

Reactions of anionic living polymers with bromomethyl-functionalized benzoyl peroxides

Baki Hazer*¹, Akira Hirao², Cüneyt Volga³

¹ Zonguldak Karaelmas University, Department of Chemistry, 67100 Zonguldak, Turkey

² Department of Polymer Chemistry, Faculty of Engineering, Tokyo Institute of Technology, Ohokayama, Meguro ku, Tokyo 152, Japan

³ Karadeniz Technical University, Department of Chemistry, 61080 Trabzon, Turkey

(Received: January 2, 1998; revised: June 8, 1998)

SUMMARY: In order to synthesize benzoyl peroxide functionalized polystyrene (PSt), polyisoprene (PI) and poly(methyl methacrylate) (PMMA), anionic living PSt, PI, and PMMA were allowed to react with an excess amount of 4-(bromomethyl)benzoyl *tert*-butyl peroxide (BMtB) or bis[3,5-bis(bromomethyl)benzoyl] peroxide (BDBP) in tetrahydrofuran (THF) at -78°C . The results indicate that coupling reactions leading to dimers are significant during the reaction. Dimer formation was avoided when the living polystyrene was modified to the alcoholate anion by reaction with ethylene oxide (EO).

Introduction

Anionic living polymers are suitable precursors for the synthesis of end-functionalized polymers with controllable molecular weights and narrow molecular weight distributions. Highly reactive but stable carbanions at living polymer chain ends can be transformed to a wide variety of useful functional groups by reaction with electrophiles. Thus, many end-functionalized polymers with well-defined structure have so far been synthesized by means of such reactions^{1–5}. In previous papers^{6–9} the successful synthesis of well-defined polystyrenes and polyisoprenes with either NH_2 , COOH , epoxy, or 1,3-butadienyl terminus by the reaction of polystyryl or polyisoprenyl anions with specially designed alkyl halides containing protected functionalities was demonstrated. In another work¹⁰ we reported the synthesis of a macroperoxide, prepared by the termination of polystyryl anions obtained by a new difunctional initiator (1,5-bis[2-(1-lithio-3,3-dimethylbutyl)]naphthalene; DDBLN) with bis[4-(bromomethyl)benzoyl] peroxide at 25°C .

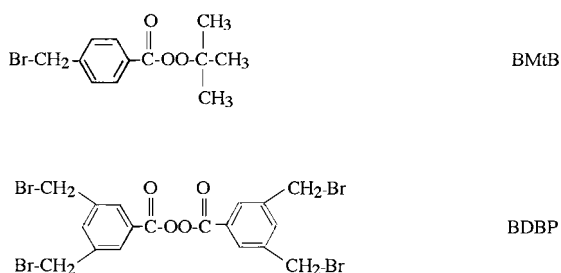
This paper refers in detail to the coupling reactions between living polymer anions and the bromomethyl functionalized benzoyl peroxides BMtB and BDBP (Scheme 1).

Experimental part

Materials

Styrene (St), methyl methacrylate (MMA), and isoprene (I) were purified by the procedures reported in ref.⁷ 4-(Bromomethyl)benzoyl bromide was synthesized from 4-methylbenzoyl chloride with *N*-bromosuccinimide according to the procedure described in ref.¹¹ BMtB was synthesized by the reac-

Scheme 1: Chemical formulae of BMtB and BDBP



tion of equimolar amounts of 4-(bromomethyl)benzoyl bromide and *tert*-butyl (t-Bu) hydroperoxide in the presence of NaOH as a catalyst at $0-5^{\circ}\text{C}$. The crude, white product was crystallized from chloroform solution chilled with pentane.

¹H NMR (CDCl_3): $\delta = 1.0$ (9H, t-Bu), 4.7 (2H, CH_2Br), 7.7–8.0 (4H, phenyl).

BDBP was synthesized according to the procedure described in ref.¹²

Coupling reactions

Coupling reactions of anionic living polymers were carried out with either BMtB or BDBP. All operations including polymerization and reaction were performed under high vacuum conditions using break-seals. The polymerization of styrene was carried out with *sec*-butyllithium (*sec*-BuLi) in THF at -78°C for 20 min. The capping with 1,1-diphenylethylene (DPE) was carried out in THF at -78°C for 10 min. The polymerization of MMA was performed in THF at -78°C for 20 min with the initiator system prepared from *sec*-BuLi and DPE in the presence of LiCl. The reactions with either terminator were carried out in THF at -78°C for 20 min for the addition and the reaction mixtures were allowed to stand for additional 20 min. The living polymer was always added dropwise to an excess of terminator. The

characteristic color disappeared immediately up on mixing, indicating the reactions are rapid and complete within seconds even at -78°C . The resulting polymers were precipitated in methanol and purified twice by reprecipitation from THF solution to methanol.

Coupling reactions in the presence of N,N,N',N' -tetramethylethylenediamine (TMEDA) at 30°C

As a typical coupling reaction, run no. 97-34 was carried out by the following procedure: Styrene (1.19 M in benzene, 8.07 mmol) was added to *sec*-BuLi (0.162 M in heptane, 0.259 mmol) to polymerize at room temperature for 1 h. The color was orange. Then, TMEDA (0.196 M in heptane, 0.261 mmol) was added at r.t. where the color changed dramatically to clear red. The mixture was divided in two portions, one of which (34 vol.-%) was terminated with methanol as a reference. The other one (66 vol.-%, 0.166 mmol of living end) was added dropwise to 4-(bromomethyl)benzoyl *tert*-butyl peroxide (0.0940 M in benzene, 0.782 mmol) at 30°C for 5 min. On mixing, the color disappeared instantaneously, indicating a rapid reaction. The mixture was allowed to stand for an additional 1 h and then precipitated in methanol. The polymer was reprecipitated two more times to remove unreacted terminator.

Modification of the living polystyryl anion to the alcoholate anion with EO (97-39 and -40).

Two kinds of living polystyrenes were prepared by BuLi (monofunctional) and 1,1,4,4-tetraphenylbutanediyl dipotassium (difunctional) initiation, respectively, according to the following initial feed.

97-39: St/THF (0.97 M, 8.94 mmol), *sec*-BuLi/heptane (0.116 M, 0.190 mmol), ethylene oxide/THF (0.718 M, 3.45 mmol), BMtB/THF (0.161 M, 0.726 mmol).

\bar{M}_n calc. = 5200, \bar{M}_n obsd. = 4780, $\bar{M}_w/\bar{M}_n = 1.07$.

97-40: St/THF (0.97 M, 10.42 mmol), 1,1,4,4-tetraphenylbutanediyl dipotassium/THF (0.0728 M, 0.334 mmol), ethylene oxide/THF (0.718 M, 3.88 mmol), BMtB/THF (0.161 M, 1.40 mmol).

\bar{M}_n calc. = 6780, \bar{M}_n obsd. = 6190, $\bar{M}_w/\bar{M}_n = 1.10$.

For the coupling procedure, the polystyryl anion was reacted with an excess of EO in THF at -78°C for 5 min at 25°C for additional 1 h. Under these conditions, the polystyryl anion is quantitatively transformed into $\text{CH}_2\text{CH}_2\text{OLi}$ of the alcoholate anion and no polymerization of EO proceeds further. BMtB was then added to this anion in THF at room temperature (ca. 15°C) and allowed to stand for one week.

Characterization

Thin-layer chromatography (TLC) was carried out on SiO_2 plates (Merck Art 5554) with a fluorescent indicator. The instrument for the TLC-flame ionization detector (FID) method was an Iatron Thinchrograph Model MK-5 from Iatron Co, Ltd. A specially designed quartz rod (150×2.0 mm), commercially available as a SII rod, was used on which silicagel was sintered. The principle for this method was described in detail in the literature¹³. Polymer

samples were usually developed with either toluene in the case of polystyrenes or toluene/hexane in the case of polyisoprenes. Using these solvents as eluents, the end-functionalized samples with peracid ester or ester remained near the spotting points, while unfunctionalized homopolymers were well mobile, to be developed almost at top.

^1H and ^{13}C NMR spectra were recorded on JEOL FX-90Q and JEOL FX-200 spectrometers in CDCl_3 .

Size exclusion chromatographs (SEC) were obtained at 40°C with a TOSOH HLC 8020 instrument with UV (254 nm) or refractive index detection. THF was used as an eluent at a flow rate of 1.0 mL/min. Three polystyrene gel columns (TSKgel G4000H_{XL}, G3000H_{XL}, G2000H_{XL}) were used. Calibration curves were made to determine \bar{M}_n and \bar{M}_w/\bar{M}_n values with standard polystyrene and polyisoprene samples.

Results and discussion

The coupling reactions of anionic living polymers with the bromomethylated benzoyl peroxides, BMtB or BDBP, as terminators were usually carried out in THF at -78°C . In addition, we have attempted to react BMtB with polystyryllithium in the presence of TMEDA in benzene at 30°C , since it has been recently reported that 4-(chloromethyl)styrene quantitatively reacts with polystyryllithium under similar conditions¹⁴. Moreover, reactions using *tert*-butyl 4-(bromomethyl)benzoate (BMtBB) instead of BMtB were carried out under identical conditions in order to elucidate the reactivity difference between peracid ester and normal ester. As mentioned in the *Experimental part*, living polymer was added dropwise into an excess amount of each terminator to minimize the peracid ester attack by the living chain end.

Coupling with BMtB

We have first examined the reaction of polystyryllithium with BMtB in THF at -78°C . Upon addition of polystyryllithium into BMtB, the characteristic orange-red color of the living polymer anion disappeared instantaneously, indicating that the reaction proceeded very rapidly even at -78°C . The reaction mixture was allowed to stand at -78°C for additional 20 min and then at 25°C . The polymer was precipitated in methanol, purified by repeated reprecipitation to remove unreacted BMtB, and freeze-dried for 24 h.

The gel permeation chromatography analysis shows that the resulting polymer possesses a bimodal distribution (Fig. 1). The polymer with the lower molecular weight peak seems to be the desired coupling product, since the \bar{M}_n value of 3600 agrees with the calculated value of 3700. A higher molecular weight peak ($\bar{M}_n = 7000$) appears monodisperse and double the molecular weight of the starting living polymer. The ratio of the low and high peak areas is 63 : 37. Such a dimer formation was often observed in these

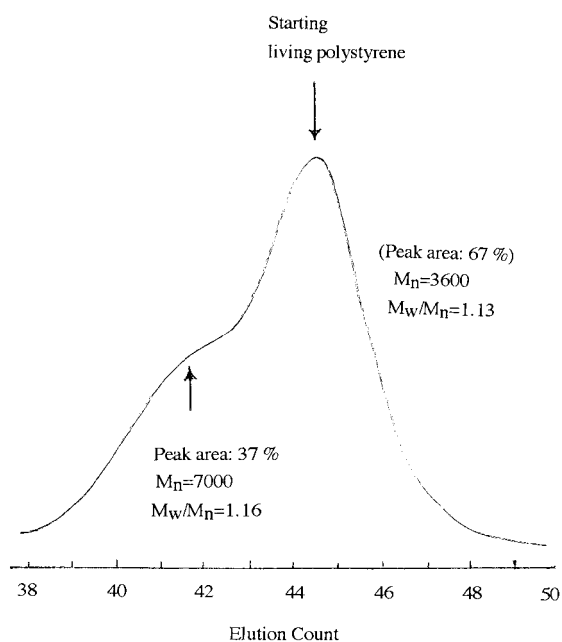


Fig. 1. SEC chart of the resulting polymer based on functionalized polystyrene and dimeric product (Run no. 96-8)

kinds of reactions of anionic living polymers with halobenzyl compounds previously reported¹⁵.

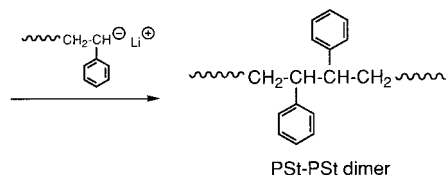
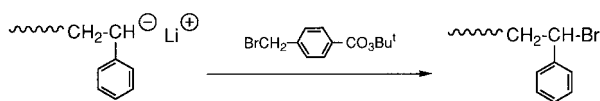
The most likely cause for a dimer formation is considered to be either a lithium-bromine exchange reaction, followed by the coupling between the brominated polystyrene and remaining polystyryllithium, or a single electron transfer, followed by the coupling between intermediate polymer radicals thus generated as shown in Scheme 2. Accordingly, these two possible reaction routes leading to a dimer formation indicate strongly that the dimer structure is unfunctionalized polystyrene.

The ¹H NMR spectrum of the resulting polymer is shown in Fig. 2. The resonance for two protons *ortho* to the benzoic peracid ester and methyl protons of the *tert*-butyl group appear at 7.8 and 0.9 ppm, respectively, while no resonance for the two protons of the bromomethyl group at 4.6 ppm is observed. Thus, the spectrum gives a direct evidence that the reaction of polystyryllithium with BMtB proceeds in the expected manner to a certain extent and that the resulting polymer is end-functionalized with the peracid ester function. However, the degree of end-functionalization estimated by this spectrum is as low as 20%.

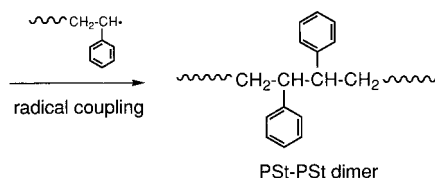
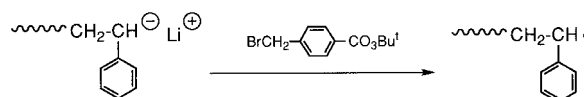
Thin layer chromatography of the resulting polymer showed two spots. The spot well mobile near the top corresponds to polystyrene, while the spot remaining around the spotting point may be the functionalized polystyrene with a peracid ester function. The amount of functionalized polymer could be determined to be 34% by means of FID detection. These analytical results by ¹H NMR and TLC-FID methods as well as SEC indicate that only about 30% of the starting polystyrene is end-functionalized with peracid

Scheme 2: The purposed side reactions during the coupling reaction of the polystyryl anion with a bromomethylbenzoyl peroxide moiety

(1) Lithium-bromine exchange



(2) Single-electron transfer



ester while the remaining 70% of the resulting polymer is unfunctionalized polystyrene. In addition to the side reaction leading to a dimer formation (37%), additional undesired side reactions may possibly take place in the reaction with BMtB. We tentatively consider a proton abstraction of the bromomethyl group and a single electron transfer pathway without coupling between generated polymer radicals as side reaction candidates.

As expected, similar results were obtained in repeated experiments. Living polystyryllithium was capped with 1,1-diphenylethylene to lower the nucleophilicity and reacted with BMtB. A monomodal peak with a relatively broad distribution ($\overline{M}_w/\overline{M}_n = 1.34$) was obtained in this case by the GPC measurement. Both ¹H NMR and TLC-FID analysis indicated about 30% end-functionalization. No improvement was realized by changing the solvent and temperature from THF, -78 °C to benzene, 30 °C. These results are summarized in Tab. 1.

The living polymer of MMA was prepared from MMA and *sec*-BuLi capped with 1,1-diphenylethylene in the presence of LiCl in THF at -78 °C, followed by treating with BMtB in THF at -78 °C (Run no. 96-15 in Tab. 1). No appreciable reaction was observed to occur. The same SEC peaks were obtained before and after reaction. The ¹H NMR spectra also indicated that no reaction occurred.

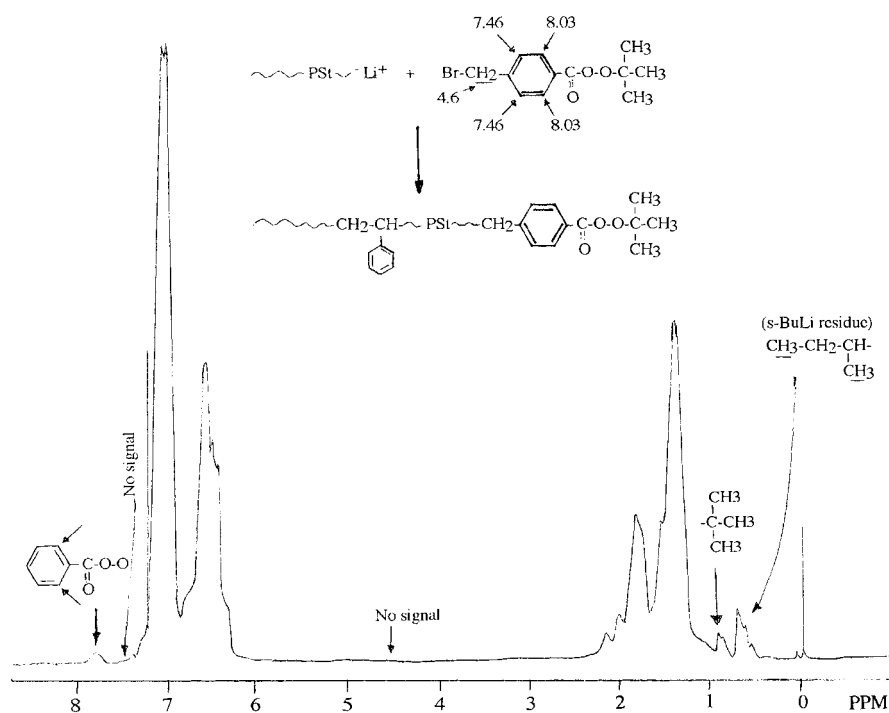


Fig. 2. ^1H NMR spectrum of the resulting polymer based on functionalized polystyrene and dimeric product (Run no. 96-8)

Tab. 1. Results of the coupling reactions between polystyryllithium and 4-(bromomethyl)benzoyl *tert*-butyl peroxide (BMtB)

Run no.	Living polymer	Terminator	calc. \bar{M}_n	obsd. \bar{M}_n	\bar{M}_w/\bar{M}_n	Peak area	Function-alization ^{a)}
						%	%
96-8	PSt	BMtB	3710	3600 7000	1.13	63 37	34
96-13 ^{b)}	PSt	BMtB	2590	2838	1.34		30
96-15 ^{b)}	PMMA	BMtB	3200	3200	1.10		≈ 0
96-23	PSt	BMtB	7240	7250 15000	1.16	79 21	45
97-4	PSt	BMtBB	3400	3600 7200	1.18	68 32	42
97-7 ^{c)}	PSt	BMtBB	8100	12400	1.24	multi-modal	$\approx 60^{\text{d)}$
97-10	PI	BMtBB	3900	4600 9200	1.13	60 40	40
96-22	PSt	BDBP	6050	6060 10700	1.24	64 36	$\approx 40^{\text{d)}$
97-34 ^{e)}	PSt	BMtB	3450	3140 4940	1.04	36 64	20
97-35 ^{e)}	PSt	BMtB	5050	5190 8460	1.02	47 53	29
97-39	PSt-alcoholate	BMtB	5200	4780	1.07		75
97-40 ^{e)}	PSt-alcoholate	BMtB	6780	6190	1.10		75

a) Determined by TLC-FID.

b) Living polymers were obtained with the *sec*-BuLi + DPE catalyst system.

c) Living polystyryl anion was obtained by 1,1,4,4-tetraphenylbutanediyli dipotassium instead of *sec*-BuLi alone as catalyst.

d) Mono- and difunctionalized products may be involved.

e) Polymerizations were carried out in benzene at r.t. and the reactions were performed in benzene in the presence of TMEDA at 30 °C.

Coupling with *tert*-butyl 4-(bromomethyl)benzoate (BMtBB)

Under identical conditions, the coupling reaction of polystyryllithium (in THF at -78°C and in benzene at 30°C), difunctional polystyrylpotassium (in THF at -78°C), or polyisoprenyllithium (in THF/heptane at -78°C) with *tert*-butyl 4-(bromomethyl)benzoate, BMtBB, was carried out to examine the difference in reactivity between peracid ester and normal ester (Run no. 97-4, 97-7, and 97-10 in Tab. 1). Very interestingly, the reaction products are similar to those obtained by the reactions with BMtB as mentioned above. Dimeric products of the starting living polymers were formed significantly in all cases and 20–40% of end-functionalization were achieved. Accordingly, undesirable side reactions leading to dimers and unfunctionalized polymers occurred to similar extents in the reactions of anionic living polymers with the corresponding normal *tert*-butyl ester. These results are also listed in Tab. 1. Considering the previous observation that the reactions of anionic living polymers and organolithium compounds with halobenzyl compounds usually proceed satisfactorily, more enhanced reactivities of the bromomethyl groups due to the electron-withdrawing character of both peracid ester and normal ester functionalities may possibly be attributable to the results obtained here. In this manner, not only an electron transfer to the halogen is possible but also to the carbonyl group, possibly depending on the redox potential.

Furthermore, several researchers previously also pointed out that side reactions as illustrated in Scheme 2 occur competitively to a certain extent in these reactions. For example, in the preparation of star polymers by means of the reaction of multifunctional halobenzyl compounds with anionic living polymers of styrene, the coupling reactions leading to a dimer formation of the starting living polymer were often observed¹⁶⁾. Metal-halogen exchange reactions were suggested as possible candidates. Höcker and Heitz reported that the dimeric product was formed considerably by a Wurtz coupling in the reaction of anionic living polystyrene with 2,5-dimethoxybenzyl bromide^{15a)}. In these cases, the dimer formation could be eliminated or suppressed considerably by changing the counterion of the living polymers from Li^+ to K^+ and a modification of the living ends with 1,1-diphenylethylene. Unfortunately, these variations showed no improvement in our reactions.

With respect to the rate of metal-halogen exchange reaction, the effect of the leaving group is generally known to be $\text{I} > \text{Br} > \text{Cl}$. Exactly the same order is expected for a single electron transfer process when considering the reduction potentials. If the side reactions proposed by Scheme 2 proceeded in our cases, their reaction rates would have been reduced by changing the reactive moiety of BMtB from bromobenzyl to the corresponding

chlorides. However, it was reported that such dimers were also more or less formed in similar reactions with chlorobenzyl compounds¹⁶⁾.

Coupling with BMtB via ethylene oxide

As another solution to avoid the dimer formation, we have modified the carbanion of living polystyrene to the alcoholate anion by reaction with ethylene oxide (EO) (see the *Experimental part* for the procedure). The reason for this is that there is either little or no possibility for the side reactions proposed by Scheme 2 in the reaction of halobenzyl compounds with alcoholate anions, while the bromomethylbenzyl group is considered to be still reactive with alcoholate anions. The resulting polymer showed a sharp monomodal SEC peak ($\bar{M}_w/\bar{M}_n = 1.07$) and a reasonable molecular weight (Run no. 97-39 and 97-40 in Tab. 1). A dimeric product was not formed in this case, although a very small high molecular weight shoulder (<3%) was observed in the SEC chart (Fig. 3). The ^1H NMR spectrum (Fig. 4), exhibited resonances at 7.75 (multiplet), 7.40 (multiplet), and 4.40 (singlet) corresponding to the aromatic protons *ortho* and *meta* to the peracid ester of BMtB and the benzyl protons ($-\text{C}_6\text{H}_4-\underline{\text{CH}_2}-\text{O}-$), respectively. Broad peaks at 3.8–4.1 ppm are the $\text{CH}_2\text{CH}_2\text{O}$ protons of ethylene oxide. This clearly indicates the incorporation of a *tert*-butyl perester functionality. The functionality determined from the ratio of the resonances at 4.4 ppm and 0.65 ppm (methyl protons of the initiator fragment) is 75%. The absence of a resonance corresponding to bromomethyl protons (4.6 ppm) provides an evidence that no reaction occurred between the $\text{CH}_2\text{CH}_2\text{OLi}$ end-group and the peracid ester of BMtB. Thus the dimer formation could be dramatically suppressed by the use of the end-functionalized polystyrene with $\text{CH}_2\text{CH}_2\text{OLi}$. However, more drastic reaction condition and/or the use of dipolar aprotic solvents such as *N,N*-dimethylformamide and dimethyl sulfoxide will be required for a completion of the functionalization reaction.

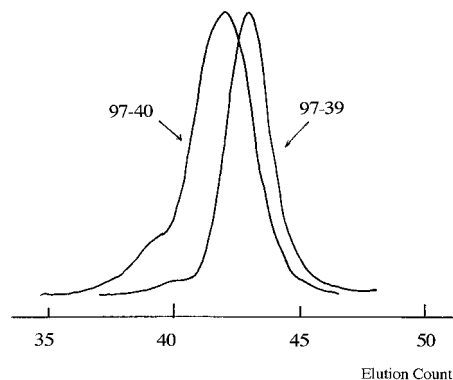


Fig. 3. SEC charts of the functionalized polystyrenes via EO coupling reactions (Run no. 97-39 and 97-40)

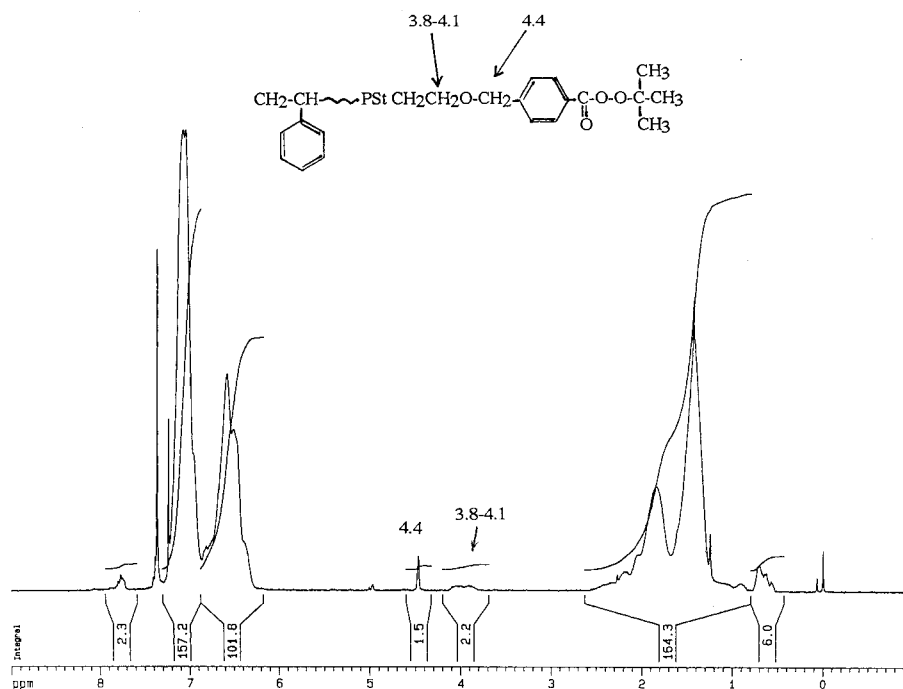


Fig. 4. ^1H NMR spectrum of the functionalized polystyrene via EO coupling reactions (Run no. 97-39)

Coupling with BDBP

The tetrafunctional bromomethylated benzoyl peroxide, BDBP, was attempted to react with polystyryllithium in THF at -78°C . The dimer was obtained in significantly more than 60% yield, but higher molecular weight materials such as the three- and four-armed star type polymers were not produced. In this case, the polymerization product may be more complex than those obtained with BMtB and is therefore more difficult to be analyzed. No information was available by ^1H NMR. TLC-FID indicates the presence of functionalized polymers with peracid esters, although they are around 40%. In order to confirm the content of peracid ester functions in the polymer, we have decomposed the resulting polymer in chlorobenzene solution in the presence of iodine at 80°C according to the procedure previously reported¹⁷. After cleavage, \bar{M}_n of the polystyrene samples changed from 10700 to 8800 (Run no. 96-22), and from 7250 to 5821 (96-23), indicating that the polymer mixture contains the dimeric product functionalized with benzoyl peroxide.

As a conclusion, in the coupling reactions of anionic living PS, PI and PMMA with bromomethyl-functionalized benzoyl peroxides, the dimer formation was significant during the reactions which yield 70% of unfunctionalized polymer. By modification of the carbanion of the living polymer with ethylene oxide to the alcoholate anion, the dimer formation was dramatically suppressed and 75% of peroxide-functionalized polymer was obtained.

- 1) R. N. Young, R. P. Quirk, L. J. Fetters, *Adv. Polym. Sci.* **56**, 1 (1984)
- 2) P. Rempp, E. Franta, J.-E. Herz, *Adv. Polym. Sci.* **86**, 145 (1988)
- 3) R. P. Quirk, J. Yin, L. E. Fetters, *Macromolecules* **22**, 85 (1989)
- 4) R. P. Quirk, J. Yin, S.-H. Guo, X.-W. Hu, G. Summers, J. Kim, L.-F. Zhu, L. E. Schock, *Makromol. Chem., Macromol. Symp.* **32**, 47 (1990)
- 5) M. O. Hunt, Jr., A. M. Belu, R. W. Linton, J. M. De Simone, *Macromolecules* **26**, 2145 (1993)
- 6) K. Takenaka, A. Hirao, S. Nakahama, *Macromol. Chem. Phys.* **196**, 1687 (1995)
- 7) K. Takenaka, A. Hirao, S. Nakahama, *Polym. Int.* **37**, 291 (1995)
- 8) A. Hirao, H. Nagahama, T. Ishizone, S. Nakahama, *Macromolecules* **26**, 2145 (1993)
- 9) K. Ueda, A. Hirao, S. Nakahama, *Macromolecules* **23**, 939 (1990)
- 10) B. Hazer, I. Çakmak, S. Küçükyavuz, T. Nugay, *Eur. Polym. J.* **28**, 1295 (1992)
- 11) B. Hazer, *Eur. Polym. J.* **26**, 1167 (1990)
- 12) B. Hazer, *Eur. Polym. J.* **27**, 975 (1995)
- 13) F. B. Padly, *J. Chromatogr.* **39**, 37 (1969)
- 14) (a) R. Asami, M. Takaki, H. Hanahata, *Macromolecules* **16**, 628 (1983); (b) Y. Tsukahara, J. Inoue, Y. Ohota, S. Kohjiya, Y. Okamoto, *Poly. J. (Tokyo)* **26**, 1013 (1994)
- 15) (a) T. Heitz, H. Höcker, *Makromol. Chem.* **189**, 777 (1988); (b) J. C. Meunier, R. van Leemput, *Makromol. Chem.* **142**, 1 (1971)
- 16) B. J. Bauer, L. J. Fetters, *Rubber Chem. Technol.* **51**, 406 (1978)
- 17) B. Hazer, B. Baysal, *Polymer* **27**, 967 (1986)