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SHORT COMMUNICATION

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The micellization of the diblock copolymer of ethylene oxide and styrene in benzene and the effect on the preparation of the star ABC triblock copolymer of ethylene oxide, styrene and methyl methacrylate

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Abstract In the preparation of the ABC star triblock copolymer of ethylene oxide, styrene and methyl methacrylate (MMA), the photoinduced charge-transfer complex (CTC) was used to initiate the polymerization of the third monomer MMA. The CTC was composed of the diblock copolymer of poly(ethylene oxide) (PEO) and polystyrene (PS), PEO-b_i-PS, with an aromatic imino group at the conjunction point and benzophenone (BP). It was confirmed that the kinetic behavior of this macromolecular initiation system is nearly the same with a general small radical initiator: the polymerization rate $R_p \propto [\text{PEO-}b_i\text{-PS}]^{0.48}[\text{BP}]^{0.45}[\text{MMA}]^{0.97}$. Moreover, if the molecular weight of the PEO block is fixed, R_p is independent of the molecular weight of the PS block.

By means of measurements of viscosity and fluorescence, it was found that the micelles of the diblock copolymer PEO-b_i-PS were formed in benzene. The aromatic imino groups were located on the boundary surfaces of the micelles and were fully exposed, and so the BP and MMA molecules easily approached them and affected the charge-transfer polymerization of MMA.

Key words Diblock copolymer – Ethylene oxide – Styrene – Micellization

Introduction

As is well known in the design and synthesis of linear and star multiblock copolymers with the same or different arms in the structure, the most common way is to couple the macroanions with multifunctional chlorosilane compounds [1, 2]. Recently, Hadjichristidis and Iatrou [3, 4] prepared star ter- and quaterpolymers with different arms using this method. These copolymers with special architecture are very interesting for polymer scientists and have promoted the development of polymer science in areas including compatibility [5], morphology [6], rheology [7], and unperturbed dimensions [8], etc. However, the number of monomers suitable for anionic polymerization is limited, so there is no universal significance by using the coupling method to prepare linear and star copolymers with arms of different polarity.

In the last few years, a great deal of work has been dedicated to the synthesis of ABC star polymers using macromonomer techniques [9–11]. Quirk and Kim [12] reported the preparation of a 1,1-diphenylethylene-functionalized poly(ethylene oxide) (PEO) macromonomer and its use for the preparation of polystyrene-*b*-poly(ethylene oxide) and the star triblock copolymer of polystyrene (PS), PEO, and poly(*t*-butyl methacrylate).

In a previous chapter [13], we described the synthesis of a star triblock copolymer of PEO-PS-poly(methyl methacrylate) (PMMA) (s-EO-S-M) with a great difference in polarity via the combination of anionic polymerization with charge-transfer polymerization. This is a special kind of amphiphilic star terpolymer: the PEO arm is strongly hydrophilic, PS is strongly hydrophobic and PMMA is weakly hydrophilic, so its solution properties, dynamics, morphology and compatibility with corresponding homopolymers are naturally interesting for us.

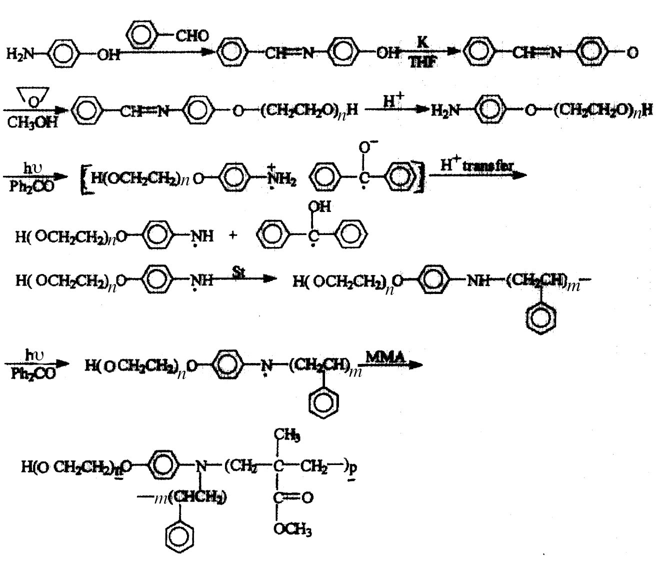
In the preparation of s-EO-S-M, the used binary initiation system is composed of PEO-b_i-PS with an aromatic imino group at the conjunction point and benzophenone (BP). As is well known the kinetic behavior of the macromolecular initiation system usually deviated or seriously deviated from the normal kinetic equation of radical polymerization [14], and this deviation was also observed from the system composed of PEO with an aniline end group (PEO_a) and BP [15]. It was found, however, if the polymerization of MMA was initiated by the system composed of PEO-b_i-PS and BP, its kinetic behavior is nearly identical with the normal radical polymerization equations, and the rate of polymerization R_p is independent of the molecular weight of the PS block if the molecular weight of PEO is fixed. This is a new and very interesting experimental fact.

In order to ascertain this unusual phenomenon, the solution properties of PEO-b_i-PS with an aromatic imino group at the conjunction point were investigated in benzene by viscometry and fluorimetry, the micellization of this block copolymer in benzene was described and the effect of this phenomenon on synthesis of s-EO-S-MMA was investigated.

Experimental

Materials and preparation of s-EO-S-MMA

The purification of monomers and solvents and the whole preparation procedure of the triblock copolymer were reported in detail in previous papers [13, 16]. Here we only described it in a brief scheme:



Scheme 1

Viscometry

The viscosity was measured in a Ubbelohde viscometer that was placed in a thermostatically controlled bath. The concentration of PEO-b_i-PS solution was 5×10^{-3} g/ml and the temperature was varied from 20 to 70 °C. The data were evaluated using the following equation [17]:

$$\eta_{sp}/c = (\eta_r - 1)/c \ . \qquad (1)$$

Here c is the polymer concentration, η_{sp} is the specific viscosity, and η_r is the viscosity ratio. When the solution is very dilute, η_r could be expressed by t/t_0 (t: the afflux time of solution, t_0: the afflux time of pure solvent).

Fluorimetry

The fluorescence spectra were recorded on a fluorometer manufactured by Zhejiang University, China. The excitation wavelength was 300 nm for the systems composed of aniline and MMA, PEO_a and MMA, or PEO-b_i-PS and MMA using slits of 4 nm width for excitation and emission. For the systems composed of PEO_a and anthracene or PEO-b-PS and anthracene, the excitation wavelength was 365 nm using the same slits.

Conversion

The degree of conversion of the monomer was obtained by isolating the block copolymer from the mixture at the different times and weighing.

Kinetics

The kinetics experiments were carried out with a modified dilatometer [15] at low conversion and at low concentration.

Results and discussion

Origin of the problem

In the preparation of PEO-b_i-PS and s-EO-S-M in benzene, it was found that the conversion of styrene (St) for the former (<10%) is much lower than that of the latter in which the conversion of MMA is as high as 61–70%. The polymerization data for both cases are given in Table 1. We think that when the charge-transfer complex composed of PEO_a and BP initiated the polymerization of St in benzene, PEO_a chains existed as random coils, and intra- or intermolecular entanglements of PEO_a chains took place because benzene is not a good solvent for them. Thus some amine groups should be covered, and the effective concentration of amine radicals decreased. This suggestion could be proved by fluorimetry using MMA as a quencher to measure the quenching constants K_D of aniline and PEO_a via the Stern–Volmer equation [18]:

$$I_0/I = 1 + K_D\,[Q] \ , \qquad (2)$$

Table 1 Polymerization data of methyl methacrylate (MMA) by the binary initiation system of poly(ethylene oxide) (*PEO*) and polystyrene (*PS*) (PEO-*b*-PS) with imino groups and benzophenone (*BP*)[a]

Sample	$M_n(\times 10^{-4})$			M_w/M_n			Conversion (%)	
	PEO	PEO-*b*-PS	s-EO-S-MMA	PEO	PEO-*b*-PS	s-EO-S-MMA	St	MMA
1	2.48	5.24	28.1	1.04	1.42	2.80	7.58	68.74
2	1.10	3.40	25.0	1.04	1.39	2.55	8.92	72.25
3	2.48	2.67	3.44	1.05	1.39	2.76	5.32	61.44

[a] Polymerization condition: [PEO-b_r-PS] = 1.0×10^{-5} mol/l, [BP] = 1.1×10^{-5} mol/l, MMA: 5 ml, polymerization time: 18 h for sample 1, 48 h for 2 and 24 h for 3.

where I_0 and I are the fluorescence intensity of the samples in the absence and in the presence of quencher, respectively, K_D is the Stern–Volmer quenching constant and $[Q]$ is the concentration of the quencher.

The effect of the concentration of quencher MMA on the relative fluorescence intensity of different systems is shown in Fig. 1. A nice linear relationship for all of them could be observed, and the K_Ds were obtained from the slopes of the straight lines. For aniline, K_D is 38.6 l/mol, and for PEO^1_a and PEO^2_a. the K_Ds are 15.1 and 10.7 l/mol, respectively. It is obvious that under the same conditions, the fluorescence of aniline was quenched more rapidly by MMA than that of PEO_a, and moreover, the higher the molecular weight of the PEO_a, the smaller the K_D. These results provided strong evidence for entanglements of the PEO_a chain leading to the being covered of a part of aniline end groups. When PEO_a, BP and St coexisted in benzene, BP molecules only approached and reacted with the aniline groups located at the surface of the PEO_a coils. If the aniline groups at the surface of PEO_a were used up, the remaining BP and St were very difficult to diffuse into the entangled coils to make the St monomers polymerize continuously: this phenomenon is more serious for PEO^2_a with a higher molecular weight due to its higher entanglement density. That is the cause for the lower conversion of St initiated by the binary initiation system of PEO_a and BP.

When the quencher MMA was added to the benzene solution of PEO-b_r-PS in which the aromatic imino groups are located at the conjunction point of the PEO and PS blocks, however, the K_Ds of the systems are close to the aniline values shown in Fig. 1: the values are 36.1 (for PEO-b_r-PS^1: molecular weights of PEO and PS are 5,000 and 12,500, respectively) and 34.2 l/mol (for PEO-b_r-PS^2: molecular weights of PEO and PS are 5,000 and 29,500, respectively), which are much greater than for the PEO_a systems. These unusual phenomena of PEO-b_r-PS in benzene are of great interest to us.

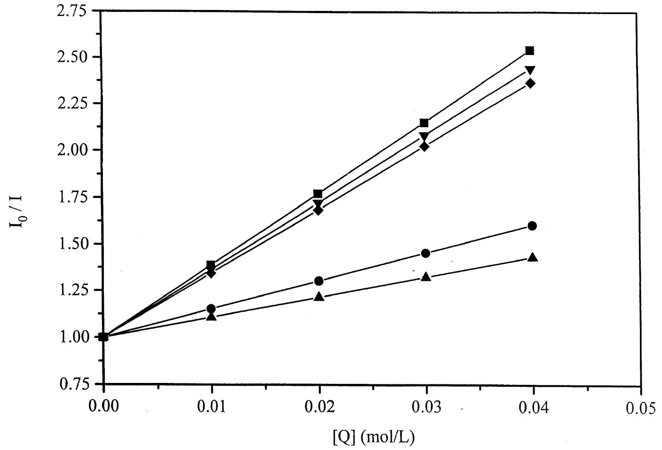


Fig. 1 Effect of quencher concentration on the relative fluorescence intensity of aniline (■), PEO^1_a (●), PEO^2_a (▲), PEO-b_r-PS^1 (▼), and PEO-b_r-PS^2 (◆). [Aniline] = [PEO_a] = [PEO-b_r-PS] = 5×10^{-4} mol/l, solvent: benzene

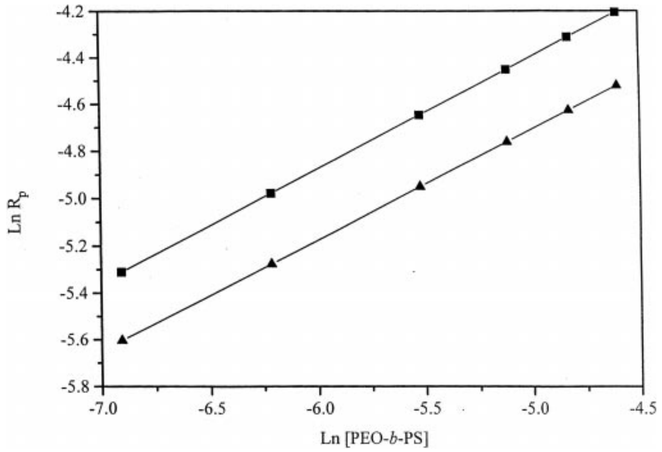


Fig. 2 Effect of concentration of PEO-b_r-PS on the rate of polymerization (R_p) PEO-b_r-PS^1 (■), PEO-b_r-PS^2 (●), [BP] = 8×10^{-3} mol/l, [MMA] = 3.143 mol/l, solvent: benzene

Polymerization kinetics of MMA initiated by the binary system PEO-b_r-PS and BP

The dependencies of the concentrations of PEO-b_r-PS, BP and MMA on the polymerization rate (R_p) are shown in Figs. 2–4. The formulas of $R_p \propto [\text{PEO-}b\text{-PS}^1]^{0.48} [\text{BP}]^{0.49} [\text{MMA}]^{0.97}$ and $R_p \alpha [\text{PEO-}b\text{-PS}^2]^{0.46} [\text{BP}]^{0.48} [\text{MMA}]^{0.95}$ were derived from the slopes of the straight lines, which illustrated the fact that R_p is approximately proportional to the first order of the monomer concentration and to one-half order of the initiator concentration, and

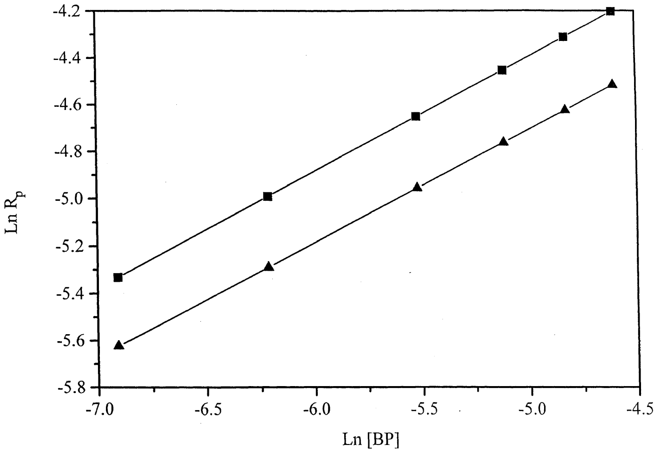


Fig. 3 Effect of concentration of benzophenone (*BP*) on R_p. PEO-b_r-PS^1 (■), PEO-b_r-PS^2 (●), [PEO-b_r-PS] = 8×10^{-3} mol/l, [MMA]= 3.143 mol/l, solvent: benzene

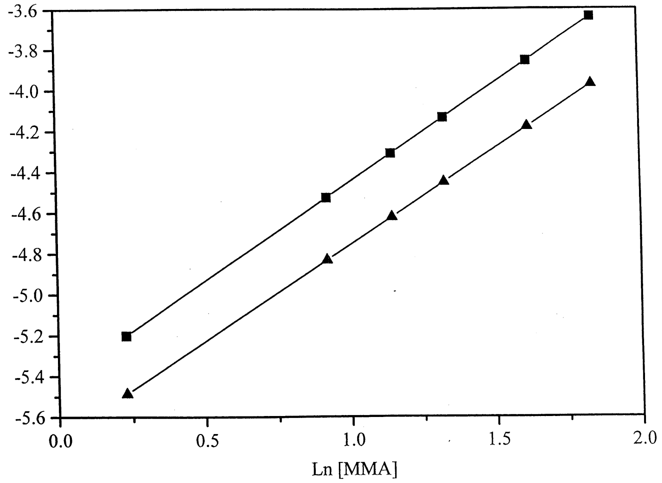


Fig. 4 Effect of concentration of methyl methacyrlate (MMA) on R_p. PEO-b_r-PS^1 (■), PEO-b_r-PS^2 (●), [PEO-b_r-PS] = [BP] = 8×10^{-3} mol/l, solvent: benzene

moreover, R_p is nearly independent of the molecular weight of PEO-*b*-PS. Compared with these results, the formulas [16] $R_p \propto [PEO_a^1]^{0.42}[BP]^{0.57}[MMA]^{0.56}$ and $R_p \propto [PEO_a^2]^{0.36}[BP]^{0.54}[MMA]^{0.36}$, which show the dependence of R_p on the concentrations of PEO$_a$, BP and MMA, seriously deviated from the normal radical kinetic equation.

Micellization of PEO-b_r-PS in benzene

In order to ascertain the causes of these unusual phenomena, the solution properties of PEO-b_r-PS were investigated. The dependence of the viscosity in benzene of PEO-b_r-PS with different molecular weights on the temperature is illustrated in Fig. 5. This is a typical micellization curve for the amphiphilic diblock copolymer in a liquid that is a good solvent for one block but a poor solvent for the other block [19]. Benzene is a good solvent for the PS chain, but a poor solvent for PEO. In this case, the entangled PEO chains aggregated and formed the cores of a micelle and the PS chains constituted the shells. At lower temperature, the solution viscosity is much lower because the block copolymer existed mainly in an associated micelle. However, the viscosity increased with increasing temperature due to the slow dissociation of micelles into copolymer macromolecules. When all the micelles were dissociated into the single PEO-b_r-PS macromolecule with further increase of temperature the viscosity of the system reached a maximum. If the temperature were raised continuously, the viscosity would drop as for the common solution. In Fig. 5, the circles and squares represent the higher and lower molecular weights of PEO-b_r-PS, respectively. In both cases, the molecular weight of the PEO block was the same, and the entanglement densities of the PEO chains which formed the cores of the micelles should be closer to each other, so the viscosity of the system is mainly dependent on the molecular weight of PS. Therefore, the viscosity of PEO-b_r-PS^2 with a higher molecular weight (M_w PS: 29,500) is greater than that of PEO-b_r-PS^1 with a lower molecular weight (M_w PS: 12,500).

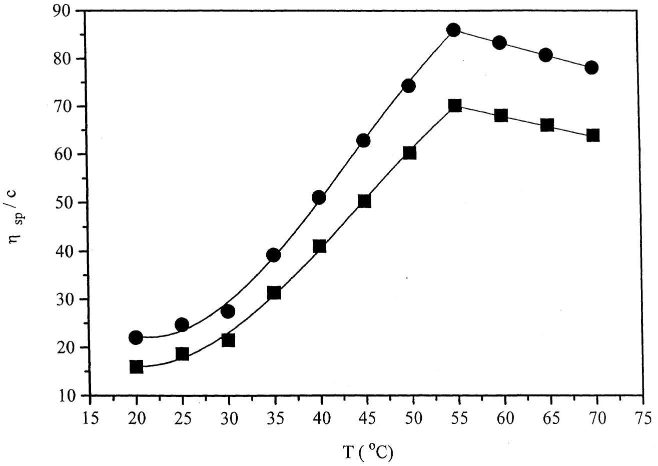


Fig. 5 Relationship of the viscosity of PEO-b_r-PS in benzene with temperature. PEO-b_r-PS^1 (■), PEO-b_r-PS^2 (●), [PEO-b_r-PS] = 0.005 g/ml, solvent: benzene

The micellization of PEO-b_r-PS in benzene can also be confirmed by measurements of the Stern–Volmer quenching constant K_D by means of fluorimetry. MMA was used as a quencher and a series of K_Ds was obtained. In this system, aniline, PEO$_a$ and PEO-b_r-PS were used to quench the fluorescence of anthracene, and another series of K_Ds shown in Table 2 was obtained. When PEO-*b*-PS^1 and PEO-*b*-PS^2 were used as quenchers, the

Table 2 Measurements of Stern–Volmer quenching constants (K_Ds) for the system of anthracene using aniline, PEO$_a$ and PEO-b_i-PS as quenchers[a]

[Q] (mol/l)	I_0/I				
	Aniline	PEO^1_a	PEO^2_a	PEO-b_i-PS^1	PEO-b_i-PS^1
0.01	1.474	1.121	1.081	1.449	1.427
0.02	1.958	1.242	1.162	1.897	1.854
0.03	2.421	1.362	1.242	2.346	2.281
0.04	2.896	1.484	1.324	2.796	2.708
K_D(l/mol)	47.4	12.1	8.1	44.9	42.7

[a] [Anthracene]: 1×10^{-2} mol/l, excitation wavelength: 365 nm, maximum fluorescence peak wavelength: 426 nm

K_Ds were 44.9 and 42.7 l/mol, respectively, which is close to the 47.4 l/mol for the system with aniline as a quencher. However, if PEO^1_a and PEO^2_a were used as quenchers, the K_Ds were only 12.1 and 8.1 l/mol, respectively.

Thus, the following conclusions could be obtained on the basis of Fig. 1 and Table 2.

1. For PEO-b_i-PS whether the molecular weight is high or low, the K_Ds are always much higher than for PEO$_a$ in benzene, whose values approached that of aniline. This means that for PEO-b_i-PS, the imino groups at the conjunction point of the PEO and PS blocks were fully exposed in benzene, and so the energy transfer between PEO-b_i-PS in the excited state and MMA in the ground state or anthracene in the excited state and PEO-b_i-PS in the ground state was much easier to carry out.
2. In benzene solution of PEO-b_i-PS with different molecular weights of the PS block, there is no sharp difference in the K_D values; that means as long as the molecular weight of PEO is fixed, the number and the environment of the imino groups is unchanged, and the PS chain length cannot exert a great effect on the activity of the imino groups due to its full extension in benzene.
3. Either PEO-b_i-PS is used as an energy donor or acceptor: the solution properties in benzene for both cases are similar. That means only the imino groups were on the boundary surfaces of PEO-b_i-PS, and so the energy transfer between PEO-b_i-PS in the excited state and MMA in the ground state or anthracene in the excited state and PEO-b_i-PS in the ground state were conducted in the same way.

Conclusions

The binary initiation system composed of BP and PEO-b_i-PS in which the aromatic imino group is at the conjunction point of the PEO and PS blocks was used to initiate the polymerization of MMA. The polymerization behavior was close to the normal radical kinetics equation. By means of viscometry and fluorimetry, it was confirmed that micelles were formed when PEO-b_i-PS dissolved in benzene, and electron and proton transfer from the aromatic imino groups located on the boundary surfaces of the PEO and PS blocks to BP could be easily carried out.

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