Effect of End Groups on the Thermotropic Behavior of Linear Poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s Prepared by ATRP and Their Topological Blends

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ABSTRACT: Linear poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s with 9−77 (GPC relative to linear polystyrene) or 7−101 (GPC$_{LS}$) repeat units were synthesized by atom transfer radical polymerization of 11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate using a mesogenic initiator, 11-(4′-cyanophenyl-4″-phenoxy)undecyl 2-bromopropionate. The biphasic regions of the smectic A to isotropic (s$_A$−i) transition of the linear polymers are extremely narrow, with full widths at half of the maximum peak intensity (fwhm) = 4.52−7.74 °C, in contrast to that of the corresponding polymer prepared by conventional radical polymerization (fwhm = 17.0 °C). The breadths of this transition do not vary with chain length, in contrast to the corresponding linear polymers with methyl propionate end groups. The breadth of the s$_A$−i biphasic region of 1:1 binary blends of poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s increases relatively linearly with the difference in end group (and therefore branching) density of the two components, regardless of the combination of molecular architectures (linear, three-arm star, or comb) or the type of end groups (bromine and hydrogen or methyl propionate).

Introduction

Many structure/property relationships have been established for side-chain liquid crystalline polymers (SCLCPs) since their discovery in 1970.[1] For example, the insertion of a flexible spacer between the backbone and the mesogen depresses the glass transition, uncovering otherwise unseen phases.[2] More thermally stable and more ordered mesophases are formed from more flexible backbones.[3] The phases exhibited by SCLCPs generally correlate with their low molar mass analogues[4] and become independent of molecular weight after 10−50 repeat units.[5] However, the effects of tacticity and polydispersity on the phase behavior of SCLCPs are not well established.

Polydispersity in molecular weight (pdi = M_w/M_n) of SCLCPs is generally believed to broaden their phase transitions.[6,7] For example, when 11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate is polymerized radically ($M_n = 2.52 \times 10^4$, pdi = 3.43), the smectic A to isotropic (s$_A$−i = 140 °C) transition of the resulting polyacrylate is broad (full width at half of the maximum peak intensity, fwhm = 17.0 °C).[7,8] However, when the polymer is fractionated, each of the fractions (M_n = (5.79−43.1) × 10^3, pdi = 1.57−2.04) exhibits a narrower phase transition (fwhm = 6.25−10.7 °C), including the fraction (fwhm = 7.14 °C) with a molecular weight ($M_n = 2.40 \times 10^4$, pdi = 1.96) similar to that of the original polymer.[8] A blend of these fractions in their original weight ratios results in a mixture ($M_n = 2.34 \times 10^4$, pdi = 3.75) with nearly identical behavior (s$_A$−i = 136 °C, fwhm = 16.5 °C) to that of the original polymer.[8]

Although conventional radical polymerizations generally produce SCLCPs with relatively broad molecular weight distributions and broad phase transitions,[7−9] SCLCPs produced more recently by controlled polymerizations have narrower phase transitions,[4,5,10] even when blended into multimodal blends.[11] Therefore, a broad polydispersity in molecular chain length cannot be the sole cause of broad phase transitions. Because chain transfer to polymer can occur in free radical polymerizations to produce branched structures, we proposed that polydispersity in molecular architecture, not molecular weight alone, is responsible for the broad phase transitions due to the limited miscibility of the resulting mixture of molecular architectures.[8,12]

The limited miscibility of molecular architectures is being explored both experimentally and theoretically. Entropic corrections to the Flory−Huggins theory predict that star and linear homopolymers with the same molecular weight will be immiscible when the star has greater than 10 arms.[13] Furthermore, immiscibility is seen experimentally in blends of deuterated star and hydrogenated linear poly(styrene).[14] After accounting for isotopic differences, a small but measurable interaction parameter, $\chi = 6 \times 10^{-5}$, exists due to architectural differences alone. Additionally, dynamic secondary ion mass spectroscopy shows that the star component of the blend preferentially segregates to the surface.[14] Blends of poly(butadiene)s with different architectures also phase separate,[15] as do blends of poly(ethylene) with different architectures[16] or with similar molecular weights but different branching densities.[17] Blends of LDPE ($M_w = 2.54 \times 10^5$, 1.6 branches per 50 repeat units) and fractionated LLDPE ($M_w = 2.13 \times 10^5$, 0.24 branches per 50 repeat units) phase separate when the composition is greater than 40% LDPE.[17]

In a preliminary study,[8] we reported the synthesis of linear and three-arm star poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s by atom transfer radical polymerization (ATRP[18]). Although all of the polymers exhibited much narrower isotropization transitions (fwhm = 4.46−8.96 °C) than the corresponding polymer prepared by conventional radical polymerization (fwhm = 17.0 °C), the breadth of the transition increased slightly with decreasing molecular weight, indicating

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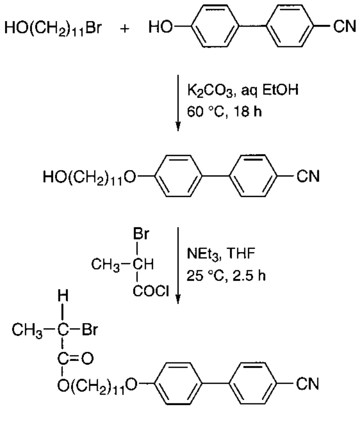
Scheme 1. Synthesis of 11-(4′-Cyanophenyl-4″-phenoxy)undecyl 2-Bromopropionate



that the end groups of both the linear and star polymers and/or the core of the star polymers have limited compatibility with the mesogenic repeat units. We also compared the thermotropic behavior of binary blends ($DP_n \approx 50$) of the three combinations of architectures. Although only the binary mixture of star polymers, with its significant difference in branching densities of the two components, exhibited a broad isotropization transition (fwhm = 15.2 °C), it also had the largest difference in the isotropization temperatures of the two components. This paper investigates both the effect of the end groups on the breadth of the isotropization transition of the linear polymers, and expands the range of chain lengths (and therefore difference in transition temperatures) incorporated into the binary blends of the new linear polymers, and the linear[8] and three-arm star[8] polymers synthesized previously, using the entire range of molecular weights. The linear polyacrylates were synthesized using a new mesogenic initiator, 11-(4′-cyanophenyl-4″-phenoxy)undecyl 2-bromopropionate (Scheme 1), that results in −H and −Br end groups (Scheme 2) rather than methyl propionate and −Br chain ends.

Results

Synthesis of Linear Polymers with −H/−Br End Groups by ATRP. To minimize the size of the end groups of the linear polymers, we synthesized the mesogenic initiator shown in Scheme 1. 11-Bromoundecanol was etherified with 4′-hydroxy-4-biphenylcarbonitrile, followed by esterification of the resulting 11-(4′-cyanophenyl-4″-phenoxy)undecanol with 2-bromopropionyl chloride. This mesogenic initiator was then used to polymerize the mesogenic monomer in bulk by ATRP in the presence of cuprous bromide as the catalyst and 4,4′-diheptyl-2,2′-dipyridyl (dHbipy) as the Cu-solubilizing ligand (Scheme 2). The mesogenic initiator introduces the same chemical structure at one chain end as in the polymer repeat units, such that the end groups of the resulting polymer can be considered −H and −Br, rather than methyl propionate and −Br as in the linear polymers produced previously[8] using methyl 2-bromopropionate as the initiator.

Since the mesogenic initiator produces a radical whose structure is nearly identical to that of the propagating radical, the rate constant of initiation should be similar to that of propagation. This should result in relatively efficient initiation with all of the chains growing for approximately the same amount of time, thereby producing polymers with relatively narrow polydispersities in the absence of detectable chain transfer and termination. The results of the bulk polymerizations using the mesogenic initiator are summarized in Table 1. Pure polymers with pdi = 1.13−1.46 based on GPC relative to polystyrene (GPC_{PSt}) were isolated in 49−82% yield after carefully removing both residual copper and unreacted monomer by the method[8] described previously.

If we consider the end groups to be −H and −Br, the theoretical degree of polymerization is equal to $[M]_0/[I]_0 + 1$ at 100% conversion. At attempted $DP_n \le 20$, the molecular weights measured by GPC_{PSt} are higher than the theoretical molecular weights at 100% conversion, evidently due to the errors in using a calibration curve based on polystyrene. At higher attempted degrees of polymerization, it was difficult to attain complete monomer conversion, and the measured molecular weights are therefore lower than the theoretical molecular weights at 100% conversion. In these cases, we used excess monomer to obtain the higher molecular weight polymers with $DP_{n,PSt}$ up to 77.

Table 1 also lists the molecular weight data measured by GPC using a light scattering detector (GPC_{LS}); the polydispersities measured by standard GPC and by GPC_{LS} are similar. Using GPC_{LS}, the measured number-average molecular weights and degrees of polymerization are similar to the attempted values based on $[M]_0/[I]_0$. However, the molecular weights determined off-line by light scattering with classical Zimm measurements are quite different from the absolute molecular weights measured by GPC_{LS}, except at the highest molecular weights. This is presumably due to the errors caused by the low scattering of low molecular weight polymers, and because the Zimm plots were extrapolated from no more than 15 data points (five concentrations measured at three angles), whereas the molecular weights calculated from the GPC_{LS} traces involve thousands of data points (elution volumes) measured at each of the three angles.

The relative accuracy of both the high and low *average* molecular weights measured by GPC_{LS} is supported by the high linear correlation coefficients ($r = 0.989$, $r^2 = 0.978$) for the plot of the GPC_{LS}-determined molecular weights vs the GPC_{PSt}-determined molecular weights shown in Figure 1. This plot has a slope of 1.49, which is the same, within experimental error, as that of the linear polymers with methyl propionate and −Br end groups (1.51).[19] Figure 1 demonstrates that $M_{n,LS} \times 10^{-3} = (1.49)(M_{n,GPC} \times 10^{-3}) - 4.10$ for the linear polymers with −H/−Br end groups. The corresponding weight-average relationship is $M_{w,LS} \times 10^{-3} = (1.47)(M_{w,GPC} \times 10^{-3}) - 4.06$.

Thermotropic Behavior of Linear Polymers with −H/−Br End Groups. Table 2 summarizes the thermotropic behavior of the linear polymers. Figure 2 shows the corresponding differential scanning calorimetry (DSC) traces obtained from the second or subsequent heating scans and from the first or subsequent cooling scans; all of the DSC scans are normalized relative to each other. The s_C−s_A transitions occur at almost the same temperature as the glass transition and are therefore not detectable in the DSC scans of the second heating; i.e., the samples were not cooled slow enough after heating through isotropization to transform from the s_A to the s_C phase before vitrification.

Scheme 2. Synthesis of Linear Poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s by ATRP Using Either 11-(4′-Cyanophenyl-4″-phenoxy)undecyl 2-Bromopropionate or Methyl 2-Bromopropionate as the Initiator; dHbipy = 4,4′-Diheptyl-2,2′-dipyridyl

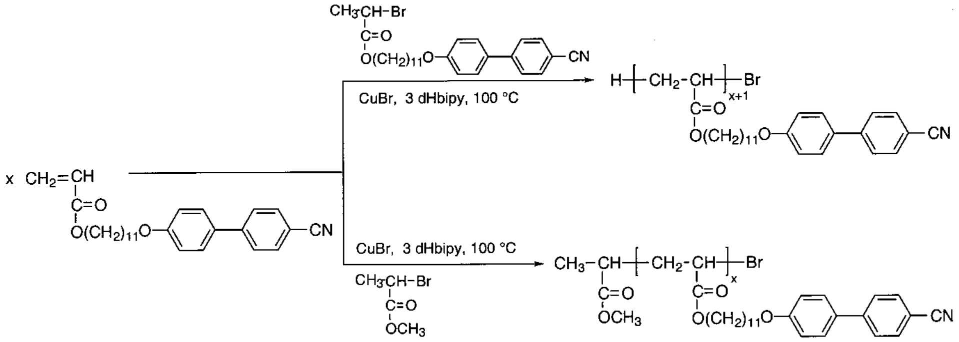


Table 1. Synthesis of Linear Poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate] with −H/−Br End Groups by ATRP[a]

$[M]_0/[I]_0$ + 1	time (h)	yield[b] (%)	theor[c] M_n × 10^{-3}	GPC$_{PSt}$[d] M_n × 10^{-3}	DP$_n$	M_w × 10^{-3}	pdi	GPC$_{LS}$[e] M_n × 10^{-3}	DP$_n$	M_w × 10^{-3}	pdi	d*n*/d*c* (mL/g)	Zimm[e] M_w × 10^{-3}
6	0.25	49	2.39	3.86	9	4.64	1.20	1.60[f]	4[f]			0.181	3.25
6	0.5	82	2.60	4.37	10	5.13	1.17	3.04	7	3.35	1.10	0.165	
8	1.3	81	3.44	5.55	13	6.45	1.16	3.29	8	3.85	1.17	0.178	5.36
12	1.3	73	5.12	6.81	16	7.71	1.13	6.04	14	7.81	1.29	0.174	
20	3.0	80	8.47	10.4	25	12.3	1.18	9.84	23	11.6	1.18	0.171	
26	3.0	56	11.0	5.86	14	7.11	1.21	5.45	13	6.45	1.18	0.171	17.4
27	4.0	68	16.4	13.1	31	15.5	1.18	15.3[f]	36[f]			0.180	16.2
50	22.5	58	21.2	17.2	41	23.6	1.37	19.2	46	32.4	1.69	0.183	
97	47	67	40.6	22.0	52	32.1	1.46	33.4	79	48.5	1.45	0.180	38.9
101	6.0	71	42.6	32.4	77	47.4	1.46	42.4	101	61.6	1.45	0.183	59.0

[a] Using 1:3:1 [CuBr]:[4,4′-diheptyl-2,2′-dipyridyl]:[initiator] at 100 °C in bulk. [b] After copper and monomer completely removed by multiple reprecipitations. [c] Theoretical M_n assuming 100% conversion and taking end groups into account: $M_n = 500.48 + (419.56[M]_0/[I]_0)$. [d] Number-average molecular weight (M_n), number-average degree of polymerization (DP$_n$), weight-average molecular weight (M_w), and polydispersity (pdi = M_w/M_n) determined by gel permeation chromatography (GPC) in THF at 35 °C relative to linear polystyrene using mean of RI and UV detectors. [e] Determined in THF at 35 °C using a light scattering detector with a Ga−As laser set at 690 nm with scattering angles of 45°, 90°, and 135°. [f] Calculated using equation from Figure 1: $M_{n,LS} \times 10^{-3} = (1.49)(M_{n,GPC} \times 10^{-3}) - 4.10$.

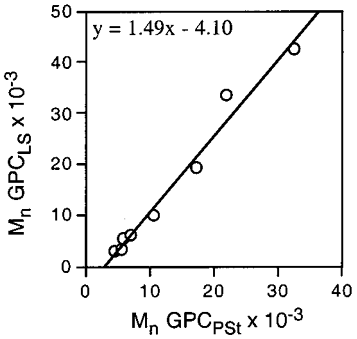


Figure 1. Comparison of the molecular weights of linear poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s with −H/−Br end groups determined by gel permeation chromatography relative to linear polystyrene (GPC$_{PSt}$) and the absolute molecular weights determined by GPC with a light scattering detector (GPC$_{LS}$); linear correlation coefficients, $r = 0.989$, $r^2 = 0.978$.

Figure 2 demonstrates that all of the linear polymers with −H/−Br end groups have equally narrow isotropization transitions (mean fwhm ∼ 6.4 °C on heating), even at short chain lengths where the end groups could have a pronounced effect. This confirms that the smaller hydrogen end group is compatible with the mesogenic polymer, in contrast to the methyl propionate end group of the linear polymers[8] synthesized previously. In addition, even the polymers with the broadest polydispersities (pdi = 1.46) have narrow s_A−i transitions. This demonstrates that a broad Gaussian-like distribution of chain lengths will not broaden the s_A−i biphasic region.

Table 2. Thermotropic Behavior of Linear Poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s with −H/−Br End Groups Synthesized by ATRP[a]

GPC$_{PSt}$ DP$_{n,PSt}$	M_n × 10^{-3}	pdi	transition temp (°C) g−s_C	s_C−s_A	s_A−i	peak width (°C) fwhm
9	3.86	1.20	4	9	99	5.71
10	4.37	1.17	4	10	105	8.72
13	5.55	1.16	7	12	108	6.22
14	5.86	1.21	9	16	114	7.10
16	6.81	1.13	7	14	116	6.13
25	10.4	1.18	11	18	128	5.95
31	13.1	1.18	12	21	133	6.18
41	17.2	1.37	12	21	137	7.74
52	22.0	1.46	13	23	139	5.81
77	32.4	1.46	15	22	142	4.52

[a] Peak width of isotropization determined by DSC on heating at 10 °C/min from the full width at half of the maximum peak intensity (fwhm); g = glass, s_C = smectic C, s_A = smectic A, i = isotropic.

Table 2 and Figure 2 also demonstrate that the glass, s_C−s_A, and s_A−i transition temperatures increase with increasing molecular weight. Figure 3 plots these transitions as a function of the absolute number-average degree of polymerization (DP$_n$) and DP$_n^{-1}$. (Figure S1 in the Supporting Information presents the corresponding plots as a function of the GPC$_{PSt}$-determined DP$_n$ and DP$_n^{-1}$.) The transition temperatures become independent of molecular weight at approximately 40 repeat units. The isotropization temperature extrapolated to DP$_n^{-1}$ = 0 for the infinite molecular weight polymer is 142 °C, which is the same within experimental error as the infinite absolute molecular weight transition temperatures of the corresponding linear polymers[19] with

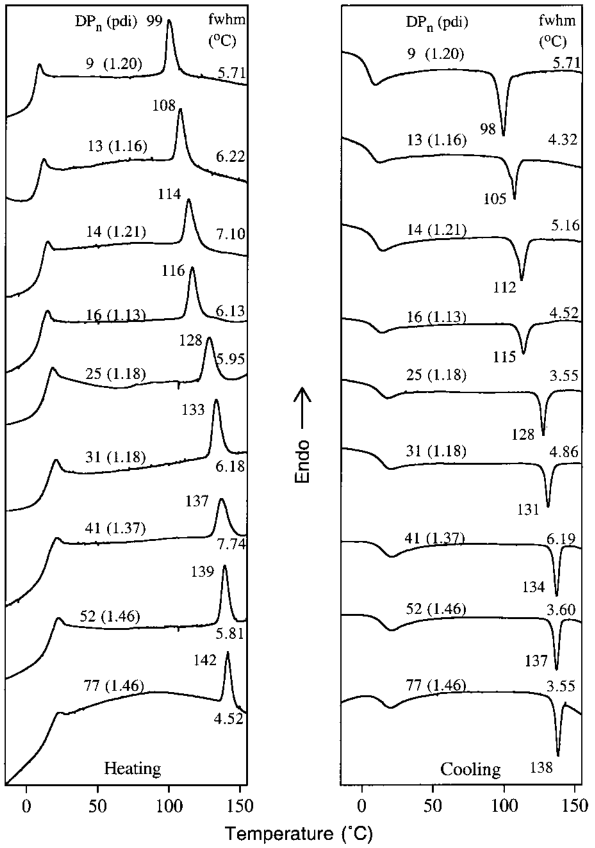


Figure 2. Normalized differential scanning calorimetry traces (10 °C/min) from the second or later heating scans and first or later cooling scans of linear poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s with −H/−Br end groups prepared by ATRP; fwhm = full width at half of the maximum peak intensity.

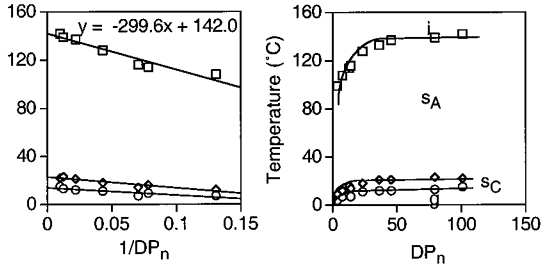


Figure 3. Dependence of the glass (○), smectic C−smectic A (◇), and smectic A−isotropic (□) phase transition temperatures of linear poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s with −H/−Br end groups prepared by ATRP as a function of the absolute number-average degree of polymerization and the inverse absolute number-average degree of polymerization determined by GPC with a light scattering detector. Infinite molecular weight transitions: g 14 s_C 23 s_A 142 i. For comparison: linear with $-CH(CH_3)CO_2CH_3/-Br$ end groups,[19] g 16 s_C 26 s_A 143 i; three-arm star,[19] g 16 s_C 27 s_A 142 i; comb,[12] g 18 s_C 27 s_A 144 i; fractionated[19] from a conventional radical polymerization, g 6 s_C 25 s_A 147 i.

propionate end groups (143 °C), the three-arm star polymers[19] (142 °C), and comb polymers[12] (144 °C) synthesized previously[8,12] by ATRP. This demonstrates that the effects of both the end groups and branch points are negligible at high molecular weight.

Binary Blends of Linear Polymers with −H/−Br End Groups. The narrow isotropization transitions of all of the mesogenic polymers (linear, 3-arm star, comb) synthesized by ATRP with the broadest polydispersities demonstrate that all of the components of these samples must be miscible in the s_A and isotropic phases. The transition should only be broadened or multimodal if the chains have limited miscibility or are phase-separated in either of the two phases that coexist at that transition. Figure 4 therefore compares the phase transitions of 1:1 binary blends of the linear polymers with −H/−Br end groups and those of the corresponding unmixed, macroscopically phase-separated samples. To investigate a broad range of chain lengths (and therefore broad differences in transition temperatures) incorporated into the binary blends of the new linear polymers, Figure 4 presents the DSC traces of blends of the highest molecular weight polymer ($DP_{n,PSt}$ = 77) with all of the lower molecular weight linear polymers. The compositions of the blends are listed in Table 3, along with their GPC_{PSt}-determined number-average degrees of polymerization and polydispersities. The measured average chain lengths generally correspond to the expected values based on composition, except when the blends exhibit bimodal GPC traces.

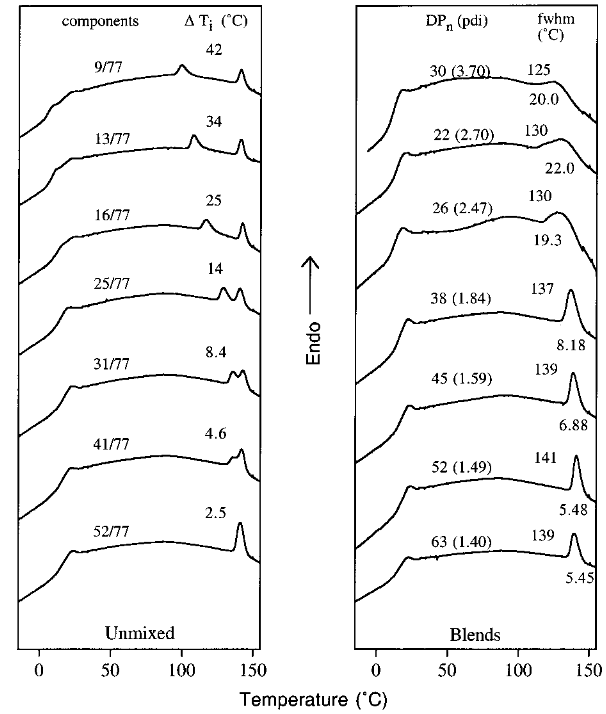


Figure 4. Normalized differential scanning calorimetry traces (10 °C/min) of 1:1 binary unmixed (physically separated) composites and blends of linear poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s with −H/−Br end groups ($DP_{n,PSt}$ = 77, pdi = 1.46) with lower molecular weight linear polymers ($DP_{n,PSt}$ = 9−52, pdi = 1.13−1.46) prepared by ATRP.

The isotropization transitions of both components of the unmixed, macroscopically phase-separated samples are at least partially resolved in all of the DSC traces in Figure 4, except for the 52/77 sample; the relative areas of the endotherms correspond to the weight (or mole repeat unit) ratio of the two components. In contrast, all of the corresponding blends exhibit a single isotropization transition at a temperature intermediate between that of the two components. This transition is only broad (fwhm ≥ 19 °C) when the differences in molecular weights and transition temperatures of the two components are large ($\Delta DP_{n,PSt} \geq 61$, $\Delta T_i \geq 25$ °C). When the differences in molecular weights and transition temperatures of the components are less ($\Delta DP_{n,PSt} \leq 52$, $\Delta T_i \leq 14$ °C), the isotropization transitions of the blends ($DP_{n,PSt}$ = 38−63, pdi = 1.40−1.84) are narrow

Table 3. Composition and Characterization of 1:1 Binary Blends of Poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s Prepared by ATRP

polymers 1/2	composition (%)				GPC_{PSt}[d]			
DP_n/DP_n[a]	polymer 1	polymer 2	recovery (%)	theor DP_n	DP_n	pdi	T_i (°C)	fwhm[e] (°C)
Linear/Linear with −H/−Br End Groups[b]								
9/77	49	51	63	44	30	3.70	125	20.0
13/77	50	50	72	45	22	2.70	130	22.0
16/77	50	50	75	47	26	2.47	130	19.3
25/77	48	52	68	52	38	1.84	137	8.18
31/77	50	50	70	54	45	1.59	139	6.88
41/77	49	51	29	59	52	1.49	141	5.48
52/77	50	50	51	65	63	1.40	139	5.45
Linear/Linear with −H/−Br End Groups[c]								
9/10	53	47	100	9	9	1.23	106	8.01
10/16	48	52	100	13	11	1.30	113	8.91
10/25	46	54	100	18	13	1.50	121	13.8
10/31	48	52	100	21	17	1.49	126	19.2
10/41	51	49	100	25	17	2.00	127	25.7
10/52	47	53	100	32	20	2.28	129	21.5
10/77	47	53	100	46	18	2.82	129	20.7
Linear (−H/−Br End Groups)/Three-Arm Star[c]								
41/37	51	49	100	39	38	1.21	131	9.09
41/42	50	50	100	41	35	1.22	128	13.1
41/49	49	51	100	45	38	1.39	135	7.15
41/55	50	50	100	48	41	1.32	134	7.29
41/60	50	50	100	51	48	1.63	127	16.5
10/57	50	50	100	57	43	2.04	120	32.8
16/57	50	50	100	38	39	1.89	132	6.96
31/57	50	50	100	45	54	1.38	134	6.42
52/57	50	50	100	56	67	1.30	136	6.79
77/57	52	48	100	68	78	1.41	140	3.39
Linear/Linear with $-CH(CH_3)CO_2CH_3/-Br$ End Groups[b]								
8/115	50	50	79	69	19	14.1	128	39.2[f]
12/115	45	55	64	76	31	7.88	132	27.3[f]
23/115	51	49	77	75	59	6.44	139	13.3
36/115	52	48	84	81	51	5.24	138	7.50
40/115	51	49	80	88	55	4.68	139	6.25

[a] Number-average degree of polymerization (DP_n) values from GPC relative to linear polystyrene. [b] Samples were blended by dissolving in THF, precipitating in methanol, and collecting the precipitate in a fritted glass filter. [c] Samples were blended by dissolving in THF, precipitating with methanol, and then evaporating off the solvent. [d] Number-average degree of polymerization (DP_n) and polydispersity (pdi = M_w/M_n) determined by gel permeation chromatography (GPC_{PSt}) relative to linear polystyrene using mean of RI and UV detectors. [e] Full width at half of the maximum peak intensity. [f] Bimodal; fwhm determined at full width at half of the maximum peak intensity of the shorter maximum.

(fwhm = 5.16−8.39 °C) and similar to those of the individual components.

To better explore the molecular weight region where the isotropization temperature of the polymer depends on molecular weight, a low molecular weight polymer ($DP_{n,PSt} = 10$) was blended with each of the remaining linear polymers. If chains of different lengths undergo isotropization separately, then all of the blends in this series should exhibit broad transitions. Figure 5 compares the phase transitions of these binary blends and their unmixed samples. Their compositions and GPC_{PSt}-determined molecular weight data are listed in Table 3. Although all of the blends were recovered quantitatively, the measured average chain lengths do not correspond well to the expected values based on composition because the GPC traces are bimodal; the measured $M_{n,PSt}$ is biased toward the larger peak in the trace. As in the previous series, isotropization is only broad (fwhm ≥ 13 °C) when there is a large difference in transition temperatures ($\Delta T_i \geq 24$ °C) of the two components, although the difference in molecular weight ($\Delta DP_{n,PSt} \geq 15$) is much smaller. This demonstrates that for some of the blends the components are miscible in the s_A and isotropic phases, even though their transition temperatures are in the molecular-weight-dependent region.

We also blended a linear polymer ($DP_{n,PSt} = 41$) with three-arm star polymers with a range of chain lengths ($DP_{n,PSt} = 37−61$) (Figure S2 in the Supporting Information) and a three-arm star polymer ($DP_{n,PSt} = 57$) with the linear polymers with a range of chain lengths ($DP_{n,PSt} = 10−77$) (Figure S3); their compositions, GPC_{PSt}-determined molecular weight data, and breadths of isotropization are listed in Table 3. In the first case, there is no correlation between the breadth of the transition and the differences in either molecular weight or transition temperature of the two components. In the second case, isotropization is broad (fwhm = 33 °C) only at the largest differences in molecular weight and transition temperatures ($\Delta DP_{n,PSt} = 47$, $\Delta T_i = 32$ °C).

Binary Blends of Linear Polymers with $-(CH_3)CHCO_2CH_3/-Br$ End Groups. As discussed in the Introduction, our original[8] investigation involved only one 1:1 binary blend, with $DP_n \approx 50$, of the linear polymers with methyl propionate/bromine end groups. We have therefore expanded this series of 1:1 binary blends using the original linear polymers with a range of chain lengths. The highest molecular weight polymer ($DP_{n,PSt} = 115$) was blended with all of the lower molecular weight linear polymers; their compositions and GPC_{PSt}-determined molecular weight data are summarized in Table 3. The measured average chain lengths do not correspond well to the expected values

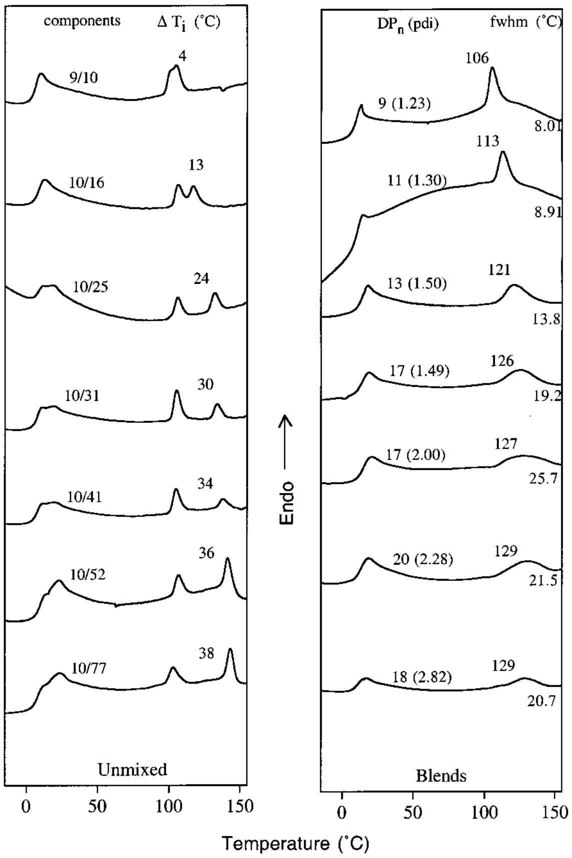


Figure 5. Normalized differential scanning calorimetry traces (10 °C/min) of 1:1 binary unmixed (physically separated) composites and blends of linear poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s with −H/−Br end groups ($DP_{n,PSt}$ = 10, pdi = 1.17) with similar and higher molecular weight linear polymers ($DP_{n,PSt}$ = 9−77, pdi = 1.13−1.46) prepared by ATRP.

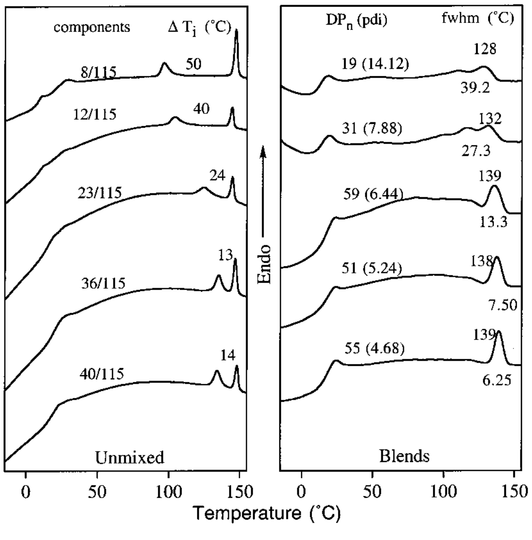


Figure 6. Normalized differential scanning calorimetry traces (10 °C/min) of 1:1 binary unmixed (physically separated) composites and blends of linear poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s with $-CH(CH_3)CO_2CH_3/-Br$ end groups ($DP_{n,PSt}$ = 115, pdi = 2.99) with lower molecular weight linear polymers[8] ($DP_{n,PSt}$ = 8−40, pdi = 1.13−1.46) prepared by ATRP.

based on composition because the GPC traces are bimodal.

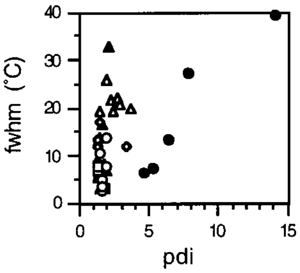


Figure 7. Dependence of the breadth of isotropization (fwhm) of 1:1 binary blends of poly[11-(4′-cyanophenyl-4″-phenoxy)-undecyl acrylate]s (△, linear/linear with −H/−Br end groups; ●, linear/linear with $-CH(CH_3)CO_2CH_3/-Br$ end groups; ▲, three-arm star/linear with −H/−Br end groups; ▼, three-arm star/linear with $-CH(CH_3)CO_2CH_3/-Br$ end groups;[8] ○, comb/comb;[12] □, comb/three-arm star;[12] ◇, comb/linear,[12] $-CH(CH_3)CO_2CH_3/-Br$ end groups) as a function of the blends' polydispersity (pdi = M_w/M_n) in molecular weight.

Figure 6 compares the DSC traces of the linear/linear binary blends and those of the corresponding unmixed samples. The two components of the unmixed, macroscopically phase-separated samples undergo separate isotropization transitions. The relative areas of the endotherms correspond to the weight (or mole repeat unit) ratio of the two components. As with the linear polymers with −H/−Br end groups, the isotropization transition of these linear/linear blends is only broad (fwhm ≥ 13 °C) when the differences in molecular weights and transition temperatures of the two components are large ($\Delta DP_{n,PSt} \geq 93$, $\Delta T_i \geq 24$ °C); two of the blends have a bimodal transition. When the differences in molecular weights and transition temperatures of the components are less ($\Delta DP_{n,PSt} \leq 79$, $\Delta T_i \leq 13$ °C), the isotropization transitions of the blends ($DP_{n,PSt}$ = 38−63, pdi = 1.40−1.84) are narrow (fwhm = 5.16−8.39 °C) and similar to those of the two components (fwhm = 6.3−7.5 °C). In these cases, isotropization occurs at a temperature intermediate between that of the two components.

Discussion

Figure 7 plots the breadth of the isotropization transition as a function of the polydispersity of the 1:1 binary blends of all of the poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s that we have synthesized by ATRP, including linear/linear blends of polymers with −H/−Br end groups, linear/linear polymers with $-(CH_3)CHCO_2CH_3/-Br$ end groups, linear/three-arm star, linear/comb,[12] comb/comb,[12] and comb/three-arm star[12] polymers. Although polydispersity in molecular weight is generally believed to broaden the phase transitions of SCLCPs,[6,7] Figure 7 demonstrates that there is no correlation between the breadth of the s_A−i transition and the polydispersity of the blend in this system. For example, binary blends with pdi = 1−2 have breadths (fwhm) ranging from 3 to 33 °C. However, some of the series presented in this paper have broad isotropization transitions when the components have large differences in molecular weight and/or transition temperature and narrow transitions when the differences are small. Figure 8 demonstrates that the correlation between the breadth of isotropization and differences in chain length of the two components does not hold for all of the series. Nevertheless, the correlation is fairly good for the breadth of the transition as a function of differences in the isotropization temperature of the two components if we consider all of the data (Figure 9), although it does not hold well for some of

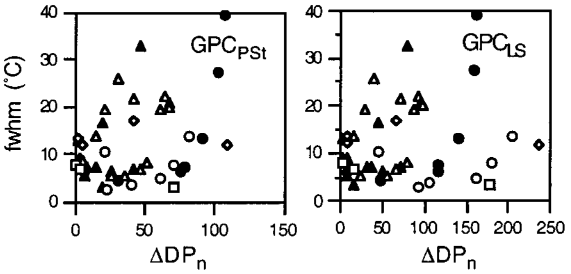


Figure 8. Dependence of the breadth of isotropization (fwhm) of 1:1 binary blends of poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s (△, linear/linear with $-$H/$-$Br end groups; ●, linear/linear with $-\mathrm{CH(CH_3)CO_2CH_3}/-\mathrm{Br}$ end groups; ▲, three-arm star/linear with $-$H/$-$Br end groups; ▼, three-arm star/linear with $-\mathrm{CH(CH_3)CO_2CH_3}/-\mathrm{Br}$ end groups;[8] ○, comb/comb;[12] □, comb/three-arm star;[12] ◇, comb/linear,[12] $-\mathrm{CH(CH_3)CO_2CH_3}/-\mathrm{Br}$ end groups) as a function of the difference in the number-average degrees of polymerization of the two components as measured by either GPC$_{PSt}$ or GPC$_{LS}$.

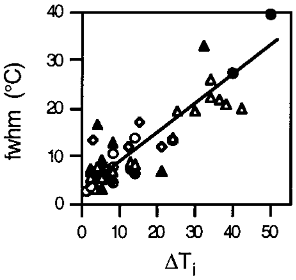


Figure 9. Dependence of the breadth of isotropization (fwhm) of 1:1 binary blends of poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s (△, linear/linear with $-$H/$-$Br end groups; ●, linear/linear with $-\mathrm{CH(CH_3)CO_2CH_3}/-\mathrm{Br}$ end groups; ▲, three-arm star/linear with $-$H/$-$Br end groups; ▼, three-arm star/linear with $-\mathrm{CH(CH_3)CO_2CH_3}/-\mathrm{Br}$ end groups;[8] ○, comb/comb;[12] □, comb/three-arm star;[12] ◇, comb/linear,[12] $-\mathrm{CH(CH_3)CO_2CH_3}/-\mathrm{Br}$ end groups) as a function of the difference in the isotropization temperatures of the two components.

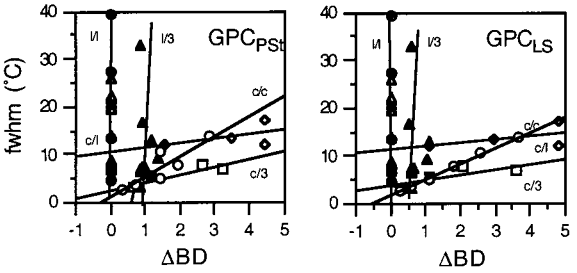


Figure 10. Dependence of the breadth of isotropization (fwhm) of 1:1 binary blends of poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s (△, linear/linear with $-$H/$-$Br end groups; ●, linear/linear with $-\mathrm{CH(CH_3)CO_2CH_3}/-\mathrm{Br}$ end groups; ▲, three-arm star/linear with $-$H/$-$Br end groups; ▼, three-arm star/linear with $-\mathrm{CH(CH_3)CO_2CH_3}/-\mathrm{Br}$ end groups;[8] ○, comb/comb;[12] □, comb/three-arm star;[12] ◇, comb/linear,[12] $-\mathrm{CH(CH_3)CO_2CH_3}/-\mathrm{Br}$ end groups) as a function of the difference in branching density (normalized to chains of 50 repeat units and based on either GPC$_{PSt}$- or GPC$_{LS}$-determined molecular weights) of the components.

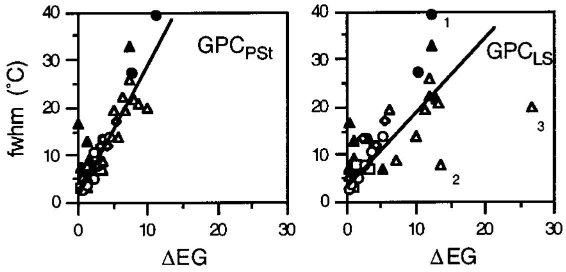


Figure 11. Dependence of the breadth of isotropization (fwhm) of 1:1 binary blends of poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s (△, linear/linear with $-$H/$-$Br end groups; ●, linear/linear with $-\mathrm{CH(CH_3)CO_2CH_3}/-\mathrm{Br}$ end groups; ▲, three-arm star/linear with $-$H/$-$Br end groups; ▼, three-arm star/linear with $-\mathrm{CH(CH_3)CO_2CH_3}/-\mathrm{Br}$ end groups;[8] ○, comb/comb;[12] □, comb/three-arm star;[12] ◇, comb/linear,[12] $-\mathrm{CH(CH_3)CO_2CH_3}/-\mathrm{Br}$ end groups) 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$_{LS}$-determined molecular weights) of the components.

the individual series; i.e., there is fairly linear correlation between the breadth of isotropization and differences in the isotropization temperature of the two components for architecturally uniform blends (linear/linear and comb/comb blends, which constitute most of the data points in Figure 9) but not for the blends with different architectures (linear/three-arm star and linear/comb blends).

Alternatively, we proposed that polydispersity in molecular architecture is responsible for the broad phase transitions exhibited by SCLCPs synthesized by conventional radical polymerizations due to the limited miscibility of the mixture of molecular architectures produced by chain transfer to polymer at high monomer conversion.[8,12] Figure 10 plots the breadth of isotropization of binary blends of the poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s as a function of the differences in branching density normalized to 50 repeat units. Although the dependence is linear within each series or combination of molecular architectures, the dependence is meaningless for the linear/linear polymers since each linear polymer has zero branches per chain.

However, each branch point in the polymer adds one end group, and the branching density can therefore be related to the density of end groups, even for the linear polymers. Figure 11 demonstrates that a plot of the breadth of isotropization vs the difference in end group density (normalized to 50 repeat units) of the two components is linear, regardless of the combination of molecular architectures, when the calculations are based on GPC$_{PSt}$-determined molecular weights; the data are more scattered when the absolute molecular weights are used, which expands the range of end group densities due to the underestimation of molecular weight of branched polymers by GPC relative to linear polystyrene. The three most outlying points are numbered in the figure. The first outlying point is due to one of the few blends with a bimodal isotropization transition. In this case, the breadth of the transition is exaggerated because we calculated it at half of the maximum peak height corresponding to the smaller peak. Outlying points 2 and 3 involve blends with the lowest molecular weight linear polymer with $-$H/$-$Br end groups ($DP_{n,PSt} = 9$). In this case, the absolute GPC$_{LS}$ molecular weight used to determine the end group density was calculated from the equation in Figure 1, rather than measured directly, due to the limited amount of sample. Any errors in this calculation will propagate to the $DP_{n,LS} = 4$ and therefore calculated end group density. If these three points are eliminated from the linear regression, the linear correlation coefficient is $r = 0.85$ for the GPC$_{LS}$ plot. The differences in branching and end group density of the blends are summarized in Table S1 of the Supporting Information.

Conclusions

Linear poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s were synthesized by atom transfer radical polymerization of 11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate using a mesogenic initiator. The small −H and −Br end groups of the resulting polymers are apparently compatible with the mesogenic repeat units, in contrast to the methyl propionate/−Br end groups generated using methyl 2-bromopropionate as the initiator; i.e., the breadth of the s_A−i transition of the linear polymers with −H/−Br end groups is independent of molecular weight and is narrow in all cases (fwhm = 4.52−8.72 °C). The breadth of isotropization of 1:1 binary blends of the mesogenic polyacrylates prepared by ATRP with a variety of architectures (linear, three-arm star, comb) increases as the difference in end group and/or branching density of the two components increases, regardless of the combination of molecular architectures or the type of end groups. Therefore, the broad isotropization transition (fwhm = 17.0 °C)[7,8] of the corresponding polymer prepared by conventional radical polymerization is evidently due to polydispersity in molecular architecture rather than polydispersity in molecular weight. This broadening of the disordering transition with increasing differences in branching density is not limited to SCLCPs but is apparently common to many polymers, such as poly(styrene),[14] poly(butadiene),[15] and poly(ethylene).[16,17,20]

Experimental Section

Materials. 2-Bromopropionyl chloride (Acros, technical grade) and cuprous bromide (Aldrich, 99.999%) were used as received. 11-(4′-Cyanophenyl-4″-phenoxy)undecanol, 11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate, and 4,4′-diheptyl-2,2′-dipyridyl were prepared as described previously.[8] With the exception of the $DP_{n,PSt} = 115$ (pdi = 2.99) linear polymer and the $DP_{n,PSt} = 37$ (pdi = 1.11) three-arm star polymer, the syntheses of the linear[8] polymers with $-CH(CH_3)CO_2CH_3/-Br$ end groups and the three-arm star[8] and comb[12] poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s by ATRP were described previously. Triethylamine (Baker, technical grade) was stirred over KOH and distilled under N_2. Reagent grade tetrahydrofuran (THF) was dried by distillation from purple sodium benzophenone ketyl under N_2. Stock solutions of methanolic ammonium chloride containing 45 mL of methanol and 15 mL of saturated aqueous NH_4Cl were prepared to remove copper salts from ATRP polymers by precipitations at −78 °C as described previously;[8] water was necessary to keep NH_4Cl in solution at low temperature. 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 Varian Gemini 300 (300 MHz) or a Varian Gemini 200 (200 MHz) spectrometer. All spectra were recorded in $CDCl_3$ with tetramethylsilane as an internal standard. Relative molecular weights were determined by gel permeation chromatography (GPC_{PSt}) 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 μ columns, a Waters 486 tunable UV/vis detector set at 275 nm, and a Waters 410 differential refractometer. Absolute molecular weights were determined by GPC with a light scattering detector (GPC_{LS}) at 35 °C using THF as solvent (1.0 mL/min), a set of 50, 500, and 10^4 Å and linear ($50-10^6$ Å) Phenogel 5 μm columns, and a Wyatt Technology miniDAWN three-angle (45°, 90°, 135°) light scattering detector equipped with a Ga−As laser (690 nm), with the concentration at each elution volume determined using a Wyatt Optilab 903 interferometeric differential refractometer (690 nm). The molecular weight data were calculated using Astra 4.72.03 software (Wyatt Technology). The light scattering detectors were calibrated using the Rayleigh ratio of toluene, and then their responses were normalized to that of the 90° detector using a solution of polystyrene (M_n < 30 000) in THF. To determine the mass concentrations at each elution volume and to determine the physical constant K^* for the light scattering measurements, refractive index increments (dn/dc) were measured off-line in THF (distilled from $LiAlH_4$ and filtered through a 0.02 μm PTFE filter) at 690 nm using the Optilab 903 interferometeric refractometer calibrated with aqueous NaCl and an Orion Sage 362 syringe pump at 0.3 mL/min. All samples were dissolved overnight and filtered through a 0.45 μm PTFE filter.

All polymers and their blends were dried overnight in vacuo at 45−60 °C 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. Transition temperatures were calibrated using indium and benzophenone standards, and enthalpy changes were calibrated using indium. 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.

Synthesis of 11-(4′-Cyanophenyl-4″-phenoxy)undecyl 2-Bromopropionate. A solution of 2-bromopropionyl chloride (1.7 g, 10 mmol) in dry THF (15 mL) was added dropwise over 40 min to a solution of 11-(4′-cyanophenyl-4″-phenoxy)undecanol (3.0 g, 8.2 mmol) and dry NEt_3 (1.2 g, 12 mmol) in dry THF (35 mL) at room temperature. After 2 h, thin-layer chromatography (TLC, silica, Et_2O) showed that 11-(4′-cyanophenyl-4″-phenoxy)undecanol (R_f = 0.67) had reacted completely (R_f = 0.92). The reaction mixture was poured into water (200 mL) and extracted three times with CH_2Cl_2 (50 mL each). The organic layer was separated and dried over $MgSO_4$ overnight. After filtration, the organic layer was concentrated by rotary evaporation to yield a light brown oil. This residue was recrystallized twice from a mixture of ethanol (85 mL) and toluene (15 mL) to yield 3.0 g (74%) of 11-(4′-cyanophenyl-4″-phenoxy)undecyl 2-bromopropionate as white crystals. ^1H NMR: 1.31 (m, $[CH_2]_7$), 1.67 (m, CH_2CH_2OAr), 1.77 (m, $CH_2CH_2O_2C$), 1.80 (d, CH_3CHBr), 4.00 (t, CH_2OAr), 4.15 (t, CH_2O_2C), 4.35 (q, $CHBr$), 6.97 (d, 2 aromatic H ortho to OCH_2), 7.51 (d, 2 aromatic H meta to OCH_2), 7.65 (m, 4 aromatic H ortho and meta to CN).

Synthesis of Linear Polymers with −H and −Br End Groups. Linear polymers were prepared by ATRP in 49−82% yield as in the following example. A mixture of 11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate (0.50 g, 1.2 mmol), 11-(4′-cyanophenyl-4″-phenoxy)undecyl 2-bromopropionate (85 mg, 0.17 mmol), CuBr (24 mg, 0.17 mmol), and 4,4′-diheptyl-2,2′-dipyridyl (0.18 g, 0.51 mmol) was degassed using six freeze−pump−thaw cycles in a sealable polymerization tube. The tube was then sealed under vacuum and stirred at 100 °C for 1.3 h. The polymer was precipitated in cold (−78 °C) methanol (50 mL) containing 1 drop of HCl, collected, and purified by reprecipitating four times from THF (5 mL) into a solution of cold (−78 °C) methanol (50 mL) and saturated aqueous NH_4Cl (2 mL). One additional precipitation from THF (4 mL) into cold (−78 °C) methanol (50 mL) containing 1 drop of HCl yielded 0.48 g (81%) of poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate] as a sticky white solid: GPC_{PSt} $M_n = 5.55 \times 10^3$, pdi = 1.16; GPC_{LS} $M_n = 3.29 \times 10^3$, pdi = 1.17.

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Supporting Information Available: Branching and end group densities of the components of the blends, dependence of the transition temperatures on GPC_{PSt}-determined DP_n and DP_n^{-1}, and DSC scans of binary blends of linear and three-arm star polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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