Effect of magnetic field on block copolymerization of styrene and methyl methacrylate by photochemical initiation in micellar solution of poly(ethylene glycol) with sensitizer end group

Junlian Huang* **and Youqian Hu**
Department of Macromolecular Science, Fudan University, Shanghai 200433, People's Republic of China

and Qinhua Song
Department of Food Processing, JiangXi University, Nanchang, JiangXi, People's Republic of China

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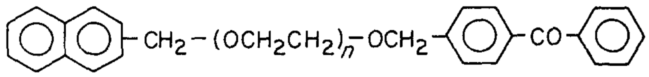
Block copolymerization of styrene and methyl methacrylate by photochemical initiation was carried out successfully in the water phase with a magnetic field. Poly(ethylene glycol) (PEG) with a naphthyl group at one end and a benzoyl benzyl group at the other end



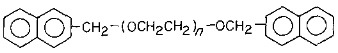
was used as triplet sensitizer. The block copolymerization is dependent on the magnetic field and the concentration of PEG sensitizer. It was found that a magnetic field of 0.035 T is sufficient to influence block copolymerization proceeding in the micelles formed by the hydrophilic PEG chain and hydrophobic sensitizer end groups. The molecular weights of polystyrene-*block*-poly(methyl methacrylate) are in the range of 10^5–10^6 and the molecular weight distribution is about 1.61–1.74.

(Keywords: magnetic field; block copolymerization; poly(ethylene glycol))

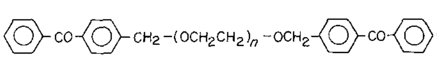
Introduction

Many methods for synthesizing block copolymers have been described. They can be prepared by the step copolymerization of polymers with functional groups capable of reacting with each other[1]. They can also be obtained by sequential addition of monomer to a living anionic polymerization system[2,3], and by transformation reactions[4,5], telechelic polymers[6,7] and coupling reactions[8]. The synthesis of block copolymers via ring-opening[9] and Ziegler–Natta polymerization[10,11] has been reported.

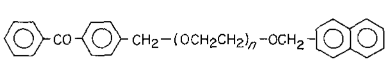
Recently, we prepared three kinds of new water-soluble poly(ethylene glycol) (PEG) with sensitizer end groups:



(N-PEG-N)



(B-PEG-B)

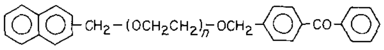


(B-PEG-N)

We confirmed that 2,2′-azoisobutyronitrile (AIBN) could be sensitized by them via triplet–triplet energy transfer under u.v. irradiation in the water phase, with B-PEG-N giving the best results[12]. It is of interest to note that in the presence of PEG sensitizers, AIBN could initiate styrene (St) to polymerize in the water phase under irradiation of 313 nm with a magnetic field, and the macromolecular radicals of polystyrene (PS) were able to initiate methyl methacrylate (MMA) to polymerize continuously in the same conditions, forming the block copolymer. However, the homopolymer of PS has only been found after the addition of MMA when the magnetic field was absent.

Experimental

Polymerization. An amount of 0.0016 g AIBN (recrystallized twice from ethanol) was dissolved in 10 ml of distilled water containing 0.49 g of N-PEG-B



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 St were poured into a quartz tube (diameter 1.5 cm) and deaerated by repeated freezing and thawing under vacuum at 77 K. The tube was sealed in argon atmosphere and placed between the two poles of an adjustable-gap electromagnet. The maximum magnetic field strength was 1.2 T when the distance between the two poles was 2.5 cm and the direct current voltage was 220 V. A variable magnetic field was produced by adjusting the voltage. The tube was irradiated with a 500 W high pressure Hg lamp (model DDZ-500, Shanghai Ya Ming Lamp Factory) at 10°C; potassium chromate aqueous solution was used as photofilter to obtain 313 nm monochromatic light. After 12 h, 1 ml of MMA (Shanghai First Reagent Factory; washed with 10% sodium hydroxide, dried over anhydrous sodium sulfate after repeated washing with distilled water,

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* To whom correspondence should be addressed

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distilled under reduced pressure, then bubbled by argon for 2 h and sealed) was injected into the quartz tube. After reacting for 4 h, polymers were precipitated in excess, stirred methanol and separated. Polymer products were extracted with cyclohexane by Soxhlet extraction to remove homopolymer PS. The dried residue was extracted again with acetonitrile to remove poly(methyl methacrylate) (PMMA) homopolymer. The remaining polymer was dissolved in benzene, then filtered. The filtrate was concentrated, then precipitated with methanol. The composition of block copolymer was measured by ^{1}H n.m.r.[13]:

$$\text{block efficiency of MMA} = \frac{\text{PMMA in PS-}b\text{-PMMA}}{\text{polymerized PMMA}}$$

The polymerization rate was obtained by isolating the PS from the reaction mixture and measuring the PS conversion.

Table 1 Effect of feed ratio of St/MMA on the composition and molecular weight of PS-*b*-PMMA[a]

Monomer feed ratio (wt St/MMA)	Composition of copolymer (St/MMA)	$M_n \times 10^{-4}$	(dl g^{-1})
4/1	93/7	38	1.546
2/1	79/21	61	2.967
1/1	70/30	57	2.304
1/2	43/57	63	3.028
1/4	11/89	47	2.189

[a] Magnetic field, 0.035 T; concentration of N-PEG-B, 6.5×10^{-4} mol l^{-1}

Table 2 Composition of block copolymerization product of St and MMA[a]

	Composition of polymerization product (%)			
Monomer feed ratio (wt St/MMA)	PS-*b*-PMMA	PS	PMMA	Block efficiency of MMA (%)
4/1	76	24	0	100.0
2/1	72	24	4	79.1
1/1	67	20	13	60.7
1/2	50	16	34	45.5
1/4	42	10	48	43.5

[a] Magnetic field, 0.035 T; concentration of N-PEG-B, 6.5×10^{-4} mol l^{-1}

Instruments. The number-average molecular weight of PS was determined by gel permeation chromatography (g.p.c.) (Shimadzu LC-3A with microcomputer): column length, 1.2 m; filler, crosslinking 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^{-1}; pump, 80 kg cm^{-2} (7.85×10^6 Pa); detecting wavelength, 254 nm; calibration by standard PS (Aldrich).

Results and discussion

Identification of block copolymer. Block copolymer of PS-*b*-PMMA was characterized by i.r., n.m.r., g.p.c. and d.s.c. *Tables 1* and *2* show the details of composition and molecular weights of block copolymerization products of St and PMMA with a magnetic field of 0.035 T in the presence of N-PEG-B. When the weight ratio of St/MMA is more than 8/1, almost no PMMA homopolymer is formed.

Effect of magnetic field on block copolymerization. When the concentration of N-PEG-B and weight ratio of St/MMA were kept constant, it was found that the molecular weight of PS and PS-*b*-PMMA increased and the molecular weight distribution (*MWD*) became narrower with the magnetic field, as *Tables 3* and *4* show. In these tables, *s* is the standard deviation and *p* is the significance level calculated by *t* test[14].

We have reported that triplet energy transfer could have occurred between the excited naphthalene or benzophenone group in the polymer chain and AIBN small molecules[15,16], so the radical pairs decomposed by AIBN are triplet too, according to the conservation law of spin[17]. However, the spins of the radical pair may change their relative orientation by hyperfine interaction, so the energy of singlet and triplet sublevels, T_+, T_0, T_-, is degenerated. The external magnetic field plays a role in making the degenerating energy levels split. The amount of triplet radical pairs with long lifetime increases, and they have much more time to contact with the monomer, so the molecular weight of PS increases. For the same reasons, the macromolecular radical of propagating PS with long lifetime can initiate MMA to polymerize continuously after the diffusion of MMA into the micelle.

Table 3 Effect of magnetic field on molecular weight (MW) of PS-*b*-PMMA in the presence of N-PEG-B[a]

	Feed ratio (wt St/MMA)								
	1/4			1/1			4/1		
Magnetic field (T)	MW ($\times 10^{-4}$)	s(%)	p	MW ($\times 10^{-4}$)	s(%)	p	MW ($\times 10^{-4}$)	s (%)	p
0	16.1	1.56	93.5–95.5	16.0	0.96	90.0–95.5	15.5	0.36	90.0–95.5
0.015	21.6	0.68	94.0–97.5	51.4	1.14	99.5–99.9	29.3	0.77	90.5–97.5
0.035	25.5	0.21	94.0–97.5	57.0	0.83	99.5–99.9	38.4	0.68	93.5–97.5
0.05	26.2	1.34	97.0–99.9	56.8	1.49	99.5–99.9	38.1	0.21	95.9–99.9
0.10	26.4	1.03	97.5–99.0	57.2	0.53	>99.9	38.3	0.34	>99.9
0.20	26.0	0.47	97.5–99.9	57.1	1.11	>99.9	38.0	1.26	>99.9
0.40	26.3	0.76	97.5–99.9	57.2	0.96	>99.9	38.2	0.71	>99.9

[a] Concentration of N-PEG-B, 6.5×10^{-4} mol l^{-1}

Besides, as the fluctuation of the lifetime of the

Table 4 Effect of magnetic field on molecular weight distribution (*MWD*) of PS-*b*-PMMA in the presence of N-PEG-B[a]

Magnetic field (T)	Feed ratio (wt St/MMA) 1/4 *MWD*	1/4 *s*(%)	1/4 *p*	1/1 *MWD*	1/1 *s*(%)	1/1 *p*	4/1 *MWD*	4/1 *s*(%)	4/1 *p*
0	2.31	0.54	90.0–95.5	2.44	1.51	90.0–95.5	2.26	0.84	90.0–95.5
0.015	2.09	1.64	94.5–97.5	1.93	1.09	94.0–97.5	1.87	1.20	95.5–99.0
0.035	1.67	0.32	94.0–97.5	1.65	0.47	97.0–99.9	1.60	0.76	94.5–97.5
0.05	1.70	1.26	97.0–99.0	1.64	0.52	>99.9	1.59	0.89	97.5–99.0
0.1	1.65	0.73	97.5–99.9	1.66	1.11	>99.9	1.62	0.24	99.0–99.9

[a] Concentration of N-PEG-B, $6.5 \times 10^{-4} \mathrm{mol\,l^{-1}}$

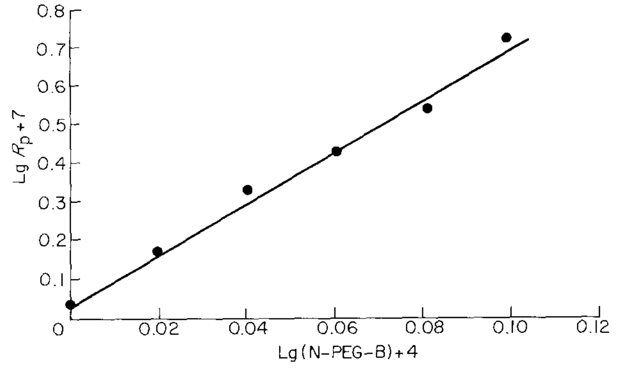

Figure 1 Relation between polymerization rate of styrene and concentration of N-PEG-B below *CMC* (magnetic field, 0.035 T)

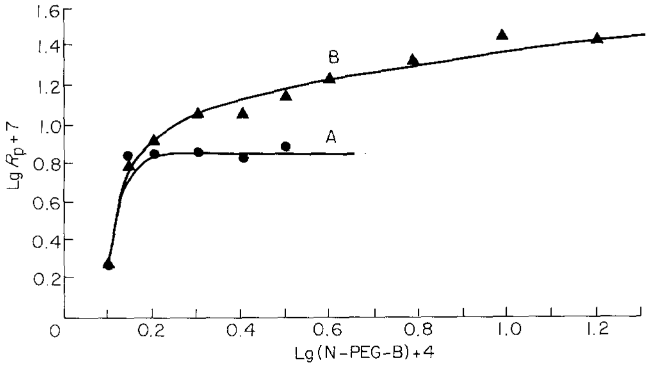

Figure 2 Relation between polymerization rate of styrene and concentration of N-PEG-B above *CMC*: A, PS; B, PS-*b*-PMMA (magnetic field, 0.035 T)

propagating triplet radical pairs is smaller than the singlet ones, so the *MWD* is much narrower.

Effect of N-PEG-B on block copolymerization. As we have reported, N-PEG-B was chosen as triplet sensitizer because of its high intersystem crossing (1.0) and long triplet life (2.3 s)[12]. PEG macromolecule chain is hydrophilic, and the sensitizer end groups, naphthyl or benzoyl benzyl, are hydrophobic, so the AIBN and St molecules are solubilized in the area enveloped by sensitizer groups.

When the concentration of sensitizer is less than the critical micelle concentration (*CMC*), no micelles are formed in the water phase; the polymerization rate of monomer St increases slowly with the concentration of PEG sensitizer due to the increasing number of activated sensitizer macromolecules. The system seems to behave like a common photosensitized solution polymerization. The polymerization rate R_p is proportional to 0.59 power of N-PEG-B concentration, as shown in *Figure 1*. When the concentration of PEG sensitizer is equal to *CMC*, *Figure 2* shows that R_p jumps, because the polymerization is carried out in the micelle, the hydrophobic sensitizer groups are arranged tightly, and efficient triplet energy transfer can occur between the activated sensitizer groups and AIBN.

However, if the monomer MMA was added to the polymerization system at *CMC* or twice *CMC*, the block copolymerization proceeded at first, then precipitate appeared. But if the concentration of N-PEG-B was increased further, for example to five or six times *CMC*, then block copolymerization proceeded successfully (*Figure 2B*) and no precipitate was produced. That means that block copolymerization should be carried out in a much higher concentration of N-PEG-B in our system. The reasons are very simple and obvious. When the block copolymer particles increase in size, they need to absorb more and more surfactant of N-PEG-B in order to maintain stability. If there are not enough N-PEG-B macromolecules, the growing block copolymer particles break free from the surrounding N-PEG-B macromolecules, and the propagation of block chain may be stopped as soon as it enters the water phase. Therefore, a higher concentration of N-PEG-B is necessary for our system in order to supply enough PEG sensitizer macromolecules for the growing block copolymer particles.

Conclusion

In the presence of N-PEG-B with the properties of surfactant and triplet sensitizer, the block copolymerization of St and MMA could be carried out with initiation by AIBN under u.v. irradiation with a magnetic field. This process is strongly dependent of the magnetic field and the concentration of N-PEG-B.

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