Free-Radical Telomerization of *tert*-Butyl Acrylate in the Presence of Bis(4-aminophenyl) Disulfide as a Useful Route to Amino-Terminated Telomers of Poly(acrylic acid)

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Received November 2, 1992; Revised Manuscript Received January 15, 1993

ABSTRACT: In this paper, we report the synthesis of telomers of *tert*-butyl acrylate (*t*BA) and of acrylic acid using bis(4-aminophenyl) disulfide as "iniferter" (*ini*tiator–trans*fer*–*ter*minator). Polymers with molecular weights of (20–50) × 10^3 (*t*BA) and polydispersities of ≈2 were formed. We found that bis(4-aminophenyl) disulfide provided significant control over the polymerization of *t*BA, while also allowing for the formation of α,ω-diamino-functionalized poly(*t*BA). The molecular weight distributions of the isolated polymers were insensitive to changes in temperature between 50 and 90 °C. Telomers of *t*BA could be hydrolyzed quantitatively to telomers of acrylic acid using *p*-toluenesulfonic acid as a catalyst in a solution of acetic acid and water.

Introduction

In this paper, we report the syntheses of amino-terminated telomers of *tert*-butyl acrylate (*t*BA) and of acrylic acid (AA) with polydispersities of ≈2. These polymers are terminated at both ends by 4-aminophenyl sulfide (APS) groups, making the chain termini selectively reactive for later modifications.

Polymer chains bearing chemically distinct terminal groups ("telomers") make convenient building blocks for larger structures, including block and graft copolymers and end-linked networks.[1] The properties of these larger structures are often sensitive to the molecular weights and polydispersities of the telomers from which they are prepared.[1] Often, the ideal telomer for an application would consist of molecules of a single, known molecular weight. The development of methods for the preparation of telomers with narrow distributions of molecular weight is an area of considerable interest in polymer science.[1,2]

We wanted to prepare model end-linked networks from telomers of poly(acrylic acid) having narrow distributions of molecular weight. While telomers prepared from neutral monomers have been reported in the literature,[1,2] telomers of acrylic acid have not. These telomers would be useful materials for basic studies and applications involving polyelectrolytes. We sought a method of telomerization that would produce poly(acrylic acid) with low polydispersity and terminal groups useful for later cross-linking.

Acrylic acid is highly reactive in free-radical polymerizations. It has a high chain extension constant,[3] and the growing polymer has a pronounced tendency to terminate through disproportionation.[3] As a result, direct free-radical telomerization of acrylic acid is often far more difficult to control than the free-radical telomerization of acrylate esters.[2,3] For that reason, we chose to prepare telomers of acrylic acid by a two-step process involving first telomerization of an acrylate ester followed by hydrolysis to poly(acrylic acid). We selected *t*BA as the monomer because poly(*t*BA) is readily hydrolyzed to poly(acrylic acid).[4–8]

Disulfides are useful coreactants in the polymerization of vinyl-derived monomers.[9,10] The S–S bond is readily cleaved to form thiyl radicals, which act both as initiators and as terminators of free-radical polymerization.[11] The disulfides also act as chain-transfer agents.[11] Scheme I shows a mechanistic outline for such polymerizations. The compounds RSSR have sometimes[11,12] been called "iniferters" (*ini*tiator–trans*fer*–*ter*minator) in reference to the three mechanistic roles performed by RSSR and RS•. The transfer and termination steps compete with chain extension and impose a kinetic limit upon the degree of polymerization.[2] For polymers that have a pronounced tendency to terminate through disproportionation this limit results in the formation of polymers with narrower distributions of molecular weight than those prepared with simple initiators.[11]

We chose to employ bis(4-aminophenyl) disulfide (BAPD) as the iniferter for the polymerization of *t*BA. We had two reasons: First, the 4-amino group provides a reactive and chemically distinct functional group for the chain termini, making selective end-linking of the polymer much easier. Second, unlike the iniferters reported in the literature[13]—which are light-sensitive oils that must be freshly prepared before use—BAPD is a stable, commercially available solid.

Homolytic cleavage of the S–S bond of BAPD did not occur at an appreciable rate below the boiling point of *t*BA. It was therefore necessary to form the thiyl radicals by reaction with a free-radical initiator. We chose α,α'-azobis(isobutyronitrile) (AIBN) because it is an efficient source of reactive radicals.[11] We demonstrate below that, under appropriate conditions, direct initiation of the polymerization of *t*BA by AIBN was not a significant complication.

We polymerized *t*BA at 50–90 °C in the presence of BAPD and a catalytic amount of AIBN. The resulting telomer, poly(*tert*-butyl acrylate)–bis(4-aminophenyl sulfide) (p*t*BA–bAPS), was readily converted to poly(acrylic

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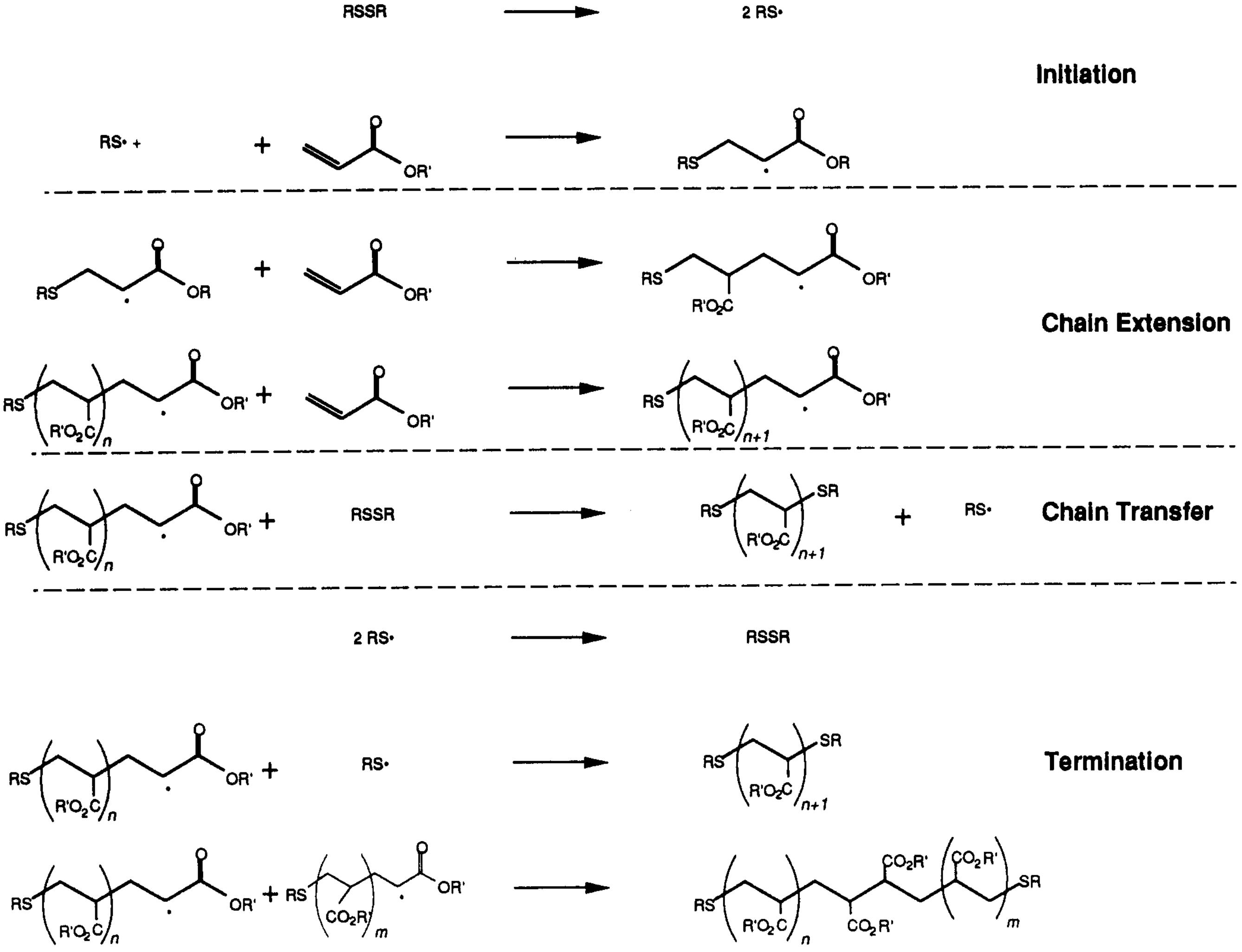
Scheme I
Mechanistic Scheme for "Iniferter"-Regulated Polymerizations



acid)–bis(4-aminophenyl sulfide) (pAA–bAPS) under acidic conditions. In the following sections, we report the effect of using different ratios of BAPD to AIBN, different temperatures, and different times of reaction upon the properties of the p*t*BA–bAPS produced. α,ω-Diamino-terminated telomers of *t*BA with molecular weights of (20–50) × 10^3 and polydispersities of 2.0 ± 0.2 are easily prepared by this method. We further report the characterization of the pAA–bAPS formed by the hydrolysis of these telomers of *t*BA.

Experimental Section

Materials. *t*BA (Aldrich) was distilled under vacuum prior to use and stored at 5 °C under N_2. Bis(4-aminophenyl) disulfide (BAPD; Aldrich), α,α'-azobis(isobutyronitrile) (AIBN; Aldrich), and *p*-toluenesulfonic acid (Aldrich) were used as received.

Telomerization of *t*BA. As discussed below, we varied the temperature and the concentration of AIBN relative to BAPD from run to run. In this section we outline the general procedures followed for all of the different combinations of conditions that we used.

A 200-mL round-bottomed flask was covered with aluminum foil, sealed with a rubber septum, and purged with N_2 for 30 min. *t*BA (100 g) and known quantities of AIBN and BAPD were added to the flask under N_2, and N_2 was bubbled through the reaction mixture for 30 min. The flask was equipped with a N_2 bubbler and immersed in an oil bath at 25 °C. The oil bath was heated to the desired temperature in ≈5 min and regulated with a thermostat. After a predetermined time, the flask was removed from the oil bath, and the reaction was quenched by immersing the flask in a slurry of dry ice and acetone for 30 min.

The reaction solution was transferred to a 600-mL beaker and diluted with an equal volume of methanol. Small portions of water were added until the polymer precipitated. The precipitate was collected by filtration and reprecipitated four or five times from methanol by the addition of water. The purified precipitate was dried under vacuum overnight at room temperature and then lyophilized for a week.

Using this technique, the molecular weight of the polymers obtained were reproducible within ±20% for each set of conditions.

Hydrolysis of pTBA–APS. A solution of p*t*BA–bAPS (5 g) and *p*-toluenesulfonic acid monohydrate (1 g) in a mixture of acetic acid (40 mL) and water (10 mL) was refluxed for 8 h at 120 °C. This temperature was sufficient to distill away the *tert*-butyl alcohol formed by the hydrolysis reaction. The residue in the flask was allowed to cool to room temperature, and chloroform was added to precipitate the crude pAA–bAPS. The crude product was isolated by filtration, dissolved in methanol, and precipitated by the addition of diethyl ether. This process was repeated from three to five times in order to remove traces of acetic acid and *p*-toluenesulfonic acid. The product was dried to a constant weight under vacuum, which usually required about 12 h. The pAA–bAPS obtained was a white solid, soluble in methanol, ethanol, dioxane, DMF, DMSO, and water.

Characterization of the Telomers. The number-average molecular weight ($\bar{M}_n$), weight-average molecular weight ($\bar{M}_w$), and molecular weight distribution (polydispersity, PD) of the polymers were determined by size-exclusion chromatography (SEC).[14] Tetrahydrofuran (THF) and methanol, respectively, were used to elute the p*t*BA–bAPS and the pAA–bAPS. The instrument was calibrated using polystyrene standards;[14] the calibration was applied to p*t*BA–bAPS and pAA–bAPS using the universal calibration.[14] The molecular weights of p*t*BA–

bAPS obtained in this way were accurate to ±10%. Unfortunately, the universal calibration was not particularly accurate for polyelectrolytes: the values of molecular weight obtained for pAA–bAPS differed by as much as 20% from the expected values. Therefore, in calculations requiring the molecular weight of the pAA–bAPS, we used the molecular weight derived arithmetically from the known molecular weight of the p*t*BA–bAPS from which it was formed. SEC on p*t*BA–bAPS was performed in our laboratories, on pAA–bAPS by ARRO Laboratories (Joliet, IL).

The functionalization of the polymers was estimated using elemental analysis. Elemental analyses were obtained from Galbraith Laboratories (Knoxville, TN). Either the sulfur content or the nitrogen content of the polymers could be used. We chose sulfur for p*t*BA–pAPS in order to avoid detection of chain termini that were derived from AIBN, which contains nitrogen. We chose nitrogen for pAA–bAPS to avoid detection of any residual *p*-toluenesulfonic acid. The value of $\bar{M}_n$ obtained from SEC and the elemental weight percent of either sulfur or nitrogen in the telomer, ϕ_E, were used to calculate the number of APS groups per chain by the following equation: $f = (\phi_E/100)(\bar{M}_n/M_E)$, where f is the average number of APS groups per chain and M_E is the atomatic mass of the element used in the analysis, 14.01 g atom for N or 32.06 g atom for S.

Solution-phase ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AM-400 400-MHz spectrometer, using either $CDCl_3$ or CD_3OD as solvent and internal reference.

Results and Discussion

Were this preparation ideal, it would produce clean, monodisperse telomers of acrylic acid with APS groups at both ends and no *t*BA residues remaining in the chain. Therefore, the terminal functionalities, the distribution of molecular weights (polydispersity), and the chemical nature of the side chains provide three indicators of how successful this preparation has been.

With BAPD the only source of free radicals, the termini of the chains would consist almost entirely of APS groups, p-$NH_2C_6H_4S$. In the presence of AIBN, however, the chains could be terminated by zero, one, or two APS groups and two, one, or zero 2-cyanopropyl groups, $CH_3C(CN)CH_3$, respectively. In the following sections, we demonstrate that under appropriate conditions, the telomerization of *t*BA in the presence of BAPD and AIBN results in bis-APS terminated telomers of *t*BA with narrow distributions of molecular weights (as measured by the polydispersity, PD = $\bar{M}_w/\bar{M}_n$).

Unhydrolyzed *t*BA residues could have a significant effect upon the properties of the telomer. Because isolation of completely hydrolyzed chains from those with some *t*BA groups remaining presented an insuperable experimental difficulty, it was essential that the hydrolysis proceed to completion. Below, we show that these p*t*BA–bAPS telomers can be completely deprotected to pAA–bAPS of the same length and degree of functionalization, *f*.

Determination of Terminal Groups. We confirmed the presence of the APS groups qualitatively by comparison of the solution-phase ^{1}H-NMR spectra of BAPD and the telomers (Figure 1). The peaks arising from the aromatic protons of the iniferter (at 6.5–6.6 and 7.15–7.25 ppm) are present in both spectra. The lower-field peak is partially masked in the spectrum of the telomer by the peak corresponding to $CDCl_3$, the solvent. The amino protons appear to shift about 0.5 ppm upfield in going from the iniferter to the telomer. The resonant frequencies of exchangeable protons are very sensitive to the properties of the solution; this difference in chemical shifts is almost certainly due to solvent effects.

We calculated the number of p-$NH_2C_6H_4S$ groups per telomer, *f*, according to the equation given in the Experimental Section. Table I presents the values of *f* calculated for each of the polymers we prepared. With the exception of polymer 2, all of the samples were terminated on both ends by APS groups. A value of *f* less than 2 indicated that species derived from AIBN—or possibly from disproportionation—competed with those derived from BAPD in the initiation and the termination steps. We found that molar excesses of BAPD over AIBN approximately 30-fold or greater were required to produce telomers with $f = 2$. Nevertheless, radicals derived from AIBN clearly reacted more rapidly with BAPD than with *t*BA: Telomer chains terminated on both ends with APS groups were readily obtained even though [*t*BA]/[BAPD] ranged from 33 to 400.

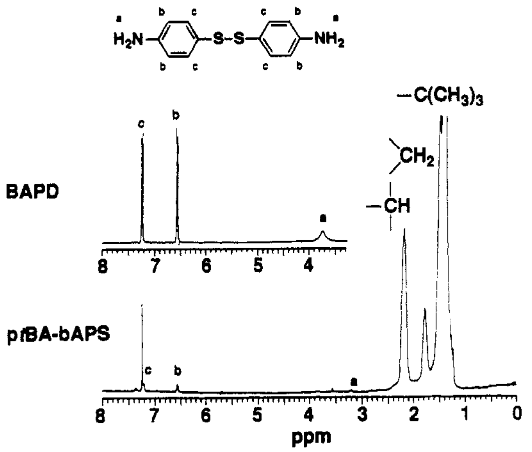


Figure 1. Solution-phase ^{1}H-NMR spectra of BAPD and poly(*t*BA) in $CDCl_3$.

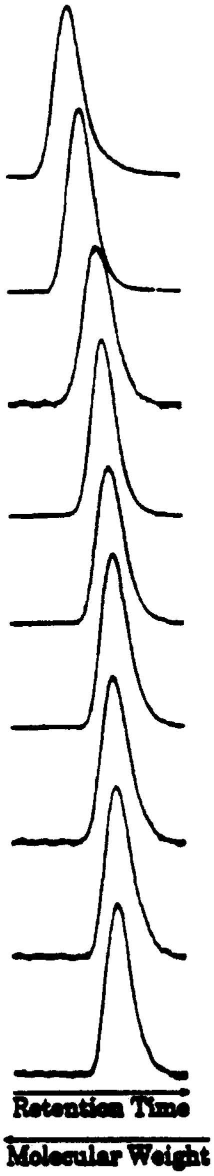
Different Concentrations of BAPD. Addition of chain-transfer agents to a polymerization reaction reduces the molecular weight and polydispersity of the resulting polymer.[11] The magnitude of this effect depends upon the concentration of the chain-transfer agent.[15] We studied the telomerization of *t*BA in the presence of different concentrations of BAPD and analyzed the polymers formed by SEC. Table I shows the peaks obtained for each of the nine polymers in this series. As expected, increases in the concentration of BAPD resulted in lower molecular weights (longer retention times) of p*t*BA–bAPS. Greater concentrations of BAPD also resulted in lower polydispersities, corresponding to more symmetric peaks in the size-exclusion chromatograms.

The effects observed in the raw SEC data are further quantified in Table I. The SEC data were used to calculate the number-average and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$ respectively) of the polymers. The polydispersity was calculated as the ratio of these two values, $\bar{M}_w/\bar{M}_n$.

In the absence of BAPD, the AIBN initiated the polymerization of *t*BA directly. The resulting polymer had the highest value of $\bar{M}_w$ and the greatest polydispersity of the polymers we prepared. The introduction of BAPD resulted in significant reductions both in measures of molecular weight and in the polydispersity. Solutions that contained between 69 and 205 mM BAPD produces polymers with a polydispersity of 2. The data in Table I show that polymers with polydispersities greater than 2 also had functionalities less than 2. (That the limiting values of polydispersity and functionality were both 2 was purely a coincidence.) Thus, a polydispersity of 2 was achieved when all of the chain ends have been formed by transfer to an added transfer agent.

Chain-Transfer Constant. The ratio of the rate constants of chain transfer and chain propagation for a polymerization is known as the chain-transfer constant,

Table I
Molecular Weight Distributions of Poly(*tert*-butyl acrylates) Prepared in the Presence of Different Concentrations of BAPD



Run[a]	SEC	[BAPD][b] × 10³ M	$\bar{M}_n$[c] × 10⁻³ g/mol	$\bar{M}_w$[c] × 10⁻³ g/mol	$\bar{M}_w/\bar{M}_n$	Sulfur Content[d] Wt-%	f [e]
1		0	100	790	7.6		
2		18	140	380	2.8	0.014	0.61
3		37	52	140	2.6	0.11	1.8
4		69	43	86	2.0	0.15	2.0
5		98	27	56	2.1	0.26	2.2
6		140	24	53	2.2		
7		158	22	46	2.0	0.36	2.5
8		180	22	44	2.0	0.33	2.2
9		205	23	40	1.8	0.28	2.0

[a] Polymerization carried out for 120 min at 90 °C in the presence of 2.7 mM (0.05 wt %) AIBN. [b] Initial concentration in moles per liter of *tert*-butyl acrylate. [c] Calculated from SEC data. [d] Determined by elemental analysis. [e] Average number of amino terminal groups per polymer chain.

C_{tr}. We determined C_{tr} for the BAPD–*t*BA system using the equation of Mayo:[16,17]

$$\frac{1}{\bar{P}_n} = \frac{1}{\bar{P}_n^{\,0}} + C_{tr}\frac{[\mathrm{BAPD}]}{[t\mathrm{BA}]} \qquad (1)$$

where [BAPD] and [*t*BA] are the initial concentrations of BAPD and *t*BA used in each run, $\bar{P}_n^0$ is the average degree of polymerization when [BAPD] = 0, and $\bar{P}_n$ is the average degree of polymerization for a given run. We stopped the reactions at conversions low enough to ensure that the ratio of [BAPD]/[*t*BA] was constant.

We obtained values of $\bar{P}_n^0$ and $\bar{P}_n$ from the SEC data for runs 1–9. Figure 2 shows a Mayo plot for these data. The data fell on a line, as expected, up to values of [BAPD]/[*t*BA] = 2 × 10⁻². Above this value, however, the degree of polymerization appeared insensitive to changes in the relative concentrations of monomer and iniferter. This observation can be explained either by lack of solubility of all of the BAPD at the higher BAPD concentration or by the effect of AIBN concentration on the initiation stage.

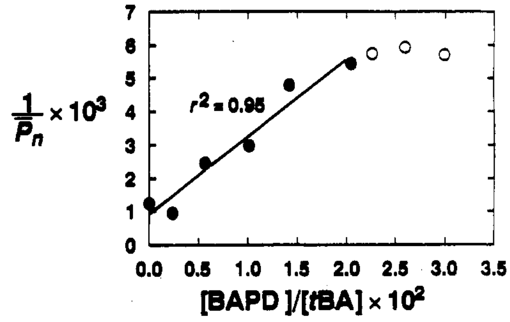


Figure 2. Reciprocal degree of polymerization of *t*BA as a function of the molar ratio of BAPD to *t*BA. Values of $\bar{P}_n$ were determined by SEC. The line is a least-squares fit to the data represented by the filled circles.

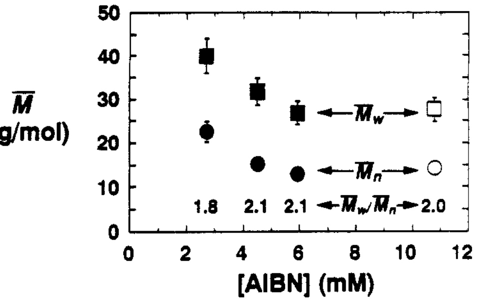


Figure 3. Changes in the concentration of AIBN affecting the molecular weight of the resulting poly(*tert*-butyl acrylate). Polymerizations were carried out at 90 °C for 120 min, starting with a concentration of 205 mM BAPD. The filled symbols represent the molecular weights of α,ω-diamino-terminated polymers; the open symbols represent the molecular weights of polymers containing less than two amino groups per chain. In the regime where bisfunctionalization was observed, the molecular weight decreased linearly as the concentration of AIBN increased.

Table II
Properties of Poly(*tert*-butyl acrylates) as a Function of the Time of Polymerization

t^a (min)	convn^b (%)	$\bar{M}_n{}^c$ ($\times10^{-3}$)	$\bar{M}_w{}^c$ ($\times10^{-3}$)	$\bar{M}_w/\bar{M}_n$
30	0.46	26	58	2.2
60	2.1	25	54	2.2
120	13	24	53	2.2
180	16	20	46	2.3
240	20	22	48	2.2

[a] Reaction carried out with 160 mM BAPD and 2.7 mM AIBN at 90 °C. [b] Ratio of the weight of recovered polymer to the initial weight of monomer. [c] Determined by size-exclusion chromatography.

Using a linear least-squares fit to the data for which [BAPD]/[*t*BA] ≤ 2×10^{-2}—represented by filled circles in Figure 2—we obtained $C_{tr} = 0.23$. This value was very near the value of 0.24 obtained for BAPD–styrene.[18,19]

Effect of AIBN Concentration. Increasing the concentration of AIBN produced polymers of lower molecular weights. Figure 3 shows the values of $\bar{M}_n$ and $\bar{M}_w$ obtained from SEC for four polymers. Each polymer was prepared from an initial concentration of BAPD of 205 mM by heating to 90 °C for 120 min. As the initial concentration of AIBN increased from 2.7 to 5.9 mM, the molecular weight of the resulting telomers decreased linearly while the polydispersity and the functionality remained constant at 2. When the initial concentration of AIBN was increased to 11 mM, however, the resulting molecular weight was significantly higher than expected from an extrapolation of the previous data, and the functionality dropped to 1.3. The initial molar ratio of BAPD to AIBN in this reaction was 17; the initial ratios for the other three cases changed from 35 to 75. These observations were consistent with the data in Table I, in which initial ratios greater than 30 were required to achieve polymers with $f = 2$.

Reaction Time. Table II shows properties of polymers prepared using different times of polymerization. The molecular weight and polydispersity of these polymers was independent of the time allowed for polymerization; only the conversion increased. The conversion did not increase linearly with time: Because the time for polymerization included the time required to heat the mixture from room temperature to 90 °C, the particular relation to conversion to time observed here was an experimental artifact. The most important conclusion derived from Table II is that the molecular weight distribution of the polymers was insensitive to the time the reaction was allowed to run up to at least 20% conversion.

Reaction Temperature. We performed two polymerizations at 50 °C in order to determine the effect of temperature upon the value of the transfer constant, C_{tr}, and upon the molecular weight distribution. Both polymerizations were run for 120 min, with an initial concentration of AIBN of 2.7 mM. The first mixture contained no BAPD and resulted in a polymer with $\bar{M}_n = 8.5 \times 10^5$, $\bar{M}_w = 1.2 \times 10^6$, and $\bar{M}_w/\bar{M}_n = 2.3$. The second mixture contained 94 mM BAPD and resulted in a polymer with $\bar{M}_n = 36\,000$, $\bar{M}_w = 88\,000$, $\bar{M}_w/\bar{M}_n = 2.4$, and $f = 1.8$. Using the equation of Mayo,[16,17] the value of C_{tr} was estimated to be 0.24, essentially the same as the value of 0.23 obtained at 90 °C. These observations suggest that the transfer constant remains the same over a broad range of temperatures. Pierson and co-workers have reported the same effect when using BAPD with styrene.[20]

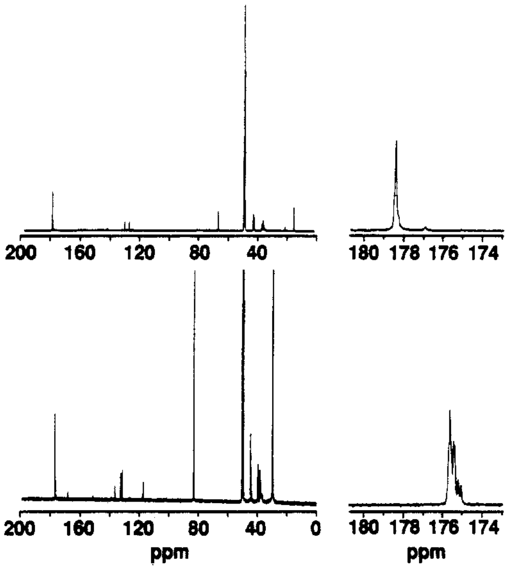


Figure 4. p*t*BA–bAPS was completely hydrolyzed when refluxed in 4:1 acetic acid–water using *p*-toluenesulfonic acid as a catalyst. Solution-phase ^{13}C-NMR spectra of the initial p*t*BA–bAPS (lower trace) and the deprotected pAA–bAPS (upper trace). The peak at 178.4 ppm corresponds to carbonyl carbon; those around 175 ppm correspond to the carbonyl carbon of an ester. No ester could be detected in the final product. No peaks corresponding to the $C(CH_3)_3$ and $C(CH_3)_3$ carbons of the *tert*-butyl esters (84 and 29 ppm, respectively) were detected in the spectra of pAA–bAPS either.

Hydrolysis of p*t*BA–bAPS to pAA–bAPS. We hydrolyzed p*t*BA–bAPS using *p*-toluenesulfonic acid in refluxing wet acetic acid (4:1 (v/v) acetic acid–water). Comparison of the solution-phase ^{13}C-NMR spectra of the polymer before and after hydrolysis (Figure 4) confirmed that the *tert*-butyl groups were removed under these conditions. The peak corresponding to the carboxyl group at 178.4 ppm was completely resolved from the ester carbon at 175.4 ppm. In addition no ester proton was detected in the ^{1}H-NMR spectra of the hydrolyzed polymer. Further, the peaks at 29 and 84 ppm, corresponding respectively to the $C(CH_3)_3$ and $C(CH_3)_3$ carbons of the *tert*-butyl groups, were entirely absent from the spectra of the hydrolyzed telomers. We conclude that the hydrolysis was quantitative.

The APS groups remained stable under the conditions we used to hydrolyze the *tert*-butyl esters. Peaks arising from the aromatic protons and carbon atoms appeared at approximately 7 and 130 ppm in the ^{1}H- and ^{13}C-NMR spectra, respectively. We calculated the functionalization, f, of pAA–bAPS using the weight percent of nitrogen in the polymer and the formula given in the Experimental Section. Table III shows the results obtained for two of the telomers used in this paper. The values of f were accurate to ±0.2 and were indistinguishable from 2,

Table III
End-Group Functionality of pAA–APS

$\bar{M}_n{}^a$ ($\times10^{-3}$)	$\phi_N{}^b$ (wt %)	$\bar{M}_n{}^c$ ($\times10^{-3}$)	f^d
13	0.23	12	2.1
8.6	0.32	8.8	2.0

[a] Calculated from the value of $\bar{M}_n$ for the p*t*BA–bAPS from which the polymer was prepared. [b] Determined by elemental analysis. [c] Calculated from the elemental analysis, assuming two 4-aminophenyl sulfide groups per polymer chain. [d] Calculated using the equation in the Experimental Section.

indicating that the bifunctionality of p*t*BA–bAPS was retained in pAA–bAPS.

Conclusions

We found that BAPS provided significant control over the polymerization of *t*BA while also introducing the chemically distinct chain termini into the telomer. The molecular weight distributions of the isolated polymers were insensitive to changes in temperature between 50 and 90 °C and to changes in the degree of conversion of monomer from 0% to 20%. When using AIBN as the principal source of radicals, we found that molar excesses of BAPD over AIBN greater than 30 were required to produce predominantly diamino-terminated chains. The free-radical polymerization of *t*BA in the presence of BAPD is therefore a useful means for preparing terminally reactive telomers of *t*BA. We also found that p*t*BA–bAPS is easily hydrolyzed to form amino-terminated telomers of acrylic acid, which are themselves potentially very useful building blocks for more complex polymers.

Acknowledgment. The authors gratefully acknowledge Prof. George Whitesides for helpful discussions and the use of lab space. The authors thank Watson Lees for assistance with the NMR spectroscopy and Gerard Guevelou for performing the SEC analyses. This work was supported by the National Science Foundation (NSF) under the Engineering Research Center Initiative by a grant to the Massachusetts Institute of Technology Biotechnology Process Engineering Center (cooperative agreement CDR-88-03014). The Bruker NMR spectrometer was provided to Chemical Laboratories of Harvard University through a grant from the NSF (CHE-8410774).

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