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Bimetallic Samarium(III) Catalysts via Electron Transfer Initiation: The Facile Synthesis of Well-Defined (Meth)acrylate Triblock Copolymers

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Abstract: A method for generating a bifunctional organolanthanide(III) initiator *in situ* from a (meth)acrylate monomer and a divalent samarium precursor, $(C_5Me_5)_2Sm$ (**1**) or $(C_5Me_5)_2Sm(THF)_2$ (**2**), is described. This process involves one-electron transfer from the Sm(II) species to monomer, forming radical anions which couple to give a bimetallic samarium(III) enolate that acts as a bisinitiator for living polymerization. Well-defined, highly syndiotactic ABA triblock copolymers containing both methacrylate and acrylate segments were prepared in two monomer addition steps with this methodology. Selective side chain deprotection may be carried out on copolymers containing poly(*tert*-butyl acrylate) or poly(benzyl methacrylate) blocks to give syndiotactic ester-acid copolymers. © 1997 Elsevier Science Ltd.

Introduction

Bifunctional polymerization initiators--those with two covalently linked active sites--provide a number of unique advantages in polymer synthesis. Their bilateral symmetry renders them inherently superior to monometallic initiators for the preparation of telechelics and triblocks, and provides access to otherwise unavailable materials (such as ABA triblocks for which monomer crossover from B to A, but not from A to B, is possible). The simplest and perhaps most elegant bifunctional polymerizations are those based on electron transfer initiation. In these systems, a bisinitiator is generated *in situ* by the addition of a one-electron reducing agent to a vinyl monomer, forming radical anions which couple to give a linked active species. This methodology was first developed by Szwarc, who used sodium naphthalide to initiate the "living" dianionic polymerization of dienes and α-olefins.[1,2] The great utility of this process for the preparation of useful polymer structures has since been demonstrated.[3]

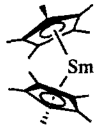
The development of special-architecture polymethacrylates and polyacrylates has been an important goal in polymer synthesis due to the high functionality, chemical resistance, and commerical importance of acrylic materials. In particular, (meth)acrylic block copolymers have been highly sought after. Poly(methyl methacrylate) (PMMA) is predicted to be an ideal component for thermoplastic elastomers due to its high glass transition temperature (T_g);[4,5] copolymers of acrylics and nonpolar monomers are desired for their potential amphiphilic properties.[6] However, the control necessary to produce well-defined poly(meth)acrylates has been an elusive goal. It is only relatively recently--with the advent of such techniques as group transfer polymerization (GTP) and ligated anionic polymerzation--that special-architecture poly(meth)acrylates such as stars, blocks, and telechelics have been widely prepared and studied.[7]

In 1992, Yasuda found that organolanthanide complexes of the type Cp*$_2$Sm-R (where Cp* = C$_5$Me$_5$ and R = hydride, alkyl, alkylaluminum) function as initiators for the highly syndiotactic, living polymerization of methacrylates.[8-13] Well-controlled polymerizations and block copolymerizations of acrylates, lactones and ethylene by these compounds were also reported.[6,10-16] We have a general interest in controlling polymer architecture through living, bisinitiated transition metal polymerization,[17-19] and report herein an unusual, facile organometallic electron transfer process for the *in situ* generation of bimetallic lanthanide(III) initiators for (meth)acrylate polymerization. This method is particularly advantageous for the synthesis of all-acrylic triblocks, including materials which may be selectively deprotected at the ester site to give syndiotactic ester-acid block copolymers. An initial report of this work has appeared previously.[20]

Samarium Electron Transfer Reagents

Electron-transfer catalysts present the most expedient route into bifunctional polymerization. Forming a bisinitiator *in situ* eliminates the necessity of preparing, isolating, and storing a preformed catalyst, a significant advantage when working with highly sensitive species. Additionally, contaminants in the polymerization solvent or monomer have a smaller effect. When added to a preformed bisinitiator prior to the addition of monomer, solvent impurities will form monoinitiaing species by deactivation of one of the two active centers; when solvent is added to an electron transfer initiator this does not occur, since the bisinitiating species has yet to be formed. Contaminants in the monomer, obviously, can continue to cause termination during propagation; however, a portion of any impurities will also react with the electron transfer agent itself and the effects of termination will be lessened.

Our initial studies of bisinitiated organolanthanide polymerization concerned the synthesis of "link-functionalized" polymers, for which preformed Cp*$_2$Sm-R-SmCp*$_2$ initiators were used.[19,21] Given the above considerations and the fact that Cp*$_2$Sm(III) complexes are extremely sensitive to air and water, we wished to develop bimetallic catalysts which could be prepared *in situ*. This goal seemed possible due to the existence of suitable precursors--the samarium(II) complex Cp*$_2$Sm (decamethylsamarocene, **1**)[22] and its tetrahydrofuran disolvate, Cp*$_2$Sm(THF)$_2$ (**2**)[23]--to act as an electron transfer agents.



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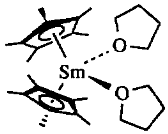

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Unlike most lanthanides, which are only stable in the [Xe] +3 oxidation state, samarium, ytterbium, and europium also exhibit metastable +2 oxidation states due to favorable shell configurations.[24] The Sm(II) species is highly reactive, with an E_0^{aq} (Sm^{3+}/Sm^{2+}) of -1.55 V.[25] For this reason, samarium(II) reagents such as SmI$_2$(THF)$_2$ have found great utility in organic synthesis as one-electron reducing agents.[24,26,27] The reaction of unsaturated substrates (N$_2$, alkenes, alkynes, aromatics, azines, azo complexes) with **1** and its THF disolvate **2** is even more interesting. Two-electron reduction of these functionalities occurs through bimetallic, 2 x 1-electron transfer from two molecules of decamethylsamarocene, giving a complex containing two trivalent Cp*$_2$Sm(III) centers linked by the doubly reduced substrate.[28-32]

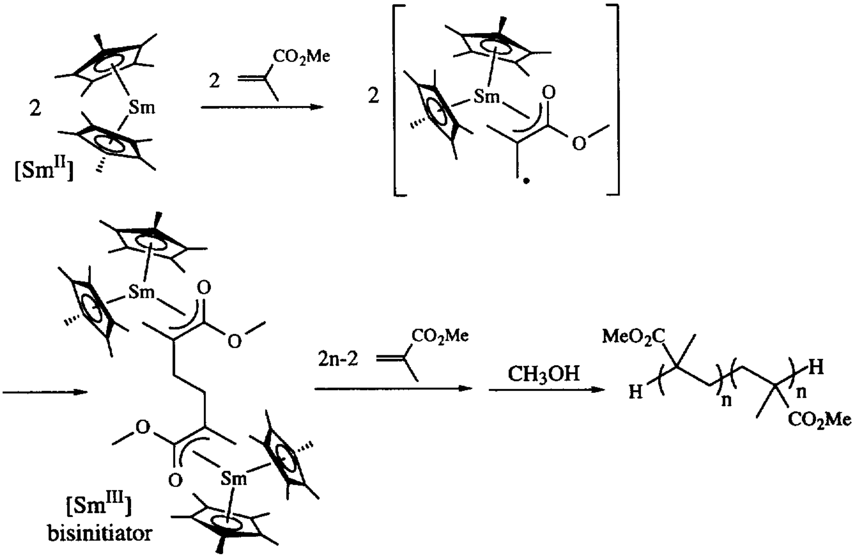
In cases where the substrate is reluctant to bear two negative charges (or in some cases, at a 1:1 Sm(II) : substrate ratio) a second mechanism occurs. The singly reduced radical anions formed by the first electron transfer step couple together to form a bimetallic complex in which the dimerized unit serves as the linking moiety. Phosphaalkynes, dienes, acridine, 1,2-bis(2-pyridyl)ethylene, benzalazine, and pyridazine react with decamethylsamarocenes in this manner.[29,31,33,34] The coupling process is typically fast and clean, and is thought to be facilitated by the protective steric hindrance of the four C_5Me_5 rings.[35] This reductive dimerization parallels the formation of styryl dianion from sodium naphthalide during electron-transfer initation, and has the potential to be used in the same capacity to initiate bimetallic polymerization if the reduced moitey is polymerizable and present in excess.

Methyl Methacrylate

During the course of lanthanide(III) polymerization investigations, Yasuda noted that lanthanide(II) complexes such as $Cp^*_2Yb(THF)_{1-3}$, $Cp^*_2Sm(THF)_2$, and $(indenyl)_2Yb(THF)_2$ possessed the ability to initiate polymerization of methyl methacrylate (MMA).[9,12] These complexes showed the same degree of living behavior as lanthanide(III) catalysts, as evidenced by high polymer yield and syndiotacticity, low polydispersity ($\approx$ 1.1), and a linear relationship between molecular weight and conversion for $Cp^*_2Yb(THF)$. However, extremely low initiator efficiencies (< 40%) were observed. Yasuda concluded that initiation with lanthanide(II) complexes proceeded through the adventitious formation of samarium(III) hydride species. Since lower efficiencies were obtained for $Cp^*_2Yb(THF)$ at higher monomer to initiator ratios, it was also concluded that contamination by water and air was also a factor in nonquantitative initiation. However, further monomer purification did not raise efficiencies past 40%.[9]

Reexamination of this process, in light of the tendency of Cp^*_2Sm complexes to reductively couple unsaturated molecules, led us to believe that initiation with this complex actually occurs through reductive dimerization of MMA to form a *bisinitiator*, comprising two samarium(III) enolates joined through their double bond termini (Scheme 1).

Scheme 1



Because the two polymerizing centers are linked the resultant PMMA has a molecular weight twice that predicted from the monomer to initiator ratio, and initiation appears to be at most 50% efficient. Known trends for both (meth)acrylates and samarium(II) reagents support this conclusion. MMA may be polymerized by electron transfer from sodium naphthalide,[36] and reductive dimerizations of methacrylates by Me_3SiCl / Li / THF[37] and substituted (meth)acrylates by Me_3SiCl / Mg / hexamethylphosphoramide[38] to give linked silyl enolates are known. Monometallic reduction of ethyl cinnamate by SmI_2 occurs exclusively at the conjugated double bond in a similar manner.[27] Very recently, Evans has used field desorption mass spectrometry to show that the polymerization of ethylene with **1** proceeds through bimetallic reduction to a bisinitiator.[39,40]

As previously reported, we monitored the molecular weight of PMMA produced with **2** as a function of the monomer to initiator (M : I) ratio in THF at -78 °C as evidence for the existence of a reductive dimerization mechanism (Figure 1).[20]

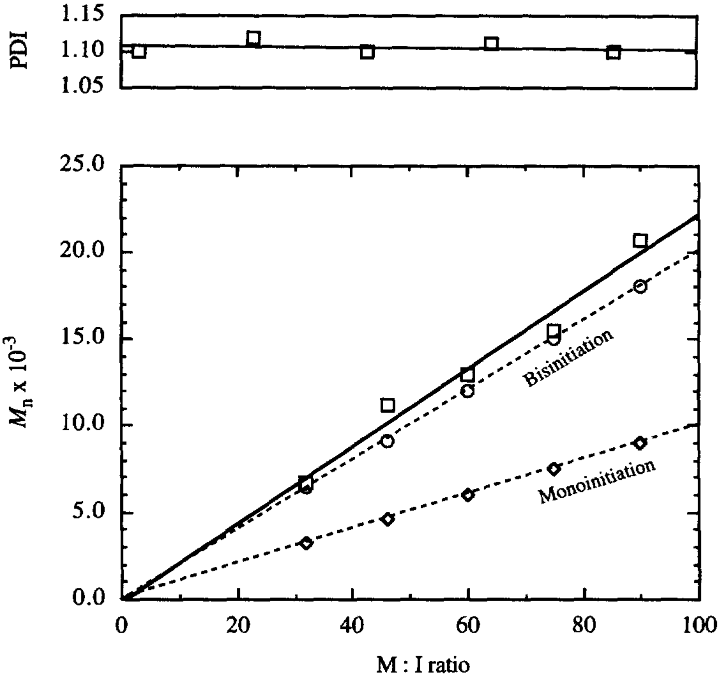
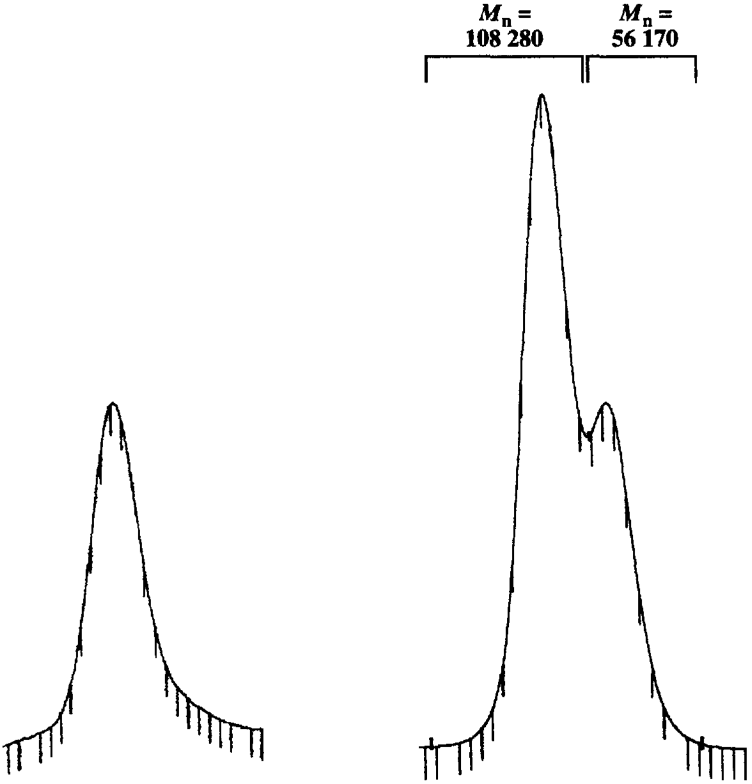


Figure 1. Polydispersity and molecular weight vs. monomer to initiator ratio for the polymerization of MMA with **2**.

Moderate rather than high M : I ratios were chosen to minimize any termination by monomer impurities. Under these conditions, it can be seen that the M_n values obtained by polymerization with **2** approach twice the values calculated from the M : I ratio, as expected for a linked, bisinitiated polymerization. Actual initiator efficiencies for this system are thus as high as 96% and parallel those seen for lanthanide(III) initiators.[9] We did not observe an inverse relationship between efficiency and monomer to initiator ratio. Additionally, the linearity of this relationship and the lack of increase in PDI with M : I ratio demonstrate a lack of chain transfer during polymerization.[41]

Polymerizations may also be carried out at 0 °C, with unsolvated **1**, or with **2** in toluene; however, THF provides the best control (monomer addition at room temperature causes some inflation of molecular weights from calculated values). In all cases polymer yields are over 90% and the resultant PMMA has high syndiotacticity and low polydispersity, although higher monomer to initiator ratios are more susceptible to small amounts of termination from impurities. Both catalysts--especially coordinatively unsaturated **1**--tend to undergo oxidation upon storage to bridged oxide species,[42] and should be freshly prepared before polym-erization. Additionally, we found the use of syringes and rubber septa during monomer and solvent addition to be problematic; when possible, vacuum transfer of reagents through an all-glass apparatus is preferred.

We were able to exploit the atmospheric sensitivity of samarocene reagents to obtain further evidence for a bisinitiated polymerization mechanism. Figure 2 shows the GPC traces of two samples of PMMA, both prepared in THF at -78 °C. Sample (a) was synthesized with meticulous exclusion of air and water while sample (b) was less carefully prepared. The molecular weight distribution of (b) exhibits a second peak at lower molecular weight, indicating the presence of two active species during polymerization. The M_n of this peak is approximately half that of the main peak, consistent with the presence of monoinitiators formed by the adventitious termination of bisinitiating species at one chain end.



(a)
No contamination
(M_n = 11 990, Figure 2.4)

(b)
Atmospheric contamination

Figure 2. Consequences of monoinitiator contamination for the molecular weight distribution of PMMA prepared with **2**.

To further show that a linked bisinitiator is present during initiation, we attempted to isolate the species formed from equimolar reaction of MMA with **2** in THF. Unfortunately, the high solubility and extreme sensitivity of samarium(III) enolates prevented this task.[43] Carrying out the reaction with unsolvated **1** in toluene did not produce a less soluble product, and attempts to obtain a more crystalline species by substituting phenyl or trityl methacrylate for MMA were unsuccessful as well. We did observe that the crude ^{1}H NMR spectrum (400 MHz, d_8-THF) of the product from **1** and MMA showed two overlapping C_5Me_5 resonances at 1.73 and 1.70, a typical pattern for many bimetallic samarium(III) complexes.[34,44] The paramagnetism of Sm(III) precludes shift predictions for the other expected resonances,[45] but large, broad absorptions were seen at 3.19, 1.29, and 1.02 ppm, consistent with a tail-to-tail MMA dimer structure having symmetrical $-OCH_3$, $-CH_3$, and $-CH_2-$ groups. One-pulse integration gave an area ratio of approximately 60:4 for the C_5Me_5 resonances and the resonance at 1.29 ppm, as would be expected if the latter peak arose from the interior $-\underline{CH_2}-$ protons.

Yasuda has analyzed the hydrolysis products of $Cp^*_2Yb(THF)_2$ reacted with MMA in ratios of 1:1 and 2:1.[9,12] With this reagent only complex mixtures of products were obtained, with one component being a head-to-tail dimer (30-35%). Given that ytterbium(II) is a much weaker reducing agent than samarium(II)[46] and does not tend to form bimetallic complexes to the same extent, this observation is not surprising.

Other Methacrylates and Acrylates

To confirm that *in situ* formation of a bisinitiator with **1** and **2** would be useful for the synthesis of triblocks, the polymerization of higher methacrylates and acrylates was investigated (Table 1).

Table 1. Polymerization of higher methacrylates and acrylates with **1** and **2**.

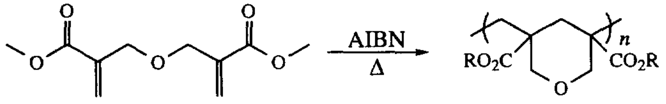
Monomer	Catalyst	Conditions	Yield (%)	M_n (GPC)	PDI (GPC)
n-hexyl methacrylate	1	0 °C toluene	n/a[a]	13 370[b]	1.17[b]
benzyl methacrylate	2	-78 °C THF	99	21 800[c]	1.25[c]
phenyl methacrylate	1	RT toluene	trace	---	---
trityl methacrylate	2	RT THF	0	---	---
trimethylsilyl methacrylate	2	0 °C THF	0	---	---
ethyl acrylate	1	-78 °C toluene	n/a[a]	42 320[c]	1.12[c]
tert-butyl acrylate	1	RT THF	39[a]	430 820[d]	1.37[d]
methyl hydroxymethyl-acrylate ether (**I**)	2	RT THF / toluene	0	---	---

[a] Not determined or low due to adhesive properties of the polymer. [b] $CHCl_3$, vs. PMMA. [c] THF, vs. polystyrene. [d] $CHCl_3$, vs. polystyrene.

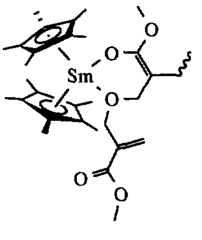
Differences in hydrodynamic properties between these polymers and those used for gel permeation chromatography (GPC) standards (PMMA or polystyrene) preclude rigorous comparisons of calculated and observed molecular weights.[47] However, it can be seen that benzyl methacrylate (BzMA), *n*-hexyl methacrylate (HMA), ethyl acrylate (EA), and *tert*-butyl acrylate (*t*BuA) are polymerized with good control (PDI = 1.12-1.37). The methodological constraints seen for MMA are operative for these polymers as well; the use of Schlenk syringe techniques gave in two cases molecular weight distributions containing a small, low-M_n shoulder. Again, this offers proof that a bisinitiator is indeed formed during polymerization.

In contrast to benzyl methacrylate, phenyl and triphenylmethyl (trityl) methacrylate were not polymerized, although a color change to yellow indicating the formation of a samarium(III) species was observed.[48] Trimethylsilyl methacrylate showed similar behavior (the color change occurred slowly over a five minute period in this case). Both trityl and trimethylsilyl methacrylate may be polymerized anionically,[49,50] illustrating the unique requirements of the $Cp^*{}_2$-ligated samarium coordination sphere. As Yasuda has successfully carried out the polymerization of isopropyl and *tert*-butyl methacrylates with $[Cp^*{}_2SmH]_2$,[9] electronic rather than steric effects may be advanced as an explanation for this phenomenon. However, the huge size of the triphenylmethyl group is undoubtedly a factor.[51]

Diacrylate ether **I** also did not polymerize. This monomer undergoes exclusive cyclopolymerization with radical or GTP initiators in dilute solution, giving a macromolecule with a pyran-type backbone (Equation 1).[52,53] The formation of a yellow samarium(III) species was again seen upon addition of **I** to **2** in either THF or toluene; however, ^1H NMR analysis of the reaction products revealed only monomer. To determine if the electron transfer / dimerization step was problematic a preformed samarium(III) initiator, the allyl complex $Cp^*{}_2Sm(\eta^3\text{-}CH_2CHCH_2)$ (**3**),[34] was tested in toluene. Again, no polymer was obtained. A random copolymerization of **I** and MMA with **2** (1:1 feed ratio) was also unsuccessful; in fact, not even homo-PMMA was produced. These observations suggest that the samarium(III) enolate of **I** is indeed formed, but is not reactive enough to undergo the Michael addition necessary for propagation. A possible explanation for this phenomenon is stabilization of the enolate by coordination of the ether oxygen to the samarium center:



(1)



This would result in the formation of a six-membered ring, which for entropic reasons would effectively shut down any further coordination of monomer, preventing polymerization.[54]

The polymers obtained were characterized by ^{1}H NMR, ^{13}C{^{1}H} NMR, IR, DSC, and TGA. In addition to PMMA, poly(benzyl) methacrylate (PBzMA) and poly(*n*-hexyl) methacrylate (PHMA) showed high degrees of syndiotacticity. The methyl and methylene regions of the ^{1}H NMR spectra of these polymers prepared with **1** / **2** are consistant with the formation of highly syndiotactic PMMA.[55] The ^{13}C{^{1}H} NMR spectra were also indicative of high syndiotacticity. Carbon spectra of heterotactic polymethacrylates typically contain many peaks in the $\underline{C}$=O, -$\underline{C}H_2$-, -$\underline{C}$C=O, and -$\underline{C}H_3$ regions; however, many of the literature peaks reported for less stereoregular PMMA, PBzMA, and PHMA were minor or absent altogether from the spectra of the polymers prepared with **1** / **2**.

Thermal gravimetric analysis (TGA) of the methacrylate polymers showed smooth, near-quantitative decomposition between 285-402 °C, characteristic of main-chain scission to give ≈ 100 % monomer (Table 2).[56]

Table 2. Thermolysis of methacrylate polymers prepared with **1** and **2**.

Polymer	Decomposition Onset (°C)	Decomposition End (°C)	Mass Loss (%)
PMMA	359	402	> 95
PBzMA	346	378	98
PHMA	285	382	98

The onset of decomposition for PMMA was near literature values for anionically prepared samples,[57] indicating a similarly lower content of sterically unstable head-to-head linkages[58,59] as compared to radically polymerized PMMA (onset ≤ 300 °C[60,61]). The decomposition of PHMA began nearly 75 degrees lower than that of PMMA, consistent with the trends for thermolysis of linear methacrylates (C_1-C_5) seen by Crawford.[62] PBzMA underwent onset of decomposition only slightly lower then PMMA itself. Further characterization of PMMA was carried out with differential scanning calorimetry (DSC). Its glass transition temperature as determined by this technique was approximately 128 °C, again indicative of high syndiotacticity.[63]

All-Acrylic Triblock Copolymers

Using monometallic Cp*$_2$Sm(III) hydride and alkyl initiators, Yasuda and coworkers have successfully prepared high molecular weight, highly syndiotactic monodisperse diblocks and triblocks of MMA and higher (meth)acrylates.[9,11,14] Poly(MMA-*b*-*n*-butyl acrylate-*b*-MMA) triblocks exhibited thermoelastic properties such as 163% elongation and an Izod impact strength of 400 J m^{-1} at a composition ratio of 8:72:20. An ABC poly(MMA-*b*-ethyl acrylate-*b*-ethyl methacrylate) copolymer showed an elongation of 276%. While these values do not approach that of Kraton SBS rubber[64] (elongations near 1000%), it is clear that further optimization of the block components and lengths of all-acrylic triblock copolymers prepared by lanthanide initiators may produce extremely useful materials.

The utility of a samarium(III) bisinitiator formed *in situ* from monomer for producing even more well-defined triblock copolymers is evident, not only for reasons of sensitivity--contamination by as little as 2% of diblock species can adversely affect the mechanical properties of triblock elastomers[65]--but because of symmetry. For most elastomers, the useful composition range of the outer "hard" blocks is very small (≤ 10% per block);

changes in modulus have been seen between triblock methacrylate ionomers containing outer segments differing by only 1% by weight.[66] Thus, elimination of the small amounts of asymmetry resulting from the necessity of two separate "A" monomer addition steps in monometallic polymerization[67] is a significant improvement. The propagating enolate groups in samarium(III) acrylate polymerization are less robust than the propagating methacrylate enolates, a concern for the incorporation of acrylate monomers into triblock structures;[13,14] elimination of one addition step through the use of a bimetallic initiator should also serve to minimize this problem.

We thus utilized **1** and **2** to prepare methacrylate-(meth)acrylate triblock copolymers via *in situ* initiator formation. Structures incorporating MMA and both higher methacrylates and acrylates as exterior or interior segments were successfully prepared (Table 3).

Table 3. (Meth)acrylic ABA triblock copolymers prepared with **1** and **2**.

Block A	Block B	Composition (A:B, wt %)[a]	Initiator	Yield	M_n (GPC)	PDI (GPC)
Benzyl MA	MMA	50:50	**2**	100	60 860[c]	1.15[c,d]
MMA	Hexyl MA	53:47	**2**	83[b]	31 960[e]	1.16[e]
MMA	Hexyl MA	77:23	**1**	84[b]	70 810[e]	1.12[e]
Ethyl AC	MMA	49:51	**1**	88	60 540[c]	1.27[c]
MMA	*t*-Butyl AC	54:46	**2**	72	76 490[c]	1.10[c,d]

[a] By ^1H NMR. Equal weight compositions were chosen for ease of characterization. [b] After a second reprecipitation; crude yield was higher. [c] THF, vs. polystyrene. [d] GPC / LS PDI = 1.01. [e] $CHCl_3$, vs. PMMA.

Low polydispersities and high yields were obtained in all cases with the exception of highly soluble poly(MMA-*t*BuA-MMA) (**II**), which was isolated in 72% yield due to loss during precipitation. It should be noted that previous attempts to synthesize poly(ethyl acrylate-*b*-MMA-*b*-ethyl acrylate) anionically have failed.[68] The potential for preparing elastomeric materials can be seen in the successful preparation of triblocks incorporating PHMA (T_g = -5 °C) and PEA (T_g = -24 °C).[69]

As with homopolymerization, the best results were again obtained under the most scrupulously air-free conditions. Small low-M_n shoulders were observed in the molecular weight distributions of PHMA-PMMA and PEA-PMMA copolymers prepared with syringe techniques. However, a PBzMA-PMMA triblock (**III**) synthesized by sequential vacuum transfer and glove box monomer addition was rigorously monomodal by GPC.[70] For the larger MMA-HMA triblock, the absence of PHMA homopolymer was confirmed by comparing its GPC trace to that of a representative homopolymer prepared at a similar monomer to initiator ratio. The distribution contained no material eluting at the retention time of the homopolymer peak, which was in this case adequately resolved from the main triblock peak. The M_n and PDI of the smaller triblock were roughly additive to those of representative homopolymers, as were those for PEA-PMMA-PEA.[71]

Tandem GPC / light scattering (GPC / LS) was used to further confirm the well-defined nature of the benzyl methacrylate-MMA copolymer, as the resolution of diblock from triblock species is not always possible with GPC chromatography alone.[72,73] Using this tandem technique, no significant decrease in molecular weight was seen in the high elution volume portion of the distribution, indicating the absence of unresolvable diblock copolymer in this region. The polydispersity of the triblock copolymer as determined by GPC / LS was 1.01.

The achievement of controlled monomer crossover between methacrylates, and from methacrylate to acrylate, was expected. However, we were surprised at the extent of advantage conferred by the bisinitiating system for crossover from acrylate to methacrylate. During the synthesis of MMA-*n*-butyl acrylate-MMA triblock copolymers with $(C_5Me_5)_2SmMe(THF)$, Yasuda noted that partial deactivation of the active acrylate chain end prior to or during addition of the second aliquot of MMA resulted in significant amounts of diblock copolymer formation.[14] This occurred even if only two minutes were allowed to pass between complete acrylate consumption and MMA addition. In THF, the percentage of diblock present was 17%; when toluene was used as solvent, fully half of the polymer sample became deactivated to give diblock copolymer. Satisfactory triblocks were obtained by exploiting the different reactivity ratios of MMA and *n*-butyl acrylate and adding both monomers at once during the second addition step.

The preparation of poly(MMA-*t*BuA-MMA) with **2**, in contrast, proceeded in a much improved manner. After vacuum transfer addition of *tert*-butyl acrylate to the catalyst in THF at 0 °C, 3.5 hours were allowed to lapse before the addition of MMA. The triblock so formed was isolated in 72% yield by precipitation from chloroform into hexanes and exhibited the same monomodality and low polydispersity (1.01 by GPC / LS) as the benzyl methacrylate-MMA triblock. We did observe a small portion of diblock in the fraction of polymer remaining in the supernatant, indicating that deactivation cannot be completely avoided. However, hexane precipitation of the triblock was apparently completely adequate for removal of this material.

All copolymers possessed ^1H NMR, $^{13}C\{^1H\}$ NMR, and IR spectra additive from homopolymer spectra, and showed compositional analyses close to feed ratio values as determined by ^1H NMR integration. Elemental analyses of the benzyl methacrylate-MMA and *tert*-butyl acrylate-MMA copolymers were also in close agreement with predicted values. The triblocks exhibited solubility behavior intermediate between their constituent homopolymers (Table 4).

Table 4. Solubility properties of MMA-HMA and MMA-EA triblock copolymers.

Solvent	PMMA	PHMA	M-H-M Triblock[a]	PMMA	PEA	E-M-E Triblock
Isopropanol, 40 °C	No	Yes	Yes	---	---	---
Hexanes, RT	No	Yes	No	---	---	---
Methanol, RT	No	Yes	No	No	Yes	Slightly
Methanol, 65 °C	---	---	---	No	Yes	Yes

[a] Polymer of M_n = 31 960.

By TGA, the methacrylic triblocks show smooth, near-quantitative decomposition at similar temperatures to their components (Table 5), while MMA-*t*BuA-MMA undergoes a multistage process in which the *tert*-butyl block decomposes first (Figure 3).[74,75] As is characteristic of polyacrylates, which undergo more complicated thermolysis than polymethacrylates,[56] a moderate amount of nonvolatile char was obtained.

Table 5. Thermolysis of methacrylate triblock copolymers.

Polymer	Decomposition onset (°C)	Decomposition end (°C)	Mass loss (%)
PBzMA-PMMA-PBzMA	325	373	97
PMMA-PHMA-PMMA[a]	323	390	96

[a] Polymer of M_n = 70 810.

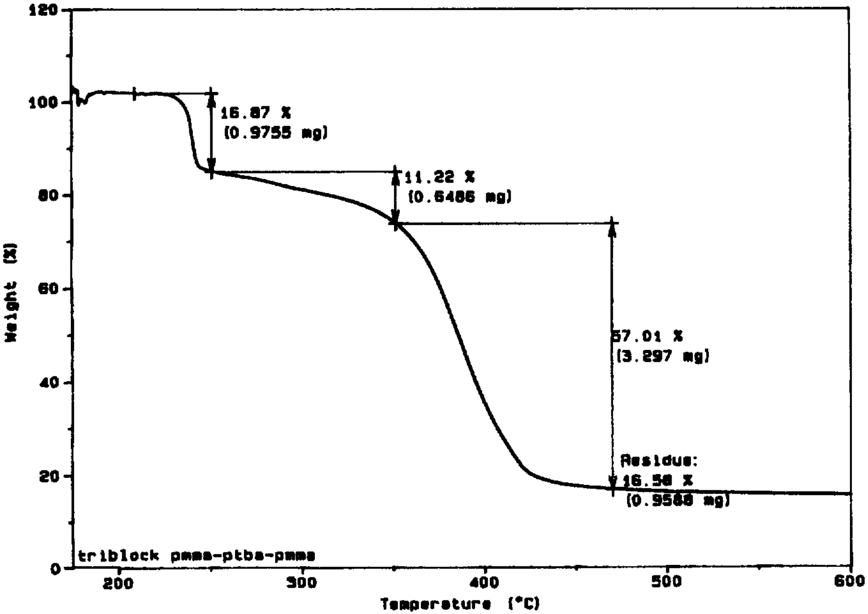


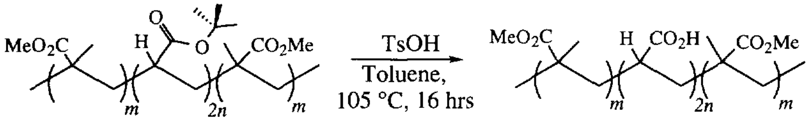
Figure 3. Thermolysis of PMMA-PtBA-PMMA: (a) Cleavage of t-butyl side chains to poly(acrylic acid); theoretical mass loss as isobutylene 20.6%. (b) Formation of poly(acrylic anhydride) with loss of H_2O; decarboxylation. (c) Chain scission of PMMA; theoretical mass loss as MMA 54.0%. (d) Nonvolatile poly(acrylate) residue.

Syndiotactic Acid-Ester Copolymers by Selective Side Chain Cleavage

In the last several years, McGrath and coworkers have shown that all-methacrylic block copolymers with acid or ionomeric segments exhibit a number of interesting properties.[66,76,77] In particular, blocks composed of an ester segment and a segment of either methacrylic acid (MA) or its alkali salts undergo phase separation much easier than all-ester copolymers. This is a result of greater dissimilarity between the block constituents and results in "more cohesive domains" and "greater network stability,"[66] both of which are adventitious for thermoplastic behavior. Since poly(methacrylic acid) (PMA) cannot be prepared by anionic initiation, these copolymers are synthesized by selective cleavage of one ester sidechain of an ester-ester copolymer. The most commonly used precursor for this process is poly(*tert*-butyl methacrylate) (P*t*BMA), since its *t*-butyl groups are easily removed as isobutylene using catalytic amounts of a strong acid.[78,79]

McGrath has noted that the use of dilithium initiators in hydrocarbon solvents produces highly isotactic P*t*BMA.[80] Since the polymer backbone is not affected by acid-catalyzed hydrolysis, cleavage of the ester offers a route into acid and ionomeric polymers also having this microstructure. We were thus interested in synthesizing highly *syndiotactic* ester-acid copolymers, available from ester-ester triblocks prepared with decamethylsamarocene catalysts. Due to the highly directing nature of the Cp*$_2$Sm(III) propagating group, all methacrylate segments in these materials--not just those derived from the bulky *t*-butyl blocks--will be highly tactic. Syndiotactic methacrylates show much higher glass transition temperatures than their iso- or atactic analogues,[69] and syndiotactic PMA is more resistant to thermolysis than isotactic PMA.[81,82] Thus, such materials may represent the most useful forms of methacrylic ester / acid block copolymers.

As an initial investigation, the synthesis of an ester-acid triblock copolymer from **II** was studied. The poly(*tert*-butyl acrylate) segment of **II** does not possess high syndiotacticity, but we wished to show that selective sidechain cleavage methodology could be extended to polyacrylates. Additionally, we desired to prepare a hydrophilic / hydrophobic acrylic triblock containing an *inner* acid segment, since only materials with the reverse architecture have been studied. The method of McGrath for the deprotection of P*t*BMA involves treatment of the polymer with catalytic *p*-toluenesulfonic acid monohydrate at elevated temperatures, eliminating the *tert*-butyl group as isobutylene.[78,79] Reaction of **II** under these conditions gave the desired poly(acrylic acid) (PAA) copolymer, PMMA-PAA-PMMA (**IV**) (Equation 2).[83]



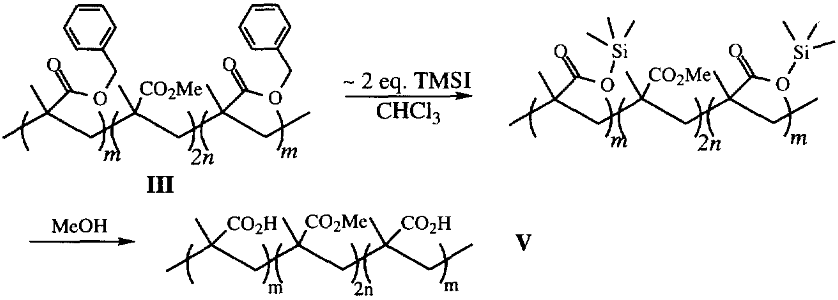
(2)

II **IV**

To prepare a rigorously syndiotactic acid-ester triblock having acid outer segments, we next employed a strategy of selective cleavage of the benzyl ester groups in **III**. Benzyl esters are a commonly used protecting group in organic synthesis[84] and may be removed by reaction with trimethylsilyl iodide (TMSI).[85,86] This process gives a trimethylsilyl ester, which is quantitatively cleaved to an acid functionality by protolysis. The selective TMSI deprotection of benzyl esters and ethers has recently been used to prepare polycyclobutenes containing alcohol and carboxylic acid side chains.[87]

Clean production of PMA-PMMA-PMA (**V**) was accomplished by treatment of **III** with approximately 2 equivalents of TMSI followed by protolysis with methanol (Scheme 2). Over 99.77% of the initial benzyl groups were removed as quantified by ^{1}H NMR, while the methyl ester groups remained intact.[88]

Scheme 2



III

V

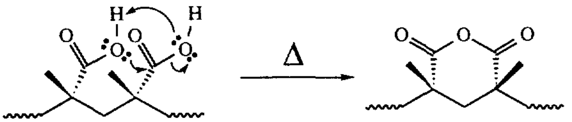
Both acid copolymers possessed spectra and behavior consistent with their predicted structures. Along with the ^1H NMR spectra, the $^{13}C\{^1H\}$ NMR spectra of the copolymers in CD_2Cl_2 and 1:3 CD_2Cl_2 / CD_3OD, respectively, also showed the complete disappearance of P*t*BuA or PBzMA peaks. However, new resonances corresponding to the deprotected acid copolymers were not present. This was somewhat expected, since the hydrophilic acid segments of these materials are likely to be "frozen out" as micelles under these conditions (*vide infra*).[78,79] Confirmation of the acid structures was easily seen by FTIR; both **IV** and **V** exhibited characteristic broad, strong O-H stretches above 3000 cm^{-1}. The disappearance of appropriate precursor absorbances, such as sp^2 C-H stretches for the debenzylated polymer, was also seen. By DSC, triblock **O** showed a typical homo-PMMA T_g of 125 °C, suggestive of phase separation. An analogous T_g for the PAA segment (reported as 106 °C)[69] was not located, however.

The loss of mass from copolymer **V** was observed by GPC chromatography. Analysis of the acid polymer gave M_n = 33 070 and PDI = 1.05, as compared to M_n = 60 860 and PDI = 1.15 for precursor **III**.[89] This 46% apparent mass loss is larger than the calculated value for the loss of the benzyl esters (26%); the extra decrease represents a change in hydrodynamic volume. This "shrinking" is also evidenced by the narrower PDI of the acid copolymer.[90]

Both triblocks showed solubility properties characteristic of hydrophilic / hydrophobic materials. Polymer **V** was soluble in THF and DMSO, slightly soluble in methanol, and insoluble in diethyl ether and hexanes. Unlike precursor **III**, it could only be dissolved in less-polar solvents such as toluene, methylene chloride, and chloroform when small amounts of a protic cosolvent (i.e. methanol) were added. This behavior has been previously documented for poly(methacrylic acid) triblocks with PHMA inner segments, and is attributed to solution aggregation through interchain hydrogen bonding of the outer acid blocks.[78,79] Polymer **IV**, with an interior rather than exterior acid block, showed additional solubility in toluene, acetone, dioxane, $CHCl_3$, and CH_2Cl_2; however, the use of a polar / protic cosolvent with toluene or chloroform was advantageous.

By TGA, a characteristic two-stage decomposition process was evident for the acid copolymers: slow formation of cyclic polyanhydrides with loss of water at 200-380 °C,[91] followed by main chain scission at 380-425 °C.[56] Additional mass loss due to PAA decarboxylation during the earlier period was seen for **IV**.[92] The increased chain scission onset and end temperatures of **IV** and **V** as compared to their precursors (end $\geq$ 390 °C) are indicative of the formation of polyanhydrides.[60] Again, a higher degree of nonvolatile char ($\approx$ 10%) was seen for polyacrylate copolymer **IV**. For comparison, a radically polymerized sample of poly(acrylic acid)[93] analyzed identically to **IV** underwent gradual decomposition from 206-457 °C to 13% char.

An advantage of these highly syndiotactic acid copolymers, improved heat resistance, may be seen in the thermolysis behavior of **V**. The formation of cyclic polyanhydrides is facilitated by an isotactic mictrostructure due to a favorable "same-side" conformation of the reacting neighboring acid units (Equation 3).[81,82]



+ H_2O (3)

A less favorable conformation, in which the reacting units are on opposite sides of the polymer chain, is achieved with syndiotactic PMA. Comparison of the thermolysis curve of **V** to the curve of radically polymerized, atactic PMA obtained by Jamieson and McNeill[60] under similar conditions shows a more gradual rate of anhydride formation for **V** in the 200-250 °C region. This observation is consistant with a highly syndiotactic structure of **V**.

Conclusions

Through the unusual one-electron transfer capabilities of divalent samarium, a lanthanide(III) polymerization system which generates a bisinitiating catalyst *in situ* from a (meth)acrylate monomer and decamethylsamarocene has been developed. This system is living and produces monodisperse, highly syndiotactic polymers in quantitative yield. Initiation with decamethylsamarocene parallels anionic electron-transfer initiation and simplifies concerns of storage and purity for air-sensitive $Cp^*{}_2Sm(III)$ reagents. *In situ* bisinitiator formation is successful for methyl methacrylate and a number of higher methacrylates and acrylates, although aromatic and extremely bulky methacrylates do not undergo polymerization.

Using this procedure, ABA triblock copolymers containing both methacrylate and acrylate segments may be synthesized in only two monomer addition steps. Controlled monomer crossover is achieved from both methacrylate to acrylate and vice-versa, giving monodisperse, well-defined materials. Structures incorporating elastomeric, low T_g blocks were successfully prepared, demonstrating the potential of this method for the preparation of acrylic-based thermoplastic elastomers. Materials incorporating cleavable sidechains were also synthesized; selective deprotection of these groups leads to copolymers containing syndiotactic acrylic or methacrylic acid segments which exhibit improved heat stability and hydrophilic / hydrophobic behavior.

Experimental Section

General Procedures and Characterizations

All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of prepurified argon using standard Schlenk techniques. Unless specified otherwise, solvents were removed under Schlenk line vacuum (approximately 0.01 Torr) rather than with a rotary evaporator. Drybox manipulations were performed under argon or nitrogen in a Vacuum Atmospheres HE-432 Dri-Lab equipped with an HE-493 Dri-Train or in a Braun Labmaster 100 drybox equipped with a Labmaster MB130 B-G Inert Gas System and an integrated SPS water-oxygen analyzer. ^1H NMR spectra were obtained at 200 and 400 MHz with Bruker AM-200 and AM-400 FT NMR spectrometers and are referenced to residual solvent proton peaks. $^{13}C\{^1H\}$ proton decoupled NMR spectra were measured at 125 MHz on the Bruker AM-500 spectrometer or at 75 MHz on a Bruker MSL-300 spectrometer are referenced to solvent carbon peaks. Minor tacticity resonances (see text) are noted; major resonances bear carbon assignments. Infrared spectra were obtained using a Perkin-Elmer 1600 Series FTIR spectrometer as KBr pellets, thin films on NaCl disks, or neat samples between NaCl disks as indicated and are uncalibrated. Elemental analyses were performed on a Control Equipment Model 240XA elemental analyzer at the Microanalytical Laboratory Research Services, Graduate School, University of Massachusetts, Amherst. Column chromatography was carried out with J. T. Baker 40-140 mesh silica gel.

Polymer Characterizations

Gel permeation chromatography (GPC) was performed on a Hewlett-Packard 1050 Series liquid chromatograph pump equipped with an HP model 1047 refractive index detector and a Hewlett-Packard model 3396A integrator. Chloroform or THF was used as the mobile phase with a flow rate of 1 mL / minute and samples were prepared as 1-2% polymer (w/v) and passed through 0.2 µm filters before injection. Separations were affected by 10^5 Å, 10^4 Å, 10^3 Å, and 500 Å Waters Ultrastyragel or Pacific Column Permagel columns run in series (an additional 10^6 Å column was used in some cases). Molecular weights were calibrated to narrow molecular weight polystyrene standards (M_n = 700 - 556 000) or poly(methyl methacrylate) (PMMA) standards (M_n = 16 200 - 164 700) purchased from Scientific Polymer Products. Tandem GPC / LS experiments were carried out in THF at 25 °C (flow rate = 1 mL / minute) using an HP 1050 Series Liquid Chromatograph pump equipped with a Wyatt / Optilab model 903 interferometric refractometer and an 18-angle Wyatt Dawn DSP-F laser photometer operating at 633 nm. GPC / LS data were analyzed using Wyatt ASTRA 1.2 or 1.4 software. Separations were affected and samples were prepared as described above. Polydispersity values for triblock copolymers were calculated by mass recovery (absolute M_n and M_w values calculated by this method are not highly accurate, but their numerical ratio is not affected). Differential Scanning Calorimetry (DSC) was peformed on a Perkin-Elmer 7 Series Thermal Analysis System equipped with a PE 7700 DSC using a temperature range of -50 °C to 200-300 °C. Thermogravimetric analysis (TGA) was carried out using a DuPont Thermal Analyst 2000 System equipped with a DuPont 2950 Thermogravimetric Analyzer from ambient temperature to 500-600 °C. In both cases measurements were made under a nitrogen flow at 10 °C / minute on 5-15 mg of polymer. Polymer samples (with the exception of **IV** and **V**) were prepared for thermal analysis by lyophilization from benzene.

Reagents

Unless indicated, all materials were purchased from commercial suppliers in reagent grade and used without further purification. Tetrahydrofuran (THF), diethyl ether, toluene, hexanes, phthalan, d_6-benzene, d_8-toluene, and d_8-THF used for air-sensitive manipulations were vacuum transferred or distilled under nitrogen from purple sodium benzophenone ketyl and stored in Schlenk solvent pots. Alternately, solvents were passed sequentially through columns of activated alumina (LaRoche A-2) and Q-5 supported copper redox catalyst (Engelhard CU-0226S) under a prepurified nitrogen atmosphere.[94] Ethyl acrylate, *tert*-butyl acrylate, *n*-hexyl methacrylate, and benzyl methacrylate were dried for several days over CaH_2 and vacuum transferred or distilled at reduced pressure into storage tubes. Methyl methacrylate (MMA) was similarly dried and transferred onto fresh CaH_2, over which it was stored, and again transferred immediately before use. All monomers were protected from heat and incident light during drying and stored below 0 °C in darkened containers. Trityl methacrylate (Monomer-Polymer Laboratories) was recrystallized twice from anhydrous diethyl ether at -40 °C.

$Cp^*_2Sm(THF)_2$ (**2**) was prepared from $SmI_2(THF)_2$ and KCp* by the method of Evans[23] and recrystallized from 1:5 THF : hexanes at -35 °C. Alternately, **2** was generated *in situ* immediately prior to polymerization from **1** and THF. $Cp^*_2Sm(\mu\text{-}\eta^3\text{-}CH_2CHCH_2)$ (**3**) was prepared from **1** and propene (dried over CaH_2 at -78 °C for 16 h) by the method of Evans.[34,95] Sodium phenoxide was prepared by NaH deprotonation of phenol in THF at 0 °C and used without further purification. The samarium metal used for the synthesis of these compounds was purchased as -40 mesh spheres (Aldrich) and stored under argon.

Experimental Procedures and Characterizations

Cp^*_2Sm (1). A specifically modified method of Evans[22] was used to prepare this complex. Greenish-purple, partially desolvated **2**[23] (3.31 g) was heated under dynamic vacuum on a Schlenk line (≈ 0.01 Torr) at 73 °C utilizing all-glass connections. A pressure surge to about 0.1 Torr was observed as further desolvation began to occur. The sample of **2** was left at 73 °C under dynamic vacuum overnight, after which the pressure surge had abated. A 0.606 g (1.44 mmol) portion of the solid was placed in a small sublimation apparatus, placed under dynamic vacuum at 73 °C, and *gradually* heated to 110 °C over a period of several hours to minimize further pressure surges from desolvation. [At higher temperatures and pressures, decomposition in addition to sublimation was observed.] At 110 °C, a small amount of purple material, presumably **2** or iodide-containing impurities, collected on the sublimation probe. After four hours green **1** began to collect as well, and the sublimation apparatus was cooled to room temperature. In the drybox, the probe was cleaned with toluene and the apparatus placed under dynamic vacuum at 110 °C for 36 hours. After this period only beige material was left in the bottom of the sublimation apparatus and 0.451 g (74%) **1** was recovered from the probe. Decamethylsamarocene is extremely sensitive to oxidizing agents and coordinating solvents, and should be handled only in a freshly flushed, ether-free drybox. It should also be stored in a flask with a ground glass or Teflon seal rather than in a capped vial. ^{1}H NMR (C_6D_6, 200 MHz): δ 1.74 (br s). Literature (C_6D_6): δ 1.0 to 1.7 (s), dependent on concentration.[96]

General procedure for polymerization and block copolymerization of methacrylates. Three methods were employed as indicated. Typical polymerizations exhibited an immediate color change from that of the catalyst solution to bright yellow upon addition to monomer, and more concentrated polymerizations (higher than approximately 0.5 M in monomer) became viscous or gelled at high conversion.

Schlenk procedure. In the drybox, a 25 or 50 mL Schlenk tube was equipped with a magnetic stirbar. Catalyst (typically 0.002-0.010 mmol, as a solid or aliquot of volumetric solution) was added to the tube, followed by solvent (0.5-2.0 mL). The tube was sealed with a glass stopper and removed to argon on a Schlenk line, where the stopper was replaced with a rubber septum. Alternately, the tube was sealed directly with a degassed rubber septum which was wired tightly to the tube upon removal from the drybox. Monomer (typically 0.9-1.8 mmol) was added to the stirred solution via syringe at 0 or -78 °C. The rubber septum was replaced with a flame-dried glass stopper, and the polymerization was closed from argon and allowed to stir for the appropriate length of time.

Drybox procedure. In the drybox, the desired amount of catalyst and solvent were measured directly into a 10 mL round-bottom flask equipped with a stirbar. The flask was sealed with a glass stopper, removed from the drybox, and immediately cooled to the desired temperature. This procedure was used for the attempted polymerizations involving phenyl and trityl methacrylate and **I**.

Vacuum transfer procedure. In the drybox, catalyst and a magnetic stirbar were added to a 25 mL Schlenk storage tube equipped with a wide-bore, 8 mm airfree stopcock. The tube was evacuated on an all-glass vacuum-transfer apparatus connected to a Schlenk line, and an appropriate amount of solvent was added by vacuum transfer direcrtly from sodium benzophenone ketyl or CaH_2. The tube was sealed from vacuum, warmed, and stirred until the catalyst had completely dissolved in the liquid solvent. It was then removed from the transfer apparatus and placed directly under vacuum on a Schlenk line (still sealed) until needed. Separately, the desired amount of monomer (approximated visually) was transferred from CaH_2 into a tared Schlenk storage tube. The tube was sealed, quickly weighed, and reattached to the apparatus. The weighed monomer was then transferred to the catalyst solution. The tube containing the polymerization components was sealed from vacuum, warmed quickly while stirring to 0 °C until homogeneous, then cooled to the desired temperature. The airfree joint was kept under vacuum during the entire polymerization period. This procedure was used for the attempted polymerization of trimethylsilyl methacrylate.

Polymer workup. After polymerization was complete the polymerization vessel was opened to air and an excess of methanol (5-10 times the volume of the polymerization solvent) was added, causing disappearance of the yellow color and, typically, precipitation of the polymer as a white solid. The polymer was isolated by filtration and purified by reprecipitation into methanol from $CHCl_3$, collected on a 0.2 µm filtration apparatus, and rinsed with additional methanol unless otherwise indicated.

Polymerization of MMA with 1 and 2. For monomer to initiator ratio experiments, the Schlenk procedure was employed; to minimize contact with ambient oxygen and moisture, multiple polymerizations were initiated simultaneously with aliquots of monomer from a single gas-tight, flame-dried microsyringe which was flushed with several volumes of argon before use. In this case the resultant polymer was not isolated by filtration due to moderate solubility in methanol; isolation was accomplished by direct removal of solvents *in vacuo* from the quenched reaction mixture. Spectral data for a PMMA sample prepared at -78 °C: ^1H NMR ($CDCl_3$, 400 MHz): δ 3.59 (s, 3 H), 1.87 and 1.80 (both br s, combined 2 H), 1.03 and 0.85 (both br s, combined 3 H). Literature ($CHCl_3$): δ 3.62 (s, $C\underline{H}_3O$-), 1.86 (br, -$C\underline{H}_2$-), 1.07 (br s, heterotactic -$C\underline{H}_3$), 0.93 (br s, syndiotactic -$C\underline{H}_3$).[97] $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 178.05 (minor peak), 177.76, 176.95 (minor peak), 54.37 (minor peak), 54.12, 51.76, 44.86 (minor peak), 44.56, 18.68 (minor peak), 16.63. Literature ($CDCl_3$): δ 178.0, 177.7, 176.9 ($\underline{C}$=O), 54.4, 53.6, 53.0 (-$\underline{C}H_2$-), 51.7 (-$O\underline{C}H_3$), 45.5, 44.9, 44.6 (-$\underline{C}C$=O), 21.1, 18.8, 16.6 (-$\underline{C}H_3$).[98] IR (thin film from $CHCl_3$): 2995 (m), 2950 (m), 2842 (sh), 1732 (vs), 1636 (sh), 1486 (m), 1448 (m), 1436 (m), 1386 (w), 1273 (m), 1243 (s), 1192 (s), 1150 (s), 1063 (w), 987 (w), 967 (w), 912 (w), 842 (w), 826 (w), 810 (w), 752 (s) cm^{-1}. Literature: 2951, 1730, 1449, 1387, 1240, 1148, 1064, 989, 753 cm^{-1}.[99]

Attempted isolation of coupled $[Cp^*_2Sm]_2[MMA]_2$ species prepared with 2. Using Schlenk procedures, a solution of MMA (37 µL, 35 mg, 0.35 mmol) in 20 mL THF was added to a soltuion of **2** (197 mg, 0.351 mmol) in 30 mL THF over a 30 minute period. A gradual color change from purple to through orange to bright yellow was observed. Removal of volatiles *in vacuo* gave approximately 120 mg of a sticky yellow solid. This material possessed a high solubility in THF, diethyl ether, toluene, and hexanes; recrystallization attempts from these solvents at -78 °C were unsuccessful. A similar reaction carried out with **1** in toluene yielded a material for which recrystallization also failed.

Attempted isolation of coupled $[Cp^*_2Sm]_2[MMA]_2$ species prepared with 1. As described above, MMA (76 µL, 72 mg, 0.72 mmol) was added to **1** (300 mg, 0.713 mmol) at -78 °C. Attempts to recrystallize the resultant sticky orange-yellow solid from toluene and hexanes at -40 °C were unsuccessful. A 100 mg portion of the material was dissolved in a minimum amount of hexanes in a 25 mL Schlenk tube. Two drops of phthalan were added to the solution, which was then concentrated *in vacuo* at 60 °C and cooled to -40 °C. After a 48 hour period, three yellow crystals had formed in the bottom of the tube. However, isolation of the crystals was complicated by the precipitation of additional material as powder when the tube was transferred from -40 °C to a -78 °C dry ice / acetone bath for Schlenk line manipulations. The crystals and powder were redissolved by warming the solution, which was then recooled to -40 °C. However, no crystalline material was recovered after this procedure. Attempts to prepare phenyl and trityl methacrylate analogues were carried out similarly.

Phenyl methacrylate. Using Schlenk techniques, methacryloyl chloride (90% technical grade, 4.89 g, 0.0421 mol) was added to sodium phenoxide (4.89 g, 0.0421 mol) in 125 mL THF at 0 °C over a two hour period. A white precipitate of NaCl was immediately observed. The flask was allowed to warm to room temperature overnight and the mixture was slowly filtered through a 0.2 µm membrane filtration apparatus. The insolubles were discarded and the filtrate cooled to -40 °C overnight, which resulted in the separation of additional

NaCl as white crystals. Removal of THF from the supernatant with a rotary evaporator gave a cloudy, reddish liquid, which was dissolved in 100 mL chloroform and extracted with distilled H_2O (1 x 100 mL) in a separatory funnel to ensure complete removal of NaCl. Disappearance of the red color was observed. The aqueous layer was back-extracted with $CHCl_3$ (2 x 50 mL) in a separatory funnel and the combined organic layers dried with $MgSO_4$ and filtered. The chloroform was removed by rotary evaporator, and further removal of volatiles was carried out under high vacuum (0.01 Torr). The crude methacrylate was dried over CaH_2 for one week at 0 °C in the dark, and distilled under vacuum at 40 °C / approximately 0.03 Torr (literature b.p. = 40 °C / 0.15 Torr[100]). However, the distillate was found to be contaminated by an impurity present in 5%, which was identified as phenol by ^1H NMR spectroscopy. Purification was accomplished by column chromatography on silica with a mobile phase of 5% v/v ethyl acetate in petroleum ether (R_f of phenyl methacrylate = 0.53). The purified monomer was redried over CaH_2 for five days, distilled under dynamic vacuum as described above, and stored in the dark at -35 °C (~ 1.0 g, 15%). ^1H NMR ($CDCl_3$, 200 MHz, referenced to TMS): δ 7.42-7.09 (m, 5 H, $-OC_6\underline{H}_5$), 6.34 (m, 1 H, $=CH\underline{H}$), 5.73 (m, 1 H, $=C\underline{H}H$), 2.06 (m, 3 H, $-C\underline{H}_3$). Literature ($CDCl_3$): δ 7.23 (m, 5 H), 6.32 (m, 1 H), 5.72 (m, 1 H), 2.03 (m, 3 H).[100] $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz): δ 165.40 ($\underline{C}=O$), 151.56 ($H_2C=\underline{C}$), 136.30 ($H_2\underline{C}=C$), 129.50, 126.84, 125.72, 121.96 ($\underline{C}_6H_5$), 18.30 ($\underline{C}H_3$). IR (neat): 3065 (w), 3043 (sh), 2992 (w), 2964 (w), 2928 (w), 1737 (s), 1637 (m), 1592 (m), 1494 (m), 1456 (m), 1401 (w), 1378 (w), 1321 (m), 1295 (m), 1200 (s), 1164 (s), 1130 (s), 1071 (w), 1025 (w), 1007 (w), 946 (m), 913 (w), 856 (w), 807 (m), 747 (m), 690 (m) cm^{-1}. Literature: 3105-2855 (s), 1743 (s), 1639 (m), 1591 (m), 1475 (m), 1454 (m), 1426 (w), 1402 (w), 1379 (w), 1318 (m), 1294 (m), 1204 (s), 1154 (s), 1124 (s), 1027 (w), 1004 (w), 946 (s) cm^{-1};[101] 750, 690 cm^{-1}.[100]

Bis(2-methoxycarbonyl-2-propenyl) ether (I). This diacrylate was prepared through a combination of the procedures of Mathias[102] and Stansbury.[103] Ethyl acrylate (12.7 g, 0.148 mol), 1,4-diazabicyclo[2.2.2]octene (DABCO) (0.834 g, 0.00743 mol), and paraformaldehyde (2.35 g, 0.0743 mol) were placed in a thick-walled, 20 mL glass ampule with a magnetic stirbar. The ampule was cooled and sealed with a methane / oxygen torch, wrapped in aluminum foil, and stirred while completely immersed in an 85 °C oil bath. After three hours, the initial white suspension became clear, and after 19 hours a white precipitate was again present in the ampule. Upon cooling to room temperature, the contents of the ampule were added to 30 mL of diethyl ether and extracted with 1% aqueous HCl (3 x 15 mL). [CAUTION! This reaction mixture contains methyl α-(hydroxymethyl)acrylate, which causes severe skin blistering.[104] All manipulations of crude **I** should be carried out with appropriate gloves and protective clothing, and all glassware used for the synthesis of this compound should be rinsed thoroughly immediately after use.] The white precipitate dissolved upon acid extraction. The ether layer was dried over $MgSO_4$ and filtered, followed by removal of solvent by rotary evaporation to give a clear oil. Further removal of volatiles from this oil on a high-vacuum line (0.01 Torr) gave a white solid (4.50 g, 29%). Column chromatography separation of the diacrylate from byproduct acetals with 10:1 v/v petroleum ether / diethyl ether on silica was attempted, but no product was obtained after collection of a large volume of eluent. The column was then eluted with 2:1 v/v methylene chloride / diethyl ether, allowing collection of pure **I** (2.37 g, 15%) (R_f of diacrylate ~ 1.0; R_f of acetals ~ 0.8). The diacrylate was then recrystallized twice from dry hexanes at -35 °C to give 2.04 g (13%) of thick white plates. ^1H NMR ($CDCl_3$, 200 MHz): δ 6.31 (m, 2 H), 5.91 (m, 2 H), 4.25 (m, 4 H), 3.76 (s, 6 H). Literature: δ 6.2 and 5.8 (4 H, $=C\underline{H}_2$), 4.2 (4 H, $-C\underline{H}_2-$), 3.7 (6 H, $C\underline{H}_3O-$).[105]

Polymerization of benzyl methacrylate with 2. The Schlenk procedure was employed. The quantities of reagents used were 120 μL (125 mg, 0.708 mmol) benzyl methacrylate, 5.7 mg **2** (0.010 mmol), and 1 mL THF; polymerization was carried out overnight. The GPC molecular weight distribution of the polymer contained a lower M_n peak due to inadequate exclusion of air during monomer addition. ^{1}H NMR (CD_2Cl_2, 200 MHz): δ 7.29 (s, 5 H, $C_6\underline{H}_5$), 4.89 (s, 2 H, $-OC\underline{H}_2-$), 1.87 and 1.78 (both br s, combined 2 H, $-C\underline{H}_2-$), 0.91 and 0.73 (both br s, combined 3 H, $-C\underline{H}_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 177.34, 177.04 (minor peak), 135.40 (minor peak), 135.17, 128.53, 128.39, 128.20, 66.75, 54.04, 45.13 (minor peak), 44.81, 16.77. Literature ($CDCl_3$): δ 177.2, 176.9, 176.4, 176.2 ($\underline{C}=O$), 135.5, 135.1 ($-OCH_2\underline{C}-$), 128.4 ($-C\underline{C}_5H_5$), 66.7 ($-O\underline{C}H_2-$), 54.5, 54.1, 53.7 ($-\underline{C}H_2-$), 45.1, 44.8 ($-\underline{C}C=O$), 18.9, 18.7, 18.4, 16.7 ($-\underline{C}H_3$).[98] IR (thin film from $CHCl_3$): 3089 (sh), 3032 (s), 2954 (s), 1953 (w), 1875 (w), 1808 (w), 1729 (vs), 1608 (w), 1588 (w), 1497 (s), 1484 (s), 1455 (vs), 1388 (m), 1367 (m), 1262 (vs), 1143 (vs), 1082 (sh), 1062 (sh), 1032 (m), 1006 (sh), 967 (s), 801 (m), 751 (vs), 697 (s), 584 (m) cm^{-1}. Literature: 2952, 1728, 1455, 1262, 1142, 1081, 966, 750, 697 cm^{-1}.[99] Calculated M_n = 24 950.

Polymerization of *n*-hexyl methacrylate with 1. The Schlenk procedure was employed. The quantities of reagents used were 100 μL *n*-hexyl methacrylate (89.0 mg, 0.523 mmol), 7.3 mg **1** (0.017 mmol), and 2 mL toluene; polymerization was carried out for 3 hours. The soft, white-to-colorless polymer, which adhered to the walls of the glass tube and was not weighed, was purified by reprecipitation from warm (> 33 °C) isopropanol into cold distilled H_2O. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.91 (br s, 2 H, $-OC\underline{H}_2-$), 1.89 (v br) and 1.79 (br s) (combined 2 H, $-C\underline{H}_2-$), 1.60 (br s, 2 H, $-OCH_2C\underline{H}_2-$), 1.31 (br s, 6 H, $-OCH_2CH_2(C\underline{H}_2)_3CH_3$), 1.01 and 0.90 (both br s, combined 6 H, $-O(CH_2)_5C\underline{H}_3$ and $-C\underline{H}_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 177.43 ($\underline{C}=O$), 64.97 ($-O\underline{C}H_2-$), 54.13 ($-\underline{C}H_2-$), 45.11 (minor peak), 44.81 ($-\underline{C}C=O$), 44.74 (minor peak), 31.39, 28.09, 25.69, 22.49 (*n*-hexyl $-\underline{C}H_2-$), 16.81 ($-\underline{C}H_3$), 14.01 (*n*-hexyl $-\underline{C}H_3$). IR (thin film from $CHCl_3$): 2955 (s), 2930 (s), 2858 (m), 1729 (vs), 1465 (m), 1387 (w), 1269 (m), 1241 (m), 1173 (s), 1149 (s), 1065 (w), 990 (w), 967 (w), 912 (w), 803 (w), 748 (w), 726 (w) cm^{-1}. Literature: 2931, 1729, 1468, 1388, 1240, 1149, 1066, 990, 749 cm^{-1}.[99] Calculated M_n = 10 260.

Polymerization of ethyl acrylate with 1. The Schlenk procedure was employed. The quantities of reagents used were 150 μL ethyl acrylate (139 mg, 1.38 mmol), 4.9 mg **1** (0.012 mmol), and 0.75 mL toluene; polymerization was carried out for 2.5 hours in the dark. During this period an increase in viscosity was observed, but no precipitate was observed upon addition of excess methanol. Solvents were removed from the reaction *in vacuo* to give a clear, rubbery solid, which adhered to the walls of the flask and could not be isolated or weighed. Attempts to purify the polymer by reprecipitation from toluene into hexanes gave a similarly intractable material. The GPC molecular weight distribution of the polymer contained a low M_n shoulder due to inadequate exclusion of air during monomer addition. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.10 (br d, J = 6.6 Hz, 2 H, $-OC\underline{H}_2CH_3$), 2.27 (br s, 1 H, $-C\underline{H}CO_2-$), 1.90, 1.63, 1.47 (all br, combined 2 H, $-C\underline{H}_2-$), 1.23 (br s, 3 H, $-OCH_2C\underline{H}_3$). Literature for atactic poly(methyl acrylate) (*o*-dichlorobenzene, 140 °C): δ 2.5 (v br m, $-C\underline{H}CO_2-$), 1.81 (v br m, $-C\underline{H}_2-$).[97] IR (KBr): 2982 (m), 2938 (sh), 2880 (sh), 1735 (vs), 1448 (m), 1381 (m), 1331 (sh), 1299 (sh), 1261 (s), 1160 (vs), 1116 (sh), 1097 (m), 1024 (m), 905 (w), 853 (w), 801 (w), 760 (sh) cm^{-1}. Literature: 2982, 1733, 1447, 1382, 1330, 1257, 1159, 1097, 1025 cm^{-1}.[99] Calculated M_n = 23 800.

Polymerization of *tert*-butyl acrylate with 1. The Schlenk procedure was employed. The quantities of reagents used were 100 μL *tert*-butyl acrylate (87.5 mg, 0.683 mmol), an unweighed amount of **1** (<

5 mg, 0.01 mmol), and 1 mL THF; polymerization was carried out for 16 hours. No increase in viscosity was observed. The polymerization was warmed to room temperature and allowed to proceed for 30 minutes, after which the solution became viscous. Addition of methanol produced no insoluble material, and solvents were removed *in vacuo* from the polymerization vessel. The clear, rubbery poly(*tert*-butyl acrylate) was isolated in 39% yield by precipitation into distilled H_2O from methanol. This figure most likely represents a loss of additional polymer in the precipitation solvent mixture. ^1H NMR ($CDCl_3$, 200 MHz): δ 2.21 (br, -C$\underline{H}$$CO_2$-), 1.77 (v br, -C$\underline{H}_2$-), 1.42 (br s, -$OC_4\underline{H}_9$). Literature for atactic poly(methyl acrylate) (*o*-dichlorobenzene, 140 °C): δ 2.5 (v br m, -C$\underline{H}$$CO_2$-), 1.81 (v br m, -C$\underline{H}_2$-).[97] IR (thin film from $CHCl_3$): 2977 (m), 2932 (m), 2868 (sh), 1728 (s), 1478 (w), 1455 (w), 1393 (m), 1367 (m), 1340 (sh), 1258 (s), 1148 (s), 1035 (w), 923 (w), 906 (w), 845 (m), 803 (w), 753 (w) cm^{-1}. Literature for poly(isobutyl acrylate): 1736 (υ C=O) cm^{-1}.[99]

Poly(methyl methacrylate-*b*-*tert*-butyl acrylate-*b*-methyl methacrylate) (II). Using the vacuum transfer procedure, *tert*-butyl acrylate (532 mg, 4.15 mmol) was added to **2** (16.2 mg, 0.029 mmol) in approximately 5 mL toluene and allowed to stir for 3.5 hours at 0 °C with incident light excluded. Methyl methacrylate (622 mg, 6.21 mmol) was then added, and the polymerization was stirred for an additional 2.5 hours at 0 °C. Addition of excess methanol produced a milky white suspension. Solvent was removed from this suspension and the polymer purified by precipitation into hexanes from $CHCl_3$ as a white solid (825 mg, 72%). The triblock was soluble in chloroform, methylene chloride, THF, acetone, benzene, toluene, and insoluble in hexanes. ^1H NMR ($CDCl_3$, 200 MHz): δ 3.57 (s, relative area 1.51), 2.21 (br, relative area 1.00), 1.79 (v br), 1.41 (s), 1.00 (s), 0.83 (br s). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 178.05 (minor peak), 177.75 (methacrylate $\underline{C}$=O), 176.95 (minor peak), 174.16 (acrylate $\underline{C}$=O), 80.39 (acrylate -O$\underline{C}$$(CH_3)_3$), 54.39 (minor peak), 54.13 (methacrylate -$\underline{C}H_2$-), 51.76 (methacrylate -O$\underline{C}H_3$), 44.89 (minor peak), 44.58 (methacrylate -$\underline{C}$C=O), 42.35, 41.89, 41.61 (acrylate -$\underline{C}H_2$-), 37.40 (acrylate -$\underline{C}$C=O), 28.06 (acrylate -OC($\underline{C}H_3)_3$), 27.98 (minor peak), 18.71 (minor peak), 16.67 (methacrylate -$\underline{C}H_3$). IR (thin film from $CHCl_3$): 2978 (m), 2950 (m), 2845 (sh), 1731 (vs), 1635 (sh), 1482 (m), 1448 (m), 1392 (m), 1367 (m), 1340 (w), 1273 (m), 1246 (s), 1192 (s), 1149 (vs), 1063 (w), 1034 (sh), 987 (w), 967 (w), 913 (w), 845 (m), 810 (w), 754 (m), 668 (w) cm^{-1}. Calculated M_n = 80 170. Analysis calculated for $PMMA_{216}$-$PtBA_{289}$-$PMMA_{216}$: C, 62.56; H, 8.71. Found: C, 61.93; H, 8.70.

Poly(benzyl methacrylate-*b*-methyl methacrylate-*b*-benzyl meth-acrylate) (III). Using the vacuum transfer procedure, MMA (544 mg, 5.43 mmol) was added to **2** (19.4 mg, 0.0345 mmol) in 5 mL THF at 0 °C and allowed to react for 2.5 hours. The sealed polymerization tube was transferred to the drybox (freshly flushed with 700 psi N_2) where benzyl methacrylate (520 µL, 540 mg, 3.06 mmol) was added by syringe while stirring. The tube was sealed, removed from the drybox, and allowed to stir for 2.5 hours at 0 °C. After addition of excess methanol, the white triblock copolymer was isolated by filtration (1.06 g, 98%) and purified by reprecipitated from chloroform into methanol (1.04 g, 96%). The polymer was soluble in acetone, methylene chloride, chloroform, THF, benzene, and toluene, and insoluble in methanol. ^1H NMR (CD_2Cl_2, 200 MHz): δ 7.28 (s), 4.88 (br s, relative area 1.00), 3.58 (s, relative area 2.63), 1.88 (br), 1.81 (br), 0.99 (br), 0.90 (br), 0.82 (br), 0.73 (br). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 178.07 (minor peak), 177.76, 177.32, 176.97 (minor peak), 135.38 (minor peak), 135.11, 128.50, 128.36, 128.17, 66.77, 54.13, 51.78, 45.10 (minor peak), 44.90 (minor peak), 44.78, 44.59, 18.75, 16.67. IR (thin film from $CHCl_3$): 3089 (sh), 3033 (sh), 2994 (m), 2949 (s), 2847 (sh), 1967 (w), 1867 (w), 1806 (w), 1730 (vs), 1608 (w), 1586 (w), 1485 (m), 1453 (m), 1387 (m), 1367 (m), 1269 (s), 1242 (vs), 1196 (vs), 1148 (vs), 1091 (sh), 1062 (m), 1029 (w), 991 (sh), 967 (m), 913 (w), 842 (w), 823 (w), 803 (w), 751 (s), 698 (m), 668 (w) cm^{-1}. Calculated M_n = 62 820. Analysis calculated for PBMA$_{89}$-PMMA-$_{315}$-PBMA$_{89}$: C, 67.45; H, 7.48. Found: C, 66.96, H, 7.32.

Poly(methyl methacrylate-*b*-*n*-hexyl methacrylate-*b*-methyl meth-acrylate). Using the Schlenk procedure, *n*-hexyl methacrylate (125 µL, 111 mg, 0.653 mmol) was added to **1** (9.1 mg, 0.022 mmol) in 5 mL toluene at 0 °C and allowed to react for 4.5 hours. Methyl methacrylate (345 µL, 326 mg, 3.25 mmol) was then added in a similar manner. The polymerization was stirred at 0 °C overnight. Partial precipitation of a white solid was observed upon addition of excess methanol. Solvents were removed from this inhomogeneous mixture *in vacuo*, and the white triblock isolated by reprecipitation from a minimum amount of $CHCl_3$ into methanol (439 mg, 100%). The GPC molecular weight distribution of the copolymer contained a small low M_n shoulder due to inadequate exclusion of air during polymerization. The shoulder was partially removed by a second reprecipitation (365 mg, 84%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.91 (br, relative area 1.00), 3.58 (s, relative area 8.41), 1.88 (br), 1.80 (br s), 1.60 (br), 1.31 (br s), 1.00 (br s), 0.90 (br), 0.84 (br). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 178.04 (minor peak), 177.75, 177.41, 176.94 (minor peak), 64.95, 54.41 (minor peak), 54.12, 51.75, 44.89 (minor peak), 44.72, 44.58, 31.38, 28.08, 25.68, 22.47, 18.69 (minor peak), 16.69, 13.98. IR (thin film from $CHCl_3$): 2994 (w), 2951 (m), 2932 (sh), 2857 (sh), 1730 (vs), 1484 (w), 1448 (w), 1434 (sh), 1387 (w), 1272 (w), 1242 (m), 1192 (m), 1149 (s), 1063 (w), 986 (w), 967 (w), 912 (w), 840 (w), 827 (w), 806 (w), 751 (m) cm^{-1}. Calculated M_n = 40 240.

A second triblock copolymer was prepared with **2** using similar methodology: *n*-Hexyl methacrylate (120 µL, 107 mg, 0.627 mmol) was added to **1** (8.6 mg, 0.020 mmol) in 2 mL THF at -78 °C and allowed to react for 3 hours. The polymerization was warmed to 0 °C and stirred for an additional 2 hours. Methyl methacrylate (115 µL, 109 mg, 1.08 mmol) was then added and the polymerization stirred for approximately 4 hours at 0 °C. Isolation of the fluffy white triblock (179 mg, 83%) by reprecipitation was carried out as described above. The material was soluble in hot isopropanol but insoluble in hexanes and boiling methanol. Its ^{1}H NMR spectrum was identical to previously described copolymer (area ratio of peaks at 3.91 and 3.58 ppm = 1.00 : 8.42). The GPC molecular weight distribution of the copolymer contained a small low M_n shoulder due to inadequate exclusion of air during polymerization. Calculated M_n = 20 890.

Poly(ethyl acrylate-*b*-methyl methacrylate-*b*-ethyl acrylate). Using the Schlenk procedure, MMA (190 µL, 179 mg, 1.79 mmol) was added to **1** (7.4 mg, 0.018 mmol) in 2 mL toluene at 0 °C and allowed to react for 2.25 hours. Ethyl acrylate (195 µL, 180 mg, 1.80 mmol) was then added in a similar manner. The polymerization was stirred at 0 °C for 2.25 hours, followed by addition of a large excess of methanol (≈ 100 mL). The precipitated white polymer was collected by filtration (317 mg, 88%). The GPC molecular weight distribution of the copolymer contained a small low M_n shoulder due to inadequate exclusion of air during polymerization. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.09 (br d, J = 6.7 Hz, relative area 1.00), 3.58 (s, relative area 1.51), 2.26 (br), 1.89 (br m), 1.80 (br s), 1.63 (br), 1.44 (br m), 1.23 (br m), 1.00 (s), 0.84 (br s). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 178.17 (minor peak), 177.78 (methacrylate $\underline{C}$=O), 174.51 (acrylate $\underline{C}$=O), 60.48 (acrylate -O$\underline{C}H_2$-), 54.16 (methacrylate -$\underline{C}H_2$-), 51.79 (methacrylate -O$\underline{C}H_3$), 44.58 (methacrylate -$\underline{C}$C=O), 41.41 (acrylate -$\underline{C}H_2$-), 36.20 (acrylate -$\underline{C}$C=O), 18.71 (minor peak), 16.67 (methacrylate -$\underline{C}H_3$), 14.15 (acrylate -$OCH_2\underline{C}H_3$). IR (thin film from $CHCl_3$): 2986 (m), 2950 (m), 2854 (sh), 1731 (vs), 1478 (m), 1448 (m), 1382 (m), 1329 (sh), 1268 (sh), 1242 (s), 1174 (sh), 1152 (s), 1097 (sh), 1062 (w), 1025 (w), 988 (w), 967 (w), 911 (w), 852 (w), 826 (w), 810 (w), 749 (w) cm^{-1}. Calculated M_n = 40 880.

Poly(methyl methacrylate-*b*-acrylic acid-*b*-methyl methacrylate) (IV). In a 50 mL round-bottom flask equipped with a stirbar, 100 mg of **II** (comprising 46.0 mg or 0.359 mmol poly(*tert*-butyl acrylate) repeat units) was dissolved in 10 mL toluene. To this solution, 18.0 mg *p*-toluenesulfonic acid monohydrate (0.0946 mmol) was added. The flask was fitted with a reflux condenser sealed with a rubber septum, and a gentle purge of nitrogen gas (to remove byproduct isobutylene) was introduced to its contents by a long needle inserted through the septum. The reaction was stirred for 16 hours at 105 °C under N_2 purge. During this period a small amount of solid polymer deposited from solution onto the sides on the flask. Acetone (≈ 2 mL) was added as a cosolvent to redissolve the polymer, which was then precipitated by the addition of a large volume of hexanes as an off-white solid, collected by filtration (86 mg, theoretical yield of fully deprotected material 80 mg), and lyophilized from 1,4-dioxane. ^{1}H NMR (1:1 $CDCl_3$ / CD_3OD, 200 MHz): δ 3.58 (s, ester -OC$\underline{H}_3$), 2.39 (v br s, acid C$\underline{H}$), 2.00-1.75 (br m, ester and acid -C$\underline{H}_2$-), 1.21 (s), 0.99 and 0.81 (both br s, combined ester -C$\underline{H}_3$). Authentic sample of poly(acrylic acid) (D_2O, 200 MHz): δ 2.42 (br, 1 H, C$\underline{H}$), 2.10-1.55 (br m, 2 H, -C$\underline{H}_2$-). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75 MHz): δ 178.38 (minor peak), 178.10 (ester $\underline{C}$=O), 177.29 (minor peak), 52.00 (ester -O$\underline{C}H_3$), 45.26 (minor peak), 44.97 (ester -$\underline{C}$C=O), 19.03 (minor peak), 16.99 (ester -$\underline{C}H_3$) (ester -$\underline{C}H_2$- resonances near 54.00 was obscured by the solvent). Authentic sample of poly(acrylic acid) (D_2O with d_6-acetone standard, 75 MHz): δ 178.28 ($\underline{C}$=O), 178.17 (minor peak), 41.15 (-$\underline{C}H_2$-), 34.33, 33.92 (-$\underline{C}$C=O). IR (KBr): 3211 (s), 3000 (m), 2952 (m), 2847 (sh), 2644 (sh), 1734 (vs), 1700 (sh), 1478 (m), 1449 (m), 1389 (w), 1363 (w), 1341 (w), 1267 (s), 1243 (s), 1189 (s), 1149 (vs), 1061 (w), 1036 (sh), 988 (w), 961 (w), 911 (w), 839 (w), 805 (w), 751 (w), 683 (w), 671 (w), 650 (sh), 572 (w), 511 (sh), 483 (w) cm^{-1}. Literature for poly(acrylic acid): 3106, 2680, 1712, 1452, 1350, 1234, 1168, 1113, 795 cm^{-1}.[99] TGA: Onset of decomposition 379 °C; end 422 °C; mass loss ≈ 90%.

Poly(methacrylic acid-*b*-methyl methacrylate-*b*-methacrylic acid) (V). In a 50 mL round-bottom flask containing a magnetic stirbar, 211.4 mg of **III** (comprising 106 mg or 0.601 mmol poly(benzyl methacrylate) repeat units) was dissolved in 30 mL CH_2Cl_2 which had been dried over 3 Å molecular sieves. Trimethylsilyl iodide (TMSI) (94.0 µL, 132 mg, 0.660 mmol) was added by syringe while stirring, and the flask immediately sealed with a glass stopper. The polymer solution underwent an immediate color change to yellow. The sealed reaction was stirred for 20 hours at room temperature, during which it darkened to a purple color characteristic of molecular I_2. After this period a 0.5 mL aliquot was removed by pipet and quenched with 1 mL methanol, resulting in a yellowish solution. Solvents were removed from the aliquot *in vacuo* and the residual polymer precipitated from acetone into hexanes and collected by filtration. The ^{1}H NMR spectrum of the white polymer in d_6-acetone (200 MHz) was taken. One-pulse integration of the benzyl ester (4.99 ppm, -OC$\underline{H}_2$-) and methyl ester (3.63 ppm, -OC$\underline{H}_3$) resonances indicated that 45.2% of the benzyl groups were intact. The sealed reaction was allowed to stir for another 4 hours and 50.0 µL (70.3 mg, 0.351 mmol) TMSI was added. After a 24 hour period, a second aliquot was removed and analyzed as described (using benzyl -OC$\underline{H}_2$- and methyl -OC$\underline{H}_3$ resonances at 5.05 and 3.62 ppm, respectively, in 1:3 CD_2Cl_2 / CD_3OD). This analysis indicated that 14.3% of the benzyl groups remained. TMS (50.0 µL, 70.3 mg, 0.351 mmol) was again added and the reaction stirred for a final 24 hour period. Analysis of a third aliquot (using benzyl -$C_6\underline{H}_5$ and methyl -OC$\underline{H}_3$ resonances at 7.34 and 3.61 ppm, respectively, in 1:3 CD_2Cl_2 / CD_3OD) indicated a residual benzyl ester content of less than

0.23%. Methanol (30 mL) was added to the reaction, giving a brown solution. Solvents were removed with a rotary evaporator and the resultant brown solid precipitated from THF into hexanes to remove benzyl iodide (the precipitation supernatant possessed a purple color). The material was repeatedly extracted with hexanes (5 x 50 mL) while being crushed with a glass stirring rod, then dried *in vacuo* at 60 °C to give a yellowish powder (130 mg, 83%). A portion of the acid copolymer was slurried for three days in basic water (pH ~ 14) and then neutralized with acidic H_2O (pH ~ 1), resulting in disappearance of the yellow color. However, the white polymer isolated from this procedure showed a small loss (≈ 7%) of methyl ester groups as compared to the precursor triblock by ^1H NMR and a decreased solubility in THF. ^1H NMR (1:3 CD_2Cl_2 / CD_3OD, 200 MHz): δ 3.59 (s, ester $-OC\underline{H}_3$), 2.05-1.75 (br m, ester and acid $-C\underline{H}_2-$), 1.30-0.90 (br m) and 0.83 (br s) (combined ester and acid $-C\underline{H}_3$). $^{13}C\{^1H\}$ NMR (1:3 CD_2Cl_2 / CD_3OD, 75 MHz): δ 179.04 (minor peak), 178.76 (ester C=O), 177.92 (minor peak), 52.33 (ester $\underline{C}H_3O-$), 45.28 (minor peak), 45.25 (ester $-\underline{C}C{=}O$), 19.26 (minor peak), 17.16 (ester $-\underline{C}H_3$) (ester $-\underline{C}H_2-$ resonances near 54 ppm were obscured by the solvent). IR (KBr): 3715-3095 (s), 3000 (m), 2956 (m), 2845 (sh), 2774 (sh), 2611 (m), 1967 (sh), 1735 (vs), 1657 (sh), 1643 (sh), 1589 (w), 1571 (w), 1553 (w), 1488 (m), 1450 (m), 1390 (m), 1370 (w), 1275 (s), 1250 (s), 1194 (s), 1151 (vs), 1061 (w), 994 (sh), 967 (m), 934 (sh), 906 (sh), 839 (w), 830 (sh), 806 (w), 751 (m), 702 (w), 670 (w), 620 (sh), 583 (sh), 518 (m), 482 (sh) cm^{-1}. Literature for poly(acrylic acid): 3106, 2680 (υ O-H).[99] M_n calculated from observed M_n (GPC) and composition (^1H NMR) of **III** = 42 300.

A second portion of **III** (240 mg, comprising 120 mg or 0.681 mmol benzyl units) was reacted under more concentrated conditions: The polymer was dissolved in 2 mL CH_2Cl_2 and treated with 107 µL (150 mg, 0.750 mmol) TMSI as described above. After a 6 hour period, the polymer solution had become a gel; ^1H NMR analysis indicated that 60% of the benzyl ester groups had been removed. The reaction was diluted with 6 mL CH_2Cl_2 and 50.0 µL (70.3 mg, 0.351 mmol) TMSI was added. After 18 hours (< 2% benzyl groups remaining), the deprotected polymer was isolated and reprecipitated as previously described. The integrated one-pulse ^1H NMR spectrum of the acid copolymer (1:2 $CDCl_3$ / CD_3OD, 200 MHz) showed no decrease in the ratio of methyl ester groups to main chain $-CH_3$ groups.

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