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Anionic Synthesis of Polymers Functionalized with a Terminal Anhydride Group

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ABSTRACT: Polymers bearing a single succinic anhydride at the chain end were synthesized using anionic polymerization techniques. Specifically, the living anions of poly(methyl methacrylate) (PMMA), polystyrene (PS), polyisoprene (PI), and poly(vinylpyridine) (PVP) were found to exclusively undergo a 1,4-conjugate addition reaction with di-*tert*-butyl maleate. Only a single maleate adds. The gel permeation chromatograms for the synthesized polymers were found to have very narrow molecular weight distributions ($M_w/M_n < 1.15$) after the end-capping reaction. Pyrolysis (235 °C, 2−12 h) of the resulting substituted di-*tert*-butyl succinate ester efficiently produced the related succinic anhydride functional polymers in the case of PMMA and PS. The functionality of these polymers ($f \geq 0.81$) was determined following derivatization reactions with various amines. Nuclear magnetic resonance (NMR) spectroscopy and gel permeation chromatography (GPC) of the resulting amides permits quantification of the extent of functionalization. Upon melt blending (200 °C) an anhydride terminal PMMA (29 kg/mol) with an amino terminal PS (18.5 kg/mol) all of the monofunctional homopolymers were converted to PS−PMMA diblock within 20 min (GPC and transmission electron microscopy, TEM). A lamellar morphology (TEM) was obtained after further annealing of this sample (72 h).

Introduction

Polymers bearing a single reactive functional group represent an intriguing class of materials having potential application in several areas including surface modification, lubrication, catalysis, drug delivery, and compatibilization of polymer blends.[1] We are interested in blending and have found that *in situ* block copolymer formation via a chemical reaction can be an effective means to compatibilize polymer blends.[2] We have determined that it can be advantageous to make block copolymer as rapidly as possible while blending; therefore, faster chemical reactions are desirable. Of the reactive pairs we have investigated, the primary aliphatic amine/cyclic anhydride system has the most promising reaction kinetics.[3] We have observed extremely fast melt-coupling reactions (homogeneous and heterogeneous) and remarkable reactive self-assembly phenomenon with this reactive pair.[4] These exciting initial results led us to develop new, straightforward methods for synthesizing monofunctional polymers. We are currently using these materials to investigate several fundamental aspects of polymer blending and reactive self-assembly. One long range goal of this work is to synthesize kilogram quantities of these materials. With this in mind, we have designed synthetic methods that utilize readily available materials as trapping agents for living polymer anions.[5] Here we report a method for the synthesis of several polymers having a single succinic anhydride at the chain end.

Takenaka *et al.* have reported a method for the synthesis of anhydride terminal polystyrenes and polydienes involving a Diels−Alder addition of maleic anhydride to a diene-terminated polymer.[6] No other methods for the synthesis of anhydride terminal polymers have been reported to our knowledge. We also believe this work to be the first reported synthesis of anhydride-terminal poly(methyl methacrylate).

It has previously been shown that poly(styryllithium) will react with diethyl maleate ($EtO_2CCH{=}CHCO_2Et$) in a 1,4-fashion to incorporate exactly two esters (i.e., one maleate unit) on the chain end.[7] We designed a complementary method utilizing di-*tert*-butyl maleate (**1**) as a trapping agent for living anions of several different polymers (polystyrene (PS), poly(methyl methacrylate) (PMMA), poly(vinylpyridine) (PVP), and polyisoprene (PI)). We envisioned that pyrolysis of a di-*tert*-butyl succinate ester into a succinic anhydride would be a facile transformation based on our previous work.[8]

Results and Discussion

Diester-Terminated PMMA. Monofunctional polymers were synthesized using anionic polymerization techniques. Notably, all monomers (except methyl methacrylate) and solvents (except THF) in this study were purified by passage through activated basic alumina to remove all protic impurities and inhibitors. Scheme 1 outlines the synthesis of di-*tert*-butyl ester terminated PMMA **5**. The *sec*-butyllithium diphenylethylene adduct **2** was treated with 260 equiv of methyl methacrylate (**3**) in THF containing anhydrous lithium chloride[9] to generate the living PMMA anion **4**. Treatment with 2 equiv of di-*tert*-butyl maleate (**1**) and quenching with methanol produced polymer **5**, which had incorporated a single di-*tert*-butyl succinate moiety (see box) arising from conjugate- (or 1,4-) addition to **1**. PMMA **5** (Table 1) was highly functional ($f > 0.96$, see below) and had a very narrow molecular weight distribution (PDI = 1.03).

To investigate the feasibility of chain extension after trapping with **1**, methyl methacrylate was reintroduced to the solution of di-*tert*-butyl maleate enolate prior to methanol quench. No propagation was observed (gel permeation chromatography (GPC)) even when that reaction temperature was increased to 0 °C. The unique stability and steric constraints of the *tert*-butyl ester enolate anion apparently prevent further propagation.

A higher molecular weight maleate-terminated PMMA (**6**, 44 kg/mol, Table 1) was also synthesized. This polymer showed reasonably high functionality ($f = 0.81$)

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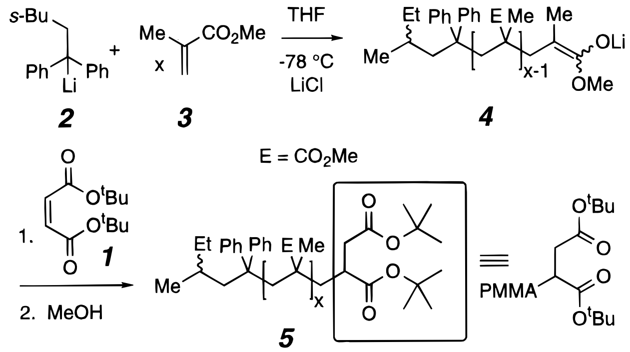
Scheme 1



and had a narrow molecular weight distribution. A similar strategy was also used to prepare diester trapped polystyrene, polyisoprene, and poly(vinylpyridine) samples **7**−**17** as summarized in Table 1 and discussed further below. In all cases, the molecular weight distributions obtained were reasonably narrow (<1.25) and the observed molecular weights (GPC) were close to those targeted.

Terminal Anhydride Formation. The di-*tert*-butyl ester terminus in polymer **5** proved to be an excellent precursor to the desired succinic anhydride by simple thermal modification (Scheme 2). When **5** was heated at 235 °C under vacuum in the melt (2−12 h) or in solution (2−8 h), the corresponding anhydride **5A** was smoothly generated. For PMMA a small amount of chain degradation was observed (GPC) after heating at this temperature for 12 h, at which time the anhydride closure was ~65% complete. Fortunately, however, when the PMMA reaction was carried out in solution at 235 °C under argon for 8 h, anhydride formation was complete and no chain cleavage was detected.[10] Similar conditions were used to convert diester-terminated polymers **6**, **9**−**13**, and **15** into anhydride-functional polymers **6A**, **9A**−**13A**, and **15A**. This transformation gave highly functional polymers ($f > 0.81$) in the case of PS and PMMA polymers.

In the melt the clear samples bubbled noticeably at first but eventually subsided as all of the *tert*-butyl groups pyrolytically eliminated isobutylene, and the resultant 1,4-diacid dehydrated to the anhydride.[11] Upon thermal modification of PVP **17**, significant polymer decomposition (black color) was witnessed, and the resulting polymer had low functionality ($f < 0.20$).

Diester-Terminated Polystyrene (and Polyisoprene and Poly(2-vinylpyridine)). Precursors to other polymers (PS, PI, and PVP, see **7**−**17** in Table 1) having anhydride terminal functionality have also been synthesized. The reaction between polystyryl anion and **1** was very sensitive to solvent polarity and temperature. When a 17.5 kg/mol polystyryllithium species was trapped with **1** at 25 or 5 °C in cyclohexane (~6 mM) the resulting GPC trace was found to have bimodal character (37.8%) with the high molecular weight peak being twice that of the low (Figure 1 and **7** and **8** in Table 1). We suspect that under these conditions a competition exists between 1,4- and 1,2-addition to the enoate present in **1** (Scheme 3). If polystyryl anion first undergoes ester attack in a 1,2-fashion, the resulting adduct still possesses a very reactive site toward 1,4-addition by another polystyryl anion. This would explain the resulting bimodal GPC behavior. This chain coupling reaction did not occur when the polymerization was performed in THF at −80 °C. The polymers obtained were highly functional ($f \geq 0.94$) and had narrow molecular weight distributions (**9** and **10**, Table 1 (1.07 and 1.06)). An α,ω-anhydrido polystyrene was also synthesized by using **1** to endcap polystyryl dipotassium (**11** in Table 1). This polymer also possessed a relatively narrow polydispersity index of 1.07 and was found to be highly functional at each terminus ($f = 1.86$). This method works well but is not very practical for increasing the reaction scale ($\geq$100 g). Approximately 5 L of THF would be required to synthesize 100 g of polymer using this protocol. We have found it difficult to control PDI at higher monomer concentrations when polymerizing in THF. It is well-known that PS's having narrow molecular weight distributions can be synthesized at relatively high monomer concentrations ($\approx$1.0−2.0 M) in hydrocarbon solvents.[12] For this reason, we looked to develop conditions for functionalization by di-*tert*-butyl maleate (**1**) in cyclohexane. We first achieved this goal by polymerizing styrene in cyclohexane at room temperature and then adding enough THF (2× the amount of cyclohexane) into the reactor to carry out the subsequent trapping reaction with **1** at −80 °C. This procedure gave polymers having narrow molecular weight distributions (**12** and **13** in Table 1), which were moderately functional ($f > 0.7$), but the procedure was tedious. We believe that lower f values were obtained as a result of chain end quenching by adventitious impurities that were introduced into the reaction during this cumbersome protocol.

We then considered that the presence of the polar additive tetramethylethylenediamine (TMEDA) might reduce the amount of 1,2-attack on **1** since that diamine is believed to decrease the association number of poly(styryllithium) from 2 to 1.[13] An association number of 2 could result in undesirable addition of two poly(styryllithiums) to **1** prior to diffusion of the second anion away from the initially formed adduct. Indeed, when TMEDA ($\approx$5 equiv) was added before the trapping reaction, the percent bimodal character of the resulting polymer was reduced nearly 3-fold (**14** in Table 1). The presence of TMEDA reduced but did not eliminate 2:1 adduct formation, so another alternative was sought.

It is well-known that organozinc compounds are much softer nucleophiles than their organolithium counterparts.[14] Organozinc compounds have also been shown to exclusively undergo 1,4-conjugate additions to enoates and enones.[15] TMEDA and solid zinc iodide were added to the poly(styryllithium). The color of the cyclohexane solution slowly changed from the characteristic deep red of PS−Li/TMEDA to a faint orange, consistent with a transmetalation event. Upon addition of maleate **1** to this species, a polymer having high functionality ($f > 0.8$) and no bimodal character was isolated (**15** in Table 1). The use of zinc-modified PS−Li reagents represents the method of choice for maleate functionalization of large quantities (> 50 g) of polystyrene. When this same method was used to functionalize polyisoprene, the resulting GPC trace was 15% bimodal (**16** in Table 1).[16]

Poly(2-vinylpyridine) was initiated with *s*-BuLi, polymerized in THF at −78 °C, and subsequently functionalized with **1** under these conditions. The isolated polymer had a fairly narrow molecular weight distribution (**17** in Table 1) and appeared to be highly functional after the initial trapping reaction. Unfortunately, the conditions required for subsequent *tert*-butyl ester pyrolysis (235 °C, 3 h) led to thermal decomposition of PVP. This method is therefore not suitable for synthe-

Table 1. Data for Maleate-Trapped Polymers 5−17 and Functionality of Derived Anhydrides

functionalized polymer	trapping conditions	M_n (K) calcd	M_n (K) exptl	PDI	% bimodal[a]	f/chain[b] method A	f/chain[b] method B
PMMA **5**	THF, LiCl, −78 °C	26	29.0	1.03	0	0.91	0.96
PMMA **6**	THF, LiCl, −78 °C	40	44.0	1.06	0	0.85	0.81
PS **7**	cyclohexane, 25 °C	17.5	15.8	1.20[c]	37.8		
PS **8**	cyclohexane, 5 °C	17.5	16.4	1.22[c]	43.2		
PS **9**	THF, −80 °C	21.5	22.3	1.07	0	0.96	0.98
PS **10**	THF, −80 °C	50	48.9	1.06	0	0.94	0.99
PS **11**	THF, −80 °C	22	22.8	1.07	0	1.78[d]	1.86[d]
PS **12**	cyclohexane/THF −78 ° C	21	22.9	1.09	0	0.76	0.72
PS **13**	cyclohexane/THF −78 ° C	50	51.3	1.08	0	0.74	0.75
PS **14**	cyclohexane/ TMEDA, 5 °C	21	23.1	1.12[c]	16.3		
PS **15**	cyclohexane/ TMEDA, ZnI_2, 5 °C	20	19.1	1.06	0	0.87	0.82
PI **16**	cyclohexane/ TMEDA, ZnI_2, 5 °C	20	23.4	1.16[c]	15.0		
PVP **17**	THF, −78 °C	23	19.0	1.15	0	0.15	0.20

[a] GPC traces for a quenched aliquot of each polymer immediately before the trapping reaction with **1** typically showed 1−2% bimodal character due presumably to either Li−H elimination/coupling or oxidative coupling of the living chain ends. % Bimodal (see Figure 1) is defined as (peak area of higher MW peak/total peak areas after the trapping reaction) − (peak area of higher MW peak/total peak areas before trapping reaction). [b] *f* is defined as the fraction of chains having one anhydride group. Method A: GPC analysis of coupling reaction with an amino-terminal PS of similar M_n (performed either in solution (~0.1 μM, THF, RT, 48 h) or in the melt (180 °C, 10 min) under shear). Method B: ^{1}H NMR analysis of PEG-derivatized polymer (see text). [c] The PDI's of polymers **7**, **8**, **14**, and **16** reflect their bimodal character. Each peak in these GPCs has a narrow PDI (~1.04). [d] For the α,ω-difunctional PS **11** *f* is the fraction of chains having two anhydride groups.

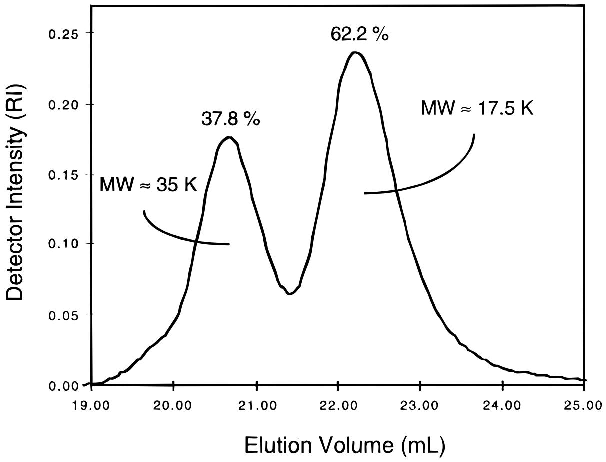
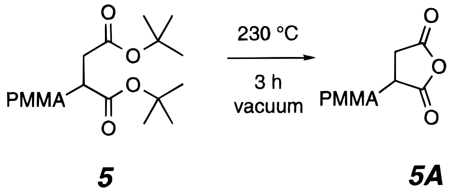


Figure 1. Gel permeation chromatogram of **7** showing bimodal character when the maleate trapping is done in cyclohexane at 25 °C. MW refers to peak molecular weight.

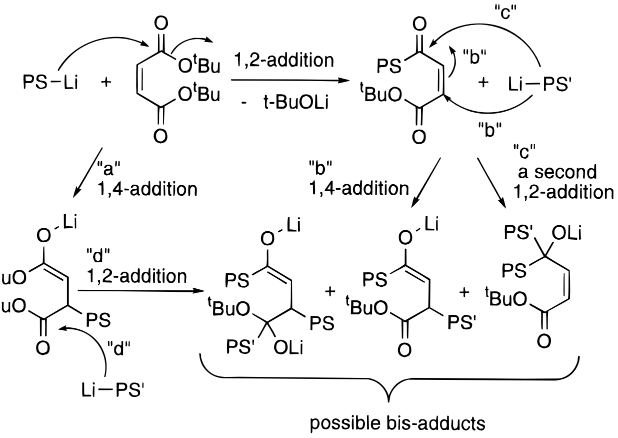
Scheme 2



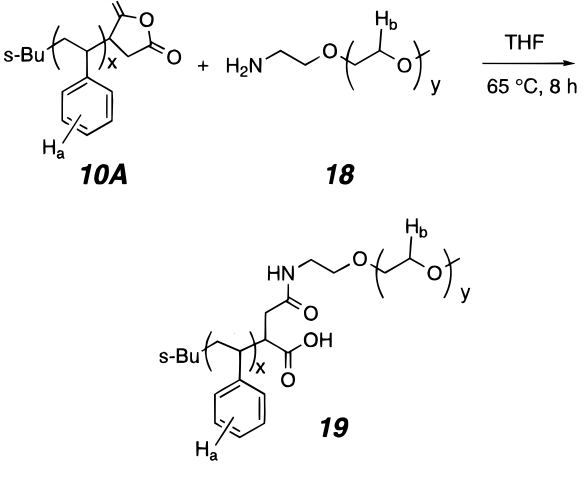
sizing PVP polymers with a single anhydride at the chain end.

Functionality Determination. Anhydride-terminal polymers were analyzed by two different methods, A and B. Method A involved derivatization with a 2-fold molar excess of the commercial 5 kg/mol amino-functional polyethylene glycol (PEG) **18** as shown in Scheme 4 for the 48.9 kg/mol PS **10A**. After derivatization for 8 h in THF at 65 °C, the excess **18** was easily separated from the high molecular weight polymer fraction (GPC (~2 mg injection through a train of two 300 × 7.8 mm, Phenogel columns (5 mm/1000 Å and 5 mm/500 Å), THF elution)). The latter contained both the PS−PEG copolymer **19** along with any unfunctional polymer molecules present in the original sample of PS **10A**. The functionality of the high molecular weight derivatized polymer sample was determined using ^{1}H NMR spectroscopy. Specifically, by comparing the integral ratio of the PS aromatic protons H_a (δ 6.3−7.3 ppm) to the PEG backbone protons H_b (δ 3.62 ppm) in the newly formed PS−PEG block copolymer, the percent functionality could be calculated. The ^{1}H NMR spectrum of **19** is shown in Figure 2. The theoretical integral ratio H_a/H_b for the resulting PS−PEG (48.9 kg/mol−5 kg/mol) diblock is 4.70/1.00. The observed

Scheme 3



Scheme 4



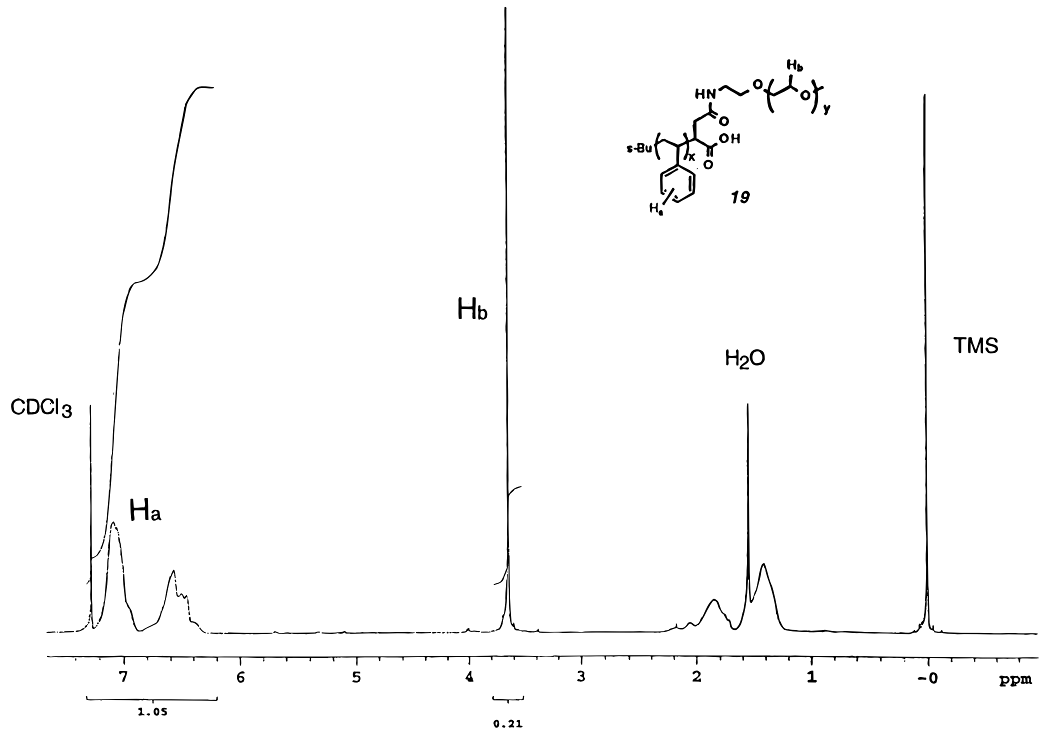
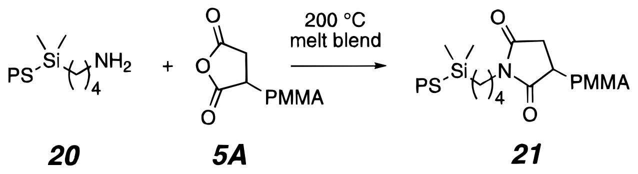


Figure 2. ^{1}H NMR spectrum after derivatization of **10A** (48.9 K) with amino functional PEG **18** (5 K).

Scheme 5



integral ratio was 5.00/1.00, indicating the presence of ~6% of unfunctional PS in the original **10A**. The functionalities listed in Table 1 for **5A**–**17A** were determined using this method.

Method B relied upon GPC analysis to determine the extent of functionality of the anhydride-terminal polymers (Table 1). In other work, we have developed methods for the synthesis of amino-terminated PS.[5] By reacting **5A**–**17A** with a known excess of a highly functional amino-terminated polymer of known (and similar) molecular weight, it is possible to form block copolymer from every anhydride functional polymer present. GPC analysis was then used to determine the extent of conversion to diblock, which is proportional to the percent functionality of the anhydride polymer.[17] From the ratio of the high molecular weight peak area to the sum of the high and low molecular weight peak areas and from the known amount of excess amino-PS, the functionality of the anhydride polymer can be deduced. Similar f values were obtained with each of the two methods.

Melt Blending Results. As further evidence that these polymers are highly functional, a heterogeneous melt blending experiment was performed in a Mini-Max parallel plate mixer.[18] Equimolar amounts of the 29 kg/mol PMMA **5A** and the 18.5 kg/mol amino-terminal polystyrene ($f = 0.7$) **20** were heated for 20 min at 200 °C to generate the diblock imide **21** (Scheme 5). The GPC of this material showed that essentially all of the amino-functional PS **20** had coupled with **5A**. The morphology of the resulting blend was then analyzed by transmission electron microscopy (TEM). Figure 3a shows the morphology of the material obtained after this initial reactive blending. We presume these nanoscopic structures to be PS–PMMA block copolymer micelles (perhaps swollen with unfunctional PS). After this blend was annealed at 200 °C for 72 h, the TEM micrograph of the resulting blend shows a lamellar microstructure (Figure 3). Little, if any, block copolymer was formed during the annealing process (GPC analysis). The lamellar widths of the PS domains (~30 nm) are larger than those for the PMMA domains (~20 nm), presumably because **20** is only 70% functional; i.e., the PS domains are likely to be swollen with unfunctional PS homopolymer. Nonetheless, these micrographs provide even more evidence that we have successfully synthesized polymers with highly functional anhydride chain ends.

Summary

A new method for the synthesis of anhydride terminal polymers has been achieved. Di-*tert*-butyl ester terminal PMMA, PS, PI, and PVP were synthesized by trapping their corresponding anions with di-*tert*-butyl maleate. This method owes its success to the fact that the maleate trapping agent adds only once to the living anion and no products of additional propagation were observed. Furthermore, the PS and PMMA diesters can be pyrolyzed to produce succinic anhydride functionality upon being heated at 235 °C (for 2–12 h) in solution or in the melt. This work, to our knowledge, constitutes *the first synthesis of PMMA with a single anhydride functional group at the chain end*. The functionality of these polymers was determined using ^{1}H NMR spectroscopy and gel permeation chromatography following derivatization reactions with various amines. Notably, we have developed a reliable technique for determining the extent of functional group incorporation in high molecular weight polymers by derivatizing them with amino-functional PEG (followed by preparatory GPC and ^{1}H NMR analysis). Using this technique (as well as other GPC coupling experiments), the *PS and PMMA polymers synthesized were determined to have a high*

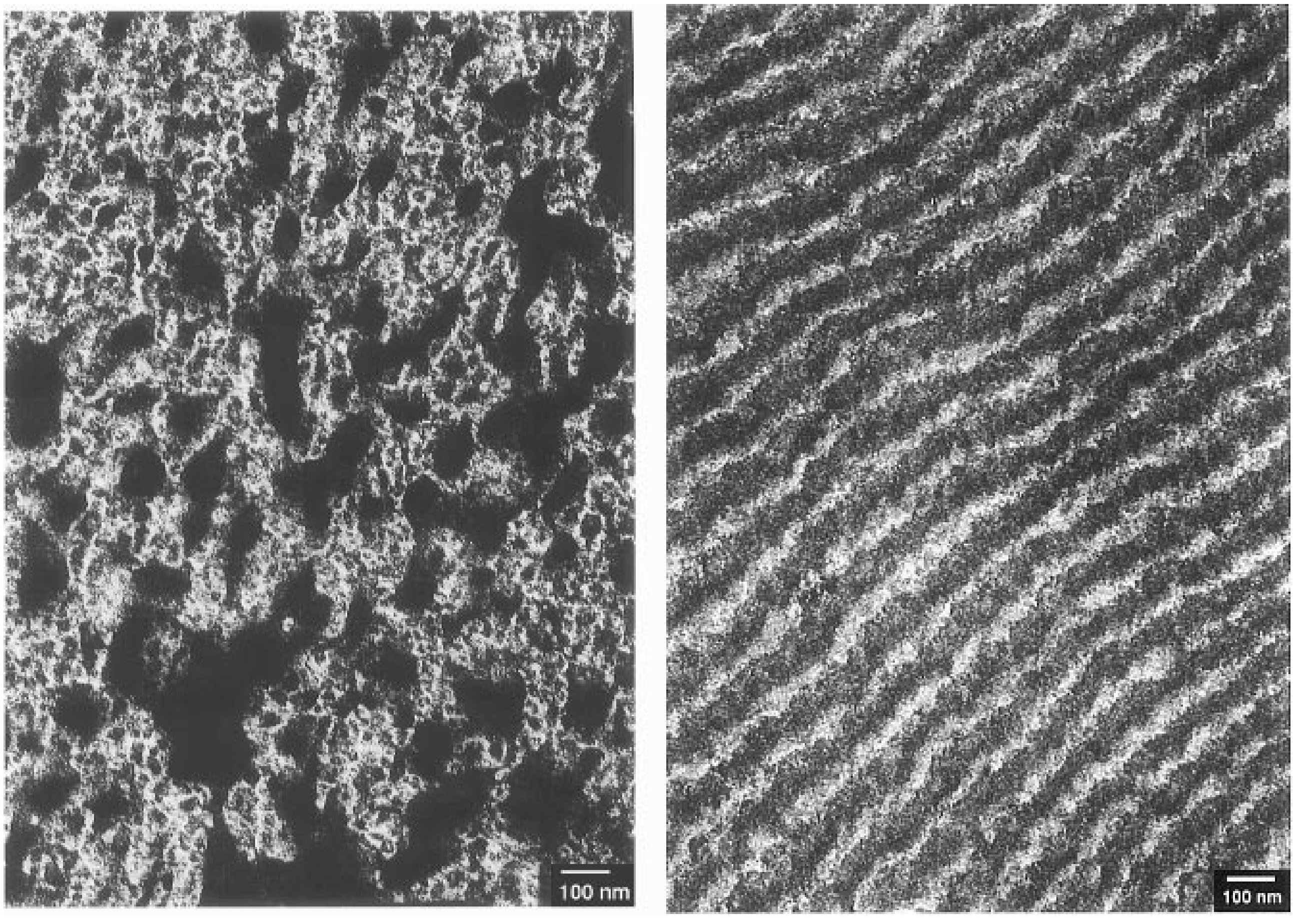


Figure 3. Transmission electron micrographs of the reaction of **5A** (29 K) with amino-terminal PS **20** (18.5 K) at 200 °C in a Mini-Max parallel plate mixer: (a, left) after 20 min of mixing at 200 °C and (b, right) this mixture after annealing at 200 °C for 72 h. PS domains have been selectively stained black with RuO_4 (PMMA domains appear white).

extent of chain-end anhydride incorporation ($f > 0.95$ in some cases). An initial melt blending experiment gave nanoscopic morphologies (transmission electron microscopy) consistent with efficient cross coupling of a highly reactive, immiscible polymer pair. Currently, we are using these materials in other polymer blending studies and investigating the phenomenon of reactive self assembly.[4]

Experimental Section

Materials. Styrene, 1,1-diphenylethylene, cyclohexane, toluene, and heptane were passed through basic alumina (Brockmann I) and stored over activated 4 Å molecular sieves under an argon atmosphere. 2-Vinylpyridine was passed twice through basic alumina and stored over activated 4 Å molecular sieves under an argon atmosphere. Isoprene was distilled from *n*-BuLi under vacuum into an addition buret immediately before use. Methyl methacrylate was first passed through basic alumina and then distilled once from triethylaluminum (1.7 M in heptane) into an addition buret immediately before use. 1,1,2,2-Tetramethylethylenediamine (TMEDA) was distilled twice from calcium hydride and stored over activated 4 Å molecular sieves under an argon atmosphere. Lithium chloride was dried in an oven at 110 °C for 24 h. Zinc iodide was stored in a glovebox and used as received (Aldrich). THF (unstabilized) and diethyl ether (unstabilized) were distilled from sodium benzophenone ketyl. *sec*-Butyllithium was stored at −20 °C and was titrated using menthol and 2,2′-bipyridyl. Amino-functional polyethylene glycol (5 kg/mol, $f = 0.99$/chain) was stored under a blanket of argon at −20 °C and used as received (Shearwater).

Polymer Synthesis. All polymers were synthesized using the pressurized argon method.[19] The reactor, magnetic stirbars, and syringes were stored in an oven (110 °C) and removed just prior to use. Each syringe was purged three times with argon before use. The reactor was then flushed and evacuated five times with argon. The inside of the reactor was rinsed with *s*-BuLi (1.4 M, 2.0 mL) to scavenge any unwanted impurities. After rinsing, the *s*-BuLi was diluted with dry cyclohexane (100 mL) and cannulated from the reactor.

Synthesis of Di-*tert*-Butyl Maleate (1).[20] Isobutylene gas was condensed (15 mL, ~0.13 mol) into a 50 mL heavy-walled pressure tube at −78 °C. The tube was then charged with maleic acid (9.0 g, 0.078 mol), dichloromethane (15 mL), and concentrated sulfuric acid (0.5 mL). The tube was affixed with a Teflon cap, attached to a mechanical stirring motor, and tumbled at 25 °C for 18 h. The tube was then cooled to −78 °C and opened. The contents were poured into 250 mL of ether and placed in a separatory funnel. The ether layer was neutralized with 1 N NaOH, washed (1 × 100 mL of water, 1 × 100 mL of 5% aqueous NaOH, and 2 × 100 mL of brine), dried over sodium sulfate, and filtered. This solution was passed through basic alumina to remove any traces of acid. Upon removal of solvent 11.0 g (62%) of **1** was obtained as a white crystalline solid. This material was stored at −20 °C under an argon atmosphere. ^{1}H NMR ($CDCl_3$): δ 6.06 (s, 2H, CH=CH) and 1.50 (s, 18H, ^{t}Bu CH_3). ^{13}C NMR ($CDCl_3$) δ 130.11, 81.78, and 28.02. GC/MS: mass (% abundance) 173 (1), 171 (1), 157 (2), 118 (1), 117 (33), 116 (2), 100 (1), 99 (10), 82 (1), 73 (4), 72 (1), 60 (1), 59 (22), 58 (6), 57 (100), 56 (18), 55 (2), 54 (3), 53 (1), 46 (1), 45 (1), 43 (3), 42 (1), and 41 (12). FTIR (KBr pellet): 3120−2800, 1720, and 1636 cm^{-1}. Anal. Calcd for $C_{12}H_{20}O_4$: C, 63.12; H, 8.84. Found: C, 63.05; H, 8.71.

Synthesis of Diester-Terminated PMMA 5, 6. THF (500 mL) was distilled directly into a 1 L reactor. The solution was cooled to −78 °C with a dry ice/acetone bath and allowed to thermally equilibrate for 15 min. 1,1-Diphenylethylene (0.3

mL, 1.69 mmol) was charged into the flask via syringe. Lithium chloride (0.25 g, 5.9 mmol) was then added to the reactor. *s*-BuLi (0.50 mL, 1.4 M in hexanes, 0.70 mmol) was then injected into the reactor via syringe through a septum causing a deep red color to immediately develop, and the resulting solution was magnetically stirred with an ~3 cm stirbar so as to maintain a vortex column in the liquid. Methyl methacrylate (17.0 g, 0.170 mol) was added slowly, dropwise from an addition buret into the reactor over a period of 15 min. The solution immediately became faint yellow upon addition of methyl methacrylate. The polymerization was allowed to continue for 1 h at −78 °C after monomer addition was complete. Di-*tert*-butyl maleate (**1**, 0.320 g, 1.40 mmol in 2 mL of THF) was added by syringe causing the yellow color to slightly intensify. The solution was allowed to warm to 0 °C and stirred for 30 min. Degassed methanol was injected through the septum to terminate the reaction. The polymer was precipitated with ~1 L of hexanes, filtered, and dried at room temperature under vacuum to yield 16.8 g (97%) of **5** (95% of **6**).

Synthesis of Diester-Terminated Polystyrenes 7−15. Procedure A (Polymers 7 and 8). Cyclohexane (200 mL) was cannulated into a 1 L reactor. Styrene (22.8 g, 0.219 mol) was charged into the reactor via syringe, and the resulting solution was magnetically stirred with an ~3 cm stirbar so as to maintain a vortex column in the liquid. *s*-BuLi (0.90 mL, 1.4 M in hexanes, 1.3 mmol) was then injected into the reactor via syringe through a septum and a characteristic orange color gradually intensified over 2 min. The polymerization was allowed to continue for 1.5 h at 25 °C. Di-*tert*-butyl maleate (**1**, 0.593 g, 2.6 mmol) was added to the poly(styryllithium) causing the orange color to change to yellow in seconds. Degassed methanol was injected through the septum to terminate the reaction. The polymer was precipitated by addition of ~600 mL of methanol, filtered, and dried at room temperature under vacuum to yield 20.2 g (87%) of **7**. (In the case of **8** (92%), the reactor was cooled to 5 °C before **1** was introduced into the reactor.)

Procedure B (Polymers 9 and 10). THF (500 mL) was distilled directly into a 1 L reactor. The solution was cooled to −80 °C with a dry ice/ether bath and allowed to thermally equilibrate for 15 min. *s*-BuLi (0.30 mL, 1.4 M in hexanes, 0.42 mmol) was then injected into the reactor via syringe through a septum, and the resulting solution was magnetically stirred with an ~3 cm stirbar so as to maintain a vortex column in the liquid. Styrene (9.1 g, 0.0875 mol) was added slowly dropwise by syringe over 15 min causing the solution to immediately become orange. The polymerization was allowed to continue for 15 min after styrene addition was complete. Di-*tert*-butyl maleate (**1**, 0.20 g, 0.84 mmol in 2 mL of THF) was added by syringe to the polystyryl anion causing the characteristic orange color to change to light yellow in seconds. Degassed methanol was injected through the septum to terminate the reaction. The polymer was precipitated with ~1 L of methanol, filtered, and dried at room temperature under vacuum to yield 9.05 g (98%) of **9**. (**10** (86%) was synthesized using the same protocol.)

Procedure C (Polymer 11). THF (500 mL) was distilled directly into a 1 L reactor. The solution was cooled to −80 °C with a dry ice/ether bath and allowed to thermally equilibrate for 15 min. Potassium naphthalenide (4 mL, 0.1 M in THF, 0.40 mmol) was then cannulated into the reactor through a septum, and the resulting dark green solution was magnetically stirred with an ~3 cm stirbar so as to maintain a vortex column in the liquid. Styrene (9.1 g, 0.0875 mol) was added slowly dropwise by syringe over 15 min causing the solution to immediately become orange-red. The polymerization was allowed to continue for 15 min after styrene addition was complete. Di-*tert*-butyl maleate (**1**, 0.182 g, 0.80 mmol in 2 mL of THF) was added by syringe to the polystyryl anion causing the characteristic orange-red color to change to light yellow in seconds. Degassed methanol was injected through the septum to terminate the reaction. The polymer was precipitated with ~1 L of methanol, filtered, and dried at room temperature under vacuum to yield 8.9 g (96%) of **11**.

Procedure D (Polymers 12 and 13). Cyclohexane (200 mL) was cannulated into a 1 L reactor. Styrene (22.75 g, 0.219 mol) was charged into the reactor via syringe, and the resulting solution was magnetically stirred with an ~3 cm stirbar so as to maintain a vortex column in the liquid. *s*-BuLi (0.78 mL, 1.4 M in hexanes, 1.09 mmol) was then injected into the reactor via syringe through a septum, and a characteristic orange color gradually intensified over 2 min. The polymerization was allowed to continue for 2 h. The solution was then cooled to −78 °C and 400 mL of THF was distilled directly into the flask. Di-*tert*-butyl maleate (**1**, 0.500 g, 2.2 mmol) was added to the polystyryl anion causing the characteristic orange color to change to yellow in seconds. Degassed methanol was injected through the septum to terminate the reaction. The polymer was precipitated with ~600 mL of methanol, filtered, and dried at room temperature under vacuum to yield 21.2 g (92%) of **12**. (**13** (90%) was synthesized using the same protocol.)

Procedure E (Polymer 14). Cyclohexane (200 mL) was cannulated into a 1 L reactor. Styrene (18.2 g, 0.175 mol) was charged into the reactor via syringe, and the resulting solution was magnetically stirred with an ~3 cm stirbar so as to maintain a vortex column in the liquid. *s*-BuLi (0.65 mL, 1.4 M in hexanes, 0.875 mmol) was then injected into the reactor via syringe through a septum and a characteristic orange color gradually intensified over 2 min. After 1.5 h, TMEDA (0.5 mL) and ether (0.5 mL) were introduced via syringe and the solution became deep red in color. Di-*tert*-butyl maleate (**1**, 0.400 g, 1.75 mmol) was added to the polystyryl anion causing the characteristic orange color to disappear in seconds and change to yellow. Degassed methanol was injected through the septum to terminate the reaction. The polymer was precipitated with ~600 mL of methanol, filtered, and dried at room temperature under vacuum to yield 18.0 g (98%) of **14**.

Procedure F (Polymers 15 and 16). Cyclohexane (200 mL) was cannulated into a 1 L reactor. Styrene (18.2 g, 0.175 mol) was charged into the reactor via syringe, and the resulting solution was magnetically stirred with an ~3 cm stirbar so as to maintain a vortex column in the liquid. *s*-BuLi (0.65 mL, 1.4 M in hexanes, 0.875 mmol) was then injected into the reactor via syringe through a septum and a characteristic orange color gradually intensified over 2 min. After 2 h, TMEDA (0.5 mL) and ether (0.5 mL) were introduced via syringe and the solution became deep red in color. After 10 min, zinc iodide (0.410 g, 1.29 mmol) was added to the reactor. The solution was stirred at 25 °C for 30 min and the color of the solution gradually lightened to orange. Di-*tert*-butyl maleate (**1**, 0.400 g, 1.75) was added to the polystyryl anion causing the characteristic orange color to disappear in seconds and change to yellow. Degassed methanol was injected through the septum to terminate the reaction. The polymer was precipitated with ~600 mL of methanol, filtered, and dried at room temperature under vacuum to yield 17.2 g (93%) of **15**. (**16** (97%) was synthesized using the same protocol.)

Synthesis of Diester-Terminated PVP 17. THF (500 mL) was distilled directly into a 1 L reactor. The solution was cooled to −78 °C with a dry ice/acetone bath and allowed to thermally equilibrate for 15 min. *s*-BuLi (0.75 mL, 1.4 M in hexanes, 1.05 mmol) was then injected into the reactor via syringe through a septum, and the resulting solution was magnetically stirred with an ~3 cm stirbar so as to maintain a vortex column in the liquid. 2-Vinylpyridine (24.4 g, 0.232 mol in 35 mL THF) was cannulated from a Schlenk flask at −78 °C into the reactor over a period of 15 min. The solution immediately became deep red upon addition of monomer. The polymerization was allowed to continue for 30 min at −78 °C after monomer addition was complete. Di-*tert*-butyl maleate (**1**, 0.480 g, 2.11 mmol in 2 mL of THF) was added by syringe causing the deep red color to change to yellow. Degassed methanol was injected through the septum to terminate the reaction. The polymer was precipitated with ~1 L of hexanes, filtered, and dried at room temperature under vacuum to yield 21.0 g (85%) of **17**.

Thermal Modification of 5A−17A. Procedure a. Polymer **10** (4.0 g) was placed in a 500 mL Schlenk flask. The flask was immersed half-way and heated in an oil bath at 235 °C under vacuum for 3 h.[21] The resulting anhydride containing polymer **10A** was then dissolved in a minimal amount of cyclohexane and freeze-dried under vacuum to yield 3.85 g (97%).

Procedure b. Polymer **5** (500 mg) was placed in a 10 mL culture tube. Dry toluene (5 mL) was added and this solution was sparged with argon for 10 min. The tube was sealed with a teflon-lined screw cap and placed in a oil bath. The solution was heated for 8 h at 235 °C (2 h for the functional PS polymers).[22] The solution was cooled to room temperature and poured into 50 mL of hexanes to precipitate the polymer. The solution was filtered and the solid filtrate was dried under vacuum for 24 h to yield 450 mg (91%) of **5A**.

Derivatization of 5A−17A with PEG-NH$_2$ (18). Derivatization of **10A** is given as an example. Anhydride functional polystyrene **10A** (25 mg, 5.11×10^{-7} mol) and amino-PEG **18** (20 mg, 4.0×10^{-6} mol) were placed in a 10 mL culture tube equipped with a magnetic stirbar. Dry THF (2 mL) was added and this solution was sparged with argon for 5 min. The tube was sealed with a Teflon-lined screw cap and placed in a oil bath. The solution was magnetically stirred for 8 h at 65 °C. The solution was cooled to room temperature and a 0.1 mL aliquot (≈2.2 mg total sample) was sampled for GPC analysis. The high (≈50 kg/mol) and low molecular weight fractions (≈5 kg/mol) from the crude reaction mixture were collected in separate round-bottomed flasks as each came off the column. Each solution (THF) was concentrated under vacuum, and analyzed by ^{1}H NMR spectroscopy (CDCl$_3$).

Compound Characterization Tools. Polymer molecular weights were estimated using a Waters 150-C A1C-BC GPC equipped with three Phenogel columns and UV and RI detectors. For these polymers, the UV detector was set at 256 nm and THF was used as the eluent. Ten standard polystyrenes were used for the calibration. Semipreparative GPC separations were carried out using a Perkin-Elmer Series 2 liquid chromatograph equipped with two analytical Phenogel columns and UV and RI detectors. ^{1}H NMR spectra were recorded on a Varian 500 MHz spectrometer. Infrared spectra were recorded on a MIDAC FTIR. Mass spectra were recorded on a Hewlett-Packard 5890/5971A-MSD tandem gas chromatograph/mass spectrometer (GC/MS).

Transmission Electron Microscopy (TEM). Ultrathin sections (∼500 Å) of the polymer blend were cut using a Reichart Ultracut diamond knife at room temperature and floated on distilled water before being skimmed onto 400 mesh copper grids. The sections were stained in the vapor phase of a 0.5% aqueous RuO$_4$ solution (20 min) and examined under bright field TEM using a JEOL 1210 electron microscope operated at 120 kV accelerating voltage.

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(21) This procedure was found to be less effective for the synthesis of PMMA **5** and **6**. Longer reaction times were required (up to 12 h) and the resulting materials were not as functional ($f \approx 0.7$). These problems were not witnessed using procedure B.

(22) Caution: this reaction vessel is under high pressure. Although we did not encounter any experimental difficulties with a heavy walled culture tube, an explosion did occur on one (out of ∼20 attempts in this type of vessel) occasion when the reaction was performed in a standard (KIMAX) culture tube with a Teflon-lined cap. For this reason, we strongly recommend use of a blast shield when following this procedure.

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