Synthesis of *end*- and *mid*-Phthalic Anhydride Functional Polymers by Atom Transfer Radical Polymerization

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ABSTRACT: Polystyrene (PS) and poly(methyl methacrylate) (PMMA) having a single di-*tert*-butyl phthalate (DTBP) group either at the chain end or in the middle of the chain were synthesized by Cu(I) ion mediated atom transfer radical polymerization (ATRP). The di-*tert*-butyl phthalate initiators **7** and **8** (for *end*-functional polymers) and **11** (for *mid*-functional polymers) were prepared from commercially available di-*tert*-butyl acetylene dicarboxylate (**1**) and myrcene (**2**) in four and six steps, respectively, with high overall yields. The DTBP functionalized polymers could be cleanly converted to the corresponding phthalic anhydride (PA) functional polymers by pyrolysis. The pyrolysis process could be easily monitored using conventional ^{1}H NMR spectroscopy, by observing the significant chemical shift change of the alkyl linker existing in the initiators. Kinetic study of the pyrolysis revealed that the mechanism of the DTBP group pyrolysis to phthalic anhydride (PA) group follows two first-order consecutive reactions having a phthalic diacid (DA) as an observable intermediate. When the PA-functionalized PMMA was subjected to reactive blending at 180 °C with an amine-functionalized PS, the conversion reached a maximum (>90%) in less than 2 min, which is considerably faster than the corresponding reaction of an aliphatic anhydride (e.g., succinic anhydride)-functionalized PMMA. A competition experiment with small molecules showed that phthalic anhydride reacts ∼5 times faster than succinic anhydride with PS−NH_2.

Introduction

Functional polymers are of great interest due to their potential applications in many research areas such as surface modification,[1] adhesion,[2] drug delivery,[3] polymeric catalysts,[4] and compatibilization of polymer blends.[5] One of the key applications requires these polymers to react with other polymers or small molecules having cross-reactive functional groups. To understand fundamental aspects of these macromolecular reactions, it is often desirable and necessary to use polymers containing only one functional group per chain. Especially in polymer blends, the reactions taking place at the polymer interface result in the formation of block or graft copolymers. These can reduce interfacial tension, prevent drop coalescence, and enhance adhesion. Although conceptually any pair of cross-reactive groups that can form covalent bonds between two polymers could be adopted in polymer−polymer coupling reactions, not many reaction types have been used in practice due to one or more of the following restrictions. Thermal stability, reaction rates, elimination of small molecule byproducts, and lack of reliable synthetic methods can limit the utility of any one coupling reaction type. Some compatibilizing reactions that are used include amine−anhydride, amine−carboxylic acid, amine−epoxy, isocyanate−hydroxyl, oxazoline−carboxylic acid, and epoxy−carboxylic acid couplings. Among these reactions, the amine−anhydride pair is superior because it not only is compatible with blending conditions but also gives very fast and clean reaction.[6] For these reasons efficient synthesis of anhydride functional polymers with controlled architecture and high functionality has been of great interest. Anionic polymerization has traditionally been one of the best ways to prepare anhydride functional polymers with controlled molecular weights and narrow molecular weight distributions. A few methods to make anhydride-functionalized polymers by anionic polymerization have been reported. Takenaka's method involves trapping the polymer anions with a butadienyl alkyl group, followed by modification with maleic anhydride by Diels−Alder reaction to give a cyclic anhydride group at the polymer chain ends.[7] Cernohous' strategy involves direct capture of the polymer anion with di-*tert*-butyl maleic ester and subsequent pyrolysis of the polymer to generate the anhydride group.[8] Jérôme and co-workers recently reported a modified protocol of Cernohous' strategy using chemical deprotection of di-*tert*-butyl groups instead of thermal pyrolysis.[9] Both methods provide anhydride bearing polymers with high functionalities and very narrow molecular weight distributions. However, they require extremely controlled experimental conditions to avoid impurities during the synthesis and/or elaborate synthesis of the trapping reagents. In addition, since these two methods adopt a trapping rather than an initiation strategy for incorporating the functional group, the functionality of the polymers can be lower than ideal (f < 1.0) depending on the experimental conditions and monomer structure.

Recently, atom transfer radical polymerization (ATRP) has emerged as a very versatile, convenient, and powerful strategy for polymer synthesis.[10] Experimental conditions of this method are not as rigorous as those for anionic polymerization, yet the polymers obtained by this method give relatively narrow polydispersities (PDI < 1.3) with good molecular weight control. Another advantage of ATRP is its greater functional group tolerance than anionic polymerization. For these reasons ATRP has proven to be very powerful for the preparation of various functional polymers.[11] So far, to our knowledge, only two methods for preparing anhydride

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functional polymers by ATRP have been reported.[11a,12] Pionteck's method[11a] involves the use of 4-(bromomethyl)phthalic anhydride as an initiator for ATRP of styrene. The resulting polymers showed moderate polydispersities (PDI = 1.31−1.43) and some loss of the anhydride functionality, probably due to hydrolysis under ATRP conditions. Kallitsis' method[12] adopts postmodification of bromo end-functional polystyrene obtained by ATRP with excess maleic anhydride and takes advantage of the fact that maleic anhydride propagates only very slowly. Since this strategy involves postsynthesis modification, there could be some functionality loss depending on the efficiency of the trapping reaction. In addition, the possibility of a reaction of the resulting α-bromo group on the succinic anhydride modified polymer with a counter-reactive group (e.g., with an amine functional polymer during reactive blending) is a concern.

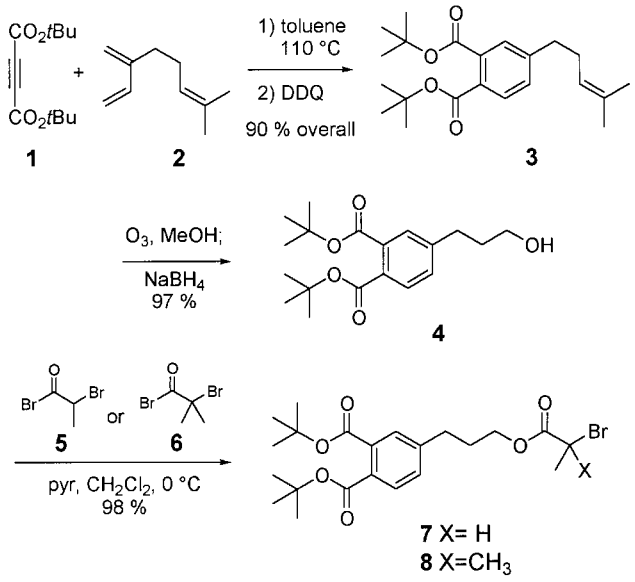
To avoid the aforementioned problems, we sought to develop an ATRP initiator bearing a protected form of the anhydride group (e.g., a 1,4-di-*tert*-butyl diester) and to use subsequent in situ pyrolysis[8,13] of the di-*tert*-butyl diester to generate the anhydride functionalized polymer. Here we report the design and synthesis of new ATRP initiators bearing a di-*tert*-butyl phthalate (DTBP) group and the use of these initiators to obtain *end*- and *mid*-DTBP functionalized poly(methyl methacrylate) (PMMA) and polystyrene (PS). Understanding reactivity differences between *end*- vs *mid*-functional polymers in reactive blending is important, since it could shed light on fundamental aspects of the effect of polymer architecture on polymer coupling reactions.[14] Very clean generation of the phthalic anhydride group was achieved by subsequent thermal pyrolysis, and this process was conveniently monitored by ^{1}H NMR spectroscopy. Generation of the anhydride group was quantitative, and reactive blending experiments with these polymers showed that phthalic anhydride reacts faster than aliphatic succinic anhydride in polymer−polymer coupling reactions.

Results and Discussion

Preparation of Di-*tert*-butyl Phthalate (DTBP) ATRP Initiators. Generally, benzylic bromides and α-bromoesters are good initiators for Cu(I)-mediated ATRP.[10] Although integration of benzylic bromide with phthalic anhydride functionality has been achieved by *N*-bromosuccinimide (NBS) bromination of 4-methylphthalic anhydride,[11a] the reaction is complicated by formation of multisite bromination products. Purification of the monobromide from the mixture is not trivial because of the reactive anhydride group. Since conventional copper-mediated ATRP conditions require ligands such as bipyridine or multidentate tertiary amines, these ligands make the solution basic. As a consequence, the presence of any moisture can hydrolyze an anhydride group to form diacid. Therefore, we decided to use a protected form of the anhydride that would survive the ATRP conditions yet be convenient for efficient conversion to anhydride after the polymer synthesis.

To introduce the bromide functionality, we first attempted NBS bromination of di-*tert*-butyl-4-methyl phthalate. However, the reaction resulted in a mixture of brominated products including di- and tribromo species. Although there are several easily accessible phthalic acid or anhydride derivatives such as trimellitic acid (or anhydride) and pyromellitic acid (or dianhydride), modification of these to useful ATRP initiators having either benzylic bromide or α-bromo ester groups is synthetically challenging. Instead, we designed a novel synthetic route to the desired DTBP functionalized ATRP initiators involving a Diels−Alder reaction as shown in Scheme 1.

Scheme 1. Synthesis of Di-*tert*-butyl Phthalate ATRP Initiators 7 and 8 for *end*-Functional Polymer Synthesis

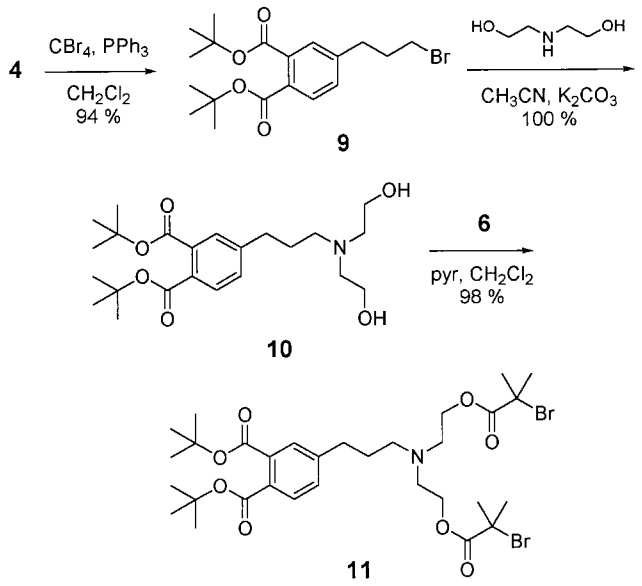


The Diels−Alder reaction between commercially available di-*tert*-butyl acetylenedicarboxylate (**1**) with myrcene (**2**) gave the cycloaddition product in 91% yield after purification. Aromatization of the resulting dihydrophthalate by DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) yielded phthalate **3** in high yield. These two sequential reactions could be done in one pot without separation of the dihydrophthalate intermediate in 90% overall yield. The terminal trisubstituted double bond was cleaved by ozonolysis and in situ reduction with sodium borohydride to give the primary alcohol **4** in close to quantitative yield. Derivatization of this alcohol **4** with either 2-bromopropionyl bromide (**5**) or 2-bromoisobutyryl bromide (**6**) provided the desired ATRP initiators **7** and **8**, respectively. Although the initiator synthesis is a multistep sequence, the overall yield is over 86%, and purifications of each intermediate were straightforward by conventional chromatography.

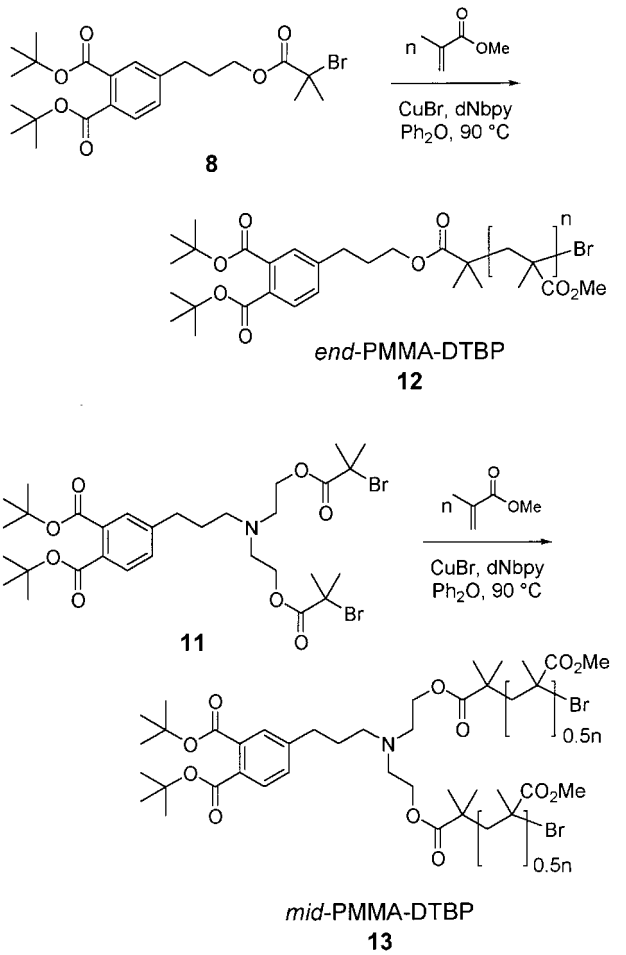
The preparation of the bidirectional ATRP initiator that could provide *mid*-DTBP functional polymers is outlined in Scheme 2. Alcohol **4** was converted to primary bromide **9** using carbon tetrabromide and triphenylphosphine in methylene chloride[15] in 94% yield. The resulting bromide in **9** was substituted with diethanolamine in acetonitrile to provide diol **10** in quantitative yield. The use of a nonnucleophilic polar solvent (CH_3CN) was critical to achieve a high yield in this reaction. For example, when the reaction was performed in ethanol, a significant amount of ethoxy-substituted product was obtained as a major product, in addition to a small quantity of **10**. Finally, derivatization of the two primary alcohol groups with 2 equiv of 2-bromoisobutyryl bromide (**6**) provided bis-α-bromo ester **11** that has a DTBP group in the middle in high overall yield (92% from **4**).

DTBP-Functional Polymer Syntheses by ATRP. Having the mono- and bidirectional initiators **7**, **8**, and

Scheme 2. Synthesis of Difunctional Di-*tert*-butyl Phthalate ATRP Initiator 11 for *mid*-Functional Polymer Synthesis



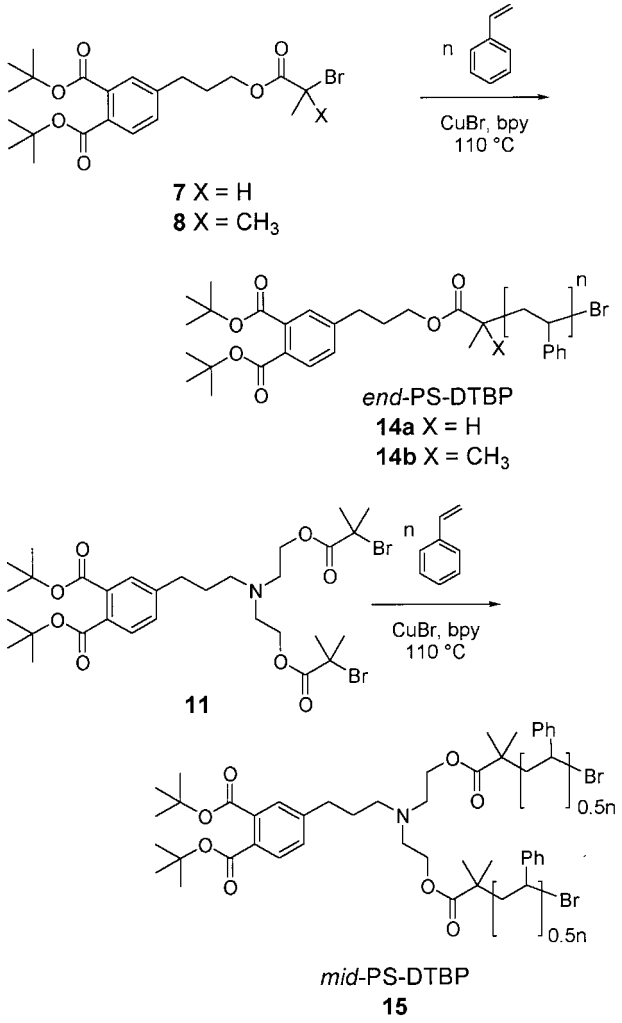
Scheme 3. Synthesis of Di-*tert*-butyl Phthalate (DTBP)-Functionalized PMMA 12 and 13 by ATRP



11 in hand, we investigated the use of these initiators for polymerization of MMA and styrene under ATRP conditions. The syntheses of DTBP-containing PMMA and PS are shown in Schemes 3 and 4, respectively.

For MMA polymerization, Matyjaszewski's conditions[16] (0.5 equiv of CuBr and 1.0 equiv of 4,4′-bis(5-nonyl)-2,2′-bipyridine to initiator with 50% monomer solution in diphenyl ether, 90 °C) were employed. Styrene was polymerized in bulk using equimolar amounts of initiator and copper(I) (CuBr:ligand = 1:2). The characterization data for the various polymers are presented in Table 1. After 19−24 h of reaction time, the yields were around 70−80% after filtration of the crude reaction mixture through a pad of alumina and precipitation. The calculated molecular weights ($M_{n,cal}$) based on these isolated yields were about 10% lower than the actual M_n values of the polymers determined by GPC. This is mainly due to polymer mass loss during the filtration of the crude solution through alumina to remove the copper complex and/or during the multiple precipitations. In fact, when the conversion was checked by ^{1}H NMR of the crude solution before filtration and precipitation, the $M_{n,cal}$ value was higher than that calculated from the isolation yield and matched well the value determined by GPC (footnotes *f* and *g* under Table 1). The GPC of all the polymers showed monomodal traces with reasonably narrow polydispersities (1.15−1.32). The use of the 4,4′-dinonyl-2,2′-bipyridine (dNbpy) ligand[16] resulted in narrower molecular weight distributions (polymer **14b** in Table 1) since the copper complexes are more soluble.

Scheme 4. Synthesis of Di-*tert*-butyl Phthalate (DTBP) Functionalized PS 14 and 15 by ATRP



The presence of the DTBP functional group could be clearly verified by ^{1}H NMR analysis. For example, in the ^{1}H NMR spectrum of *end*-PMMA−DTBP (**12**), two

Table 1. Polymer Characterization Data

polymer	conditions[a]	time (h)	yield[b] (%)	$M_{n,cal}$[c] (g/mol)	$M_{n,SEC}$ (g/mol)	$M_{n,NMR}$[d,e] (g/mol)	M_w/M_n
end-PMMA−DTBP **12**	CuBr, dNbpy, Ph_2O, 90 °C	19	70	17 500	21 000	18 500	1.20
mid-PMMA−DTBP **13**	CuBr, dNbpy, Ph_2O, 90 °C	20	71	17 800	19 400	17 800	1.26
end-PS−DTBP **14a**	CuBr, bpy, 110 °C	22	76	15 200	16 300	16 600	1.20
end-PS−DTBP **14b**	CuBr, dNbpy, 110 °C	24	62 (78[f])	12 400 (15 800[g])	16 000	16 200	1.15
mid-PS−DTBP **15**	CuBr, bpy, 110 °C	20	72	28 800	32 600	39 000	1.32

[a] For PMMAs, initiator/CuBr/ligand = 1/0.5/1, monomer/Ph_2O = 1/1 (wt). For PS, initiator/CuBr/ligand = 1/1/2 in bulk styrene. [b] Yields after filtration through an alumina column and precipitation in proper solvents. Some loss of polymer mass (∼10%) during the filtration through an alumina column was observed. [c] Calculation of the $M_{n,cal}$ was based upon the isolated yields. [d] Number-average molecular weight of the purified polymers based on ^{1}H NMR analysis. [e] Di-*tert*-butyl ester "functionality" was assumed to be high since every chain was initiated by a phthalate containing α-bromoester. [f] This yield is based on the conversion of the monomer determined by the ^{1}H NMR analysis of the crude reaction mixture. [g] Calculated $M_{n,cal}$ based upon the conversion from ^{1}H NMR of the crude reaction mixture.

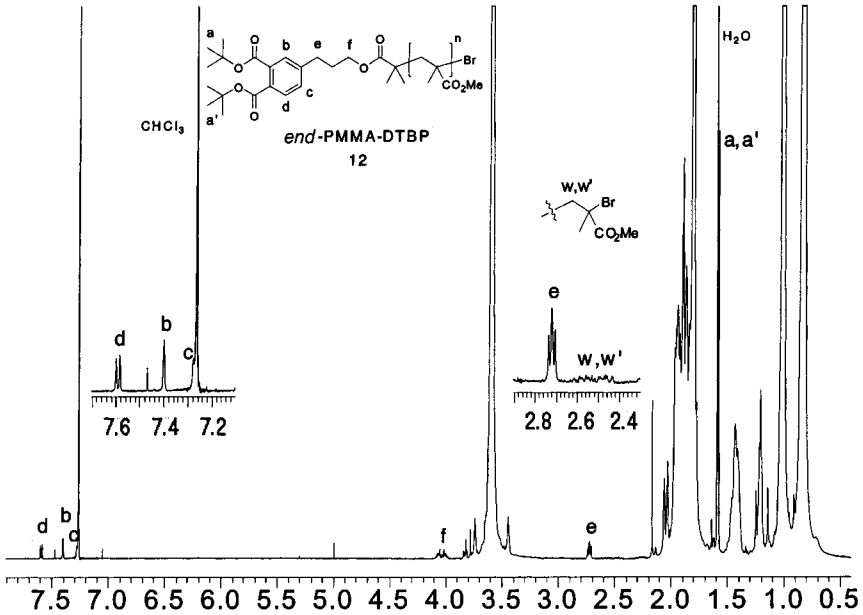


Figure 1. ^{1}H NMR (500 MHz) spectrum of *end*-PMMA−DTBP **12** (M_n = 21 000 g/mol) in $CDCl_3$.

tert-butyl groups (*a* and *a′*) of the DTBP group appear at δ 1.59 and δ 1.60 as singlets (Figure 1). The resonance of the benzylic methylene protons (*e*) appears at δ 2.72 as a triplet. The methylene protons *f* next to the ester appear at δ 4.03 as complex multiplets due to the stereoisomerism (tacticity) of the polymer backbone. All three aromatic protons (*b*, *c*, and *d*) could be easily found at δ 7.40, 7.26, and 7.60, respectively. The chemical shift of the proton *c* happens to be very close to that of the chloroform (NMR solvent), and the signal is overlapped with the solvent peak. The presence of the α-bromoester moiety at the other terminus could also be verified by several downfield shifted methyl ester groups (δ 3.7−3.9). A broad resonance at δ 2.4−2.6 is assigned to the diastereotopic methylene protons *w*, *w′*, which are deshielded by the β-bromide substituent.

The spectrum of the *mid*-functional DTBP group of *mid*-PMMA−DTBP **13** could also be assigned clearly as shown in Figure 2. Resonances of *tert*-butyl groups (*a* and *a′*) and aromatic peaks (*b*, *c*, and *d*) are similar to those in *end*-PMMA−DTBP **12**. Methylene protons next to the ester groups (*h*) also appear as multiplets, slightly more downfield (δ 4.08) than those (δ 4.03) in *end*-PMMA−DTBP **12**, probably due to the amino group at their β-position. However the multiplicity of these peaks is now more complicated than in *end*-PMMA−DTBP **12**. They are influenced by anisotropy arising from tacticity differences in both of the flanking PMMA arms in **13**. The benzylic protons (*e*) are now shifted upfield (δ 2.66)

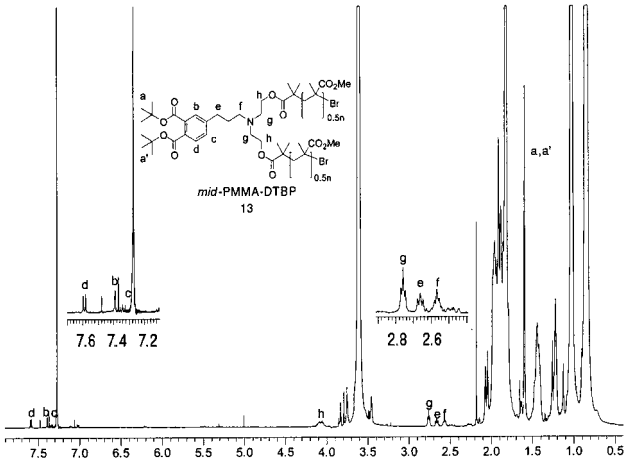


Figure 2. ^{1}H NMR (500 MHz) spectrum of *mid*-PMMA−DTBP **13** (M_n = 19 400 g/mol) in $CDCl_3$.

compared with **12** (δ 2.72) since the β-substituent is nitrogen rather than oxygen. Two methylene groups (*g*) appear as a triplet at δ 2.76, and another methylene group (*f*) next to the nitrogen now appears at δ 2.57 as a multiplet. Finally, the presence of methyl ester groups at δ 3.75−3.90 and terminal methylene group at δ 2.4−2.6 indicates that the chain ends still contain bromines.

For polystyrenes, the resonances from DTBP groups could also be assigned, but the peak shapes are broadened due to stronger anisotropic effects of the polymer

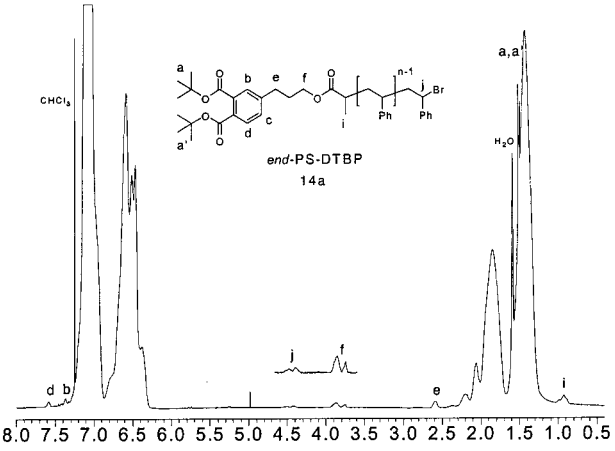


Figure 3. ^{1}H NMR (500 MHz) spectrum of *end*-PS-DTBP **14a** (M_n = 16 300 g/mol) in $CDCl_3$.

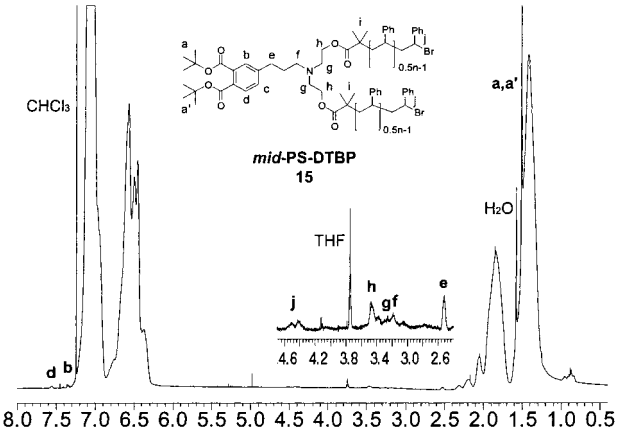


Figure 4. ^{1}H NMR (500 MHz) spectrum of *mid*-PS-DTBP **15** (M_n = 32 600 g/mol) in $CDCl_3$.

backbone (Figure 3 and Figure 4). In the case of *end*-PS-DTBP **14a**, the resonances for the aromatic protons *d* and *b* lose their fine structures and appear at δ 7.59 and 7.37 as broad peaks. The signal for proton *c* is buried under the polystyrene backbone. The benzylic methylene group (*e*) appears as a broad singlet at δ 2.59, while resonances of the methylene protons *f*, which reside closer to the backbone stereocenters, appear as two separate broad peaks at δ 3.95−3.70. The α-methyl group (*i*) appears at δ 0.95. Two *tert*-butyl groups (*a*, *a*′) at δ 1.59 and δ 1.60 appear as separate sharp singlets extruding from the broad peak arising from backbone methylene protons. The presence of a terminal bromine was indicated by the benzylic methine resonance (*j*) at around δ 4.4−4.6. For another *end*-PS-DTBP **14b**, derived from the initiator **8** containing a geminal dimethyl group instead of monomethyl group at the α-position of the ester, the methylene peaks corresponding to *f* and *e* appeared at more shielded positions [δ ∼3.5 (vs δ ∼3.8 in **14a**) and δ ∼2.5 (vs δ ∼2.6 in **14a**), respectively] due to a conformational buttressing (cf. "*gem*-dimethyl effect"[17]). It is notable that analysis of chemical shift differences can provide insight about local conformational effects within the polymer structure.

Since the *mid*-PS-DTBP **15** sample was of higher molecular weight (M_n = 32 600 g/mol), the signal-to-noise ratio for the unique resonances in the ^{1}H NMR spectrum is lower (Figure 4). Nonetheless, resonances for the methylenes (*h*, *g*, and *f*), benzylic methylene (*e*),

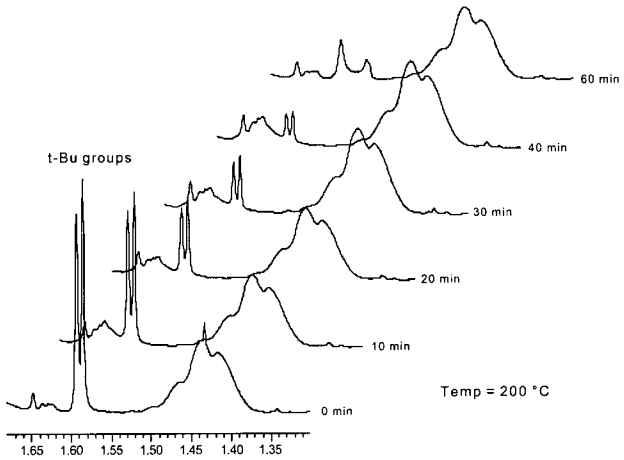


Figure 5. ^{1}H NMR monitoring of pyrolysis of *end*-PMMA−DTBP **12**: *tert*-butyl group region (temperature = 200 °C).

tert-butyl (*a* and *a*′), and aromatic (*b* and *d*) groups could be identified.

Number-average molecular weights (M_n) of the polymers could also be calculated from the integration ratios between backbone signals and one of these end group signals and the values matched reasonably well with those from SEC (Table 1).

Pyrolysis of Di-*tert*-butyl Phthalate (DTBP)-Functionalized Polymers to Phthalic Anhydride (PA)-Functionalized Polymers. Pyrolysis of Poly(methyl methacrylate)−Di-*tert*-butyl Phthalate (PMMA−DTBP). Having the DTBP-functionalized polymers in hand, we investigated the pyrolysis of the DTBP-group pyrolysis to phthalic anhydride (PA). For the previously studied di-*tert*-butyl succinyl functionalized PMMA or PS,[8] quantitative monitoring of the pyrolysis was not feasible by NMR analysis. However, the resonances from the DTBP groups in **12**−**15** are well-suited for such analysis. Polymer samples were loaded as powder in NMR tubes, and each tube was heated under nitrogen. Disappearance of *tert*-butyl group resonances at δ 1.58−1.59 could be clearly observed over time (Figure 5). When the pyrolysis was performed at 200 °C, the *tert*-butyl groups were nearly completely removed (>90%) after about an hour. (The broad peak at δ ∼1.59 in the spectrum of the 60 min sample is presumed to be water, which either could be introduced as a contaminant in the $CDCl_3$ or, since it is a byproduct of the reaction itself, should have been present in the headspace of the reaction NMR tube when the $CDCl_3$ was added.) The same extent of reaction was also observed in other regions of the spectra (see Figures 6 and 7).

The most diagnostic peak of the pyrolysis process was the benzylic methylene resonances (*e*) of the end group (Figure 6). After 10 min, a new broad peak at δ 2.86 (*e*′) appeared while the triplet for the benzylic protons (peak *e* from H_e) of the DTBP species was reduced in intensity. After 20 min, another new peak at δ 2.93 (*e*″) with a fine structure (triplet) appeared while the peaks *e* and *e*′ were reduced in intensity.

A similar pattern was also observed for the aromatic resonances from the phthalate group (Figure 7). Signals from PMMA−DTBP (*b* and *d*) disappeared slowly over 40 min, and new sets of transient peaks (*b*′, *c*′, and *d*′) rose and fell over time, while new peaks (*b*″, *c*″, and *d*″) developed slightly downfield. The species were assigned as di-*tert*-butyl phthalate (DTBP), diacid (DA),

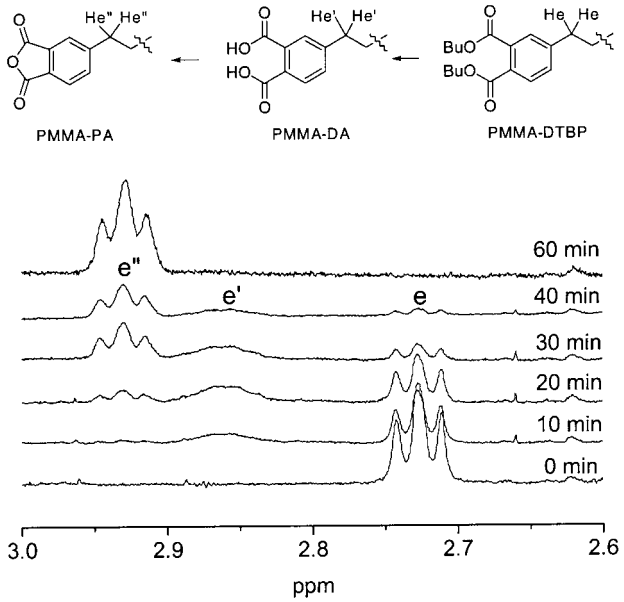


Figure 6. ^{1}H NMR monitoring of pyrolysis of *end*-PMMA−DTBP **12**: benzylic methylene region (temperature = 200 °C).

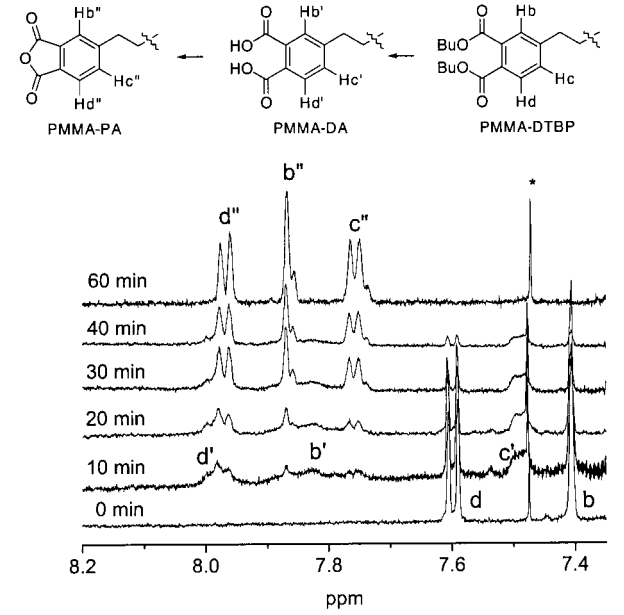


Figure 7. ^{1}H NMR monitoring of pyrolysis of *end*-PMMA−DTBP **12**: aromatic region (temperature = 200 °C). Peak * is a C_{13}−H coupled sideband of residual $CHCl_3$ in the NMR solvent ($CDCl_3$).

and phthalic anhydride (PA), respectively (Figures 6 and 7). The existence of the phthalic anhydride group could also be verified by IR spectroscopy. While the ester carbonyl at 1728 cm^{-1} disappeared, two new peaks at 1783 and 1850 cm^{-1} developed during the pyrolysis.

From careful analysis of the NMR spectra during the pyrolysis process, several pieces of important mechanistic information could be obtained. First, since the pyrolysis was performed in a closed system without vacuum, the volatile side products were trapped in the NMR tube and detected by NMR spectroscopy after dissolving the polymer with $CDCl_3$. Surprisingly, isobutene could be clearly detected (see the NMR spectrum in Supporting Information). However no indication of the presence of *tert*-butyl alcohol was present in the NMR spectra (δ 1.27). No direct evidence was

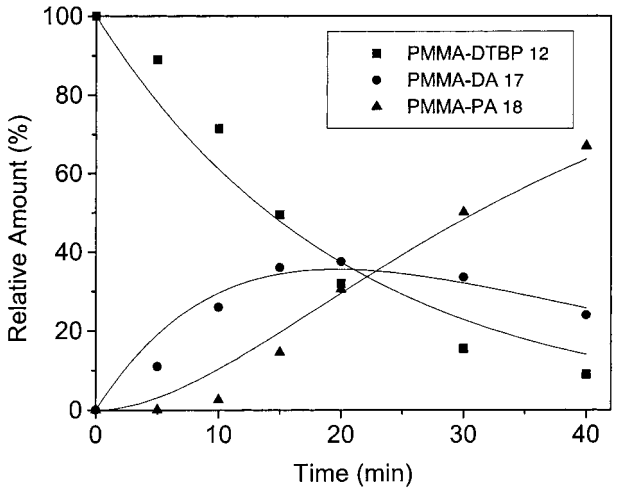
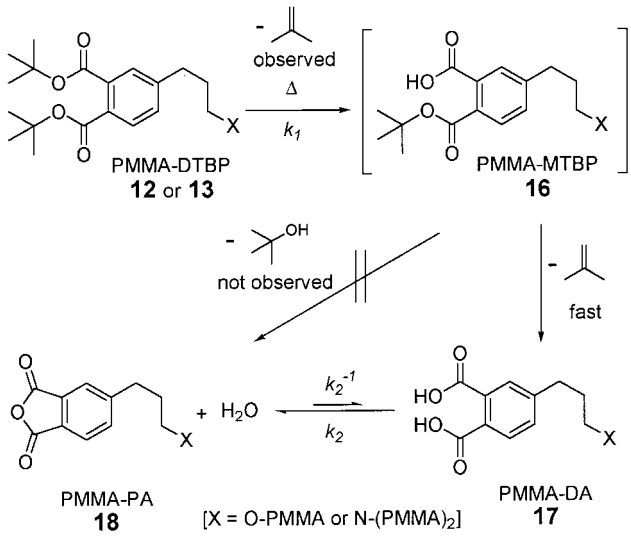


Figure 8. Time dependence of relative concentrations of *end*-PMMA−DTBP (**12**), −DA (**17**), and −PA (**18**) species during the pyrolysis of **12** at 200 °C. Each relative concentration was determined by ^{1}H NMR integration of benzylic methylene resonances **b**, **c**, and **d** for each species as shown in Figure 6.

Scheme 5. A Proposed Mechanism for the Thermal Conversion of PMMA−DTBP (12 and 13) to PMMA−PA



observed for the accumulation of the intermediate mono-*tert*-butyl phthalate **16** (Scheme 5).

A mechanism consistent with these observations is presented in Scheme 5. Namely, PMMA−DTBP is first pyrolyzed into PMMA−MTBP (**16**), releasing one isobutene molecule with a rate constant k_1 followed by a rapid loss of a second isobutene to form PMMA−DA (**17**). This might be due to self-catalysis by the adjacent carboxylic acid group generated by the first pyrolysis event. Because there was no indication of *tert*-butyl alcohol, direct formation of the phthalic anhydride species, PMMA−PA (**18**), the route from the PMMA−MTBP (**16**) to PMMA−PA (**18**) is ruled out. The accumulation of diacid species PMMA−DA (**17**) indicates that the rate of cyclization of the diacid **17** to phthalic anhydride **18**, k_2, is comparable to the first *tert*-butyl group pyrolysis rate, k_1. Therefore, the overall process can be explained by two first-order consecutive reactions.[18] A plot of experimental (individual points) and theoretical data (solid curves) obtained from the ^{1}H NMR spectra and eqs 4−6,[18] respectively, is shown in Figure 8. Rate constants k_1 and k_2 could be calculated from these data.

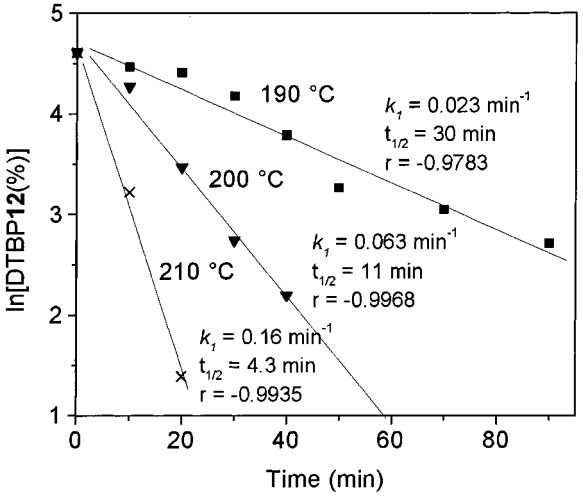


Figure 9. Plots of ln[PMMA−DTBP (**12**)] over time at various temperatures. Rate constants of the first pyrolysis step (k_1) and half-lives of PMMA−DTBP (**12**) at each temperature are shown.

The pyrolysis was carried out at three different temperatures (190, 200, and 210 °C), and linear relationships ($r = -0.9783$, -0.9968, and -0.9935, respectively) of ln[PMMA−DTBP(**12**)] vs time were obtained (Figure 9). Half-lives for the initial pyrolysis of the DTBP species **12** were 30, 11, and 4.3 min at these three temperatures. The activation enthalpy ($\Delta H^{\ddagger}$) and activation entropy ($\Delta S^{\ddagger}$) of this process were calculated to be about 42 kcal/mol and 16 cal/(mol K), respectively.

Pyrolysis of Polystyrene−Di-*tert*-butyl Phthalate (PS−DTBP). Pyrolysis of PS−DTBP could be monitored by ^{1}H NMR spectroscopy in the same manner as that of PMMA−DTBP. One significant difference was that the bromine at the chain end of the PS−DTBP **14a** was lost during the pyrolysis. New broad olefinic resonances at δ 6.0−6.3 [*k* and *j″* in spectra B and C of Figure 10] and an allylic resonance at δ 3.1 (*l*) suggested that dehydrobromination took place under the pyrolysis conditions.

Pyrolysis of PS−DTBP proceeded somewhat more quickly. The formation of the anhydride was complete in 30 min at 190 °C while it took over 1 h for the analogous PMMA at the same temperature (Figure 11). A similar trend had been observed for di-*tert*-butyl succinate functional polymer pyrolysis. Pyrolysis of PS-succinate derivatives required milder conditions (about 1 h at 210−220 °C) than those of PMMA derivatives (8 h at 235 °C in toluene).[8]

Reactive Melt Blending. Reactivities of these PMMA−PA polymers with a PS-amine were tested under polymer blending conditions. *end*-PMMA−PA **18** (obtained from *end*-PMMA−DTBP **12**) was mixed with *end*-PS−NH_2[19] (M_n = 15 700 g/mol, M_w/M_n = 1.02, functionality ∼99%) in a 38:62 weight ratio and subjected to shear blending in a MiniMAX mixer[20] (Custom Scientific Instruments, Cedar Knolls, NJ) at 180 °C with 320 rpm rotor speed. Three stainless steel ball bearings were added to the cup to obtain more uniform mixing.[21] Periodically the mixer was opened, and a sample was removed from the mixer and checked by GPC (gel permeation chromatography) to measure the amount of diblock copolymer formed. The same experiment was done with *mid*-PMMA−PA (*mid*-**18**, obtained from *mid*-PMMA−DTBP **13**). The conversion data of these reactive blending experiments are shown in Figure 12.

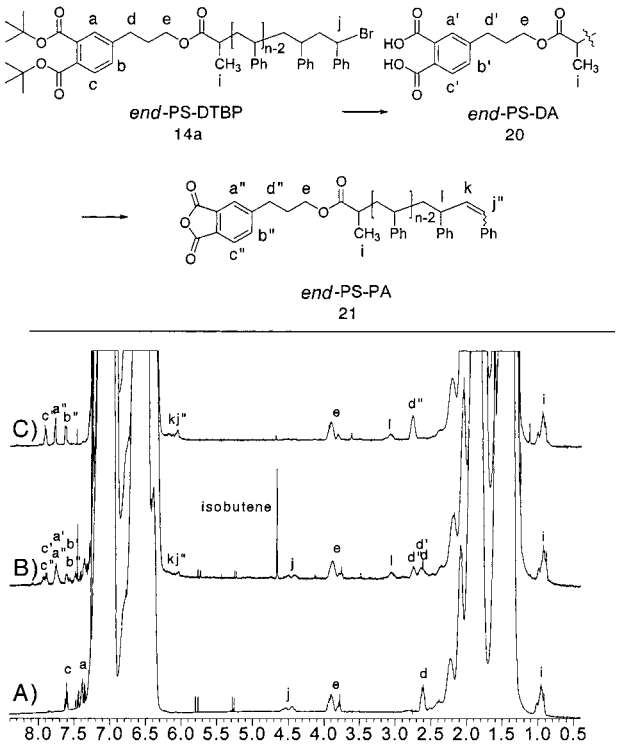


Figure 10. Monitoring of pyrolysis of *end*-PS-DTBP (**14a**): (A) represents the ^{1}H NMR of *end*-PS-DTBP (**14a**). (B) represents the ^{1}H NMR of **14a** after 10 min at 190 °C under 1 atm. (C) represents the ^{1}H NMR of **14a** after 40 min at 190 °C under vacuum. Resonances at δ 5.76 and δ 5.24 in (B) and (C) are from residual styrene monomer in the sample.

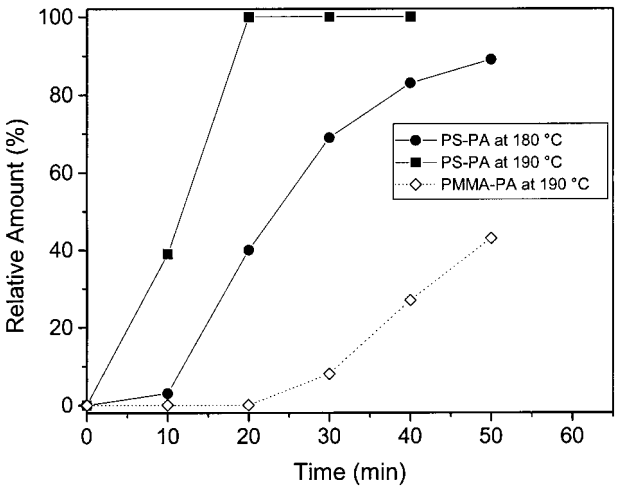


Figure 11. Time dependence of the relative amounts of *end*-PS−PA (**21**) at various temperatures.

Compared with the data obtained by Orr et al.,[6] who studied many different reaction pairs under similar conditions, these two phthalic anhydride functionalized PMMAs exhibited faster reaction rates (maximum conversion in ≤2 min) with higher conversion (92% for *end*-functional and 85% for *mid*-functional PMMA). For example, *end*-succinic anhydride functional PMMA achieved only 40% conversion in 20 min (see Figure 12). This high conversion for reactive heterogeneous polymer coupling is attributed to the higher reactivity of phthalic anhydride compared to an aliphatic anhydride (ca. succinic anhydride). To verify the reactivity difference between these two classes of anhydrides, a competition reaction experiment was performed (Scheme 6).

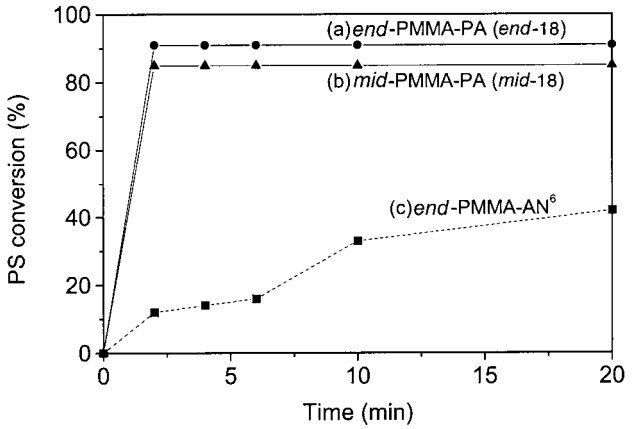
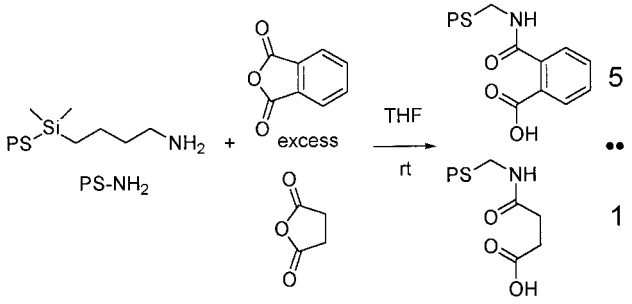


Figure 12. Conversion of limiting reagent vs time in blends of *end*- or *mid*-PMMA−PA with PS−NH_2. Blends were prepared in the MiniMax mixer at 180 °C and 320 rpm under a nitrogen blanket. The conversions were measured by analysis of the UV trace from GPC run of each sample. The UV response of PMMA fraction was negligible compared to that of PS fraction. (a) represents a blend of 38% *end*-PMMA−PA (*end*-**18**, $M_n = 21\,000$ g/mol) with 62% PS−NH_2 ($M_n = 15\,000$ g/mol, $f \sim 0.99$). (b) represents a blend of 36% *end*-PMMA−PA (*end*-**18**, $M_n = 19\,400$ g/mol) with 64% PS−NH_2 ($M_n = 15\,000$ g/mol, $f \sim 0.99$). (c) represents a blend of 30% *end*-PMMA-succinic anhydride ($M_n = 29\,000$ g/mol, $f = 0.95$) and 70% PS−NH_2 ($M_n = 20\,900$ g/mol, $f = 0.99$). The conversion data for (c) are adopted from Orr's thesis[6] for comparison. Conversions are normalized by the maximum possible conversion value (100%) of PMMA−PA.

Scheme 6. Competition Experiment of Phthalic Anhydride vs Succinic Anhydride with PS−NH_2



When *end*-PS−NH_2 was dissolved at room temperature in THF containing excess phthalic anhydride (50 mol equiv) and succinic anhydride (50 mol equiv), end group analysis of the polymer by ^{1}H NMR spectroscopy after purification showed that phthalic anhydride reacted about 5 times faster than succinic anhydride.

Since the coupling reactions were so fast for both *end*- and *mid*-functional PMMAs, the rate difference arising from the position of the reactive group along the polymer chain could not be measured. To accomplish this goal, we are currently studying the preparation and use of fluorescently labeled reactive polymers to measure the reaction rates at high dilution.[13]

Conclusions

We have described a new way to introduce a single phthalic anhydride group either at the end or in the middle of polymer chains by using atom transfer radical polymerization (ATRP). Di-*tert*-butylphthalic ester (DTBP) functionalized polymers were prepared and subsequently pyrolyzed to generate the phthalic anhydride functionalities. This method provided phthalic anhydride functionalized PMMA and PS with high functionality and good architecture control. The necessary DTBP functionalized ATRP initiators were synthesized from easily accessible di-*tert*-butylacetylene dicarboxylate (**1**) and myrcene (**2**) in four or six step efficient reaction sequences. The key feature of the methodology, pyrolysis of the di-*tert*-butylphthalic ester (DTBP) group to the phthalic anhydride group (PA), could be easily monitored by conventional ^{1}H NMR spectroscopy. From this study, it was revealed that pyrolysis of PMMA−DTBP polymers follows two first-order consecutive reactions in which phthalic acid is a transient species. In addition, conversion to the phthalic anhydride species was faster for PS than for PMMA. The functionality of these polymers was determined by ^{1}H NMR analysis. These PA functionalized PMMAs showed faster coupling kinetics than the corresponding aliphatic anhydride (e.g., succinic anhydride functional PMMA) in a heterogeneous reactive melt blending experiment with PS−NH_2. Experiments are in progress to determine the reactivity difference between *end*- and *mid*-functional anhydride polymers (*end*-**18** and *mid*-**18**).

Experimental Section

Materials. Toluene and diphenyl ether were passed through basic alumina (Brockmann I) and stored over activated 4 Å molecular sieves under an argon atmosphere. Acetonitrile was stored over 4 Å molecular sieves. Methanol was used as received. Methylene chloride was dried over an activated alumina column. THF was distilled over sodium/benzophenone. Myrcene (Aldrich) was purified by simple vacuum distillation to remove any dimer and stored in a refrigerator. Styrene and methyl methacrylate were passed through a pad of basic alumina (Brockmann I) and purged with argon for at least 15 min prior to use. Di-*tert*-butyl acetylenedicarboxylate (**1**), 2,2′-bipyridine, and 4,4′-dinonyl-2,2′-dipyridine were purchased from Aldrich and used as received. *end*-Functional polystyrene−amine ($M_n = 15\,700$ g/mol, $M_w/M_n = 1.02$, functionality ~99%) was synthesized by a described protocol.[19] If not specified, all chemicals were purchased from Aldrich and used as received. MPLC refers to medium-pressure liquid chromatography (20−40 psi) using hand-packed columns of E. Merck or Bodman silica gel (230−400 mesh), a Fluid Metering Inc. solvent pump, and a Waters differential refractive index detector.

Polymer Characterization. Polymer molecular weights were measured using a Waters GPC system equipped with a Waters 590 HPLC pump, a Waters 717 plus autosampler, three Phenogel columns (i.d. 7.8 mm; 5 μm particle size; 500, 10^3, and 10^4 Å pore sizes), and UV (Spectra-Physics) and RI (Waters 410) detectors. The UV detector was set at 256 nm, and THF was used as the eluent at a flow rate of 1 mL/min. Ten standard polystyrenes were used for the calibration: 380, 156, 96.0, 49.9, 22.0, 11.6, 5.05, 2.95, 1.32, and 0.58 × 10^3 g/mol. Molecular weights of PMMAs were corrected by universal calibration based on the Mark−Houwink equation from the PS standards using a subroutine[6] in Microcal Origin (Microcal Software, Inc., Northampton, MA). GPC samples were prepared by dissolving 5 mg of polymer in 4 mL of THF, and 100 μL of the solution was injected for each run. For GPC runs of samples containing amine reactive groups, the samples were pretreated with acetic anhydride (~25 μL per 1 mL of THF) to prevent further coupling reaction in solution and/or adsorption of the amine functionalized polymer to the column stationary phase. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian VI-500 or a Varian VI-300 spectrometer. Infrared spectra were recorded on a MIDAC FT-IR spectrometer.

Melt Coupling Reactions. Coupling reactions were carried out in a MiniMAX cup and rotor mixer at 180 °C under a continuous nitrogen purge. Total sample mass was typically ~300 mg, and the mixer was operated at 320 rpm. Three stainless steel ball bearings were added to the cup to obtain

more uniform mixing.[21] Blend components were weighed and coarsely mixed at room temperature prior to being placed in the mixer. Samples (10−20 mg) were taken at 2, 4, 6, 10, and 20 min with a tweezer. Samples were then dissolved in THF (1 mg of polymer/1 mL of THF) and doped with acetic anhydride (∼2.5%) to quench any unreacted amine functionality, thereby preventing coupling in solution. Each solution (100 μL) was injected on the GPC for analysis.

4-(4-Methyl-3-pentenyl)-1,4-cyclohexadiene-1,2-dicarboxylic Acid, Bis(1,1-dimethylethyl) Ester. To a solution of di-*tert*-butylacetylene dicarboxylate (**1**) (1.57 g, 6.95 mmol) and myrcene (**2**, 1.89 g, ∼13 mmol, technical grade, about 75% pure, the main impurity was limonene) in toluene (5 mL) was added a small amount of trimethyl orthoformate (100 μL, acid scavenger). The resulting solution was placed in a pressure tube, capped with a Teflon screw cap, and heated at 110 °C for 6 h. After being cooling to room temperature, the tube was opened and the reaction mixture was transferred to a round-bottom flask. The solvent was removed, and the residue was purified by MPLC (hexanes:EtOAc = 9:1) to yield pure product as a colorless oil (2.52 g, 91%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.38 (br s, 1H, C=C*H*), 5.08 (br t, J = 8.3 Hz, 1H, $(CH_3)_2C$=C*H*), 2.96 (br t, J = 7.5 Hz, 2H, C=CCH_2CH=C), 2.85 (t, J = 7.5 Hz, 2H, C=CCH_2C=CH), 2.09 (m, 2H, CH_2C=CH), 2.00 (m, 2H, C=CHCH_2), 1.68 (s, 3H, CH_3C=CH), 1.60 (s, 3H, CH_3C=CH), 1.51 (s, 9H, C(CH_3)$_3$), and 1.50 (s, 9H, C(CH_3)$_3$).

^{13}C NMR ($CDCl_3$, 75 MHz): δ 167.47, 167.37, 133.47, 132.75, 132.60, 131.80, 123.79, 116.54, 81.26, 81.18, 36.62, 30.85, 28.69, 28.00, 27.88, 25.83, 25.66, and 17.71.

IR (neat): 2977 (s), 2929 (s), 2824 (w), 1720 (vs), 1692 (m), 1656 (w), 1652 (w), 1477 (w), 1453 (w), 1391 (m), 1368 (m), 1277 (s), 1256 (s), 1152 (s), 1066 (m), 1044 (w), 1028 (m), 936 (w), 884 (w), 846 (m), 791 (w), and 743 cm^{-1} (w).

Anal. Calcd for $C_{22}H_{34}O_4$: C, 72.89; H, 9.45. Found: C, 73.04; H, 9.36.

4-(4-Methyl-3-pentenyl)-1,2-benzenedicarboxylic Acid, Bis(1,1-dimethylethyl) Ester (3). To a solution of 4-(4-methyl-3-pentenyl)-1,4-cyclohexadiene-1,2-dicarboxylic acid, bis(1,1-dimethylethyl) ester (1.82 g, 5.02 mmol) in toluene (10 mL) was added DDQ (1.25 g, 5.52 mmol). The resulting purple solution was allowed to stir for 1 h at ∼80−90 °C. The solution turned brown upon reaction. After cooling to room temperature, the solids were removed by filtration through a pad of silica gel, and the filtrate was concentrated. The resulting crude product was purified by MPLC (hexanes:EtOAc = 9:1) to give the pure product **3** (1.59 g, 88%) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.57 (d, J = 7.2 Hz, 1H, ArH_a), 7.40 (s, 1H, ArH_b), 7.26 (d, J = 7.2 Hz, 1H, ArH_c), 5.13 (t, J = 7.1 Hz, 1H, C=C*H*), 2.67 (t, J = 7.8 Hz, 2H, ArCH_2), 2.29 (dt, J = 7.5 and 7.5 Hz, C=CHCH_2), 1.68 (s, 3H, CH_3), 1.59 (s, 9H, C(CH_3)$_3$), 1.58 (s, 9H, C(CH_3)$_3$), and 1.56 (s, 3H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz): δ 167.43, 166.58, 145.40, 134.32, 132.69, 130.75, 130.08, 128.94, 128.62, 123.02, 81.70, 81.46, 35.72, 29.44, 28.05, 28.01, 25.64, and 17.69.

IR (neat): 3004 (w), 2978 (s), 2931 (s), 2860 (w), 1721 (vs), 1607 (w), 1572 (w), 1478 (w), 1455 (m), 1414 (w), 1392 (m), 1368 (s), 1300 (vs), 1257 (s), 1167 (s), 1130 (s), 1071 (m), 1036 (w), 848 (m), 795 (w), 771 (w), 750 (w), and 704 cm^{-1} (w).

4-(3-Hydroxypropyl)-1,2-benzenedicarboxylic Acid, Bis(1,1-dimethylethyl) Ester (4). Ozone was passed through a solution of diester **3** (1.15 g, 3.19 mmol) in methanol (20 mL) at −78 °C until the solution turned blue (∼5 min). Excess ozone was removed by purging with oxygen. After the addition of $NaBH_4$ (242 mg, 6.37 mmol) the reaction mixture was allowed to warm to room temperature. The majority of the methanol was removed by rotary evaporation, and the residue was partitioned between ether and water. The ether layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated to give 1.16 g of crude product. Further purification by MPLC (hexanes:EtOAc = 1:1) on silica gel provided pure alcohol **4** (1.04 g, 97%) as a viscous oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.58 (d, J = 7.2 Hz, 1H, ArH_a), 7.41 (d, J = 2.4 Hz, 1H, ArH_b), 7.28 (dd, J = 7.2 and 2.4 Hz,_1H, ArH_c), 3.66 (t, J = 6.3 Hz, 2H, CH_2OH), 2.75 (t, J = ∼8 Hz, 2H, CH_2Ar), 1.88 (m, 2H, CH_2CH_2CH_2), 1.59 (s, 9H, C(CH_3)$_3$), and 1.58 (s, 9H, C(CH_3)$_3$).

^{13}C NMR ($CDCl_3$, 75 MHz): δ 167.33, 166.65, 144.96, 134.43, 131.00, 130.11, 129.09, 128.57, 81.84, 81.56, 61.83, 33.73, 31.74, 28.05 and 28.01.

IR (neat): 3441 (br m), 2978 (m), 2932 (m), 2872 (w), 1709 (vs), 1366 (m), 1305 (s), 1258 (m), 1161 (s), 1135 (s), and 1071 cm^{-1} (m).

Anal. Calcd for $C_{19}H_{28}O_5$: C, 67.83; H, 8.39. Found: C, 67.84; H, 8.06.

4-(3-Bromopropyl)-1,2-benzenedicarboxylic Acid, Bis(1,1-dimethylethyl) Ester (9). Diester alcohol **4** (474 mg, 1.41 mmol) and CBr_4 (514 mg, 1.55 mmol) were dissolved in CH_2Cl_2 (3 mL) and cooled to 0 °C under inert atmosphere. To this solution was added a solution of triphenylphosphine (370 mg, 1.41 mmol) in CH_2Cl_2 (2 mL), and the resulting mixture was allowed to stir for 1 h at 0 °C. Most of the CH_2Cl_2 was removed and the residue was filtered through a pad of silica gel (hexanes:EtOAc = 3:1). The filtrate was concentrated and purified by MPLC (hexanes:EtOAc = 19:1) to give pure bromide **9** (531 mg, 94%) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.59 (d, J = 7.8 Hz, 1H, ArH_a), 7.42 (d, J = 1.5 Hz, 1H, ArH_b), 7.29 (dd, J = 7.8 and 1.5 Hz, 1H, ArH_c), 3.38 (t, J = 6.3 Hz, 2H, CH_2Br), 2.82 (t, J = 7.8 Hz, 2H, CH_2Ar), 2.16 (m, 2H, CH_2CH_2CH_2), 1.59 (s, 9H, C(CH_3)$_3$), and 1.58 (s, 9H, C(CH_3)$_3$).

^{13}C NMR ($CDCl_3$, 75 MHz): δ 167.11, 166.42, 143.51, 134.53, 131.38, 130.24, 129.18, 128.64, 81.89, 81.63, 33.58, 33.59, 32.64, 28.02, and 28.00.

IR (neat): 2979 (m), 2931 (w), 2872 (w), 1716 (vs), 1609 (w), 1572 (w), 1392 (w), 1368 (m), 1305 (s), 1257 (m), 1160 (m), 1132 (s), 1072 (m), and 847 cm^{-1} (m) .

Anal. Calcd for $C_{19}H_{27}BrO_4$: C, 57.15; H, 6.82. Found: C, 57.11; H, 7.03.

4-[3-(2-Bromopropionyloxy)propyl]-1,2-benzenedicarboxylic Acid, Bis(1,1-dimethylethyl) Ester (7). To a solution of alcohol **4** (304 mg, 0.905 mmol), pyridine (88 mg, 1.1 mmol), and DMAP (∼2 mg) in dry CH_2Cl_2 (2 mL) was added 2-bromopropionyl bromide (215 mg, 0.996 mmol) via a microsyringe dropwise at 0 °C. After stirring for 10 min, the excess 2-bromopropionyl bromide was quenched by adding 1 drop of water. The reaction mixture was filtered through a short pad of silica gel (∼ 5 cm) with hexanes:EtOAc (1:1). The filtrate was concentrated and further purified by MPLC (hexanes:EtOAc = 3:1) to give pure bromoester **7** (398 mg, 93%) as a colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.59 (d, J = 7.8 Hz, 1H, ArH_a), 7.42 (d, J = 1.0 Hz, 1H, ArH_b), 7.29 (dd, J = 7.8 and 1.0 Hz, 1H, ArH_c), 4.38 (q, J = 7.0 Hz, 1H, C*H*Br), 4.21 (dt, J = 10.5 and 6.5 Hz, 1H, O=COCH_aH$_b$), 4.15 (dt, J = 10.5 and 6.5 Hz, 1H, O=COCH_aH$_b$), 2.77 (t, J = 7.8 Hz, 2H, CH_2Ar), 2.01 (pent, J = 6.5 Hz, 2H, CH_2CH_2CH_2), 1.83 (d, J = 7.0 Hz, 3H, CH_3CHBr), 1.59 (s, 9H, C(CH_3)$_3$), and 1.58 (s, 9H, C(CH_3)$_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.13, 167.13, 166.42, 143.92, 134.51, 131.31, 130.10, 129.17, 128.55, 81.86, 81.59, 64.74, 39.99, 31.66, 29.58, 28.03, 27.99, and 21.54.

IR (neat): 2978 (s), 2933 (m), 2872 (w), 1720 (vs), 1608 (w), 1572 (w), 1477 (m), 1452 (m), 1415 (w), 1392 (m), 1368 (s), 1301 (vs), 1259 (s), 1223 (s), 1163 (vs), 1132 (vs), 1072 (s), 1037 (w), 1019 (w), 989 (w), 940 (w), 914 (w), 847 (m), 815 (w), 795 (w), 771 (w), 751 (w), 704 (w), and 675 cm^{-1} (w).

4-[3-(2-Bromo-2-methyl-propionyloxy)propyl]-1,2-benzenedicarboxylic Acid, Bis(1,1-dimethylethyl) Ester (8). To a solution of alcohol **4** (520 mg, 1.55 mmol), pyridine (185 mg, 2.32 mmol), and DMAP (∼2 mg) in dry CH_2Cl_2 (5 mL) was added 2-bromoisobutyryl bromide (428 mg, 1.86 mmol) via a microsyringe dropwise at 0 °C. After stirring for 10 min, the excess 2-bromopropionyl bromide was quenched by adding 1 drop of water. The reaction mixture was filtered through a short pad of silica gel (∼5 cm) with hexanes:EtOAc (1:1). The filtrate was concentrated and further purified by MPLC (hexanes:EtOAc = 3:1) to give pure bromoester **8** (709 mg, 95%) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.59 (d, J = 8.1 Hz, 1H, ArH_a), 7.43 (d, J = 1.8 Hz, 1H, ArH_b), 7.29 (dd, J = 8.1 and 1.8 Hz, 1H, ArH_c), 4.18 (t, J = 6.3 Hz, 2H, CO_2CH_2), 2.79 (t, J = 7.7 Hz, 2H, CH_2Ar), 2.02 (m, 2H, $CH_2CH_2CH_2$), 1.94 (s, 6H, $(CH_3)_2CBr$), 1.59 (s, 9H, $C(CH_3)_3$), and 1.58 (s, 9H, $C(CH_3)_3$).

^{13}C NMR ($CDCl_3$, 75 MHz): δ 171.54, 167.14, 166.45, 143.95, 134.49, 131.30, 130.14, 129.17, 128.58, 81.86, 81.59, 64.72, 55.81, 31.67, 30.68, 29.58, 28.02, and 27.99.

IR (neat): 2977 (m), 2931 (w), 1720 (vs), 1607 (w), 1572 (w), 1459 (m), 1391 (m), 1368 (m), 1298 (s), 1164 (vs), 1131 (s), 1072 (m), 1023 (w), 847 (m), 795 (w), and 770 (w) cm^{-1}.

Anal. Calcd for $C_{23}H_{33}BrO_6$**:** C, 56.91; H, 6.85. Found: C, 56.81; H, 6.97.

4-{3-[Di(2-hydroxyethyl)]aminopropyl}-1,2-benzenedicarboxylic Acid, Bis(1,1-dimethylethyl) Ester (10). Diethanolamine (204 μL, 2.13 mmol) and bromide **9** (284 mg, 0.711 mmol) were dissolved in CH_3CN (3 mL). The solution was placed in a reaction culture tube with a stir bar. After adding K_2CO_3 (294 mg, 2.13 mmol), the resulting suspension was degassed by sparging argon for 5 min. The culture tube was capped with a Teflon lined screw cap and heated at 80 °C for 16 h. After cooling the solution to room temperature, the suspension was filtered through a fritted glass filter (10−20 μm pore size) to remove solid K_2CO_3. The filtered solid was washed with ethyl acetate. The combined filtrate was concentrated to give 430 mg of yellow viscous oil, which was further purified by MPLC (EtOAc:MeOH = 1:1) on silica gel to give pure product **10** (300 mg, 100%) as a yellowish viscous oil.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.58 (d, J = 8.0 Hz, 1H, ArH_a), 7.41 (d, J = 1.5 Hz, 1H, ArH_b), 7.28 (dd, J = 8.0 and 1.5 Hz, 1H, ArH_c), 3.58 (t, J = 5.5 Hz, 4H, CH_2OH), 2.67 (t, J = 7.5 Hz, 2H, CH_2Ar), 2.62 (t, J = 5.5 Hz, 4H, NCH_2CH_2OH), 2.54 (t, J = 7.5 Hz, 2H, $NCH_2CH_2CH_2Ar$), 1.80 (pent, J = 7.5 Hz, 2H, $CH_2CH_2CH_2$), 1.59 (s, 9H, $C(CH_3)_3$), and 1.58 (s, 9H, $C(CH_3)_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.54, 166.41, 145.09, 134.38, 130.76, 129.93, 129.06, 128.52, 81.90, 81.52, 59.48, 55.81, 53.88, 32.88, 28.11, 27.97, and 27.91.

IR (neat): 3393 (br s, OH), 3000 (w), 2977 (m), 2933 (m), 2871 (m), 2819 (w), 1715 (s), 1606 (w), 1573 (w), 1459 (m), 1393 (m), 1367 (m), 1297 (s), 1258 (s), 1165 (s), 1132 (s), 1072 (s), 1036 (m), 852 (m), and 754 cm^{-1} (w).

Anal. Calcd for $C_{23}H_{37}NO_6$: C, 65.22; H, 8.81. Found: C, 65.08; H, 8.88.

4-{3-{Di[2-(2-bromo-2-methyl-propionyloxy)-ethyl]}-aminopropyl}-1,2-benzenedicarboxylic Acid, Bis(1,1-dimethylethyl) Ester (11). To a solution of diol **10** (290 mg, 0.685 mmol), pyridine (134 mg, 1.70 mmol), and DMAP (~1 mg) in dry CH_2Cl_2 (5 mL) was added 2-bromoisobutyryl bromide (346 mg, 1.50 mmol) via a microsyringe through a septum at 0 °C while stirring. After 10 min excess 2-bromoisobutyryl bromide was quenched by adding 1 drop of water. The majority of the methylene chloride was removed, and the residue was loaded on a silica gel column and eluted with hexanes:EtOAc (2:1) to give pure product **11** (390 mg, 79%) as a colorless viscous oil.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.58 (d, J = 7.5 Hz, 1H, ArH_a), 7.40 (d, J = 1.5 Hz, 1H, ArH_b), 7.27 (dd, J = 7.5 and 1.5 Hz, 1H, ArH_c), 4.24 (t, J = 5.8 Hz, 4H, $CH_2OC{=}O$), 2.86 (t, J = 6.0 Hz, 4H, NCH_2CH_2O), 2.68 (t, J = 7.5 Hz, 2H, CH_2-Ar), 2.60 (t, J = 7.0 Hz, 2H, $NCH_2CH_2CH_2Ar$), 1.92 (s, 12H, $(CH_3)_2CBr$), 1.79 (pent, J = 7.5 Hz, 2H, $CH_2CH_2CH_2$), 1.59 (s, 9H, $C(CH_3)_3$), and 1.58 (s, 9H, $C(CH_3)_3$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 171.63, 167.31, 166.53, 145.17, 134.46, 130.96, 130.04, 129.11, 128.51, 81.81, 81.54, 64.24, 55.65, 54.15, 52.38, 32.93, 30.77, 29.00, 28.06, and 28.03.

IR (neat): 3003 (w), 2978 (m), 2934 (m), 2865 (w), 2823 (w), 1731 (s), 1716 (s), 1607 (w), 1573 (w), 1461 (m), 1391 (m), 1369 (m), 1296 (s), 1164 (s), 1131 (s), 1111 (m), 1073 (m), 1015 (w), 985 (w), 847 (w), 795 (w), and 770 cm^{-1} (w).

General Procedure for Poly(methyl methacrylate)−Di-*tert*-butyl Phthalate Synthesis by ATRP. CuBr (21.7 mg, 0.152 mmol), 4,4′-dinonyl-2,2′-dipyridyl (124 mg, 0.303 mmol), and a stir bar were placed in a Pyrex culture tube. The tube was capped with a screw cap with a Teflon lined silicone rubber septum. It was cycled between vacuum and argon five times to remove the oxygen. In a separate round-bottom flask were placed initiator **8** (147 mg, 0.303 mmol), freshly alumina-filtered methyl methacrylate (7.58 g, 75.8 mmol), and diphenyl ether (8.0 mL). After capping the flask with a rubber septum, the solution was degassed by sparging with argon through a needle while venting through an additional needle for 15 min. The degassed solution was transferred to the culture tube via a gastight syringe. The septum screw cap was replaced with a closed screw cap in a drybox. The culture tube was placed in an oil bath and heated at 90 °C for 19 h. The brown solution gradually became more viscous. After the reaction time, the culture tube was cooled to room temperature, and the content was diluted with THF (50 mL). The greenish-brown solution was filtered through a short pad of basic alumina (~10 cm), and the column was washed with additional THF (~60 mL). The colorless combined filtrate was dripped into stirred hexanes (400 mL) to precipitate the polymer. After filtration, the white polymer was dissolved in THF (120 mL) and reprecipitated in hexanes (400 mL). The precipitated polymer was filtered and dried in a vacuum oven at ~50 °C overnight to give pure white poly(methyl methacrylate)-di-*tert*-butylphthalate **12** (5.32 g, 70%).

GPC: M_w = 25.1 K, M_n = 21.0 K, PDI = 1.20

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.60 (d, 1H, J = 8.0 Hz, ArH_a), 7.28 (d, 1H, J = 8.0 Hz, ArH_b), 7.16 (s, 1H, ArH_c), 4.04 (m, 1H, $CH_aH_bOC{=}O$), 4.01 (m, 1H, $CH_aH_bOC{=}O$), 3.83 (s, 3/2H, $C(CH_3)Br(CO_2CH_3)$), 3.76 (s, 3/2H, $C(CH_3)Br(CO_2CH'_3)$), 3.60 (br s, CO_2CH_3's, backbone), 2.73 (t, 2H, J = 7.5 Hz, $ArCH_2$), 2.10−1.65 (br m, CH_2's, backbone), 1.60 (s, 9H, $C(CH_3)_3$), 1.59 (s, 9H, $C(CH_3)_3$), 1.50−0.60 (br, CH_3's, backbone).

General Procedure of Polystyrene−Di-*tert*-butyl Phthalate Synthesis by ATRP. A reaction mixture [CuBr (60.8 mg, 0.414 mmol), 2,2-bipyridine (188 mg, 1.26 mmol), initiator **7** (200 mg, 0.424 mmol), and styrene (8.4 g, 81 mmol)] was prepared in a screw-capped culture tube in a similar manner as mentioned above. The culture tube was placed in an oil bath and heated at 110 °C for 22 h. The mixture was cooled to room temperature, diluted with THF (50 mL), and filtered through a short pad of basic alumina (~10 cm), and the column was washed with additional THF (~60 mL). The colorless combined filtrate was dripped into stirred MeOH (400 mL) to precipitate the polymer. After filtration, the white polymer was dissolved in THF (120 mL) and reprecipitated in MeOH (400 mL). The precipitated polymer was filtered and dried in a vacuum oven at ~50 °C overnight to give pure white polystyrene-di-*tert*-butylphthalate **14a** (6.38 g, 76%).

GPC: M_w = 19.5 K, M_n = 16.3 K, PDI = 1.20.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.58 (br, 1H, ArH_a), 7.36 (br, 1H, ArH_b), 7.3−6.25 (ArH, backbone), 4.40−4.36 (br, 1H, $CHBrPh$), 3.95−3.72 (br, 2H, $CH_2OC{=}O$), 2.59 (br, 2H, $ArCH_2$), 2.40−1.20 (CH_2, CH, backbone), 1.00−0.85 (br, CH_3).

^{1}H NMR Monitoring of the Pyrolysis of DTBP-Functionalized Polymers. Five NMR tubes were each loaded with ~15 mg of dry DTBP-functionalized polymer, and each tube was capped with a plastic cap after purging with argon. The tubes were immersed in an oil bath set at a designated temperature (e.g., 190, 200, and 210 °C for each set of experiments). Each NMR tube was removed from the silicone oil bath after a designated time (5, 10, 15, 20, and 40 min) and cooled in cold water. To each NMR tube was added $CDCl_3$ (~0.6 mL) to dissolve the polymer samples, and each sample was checked by ^{1}H NMR (500 MHz) spectroscopy.

General Procedure of Pyrolysis in Bulk Scale. DTBP-functionalized PMMA **12** (1.50 g) was placed in a Schlenk flask (50 mL) and capped with a septum. The sidearm was connected to a vacuum line, and vacuum was applied (~0.15 mmHg). The flask was immersed in an oil bath and heated at 210 °C for 1 h. The polymer started to melt immediately after heating, and bubbling continued over 40 min. After the reaction time, the flask was cooled to room temperature in a water bath and further cooled in a liquid nitrogen bath. It was warmed to room temperature rapidly by flowing cold water and cooled again in a liquid nitrogen bath. This was repeated if necessary to

make the polymer chunk fragile. The polymer chunk was broken with a sharp tipped awl into small pieces and recovered into a vial (1.50 g, 83%). In the case of polystyrene, the procedure is similar except for the pyrolysis temperature (190 °C). ^{1}H NMR spectra of the sample indicated complete conversion of di-*tert*-butyl phthalate group to phthalic anhydride.

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Supporting Information Available: A copy of the ^{1}H NMR spectrum of partially pyrolyzed *end*-PMMA−DTBP **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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(18) The kinetic equations can be presented as the following:

$$\frac{d[DTBP]}{dt} = -k_1[DTBP] \quad (1)$$

$$\frac{d[DA]}{dt} = k_1[DTBP] - k_2[DA] \quad (2)$$

$$\frac{d[PA]}{dt} = k_2[DA] \quad (3)$$

$$[DTBP] = [DTBP]_0 e^{-k_1 t} \quad (4)$$

$$[DA] = \frac{k_1[DTBP]_0}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t}) \quad (5)$$

$$[AN] = [DTBP]_0\left[1 + \frac{1}{k_1 - k_2}(k_2 e^{-k_1 t} - k_1 e^{-k_2 t})\right] \quad (6)$$

(19) This polymer has been synthesized by Jeff Cernohous by anionic polymerization following the procedure described in the paper (Cernohous, J. J.; Macosko, C. W.; Hoye, T. R. *Macromolecules* **1998**, *31*, 3759).
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