

MOLECULAR ENGINEERING OF SIDE-CHAIN LIQUID CRYSTALLINE POLYMERS BY LIVING POLYMERIZATIONS

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Abstract – “Living” anionic, cationic, metalloporphyrin and ring-opening metathesis polymerizations have been used to prepare well-defined side-chain liquid crystalline homopolymers, block and graft copolymers and statistical copolymers. This paper analyzes their successes and failures by reviewing the mechanistic aspects and experimental conditions of each type of polymerization, and identifies other classes of mesogenic monomers that could be polymerized in a controlled manner in the future. The emerging structure/property relationships are then identified using well-defined SCLCPs in which only one structural feature is varied while all others remain constant.

The thermal transitions of liquid crystalline polymethacrylates, polynorbornenes and poly(vinyl ether)s reach their limiting values at less than 50 repeat units, which are generally equal to those of the corresponding infinite molecular weight polymers. Increasing spacer length depresses the glass transition of SCLCPs, and consequently often uncovers mesophases that are not observed without a spacer. The crystalline melting of tactic SCLCPs also tends to decrease (with odd-even alternation) with increasing spacer length. Without additional order within the polymer backbone due to high tacticity, mesogenic side-chains generally do not crystallize until the spacer contains at least nine carbon atoms. As the flexibility of the polymer backbone increases, the glass transition temperature decreases, and the side chains are able to crystallize at shorter spacer lengths and form more ordered mesophases. The isotropization temperature ($T_i = \Delta H_i / \Delta S_i$) also increases since the change in entropy decreases more rapidly than the change in enthalpy with increasing backbone flexibility. However, the mesogenic side groups of most highly tactic polymers, which are less flexible than the corresponding atactic polymers, are evidently in the proper configuration to crystallize and/or form ordered phases. If the mesogen density is taken into account, the increase in ΔH_i and ΔS_i per methylenic unit in the spacer are equivalent for a given mesophase, and increase as the order of the mesophase increases. The discontinuity and/or change in the slope of $\Delta \Delta H_i / -CH_2-$ and $\Delta \Delta S_i / -CH_2-$ with a change in the type of mesophase can be used to confirm that a phase change has occurred with the addition or subtraction of one methylenic unit in the spacer of a homologous series.

Model compounds corresponding to exactly one repeat unit of the polymer, or which take into account only the (appropriately substituted) mesogen and spacer, mimic the phase behavior of the corresponding SCLCPs well. The monomers themselves, which have chemical structures very different from that of the polymer backbone, are the least appropriate model compounds for most SCLCPs. The effect of polydispersity has not been clarified yet, although it may manifest itself in broad phase transitions if the broad polydispersity is accompanied by polydispersity in molecular architecture, and the molecular architectures are immiscible.

Liquid crystalline block and graft copolymers microphase separate into classic morphologies, but with the mesogens within the liquid crystalline block organize anisotropically if the blocks are sufficiently long. Although the same mesophase is generally formed by the copolymers and homopolymer, the phase diagram is asymmetric and less ordered mesophases may result if spheres of the liquid crystalline block are dispersed in a matrix of the other block. The morphology and thermotropic behavior of diblock and ABA and BAB triblock copolymers of

2-(cholesterylloxycarbonyloxy)ethyl methacrylate and styrene are identical when the volume fraction of the blocks are equal. Statistical copolymers also require a minimum concentration of the mesogenic monomer to form a mesophase. The isotropization temperatures of statistical copolymers based on two mesogenic monomers whose homopolymers exhibit identical mesophases follow ideal solution behavior as a function of copolymer composition. Copolymers based on structural units which are not isomorphic do not exhibit their respective mesophases over the entire copolymer composition, and intermediate compositions may exhibit an entirely different phase. © 1997 Elsevier Science Ltd

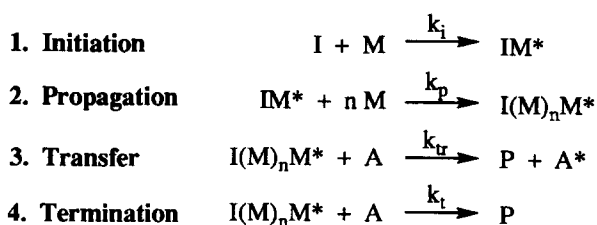
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1. INTRODUCTION

1.1. Chain polymerizations¹

Until recently, most side-chain liquid crystalline polymers (SCLCPs) were prepared by either hydrosilations of mesogenic olefins with poly(methylsiloxane)s or by free radical polymerizations of acrylates, methacrylates and chloroacrylates.^{2,3} Both routes involve



Scheme 1. Four elementary reactions of a chain polymerization.

chain polymerizations, either directly or prior to a polymer analogous reaction. Chain polymerizations involve the four elementary reactions shown in Scheme 1. In contrast to step polymerizations, chain polymerizations require an initiator (I) to produce reactive centers. In order for a vinyl monomer to be polymerizable, it must contain a substituent capable of stabilizing the resulting active site. Therefore, most 1-substituted alkenes undergo facile radical polymerizations (although α -olefins do not), whereas an electron-donating substituent is required to activate olefins to cationic initiation and propagation, and an electron-withdrawing substituent is required to activate olefins to anionic polymerizations.

In addition to initiation and propagation, chain polymerizations may also undergo transfer and termination reactions (with reagent A for example), in which inactive chains (P) are formed. Chain transfer may occur to monomer, solvent, polymer, or a chain transfer agent. In order for this to be a transfer reaction rather than termination, the molecule (A^*) generated must be reactive enough to reinitiate polymerization. Solvent is not required in radical polymerizations, although it retards autoacceleration and helps to diffuse heat; solvent is required in ionic polymerizations to control the heat generated. Since solvent is the component present in the highest concentration in most ionic polymerizations, solvents which either terminate the active sites or which act as chain transfer agents must be avoided. In contrast to chain transfer to solvent which would be prevalent from the initial stages of a polymerization due to the solvent's high concentration, chain transfer to polymer often does not compete noticeably with propagation until the end of the polymerization when monomer is depleted.

Termination can be avoided or suppressed in ionic and metathesis polymerizations under appropriate conditions. In contrast to ionic polymerizations in which the growing species cannot react with each other due to their like charge, termination does occur in radical polymerizations by combination or disproportionation of two growing polymeric radicals. Therefore, termination is unavoidable in radical polymerizations.

In contrast to the synthesis of small molecules, it is impossible to obtain a completely pure product from a polymerization that has a unique chain length and therefore a unique molecular weight. Chains of vastly different lengths will form if there are multiple propagating species with varying activities which do not exchange rapidly. This distribution of chain lengths and molecular weights is described by the moments of a statistical distribution of molecular weights [eqn (1)].

$$\bar{M}_n = \frac{\sum n_i M_i}{\sum n_i} = \frac{\sum w_i}{\sum n_i} \quad (1)$$

$$\bar{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i} = \frac{\sum w_i M_i}{\sum w_i}$$

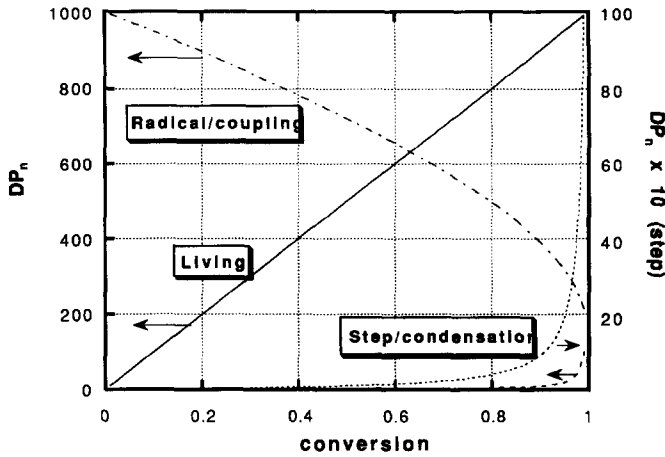


Fig. 1. Polymer molecular weight as a function of monomer conversion in chain-growth, step-growth and living polymerizations.⁴

$$\bar{M}_z = \frac{\sum n_i M_i^3}{\sum n_i M_i^2} = \frac{\sum w_i M_i^2}{\sum w_i M_i}$$

n_i = number of chains of length i

M_i = molecular weight of chains of length i

The first moment of the distribution is the number average molecular weight (\bar{M}_n), which is the total weight of the sample ($\sum w_i$) divided by the number of chains in that sample ($\sum n_i$). The weight (\bar{M}_w) and z -average (\bar{M}_z) molecular weights are the second and third moments of the distribution, respectively. That is, $\bar{M}_z > \bar{M}_w > \bar{M}_n$.

However, the thermotropic behavior of SCLCPs is generally most accurately described as a function of the number average degree of polymerization (DP_n), rather than the average molecular weight. As shown in eqn (2), the number (DP_n), weight (DP_w) and z -average (DP_z)

$$\bar{M}_n = DP_n M_0 \quad \bar{M}_w = DP_w M_0 \quad \bar{M}_z = DP_z M_0 \quad (2)$$

M_0 = molecular weight of repeat unit and/or monomer

degrees of polymerization correspond to the number, weight and z -average molecular weights, respectively. Since the number of polymer chains resulting from a chain polymerization is proportional to the amount of initiator used, the degree of polymerization is inversely proportional to initiator concentration. The ratio of the concentration of reacted monomer and polymer chains is determined by the ratio of the rates of propagation (R_p) and all chain forming reactions, including transfer (R_{tr}) [eqn (3)].

$$DP_n = \frac{\Delta[M]}{[\text{Polymer}]} = \frac{R_p}{R_i + R_{tr} + \dots} \quad (3)$$

As shown in Fig. 1, high molecular weight polymer forms rapidly in a chain polymerization if initiation is slow and propagation is relatively fast, as in classic radical

polymerizations. The molecular weight is limited by one of the chain breaking reactions (transfer or termination). In this case, the polymerization system consists of monomer and high molecular weight polymer at all stages of the polymerization, with only the yield of polymer increasing with increasing monomer conversion. In a radical polymerization which terminates by coupling and which has a constant rate of initiation, high molecular weight polymer forms at low ($< 1\%$) conversion. However, the average molecular weight decreases with further conversion since the number average degree of polymerization (DP_n) is determined by the ratio of the rates of propagation and initiation.

The breadth of the molecular weight distribution is described by the ratio of the weight and number average molecular weights or degrees of polymerization, and is referred to as the polydispersity index (pdi) or molecular weight distribution (mwd) [eqn (4)].

$$\text{pdi} = \frac{\bar{M}_w}{\bar{M}_n} = \frac{DP_w}{DP_n} \quad (4)$$

Chain polymerizations which do not terminate by bimolecular chain coupling generally result in polymers with the most probable molecular weight distribution of 2.0; free radical polymerizations which terminate by bimolecular chain coupling result in $\text{pdi} = 1.5$. However, chain transfer to polymer, autoacceleration, slow initiation, and slow exchange between active species of different reactivities result in much higher polydispersities.

1.2. Living polymerizations

Since the 1960s, much of the research in polymer synthesis has been directed at establishing living conditions for chain polymerizations.⁵⁻⁸ The only requirement for a polymerization to be considered truly living is that all chain breaking reactions such as chain transfer and termination are absent. That is, the rate constants of both chain transfer and termination should be equal to zero ($k_{tr} = 0$, $k_t = 0$). As shown in Fig. 2 for a polymerization which is first order in monomer, a change in the number of active species due to termination is detected by a nonlinear dependence of monomer conversion as a function of time. (Such plots have never been used to detect termination in polymerizations of mesogenic monomers.)

In contrast, transfer reactions are not detected by following the monomer conversion if the rate of reinitiation is comparable to that of propagation. In this case, transfer is detected by a nonlinear dependence of the polymer molecular weight or degree of polymerization as a function of polymer yield.

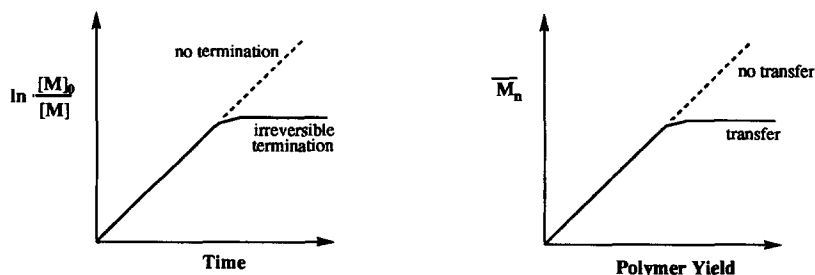


Fig. 2. The effect of termination and transfer reactions on monomer conversion and polymer molecular weight.

function of monomer conversion, polymer yield or the ratio of monomer to initiator concentrations, $[M]_0/[I]_0$ (Fig. 2). However, a linear dependence of molecular weight vs conversion is often used erroneously to demonstrate that a polymerization is living.⁹⁻¹¹ That is, termination does not affect the number of chains in the system, and therefore does not affect M_n or DP_n if initiation is fast and monomer conversion goes to completion; i.e. if all of the chains are not terminated.

In practice, linear semilogarithmic kinetic plots and linear dependencies of molecular weight on monomer conversion require only that the rate constants of chain transfer and termination are much less than that of propagation ($k_p/k_{tr} \geq 10 \times [M]_0/[I]_0 \sim 10 \times DP_n$; $k_p/k_{tr} \geq 10 \times [M]_0/[I]_0 \sim 10 \times DP_n$).^{10,11} Termination is therefore less important at lower ratios of monomer to initiator [eqn (5)]. This is therefore the practical requirement for the synthesis of

$$\ln([M]_0/[M]_\infty) = [I]_0 k_p / k_t \quad (5)$$

well-defined polymers, such that complete monomer conversion can be reached and the chain ends can be quantitatively functionalized. However, since chain breaking reactions are actually present, such systems are more appropriately labeled controlled polymerizations rather than living polymerizations. In fact, conditions have recently been established for controlled radical polymerizations, even though it is impossible to avoid bimolecular termination.¹²⁻²⁰ The extent of the "livingness" or controllability of a polymerization can be ranked if the individual or relative rate constants of propagation, transfer and termination are known.^{10,11}

If initiation is also faster than, or at least comparable to propagation, all chains begin growing simultaneously and the molecular weight of the polymer increases linearly with conversion. In this case, the degree of polymerization is determined by the ratio of the concentrations of reacted monomer and initiator [eqn (6)]. Although this formally requires

$$DP_n = \frac{\Delta[M]}{[I]_0} = \frac{[M]_0 - [M]_t}{[I]_0} \quad (6)$$

that $k_i = \infty$, controllable molecular weight is obtained if the rate constant of initiation is greater than or comparable to that of propagation ($k_i \geq k_p$).²¹ If initiation is slow, the number average molecular weight is initially too high but becomes equal to the theoretical value once initiator is consumed.

In addition to the absence of chain breaking reactions and fast initiation, two additional requirements must be met to obtain polymers with narrow molecular weight distributions: all chains must have equal reactivity ($k_p^x = k_p^y = k_p^z$, etc.) or the active sites must exchange rapidly, and propagation must be irreversible ($k_p \gg k_d$). In this case, the molecular weight distribution depends on only the degree of polymerization as defined by the Poisson distribution [eqn (7)].

$$\frac{DP_w}{DP_n} = 1 + \frac{DP_n}{(1 + DP_n)^2} = 1 + \frac{1}{DP_n} \cong 1 \quad (7)$$

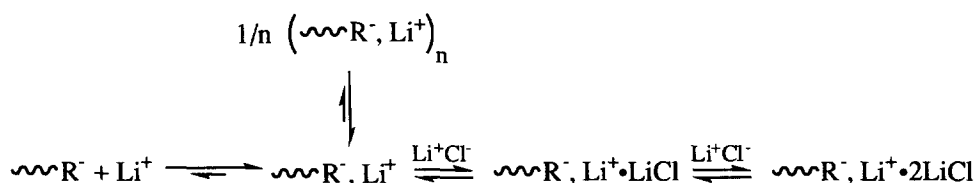
Living polymerizations in which initiation is fast and quantitative and which have irreversible growth offer several advantages over conventional polymerizations. In addition to the ability to obtain polymers with controlled molecular weights and narrow molecular weight distributions, it is also possible to control the polymer architecture and chain end



2. "LIVING" POLYMERIZATIONS USED TO SYNTHESIZE SCLCPS

2.1. Anionic and group transfer polymerizations of olefins^{5,6,24}

$$\text{CH}_2=\text{C} \begin{array}{c} \text{CN} \\ | \\ \text{CO}_2\text{R} \end{array} > \text{CH}_2=\text{CH} \begin{array}{c} | \\ \text{CN} \end{array} > \text{CH}_2=\text{CH} \begin{array}{c} | \\ \text{CO}_2\text{R} \end{array} > \text{CH}_2=\text{C} \begin{array}{c} \text{CH}_3 \\ | \\ \text{CO}_2\text{R} \end{array} > \text{CH}_2=\text{CH} \begin{array}{c} | \\ \text{C}_6\text{H}_5 \end{array} \quad (8)$$



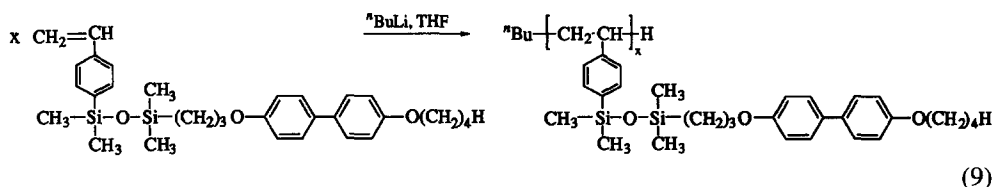
Scheme 3.

corresponds to the electron-withdrawing ability of their substituents. However, the reactivity of the growing carbanions (and enolate anions) follows the opposite order shown in eqn (8), with the most stable carbanions being the least reactive.

The choice of initiator is very important for a controlled anionic polymerization. The initiator will be nucleophilic enough to initiate polymerization if the pK_a of the conjugate acid is similar to or greater than that of the propagating anion.²⁵ However, the initiator should not be so reactive that it causes side reactions. Common solvents for anionic polymerizations include hydrocarbons and ethers. Protonic solvents, dissolved oxygen and carbon dioxide result in either transfer or termination in most anionic polymerizations, depending on the nucleophilicity of the anion generated, and are therefore not used. Halogenated solvents also terminate anionic polymerizations and should be avoided.

In contrast to radical polymerizations in which there is only one type of propagating species, ionic polymerizations may involve several active species, each with different reactivities and/or lifetimes. As outlined in Scheme 2, ionic polymerizations may potentially involve equilibria between covalent dormant species, contact ion pairs, aggregates, solvent separated ion pairs, and free ions. Although ion pairs involving alkali metal counteranions can not collapse to form covalent species, group transfer polymerization apparently operates by this mechanism. In anionic polymerizations, free ions are much more reactive than ion pairs ($k_p^- \approx 10^5 k_p^\pm$), although the dissociation constants are quite small ($K_D \approx 10^{-7}$).⁵ The equilibria between these different species in anionic polymerizations of nonpolar alkenes are dynamic enough relative to the rate of propagation to generate monomodal and narrow molecular weight distributions.^{26,27}

Although anionic polymerizations of nonpolar monomers such as styrene and butadiene are the most inherently living polymerizations available,^{5,6} only one mesogenic styrene has been polymerized by an anionic mechanism.²⁸ As shown in eqn (9), 4-{3-[3-((4'-*n*-butoxy-(4''-phenyl)phenoxy)propyl)tetramethyldisiloxanyl]styrene was polymerized using $n\text{BuLi}$ as



the initiator in THF (unreported temperature) in order to determine the effect of a siloxane spacer. In this case, the polymerizations were not well-controlled, with degrees of polymerization much higher than those calculated from $[M]_0/[I]_0$ despite the low conversions

Table 1. Anionic polymerizations of *n*-[4'-(4"-methoxyphenyl)phenoxy]alkyl methacrylates (*n* = 2–6)

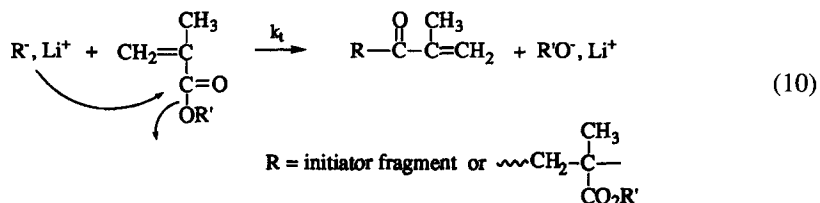
$x \text{ CH}_2=\text{C}(\text{CH}_3)\text{CO}_2(\text{CH}_2)_n\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{OCH}_3 \longrightarrow \left[\text{CH}_2-\text{C}(\text{CH}_3)(\text{CO}_2(\text{CH}_2)_n\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{OCH}_3) \right]_x$							
Initiating System	Solvent	Temp. (°C)	$\frac{[M]_0}{[I]_0}$	GPC ^a		Tacticity	Ref.
				DP_n	pdi		
^t BuMgBr/Et ₂ O	CHCl ₃	– 30 to – 20	10	13–39	1.54–3.06	(mm) = 0.90–0.93	42
			20	24–68	2.35–14.0	(mm) = 0.90–0.96	42
^t BuMgBr/Et ₂ O	THF	– 78 to – 60	10	14–21	1.23–2.27	(rr) = 0.79–0.81	42
			20	19–33	1.23–1.57	(rr) = 0.79–0.85	42
$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{Ph})\text{C}^-\text{Li}^+$	THF	– 40	11	13 ^b	1.13	(rr) = 0.80	44
3LiCl			22	23 ^b	1.26	(rr) = 0.80	44

^arelative to polystyrene standards

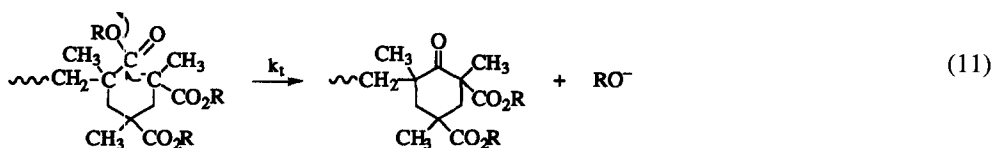
^brelative to PMMA standards

(62–80% yield); pdi = 1.2–1.6. However, the degree of polymerization increased steadily as $[M]_0/[I]_0$ increased.

With the previous exception,²⁸ only mesogenic methacrylates have been used in an attempt to prepare well-defined SCLCPs directly by an anionic addition mechanism. In this case, the most troublesome side reactions to avoid are intermolecular [eqn (10)] and intramolecular



[eqn (11)] termination by nucleophilic attack at the carbonyl group of the monomer or



polymeric repeat unit to produce unreactive alkoxide anions;²⁹ other electrophilic functionalities within the mesogen are also susceptible to nucleophilic attack. This is minimized in the initiation step by using a bulky initiator such as 1,1-diphenylhexyl lithium at low temperature (– 78°C). Low temperature and more polar solvents such as THF also minimize nucleophilic attack by the relatively hindered enolate anion during propagation.³⁰

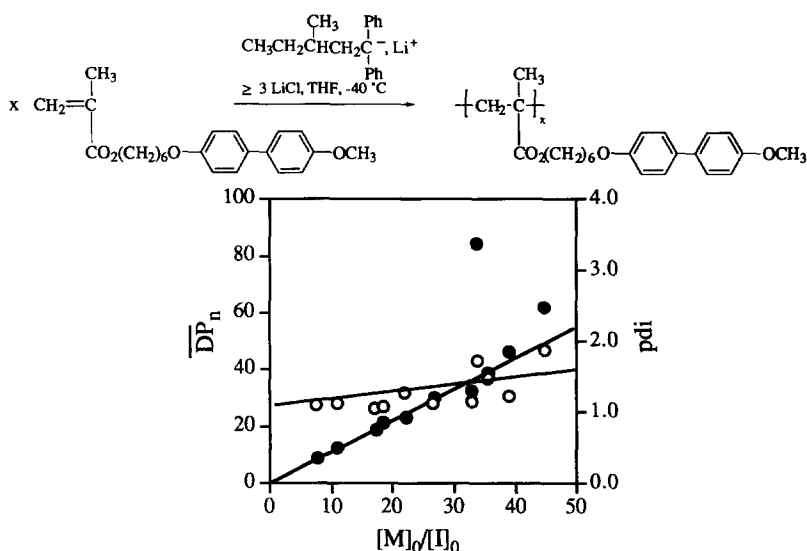
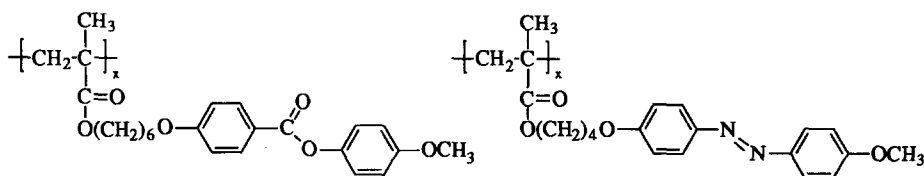
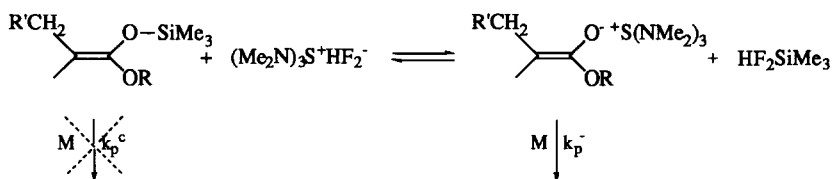


Fig. 3. Degree of polymerization (●) and polydispersity (○) resulting from anionic polymerizations of 6-[4'-(4"-methoxyphenyl)phenoxy]hexyl methacrylate initiated by 1,1-diphenyl-3-methylpentyl lithium/3 LiCl in THF at -40°C .⁴⁴

In addition, the propagating ion pairs and free ions of these polar monomers may exchange slowly relative to propagation to produce polymers with multimodal molecular weight distributions.^{31–34} For example, anionic polymerization of 'butyl methacrylate results in broad ($\text{pdi} = 2.00\text{--}2.72$) and multimodal molecular weight distributions when performed in a mixture of toluene and THF at -78°C using 1,1-diphenylhexyl lithium as the initiator.³⁵ However, narrow and unimodal molecular weight distributions are produced in either pure THF or pure toluene, in which propagation apparently occurs exclusively by free ions or ion pairs, respectively. Although 1,1-diphenyl-3-methylpentyl lithium and 1,1-diphenylhexyl lithium initiated polymerizations of methyl methacrylate in THF at -78°C effectively yield "living" polymers with narrow molecular weight distributions ($\text{pdi} \approx 1.15$), addition of lithium chloride decreases the rate of polymerization and narrows the polydispersity to 1.09.³⁶ These conditions are also effective at controlling the anionic polymerization of 'butyl acrylate.³⁷ As outlined in Scheme 3, lithium chloride narrows the polydispersity by shifting the equilibrium to LiCl adducts, thereby breaking up less reactive aggregates of the propagating polymer and shifting the equilibrium from free ions to ion pairs.³⁸



Scheme 4.



Scheme 5.

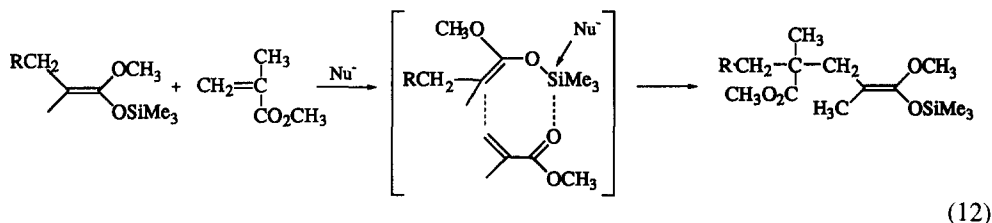
In addition to determining the effect of molecular weight on the thermotropic behavior of SCLCPs, “living” anionic polymerizations have been used extensively to study the effect of tacticity. Although toluene is generally used as the nonpolar solvent in anionic polymerizations of methacrylates to promote association and isotactic placement,^{39,40} it is a poor solvent for mesogenic methacrylates and/or the corresponding polymers. This results in only low yields of low molecular weight polymers with insufficient levels of isotacticity. Highly isotactic poly{6-[4'-(4''-(S)-2'''-methylbutoxy)phenyl]phenoxy}hexyl methacrylate} and poly([4-(4'-methoxyphenyl)phenoxy]-*n*-alkyl methacrylate)s ($n = 2-6$) were instead obtained in chloroform in the temperature range from -20 to -30°C using 'BuMgBr as the initiator (Table 1), although termination evidently broadened the polydispersity to 1.54–3.06 at $[M]_0/[I]_0 = 10$, and to $\text{pdi} = 2.35-14.0$ at $[M]_0/[I]_0 = 20$.^{41,42} Termination of the propagating chains is also demonstrated by the lower conversions at higher attempted degrees of polymerization, whereas partial consumption of the initiator is demonstrated by the much higher degrees of polymerization obtained relative to the theoretical values, even at these low polymer yields.

Table 1 demonstrates that 'BuMgBr initiated polymerizations in THF in the temperature range from -60 to -78°C are more controlled, yielding polymers with narrower polydispersities.^{41,42} These conditions involve freely propagating chains and therefore result in syndiotactic polymers at low temperature.⁴³ Although “living” polymethacrylates with the highest syndiotacticities $[(rr) = 0.92-0.96]$ have been achieved using $\text{'BuMgBr}/(^n\text{C}_8\text{H}_{17})_3\text{Al}$ (1:3) in toluene at -78°C ,⁴⁰ these conditions have not been applied to mesogenic methacrylates, probably because of the corresponding polymers' limited solubility in toluene. Instead, the initiating system developed by Teyssié³⁶ of 1,1-diphenyl-3-methylpentyl lithium in THF in the presence of at least three equivalents of LiCl has been used most successfully for preparing well-defined syndiotactic poly{*n*-[4'-(4'-methoxyphenyl)phenoxy]alkyl methacrylate}s with narrow molecular weight distributions ($\text{pdi} = 1.05-1.46$) (Table 1).⁴⁴ Although the polymers precipitated during the polymerization at -78°C , Fig. 3 demonstrates that the polymerization is controlled and transfer is not detectable at -40°C . However, the polymers precipitate during the polymerization when $[M]_0/[I]_0 > 40$, even at -40°C , resulting in bimodal molecular weight distributions.

In the absence of LiCl, 1,1-diphenyl-3-methylpentyl lithium initiated polymerizations of 6-[4'-(4''-methoxyphenoxy)phenoxy]hexyl methacrylate⁴⁵ and 4-[4'-(4''-methoxyphenoxy)phenoxy]butyl methacrylate⁴⁶ in THF at -70°C yielded polymers (Scheme 4) with $\text{pdi} = 1.09-1.31$ and molecular weights close to the theoretical values up to $[M]_0/[I]_0 = 50$. In the latter case, the (co)polymerization was improved by adding a trace amount of triisobutylaluminum to the monomer solution in order to consume any residual water.⁴⁶

SCLCPs have also been prepared by group transfer polymerization (GTP) of mesogenic

methacrylates at room temperature.^{47,48} The livingness of the nucleophilic catalysed GTP was originally attributed to a new mechanism [eqn (12)] involving a (symmetry-forbidden^{49,50})

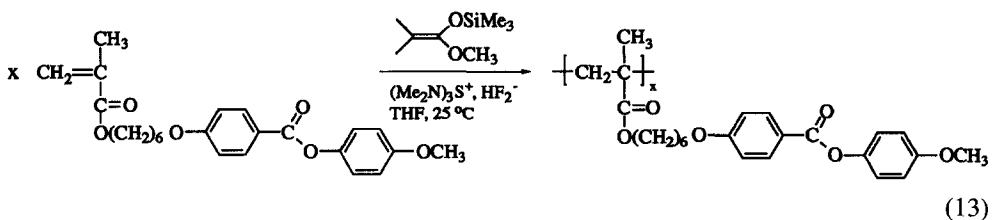


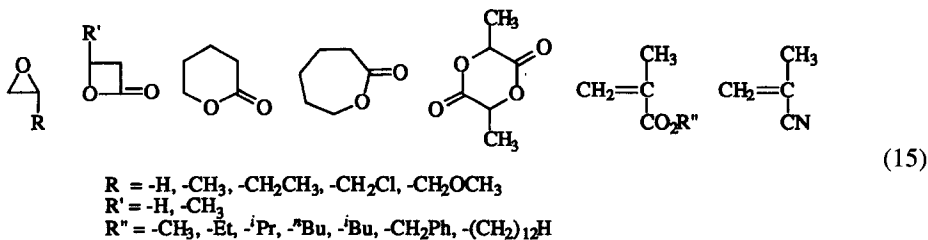
eight-member cyclic transition state in which the trialkylsilyl group is transferred from the growing chain end to the incoming monomer.⁵¹

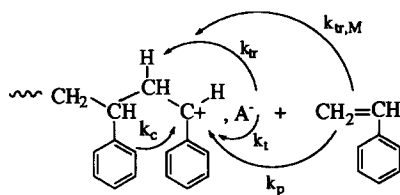
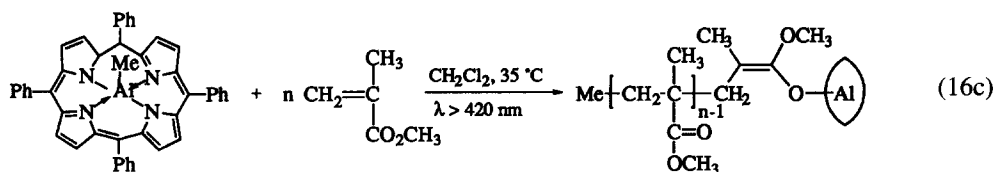
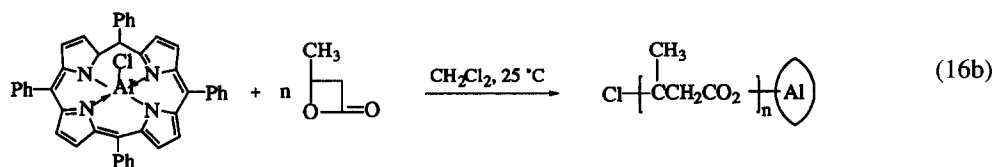
Alternatively, GTP may be an anionic polymerization in which a small concentration of enolate anions are in dynamic equilibrium with dormant silyl ketene acetal chain ends (Scheme 5). This dynamic equilibrium between a small concentration of enolate anions and a high concentration of dormant chain ends would reduce the lifetime of the active enolate anions, thereby accounting for the reduced rate^{52,53} of polymerization compared to classic anionic polymerizations of methacrylates. This shift in the equilibrium to only one type of active species would also account for the narrower polydispersities. Since the counteranions are bulky tris(dimethylamino)sulfonium⁵¹ or tetrabutylammonium⁵⁴ ions, the active species would be free ions stabilized by solvent, which are less reactive towards intramolecular backbiting [eqn (11)].

Most experimental results indicate that GTP is a classic anionic polymerization operating by reversible termination (dissociative mechanism),^{55,56} and/or degenerative transfer.^{57,58} For example, termination occurs once monomer is consumed by backbiting at the pen-penultimate carbonyl to generate cyclic β -ketoester endgroups as in classic anionic polymerizations [eqn (11)].⁵⁹ Acids with $\text{pK}_a < 18$ also terminate "group transfer" polymerizations, whereas acids with $\text{pK}_a = 18\text{--}25$ act as chain transfer agents.⁶⁰ The reactivity ratios in GTP copolymerizations of methacrylates are also similar to those in anionic copolymerizations,^{55,61,62} rather than $r_1 \approx r_2 \approx 1$ as expected for an associative mechanism. However, the most compelling evidence supporting an anionic mechanism is that the stereochemistry resulting from group transfer polymerizations is nearly identical to that of an anionic polymerization involving freely propagating enolate anions.^{55,63,64} That is, the polymers are not highly isotactic as expected for the coordinated chain ends in an associative mechanism. Instead, freely propagating chains favor syndiotactic placement, especially at low temperature. In addition, ¹H-NMR experiments recently demonstrated that the silyl end groups of two different living polymethacrylates exchange in the presence of tris(dimethylamino)sulfonium bifluoride.⁶⁵

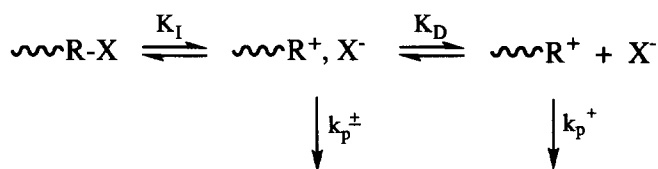
6-[4'-(4"-Methoxyphenoxy)carbonyl]phenoxy]hexyl methacrylate was first polymerized by GTP using 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene as the initiator and tris(dimethylamino)sulfonium bifluoride as the catalyst in THF at room temperature [eqn (13)].⁴⁷



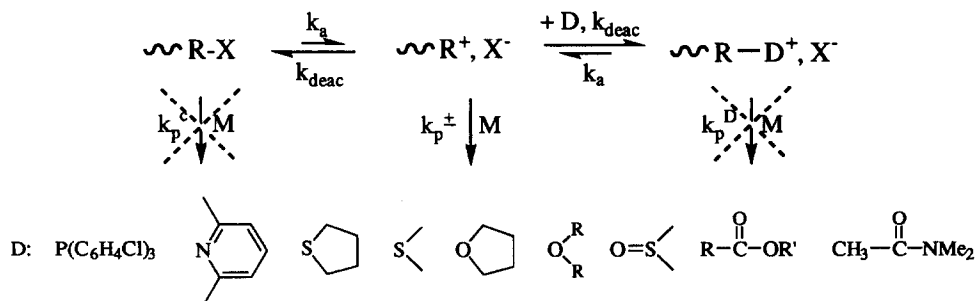




Scheme 7.



Scheme 8.

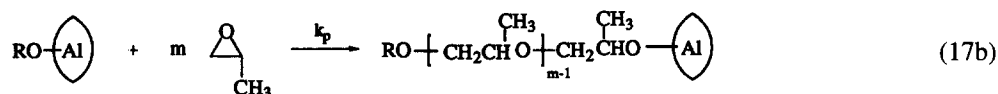
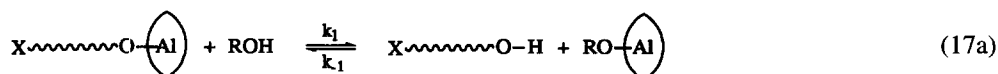


Scheme 9.

Table 2. Relative rates of initiation in cationic polymerizations initiated by covalent initiators in the presence of a Lewis acid catalyst.¹¹³

Initiator	fast initiation	similar initiation and propagation rates	slow initiation
$\text{CH}_3\text{-CH(X)-OR}$	$\text{CH}_2=\text{C}(\text{CH}_3)\text{-C}_6\text{H}_5$	$\text{CH}_2=\text{CHOR}$	
$\text{CH}_3\text{-C(CH}_3\text{)(X)-C}_6\text{H}_5$	$\text{CH}_2=\text{CH-C}_6\text{H}_5$, $\text{CH}_2=\text{C(CH}_3\text{)}_2$	$\text{CH}_2=\text{C(CH}_3\text{)-C}_6\text{H}_5$	$\text{CH}_2=\text{CHOR}$
$\text{CH}_3\text{-CH(X)-C}_6\text{H}_5$		$\text{CH}_2=\text{CH-C}_6\text{H}_5$	$\text{CH}_2=\text{C(CH}_3\text{)-C}_6\text{H}_5$, $\text{CH}_2=\text{CH-C}_6\text{H}_4\text{(CH}_3\text{)}$
$\text{CH}_3\text{-C(CH}_3\text{)(X)-CH}_3$		$\text{CH}_2=\text{C(CH}_3\text{)}_2$	

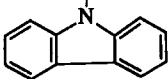



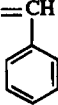

monomer into the aluminum – axial ligand bond of (5,10,15,20-tetraphenylporphinato)-aluminum derivatives [(TPP)AlCl, (TPP)AlMe, (TPP)AlOMe] to generate an aluminum alkoxide (oxiranes,⁶⁹ δ -valerolactone,⁷³ ϵ -caprolactone,⁷⁸ D-lactide⁷⁵), aluminum carboxylate (β -lactones),⁷¹ or aluminum enolate (methacrylates)⁷⁶ as the growing species. Inoue coined the term “immortal”⁷⁹ to describe these polymerizations because the active chain ends are not “killed” by proton sources. For example, the oxirane polymerizations undergo rapid and reversible exchange with alcohols such as methanol, hydroxyethyl methacrylate and polyethylene glycol [eqn (17)];^{78–81} lactone chain ends exchange rapidly with carboxylic



acids.⁸¹ In this case, the degree of polymerization corresponds to the molar ratio of reacted monomer to the sum of the initial concentrations of initiator and proton source ($\Delta[M]/[\text{TPP-AIX}] + [\text{ROH}]_0$). Since this reversible termination is rapid compared to propagation ($k_i/k_p = 10$),⁸¹ the polydispersity of the resulting polymers remains narrow at $\text{pdi} \approx 1.1$.

Although the aluminum porphyrin initiated polymerizations take days or weeks to go to complete monomer conversion in the presence of a proton source, their rate is increased

Table 3. Examples of “living” cationic polymerizations of alkenes.

Type	Polymerization System	Solvent, Temp. (°C)	Reference
HA	HI, $\text{CH}_2=\text{CH}$ 	CH_2Cl_2 , - 78	115
HA or RX/LA	HI, I_2 , $\text{CH}_2=\text{CH}$ 	<i>n</i> -hexane, - 15	116
	CumOAc, BCl_3 , 	CH_2Cl_2 , - 30	117
HA or RX LA/ N^+X^-	$\text{CH}_3-\text{CH}-\text{Cl}$, SnCl_4 , $\text{Bu}_4\text{N}^+\text{Cl}^-$, $\text{CH}_2=\text{CH}$  	CH_2Cl_2 , - 15	119
HA/Nu	$\text{CF}_3\text{SO}_3\text{H}$, SMe_2 , $\text{CH}_2=\text{CH}$ 	CH_2Cl_2 , - 15	107

substantially by adding a sterically hindered Lewis acid such as methylaluminum bis(2,6-di-*t*-butyl-4-methylphenolate).⁸² In contrast to the oxirane and β -lactone polymerizations, ϵ -caprolactone and 2,2-dimethyltrimethylene carbonate are polymerized by methylaluminum bis(2,6-diphenylphenolate) in the absence of an aluminum porphyrin; these polymerizations are relatively rapid and controlled in the presence of *i*-propanol or methanol.⁸³

In contrast to the heterocyclic polymerizations, (TPP)AlCl does not initiate polymerization of methacrylates⁷⁶ and methacrylonitrile,⁷⁷ whereas (TPP)AlMe initiation requires irradiation by visible light. These extremely slow polymerizations are also accelerated by addition of bulky Lewis acids such as methylaluminum bis(2,6-di-*t*-butylphenolate),^{77,84–86} triphenylphosphine,⁸⁶ or organoborane⁸⁷ compounds such as triphenylborane or tris(pentafluorophenyl)borane.⁸⁸ These Lewis acids accelerate the polymerization by coordinating to the monomer's carbonyl group, thereby increasing the olefin's electrophilicity. In addition, light is not needed to polymerize methacrylates if more nucleophilic thiolatealuminum porphyrins such as propylthio- and phenylthio(5,10,15,20-tetraphenylporphinato)aluminum [(TPP)AlSPr, (TPP)AlSPh] are used, preferably in the presence of methylaluminum bis(2,6-di-*t*-butyl-4-methylphenolate).⁸⁹ In all cases, the molecular weight is determined by the ratio of the concentrations of reacted monomer to initiator up to at least $[M]/[I]_0 = 300$, and the polydispersity is narrow at $\text{pdi} = 1.05\text{--}1.2$.

Photoirradiated (TPP)AlMe was used to polymerize 6-[4'-(4"-methoxyphenoxy)carbonyl]phenoxy]hexyl methacrylate,⁹⁰ 6-[4'-(4"-*n*-butoxyphenoxy)carbonyl]phenoxy]hexyl methacrylate⁹¹ and 6-[4'-(4"-cyanophenoxy)carbonyl]phenoxy]hexyl methacrylate⁹² in order to determine the effect of molecular weight and tacticity ($[\text{rr}] \approx 0.75$). Although “high speed” conditions^{84–89} were not used, the polymerizations reached 76–92% conversion in 10 h to

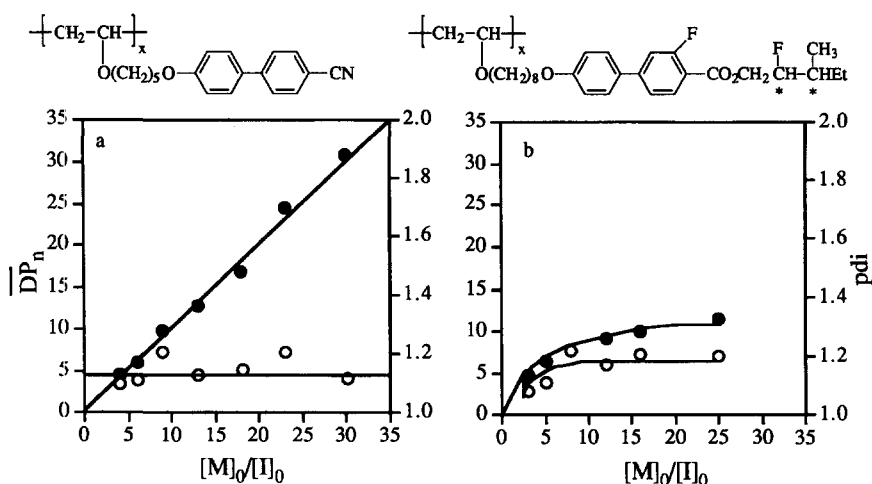
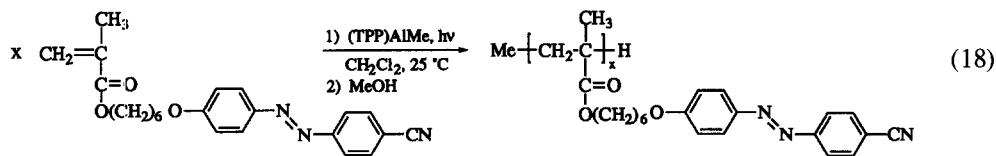
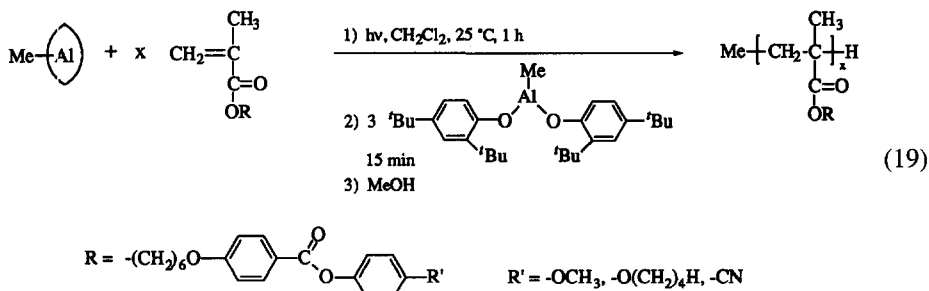


Fig. 4. Degree of polymerization (●) and polydispersity (○) resulting from cationic polymerizations of (a) 5-[(4'-(4''-cyanophenyl)phenoxy)pentyl]vinyl ether^{125,126} and (b) 8-[(4'-(2R, 3S)-2-fluoro-3-methylpentylloxycarbonyl)-3'-fluorophenyl-4''-phenoxy]octyl]-vinyl ether¹³⁹ initiated by triflic acid in CH_2Cl_2 at 0°C in the presence of dimethyl sulfide.

produce polymers with the expected molecular weight ($DP_n < 35$) and $pdi = 1.09\text{--}1.35$. In contrast, that of 6-[4'-(4''cyanophenylazo)phenoxy]hexyl methacrylate [eqn (18)] required

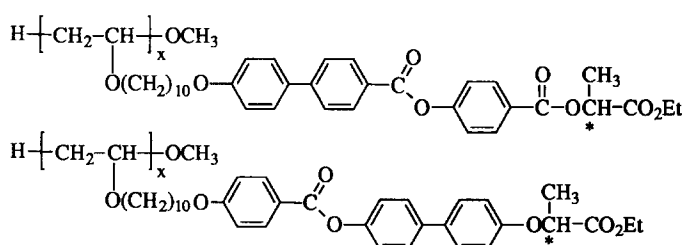


70 h to reach 90% conversion.⁹⁰ Nevertheless, methylaluminum bis(2,4-di-*t*-butylphenolate) accelerated polymerization of only the first three monomers to achieve 80–95% conversion in 15 min following its addition [eqn (19)], but terminated polymerization of 6-[4'-(4''-cyanophenylazo)phenoxy]hexyl methacrylate.⁹⁰



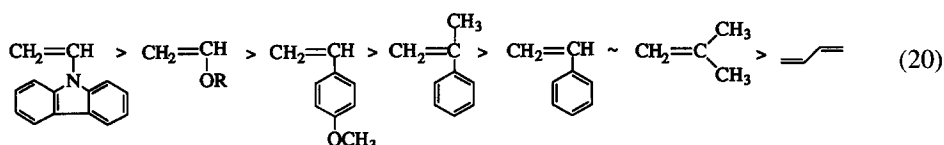
2.3. Cationic polymerizations of olefins⁸

Alkenes polymerize cationically by electrophilic addition of the monomer to a growing carbenium ion. Therefore, the monomer must be nucleophilic and capable of stabilizing the



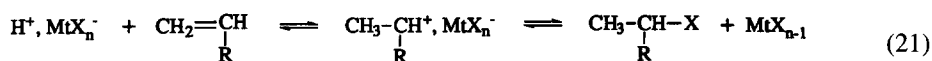
Scheme 10.

resulting positive charge. In addition, the double bond must be the most nucleophilic functionality in the monomer. Some vinyl monomers which polymerize cationically are listed in eqn (20) in their order of reactivity, which corresponds to the electron-donating ability of



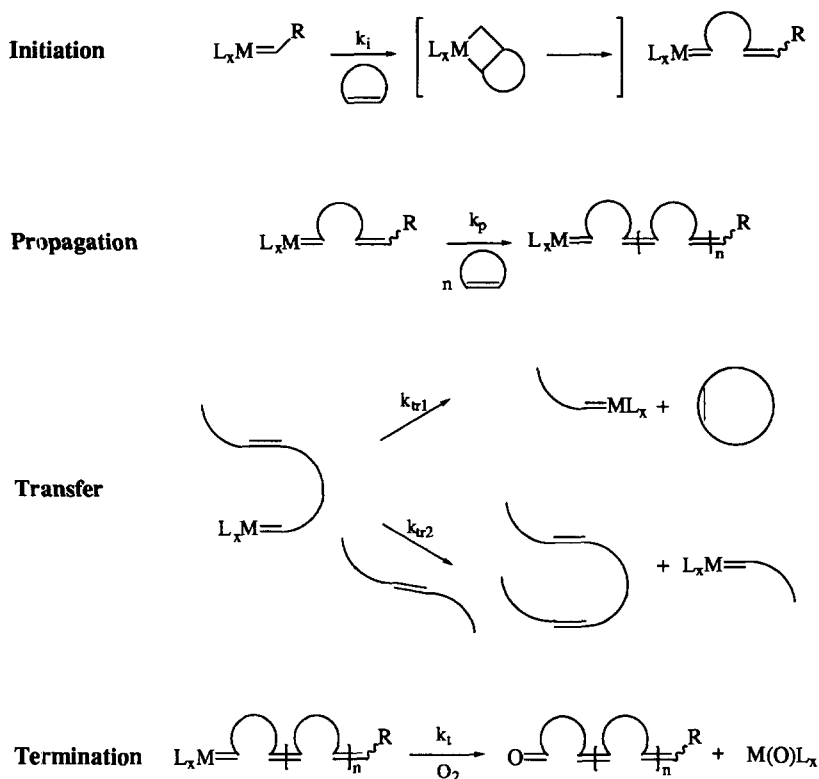
their substituents. Sufficiently nucleophilic alkenes such as vinyl ethers, styrenes and isobutylene polymerize cationically to generate stabilized carbenium ions as the propagating species. However, the reactivity of the growing carbenium ions follows the opposite order shown above, with the most stable carbenium ions being the least reactive.

Initiators include strong protonic acids and the electrophilic species generated by reaction of a Lewis acid with water, an alcohol, ester or alkyl halide (Scheme 6). In this case, initiation occurs by electrophilic addition of the vinyl monomer to the proton or carbenium ion, which may be accompanied by reversible or irreversible collapse of the ion pair [eqn (21)]. As



demonstrated by the styrene polymerization in Scheme 7, propagation occurs in carbocationic polymerizations by electrophilic addition of the vinyl monomer to a growing carbenium ion. The resulting carbenium ions are very reactive and therefore difficult to control, with rate constants of propagation $k_p = 10^4$ – 10^6 L/mol s. In addition, a significant amount of the positive charge is distributed over the β -H atoms, making them prone to abstraction by either monomer ($k_{tr,M}$) or counteranion (k_{tr}). Chain transfer by β -proton elimination from the propagating carbenium ions is the most common and detrimental side reaction in cationic polymerizations of alkenes. The first requirement for a controlled cationic polymerization is therefore to use only components which are nonbasic in order to reduce the possibility of transfer by β -proton elimination. In the case of styrene polymerizations, transfer also occurs by intramolecular Friedel–Crafts cyclization (k_c) to form polymers with indanyl end groups, especially at high conversion.

However, due to their higher activation energies compared to propagation, these chain transfer reactions can be suppressed by polymerizing at lower temperatures in hydrocarbon and chlorinated solvents;⁹³ nitro solvents are also used. Protonic solvents and amines which



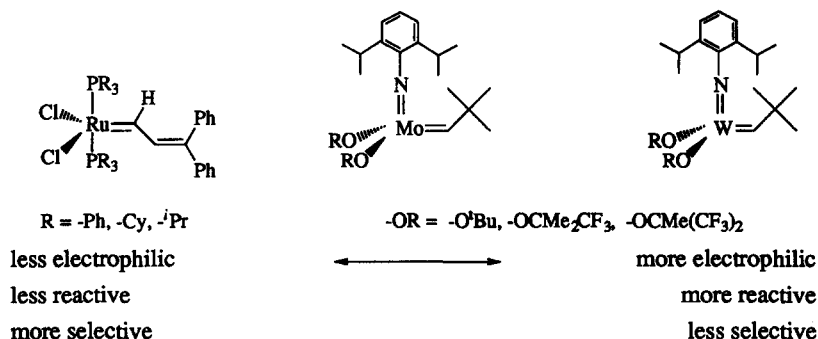
Scheme 11.

result in either transfer or termination should be avoided. In the absence of impurities and/or terminating agents, termination generally occurs in cationic polymerizations by unimolecular collapse of the ion pair (k_t). However, termination may be reversible depending on the nature of the ligand. For example, anions containing chloride and bromide ligands such as $SnCl_5^-$, $SbCl_6^-$, $SnBr_5^-$, BCl_4^- and BBr_4^- usually decompose reversibly. Reversible systems which exchange fast in comparison to propagation provide “living” systems with narrow molecular weight distributions.

Cationic polymerizations often involve both contact ion pairs and free ions as the propagating species (Scheme 8); solvent-separated ion pairs have not been identified spectroscopically. Propagation via covalent species has also been proposed for many of the new living carbocationic systems.⁹⁴ However, ions have been detected indirectly using optically active compounds and/or by various salt, substituent and solvent effects,⁸ and more directly by 1H -NMR of exchange reactions in polymerizations and model systems.⁹⁵⁻⁹⁹ Although the reactivities of these ion pairs and free ions are similar ($k_p^\pm \approx k_p^+$),¹⁰⁰⁻¹⁰² their different lifetimes lead to high polydispersities.^{10,103}

In order to achieve more controlled cationic polymerization conditions, the overall rate of polymerization must be decreased, thereby increasing the time available for functionalizing the chain ends. This has been accomplished by decreasing the stationary concentration of

Table 4. Metathesis of *cis*-pentene in toluene or benzene at 25°C



Catalyst	Turnovers per second	Reference
W(CH ^t Bu)(N-2,6-C ₆ H ₃ - ⁱ Pr ₂)[OCMe(CF ₃) ₂] ₂	1.7×10^1	164
Mo(CH ^t Bu)(N-2,6-C ₆ H ₃ - ⁱ Pr ₂)[OCMe(CF ₃) ₂] ₂	4.1×10^0	166
RuCl ₂ (CHCH=CPh ₂)(PCy ₃) ₁	7.2×10^{-3}	162
RuCl ₂ (CHCH=CPh ₂)(P ⁱ Pr ₃) ₂	6.1×10^{-3}	162
Mo(CH ^t Bu)(N-2,6-C ₆ H ₃ - ⁱ Pr ₂)[OCMe ₂ CF ₃] ₂	1.4×10^{-3}	166
W(CH ^t Bu)(N-2,6-C ₆ H ₃ - ⁱ Pr ₂)(O ^t Bu) ₂	5.5×10^{-4}	7
Mo(CH ^t Bu)(N-2,6-C ₆ H ₃ - ⁱ Pr ₂)(O ^t Bu) ₂	$\sim 2 \times 10^{-5}$	166
RuCl ₂ (CHCH=CPh ₂)(PPh ₃) ₂	0	161

active carbenium ions by shifting the equilibrium to dormant species. Since most cationic polymerizations involve an equilibrium between covalent adducts and ionic species, the equilibrium can be shifted from free ions to dormant covalent species by adding a salt with a common counteranion.¹⁰⁴ Alternatively, the carbenium ions can be deactivated with nucleophiles, such as phosphines,¹⁰⁵ hindered amines,¹⁰⁶ dialkyl sulfides,^{107,108} ethers,¹⁰⁹ sulfoxides,¹¹⁰ esters¹¹¹ and amides¹¹² to generate dormant onium ions (Scheme 9). The rapid dynamic exchange between active and dormant species, and the trapping of free carbenium ions with salts or nucleophiles also decreases the polydispersities (*pdi* < 1.2).

The choice of initiator is also very important for a controlled cationic polymerization since initiation is often not quantitative in classic systems. Covalent initiators will be reactive enough to initiate polymerization if the initiator ionizes faster than the (dormant) propagating chain ends. Many of the new “living” systems therefore use initiators with better leaving groups and tertiary versus secondary active centers. The emerging relative rates of initiation that are summarized in Table 2 correlate with the order of monomer reactivity listed in eqn (20); completion of the table should therefore be obvious. Nevertheless, the new “living” systems also use a much higher concentration of these well-defined initiators. This results in lower molecular weight polymers than in classic systems, which makes transfer less easily detected,¹¹⁴ and decreases the probability of spontaneous coininitiation with adventitious moisture.

Examples of the different types of “living” cationic polymerization systems are listed in Table 3. All involve relatively fast initiation and optimal equilibria between a low concentration of active carbenium ions and a high concentration of dormant species (Scheme 9).

Only hydroiodic acid initiated polymerizations of *N*-vinyl carbazol are controlled in the absence of a Lewis acid activator or a nucleophilic deactivator.¹¹⁵ In contrast, all other adducts generated by addition of HI to the monomer's double bond require activation with a Lewis acid such as I₂.¹¹⁶ Similarly, cumyl acetate requires activation by a Lewis acid to initiate polymerization of isobutylene¹¹⁷ to produce polymers with -Cl terminated chains since boron has a greater affinity for acetate ligands than for chlorine.¹¹⁸ The BCl₃ system therefore has the added advantage that the initiator with an acetate leaving group is more easily ionized than the propagating chain with a chlorine leaving group.¹¹⁸ Table 3 also provides two examples in which it is necessary to add a common ion salt¹¹⁹ or a nucleophile¹⁰⁷ to decrease the concentration of carbenium ions.

Although many controlled cationic polymerizations have been developed,¹²⁰ only mesogenic vinyl ethers have been used in an attempt to prepare well-defined SCLCPs by a cationic addition mechanism.¹²¹ Nevertheless, these polymerizations (and copolymerizations) provide the most complete series of SCLCPs with the widest range of structural variables. As shown in eqn (22), most of these monomers, including *n*-[(4'-(4''-cyano-

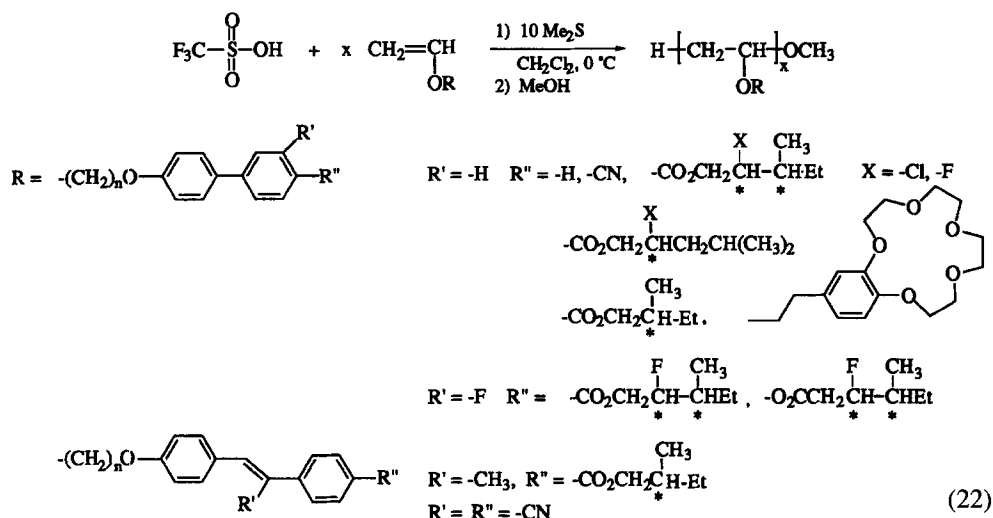


Table 5. Relative rates of initiation and propagation in ring-opening metathesis polymerizations of norbornene in C₆D₆ at 17–22°C

Initiator	k_i/k_p	Reference
RuCl ₂ (CHCH=CPh ₂)(PPh ₃) ₂	0.006	185
Mo(CH'Bu)(N-2,6-C ₆ H ₃ -iPr ₂)(O'Bu) ₂	0.083	186
RuCl ₂ (CH- <i>p</i> -C ₆ H ₄ X)(PPh ₃) ₂		
X = -Cl	1.2	185
X = -NO ₂	2.3	185
X = -NMe ₂	2.6	185
X = -OCH ₃	2.6	185
X = -CH ₃	2.9	185
X = -F	4.8	185
X = -H	9.0	185

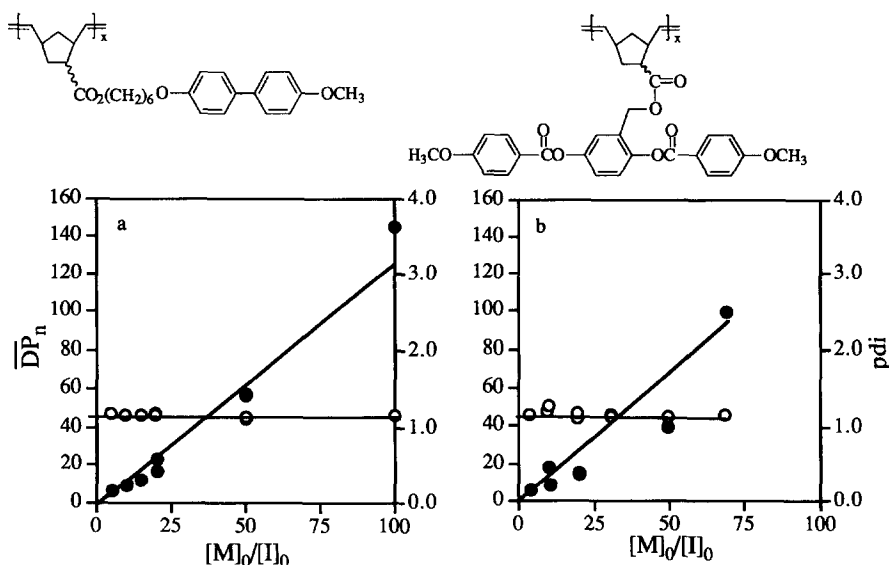
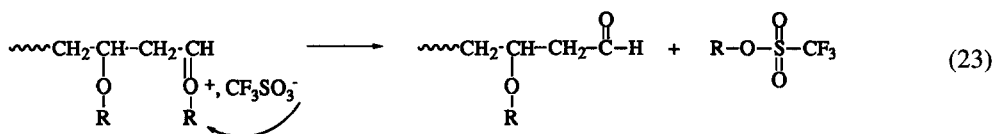
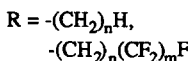
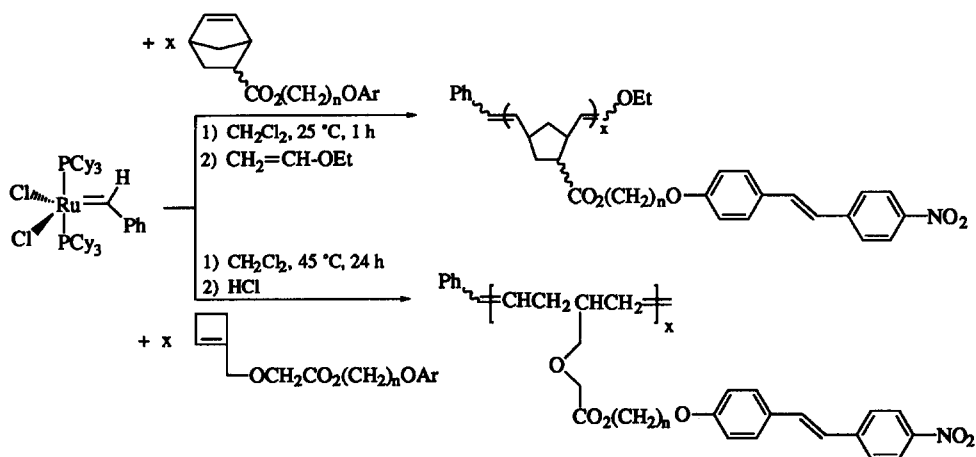


Fig. 5. Degree of polymerization (●) and polydispersity (○) resulting from ring-opening metathesis polymerizations of (a) 5-[[6'-[4''-(4'-methoxyphenyl)phenoxy]hexyl]carbonyl]bicyclo[2.2.1]hept-2-ene²² and (b) 5-[[[2',5'-bis[4''-methoxybenzoyl]oxy]benzyl]oxy]carbonyl]bicyclo[2.2.1]hept-2-ene¹⁸² initiated by $\text{Mo}(\text{CH}'\text{Bu})(\text{N}-2,6\text{-C}_6\text{H}_3\text{-}^i\text{Pr}_2)(\text{O}'\text{Bu})_2$ or $\text{Mo}(\text{CHCMe}_2\text{Ph})(\text{N}-2,6\text{-C}_6\text{H}_3\text{-}^i\text{Pr}_2)(\text{O}'\text{Bu})_2$, respectively, in THF at 25°C.

phenyl)phenoxy]alkyl]vinyl ethers ($DP_n = 2.1\text{--}32$, $pdi = 1.02\text{--}1.54$),^{122–127} 2-[(4'-biphenyl-oxy)ethyl]vinyl ether ($DP_n = 3.8\text{--}22$, $pdi = 1.07\text{--}1.11$),¹²⁸ n -[(4'-(S(-)-2-methyl-1-butoxy)-4''- α -methylstilbeneoxy)alkyl]vinyl ethers ($DP_n = 4\text{--}24$, $pdi = 1.07\text{--}1.12$),¹²⁹ 11-[(4'-cyano-4''- α -cyanostilbene)oxy]alkyl]vinyl ethers ($DP_n = 4\text{--}30$, $pdi = 1.05\text{--}1.09$),¹³⁰ n -[(4'-(S(-)-2-methyl-1-butoxy)phenyl-4''-phenoxy)alkyl]vinyl ethers ($DP_n = 4\text{--}26$, $pdi = 1.04\text{--}1.10$),^{131,132} n -[(4'-(2S,3S)-(+)-2-chloro-3-methylpentyloxycarbonyl)phenyl-4''-phenoxy]alkyl]vinyl ethers ($DP_n = 4\text{--}21$, $pdi = 1.07\text{--}1.16$),^{133,134} n -[(4'-(2R(2S),3S)-2-fluoro-3-methylpentyloxycarbonyl)phenyl-4''-phenoxy)alkyl]vinyl ethers ($DP_n = 3.4\text{--}16$, $pdi = 1.05\text{--}1.20$),^{135,136} n -[(4'-(2R(2S),3S)-2-fluoro-3-methylpentanoate)phenyl-4''-phenoxy)alkyl]vinyl ethers ($DP_n = 3.5\text{--}15$, $pdi = 1.04\text{--}1.20$),¹³⁷ n -[(4'(2R,3S)-2-fluoro-3-methylpentanoate)-3'-fluorophenyl-4''-phenoxy]alkyl]vinyl ethers ($DP_n = 4.0\text{--}16$, $pdi = 1.06\text{--}1.13$)¹³⁸ n -[(4'-(2R,3S)-2-fluoro-3-methylpentyloxycarbonyl)-3'-fluorophenyl-4''-phenoxy]alkyl]vinyl ethers ($DP_n = 4.5\text{--}27$, $pdi = 1.08\text{--}1.22$),¹³⁹ 8-[(4'-(2R(2S))-2-chloro-4-methylpentyloxycarbonyl)phenyl-4''-phenoxy]octyl]vinyl ethers ($DP_n = 3.9\text{--}15$, $pdi = 1.12\text{--}1.22$),¹⁴⁰ 8-[(4'-(2R(2S))-2-fluoro-4-methylpentyloxycarbonyl)phenyl-4''-phenoxy]octyl]vinyl ethers ($DP_n = 4.1\text{--}16$, $pdi = 1.11\text{--}1.33$)¹⁴¹ and 4-{2-[4'-(11-vinyloxyundecyloxy)biphenyl-4-yl]ethyl]benzo-15-crown-5 ($DP_n = 6\text{--}19$)¹⁴² were polymerized using triflic acid as the initiator and dimethyl sulfide as a deactivator in CH_2Cl_2 at 0°C.

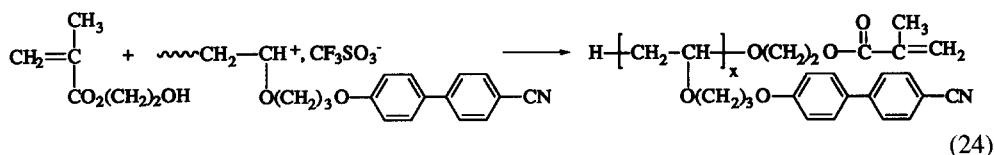
Although Webster *et al.* found that triflic acid/dimethyl sulfide initiated polymerizations of *t*-butylvinyl ether are not living at 0°C in CH_2Cl_2 ,¹⁰⁷ plots of the degree of polymerization vs $[M]_0/[I]_0$ demonstrate that transfer is usually not detectable at the molecular weights





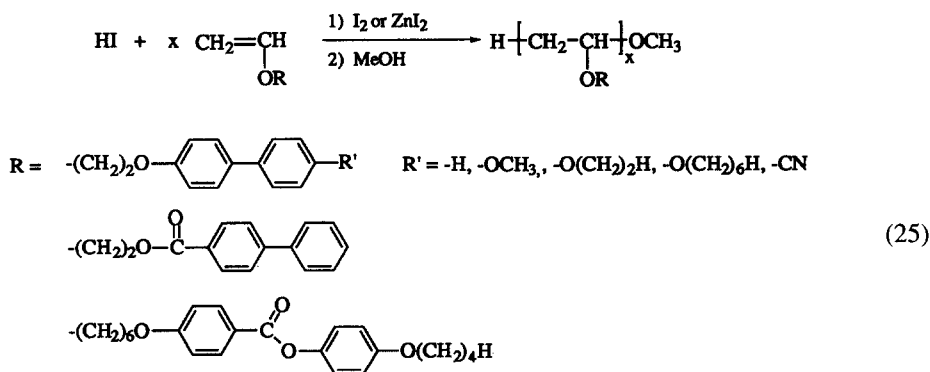
Scheme 13.

absent or barely detectable, respectively, for poly{11-[(4'-cyanophenyl-4''-phenoxy)undecyl]vinyl ether}s with $DP_n \leq 30$.¹⁴⁵ The ability to endcap growing polymers of 3-[(4'-4''-cyanophenyl)phenoxy]propyl]vinyl ether with 2-hydroxyethyl methacrylate [eqn (24)], 10-



undecene-1-ol and 2-[2'-(2''-allyloxyethoxy)ethoxy]ethanol also demonstrates that transfer and termination are negligible at low degrees of polymerization ($DP_n = 5-7$).¹⁴⁶

As shown in eqn (25), well-defined poly{(2-[(4'-biphenyloxy)ethyl]vinyl ether}s ($DP_n =$



22-50, $\text{pdi} = 1.2$),¹⁴⁷ poly{2-[(4'-*n*-alkoxyphenyl-4''-phenoxy)ethyl]vinyl ether}s ($DP_n = 7.0-24$, $\text{pdi} = 1.02-1.4$),^{147,148} poly{2-[(4'-cyanophenyl-4''-phenoxy)ethyl]vinyl ether}s ($DP_n = 4.9-28$, $\text{pdi} = 1.04-1.2$)¹⁴⁹ and poly{4-(2'-vinylloxyethyl)-4''-phenylbenzoate}s ($DP_n = 18-32$, $\text{pdi} = 1.2-1.3$)¹⁴⁷ were prepared using HI as the initiator and either I_2 or

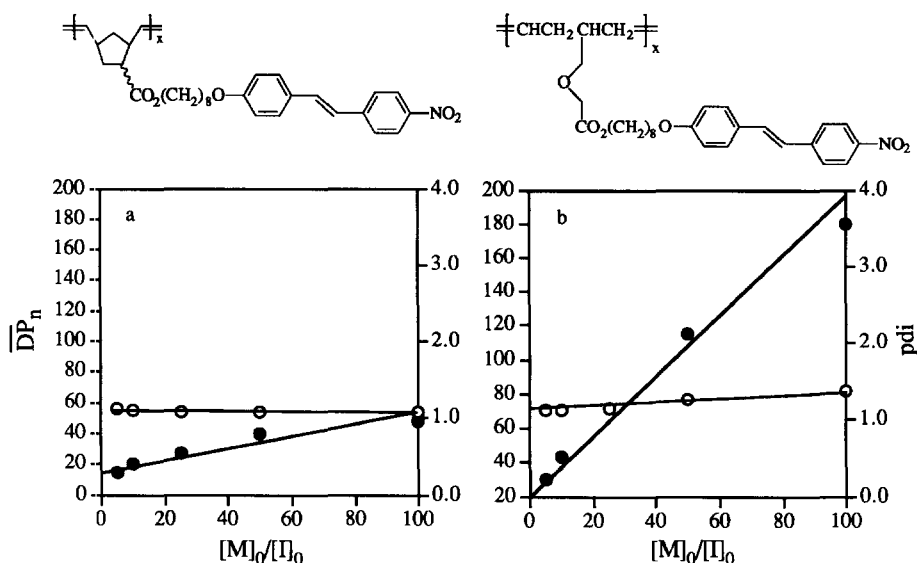


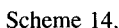
Fig. 6. Degree of polymerization (●) and polydispersity (○) resulting from ring-opening metathesis polymerizations of (a) 5-[[8'-(4''-(4'''-nitrostilbeneoxy)octyl)carbonyl]bicyclo[2.2.1]hept-2-ene and (b) poly{3-[[8'-(4''-(4'''-nitrostilbeneoxy)octyl)carbonyl]methyleneoxy)methyl]cyclobutene} initiated by $\text{RuCl}_2(\text{CHPh})(\text{PPh}_3)_2$ in CH_2Cl_2 at 25 and 45°C, respectively.¹⁸⁷

ZnI_2 as the catalyst in CH_2Cl_2 at -5°C . 6-[(4'-*n*-Butoxyphenyl-4''-benzoate)hexyl]vinyl ether ($DP_n = 7.6\text{--}38$, $pdi = 1.10\text{--}1.15$) was polymerized similarly using HI/I_2 , except that toluene was used as the solvent at -40°C .¹⁵⁰ Low molecular weight oligo(vinyl ether)s ($DP_n = 10\text{--}19$, $pdi = 1.07\text{--}1.22$) containing olefinic, nitro and cyano groups were also prepared in CH_2Cl_2 using residual H_2O as the initiator and AlCl_2Et as catalyst in presence of dimethyl sulfide at 0°C .^{151,152}

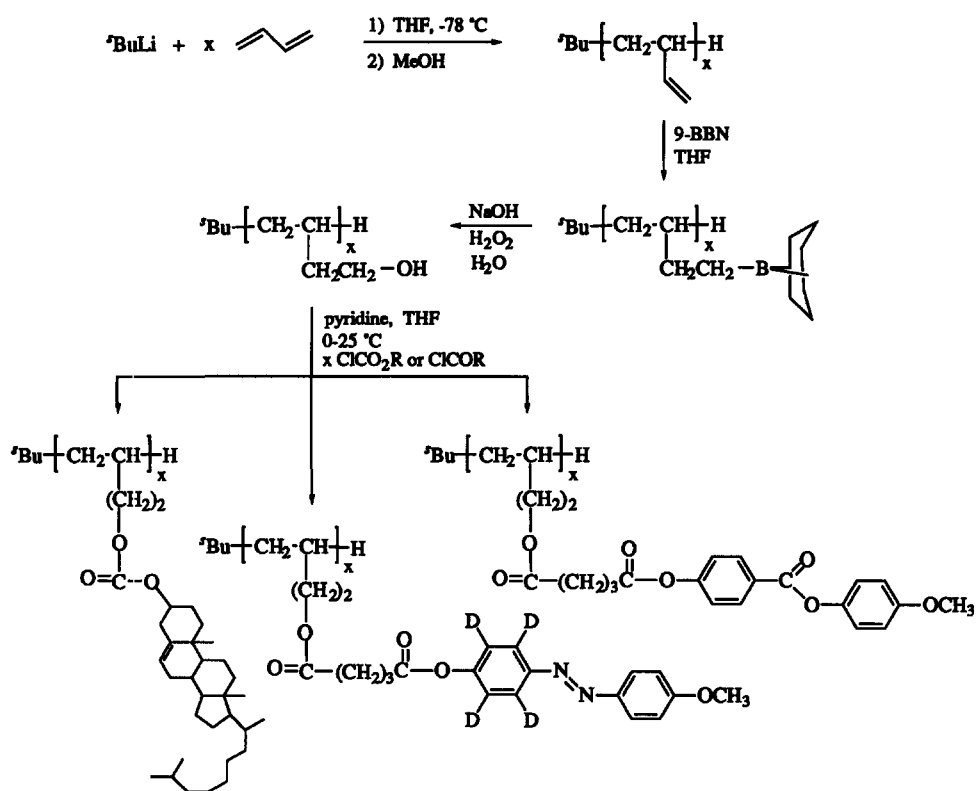
2.4. Ring-opening metathesis polymerizations^{7,153,154}

As outlined in Scheme 11, cycloolefins polymerize by ring-opening metathesis polymerization (ROMP) via a $[2 + 2]$ cycloaddition with a propagating metallaolefin to form a metallocyclobutane intermediate, which then ring opens to regenerate a metallaolefin at the terminus of the growing chain.^{153,154} The overall ring opening of the cyclic monomer therefore occurs by cleavage of the double bond. Since polymers with narrow molecular weight distributions are only obtained if propagation is irreversible ($k_p \gg k_d$), only highly strained cyclobutene derivatives and derivatives of the bicyclo[2.2.1]hept-2-ene ring system, including norbornenes, norbornadienes, 7-oxanorbornenes and 7-oxanorbornadienes, are candidates for controlled ROMP [eqn (26)].

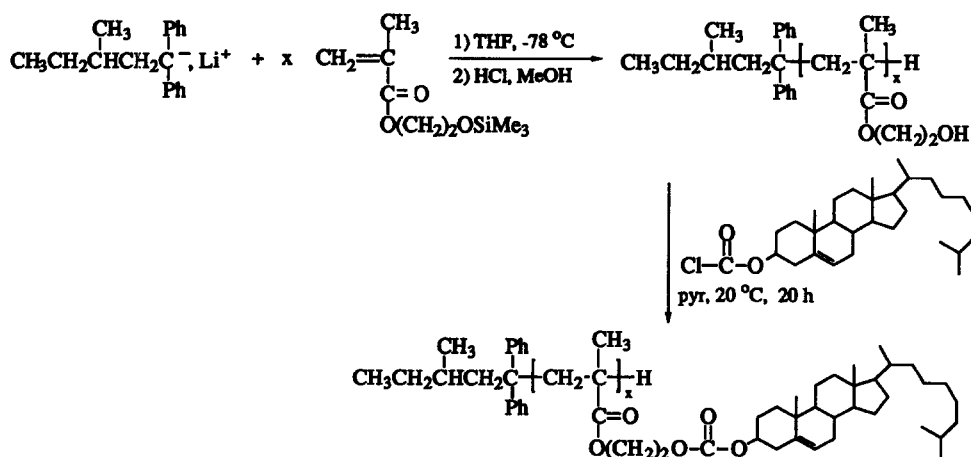




In addition to preventing spontaneous termination, increased stability of the metal center also minimizes chain transfer and other termination reactions. The elementary reactions



Scheme 15.



Scheme 16.

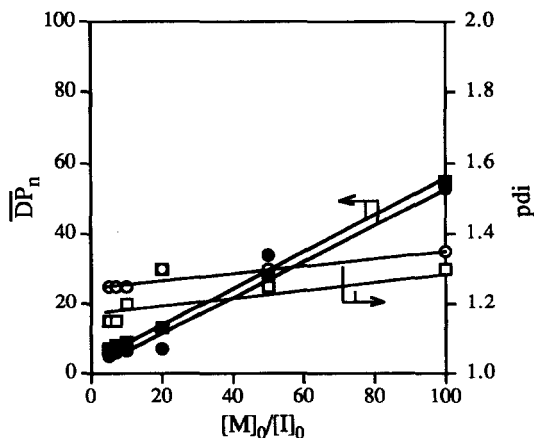


Fig. 7. Degree of polymerization (●,■) and polydispersity (○,□) of the precursor polymer resulting from the cationic polymerization of 6-chlorohexylvinyl ether (●,○) initiated by HI/I_2 in toluene at -40°C , and of the final poly{6-[(4'-*n*-ethoxy-4"-azobenzene)hexyl]vinyl ether}s prepared by polymer analogous reactions (■,□).²¹⁴

outlined in Scheme 11 demonstrate that each repeat unit of the polymer contains a double bond which may participate in secondary metathesis reactions. Therefore, the most troublesome chain transfer reaction to eliminate from ring-opening metathesis polymerizations is chain transfer to polymer. Intramolecular chain transfer to polymer results in macrocycle formation with elimination of a shorter linear chain endcapped with the metallaolefin (or metallacyclobutane). Intermolecular chain transfer to polymer results in randomization of the chain lengths and broadening of the molecular weight distribution to the most probable distribution ($\text{pdi} = 2$).

Secondary metathesis is prevented by using initiators which do not metathesize internal olefins. That is, if the metallaolefin or metallacyclobutane complex is reactive enough to metathesize an internal olefin, it is generally too reactive to obtain a living polymerization. As shown in Table 4, the reactivities and selectivities of the commonly used initiators correlate with their rates of metathesis of *cis*-2-pentene. In general, the reactivity increases and selectivity decreases with increasing electrophilicity of the metal center. This is determined by both the metal itself and the electronegativity of the ligands. For example, $\text{W}(\text{CH}^t\text{Bu})(\text{N}-2,6\text{-C}_6\text{H}_3\text{-}^i\text{Pr}_2)[\text{OCMe}(\text{CF}_3)_2]_2$ metathesizes *cis*-2-pentene at over 17 turnovers per second in toluene at 25°C, and therefore does not produce a well-defined polynorbornene.¹⁶⁴ In contrast, $\text{Mo}(\text{CH}^t\text{Bu})(\text{N}-2,6\text{-C}_6\text{H}_3\text{-}^i\text{Pr}_2)(\text{O}^t\text{Bu})_2$ metathesizes *cis*-2-pentene at only $\sim 2 \times 10^{-5}$ turnovers per second at 25°C and is therefore much more selective at producing well-defined polynorbornene.¹⁶⁶

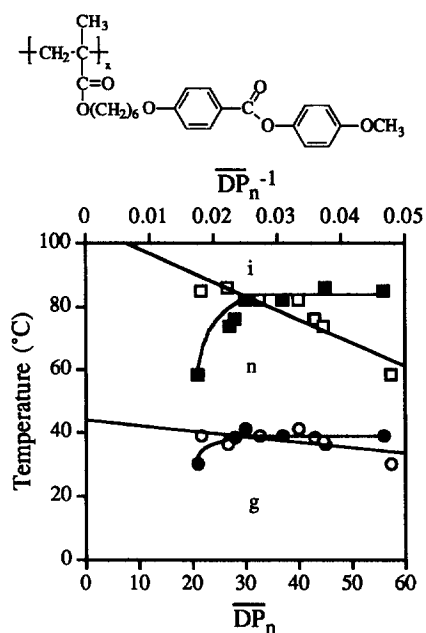


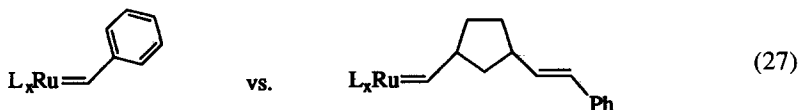
Fig. 8. Dependence of the glass (●,○) and nematic–isotropic (■,□) phase transition temperatures of syndiotactic $[(r) = 0.70\text{--}0.77]$ poly{6-[4'-(4''-methoxyphenoxy)carbonyl]-phenoxy]hexyl methacrylate} as a function of the number average degree of polymerization (●,■) and the inverse number average degree of polymerization (○,□).⁴⁵ Infinite molecular weight transitions: *g* 44 *n* 105 *i*.

These transfer reactions can also be minimized by working with bicyclic monomers such as norbornene derivatives, which generate polymers whose double bonds are sterically hindered and therefore resistant to secondary metathesis.¹⁵³ Polymerizations of cyclobutene monomers are less controlled than norbornene polymerizations because the double bonds in the resulting polymers are highly susceptible to secondary metathesis reactions. However, well-defined polymers of cyclobutene^{169,170} and methylcyclobutene^{171,172} are obtained by adding a Lewis base (PR₃) to W(CH^tBu)(N-2,6-C₆H₃-ⁱPr₂)(O^tBu)₂ initiated polymerizations, thereby decreasing the reactivity of the initiator and growing chain ends and increasing the rate of initiation relative to that of propagation. In addition, 3,3-¹⁷³ and 3,4-disubstituted^{174,175} cyclobutenes generate polymers with sterically hindered double bonds, and are therefore polymerized in a controlled manner using Mo(CH^tBu)(N-2,6-C₆H₃-ⁱPr₂)(O^tBu)₂ without an additive.

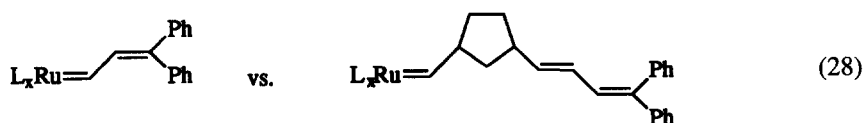
Molecular oxygen and sometimes the carbonyl groups of aldehydes, ketones, esters and amides terminate the active metallaolefin chain ends of all but the new ruthenium initiators. For example, reaction of the growing chain with molecular oxygen generates a metal oxide and an aldehyde terminated polymer (Scheme 11). The resulting aldehyde chain end can then react with the active end of another polymer chain to generate a second molecule of the metal oxide and a polymer of higher molecular weight.^{176,177} Since the rate of reaction with molecular oxygen is slower than the rate of propagation in polymerizations using the molybdenum and tungsten alkylidene initiators, it occurs at the end of the polymerization, resulting in a double molecular weight fraction.^{176,177}

Of the molybdenum and tungsten alkylidene initiators shown in Table 4, Mo(CH^tBu)(N-2,6-C₆H₃-ⁱPr₂)(O^tBu)₂ is the least reactive and therefore the most selective initiator for ROMP. Its polymerizations are endcapped with benzaldehyde, pivaldehyde and acetone (benzophenone is less efficient),⁷ although it tolerates a variety of non-protonic functional groups, including acetate, cyano, ethers, esters, phenyl benzoates, N-substituted imides and trifluoromethyl groups in both the monomer^{175,177–182} and endcapping¹⁸³ agent. With the exception of cyano groups,¹⁸⁴ ruthenium(II) complexes tolerate the same groups, as well as alcohols, aldehydes and ketones.¹⁶² These polymerizations are terminated with ethyl vinyl ether.

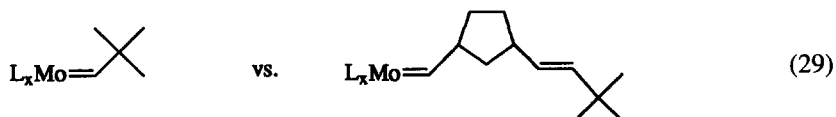
The final requirement for a controlled ring-opening metathesis polymerization is that the rate of initiation be greater than or equal to that of propagation. As shown in Table 5 for the most selective initiators, only the RuCl₂(CHAr)(PPh₃)₂ complexes initiate norbornene polymerizations faster than propagation occurs, thereby producing polymers with very narrow molecular weight distributions (pdi = 1.04–1.10).¹⁸⁵ Although one would expect the rate of initiation to be highest with benzylidenes substituted with electron-withdrawing groups (most electrophilic metal center), the electronic effect of the alkylidene substituents is obviously minor. The aryl alkylidene is therefore evidently less sterically demanding than the insertion product [eqn (27)]. In contrast, the low initiation rates of the ruthenium diphenyl-



vinyl alkylidenes produce polynorbornenes with polydispersities of approximately 1.25,¹⁸⁵ although the diphenylvinyl alkylidene appears to be less sterically demanding than the cyclopentylidene insertion product [eqn (28)]. Its lower reactivity was attributed to conjugation.¹⁸⁵ The rate constant of initiation using Mo(CH^tBu)(N-2,6-C₆H₃-ⁱPr₂)(O^tBu)₂ is also



slightly less than that of propagation, producing polynorbornenes with $\text{pdi} < 1.10$.¹⁸⁶ This is apparently because the neopentylidene ligand with a tertiary carbon β to the metal is more sterically demanding than the insertion products, which contain secondary carbons β to the metal [eqn (29)].



With one exception,¹⁸⁷ only mesogenic norbornenes have been used to prepare well-defined SCLCPs by a ring-opening metathesis mechanism. Norbornene monomers containing terminally attached *p*-methoxybiphenyl^{22,188–190} and *p*-cyanobiphenyl^{189–191} mesogens were polymerized using $\text{Mo}(\text{CH}^i\text{Bu})(\text{N}-2,6\text{-C}_6\text{H}_3\text{-}^i\text{Pr}_2)(\text{O}^i\text{Bu})_2$ as the initiator in order to determine the effect of molecular weight, polydispersity, flexible spacer length and mesogen density on

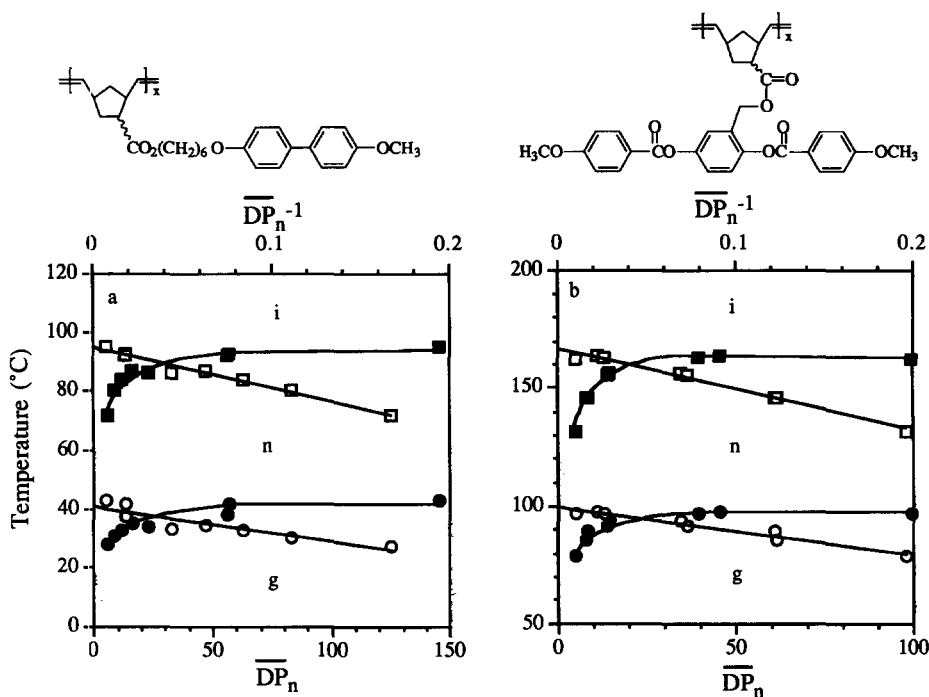


Fig. 9. Dependence of the glass (●,○) and nematic–isotropic (■,□) phase transition temperatures of (a) poly{5-[[6'-[4''-(4-methoxyphenyl)phenoxy]hexyl]carbonyl]bicyclo[2.2.1]hept-2-ene}²² and (b) poly{5-[[[2',5'-bis[(4''-methoxybenzoyl)oxy]benzyl]oxy]carbonyl]bicyclo[2.2.1]hept-2-ene}¹⁸² as a function of the number average degree of polymerization (●,■) and the inverse number average degree of polymerization (○,□). Infinite molecular weight transitions: (a) T_g 41 T_{ni} 95 i; (b) T_g 99 T_{ni} 167 i.

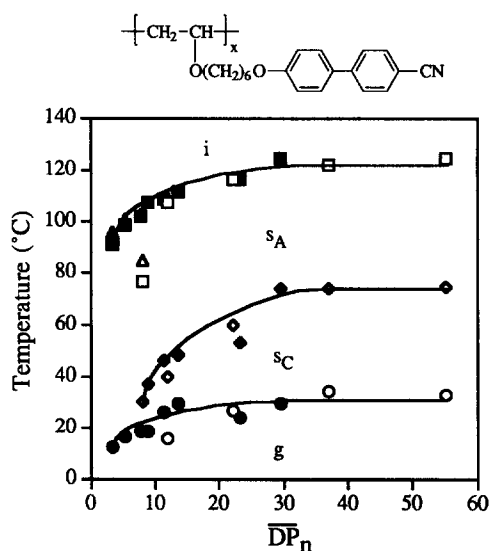


Fig. 10. Dependence of the transition temperatures from the glass (●,○), *s_C* (◆,◇), *s_A* (■,□) and nematic (▲,△) phases of poly{6-[(4'-cyanophenyl-4''-phenoxy)hexyl]vinyl ether} prepared by direct cationic polymerization (●,◆,■)¹²⁴ and by polymer analogous reactions (○,◇,□)^{212,213} as a function of the GPC-determined degree of polymerization. Infinite molecular weight transitions: *g* 31 *s_C* 81 *s_A* 122 *i*.

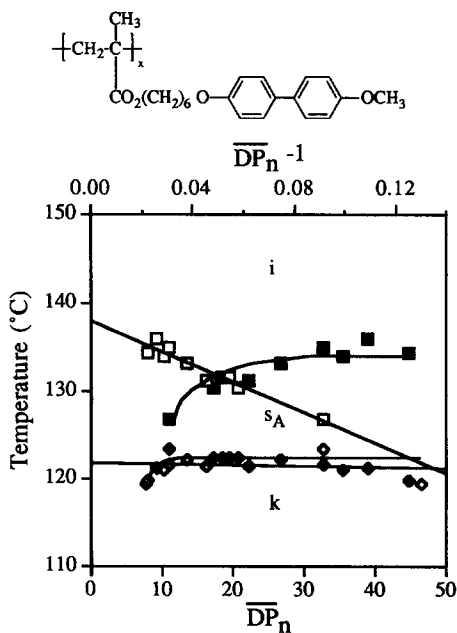
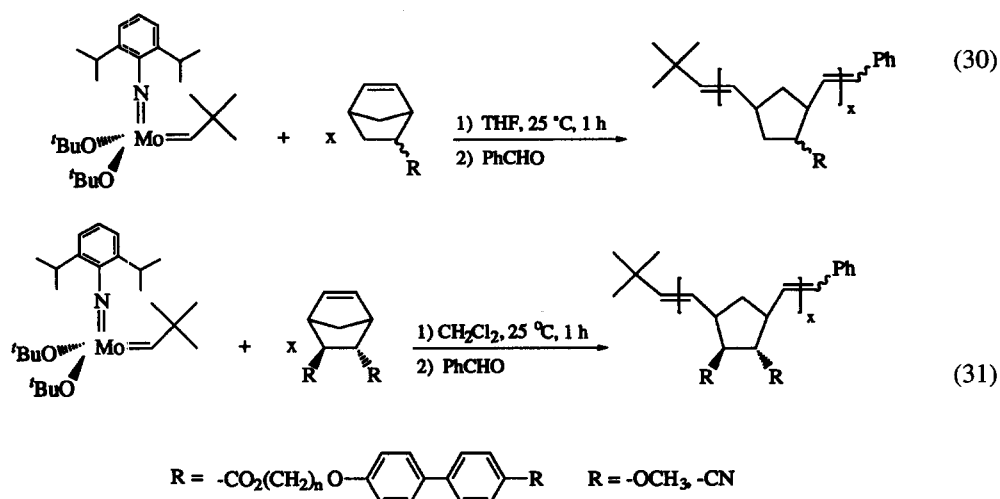


Fig. 11. Dependence of the transition temperatures from the crystalline (◆,◇) and *s_A* (■,□) phases of syndiotactic [(*rr*) = 0.80] poly[*n*-[4-(4'-methoxyphenyl)phenoxy]hexyl methacrylate] as a function of the number average degree of polymerization (◆,■) and the inverse number average degree of polymerization (◇,□).⁴⁴ Infinite molecular weight transitions: *k* 122 *s_A* 138 *i*.

the thermotropic behavior of SCLCPs with polynorbornene backbones [eqns (30) and (31)]. As



shown in Fig. 5a using a 5-[[*n*-[4'-(4"-methoxyphenyl)phenoxy]alkyl]carbonyl]bicyclo[2.2.1]hept-2-ene as an example, the GPC-determined number average degree of polymerization (relative to polystyrene) agrees well with the initial ratio of monomer to initiator. In this case, the degree of polymerization varied from 6 to 151, with polydispersities of 1.05–1.28.^{22,188} Polymerizations of 5-[[*n*-[4'-(4"-methoxyphenyl)phenoxy]alkyl]methyleneoxy]bicyclo[2.2.1]hept-2-enes ($DP_n = 9\text{--}342$, $pdi = 1.15\text{--}1.19$)¹⁸⁹ and 5-[[*n*-[4'-(4"-cyano-phenyl)phenoxy]alkyl]carbonyl]bicyclo[2.2.1]hept-2-ene ($DP_n = 7\text{--}290$, $pdi = 1.08\text{--}1.27$)¹⁸⁹ yielded similar results. The higher polydispersities were usually the result of a minor amount of a double molecular weight fraction in addition to the expected molecular weight due to insufficient degassing of molecular oxygen. Higher polydispersities were obtained in $\text{Mo}(\text{CH}^i\text{Bu})(\text{N}-2,6\text{-C}_6\text{H}_3\text{-}^i\text{Pr}_2)(\text{O}^i\text{Bu})_2$ and $\text{Mo}(\text{CH}^i\text{Bu})(\text{N}-2,6\text{-C}_6\text{H}_3\text{-}^i\text{Pr}_2)(\text{OCH}_3(\text{CF}_3)_2)_2$ initiated polymerizations of (\pm)-endo,exo-5,6-di[[*n*-[4'-(4-cyanophenyl)phenoxy]alkyl]carbonyl]bicyclo[2.2.1]hept-2-ene ($pdi = 1.21\text{--}1.60$)¹⁹¹ and (\pm)-endo,exo-5,6-di[[*n*-[4'-(4"-methoxyphenyl)phenoxy]alkyl]carbonyl]bicyclo[2.2.1]hept-2-ene ($pdi = 1.20\text{--}2.75$),¹⁹⁰ respectively, due to oxygen and monomer impurities [eqn (31)]. The degrees of polymerization ($DP_n = 41\text{--}266$) were substantially different from the attempted ratio of monomer to initiator ($[M]_0/[I]_0 = 100$), which were attributed to difficulties in actually controlling this ratio. Surprisingly, the "absolute" molecular weights determined using a GPC with a viscometry detector and a universal calibration curve were even higher, with degrees of polymerization ($DP_n = 87\text{--}372$) approximately twice those calculated relative to polystyrene.¹⁹¹

Several polynorbornenes with laterally attached mesogens have also been prepared using $\text{Mo}(\text{CHCMe}_2\text{Ph})(\text{N}-2,6\text{-C}_6\text{H}_3\text{-}^i\text{Pr}_2)(\text{O}^i\text{Bu})_2$ as the initiator in order to determine the effect of molecular weight,¹⁸² the effect of the length of the *n*-alkoxy substituent,^{182,192–197} as well as to design polymers with *s*_C mesophases by proper choice of the mesogen,^{192,193,196,197} and to test various concepts for inducing smectic layering in nematic liquid crystals (Scheme 12).^{192–195} In particular, polymerizations of both 5-[[[2',5'-bis[(4"-*n*-alkoxybenzoyl)oxy]benzyl]oxy]carbonyl]bicyclo[2.2.1]hept-2-enes ($DP_n = 5.1\text{--}168$, $pdi = 1.12\text{--}1.27$) and 5,8-bis[(4'-*n*-alkoxybenzoyl)oxy]-1,2,3,4-tetrahydronaphthalene ($DP_n = 40\text{--}101$, $pdi = 1.06\text{--}1.21$) are fairly

well controlled as demonstrated by the similar degrees of polymerization and $[M]_0/[I]_0$ (Fig. 5b), and by the polymers' narrow polydispersities.¹⁸² Polymerization of 5-[[[2',5'-bis[2-(3''-fluoro-4''-*n*-alkoxyphenyl)ethynyl]benzyl]oxy]carbonyl]bicyclo[2.2.1]hept-2-enes also results in the expected molecular weights ($DP_n = 39\text{--}76$, $pdi = 1.09\text{--}1.29$) at $[M]_0/[I]_0 \sim 50$.^{196,197} In this case, higher polydispersities result when the monomers are viscous oils which can not be purified by recrystallization. 5-[[[2',5'-Bis[(4''-*n*-((perfluoroalkyl)alkoxy)-benzoyl]oxy]benzyl]oxy]carbonyl]bicyclo[2.2.1]hept-2-enes were also polymerized by ROMP, although it was necessary to use higher temperatures (40°C) in order to prevent the polymer from precipitating out of solution during the polymerization; this broadens the polydispersity to $pdi \sim 1.5$.¹⁹⁵

Both norbornene and butene monomers containing terminally attached *p*-nitrostilbene mesogens were recently polymerized using $RuCl_2(CHPh)(PPh_3)_2$ as the initiator in order to determine the effect of molecular weight and flexibility of the polymer backbone on their thermotropic behavior (Scheme 13).¹⁸⁷ Although the polydispersities are quite narrow

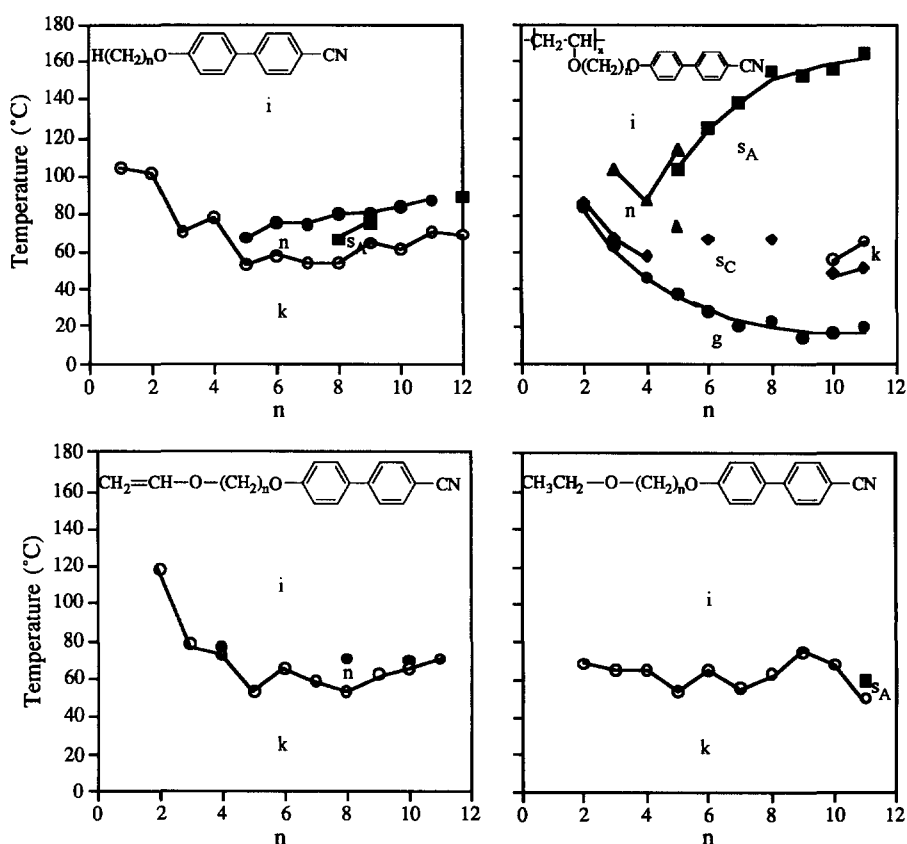


Fig. 12. Transition temperatures observed on heating 4-*n*-alkoxy-4'-cyanobiphenyls,²²⁸ poly[*n*-[(4'-(4''-cyanophenyl)phenoxy)alkyl]vinyl ether]s ($DP_n = 17\text{--}32$, $pdi = 1.09\text{--}1.21$),^{122–127,212,213} *n*-[(4'-(4''-cyanophenyl)phenoxy)alkyl]vinyl ethers^{122–127} and α -ethoxy- ω -(4-*n*-alkoxy-4'-cyanobiphenyl)s^{122–127} from the glassy (●), crystalline (○), s_C (◆), s_A (■) and nematic (▲) states.

Table 6. Thermotropic behavior of 4-*n*-alkoxy-4'-cyanobiphenyls,²²⁸ poly{*n*-[(4'-(4''-cyanophenyl)phenoxy)alkyl]vinyl ether}s ($DP_n = 17-32$, $pdi = 1.09-1.21$),^{122-127,212,213} *n*-[(4'-(4''-cyanophenyl)phenoxy)alkyl]vinyl ethers¹²²⁻¹²⁷ and α -ethoxy- ω -(4-*n*-alkoxy-4'-cyanobiphenyl)s.¹²²⁻¹²⁷

n

Thermotropic Behavior (°C)

$$\text{H}(\text{CH}_2)_n\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$$

$$\left[\text{CH}_2-\underset{\text{O}(\text{CH}_2)_n\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}}{\text{CH}} \right]_x$$

1	k 104	(n 86) i		
2	k 102	(n 91) i	g 81 × 86	i
3	k 71	(n 64) i	g 64 × 68	n 104 i
4	k 78	(n 76) i	g 47 × 58	n 88 i
5	k 53	n 68 i	g 38	n_{re} 69 s_A 104 n 115 i
6	k 58	n 76 i	g 29	s_C 67 s_A 125 i
7	k 54	n 75 i	g 21	s_A 139 i
8	k 54	s_A 67 n 80 i	g 23	s_C 67 s_A 155 i
9	k 65	s_A 76 n 80 i	g 14	s_A 152 i
10	k 61	n 84 i	g 17 k	56 (s_C 49) s_A 156 i
11	k 71	n 87 i	g 21 k	66 (s_C 52) s_A 165 i
12	k 69	s_A 89 i		

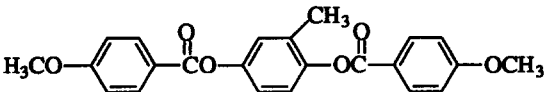
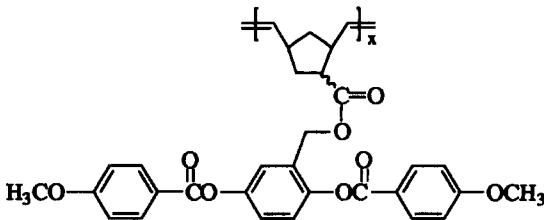
$$\text{CH}_2=\text{CH}-\text{O}-(\text{CH}_2)_n\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$$

$$\text{CH}_3\text{CH}_2-\text{O}-(\text{CH}_2)_n\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$$

2	k 118	i	k 69	i
3	k 79	i	k 65	i
4	k 73	n 77 i	k 65	(n 33) i
5	k 54	(n 39) i	k 54	(n 35) i
6	k 65	(n 60) i	k 65	(n 60) i
7	k 59	(n 54) i	k 56	(n 55) i
8	k 54	n 71 i	k 63	(s_A 58 n 61) i
9	k 63	(n 59) i	k 75	(s_A 41 n 50) i
10	k 65	n 70 i	k 69	(s_A 65) i
11	k 71	(s_A 61 n 71) i	k 69	s_A 60 i

($pdi = 1.07-1.11$), Fig. 6a shows that the molecular weight resulting from polymerizations of 5-{*n*-[4'-(4''-nitrostilbeneoxy)alkyl]carbonyl}bicyclo[2.2.1]hept-2-enes ($DP_n = 15-47$) using $\text{RuCl}_2(\text{CHPh})(\text{PPh}_3)_2$ as the initiator may be slightly less controlled than those using $\text{Mo}(\text{CHCMe}_2\text{R})(\text{N}-2,6-\text{C}_6\text{H}_3-\text{}^i\text{Pr}_2)(\text{O}^t\text{Bu})_2$ to polymerize norbornene monomers, although nitro groups do react slowly with the latter initiator.¹⁸³ That is, Fig. 5 demonstrates that the number average degree of polymerization of mesogenic polynorbornenes determined relative to polystyrene standards generally match $[M]_0/[I]_0$ quite closely. In contrast to the 5-{*n*-[4'-(4''-nitrostilbeneoxy)octyl]alkyl]carbonyl}bicyclo[2.2.1]hept-2-enes, Fig. 6b

Table 7. Thermotropic behavior of 2,5-bis[(4'-*n*-alkoxybenzoyl)oxy]toluenes²²⁸ and poly{5-[[[2',5'-bis[(4''-methoxybenzoyl)oxy]benzyl]oxy]carbonyl]bicyclo[2.2.1]hept-2-ene}s ($DP_n = 23-100$), $pdi = 1.12-1.24$.¹⁸²

<i>n</i>	Thermotropic Behavior (°C)		
			
			
1	k 166 n 252 i		g 98 n 164 i
2	k 187 n 248 i		g 92 n 172 i
3	k 138 n 209 i		g 83 n 140 i
4	k 115 n 206 i		g 73 n 138 i
5	k 90 n 178 i		g 60 n 123 i
6	k 88 n 173 i		g 56 n 126 i

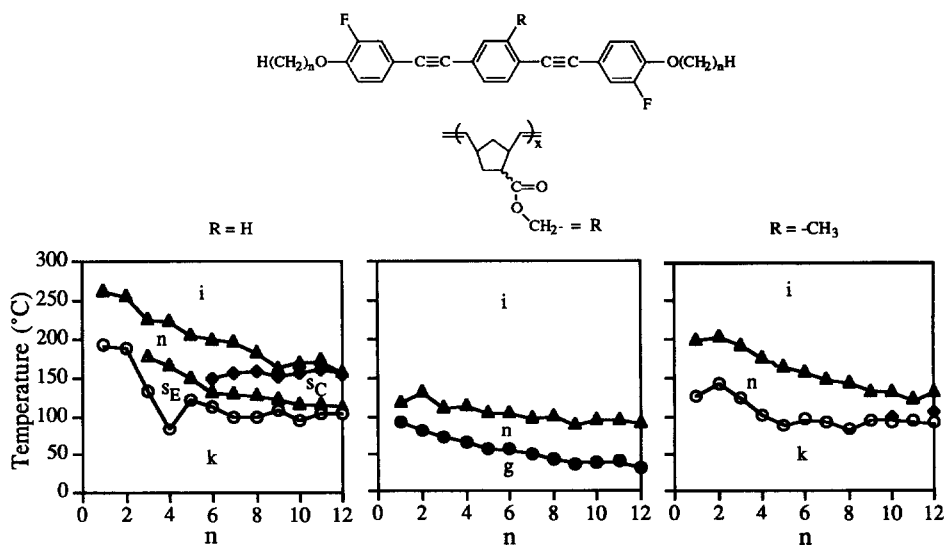


Fig. 13. Transition temperatures of 1,4-bis[(3'-fluoro-4'-*n*-alkoxyphenyl)ethynyl]benzenes,^{193,196} 1,4-bis[(3'-fluoro-4'-*n*-alkoxyphenyl)ethynyl]toluenes¹⁹⁶ and poly{5-[[[2',5'-bis[2-(3''-fluoro-4''-*n*-alkoxyphenyl)ethynyl]benzyl]oxy]carbonyl]bicyclo[2.2.1]hept-2-ene}s ($DP_n = 31-59$, $pdi = 1.09-1.60$);¹⁹⁷ from the glassy (●), crystalline (○), s_E (Δ), s_C (◆) and nematic (▲) states as a function of the length of the *n*-alkoxy substituents.

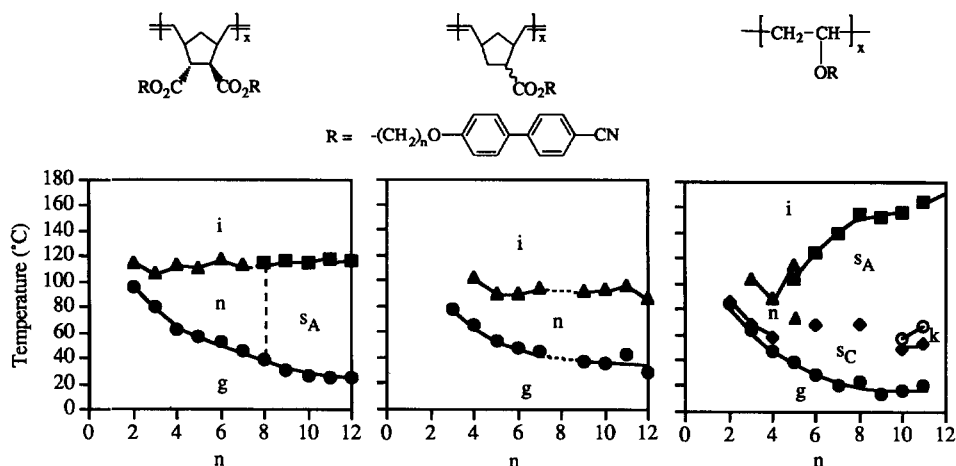


Fig. 14. Transition temperatures of poly{(±)-endo,exo-5,6-di{[*n*-[4'-(4"-cyanophenyl)phenoxy]alkyl]carbonyl}bicyclo[2.2.1]hept-2-ene}s ($DP_n = 41-266$, $pdi = 1.21-1.60$),¹⁹¹ poly{5-([*n*-[4'-(4"-cyanophenyl)phenoxy]alkyl]carbonyl}bicyclo[2.2.1]hept-2-ene}s ($DP_n = 43-290$, $pdi = 1.08-1.27$)¹⁸⁹ and poly{*n*-[4'-(4"-cyanophenyl)phenoxy]alkyl}vinyl ether}s ($DP_n = 17-32$, $pdi = 1.09-1.21$)^{122-127,212,213} as a function of the number of methylenic units in their *n*-alkyl spacers; from the glassy (●), crystalline (○), s_C (◆), s_A (■) and nematic (▲) states.

shows that polymerization of the corresponding cyclobutene monomers yield polymers with degrees of polymerizations which are from two to six times higher than $[M]_0/[I]_0$ ($DP_n = 30-72$, $pdi = 1.11-1.38$).

$\text{Mo}(\text{CHCMe}_2\text{Ph})(\text{N}-2,6\text{-C}_6\text{H}_3\text{-}^i\text{Pr}_2)(\text{O}^t\text{Bu})_2$ has also been used to prepare low molar mass liquid crystalline polyenes.¹⁹⁸

2.5. Polymer analogous reactions on well-defined precursor polymers

In order to synthesize homopolymers by polymer analogous reactions, the reaction must go to 100% conversion. Hydrosilations of mesogenic olefins are the most common polymer analogous reactions used to prepare SCLCPs.¹⁹⁹ However, the precursor poly(methyl siloxane)s are generally not prepared by living polymerizations, nor do the hydrosilations readily go to completion. Only recently has a communication appeared describing a well-defined side-chain liquid crystalline polysiloxane.²⁰⁰ As shown in Scheme 14, the precursor polysiloxane ($DP_n \sim [M]_0/[I]_0$, $pdi < 1.2$) was prepared by anionic ring-opening polymerization of pentamethylvinylcyclotrisiloxane using lithium trimethylsilanolate as the initiator in THF at 0°C, followed by termination with *t*-butyldimethylsilyl chloride. The resulting poly(dimethylsiloxane-co-methylvinylsiloxane) was functionalized by hydrosilation of the vinyl groups with the monoadduct of a mesogenic olefin and 1,1,3,3-tetramethylsiloxane. The thermotropic behavior of these (co)polymers has not been reported yet.

Polybutadiene was the first well-defined polymer used in a polymer analogous reaction to synthesize SCLCPs,²⁰¹⁻²⁰³ primarily for comparison to the corresponding block copolymers discussed in Section 4.1.1. As shown in Scheme 15, butadiene was polymerized by a living anionic mechanism using *n*-butyl lithium as the initiator in THF at -78°C to produce

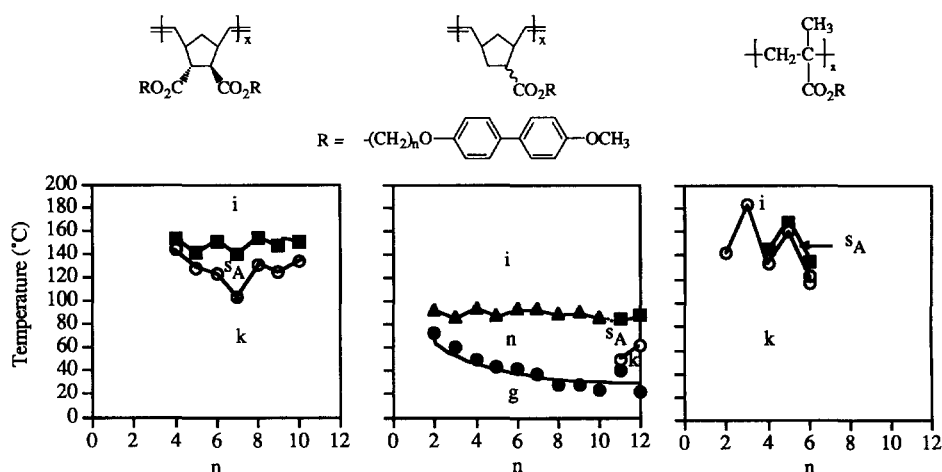


Fig. 15. Transition temperatures of (presumably) isotactic poly{[(\pm)-endo,exo-5,6-di{[n -[4'-(4"-methoxyphenyl)phenoxy]alkyl]carbonyl}bicyclo[2.2.1]hept-2-ene}s ($DP_n = 30$ –173, $pdi = 1.20$ –2.75),¹⁹⁰ poly{5-{[n -[4'-(4"-methoxyphenyl)phenoxy]alkyl]carbonyl}bicyclo[2.2.1]hept-2-ene}s ($DP_n = 72$ –151, $pdi = 1.05$ –1.28)^{22,188} and syndiotactic [(rr) = 0.79–0.86] poly{ n -[4'-(4"-methoxyphenyl)phenoxy]alkyl methacrylate}s ($DP_n = 19$ –33, $pdi = 1.14$ –2.08)^{42,44} as a function of the number of methylenic units in their n -alkyl spacers, from the glassy (●), crystalline (○), s_A (■) and nematic (▲) states.

poly(1,2-butadiene) ($DP_n = 1.1 \times 10^3$, $pdi = 1.10$). Poly{[(2-cholesterylloxycarbonyloxy)ethyl]ethylene}²⁰¹ ($pdi = 1.13$), poly{[4-(4'-methoxyphenylazo)(2'',3'',4'',6''-D₄)phenyl glutarate]ethylene}²⁰² ($pdi = 1.15$) and poly{[4-(4'-methoxyphenylcarbonyl)phenyl glutarate]ethylene}²⁰³ were then prepared by hydroboration of the remaining double bonds with 9-borabicyclo[3.3.1]nonane (9-BBN), followed by oxidation and formylation or esterification with the corresponding mesogenic chloroformate or acid chloride. Another cholesterol-containing polymer, poly[(2-cholesterylloxycarbonyloxy)ethyl methacrylate], was prepared by anionic polymerization of a protected hydroxyethyl methacrylate for comparison to the corresponding diblock and triblock copolymers (Section 4.1.1).^{204–210} As shown in Scheme 16, 2-(trimethylsiloxy)ethyl methacrylate was polymerized in THF at -78°C using 1,1-diphenyl-3-methylpentyl lithium as the initiator, which was generated *in situ* by reacting *t*-butyl lithium with 1,1-diphenylethylene. The trimethylsilyl protecting group was removed when the polymer was quenched and precipitated in acidic methanol. The resulting poly(2-hydroxyethyl methacrylate) block was then quantitatively functionalized with cholesterylchloroformate. Although the molecular weight distribution of poly[(2-trimethylsiloxy)ethyl methacrylate] is reported to be broad ($pdi = 1.30$) when polymerized under these conditions and narrow ($pdi = 1.08$) when polymerized in the presence of 10 equiv LiCl,²¹¹ the molecular weight distribution of the final poly[(2-cholesterylloxycarbonyloxy)ethyl methacrylate]s prepared in these studies varied from $pdi = 1.0$ –1.2 when $DP_n < 159$,^{204,208} and $pdi = 1.90$ when $DP_n = 461$.²⁰⁸

In contrast to the direct cationic polymerizations of mesogenic vinyl ethers discussed in Section 2.3, poly{ n -[(4'-cyanophenyl-4"-phenoxy)alkyl]vinyl ether}s can also be prepared by (quantitative) etherification of poly[n -(chloroalkyl)vinyl ether]s as shown in Scheme 17,^{212,213} with reportedly no change in the polydispersity ($pdi = 1.1$ –1.3) and only the

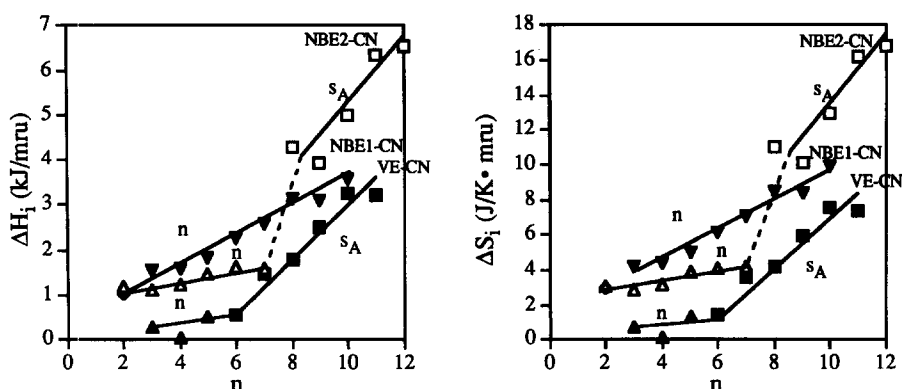


Fig. 16. Changes in enthalpy and entropy of isotropization from the nematic (Δ) and s_A (\square) mesophases of poly(\pm)-endo, exo-5,6-di{[n -[4'-(4''-cyanophenyl)phenoxy]alkyl]carbonyl}bicyclo[2.2.1]hept-2-ene}s (NBE2-CN, $DP_n = 41$ –266, $pdi = 1.21$ –1.60);¹⁹¹ from the nematic (∇) mesophase of poly{5-{[n -[4'-(4''-cyanophenyl)phenoxy]alkyl]carbonyl}bicyclo[2.2.1]hept-2-ene}s (NBE1-CN, $DP_n = 43$ –290, $pdi = 1.08$ –1.27);¹⁸⁹ and from the nematic (\blacktriangle) and s_A (\blacksquare) mesophases of poly{ n -[4'-(4''-cyanophenyl)phenoxy]alkyl}vinyl ether}s (VE-CN, $DP_n = 17$ –32, $pdi = 1.09$ –1.21)^{122–127} as a function of the number of methylenic units in their n -alkyl spacers.

expected increase in molecular weight. However, the more complete set of data plotted in Fig. 7 shows that the degrees of polymerization of poly(6-[4'-(4''-ethoxyphenyl)azo]phenoxyhexyl)vinyl ether}s and their precursor polymers are lower than expected from $[M]_0/[I]_0$.²¹⁴ In this case, the extent of grafting was less than quantitative at 80–97%.

SCLCPs have also been prepared by alkylation and/or quaternization of linear poly(ethylene imine)s^{215,216} and poly(4-vinylpyridine)s^{217–223} with mesogenic alkyl halides or carboxylic acids. Although these precursor polymers can be prepared by controlled cationic²²⁴ and anionic^{225,226} polymerizations, respectively, “living” polymerizations were either not used to prepare the SCLCPs, or the molecular weight and polydispersity data were

Table 8. Normalized²³² changes in enthalpy and entropy of isotropization per methylenic unit in the spacer of poly(\pm)-endo,exo-5,6-di{[n -[4'-(4''-cyanophenyl)phenoxy]alkyl]carbonyl}bicyclo[2.2.1]hept-2-ene}s (NBE2-CN),¹⁹¹ poly{5-{[n -[4'-(4''-cyanophenyl)phenoxy]alkyl]carbonyl}bicyclo[2.2.1]hept-2-ene}s (NBE1-CN),¹⁸⁹ poly{ n -[4'-(4''-cyanophenyl)phenoxy]alkyl}vinyl ether}s (VE-CN),^{122–127} poly(\pm)-endo,exo-5,6-di{[n -[4'-(4''-methoxyphenyl)phenoxy]alkyl]carbonyl}bicyclo[2.2.1]hept-2-ene}s (NBE2-MeO),¹⁹⁰ and poly{5-{[n -[4'-(4''-methoxyphenyl)phenoxy]alkyl]carbonyl}bicyclo[2.2.1]hept-2-ene}s (NBE1-MeO)^{22,188}

SCLCP	$\Delta\Delta H_i/-CH_2- (kJ/mru)$		$\Delta\Delta S_i/-CH_2- (J/K mru)$	
	nematic	smectic A	nematic	smectic A
NBE2-CN	0.044	0.28	0.12	0.70
NBE1-CN	0.051	[—]	0.14	[—]
VE-CN	0.058	0.28	0.14	0.62
NBE2-MeO	[—]	0.32	[—]	0.76
NBE1-MeO	0.038	[—]	0.11	[—]
mean	0.048 ± 0.008	0.29 ± 0.02	0.13 ± 0.02	0.69 ± 0.06

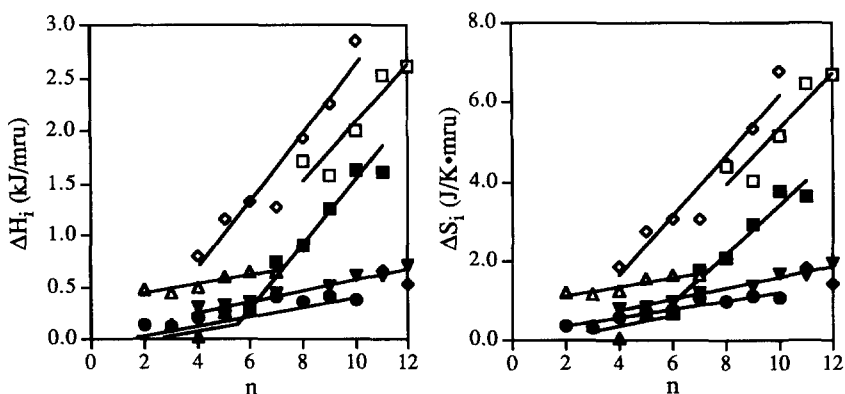


Fig. 17. Normalized²³² changes in enthalpy and entropy of isotropization from the nematic (Δ) and s_A (\square) mesophases of poly $\{(\pm)$ -endo,exo-5,6-di $\{[n$ -[4'-(4"-cyanophenyl)phenoxy]alkyl]carbonyl}bicyclo[2.2.1]hept-2-ene $\}$ s (NBE2-CN, $DP_n = 41$ –266, $pdi = 1.21$ –1.60);¹⁹¹ from the nematic (\blacktriangledown) mesophase of poly $\{5$ - $\{[n$ -[4'-(4"-cyanophenyl)phenoxy]alkyl]carbonyl}bicyclo[2.2.1]hept-2-ene $\}$ s (NBE1-CN, $DP_n = 43$ –290, $pdi = 1.08$ –1.27);¹⁸⁹ from the nematic (\blacktriangle) and s_A (\blacksquare) mesophases of poly $\{n$ - $\{[4'-(4"-cyanophenyl)phenoxy]alkyl\}$ vinyl ether $\}$ s (VE-CN, $DP_n = 17$ –32, $pdi = 1.09$ –1.21);^{122–127} from the s_A (\diamond) mesophase of poly $\{(\pm)$ -endo,exo-5,6-di $\{[n$ -[4'-(4"-methoxyphenyl)phenoxy]alkyl]carbonyl}bicyclo[2.2.1]hept-2-ene $\}$ s (NBE2-OMe, $DP_n = 30$ –173, $pdi = 1.20$ –2.75);¹⁹⁰ and from the nematic (\bullet) and s_A (\blacklozenge) mesophases of poly $\{5$ - $\{[n$ -[4'-(4"-methoxyphenyl)phenoxy]alkyl]carbonyl}bicyclo[2.2.1]hept-2-ene $\}$ s (NBE1-OMe, $DP_n = 72$ –151, $pdi = 1.05$ –1.28)^{22,188} as a function of the number of methylenic units in their n -alkyl spacers.

not reported for the precursor polymers and the resulting SCLCPs. These systems are therefore not discussed here.

3. STRUCTURE/PROPERTY CORRELATIONS DETERMINED USING “LIVING” POLYMERIZATIONS

3.1. The effect of molecular weight

The most basic and fundamental structure/property question that must be answered with any new system, especially one prepared by a living polymerization, is the molecular weight or degree of polymerization at which its thermotropic behavior no longer depends on the addition or subtraction of another repeat unit. (However, the isotropization enthalpy of SCLCPs is essentially molecular weight independent.) Comparisons of additional structural variables can then be made between samples whose thermotropic behavior is independent of molecular weight.

The thermal transitions of liquid crystalline polymethacrylates reach their limiting values at less than 50 repeat units. For example, Fig. 8 shows that the glass and nematic–isotropic transition temperatures of syndiotactic $[(rr) = 0.70$ – $0.77]$ poly $\{6$ -[4'-(4"-methoxyphenoxy-carbonyl)phenoxy]hexyl methacrylate $\}$ prepared by controlled anionic polymerization levels off at approximately 35 repeat units.⁴⁵ This is in contrast to the corresponding polymers prepared by radical polymerizations, which have transition temperatures that are substantially higher and level off at approximately 25 repeat units;⁴⁵ in addition to having different end

Table 9. Comparison of the thermotropic behavior of poly{6-[4'-(4''-*n*-butoxyphenoxy)carbonyl]phenoxy]hexyl methacrylate} and poly{6-[(4'-*n*-butoxyphenyl)-4''-benzoate]hexyl]vinyl ether}

Polymer Backbone	DP_n	pdi	Thermotropic Behavior (°C)	Ref.
methacrylate	19	1.13	$g\ 38\ s_A\ 104\ n\ 110\ i$	91
vinyl ether	38	1.15	$s\ 47\ s_C\ 106\ n\ 111\ i$	150

groups and perhaps branched architectures, the radically prepared polymers are also less syndiotactic [(*rr*) = 0.40–0.66]. However, Fig. 8 also plots the transition temperature(s) as a function of the inverse degree of polymerization in order to calculate the transition temperatures of an infinite molecular weight polymer from the intercepts. Although the transition temperatures plateau as a function of the degree of polymerization, they do not correspond to the transitions of an infinite molecular weight polymer, which is similar to that of the radically prepared polymers. Nevertheless, the rapid increase in transition temperatures upon going from $DP_n = 20$ to $DP_n = 30$ indicate that this discrepancy may be due simply to errors in the calculated molecular weight of the low molecular weight polymers, and therefore to an inaccurately high (absolute) slope used for the extrapolation.

The g - s_A - n - i transition temperatures of syndiotactic poly{6-[4'-(4''-*n*-butoxyphenoxy)carbonyl]phenoxy]hexyl methacrylate} prepared by aluminum porphyrin initiated polymerizations also level off at approximately 25 repeat units.⁹¹ Similarly, the glass and nematic–isotropic transition temperatures of poly[6-(4'-methoxy-4''- α -methylstilbeneoxy)hexyl methacrylate] prepared by group transfer polymerization become independent of molecular weight at approximately 20 repeat units.⁴⁸ Both polymethacrylates reach the same transition temperatures as the corresponding polymers prepared by radical polymerizations, which have nearly identical tacticities.

The thermotropic behavior of liquid crystalline polynorbornenes also reach their limiting values at 50 repeat units or less.^{22,182,188–190} For example, Fig. 9 demonstrates that the glass and nematic–isotropic transitions of both terminally and laterally attached systems level off at 25–50 repeat units, and correspond to the transition temperatures of the infinite molecular weight polymers. The same is true of the crystalline melting and smectic–isotropic transition temperatures of poly {(±)-endo, exo-5, 6-di{[*n*-[4'-(4''-methoxyphenyl)phenoxy]hexyl]carbonyl}bicyclo[2.2.1]hept-2-ene}.¹⁹⁰

Although most well-defined SCLCPs have been prepared by cationic polymerizations of mesogenic vinyl ethers, most of these studies did not prepare polymers of high enough molecular weight to prove that the transition temperatures had leveled off. For example, the highest molecular weight poly{6-[(4'-cyanophenyl)-4''-phenoxy]hexyl]vinyl ether} prepared by direct cationic polymerization contains approximately 30 repeat units.¹²⁴ Figure 10 compares the thermotropic behavior of these poly(vinyl ether)s to the same polymers prepared by polymer analogous^{212,213} reactions. The higher molecular weight polymers prepared by polymer analogous reactions confirm that the glass and isotropization transitions saturate at

approximately 30 repeat units, although the s_C – s_A transition has not leveled off yet. Similarly, the crystalline–nematic and nematic–isotropic transitions of poly{6-[4'-(4"-ethoxyphenylazo)phenoxyhexyl]vinyl ether} prepared by polymer analogous reactions reaches their limiting values at 27 repeat units.²¹¹

The systems shown in Figs 8 and 9 display very simple thermotropic behavior, with the same phase sequence observed at all molecular weights. However, Fig. 10 exemplifies systems in which the number and type of mesophases vary as a function of molecular weight. This is simply due to the phases having different dependencies on molecular weight. That is, the slope of the glass transition vs degree of polymerization of poly{6-[(4'-(4"-cyanophenyl)-4"-phenoxy)hexyl]vinyl ether} is less than that of the s_C – s_A transition; the smectic C mesophase is therefore observed only at higher molecular weights, whereas a nematic mesophase is observed only at very low molecular weights. Figure 11 shows a second example in which the s_A –isotropic transition temperature of syndiotactic poly{*n*-[4-(4'-methoxyphenyl)phenoxy]hexyl methacrylate} increases and levels off at approximately 30 repeat units, whereas the crystalline melting temperature is relatively constant.⁴⁴ In this case, the lowest molecular weight oligomer melts directly to the isotropic state. The crystalline melting of isotactic poly{*n*-[4'-(4"-methoxyphenyl)phenoxy]hexyl methacrylate} fractionated into samples with $DP_n = 16$ –133 (pdi = 1.16–1.24) is also essentially constant (3.4°C variation).⁴²

As explained by Percec and Keller,²²⁷ the temperature range of at least the highest temperature mesophase therefore increases with increasing polymer molecular weight due to the greater dependence of isotropization on the degree of polymerization compared to crystalline melting and the glass transition. This is due to a greater decrease in entropy and increase in free energy of the isotropic liquid with increasing molecular weight compared to that of the more ordered phases.

3.2. The effect of the mesogen

The extensive literature on low molar mass liquid crystals demonstrates that specific mesogens (specific chemical structures) tend to form specific mesophases, which vary somewhat with the length of the flexible substituent. We therefore expect that the type of mesogen, including the terminal substituent(s) and the length of the spacer should be the primary factors determining the specific mesophase(s) exhibited by a given SCLCP. The nature of the polymer backbone, tacticity, polydispersity, etc. should then be secondary factors in enhancing, altering or disrupting the natural ordering of the mesogenic side chains.

If the mesogen and the length of the spacer are the primary factors determining the specific mesophase(s) exhibited by a given SCLCP, then its thermotropic behavior should be predictable by comparison to an appropriate model compound. Three possibilities for an appropriate model compound are shown in Table 6 and Fig. 12 using poly{*n*-[(4'-(4"-cyanophenyl)phenoxy)alkyl]vinyl ether}s^{122–127,212,213} as an example. Not surprisingly, the monomers themselves, which contain olefin endgroups that are very different from the chemical structure of the polymer backbone, are the least appropriate model compounds for poly{*n*-[(4'-(4"-cyanophenyl)phenoxy)alkyl]vinyl ether}s. That is, the polymer exhibits enantiotropic nematic mesophases at spacer lengths of $n = 3$ –5 and enantiotropic smectic A mesophases at spacer lengths of $n = 5$ –12. In addition, enantiotropic and monotropic s_C mesophases are sometimes observed, as well as a higher ordered phase. In contrast, the monomer forms a s_A mesophase only at $n = 11$, which is monotropic; the nematic mesophases observed at $n = 4$ –11 are also primarily monotropic.

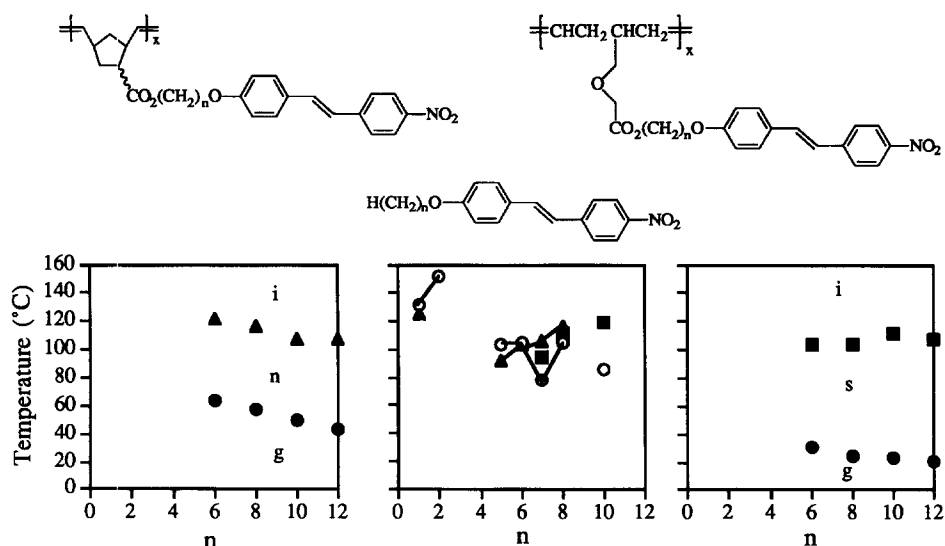


Fig. 18. Transition temperatures from the glass (●), crystalline (○), nematic (▲) and smectic (■) phases of poly{5-[*n*-(4'-nitrostilbeneoxy)alkyl]carbonyl}bicyclo[2.2.1]-hept-2-ene}s ($DP_n = 27-42$, $pdi = 1.08-1.11$),¹⁸⁷ 4-*n*-alkoxy-4'-nitro(stilbene)²²⁸ and poly{3-[[*n*-(4'-nitrostilbeneoxy)alkyl]carbonyl]methylenoxy)methylcyclobutene}s ($DP_n = 61-72$, $pdi = 1.14-1.16$)¹⁸⁷ as a function of the number of methylenic carbons in their *n*-alkyl spacers.

The more obvious choice for a model compound corresponds to exactly one repeat unit of the polymer. The α -ethoxy- ω -(4-*n*-alkoxy-4'-cyanobiphenyl)s exhibit nematic mesophases at $n = 4-9$ and s_A mesophases at $n = 8-11$, and therefore match the thermotropic behavior of the polymer better than the vinyl ether monomers. However the s_A mesophase is enantiotropic only at $n = 11$, and the nematic mesophase is monotropic at all of these spacer lengths. Compounds which take into account only the mesogen and spacer are also good, if not better, models of the polymers. In contrast to the ethyl ethers, all of the s_A and most of the nematic mesophases are enantiotropic, which means that the melting temperature mimics the relative temperature of the glass transition of the polymer backbone better. However, the nematic mesophase still appears at $n = 6-11$, and the s_A mesophase does not appear at $n = 5-7, 10, 11$. Nevertheless, the poly(vinyl ether)s and all of these model compounds demonstrate that liquid crystals based on cyanobiphenyl mesogens tend to form nematic and s_A mesophases.

Model compounds which take into account only the mesogen and spacer also mimic the thermotropic behavior of laterally attached SCLCPs well. For example, Table 7 demonstrates that both 2,5-bis[(4'-*n*-alkoxybenzoyl)oxy]toluenes²²⁸ and all corresponding SCLCPs, such as polynorbornenes,¹⁸² laterally attached through a one carbon spacer with 2,5-bis[(4'-*n*-alkoxybenzoyl)oxy]benzene mesogens exhibit only nematic mesophases. (However, Section 5 will demonstrate that smectic layering can be induced in these SCLCPs and their low molar mass analogs by terminating the mesogen's *n*-alkoxy substituents with immiscible fluoro-carbon segments.¹⁹³⁻¹⁹⁵)

In order to determine whether or not the alkyl substituent is necessary for low molar mass liquid crystals to mimic the thermotropic behavior of laterally attached SCLCPs, both

Table 10. Changes in enthalpy and entropy of isotropization of poly{(±)endo,exo-5,6-di{[*n*-[4'-(4"-cyanophenyl)phenoxy]alkyl]carbonyl}bicyclo[2.2.1]hept-2-ene}s (NBE2-CN),¹⁹¹ poly{5-[[*n*-[4'-(4"-cyanophenyl)phenoxy]alkyl]carbonyl}bicyclo[2.2.1]hept-2-ene}s (NBE1-CN),¹⁸⁹ poly{*n*-[(4'-(4"-cyanophenyl)phenoxy)alkyl]vinyl (VE-CN) ethers.¹²²⁻¹²⁷

SCLCP	<i>n</i>	Δ <i>H</i> _i (kJ/mru)	Δ <i>S</i> _i (J/K mru)	<i>T</i> _i (°C)	Mesophase
NBE2-CN	4	0.492	1.27	114	nematic
NBE1-CN	4	0.312	0.830	103	
VE-CN	4	0.0314	0.0870	104	
NBE2-CN	5	0.596	1.56	110	
NBE1-CN	5	0.322	0.884	91	
VE-CN	5	0.262	0.675	115	
NBE2-CN	9	1.58	4.05	116	smectic A
VE-CN	9	1.26	2.96	152	
NBE2-CN	10	2.00	5.17	115	
VE-CN	10	1.63	1.70	156	
NBE2-CN	11	2.53	6.46	118	
VE-CN	11	1.61	1.68	165	

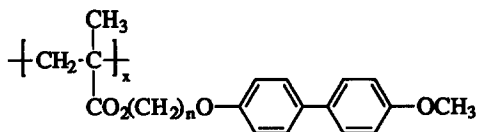
1,4-bis[(3'-fluoro-4'-*n*-alkoxyphenyl)ethynyl]benzenes^{193,196} and 1,4-bis[(3'-fluoro-4'-*n*-alkoxyphenyl)ethynyl]toluenes¹⁹⁶ were synthesized and their thermotropic behavior compared to that of poly{5-[[2',5'-bis[2-(3"-fluoro-4"-*n*-alkoxyphenyl)ethynyl]benzyl]oxy]carbonyl}-bicyclo[2.2.1]hept-2-ene}s.¹⁹⁷ As shown in Fig. 13, the 1,4-bis[(3'-fluoro-4'-*n*-alkoxyphenyl)ethynyl]benzenes exhibit a *s_E-s_C-n-i* phase sequence when *n* = 6–12. In contrast, the polymers exhibit only nematic mesophases. The 1,4-bis[(3'-fluoro-4'-*n*-alkoxyphenyl)ethynyl]benzenes are therefore not appropriate model compounds for these polynorbornenes, evidently because they do not take the benzylic spacer into account. In contrast, the corresponding 1,4-bis[(3'-fluoro-4'-*n*-alkoxyphenyl)ethynyl]toluenes mimic the polynorbornene's thermotropic behavior quite well. For example, Fig. 13 demonstrates that a *s_E* mesophase is not observed at any substituent length, whereas an enantiotropic *s_C* mesophase is observed over a very narrow temperature range when *n* = 10,12; the *s_C* mesophase is monotropic when *n* = 11.

Further comparisons to appropriate model compounds and the effect of increased mesogen density are discussed in the next sections.

3.3. The effect of the spacer

Increasing the spacer length has much the same effect on the thermotropic behavior of SCLCPs as increasing the length of the flexible substituent has on that of low molar mass liquid crystals. That is, it destabilizes some phases and stabilizes others. For example, just as increasing the length of the flexible substituent depresses the melting point of low molar mass liquid crystals, increasing the spacer length depresses the glass transition of SCLCPs, and consequently often uncovers mesophase(s) that are not observed without a spacer. Therefore, many of the first SCLCPs synthesized with the mesogen directly attached to the polymer backbone did not exhibit liquid crystallinity.² It was only after Finkelmann *et al.* introduced the spacer concept in 1978,²²⁹ that SCLCPs were synthesized routinely. Rather than simply suppressing the glass transition and/or crystalline melting, they attributed the spacer concept

Table 11. Comparison of the thermotropic behavior of isotactic and syndiotactic poly{*n*-[4'-(4"-methoxyphenyl)phenoxy]alkyl methacrylate}s.



<i>n</i>	GPC			%		Phase Transitions (°C)	Ref.
	<i>DP_n</i>	pdi	(mm)	(mr)	(rr)		
2	37	2.35	94	6	0	<i>k</i> 193 <i>i</i>	42
2	23	1.43	2	19	79	<i>k</i> 142 <i>i</i>	42
3	68	2.80	97	3	0	<i>k</i> 147 <i>i</i>	42
3	33	2.08	5	12	83	<i>k</i> 183 <i>i</i>	42
4	24	3.22	95	4	1	<i>k</i> 141 <i>i</i>	42
4	26	1.23	2	12	86	<i>k</i> 133 <i>s_A</i> 145 <i>i</i>	42
5	36	14.0	96	3	1	<i>k</i> 145 <i>i</i>	42
5	19	1.57	2	18	80	<i>k</i> 160 <i>s_A</i> 167 <i>i</i>	42
6	20	2.21	90	9	1	<i>k</i> 136 <i>i</i>	42
6	28	1.41	1	14	85	<i>k</i> 116 <i>s_A</i> 131 <i>i</i>	42
6	33	1.14	—	—	~80	<i>k</i> 122 <i>s_A</i> 135 <i>i</i>	44

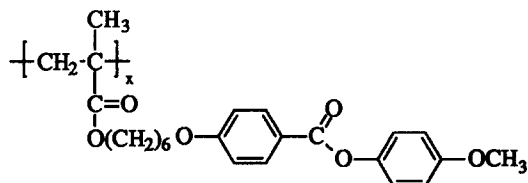
to a decoupling of the motions of the mesogens, which want to order anisotropically, from that of the polymer backbone, which tends to adopt a random coil conformation. However, neutron scattering experiments have demonstrated that the polymer backbone is deformed in both nematic and smectic mesophases, and that it is therefore impossible to completely decouple its motions from those of the mesogens to which it is chemically linked.²³⁰

In spite of the number of well-defined SCLCPs described in Section 2, only a few poly(vinyl ether)s and polynorbornenes have been synthesized with a complete and homologous set of spacer lengths. Figure 14 plots the phase diagrams of three polymers with terminally attached 4-(4'-cyanophenyl)phenoxy mesogens as a function of the spacer length; Fig. 15 plots the corresponding phase diagrams of three polymers terminally attached with 4-(4'-methoxyphenyl)phenoxy mesogens. Both figures demonstrate that the glass transition decreases as the length of the spacer increases. This is due to decreased packing density, and is often referred to as internal plasticization.

The temperature of crystalline melting of tactic SCLCPs also decreases as the spacer length increases (Fig. 15), albeit in an odd-even alternation as in low molar mass liquid crystals as a function of the length of the flexible substituent. However, without additional order within the polymer backbone itself due to high tacticity (Section 3.4 and 3.5), the mesogenic side chains are generally not able to crystallize until the spacer is sufficiently long. Therefore, both poly{*n*-[4'-(4"-cyanophenyl)phenoxy]alkyl}vinyl ether}s¹²²⁻¹²⁷ (Fig. 14) and poly{5-[[*n*-[4'-(4"-methoxyphenyl)phenoxy]alkyl]carbonyl}bicyclo[2.2.1]hept-2-ene}s¹⁸⁸ (Fig. 15) undergo side-chain crystallization only when *n* ≥ 10, or when polymers with slightly shorter spacers are of low molecular weight.

Depending on the specific mesogen, the nematic mesophase of low molar mass liquid crystals is generally destabilized by increasing substituent length, whereas smectic mesophases tend to be stabilized.²²⁸ That is, long alkyl or alkoxy substituents favor smectic

Table 12. Comparison of the thermotropic behavior of poly[6-[4'-(4"-methoxyphenoxy)carbonyl]phenoxy]hexyl methacrylate} with different tacticities



Polymerization Mechanism	GPC		%			Phase Transitions (°C)	Ref.
	DP_n	pdi	(mm)	(mr)	(rr)		
Radical	48	1.51	—	41	59	g 39 s_A 71 n 107 i	45
Radical	84	3.65	1	34	65	g 40 n 107 i	90
Radical	290	3.10	—	34	66	g 38 n 112 i	45
Radical	953	1.23	—	—	—	g 41 s_A 72 n 111 i	248
GTP	42	1.71	—	44	50	g 42 n 107 i	47
Anionic	37	1.24	—	28	72	g 39 n 82 i	45
(TPP)AlMe ^a	21	1.31	—	28	72	g 38 s_A 64 n 105 i	90
(TPP)AlMe-ALC ^b	30	1.43	—	22	78	g 40 n 107 i	90

^aMethyl(5,10,15,20-tetraphenylporphinato)aluminum.

^bMethyl(5,10,15,20-tetraphenylporphinato)aluminum and methylaluminum bis(2,4-di-^tbutylpheno-
late).

mesophases, whereas short substituents favor nematic mesophases. Figures 14 and 15 confirm that long spacers also favor smectic mesophases, and that short spacers favor nematic mesophases. These plots also seem to confirm that the transition temperature of nematic disordering decreases slightly with increasing spacer length in SCLCPs, whereas that of the s_A mesophase tends to increase, with at least a slight odd–even alternation. Nevertheless, since the glass transition temperature decreases more rapidly than isotropization with increasing spacer length, the temperature window over which these mesophase(s) are observed increases.

Figure 16 shows the change in enthalpy and entropy as a function of the length of the spacer for the three polymer series plotted in Fig. 14. It demonstrates that both the change in enthalpy and entropy of isotropization from the nematic and s_A mesophases increase linearly with increasing spacer length. Although such increases in ΔH_i and ΔS_i have been attributed to more efficient decoupling of the mesogen from the polymer backbone and therefore to increased order,²³¹ it simply corresponds to a constant increase in ΔH_i and ΔS_i per methylenic unit, and therefore to the disordering of an additional $-\text{CH}_2-$ unit of the spacer. The slope of these lines ($\Delta\Delta H_i/-\text{CH}_2-$ and $\Delta\Delta S_i/-\text{CH}_2-$) are nearly equivalent for both nematic and smectic disordering, respectively, of poly{[(±)-endo, exo-5,6-di{[n-[4'-(4"-cyanophenyl)phenoxy]alkyl]carbonyl}bicyclo[2.2.1]hept-2-ene} and poly(n-[(4'-(4"-cyanophenyl)phenoxy)alkyl]vinyl ether)}, and are half those values of poly{5-[[n-[4'-(4"-cyanophenyl)phenoxy]alkyl]carbonyl}bicyclo[2.2.1]hept-2-ene} since the latter has half as many mesogenic side chains. Therefore, if the mesogen density is taken into account for the

four amorphous polymer series plotted in Figures 14 and 15,²³² $\Delta\Delta H_i/-\text{CH}_2-$ and $\Delta\Delta S_i/-\text{CH}_2-$ are equivalent for the same mesophase (Fig. 17, Table 8), regardless of the type of polymer [poly(vinyl ether), mono- and di-substituted polynorbornene] and regardless of the mesogen [4-4'-cyanophenyl)phenoxy and 4-(4'-methoxyphenyl)phenoxy mesogens].

As expected, Figs 16 and 17 and Table 8 also demonstrate that the enthalpy and entropy of isotropization from the more ordered smectic mesophase is higher than those from the nematic phase. This discontinuity and/or change in the slope with a change in the type of mesophase can therefore be used as additional confirmation that a phase change has occurred with the addition or subtraction of one methylenic unit in the spacer of a homologous series.

The effect of varying the nature of the spacer from hydrocarbon to siloxane is starting to be investigated using living polymerizations.²⁸ However, these polymers have not been characterized yet.

3.4. The effect of the nature of the polymer backbone

Since the effect of the nature of the polymer backbone has not been studied extensively using well-defined polymers, it is worth summarizing the observations from less controlled systems based on comparisons of poly(phosphazene), poly(methylsiloxane), poly(vinyl ether), poly(acrylate), poly(methacrylate), poly(chloroacrylate) and polystyrene backbones.²³³⁻²⁴¹ In general, the mesogen is more "decoupled" from the polymer backbone as the latter's flexibility increases. This is because the dynamics of ordering increase with increasing flexibility, which increases the ability of the mesogenic side-chains to form more ordered mesophases and/or crystallize. (The relative dynamics of these SCLCPs correlate directly with the speed with which they form identifiable microscopic textures between crossed polarizers.²³⁵) In addition, the side chains are able to crystallize at shorter spacer lengths as the polymer flexibility increases.²³⁶⁻²³⁸ Therefore, SCLCPs with extremely flexible backbones may form only a monotropic or virtual mesophase, whereas an analogous polymer with a more rigid backbone is more likely to form an enantiotropic mesophase. However, as the flexibility of the backbone increases, the glass transition temperature usually decreases, whereas that of (melting and) isotropization typically increase. Additional mesophases may therefore be revealed if the glass transition is low enough, and if the mesophase is thermodynamically stable relative to the crystalline phase.

Secondary structural variables, including the nature of the polymer backbone, will only be elucidated by synthesizing complete and homologous series of well-defined polymers. As discussed previously, only a few of the poly(vinyl ether)s, polynorbornenes and polymethacrylates contain both identical mesogens and spacers. These systems confirm the above trends. For example, when (4'-*n*-butoxyphenoxy)carbonyl)phenoxy mesogens are attached to polymethacrylate and poly(vinyl ether) backbones through an *n*-hexyl spacer, the more flexible poly(vinyl ether) forms a highly ordered s_F or s_I mesophase with no evidence of a glass transition (Table 9). In contrast, the less flexible polymethacrylate is glassy. Otherwise, both have nearly identical mesophases and transition temperatures, except poly{6-[(4'-*n*-butoxyphenyl-4''-benzoate)hexyl]vinyl ether} forms a s_C mesophase (X-ray evidence) in addition to the nematic mesophase, whereas poly{6-[4'-(4''-*n*-butoxyphenoxy)carbonyl)phenoxy]hexyl methacrylate} reportedly forms a s_A mesophase in the same temperature range.

Comparison of the phase diagrams plotted in Fig. 14 of poly{5-[[*n*-(4'-(4''-cyanophenyl)-phenoxy]alkyl)carbonyl]bicyclo[2.2.1]hept-2-ene}s¹⁸⁹ and poly{n-[(4'-(4''-cyanophenyl)-

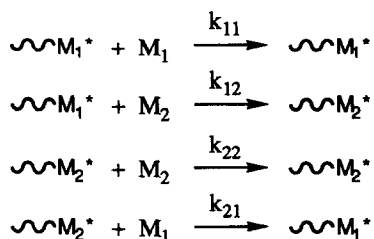
RANDOM	poly(A- <i>ran</i> -B)	AABAABBBABBAABABAABB
BLOCK	poly(A- <i>block</i> -B)	AAAAAAAAAABBBBBBBBBB
ALTERNATING	poly(A- <i>alt</i> -B)	ABABABABABABABABABA
GRAFT	poly(A- <i>graft</i> -B)	AAAAAAAAAAAAAAAAAAAAAA BBBB BBBB BBBB BBBB

Scheme 18.

phenoxy]alkyl]vinyl ether}s^{122-127,212,213} which contain a single mesogen per repeat unit demonstrates that the glass transition temperature decreases as the flexibility of the polymer backbone increases from polynorbornene to poly(vinyl ether), whereas the isotropization temperature increases. In addition to revealing additional mesophases at lower temperatures, this increase in polymer flexibility enables the poly(vinyl ether)s to form more ordered mesophases. That is, poly{5-([*n*-[4'-(4"-cyanophenyl)phenoxy]alkyl]carbonyl)-bicyclo[2.2.1]hept-2-ene} exhibits only a nematic mesophase at all spacer lengths, whereas the corresponding poly(vinyl ether) exhibits s_A and s_C mesophases with increasing spacer lengths, and also undergoes side chain crystallization at spacer lengths of 10–11 carbons, (at which point the s_C mesophase becomes monotropic).

When the polynorbornene is substituted with two mesogens rather than one, the internal mobility of the chain should not change, although its overall flexibility and free volume should decrease. As shown in Fig. 14, doubling the mesogen density has very little effect on the glass transition, but causes an increase in the temperature of isotropization, especially at longer spacer lengths. Increasing the mesogen density also enables the mesogens to form smectic layers when the spacer length reaches eight carbon atoms, which is typical of SCLCPs terminally attached with cyano-substituted mesogens.²

Since the glass transition of a polymer is determined not only by the polymer flexibility, but also by the packing density (free volume), the interactions between chains and the chain length, it is difficult to assess the relative flexibility of two polymers from the glass transition alone. Therefore, it is not immediately obvious from the glass transitions of syndiotactic poly(methyl methacrylate) (105°C) and polynorbornene (43°C) which of the two backbones are more flexible. That is, although polynorbornene has the lower T_g , the double bonds and



Scheme 19.

cyclopentane ring along the backbone should be more constrained than the single bonds along a polymethacrylate backbone.

The phase diagrams of syndiotactic $[(rr) = 0.79-0.86]$ poly $\{n\text{-}[4'-(4''\text{-methoxyphenyl})\text{-phenoxy}]\text{alkyl methacrylate}\}$,^{42,44} poly $\{5\text{-}\{[n\text{-}[4'-(4''\text{-methoxyphenyl})\text{-phenoxy}]\text{alkyl}\}\text{-carbonyl}\}\text{bicyclo}[2.2.1]\text{hept-2-ene}\}$,^{22,188} and poly $\{(\pm)\text{-endo,exo-5,6-di}\{[n\text{-}[4'-(4''\text{-methoxyphenyl})\text{-phenoxy}]\text{alkyl}\}\text{carbonyl}\}\text{bicyclo}[2.2.1]\text{hept-2-ene}\}$ ¹⁹⁰ were plotted in Fig. 15. Assuming that the polynorbornene backbone is more rigid than the polymethacrylate backbone, increasing the backbone flexibility increases the ability of the side chains to form more ordered mesophases and crystallize at shorter spacer lengths as expected. However, the more ordered side chains of the poly $\{n\text{-}[4'-(4''\text{-methoxyphenyl})\text{-phenoxy}]\text{alkyl methacrylate}\}$ s may also be due to their high tacticity as discussed in Section 3.5.

Increasing the mesogen density from one to two mesogenic groups per repeat unit of the polynorbornene backbone again allows the side chains to organize into smectic layers. However, in this case, $\text{Mo}(\text{CH}'\text{Bu})(\text{N-2,6-C}_6\text{H}_3\text{-}^i\text{Pr}_2)(\text{OCH}_3(\text{CF}_3)_2)_2$ was used as the initiator to polymerize the $(\pm)\text{-endo,exo-5,6-di}\{[n\text{-}[4'-(4''\text{-methoxyphenyl})\text{-phenoxy}]\text{alkyl}\}\text{-carbonyl}\}\text{bicyclo}[2.2.1]\text{hept-2-ene}$ s instead of $\text{Mo}(\text{CH}'\text{Bu})(\text{N-2,6-C}_6\text{H}_3\text{-}^i\text{Pr}_2)(\text{O}'\text{Bu})_2$.¹⁹⁰ $\text{Mo}(\text{CH}'\text{Bu})(\text{N-2,6-C}_6\text{H}_3\text{-}^i\text{Pr}_2)(\text{OCH}_3(\text{CF}_3)_2)_2$ polymerizes $(\pm)\text{-endo,exo-5,6-}[\text{disubstituted}]\text{bicyclo}[2.2.1]\text{hept-2-ene}$ s to produce isotactic polymers with approximately 85% *cis* double bonds, whereas the corresponding $\text{Mo}(\text{CH}'\text{Bu})(\text{N-2,6-C}_6\text{H}_3\text{-}^i\text{Pr}_2)(\text{O}'\text{Bu})_2$ polymerizations produce atactic polymers with approximately 95% *trans* double bonds.²⁴² Therefore, the poly $\{(\pm)\text{-endo,exo-5,6-di}\{[n\text{-}[4'-(4''\text{-methoxyphenyl})\text{-phenoxy}]\text{alkyl}\}\text{carbonyl}\}\text{bicyclo}[2.2.1]\text{hept-2-ene}\}$ s shown in Fig. 15 are presumably highly isotactic and able to undergo side-chain crystallization, in contrast to the atactic poly $\{(\pm)\text{-endo,exo-5,6-di}\{[n\text{-}[4'-(4''\text{-cyanophenyl})\text{-phenoxy}]\text{alkyl}\}\text{carbonyl}\}\text{bicyclo}[2.2.1]\text{hept-2-ene}\}$ s presented in Fig. 14. Although a more ordered mesophase is formed by the more tactic polymers, the increased ability of the side chains to crystallize also results in much narrower temperature ranges over which the liquid crystalline phase is observed.

A final example demonstrating that more ordered phases are possible when more flexible polymer backbones are used is shown in Fig. 18. Although this is not a complete series with

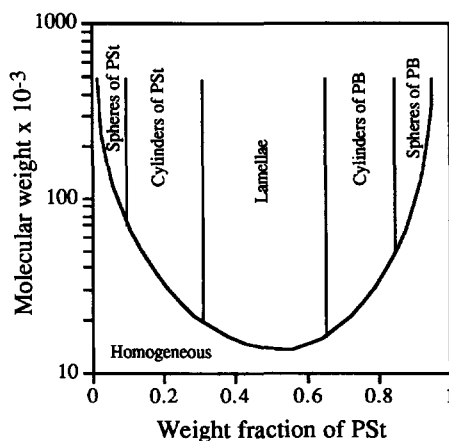


Fig. 19. Morphology of poly(styrene-*block*-butadiene) as a function of molecular weight and composition.²⁵

consecutive spacer lengths, it does demonstrate that the more flexible polybutadiene backbone allows *n*-[4'-(4"-nitrostilbeneoxy)alkyl] side chains with 6–12 carbons in the spacer to organize into smectic layers, whereas the corresponding polynorbornenes exhibit only nematic mesophases.¹⁸⁷ This is especially interesting since the corresponding low molar mass liquid crystals transform from a monotropic nematic phase when the alkoxy substituent contains six carbons, to an enantiotropic smectic and nematic sequence at 7–8 carbons, and finally to only enantiotropic smectic at 10 carbons.²²⁸ The corresponding polymers with less than six carbons in the spacer (as well as the rest of the series) should therefore be synthesized and characterized to determine to what extent the polymer backbone overrides the natural ordering tendency of the side chains.

As discussed in Section 3.3, the change in enthalpy and entropy of isotropization increases linearly with increasing spacer length. The slopes of these lines ($\Delta\Delta H_i/(-CH_2-)$ and $\Delta\Delta S_i/(-CH_2-)$) therefore correspond to the disordering of one methylenic unit of the spacer, and are evidently equivalent for a given mesophase if they are normalized²³² over the mesogen density. This is true regardless of the type of polymer [polynorbornene or poly(vinyl ether)] and regardless of the mesogen (*p*-cyanobiphenyl or *p*-methoxybiphenyl). Since the slope of the normalized changes in enthalpy and entropy of isotropization are equivalent for a specific mesophase, the degree of order of at least the spacer, and presumably the mesogen, within a specific mesophase must be equivalent for the five polymer series summarized in Fig. 17 and Table 8. However, the different absolute values (e.g. the intercepts) of these lines indicate that the disordering of the spacer is not independent of the rest of the polymer, and instead varies with the polymer backbone to which it is chemically linked.

The data in Table 10 demonstrates that for a constant spacer length and mesophase, both the change in enthalpy and entropy of isotropization decrease as the flexibility of the polymer backbone increases from polynorbornene to poly(vinyl ether). However, the change in entropy decreases more rapidly than the change in enthalpy, and the isotropization temperature ($T_i = \Delta H_i/\Delta S_i$) therefore increases with increasing flexibility. Since lower entropies of fusion are associated with more rigid structures, the lower entropy of isotropization of poly(vinyl ether)s is obviously not due to a lack of inherent flexibility of its polymer backbone, but rather to the more flexible backbone being more ordered and therefore more constrained (anisotropic) within the mesophase, as was recently demonstrated by neutron scattering experiments.²³⁰

3.5. The effect of tacticity

The effects of tacticity were first observed and discussed in 1981.^{243–245} However, relatively little effort has been made in examining the effect of tacticity on well-defined SCLCPs prepared through living polymerizations. Although these limited results are contradictory, we believe that trends are emerging which indicate that high tacticity in SCLCPs will cause either of two effects. In most systems, the high tacticity evidently places the mesogenic side groups in the proper configuration to crystallize and/or form more ordered mesophases. However, if the mesogenic groups are not in the proper configuration to form ordered phases, the primary effect of increasing the tacticity is to decrease the flexibility of the polymer backbone relative to that of the atactic polymer.

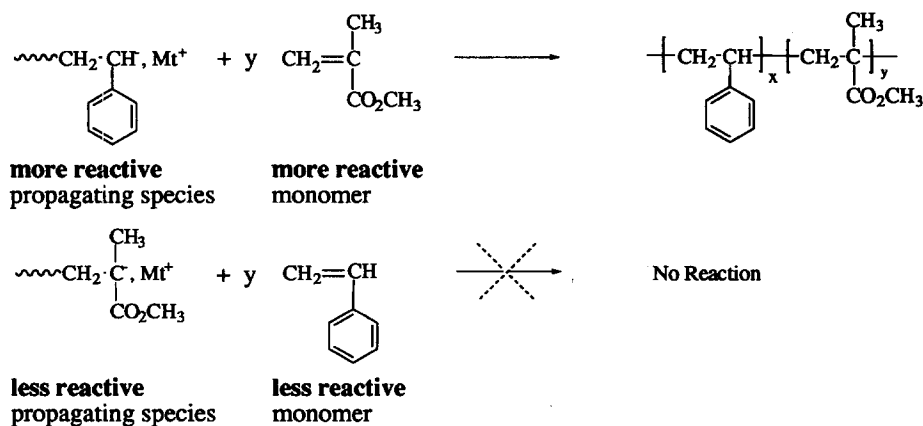
Discussion of the effect of the polymer backbone in Section 3.4 already provided examples of highly isotactic poly{(±)-endo,exo-5,6-di{[*n*-[4'-(4"-methoxyphenyl)phenoxy]alkyl]-

Table 13. Monomer and propagating anion's reactivity in anionic polymerizations

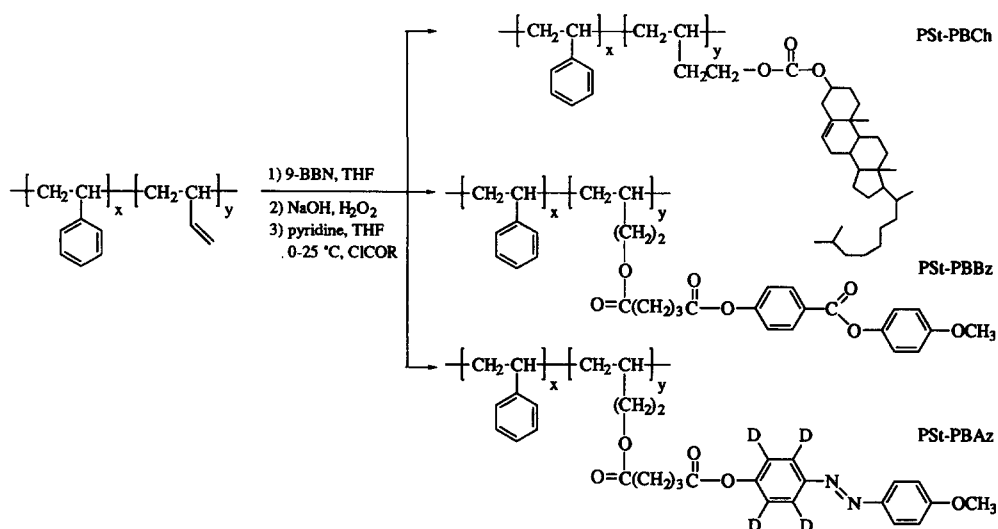
Monomer	pK _a	Ref.
Styrenes	41–42	25
Dienes	43	25
2-Vinyl Pyridine	29	304
Methacrylic Esters	27–28	25
Acrylonitrile	32	25
4-Vinyl Pyridine	26	304
Vinyl Ketones	19	25
Oxiranes	16–18	25
Thiiranes	12–13	25
Siloxanes	10–14	25
Cyanoacrylates	11–13	25
Nitroalkanes	10–14	25
Lactones	4–5	25

carbonyl}bicyclo[2.2.1]hept-2-ene}s¹⁹⁰ and syndiotactic poly{*n*-[4'-(4"-methoxyphenyl)phenoxy]alkyl methacrylate}s^{42,44} which crystallize and form more ordered mesophases than those of the corresponding atactic polymers (Fig. 15). Although more flexible backbones are more able to achieve the conformations necessary to order, the side chains are evidently already attached to the polymer backbone of these tactic polymers with the proper configuration to order, which obviates the need to distort their conformation for such purposes.

As discussed in Section 2.1, isotactic poly{*n*-[4'-(4"-methoxyphenyl)phenoxy]alkyl methacrylate}s have also been prepared, although the isotactic polymerizations are much less controlled than the syndiotactic polymerizations.^{42,44} The thermotropic behavior of both the isotactic and syndiotactic poly{*n*-[4'-(4"-methoxyphenyl)phenoxy]alkyl methacrylate}s is summarized in Table 11. All of the tactic polymers crystallize. With the exception of poly{2-[4'-(4"-methoxyphenyl)phenoxy]ethyl methacrylate} (*n* = 2), the melting temperature of the isotactic polymers is almost independent of the spacer length. In contrast, the



Scheme 20.

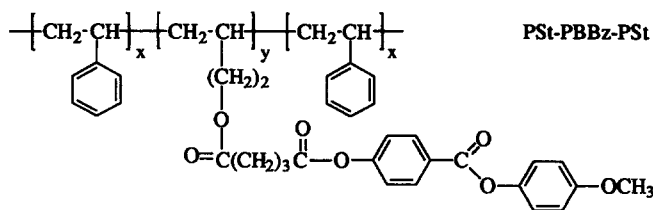


Scheme 21.

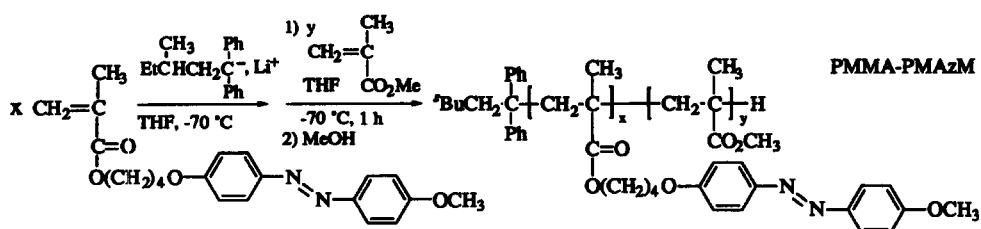
syndiotactic polymers melt with a large odd–even alternation. However, only the syndiotactic polymers with at least four carbons in the spacer exhibit an enantiotropic smectic mesophase, which occurs over only a very narrow temperature range. The greater order of the isotactic polymers is evidently due to the greater segmental mobility of isotactic vs syndiotactic polymethacrylate backbones.^{246,247}

Surprisingly, the mesogenic groups of syndiotactic [(*rr*) = 0.70–0.78] poly{6-[4'-(4"-methoxyphenoxy)carbonyl]phenoxy]hexyl methacrylate}s are not in the proper configuration to crystallize,^{45,90} and the primary effect is therefore that of decreased flexibility compared to the atactic polymer. As discussed in Section 3.4, more rigid backbones suppress side-chain crystallization and the formation of more ordered mesophases. In addition, the glass transition temperature increases whereas that of isotropization tends to decrease.

However, as shown in Table 12, the glass transition temperature of poly{6-[4'-(4"-methoxyphenoxy)carbonyl]phenoxy]hexyl methacrylate} is essentially independent of tacticity. With the exception of the polymer prepared by anionic polymerization,⁴⁵ the nematic–isotropic transition also appears to be independent of tacticity. However, as demonstrated by the data in Fig. 8, the extrapolated transition temperatures (*g* 44 *n* 105 *i*) of an infinite molecular weight polymer prepared by anionic polymerization are nearly identical to those of the rest of the polymers presented in Table 12.



Scheme 22.



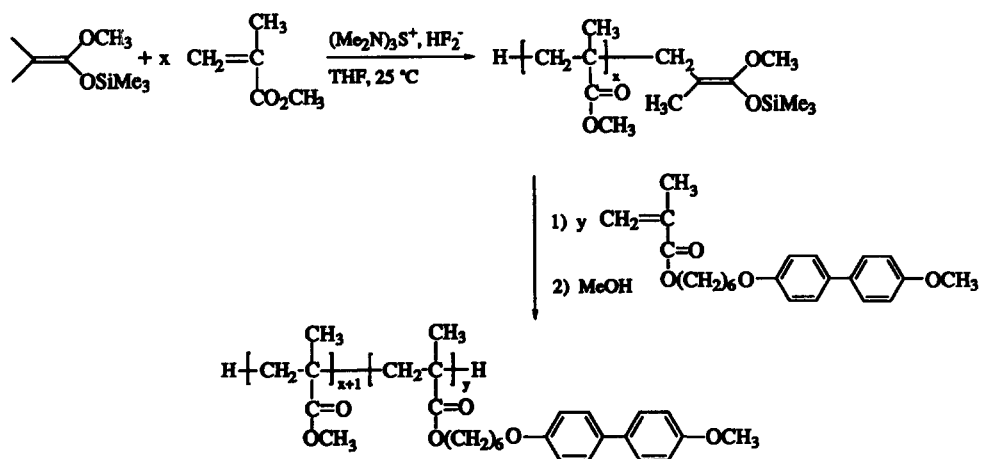
Scheme 23.

Although the more ordered s_A mesophase is not detected in two of the three more syndiotactic poly{6-[4'-(4''-methoxyphenoxy)hexyl methacrylate]}s, it is also not detected in some of the less tactic polymers prepared by free radical and group transfer polymerizations. These results are therefore inconclusive as to whether or not increasing syndiotacticity and decreasing flexibility suppresses the formation of the more ordered s_A mesophase in poly{6-[4'-(4''-methoxyphenoxy)hexyl methacrylate]}s.

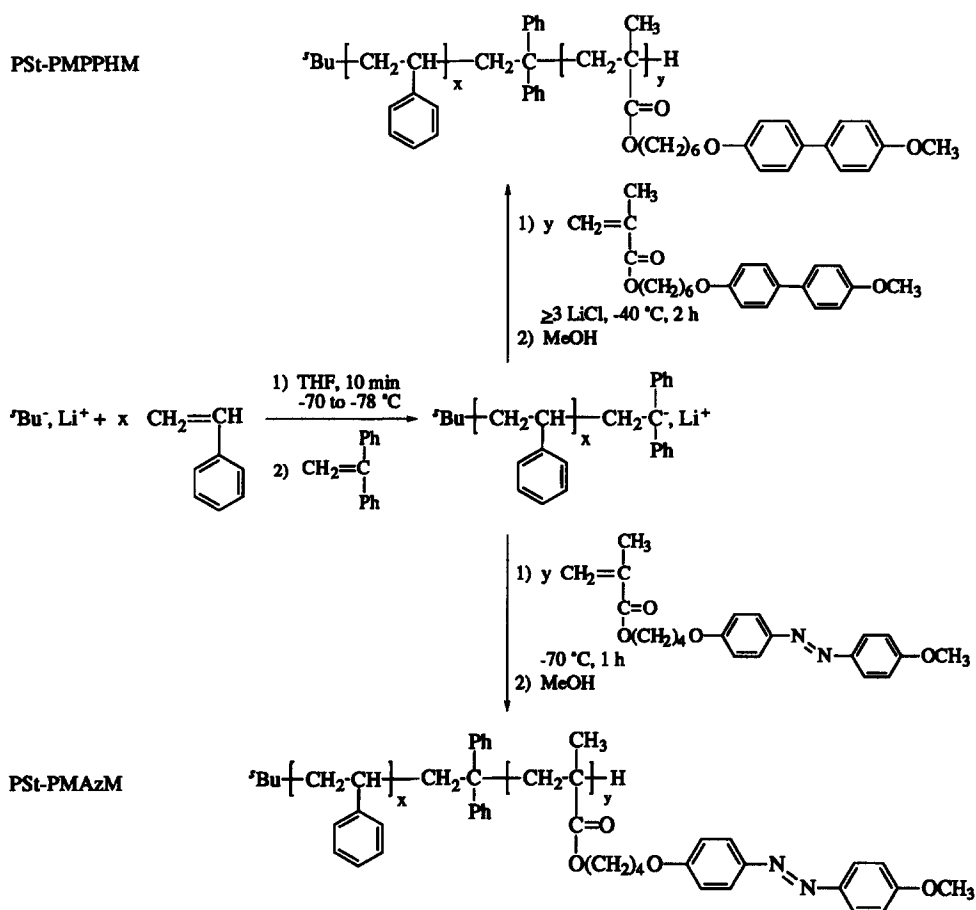
3.6. The effect of polydispersity

One of the most fundamental questions still open regarding the structure/property relationships of SCLCPs is the effect of polydispersity. In some cases, the temperature and nature of the mesophase(s) depend not only on the degree of polymerization, but also on the molecular weight distribution.^{147-149,212} For example, the s_C mesophase of the broad polydispersity (pdi = 1.9) poly{6-[(4'-cyanophenyl-4''-phenoxy)hexyl]vinyl ether} prepared by direct polymerization was not detected by DSC, although it was readily apparent in samples prepared by polymer analogous reactions (pdi = 1.2).²¹²

However, broad polydispersity is generally believed to manifest itself in broad phase transitions. In contrast to low molar mass liquid crystals (LMLLCs) which undergo phase transitions over a few degrees, SCLCPs often exhibit extremely broad transitions. This wide



Scheme 24.



Scheme 25.

(and even split^{249,250}) biphasic region, in which a mesophase coexists with either the isotropic melt or another mesophase,²⁵¹ is evidently due to the fact that polymers are polydisperse. For example, fractionated samples of poly{6-[(4'-cyanophenyl-4"-phenoxy)undecyl] acrylate} undergo (s_C-s_A , s_A-i) transitions over a narrower temperature range ($15-25^\circ\text{C}$) than the original polymer (40°C) prepared by free radical polymerization.²⁵² (Unfortunately, the actual molecular weight and polydispersity were not determined for any of the samples.)

In contrast, the transitions of most well-defined SCLCPs prepared by controlled polymerizations are relatively narrow. The effect of polydispersity was therefore investigated by blending well-defined ($\text{pdi} < 1.28$) poly{5-[[6'-[4"- (4'''-methoxyphenyl)phenoxy]alkyl]carbonyl]bicyclo[2.2.1]hept-2-ene}s of varying molecular weights ($DP_n = 5, 10, 15, 20, 50, 100$) to create polydisperse samples ($\text{pdi} = 2.50-4.78$).²² In this case, both monodisperse samples and multimodal blends underwent the nematic-isotropic transition over a narrow temperature range. Polydispersity also had no effect on the transition temperatures, which were determined simply by the number average degree of polymerization.

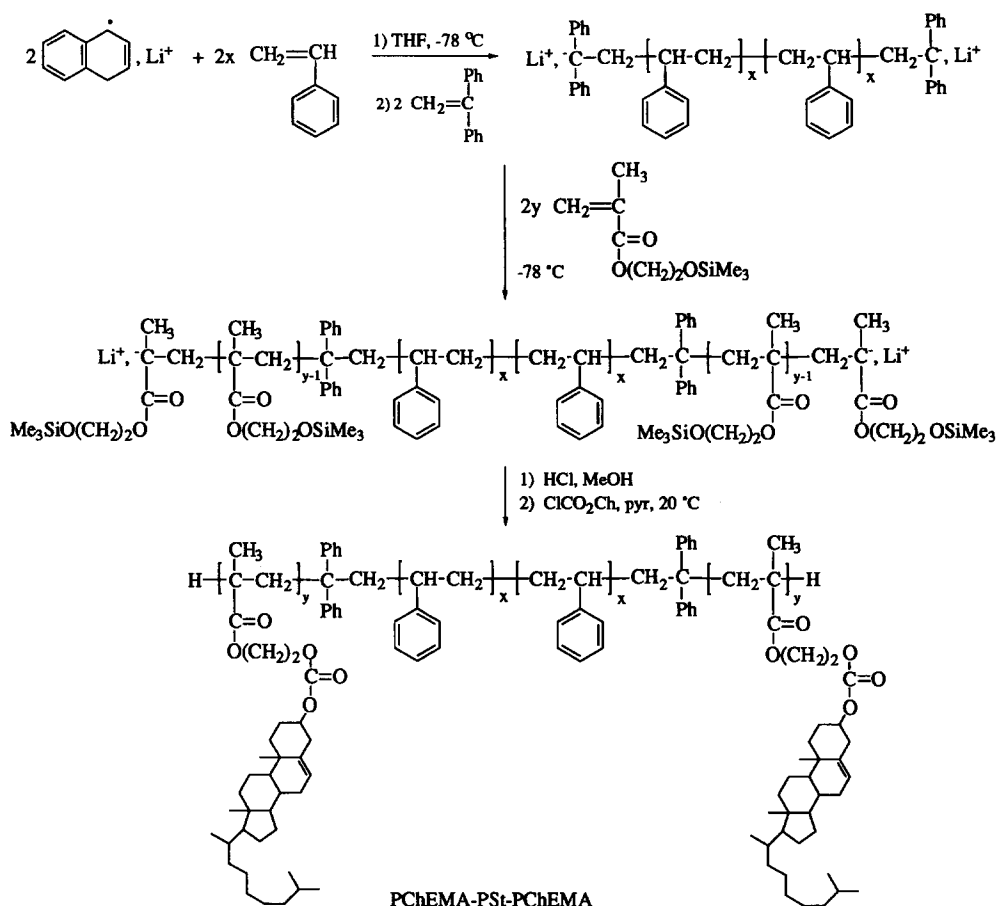
Since polydispersity created by blending linear polymers has no effect on the thermotropic



behavior of polynorbornenes,²² whereas fractionation of polyacrylates prepared by radical polymerization results in narrower biphasic regions,²⁵² we must consider what the various sources of polydispersity are. Most SCLCPs are still prepared by free radical polymerizations. Since mesogenic monomers are highly functionalized with a number of sites which can cause chain transfer, their free radical polymerizations should result in chain branching and broad polydispersity at high monomer conversion. In addition, entanglements are trapped in high molecular weight polymers.

4. CHAIN COPOLYMERIZATIONS¹

Polymers which contain more than one type of monomeric repeat unit are called copolymers. By copolymerizing two or more monomers in varying ratios and arrangements,

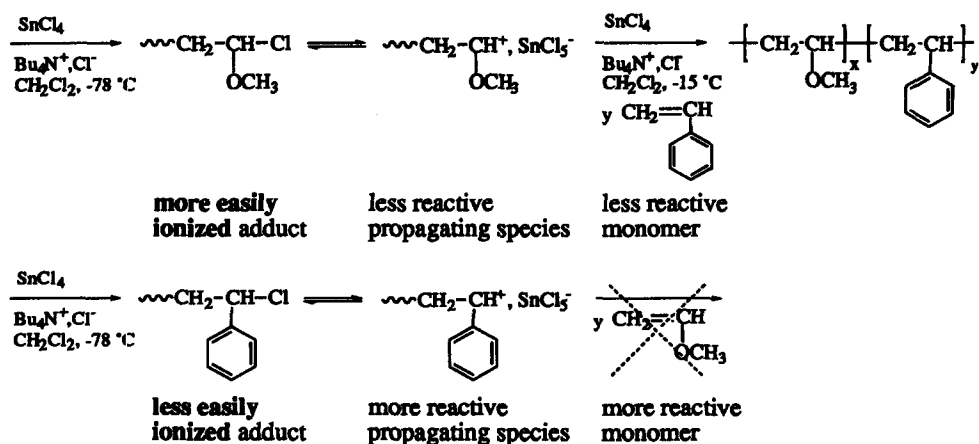


Scheme 27.

polymeric products with an almost limitless variety of properties can be obtained. As shown in Scheme 18, there are four basic types of copolymers as defined by the distribution of, for example, comonomers A and B. While the properties of a random copolymer are intermediate between those of the two homopolymers, block and graft copolymers exhibit the properties of both homopolymers. The properties of an alternating copolymer are usually unique.

The first three types of copolymers can be prepared by polymerizing a mixture of the two monomers simultaneously. In this case, the distribution of comonomers is determined by their relative concentrations and reactivity ratios. The reactivity ratios (r_1 , r_2 , etc.) are the ratios of the rate constants of homopropagation and cross-propagation [eqn (32)]. Using the terminal model of copolymerization, there are four possibilities for propagation (Scheme 19). If there are only two active sites (M_1^* and M_2^*) whose concentration are at steady state and if

$$r_1 = \frac{k_{11}}{k_{12}} \quad r_2 = \frac{k_{22}}{k_{21}} \quad (32)$$

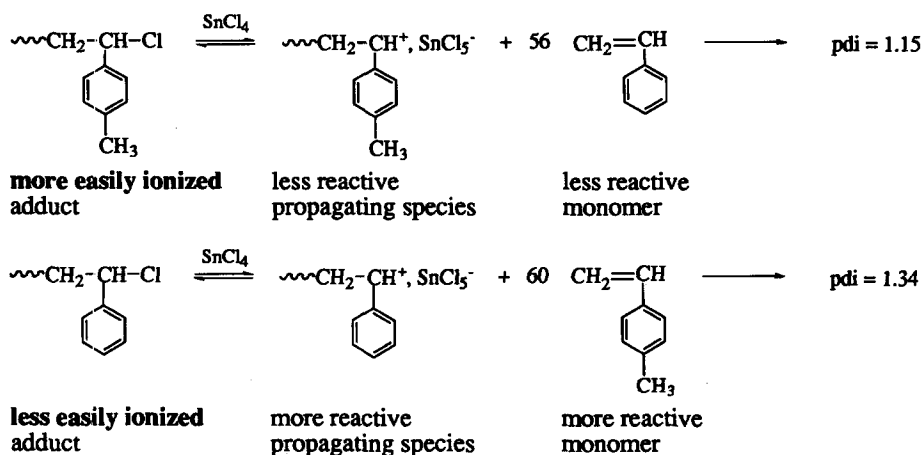


Scheme 28.

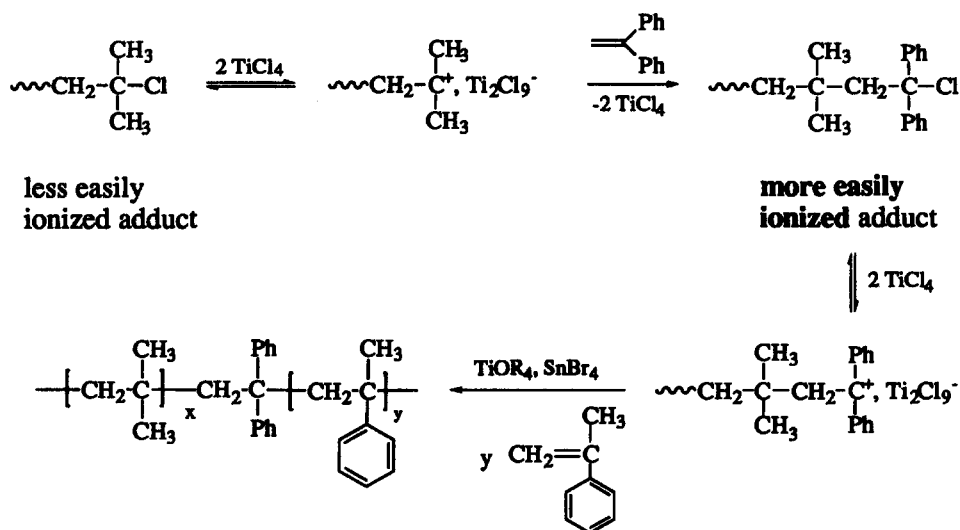
monomer is consumed entirely by propagation, the molar ratio of the two monomer units in the polymer ($d[M_1]/d[M_2]$) is defined by eqn (33), in which $[M_1]$ and $[M_2]$ are the concentrations of the two monomers in the polymer feed.

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1 [M_1] + [M_2]}{r_2 [M_2] + [M_1]} \quad (32)$$

Random copolymers in which the comonomer distribution follows Bernoullian or zero-order statistics are formed by ideal copolymerizations in which $r_1 r_2 = 1$. However, a truly random distribution of the two units results only if the Bernoullian distribution is symmetric, i.e. when $r_1 = r_2 = 1$. In this case, the two monomers have equal probability of reacting with a



Scheme 29.

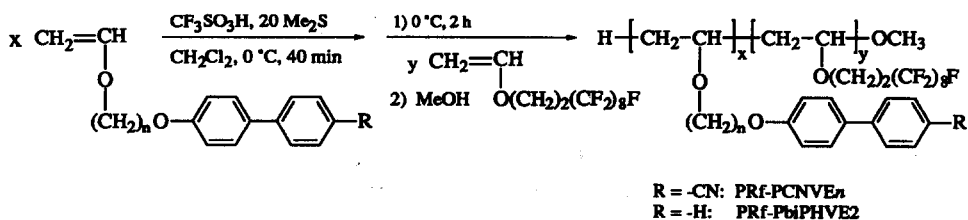


Scheme 30.

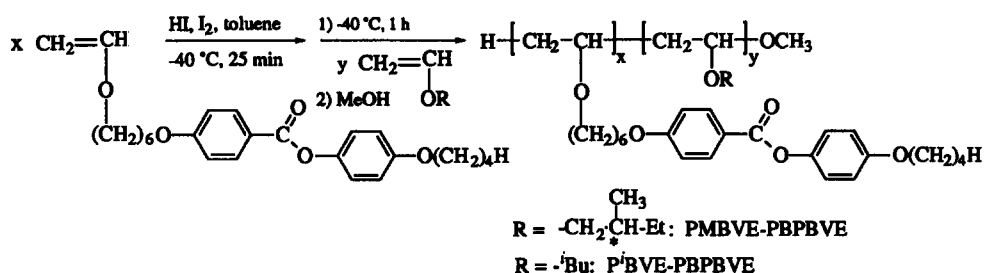
given active center, regardless of the monomer it is derived from, and the copolymer composition equals the comonomer feed composition at all conversions. Random copolymers are generally formed by radical copolymerizations, whereas ionic copolymerizations tend to favor propagation of one of the comonomers much more than the other, yielding blocky sequences of that comonomer. That is, it is usually difficult to copolymerize monomers by an ionic mechanism due to large differences in their reactivity ratios: $r_1 \gg 1$, $r_2 \ll 1$. Alternating copolymers result when both reactivity ratios are close to zero due to little tendency of either monomer to homopolymerize ($r_1 = r_2 = 0$).

Block copolymers containing long blocks of each homopolymer in a diblock, triblock, or multiblock sequence are formed by simultaneous polymerization of the two comonomers only when $r_1 \gg 1$ and $r_2 \gg 1$. However, block copolymers are more effectively prepared by either sequential monomer addition in living polymerizations, or by coupling two or more telechelic homopolymers subsequent to their homopolymerization. Alternatively, if the two monomers do not polymerize by the same mechanism, a block copolymer can still be formed by sequential monomer addition if the active site of the first block is transformed to a reactive center capable of initiating polymerization of the second monomer.

Living polymerizations have been used to prepare copolymers based on either two



Scheme 31.



Scheme 32.

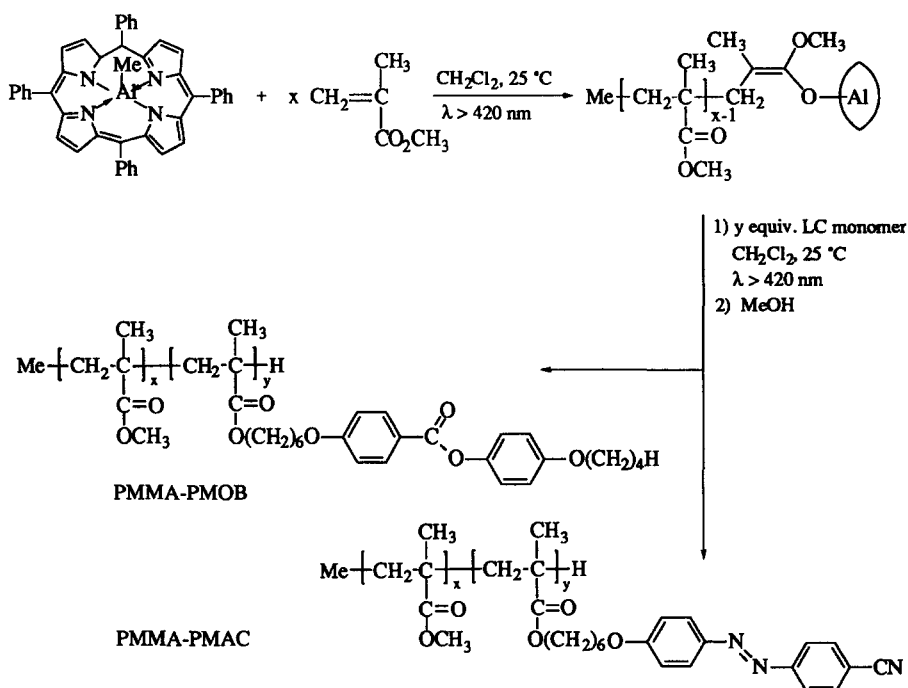
mesogenic monomers, or one mesogenic monomer and one non-mesogenic monomer, with the comonomers distributed either statistically or in blocks or grafts.

4.1. Block copolymers

Block and graft copolymers based on two or more incompatible polymer segments phase separate and self-assemble into spatially periodic structures when the product (χN) of the Flory–Huggins interaction parameter and the total number of statistical segments in the copolymer exceeds a critical value.^{25,262,263} Since the incompatible blocks are chemically linked to each other, macroscopic phase separation is prevented, and phase separation is instead limited to the microscopic level. The resulting morphology minimizes the free energy of the system by minimizing unfavorable contacts and the interfacial curvature energy, while maximizing the conformational entropy and maintaining a uniform segment density throughout the phase.^{262–266} The geometry and size of the microdomains are therefore determined not only by the degree of incompatibility χN , but also by the volume fraction (ϕ_A , ϕ_B) of the different blocks, the block length(s), the total molecular weight, the conformational asymmetry and fluctuations.^{262–271}

An isothermal morphology diagram of poly(styrene-*block*-butadiene) is shown in Fig. 19 as a function of molecular weight and copolymer composition; the classic morphologies include spherical microdomains ($0 \leq \phi_A \leq 0.15$) packed in a body-centered cubic lattice, hexagonally packed cylindrical microdomains ($0.15 \leq \phi_A \leq 0.3$), and alternating lamellae of approximately symmetric diblocks ($0.3 \leq \phi_A \leq 0.5$). Several new morphologies, and thermotropic transitions were discovered by blending diblock copolymers with homopolymer^{272–278} or diblock^{279,280} copolymer, and by varying temperature^{281,282} or hydrostatic pressure²⁸³ in order to change χ at a fixed composition. Although the first non-classic morphology was characterized as an ordered bicontinuous double diamond phase,^{284–289} it has since been identified as a gyroid bicontinuous cubic phase,^{278,290} which is apparently unstable.²⁹¹ Linear ABA triblock,^{25,267–270} diblock star^{289,292} and cyclic diblock²⁹³ copolymers generally form the same morphologies as diblock copolymers of the same composition. However, a new tricontinuous cubic structure was recently discovered in miktoarm star copolymers²⁹⁴ and ABC triblock^{295–297} copolymers; ABC triblock copolymers also form spheres and cylinders at lamellae interfaces.^{298–301}

Block copolymers containing a side-chain liquid crystalline segment are being synthesized in order to answer structure/property questions, and to create new materials that combine



Scheme 33.

the anisotropic ordering of liquid crystals with the mechanical properties of block copolymers. For example, in contrast to block copolymers which have more uniform mechanical properties, even main-chain liquid crystalline polymers are notorious for lacking strength in the direction transverse to chain extension. Self-supported liquid crystalline materials should also be possible by synthesizing liquid crystalline thermoplastic elastomers, in which the ABA triblock copolymer contains a liquid crystalline B block with hard segments as the A blocks.

However, understanding the thermodynamics of phase separation in liquid crystalline block copolymers is in its infancy. The morphology of such block copolymers will be influenced by the competition between microphase separation of the chemically-different blocks and anisotropic ordering of the liquid crystalline block(s). This may result in unique morphologies, such as those recently observed with rod-coil diblock copolymers of poly(styrene-*block*-hexyl isocyanate).^{302,303} This microphase separation may also influence the equilibrium packing of the mesogens, and therefore the onset, nature and stability of the mesophase(s), especially at the interfaces and especially at curved surfaces.

The molecular weight, block lengths and volume fraction of each block are three factors controlling the morphology of block copolymers. In addition, phase separation should be most discrete with the narrowest interfacial areas when the block lengths are monodisperse.²⁵ Block copolymers are therefore generally synthesized using living polymerizations which readily control both the molecular weight and result in copolymers with narrow polydispersity. Conversely, the ability to form well-defined block copolymers by sequential

Table 14. Phase behavior of block copolymers of methyl methacrylate and 6-[4'-(4"-*n*-butoxyphenoxy-carbonyl)phenoxy]hexyl methacrylate (PMMA-PMOB)^{90,91} and 6-[4'-(4"-cyanophenylazo)phenoxy]-hexyl methacrylate (PMMA-PMAC)⁹⁰ (Scheme 33)

Entry	Copolymer	Block length		Wt. ratio PMMA/LC	Thermotropic Behavior (°C)	Ref.
		PMMA	LC			
1	PMMA-PMOB	56	13	50/50	<i>g</i> 75 <i>i</i>	90
2		109	12	67/33	<i>g</i> 40 <i>g</i> 108 <i>i</i>	91
3		109	24	50/50	<i>g</i> 42 <i>g</i> 100 <i>s_A/n</i> 100 <i>i</i>	91
4	PMMA-PMAC	28	8	51/49	<i>g</i> 44 <i>g</i> 92 <i>i</i>	90

monomer addition provides further evidence that a polymerization and its propagating chain ends are living. All of the "living" polymerization mechanisms used to prepare well-defined SCLCPs have been used to prepare block copolymers containing a liquid crystalline block, and all of the well-defined side-chain liquid crystalline block copolymers have been prepared by sequential monomer addition. In this case, the liquid crystalline monomer is either polymerized directly or the mesogen is introduced in a polymer analogous reaction. When the liquid crystalline block is generated by a polymer analogous reaction, well-defined blocks require quantitative functionalization.

4.1.1. Anionic and group transfer copolymerizations

In order to prepare block copolymers by sequential monomer addition, the crossover reaction must be efficient. The order of monomer addition is therefore extremely important in anionic polymerizations, since the propagating anion of the first block must be nucleophilic enough to initiate polymerization of the second monomer. Since the reactivity of the

Table 15. Phase behavior of block copolymers of 6-[4'-(4"-*n*-butoxyphenoxy-carbonyl)phenoxy]hexyl vinyl ether with ^tbutyl vinyl ether (P^tBVE-PBPBVE) or (S)-2-methylbutyl vinyl ether (PMBVE-PBPBVE) (Scheme 32)¹⁵⁰

Entry	Copolymer	Theoretical block length		Actual wt. ratio non-LC/LC	Thermotropic Behavior (°C) ^a	$\Delta H_{i,co}^b$
		non-LC	LC			$\Delta H_{i,homo}$
1	P ^t BVE-PBPBVE	2	10	3/97	<i>s</i> 28 <i>s_C</i> 87 <i>n</i> 97 <i>i</i>	1.1
2		3	10	8/92	<i>s</i> 24 <i>s_C</i> 83 <i>n</i> 93 <i>i</i>	1.1
3		10	10	10/90	<i>s</i> 25 <i>s_C</i> 83 <i>n</i> 94 <i>i</i>	0.99
4		25	10	25/75	<i>s</i> 29 <i>k</i> 43 <i>s_C</i> 83 <i>n</i> 93 <i>i</i>	0.85
5	PMBVE-PBPBVE	10	10	21/79	<i>k</i> 27 <i>s</i> 33 <i>s_C</i> 60 <i>n</i> 70 <i>i</i>	nr
6		25	10	32/68	<i>k</i> 20 <i>s</i> 28 <i>i</i>	nr

^aPBPBVE homopolymer $DP_n = 10$: *s* 31 *s_C* 92 *n* 102 *i*; ¹⁵⁰ PBPBVE homopolymer $DP_n = 38$: *s* 47 *s_C* 106 *n* 111 *i*. ¹⁵⁰ P^tBVE: $T_g - 20^\circ\text{C}$; ³⁴⁴ T_m 110°C; ³⁴⁵ T_m 165°C. ³⁴⁶
^bnr = not reported.

Table 16. Phase behavior of block copolymers of (perfluorooctyl)ethyl vinyl ether and *n*-[(4'-(4"-cyanophenyl)phenoxy)alkyl]vinyl ethers (PR_F-PCNVE*n*) or 2-[(4'-biphenyloxy)ethyl]vinyl ether (PR_F-PbiPHVE2) (Scheme 31)³¹⁷

Copolymer	Block length		Wt. ratio	Thermotropic Behavior (°C) ^a		$\Delta H_{i,co}$
	PR _F	LC		Copolymer	Poly(LC) ^b	
PR _F -PCNVE2	7	14	45/55	k -6 k 22 g 75 x 83 lc 250 dec	g 78 x 86 i	0.61
PR _F -PCNVE3	8	15	54/46	k -12 k 15 g 60 x 64 n 97 lc 250 dec	g 60 x 64 n 98 i	0.43
PR _F -PCNVE9	5	16	32/68	k -7 g 12 k 23 s _C 41 s _A 140 i	g 14 s _A 142 i	0.81
PR _F -PCNVE11	5	14	31/69	g 10 k 54 k 64 s _A 146 i	g 17 66 s _A 155 i	0.95
PR _F -PbiPHVE2	6	13	44/56	k 30 k 66 lc 250 dec	g 59 k 70 i	0.79

^aPR_F homopolymer: k 23 s 41 i,³⁴⁷ x = unidentified phase, lc = unidentified liquid crystalline phase, dec = decomposes.

^bof comparable molecular weight to the liquid crystalline block length.

propagating anion correlates with the pK_a of its conjugate acid, any monomer listed in Table 13 (such as styrene) will polymerize any monomer listed below it (such as methyl methacrylate) with a similar or lower pK_a.²⁵ As outlined in Scheme 20, this means that the more reactive propagating species is used to polymerize the more reactive monomer, whereas the less reactive propagating species can not initiate polymerization of the less reactive monomer.

Block copolymers of butadiene and styrene are therefore readily synthesized anionically, with either of the two monomers polymerized first. Precursor copolymers of poly(styrene-*block*-butadiene) have been used to prepare well-defined liquid crystalline block copolymers by the same polymer analogous reaction described in Section 2.5 (Scheme 21).²⁰¹⁻²⁰³ Following anionic polymerization by sequential monomer addition, the polymer analogous reactions of the cholesterol (PSt-PBCh)²⁰¹ and azobenzene (PSt-PBAz)²⁰³ derivatives were essentially quantitative, while that of the phenyl benzoate (PSt-PBBz) block went to up to 94% conversion.²⁰² The polydispersities of the liquid crystalline copolymers (pdi = 1.13–1.23) were nearly as narrow as those of their precursor copolymers (pdi = 1.08–1.21, $M_n = 8.0\text{--}9.2 \times 10^4$).^{201,203}

The ability of butadiene anions to initiate styrene polymerization, and *vice versa*, is demonstrated by the synthesis of triblock poly(styrene-*block*-butadiene-*block*-styrene) by three sequential monomer additions, which was then used to synthesize the liquid crystalline triblock copolymer shown in Scheme 22.

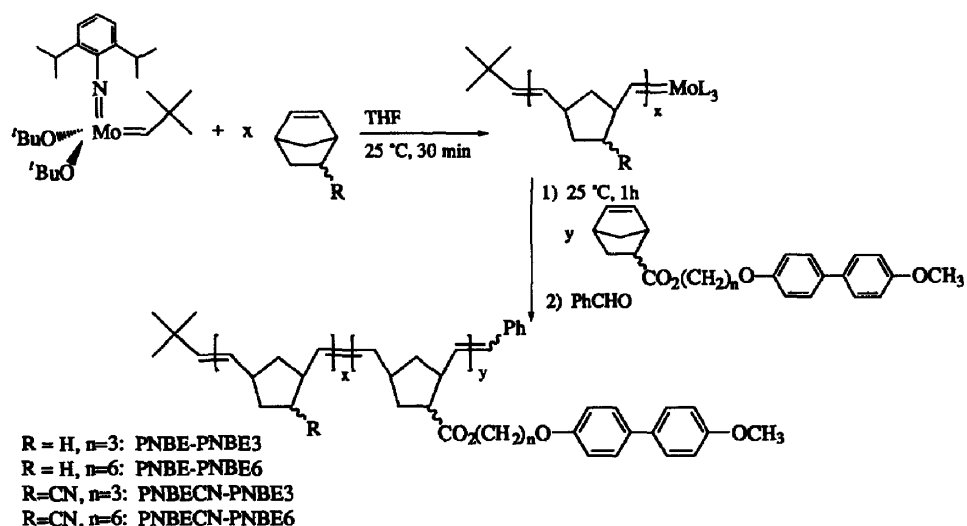
Similarly, diblock copolymers involving two (or more) methacrylate monomers can generally be polymerized in the order which is most convenient since the two propagating anions should have similar pK_as. For example, diblock copolymers of methyl methacrylate and 4-[4'-(4"-methoxyphenylazo)phenoxy]butyl methacrylate (PMMA-PMaZM) were synthesized by polymerizing the mesogenic block first (Scheme 23).⁴⁶

Although block copolymers of methyl methacrylate and 6-[4'-(4"-methoxyphenyl)-phenoxy]hexyl methacrylate have been synthesized by group transfer polymerization (Scheme 24),³⁰⁵ they have not been characterized. This same block copolymer has also been synthesized by coupling (acyl chloride)-endcapped polystyrene with hydrazide-endcapped poly{6-[4'-(4"-methoxyphenyl)phenoxy]hexyl methacrylate}.³⁰⁶ However, the two coupled

Table 17. Phase behavior of polynorbornene block copolymers (Schemes 34 and 35)³⁴³

Copolymer	Block Length		wt. ratio amorph/LC	Thermotropic Behavior (°C)			$\Delta H_{i,co}$
	amorph.	LC		Copolymer	Poly(amorph)	Poly(LC)	$\Delta H_{i,homo}$
PNBE-PNBE3	300	20	48/52	<i>g 44 g 58 n 84 i</i>	<i>g 43 i</i>		*
	100	20	22/78	<i>g 39 g 55 n 92 i</i>		<i>g 57 n 79 i</i>	0.65
PNBECN-PNBE3	180	20	45/55	<i>g 112 i</i>	<i>g 116 i</i>		
PNBE-PNBE3	100	50	11/89	<i>g 39 g 59 n 86 i</i>	<i>g 43 i</i>		0.97
	50	50	6/94	<i>g 36 g 60 n 87 i ii</i>			0.90
PNBECN-PNBE3	180	50	27/73	<i>g 67 n 88 g 119 i</i>		<i>g 61 n 86 i</i>	*
	89	50	13/87	<i>g 63 n 82 i</i>	<i>g 116 i</i>		0.49
	36	50	9/91	<i>g 63 n 82 i</i>			0.40
PNBE-PNBE6	300	20	40/60	<i>g 42 n 97 i</i>	<i>g 43 i</i>		*
	100	20	18/82	<i>g 38 n 94 i</i>			0.75
PMTD-PNBE6	100	20	46/54	<i>g 41 n 85 g 208 i</i>	<i>g 214 i</i>	<i>g 35 n 87 i</i>	*
PNBECN-PNBE6	180	20	40/60	<i>g 40 n 87 g 112 i</i>	<i>g 116 i</i>		*
PNBE-PNBE6	100	50	9/91	<i>g 38 n 91 i</i>	<i>g 43 i</i>		0.97
	56	50	5/95	<i>g 38 n 93 i</i>			0.93
PMTD-PNBE6	100	50	27/73	<i>g 41 n 92 g 207 i</i>	<i>g 214 i</i>	<i>g 42 n 93 i</i>	0.60
PNBECN-PNBE6	180	50	23/77	<i>g 43 n 93 g 114 i</i>			0.60
	89	50	15/85	<i>g 43 n 91 i</i>	<i>g 116 i</i>		0.82
	36	50	7/93	<i>g 45 n 91 i</i>			0.81

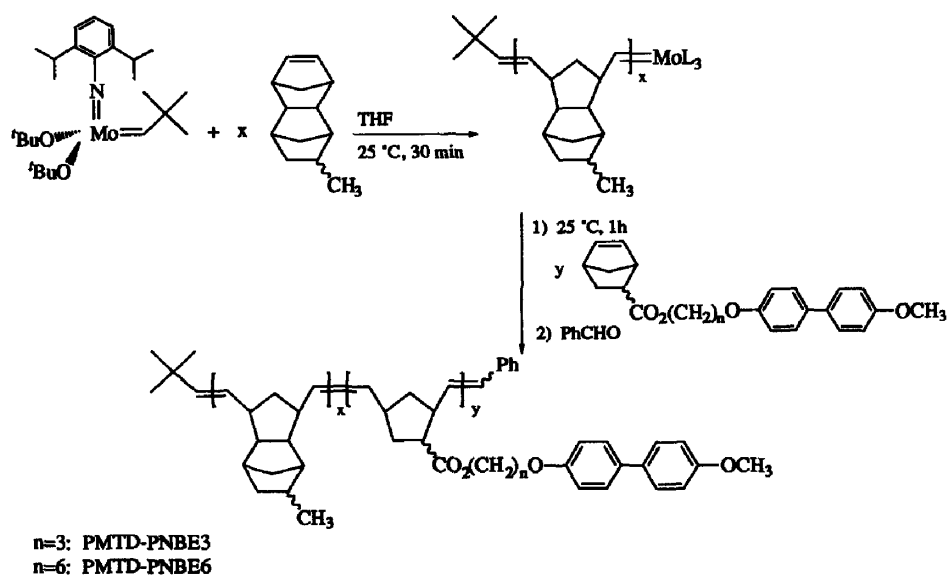
*transition too broad to accurately calculate enthalpy.



Scheme 34.

homopolymers were prepared by radical polymerizations, and the resulting block copolymers are therefore not monodisperse in either block length or molecular weight.

In contrast to block copolymers of two methacrylates, block copolymers of a methacrylate and styrene can only be prepared anionically by polymerizing styrene first. As shown in



Scheme 35.

Table 18. Phase behavior of polystyrene block copolymers (Schemes 21, 22 and 25)

Copolymer	Block Length		wt. ratio	Thermotropic Behavior (°C)*		$\Delta H_{i,co}$	Ref.
	St	LC		Copolymer	Poly (LC)		
PSt-PBCh	692	165	48/52	<i>g</i> 98 <i>s</i> 203 <i>i</i>	<i>g</i> 75 <i>s</i> 206 <i>i</i>	0.38	201
PSt-PBBz	725	183	50/50	<i>g</i> 27 <i>s</i> _C 58 <i>n</i> 101 <i>i</i>	<i>g</i> 24 <i>s</i> _C 60 <i>n</i> 101 <i>i</i>	0.30	202
PSt-PBBz-PSt	306	313	11/89	<i>g</i> 20 <i>n</i> 88 <i>i</i>	<i>g</i> 18 <i>n</i> 53 <i>i</i>	1.29	202
PSt-PMPPHM	180	41	55/45	<i>g</i> 90 <i>k</i> 104 <i>s</i> _A 132 <i>i</i>		0.71	44
	144	41	50/50	<i>g</i> 92 <i>k</i> 105 <i>s</i> _A 133 <i>i</i>	<i>k</i> 121 <i>s</i> _A 135 <i>i</i>	0.69	44
	103	49	37/63	<i>g</i> 91 <i>k</i> 106 <i>s</i> _A 135 <i>i</i>		0.77	44

*amorphous PSt: $T_g = 85^\circ\text{C}$.

Scheme 25, well-defined ($\text{pdi} = 1.03\text{--}1.11$) diblock copolymers of styrene and 6-[4'-(4"-methoxyphenyl)phenoxy]hexyl methacrylate (PSt-PMPPHM) were synthesized directly by sequential anionic polymerization of styrene and then the methacrylate in THF at -78°C using $^t\text{BuLi}$ as the initiator.⁴⁴ The reactivity of the growing polystyrene anions was reduced by reaction with 1,1-diphenylethylene before polymerizing 6-[4'-(4"-methoxyphenyl)phenoxy]hexyl methacrylate at -40°C in the presence of lithium chloride. Diblock copolymers of styrene and 4-[4'-(4"-methoxyphenylazo)phenoxy]butyl methacrylate (PSt-PMAzM) were prepared similarly (Scheme 25), except that the methacrylate block was polymerized at -70°C without adding lithium chloride.⁴⁶

Poly[styrene-*block*-2-(cholesterylloxycarbonyloxy)ethyl methacrylate] (PSt-PChEMA) copolymers and similar diblock copolymers with amorphous butadiene (PB-PChEMA)²⁰⁴ and *n*-butylmethacrylate (PBMA-PChEMA)^{204,210} blocks were synthesized by a route analogous to that shown in Scheme 16, except that the non-mesogenic block was polymerized first. For example, styrene was polymerized first in THF at -78°C using $^t\text{BuLi}$ as the initiator (Scheme 26). Diblock PSt-PChEMA copolymers were generated by reacting the growing polystyrene anions with 1,1-diphenylethylene before polymerizing 2-(trimethylsiloxy)ethyl methacrylate, followed by deprotection and reaction of the poly(2-hydroxyethyl methacrylate) block with cholesterylchloroformate. The molecular weights of the diblock copolymers corresponded to $DP_n = [M_1]_0 + [M_2]_0/[I]_0$; the polydispersities of PB-PChEMA ($\text{pdi} = 1.3$),²⁰⁴ PBMA-PChEMA ($\text{pdi} = 1.2$)²⁰⁴ and PSt-PChEMA ($\text{pdi} = 1.02\text{--}1.18$)^{205,207,209} were generally very narrow.

Since triblock copolymers cannot be synthesized anionically by a third monomer addition of styrene to the growing methacrylate anion, PSt-PChEMA-PSt triblock copolymers were generated by coupling the living diblock copolymers with terephthaloyl chloride before quenching/deprotection (Scheme 26). Alternatively, triblock PChEMA-PSt-PChEMA copolymers can be prepared using a difunctional initiator as shown in Scheme 27. All of the triblock PSt-PChEMA-PSt ($\text{pdi} = 1.07\text{--}1.25$)²⁰⁹ and PChEMA-PSt-PChEMA ($\text{pdi} = 1.01\text{--}1.47$)^{206,207,209} copolymers are also well-defined in terms of molecular weight and polydispersity. Although only 70–88% of the 2-hydroxyethyl methacrylate groups were initially functionalized with cholesterylcarbonate,²⁰⁴ complete conversion was subsequently achieved using 100% excess cholesterylchloroformate and longer reaction times of up to 4 days.²⁰⁸

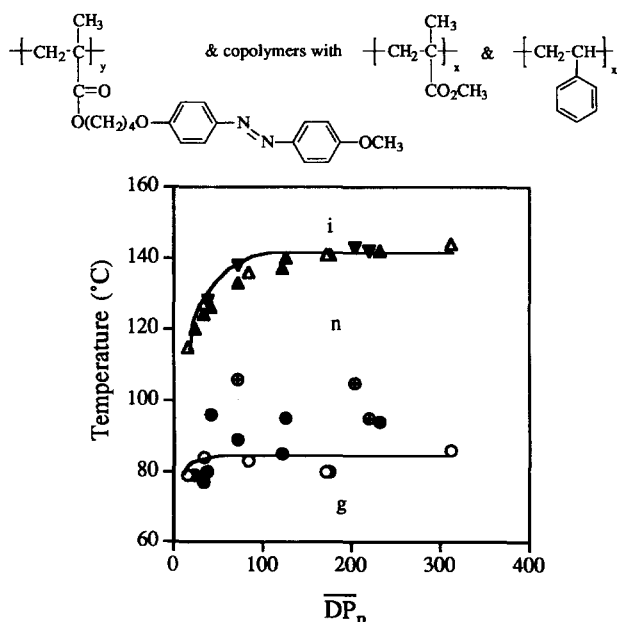


Fig. 20. Thermotropic behavior of poly[4-[4'-(4''-methoxyphenylazo)phenoxy]butyl methacrylate] (\circ, \diamond), poly{(methyl methacrylate)-*block*-[4-[4'-(4''-methoxyphenylazo)phenoxy]butyl methacrylate]} (\bullet, \blacktriangle) (Scheme 23) and poly{styrene-*block*-[4-[4'-(4''-methoxyphenylazo)phenoxy]butyl methacrylate]} ($\oplus, \blacktriangledown$) (Scheme 25) as a function of the number of repeat units in the liquid crystalline block.⁴⁶

4.1.2. Cationic copolymerizations

As in anionic copolymerizations, the order of monomer addition is extremely important in achieving efficient crossover reactions in cationic copolymerizations. However, in contrast to anionic polymerizations, the most efficient crossover reaction is not achieved by reacting the more reactive monomer with the more reactive propagating species. Instead, initiation of the second monomer is apparently fast and quantitative if the most reactive monomer is polymerized first. As demonstrated by the examples in Scheme 28, this generates the more easily ionized covalent chain end, which therefore corresponds to the efficiency of covalent initiators discussed in Section 2.3 and outlined in Table 2. However, since the optimum polymerization conditions generally vary with each monomer, the temperature and catalyst type and concentration may have to be adjusted accordingly with each monomer addition. For example, Scheme 28 shows that fairly well-defined ($\text{pdi} = 1.33$) diblock copolymers of styrene (45 repeat units) and methyl vinyl ether (20 repeat units) are obtained when the vinyl ether is polymerized first, although the second stage polymerization requires higher temperature and a higher concentration of the Lewis acid in conjunction with a common ion salt.³⁰⁷ The synthesis of block copolymers of styrene-2-chloroethyl vinyl ether,³⁰⁷ *p*-methoxystyrene-*i*-butyl vinyl ether,³⁰⁸ *p*-methoxystyrene-methyl vinyl ether,³⁰⁸ *p*-*i*-butoxystyrene-*i*-butyl vinyl ether,³⁰⁹ and *p*-methylstyrene-*i*-butyl vinyl ether³⁰⁹ also require polymerization of the most

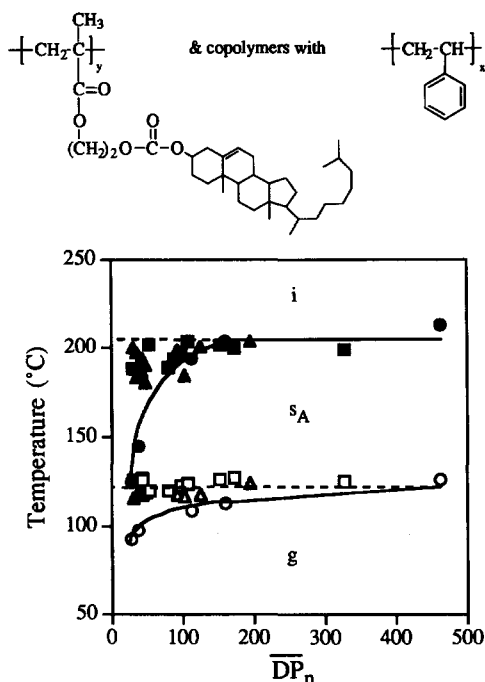


Fig. 21. Thermotropic behavior of poly[2-(cholesteryloxy)ethyl methacrylate] (○,●), and diblock (PSt-PChEMA)^{208,209} (□,■) and triblock [PChEMA-PSt-PChEMA]²⁰⁸ (Δ,▲) and PSt-PChEMA-PSt²⁰⁹ (▽,▼) copolymers of 2-(cholesteryloxy)ethyl methacrylate and styrene (Schemes 26 and 27) as a function of the number of repeat units in the liquid crystalline block.

reactive monomer first. The opposite order of first stage polymerization of the less reactive monomer generally produces a mixture of the block copolymer and the homopolymer of the second monomer.³⁰⁷⁻³¹¹

Monomer pairs of similar reactivity, such as *p*-*t*-butoxystyrene-*p*-methoxystyrene,³⁰⁹ and α -methylstyrene-2-chloroethyl vinyl ether³¹⁰ can be polymerized starting from either monomer. However, even monomer pairs with similar stabilities and reactivities have an optimum order of addition. For example, Scheme 29 shows that the molecular weight distribution of triblock copolymers of styrene (50–56 repeat units) and *p*-methylstyrene (60–62 repeat units) is narrower when *p*-methylstyrene is polymerized first (using a difunctional initiator),³¹² thereby generating a more easily ionized macroinitiator.

Nevertheless, efficient crossover reactions can be achieved even when the second monomer is more reactive than the first monomer by endcapping the first block with a more easily ionized, but non-polymerizable monomer. As outlined in Scheme 30, Faust *et al.* prepared well-defined (*pdi* < 1.1) diblock and triblock copolymers of isobutylene and α -methylstyrene (or other styrene derivatives) with 100% crossover efficiencies by reacting the first block with 1,1-diphenylethylene before adding α -methylstyrene.³¹³⁻³¹⁵ In this case, it is also necessary to deactivate the first Lewis acid (TiCl₄) by adding titanium(IV) isopropoxide or butoxide,

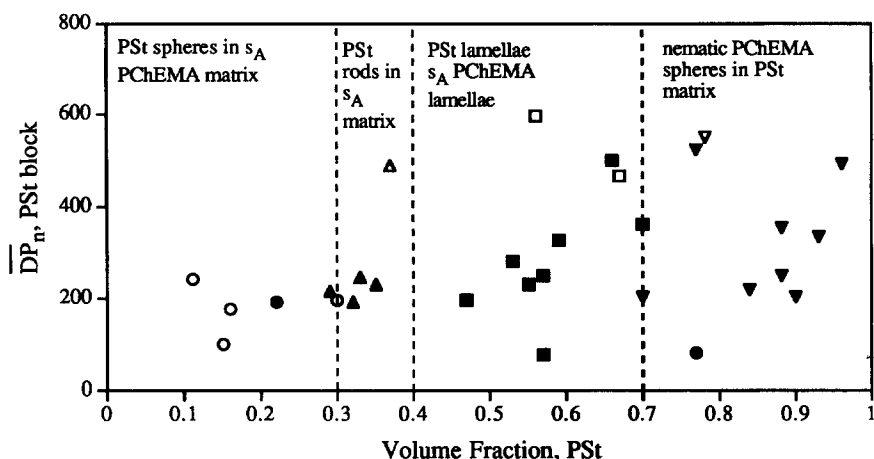


Fig. 22. Morphology of AB diblock (○, △, □, ▽) and ABA and BAB triblock (●, ▲, ■, ▼) copolymers of styrene and 2-(cholesteryloxycarbonyloxy)ethyl methacrylate (Scheme 26 and Scheme 27): PSt spheres in a smectic A PChEMA matrix (○, ●); PSt rods in a smectic A PChEMA matrix (△, ▲); alternating lamellae of PSt and smectic A PChEMA (□, ■); nematic PChEMA spheres in a PSt matrix (▽, ▼).^{208,209}

and to add a second Lewis acid (SnBr_4).³¹⁵ Diblock copolymers ($\text{pdi} < 1.1$) of isobutylene and methyl vinyl ether were prepared similarly.³¹⁶

Therefore, techniques are emerging for generating well-defined block copolymers by sequential monomer addition in cationic polymerizations of vastly different vinyl monomers. However, side-chain liquid crystalline block copolymers have only been prepared by sequential monomer addition of two vinyl ethers of approximately the same reactivity. Both diblock copolymers of [(perfluorooctyl)ethyl]vinyl ether and *n*-[(4'-(4''-cyanophenyl)phenoxy)alkyl]vinyl ethers ($\text{PR}_f\text{-PCNVEn}$) or 2-[(4'-biphenyloxy)ethyl]vinyl ether ($\text{PR}_f\text{-PbiPHVE2}$) were prepared by polymerizing the mesogenic block first using triflic acid as the initiator and dimethyl sulfide as a deactivator in CH_2Cl_2 at 0°C , followed by addition of the less soluble fluorocarbon monomer (Scheme 31).³¹⁷ Somewhat well-defined ($\text{pdi} = 1.30\text{--}1.40$) diblock copolymers of 6-[4'-(4''-*n*-(*S*)-2-methylbutyl)] vinyl ether (PMBVE-PBPBVE) were also prepared by polymerizing the mesogenic block first, except that HI was used as the initiator and I_2 as the catalyst in toluene at -40°C , followed by addition of the non-mesogenic monomer (Scheme 32).¹⁵⁰ Although a minor amount of homopolymer was obtained from the second stage polymerization, this was removed by selective extraction.

4.1.3. Copolymerizations with metalloporphyrins

Aluminum porphyrins have been used to prepare block copolymers by sequential monomer addition of two oxiranes,^{68,318} of two β -lactones,³¹⁹ of a β -lactone and an oxirane,³¹⁹ of ethylene oxide and ϵ -caprolactone,⁷⁴ of propylene oxide and D-lactide,⁷⁵ and of two methacrylates.⁷⁶ In the one example involving monomer pairs (β -lactone and oxirane) which generate two different types of propagating species, the β -lactone had to be polymerized

first since the resulting aluminum carboxylate was able to initiate polymerization of the oxiranes, whereas aluminum alkoxides were unable to initiate polymerization of β -lactone.³¹⁹ Metalloporphyrins have also been useful in preparing liquid crystalline block copolymers of methyl methacrylate and either 6-[4'-(4"-*n*-butoxyphenoxy)carbonyl]phenoxy]hexyl methacrylate (PMMA-PMOB)^{90,91} or 6-[4'-(4"-cyanophenylazo)phenoxy]hexyl methacrylate (PMMA-PMAC)⁹⁰ with narrow polydispersity (pdi = 1.14–1.19) and the expected molecular weight using methyl(5,10,15,20-tetraphenylporphinato)aluminum as the initiator (Scheme 33).

4.1.4. Ring-opening metathesis copolymerizations

Well-defined diblock and triblock copolymers (pdi = 1.08–1.14) were first prepared by ring-opening metathesis polymerization by sequential monomer addition of norbornene, dicyclopentadiene and benzonorbornadienes using the bis(η^5 -cyclopentadienyl)titanacyclobutane derivative of 3,3-dimethylcyclopropene as the initiator.^{320,321} Norbornenes and norbornadienes have also been sequentially polymerized using $M(\text{CHCMe}_2\text{R})(\text{N}-2,6\text{-C}_6\text{H}_3\text{-}^i\text{Pr}_2)(\text{O}^t\text{Bu})_2$ ($M = \text{Mo}, \text{W}$; $\text{R} = \text{-CH}_3, \text{-Ph}$) as the initiator (pdi = 1.05–1.12, up to 488 repeat units per block),^{7,186,322–334} as have norbornenes and cyclobutene derivatives (pdi = 1.04–1.23, up to 200 repeat units per block).^{335–339} In these systems, reversing the order of monomer addition has no effect on the copolymerization. More recently, block copolymers of norbornenes and 7-oxanorbornenes (pdi = 1.21–1.26, up to 292 repeat units per block),³⁴⁰ and of an oxanorbornadiene and a functionalized norbornene (pdi = 1.32)³⁴¹ were prepared using $\text{RuCl}_2(\text{CHCH}=\text{CPh}_2)(\text{PR}_3)_2$ and $\text{RuCl}_2(\text{CHPh})(\text{PPh}_3)_2$, respectively, as the initiator. Triblock copolymers of 7-oxanorbornenes have also been prepared using a difunctional $(\text{PCy}_3)_2\text{Cl}_2\text{RuCH-Ph-CHRuCl}_2(\text{PCy}_3)_2$ initiator (pdi = 1.11–1.26, up to 200 repeat units per block).³⁴²

However, only $\text{Mo}(\text{CH}^i\text{Bu})(\text{N}-2,6\text{-C}_6\text{H}_3\text{-}^i\text{Pr}_2)(\text{O}^t\text{Bu})_2$ has been used to prepare well-defined, liquid crystalline block copolymers. As shown in Schemes 34 and 35, the non-mesogenic monomer was polymerized first in THF at 25°C, followed by addition of 5- $\{[n\text{-}[4'-(4''\text{-methoxyphenyl})phenoxy]alkyl]carbonyl\}$ bicyclo[2.2.1]hept-2-ene ($n = 3$: PNBE3; $n = 6$: PNBE6), to produce diblock copolymers (pdi = 1.06–1.25) with norbornene (PNBE), methyltetracyclodecene (PMTD) and 5-(cyano)bicyclo[2.2.1]hept-2-ene (PNBECN).³⁴³

4.1.5. Morphology and thermotropic behavior of side-chain liquid crystalline block copolymers

The amorphous segment of microphase-separated amorphous/liquid crystalline block copolymers may influence the ordering of the mesogens at the interface, as well as the size and discreteness of that interface. Living copolymerizations are therefore being used to determine the effect of the morphology and domain size on the thermotropic behavior of side-chain liquid crystalline block copolymers.

As summarized in Table 14, block copolymers of methyl methacrylate and 6-[4'-(4"-*n*-butoxyphenoxy)carbonyl]phenoxy]hexyl methacrylate (PMMA-PMOB)^{90,91} or 6-[4'-(4"-cyanophenylazo)phenoxy]hexyl methacrylate (PMMA-PMAC)⁹⁰ demonstrate that liquid crystalline block copolymers behave similarly to standard block copolymers.

Table 19. Phase behavior of poly{6-[4'-(4"-cyanophenoxy)carbonyl]phenoxy}hexyl methacrylate-graft-methyl methacrylate}s (equation 35).^{354,355}

Entry	(number average) block length ^a		wt. ratio ^b PMMA/LC	Thermotropic Behavior (°C) ^c	weighted average ^c T _g (°C)
	PMMA	LC			
1	73	35	55/45	<i>g</i> 46 <i>s</i> _A , <i>n</i> 114 <i>i</i>	87
2	73	37	55/45	<i>g</i> 56 <i>s</i> _A , <i>n</i> 112 <i>i</i>	87
3	73	48	59/41	<i>g</i> 58 <i>s</i> _A , <i>n</i> 106 <i>i</i>	89
4	73	88	63/37	<i>g</i> 56 <i>s</i> _A , <i>n</i> 98 <i>i</i>	92
5	73	74	67/33	<i>g</i> 103 <i>i</i>	94
6	73	50	74/26	<i>g</i> 91 <i>i</i>	98
7	28	76	57/43	<i>g</i> 54 <i>i</i>	77
8	59	64	64/36	<i>g</i> 74 <i>i</i>	88
9	85	71	70/30	<i>g</i> 105 <i>i</i>	97
10	127	53	75/25	<i>g</i> 113 <i>i</i>	101

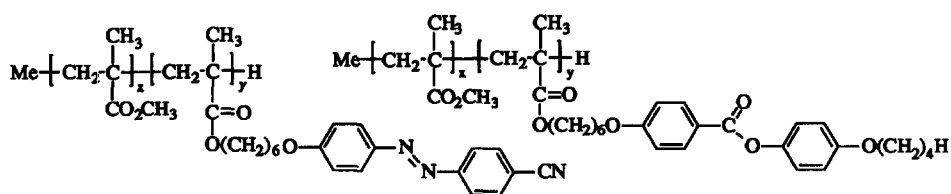
^aCalculated assuming pdi of LC main chain is equivalent to pdi of copolymer.

^bCalculated using weight average molecular weight of graft and LC main chain relative to PMMA standards.

^cPMMA graft: T_g = 94–117°C depending on block length; poly{6-[4'-(4"-cyanophenoxy)carbonyl]phenoxy}hexyl methacrylate}: *g* 54 *s*_A 104 *n* 110 *i*.³⁵⁴

That is, entry 1 shows that short blocks are miscible, such that this PMMA-PMOB copolymer exhibits a single glass transition at a temperature intermediate between that of poly(methyl methacrylate) (105°C) and poly{6-[4'-(4"-*n*-butoxyphenoxy)carbonyl]phenoxy}hexyl methacrylate} (*g* 38 *s*_A 104 *n* 110 *i*); increasing the poly(methyl methacrylate) block length causes it to phase separate (entry 2). In addition, the mesogenic block must be sufficiently long for it to organize anisotropically (entry 3). The final entry demonstrates that poly(methyl methacrylate) and poly{6-[4'-(4"-cyanophenylazo)phenoxy]hexyl methacrylate} (*g* 47 *s*_A 154 *i*) are evidently more incompatible than PMMA-PMOB since phase separation occurs at lower block lengths, although the mesogenic block length is still not long enough to exhibit liquid crystallinity. (The morphology of these block copolymers was not determined.)

In contrast, block copolymers of 6-[4'-(4"-*n*-butoxyphenoxy)carbonyl]phenoxy}hexyl vinyl ether and ^tbutyl vinyl ether (P^tBVE-PBPBVE) or (S)-2-methylbutyl vinyl ether (PMBVE-PBPBVE) exhibit liquid crystallinity even at very short block lengths (Table 15). However, the weight fraction of the liquid crystalline segment is 68–98%, which should correspond to cylinders or spheres of the non-mesogenic block in a matrix of poly{6-[4'-(4"-*n*-butoxyphenoxy)carbonyl]phenoxy}hexyl vinyl ether}. Without microscopic or X-ray evidence, it is also not clear from the data presented in Table 15 that microphase separation occurs, especially at block lengths of two to three repeat units of the non-mesogenic poly(vinyl ether). That is, transitions due to poly(^tbutyl vinyl ether) are not observed in the first three entries, and all of the transition temperatures of the poly{6-[4'-(4"-*n*-butoxyphenyl-4"-benzoate)hexyl]vinyl ether} segment are depressed relative to those of the homopolymer. The transition temperatures are even further depressed in those block copolymers (entries 4–6) which exhibit a crystalline melting, presumably due to the non-mesogenic, semi-crystalline block. The fact that this transition (43°C) is substantially depressed relative



Scheme 36.

to that of poly(^tbutyl vinyl ether) (110³⁴⁵–165³⁴⁶ °C depending on tacticity) further indicates that some mixing of the blocks occurs.

Microphase separation does occur at shorter block lengths when the two blocks are highly immiscible, such as with hydrocarbon and fluorocarbon blocks. For example, all of the diblock copolymers of (perfluorooctyl)ethyl vinyl ether and *n*-[(4'-cyanophenyl-4''-phenoxy)alkyl]vinyl ethers (PR_F-PCNVE_n) or 2-[(4'-biphenyloxy)ethyl]vinyl ether (PR_F-PbiPHVE2) listed in Table 16 exhibit the phases characteristic of both of the corresponding homopolymers. However, the three copolymers with the shortest spacers reportedly remain in an ordered state above temperatures corresponding to isotropization of the homopolymers.

Table 17 presents the thermotropic behavior of diblock copolymers of 5-[[*n*-(4'-(4''-methoxyphenyl)phenoxy)alkyl]carbonyl]-bicyclo[2.2.1]hept-2-ene (*n* = 3: PNBE3; *n* = 6: PNBE6) with norbornene (PNBE), methyltetra cyclodecene (PMTD) and 5-(cyano)bicyclo[2.2.1]hept-2-ene (PNBECN) with at least 50 wt% liquid crystalline blocks of 20 or 50

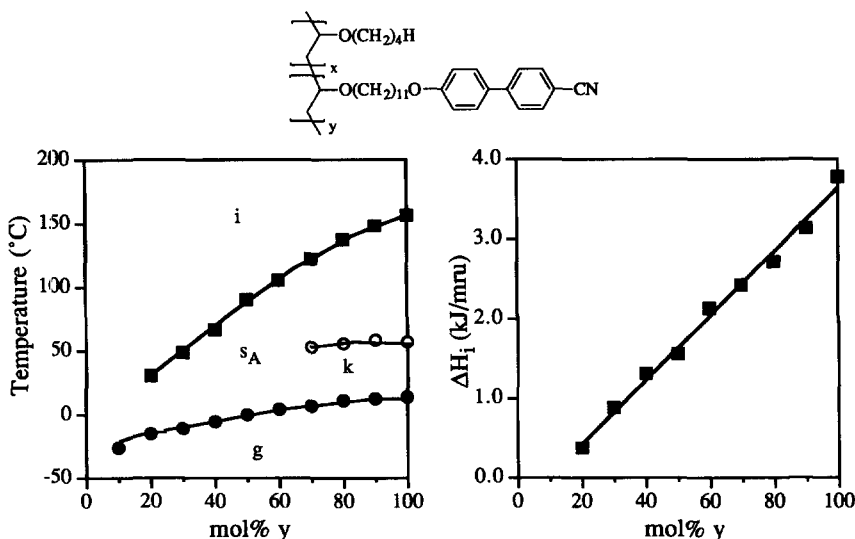
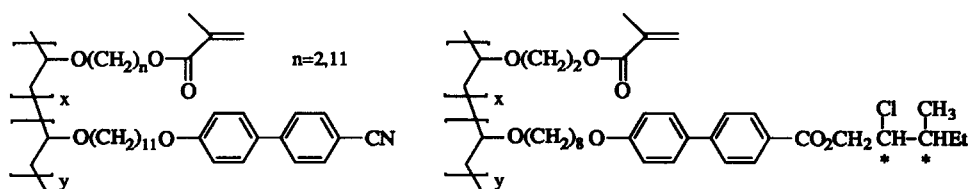


Fig. 23. Phase transition temperatures from the glass (●), crystalline (○) and *s_A* (■) phases of poly{(ⁿbutyl vinyl ether)-co-[11-[(4'-(4''-cyanophenyl)phenoxy)undecyl]vinyl ether]} ($DP_n = 17\text{--}22$, $pdi = 1.07\text{--}1.15$),³⁵⁷ and the corresponding changes in enthalpy of isotropization; first heat.



Scheme 37.

repeat units.³⁴³ With the exception of 45/55 wt% PNBE-CN-PNBE3, all of the diblock copolymers exhibit enantiotropic nematic mesophases and undergo phase transitions at approximately the same temperatures as the two corresponding homopolymers, although both glass transitions are not always detectable when they either occur in the same temperature region, or when the corresponding block is present as a low weight fraction of the copolymer. The ability of the mesogen to pack into microphase separated liquid crystalline regions is therefore independent of the identity of the amorphous block in these systems.

Well-defined PSt-PBCh,²⁰¹ PSt-PBBz²⁰² and PSt-PBAx²⁰³ (Scheme 21) diblock copolymers with extremely long liquid crystalline block lengths (10^2 repeat units) form distinct lamellae typical of 50:50 wt% block copolymers, although the glass transitions of both blocks are not always detected due to either their similar temperatures or masking by a liquid crystalline transition; the morphology of the PSt-PBBz-PSt triblock copolymer (Scheme 22) has not been determined. As summarized in Table 18, the diblock copolymers form the same phases at the same temperatures as the corresponding homopolymers.

The same is true of diblock copolymers of styrene and 6-[4'-(4"-methoxyphenyl)phenoxy]-hexyl methacrylate (PSt-PMPPHM) with at least 45 wt% liquid crystalline blocks of 40-50 repeat units (Table 18).⁴⁴ That is, the glass transition of polystyrene and the s_A to isotropic transition of poly{6-[4'-(4"-methoxyphenyl)phenoxy]hexyl methacrylate} occur at essentially the same temperatures in the copolymers. However, the crystalline melting of the liquid crystalline block is depressed in the block copolymers, which broadens the temperature range of the s_A mesophase. All of the diblock copolymers form well-defined lamellae, although the layer spacings of the mesogens in the diblock copolymers are slightly lower than that in the homopolymer. In addition, the lamellae orient perpendicular to the interface of the two blocks in the copolymer and therefore perpendicular to the fiber axis, in contrast to the orientation in the homopolymers.

Although the temperatures of the transitions of the liquid crystalline block generally match those of the corresponding homopolymer, the transition temperatures may be molecular weight dependent. For example, Fig. 20 demonstrates that the glass and nematic-isotropic transition temperatures of poly{4-[4'-(4"-methoxyphenylazo)phenoxy]butyl methacrylate} level off at approximately 100 repeat units.⁴⁶ In addition, the isotropization temperature of its diblock copolymers with styrene (PSt-PMaZM) and methyl methacrylate (PMMA-PMaZM) follow approximately the same dependence on the block length of the liquid crystalline block, although the polystyrene (19-365) and poly(methyl methacrylate) (30-529) block lengths vary widely; the glass transition temperatures of the block copolymers are much more scattered.

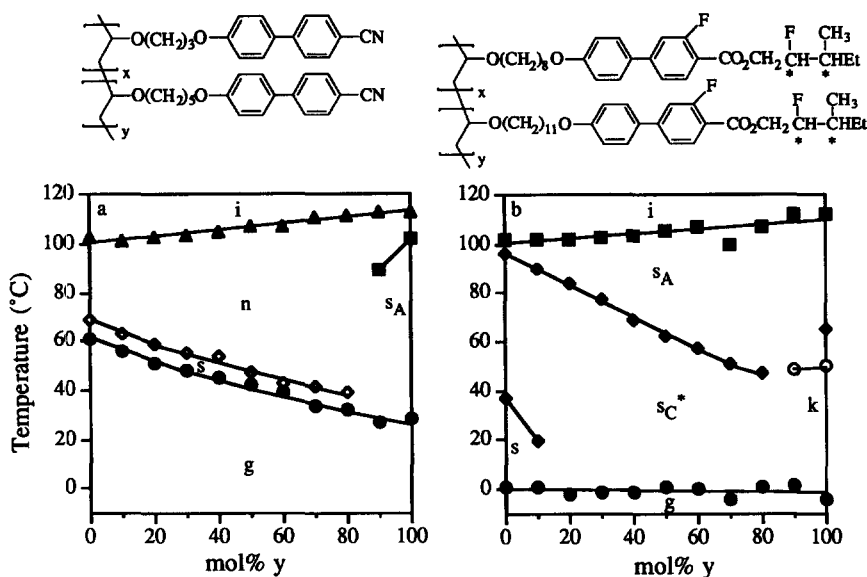


Fig. 24. Dependence of the phase transition temperatures from the glass (●), crystalline (○), unidentified smectic (◇), s_C^* (◆), s_A (■) and nematic (▲) phases of: (a) poly{[3-[(4'-(4''-cyanophenyl)phenoxy)propyl]vinyl ether]-co-[5-[(4'-(4''-cyanophenyl)phenoxy)pentyl]vinyl ether]} ($DP_n = 16-21$, $pdi = 1.09-1.25$);³⁶⁴ and (b) poly{[8-[(4'-(2R,3S)-2-fluoro-3-methylpentylloxycarbonyl)-3'-fluorophenyl-4''-phenoxy]octyl]vinyl ether]-co-[11-[(4'-(2R,3S)-2-fluoro-3-methylpentylloxycarbonyl)-3'-fluorophenyl-4''-phenoxy]undecyl]vinyl ether]} ($DP_n = 9-15$, $pdi = 1.09-1.22$);¹³⁹ first heat.

In contrast, the data in Table 17 demonstrate that the nematic-isotropic transition temperature of polynorbornene copolymers with either 20 or 50 repeat units in the liquid crystalline block are more similar to the higher molecular weight homopolymer than to that with 20 repeat units. This trend is demonstrated more conclusively by the diblock (PSt-PChEMA)^{208,209} and triblock (PChEMA-PSt-PChEMA²⁰⁸ and PSt-PChEMA-PSt²⁰⁹) copolymers of 2-(cholesterylloxycarbonyloxy)ethyl methacrylate and styrene. Although the exact temperatures vary greatly, Fig. 21 shows that the glass and smectic A-isotropic transition temperatures vary much less as a function of the length of the liquid crystalline block, and are essentially independent of the type of block copolymer and the morphology.

Studies of the copolymers discussed so far have therefore demonstrated that the mesogens within the liquid crystalline segment of block copolymers can organize anisotropically, and that the same mesophase is generally formed by both the homopolymer and copolymers containing at least 50 wt% of the liquid crystalline block. However, systematic studies of diblock (PSt-PChEMA) and triblock (PSt-PChEMA-PSt, PChEMA-PSt-PChEMA) copolymers of styrene and (2-cholesterylloxycarbonyloxy)ethyl methacrylate have demonstrated that this varies with lower weight or volume fractions of the liquid crystalline block.²⁰⁴⁻²⁰⁹ Most importantly, the morphology and thermotropic behavior of the diblock (PSt-PChEMA)^{208,209} and triblock (PChEMA-PSt-PChEMA²⁰⁸ and PSt-PChEMA-PSt²⁰⁹) copolymers of 2-(cholesterylloxycarbonyloxy)ethyl methacrylate and styrene

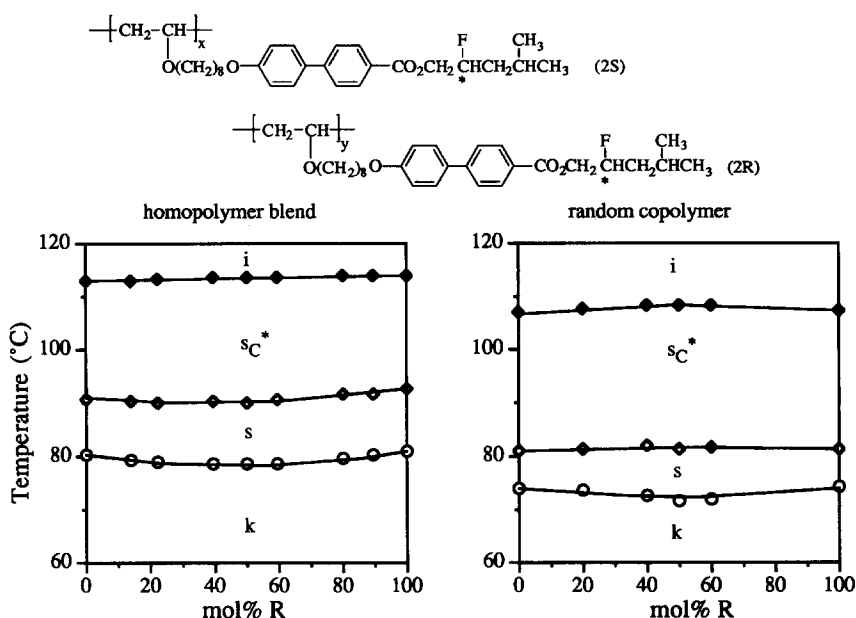


Fig. 25. Dependence of the phase transition temperatures from the crystalline (○), unidentified smectic (◇) and s_C^* (◆) phases of (a) blends of poly{[8-[(4'-(2R)-2-fluoro-4-methylpentylloxycarbonyl)phenyl-4''-phenoxy]octyl]vinyl ether} ($DP_n = 16.3$, $pdi = 1.14$) and poly{8-[(4'-(2S)-2-fluoro-4-methylpentylloxycarbonyl)phenyl-4''-phenoxy]octyl]vinyl ether} ($DP_n = 15.2$, $pdi = 1.14$); and (b) poly{[8-[(4'-(2R)-2-fluoro-4-methylpentylloxycarbonyl)phenyl-4''-phenoxy]octyl]vinyl ether}-co-[8-[(4'-(2S)-2-fluoro-4-methylpentylloxycarbonyl)phenyl-4''-phenoxy]octyl]vinyl ether} ($DP_n = 12.5-12.9$, $pdi = 1.13-1.16$);¹⁴¹ second heat.

are identical when the volume fraction of the blocks are equal, which is consistent with the behavior of amorphous AB and ABA block copolymers.^{25,267-270} This is true regardless of the length of the individual blocks. That is, the extent of immiscibility of all of the block copolymers is above the critical value ($\chi N > \chi N_{ODT}$), and the order-disorder transition (ODT) is not observed in any of the copolymers studied. As summarized in Fig. 22, those samples with volume fractions of polystyrene $0 < \phi_{PSI} < 0.7$ exhibit the classic morphologies of polystyrene spheres or rods embedded in a smectic A matrix of poly[2-(cholesterylformyl)ethyl methacrylate], and alternating lamellae of polystyrene and poly[2-(cholesterylformyl)ethyl methacrylate] (s_A). However, the phase diagram is asymmetric about $\phi_{PSI} = 0.5$. Such asymmetry is observed in amorphous block copolymers when the conformational and volume-filling characteristics of the two blocks are different.^{263,348} The extreme asymmetry of the phase diagram shown in Fig. 22 is therefore consistent with the conformational asymmetry of amorphous/side-chain liquid crystalline block copolymers.

In contrast to samples with $\phi_{PSI} < 0.7$, those with $\phi_{PSI} > 0.7$ exhibit only a spherical morphology of *nematic* poly[2-(cholesterylformyl)ethyl methacrylate] spheres in a polystyrene matrix, with no occurrence of PChEMA rods in a polystyrene matrix. As

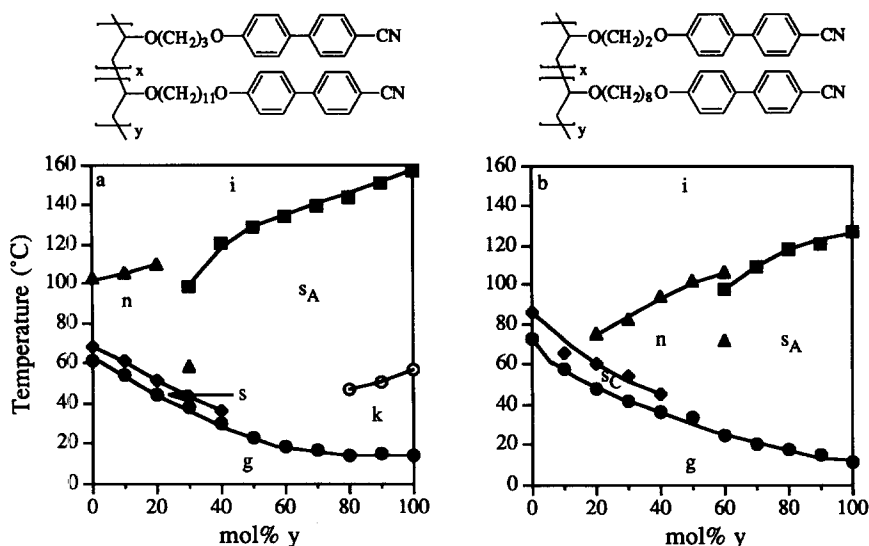
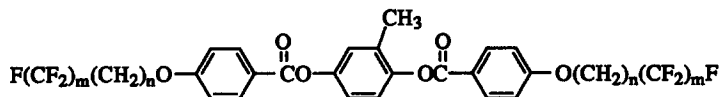


Fig. 26. Dependence of the phase transition temperatures from the glass (●), crystalline (○), unidentified smectic (◇), s_C (◆), s_A (■) and nematic (▲) phases of: (a) poly{ {3-[(4'-(4''-cyanophenyl)phenoxy)propyl]vinyl ether}-co-{11-[(4'-(4''-cyanophenyl)phenoxy)undecyl]vinyl ether} } ($DP_n = 17-21$, $pdi = 1.07-1.12$);³⁶⁴ and (b) poly{ {2-[(4'-(4''-cyanophenyl)phenoxy)ethyl]vinyl ether}-co-{8-[(4'-(4''-cyanophenyl)phenoxy)octyl]vinyl ether} } ($DP_n = 9-11$, $pdi = 1.10-1.17$);^{125,366} first heat.

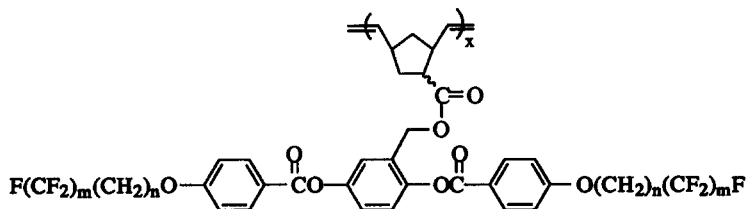
proposed by the researchers, both the curvature of the interface and the small size of the spheres (170 Å) evidently prevent the liquid crystalline block from organizing into its equilibrium smectic A structure, which has a layer distance of 45 Å. That is, the equilibrium packing of the mesogens is constrained in the microphase separated regions, which results in

Table 20. Thermotropic behavior of 2,5-bis{[4'-*n*-(perfluoroalkyl)alkoxybenzoyl]oxy}toluenes¹⁹⁵



<i>n</i>	<i>m</i>	Phase Transitions (°C)
4	6	<i>k</i> 106 s_C 205 s_A 214 <i>i</i>
5	6	<i>k</i> 101 s_C 197 s_A 207 <i>i</i>
6	6	<i>k</i> 99 s_C 197 s_A 203 <i>i</i>
8	6	<i>k</i> 102 s_C 189 s_A 192 <i>i</i>
4	7	<i>k</i> 124 s_C 215 s_A 222 <i>i</i>
5	7	<i>k</i> 119 s_C 208 s_A 216 <i>i</i>
6	7	<i>k</i> 129 s_C 206 s_A 212 <i>i</i>
8	7	<i>k</i> 120 s_C 197 s_A 200 <i>i</i>
4	8	<i>k</i> 130 s_C 218 s_A 226 <i>i</i>
5	8	<i>k</i> 122 s_C 214 s_A 221 <i>i</i>
6	8	<i>k</i> 130 s_C 211 s_A 217 <i>i</i>
8	8	<i>k</i> 124 s_C 201 s_A 205 <i>i</i>

Table 21. Thermotropic behavior of poly{5-[[[2',5'-bis[(4''-*n*-((perfluoroalkyl)alkoxy)benzoyl)oxy]-benzyl]oxy]carbonyl]bicyclo[2.2.1]hept-2-ene}_s¹⁹⁵



<i>n</i>	<i>m</i>	Phase Transitions (°C)
4	6	<i>g</i> 106 <i>s_C</i> 227 <i>s_A</i> 234 <i>i</i>
5	6	<i>g</i> 96 <i>s_C</i> 228 <i>s_A</i> 231 <i>i</i>
6	6	<i>g</i> 90 <i>s_C</i> 216 <i>s_A</i> 223 <i>i</i>
8	6	<i>g</i> 77 <i>s_C</i> 213 <i>s_A</i> 216 <i>i</i>
4	7	<i>g</i> 90 <i>s_C</i> 242 <i>s_A</i> 251 <i>i</i>
5	7	<i>g</i> 96 <i>s_C</i> 239 <i>s_A</i> 248 <i>i</i>
6	7	<i>g</i> 93 <i>s_C</i> 230 <i>s_A</i> 236 <i>i</i>
8	7	<i>g</i> 97 <i>s_C</i> 228 <i>s_A</i> 232 <i>i</i>
4	8	<i>g</i> 93 <i>s_C</i> 251 <i>s_A</i> 264 <i>i</i>
5	8	<i>g</i> 93 <i>s_C</i> 258 <i>s_A</i> 262 <i>i</i>
6	8	<i>g</i> 98 <i>s_C</i> 250 <i>s_A</i> 261 <i>i</i>
8	8	<i>g</i> 98 <i>s_C</i> 231 <i>s_A</i> 234 <i>i</i>

further asymmetry in the phase diagram. However, no new morphologies are observed. Diblock PBMA-PChEMA copolymers exhibit a very similar, asymmetric phase diagram, which lacks the morphology of PChEMA rods in the amorphous matrix; PChEMA is also nematic in the PChEMA sphere morphology.²¹⁰

The last structure/property relationship to be studied in side-chain liquid crystalline block copolymers is the change in enthalpy of the liquid crystalline transitions per mol mesogenic repeat unit. Tables 14–18 list the relative changes in enthalpy of isotropization for the copolymers and corresponding liquid crystalline homopolymers whenever possible. As shown, the change in enthalpy is often depressed relative to that of the homopolymer, although higher percentages seem to be obtained when the block copolymer contains a greater fraction of the liquid crystalline block. Nevertheless, it is just as often close to 100%, as in poly{(methyl methacrylate)-*block*-4-[4'-(4''-methoxyphenylazo)phenoxy]butyl methacrylate} (75–120%; Scheme 23) and poly{styrene-*block*-4-[4'-(4''-methoxyphenylazo)phenoxy]butyl methacrylate} (100–110%; Scheme 25).⁴⁶

The relative decrease in enthalpy should represent the extent of disorder at the interface of the two blocks, and has actually been directly correlated to the thickness of the interphase. That is, the ΔH of isotropization of lamellar PSt-PChEMA (Scheme 26) containing $\phi_{\text{PChEMA}} = 0.56$ is 81.4% of that of the homopolymer, indicating that the interphase should be approximately 18.6% of the liquid crystalline lamellae (12.5 nm). The calculated value of 2.3 nm corresponds very well to that measured by TEM following preferential staining of the interphase.²⁰⁷ Nevertheless, variations in the extent of disorder at the interface as measured by decreased enthalpies of transitions may be due to variations in sample

preparation and thermal history. For example, Gronski *et al.*'s ^2H -NMR experiments on deuterated PSt-PBAz (Scheme 21) indicate that the disordered interphase present in powder samples is eliminated when the samples are oriented by shear for extensive time in the nematic mesophase.²⁰³

4.2. Graft copolymers

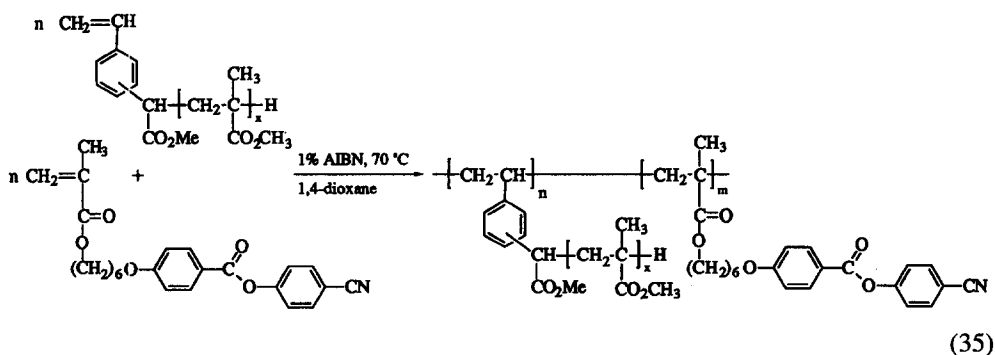
Although copolymers with equivalent compositions but different molecular architectures generally form the same morphology, the temperature of the order–disorder transition (T_{ODT}) varies.³⁴⁹ This is because the critical value of χN , in which χ is inversely proportional to temperature, varies with molecular architecture. For example, when $\phi_A = 0.5$ weak segregation theory calculates (in the absence of fluctuation corrections) that ordering occurs when $\chi N \geq 10.5$ for linear diblock copolymers,²⁶⁴ $\chi N \geq 11$ for graft copolymers (depending on the number of grafts),^{350,351} and $\chi N \geq 18$ for linear triblock copolymers [eqn (34)].³⁵²

$$(\chi N)_{\text{ODT,blend}} < (\chi N)_{\text{ODT,diblock}} < (\chi N)_{\text{ODT,graft}} < (\chi N)_{\text{ODT,triblock}} \quad (34)$$

Therefore, graft copolymers are more likely to remain homogeneous at a given temperature than the corresponding diblock copolymers.

In addition, both the shape and distribution of the domains of the minor phase in the matrix of the major phase of graft copolymers is more irregular than the spatially periodic structures of block copolymers.³⁵³ This is probably due to the greater limitations to phase separation due to the greater number of connections between the two blocks, as well as to the generally random distribution of grafts along the length of the main-chain block.

As shown in eqn (35), graft copolymers containing a mesogenic monomer have been



synthesized by free radical copolymerization of styryl-terminated poly(methyl methacrylate) and 6[4'-(4''-cyanophenoxy)hexyl methacrylate].^{354,355} In this case, the block length of the graft is nearly monodisperse ($DP_n = 28\text{--}127$, $\text{pdi} \leq 1.10$). However, the copolymers are not well-defined in molecular weight ($\text{pdi} = 2.21\text{--}4.00$) since a living mechanism was not used for the copolymerization. More importantly, the distance between

grafts along the backbone is not uniform. Nevertheless, the copolymers contain nearly the same ratio of the comonomers as was present in the feed, with total molecular weights up to $M_w = 2.5 \times 10^5$.

Table 19 presents the thermotropic behavior of these graft copolymers with varying compositions and graft lengths. Only the first four entries are microphase separated with the mesogenic block organized anisotropically. In these cases, the glass transition of the PMMA block overlaps the s_A-n-i transitions. All other entries exhibit a single glass transition. However, only entries 6 and 8 appear to form a homogenous solution with a glass transition corresponding to the weighted average of the two blocks. The glass transition of the other entries seems to correspond to either the PMMA graft (entries 5,9,10) or the mesogenic main-chain (entry 7). The T_g of the mesogenic main-chain is apparently not detected in entries 5, 9 and 10 because of its low weight fraction, whereas the T_g of PMMA is not detected in the sample in which it is present in the lowest weight fraction (entry 7). (The actual morphology and therefore confirmation of phase separation by these graft copolymers has not been determined.)

Comparison of the data in Tables 19 and 14 of graft and block copolymers, respectively, based on methyl methacrylate and a mesogenic methacrylate confirm that block copolymers phase separate more easily than graft copolymers. Although not exactly comparable due to the different mesogenic methacrylates, the block copolymers phase separate at shorter block lengths than the graft copolymers. In addition, the distribution of amorphous grafts along the mesogenic block disrupts the ability of the mesogens to organize anisotropically much more than the single connection in diblock copolymers.

4.3. Statistical binary copolymers

As discussed in the beginning of Section 4, a truly random distribution of two comonomers is achieved only in an azeotropic copolymerization in which $r_1 = r_2 = 1$. In this case, the two monomers have equal probability of reacting with a given active center, regardless of the monomer it is derived from, and the copolymer composition equals the comonomer feed composition at all conversions. Therefore, if the copolymerization also follows a "living" mechanism, all of the copolymer chains will have approximately the same chain length and the same random distribution of comonomer units. If $r_1 \neq r_2 \neq 1$, not only will the comonomers not be randomly distributed along the copolymer chain, but the comonomer feed and therefore the copolymer composition will also change as a function of conversion, resulting in a mixture of chemically heterogeneous chains.

With one exception,⁹⁰ side-chain liquid crystalline binary copolymers have only been prepared by a "living" mechanism using cationic polymerizations of vinyl ether comonomers [eqn (36)]. However, these copolymers are based on biphenyl-mesogenic monomers



with a variety of substituents which are copolymerized with either non-mesogenic vinyl ethers or vinyl ethers containing other biphenyl mesogens. The reactivity ratios

of the two comonomers have not been determined in any of these systems. Nevertheless, the reactivity of a given functional group is independent of a second functional group if they are separated by at least three methylenic carbons.³⁵⁶ Therefore, the reactivity ratio of a given mesogenic monomer should be identical to that of the corresponding *n*-alkyl substituted ($n \geq 3$) monomer with an identical polymerizable group if the *n*-alkyl spacer also contains at least three carbons. Similarly, the reactivity ratio of a mesogenic monomer should be independent of the length of the *n*-alkyl spacer if it contains at least three carbons.

If a mesogenic monomer is copolymerized with a non-mesogenic monomer, the meso-phase is observed above a minimum concentration of the mesogenic monomer. For example, neither poly{(methyl methacrylate)-*co*-[6-[4'-(4''-cyanophenylazo)phenoxy]hexyl methacrylate]} ($DP_n \sim 35$, $pdi = 1.35$) nor poly{(methyl methacrylate)-*co*-[6-[4'-(4''-n-butoxyphenoxy)carbonyl]phenoxy]hexyl methacrylate]} ($DP_n \sim 69$, $pdi = 1.12$) (Scheme 36) prepared by metalloporphyrin-initiated copolymerizations and containing 18–20 mol% of the mesogenic monomer exhibit the s_A mesophase of the corresponding SCLCPs.⁹⁰

However, the s_A mesophase of poly{[^tbutyl vinyl ether]-*co*-[11-[(4'-cyanophenyl-4''-phenoxy)undecyl]vinyl ether]} is retained at compositions containing at least 20 mol% of the mesogenic monomer (Figure 23); the crystalline phase is suppressed at much lower concentrations of the non-mesogenic units.³⁵⁷ Figure 23 also demonstrates that all of the transition temperatures decrease as the amount of ^tbutyl vinyl ether in the copolymer increases, with the change in enthalpy of isotropization decreasing accordingly. In this case,^{357,358} the glass transition decreases as the copolymer becomes more like poly(^tbutyl vinyl ether) due to its lower T_g (– 55°C at high molecular weight).³⁴⁴

Therefore, copolymerization of a mesogenic monomer with a non-mesogenic monomer whose homopolymer has a lower glass transition temperature can be used to both eliminate side-chain crystallization and to depress the glass transition temperature of the corresponding SCLCP. If the glass transition and/or more ordered phases are depressed, additional mesophases may be revealed.³⁵⁷ However, the biphasic region or temperature range over which the phase transitions occur increases as the concentration of the non-mesogenic unit increases.³⁵⁷ The thickness of the s_A layers in similar copolymers with ^tbutyl vinyl ether increases as the concentration of ^tbutyl vinyl ether increases, and apparently changes from interdigitated bilayer to (non-interdigitated) bilayer packing.³⁵⁹

In contrast, poly{[^tbutyl vinyl ether]-*co*-[2-[(4'-cyanophenyl-4''-phenoxy)ethyl]vinyl ether]} must contain at least 60 mol% of the mesogenic monomer to exhibit a s_C mesophase.³⁵⁷ Similar copolymers (Scheme 37) containing polymerizable methacrylate pendant groups and at least 40–60% of the mesogenic monomer can be subsequently crosslinked to generate networks which exhibit the s_A or s_C^* mesophase of the corresponding homopolymer.^{360–362} In addition, the crystalline and/or more ordered smectic mesophases of these homopolymers are eliminated when the networks contain 10–30% of the crosslinkable methacrylate monomer; less 2-vinyloxyethyl methacrylate than 11-vinyloxyundecanyl methacrylate is required to eliminate the ordered phases.

Several vinyl ether comonomers based on the same biphenyl mesogen with different spacers and/or different substituents were also copolymerized using the same conditions [eqn (36)]. All of the copolymerizations were assumed to be azeotropic ($r_1 = r_2 = 1$), and most were based on copolymer pairs containing at least three carbons in the spacer. Although the copolymers prepared by cationic polymerizations were not of high enough molecular

weight for their transitions to be independent of molecular weight,³⁶³ they were compared to homopolymers of the same degree of polymerization.

If the copolymer is based on monomers whose homopolymers exhibit identical mesophases, its phase diagram follows ideal solution behavior with a continuous, linear or slightly curved dependence of the transition temperature and enthalpy of at least the highest temperature mesophase on copolymer composition.^{132,134,136-140,364} For example, Fig. 24a demonstrates that the two structural units of poly{[3-[(4'-(4''-cyanophenyl)phenoxy)propyl]vinyl ether]-co-[5-[(4'-(4''-cyanophenyl)phenoxy)pentyl]vinyl ether]} are isomorphic within the nematic mesophase, although they are not isomorphic within the smectic mesophases.³⁶⁴ Similarly, the two structural units of poly{[8-[(4'-(2R,3S)-2-fluoro-3-methylpentylloxycarbonyl)-3'-fluorophenyl-4''-phenoxy]octyl]vinyl ether]-co-[11-[(4'-(2R, 3S)-2-fluoro-3-methylpentylloxycarbonyl)-3'-fluorophenyl-4''-phenoxy]undecyl]vinyl ether]} are isomorphic within both the s_C^* and s_A mesophases, but not the more ordered phases (Fig. 24b).¹³⁹ Therefore, copolymerization can be used to eliminate the crystalline and/or more ordered smectic phases of the corresponding homopolymer(s).

The isotropization temperature shows a slightly positive deviation from the additive values if the hetero-monomer interactions are stronger than the homo-monomer interactions,^{141,365} as shown by the copolymers and blends of homopolymers of 8-[(4'-(2R)-2-fluoro-4-methylpentylloxycarbonyl)phenyl-4'-phenoxy]octyl]vinyl ethers and 8-[(4'-(2S)-2-fluoro-4-methylpentylloxycarbonyl)phenyl-4'-phenoxy]octyl]vinyl ethers based on biphenyl mesogens with diastereomeric substituents (Fig. 25). However, this positive deviation decreases with increasing molecular weight,¹⁴¹ and will apparently vanish as the thermotropic behavior becomes independent of molecular weight (see Section 3.1). In contrast, the crystalline melting of such systems shows a negative deviation from ideal solution behavior due to the different physical properties of diastereomers.^{136,137,141}

If the copolymer is based on structural units which are not isomorphic, their respective mesophases are not exhibited over the entire composition (Fig. 26),^{125,133,135,364-367} and intermediate compositions may exhibit an entirely different³⁶⁶ phase (Fig. 26b), or the corresponding chiral mesophase³⁶⁵ if the comonomer is chiral.³⁶⁸ The transition temperature and enthalpy of at least the highest temperature mesophase generally also follow a continuous, slightly curved dependence on copolymer composition. Several of the copolymer pairs exhibit a reentrant nematic mesophase at a composition close to that which exhibits both mesophases of the corresponding two homopolymers.^{125,364,366,367}

Copolymerizations and the resulting phase diagrams can therefore be used to confirm or disprove the tentative assignment of a given mesophase.

5. OTHER FACTORS CONTROLLING THE THERMOTROPIC BEHAVIOR OF SCLCPS AS STUDIED USING LIVING POLYMERIZATIONS: INDUCTION OF SMECTIC LAYERING USING IMMISCIBLE COMPONENTS

Although liquid crystals were discovered in 1888,³⁶⁹ chemical concepts are only now being developed for converting the type of mesophase exhibited by a given chemical structure. Compounds which normally form only nematic mesophases can be forced to order into smectic layers by incorporating immiscible fluorocarbon units into their

hydrocarbon chemical structure. Comparison of the data in Table 7 and Table 20 and Table 21 demonstrate that smectic layering is induced not only in low molar mass liquid crystals, but also in the corresponding side-chain liquid crystalline polynorbornenes with laterally attached mesogens. The latter architecture is the most convincing system possible for demonstrating this concept since lateral attachment of the mesogens to a polymer backbone had previously precluded smectic layering.^{182,370-374}

6. FUTURE

Additional well-defined side-chain liquid crystalline polymers should be synthesized by controlled polymerizations of mesogenic acrylates (anionic or free radical polymerizations), styrenes (anionic, cationic or free radical), vinyl pyridines (anionic), various heterocyclic monomers (anionic, cationic and metalloporphyrin-initiated), cyclobutenes (ROMP), and 7-oxanorbornenes and 7-oxanorbornadienes (ROMP). Ideally, the kinetics of these "living" polymerizations will be determined by measuring the individual rate constants for termination and transfer, or at least the ratios of k_p/k_t and k_p/k_t . In addition, future studies should attempt to detect termination by plotting $\ln[M]_0/[M]$ vs time in addition to plots of molecular weight vs conversion or $[M]_0/[I]_0$ to detect transfer.

In addition to conclusively establishing the molecular weight dependence of their thermal transitions, these new SCLCPs will confirm or modify the structure/property correlations that have emerged thus far by synthesizing and studying only SCLCPs with a complete and homologous set of spacer lengths. In particular, the effect of tacticity should be studied using more controlled polymerization systems, rather than only those generated by anionic polymerizations. The effect of polydispersity and/or mixtures of immiscible molecular architectures and chain entanglements should also be determined, perhaps by comparing SCLCPs prepared by controlled radical polymerizations with those first prepared by classic radical polymerizations.

The range of well-defined block and graft copolymers containing at least one mesogenic block should also be expanded in order to elucidate the thermodynamics of phase separation, and perhaps, to discover new morphologies. (Living polymerizations should be used to synthesize both the macromonomer and the graft copolymer.) This will require better characterization of their thermotropic behavior and resulting morphologies. For example, overlapping transitions and glass transitions should be determined by dynamic mechanical analysis and/or dynamic DSC when necessary. The mechanical properties of these copolymers should also be determined in order to establish whether or not they behave as thermoplastic elastomers and if their transverse strength is greater than that of the corresponding homopolymers.

We expect that the range of well-defined statistical copolymers will also increase, primarily to manipulate the phases formed and the transition temperatures of the corresponding homopolymers.

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