Solution Behavior of Topological Isomers of Poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s Prepared by Atom Transfer and Conventional Radical Polymerizations

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ABSTRACT: The solution behavior of linear, three-arm star, and comb poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s previously synthesized by atom transfer radical polymerization was investigated by gel permeation chromatography (GPC_{PSt}) and light scattering measurements in CH_2Cl_2, THF, and $CHCl_3$ in order to correlate their size and shape with their molecular architecture and in order to investigate the extent of branching in the corresponding polymer prepared by conventional radical polymerization. The inaccuracy of the GPC_{PSt} molecular weights increases as the polymers become more branched: linear < three-arm star < comb; the discrepancy between the GPC_{PSt} and absolute molecular weights of polymers fractionated from the conventional radical polymerization is between those of the three-arm star and comb polymers in all three solvents. Light scattering studies demonstrate that CH_2Cl_2 is the best solvent for all of the polymers, resulting in either no aggregation or an insignificant amount of aggregation, whereas all of the topologies except the comb polymers tend to aggregate in THF and $CHCl_3$; nevertheless, the extent of aggregation is not great enough to be detected by variations in the average GPC_{LS}-determined molecular weights measured in any of these solvents. The tendency to aggregate in all of the solvents and the radius of gyration in CH_2Cl_2 decrease as the branching increases: linear > three-arm star > comb, with the polymer prepared by conventional radical polymerization being similar to the branched polymers. The scaling coefficients ($R_g = KM^{\nu}$) of all of the polymers are similar in CH_2Cl_2, with $\nu = 0.37$ for the three-arm star polymers, $\nu = 0.39$ for the comb polymers, and $\nu = 0.32$ for the polymer prepared by conventional radical polymerization. The relative values of the contraction factors, $g = \langle R_g^2\rangle_{br}/\langle R_g^2\rangle_{lin}$, decrease in the order $g_{star} > g_{comb} > g_{radical}$ for the three-arm star polymers, the comb polymers, and the polymer prepared by conventional radical polymerization, respectively, in CH_2Cl_2.

Introduction

To test the hypothesis that the broad phase transitions often exhibited by side-chain liquid crystalline polymers (SCLCPs) are due to the limited miscibility of a mixture of branched structures produced by chain transfer to polymer at high monomer conversion in radical polymerizations,[1] we have synthesized a series of linear,[1,2] three-arm star,[1] and comb[3] poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s (Scheme 1) by atom transfer radical polymerization (ATRP[4]) and determined the thermotropic behavior of the individual isomers and binary blends of all combinations of the topological isomers. The breadth of the smectic A to isotropic (s_A−i) biphasic region of the 1:1 binary blends increases relatively linearly with the difference in end group (and therefore branching) density of the two components, regardless of the combination of molecular architectures or the type of end groups.[2,3] The narrow transitions of all of the polymers produced by ATRP, including those with broad polydispersities, suggest that they have rather uniform molecular architectures. The differences in the thermotropic behavior of the polymers are consistent with their different topologies. In general, the transition temperatures of the polymers decrease with increasing branching (linear > three-arm star > comb) at identical molecular weights (determined by gel permeation chromatography relative to linear polystyrene, GPC_{PSt}), although they extrapolate to essentially the same values (g 18 s_C 28 s_A 146 i) at infinite molecular weight due to the insignificance of two to seven end groups and zero to five branches at high molecular weight; the s_A−i transition temperature of polymers fractionated from the polymer produced by a conventional radical polymerization extrapolates to a significantly higher value (T_i = 154 °C) at infinite GPC_{PSt}-determined molecular weight.

Although the differences in the thermotropic behavior of the polymers are consistent with their different topologies, better support for the molecular architectures shown in Scheme 1 may be provided by their solution properties. This paper investigates the solution behavior of the linear, three-arm star, and comb poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s, previously synthesized by ATRP, by GPC_{PSt}, and by light scattering measurements at either three (45°, 90°, 135°) or 18 (17°−155°) angles in CH_2Cl_2, THF, and $CHCl_3$ in order to correlate their size and shape with their molecular architecture and in order to investigate the extent of branching in the corresponding, potentially heterogeneously branched polymer produced in a conventional radical polymerization (designated "radical" throughout the rest of this paper).

There are relatively few studies on the absolute molecular weights and solution behavior of SCLCPs, all of which were prepared by conventional radical polymerizations, in organic solvents.[5−12] Homopolymers and random copolymers of (4′-methoxyphenyl-4″-phenoxy)-oligooxyethylene methacrylates with different spacer lengths (zero to four oxyethylene units) were characterized by GPC in THF using a light scattering detector

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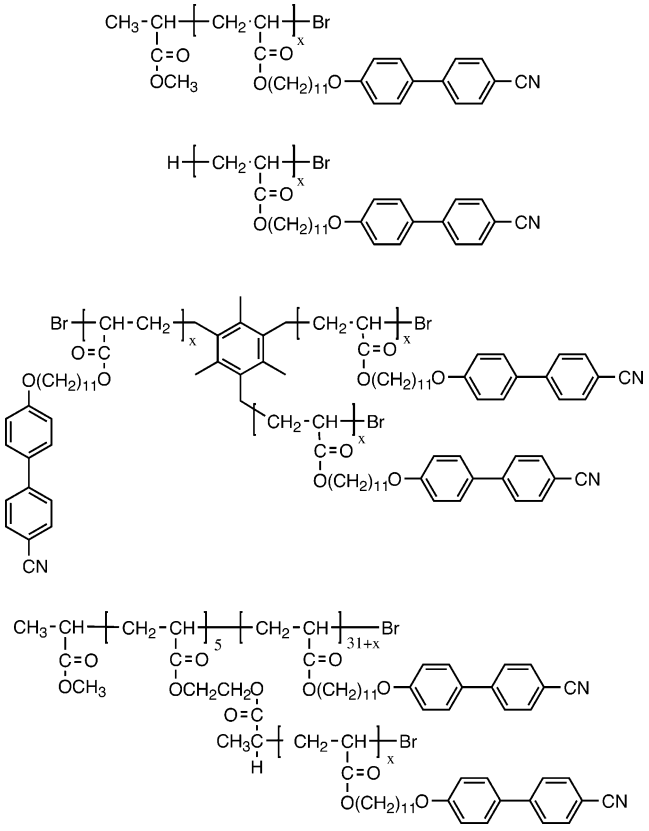
Scheme 1. Linear, Three-Arm Star, and Comb Poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s Synthesized by Atom Transfer Radical Polymerization



at 90°.[6] The absolute molecular weights were significantly higher than the GPC_{PSt}-determined molecular weights, which demonstrates that the hydrodynamic volumes of the SCLCPs and copolymers are smaller than that of linear polystyrene. The absolute molecular weights determined by light scattering measurements of fractionated poly{6-[4′-(4″-methoxyphenoxycarbonyl)-phenoxy]hexyl methacrylate} were also much higher than the GPC_{PSt}-determined molecular weights.[11]

Many of these SCLCPs aggregate in organic solvents,[5−12] evidently due to strong mesogen−mesogen interactions. The formation of an excimer by poly[3-(4′-cyanophenyl-4″-phenoxy)propyl acrylate] in THF at dilute concentrations, but not by 3-(4′-cyanophenyl-4″-phenoxy)pentane, indicates that (intramolecular) mesogen−mesogen interactions are stronger in SCLCPs than in the corresponding low molar mass liquid crystals.[13] Although the strength of the intramolecular mesogen−mesogen interactions apparently decreases with increasing spacer length,[13] the ability to associate via intermolecular mesogen−mesogen interactions increases with increasing spacer length.[9,12]

There are far more studies on the solution properties of common polymers with different topologies.[14] In general, branched polymers are more compact than the corresponding linear polymers at the same molecular weight. For example, the intrinsic viscosity of randomly branched poly(methyl methacrylate) (PMMA) is lower than that of linear PMMA at high molecular weights, although their radii of gyration are indistinguishable.[15] The scaling relationship between molecular weight and radius of gyration ($R_g = KM^{\nu}$) is also an indication of the conformation of a polymer in solution, with typical values of $\nu = 0.33$ for a hard sphere, $\nu = 0.50$ for an unperturbed chain in a Θ solvent, $\nu = 0.588$ for a random coil in a good solvent, and $\nu = 1.0$ for a polymer with an extended rodlike conformation.[14] Nevertheless, values of the scaling parameter below the hard-sphere limit have been reported for extremely branched polymers, such as those measured by small-angle neutron scattering of arborescent polystyrene in a linear deuterated matrix of either polystyrene or poly(vinyl methyl ether) ($\nu = 0.26$ and 0.28, respectively),[16] as predicted by de Gennes and Hervet.[17]

Experimental Section

Materials. The syntheses of the linear poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s with methyl propionate and bromide end groups,[1] and with hydrogen and bromide end groups,[2] and of the three-arm star[1] and comb[3] poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s by ATRP were described previously. The synthesis of the corresponding polymer by conventional radical polymerization using azobis(isobutyronitrile) (AIBN) as the initiator in benzene at 60 °C for 29 h was also reported previously, as was its fractionation.[1] Blends of the individual architectures were prepared by dissolving the components in a minimum amount of THF, precipitating with cold methanol, removing all solvents in vacuo and drying the precipitated residue in vacuo at 60 °C overnight. THF was distilled from $LiAlH_4$ for light scattering measurements. All other HPLC grade solvents were commercially available and used as received.

Techniques. Molecular weights relative to linear polystyrene were determined by gel permeation chromatography from calibration curves of log M_n vs elution volume at 35 °C using THF, CH_2Cl_2, or $CHCl_3$ as solvent (1.0 mL/min). The instrument using THF as solvent consisted of a set of 50 Å, 100 Å, 500 Å, 10^4 Å, and linear (50−10^4 Å) Styragel 5 μm columns, a Waters 486 tunable UV/vis detector set at 275 nm, and a Waters 410 differential refractometer. The instrument using CH_2Cl_2 and $CHCl_3$ as solvent consisted of a set of 50 Å, 500 Å, 10^4 Å, and linear (50−10^6 Å) Phenogel 5 μm columns and a Wyatt Optilab 903 interferometeric differential refractometer (690 nm).

Absolute molecular weights were determined by GPC with a light scattering detector (GPC_{LS}) at 35 °C using either THF, CH_2Cl_2, or $CHCl_3$ as solvent (1.0 mL/min), a set of 50 Å, 500 Å, 10^4 Å, and linear (50−10^6 Å) Phenogel 5 μm columns, and a Wyatt Technology miniDAWN three-angle (46°, 90°, 134° in CH_2Cl_2; 45°, 90°, 135° in THF; 46°, 90°, 134° in $CHCl_3$) light scattering detector equipped with a Ga−As laser (690 nm, 20 mW), 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 4.90.07 software (Wyatt Technology) and a Zimm fit according to the following equation

$$\frac{K^*c}{R(\theta)} = \frac{1}{M_w}\left[1 + \frac{16\pi^2 {n_0}^2}{3{\lambda_0}^2}\langle {R_g}^2\rangle \sin^2(\theta/2)\right] \qquad (1)$$

where θ is the angle between the incident and scattered rays, $R(\theta)$ is the excess Rayleigh ratio of scattered light at angle θ, K^* is the optical constant

$$K^* = \frac{4\pi^2 {n_0}^2 (\mathrm{d}n/\mathrm{d}c)^2}{N_A {\lambda_0}^4} \qquad (2)$$

c is the mass/volume concentration of the solute, n_0 is the refractive index of the solvent at the wavelength, λ_0, of the incident light, and N_A is Avogadro's number. Equation 1 assumes that the concentration at each elution slice is negligible and that the scattering function $P(\theta)$ does not require higher-order terms that are nonlinear in $\sin^2(\theta/2)$. The light scattering detectors were calibrated using the Rayleigh

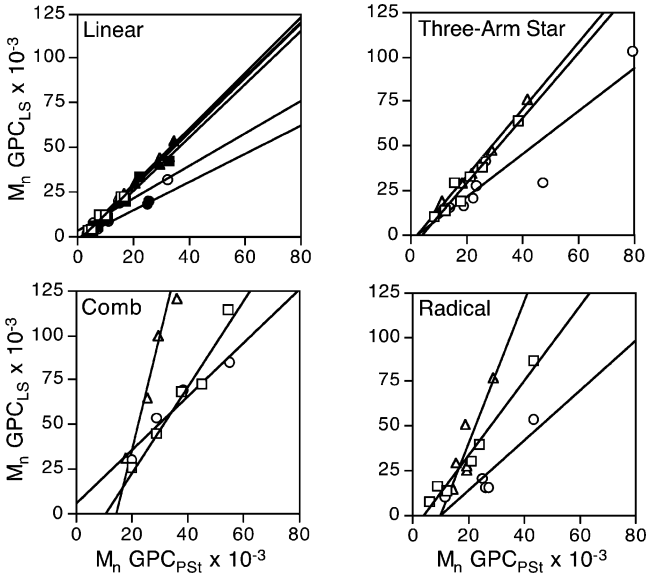


Figure 1. Comparison of $GPCP_{St}$- and GPC_{LS}-determined molecular weights of linear (−CH(CH$_3$)CO$_2$CH$_3$/−Br end groups (open symbols) and −H/−Br end groups[2] (filled symbols), three-arm star, and comb poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s synthesized by ATRP and the corresponding polymers fractionated from a conventional radical polymerization in CH_2Cl_2 (○, ●), THF (□, ■), and $CHCl_3$ (△, ▲).

ratio of toluene, and their responses were then normalized to that of the 90° detector using a solution of a narrow distribution polystyrene (M_n < 30 000) standard in the solvent used for each experiment. The root-mean-square radii of gyration ($\langle R_g^2\rangle^{1/2}$) in THF, CH_2Cl_2, and $CHCl_3$ were measured from GPC chromatograms under the same conditions, except that a Wyatt Technology DAWN-EOS 18-angle (20°−153° in CH_2Cl_2; 17°−155° in THF; 21°−152° in $CHCl_3$) light scattering detector equipped with a Ga−As laser (690 nm, 30 mW) was used instead of the miniDAWN detector. To determine the mass concentrations at each elution volume and the physical constant K^* for the light scattering measurements, refractive index (RI) increments (dn/dc, using 0.1, 0.2, 0.3, 0.4, and 0.5 mg/mL) were measured off-line in THF (distilled from $LiAlH_4$ and filtered through a 0.02 μm PTFE filter; dn/dc = 0.180 mL/g), CH_2Cl_2 (dn/dc = 0.176 mL/g), and $CHCl_3$ (dn/dc = 0.146 mL/g) at room temperature 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.

Results and Discussion

Absolute vs GPC_{PSt} Molecular Weights. Figure 1 plots the number-average molecular weights measured by gel permeation chromatography using a three-angle light scattering detector (GPC_{LS}) as a function of the GPC_{PSt}-determined molecular weights measured in CH_2Cl_2, THF, and $CHCl_3$ for all of the architectures shown in Scheme 1, including the data reported previously in THF for the linear[2] polymers with −H/−Br end groups and the comb[3] polymers; the molecular weight data are summarized in Tables S1−S3 of the Supporting Information. Table 1 lists the slope (m) and intercept (b) of each line according to $M_{n,LS} \times 10^{-3} = m(M_{n,GPC} \times 10^{-3}) + b$; the slope and intercept would presumably equal 1.0 and 0.0, respectively, if the polymers had the same hydrodynamic volume as polystyrene. Figure 1 and Table 1 demonstrate that the slopes of the two linear polymers are closest to one in CH_2Cl_2 and are higher but nearly identical in THF and $CHCl_3$, with similar deviations from the origin in all three solvents. The inaccuracies of the GPC_{PSt} molecular weights of the three-arm star polymers are higher than those of the linear polymers, and the comb polymers have the highest error in all three solvents, with the deviations being greatest in $CHCl_3$. Since branched polymers have more compact structures than the analogous linear polymers,[14] the increasing error in the GPC_{PSt}-determined molecular weights is consistent with the structures drawn in Scheme 1, i.e., with the extent of branching increasing from the "linear" to the "three-arm star" to the "comb polymers". The variation in the deviations of the GPC_{PSt} molecular weights from the GPC_{LS} molecular weights with solvent demonstrates that the differences in the hydrodynamic volumes of polystyrene and poly[11-(4′-cyanophenyl-4″-phenoxy)-undecyl acrylate] are greater in $CHCl_3$ than in THF, which are greater than in CH_2Cl_2. Figure 1 and Table 1 also include the GPC_{LS}- and GPC_{PSt}-determined molecular weights of the polymer synthesized from a conventional radical polymerization and its fractions. The errors in the GPC_{PSt}-determined molecular weights of these polymers do not correspond to those of the linear polymers and are instead closest to those of the comb polymers.

Although we did not have enough of all samples to measure their molecular weights in all three solvents, many of the data in Figure 1 do involve identical samples. (See identical sample numbers in Tables S1−S3 of the Supporting Information, which are summarized in Table 2.) The measured molecular weights tend to be similar in the three solvents, albeit slightly higher in THF and $CHCl_3$ than in CH_2Cl_2. This indicates that CH_2Cl_2 may be a better solvent than THF and $CHCl_3$ for these polymers and/or that the polymers may aggregate in the latter two solvents.

Size and Shape in Solution. If the structures drawn in Scheme 1 are correct, their solution properties should vary according to the more branched structures having more compact shapes.[14] We have therefore determined the root-mean-square radius of gyration ($\langle R_g^2\rangle^{1/2}$) and scaling coefficient relating R_g to molecular weight ($R_g = KM^\nu$) for the three architectures shown and for the polymer prepared by a conventional radical polymerization, as well as the contraction factors ($g = \langle R_g^2\rangle_{br}/\langle R_g^2\rangle_{lin}$) of the branched structures relative to the linear polymers. These values must be compared at identical molecular weight, preferably using monodisperse polymers. Since GPC effectively fractionates polymers according to differences in hydrodynamic volume, with each elution slice (V_i) corresponding to a single size polymer or a fraction of narrow polydispersity, the solution behavior of a broad range of molecular weight polymers can be studied using a single GPC chromatogram,[14,15,18] especially if that chromatogram involves a sample with a very broad molecular weight distribution.[19] This technique of using a chromatogram corresponding to a sample with a broad polydispersity, rather than multiple chromatograms corresponding to monodisperse samples, also minimizes the amount of data taken from the molecular weight extremities near the baseline where the scattering error is greatest. We therefore attempted to blend a range of molecular weights of the linear (−H/−Br end groups), three-arm star, and comb polymers synthesized by ATRP into polydisperse, monomodal, Gaussian-like blends of each architecture and studied their solution behavior using a somewhat more powerful light scattering detector with

Table 1. Linear Equations [$M_{n,LS} \times 10^{-3} = m(M_{n,GPC} \times 10^{-3}) + b$] Corresponding to the Data in Figure 1 Relating the Molecular Weights of Poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate] Determined by Light Scattering as a Function Those Determined by Gel Permeation Chromatography Relative to Linear Polystyrene in CH_2Cl_2, THF, and $CHCl_3$

architecture	slope, m	intercept, b	linear correlation coeff, r
CH_2Cl_2			
linear, (−CH(CH_3)CO_2CH_3/−Br end groups)	0.910	+3.40	0.990
linear, (−H/−Br end groups)	0.789	−0.939	0.997
three-arm star	1.20	−2.51	0.927
comb	1.50	+5.89	0.969
radical and fractions	1.40	−14.11	0.902
THF			
linear, (−CH(CH_3)CO_2CH_3/−Br end groups)	1.52	−2.27	0.986
linear, (−H/−Br end groups)	1.49	−4.10	0.989
three-arm star	1.82	−6.87	0.971
comb	2.40	−24.6	0.982
radical and fractions	2.09	−7.54	0.986
$CHCl_3$			
linear, (−CH(CH_3)CO_2CH_3/−Br end groups)	1.52	−1.11	0.994
linear, (−H/−Br end groups)	1.56	−1.82	1.00
three-arm star	1.88	−4.73	0.997
comb	6.42	−92.3	0.987
radical and fractions	4.00	−40.0	0.888

Table 2. Effect of Solvent on the "Absolute" Molecular Weights of Identical Samples of Poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate] Determined by Gel Permeation Chromatography Using a Three-Angle Light Scattering Detector[a]

	$M_n \times 10^{-3}$			$M_w \times 10^{-3}$		
sample[b]	CH_2Cl_2	THF	$CHCl_3$	CH_2Cl_2	THF	$CHCl_3$
Linear, −CH(CH_3)CO_2CH_3/−Br End Groups						
1	6.97	11.9	7.50	8.23	15.0	8.89
3	19.0	22.3	21.9	22.9	30.4	26.2
Linear, −H/−Br End Groups						
6	4.00	3.29	3.87	5.11	3.85	4.57
8	8.42	9.84	9.61	10.3	11.6	11.5
9	18.0	19.2	23.9	27.8	32.4	32.8
Three-Arm Star						
11	14.7	13.9	13.7	19.2	17.4	17.0
12	14.5	29.2	18.8	18.1	33.0	20.9
16	27.5	33.1	29.5	30.9	39.7	40.1
18	29.5	38.3	47.5	63.1	84.4	80.3
19	103	64.0	75.8	161	150	149
Comb						
20	30.0	26.0	31.2	35.8	35.4	38.8
21	53.4	44.4	64.9	80.6	73.3	77.9
22	68.8	68.3	100	103	110	110
23	84.5	73.1	120	128	125	130
Radical and Fractions						
24	15.7	29.1	25.2	50.2	87.3	60.8
25	10.1	13.3	14.3	23.5	20.4	37.4
26	20.6	30.5	28.9	45.8	64.8	50.9
27	53.7	86.5	51.0	93.9	144	108
28	15.5	25.2	27.4	57.0	81.8	62.5

[a] Number-average molecular weight (M_n) and weight-average molecular weight (M_w) determined at 35 °C using a light scattering detector with a Ga−As laser set at 690 nm. [b] Corresponds to sample numbers in Tables S1−S3 of the Supporting Information.

Table 3. Effect of Solvent on the Average Molecular Weights of the Blends of Poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate] Measured by Gel Permeation Chromatography Using an 18-Angle Light Scattering Detector[a]

blend	solvent	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	PDI
linear	CH_2Cl_2	10.2	19.2	1.88
	THF	12.0	26.0	2.16
	$CHCl_3$	9.56	19.7	2.06
	calculated[b]	10.9		
3-arm star	CH_2Cl_2	25.6	36.5	1.43
	THF	28.0	39.8	1.42
	$CHCl_3$	26.1	38.3	1.47
	calculated[b]	28.2		
comb	CH_2Cl_2	56.0	94.6	1.69
	THF	60.7	106	1.75
	$CHCl_3$	67.2	105	1.56
	calculated[b]	68.2		
radical	CH_2Cl_2	15.7	50.2	3.20
	THF	18.6	50.8	2.73
	$CHCl_3$	18.2	54.3	2.99

[a] 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_{LS}) using an 18-angle light scattering detector with a Ga−As laser set at 690 nm using dn/dc = 0.176 mL/g in CH_2Cl_2, dn/dc = 0.180 mL/g in THF, and dn/dc = 0.146 mL/g in $CHCl_3$. [b] Calculated using the absolute molecular weight of each component in CH_2Cl_2, as listed in Table S4.

18 angles. The compositions of the polydisperse blends are listed in Table S4 of the Supporting Information, and their GPC_{LS} molecular weights determined in CH_2Cl_2, THF and $CHCl_3$ are summarized in Table 3. The original polymer prepared by conventional radical polymerization had a broad polydispersity as synthesized and was used directly.

Figures 2−5 show the GPC chromatograms of the three architectural blends and the polymer prepared by the conventional radical polymerization, using concentrations of approximately 0.5 g/L. The chromatograms from the differential RI and light scattering detectors are corrected for the interdetector delay; the apparent shift in the light scattering chromatograms to lower elution volumes relative to the RI chromatograms corresponds to the polydispersity of the samples. The shapes of the chromatograms may be slightly different because the RI detector response (∝ concentration, c_i) is not sensitive to molar mass (M_i), in contrast to that of the light scattering detector (∝ c_iM_i).

The RI chromatogram of the linear blend in CH_2Cl_2 (Figure 2) demonstrates that although we successfully generated a polydisperse blend, its distribution is slightly bimodal. The light scattering chromatograms are similar, although a slight amount of a high molecular weight fraction is also detectable, due to the greater sensitivity of the light scattering detector to molar mass, at low elution volume. This higher molecular weight fraction is presumably due to aggregation via intermolecular mesogen−mesogen interactions, as observed in

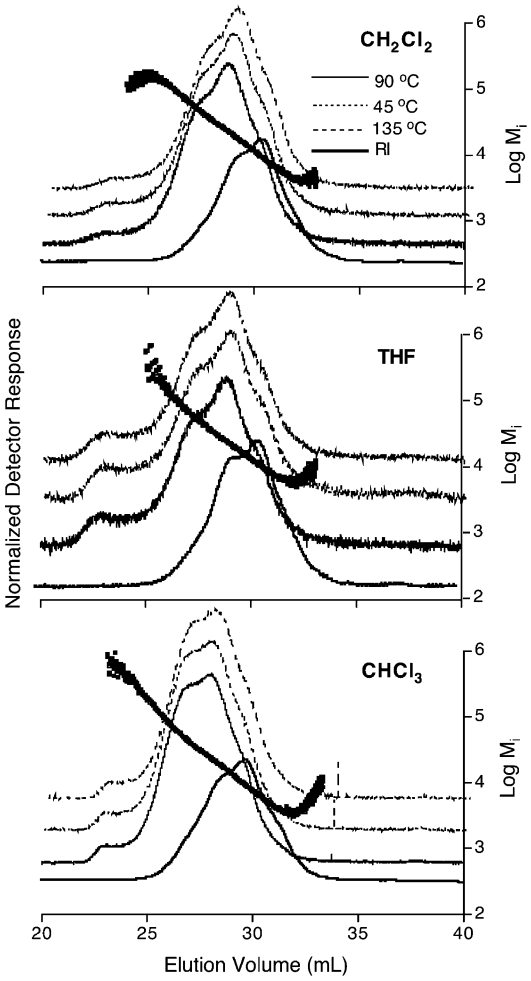


Figure 2. Gel permeation chromatography (GPC) refractive index and three of the 18 light scattering detector responses and log M_i calibration curves (■) of the blends of the linear (−H/−Br end groups) poly[11-(4′-cyanophenyl-4″-phenoxy)-undecyl acrylate]s in CH_2Cl_2, THF, and $CHCl_3$.

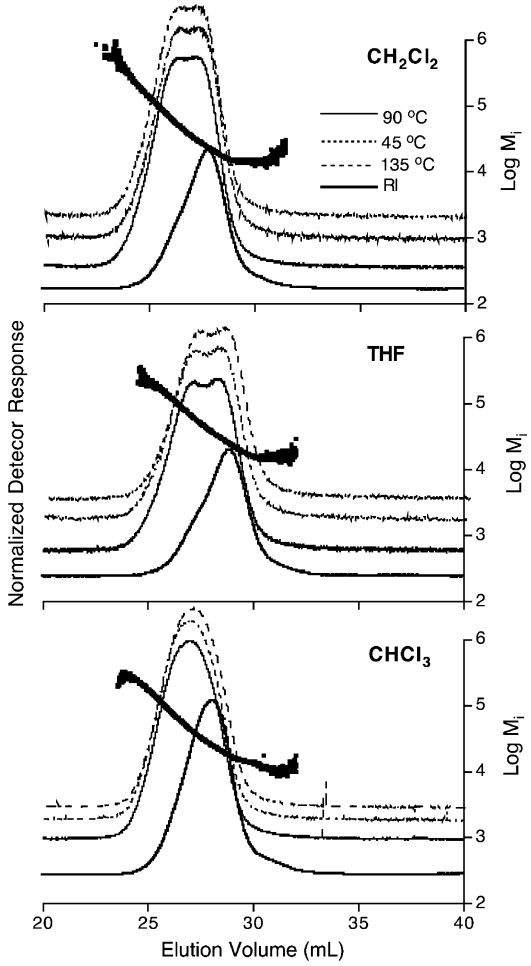


Figure 3. Gel permeation chromatography (GPC) refractive index and three of the 18 light scattering detector responses and log M_i calibration curves (■) of the blends of the three-arm star poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s in CH_2Cl_2, THF, and $CHCl_3$.

previous[5−12] solution studies of SCLCPs. Aggregation is even more prominent in the light scattering chromatograms of the linear polymer in THF ($\epsilon = 7.52$ at 20 °C) and $CHCl_3$ ($\epsilon = 4.81$ at 20 °C), which are less polar solvents than CH_2Cl_2 ($\epsilon = 8.93$ at 20 °C). In addition, the shapes of the main peak are shifted more to the high molecular weight side in $CHCl_3$ than in CH_2Cl_2 and THF in both the RI and light scattering chromatograms, which may also be indicative of aggregation, but to a lesser extent than that which elutes separately from the main peak. Therefore, Figure 2 demonstrates that CH_2Cl_2 is the best of the three solvents for poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate], which tends to aggregate more extensively in THF and $CHCl_3$; nevertheless, this level of aggregation is not high enough to significantly influence the average molecular weights measured (Table 3). Similarly, poly-[(4′-methoxyphenyl-4″-phenoxy)oligooxyethylene methacrylate]s[6] with zero or one oxyethylene units in the spacer aggregate in THF and $CHCl_3$ at the concentrations used for GPC measurements (∼0.5 g/L), whereas poly[4′-(4″-*n*-dodecyloxyphenoxycarbonyl)phenoxy methacrylate][10] aggregates in $CHCl_3$ only at concentrations greater than 200 g/L. Poly{6-[4′-(4″-methoxyphenoxycarbonyl)phenoxy])hexyl methacrylate} tends to aggregate more in $CHCl_3$[8] than in THF.[7,8,11]

As shown by the RI chromatogram in CH_2Cl_2 in Figure 3, we were fairly successful at preparing a Gaussian-like blend of the three-arm star polymers, although the light scattering peak shapes are slightly bimodal. In contrast to the linear polymers, there is no evidence for aggregation at low elution volume in any of the solvents, although the shapes of the light scattering chromatograms are shifted more to the high molecular weight side in THF than in CH_2Cl_2, and the light scattering chromatograms are actually monomodal in $CHCl_3$ due to an even greater detector response on the high molecular weight side. Therefore, the three-arm star polymers have less tendency than the linear polymers to aggregate in any of the solvents, although the peak shapes are shifted to the higher molecular weight side in THF, and especially $CHCl_3$, compared to those in CH_2Cl_2.

The molecular weight distribution of the comb polymer blend is also Gaussian-like, as reflected in its RI chromatograms in all three solvents (Figure 4). There is essentially no evidence in the chromatograms for aggregation of the comb polymers, which have an average of five branches per chain,[3,20] by scattering at low elution volume or by a change in the light scattering peak shapes with changing solvent. The decreasing tendency to aggregate in solution, which would involve intermolecular mesogen−mesogen interactions, with

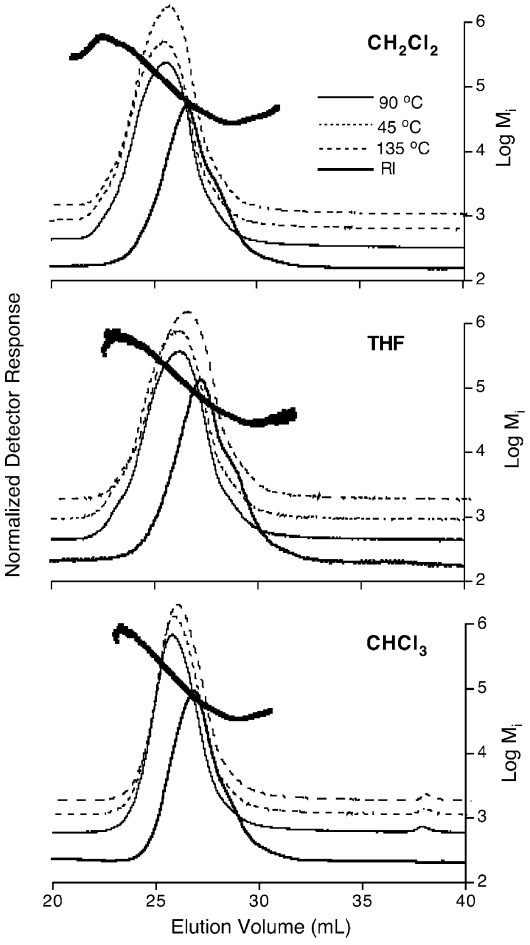


Figure 4. Gel permeation chromatography (GPC) refractive index and three of the 18 light scattering detector responses and log M_i calibration curves (■) of the blends of the comb poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s in CH_2Cl_2, THF, and $CHCl_3$.

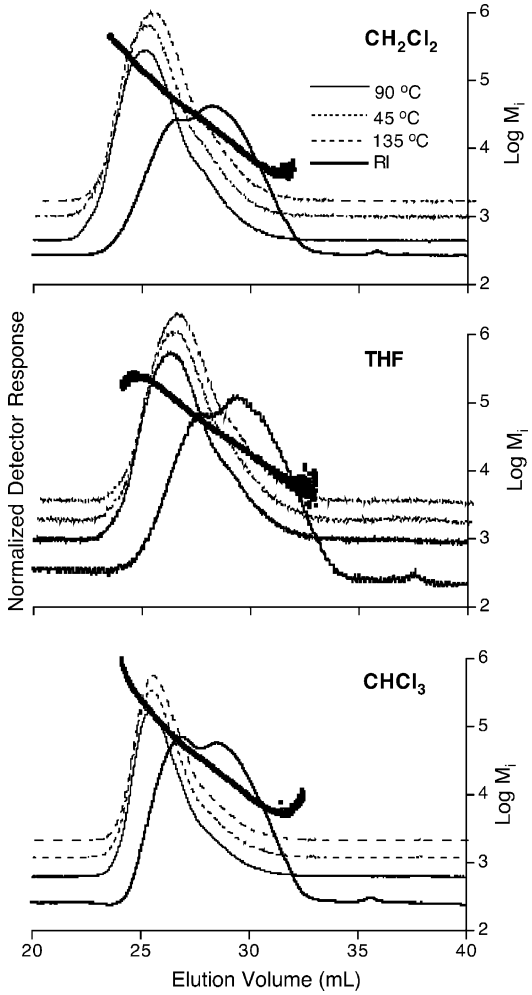


Figure 5. Gel permeation chromatography (GPC) refractive index and three of the 18 light scattering detector responses and log M_i calibration curves (■) of the poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate] synthesized by conventional radical polymerization in CH_2Cl_2, THF, and $CHCl_3$.

increasing branching density is consistent with the structures drawn in Scheme 1.

The corresponding chromatograms of the polymer prepared by conventional radical polymerization are shown in Figure 5. The RI chromatogram in CH_2Cl_2 demonstrates that this polymer has a bimodal molecular weight distribution, as also observed by GPC with a UV detector. Comparison of the RI and light scattering chromatograms in each solvent and of the RI chromatograms in the three different solvents demonstrates that its chromatography behavior is most similar to that of the three-arm star polymers prepared by ATRP; i.e., there is no evidence of aggregates eluting separately at low volume, although the peak shapes are shifted to the higher molecular weight side in both the light scattering and RI chromatograms in $CHCl_3$. Nevertheless, Table 3 demonstrates that, with the exception of M_w of the linear polymers, the solvent has little influence on the average molecular weights measured for any of the polymers and that the measured M_n values are close to those calculated using the composition and M_n values of each component determined in CH_2Cl_2 (Table S4).

Figures 2−5 also include the calibration curves corresponding to the logarithmic molecular weight of the polymer at each elution volume as calculated by extrapolation of the 18 light scattering responses to zero angle. The curves are fairly linear, with greater noise at the high molecular weight extremities due to the low concentration and therefore low light scattering responses and at the low molecular weight extremities due to the low light scattering responses resulting from both the low concentration and low molar mass.

Using the chromatograms in Figures 2−5 between the two molecular weight extremities at which the calibration curves are most scattered and/or deviate significantly from linearity,[21] the root-mean-square radii of gyration were measured at elution slices of approximately every 8 μL from the angular dependence of the scattered light, assuming that the concentration at each elution slice is negligible. Although this includes lower molecular weights that are close to the limit for calculating $\langle R_g^2\rangle^{1/2}$ because the angular dependence is low, the error seems to be relatively small. For example, Figure 6 shows the Debye plots and corresponding calculated $\langle R_g^2\rangle^{1/2}$ values taken from the three different elution slices marked on the accompanying GPC_{LS} trace of the comb polymer blend in CH_2Cl_2. Even in the lower molecular weight range, there is only a 5% uncertainty in the calculated radius, which decreases to 1% and 2% from the middle and higher molecular weight slices, respectively. The radius of 7.5 nm corresponding to the low molecular weight slice is at the lower limit that can be accurately measured at 690 nm with this system.[18]

Since aggregation of the linear polymers is barely detectable in CH_2Cl_2, with no evidence for aggregation

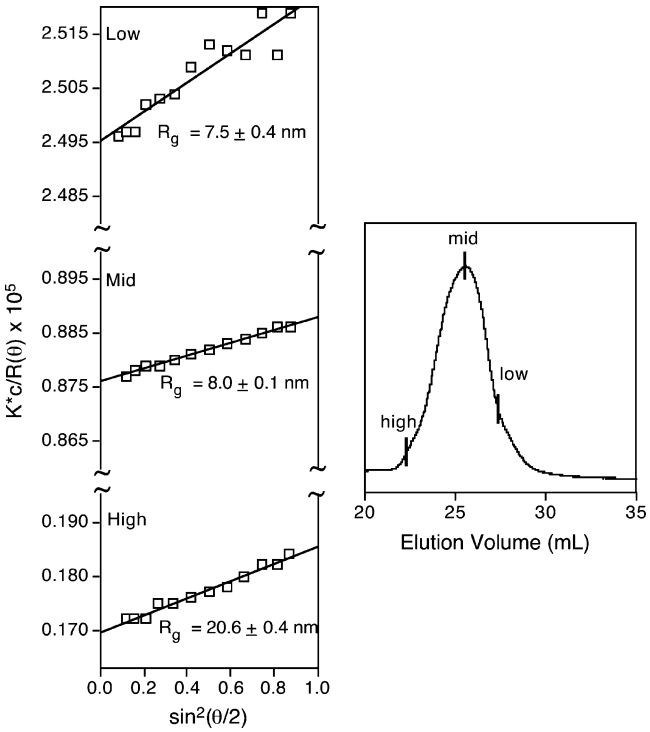


Figure 6. Debye plots of the scattering intensity and the calculated root-mean-square radii of gyration (R_g) from the three elution slices designated on the accompanying 90° GPC_{LS} chromatogram of the blend of the comb ($M_n = 5.60 \times 10^4$, PDI = 1.69) poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s in CH_2Cl_2.

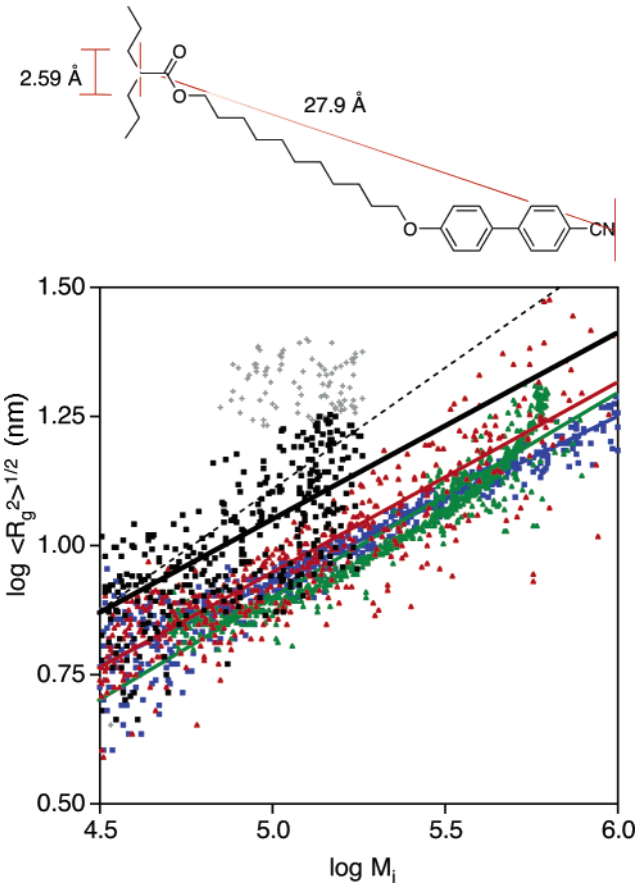


Figure 7. Log−log plots of the root-mean-square radii of gyration ($\langle R_g^2 \rangle^{1/2}$) of the linear (black, −H/−Br end groups, $y = 0.47x - 1.3$ using all of the data or $y = 0.36x - 0.76$ if the data represented by + are eliminated, least-squares fit), three-arm star (red, $y = 0.37x - 0.90$, least-squares fit), and comb (green, $y = 0.39x - 1.1$, least-squares fit) poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s prepared by ATRP and the corresponding polymer prepared by conventional radical polymerization (blue, $y = 0.32x - 0.68$, least-squares fit) as a function of molecular weight in CH_2Cl_2 using the GPC_{LS} chromatograms shown in Figures 2−5.

of either the three-arm star or comb polymers, Figure 7 compares the log−log plots of the root-mean-square radii of gyration of the polymers in CH_2Cl_2 over the molecular weight range that is ≥20K−30K Da and covered by the GPC chromatograms shown in Figures 2−5.[21] The values are all below the upper size limit of approximately 50 nm where the scattering function of rodlike structures and aggregates require terms that are nonlinear in $\sin^2(\theta/2)$ (and are not included in eq 1) and would necessitate extrapolation of only the lower scattering angles. Although the data are scattered, the trends are clear. The three-arm star polymers occupy less volume than the linear polymers, with a lower R_g at any given molecular weight, and the comb polymers are smaller than the linear and three-arm star polymers at similar molecular weights. This confirms that the comb polymers are more branched. The polymer prepared by conventional radical polymerization is similar in size to the three-arm star polymers at lower molecular weights and the comb polymers at higher molecular weights, indicating that the higher molecular weight fractions are more branched.

However, the data in Figure 7 for the linear polymer blend seem to have some anomalous points at the highest molecular weights, which indicates that we did not eliminate all of the data corresponding to aggregated species. The slope of these log−log plots corresponds to the scaling coefficient, ν, in the relationship between molecular weight and radius of gyration, $R_g = KM^{\nu}$. The scaling coefficients of the three-arm star polymers (ν = 0.37), comb polymers (ν = 0.39), and the polymer prepared by conventional radical polymerization (ν = 0.32) are nearly identical, whereas that of the linear polymer based on all of the data is $\nu = 0.47$. With the exception of branched polymers based on wormlike chains,[22] the scaling coefficient should be identical for linear and branched polymers based on the same chemical structure, provided the arms are sufficiently long;[14,23−25] we therefore eliminated the apparently anomalous data points from the linear polymer blend (denoted by + in Figure 7) until the slope of its log−log plot corresponded to the mean of those of the three other architectures ($\nu = 0.36$). This value of $\nu = 0.36$ is smaller than the lower limit of $\nu = 0.50$ for a random coil in a Θ solvent (Gaussian limit)[26] and close to the hard-sphere limit of $\nu = 0.33$. This indicates that the average segment density of these SCLCPs is greater than that for a Gaussian chain and approaches that for a bulk polymer, presumably due to both the strong intramolecular mesogen−mesogen interactions and the presence of a long mesogenic side chain in every repeat unit, causing the polymer to behave as a system that is more branched than the nominal branching drawn in Scheme 1; as shown in Figure 7, the length of the mesogenic side chain is more than 10 times greater than the distance between repeat units. As mentioned in the Introduction, values even lower than the hard-sphere limit have been observed experimentally.[16] Zimm and Stockmayer have also predicted that a Cayley tree will have a scaling exponent of $\nu = 0.25$ in the limit of large

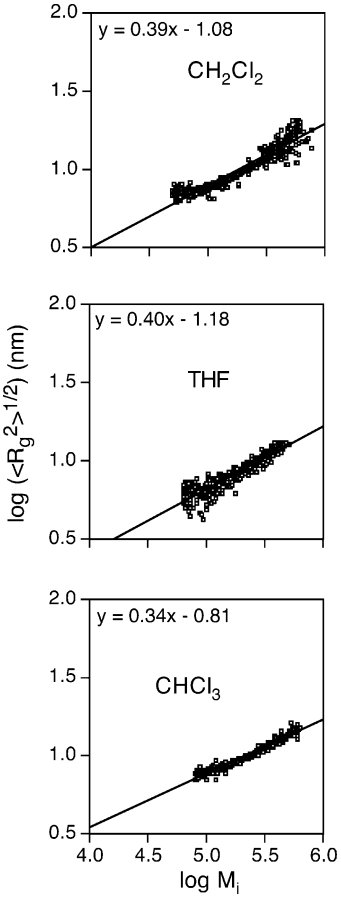


Figure 8. Log−log plots and least-squares fits of the root-mean-square radii of gyration ($\langle R_g^2\rangle^{1/2}$) of the comb poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s prepared by ATRP as a function of molecular weight in CH_2Cl_2, THF, and $CHCl_3$ using the GPC_{LS} chromatograms shown in Figure 5.

molar mass,[27] and de Gennes and Hervet predicted that dendritic polymers will have a scaling exponent of $\nu = 0.20$.[17]

Since the comb polymers did not aggregate in any of the three solvents, Figure 8 compares the log−log plots of the root-mean-square radius of gyration as a function of molecular weight of the comb polymers in CH_2Cl_2, THF, and $CHCl_3$; the plots again do not contain data at the molecular weight extremities of the chromatograms.[28] The scaling coefficients are nearly identical in CH_2Cl_2 ($\nu = 0.39$) and THF ($\nu = 0.40$) and demonstrate that the comb polymers have a spherical shape in both solvents. The scaling coefficient is slightly smaller in $CHCl_3$ ($\nu = 0.34$), evidently because $CHCl_3$ is not as good of a solvent for poly[11-(4′-cyanophenyl-4″-phenoxy)-undecyl acrylate].

The contraction factor, $g = \langle R_g^2\rangle_{br}/\langle R_g^2\rangle_{lin}$ at identical molecular weight,[27] is a measure of the compactness of a branched polymer relative to the corresponding linear polymer. The contraction factors, g, as measured by the ratio of the corresponding lines in Figure 7, are plotted in Figure 9 as a function of molecular weight for each of the branched topologies in CH_2Cl_2. Since we are assuming that the linear polymers have the same scaling coefficient as the branched polymers (Figure 7), g is essentially constant at higher molecular weights where the effect of the high core segment density is negligible; we will use the plateau values at $M_i = 10^6$ for comparison. The contraction factor of the comb

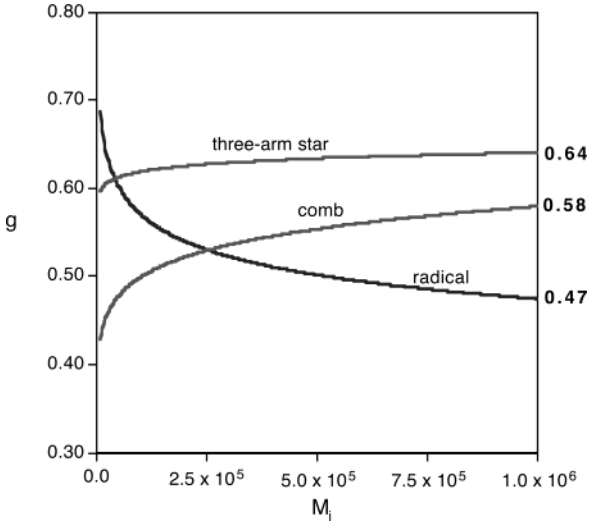


Figure 9. Contraction factors, $g = \langle R_g^2\rangle_{br}/\langle R_g^2\rangle_{lin}$ at same molecular weight, of the three-arm star and comb poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s prepared by ATRP and the corresponding polymer prepared by conventional radical polymerization as a function of molecular weight in CH_2Cl_2 using the lines in Figure 7.

polymer is smaller than that of the three-arm star polymer, which is consistent with the comb polymers being more branched. The contraction factor of the polymer prepared by a conventional radical polymerization is even lower than that of the comb polymers, which again confirms that its structure does not correspond to a linear polymer.

These SCLCPs may contract simply because of the topological constraints imposed by branching and/or because of an enhancement of their relatively strong intramolecular mesogen−mesogen interactions ($\nu \sim 0.36$ in CH_2Cl_2) facilitated by the branched topologies. Theories relating $g = \langle R_g^2\rangle_{br}/\langle R_g^2\rangle_{lin}$ to the number of branches in the branched polymer are based on radii of gyration under theta conditions ($\nu = 0.50$)[14,27] and therefore predict that contraction is due exclusively to topological constraints, with the intramolecular interactions being constant upon going from linear to branched structures. Nevertheless, g is a dimensionless ratio that varies little with solvent quality, at least when comparing values measured in a good solvent ($\nu = 0.588$) to those measured under theta conditions ($\nu = 0.50$),[29] presumably because those branched and linear polymers have the same expansion coefficients. We will therefore compare the g values measured for these SCLCPs to those predicted by theory under theta conditions and assume that the theories are also valid when $\nu \sim 0.36$. For the three-arm star polymers, the value of $g = 0.64$ is intermediate between the values calculated for a star polymer at the Gaussian limit with three monodisperse arms ($g = 0.78$) and three polydisperse arms ($g = 0.56$).[30] This may indicate that the arm lengths are fairly uniform, but not mondisperse, and/or that the arm lengths are fairly uniform, but the polymer behaves as a system that is more branched than the nominal three branches drawn in Scheme 1 due to the long mesogenic side chains in each repeat unit. The value of $g = 0.58$ for the comb polymers, which have five grafts according to NMR combined with molecular weight analyses,[3,20] is lower than that calculated for a randomly branched material with five trifunctional branch points ($g = 0.70$),[31] indicating that it also behaves in solution as a

structure that is more branched than the nominal five/six[20] branches drawn in Scheme 1.

Conclusions

The solution properties of the poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s synthesized by ATRP are consistent with the extent of branching increasing from "linear" to "three-arm star" to "comb" topologies according to their synthetic design. The error in the GPC_{PSt}-determined molecular weights increase with increasing branching: linear < three-arm star < comb. The tendency to aggregate in solution decreases with increasing branching, as does the root-mean-square radius of gyration in CH_2Cl_2 (linear > three-arm star > comb). The scaling coefficients, ν, in the relationship $R_g = KM^{\nu}$ are smaller in CH_2Cl_2 than the lower limit of $\nu = 0.50$ for a random coil in a Θ solvent, presumably due to the long mesogenic side chains and strong intramolecular mesogen−mesogen interactions increasing the average segment density. The value of the contraction factor, $g = \langle R_g^2\rangle_{br}/\langle R_g^2\rangle_{lin}$, of the comb polymer is lower than that of the three-arm star polymer in CH_2Cl_2.

The solution behavior of the poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate] prepared by conventional radical polymerization is not consistent with it being a linear polymer. The errors in the GPC_{PSt}-determined molecular weights of its fractions are between those of the three-arm star and comb polymers and vary with solvent similar to those of the comb polymers. Its aggregation behavior is most similar to that of the three-arm star polymers. Its size ($\langle R_g^2\rangle^{1/2}$) and shape are similar to both branched polymers in CH_2Cl_2. Its low contraction factor ($g = 0.47$) confirms that it is more branched than the linear polymer prepared by ATRP.

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Supporting Information Available: Tabulated molecular weight values corresponding to Figure 1 and of the components of the blends. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) According to ^{1}H NMR analysis combined with the absolute molecular weight data,[3] the comb polymers contain five grafts along the backbone separated by an average of five repeat units, with a sixth branch resulting from growth at the chain end upon grafting; the six "branches" vary in length from approximately four to 34 repeat units.
(21) This excludes the region where a small amount of aggregates elute separately from the main peak of the linear polymers. The log M_i cutoff limits in CH_2Cl_2 were 4.25−5.26 (18K−182K g/moL) for the linear polymers, 4.50−6.40 (32K−2512K g/moL) for the three-arm star polymers, 4.70−5.89 (50K−776K g/moL) for the comb polymers, and 4.50−6.00 (32K−1000K g/moL) for the polymer prepared by conventional radical polymerization.
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(30) For star polymers with f Gaussian arms, $g = (3f - 2)/f^2$ if the arm lengths are monodisperse[27] and $g = 3f/(f+1)^2$ if the arm lengths are polydisperse.[14]
(31) For a randomly branched material with trifunctional branch points, $g_3 = [(1 + n/7)^{0.5} + 4n/9\pi]^{-0.5}$, where n = the number of branching units.[27]

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