Block Copolymerization of Ethylene Oxide and Styrene by Sequential Initiation of an Anion and a Photoinduced Charge Transfer Complex

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ABSTRACT: A block copolymer composed of crystalline polyethylene oxide (PEO) and noncrystalline polystyrene (PS) was prepared by the combination of anion and photoinduced charge transfer polymerization (CTP) using *p*-aminophenol as the parent compound. The whole copolymerization was divided into two stages. In the first stage, the amino group of *p*-aminophenol was protected by benzaldehyde first and then reacted with metallic potassium. The phenoxy anion formed initiated polymerization of EO. In the second stage, the PEO prepolymer with the Schiff base end group was deprotected by acidolysis with acetic acid. Then the recovered amino group and added benzophenone (BP) constituted a charge transfer complex (CTC) under UV irradiation to initiate the polymerization of styrene. The block copolymer of EO and St (PEO-*b*-PS) and the intermediates were characterized in detail by elemental analysis, GPC, UV, DSC, IR, and NMR.

Introduction

As is well-known, existing polymerization methods except condensation polymerization are essentially arranged under three general mechanistic categories, that is, radical, ion, and coordination polymerization, according to the properties of the species. However each process is limited to certain types of monomers and excludes other monomers that polymerize by other mechanisms. There is not yet a general acceptable polymerization method which is suitable for all monomers. Therefore some bifunctional and polyfunctional initiators have been designed and prepared[1] in order to satisfy different polymerization mechanism demands for monomer structure. In this strategy, one kind of polymer, prepared by one mechanism, is terminally funtionalized, separated, and subsequently used to initiate a second monomer to polymerize by a different mechanism.[2] In principle, any block copolymers which were very difficult to prepare by a single polymerization mechanism could be designed and synthesized by this approach.

At the present time, most bifunctional initiators prepared and widely used are still governed by a single reaction mechanism. For example, azo–peroxide initiators[3] which possess functional groups of different thermal stabilities and azo–benzoin initiators[4] which possess photosensitive and thermosensitive functional groups in a single molecule function by the radical polymerization mechanism for both steps of the reaction.

Recently, Yagci[5] reported the preparation of a block copolymer of cyclohexene oxide and styrene by a combination of radical and cationic polymerization. They still used an azo–benzoin system as initiator, but after the thermal polymerization of styrene, the polystyrene macroradicals with benzoin end groups were oxidized to the corresponding carbocations in the presence of onium salts. These then initiate the polymerization of cyclohexene oxide, resulting in the formation of a block copolymer. This is a limited bifunctional initiator example really controlled by a different polymerization mechanism.

In the present paper, we reported the research results of sequential initiation of anion and photoinduced CTC to prepare PEO-*b*-PS using *p*-aminophenol as the parent compound.

Experimental Section

Materials. Styrene (St), EO, and tetrahydrofuran (THF) were dried by calcium hydride and then distilled under N_2 atmosphere before use. All other solvents were purified by conventional drying and distillation procedures. *p*-Aminophenol (from Tao Yuan Reagent Factory, WuJian county, ShuZhou City, China) was recrystallized two times with alcohol and then water, giving crystals with a dark yellow color in a yield of 83.2%, mp 187–188 °C; benzophenone (BP) was also purified by recrystallization with alcohol. *N*-benzylidene *tert*-butyl nitrone (BBN) was prepared according to the references.[6,7] Mp of purified product: 69 °C.

Protection of the Amino Group of *p*-Aminophenol. In a three-neck flask fitted with a stirrer, 3 g (0.027 mol) of *p*-aminophenol in alcohol (20 mL) was introduced, and the system was placed in a water bath at 50 °C. After dissolution of the *p*-aminophenol, 4.5 mL of benzaldehyde was added dropwise from a funnel. The reaction was stirred for 1 h. Yellow needle crystals of 4-[(phenylmethylene)amino]phenol formed as soon as the system was cooled to temperature, yield 78%. The product could be purified by recrystallization with alcohol, mp of purified sample 177–178 °C. Anal. Calc: C, 79.19; H, 5.58; N, 7.11. Found: C, 79.20; H, 5.80; N, 6.87. Molecular formula: $C_{13}H_{11}NO$. IR (KBr, cm^{-1}): 3420 (OH), 1619 (C=N), 1503, 1586, 1603 (benzene ring). ^1H NMR ($CDCl_3$, ppm): 8.34 (CH=N), 9.28 (OH in benzene), 6.64–7.86 (benzene ring).

Preparation of the Phenoxy Anion. *p*-[(Phenylmethylene)amino]phenol (PMAP) (1.0016 g, 0.005 mol) was added to a 100 mL ampule containing 30 mL of dried THF, and then 0.2 g (0.0055 mol) of potassium with a fresh surface was introduced. After three cycles of freezing at 77 K and thawing under a vacuum system, the sealed ampule was magnetically stirred for 24 h at 60 °C. The solution, with a golden yellow color in the beginning of the reaction, turned to a violet red at the end. It was then cooled to room temperature for use.

Anionic Polymerization of EO. To a 100 mL ampule which was deaerated was added 1 mL of the PMAP/THE solution. The dark green color appeared as soon as 20 mL of EO was introduced. After sealing the ampule, the reaction

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was conducted at 70 °C for 12 h. At this point the system viscosity was so great that it was very difficult to pour out. Thus 5 mL of methanol was added to terminate the reaction. The polymerized product was dissolved in 10 mL of dichloromethane and then precipitated with ether with a conversion of 92%. The polymer could be purified by redissolution in dichloromethane and reprecipitation in ether. The purified product is a milky white powder formed with a yield of 80%. IR (cm^{-1}): 1105 (C−O−C). UV (nm): 335 (conjugation shifts base $\pi \rightarrow \pi^*$). ^1H NMR (ppm): 7.27−7.29 (m, benzene ring).

Deprotection of PEO Macromolecules with the Schiff Base End Group (PEO_S). PEG_S (1.84 g) was dissolved into 5 mL of dichloromethane, then 8 mL of acetic acid was added with stirring, the acidolysis was carried out at room temperature for 24 h, and the product could be precipitated with ether and purified with chloroform/ether in a yield of 53.5%. UV (nm): 315 (benzene ring with amino group $\pi \rightarrow \pi^*$). GPC analysis showed no chain cleavage of prepolymer PEO_S after acidolysis with acetic acid.

Photoinduced CTP of Styrene. In a 100 mL ampule containing 0.3 g (1.2×10^{-5} mol) of PEO prepolymer with the aniline end group, 0.0028 g (1.5×10^{-5} mol) of BP in 3 mL of benzene and 6 mL, styrene were added; then the ampule was linked to the vacuum system for degassing. After three cycles of freeze−pump−thaw at 77 K, the ampule was sealed and irradiated by means of a 125 W high-pressure mercury lamp (Model DDZ-125, manufactured by Shanghai Ya Ming Lamp Factory) for 48 h at a constant 30 °C. Cupric sulfate aqueous solution was used as the photofilter to obtain 365 nm monochromatic light. The block copolymer was precipitated by *n*-hexane and then extracted with acetonitrile to remove PEO prepolymer. The remaining dried residue was extracted again with cyclohexane to remove any possible homopolymer PS that might have formed in the process of block copolymerization. However, we did not find any traces of PS homopolymer from the cyclohexane extraction, either by precipitation with methanol or by GPC measurement. The last weight of purified block copolymer is 0.62 g.

Instruments. IR spectra were obtained on a Perkin-Elmer 983 G IR spectrometer. ^1H NMR spectra were recorded on a Varian XL-300 NMR spectrometer with TMS as the internal standard and $CDCl_3$ as the solvent. UV spectra were scanned on a Beckman DU-7 spectrometer. Fluorescence measurements were carried out using a Hitachi 650−60 fluorescence spectrometer. DSC studies were conducted with a SETARAM DSC 92 in a nitrogen atmosphere at a heating rate of 10 °C/min. Elemental analysis was carried out with Perkin-Elmer 240C element analyzer. ESR spectra were scanned by a Bruker ER-200D/SRC electron spin resonance spectrometer. The number-average molecular weight of the polymer was derived with a Shimadzu LC-3A gel permeation chromatograph (GPC) with a microcomputer. Conditions: column length, 1.2 m; filler, cross-linked PS gel (1250 mesh, manufactured by Ji Lin University of China); injection volume, 0.1 mL (concentration, 0.1 g/mL); solvent and eluent, THF; flow rate, 1.2 mL/min; pump pressure, 60 kg/cm^2 (5.98×10^6 Pa); detecting wavelength, 254 nm. The GPC was calibrated with standard poly(ethylene glycol) samples (Tokyo Kasei Kogyo Co., Ltd).

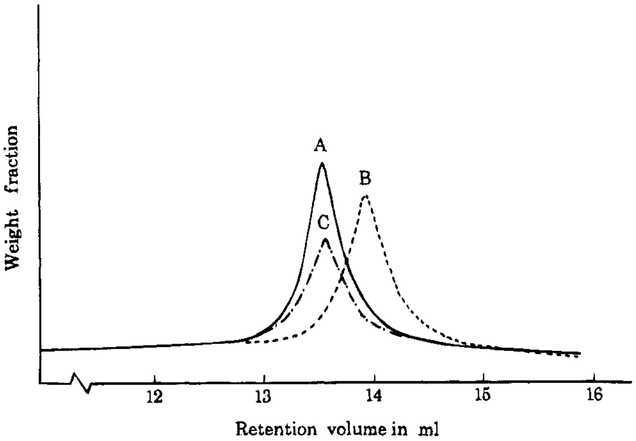


Figure 1. GPC measurement of PEO prepolymer before (A) and after acidolysis with (B) HCl and (C) acetic acid.

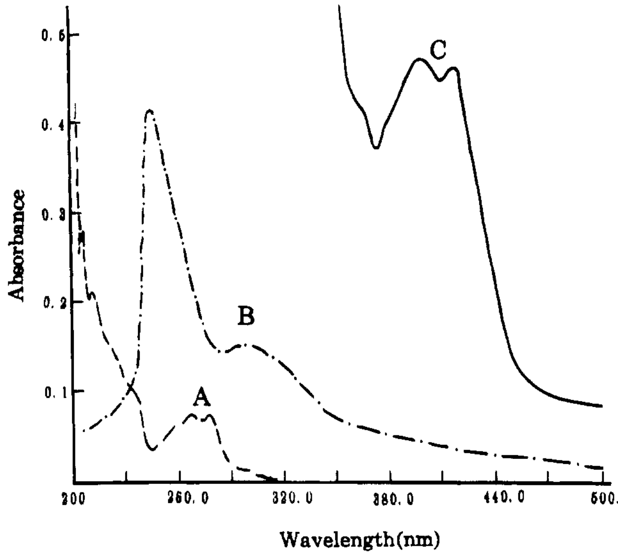


Figure 2. UV spectra of (A) TCNE, (B) acidolyzed PEO_S, and (C) a mixture of TCNE and PEO_S with the ratio of 1:1 (mol/mol) (solvent, $CHCl_3$; concentration, 1.0×10^{-4} mol/L for all samples).

Results and Discussion

Characterization of the PEO Prepolymer. Figure 1 gives molecular weight information about the PEO before (A) and after acidolysis with (B) HCl and (C) acetic acid. The molecular weight and molecular weight distribution of PEO prepolymer are about 24 800 and 1.04, respectively, before acidolysis. The presence of the Shiffs base end group of PEO prepolymer was determined by UV, IR, and ^1H NMR measurements as described in the Experimental Section. We found that if PEO prepolymer with the Schiff base end group (PEO_S) was acidolyzed by 1 N HCl, Figure 1B,C show that degradation would occur (with the HCl, the molecular weight of PEO decreased from 24 800 to 12 900), but when acetic acid was used in place of 1 N HCl, no scission of the PEO chain was detected. The presence of the recovered amino group could be established by the UV spectra of the complex formed with tetracyanoethylene (TCNE) and the acidolyzed product of PEO_S. In Figure 2, A and B are the UV absorbance spectra of TCNE and the acidolyzed PEO_S, their maximum absorbance peaks located at 267, 276.5, and 315 nm, respectively, but when they were mixed with each other in the ratio of 1:1 (mol/mol), some new bands appear at ca. 399 and 417 nm, as Figure 2C showed. It was attributed to the formation of complex between TCNE and the aniline end group of PEO through charge transfer. This is a very sensitive method to check whether the aniline group existed in a molecule or not.[8] Figure 3 shows the UV spectra of a small molecule aniline (A), PEO_S (B), and acidolyzed PEO_S (C). For PEO_S, the maximum absorbance peak appears at 335 nm, but the peaks of aniline and acidolyzed PEO_S all appeared at 315 nm. This means that for the acidolyzed PEO_S, the maximum absorbance peak has shifted by about 20 nm to shorter wavelength due to the decomposition of the Shiffs base and recovery of the aniline end group. Figure 4 shows their fluorescence spectra. When the samples of aniline (A) and acidolyzed PEO_S (C) were excited with the 250 nm light, their fluores-

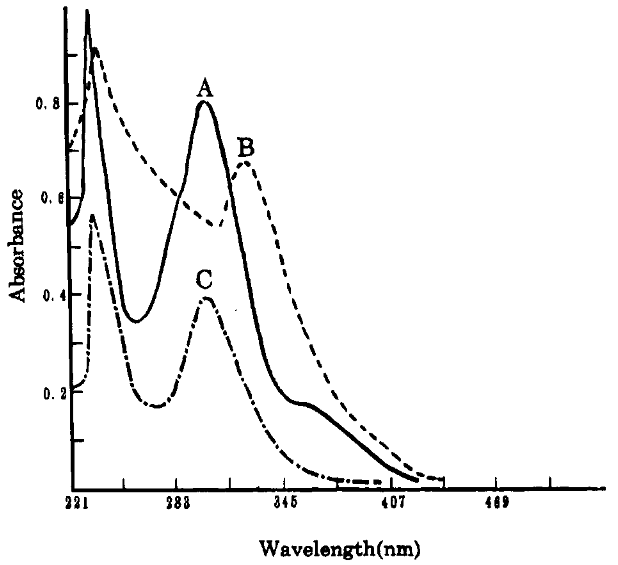


Figure 3. UV spectra of (A) aniline, (B) PEO$_S$, and (C) acidolyzed PEO$_S$ (solvent, CHCl$_3$; concentration, 2 × 10^{-4} mol/L for (A) and 1 × 10^{-4} mol/L for (B) and (C).

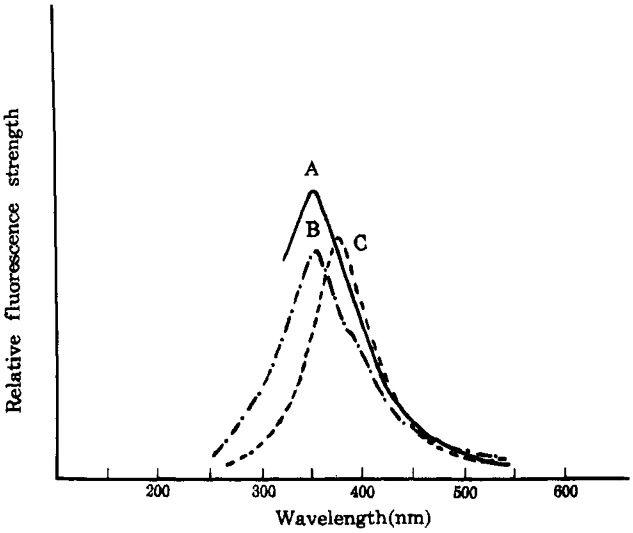


Figure 4. Fluorescence spectra of (A) aniline, (B) PEO$_S$ and (C) acidolyzed PEO$_S$ (solvent, CHCl$_3$; concentration, 2 × 10^{-4} mol/L for (A) and 1 × 10^{-4} mol/L for (B) and (C); excitation wavelength, 250 nm for (A) and (C) and 320 nm for (B)).

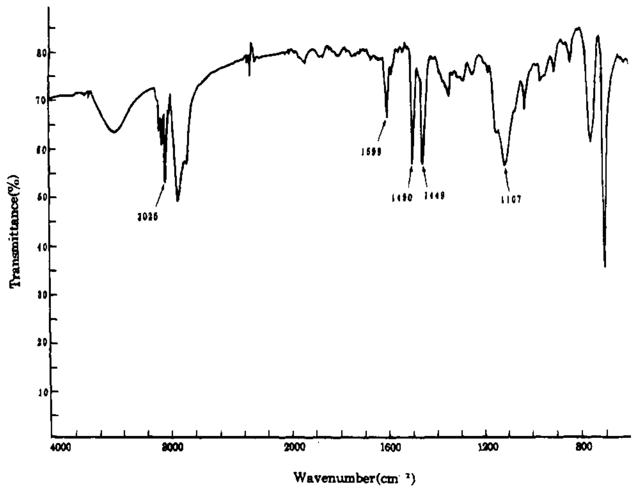


Figure 5. IR spectrum of PEO-*b*-PS.

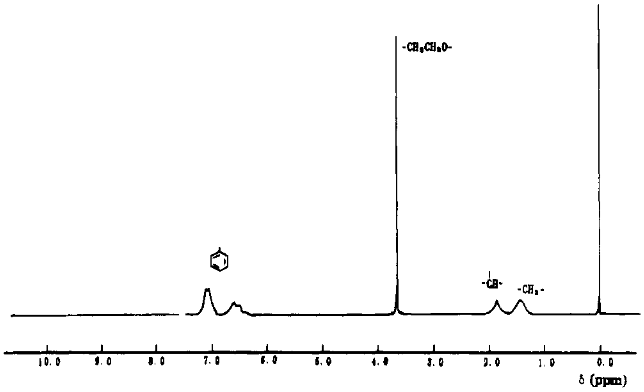


Figure 6. ^{1}H NMR spectrum of PEO–PS.

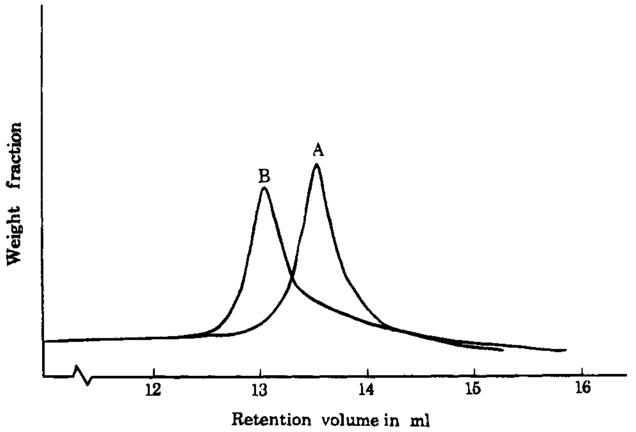


Figure 7. GPC measurement of (A) PEO prepolymer and (B) PEO-*b*-PS.

cence peaks all appear at 364 nm, but the fluorescence peak of PEO$_S$ appears at 375 nm if it was excited with 320 nm light. These data provide very strong supports for the existence of an aniline end group in the acidolyzed PEO$_S$.

Determination of PEO-*b*-PS. The purified PEO-*b*-PS was characterized in detail by IR, NMR, GPC, and DSC. Figure 5 shows its IR spectrum. The strong band at 1107 cm^{-1} (C—O—C) attributed to PEO and 3025 (benzene ring =C—H), 1599, 1490, and 1449 (benzene bend vibration) attributed to PS confirm the formation of PEO-*b*-PS. From ^{1}H NMR (Figure 6), the chemical shift values of 1.42 (–CH$_2$–), 1.84 (–CH– with benzene ring), 3.64 (–CH$_2$CH$_2$O–), and 6.46–7.09 (benzene ring) also establish the existence of PEO-*b*-PS. Figure 7 gives the GPC curves for PEO-*b*-PS. (A) shows the retention volume of the PEO prepolymer; its molecular weight is about 24 800. (B) shows the retention volume of block copolymer; its molecular weight is about 74 500 which is 3 times greater than that of the PEO prepolymer. Moreover there is only one peak for block copolymer sample in (B). Therefore we could conclude the PEO-*b*-PS was prepared by sequential initiation of anionic and photoinduced charge transfer complex polymerizations.

Figure 8 shows the DSC measurement result of PEO-*b*-PS. For the common block copolymers composed of two immiscible systems, there should appear two T_g's in the DSC curve. At first we did not find two distinct T_g's, and the T_g of the PEO chain segment was missing. It may be attributed to the higher crystallinity and faster crystallization rate of the PEO chain segment in common conditions; so the contents of the amorphous portion in PEO are too small to be detected.[9,10] However when the PEO-*p*-PS sample was melted at 150 °C and then immediately quenched in liquid nitrogen in order

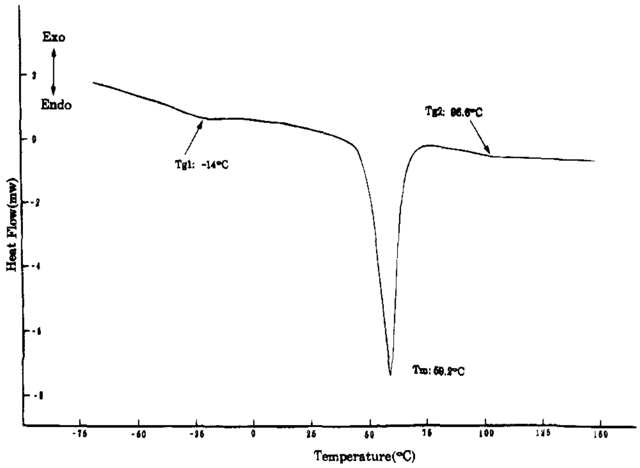


Figure 8. DSC measurement of (A) PEO_S and (B) PEO-*b*-PS.

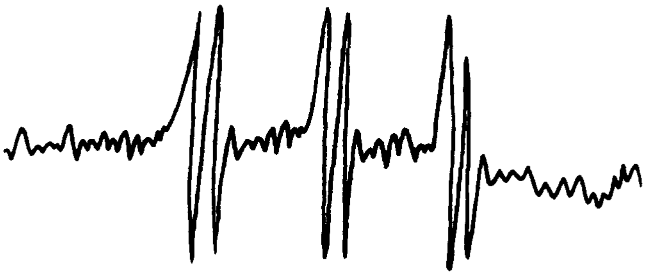
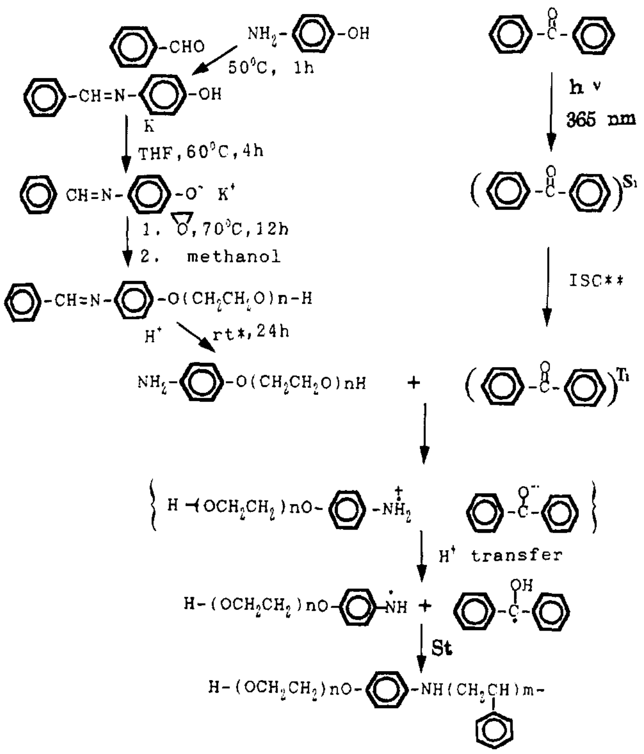


Figure 9. ESR spectrum of acidolyzed PEO_S radical captured by BBN under UV irradiation for 0.5 h (solvent, benzene; concentration, 2×10^{-2} mol/L).

Scheme 1



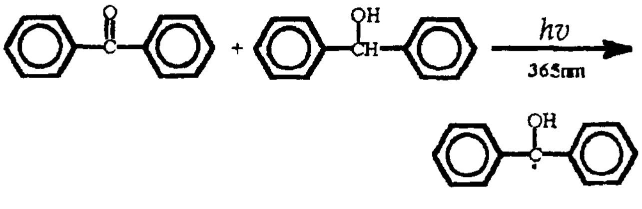
*: room temperature; **: intersystem crossing.

to inhibit crystallization of the PEO, we could observe a second T_g. The T_g of the PEO chain segment appeared as shown in Figure 8. Its value is about −19 °C, which is about 22 °C higher that of ordinary PEO (−41 °C[11]) with the same molecular weight. At the same time, the crystal melting temperature of the PEO segment in PEO-*b*-PS is shifted from 65 °C for the pure PEO homopolymer to 59.2 °C for the block copolymer. This difference may be caused by the decrease in the packing density of PEO chains due to the insertion of PS chain segments. The T_g of the PS chain segment in the block copolymer is about 98.2 °C, which is close to the T_g or ordinary PS (T_g: 100 °C[12]).

Mechanism. CTP mechanism via initiation of a small molecule aromatic amine and BP has been studied by many groups.[13−15] However, what shall happen when the PEO with an aniline end group (PEO_a) is used to replace the small molecule aniline in the charge transfer photochemical reaction? Figure 9 shows the ESR spectrum of the radical formed by irradiating the mixture of PEO_a and BP in THF containing the radical scavenger *N*-benzylidene *tert*-butyl nitrone (BBN). Its splitting constants a_N and a_H are about 13.5 and 1.98 G, respectively.

As is well-known, when the binary initiation system of BP and aromatic amine is irradiated with 365 nm light, BP molecules, after they absorb the photons, are in the excited singlet state. They then decay to the excited triplet by intersystem crossing (ISC). In this state they can combine with an aromatic amine to form an exciplex, from which an aromatic amine radical and diphenylmethanol radical would be produced through the transfer of a proton from the aromatic amine to BP.[16] Now the question in our system is which kind of radical is captured by BBN and is responsible for the ESR signal?

In order to answer this question, a comparative experiment is carried out, that is, irradiating the system composed of BP, diphenylmethanol, and BBN. Here, no ESR signal could be detected. Irradiating the mixture of BP and diphenylmethanol produces the diphenylmethanol radical, as the following equation shows:



The fact that no ESR signal appears means that this kind of radical cannot be captured by BBN; so it could be concluded that in our system, the ESR signal stems from the capture of a macroradical with an aniline end group by BBN.

Thus the whole block copolymerization of ethylene oxide and styrene by sequential initiation of an anion and a photoinduced charge transfer complex could be summarized by Scheme 1.

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