5222 *Macromolecules* **2010**, *43*, 5222–5232
DOI: 10.1021/ma100416p

Macromolecules
ARTICLE

Synthesis of Hyperbranched Polyacrylates by a Chloroinimer Approach

Coleen Pugh,* Anirudha Singh, Reichel Samuel, and Karla M. Bernal Ramos

Department of Polymer Science, Maurice Morton Institute of Polymer Science, The University of Akron, Akron, Ohio 44325-3909

Received February 22, 2010; Revised Manuscript Received April 26, 2010

ABSTRACT: (2-Chloro-2-alkoxycarbonyl)ethyl acrylates with methyl, dodecyl, perfluoroalkyl, siloxane, oligooxyethylene, and mesogenic ester substituents were synthesized as inimers for self-condensing vinyl polymerization (SCVP) to produce hyperbranched polyacrylates. The inimers were polymerized by atom transfer radical polymerization under a variety of conditions to produce soluble polymers with broad polydispersities (up to PDI = 5.24) characteristic of hyperbranched polymers, although the isolated polymers had narrower polydispersities. The molecular weight distribution was followed as a function of time and inimer conversion for the polymerization of the mesogenic inimer. The first-order inimer conversion was linear with time. The buildup of a hyperbranched structure during the SCVP was confirmed by comparison of the error in the GPC_{PSt}-determined molecular weights of the mesogenic polymer with those of the corresponding linear, three-arm star, and comb architectures.

Introduction

The architectural effects of branching are being investigated extensively for polymers based on styrene and butadiene and condensation polymers in the case of dendrimers. At identical molecular weights, branched polymers are generally more compact than the corresponding linear polymers,[1] with the radius of gyration (R_g) decreasing with increasing branching. Although the physical properties of dendrimers have rarely been compared to exact linear analogues, many of their properties are unique. For example, their solution properties are characterized by a low viscosity, with the intrinsic viscosity ([η]) passing through a maximum as a function of generation number and therefore molecular weight.[2,3] The conformation of the polymer in solution is described by the scaling relationship between its molecular weight (M) and its radius of gyration ($R_g = KM^{\nu}$); the scaling coefficient, ν, is typically 0.588 for a random coil in a good solvent,[1] 0.50 for a random coil in a theta solvent,[1] and 0.33 for a dendrimer in any quality of solvent according to molecular dynamics simulations.[4]

In the solid state, the glass transition temperature (T_g) of dendrimers increases with increasing molecular weight and increasing generation number,[3,5] but is apparently independent of architecture for linear, hyperbranched, and dendritic polymers of the same chemical structure.[6] Except at very low molecular weights, the transition temperatures of side-chain liquid crystalline polymers (SCLCPs) are also similar for linear,[7,8] three-arm star,[7,9] comb,[10] and six-arm star[11] polymers at identical absolute molecular weights.

In the melt, the viscosity of dendrimers increases with increasing generation number[12] and fits a master curve when plotted as a function of molecular weight.[3] In contrast to linear polymers, there is apparently no critical (entanglement) molecular weight with an abrupt increase in the exponent a in the relationship $\eta = KM^a$ in either the bulk[12,13] or concentrated solutions[14] of dendrimers and some hyperbranched[13] polymers; however, the rheological properties of other hyperbranched polymers with a more open structure exhibit viscoelastic effects attributable to entanglements.[13]

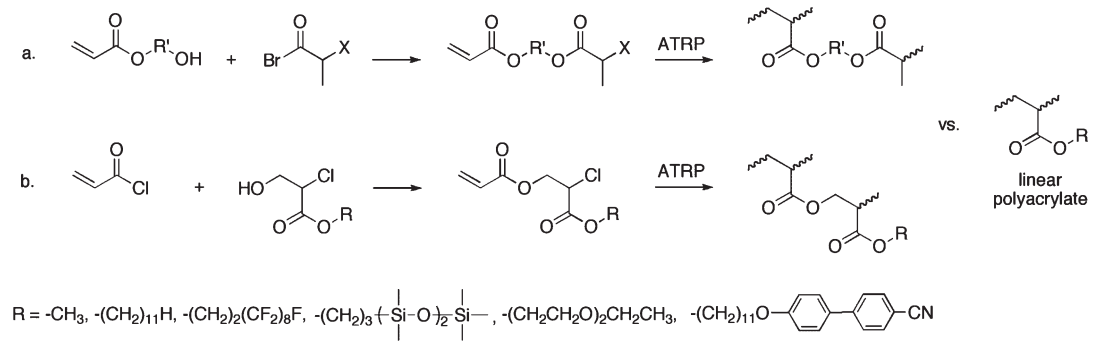
Because of synthetic challenges, the effect of branching on the solution and/or solid-state properties of poly(meth)acrylates has rarely been studied.[15] One of the most viable approaches for synthesizing polyacrylates with the maximum amount of branching should be by a self-condensing vinyl homopolymerization (SCVP)[16] of an inimer, which is a molecule that contains both an initiating site and a polymerizable group. Although "hyperbranched polyacrylates" have reportedly[17] been synthesized by homopolymerization of inimers by atom transfer radical polymerization (ATRP), they cannot be considered analogues of any specific linear polyacrylate, whose properties could be compared to determine the architectural effects of hyperbranching in this class of polymers. As shown in Scheme 1a, all of the hyperbranched polyacrylates synthesized to date by SCVP by an ATRP homopolymerization start from a monomer such as hydroxyethyl acrylate and incorporate the alkyl ester into the inimer and resulting polymer backbone upon branching, with only unreacted initiator fragments being free alkyl ester side chains. The "hyperbranched polyacrylates" are also not analogues of the branched polyacrylates produced in conventional radical polymerizations of commodity monomers, in which branching occurs by chain transfer at a site along the polymer backbone,[18] rather than at the ester side chains.[19]

We have therefore designed the new type of acrylate inimers shown in Scheme 1b,[20] which incorporate a *free* alkyl ester substituent, in addition to the requisite acrylate and α-halo functional groups. Homopolymerization of this type of inimer will therefore produce a polymer with an ester group attached to every other carbon atom along the polymer backbone, with a nonfunctionalized alkyl ester attached as a free side chain, both of which are features of linear polyacrylates. Any alcohol, including aliphatic or nonaliphatic, hydrocarbon or nonhydrocarbon, linear or branched, and mesogenic or nonmesogenic, can be attached as the free ester side chain of the hyperbranched polyacrylate backbone in order to tune its properties and provide a truly hyperbranched analogue of any specific linear polyacrylate. As representative examples, this paper describes the synthesis and polymerization of a methyl chloroinimer to produce the hyperbranched

*To whom correspondence should be addressed.

 Published on Web 05/20/2010

Scheme 1. Synthesis and Self-Condensing Vinyl Homopolymerization of (a) Conventional Acrylate Inimers and (b) (2-Chloro-2-alkoxycarbonyl)ethyl Acrylate Inimers with Representative Ester Substituents by Atom Transfer Radical Polymerization (ATRP)



analogue of poly(methyl acrylate) as well as chloroinimers that produce hyperbranched polymers with fluorocarbon, oligo(oxyethylene), and siloxane substituents and a chloroinimer that produces a hyperbranched SCLCP. This chemistry can therefore be used to produce polyacrylates that are hydrophobic or hydrophilic, oleophobic or oleophilic, oxygen permeable or nonoxygen permeable, and liquid crystalline or nonliquid crystalline, simultaneously with maintaining the desirable properties of the branched architecture, including low viscosity and a large number of reactive end groups that can subsequently be modified to impart additional functionality and properties.

Experimental Section

Materials. Allyl alcohol (Aldrich, 99%), anisole (Aldrich, anhydrous, 99.7%), 2,2′-bipyridine (Lancaster, 99%), dodecanol (Alfa Aeser, 98%), 2-(2′-ethoxyethoxy)ethanol (Aldrich, 99%), hydrochloric acid (EMD, GR ACS, 38% w/v aq), *N,N,N′,N″*-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%), pentamethydisiloxane (Gelest), platinum divinyltetraethyldisiloxane (Gelest, 3−3.5% Pt), 1*H*,1*H*,2*H*,2*H*-perfluoro-1-decanol (Riedel-de Haen, 95%), potassium chloride (Fisher Scientific, reagent grade), DL-serine (Acros Organics, 99%), and *p*-toluenesulfonic acid (*p*TSA, Mallinckrodt, ≥97.2%) were used as received. Acryloyl chloride (Aldrich, 96%) was distilled under N_2 and stored in a refrigerator at −10 °C. Cuprous bromide (Aldrich, 98%) and cuprous chloride (Alrich, 98.999%) were purified by stirring with glacial acetic acid overnight and then washing several times with ethanol.[21] 11-(4′-Cyanophenyl-4″-phenoxy)undecanol and 11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate were synthesized as described previously.[7] Tris(2-(dimethylamino)ethyl)amine (Me_6TREN) was synthesized by a literature procedure.[22] Benzene was washed with H_2SO_4, vacuum-distilled from CaH_2, and stored over 4 Å molecular sieves. Dimethyl sulfoxide (DMSO, Fischer Scientific) was distilled from 4 Å molecular sieves under N_2. Methanol was dried by storing over 4 Å molecular sieves. Triethylamine (EM Sciences, 98%) was distilled from KOH under N_2. Reagent grade tetrahydrofuran (THF) was dried by distillation from purple sodium benzophenone ketyl under N_2. All other reagents and solvents were commercially available and used as received.

Techniques. All reactions were performed under a N_2 atmosphere using a Schlenk line unless noted otherwise. The hyperbranched SCLCP with GPC_{PSt} $M_n = 1.03 \times 10^4$, PDI = 2.06 was fractionated into four fractions using our previously described procedure.[7] Thin-layer chromatography (TLC) was preformed using silica gel plates (Sorbent Technologies, 200 μm particle size w/UV254) with polyester backing. Elemental analyses were performed on a PE 2400 Series II CHNS/O Analyzer. ^{1}H and ^{13}C NMR spectra (δ, ppm) were recorded on either a Varian Mercury 300 (300 and 75 MHz, respectively) instrument. Unless noted otherwise, all spectra were recorded in $CDCl_3$, and the resonances were measured relative to residual solvent resonances and referenced to tetramethylsilane.

Number-average (M_n) and weight-average (M_w) molecular weights relative to linear polystyrene (GPC_{PSt}) and polydispersities (PDI = M_w/M_n) were determined by gel permeation chromatography (GPC) from calibration curves of log M_n vs elution volume at 35 °C using THF (unless noted otherwise) as solvent (1.0 mL/min), a guard column and set of 50 Å, 100 Å, 10^4 Å, and linear (50−10^4 Å) Styragel 5 μm columns, and sometimes a 500 Å column, a Waters 486 tunable UV/vis detector set at 254 nm, a Waters 410 differential refractometer, and Millenium Empower 2 software. Absolute molecular weights were determined by GPC with a light scattering detector (GPC_{LS}) at 35 °C using THF (unless noted otherwise) as solvent (1.0 mL/min), a set of 100 Å and two linear (50−10^4 Å, 10^3−10^6 Å) Styragel 5 μm columns, and a Wyatt Technology DAWN-EOS 18-angle (20°−153°) light scattering detector equipped with a Ga−As laser (690 nm, 30 mW), with the concentration at each elution volume determined using a Waters 410 differential refractometer (930 nm). The molecular weight data were calculated using Astra 4.0.07 software (Wyatt Technology) and a Zimm fit, assuming 100% mass recovery for refractive index (RI) dn/dc measurements. All samples (∼0.5 g/L) were dissolved overnight and filtered through a 0.45 μm PTFE filter.

Synthesis of *n*-(Pentamethyldisiloxyl)propanol by Hydrosilylation of Allyl Alcohol with Pentamethydisiloxane. A solution of pentamethyldilsiloxane (8.4 g, 56 mmol), allyl alcohol (3.1 g, 54 mmol), and a catalytic amount of platinum divinyltetraethyldisiloxane complex (1 drop) was stirred at room temperature for 18 h. The reaction mixture was passed through a plug of basic activated alumina using Et_2O as the eluant to yield 10 g (89%) of *n*-(pentamethyldisiloxyl)propanol as a slightly brown liquid, which was used without further purification. ^{1}H NMR: 0.07 (s, CH_3, 15H), 0.53 (t, CH_2Si, J = 8.5 Hz), 1.59 (quint, CH_2CH$_2$Si, J = 7.6 Hz), 3.60 (t, CH_2O, J = 6.6 Hz). ^{13}C NMR: 0.4 (Si[CH_3]$_3$), 2.1 (Si[CH_3]$_2$), 14.3 (CH_2Si), 26.8 (CH_2CH_2O), 65.8 (CH_2O).

Synthesis of 2-Chloro-3-hydroxypropionic Acid by Deaminochlorination of Serine. 2-Chloro-3-hydroxypropionic acid was synthesized in 45−58% yield as in the following example. Sodium nitrite (68 g, 0.99 mol) was added in portions over 3 h to a solution of DL-serine (52 g, 0.50 mol), HCl (116 g, 38% w/w aq, 1.2 mol), and potassium chloride (130 g, 1.8 mol) in water (490 mL) at ∼−10 °C. After stirring at room temperature for 24 h, the light-greenish solution was saturated with NaCl and extracted five times with ethyl acetate (100 mL each). The combined organic extracts were washed five times with saturated aqueous NaCl (50 mL each) and dried over Na_2SO_4. After filtration and removing the solvent by trap-to-trap distillation, the residue was recrystallized from CH_2Cl_2 to obtain 36 g (58%) of 2-chloro-3-hydroxypropionic acid as a white solid; mp 28−29 °C. ^{1}H NMR ($CDCl_3$/DMSO-d_6): 3.96 (dd, CHHOH, ^2J = 11.9 Hz, ^3J = 5.7 Hz), 4.01 (dd, CHHOH, ^2J = 12.2 Hz, ^3J = 5.7 Hz), 4.40 (dd, CHCl, ^3J = ^3J = 5.7 Hz), 7.12 (br s, CO_2H and OH). ^{13}C NMR ($CDCl_3$/DMSO-d_6): 57.8 (CHCl), 64.3 (CH_2OH), 170.4 (C=O). Elemental Analysis ($C_3H_5ClO_3$): calcd C 28.94, H 4.04; found C 28.60, H 3.80.

Synthesis of Methyl 2-Chloro-3-hydroxypropionate by Esterification of 2-Chloro-3-hydroxypropionic Acid with Methanol. Methyl 2-chloro-3-hydroxypropionate was synthesized in 68−88% yield as in the following example. A solution of 2-chloro-3-hydroxypropionic acid (20 g, 0.16 mol) and a catalytic amount of HCl (9 drops) in methanol (200 mL, 5.0 mol) was stirred at 65 °C for 22 h. Excess methanol was then removed by rotary evaporation. CH_2Cl_2 (100 mL) was added to the brownish liquid residue, and the resulting solution was washed twice with dilute aqueous $NaHCO_3$ (50 mL each) and once with saturated aqueous NaCl (50 mL) and then dried over Na_2SO_4. After filtration and removing the solvent by rotary evaporation, the resulting slightly yellow liquid was purified by column chromatography ($R_f = 0.51$) using silica gel as the stationary phase and $CHCl_3/Et_2O$ (9:1 v/v) as the eluant to yield 17 g (76%) of methyl 2-chloro-3-hydroxypropionate as a colorless liquid. ^{1}H NMR: 2.55 (br s, O*H*), 3.82 (s, CH_3), 3.96 (dd, C*H*HOH, $^2J = 12.0$ Hz, $^3J = 5.6$ Hz), 4.04 (dd, CH*H*OH, $^2J = 11.9$ Hz, $^3J = 5.9$ Hz), 4.41 (dd, C*H*Cl, $^3J = {}^3J = 5.7$ Hz). ^{13}C NMR: 53.4 (*C*H_3), 57.0 (*C*HCl), 64.2 (*C*H_2OH), 169.0 (*C*═O). Anal. C, H: calcd 34.68, 5.09; found 34.33, 4.99.

Synthesis of 11-(4′-Cyanophenyl-4″-phenoxy)undecyl 2-Chloro-3-hydroxypropionate by Esterification of 2-Chloro-3-hydroxypropionic Acid. A solution of 2-chloro-3-hydroxypropionic acid (2.1 g, 20 mmol), 11-(4′-cyanophenyl-4″-phenoxy)undecanol (5.2 g, 10 mmol), and a catalytic amount of HCl (7 drops) was stirred at 65 °C for 44 h. ^{1}H NMR spectroscopy demonstrated that 80% of the CH_2OH resonance (3.72 ppm) of 11-(4′-cyanophenyl-4″-phenoxy)undecanol had converted to product. After cooling to room temperature, 8.6 g (46%) of 11-(4′-cyanophenyl-4″-phenoxy)undecyl 2-chloro-3-hydroxypropionate was isolated as a white solid by column chromatography ($R_f = 0.77$) using silica gel as the stationary phase and 7:3 $CHCl_3/Et_2O$ as the eluant. DSC mp 56 °C. ^{1}H NMR: 1.32 (br m, [CH_2]$_6$), 1.49 (quint, CH_2CH$_2$CH$_2$OAr, $J = 7.4$ Hz), 1.69 (quint, CH_2CH$_2$O$_2$C, $J = 6.5$ Hz), 1.82 (quint, CH_2CH$_2$OAr, $J = 6.5$ Hz), 2.40 (br s, O*H*), 3.96 (dd, C*H*HOH, $^2J = 11.9$ Hz, $^3J = 6.7$ Hz), 4.02 (t, CH_2OAr, $J = 6.5$ Hz), 4.06 (dd, CH*H*OH, $^2J = 13.1$ Hz, $^3J = 5.9$ Hz), 4.22 (m, CH_2O$_2$C), 4.36 (dd, C*H*Cl, $^3J = {}^3J = 6.4$ Hz), 7.00 (d, 2 aromatic H *ortho* to OCH$_2$, $J = 9.0$ Hz), 7.54 (d, 2 aromatic H *meta* to OCH$_2$, $J = 8.6$ Hz), 7.68 (AA′XX′, 2 aromatic H *ortho* and *meta* to CN, $^3J = 16.6$ Hz, $^4J = 8.3$ Hz). ^{13}C NMR: 25.8 (*C*H$_2$[CH$_2$]$_2$O$_2$C), 26.1 (*C*H$_2$[CH$_2$]$_2$OAr), 28.5 *C*H$_2$CH$_2$O$_2$C), 29.2 (*C*H$_2$), 29.3 (*C*H$_2$), 29.4 (*C*H$_2$), 29.5 ([*C*H$_2$]$_2$), 29.6 (*C*H$_2$CH$_2$OAr), 57.2 (*C*HCl), 64.2 (*C*H$_2$OH), 66.6 (*C*H$_2$O$_2$C), 68.3 (*C*H$_2$OAr), 110.0 (*C*CN), 115.2 (2 aromatic *C ortho* to OCH$_2$), 119.2 (*C*N), 127.1 (2 aromatic C *meta* to CN), 128.4 (2 aromatic C *meta* to OCH$_2$), 131.3 (aromatic C *para* to OCH$_2$), 132.6 (2 aromatic C *ortho* to CN), 145.4 (aromatic C *para* to CN), 159.9 (aromatic *C*O), 168.6 (*C*═O).

Synthesis of Dodecyl 2-Chloro-3-hydroxypropionate by Esterification of 2-Chloro-3-hydroxypropionic Acid with Dodecanol. A solution of 2-chloro-3-hydroxypropionic acid (4.8 g, 30 mmol), dodecanol (6.0 g, 30 mmol), and *p*-toluenesulfonic acid (25 mg, 0.26 mmol) in dry benzene (5 mL) was stirred at 75−80 °C for 40 h while collecting the benzene−water azeotrope in a Dean−Stark trap. ^{1}H NMR spectroscopy demonstrated that 85% of the CH_2OH resonance (3.63 ppm) of dodecanol had been converted. Another aliquot of 2-chloro-3-hydroxypropionic acid (1.0 g, 8.0 mmol) was added, and the reaction was stirred at 75−80 °C for an additional 20 h. ^{1}H NMR spectroscopy showed almost complete conversion. After cooling to room temperature, CH_2Cl_2 (100 mL) was added, the organic phase was washed twice with dilute aqueous $NaHCO_3$ (50 mL each) and once with saturated aqueous NaCl (50 mL), and then dried over Na_2SO_4. After filtration and removing the solvent by rotary evaporation, 7.8 g (78%) of dodecyl 2-chloro-3-hydroxypropionate was obtained as a slightly yellow liquid. It was used in the next reaction without further purification. ^{1}H NMR: 0.87 (t, CH_3, $J = 6.6$ Hz), 1.26 (m, [CH_2]$_9$), 1.67 (quint, CH_2CH$_2$O$_2$C, $J = 7.0$ Hz), 2.66 (br s, O*H*), 3.94 (dd, C*H*HOH, $^2J = 11.9$ Hz, $^3J = 5.8$ Hz), 4.01 (dd, CH*H*OH, $^2J = 11.9$ Hz, $^3J = 5.5$ Hz), 4.20 (t, CH_2O$_2$C, $J = 6.8$ Hz), 4.39 (dd, C*H*Cl, $^3J = {}^3J = 5.9$ Hz). ^{13}C NMR: 14.3 (*C*H_3), 22.9 (*C*H$_2$CH$_3$), 25.9 (*C*H$_2$[CH$_2$]$_2$O$_2$C), 28.6 (*C*H$_2$CH$_2$O$_2$C), 29.3 (*C*H$_2$[CH$_2$]$_4$H), 29.5 (*C*H$_2$), 29.6 (*C*H$_2$), 29.7 (*C*H$_2$), 29.8 (*C*H$_2$[CH$_2$]$_3$H), 32.1 (*C*H$_2$CH$_2$CH$_3$), 57.2 (*C*HCl), 64.4 (*C*H$_2$OH), 66.8 (*C*H$_2$O$_2$C), 168.7 (*C*═O).

Synthesis of 2-(2′-Ethoxyethoxy)ethyl 2-Chloro-3-hydroxypropionate by Esterification of 2-Chloro-3-hydroxypropionic Acid. A solution of 2-chloro-3-hydroxypropionic acid (5.0 g, 40 mmol) and a catalytic amount of *p*-toluenesulfonic acid (30 mg, 0.17 mmol) in 2-(2′-ethoxyethoxy)ethanol (5.4 g, 40 mmol) was stirred at 60 °C in vacuo for 48 h. Diethyl ether (100 mL) was added, the organic phase was washed twice with dilute aqueous $NaHCO_3$ (50 mL each) and once with saturated aqueous NaCl (50 mL), and then dried over Na_2SO_4. After filtration and removing the solvent by rotary evaporation, 4.8 g (47%) of 2-(2′-ethoxyethoxy)ethyl 2-chloro-3-hydroxypropionate was obtained as a slightly yellow liquid. It was used in the next reaction without further purification. ^{1}H NMR: 1.22 (t, CH_3, $J = 7.0$ Hz), 2.86 (br s, O*H*), 3.54 (q, OCH_2CH$_3$, $J = 7.0$ Hz), 3.60 (t, CH_2OCH$_2$CH$_3$, $J = 5.0$ Hz), 3.63 (t, CH_2OCH$_2$CH$_2$O$_2$C, $J = 5.0$ Hz), 3.75 (t, CH_2CH$_2$O$_2$C, $J = 4.8$ Hz), 3.96 (dd, C*H*HOH, $^2J = 11.9$ Hz, $^3J = 5.2$ Hz), 4.05 (dd, CH*H*OH, $^2J = 11.9$ Hz, $^3J = 6.7$ Hz), 4.35 (t, CH_2O$_2$C, $J = 4.7$ Hz), 4.4 (dd, C*H*Cl, $^3J = 5.2$ Hz, $^3J = 6.7$ Hz). ^{13}C NMR: 15.2 (*C*H_3), 57.1 (*C*HCl), 64.5 (*C*H$_2$OH), 65.0 (*C*H$_2$O$_2$C), 66.9 (*C*H$_2$CH$_3$), 68.8 (*C*H$_2$OCH$_2$CH$_3$), 69.9 (*C*H$_2$OCH$_2$CH$_2$O$_2$C), 70.7 (*C*H$_2$CH$_2$O$_2$C), 168.6 (*C*═O).

Synthesis of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl 2-Chloro-3-hydroxypropionate by Esterification of 2-Chloro-3-hydroxypropionic Acid. 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl 2-chloro-3-hydroxypropionate (white solid; mp 45 °C) was synthesized in 67% yield using the same procedure as for 11-(4′-cyanophenyl-4″-phenoxy)undecyl 2-chloro-3-hydroxypropionate, except that 0.8 equiv of 1*H*,1*H*,2*H*,2*H*-perfluoro-1-decanol was used instead of 0.5 equiv of 11-(4′-cyanophenyl-4″-phenoxy)undecanol, the reaction time was 36 h, and unreacted 1*H*,1*H*,2*H*,2*H*-perfluoro-1-decanol was sublimed off of the crude product at 70 °C in vacuo. ^{1}H NMR: 2.55 (tt, CH_2CF$_2$, $^3J_{HF} = 18.1$ Hz, $^3J_{HH} = 6.3$ Hz), 3.20 (br s, O*H*), 3.99 (dd, C*H*HOH, $^2J = 10.7$ Hz, $^3J = 6.1$ Hz), 4.05 (dd, CH*H*OH, $^2J = 11.3$ Hz, $^3J = 5.7$ Hz), 4.44 (dd, C*H*Cl, $^3J = {}^3J = 5.6$ Hz), 4.53 (t, CO$_2$CH_2CH$_2$, $J = 6.4$ Hz). ^{13}C NMR: 30.6 (t, *C*H$_2$CF$_2$), 57.0 (*C*HCl), 58.3 (*C*H$_2$O$_2$C), 64.4 (*C*H$_2$OH), 168.3 (*C*═O); the *C*F resonances are barely detectable in the region from 104 to 121 ppm.

Synthesis of *n*-(Pentamethyldisiloxyl)propyl 2-Chloro-3-hydroxypropionate by Esterification of 2-Chloro-3-hydroxypropionic Acid. *n*-(Pentamethyldisiloxyl)propyl 2-chloro-3-hydroxypropionate (colorless liquid) was synthesized in 51% yield using the same procedure as for 2-(2′-ethoxyethoxy)ethyl 2-chloro-3-hydroxypropionate, except that *n*-(pentamethyldisiloxyl)propanol was used instead of 2-(2′-ethoxyethoxy)ethanol, 1 mol % instead of 0.4 mol % of *p*-TSA was used, the reaction was performed at atmospheric pressure, and the product was purified by column chromatography ($R_f = 0.78$) using silica gel as the stationary phase and CH_2Cl_2/Et_2O (9:1 v/v) as the eluant. ^{1}H NMR: 0.08 (s, CH_3, 15 H), 0.54 (t, CH_2Si, $J = 8.5$ Hz), 1.71 (quint, CH_2CH$_2$Si, $J = 7.8$ Hz), 2.36 (t, O*H*, $J = 7.2$ Hz), 3.97 (ddd, C*H*HOH, $^2J = 13.2$ Hz, $^3J = 7.3$ Hz, $^3J = 5.6$ Hz), 4.04 (ddd, CH*H*OH, $^2J = 11.6$ Hz, $^3J = 7.0$ Hz, $^3J = 5.9$ Hz), 4.18 (t, CH_2O$_2$C, $^3J = 7.1$ Hz), 4.41 (dd, C*H*Cl, $^3J = {}^3J = 5.9$ Hz). ^{13}C NMR: 0.4 (Si[*C*H$_3$]$_3$), 2.1 (Si[*C*H$_3$]$_2$), 14.1 (*C*H$_2$Si), 22.6 (*C*H$_2$CH$_2$Si), 57.2 (*C*HCl), 64.3 (*C*H$_2$OH), 69.0 (*C*H$_2$O$_2$C), 170.9 (*C*O$_2$).

Synthesis of (2-Chloro-2-methoxycarbonyl)ethyl Acrylate. (2-Chloro-2-methoxycarbonyl)ethyl acrylate was synthesized in 34−50% yield as in the following example. A solution of triethylamine (6.6 g, 65 mmol) in THF (25 mL) was added dropwise over 30 min to an ice-cooled solution of methyl 2-chloro-3-hydroxypropionate (5.0 g, 35 mmol) and acryloyl chloride (5.8 g, 63 mmol) in THF (5 mL). After stirring at room

temperature for 16 h, the solution was poured into ice water (200 mL) and stirred for 6 h to partially evaporate THF. Since no precipitate formed, the aqueous mixture was extracted five times with CH_2Cl_2 (50 mL each). The combined organic extracts were washed twice with dilute aqueous $NaHCO_3$ (50 mL each) and once with saturated aqueous NaCl (50 mL), and dried over Na_2SO_4. After filtration and removing the solvent by rotary evaporation, the yellow liquid residue was distilled (94−96 °C/3 mm Hg) to yield 3.4 g (50%) of (2-chloro-2-methoxycarbonyl)ethyl acrylate as a colorless liquid. ^{1}H NMR: 3.79 (s, CH_3), 4.47 (dd, CHHO$_2$C, ^2J = 11.6 Hz, ^3J = 7.9 Hz), 4.52 (dd, CHCl, ^3J = ^3J = 7.9 Hz), 4.56 (dd, CHHO$_2$C, ^2J = 11.6 Hz, ^3J = 8.0 Hz), 5.86 (dd, CHH_b = trans to CO$_2$, $^2J_{ab}$ = 1.2 Hz, $^3J_{bc}$ = 10.4 Hz), 6.10 (dd, =CH_c, $^3J_{ac}$ = 17.3 Hz, $^3J_{bc}$ = 10.4 Hz), 6.41 (CH_aH = cis to CO$_2$, $^2J_{ab}$ = 1.2 Hz, $^3J_{ac}$ = 17.3 Hz). ^{13}C NMR: 53.5 (*C*H$_3$), 53.7 (*C*HCl), 64.6 (*C*H$_2$O$_2$C), 127.6 (*C*H=), 132.3 (*C*H$_2$=), 165.4 (acrylate *C*=O), 167.9 (*C*O$_2$CH$_3$). Anal. C, H: calcd 43.65, 4.71; found 43.48, 4.73.

Synthesis of {2-Chloro-2-[11′-(4″′-cyanophenyl-4′″-phenoxy)-undecan-1-oxycarbonyl]}ethyl Acrylate. A solution of acryloyl chloride (1.8 g, 20 mmol) in THF (5 mL) was added dropwise over 4 min to an ice-cooled solution of 11-(4′-cyanophenyl-4″-phenoxy)undecyl 2-chloro-3-hydroxypropionate (6.0 g, 13 mmol) and triethylamine (1.9 g, 20 mmol) in THF (200 mL) and stirred at room temperature for 17 h. The reaction mixture was poured into ice water (200 mL) and stirred overnight to evaporate THF. The resulting white precipitate was collected in a fritted glass filter and dried in vacuo. This crude product was purified by column chromatography (R_f = 0.70) using silica gel as the stationary phase and $CHCl_3$/Et_2O (95:5 v/v) as the eluant, followed by recrystallization from ethanol (200 mL) to yield 3.3 g (50%) of {2-chloro-2-[11′-(4″′-cyanophenyl-4′″-phenoxy)-undecan-1-oxycarbonyl]}ethyl acrylate as a white solid. DSC mp 69 °C. ^{1}H NMR: 1.31 (br m, [CH_2]$_6$), 1.48 (quint, CH_2-CH$_2$CH$_2$OAr, J = 7.3 Hz), 1.68 (quint, CH_2CH$_2$O$_2$C, J = 6.9 Hz), 1.82 (quint, CH_2CH$_2$OAr, J = 6.9 Hz), 4.01 (t, CH_2OAr, J = 6.6 Hz), 4.22 (t, CH$_2$CH_2O$_2$C, J = 6.6 Hz), 4.51 (dd, CHHO$_2$C, ^2J = 14.0 Hz, ^3J = 9.4 Hz), 4.53 (dd, CHCl, ^3J = ^3J = 8.1 Hz), 4.59 (dd, CHHO$_2$C, ^2J = 12.1 Hz, ^3J = 8.4 Hz), 5.90 (dd, CHH_b = trans to CO$_2$, $^2J_{ab}$ = 1.5 Hz, $^3J_{bc}$ = 10.6 Hz), 6.13 (dd, =CH_c, $^3J_{ac}$ = 17.2 Hz, $^3J_{bc}$ = 10.4 Hz), 6.46 (CH_aH = cis to CO$_2$, $^2J_{ab}$ = 1.4 Hz, $^3J_{ac}$ = 17.4 Hz), 7.00 (d, 2 aromatic H *ortho* to OCH$_2$, J = 8.7 Hz), 7.54 (d, 2 aromatic H *meta* to OCH$_2$, J = 8.8 Hz), 7.68 (AA′XX′, 2 aromatic H *ortho* and *meta* to CN, ^3J = 15.9 Hz, ^4J = 8.3 Hz). ^{13}C NMR: 25.9 (*C*H$_2$[CH$_2$]$_2$O$_2$C), 26.2 (*C*H$_2$-[CH$_2$]$_2$OAr), 28.6 *C*H$_2$CH$_2$O$_2$C), 29.2 (*C*H$_2$), 29.4 (*C*H$_2$), 29.6 ([CH$_2$]$_3$), 29.7 (*C*H$_2$CH$_2$OAr), 53.9 (*C*HCl), 64.7 (*C*H$_2$CHCl), 66.8 (CO$_2$*C*H$_2$CH$_2$), 68.4 (*C*H$_2$OAr), 110.2 (*C*CN), 115.3 (2 aromatic C *ortho* to OCH$_2$), 119.3 (*C*N), 127.2 (2 aromatic *C* *meta* to CN), 127.6 (*C*H=), 128.5 (2 aromatic C *meta* to OCH$_2$), 131.4 (aromatic *C* *para* to OCH$_2$), 132.3 (*C*H$_2$=), 132.7 (2 aromatic C *ortho* to CN), 145.5 (aromatic C *para* to CN), 160.0 (aromatic *C*O), 165.4 (acrylate *C*=O), 167.4 (*C*O$_2$CH$_2$). Anal. C, H, N: calcd 68.49, 6.90, 2.66; found 68.24, 6.88, 2.93.

Synthesis of (2-Chloro-2-*n*-dodecan-1-oxycarbonyl)ethyl Acrylate. (2-Chloro-2-*n*-dodecan-1-oxycarbonyl)ethyl acrylate (colorless liquid; R_f = 0.47 on silica using 95:5 v/v hexanes/ethyl acetate as the eluant) was synthesized in 59% yield using the same procedure as for {2-chloro-2-[11′-(4″′-cyanophenyl-4′″-phenoxy)undecane-1-oxycarbonyl]}ethyl acrylate, except that dodecyl 2-chloro-3-hydroxypropionate was used instead of 11-(4′-cyanophenyl-4″-phenoxy)undecyl 2-chloro-3-hydroxypropionate, the reaction time was 21 h, and the crude product was extracted from water into CH_2Cl_2 and washed with dilute aqueous $NaHCO_3$ and saturated aqueous NaCl. ^{1}H NMR: 0.88 (t, CH_3, J = 6.7 Hz), 1.26 (m, [CH_2]$_8$), 1.67 (quint, CH_2CH$_2$O$_2$C, J = 6.6 Hz), 4.21 (t, CH$_2$CH_2O$_2$C, J = 6.8 Hz), 4.50 (dd, CHHO$_2$C, ^2J = 11.8 Hz, ^3J = 7.8 Hz), 4.53 (dd, CHCl, ^3J = ^3J = 8.1 Hz), 4.58 (dd, CHHO$_2$C, ^2J = 10.9 Hz, ^3J = 8.4 Hz), 5.90 (dd, CHH_b = trans to CO$_2$, $^2J_{ab}$ = 1.5 Hz, $^3J_{bc}$ = 10.4 Hz), 6.13 (dd, =CH_c, $^3J_{ac}$ = 17.3 Hz, $^3J_{bc}$ = 10.4 Hz), 6.46 (CH_aH = cis to CO$_2$, $^2J_{ab}$ = 1.4 Hz, $^3J_{ac}$ = 17.3 Hz). ^{13}C NMR: 14.3 (*C*H$_3$), 22.9 (*C*H$_2$CH$_3$), 25.9 (*C*H$_2$-[CH$_2$]$_2$O$_2$C), 28.6 (*C*H$_2$CH$_2$O$_2$C), 29.3 (*C*H$_2$[CH$_2$]$_4$H), 29.5 (*C*H$_2$), 29.6 (*C*H$_2$), 29.7 (*C*H$_2$), 29.8 (*C*H$_2$[CH$_2$]$_3$H), 32.1 (*C*H$_2$-CH$_2$CH$_3$), 53.9 (*C*HCl), 64.7 (*C*H$_2$CHCl), 66.9 (CO$_2$*C*H$_2$CH$_2$), 127.6 (*C*H=), 132.2 (*C*H$_2$=), 165.4 (acrylate *C*=O), 167.4 (*C*O$_2$CH$_2$). Anal. C, H: calcd 62.32, 9.01; found 62.19, 9.36.

Synthesis of [2-Chloro-2−2′-(2″-ethoxyethoxy)ethan-1-oxycarbonyl]ethyl Acrylate. [2-Chloro-2,2′-(2″-ethoxyethoxy)ethan-1-oxycarbonyl]ethyl (colorless liquid; R_f = 0.36 on silica using 60:40 v/v hexanes/ethyl acetate as the eluant) was synthesized in 67% yield using the same procedure as for {2-chloro-2-[11′-(4″′-cyanophenyl-4′″-phenoxy)undecan-1-oxycarbonyl]}ethyl acrylate, except that 2-(2′-ethoxyethoxy)ethyl 2-chloro-3-hydroxypropionate was used instead of 11-(4′-cyanophenyl-4″-phenoxy)-undecyl 2-chloro-3-hydroxypropionate, and after a reaction time of 18 h, precipitated $NEt_3H^+Cl^-$ was filtered off and all volatiles were removed from the crude product by rotary evaporation. ^{1}H NMR: 1.22 (t, CH_3, J = 7.0 Hz), 3.53 (q, OCH_2CH$_3$, J = 7.2 Hz), 3.58 (t, CH_2OCH$_2$CH$_3$, J = 5.1 Hz), 3.66 (t, CH_2OCH$_2$CH$_2$O$_2$C, J = 5.0 Hz), 3.75 (t, CH_2CH$_2$O$_2$C, J = 5.0 Hz), 4.38 (t, CH$_2$CH_2O$_2$C, J = 4.9 Hz), 4.53 (dd, CHHO$_2$C, ^2J = 11.7 Hz, ^3J = 8.0 Hz), 4.57 (dd, CHCl, ^3J = ^3J = 8.1 Hz), 4.60 (dd, CHHO$_2$C, ^2J = 11.4 Hz, ^3J = 7.6 Hz), 5.90 (dd, CHH_b = trans to CO$_2$, $^2J_{ab}$ = 1.3 Hz, $^3J_{bc}$ = 10.4 Hz), 6.14 (dd, =CH_c, $^3J_{ac}$ = 17.4 Hz, $^3J_{bc}$ = 10.6 Hz), 6.46 (CH_aH = cis to CO$_2$, $^2J_{ab}$ = 1.5 Hz, $^3J_{ac}$ = 17.4 Hz). ^{13}C NMR: 15.2 (*C*H$_3$), 53.8 (*C*HCl), 64.6 (*C*H$_2$CHCl), 65.6 (CO$_2$*C*H$_2$CH$_2$), 66.8 (*C*H$_2$CH$_3$), 68.8 (*C*H$_2$OCH$_2$CH$_3$), 69.9 (*C*H$_2$OCH$_2$CH$_2$O$_2$C), 70.9 (*C*H$_2$CH$_2$O$_2$C), 127.6 (*C*H=), 132.2 (*C*H$_2$=), 165.3 (acrylate *C*=O), 167.3 (*C*O$_2$CH$_2$). Anal. C, H: calcd 48.90, 6.50; found: 48.59, 6.42.

Synthesis of [2-Chloro-2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecan-1-oxycarbonyl)]ethyl Acrylate. [2-Chloro-2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecan-1-oxycarbonyl)]ethyl acrylate was synthesized in 43% yield using the same procedure as for (2-chloro-2-methoxycarbonyl)ethyl acrylate, except that 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl 2-chloro-3-hydroxypropionate was used instead of methyl 2-chloro-3-hydroxypropionate, the reaction time was 12 h, and the product was purified by column chromatography (R_f = 0.61−0.74) using silica gel as the stationary phase and $CHCl_3$ as the eluant. ^{1}H NMR: 2.52 (tt, CH_2CF$_2$, $^3J_{HF}$ = 18.0 Hz, $^3J_{HH}$ = 6.3 Hz), 4.46 (dd, CHHO$_2$C, ^2J = 11.8 Hz, ^3J = 10.0 Hz), 4.51 (dd, CHCl, ^3J = ^3J = 6.4 Hz), 4.55 (t, CH$_2$CH_2O$_2$C, J = 8.8 Hz), 4.56 (dd, CHHO$_2$C, ^2J = 10.0 Hz, ^3J = 6.4 Hz), 5.88 (dd, CHH_b = trans to CO$_2$, $^2J_{ab}$ = 1.1 Hz, $^3J_{bc}$ = 10.5 Hz), 6.11 (dd, =CH_c, $^3J_{ac}$ = 17.2 Hz, $^3J_{bc}$ = 10.5 Hz), 6.44 (CH_aH = cis to CO$_2$, $^2J_{ab}$ = 0.9 Hz, $^3J_{ac}$ = 17.4 Hz). ^{13}C NMR: 30.5 (t, *C*H$_2$CF$_2$), 53.4 (*C*HCl), 58.4 (CO$_2$*C*H$_2$CH$_2$), 64.4 (*C*H$_2$CHCl), 127.5 (*C*H=), 132.3 (*C*H$_2$=), 165.4 (acrylate *C*=O), 167.2 (*C*O$_2$CH$_2$); the *C*F resonances are barely detectable in the region from 104 to 121 ppm. Anal. C, H: calcd 30.76, 1.71; found 30.84, 1.55.

Synthesis of [*n*-(Pentamethyldisiloxyl)propan-1-oxycarbonyl]-ethyl Acrylate. [*n*-(Pentamethyldisiloxyl)propan-1-oxycarbonyl]-ethyl acrylate (colorless liquid; R_f = 0.74 on silica using CH_2Cl_2 as the eluant) was synthesized in 67% yield using the same procedure as for {2-chloro-2-[11′-(4″′-cyanophenyl-4′″-phenoxy)-undecan-1-oxycarbonyl]}ethyl acrylate, except *n*-(pentamethyldisiloxyl)propyl 2-chloro-3-hydroxypropionate was used instead of 11-(4′-cyanophenyl-4″-phenoxy)undecyl 2-chloro-3-hydroxypropionate, and after a reaction time of 21 h, precipitated $NEt_3H^+Cl^-$ was filtered off and all volatiles were removed from the crude product by rotary evaporation. ^{1}H NMR: 0.06 (s, CH_3, 15 H), 0.52 (t, CH_2Si, J = 8.6 Hz), 1.68 (quin, CH_2CH$_2$Si, J = 8.1 Hz), 4.17 (t, CH$_2$CH_2O$_2$C, J = 7.1 Hz), 4.50 (dd, CHHO$_2$C, ^2J = 11.5 Hz, ^3J = 7.6 Hz), 4.54 (dd, CHCl, ^3J = ^3J = 6.8 Hz), 4.58 (dd, CHHO$_2$C, ^2J = 11.6 Hz, ^3J = 8.9 Hz), 5.88 (dd, CHH_b = trans to CO$_2$, $^2J_{ab}$ = 1.3 Hz, $^3J_{bc}$ = 10.4 Hz), 6.12 (dd, =CH_c, $^3J_{ac}$ = 17.1 Hz, $^3J_{bc}$ = 10.5 Hz), 6.45 (CH_aH = cis to

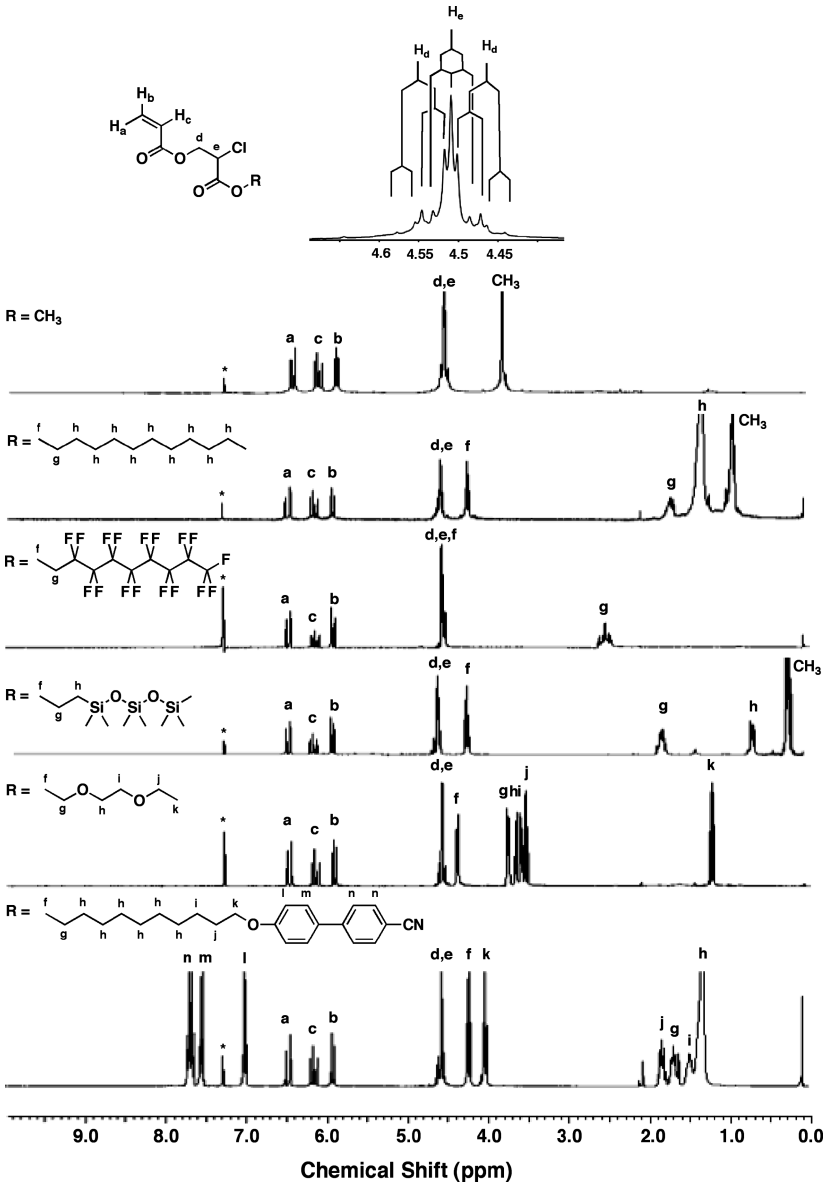


Figure 1. ^{1}H NMR (300 MHz) spectra of (2-chloro-2-alkoxycarbonyl)ethyl acrylate inimers with a variety of ester substituents and an expanded region of the R = CH_3 inimer; ∗ = $CHCl_3$.

CO_2, $^2J_{ab}$ = 1.3 Hz, $^3J_{ac}$ = 17.2 Hz). ^{13}C NMR: 0.4 (Si[CH_3]$_3$), 2.1 (Si[CH_3]$_2$), 14.1 (CH_2Si), 22.7 (CH_2CH_2Si), 53.9 (CHCl), 64.7 (CH_2CHCl), 69.1 ($CO_2CH_2CH_2$), 127.7 (CH=), 132.2 (CH_2=), 165.4 (acrylate C=O), 167.4 (CO_2CH_2). Anal. C, H: calcd 45.82, 7.42; found 45.69, 7.42.

Polymerizations. In a typical procedure, (2-chloro-2-methoxycarbonyl)ethyl acrylate (0.28 g, 1.5 mmol) was added under a stream of nitrogen to a well-stirred mixture of CuCl (3.3 mg, 33 μmol) and Me_6TREN (6.6 mg, 28 μmol) in a dry Schlenk tube, and the tube was sealed with a glass stopper. After stirring at room temperature for 10 min, the inimer mixture was degassed by five freeze−(30 min) pump−thaw cycles, and the polymerization tube was backfilled with N_2. The polymerization mixture was stirred at 50 °C for 46 h, and then the polymerization was quenched by immersing the Schlenk tube into liquid N_2. The contents of the polymerization tube were thawed, exposed to the atmosphere, diluted with THF (5 mL), and precipitated into water/methanol (3/7 v/v) (25 mL). The precipitate was collected and reprecipitated twice from THF (5 mL) into water/methanol (3/7 v/v) (25 mL) to yield 0.13 g (43%) of hyperbranched poly(methyl acrylate) as a slightly yellow waxy solid. GPC_{PSt} $M_n = 1.92 \times 10^4$, PDI = 2.15.

Copolymerizations. In a typical procedure, a solution of {2-chloro-2-[11′-(4′′-cyanophenyl-4′′′-phenoxy)undecan-1-oxycarbonyl]}ethyl acrylate (20 mg, 40 μmol) and 11-(4′-cyanophenyl-4′′-phenoxy)undecyl acrylate (0.30 g, 0.72 mmol) in anisole (0.6 mL) was added under a stream of nitrogen to a well-stirred mixture of CuCl (4.1 mg, 40 μmol) and PMDETA (6.2 mg, 40 μmol) in a dry Schlenk tube, and the tube was sealed with a glass stopper. After stirring at room temperature for 10 min, the comonomer mixture was degassed by three freeze−(30 min) pump−thaw cycles, and the polymerization tube was backfilled with N_2. The copolymerization mixture was stirred at 130 °C for 18 h, and then the copolymerization was quenched by immersing the Schlenk tube into liquid N_2. The contents of the polymerization tube were thawed, exposed to the atmosphere, diluted with THF (5 mL), and precipitated into saturated aqueous NH_4Cl (25 mL). The precipitate was collected and reprecipitated from THF (5 mL) into methanol (25 mL) to yield 0.10 g (30%) of the branched copolymer as a tan solid; GPC_{PSt} $M_n = 1.03 \times 10^4$, PDI = 1.22.

Results and Discussion

Synthesis of Inimers. As shown in Scheme 1, the key intermediate for the chloroinimers is a chlorohydrin in which

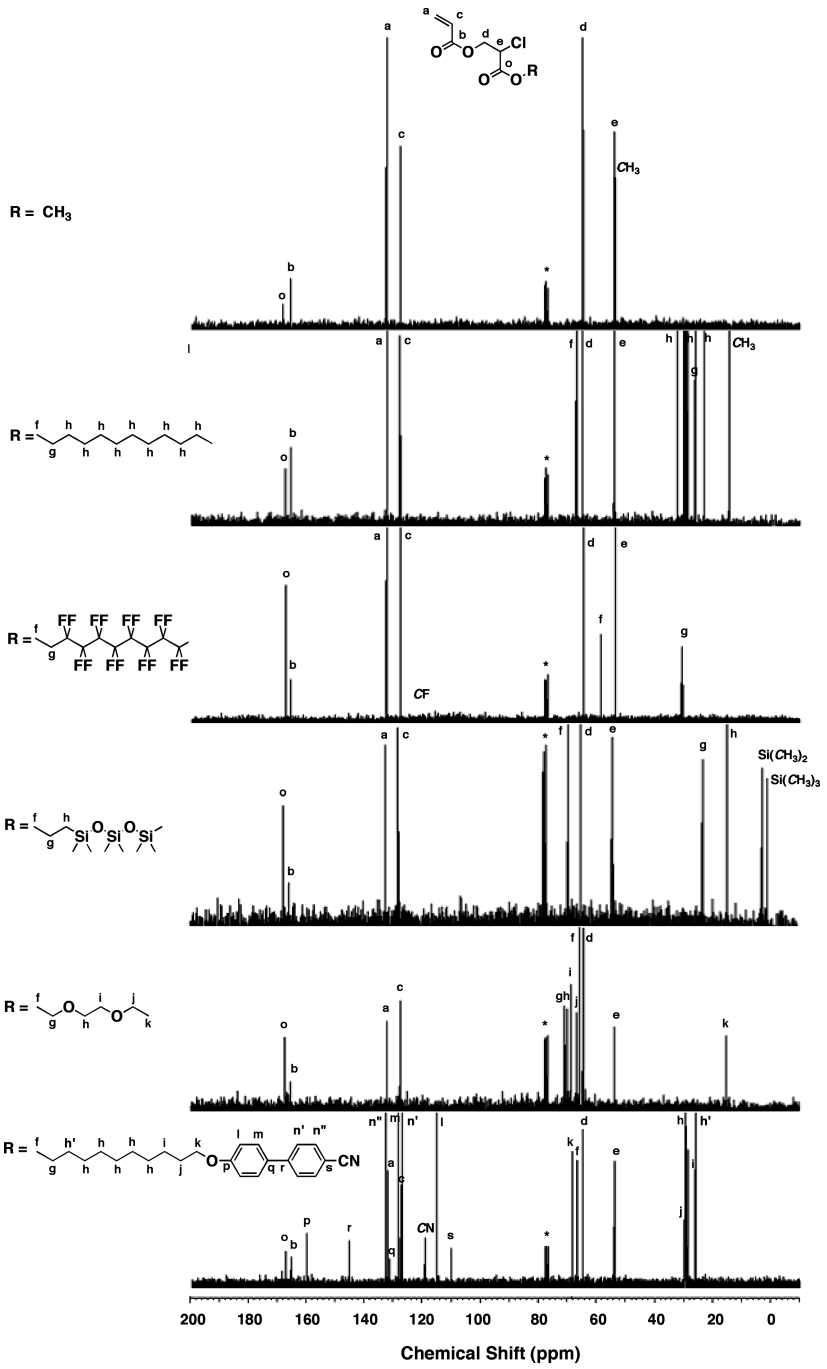


Figure 2. ^{13}C NMR (75 MHz) spectra of (2-chloro-2-alkoxycarbonyl)ethyl acrylate inimers with a variety of ester substituents; ∗ = $CHCl_3$.

the chlorine atom is alpha to the ester group and the hydroxy group is beta; this chlorohydrin was synthesized regioselectively by deaminochlorination of DL-serine via diazotization using sodium nitrite in the presence of HCl and potassium chloride, similar to the conversion of L-serine and/or other α-amino acids using either H_2SO_4[23] or HBr[24,25] and potassium bromide, followed by acid-catalyzed esterification of 2-chloro-3-hydroxypropionic acid at ≤85 °C to prevent self-condensation. The methyl ester was prepared in methanol as solvent; however, the higher molecular weight esters were prepared essentially in bulk using an excess of the chlorohydrin, which is easier to completely remove from the product than the higher molecular weight alcohols. The alkyl 2-chloro-3-hydroxypropionates were then esterified with acryloyl chloride to produce the chloroinimers.

Figure 1 presents the ^{1}H NMR spectra of the chloroinimers with a variety of ester substituents. In addition to the resonances at ~5.88 ppm (dd, CH*H*= trans to CO_2), 6.12 ppm (dd, =C*H*), and 6.44 ppm (CH*H*= cis to CO_2) due to the acrylate double bond, all of the inimers exhibit resonances at 4.53 ppm due to the C*H*Cl methine and at 4.49 and 4.57 ppm due to the diastereotopic methylene protons alpha to chlorine. Although the two methylene resonances overlap the methine resonance, the expansion of this region for the methyl inimer in Figure 1 demonstrates that the doublet-of-doublet splitting pattern is clear for each resonance. The corresponding ^{13}C NMR spectra of all of the inimers are presented in Figure 2, using as close to the same labeling system as possible to that in Figure 1. In addition to the resonances at 127.6 ppm (*C*H=), 132.3 ppm (*C*H_2=), and

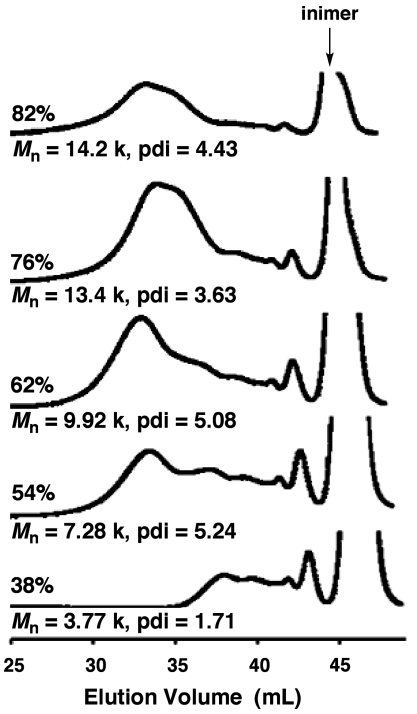


Figure 3. Gel permeation chromatograms (guard plus four columns) and the corresponding inimer conversions of aliquots taken from duplicate atom transfer radical polymerizations of {2-chloro-2-[11′-(4″-cyanophenyl-4‴-phenoxy)undecan-1-oxycarbonyl]}ethyl acrylate in anisole at 120 °C using CuBr as the catalyst and *N,N,N′,N′*-pentamethyldiethylenetriamine (PMDETA) as the ligand; inimer:CuBr:PMDETA = 80:1:1.1.

165.4 ppm (*C*═O) due to the acrylate group, all of the inimers exhibit resonances at 53.7 ppm (*C*HCl), 64.6 ppm (CH_2O_2C), and 167.9 ppm (CO_2R), regardless of the ester substituent. Only the ^{1}H and ^{13}C NMR resonances of the free ester substituent vary as the substituent is varied.

Synthesis and Characterization of Hyperbranched Polyacrylates. Since self-condensing vinyl polymerizations involve both step and chain propagation steps, they produce polymers with characteristically broad polydispersities.[26,27] Figure 3 presents the GPC traces of aliquots taken from duplicate ATRP polymerizations of {2-chloro-2-[11′-(4″-cyanophenyl-4‴-phenoxy)undecan-1-oxycarbonyl]}ethyl acrylate in anisole at 120 °C; these polymerizations were stopped at <90% conversion to prevent cross-linking. The GPC traces demonstrate that a low molecular weight oligomer, presumably dimer, is prominent at less than 65% conversion; its concentration becomes negligible before the inimer is completely consumed. This demonstrates that the inimer is more likely to add to oligomers and polymer at higher conversions than to dimerize. The molecular weight distributions of all of the samples are characteristically broad and therefore qualitatively consistent with the production of a hyperbranched polymer by an SCVP mechanism. Nevertheless, the M_n and polydispersity values reported with the GPC traces in Figure 3 are slightly underestimated because the inimer peak, which was not included in the calculations of these values, is not completely resolved from the polymer peaks.

Figure 4a presents the inimer conversions measured by comparison of the vinyl and aromatic ^{1}H NMR resonances of the samples represented in Figure 3; although scattered, the first-order vinyl group conversion is linear with time, which is consistent with a controlled or "living" polymerization. Figure 4b presents the corresponding molecular weights of these samples, calculated both with and without

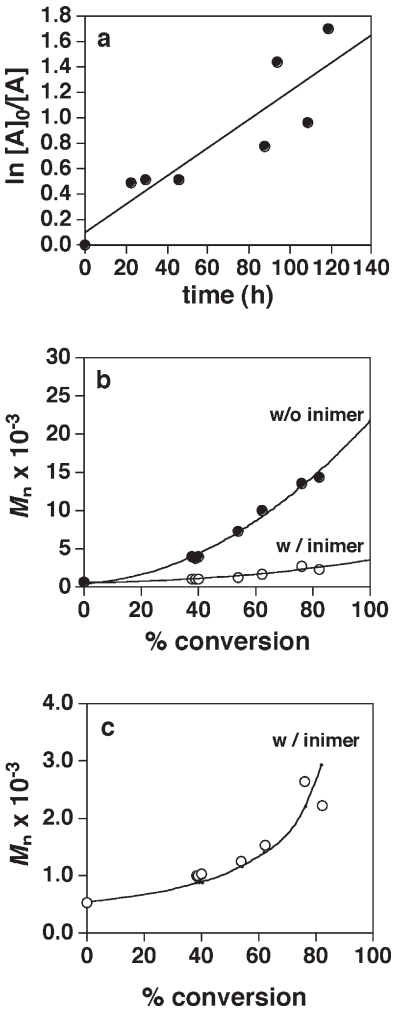


Figure 4. Data corresponding to the duplicate experiments in Figure 3 of the atom transfer radical polymerizations of {2-chloro-2-[11′-(4″-cyanophenyl-4‴-phenoxy)undecan-1-oxycarbonyl]}ethyl acrylate: (a) first-order kinetics of the conversion of the vinyl group as measured by ^{1}H NMR spectroscopy; (b) number-average molecular weight (M_n) measured by gel permeation chromatography relative to linear polystyrene as a function of inimer conversion; (c) comparison of the measured (open circles) and theoretical (line) M_n values calculated without including the inimer in the calculation as a function of inimer conversion.

inclusion of the unreacted inimer, as a function of vinyl conversion. The GPC molecular weights that excluded the unreacted inimer in the calculations are obviously much higher than those that include the inimer. Both Figures 3 and 4 demonstrate that the average molecular weight of the polymer increases exponentially with inimer conversion, although we were not able to follow this increase to the infinitely high values predicted by theory[26,27] due to cross-linking of the material at higher conversions. Nevertheless, the molecular weight values that include unreacted inimer in the calculation can be compared to theoretical values. In this case, M_n is theoretically independent of the reactivity ratio,[28] and $M_n = M_0/(1 - x)$, in which x equals the conversion and M_0 is the molecular weight of the inimer repeat unit.[26] Although the GPC molecular weights are relative to linear polystyrene, Figure 4c demonstrates that the increase in the molecular weight of the mesogenic polymer as a function of inimer conversion is consistent with the theoretical prediction up to the 82% conversion studied.

The polymerizations of the mesogenic chloroinimer reported in Figures 3 and 4 used CuBr as the catalyst and

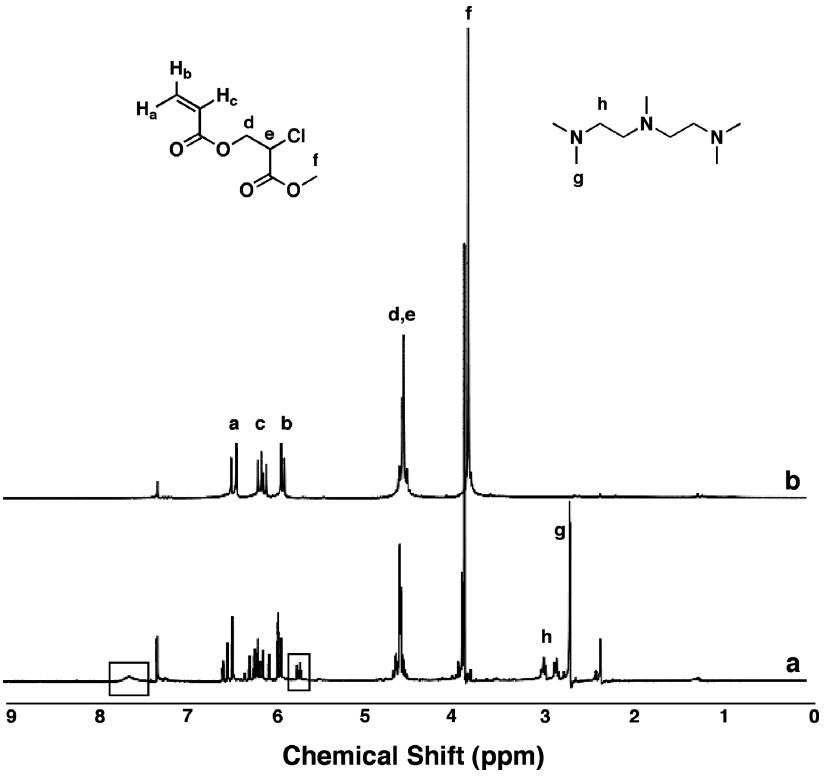


Figure 5. ^{1}H NMR spectra (300 MHz) of a mixture of (2-chloro-2-methoxycarbonyl)ethyl acrylate and *N,N,N′,N′*-pentamethyldiethylenetriamine (PMDETA) after 2.5 h at 25 °C: (a) without added catalyst and (b) in the presence of CuBr (inimer:CuBr:PMDETA = 80:1:1.1; PMDETA was mixed with CuBr for 15 min before adding the inimer).

PMDETA as the ligand. Although PMDETA does not displace the chlorine atom of methyl 2-chloropropionate,[29] the ^{1}H NMR spectrum in Figure 5a demonstrates that PMDETA reacts with the (2-chloro-2-alkoxycarbonyl)ethyl acrylate inimers in the absence of catalyst. On the basis of the broad resonance at 7.6 ppm (presumably N^+H) and the additional resonances in the vinyl region, this side reaction appears to be elimination; a new CHN^+ methine resonance due to nucleophilic substitution of chlorine by PMDETA would likely be overlapped with the resonance at 4.5 ppm. Since this side reaction did not occur when we complexed PMDETA with the catalyst before adding the inimer (Figure 5b), all of the polymerizations reported here were performed by premixing the catalyst and ligand and then adding the inimer. Complexation was detectable by a color change even when both the copper catalyst and ligand, such as 2,2′-bipyridine, were solids.

Table 1 summarizes a variety of ATRP conditions that produced soluble materials upon polymerization of the various (2-chloro-2-alkoxycarbonyl)ethyl acrylate inimers and the results of the polymerizations following precipitation and isolation of the polymers. Although these conditions are not necessarily optimized, the polymerization conditions vary widely, primarily due to differences in the solubility of the inimers and resulting polymers with a broad range of ester substituents. However, it was also necessary to use milder conditions in terms of a less active ligand, less polar solvent, and shorter reaction time to polymerize the fluorinated inimer, since conditions similar to those used to polymerize the other inimers generate a higher concentration of radicals and produced only cross-linked material. The methyl inimer is also challenging to polymerize by ATRP at elevated temperatures due to its high volatility. In addition, the polymerization of the methyl inimer in water was not reproducible; not surprising, all subsequent polymerizations of the methyl inimer in water produced cross-linked material during the degassing step, before the polymerizations were even heated. Nevertheless, this sample was used for further NMR characterization experiments.

In addition to homopolymerizations, the inimers can be copolymerized with conventional monomers. For example, a small amount of the mesogenic inimer was used as both an initiator and comonomer with the corresponding acrylate monomer, 11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate (5:95 inimer/monomer), to produce a branched polyacrylate with GPC_{PSt} $M_n = 1.03 \times 10^4$ and PDI = 1.22 (see Experimental Section).

Figure 6 presents the ^{1}H NMR spectra of the four hyperbranched poly(methyl acrylate)s reported in Table 1. All of these polymers were synthesized using a constant ratio of inimer to catalyst of ~50, but using a variety of conditions in terms of ligand, solvent, and temperature. As expected, all of the ^{1}H NMR resonances of the polymers are broad. The vinyl resonances due to the initiating terminus of the polymers appear at 5.8−6.5 ppm and the resonances due to the methyl ester appear at 3.9 ppm. The methylene and chloromethine resonances of the acrylate ester portion of the polymer overlap at ~4.5 ppm. The resonances at 1.0−3.5 ppm are due to the polymer backbone and vary significantly with the different polymerization conditions, which indicates that the extent of branching also varies with the different polymerization conditions. However, the chemical similarity of these branched polyacrylates and linear polyacrylates makes positively identifying the branch points very challenging; we will therefore report the extensive multidimensional NMR characterization of selected hyperbranched polymers in a subsequent paper.

Nevertheless, as discussed in the Introduction, many of the physical properties of polymers vary with the degree of branching and can therefore be used to confirm a branched

Table 1. Synthesis of Hyperbranched Polyacrylates by Atom Transfer Radical Polymerization of (2-Chloro-2-alkoxycarbonyl)ethyl Acrylate Inimers with a Variety of Ester Substituents (R)[a]

								GPC_{PSt}		GPC_{LS}	
R	$[inimer]_0$ (mol/L)	catalyst/ligand (~1:1 mol/mol)	[inimer]/ [catalyst]	solvent	temp (°C)	time (h)	yield (%)	$M_n \times 10^{-3}$	PDI	$M_n \times 10^{-3}$	PDI
$-CH_3$	bulk	CuCl/Me_6TREN	44		50	46	43	19.2	2.15		
$-CH_3$	bulk	CuCl/PMDETA	42		100	46	20	2.65	2.20		
$-CH_3$	5.2	CuCl/Me_6TREN	50	H_2O[b]	50	46	40	11.6	2.48	107	1.98
$-CH_3$	5.2	CuCl/PMDETA	48	methanol	50	46	20	5.47	1.37		
$-(CH_2)_{12}H$	2.5	CuBr/PMDETA	50	anisole	130	6	30	9.70	2.14	11.3	1.80
$-(CH_2)_2(CF_2)_8F$	2.8	CuCl/2,2′-bipy	55	toluene	90	6	22	49.9	2.39	124	1.93
$-(CH_2)_3[Si(Me)_2O]_2Si(Me)_3$	1.6	CuBr/PMDETA	20	anisole	120	96	28	2.01	1.44		
$-(CH_2CH_2O)_2CH_2CH_3$	1.3	CuBr/PMDETA	21	CH_3CN/H_2O[c]	25	6	24	38.0	2.33		
$-(CH_2)_{11}OC_6H_4C_6H_4CN$	1.1	CuCl/Me_6TREN	44	CH_3CN/H_2O[d]	90	46	12	7.82	1.47	16.6	1.37
$-(CH_2)_{11}OC_6H_4C_6H_4CN$	1.1	CuBr/PMDETA	53	anisole	120	24	70	8.40	1.51		
$-(CH_2)_{11}OC_6H_4C_6H_4CN$	1.8	CuBr/PMDETA	78	anisole	120	143	50	10.3	2.06	21.0	2.65
$-(CH_2)_{11}OC_6H_4C_6H_4CN$	0.8	CuCl/Me_6TREN	11	CH_3CN/H_2O[d]	90	6	44	13.3	1.44	27.9	1.58
$-(CH_2)_{11}OC_6H_4C_6H_4CN$	1.8	CuBr/PMDETA	70	anisole	120	168	57	16.3	1.57	30.3	2.09
$-(CH_2)_{11}OC_6H_4C_6H_4CN$	0.8	CuCl/Me_6TREN	34	CH_3CN/H_2O[d]	90	120	66	17.2	1.89	46.8	2.39

[a] Me_6TREN = tris(2-(dimethylamino)ethyl)amine; PMDETA = *N,N,N′,N′*-pentamethyldiethylenetriamine; 2,2′-bipy = 2,2′-bipyridine. Number- (M_n) and weight-average (M_w) molecular weights and polydispersities (pdi = M_w/M_n) were measured by gel permeation chromatography relative to linear polystyrene (GPC_{PSt}) or with a light scattering detector (GPC_{LS}), both in tetrahydrofuran at 35 °C, except for the fluorinated polymer, which was measured in trichlorobenzene at 135 °C. [b] This polymerization was not reproducible, but the polymer was used for further characterization. [c] 1:1 v/v. [d] 5:1 v/v.

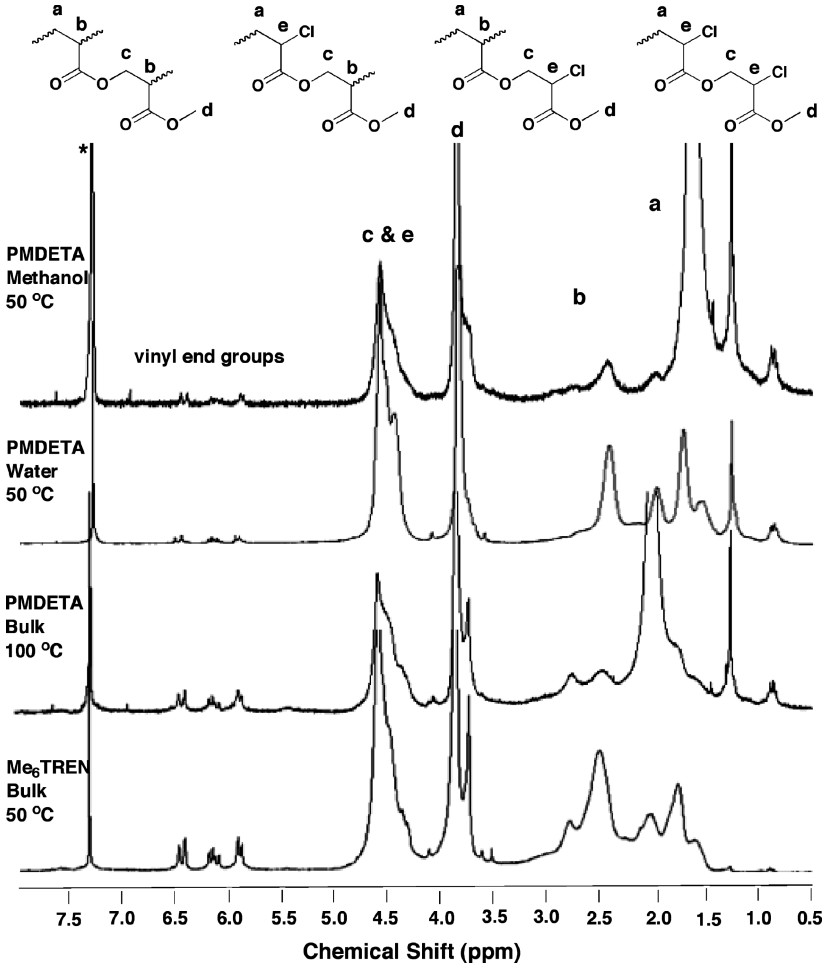


Figure 6. ^1H NMR spectra (300 MHz) of poly(methyl acrylate)s synthesized by self-condensing vinyl polymerization of (2-chloro-2-methoxycarbonyl)ethyl acrylate (inimer:CuCl:ligand ~50:1:1) under various atom transfer radical polymerization conditions ($[inimer]_0 = 5.2$ M in solution; 44−46 h) as summarized in Table 1; ∗ = $CHCl_3$ solvent, PMDETA = *N,N,N′,N′*-pentamethyldiethylenetriamine, Me_6TREN = tris(2-(dimethylamino)ethyl)amine.

structure. One of the simplest properties to compare is the error in the GPC-determined molecular weights as a function of branching,[8,11,30] which is caused by the more compact[1] shape of branched polymers compared to the linear polymer standards used to relate elution volume to molecular weight. Table 1 lists the molecular weights of many of the polymers determined by both GPC relative to linear polystyrene and by 18-angle light scattering detection of the polymers eluted from the GPC by THF. In all of these cases, the absolute[31] molecular weights are significantly higher than those

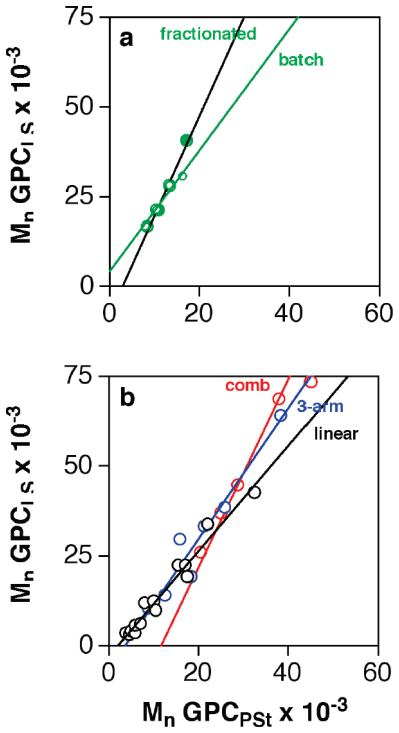


Figure 7. Comparison of the plots of the number-average molecular weights (M_n) of poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s determined by gel permeation chromatography (GPC) with a light scattering detector (GPC_{LS}) as a function of those determined by GPC relative to linear polystyrene (GPC_{PSt}) in tetrahydrofuran at 35 °C: (a) hyperbranched polymers from Table 1 that were synthesized batchwise (open green circles) and hyperbranced polymers (filled green circles) fractionated from the sample in Table 1 prepared at 120 °C in anisole for 143 h (GPC_{PSt} M_n = 1.03 × 10^4, PDI = 2.06) and (b) linear (black), three-arm star (blue), and comb (red) polymers reported[30] previously.

measured by GPC_{PSt}, which is consistent with a branched architecture.

We previously synthesized the linear,[7,8] three-arm star,[7,9] comb,[10] and six-arm star[11] analogues of the polymers produced by SCVP of the mesogenic inimer and determined the error in the GPC_{PSt}-determined molecular weights of the first three architectures in THF.[8,30] Figure 7a plots the absolute number-average molecular weights measured by GPC_{LS} as a function of the GPC_{PSt}-determined molecular weights in THF for four of the "hyperbranched" SCLCPs in Table 1. The data are plotted using the same axes as the corresponding data plotted in Figure 7b for the linear, three-arm star, and comb polymers reported previously. The linear equations corresponding to the data in Figure 7 are summarized in Table 2. Although different conditions were used to polymerize the mesogenic inimer, the data are linear with a fairly high linear correlation coefficient. Figure 7 and Table 2 demonstrate that the error in the GPC_{PSt}-determined molecular weights of the mesogenic architectures reported previously[8,30] increases with increasing branching. The error in the GPC_{PSt}-determined molecular weights of the hyperbranched polymers prepared batchwise is similar to that of the three-arm star polymers and perhaps the comb polymers. However, in contrast to the other architectures, the degree of branching of polymers produced by SCVP of an inimer increases as the conversion increases, simultaneously with increasing molecular weight.[27] We therefore also fractionated the hyperbranched polymer with GPC_{PSt} M_n = 1.03 × 10^4, and PDI = 2.06 into four fractions. In this case, the error in the GPC_{PSt}-determined molecular weights is even higher than those of the comb polymers, evidently because the higher molecular weight samples are more branched. Therefore, the error in the GPC_{PSt}-determined molecular weights of the SCLCPs prepared by ATRP polymerization of the mesogenic inimers is consistent with a SCVP to produce hyperbranched polymers.

Table 2. Linear Equations [$M_{n,LS} \times 10^{-3} = m(M_{n,GPC} \times 10^{-3}) + b$] Corresponding to the Data in Figure 7 Relating the Number-Average Molecular Weights of Poly[11-(4′-cyanophenyl-4″-phenoxy)undecyl acrylate]s of Different Molecular Architectures Determined by Gel Permeation Chromatography (GPC) with a Light Scattering Detector (GPC_{LS}) as a Function of Those Determined by GPC Relative to Linear Polystyrene (GPC_{PSt}) in Tetrahydrofuran at 35 °C

architecture	*m*, slope	*b*, intercept	r^a
linear[b]	1.46	−2.92	0.985
3-arm star[30]	1.82	−6.87	0.927
comb[30]	2.62	−30.4	0.969
hyperbranched from separate batches	1.69	3.73	0.983
fractionated hyperbranched[c]	2.76	−7.54	0.996

[a] r = linear correlation coefficient. [b] Using all of the linear polymers with two different end groups reported in refs 8 and 30. [c] Fractionated from the hyperbranched SCLCP with GPC_{PSt} M_n = 1.03 × 10^4 and PDI = 2.06 (Table 1).

Conclusions

(2-Chloro-2-alkoxycarbonyl)ethyl acrylates are ideal inimers for producing hyperbranched analogues of linear polyacrylates by self-condensing vinyl polymerization, not only because they have a free ester side chain that can be matched to the polyacrylate of interest but also because polymerization results in an ester group attached to every other carbon atom along the polymer backbone. Any alcohol, including aliphatic or nonaliphatic, hydrocarbon or nonhydrocarbon, linear or branched, and mesogenic or nonmesogenic, can be attached as the free ester side chain of the hyperbranched polyacrylate backbone. The (2-chloro-2-alkoxycarbonyl)ethyl acrylate inimers can be polymerized by atom transfer radical polymerization to generate soluble polymers under conditions that vary with the type of ester substituent, primarily because of variations in the solubility of the inimer and resulting polymer. The increase in molecular weight as a function of conversion and the broad polydispersities are consistent with a self-condensing vinyl polymerization mechanism to produce hyperbranched polymers. The hyperbranched structure was also confirmed by the greater error in the GPC_{PSt}-determined molecular weights of a mesogenic polymer compared to the corresponding linear, three-arm star, and comb architectures.

Acknowledgment. Acknowledgment is made to the National Science Foundation for support of this research through DMR-0322338 and its Special Creativity Award (DMR-0630301) and for inclusion of KBR in The University of Akron NSF-REU Site for Polymer Science and Engineering (DMR-0648318). We also acknowledge Professor Dámaso Navarro Rodríguez and the Centro de Investigacion en Quimica Aplicada of Saltillo, Mexico for financial support of K.B.R.'s internship.

References and Notes

(1) Burchard, W. *Adv. Polym. Sci.* **1999**, *143*, 113–194.
(2) (a) Mourey, T. H.; Turner, S. R.; Rubinstein, M.; Fréchet, J. M. J.; Hawker, C. J.; Wooley, K. L. *Macromolecules* **1992**, *25*, 2401–2406. (b) Rietveld, I. B.; Smit, J. A. M. *Macromolecules* **1999**, *32*, 4608–4614.
(3) Farrington, P. J.; Hawker, C. J.; Fréchet, J. M. J.; Mackay, M. E. *Macromolecules* **1998**, *31*, 5043–5050.
(4) Murat, M.; Grest, G. S. *Macromolecules* **1996**, *29*, 1278–1285.
(5) Wooley, K. L.; Hawker, C. J.; Pochan, J. M.; Fréchet, J. M. J. *Macromolecules* **1993**, *26*, 1514–1519.

(6) Wooley, K. L.; Fréchet, J. M. J.; Hawker, C. J. *Polymer* **1994**, *35*, 4489–4495.
(7) Kasko, A. M.; Heintz, A. M.; Pugh, C. *Macromolecules* **1998**, *31*, 256–271.
(8) Kasko, A. M.; Grunwald, S. R.; Pugh, C. *Macromolecules* **2002**, *35*, 5466–5474.
(9) Pugh, C.; Kasko, A. M.; Grunwald, S. R. *J. Polym. Sci., Polym. Chem. Ed.* **2008**, *46*, 4363–4382.
(10) Chang, C.; Pugh, C. *Macromolecules* **2001**, *34*, 2027–2039.
(11) Kasko, A. M.; Pugh, C. *Macromolecules* **2006**, *39*, 6800–6810.
(12) Hawker, C. J.; Farrington, P. J.; Mackay, M. E.; Wooley, K. L.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1995**, *117*, 4409–4410.
(13) Sendijarevic, I.; McHugh, A. J. *Macromolecules* **2000**, *33*, 590–596.
(14) Uppuluri, S.; Keinath, S. E.; Tomalia, D. A.; Dvornic, P. R. *Macromolecules* **1998**, *31*, 4498–4510.
(15) (a) Saunders, G.; Cormack, P. A. G.; Graham, S.; Sherrington, D. C. *Macromolecules* **2005**, *38*, 6418–6422. (b) Chisholm, M.; Hudson, N.; Kirtley, N.; Viela, F.; Sherrington, D. C. *Macromolecules* **2009**, *42*, 7745–7752.
(16) Frechet, J. M. J.; Henmi, M.; Gitsov, I.; Aoshima, S.; Leduc, M. R.; Grubbs, R. B. *Science* **1995**, *269*, 1080–1083.
(17) (a) Matyjaszewski, K.; Gaynor, S. G.; Kulfan, A.; Podwika, M. *Macromolecules* **1997**, *30*, 5192–5194. (b) Matyjaszewski, K.; Gaynor, S. G. *Macromolecules* **1997**, *30*, 7042–7049. (c) Matyjaszewski, K.; Pyun, J.; Gaynor, S. G. *Macromol. Rapid Commun.* **1998**, *19*, 665–670. (d) Yoo, S. H.; Yoon, T. H.; Jho, J. Y. *Macromol. Rapid Commun.* **2001**, *22*, 1319–1324. (e) Hong, C. Y.; Pan, C. Y. *Polymer* **2001**, *42*, 9385–9391. (f) Ishizu, K.; Shibuya, T.; Mori, A. *Polym. Int.* **2002**, *51*, 424–428. (g) Yoo, S. H.; Lee, J. H.; Lee, J. H.; Jho, J. Y. *Macromolecules* **2002**, *35*, 1146–1148. (h) Jiang, B.; Yang, Y.; Jian, D.; Fu, S.; Zhu, R.; Hao, J.; Wang, W. *J. Appl. Polym. Sci.* **2002**, *83*, 2114–2123. (i) Hong, C. Y.; You, Y. Z.; Wu, D.; Liu, Y.; Pan, C. Y. *Macromolecules* **2005**, *38*, 2606–2611.
(18) (a) Kloosterboer, J. G.; Lijten, G. F. C. M.; Greidanus, F. J. A. M. *Polym. Commun.* **1986**, *27*, 268–271. (b) Lovell, P. A.; Shah, T. H.; Heatley, F. *Polym. Commun.* **1991**, *32*, 98–103. (c) Ahmad, N. M.; Heatley, F.; Lovell, P. A. *Macromolecules* **1998**, *31*, 2822–2827. (d) Ahmad, N. M.; Britton, D.; Heatley, F.; Lovell, P. A. *Macromol. Symp.* **1991**, *143*, 231–241. (e) Roos, S. G.; Müller, A. H. E. *Macromol. Rapid Commun.* **2000**, *21*, 864–867. (f) Heatley, F.; Lovell, P. A.; Yamashita, T. *Macromolecules* **2001**, *34*, 7636–7641. (g) Britton, D. J.; Lovell, P. A.; Heatley, F.; Venkatesh, R. *Macromol. Symp.* **2001**, *175*, 95–104. (h) Farcet, C.; Belleney, J.; Charleux, B.; Pirri, R. *Macromolecules* **2002**, *35*, 4912–4918. (i) Bian, K.; Cunningham, M. F. *Macromolecules* **2005**, *38*, 695–701.
(19) Pugh, C.; Fan, G.; Kasko, A. M. *Macromolecules* **2005**, *38*, 8071–8077.
(20) Pugh, C.; Singh, A. WO2008045299, April 17, **2008**.
(21) Keller, R. N.; Wycoff, H. D. *Inorg. Synth.* **1946**, *2*, 1–4.
(22) Queffelee, J.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* **2000**, *33*, 8629–8639.
(23) (a) Izumiya, N. *Bull. Chem. Soc. Jpn.* **1953**, *26*, 53–56. (b) Shimohigashi, Y.; Waki, M.; Izumiya, N. *Kyushu Univ. Ser. C* **1978**, *11*, 217–224.
(24) (a) Larchevêque, M.; Petit, Y. *Tetrahedron Lett.* **1987**, *28*, 1993–1996. (b) Larchevêque, M.; Petit, Y. *Bull. Soc. Chim. Fr.* **1989**, 130–139. (c) Souers, A. J.; Schürer, S.; Kwack, H.; Virgilio, A. A.; Ellman, J. A. *Synthesis* **1999**, 583–585.
(25) Pugh, C.; Raveendra, B.; Singh, A.; Samuel, R.; Garcia, G., submitted.
(26) Müller, A. H. E.; Yan, D.; Wulkow, M. *Macromolecules* **1997**, *30*, 7015–7023.
(27) Yan, D.; Müller, A. H. E.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 7024–7033.
(28) The reactivity ratio (r) in a self-condensing vinyl polymerization of an AB* inimer is defined as $r = k_A/k_B$, in which k_A is the rate constant for reaction of the double bond with a new A* initiating site that results from prior addition of a B* initiating site to an A vinyl group and k_B is the rate constant for reaction of the double bond with an original B* initiating site.[26]
(29) Coessens, V.; Matyjaszewski, K. *J. Macromol. Sci., Pure Appl. Chem.* **1999**, *A36*, 811–826.
(30) Kasko, A. M.; Pugh, C. *Macromolecules* **2004**, *37*, 4993–5001.
(31) GPC_{LS} measures the absolute weight-average molecular weight at each elution slice, in which each elution slice of the GPC chromatogram corresponds to a single size polymer ($M_n = M_w$) or a fraction of very narrow polydispersity. Therefore, each moment (M_n, M_w, M_z, etc.) of the molecular weight distribution can be considered an absolute molecular weight.