

Photochemical-Induced Polymerization Kinetics of Styrene and Methyl Methacrylate by Initiation of Binary System Composed of Polyethylene Oxide with Aniline End Group and Benzophenone

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ABSTRACT: The kinetics of photochemical polymerization of styrene (St) and methyl methacrylate (MMA) using a binary initiation system composed of poly(ethylene oxide) with an aniline end group (PEO_a) and benzophenone (BP) was investigated by a modified dilatometer. The effect of the concentration of the monomer, BP and PEO_a, and of the molecular weight of PEO_a on the polymerization rate (R_p) and conversion of monomers is discussed in detail. The formulas of $R_p \propto [\text{PEO}_a]^{0.38} [\text{St}]^{0.33} [\text{BP}]^{0.56}$ and $R_p \propto [\text{PEO}_a]^{0.36} [\text{MMA}]^{0.30} [\text{BP}]^{0.54}$ using benzene as a solvent are derived when the molecular weight of PEO is 11,000 (PEO_a = 11,000). Compared with the small aminophenol (AP), there existed a critical PEO_a concentration to affect the R_p and conversion of the monomers and the critical concentration is strongly dependent on the polarity of the solvents and molecular weight of PEO_a. It is confirmed that in the same conditions the solution polymerization behavior of St and MMA initiated by the imino radical of PEO would not be affected by the properties of the second block although PMMA is miscible and PS is immiscible with PEO_a in the bulk. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 2095–2103, 1997

Key words: kinetics; binary initiation system; charge-transfer polymerization; poly(ethylene oxide); benzophenone

INTRODUCTION

In block copolymerization, the research of polymerization kinetics of a second monomer is quite difficult due to the high reactivity and easy deactivation of the species and high conversion of the monomers. However, how is the chain propagation of the second monomer carried out, and if the first block is miscible or immiscible with the

second block in the bulk, is there any difference about the formation of the second block in solution polymerization? All these questions are always very interesting to polymer chemists.

In the preparation of diblock copolymers of PEO-*b*-PS (Ref. 1) and PEO-*b*-PAN (Ref. 2) by sequential initiation of the anion and charge-transfer compound (CTC), the poly(ethylene oxide) (PEO) block with an aniline end group (PEO_a) is formed first, then PEO_a combined with benzophenone (BP) under UV-irradiation to initiate the polymerization of a second monomer. So, this supplies an ideal opportunity for us to investigate the solution polymerization kinetics of a second block which is immiscible or miscible with the

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first block in the bulk because the first block of PEO_a could be easily separated and purified.

Commonly, it is considered that the CTC is formed by mono-electron transfer from aniline to benzophenone under UV-irradiation first, then aromatic imine and diphenyl methanol radicals are produced via proton transfer; the efficient species is aromatic imine which initiated the polymerization of the monomer.^{3,4}

In our experiments, three unexpected phenomena were found: (1) the conversion of the second monomer is much lower, usually no more than 10%, no matter what kinds of monomers and solvents are used and how long the polymerization time is; (2) the polymerization rate and conversion of the monomers is strongly dependent on the concentration and molecular weight of PEO_a and there exists a critical PEO_a concentration for each sample; and (3) in benzene or acetonitrile, the polymerization of styrene (St) and methyl methacrylate (MMA) initiated by CTC composed of PEO_a and BP is not affected by the properties of the PS or PMMA blocks; their polymerization behavior is quite similar in comparing the kinetic constants. In the present contribution, detailed kinetic results in different polymerization conditions are described and the critical entanglement density of PEO_a which affected the polymerization rate is determined.

EXPERIMENTAL

Materials

St and ethylene oxide (EO) were dried by calcium hydride and distilled under N₂ before use; MMA was washed with 10% NaOH and dried over anhydrous sodium sulfate after repeated washing with distilled water, then distilled under reduced pressure before use. All solvents were purified by normal drying and distillation procedures. *p*-Aminophenol (AP), from Tao Yuan Reagent Factory, Wujiang County, ShuZhou City, Jiang Shu Province, China) was recrystallized twice with alcohol and then water, giving the crystals with a dark yellow color in a yield of 83.2%; mp 187–188°C. BP was also purified by recrystallization with alcohol.

Kinetics Measurement

A kinetics investigation was carried out with a modified dilatometer which could be vacuumed

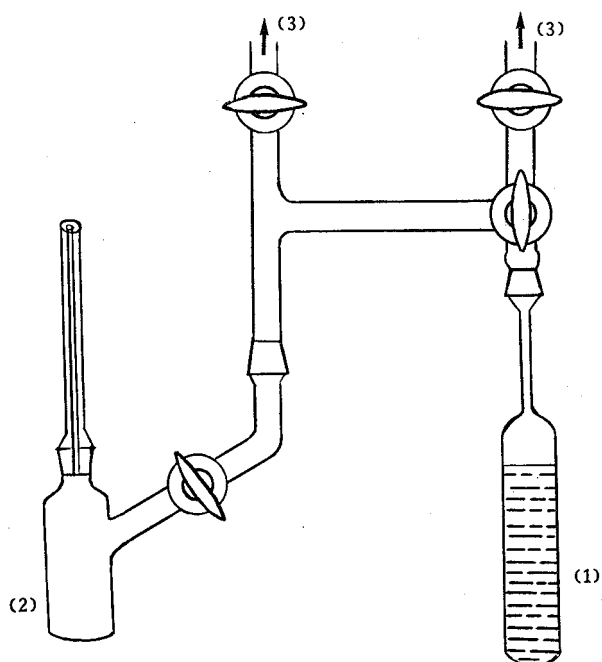


Figure 1 Modified dilatometer: (1) ampule; (2) dilatometer; (3) vacuum system.

as Figure 1 shows. Thus, the difficulties of the measurement of polymerization kinetics in the low initiator concentration due to the influence of oxygen on the polymerization were overcome. The PEO_as with different molecular weights were prepared by anionic polymerization as we reported previously.¹ The capillary diameter and the volume of the underneath container in the dilatometer were calibrated three times each with water and mercury at 25°C and an average value of each was obtained. The whole measurement procedure is described as follows: To a 50 mL ampule containing a certain amount of PEO_a dissolved into 10 mL benzene, MMA and BP were added. After three cycles of freezing at 77 K and thawing under a vacuum system, the reacting solution was pressed into the dilatometer which was also attached to the vacuum system via a branch tube until the liquid level increased to a definite height. Then, the top end of the dilatometer was sealed and placed in a water bath of 25°C. After the liquid level was raised to a maximum, the readings started to record, and at the same time, the dilatometer was irradiated by a 300 W high-pressure mercury lamp (Model GGZ-300, manufactured by Shanghai First Lamp Factory) at a constant 25°C. The cupric sulfate aqueous solution was used as the photofilter to obtain a 365 nm monochromatic light and the incident light intensity on the surface of the dilatometer was 0.5 kW/m². The whole

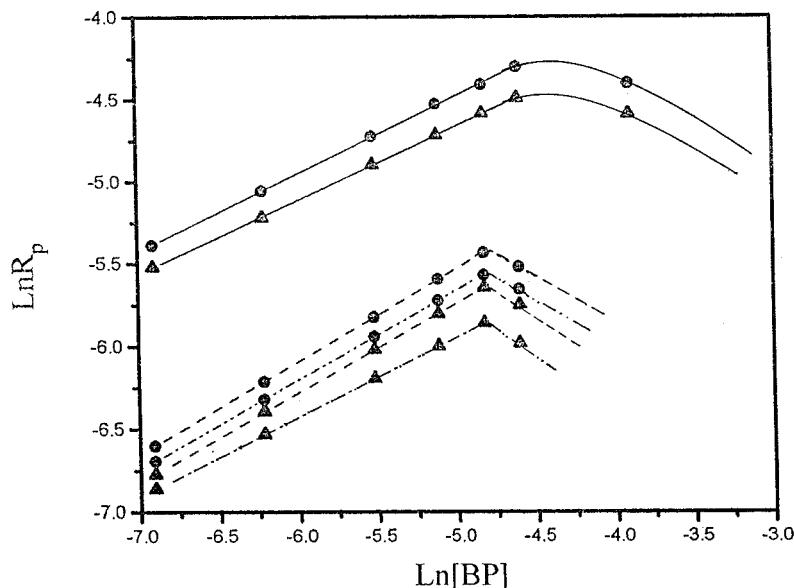


Figure 2 Effect of BP concentration on the polymerization rate. $[\text{PEO}_a - 11,000]: 8 \times 10^{-3}$ mol/L, $[\text{St}], [\text{MMA}]: 3.14$ mol/L. (●) St; (▲) MMA; (— · —) PEO_a (in acetonitrile); (---) PEO_a (in benzene); (—) AP (in acetonitrile).

measurement lasted about 40 min, and the readings were recorded at intervals of 5 min.

Instruments

UV spectra were obtained on a Beckman DU-7 spectrometer; phosphorescence spectra were recorded on a Hitachi MPF-4 fluorescence spectrometer with accessories for the measurement of phosphorescence which has been calibrated.

RESULTS AND DISCUSSION

Effect of Concentration of BP and Monomers on the Polymerization

Figure 2 shows the effect of concentration of BP on the polymerization with a fixed concentration of monomers and PEO_a and the molecular weight of PEO_a in benzene. The order of the reaction with respect to the BP concentration could be derived from the slope of the straight line portion of the plot of $\ln R_p$ vs. $\ln [\text{BP}]$, which is approximately 0.56 for St and 0.54 for MMA. When the BP concentration exceeds 8.0×10^{-3} mol/L for St and MMA, the rate decreased with the BP concentration. It could also be observed when a small amount of aminophenol (AP) was used as an initiator the $R_p \propto [\text{BP}]^{0.48}$ for St and $R_p \propto [\text{BP}]^{0.45}$ for MMA could be obtained. However, for St and MMA in the latter with the initiator AP when the

BP concentration exceeds 1.0×10^{-2} mol/L, the R_p starts to descend, which is greater than that of PEO_a . It may attributed to the following fact: If the BP concentration exceeded a definite value, the energy transfer not only could be carried out between excited BP and AP, or the amino group of PEO_a , but also led to the decrease of the energy-transfer efficiency at a higher concentration of BP.⁵ For the PEO_a , however, there is another reason that caused the R_p to drop, i.e., the excited BP could also be quenched by the PEO chain. Figure 3 shows the dependence of the phosphorescence intensity of BP on the AP and PEO_a concentrations. The variation of I_0/I_a (I_0 and I_a : the phosphorescence intensities of BP in the absence and presence of AP or PEO_a , respectively) for PEO_a dropped faster than that of AP as Figure 4 indicates. It is proved that the triplet BP could not only transfer the energy to the ground-state BP, with AP or with the amino group of PEO, but also to the PEO chain, which leads to the phosphorescence intensity decay of the excited triplet BP with PEO_a which is faster than that with small AP.

Figure 5 shows a linear relationship between $\ln R_p$ and $\ln [\text{MMA}]$ and $\ln [\text{St}]$ in the fixed concentrations of BP and $\text{PEO}_a - 11,000$; the slope of the plot gives the monomer exponent as 0.33 for St and 0.30 for MMA. Compared with the case of small AP, in the same polymerization conditions, the formulas of $R_p \propto [\text{St}]^{0.98} [\text{BP}]^{0.48}$ and $[\text{MMA}]^{0.94} [\text{BP}]^{0.41}$ are obtained, which indicates

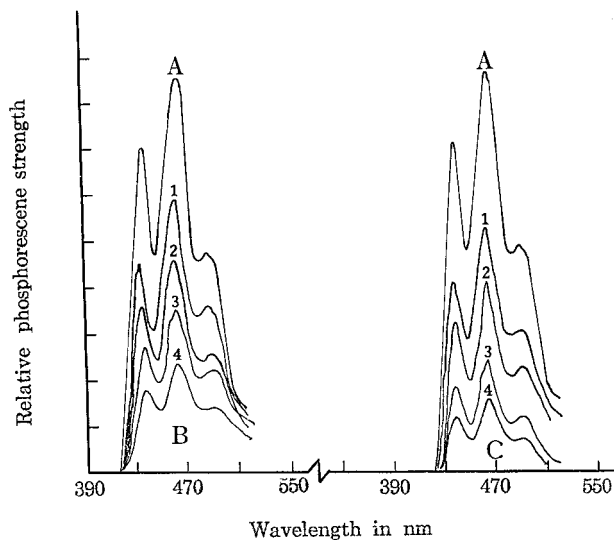


Figure 3 Phosphorescence spectra of BP in the (A) absence and presence of (B) AP and (C) PEO_a. [BP]: 1×10^{-4} mol/L; [AP] and [PEO_a]: 1×10^{-4} mol/L; solvent: CHCl₃, 77 K.

that when CTC composed of AP and BP is used as an initiator as good as a normal kinetic relationship could be obtained. R_p is nearly proportional with the square root of initiator concentration and first power of the monomer concentration. However, why does the sharp deviation for the case of PEO_a occur? We think that it may be caused by the following two reasons: (1) the amino groups are enveloped by the entanglements of PEO chains in the case of PEO_a, so the propaga-

tion via the addition between the radical and monomers is restricted; and (2) the intra- and intermolecular hydrogen-bonding interaction between the amino group and the PEO chain hindered the formation of CTC between the amino group and BP via the transfer of electrons under UV irradiation, so the formation of radicals is more difficult than that in the case of small AP. The UV spectra of small AP (A) and PEO_a (B) in chloroform (Fig. 6) supply direct evidence for the interaction between the PEO chain and amino groups. For AP, the absorption for the $n \rightarrow \pi^*$ transition locates at 296 nm; however, 306 nm is found for PEO_a. The 10 nm red shift of the latter is attributed to the formation of hydrogen bonding between the amino group and PEO_a chains. Nevertheless, a good linear relationship between R_p vs. concentration of the monomer in the conditions of the fixed concentrations of PEO_a and BP is still observed.

Effect of Concentration of PEO_a on the Polymerization

The dependence of R_p on the concentration of PEO_a is complicated. Figure 7 gives the experimental results. When the concentration of BP, St, and MMA and the molecular weight of PEO_a (11,000) is fixed, the R_p initially increases with the PEO_a concentration up to about 6.05×10^{-3} mol/L for St and 6.40×10^{-3} mol/L for MMA in benzene, beyond which the rates decreased

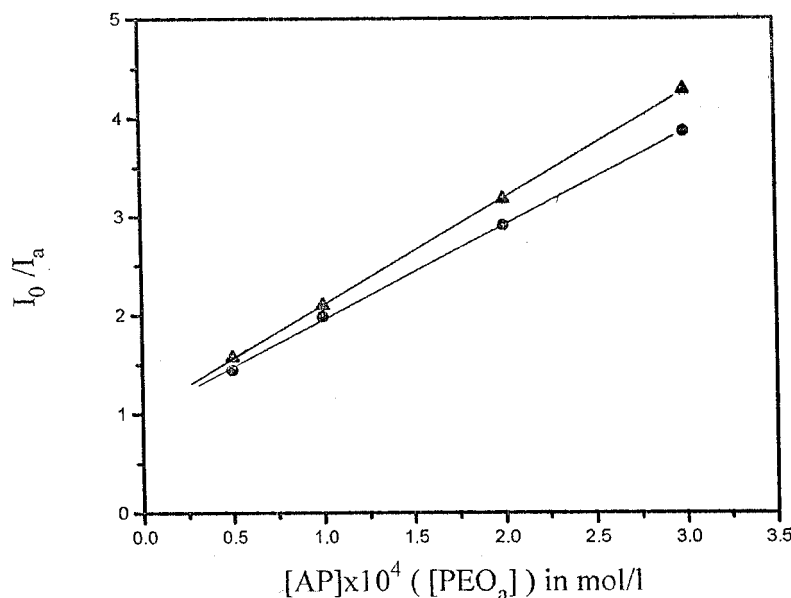


Figure 4 Dependence of I_0/I_a on the concentrations of (●) AP and (▲) PEO_a.

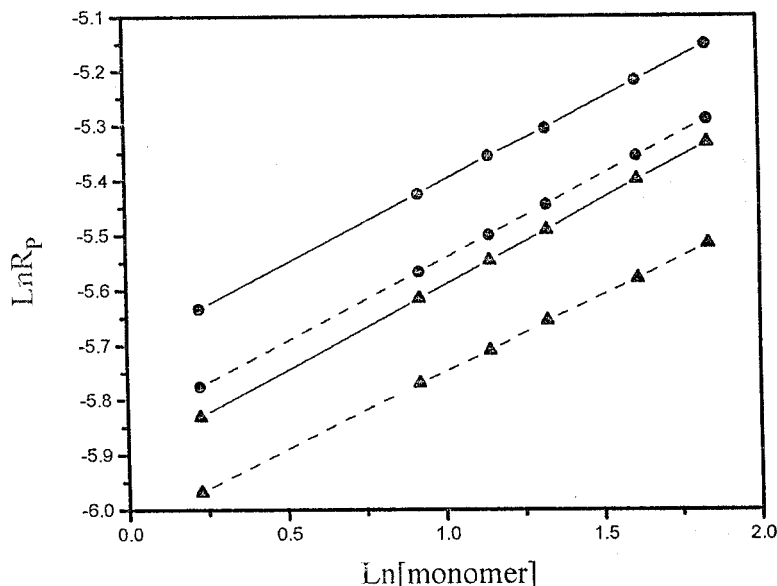


Figure 5 Relationship between $\ln R_p$ and \ln St and \ln MMA. $[\text{PEO}_a - 11,000]$, $[\text{BP}]$: 8×10^{-3} mol/L; (●) St; (▲) MMA; (—) in benzene; (---) in acetotriple.

sharply with the PEO_a concentration. The order of the reaction with respect to the PEO_a concentration is determined from the ascending portion of the plots in Figure 7 and is found to be approximately 0.38 for St and 0.36 for MMA in benzene, which still deviates from the common kinetic equation. This concentration of PEO_a corresponding to the maximum R_p , as Figure 7 shows, beyond which the R_p decreased sharply, is called a critical concentration. Only when the PEO_a concentration reached this value can the R_p drop rap-

idly. When the PEO_a concentration is less than the critical one, the amino group is only enveloped and not covered, although the R_p is less than that in the case of small AP, but as good as a linear relationship between R_p vs. the concentration of monomers and BP could still be derived. However, if the PEO_a concentration is more than the critical one, the chain entanglement density of PEO_a is so great that part of the amino groups are covered, leading to decrease of the radical concentration. The critical concentration of PEO_a , as Table I indicates, is strongly dependent on the polarity of the solvents and molecular weight of PEO_a .

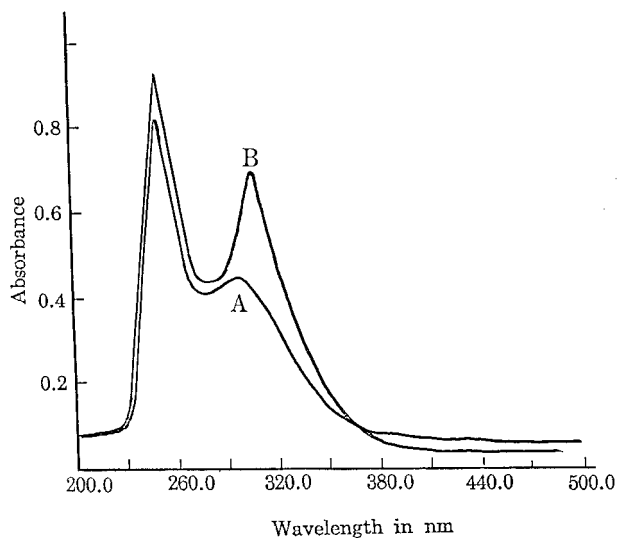


Figure 6 UV spectra of (A) AP and (B) $\text{PEO}_a - 11,000$. Solvent: CHCl_3 , $[\text{AP}]$: 2.0×10^{-4} mol/L; $[\text{PEO}_a - 11,000]$: 1.0×10^{-4} mol/L.

Effect of Molecular Weight of PEO_a on the Polymerization

As well known, in radical polymerization, the variety and the properties of the initiators do not exert great influence on the polymerization behavior of the monomers.⁶ However, for our system, the orders of concentration of the monomers, BP, and PEO_a , in kinetic equations increase with decrease of the molecular weight of PEO_a , which is shown in Table II. For example, when the molecular weight of PEO_a changes from 11,000 to 5,000, the formulas of $R_p \propto [\text{St}]^{0.33} [\text{BP}]^{0.56} [\text{PEO}_a]^{0.38}$ and $[\text{MMA}]^{0.30} [\text{BP}]^{0.54} [\text{PEO}_a]^{0.36}$ are changed to $R_p \propto [\text{St}]^{0.71} [\text{BP}]^{0.59} [\text{PEO}_a]^{0.46}$ and $[\text{MMA}]^{0.56} [\text{BP}]^{0.57} [\text{PEO}_a]^{0.42}$. The critical concentrations of PEO_a are also changed from 6.05×10^{-3} mol/L in the case of St for $\text{PEO}_a - 11,000$

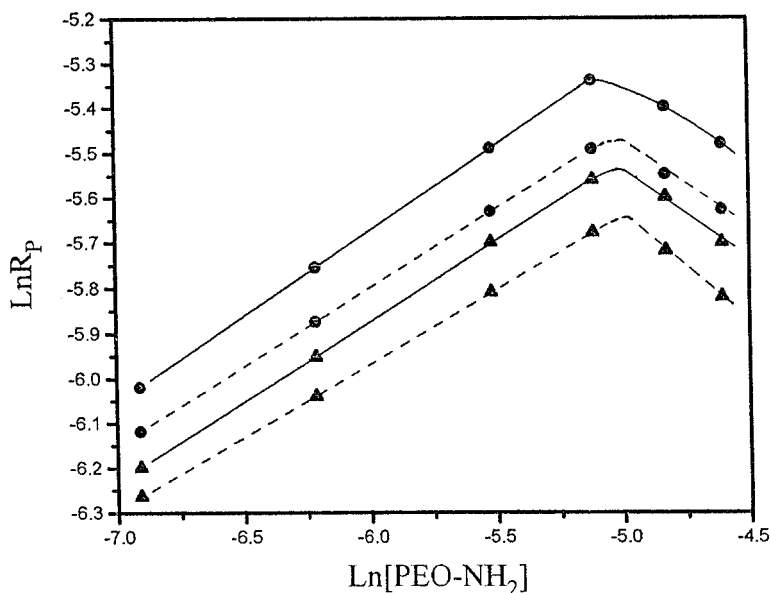


Figure 7 Dependence of R_p on the concentration of $\text{PEO}_a - 11,000$. $[\text{BP}] : 8 \times 10^{-3}$ mol/L; $[\text{MMA}], [\text{St}] : 3.14$ mol/L; (\bullet) St; (\blacktriangle) MMA; (—) in benzene; (---) in acetonitrile.

to 6.89×10^{-3} mol/L for $\text{PEO}_a - 5,000$ and from 6.32×10^{-3} mol/L to 7.4×10^{-3} mol/L for MMA, as Figure 8 indicates.

When the molecular weight of PEO_a decreases, its entanglement density would be decreased compared with the PEO_a with a high molecular weight in the same concentration. Thus, the critical concentration for PEO_a with a low molecular weight should be increased in order to form the sufficient entanglement to effect the polymerization. The relationship between R_p and the concentration of BP, MMA, and PEO_a is observed to be close to the normal kinetic equation with the decrease of the PEO_a molecular weight due to the decrease of the entanglement density of PEO_a .

The Effect of the Solvent Polarity on the Polymerization

The effect of solvent polarity on the polymerization of St or MMA is quite striking. R_p and the conversion of monomers decrease with increase of the solvent polarity when PEO_a is used. Figure 9 gives the dependence of the conversion of monomers on the solvent polarity. Whether St or MMA is used as the monomer, the conversion is always higher in benzene than that in acetonitrile. Tables III and IV list the detailed kinetic experiment results and the data of the molecular weight of the diblock copolymers in the different solvents. We also found that the R_p decreases with increase of

Table I Data of Critical Concentration of PEO_a in the Different Polymerization Conditions

Monomer	Monomer (mol/L)	MW (PEO_a) ($\times 10^{-4}$)	BP ($\times 10^3$ mol/L)	Solvent	PEO_{crit} ($\times 10^3$ mol/L)
St	3.14	1.1 ^a	8	Benzene	6.05
	3.14	1.1	8	Acetonitrile	6.31
	3.14	0.5 ^b	8	Benzene	6.89
	3.14	0.5	8	Acetonitrile	7.21
MMA	3.14	1.1	8	Benzene	6.32
	3.14	1.1	8	Acetonitrile	6.56
	3.14	0.5	8	Benzene	7.41
	3.14	0.5	8	Acetonitrile	7.66

^a Molecular weight distribution of PEO_a : 1.05.

^b Molecular weight distribution of PEO_a : 1.04.

Table II Comparison of Kinetic Constants of PEO_a with Small AP in the Different Polymerization Conditions

Initiator	Solvent	Monomer	Kinetic Constants
AP	Acetonitrile	St	$R_p \propto [\text{St}]^{0.98}[\text{BP}]^{0.48}[\text{AP}]^{0.45}$
	Acetonitrile	MMA	$R_p \propto [\text{MMA}]^{0.94}[\text{BP}]^{0.45}[\text{AP}]^{0.41}$
PEO _a -11,000 ^a	Benzene	St	$R_p \propto [\text{St}]^{0.33}[\text{BP}]^{0.56}[\text{PEO}_a]^{0.38}$
	Benzene	MMA	$R_p \propto [\text{MMA}]^{0.30}[\text{BP}]^{0.54}[\text{PEO}_a]^{0.36}$
	Acetonitrile	St	$R_p \propto [\text{St}]^{0.31}[\text{BP}]^{0.54}[\text{PEO}_a]^{0.35}$
	Acetonitrile	MMA	$R_p \propto [\text{MMA}]^{0.28}[\text{BP}]^{0.48}[\text{PEO}_a]^{0.32}$
PEO _a -5,000 ^b	Benzene	St	$R_p \propto [\text{St}]^{0.71}[\text{BP}]^{0.59}[\text{PEO}_a]^{0.46}$
	Benzene	MMA	$R_p \propto [\text{MMA}]^{0.56}[\text{BP}]^{0.57}[\text{PEO}_a]^{0.42}$
	Acetonitrile	St	$R_p \propto [\text{St}]^{0.68}[\text{BP}]^{0.57}[\text{PEO}_a]^{0.42}$
	Acetonitrile	MMA	$R_p \propto [\text{MMA}]^{0.53}[\text{BP}]^{0.52}[\text{PEO}_a]^{0.38}$

^a Molecular weight distribution: 1.05.^b Molecular weight distribution: 1.04.

the solvent polarity; on the contrary, the molecular weight of PS or PMMA in a diblock copolymer is higher in acetonitrile than that in benzene.

As well known, when aromatic amine and BP are mixed, the CTC composed of a cation-radical of PEO—NH₂⁺ and an anion-radical of Ph₂C—O⁻ would be formed via the electron transfer from the aromatic amine to the BP under UV-irradiation. In a nonpolar solvent such as benzene, the proton transfer from the cation-radical to the anion-radical is much easier, so the radicals of PEO—NH and Ph₂C[•]OH could be formed on a common route; then the former initiate the polymerization of the

monomers. However, in a polar solvent such as acetonitrile, the cation- and anion-radicals are solvated⁷ and the tightly bound ion radical pairs are turned into loose pairs; thus, the proton transfer between them may be difficult to carry out due to increase of the interaction distance between ion pairs. Hence, the concentration of the radical decreases, leading to the drop of R_p and conversion of the monomers. At the same time, the molecular weight of second blocks is increased due to the inverse dependence of the molecular weight on the concentration of radicals in radical polymerization.

We also found that for the case of PEO_a even

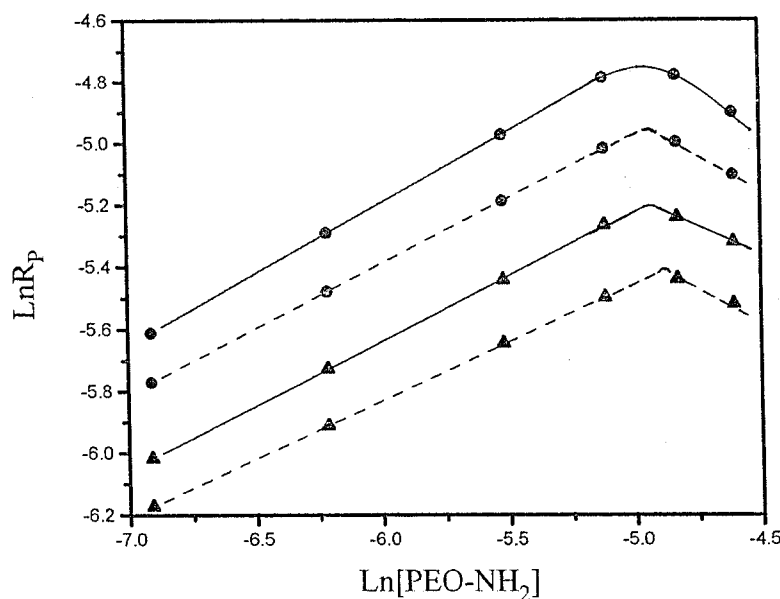


Figure 8 Dependence of R_p on the concentration of PEO_a - 5,000. [BP]: 8×10^{-3} mol/L; [MMA], [St]: 3.14 mol/L; (●) St; (▲) MMA; (—) in benzene; (----) in acetonitrile.

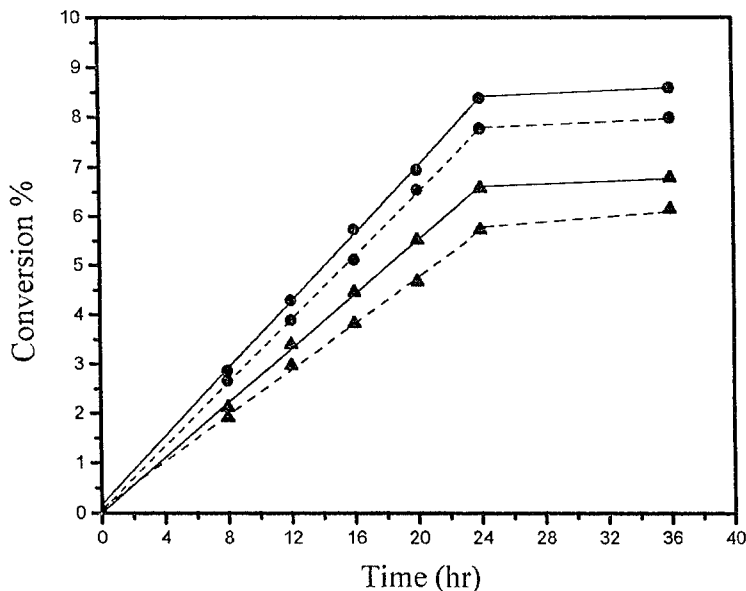


Figure 9 Effect of solvent polarity on conversion of monomers. $[\text{PEO}_a - 5,000]$, $[\text{BP}]$: 8×10^{-3} mol/L; $[\text{MMA}]$, $[\text{St}]$: 3.14 mol/L; (—) in benzene; (----) in acetonitrile.

when the concentration of PEO_a is less than the critical concentration the conversion of the monomers is still less than 10% no matter how long the polymerization time is. This phenomenon could be observed from both cases of St and MMA; obviously, chain entanglement density is responsible for it. Further research is now going on.

Effect of Second Block Compatibility with First Block on the Polymerization of Second Monomer

It is well known that PEO is miscible with PMMA and immiscible with PS in the bulk, but is there any difference for their kinetic behaviors when St and MMA are polymerized by imino radicals of

Table III Effect of Solvent Polarity on the Composition of Product^a

M ^b	PEO_a ($\times 10^{-3}$ mol/L)	Conversion (%) ^c	Composition (%) of Reaction Mixture		Block Copolymer Composition (W %) ^d	
			PEO	Copolymer	PEO	PS
St	4.0	9.61 (9.00) ^e	21.43 (32.43)	78.57 (67.57)	14.55 (12.00)	85.45 (88.00)
	6.0	9.00 (8.38)	30.34 (34.88)	69.66 (65.12)	29.03 (26.79)	70.97 (73.21)
	8.0	8.38 (7.77)	28.71 (34.69)	71.29 (65.31)	43.06 (40.62)	56.94 (59.38)
MMA	4.0	8.05 (7.42)	33.82 (38.46)	66.18 (61.54)	15.56 (12.50)	84.44 (87.50)
	6.0	7.20 (6.59)	37.97 (43.42)	62.03 (56.58)	30.61 (27.91)	69.39 (72.09)
	8.0	6.57 (5.72)	36.26 (43.68)	63.74 (56.32)	46.55 (44.90)	53.45 (55.10)

^a Concentration of St and MMA: 3.14 mol/L; BP concentration: 8×10^{-3} mol/L; MW of PEO_a : 5,000; polymerization time: 24 h; solvent: benzene.

^b Monomer.

^c Overall monomer conversion.

^d Determined by pyrolysis gas chromatography using known homopolymer PEO, PS, and PMMA as standards.

^e The values in parentheses are obtained in acetonitrile.

Table IV Effect of Solvent Polarity on Polymerization^a

Monomer	PEO _a	M_n^b ($\times 10^{-3}$ mol/L)	M_w/M_n ($\times 10^{-4}$)
St	4.0	3.45 (4.20) ^c	1.50 (1.62)
	6.0	1.75 (1.94)	1.24 (1.27)
	8.0	1.20 (1.28)	1.15 (1.17)
MMA	4.0	3.30 (4.05)	1.47 (1.60)
	6.0	1.70 (1.90)	1.22 (1.26)
	8.0	1.10 (1.15)	1.12 (1.13)

^a Concentration of monomers: 3.14 mol/L; concentration of PEO_a and BP: 8×10^{-3} mol/L; MW of PEO_a: 500; M_w/M_n : 1.04; solvent: benzene.

^b Determined by GPC.

^c The values in parentheses are obtained in acetonitrile.

PEO in solution? Our answer is negative. The experimental results confirmed that no difference could be found for their polymerization behaviors. As long as the cosolvents could be found, the polymerization of the second monomers would not be affected by the properties of the second blocks no

matter whether they are miscible or immiscible with the first block.

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REFERENCES

1. J. L. Huang, X. Y. Huang, and S. Zhang, *Macromolecules*, **28**(13), 4421 (1995).
2. J. L. Huang, X. Y. Huang, W. B. Wu, and W. Q. Lou, *J. Polym. Sci. Part A Polym. Chem.*, **34**(8), 1317 (1996).
3. S. Arimitzu and H. Masahara, *Chem. Phys. Lett.*, **22**, 543 (1973).
4. M. R. Sandner, C. L. Oshorn, and D. J. Trecher, *Polymer*, **14**, 250 (1973).
5. J. L. Huang, P. Zhu, C. G. Ji, and W. X. Ruan, *Makromol. Chem.*, **193**, 243 (1992).
6. O. George, *Principles of Polymerization*, 2nd ed., Wiley, New York, 1970, p. 340.
7. T. Sato, S. Kita, and T. Otsu, *Makromol. Chem.*, **176**, 561 (1975).