Synthesis and Miscibility of Comb Poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s Prepared by ATRP

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ABSTRACT: Comb poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s were synthesized by atom transfer radical polymerization (ATRP) of 11-[(4′-cyanophenyl-4″-phenoxy)undecyl] acrylate from a multifunctional macroinitiator. The macroinitiator was prepared by first copolymerizing 2-[(2′-tetrahydropyranyl)oxy]ethyl acrylate ($r_1 = 0.88$) with 11-[(4′-cyanophenyl-4″-phenoxy)undecyl] acrylate ($r_2 = 1.11$) under ATRP conditions, followed by hydrolysis of the randomly distributed tetrahydropyranyl groups and conversion of the resulting hydroxyethyl acrylate groups to 2-(2′-bromopropanoate)ethyl acrylate initiating sites. The comb polymers contained 45−128 repeat units according to GPC measurements relative to linear polystyrene or 52−237 repeat units according to GPC−RI−viscometry−right angle laser light scattering measurements. The biphasic regions of the smectic A to isotropic transition of the comb polymers with pdi = 1.27−1.87 are extremely narrow, with full widths at half of the maximum peak intensity (fwhm) = 2.38−8.28 °C, in contrast to that of the corresponding polymer prepared by conventional radical polymerization (fwhm = 17 °C). The breadth of the biphasic region of binary blends of the comb polymers with poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s of a variety of architectures (linear, three-arm star, comb) increases linearly with the difference in the end group (and therefore branching) density of the two components, regardless of the combination of molecular architectures.

Introduction

One of the least studied structural variables in side-chain liquid crystalline polymers (SCLCPs) is the effect of polydispersity.[1] In contrast to low molar mass liquid crystals (LMMLCs), which are composed of a single molecular species and undergo phase transitions over a few degrees, SCLCPs are characterized by a distribution of molecular weights (pdi = M_w/M_n). This polydispersity is generally believed to cause broad phase transitions and is supported by studies on poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s prepared by conventional radical polymerization.[2,3] In these cases, fractionated samples undergo the smectic A−isotropic (s_A−i) transition over a narrower temperature range (full width at half of the maximum peak intensity, fwhm = 6.25−10.7 °C) than the original polymer (fwhm = 17.0 °C).[3] Even a fraction with a molecular weight ($M_n = 24.0 \times 10^3$, pdi = 1.96) similar to that of the original sample ($M_n = 25.2 \times 10^3$, pdi = 3.43) has a much narrower transition (fwhm = 7.14 °C).[3] In contrast, most well-defined linear SCLCPs prepared by controlled polymerizations exhibit relatively narrow transitions,[1] even when blended into multimodal, polydisperse blends.[4]

Since polydispersity created by blending linear SCLCPs (polynorbornenes) has no effect on their thermotropic behavior,[4] whereas fractionation of mesogenic polyacrylates prepared by radical polymerization results in narrower biphasic regions,[2,3] we proposed that the broad phase transitions of SCLCPs may be caused by the limited miscibility of a mixture of branched structures caused by chain transfer to polymer at high monomer conversion in radical polymerizations.[3] This was demonstrated by preliminary studies that compared the thermotropic behavior of linear and three-arm star poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s prepared by atom transfer radical polymerization (ATRP) and their binary blends and unmixed composites. The biphasic regions of linear polymers (pdi = 1.15−1.49, fwhm = 4.46−6.70 °C) and their binary mixtures (fwhm = 4.46−6.25 °C) were extremely narrow. However, although the three-arm star polymers (pdi = 1.11−2.20) also exhibited narrow isotropization transitions (fwhm = 4.46−8.96 °C), their binary mixtures with a significant difference in branching density had broad transitions (fwhm = 8.93−15.18 °C), evidently due to their limited miscibility.

This paper extends our preliminary study[3] on determining whether the broad phase transitions of SCLCPs prepared by conventional radical polymerizations are due to polydispersity in molecular architecture and/or to polydispersity in chain length. We have synthesized the corresponding comb poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s, in which the mesogens are attached to both the main chain and the grafts, by ATRP. The thermotropic behavior of the comb polymers will be compared to that of the linear and three-arm star polymers and to their binary blends and unmixed composites of the various molecular architectures.

Results and Discussion

Synthesis of Poly{[2-(2′-bromopropanoate)ethyl acrylate]-*ran*-[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]} Macroinitiator by ATRP. As outlined in Scheme 1, the linear poly{[2-(2′-bromopropanoate)ethyl acrylate]-*ran*-[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]} multifunctional macroinitiator was synthesized by first copolymerizing a tetrahydropyran (THP) protected hydroxyethyl acrylate and the mesogenic monomer under ATRP conditions using methyl 2-bromopropionate as the initiator, cuprous bromide as the catalyst, and 4,4′-diheptyl-2,2′-dipyridyl

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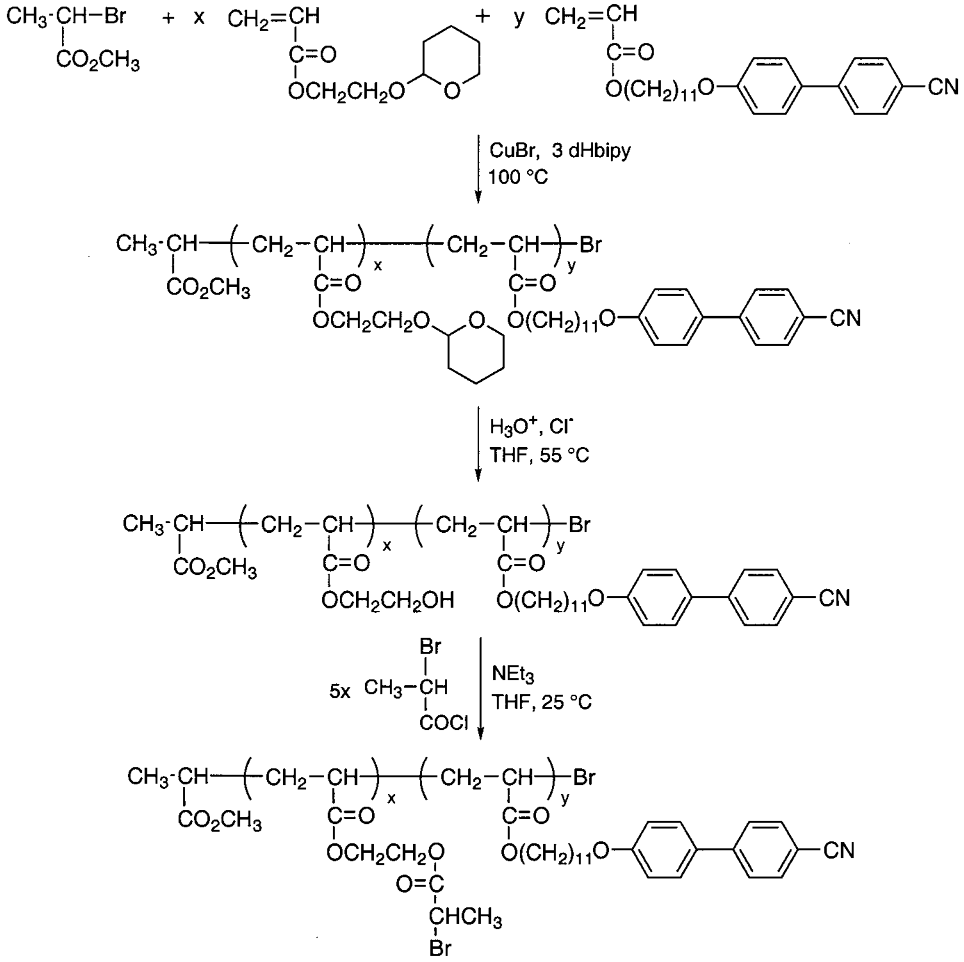
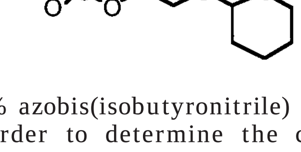
Scheme 1. Synthesis of Poly{[2-(2′-bromopropanoyl)ethyl acrylate]-*ran*-[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]}; dHbipy = 4,4′-Diheptyl-2,2′-dipyridyl



(dHbipy) as a ligand that presumably solubilizes the copper complexes and reduces the oxidation potential of Cu(I).

The hydroxy group of hydroxyethyl acrylate was protected in order to isolate it from dimer impurities that would generate cross-links and to prevent any transesterification during the polymerization. However, the THP-protecting group could also potentially act as a cross-linking and/or chain transfer site. The anomeric hydrogen of the THP group should be the most easily abstracted atom since this would generate a tertiary radical stabilized by resonance with the lone pair of electrons from two α-oxygen atoms. We therefore polymerized methyl acrylate in the presence of 2-(2′-tetrahydropyranyloxy)ethyl propionate



using 1 mol % azobis(isobutyronitrile) (AIBN) as the initiator in order to determine the chain transfer constant to a model compound representing one repeat unit of the corresponding polyacrylate. The chain transfer constant to 2-(2′-tetrahydropyranyloxy)ethyl propionate was determined by measuring the decrease in the degree of polymerization of poly(methyl acrylate) in its presence and plotting DP_n^{-1} vs the ratio of the concentrations of chain transfer agent ([TA]) and monomer ([M]) according to the Mayo equation (eq 1)[5]

$$\frac{1}{DP_n} = \left[\frac{1}{DP_n}\right]_0 + C_X \frac{[TA]}{[M]} \qquad (1)$$

where $(1/DP_n)_0$ is the inverse number-average degree of polymerization in the absence of the chain transfer agent. As shown in Figure 1 (data in Supporting Table 1), the chain transfer constant of 2-(2′-tetrahydropyranyloxy)ethyl propionate in a radical polymerization of methyl acrylate in benzene at 60 °C is approximately $C_X = k_{tr}/k_p = 1.1 \times 10^{-3}$. This means that chain transfer to 2-(2′-tetrahydropyranyloxy)ethyl propionate will be insignificant if $[M]_0/[I]_0 \leq 10^2$.[6] We have therefore copolymerized the THP-protected and mesogenic monomers using $[M_1 + M_2]_0/[I]_0 < 50$.

Since both the THP-protected and mesogenic monomers are acrylates, their reactivity ratios should be approximately equal to one. This was confirmed by determining the monomer reactivity ratios in a conventional free radical polymerization. The composition of the copolymers (Supporting Table 2) was calculated by ^{1}H NMR using the integral of the OC*H*O resonance (4.63 ppm) of the THP-protected repeat unit (M_1) and the sum of the integrals of the aromatic resonances (6.95 and 7.40−7.75 ppm) of the mesogenic repeat unit (M_2) (Supporting Figure 1). The monomer reactivity ratios, $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$, were determined from the copolymer composition using both the Fineman−Ross[7] and Kelen−Tüdos[8] methods as described in the Sup-

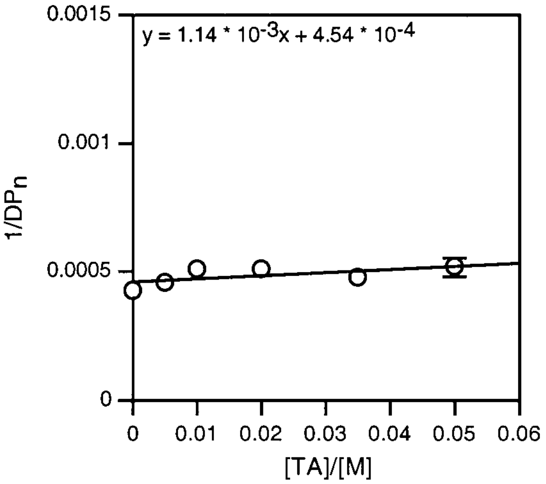


Figure 1. Determination of the chain transfer constant to poly[2-(2′-tetrahydropyranyloxy)ethyl acrylate] under conventional free radical conditions in benzene at 60 °C using 1 mol % AIBN as the initiator.

porting Information; the calculated parameters for these expressions are listed in Supporting Table 3. According to the Fineman−Ross plot (Supporting Figure 2), $r_1 = 0.87$ and $r_2 = 1.1$, in which we have labeled the THP-protected monomer M_1 and the mesogenic monomer M_2. If we invert these labels, $r_1 = r_{mes} = 1.1$ and $r_2 = r_{THP} = 0.92$. According to the Kelen−Tüdos plot (Supporting Figure 3), $r_1 = r_{THP} = 0.88$ and $r_2 = r_{mes} = 1.1$; if the labels for M_1 and M_2 are reversed, the calculated values are $r_1 = r_{mes} = 1.1$ and $r_2 = r_{THP} = 0.87$. These values of r_1 and r_2 from both the Fineman−Ross and Kelen−Tüdos methods demonstrate that the two monomers have comparable reactivities toward the propagating chain, with the mesogenic monomer being only slightly more reactive. The two monomers should therefore be randomly distributed along the copolymer chain.

The data in Table 1 confirm that the mesogenic monomer is slightly more reactive than the THP-protected monomer in their atom transfer radical copolymerizations. The small scale (1 g) syntheses demonstrate that the two monomers can be copolymerized with up to 41% of the THP-protected monomer incorporated into a copolymer with approximately 32 repeat units using a 1:1 comonomer feed composition. The copolymerization was then scaled up, first to 2 g and then to 10 g, using only 15% THP-protected monomer in the comonomer feed and a total monomer-to-initiator ratio of 30. The copolymer produced on a 10 g scale contained 13% of the THP-protected monomer and approximately 30 repeat units. The number-average degrees of polymerization and average number of each type of repeat unit (*x* and *y* in Table 1) were calculated using the molecular weight determined by GPC and the copolymer composition determined by ^{1}H NMR. Since the chemical structure and therefore the reactivity of the initiator and propagating polymer are similar, the resulting copolymers have relatively narrow (pdi = 1.17−1.29), monomodal molecular weight distributions.

The copolymer in Table 1 produced on a 10 g scale that contained 13% of the THP-protected monomer and approximately 30 repeat units was used for the macroinitiator synthesis and the remaining experiments described in this paper. After hydrolysis of this copolymer (Supporting Figure 1) in aqueous HCl at 55 °C, the ^{1}H NMR resonance at 4.63 ppm corresponding to $OCHO$ of THP in the THP-protected repeat unit almost disappeared (Supporting Figure 4). The resulting polyol was then reacted with excess 2-bromopropionyl chloride to introduce 2-bromopropanoate initiating sites (Scheme 1). The ^{1}H NMR spectrum of the resulting macroinitiator (Supporting Figure 5) demonstrated that the CH_2OH resonance (3.78 ppm) is absent. Its molecular weight distribution (pdi = 1.18) is similar to that of its two precursors (pdi = 1.21 and 1.25). Therefore, both the hydrolysis and reaction with 2-bromopropionyl chloride were essentially complete.

Synthesis of Comb Polymers by ATRP. Scheme 2 outlines the atom transfer radical polymerization of the mesogenic monomer using the multifunctional macroinitiator to produce comb polymers. This synthetic route minimizes the portion of chemical structures that are different from, or in addition to, those present in the corresponding mesogenic linear polymers; i.e., only $-CH_2CHCO_2CH_2CH_2O_2C(CH_3)H-$ branches are present in addition to the chemical structure of the linear polymer. According to the GPC_{PSt} and ^{1}H NMR results (Table 1), the macroinitiator contains an average of four initiating sites along the backbone, plus one at the polymer terminus. This macroinitiator should therefore produce comb polymers with an average of four grafts per chain.

Table 2 summarizes the results of the atom transfer radical polymerizations using $[M]_0/[\text{macroinitiator}]_0 < 300$ and $[M]_0/[I]_0 < 55$, where $[I]_0$ is the initial concentration of initiating sites. It was difficult to attain complete monomer conversion at high monomer-to-initiator ratios. The highest molecular weight comb polymer containing an average of 128 repeat units was therefore synthesized using a much higher monomer-to-initiator ratio. The final comb polymers used in this

Table 1. Synthesis of Poly{[2-(2′-tetrahydropyranyloxy)ethyl acrylate]-*ran*-[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]}s by Atom Transfer Radical Polymerizations[a]

scale (g)	$([M_1 + M_2]_0)/[I]_0$	$[M_1]_0/[I]_0$	$[M_2]_0/[I]_0$	comonomer comp (mol %)		time (h)	yield[b] (%)	copolymer comp[c] (mol %)		theor[d]	GPC$_{PSt}$[e]		GPC$_{PSt}$ + NMR		
				M_1	M_2			M_1	M_2	$M_n \times 10^{-4}$	$M_n \times 10^{-4}$	pdi	$DP_{n,total}$	x[f]	y[g]
1	31	3	28	10	90	10	76	4	96	1.24	1.49	1.25	35	1	34
1	19	4	15	21	79	24	78	18	82	0.716	1.00	1.26	26	5	21
1	40	20	20	50	50	14	74	41	59	1.24	1.08	1.29	32	13	19
2	29	4	25	14	86	11	85	9	91	1.13	1.02	1.17	25	2	23
10	30	5	25	15	85	10	91	13	87	1.16	1.20	1.25	30	4	26

[a] Using 1:3:1 [CuBr]/[4,4′-diheptyl-2,2′-dipyridyl]/[initiator] at 100 °C in bulk; M_1 = 2-(2′-tetrahydropyranyloxy)ethyl acrylate, M_2 = 11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate. [b] After copper and monomer completely removed by multiple reprecipitations. [c] Copolymer composition obtained from ^{1}H NMR by comparing the integrals of the $OCHO$ resonance of THP (4.63 ppm) with the sum of the aromatic protons (6.95 and 7.40−7.75 ppm). [d] Assuming 100% conversion and taking end groups into account: $M_n = 167.01 + 200.23[M_1]_0/[I]_0 + 419.56[M_2]_0/[I]_0$. [e] Number-average molecular weight (M_n) and polydispersity (pdi = M_w/M_n) determined by gel permeation chromatography (GPC) relative to linear polystyrene using mean of RI and UV detectors. [f] Average number of THP-protected repeat units per copolymer chain. [g] Average number of mesogenic repeat units per copolymer chain.

Scheme 2. Synthesis of Comb Poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate] by ATRP Using a Multifunctional Initiator; dHbipy = 4,4′-Diheptyl-2,2′-dipyridyl

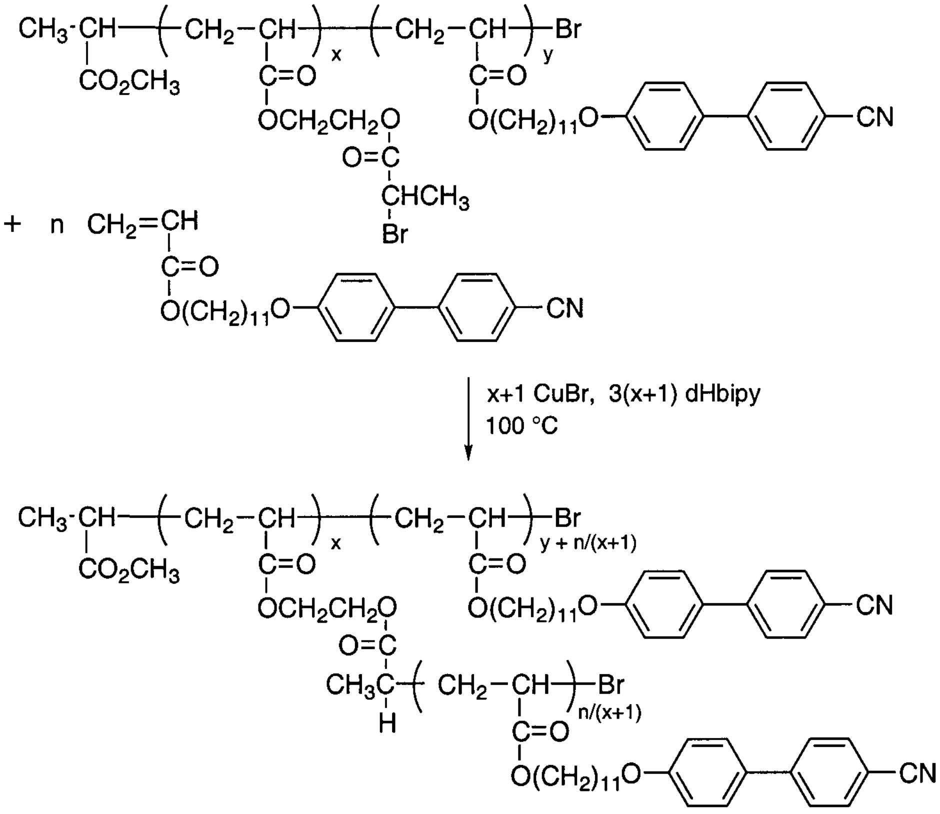


Table 2. Synthesis of Comb Poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s by Atom Transfer Radical Polymerizations[a]

					GPC$_{PSt}$[d]		
[M]$_0$/[macroinitiator]$_0$	[M]$_0$/[I]$_0$	theor[b] $M_n \times 10^{-4}$	time (h)	yield[c] (%)	$M_n \times 10^{-4}$	DP$_{n,\mathrm{total}}$	pdi
27	5	2.45	4.5	76	2.02	45	1.27
53	11	3.58	4.0	62	2.50	57	1.31
80	16	4.70	4.0	73	2.88	66	1.56
105	21	5.75	6.2	41	3.78	87	1.48
161	32	8.10	4.0	50	4.50	104	1.56
214	43	10.3	4.0	43	5.45	127	1.70
268	54	12.6	3.8	60	5.50	128	1.88

[a] Using 1:3:1 [CuBr]/[4,4′-diheptyl-2,2′-dipyridyl]/[initating site] at 100 °C in bulk monomer. [b] Assuming 100% conversion and taking end groups into account: $M_n = 1.33 \times 10^4 + (419.56\ [\mathrm{M}]_0/[\mathrm{macroinitiator}]_0)$. [c] After copper and monomer completely removed by multiple reprecipitations. [d] Number-average molecular weight (M_n), number-average degree of polymerization (DP$_{n,\mathrm{total}}$), and polydispersity (pdi $= M_w/M_n$) determined by gel permeation chromatography (GPC) relative to linear polystyrene using mean of RI and UV detectors.

study contain an average of 45−128 repeat units according to GPC analysis relative to linear polystyrene, which correspond to 3−20 repeat units per graft (Table 3). Their molecular weight distributions (pdi = 1.27−1.88) are broader than those of the corresponding linear and three-arm star polymers that we[3] previously reported.

Our previous study indicated that GPC was a reasonable method for comparing the molecular weights of the linear and three-arm star polymers.[3] That is, both series extrapolated to exactly the same isotropization temperature (145 °C) at infinite molecular weight, which is significantly lower than that of the fractionated polymers prepared by conventional free radical polymerization (154 °C). In addition, the transition temperatures of the star polymers were lower than those of the linear polymers with identical DP$_n$. However, since standard GPC analysis underestimates the molar masses of branched macromolecules due to their compact shape,[9] the molecular weight data summarized in Table 2 are only apparent values. The GPC-determined molecular weights should become less accurate and less comparable to the linear polymers as the branch content increases. Absolute molar masses of the branched polymers can presumably be determined by GPC using refractive index, viscometry, and right angle laser light scattering triple detectors (GPC−RI−Visco−RALLS = GPC$_{\mathrm{triple}}$).

Table 3 compares the GPC$_{PSt}$-determined molecular weights and polydispersities of the comb polymers with those determined by GPC$_{\mathrm{triple}}$ measurements. The molecular weights of the macroinitiator obtained from GPC relative to linear polystyrene and from GPC−RI−Visco−RALLS are 1.33 × 10^4 and 1.44 × 10^4 Da, respectively. On the basis of the GPC$_{PSt}$-determined molecular weight, the macroinitiator contains a total of five initiating sites including the chain end. On the basis of the GPC$_{\mathrm{triple}}$ molecular weight, it contains a total of six initiating sites. Therefore, the initial ratio of the concentrations of monomer to initiating sites in Table 3 are different

Table 3. Comparison of the Number-Average Molecular Weights and Polydispersities of the Comb Poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s Determined by Standard GPC (GPC_{PSt}) and by GPC−RI−Visco−RALLS (GPC_{triple}) in THF

$[M]_0/[I]_0$		theor[a] $M_n \times 10^{-4}$		GPC_{PSt}[b]				GPC_{triple}[c]			
GPC_{PSt}	GPC_{triple}	PSt	triple	$M_n \times 10^{-4}$	$DP_{n,total}$	$DP_{n,arm}$	pdi	$M_n \times 10^{-4}$	$DP_{n,total}$	$DP_{n,arm}$	pdi
5	5	2.45	2.65	2.02	45	3	1.27	2.34	52	4	1.91
11	10	3.58	3.86	2.50	57	6	1.31	3.71	85	9	1.69
16	14	4.70	5.07	2.88	66	7	1.56	4.78	111	13	1.89
21	19	5.75	6.21	3.78	87	12	1.48	6.31	147	19	1.99
32	29	8.10	8.75	4.50	104	15	1.56	7.63	178	24	2.00
43	38	10.3	11.1	5.45	127	20	1.70	9.45	222	32	2.33
54	48	12.6	13.6	5.50	128	20	1.88	10.1	237	34	2.53

[a] Assuming 100% conversion and taking end groups into account: Theoretical $M_{n,PSt} = 1.33 \times 10^4 + (419.56[M]_0/[I]_0)$; theoretical $M_{n,triple} = 1.44 \times 10^4 + (419.56[M]_0/[I]_0)$. [b] $DP_{n,total,PSt} = [M_n - 167.01 - (4)(251.08)]/419.56$; $DP_{n,arm,PSt} = (DP_{n,total,PSt} - 29)/5$. [c] $DP_{n,total,triple} = [M_n - 167.01 - (5)(251.08)]/419.56$; $DP_{n,arm,triple} = (DP_{n,total,PSt} - 31)/6$.

Table 4. Comparison of the Weight-Average Molecular Weights and Polydispersities of the Comb Poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s Determined by Multiple Methods in THF

	d*n*/d*c* (mL/g)		GPC_{LS}[c]		GPC_{PSt}		GPC_{triple}	
$DP_{n,total,PSt}$	633 nm on-line[a]	690 nm off-line[b]	$M_w \times 10^{-4}$	pdi	$M_w \times 10^{-4}$	pdi	$M_w \times 10^{-4}$	pdi
45	0.162	0.185	3.54	1.36	2.57	1.27	4.47	1.91
57	0.165	0.187	5.26	1.44	3.25	1.30	6.27	1.69
66	0.167	0.192	7.33	1.65	4.46	1.55	9.03	1.89
87	0.161	0.183	11.0	1.61	5.56	1.47	12.6	1.99
104	0.171	0.186	12.5	1.71	7.02	1.56	15.3	2.00
127	0.168				9.26	1.70	22.0	2.33
128	0.163	0.180	23.1	1.87	10.3	1.87	25.6	2.53

[a] Measured on-line at 633 nm by GPC−RI−Visco−RALLS analyses; assumes 100% mass recovery. [b] Measured off-line at 690 nm using Optilab 903 differential refractometer and used to determine M_w by GPC_{LS}. [c] Using a He−Ne laser set at 690 nm with scattering angles of 45°, 90°, and 135°.

for the two techniques. The results in Table 3 demonstrate that the four or five branches along the polymer backbone indeed cause an underestimation of the GPC_{PSt}-determined molecular weights. For example, the highest molecular weight comb polymer is 5.50×10^4 and 10.1×10^4 Da by GPC_{PSt} and GPC_{triple}, respectively; the GPC_{PSt}-determined value is only half that from GPC_{triple}. The discrepancy between the GPC_{PSt}- and GPC_{triple}-determined molecular weights increases as the length of the branches increase, and the polymer becomes more compact. The number-average degrees of polymerization per graft ($DP_{n,arm,triple}$) in Table 3 agree well with the theoretical values when $[M]_0/[I]_0 < 40$ and become less comparable as the initial ratio of monomer to initiating site increases due to incomplete monomer conversion (Table 2). The comb polymers used in this study contain 4−34 repeat units per graft, which corresponds to 52−237 repeat units based on the GPC_{triple}-determined number-average molecular weight.

The molecular weights and molecular weight distributions of the comb polymers were also measured by GPC with a three-angle laser light scattering detector (GPC_{LS}). As summarized in Table 4, the weight-average molecular weights obtained by GPC_{LS} and GPC_{triple} agree well, whereas the polydispersities obtained by GPC_{LS} correspond well to the GPC_{PSt} data; the GPC_{triple}-determined polydispersities are probably inflated because of band broadening[10] and the opposing molecular weight dependencies of the interdetector delays[11] for the two pairs of detectors. The refractive index increment (d*n*/d*c*) is roughly constant for the individual on-line and off-line measurements within the molecular weight range studied (Table 4).

Thermotropic Behavior of Comb Polymers Prepared by ATRP. All of the polymers prepared by ATRP were carefully purified to remove both residual copper and any unreacted monomer. Residual copper significantly decreases the decomposition onset temperature of the polymer and broadens high-temperature transitions.[3] Copper complexes were stringently removed by extracting them into aqueous methanolic solutions of ammonium chloride. Residual monomer depresses the transition temperatures and broadens the isotropization transitions of the polymer[3] and was removed by reprecipitating the polymers from THF into a warm solution of ethanol and toluene (5:1), followed by slowly cooling to −78 °C before collecting the polymer.

Figure 2 presents the normalized DSC traces of the comb polymers with GPC_{PSt}-determined degrees of polymerization of 45−128 (Table 2). Although these polymers also exhibit a smectic C−smectic A (s_C−s_A) transition at a temperature above the glass transition, it is barely detectable in these scans because the polymers were not annealed for sufficient time after heating through isotropization. In contrast, the s_A−i transition is not affected by annealing. As shown by the representative polarized optical micrographs in Figure 3, linear ($DP_n = 55$, pdi = 1.27), three-arm star ($DP_n = 57$, pdi = 1.30), and comb ($DP_{n,triple} = 52$, pdi = 1.27) polymers exhibit similar focal−conic fan textures after annealing for only a short time in the s_A mesophase, although there are fewer defects in the texture of the linear polymer.

As shown in Figure 2 and summarized in Table 5, the temperatures of the glass and isotropization transitions increase as the molecular weight increases. However, using the data reported previously for the linear and three-arm star polymers,[3] the isotropization temperatures decrease slightly in the order of linear > three-arm star > comb polymers with similar molecular weights, which confirms that their molecular architectures are different. For example, the linear polymer with $DP_n = 55$ undergoes isotropization at 140 °C, whereas the three-arm star and comb polymers with $DP_n = 55$

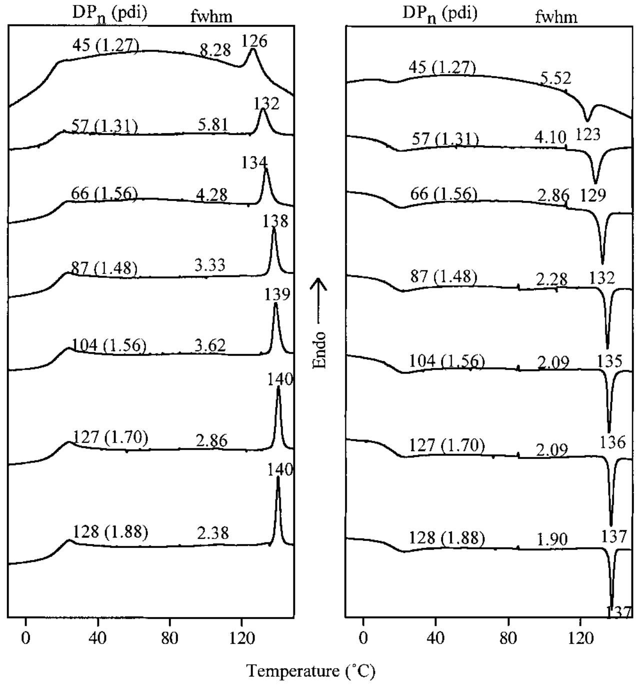


Figure 2. Normalized differential scanning calorimetry traces (10 °C/min) of comb poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s prepared by ATRP; fwhm = full width at half of the maximum peak intensity.

and $DP_{n,triple} = 52$ undergo isotropization at 135 and 126 °C, respectively. This lower temperature also does not correspond to the isotropization temperature of a single arm and/or branch, since the corresponding linear polymers with $DP_n = 18$ and $DP_n = 8$ undergo isotropization at 119 and 97 °C, respectively. The isotropization transitions of the linear and three-arm star polymers also level off at slightly lower degrees of polymerization ($DP_n \approx 40$ and 50, respectively)[3] than that of the comb polymers ($DP_n \approx 60$) (Figure 4), which again is consistent with their different molecular architectures. In addition, the comb polymers extrapolate to a similar but slightly higher isotropization temperature (148 °C) at infinite molecular weight compared to the linear and three-arm star polymers (144 and 145 °C, respectively)[3] based on GPC_{PSt}-determined number-average degrees of polymerization. Figure 5 plots the dependence of the glass and phase transition temperatures of the comb polymers as a function of the GPC_{triple}-determined number-average degree of polymerization and the inverse number-average degree of polymerization. In this case, the comb polymers extrapolate to exactly the same isotropization temperature (144 °C) at infinite molecular weight as the linear[3] and three-arm star[3] polymers. This demonstrates that the effect of one to five branch points is insignificant at infinite molecular weight for side-chain liquid crystalline poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s and that the GPC−RI−Visco−RALLS triple detector analysis is more appropriate for characterizing the molecular weight of the comb polymers. The glass and s_C−s_A transitions of the comb polymers are less sensitive to increasing molecular weight.

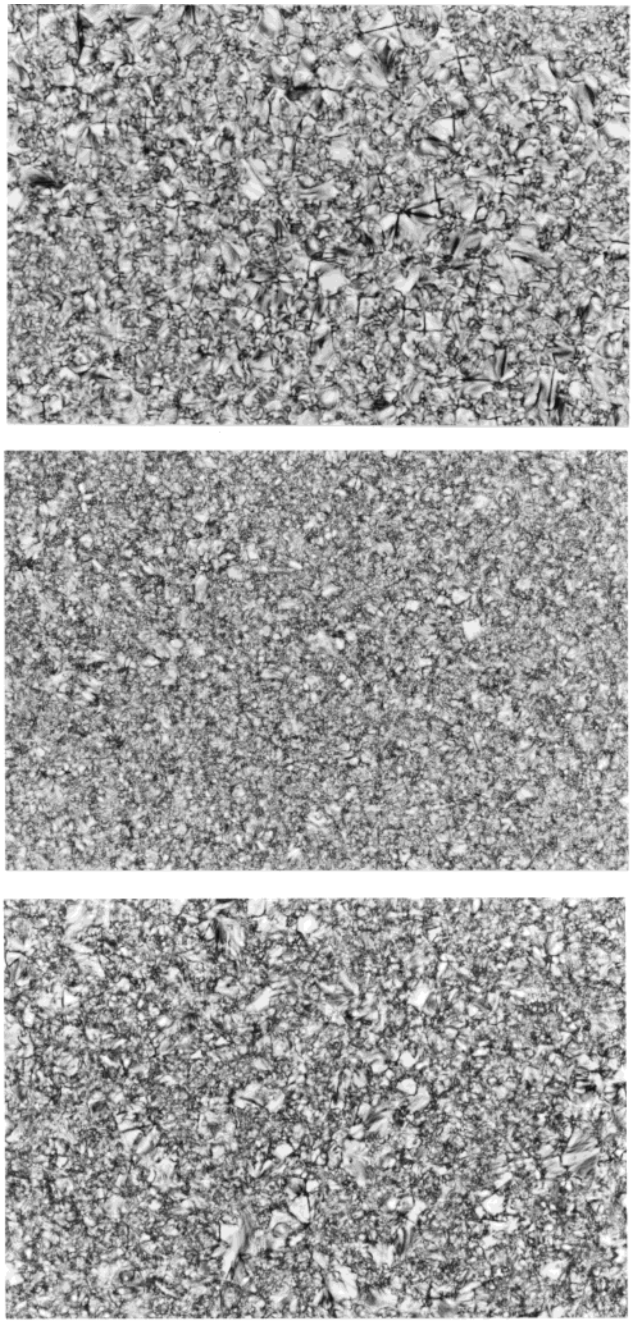


Figure 3. Polarized optical micrographs (200×) of the s_A focal−conic fan textures observed after annealing for 30 min upon cooling poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate] from the isotropic melt: (top) 137 °C, linear polymer ($DP_n = 55$, pdi = 1.27); (middle) 134 °C, three-arm star polymer ($DP_n = 57$, pdi = 1.30); (bottom) 123 °C, comb polymer ($DP_{n,triple} = 52$, pdi = 1.27).

Table 5 also lists the fwhm of the isotropization transitions of the comb polymers prepared by ATRP. In contrast to the polymer prepared by conventional free radical polymerization, which has a broad monomodal, Gaussian-like molecular weight distribution and exhibits a very broad isotropization transition (fwhm = 17.0 °C),[3] all of the isotropization transitions of the comb polymers are narrow (fwhm = 2.38−8.28 °C). The breadth of the transitions also decreases with increasing molecular weight. Although the end groups are relatively small and are chemically bonded to the polymers, this indicates that the end groups have limited miscibility with the mesogenic side chains. Since end groups have a greater influence as the molecular weight decreases, they evidently broaden the breadth of the phase transitions of lower molecular weight polymers. The two highest molecular weight comb polymers ($DP_{n,PSt} = 127$ and 128) have the narrowest transitions

Table 5. Thermotropic Behavior of Poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s Prepared by ATRP and Used in Blends with the Comb Polymers

	GPC$_{PSt}$		transition temp (°C)			peak width[a]
DP$_{n,PSt}$	$M_n \times 10^{-4}$	pdi	g–s$_C$	s$_C$–s$_A$	s$_A$–i	(°C) fwhm
			Linear			
8[b]	0.368	1.15	7	12	97	6.70
18	0.785	1.18	11	17	119	7.85
36[b]	1.54	1.34	14	23	134	5.36
40[b]	1.68	1.30	12	21	133	5.36
40	1.70	1.20	17	23	138	3.83
55	2.33	1.27	18	24	140	3.74
70[b]	2.94	1.49	17	26	141	4.46
86	3.62	1.25	15	24	141	2.34
			Three-Arm Star			
29[b]	1.25	1.24	15	24	123	7.14
42[b]	1.81	1.11	17	23	132	5.14
55[b]	2.35	1.25	16	26	135	5.36
57	2.42	1.30	16	23	137	4.25
			Comb			
45	2.02	1.27	13	18	126	8.28
57	2.50	1.31	14	21	132	5.81
66	2.88	1.56	15	23	134	4.28
87	3.78	1.48	16	24	138	3.33
104	4.50	1.56	16	25	139	3.62
127	5.45	1.70	17	25	140	2.86
128	5.50	1.88	17	25	140	2.38

[a] Peak width of isotropization determined by DSC on heating at 10 °C/min from the full width at half of the maximum of the peak intensity (fwhm). [b] From ref 3.

(fwhm = 2.86 and 2.38 °C), although these two samples have the broadest polydispersities (pdi = 1.70 and 1.88). This demonstrates that a broad monomodal, Gaussian-like distribution of chain lengths of a single architecture is not sufficient to broaden the breadth of the s$_A$–i transition of poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate].

Binary Blends of Polymers Prepared by ATRP. Since a broad Gaussian-like distribution of chain lengths is not sufficient to broaden the isotropization transition of poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate], the broad phase transition of the conventionally prepared polymer may be due to an immiscible mixture of molecular architectures caused by chain branching at high monomer conversion. That is, if the components of the polymer have limited miscibility and/or are phase-separated in the mesophase and/or isotropic melt, the transition should be either broadened or exhibit multiple maxima. If the components of the polymer are miscible in both phases coexisting at that transition, the polymer should exhibit a single, relatively narrow transition representing an average of the individual components. This is demonstrated in Figures 6–9 by comparing the phase transitions of comb/comb, comb/linear, and comb/star binary blends to those of the corresponding unmixed samples. The two components of the unmixed composites were physically separated within the same DSC sample pan by an extra lid, whereas the blends were prepared by codissolving the two components in a minimum amount of THF and precipitating the blend in methanol at −78 °C. The resulting compositions of the blends are listed in Table 6, along with their GPC$_{PSt}$-determined degrees of polymerization and polydispersities, as well as their isotropization temperatures. The isotropization temperatures of all of the blends correspond fairly well to the expected values based on composition. However, the average chain lengths are evidently underestimated by GPC$_{PSt}$ considering that the polymer blends were recovered almost quantitatively.

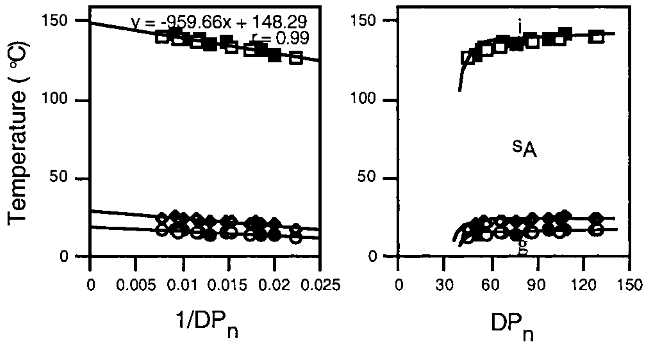


Figure 4. Dependence of the glass (○, ●), smectic C–smectic A (◇, ◆), and smectic A–isotropic (□, ■) phase transition temperatures of comb poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s prepared by ATRP (○, ◇, □) and their binary blends (●, ◆, ■) as a function of the GPC$_{PSt}$-determined number-average degree of polymerization and the inverse number-average degree of polymerization. Infinite molecular weight transitions: g 19 s$_C$ 29 s$_A$ 148 i. For comparison:[3] linear, g 16 s$_C$ 26 s$_A$ 144 i; three-arm star, g 16 s$_C$ 27 s$_A$ 145 i.

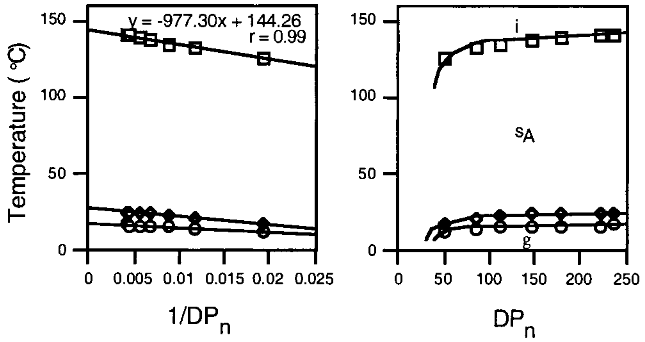


Figure 5. Dependence of the glass (○), smectic C–smectic A (◇), and smectic A–isotropic (□) phase transition temperatures of comb poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s prepared by ATRP as a function of the GPC$_{triple}$-determined number-average degree of polymerization and the inverse number-average degree of polymerization. Infinite molecular weight transitions: g 18 s$_C$ 27 s$_A$ 144 i. For comparison:[3] linear, g 16 s$_C$ 26 s$_A$ 144 i; three-arm star, g 16 s$_C$ 27 s$_A$ 145 i.

The binary blends of the comb polymers prepared by ATRP with DP$_{n,PSt}$ = 45 (pdi = 1.27) and DP$_{n,PSt}$ = 66 (pdi = 1.56) are monodisperse in molecular architecture and polydisperse in molecular weight (pdi = 1.39–1.56). Figure 6 presents their DSC scans and those of the unmixed samples. It demonstrates that the phase-segregated, unmixed samples exhibit two isotropization maxima at 126 and 134 °C, which correspond to the isotropization temperatures of the two components. Their relative areas correspond to the weight (or mole) ratio of the two components. In contrast, the corresponding binary blends of the two comb polymers exhibit a single s$_A$–i transition at an intermediate temperature, corresponding essentially to their weight averages (Table 6). Therefore, the isotropization transitions, as well as the glass and s$_C$–s$_A$ transitions of the comb binary blends, fit on the same molecular weight dependencies of the transition temperatures of the individual comb polymers (Figure 4). However, the isotropization transitions are broader (fwhm = 8.60–10.56 °C) than those of either of the two components (fwhm = 4.28–8.28 °C). This suggests that the two comb components of these binary blends do not mix well, although the breadth of the transition does not cover

Table 6. Composition of Binary Blends of Poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s Prepared by Atom Transfer Radical Polymerizations[a]

	composition (%)				GPC_{PSt}[d]		T_i (°C)	
DP_n/DP_n[b]	lower DP_n	higher DP_n	rec[c] (%)	theor DP_n	DP_n	pdi	theor[e]	DSC
			Comb/Comb					
45/66	75	25	83	50	50	1.39	129	129
	50	50	91	56	54	1.48	131	132
	25	75	86	61	56	1.56	132	134
127/45	49	51	98	87	67	1.96	134	137
127/57	48	52	99	93	77	1.85	136	136
127/66	51	49	98	106	98	1.67	137	138
127/87	50	50	99	106	98	1.67	139	139
127/104	48	52	84	116	107	1.60	140	142
			Comb/Linear					
45/40	50	50	95	43	40	1.23	132	132
57/55	49	51	98	56	53	1.25	136	132
45/86	50	50	88	66	59	1.40	134	138
127/18	50	50	91	73	31	3.36	130	130
			Comb/Three-Arm Star					
45/37	48	52	95	41	37	1.26	129	129
57/57	50	50	97	57	56	1.29	135	134
127/57	50	50	91	92	75	1.75	139	138

[a] Polymers were blended by codissolving in THF and precipitating in methanol. [b] Number-average degree of polymerization (DP_n) values from GPC_{PSt} relative to linear polystyrene. [c] % recovered. [d] Number-average degree of polymerization (DP_n) and polydispersity (pdi = M_w/M_n) determined by gel permeation chromatography (GPC) relative to polystyrene standards using mean of RI and UV detectors. [e] Weight-average T_i if miscible blend.

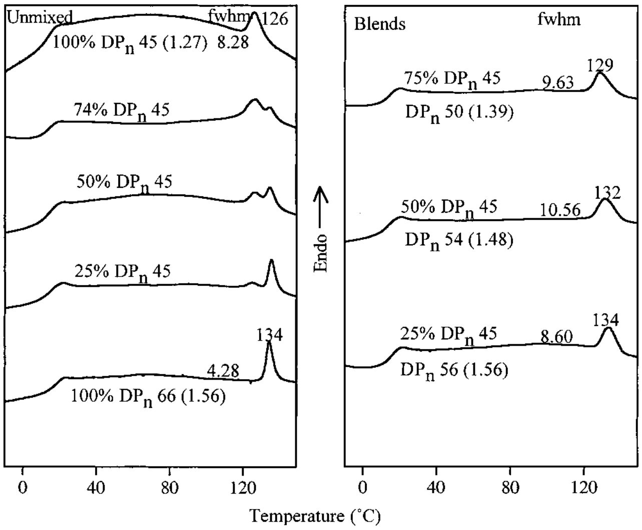


Figure 6. Normalized differential scanning calorimetry traces (10 °C/min) of binary unmixed (physically separated) composites and blends of comb poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s ($DP_{n,PSt}$ = 45, pdi = 1.27; $DP_{n,PSt}$ = 66, pdi = 1.56) prepared by ATRP.

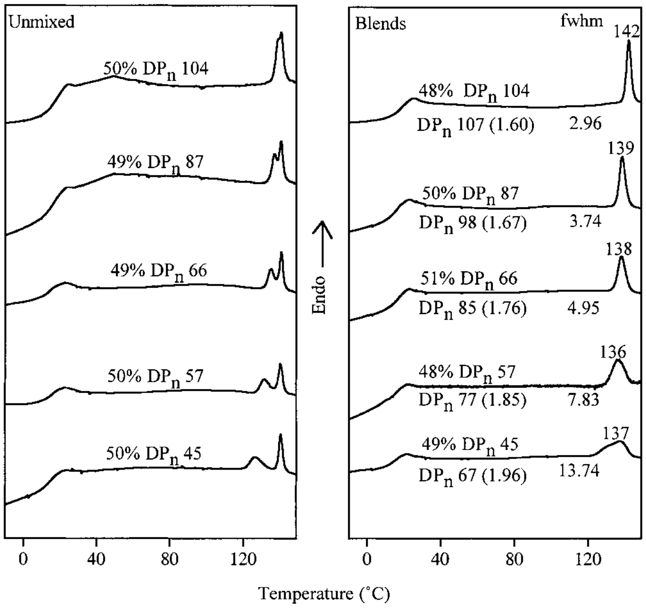


Figure 7. Normalized differential scanning calorimetry traces (10 °C/min) of 1:1 binary unmixed (physically separated) composites and blends of comb poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s ($DP_{n,PSt}$ = 127, pdi = 1.70) with all lower molecular weight comb polymers ($DP_{n,PSt}$ = 45−104, pdi = 1.27−1.56) prepared by ATRP.

the entire temperature range of isotropization of the two components.

Figure 7 presents the DSC scans of 1:1 blends of the comb polymer with $DP_{n,PSt}$ = 127 (pdi = 1.70) and all lower molecular weight samples ($DP_{n,PSt}$ = 45−104, pdi = 1.27−1.56). The molecular weight and thermotropic behavior of the individual components are shown in Figure 2 and summarized in Table 5. Again, the DSC scans of the unmixed composites in Figure 7 demonstrate that the phase-separated, unmixed samples exhibit two isotropization maxima corresponding to those of the individual components, even when their transition temperatures are nearly identical; the relative areas represent the weight (or mole) averages of the individual components. Figure 7 also demonstrates that the phase transitions of the binary blends of the comb polymers broaden with increasing differences in the molecular weights and isotropization temperatures of the two corresponding components. The blend of the comb polymers with $DP_{n,PSt}$ = 45 and $DP_{n,PSt}$ = 127 exhibits two unresolved isotropization maxima, which demonstrates that the two components do not mix well. The isotropization transitions of all of these binary blends occur at a temperature approximately equal to the weight-average temperature of the individual components (Table 6).

Although these comb polymers have the same molecular architecture, their branching density varies with molecular weight (Table 7) since the comb polymers correspond to a linear polymer with an average of four branch points along the polymer backbone. For example,

Table 7. Branching and End Group Densities of Poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s Prepared by ATRP[a]

GPC$_{\text{PSt}}$			GPC$_{\text{triple}}$		
DP_n	branching density (branches/chain)	end group density (EGs/chain)	DP_n	branching density (branches/chain)	end group density (EGs/chain)
		Linear			
18	0	5.56			
36[b]	0	2.78			
40[b]	0	2.50			
40	0	2.50			
55	0	1.82			
70[b]	0	1.43			
86	0	1.16			
		Three-Arm Star			
29[b]	1.72	5.17			
42[b]	1.19	3.57			
55[b]	0.91	2.73			
57	0.88	2.63			
		Comb			
45	4.44	6.67	52	4.81	6.73
57	3.51	5.26	85	2.94	4.12
66	3.03	4.55	111	2.25	3.15
87	2.30	3.45	147	1.70	2.38
104	1.92	2.88	178	1.40	1.97
127	1.57	2.36	222	1.13	1.58

[a] Branching and end group density normalized to chain of 50 repeat units. [b] From ref 3.

the branching densities of the comb polymers normalized to 50 repeat units are 4.44 branches/chain$_{50}$ when $DP_{n,PSt} = 45$, 1.92 branches/chain$_{50}$ when $DP_{n,PSt} = 104$, and 1.57 branches/chain$_{50}$ when $DP_{n,PSt} = 127$. The difference in branching density of the two components (ΔBD) is much higher in the binary blend with $DP_{n,PSt} = 45$ and 127 (2.87 branches/50 repeat units) than that with $DP_{n,PSt} = 104$ and 127 (0.35 branches/50 repeat units) (Table 8). The broad phase transition of the former binary blend (fwhm = 13.74 °C) with a large difference in branching density suggests that branching is the cause of the broad isotropization transitions of poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s prepared by conventional free radical polymerizations.

The binary blends of the comb and linear polymers prepared by ATRP are polydisperse in both molecular architecture and molecular weight. As shown in Figure 8 and summarized in Table 6, the comb/linear binary unmixed composites exhibit two isotropization transitions at temperatures corresponding to those of the individual components, whereas the corresponding binary blends exhibit a single isotropization transition that is much broader (fwhm = 11.87−17.01 °C) than those of either of the two components (fwhm = 2.34−8.28 °C). These transitions cover almost the entire temperature range of isotropization of the two components, which indicates that they mix very poorly, presumably due to their differences in branching density. For example, the binary blend of the comb polymer with $DP_{n,PSt} = 45$ and the linear polymer with $DP_n = 86$ exhibits the broadest phase transition and has one of the greatest differences in branching densities (Table 8). According to GPC relative to linear polystyrene, the comb polymer with $DP_{n,PSt} = 127$ has 20 repeat units on each linear graft. Its binary blend with the linear sample of similar length ($DP_n = 18$) also exhibits a broad isotropization transition (fwhm = 11.87 °C).

Table 8. Influence of Differences in Branching and End Group Densities of 1:1 Binary Blends of Poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s on the Breadth of Their Isotropization Transitions

	GPC$_{\text{PSt}}$		GPC$_{\text{triple}}$[c]		
DP_n/DP_n[a]	ΔBD[b]	ΔEG[b]	ΔBD[b]	ΔEG[b]	fwhm[d] (°C)
		Linear/Linear			
40/70[e]	0	1.07			4.46
		Three-Arm/Three-Arm Star			
29/55[e]	0.81	2.44			15.18
		Linear/Three-Arm Star			
36/42[e]	1.19	0.79			5.36
		Comb/Comb			
45/66	1.41	2.12	2.56	3.58	10.56
45/127	2.87	4.31	3.68	5.15	13.74
57/127	1.94	2.90	1.81	2.54	7.83
66/127	1.46	2.19	1.12	1.57	4.95
87/127	0.73	1.09	0.57	0.80	3.74
104/127	0.35	0.52	0.27	0.39	2.96
		Comb/Linear			
45/40	4.44	4.17	4.81	4.23	12.06
57/55	3.51	3.44	2.94	2.30	13.55
45/86	4.44	5.51	4.81	5.57	17.01
127/18	1.57	3.20	1.13	3.98	11.87
		Comb/Three-Arm Star			
45/42	3.25	3.10	3.62	3.16	6.73
57/57	2.63	2.63	2.06	1.49	7.93
127/57	0.69	0.27	0.25	1.05	3.35

[a] Number-average degrees of polymerization (DP_n) from GPC relative to linear polystyrene. [b] Difference in branching density (ΔBD) and end group density (ΔEG) of the components normalized to chains of 50 repeat units. [c] Comb polymers by GPC$_{\text{triple}}$; linear and three-arm star polymers by GPC$_{\text{PSt}}$. [d] Full width at half of the maximum of the peak intensity. [e] From ref 3.

The binary blends of the comb and three-arm star polymers are also polydisperse in both molecular architecture and molecular weight. Figure 9 presents the DSC scans of the binary blends and unmixed composites of the comb polymers with $DP_{n,PSt} = 45$, 57, and 127 and three-arm star samples with $DP_n = 42$ and 57. The isotropization transitions of these comb/three-arm star polymer binary blends are narrower (fwhm = 3.35−7.93 °C) than those of the comb/linear polymer binary blends (fwhm = 11.87−17.01). Figure 9 again demonstrates that a difference in molecular weight alone is not sufficient to broaden the phase transition. For example, although the comb polymer with $DP_{n,PSt} = 127$ and

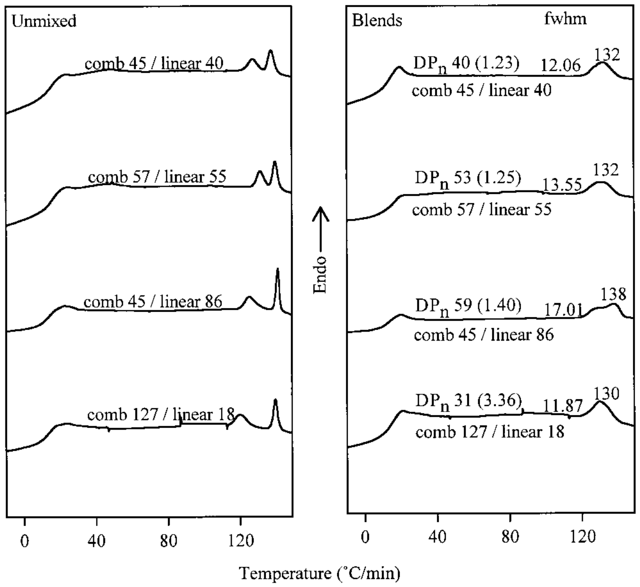


Figure 8. Normalized differential scanning calorimetry traces (10 °C/min) of 1:1 binary unmixed (physically separated) composites and blends of comb ($DP_{n,PSt} = 45-127$, pdi = 1.27–1.70) and linear ($DP_n = 18-86$, pdi = 1.18–1.27) poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s prepared by ATRP.

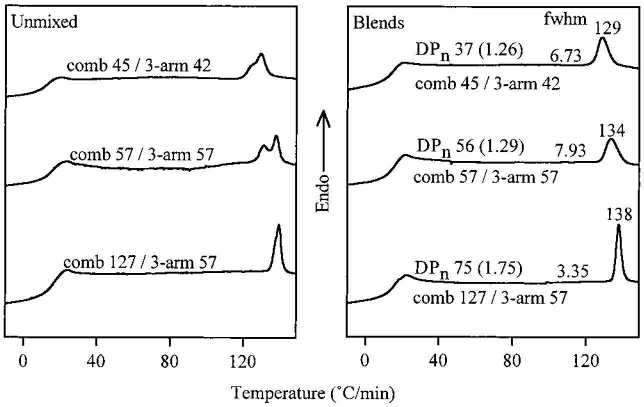


Figure 9. Normalized differential scanning calorimetry traces (10 °C/min) of 1:1 binary unmixed (physically separated) composites and blends of comb ($DP_{n,PSt} = 45-127$, pdi = 1.27–1.70) and three-arm star ($DP_n = 42-57$, pdi = 1.11–1.30) poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s prepared by ATRP.

three-arm star sample with $DP_n = 57$ have the greatest difference in their molecular weights ($\Delta DP_{n,PSt} = 70$), their binary blend exhibits the sharpest isotropization transition (fwhm = 3.35 °C). However, these two branched components have the smallest difference in branching densities (Table 8), and the same average number of repeat units per arm/graft ($DP_{n,arm,PSt} = 20$).

Conclusions

In contrast to poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate] prepared by conventional radical polymerization, whose biphasic region has a breadth of 17 °C,[3] the corresponding linear,[3] three-arm star,[3] and comb polymers prepared by atom transfer radical polymerization exhibit extremely narrow transitions, even when their polydispersities in molecular weight are broad. Therefore, a broad, monomodal, Gaussian-like distribution of chain lengths of a single architecture is not sufficient to broaden the phase transition of side-chain liquid crystalline polymers. However, the biphasic region of 1:1 binary blends of these polymers may be broad, apparently due to the limited miscibility of the two components. As plotted in Figure 10, the breadths of the isotropization transitions of comb/comb, comb/linear, and comb/three-arm star binary blends increase as their differences in branching densities increase (normalized to chains of 50 repeat units).

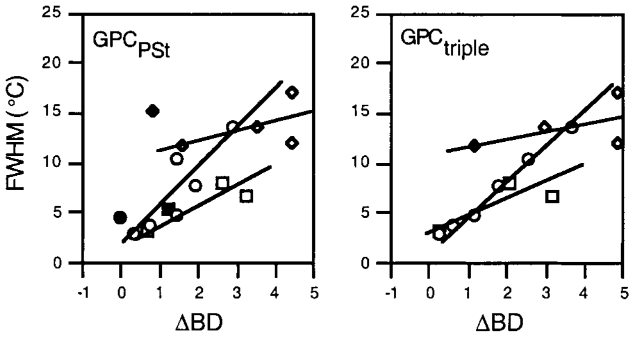


Figure 10. Dependence of the breadth of isotropization of poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate] binary blends (● = linear/linear;[3] ○ = comb/comb; ■ = linear/three-arm star;[3] □ = comb/three-arm star; ◆ = three-arm star/three-arm star;[3] ◇ = comb/linear) as a function of the difference in branching density (normalized to chains of 50 repeat units and based on either GPC_{PSt}- or GPC_{triple}-determined molecular weights) of the corresponding components.

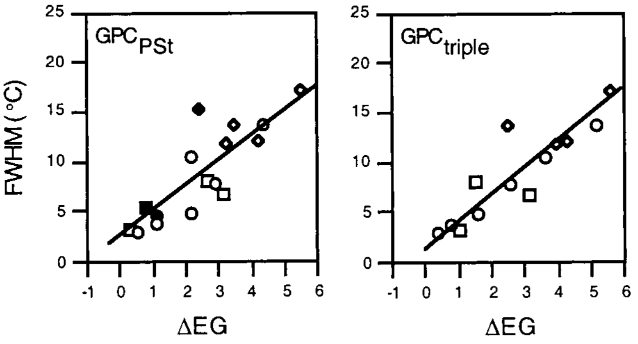


Figure 11. Dependence of the breadth of isotropization of poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate] binary blends (● = linear/linear;[3] ○ = comb/comb; ■ = linear/three-arm star;[3] □ = comb/three-arm star; ◆ = three-arm star/three-arm star;[3] ◇ = comb/linear) as a function of the difference in end group density (normalized to chains of 50 repeat units and based on either GPC_{PSt}- or GPC_{triple}-determined molecular weights) of the corresponding components.

However, the linear polymers have zero branches per chain regardless of molecular weight, and the breadth of the transitions of the linear/linear binary blends are therefore independent of differences in their branching density. Nevertheless, since each branch point adds one additional end group, differences in branching density can be related to differences in end group density. Figure 11 plots the dependence of the breadth of the phase transitions of the binary blends as a function of the difference in their end group densities (ΔEG, normalized to chains of 50 repeat units). In this case, all of the experimental points are distributed along a single straight line regardless of the combination of molecular architectures. The data are less scattered when the differences in end group density are based on GPC_{triple}-determined molecular weights of the comb polymers (Table 7). Therefore, the broad isotropization transition of polymer prepared by conventional radical polymerization is apparently due to a mixture of branched structures of limited miscibility, which are produced by chain transfer to polymer at high monomer conversion. This increasingly limited miscibility with increasing differences in branching density is not limited to SCLCPs but is apparently common to polymers of vastly different structures. For example, although blends of linear polyethylene (PE) form homogeneous solid mixtures,[12] blends of linear and branched PE tend to phase segregate in the solid state.[13] In addition, blends of branched PE with different branching densities tend to phase segregate in the solid state, with the immiscibility increasing as the branch content becomes more dissimilar.[14] Even the melts of blends of HDPE and LLDPE with high branch contents (>8 branches per 50 repeat units, $M_w \sim 50$) are heterogeneous.[15]

Experimental Section

Materials. Acryloyl chloride (96%), cuprous bromide (99.999%), 2-hydroxyethyl acrylate (96%), methyl 2-bromopropionate (99%), propionyl chloride (98%), and pyrogallol (98%) were used as received from Aldrich. 2-Bromopropionyl chloride (Acros, tech), 3,4-dihydro-2*H*-pyran (Fluka, 97%), and *p*-toluenesulfonic acid (Mallinckrodt, monohydrate) were used without further purification. Azobis(isobutyronitrile) (AIBN, Johnson Mathey, 99%) was recrystallized from methanol below 40 °C and stored in a freezer at <-10 °C. Benzene (Fisher Scientific, Certified A.C.S) was shaken with concentrated sulfuric acid (Fisher Scientific, Certified A.C.S. Plus) to remove thiophene, washed sequentially with 6 M aqueous NaOH and deionized water, and then distilled from CaH_2 under N_2. Ethylene glycol (EM Science, 99%) was vacuum distilled from anhydrous $MgSO_4$. Methyl acrylate (MA, Acros, 99%) was washed sequentially with aqueous NaOH (10 wt %) and water and vacuum distilled from $MgSO_4$. Reagent-grade tetrahydrofuran (THF, Fisher Scientific) was dried by distillation from purple sodium benzophenone ketyl under N_2 and stored over 4 Å molecular sieves. 4,4′-Diheptyl-2,2′-dipyridyl was synthesized as described previously.[3] Linear and three-arm star poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate] were synthesized by ATRP as described previously.[3] Triethylamine (NEt_3, Acros, 99%) was distilled from KOH under N_2. All other reagents and solvents were commercially available and used as received.

Techniques. All reactions were performed under a N_2 atmosphere using a Schlenk line unless noted otherwise. ^1H NMR spectra (δ, ppm) were recorded on either a Mercury Gemini 300 (300 MHz) or a Varian Gemini 200 (200 MHz) spectrometer. Unless noted otherwise, all spectra were recorded in $CDCl_3$ with TMS as an internal standard. Relative molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) at 35 °C using THF as solvent (1.0 mL/min), a set of 50, 100, 500, and 10^4 Å and linear ($50-10^4$ Å) Styragel 5 μm columns, a Waters 486 tunable UV/vis detector set at 254 nm, and a Waters 410 differential refractometer (RI). Monomer conversion was determined in the monomer reactivity studies directly from GPC by comparison of the polymer peak area and the sum of the individual monomer peak areas from the RI detector; this overestimates the conversion since each point of the GPC trace needs to be divided by the molecular weight at that elution time in order to convert weight distribution to number distribution. Absolute molecular weights were determined by GPC−RI−viscometry−right angle laser light scattering (GPC−RI−Visco−RALLS) using a Waters 410 differential refractometer combined with a Viscotek 100 differential viscometer and a Wyatt Technology DAWN F photometer equipped with a He−Ne laser (633 nm), THF as solvent (1.0 mL/min) at 35 °C, and a set of 100 Å and two linear mixtures ($50-10^4$ and 10^4-10^6 Å) Styragel 5 μm columns. Absolute molecular weights were also determined by GPC−light scattering (GPC−LS) using a Wyatt Technology miniDAWN three-angle light scattering detetector equipped with a He−Ne laser (690 nm), a Wyatt Technology Optilab 903 differential refractometer (690 nm), THF as solvent (1.0 mL/min) at 35 °C, and a set of 50, 500, and 10^4 Å and linear ($50-10^6$ Å) Phenogel 5 μm columns. Refractive index increments (d*n*/d*c*) were measured off-line at 690 nm using a Wyatt Technology Optilab 903 differential refractometer calibrated with aqueous NaCl, using an Orion Sage 362 syringe pump at 0.3 mL/min. All samples were dissolved in THF (distilled from $LiAlH_4$ and filtered through a 0.02 μm PTFE filter) overnight and filtered through a 0.45 μm PTFE filter.

All polymers and their blends were dried overnight in vacuo at room temperature before analyzing their thermotropic behavior. A Perkin-Elmer Pyris 1 differential scanning calorimeter was used to determine the thermal transitions, which were read as the maximum or minimum of the endothermic or exothermic peaks, respectively. Glass transition temperatures (T_g's) were read as the middle of the change in heat capacity. All heating and cooling rates were 10 °C/min. Both enthalpy changes and transition temperatures were calibrated using indium and benzophenone standards. Binary unmixed samples were prepared by physically separating two components within the same DSC sample pan by a lid, whereas binary blends were created by codissolving the components in a minimum amount of THF and precipitating them in methanol at −78 °C. A Leitz Laborlux 12 Pol S polarized optical microscope (magnification 200×) equipped with a Mettler FP82 hot stage and a Mettler FP90 central processor was used to observe the thermal transitions and to analyze the anisotropic textures. Thin samples were prepared by melting a minimum amount of compound between a clean glass slide and a coverslip and rubbing the coverslip with a spatula.

Synthesis of THP-Protected Monomer and Chain Transfer Agent. 2-[(2′-Tetrahydropyranyl)oxy]ethyl Acrylate. 2-[(2′-Tetrahydropyranyl)oxy]ethyl acrylate was prepared in 83−92% yield as in the following example. A solution of 3,4-dihydro-2*H*-pyran (10 g, 0.12 mol) in dry THF (25 mL) was added dropwise over 1.5 h to an ice-cooled solution of 2-hydroxyethyl acrylate (12 g, 0.10 mol) and *p*-toluenesulfonic acid (0.52 g, 3.0 mmol) in dry THF (50 mL). The reaction was warmed to room temperature and stirred for 18 h. Sodium carbonate (0.20 g, 1.9 mmol) was added, and the mixture was stirred for an additional 2 h. The resulting mixture was poured into water (100 mL). The aqueous phase was extracted twice with Et_2O (100 mL total). The combined organic layers were washed twice with dilute (10 wt %) aqueous $NaHCO_3$ (100 mL total) and once with water (50 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed by rotary evaporation. The residue was purified by column chromatography using silica gel as the stationary phase and Et_2O/petroleum ether (1:1) as the eluant ($R_f = 0.70$) to yield 17 g (83%) of 2-[(2′-tetrahydropyranyl)oxy]ethyl acrylate as a clear, colorless oil. ^1H NMR: 1.54 (m, $(CH_2)_3CH_2O$ of THP), 3.47 (m, CH_2O of THP, 1 H), 3.63 (m, CH_2O of THP, 1 H), 3.85 (m, CH_2OTHP), 4.26 (t, CH_2O_2C), 4.60 (m, OC*H*O of THP), 5.83 (dd, 1 olefinic H trans to CO_2), 6.12 (dd, 1 olefinic H *gem* to CO_2), 6.41 (dd, 1 olefinic H cis to CO_2).

2-Hydroxyethyl Propionate. A solution of propionyl chloride (7.9 g, 86 mmol) in dry THF (40 mL) was added dropwise over 1.8 h to an ice-cooled solution of ethylene glycol (50 g, 0.81 mol) and dry NEt_3 (12 g, 0.12 mol) in dry THF (200 mL). The reaction was warmed to room temperature, stirred for 20 h, and then filtered to remove $NEt_3\cdot HCl$. The filtrate was condensed and extracted four times with Et_2O (200 mL total). The combined Et_2O extracts were then dried over anhydrous $MgSO_4$. After filtration, the solvent was removed by rotary evaporation. The residue was purified by column chromatography using silica gel as the stationary phase and CH_2Cl_2 as the eluant. After removing the solvent, the residue was distilled (58−62 °C/3 mmHg) to yield 4.9 g (48%) of 2-hydroxyethyl propionate as a colorless oil. ^1H NMR: 1.12 (t, CH_3), 2.34 (q, CH_2CH_3), 3.80 (m, CH_2OH), 4.18 (t, CH_2O_2C).

2-[(2′-Tetrahydropyranyl)oxy]ethyl Propionate. A solution of 3,4-dihydro-2*H*-pyran (1.8 g, 21 mmol) in dry THF (5 mL) was added dropwise to an ice-cooled solution of 2-hydroxyethyl propionate (2.0 g, 17 mmol) and *p*-toluenesulfonic acid (99 mg, 0.52 mmol) in dry THF (10 mL). The reaction was warmed to room temperature and stirred for 20 h. Sodium carbonate (30 mg, 0.28 mmol) was added, and the mixture was stirred for an additional 2 h. The resulting mixture was poured into water (30 mL), and the aqueous phase was extracted three times with CH_2Cl_2 (45 mL total). The combined organic layers were washed twice with dilute (10 wt %) aqueous $NaHCO_3$ (40 mL total) and once with water (20 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed by rotary evaporation. The residue was then distilled (85−88 °C/3 mmHg) to yield 2.8 g (85%) of 2-[(2′-tetrahydropyranyl)oxy]ethyl propionate as a colorless oil. ^1H NMR: 1.13 (t, CH_3), 1.54 (m, $(CH_2)_3CH_2O$ of THP), 2.37 (q, CH_2CH_3), 3.50 (m, CH_2O of THP, 1 H), 3.62 (m, CH_2O of THP, 1 H), 3.85 (m, CH_2OTHP), 4.24 (t, CH_2O_2C), 4.64 (m, OC*H*O of THP). Anal. ($C_{10}H_{18}O_4$) C, H: calcd 59.39, 8.97: found 59.32, 9.11.

Measurement of the Chain Transfer Constant to 2-[(2′-Tetrahydropyranyl)oxy]ethyl Propionate in a Conventional Free Radical Polymerization of Methyl Acrylate. The chain transfer study involved the following six ratios of the concentrations of chain transfer agent and monomer: $[\text{transfer agent}]_0/[\text{monomer}]_0 = [TA]_0/[M]_0 = 0.0, 0.005, 0.01, 0.02, 0.035$, and 0.05. The stock monomer solution was prepared by adding benzene to freshly distilled methyl acrylate (4.3 g, 50 mmol) and AIBN (82 mg, 0.50 mmol) in a 25 mL volumetric flask to bring the total volume to 25 mL. The chain transfer solution was prepared by adding benzene to 2-[(2′-tetrahydropyranyl)oxy]ethyl propionate (0.20 g, 1.0 mmol) in a 10 mL volumetric flask to bring the total volume to 10 mL. The terminator solution was prepared by adding THF to pyrogallol (0.63 g, 5.0 mmol) in a 5 mL volumetric flask to bring the total volume to 5 mL. Each of the six polymerization solutions was prepared in 4 mL volumetric flasks. In a typical procedure, a $[TA]_0/[M]_0 = 0.005$ solution was prepared by adding benzene to 2.0 mL of monomer solution (4.0 mmol MA, 0.04 mmol AIBN) and 0.2 mL of chain transfer solution (0.02 mmol) in a 4 mL volumetric flask to bring the total volume to 4 mL. The $[TA]_0/[M]_0 = 0.0, 0.01, 0.02, 0.035$, and 0.05 solutions were prepared by the same procedure. The $[TA]_0/[M]_0 = 0.0, 0.005, 0.01, 0.02, 0.035$, and 0.05 solutions were poured separately into glass ampules and attached to a high-vacuum line. The six ampules were exhaustively degassed using five freeze−pump−thaw cycles, each with 30 min degas cycles at 10^{-6} Torr. The ampules were sealed under vacuum (3.0×10^{-7} Torr) and placed in a 60 °C oil bath, and the polymerizations were stirred for 5 min. The ampules were then plunged into an ice bath and opened, and 50 μL of the 1 M pyrogallol solution (0.05 mmol) was added to quench the polymerizations. The quenched polymerizations were stored in a −20 °C freezer until they were analyzed by GPC. A plot of four replications of DP_n^{-1} vs $[TA]_0/[M]_0$ generated a line whose slope is $C_p = 1.1 \times 10^{-3}$.

Measurement of the Monomer Reactivity Ratios in a Conventional Free Radical Polymerization. The copolymerizations were performed using monomer feed compositions from 0.10 to 0.90 of 2-[(2′-tetrahydropyranyl)oxy]ethyl acrylate and 0.90 to 0.10 of 11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate. In a typical procedure, a solution of 11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate (1.3 g, 3.0 mmol), 2-[(2′-tetrahydropyranyl)oxy]ethyl acrylate (0.60 g, 3.0 mmol), and AIBN (11 mg, 64 μmol) in benzene (20 mL) was degassed by three freeze−pump−thaw cycles. The flask was sealed under vacuum and stirred at 60 °C for 1 h. A sample was taken and diluted with THF to determine the conversion by GPC (5.0%). The remaining solution was precipitated into cold (−78 °C) methanol (150 mL). The resulting precipitate was separated by column chromatography using silica gel as the stationary phase. Unreacted 11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate was recovered using CH_2Cl_2 as the eluant, and the copolymer product was then isolated with THF as the eluant. After removing the solvent by rotary evaporation, the residue was precipitated from THF (1 mL) into cold (−78 °C) methanol (10 mL) to yield pure copolymer. According to ^1H NMR, the copolymer contained 49 mol % 2-[(2′-tetrahydropyranyl)oxy]ethyl acrylate repeat units (4.63 ppm, br s, OC*H*O of THP) and 51 mol % 11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate repeat units (6.95 and 7.40−7.75 ppm, m, 8 aromatic H).

Synthesis of the Multifunctional Macroinitiator: Poly{[2-(2′-bromopropanoyl)ethyl acrylate]-*ran*-[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]}. Copolymerization of 2-[(2′-Tetrahydropyranyl)oxy]ethyl Acrylate and 11-(4′-Cyanophenyl-4″-phenoxy)undecyl Acrylate by ATRP. The linear copolymer precursors were prepared by ATRP in 27−91% yield as in the following example. A mixture of 2-[(2′-tetrahydropyranyl)oxy]ethyl acrylate (0.85 g, 4.2 mmol), 11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate (10 g, 24 mmol), methyl-2-bromopropionate (0.16 g, 0.94 mmol), CuBr (0.14 g, 0.95 mmol), and 4,4′-diheptyl-2,2′-dipyridyl (0.99 g, 2.8 mmol) was degassed by five freeze−pump−thaw cycles. The flask was then sealed under vacuum and stirred at 100 °C for 10.5 h. The copolymer was precipitated into cold (−78 °C) methanol (150 mL), collected, and purified by reprecipitating once from THF (20 mL) into cold (−78 °C) methanol (150 mL), twice from THF (20 mL) into cold (−78 °C) saturated NH_4Cl in methanol (1:3, 75 mL), and then twice from THF (20 mL) into cold (−78 °C) methanol (150 mL) to yield 9.9 g (91%) of poly{[2-(2′-tetrahydropyranyloxy)ethyl acrylate]-*ran*-[11-(4′-cyanophenyl-4″-phenoxy) undecyl acrylate]} as a sticky solid; GPC $M_n = 1.20 \times 10^4$, pdi = 1.25. According to ^1H NMR, the copolymer contained 13 mol % 2-[(2′-tetrahydropyranyl)oxy]ethyl acrylate repeat units (4.63 ppm, br s, −OC*H*O− of THP) and 87 mol % 11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate repeat units (6.95 and 7.40−7.75 ppm, m, 8 aromatic H), which corresponds to 4 and 26 repeat units, respectively. GPC−RI−Visco−RALLS $M_n = 1.49 \times 10^4$ (pdi = 1.23), corresponding to 5 and 33 repeat units, respectively.

Synthesis of Poly{[(2-hydroxyethyl) acrylate]-*ran*-[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]} by Hydrolysis of Poly{[2-(2′-tetrahydropyranyloxy)ethyl acrylate]-*ran*-[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]}. A solution of concentrated HCl (1.5 mL, 67 μmol) in water (14 mL) was added to a solution of poly{[2-(2′-tetrahydropyranyloxy)ethyl acrylate]-*ran*-[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]} (9.6 g, 3.2 mmol −OTHP) in dry THF (70 mL). The solution was stirred at 55 °C for 3 h and then cooled to room temperature. The copolymer was precipitated into cold (−78 °C) methanol (400 mL) to yield 8.2 g (86%) of poly{[(2-hydroxyethyl) acrylate]-*ran*-[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]} as a sticky white solid; GPC $M_n = 1.31 \times 10^4$, pdi = 1.21. ^1H NMR: 1.30 (m, $(CH_2)_7$, 14*y* H), 1.65 (br s, CH_2CH_2OAr, 2*y* H), 1.80 (br s, $CH_2CH_2CH_2O_2C$, 2*y* H), 1.40−1.80 (overlapped m, $CH_2CH(CO_2)$, $2(x + y)$ H), 2.28 (br s, $CH(CO_2)$, $(x + y) - 1$ H), 3.78 (br s, CH_2OH, 2*x* H), 3.97 (br s, $CO_2CH_2(CH_2)_9CH_2OAr$, 4*y* H), 4.20 (br s, CH_2CH_2OH and $CH(CO_2)Br$, $2x + 1$ H), 6.95 (br s, 2*y* aromatic H *ortho* to OCH_2, 7.53 (br s, 2*y* aromatic H *meta* to OCH_2), 7.66 (br d, 4*y* aromatic H *ortho* and *meta* to CN), where x = number of 2-hydroxyethyl acrylate repeat units and y = number of 11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate repeat units per polymer chain.

Synthesis of Poly{[2-(2′-bromopropanoyl)ethyl acrylate]-*ran*-[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]} Macroinitiator. A solution of 2-bromopropionyl chloride (2.5 g, 15 mmol) in dry THF (15 mL) was added dropwise over 1 h to an ice-cooled solution of poly{[(2-hydroxyethyl) acrylate]-*ran*-[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]} (7.3 g, 2.8 mmol −OH) and dry NEt_3 (1.6 g, 15 mmol) in dry THF (40 mL). The reaction was warmed to room temperature, stirred for 48 h, and then precipitated into cold (−78 °C) methanol (450 mL) to yield 7.0 g (86%) of poly{[2-(2′-bromopropanoyl)ethyl acrylate]-*ran*-[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]} as a sticky white solid; GPC $M_n = 1.33 \times 10^4$, pdi = 1.18. GPC−RI−Visco−RALLS $M_n = 1.44 \times 10^4$, pdi = 1.18. ^1H NMR: 1.30 (m, $(CH_2)_7$, 14*y* H), 1.65 (br s, CH_2CH_2OAr, 2*y* H), 1.80 (br m, $CH_2CH_2CH_2O_2C$ and $CH_3CH(Br)$, $2y + 3x$ H), 1.40−1.80 (overlapped m, $CH_2CH(CO_2)$, $2(x + y)$ H), 2.28 (br s, $CH(CO_2)$, $(x + y) - 1$ H), 3.97 (br m, $CO_2CH_2(CH_2)_9CH_2OAr$, 4y H), 4.26 (br m, $CH_2CH_2O_2CCH(Br)CH_3$ and $CH(CO_2)Br$, $5x + 1$ H), 6.95 (br d, 2*y* aromatic H *ortho* to OCH_2), 7.53 (br d, 2*y* aromatic H *meta* to OCH_2), 7.66 (br s, 4*y* aromatic H *ortho* and *meta* to CN), where x = number of 2-(2′-bromopropanoyl)ethyl acrylate repeat units and y =

number of 11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate repeat units per polymer chain.

Synthesis of Comb Poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate] by ATRP. The comb polymers were prepared by ATRP in 41−76% yield as in the following example. A mixture of 11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate (0.30 g, 0.71 mmol), poly{[2-(2′-bromopropanoyl)ethyl acrylate]-*ran*-[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]} (0.36 g, 0.13 mmol initiator sites), CuBr (20 mg, 0.14 mmol), and 4,4′-dihepty-2,2′-dipyridyl (0.15 g, 0.43 mmol) was degassed by three freeze−pump−thaw cycles in a sealable tube. The tube was then sealed under vacuum and stirred at 100 °C for 4.5 h. The polymer was diluted with THF (3 mL), precipitated into cold (−78 °C) methanol (50 mL), and purified by reprecipitating once from THF (4 mL) into cold (−78 °C) methanol (50 mL), twice from THF (4 mL) into cold (−78 °C) saturated NH_4Cl in methanol (1:3, 15 mL), once again from THF (4 mL) into cold (−78 °C) methanol (50 mL), and twice from THF (4 mL) into a warm (50 °C) solution of ethanol/toluene (5:1, 50 mL). After cooling to −78 °C, the precipitate was collected to yield 0.50 g (76%) of comb poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate] as a sticky solid; GPC $M_n = 2.02 \times 10^4$, pdi = 1.26; GPC−RI−Visco−RALLS $M_n = 2.34 \times 10^4$, pdi = 1.91.

Preparation of Binary Blends of Poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s. The binary polymer blends were prepared in 83−99% yield. In a typical procedure, a cold (−78 °C) solution of concd HCl (1 drop) in methanol (10 mL) was added dropwise to a solution of $DP_n = 45$ comb polymer (10 mg) and $DP_n = 66$ comb polymer (10 mg) in a minimum amount of THF (<0.5 mL) until a white precipitate formed (∼2 mL). The precipitate was collected to yield 18 mg (91%) of the 50/50 comb binary blend as a sticky white solid; GPC $M_n = 2.40 \times 10^4$, pdi = 1.48.

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Supporting Information Available: Data used to determine the chain transfer constant to 2-(2′-tetrahydropyranyloxy)ethyl propionate in the radical polymerization of methyl acrylate; measurement of the reactivity ratios in the copolymerization of 2-(2′-tetrahydropyranyloxy)ethyl acrylate and 11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate under conventional radical polymerization conditions; and ^1H NMR spectra of the macroinitiator and its precursors. This material is available free of charge via the Internet at http://pubs.acs.org.

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