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Measurement of Chain Transfer Constants to Polymer Using Oligomers and Model Compounds: Chain Transfer to Poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate] in Radical Polymerization

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ABSTRACT: The chain transfer constant to polymer (C_P) for poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate] was measured directly by the Mayo method by following the decrease in molecular weight at low monomer conversion by gel permeation chromatography of poly(methyl acrylate) generated in the presence of increasing amounts of 11-(4′-cyanophenyl-4″-phenoxy)undecyl propionate ($C_P = (6.62 \pm 0.476) \times 10^{-3}$) and 11-(4′-cyanophenyl-4″-phenoxy)undecyl isobutyrate ($C_P = (4.27 \pm 0.858) \times 10^{-3}$) as model compounds that mimic one repeat unit of the polymer and oligo[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate] with nine repeat units ($C_P = (5.54 \pm 0.608) \times 10^{-3}$) synthesized by atom transfer radical polymerization. The mean chain transfer constant, $C_P = 5.48 \times 10^{-3}$, was used to calculate the extent of branching (ρ) in poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate] ($DP_n = 37$) synthesized by conventional radical polymerization: $\rho = 0.0042-0.020$ at 72−99% conversion, which corresponds to one branch per 6.4−1.4 chains, respectively, of 37 repeat units.

Introduction

Controlled radical polymerizations minimize termination ($R_t = k_t[M^\bullet]^2$ in which k_t is the rate constant of termination) relative to propagation ($R_p = k_p[M^\bullet][M]$ in which k_p is the rate constant of propagation and [M] is the monomer concentration) by maintaining a low concentration of propagating radicals ($[M^\bullet]$) in dynamic equilibrium with a high concentration of dormant covalent chains.[1] However, chain transfer is not affected since both propagation and chain transfer ($R_{trX} = k_{trX}[M^\bullet][X]$ in which [X] is the concentration of chain transfer agent) are first order in propagating radicals. This may be especially troublesome in the synthesis of side-chain liquid crystalline polymers (SCLCPs), which are highly functionalized polymers with a number of sites capable of chain transfer; in addition to the aliphatic spacers and aromatic rings of the mesogen, the mesogens often contain multiple bonds and are typically functionalized with alkoxy, halo, cyano, or nitro groups.[2] Chain transfer to polymer will produce a mixture of branched and linear architectures in controlled radical polymerizations if the chain transfer constant to polymer ($C_P = k_{trP}/k_P$ in which k_{trP} is the rate constant of chain transfer to polymer) is high. For example, branches have been detected in polyacrylates prepared by both atom transfer[3] and nitroxide-mediated[4] radical polymerizations of *n*-butyl acrylate and nitroxide-mediated radical polymerization of 2-hydroxyethyl acrylate.[5]

Chain transfer to polymer becomes more prevalent as the concentration of polymeric repeat units increases with increasing monomer conversion. In conventional radical polymerizations, the polymer yield rather than molecular weight increases with reaction time, with high molecular weight polymer produced even at low conversion.[6] Therefore, although the rate of chain transfer to polymer is low in the early stages of the polymerization due to the low polymer concentration, the polymers produced during this stage will be available for chain transfer for longer periods of time than those produced at the end of the polymerization and will therefore experience greater branching,[7] which means that the branching density per chain varies with monomer conversion. In addition, gelation can occur in systems that undergo both chain transfer to polymer and termination by combination.[8,9] We[10−12] have provided evidence that the limited miscibility of a mixture of branched[13] structures broadens the phase transitions of poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate] prepared by conventional radical polymerization. Nevertheless, there is no quantitative information in the SCLCP literature on chain transfer constants to polymer, which could be used to correlate the monomer conversion (p) to the extent of branching (ρ) according to Flory's equation (eq 1).[14]

$$\rho = -C_P\left[1 + \left(\frac{1}{p}\right)\ln(1-p)\right] \tag{1}$$

Chain transfer constants have recently been measured by the chain length distribution procedure.[15] However, chain transfer constants to monomer ($C_M = k_{trM}/k_p$ in which k_{trM} is the rate constant of chain transfer to monomer), initiator ($C_I = k_{trI}/k_p$ in which k_{trI} is the rate constant of chain transfer to initiator), solvent, or added chain transfer agent ($C_X = k_{trX}/k_p$ in which k_{trX} is the rate constant of chain transfer to solvent or chain transfer agent) are more frequently measured,[16] with similar results,[17] by following the decrease in molecular weight (DP_n or $DP_w/2$ in which DP_n and DP_w are the number- and weight-average degrees of polymerization, respectively) as a function of the rate of polymerization, ratio of the concentrations of initiator ([I]) and monomer, or ratio of the concentrations of chain transfer agent and monomer, respectively,

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according to the Mayo equation (eq 2,

$$\frac{1}{\mathrm{DP_n}} = \frac{k_t R_p}{b k_p{}^2 [\mathrm{M}]^2} + C_\mathrm{M} + C_\mathrm{I}\frac{[\mathrm{I}]}{[\mathrm{M}]} + C_\mathrm{X}\frac{[\mathrm{X}]}{[\mathrm{M}]} \qquad (2)$$

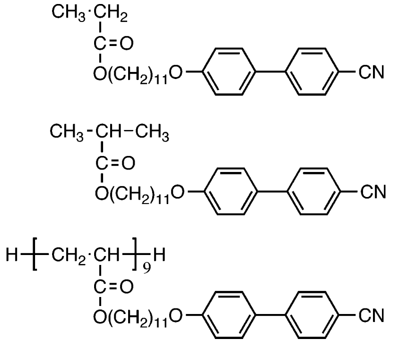
in which b is the average number of initiating primary radicals incorporated into the polymer chains due to termination by combination ($b = 2$) and disproportionation ($b = 1$)) at low monomer conversion (<5−10%).[18] Unfortunately, chain transfer constants to polymer are difficult to measure by simply adding a term for polymer to the Mayo equation and following the change in molecular weight in the presence of added polymer, since the measured molecular weight is only meaningful if the resulting grafted polymer (or its contribution to, for example, the intrinsic viscosity[19]) can be separated from the polymer generated in its presence. For example, the chain transfer constants of propagating polystyrene (PSt) to natural rubber[20] and to poly(methyl methacrylate)[21] were measured by extracting or fractionally precipitating, respectively, PSt from the graft copolymerization mixtures and measuring its decrease in $\mathrm{DP_n}$ as a function of the concentration of added polymer (eq 3, in which $[1/\mathrm{DP_n}]_0$ is the inverse number-average degree of polymerization in the absence of the chain transfer agent).

$$\frac{1}{\mathrm{DP_n}} = \left[\frac{1}{\mathrm{DP_n}}\right]_0 + C_\mathrm{X}\frac{[\mathrm{X}]}{[\mathrm{M}]} \qquad (3)$$

Similarly, we should be able to measure the chain transfer constant to polymer by following the decrease in molecular weight by gel permeation chromatography (GPC) of a polymer generated in the presence of increasing amounts of added polymer if the two polymers are separated in the GPC chromatograms. Since conventional radical polymerization generates high molecular weight polymer at low monomer conversion, and chain transfer to the added polymer will produce a higher molecular weight graft (co)polymer, resolution of the two polymers by GPC will be most readily achieved starting with a low molecular weight polymer. Alternatively, since the chain transfer constants to polymer are per repeat unit of the polymer, rather than per polymer chain, one can estimate C_P using eq 3 and model compounds corresponding to one ($C_\mathrm{p} = C_\mathrm{X}$) or more repeat units of the polymer. For example, Lím and Wichterle[22] measured the chain transfer constants to methyl isobutyrate ($C_\mathrm{X} = 1.4 \times 10^{-4}$), dimethyl 2,4-dimethylglutarate ($C_\mathrm{X} = 4.5 \times 10^{-5}$), and trimethyl heptane-2,4,6-tricarboxylate ($C_\mathrm{X} = 5.4 \times 10^{-5}$) as model compounds of poly(methyl acrylate) (PMA). In their experiments, the chain transfer constant to the model unimer was greater than those of the model dimer and trimer, and they therefore assumed that the chain transfer constant to PMA is similar to that of the trimer, i.e., $C_\mathrm{P} = 5 \times 10^{-5}$, although this is an order of magnitude lower than accepted values of C_P for polyacrylates.[6,23]

This paper will compare the chain transfer constants to poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate] determined by the Mayo method by following triplicate measurements of the decrease in molecular weight of PMA in the presence of increasing amounts of 11-(4′-cyanophenyl-4″-phenoxy)undecyl propionate and 11-(4′-cyanophenyl-4″-phenoxy)undecyl isobutyrate as model compounds that mimic one repeat unit of the polymer and an oligomer of 11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate (Scheme 1); we are using radical polymerizations of methyl acrylate in order to provide both a nonfunctionalized monomer/polymer ($-\mathrm{CH_3}$ vs mesogenic side chain) and a constant reference propagating polyacrylate radical for comparison of the chain transfer constants to different SCLCPs.[24] The oligomer was prepared by atom transfer radical polymerization (ATRP[25]) of 11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate,[12] followed by reduction of the −Br end group to −H. Therefore, one end group of the oligomer is a primary hydrogen atom, and the other end group is a secondary hydrogen atom, both of which should be much less reactive than possible chain transfer sites either along the polymer backbone or within the mesogenic side chains;[26] in nonmesogenic polyacrylates, studies using ESR[27,28] and ^{13}C NMR[4,28,29] spectroscopies demonstrated that chain transfer to polymer occurs by inter- and/or intramolecular abstraction of a methine hydrogen atom alpha to the carbonyl group to generate a relatively stable tertiary radical. In addition to oligo[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate], we investigated the two model compounds in order to determine whether chain transfer occurs by abstraction of a tertiary hydrogen atom from the polymer backbone or by a reaction involving the mesogenic side chain; i.e., if chain transfer involves the polymer backbone, the chain transfer constant to 11-(4′-cyanophenyl-4″-phenoxy)undecyl propionate should be lower than the others since it would generate a less stable secondary radical. This chain transfer to polymer data will be used to quantify the amount of branching that occurs in the conventional free radical polymerization of 11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate.

Scheme 1. 11-(4′-Cyanophenyl-4″-phenoxy)undecyl Propionate and 11-(4′-Cyanophenyl-4″-phenoxy)undecyl Isobutyrate Model Compounds and Oligo[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate] Used To Determine the Chain Transfer Constant to Polymer in the Radical Polymerization of 11-(4′-Cyanophenyl-4″-phenoxy)undecyl Acrylate



Experimental Section

Materials. Cuprous bromide (Aldrich, 99.999%), 4,4′-dimethyl-2,2′-dipyridyl (Aldrich, 99%), isobutyryl chloride (Aldrich, 98%), propionyl chloride (Aldrich, 98%), pyrogallol (Aldrich, 98%), and tributyltin hydride (Lancaster, 97%) were used as received. 2,2′-Azobis(isobutyronitrile) (AIBN, Pfaltz and Bauer, 98%) was recrystallized from methanol below 40 °C and then stored at −20 °C. 11-(4′-Cyanophenyl-4″-phenoxy)undecanol,[10] 11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate,[10] and 11-(4′-cyanophenyl-4″-phenoxy)undecyl 2-bromopropionate[12] were prepared as described previously. Benzene was washed sequentially with $\mathrm{H_2SO_4}$ and water, stored over $\mathrm{CaCl_2}$, and then distilled from $\mathrm{CaH_2}$ under $\mathrm{N_2}$. Methyl acrylate

(Aldrich, 99%) was washed with aqueous Na_2CO_3, dried over $MgSO_4$, and then distilled under N_2. Triethylamine (Fisher, ≥98) was distilled from KOH under N_2. Reagent grade tetrahydrofuran (THF) was dried for synthetic purposes by distillation from purple sodium benzophenone ketyl under N_2. THF was distilled from $LiAlH_4$ for GPC. All other 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. Elemental analyses were performed on a Perkin-Elmer 2400 Series II CHNS/O analyzer. ^{1}H NMR spectra (δ, ppm) were recorded on either a Varian Gemini 300 (300 MHz) or a Varian Gemini 200 (200 MHz) spectrometer. ^{13}C NMR spectra (δ, ppm) were recorded on either a Varian Gemini 300 (75 MHz) or a Varian Gemini 200 (50 MHz) spectrometer. All spectra were recorded in $CDCl_3$, and the resonances were measured relative to residual solvent resonances and referenced to tetramethylsilane. Monomer conversions were determined from the GPC samples of the chain transfer experiments using the two model compounds by calculating the contribution of the overlapped polymer (3.81 ppm) and monomer (3.87 ppm) CH_3O_2C resonances using the integral per polymer proton from the vinyl resonances at 5.7−6.5 ppm and after subtracting the contribution from four THF protons using the integral per THF proton from the CH_2CH_2O THF resonance at 1.95 ppm. Matrix-assisted laser desorption time-of-flight mass spectrometry (MALDI-ToF MS) was performed by the laboratory of Professor Chrys Wesdemiotis in the Department of Chemistry at The University of Akron using a Bruker Daltonics Reflex III mass spectrometer equipped with a 337 nm nitrogen laser and a pulsed ion extraction source. Data were collected in the reflectron detection mode, and the ion source and reflector lens potentials were held at 20 and 22.5 keV, respectively. Aliquots of the matrix (dithranol = 1,8,9-anthracenetriol, Fluka, 99%; 20 mg/mL in THF), polymer (10 mg/mL in THF), and salt (silver trifluoroacetate, Aldrich, 98%; 10 mg/mL in THF) solutions were mixed in a 10:2:1 ratio, and 0.5 μL of the final mixture was applied to the stainless steel sample target for analysis.

Molecular weights relative to linear PSt (GPC_{PSt}) or PMA standards were determined by gel permeation chromatography from calibration curves of log M_n vs elution volume at 35 °C using THF at 1 mL/min, a set of 50 Å, 100 Å, 500 Å, 10^4 Å, and linear (50−10^4 Å) Styragel 5 μm columns, either a Waters 410 differential refractometer or a Waters 2414 refractive index detector for the chain transfer experiments, and a Waters 486 tunable UV/vis detector set at 275 nm for the mesogenic oligomer. The absolute molecular weight of the oligo[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate] was determined by gel permeation chromatography with a light scattering detector (GPC_{LS}) at 35 °C using THF 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 (45°, 90°, 135°) 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) using dn/dc = 0.180.[13] The molecular weight data were calculated using Astra 4.90.07 software (Wyatt Technology) and a Zimm fit according to the following equation

$$\frac{K^*c}{R(\theta)} = \frac{1}{M_w}\left[1 + \frac{16\pi^2 n_0^{\,2}}{3\lambda_0^{\,2}}\langle R_g^{\,2}\rangle \sin^2(\theta/2)\right] \qquad (4)$$

in which 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 (eq 5)

$$K^* = \frac{4\pi^2 n_0^{\,2}(\mathrm{d}n/\mathrm{d}c)^2}{N_A \lambda_0^{\,4}} \qquad (5)$$

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 4 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 ratio of toluene, and their responses were then normalized to that of the 90° detector using a solution of a narrow distribution PSt (M_n < 30 000) standard in THF. The sample was dissolved overnight and filtered through a 0.45 μm PTFE filter.

Synthesis of 11-(4′-Cyanophenyl-4″-phenoxy)undecyl Propionate. A solution of propionyl chloride (0.61 g, 6.6 mmol) in THF (20 mL) was added dropwise over 15 min to an ice-cooled solution of 11-(4′-cyanophenyl-4″-phenoxy)undecanol (2.0 g, 5.5 mmol; R_f = 0.67 silica/Et_2O) and NEt_3 (0.84 g, 8.3 mmol) in THF (80 mL). After 2 h at room temperature, thin-layer chromatography (TLC; 11-(4′-cyanophenyl-4″-phenoxy)-undecyl propionate R_f = 0.94 silica/Et_2O) demonstrated that the reaction was incomplete; NEt_3 (0.56 g, 5.5 mmol) and propionyl chloride (0.50 g, 5.4 mmol) were therefore added, and the reaction mixture was stirred at room temperature until the conversion was complete according to TLC (2.5 h). The reaction mixture was poured into ice water (500 mL), and the resulting white precipitate was collected on a fritted glass filter. The crude product was purified by flash chromatography on a column of silica gel (5 in.) topped with basic activated alumina (1 in.) using CH_2Cl_2 as the eluent. The solvent was removed by rotary evaporation, and the residue was recystallized from ethanol/toluene (5:1, 300 mL) to yield 2.1 g (89%) of 11-(4′-cyanophenyl-4″-phenoxy)undecyl propionate as a white solid. ^{1}H NMR: 1.14 (t, CH_3), 1.41 (m, $(CH_2)_7$), 1.62 (m, $CH_2CH_2O_2C$), 1.81 (m, CH_2CH_2OAr), 2.32 (q, CH_2CH_3), 4.01 (t, CH_2O_2C), 4.06 (t, CH_2OAr), 6.99 (d, 2 aromatic H *ortho* to OCH_2), 7.53 (d, 2 aromatic H *meta* to OCH_2), 7.67 (m, 4 aromatic H *ortho* and *meta* to CN). ^{13}C NMR: 9.41 (CH_3), 26.13 (CH_2CH_3), 27.86−29.76 ($[CH_2]_9$), 64.69 (CH_2O_2C), 68.38 (CH_2OAr), 110.26 (aromatic *C*−CN), 115.30 (aromatic C *para* to OCH_2), 119.36 (*C*N), 127.30 (aromatic C *meta* to CN), 128.54 (aromatic C *ortho* to CN), 131.47 (aromatic C *meta* to OCH_2), 132.79 (aromatic C *ortho* to OCH_2), 145.51 (aromatic C *para* to CN), 160.03 (aromatic *C*-OCH_2), 174.85 (*C*=O). Elemental Analysis: Calcd C 76.92, H 8.34, N 3.32; Found C 77.28, H 8.63, N 3.08.

Synthesis of 11-(4′-Cyanophenyl-4″-phenoxy)undecyl Isobutyrate. 11-(4′-Cyanophenyl-4″-phenoxy)undecyl isobutyrate (TLC R_f = 0.97 silica/Et_2O) was synthesized in 94% yield by the same procedure as above, using isobutyryl chloride instead of propionyl chloride. ^{1}H NMR: 1.16 (d, CH_3, 6 H), 1.42 (m, $(CH_2)_7$), 1.62 (m, $CH_2CH_2O_2C$), 1.81 (m, CH_2CH_2OAr), 2.54 (m, C*H*), 4.01 (t, CH_2O_2C), 4.06 (t, CH_2OAr), 6.99 (d, 2 aromatic H *ortho* to OCH_2), 7.53 (d, 2 aromatic H *meta* to OCH_2), 7.67 (m, 4 aromatic H *ortho* and *meta* to CN). ^{13}C NMR: 19.26 (CH_3, 2 C), 34.27 (*C*H), 27.86−29.76 ($[CH_2]_9$), 64.60 (CH_2O_2C), 68.37 (CH_2OAr), 110.24 (aromatic *C*−CN), 115.30 (aromatic C *para* to OCH_2), 119.34 (*C*N), 127.28 (2 aromatic C *meta* to CN), 128.54 (2 aromatic C *ortho* to CN), 131.44 (2 aromatic C *meta* to OCH_2), 132.78 (2 aromatic C *ortho* to OCH_2), 145.49 (aromatic C *para* to CN), 160.04 (aromatic *C*−OCH_2), 177.47 (*C*=O). Elemental Analysis: Calcd C 77.20, H 8.56, N 3.22; Found C 76.86, H 8.53, N 3.14.

Oligomerization of 11-(4′-Cyanophenyl-4″-phenoxy)-undecyl Acrylate by ATRP. A mixture of 11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate (1.6 g 3.8 mmol), 11-(4′-cyanophenyl-4″-phenoxy)undecyl 2-bromopropionate (0.33 g, 0.66 mmol), CuBr (0.10 g, 0.71 mmol), and 4,4′-dimethyl-2,2′-dipyridyl (0.35 g, 1.9 mmol) was degassed using five freeze−pump (30 min)−thaw cycles in a sealable polymerization tube. The tube was sealed under vacuum and stirred at 100 °C for 25 min. The polymer was precipitated in cold (−78 °C) methanol (50 mL) containing one drop of concentrated HCl. Copper and ligand were removed from the precipitate by flash chromatography using basic activated alumina as the stationary phase and THF as the eluent, and the monomer was removed by precipitating the polymer from THF (50 mL) into warm ethanol (200 mL), followed by cooling to −20 °C. The precipitate was collected and dried to yield 1.3 g (67%) of poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate] as a sticky white solid; GPC$_{PSt}$ $M_n = 4.3 \times 10^3$, PDI = 1.49.

Reduction of the Bromine End Groups of Poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl Acrylate]. A solution of oligo[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate] (1.1 g, 0.25 mmol), AIBN (2.1 mg, 13 μmol), and $HSnBu_3$ (92 mg, 0.31 mmol) in benzene (10 mL) was stirred at 60 °C for 1.25 h and then passed through a short column (1 in.) of basic activated alumina to yield 1.0 g (93%) of the polymer with −H/−H end groups as a white sticky solid after drying in vacuo. To isolate a lower molecular weight oligomer for the chain transfer studies, methanol was added dropwise to a solution of the polymer in THF (300 mL) until the solution became cloudy (78 mL of methanol). After 2 days, the solution was filtered to remove 0.12 g (12%) of a higher molecular weight fraction (GPC$_{PSt}$ $M_n = 9.8 \times 10^3$, PDI = 1.26), and the filtrate was concentrated in vacuo. The resulting solid was precipitated from THF (5 mL) into cold (−78 °C) methanol (50 mL) to yield 0.88 g (88%) of a lower molecular weight fraction (GPC$_{PSt}$ $M_n = 4.07 \times 10^3$, PDI = 1.24; GPC$_{LS}$ $M_n = 3.82 \times 10^3$, PDI = 1.31) as a sticky white solid. MALDI-Tof MS: $M_n = 2435$, PDI = 1.43; 97.4% reduced chain ends, 2.6% −Br chain ends observed as the −HBr elimination product.

Chain Transfer Studies. The chain transfer measurements were performed in triplicate. To ensure that each chain transfer plot had at least four data points, each chain transfer study involved the following six ratios of the concentrations of chain transfer agent and monomer: $[X]_0/[M]_0 = 0.0, 0.005, 0.01, 0.02, 0.035, 0.05$. All glassware were dried overnight at 150 °C and cooled in vacuo.

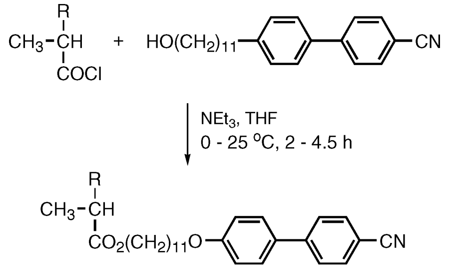
Monomer/Initiator Solution. Stock monomer solutions containing 1 mol % initiator were prepared immediately before each chain transfer experiment and were used to prepare the six polymerization solutions for a single study, each with a final concentration of 1 M monomer and 0.01 M initator. The stock solutions were 2 M in monomer and 0.02 M in initiator. For example, benzene was added 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.

Chain Transfer Agent. The chain transfer agents were measured from 0.1 M solutions. For example, benzene was added to 11-(4′-cyanophenyl-4″-phenoxy)undecyl propionate (0.41 g, 1.0 mmol) in a 10 mL volumetric flask to bring the total volume to 10 mL. The final concentrations of chain transfer agent used in each chain transfer study were 0, 0.005, 0.01, 0.02, 0.035, and 0.05 M.

Terminator Solution. A 1 M solution of pyrogallol was used to quench each polymerization. For example, THF was added to pyrogallol (0.63 g, 5.0 mmol) in a 5 mL volumetric flask to bring the total volume to 5 mL.

Chain Transfer Experiments. Each of the six polymerization solutions were prepared in 4 mL volumetric flasks. In a typical procedure, a $[X]_0/[M]_0 = 0.005$ solution of 11-(4′-cyanophenyl-4″-phenoxy)undecyl propionate was prepared by adding benzene to 2.0 mL of monomer solution (4.0 mmol of MA, 0.040 mmol of AIBN) and 0.20 mL of chain transfer solution (0.020 mmol of 11-(4′-cyanophenyl-4″-phenoxy)undecyl propionate) in a 4 mL volumetric flask to bring the total volume to 4 mL. The $[X]_0/[M]_0 = 0, 0.01, 0.02, 0.035$, and 0.05 solutions were prepared by the same procedure. The $[X]_0/[M]_0 = 0.0, 0.005, 0.01, 0.02, 0.035$, and 0.05 solutions were poured separately into glass ampules containing a stir bar 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 flame-sealed under vacuum (2.6×10^{-6} Torr), placed in a 60 °C oil bath, and the polymerizations were stirred for 5 min. The ampules were then plunged into an ice bath, broken open, 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 ^{1}H NMR spectroscopy for monomer conversion (4.9%, 5.2%, 3.24%, 6.4%, 4.4%, and 7.9% for the $[X]_0/[M]_0 = 0.0, 0.005, 0.01, 0.02, 0.035$, and 0.05 solutions, respectively) using THF as the internal standard (1.95 ppm, CH_2CH_2O) for the relative integrals of the CO_2CH_3 monomer (3.87 ppm) and polymer (3.81 ppm) resonances and by GPC$_{PSt}$ for molecular weight.

Scheme 2. Synthesis of Chain Transfer Agents, 11-(4′-Cyanophenyl-4″-phenoxy)undecyl Propionate (R = −H) and 11-(4′-Cyanophenyl-4″-phenoxy)undecyl Isobutyrate (R = −CH$_3$)^a



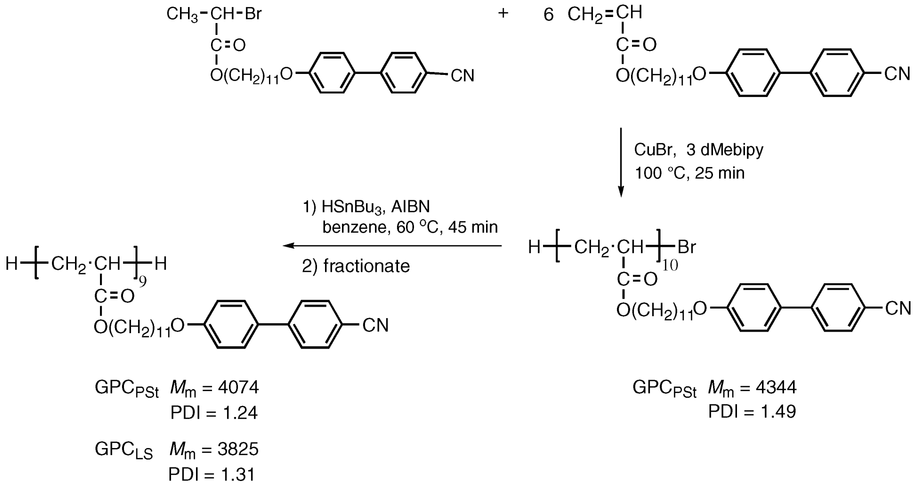
^{a} THF = tetrahydrofuran.

Results and Discussion

As outlined in Scheme 2, the two model compounds were synthesized by esterifying 11-(4′-cyanophenyl-4″-phenoxy)undecyl alcohol with propionyl chloride or isobutyryl chloride in the presence of triethylamine. Oligo[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate] was prepared by first polymerizing 11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate by ATRP using 11-(4′-cyanophenyl-4″-phenoxy)undecyl 2-bromopropionate as the initiator in the presence of cuprous bromide as the catalyst and 4,4′-dimethyl-2,2′-dipyridyl as a Cu-solubilizing ligand (Scheme 3). Since the initiator introduces the same chemical structure at one chain end as in the polymer repeat units, the end groups of the resulting oligomer can be considered −H and −Br.[12] Using a $[M]_0/[I]_0$ ratio of six, we obtained an oligomer with 10 repeat units (−H/−Br end groups) according to GPC relative to linear PSt. The bromine end group was then reduced to −H using tributyltin hydride catalyzed by AIBN (Scheme 3), and the oligomer was fractionated using THF and methanol to obtain a slightly lower molecular weight fraction with nine repeat units according to GPC$_{LS}$. Although no bromine end groups were detectable by ^{1}H NMR spectroscopy, 2.6% of the chains still contain a bromine end group according to MALDI-ToF MS; this may slightly inflate the measured value of the chain transfer constant to the oligomer.

As discussed in the Introduction, we can measure the chain transfer constant to poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate] directly by the Mayo method by following the decrease in molecular weight at low monomer conversion by GPC of PMA generated in the presence of increasing amounts of oligo[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate] if the oligomer and the generated PMA are separated in the GPC chromatograms. Figure 1 presents the GPC chromatograms of one of the triplicate sets of polymerizations of MA in the presence of the oligomer and demonstrates that the generated PMA is well resolved from the added oligomer at all six ratios of chain transfer agent to monomer ($[X]/[M] = 0, 0.005, 0.01, 0.02, 0.035, 0.05$). The elution volume of PMA (27−31 mL) increases, and therefore its molecular weight decreases with increasing concentration of the added oligomer due to chain transfer to the oligomer. This corresponds to a very slight decrease in elution volume of added oligomer and therefore a slight increase in its molecular weight due to grafting of the oligomer with PMA following chain transfer; the size

Scheme 3. Synthesis, Reduction, and Fractionation of Oligo[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate][a]



[a] dMebipy = 4,4′-dimethyl-2,2′-dipyridyl, AIBN = 2,2′-azobis(isobutyronitrile), and THF = tetrahydrofuran.

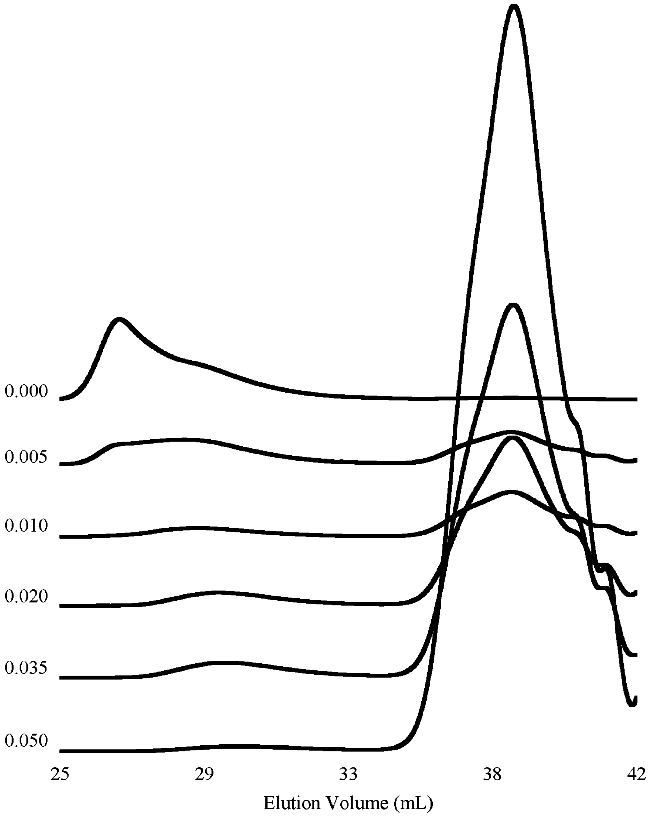


Figure 1. Refractive index detected gel permeation chromatograms of poly(methyl acrylate) (low elution volume peak) generated by polymerizing methyl acrylate (M) for 5 min in the presence of oligo[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate] (X; high elution volume peak) in benzene at 60 °C using 1 mol % 2,2′-azobis(isobutyronitrile) as the initiator; plots are labeled with [X]/[M] = 0.0, 0.005, 0.01, 0.02, 0.035, or 0.05. (The plots are not normalized relative to each other.)

of the PMA peak is small relative to the added polymer due to the low monomer conversions required for measuring chain transfer constants using the Mayo equation.

Tables S1−S4 of the Supporting Information summarize the monomer conversions and the molecular weight data used to measure the chain transfer constants to poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]; these polymerizations of methyl acrylate in benzene in the presence of the chain transfer agents at 60 °C for 5 min using 1 mol % AIBN as the initiator resulted in approximately 6% monomer conversion (2.7−13.5%). Figure 2 presents the Mayo plots of the chain transfer experiments of PMA to the two model compounds and the oligomer, and Table 1 summarizes the measured chain transfer constants. The first Mayo plot in Figure 2 compares the results from chain transfer to 11-(4′-cyanophenyl-4″-phenoxy)undecyl propionate using molecular weights of PMA measured relative to PSt and relative to PMA. The slopes of the plots, which correspond to the chain transfer constants ($C_P = 6.62 \pm 0.476$ and 6.82 ± 0.222, respectively), are equal within experimental error. Therefore, the chain transfer constants can be determined by measuring the molecular weight of PMA by GPC relative to PSt, which is the most commonly used GPC calibration standard.

The intercepts of the Mayo plots correspond to the molecular weight of PMA generated in the absence of the chain transfer agents and therefore should be equal under similar experimental conditions. Although identical experimental conditions were used, the intercepts of the three sets of data based on PSt-equivalent molecular weights vary, primarily due to different aging times of the initiator and perhaps also to errors in weighing the initiator. The different aging times of the initiator are also the primary source of error in the individual data points; i.e., there is less variation in the individual data points the closer in time that the chain transfer experiments were performed.

Table 1 and the slopes of the Mayo plots in Figure 2 also compare the chain transfer constants of PMA to the two model compounds and the oligomer. The chain transfer constant to the oligomer is the same as those of both model compounds within experimental error, although that of the isobutyrate is slightly lower than that of the propionate. This confirms that both model compounds effectively mimic one repeat unit of the mesogenic polyacrylate. However, the fact that the chain transfer constants to both model compounds and the oligomer are essentially equal demonstrates that the chain transfer event cannot be occurring by abstraction of the methine hydrogens from the polymer backbone as in nonmesogenic polyacrylates; i.e., if chain transfer involved the polymer backbone, the chain transfer constant to the oligomer and to 11-(4′-cyanophenyl-4″-phenoxy)undecyl isobutyrate would be greater than that to the propionate since the latter cannot generate a

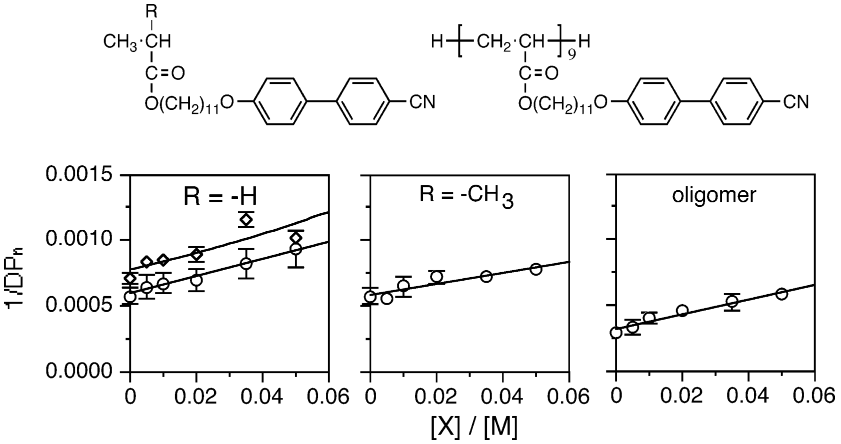


Figure 2. Mayo[18] plots of the inverse number-average degree of polymerization (1/DP$_n$) of poly(methyl acrylate) generated by polymerizing methyl acrylate (M) for 5 min in the presence of 11-(4′-cyanophenyl-4″-phenoxy)undecyl propionate, 11-(4′-cyanophenyl-4″-phenoxy)undecyl isobutyrate, or oligo[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate] (X) in benzene at 60 °C using 1 mol % 2,2′-azobis(isobutyronitrile) as the initiator, as a function of the ratio of the concentrations of chain transfer agent and monomer ([X]/[M]); ○, molecular weight measured by gel permeation chromatography (GPC) relative to polystyrene; ◊, molecular weight measured by GPC relative to PMA.

Table 1. Chain Transfer Constants (C_P) of Poly(methyl acrylate) (PMA) to 11-(4′-Cyanophenyl-4″-phenoxy)undecyl Propionate (R = −H), 11-(4′-Cyanophenyl-4″-phenoxy)undecyl Isobutyrate (R = −CH$_3$), and Oligo[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate] (Oligomer) in Benzene at 60 °C[a]

transfer agent[b]	GPC calibrant[c]	$C_P \times 10^3$	r[d]
R = −H	PSt	6.62 ± 0.476	0.990
R = −H	PMA	6.82 ± 0.222	0.838
R = −CH$_3$	PSt	4.27 ± 0.858	0.928
oligomer	PSt	5.54 ± 0.608	0.977

[a] Measured by the Mayo method[18] from triplicate polymerizations using 1 mol % 2,2′-azobis(isobutyronitrile) as the initiator, except R = H relative to PMA, which used two sets of polymerizations. [b] Transfer agent used in concentrations of [X]/[MA] = 0.0, 0.005, 0.01, 0.02, 0.035, and 0.05. [c] GPC = gel permeation chromatography; PSt = polystyrene. [d] r = linear correlation coefficient.

Table 2. Calculated Branching Densities of Poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate][10] Synthesized by Conventional Radical Polymerization[a]

monomer conv (p)	branching density (ρ)	1 branch per every X repeat units	branches per chain[b]	1 branch per every X chains[b]
0.72	0.0042	208	0.16	6.4
0.85	0.0068	149	0.25	4.0
0.99	0.020	50	0.74	1.4

[a] Calculated using eq 1 and $C_P = 5.48 \times 10^{-3}$; 72% isolated yield. [b] Using a chain with 37 repeat units, from the absolute molecular weight of poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate][10] measured in CH$_2$Cl$_2$.[13]

tertiary radical. In addition, the chain transfer constants are at least 1 order of magnitude higher than values of C_P for nonmesogenic polyacrylates.[6,22,23] Chain transfer must therefore involve the mesogenic side chains, although we have not been able to identify the chain transfer event by NMR spectroscopy.

The mean value of the chain transfer constants to the two model compounds and the oligomer using PSt-equivalent molecular weights is $C_P = 5.48 \times 10^{-3}$. Using Flory's equation for branching (eq 1)[14] and a monomer conversion of 72%, which was the isolated yield of the polymer after repeated precipitations,[10] the extent of branching present in the poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate] synthesized by conventional radical polymerization is $\rho = 4.2 \times 10^{-3}$ (Table 2). This means that there are 4.2 branches per 10^3 repeat units or 1 branch per 208 repeat units. Since the absolute molecular weight of this polymer corresponded to DP$_n$ = 37, $\rho = 4.2 \times 10^{-3}$ corresponds to 0.16 branches per polymer chain or 1 branch per 6.4 polymer chains of 37 repeat units. However, the actual monomer conversion must be higher than the isolated yield of the polymer. Table 2 therefore also presents the calculated branching densities using 85% and 99% monomer conversions and demonstrates that the polymer synthesized by conventional radical polymerization may contain up to 0.74 branches per chain of 37 repeat units or a single branch per 1.4 chains. This corresponds to 1 branch per 50 repeat units; since the polydispersity of this polymer is broad (PDI = 3.20), there are many chains with both less than and more than 37 repeat units. Therefore, according to these calculations, the previously synthesized polymer is a mixture of linear and variously branched chains. This is consistent with its solution behavior.[13] For example, the errors in the GPC$_{PSt}$-determined molecular weights of the fractionated polymer prepared by conventional radical polymerization were between those of the corresponding three-arm star and comb polymers prepared by ATRP and varied with solvent quality similar to those of the comb polymers. Its aggregation behavior was most similar to that of the three-arm star polymers, and its size (mean-square radius of gyration, $\langle R_g^2\rangle^{1/2}$) and shape were similar to both branched polymers in CH$_2$Cl$_2$. Its low contraction factor ($g = 0.47$) also confirmed that it is more branched than the corresponding linear polymers prepared by ATRP.

Conclusions

Chain transfer constants to polymer can be measured directly by the Mayo method by following the decrease in molecular weight by GPC of polymer generated in the presence of increasing amounts of an added oligomer if the oligomer and the generated polymer are separated in the GPC chromatograms. Using this technique, the chain transfer constants of PMA to 11-(4′-cyanophenyl-4″-phenoxy)undecyl propionate, 11-(4′-cyanophenyl-4″-phenoxy)undecyl isobutyrate, and an oligomer of poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate] with an average of nine repeat units are the same within experimental error, using either PMA- or PSt-equivalent molecular weights. The mean value of the chain transfer constants to the two model compounds and the oligomer ($C_P = 5.48 \times 10^{-3}$) is an order of magnitude larger than those to nonmesogenic polyacrylates. Therefore, chain transfer to poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate] involves the mesogenic side chains rather than the polymer backbone. Using Flory's equation for branching and monomer conversions of 72−99%, the extent of branching present in the poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate] synthesized by conventional radical polymerization is $\rho = 0.0042{-}0.020$, which corresponds to 1 branch per 208−54 repeat units, respectively. Therefore, the architecture of this SCLCP is not linear as is typically drawn for conventional radical polymerizations of mesogenic monomers, but rather a mixture of linear and variously branched structures. This mixture of branched structures and their limited miscibility may cause the broad phase transitions often exhibited by SCLCPs synthesized by conventional radical polymerizations.

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Supporting Information Available: Data used to determine the chain transfer constants to 11-(4′-cyanophenyl-4″-phenoxy)undecyl propionate, 11-(4′-cyanophenyl-4″-phenoxy)undecyl isobutyrate, and oligo[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate] in the radical polymerization of methyl acrylate. This material is available free of charge via the Internet at http://pubs.acs.org.

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