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Effect of Poly(ethylene glycol) with Sensitizer Groups at Both Ends on the Photoinitiated Polymerization of Styrene in the Water Phase in the Presence of a Magnetic Field

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ABSTRACT: A photoinitiated polymerization of styrene in the water phase in the presence of a magnetic field has been performed by using AIBN initiator and poly(ethylene glycol) (PEG) with naphthyl end groups (N-PEG-N), PEG with benzoylbenzyl end groups (B-PEG-B), and PEG with a naphthyl group at one end and a benzoylbenzyl group at the other end (B-PEG-N) as triplet sensitizers. The PS molecular weights are in the range 10^5–10^6 and the $\bar{M}_w/\bar{M}_n$ is in the range 1.52–1.66. For B-PEG-B and B-PEG-N, a magnetic field of 0.035 T is sufficient to influence the polymerization, but it has to be above 0.2 T for N-PEG-N. Best results were obtained when B-PEG-N was used. A triplet amplifier mechanism for B-PEG-N is suggested.

Introduction

Interest in the investigation of chemical reactions in a magnetic field has grown in recent years. Some work on the magnetic field influence on the cross-linking of synthetic rubbers such as 1,4-polybutadiene,[1] poly(styrene-*co*-butadiene),[2] etc., has been published. The effect of a magnetic field on the emulsion polymerization of styrene initiated by dibenzyl ketone under UV irradiation was also reported by Turro et al.,[3] and they showed that application of relatively weak magnetic fields (<0.05 T) enhances substantially the efficiency of escape of radicals from the micelle aggregates, so that the molecular weight of PS and the polymerization rate were increased.

In these systems, the influence of a magnetic field on some radicals could be interpreted by the radical pair theory,[4] which is also the basis for the chemically induced dynamic nuclear polarization (CIDNP).[5]

In a previous study, we dealt with the magnetic field influence on the bulk polymerization of styrene and methyl methacrylate by photochemical initiation in the presence of polymer triplet sensitizers. The extent of the influence of a magnetic field is strongly dependent on the molecular weight and concentration of polymer sensitizers.[6,7]

In the present investigation, three new water-soluble polymer triplet sensitizers were used, and their effect on the photoinduced polymerization of styrene in a magnetic field in the water phase is described.

Experimental Section

Materials. Styrene (Shanghai Jin Shan Petroleum Chemical Engineering Factory) was washed with 10% sodium hydroxide and dried over anhydrous sodium sulfate after repeated washings with distilled water. The styrene was purified by distillation under reduced pressure and stored at 0 °C under nitrogen. AIBN (Shanghai First Reagent Factory) was purified by two recrystallizations from ethanol. PEG (Tokyo Kasei, $\bar{M}_n$ = 600) was dried by azeotropic distillation with toluene. 4-Methylbenzophenone (MBP, Aldrich) was twice recrystallized from petroleum ether. 2-(Bromoethyl)naphthalene (BMN), and phosphorus tribromide (Aldrich) were used as received. *N*-Bromosuccinimide (NBS, Fluka AG) was dried overnight at 0.1 Torr and room temperature over P_2O_5.

Preparation of N-PEG-N. BMN (33.2 g, 0.15 mol) was dissolved in 600 mL of chloroform containing 9 g (0.015 mol) of PEG, and 2.38 g (0.03 mol) of dried pyridine was added. The reaction proceeded under reflux for 8 h, and the product was precipitated by ethyl ether and purified by dissolution in chloroform and reprecipitation with ether. The final PEG with a naphthyl end group was a yellowish solid, yield 14.23 g (91%). ^{1}H NMR (DMSO-d_6; δ): 3.50–3.68 (m, 4*n* H), 4.45 (s, 2 H × 2), 7.21–7.83 (m, 14 H), no peak for OH at δ 4.56.[8] IR (Nujol; cm^{-1}): 2856 (CH_2 in naphthyl), 1590, 1485 (C=C, ring), 1111 (CH_2-OCH_2), 735, 815, 862 (naphthalene ring), no absorption for OH of PEG at 3417 cm^{-1}.

Preparation of 4-(Bromomethyl)benzophenone (BMB). MBP (19.6 g, 0.1 mol) was dissolved in 100 mL of carbon tetrachloride containing 19.5 g (0.11 mol) of NBS and refluxed for 4 h. The reacted mixture was distilled and washed three times with boiling water. After separation the product was recrystallized from ethanol with the yield 23.6 g (86%). ^{1}H NMR ($CDCl_3$; δ): 4.43 (s, 2 H, CH_2Br), 7.02–7.46 (m, 9 H). IR (Nujol; cm^{-1}): 2930 (CH_2 in bromobenzyl), 1639 (C=O), 693 (CH_2Br). Anal. Calcd for $C_{14}H_{11}BrO$: C, 61.02; H, 4.00; Br, 28.78. Found: C, 61.17; H, 4.04; Br, 28.52.

Preparation of B-PEG-B. B-PEG-B was prepared using 24.8 g (0.1 mol) of purified BMB, 6 g of PEG (0.01 mol), and 1.59 g (0.02 mol) of dried pyridine in 500 mL of chloroform under reflux. The reaction was stopped after 6 h. The procedure of separation and purification is the same as before, yield 8.00 g (73%). ^{1}H NMR (DMSO-d_6; δ): 3.52–3.68 (m, 4*n* H), 4.44 (s, 2 H × 2), 7.23–7.35 (m, 18 H), no peak for OH at 4.56. IR (Nujol; cm^{-1}): 2863 (CH_2 in benzyl), 1661 (C=O), 1592, 1488 (C=C ring), no absorption for OH at 3417 cm^{-1}.

Preparation of B-PEG-N. Purified BMB (12.4 g, 0.05 mol) was dissolved in 200 mL of chloroform containing 7.4 g (0.01 mol) of mononaphthyl-substituted PEG, and 0.79 g (0.01 mol) of dried pyridine was added. The reaction was carried out under reflux for 5 h, and the product was precipitated by ether and purified by dissolution in chloroform and reprecipitation with ether, yield 8.6 g (87%). ^{1}H NMR (DMSO-d_6; δ): 3.50–3.67 (m, 4*n* H), 4.45 (s, 2 H × 2), 7.20–7.81 (m, 16 H), no OH peak at 4.56. IR (Nujol; cm^{-1}): 2864 (CH_2 in benzyl), 2858 (CH_2 in naphthyl), 1660 (C=O), 1589, 1486 (C=C ring), 735, 811, 864 (naphthalene ring).

Polymerization. AIBN (0.0016 g) was dissolved in 10 mL of distilled water containing 0.49 g of N-PEG-N, 0.54 g of B-PEG-B, and 0.48 g of B-PEG-N, respectively, by shaking the solution overnight at room temperature and protecting it from light. After filtration 5 mL of the resulting solution and 1 mL of freshly distilled styrene were poured into a 1.5-cm-diameter quartz tube and deaerated by repeated freezing and thawing under vacuum at 77 K. The tube was sealed by a glass rod in argon and placed between two poles of an adjustable-gap electromagnet. Its

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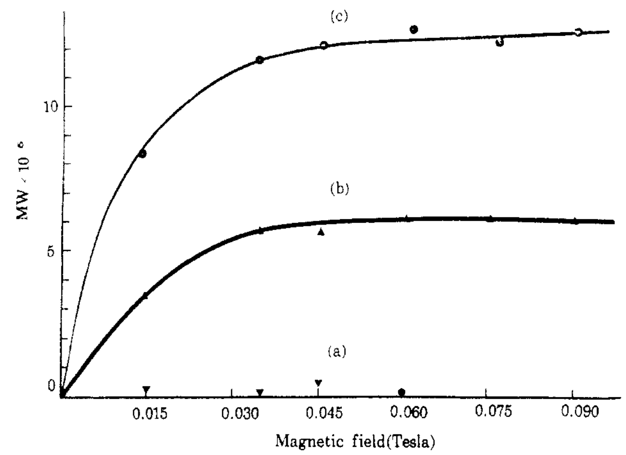

Figure 1. Effect of magnetic field (<0.1 T) on the MW of PS with PEG sensitizers: (a) N-PEG-N; (b) B-PEG-B; (c) B-PEG-N. Concentration of PEG sensitizers: 1.45×10^{-4} mol/L.

maximum magnetic field strength was 1.2 T when the distance between the two poles was 2.5 cm and direct current voltage was 220 V. A variable magnetic field was produced by adjusting the voltage. The tube was irradiated with a DDZ-500 500-W high-pressure Hg lamp (from Shanghai Ya Ming Lamp Factory) at 10 °C; potassium chromate aqueous solution was used to obtain 320 10 nm monochromatic light. The polymer was precipitated in excess, stirred methanol and separated.

Instruments. ^{1}H NMR spectra were recorded on a Varian XL-300 NMR spectrometer with TMS as an internal standard and $CDCl_3$ and DMSO-d_6 as solvents, IR spectra were obtained on a Perkin-Elmer 983 G IR spectrometer, UV spectra were obtained on a Shimadzu UV-340 spectrometer, and phosphorescence spectra were measured on a Spex Fluorolog 212 fluorescence spectrometer with accessories for measurement of phosphorescence which had been calibrated. The number-average molecular weights of PS were obtained with a Shimadzu LC-3A gel permeation chromatograph (GPC) with a microcomputer (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/100 mL); solvent and eluent, tetrahydrofuran; flow rate, 1.2 mL/min; pump pressure, 80 kg/cm^2 (7.85×10^6 Pa); detecting wavelength, 254 nm). The GPC was calibrated with standard PS (Aldrich). The surface tensions of N-PEG-N, B-PEG-B, and B-PEG-N were measured by a JZHY-180 surface tension meter (manufactured by Cheng De Experiment Machine Factor, He Bei, China) to calculate the critical micelle concentration (cmc), and the values are 1.26×10^{-4}, 1.41×10^{-4}, and 1.30×10^{-4} mol/L respectively for N-PEG-N, B-PEG-B, and B-PEG-N.

The polymerization rate was obtained by isolating the PS from the reaction mixture at various times.

Results

Figures 1 and 2 show the molecular weights of PS with and without a magnetic field in the presence of (a) N-PEG-N, (b) B-PEG-B, and (c) B-PEG-N. The molecular weights of PS are in the range 10^5–10^6, whereas no polymer is obtained in the absence of PEG sensitizers. For B-PEG-B and B-PEG-N a weak magnetic field (0.035 T) was sufficient to affect the molecular weight of PS (Figure 1). But in the case of N-PEG-N, only a stronger magnetic field (>0.2 T) exerts an influence on the molecular weights of PS. The best result could be found in (c); the molecular weight of PS is 1.13×10^6.

Table I lists $\bar{M}_w/\bar{M}_n$ data which are in the range 1.52–1.66. B-PEG-N exerts the greatest effect on the MWD of the polymerization system, with $\bar{M}_w/\bar{M}_n$ approximately 1.5. A statistical evaluation of the molecular weight of PS is given in Table I; s is the standard deviation and p is the significance level calculated by the t-test.[8]

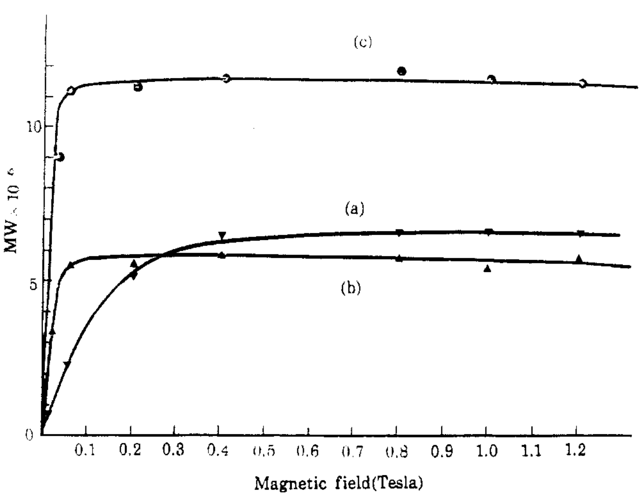

Figure 2. Effect of magnetic field (>0.2 T) on the MW of PS with PEG sensitizers: (a) N-PEG-N; (b) B-PEG-B; (c) B-PEG-N. Concentration of PEG sensitizers: 1.45×10^{-4} mol/L.

Comparative results of the PS conversion below and above the cmc are given in Figures 3 and 4. At the lower concentration of PEG sensitizers (<cmc), the polymerization rate (R_p) increased slowly with the concentration of PEG sensitizers, as in ordinary photoinduced solution polymerization. A linear logarithmic plot with a slope of 0.41 and 0.45 was obtained for N-PEG-N and B-PEG-B, but the slope was 0.59 for B-PEG-N. At the cmc a discontinous jump of R_p is observed for all sensitizers (Figure 4); R_p then dropped slowly with increasing PEG concentration.

Discussion

Magnetic Field Dependence. Our experimental results can be interpreted by radical pair theory.[4] PEG macromolecules with triplet sensitizer end groups are not only a surfactant but also a triplet sensitizer. We have indicated that triplet energy transfer between the excited naphthalene or benzophenone groups in the polymer chain and AIBN could have occurred;[9] the radical pair formed by AIBN decomposition is also triplet because of spin conservation.[10] However, the spins of the radical pair may change their relative orientations by hyperfine interaction between the spin of the unpaired electron in the radicals and the spin of the nucleus. The energies of the single S and the triplet sublevels T, T_0, and T_- are degenerated in the absence of a magnetic field. If the external magnetic field is switched on, the degeneracy is lifted: T and T_- do not lie at the same energy level with T_0, and only T_0 remains degenerate with S. Thus about two-thirds of the radical pairs are still in the triplet state. The PEG macromolecules are hydrophilic, and the sensitizer end groups, naphthalene or benzophenone, are hydrophobic, so the AIBN and styrene are solubilized in the area enveloped by the sensitizer groups. It has been proposed that another function of a magnetic field is to increase the efficiency of escape of radicals from radical pairs produced in micellar aggregates by inhibiting the competing geminate cage recombination.[11] Thus the triplet radicals formed by decomposition of AIBN sensitized by N-PEG-N, B-PEG-B, and B-PEG-N have a better chance to contact styrene monomers because of their long lifetime, so that the molecular weight of PS is significantly increased, especially in the case of B-PEG-N. Besides, the spins of unpaired electrons in triplet radical pairs are parallel, and it is more difficult for them to recombine. As the fluctuation of the lifetime of propagating triplet radical pairs is smaller than

Table I
Effect of Magnetic Field on PDI of PS in the Presence of PEG Sensitizers

	N-PEG-N			B-PEG-B			B-PEG-N		
MF[a] (T)	$\bar{M}_w/\bar{M}_n$	s, %	P	$\bar{M}_w/\bar{M}_n$	s, %	P	$\bar{M}_w/\bar{M}_n$	s, %	P
0.00	2.27	1.57	94.5–97.5	2.31	0.36	90.0–95.5	2.31	0.55	90.0–95.5
0.015	2.31	1.13	94.5–97.5	2.01	0.87	94.0–97.5	1.63	1.17	95.5–99.0
0.035	2.29	0.98	94.0–97.5	1.58	1.14	>99.9	1.52	0.68	>99.9
0.05	2.24	0.46	94.0–97.5	1.59	1.26	99.5–99.9	1.52	0.32	>99.9
0.10	2.28	1.32	94.0–97.5	1.54	0.59	>99.9	1.53	0.74	>99.9
0.20	1.66	0.21	97.0–99.9						
0.40	1.62	1.04	97.5–99.0						
0.80	1.54	0.57	97.5–99.0						

[a] MF: magnetic field; concentration of PEG sensitizers: 1.45×10^{-4} mol/L.

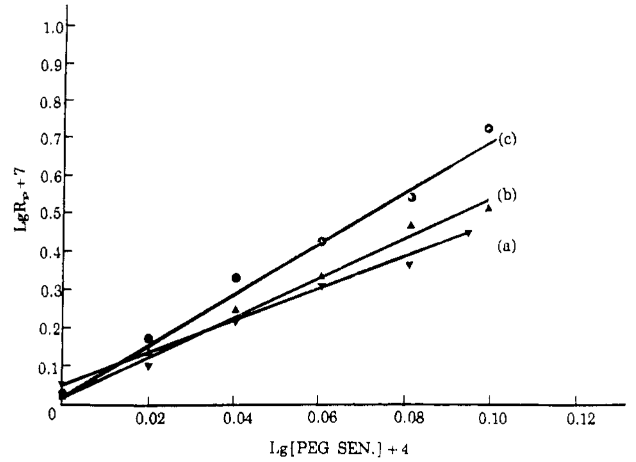

Figure 3. Relationship between polymerization rate of styrene and concentration (<cmc) of PEG sensitizers: (a) N-PEG-N; (b) B-PEG-B; (c) B-PEG-N. Magnetic field: 0.8 T.

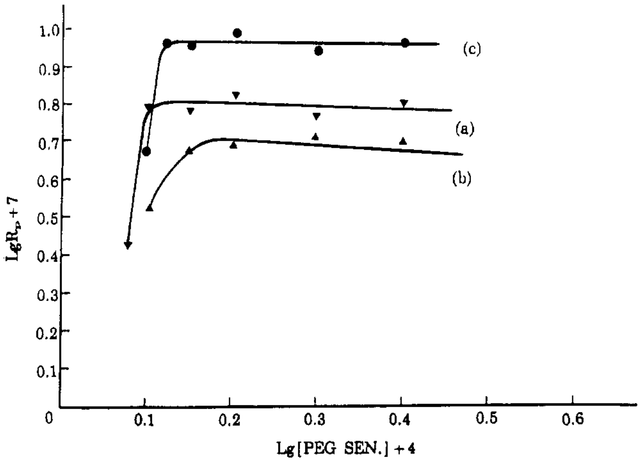

Figure 4. Relationship between polymerization rate of styrene and concentration (>cmc) of PEG sensitizers: (a) N-PEG-N; (b) B-PEG-B; (c) B-PEG-N. Magnetic field: 0.8 T.

the singlet ones, the MWD of PS is much narrower (Table I).

The Δg mechanism was not considered in our system; the radical pair produced by homolysis of AIBN in the presence of PEG triplet sensitizer possesses $\Delta g = 0$.

Action of N-PEG-N, B-PEG-B, and B-PEG-N. Figures 1 and 2 show that the three kinds of PEG sensitizers exert an effect on the polymerization in a different range of the magnetic field. For B-PEG-B and B-PEG-N, 0.035 T is sufficient, but more than 0.2 T is required for N-PEG-N. Benzophenone is widely used as a triplet sensitizer; its intersystem crossing efficiency (ISC) is nearly equal to 1.0 and much higher than that of naphthalene (0.39).[12] Thus a weak magnetic field is sufficient to inhibit the crossing S ↔ T of B-PEG-B and B-PEG-N. For N-PEG-N no magnetic field effect could be detected with 0.035 T; i.e., there is not enough triplet N-PEG-N left because of its lower ISC, and no effective energy transfer between AIBN and N-PEG-N occurs under this condition. In a stronger magnetic field (>0.2 T), the crossing S ↔ T of triplet N-PEG-N was inhibited, triplet N-PEG-N macromolecules with a much longer lifetime (2.3 s) than B-PEG-B (0.001 s)[13] have more time to collide with AIBN, the probability for decomposition of AIBN into triplet radical pairs was increased, and N-PEG-N could exert a much greater influence on the system (Figure 2).

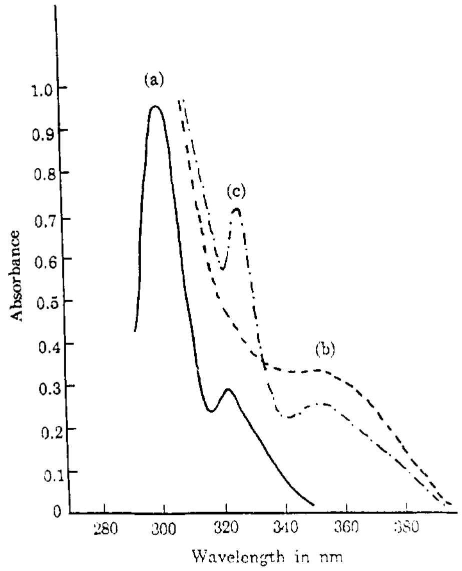

Figure 5. UV absorption spectra of PEG sensitizers: (a) N-PEG-N, concentration: 1.32×10^{-4} mol/L; (b) B-PEG-B, concentration: 1.48×10^{-4} mol/L; (c) B-PEG-N, concentration: 1.41×10^{-4} mol/L. Solvent: alcohol.

On the basis of these results, i.e., that B-PEG-B has a high ISC and a low triplet lifetime whereas N-PEG-N has a low ISC and a long triplet lifetime, we decided to combine the merit of the high ISC of B-PEG-B with the characteristic of long lifetime of N-PEG-N to obtain a PEG sensitizer with a high efficiency. B-PEG-N was designed to satisfy these conditions.

Figure 5 shows the absorption spectra of (a) N-PEG-N, (b) B-PEG-B, and (c) B-PEG-N; the spectrum of B-PEG-N is nearly equal to the overlap of (a) and (b).

Figure 6 indicates the phosphorescence spectra of (b) B-PEG-B and (c) B-PEG-N, which were excited by 370 nm, but no phosphorescence of N-PEG-N could be found because the napthyl group did not absorb above 350 nm. The phosphorescence of the benzoylbenzyl group is in the range of 410–460 nm. However, in the case of B-PEG-N, the phosphorescence of naphthyl appeared in the range of 490–570 nm besides the phosphorescence of benzoylbenzyl, which is much weaker compared to B-PEG-B.

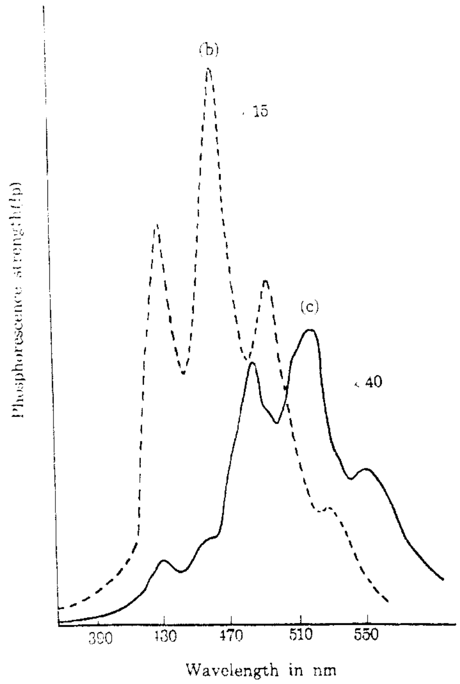

Figure 6. Phosphorescence spectra of PEG sensitizers: (b) B-PEG-B, concentration: 1.39×10^{-4} mol/L; (c) B-PEG-N, concentration: 1.35×10^{-4} mol/L. Solvent: ether/isopentane/ethanol (EPA) = 2:2:3 (v/v/v); 77 K; excitation wavelength: 370 nm.

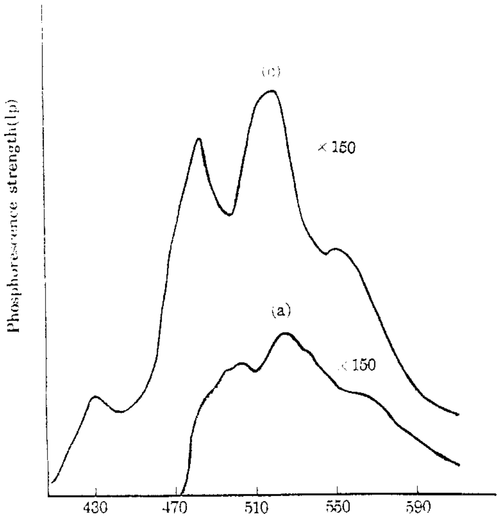

Figure 7. Phosphorescence spectra of PEG sensitizers: (a) N-PEG-N, concentration: 1.41×10^{-4} mol/L; (c) B-PEG-N, concentration: 1.35×10^{-4} mol/L. Solvents: EPA = 2:2:3 (v/v/v); 77 K; excitation wavelength: 313 nm.

Obviously, this was due to the energy transfer from the excited benzoylbenzyl group to naphthyl.

Figure 7 shows the phosphorescence spectra of (a) N-PEG-N and (c) B-PEG-N, which were excited by 313 nm. The phosphorescence strength of the naphthyl group in B-PEG-N is much higher than N-PEG-N. The singlet energy levels of naphthyl and benzoylbenzyl are about 92 and 75 kcal/mol,[14] respectively, and their triplet levels are about 61 and 69 kcal/mol;[14] i.e., the singlet energy level of naphthyl is higher than benzoylbenzyl and the triplet one is lower. Thus the singlet naphthyl of B-PEG-N excited by 313 nm transmitted energy to the benzoylbenzyl group of S ↔ S transfer, and the activated singlet of the latter transformed to its triplet state by the high ISC and then transmitted energy to the naphthyl group anew by T ↔ T transfer. After this cycle, the phosphorescence of naphthyl was enhanced due to the higher ISC of the benzoylbenzyl group. Secondly, the singlet benzoylbenzyl group of B-PEG-N excited at 313 nm is transformed into a triplet by ISC and then transmits its energy to napthyl by T ↔ T transfer, so that the phosphorescence of naphthyl in B-PEG-N is actually the sum of two processes. However, in the case of N-PEG-N, the phosphorescence of the naphthyl group is weak because of the low ISC efficiency. Consequently, the benzoylbenzyl group in B-PEG-N acts as an amplifier for triplet naphthyl, resulting in a much greater influence on the photoinduced polymerization of styrene in the presence of a magnetic field.

Concentration of PEG Sensitizers. When the concentration of PEG sensitizer is less than the cmc, no micelles form in the water phase and the polymerization rate increases with the concentration of PEG sensitizers due to the increasing sensitizer number. The system behaves like a common photosensitized solution polymerization, with R_p proportional to the 0.45, 0.41, and 0.59 power of the concentration for N-PEG-N, B-PEG-B, and B-PEG-N. When the concentration of PEG sensitizer is equal to the cmc, R_p suddenly increases because the polymerization is carried out in the micelles. The hydrophobic sensitizer groups are arranged tightly, even if the cmc of PEG sensitizers is less than 10^{-2} mol/L, which is the critical concentration for T ↔ T transfer (calculated from the critical distance of 10–15 Å for T ↔ T transfer[15]). Efficient triplet energy transfer can still occur between activated naphthyl or benzoylbenzyl groups and small molecules of AIBN solubilized in the micelles, due to the higher local concentration of PEG sensitizers in the water phase.

A further increase of the concentration of PEG sensitizer exerted no great effect on the system because of the self-quenching of the excited PEG sensitizers.

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