Synthesis of Amphiphilic Block Copolymer of Acrylamide with Styrene Using Free Radical Interfacial Copolymerization

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ABSTRACT: A novel free radical interfacial copolymerization was proposed and used to prepare the amphiphilic block copolymer of acrylamide (AM) with styrene (S). In this copolymerization, a synthesized new kind of initiator, namely, amphiphilic bifunctional initiator, which has not only a hydrophilic and a hydrophobic group but also two functional groups generating radicals in both ends of its molecule, was used to initiate the interfacial copolymerization. The generated amphiphilic block copolymer was characterized by infrared analysis, differential scanning calorimetry, elemental analysis, and dissolution behavior. The migration of generated copolymer from interface to water phase was discussed. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 443–449, 1998

Key words: free radical interfacial copolymerization; amphiphilic copolymer; amphiphilic bifunctional initiator

INTRODUCTION

A chemical reaction can occur only when the molecules, which will take part in the reaction, approach each other in the distance of angstrom order. Two kinds of monomers with a great difference in polarity have low compatibility and usually form two phases in a reaction system, leading to the difficulty for the molecules to approach each other in the necessary reaction distance. Therefore, the copolymerization of two monomers with a great difference in polarity, such as the copolymerization of a water-soluble monomer with a oil-soluble monomer, is very difficult to carry out.

There are some methods used for such copolymerization, but these methods have certain drawbacks; for example, copolymerization efficiency is very low in the micellar copolymerization,[1] ultrasonic copolymerization and homogeneous copolymerization in a cosolvent lead to a statistical copolymer with extremely low molecular weight,[2] and the polymer postfunctionalization has limited uses due to its special monomer selectivity.[3]

On the other hand, there has been considerable interest in amphiphilic block copolymers due to their potential applications as viscosifiers for enhanced oil recovery, as surface-active polymers for personal care products, as biocompatible materials in the biomedical field, as moisture-sensitive materials in the sensor technology, and for some other purposes. Therefore, to develop a novel method for preparation of amphiphilic copolymers is very important both in theory and in practice.

We have proposed a novel free radical interfacial copolymerization in which an amphiphilic bifunctional initiator was used for the synthesis of an amphiphilic block copolymer.[4] The initiator molecule not only has a hydrophilic and a hydrophobic group at both ends but also has two

functional groups generating free radicals at both ends of the molecule. In a two-phase reaction system, the initiator molecules can preferentially orient at the interface between the water phase containing a water-soluble monomer and the oil phase containing an oil-soluble monomer with the hydrophilic group, drawing one functional group into the water phase and the hydrophobic group drawing another functional group into the oil phase. Under certain conditions, the two functional groups can generate free radicals to initiate the polymerization of the two monomers in their respective phases. As a result, an amphiphilic two-block copolymer is formed at the oil–water interface. This interfacial free radical copolymerization can be schematically shown, as follows.

(a)   (b)   (c)

Hydrophobic group   Hydrophilic group

Amphiphilic bifunctional initiator   Free radical   Propagating polymer chain
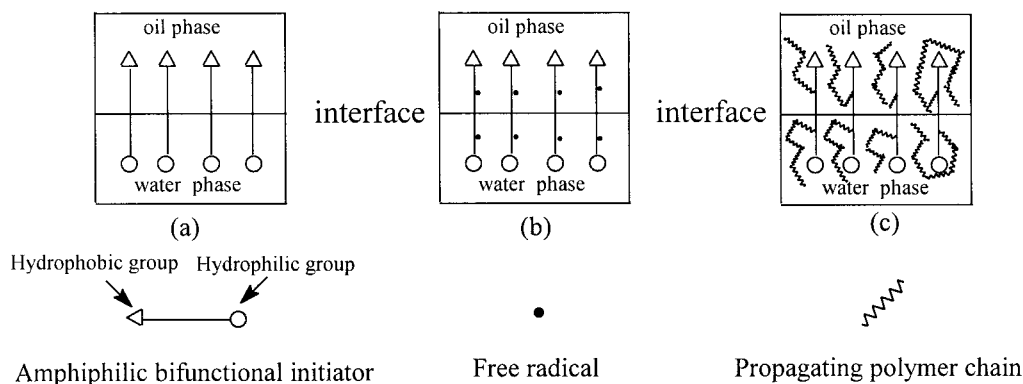
The scheme shows the following.

(a) Hydrophilic and hydrophobic monomer are dissolved in water and oil phases, respectively. The molecules of the amphiphilic bifunctional initiator orient at the oil–water interface.

(b) The amphiphilic bifunctional initiator generates free radicals in the water phase and the oil phase, respectively.

(c) The generated free radicals initiate the polymerization of hydrophilic and hydrophobic monomers in two phases, respectively, to form amphiphilic copolymer at the oil–water interface.

In this article, the free radical interfacial copolymerization of acrylamide (AM) with styrene (S) was carried out to form amphiphilic polyacrylamide-*b*-polystyrene, and the mechanism of this interfacial copolymerization was discussed.

EXPERIMENTAL

Materials

Acrylamide was recrystallized from acetone. Styrene was first washed with 10% NaOH solution and distilled water, then dried using $CaCl_2$, and distilled under reduced pressure. Decane was washed first with a small amount of fuming sulfuric acid several times until the acid was colorless, then washed with distilled water, 20% NaOH solution, and distilled water again, then dried with KOH and distilled under reduced pressure.

The amphiphilic bifunctional initiator was synthesized according to the following reactions.
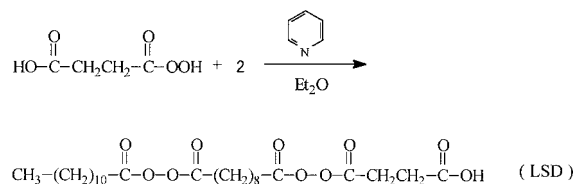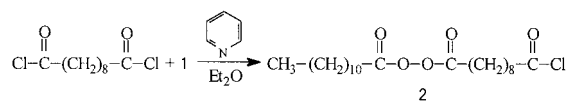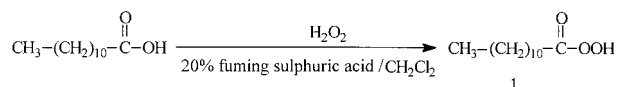
The obtained amphiphilic bifunctional initiator lauroyl (3-carboxy propionyl) sebacoyl diperoxide (LSD) was characterized using infrared (IR), nuclear magnetic resonance (NMR), mass spectrometry (MS) and elemental analysis. The detailed description of the synthesis procedure and the characterization of the synthesized amphiphilic bifunctional initiator LSD were given elsewhere.[5,6]

Table I   Recipe for the Radical Interfacial Copolymerization of Acrylamide with Styrene

Water phase	
Amount of acrylamide	5.00 g
Amount of water	20.65 g
Volume of water phase	25.0 mL
Oil phase	
Amount of styrene	10.00 g
Amount of decane	9.36 g
Volume of oil phase	25.0 ml
Amount of amphiphilic	
bifunctional initiator (LSD)	15 mg
Diameter of interface	4.50 cm
Temperature	75°C

Measurements

The IR spectra were recorded on a Perkin–Elmer 1600 IR spectrophotometer. DSC experiments were run on a Perkin–Elmer DSC-7 differential scanning calorimeter with a heating rate of 10°C/min. The π–A curve was obtained from an LB-membrane instrument (Joyce-Loebl Ltd., Britain) by dropping the dilute chloroform solution of initiator on the water surface at 20°C. The molecular weight of the polymer was determined using a Ubbelodhe viscosmeter. For polyacrylamide, the intrinsic viscosity was measured at 30°C using $1M$ NaCl aqueous solution as the solvent, and the molecular weight was calculated according to the equation $M_\eta = 148.25[\eta]^{1.52}$.[7] For polystyrene, the intrinsic viscosity was measured at 30°C using benzene as the solvent, and the molecular weight was calculated using the equation $M_\eta = 86.96[\eta]^{1.37}$.[8]
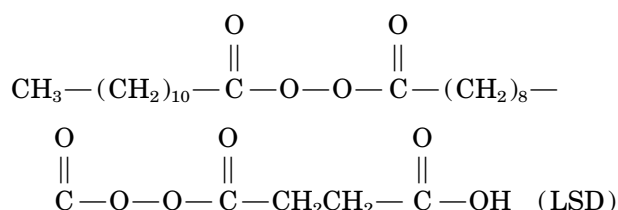
Free Radical Interfacial Copolymerization

Acrylamide was dissolved in water, and styrene was dissolved in decane. The two phases were degassed using a continuous stream of nitrogen for 30 min, respectively. Under a nitrogen atmosphere, the water phase was first added into a Pyrex vial, the amphiphilic bifunctional initiator was then added to the water phase, and the oil phase was finally added into the reaction vial. The vial was then quickly sealed with a rubber stopper equipped a thermometer and was put in a thermostat to keep the inner temperature in the vial at 75°C for 10 h. The resulting polymers were then precipitated from methanol and washed with it several times. The precipitate was th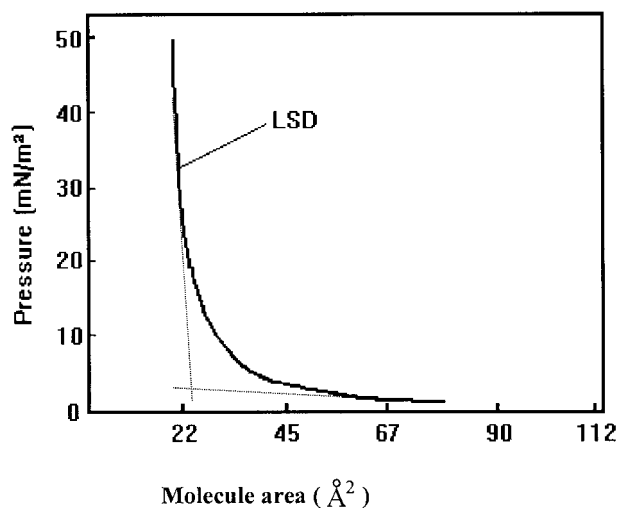en filtered and dried in vacuum at room temperature. The crude polymers were extracted using water to remove homopolyacrylamide and benzene to remove homopolystyrene. At last, the polymer which dissolved neither in water nor in benzene was obtained as copolymer and was characterized using IR, DSC, and elemental analysis. The polymerization recipe is shown in Table I.

RESULTS AND DISCUSSION

The synthesized amphiphilic bifunctional initiator LSD was characterized using IR, NMR, MS, and elemental analysis and its structure can be given as follows[5,6]:

$$CH_3-(CH_2)_{10}-\overset{\overset{\displaystyle O}{\|}}{C}-O-O-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_8-$$

$$\overset{\overset{\displaystyle O}{\|}}{C}-O-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH \quad (LSD)$$

To verify the surface-active (amphiphilic) property of the initiator, a dilute chloroform solution of LSD was dropped on a water surface to measure the molecular occupied surface area, and the resulting π–A curve is shown in Figure 1. The obtained molecular occupied surface area of 26.1 Å^2 for LSD is reasonable compared with the molecular occupied surface area of 21.0 Å^2 for octadecylic acid in the same condition. This result means that

**Figure 1** π–A curve of amphiphilic bifunctional initiator LSD.
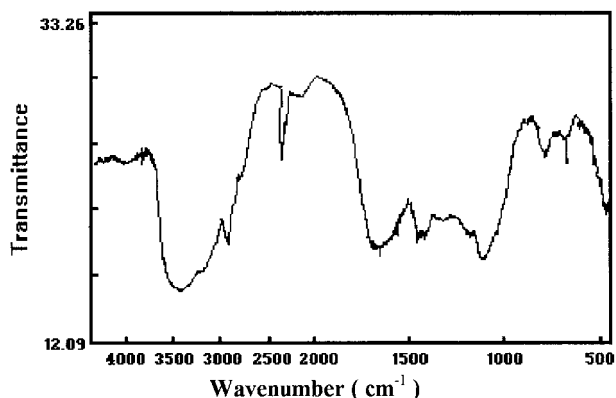
Figure 2 IR spectrum of poly(AM-*b*-S) block copolymer.

the initiator forms a monomalecular layer at the water–air interface and implies the amphiphilic properties of the initiator.

The obtained crude polymers were extracted using water to remove homopolyacrylamide and benzene to remove homopolystyrene. The polymer, which dissolved neither in water nor in benzene, was then characterized using IR (Fig. 2) and DSC (Fig. 3). The characteristic absorption bands in IR spectra at 3200, 1668, 1616, and 1416 cm^{-1} show that the polymer contains polyacrylamide segments; those at 1495, 760, and 700 cm^{-1} show that the polymer contains also polystyrene segments in its chains. The measured glass transition temperature T_g by DSC are 222 and 68°C for homopolyacrylamide and homopolystyrene, respectively. The DSC curve (Fig. 3), obtained under the same condition as for the homopolymers, of the polymer, which dissolved neither in water nor in benzene, shows two glass transition temperatures, at 233°C, corresponding to the T_g of PAM segments and, at 70°C, corresponding to the T_g of PS segments. These IR and DSC results mean that the obtained polymer, which dissolved neither in water nor in benzene, contains both PAM and PS segments in its chains.

To determine whether the obtained polymer, which dissolved neither in water nor in benzene, is a block copolymer of acrylamide with styrene or a mixture of crosslinked PAM and PS, the polymerization was also carried out using LSD as the initiator in the case of no styrene in the oil phase (only acrylamide in the water phase) and, on the contrary, no acrylamide in the water phase (but only styrene in the oil phase). In the former case,

the produced crude polymers are all soluble in water; in the latter case, the obtained crude polymers are all soluble in benzene. This results mean that the synthesized initiator LSD produced no crosslinked homo-PAM and homo-PS under the given polymerization conditions. It is ture that the DSC curve of an interpenetrating polymer network (IPN) of PAM and PS could also show two glass transition temperatures, but, if it is the case, the two glass transition temperatures should be more different from the glass transition temperatures of the corresponding homopolymers because the polymer chains are crosslinked and the crosslinked chains of one kind of polymer are surrounded by the crosslinked chains of another kind of polymer in an IPN. On the other hand, it is also difficult to explain how an IPN of PAM and PS could be formed if the initiator produced no crosslinked homopolymers. Based on these findings and the experimental results given later, the obtained polymer, which dissolved neither in water nor in benzene is more likely an amphiphilic block copolymer of acrylamide with styrene. The formation mechanism of this amphiphilic copolymer could be proposed as a free radical interfacial copolymerization. Under the polymerization conditions, the amphiphilic bifunctional initiator (LSD) will preferentially orient at the interface with its hydrophilic group (—COOH) drawing a functional group [—C(O)OOC(O)—] into the water phase and the hydrophobic group [CH$_3$-(CH$_2$)$_{10}$—] drawing another functional group [—C(O)OOC(O)—] into the oil phase. The initiator could be decomposed into radicals $^•$OC(O)(CH$_2$)$_8$C(O)CO$^•$, CH$_3$(CH$_2$)$_{10}$C(O)O$^•$, and $^•$OC(O)(CH$_2$)$_2$C(O)OH at 75°C. The free radical $^•$OC(O)(CH$_2$)$_8$C(O)O$^•$ at the interface will initiate the polymerization of the two monomers in their respective phases, leading to the formation of the amphiphilic copolymer PAM-*b*-PS at the interface. The free radicals CH$_3$(CH$_2$)$_{10}$C(O)O$^•$
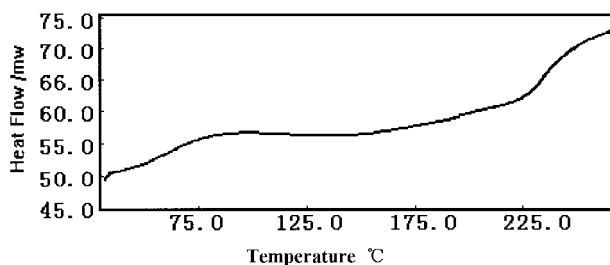
Figure 3 DSC curve of poly(AM-*b*-S) block copolymer.

and $\cdot OC(O)(CH_2)_2C(O)OH$ initiate the polymerization of acrylamide and styrene in their respective phases, leading to the formation of homopolyacrylamide and homopolystyrene. The proposed polymerization process can be represented as follows.
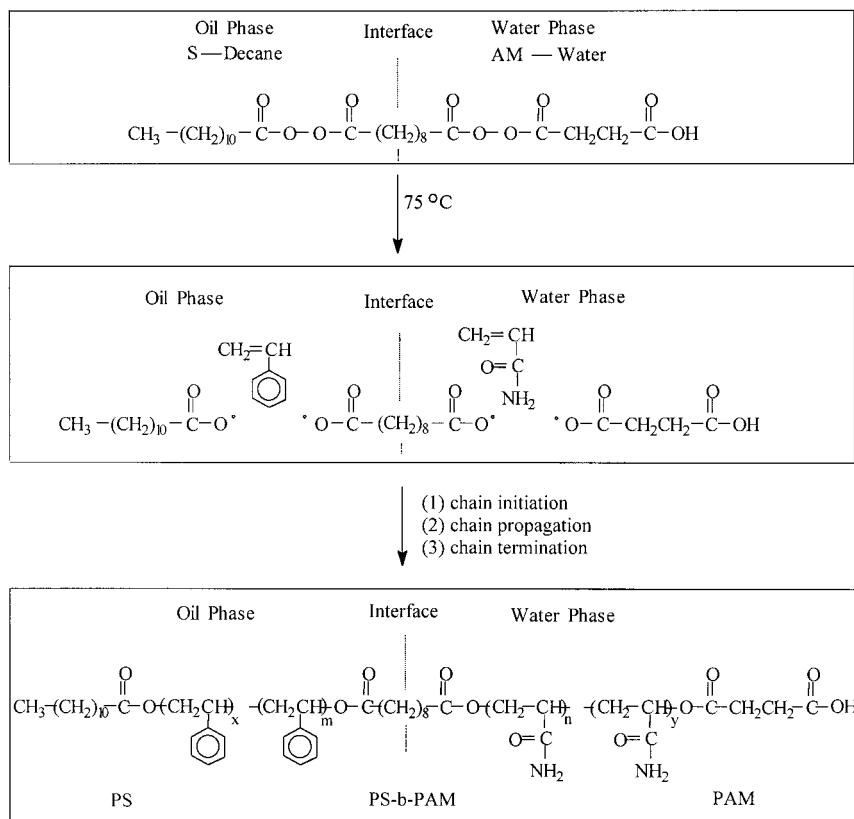
The crude polymer was precipitated from methanol and extracted using water to remove homopolyacrylamide and benzene to remove homopolystyrene. The separation results are shown in Table II. The amount of acrylamide in block copolymer was calculated from the results of elemental analysis of the block copolymer.

Most solvents, such as toluene, tetrahydrofuran, chloroform, ethanol, and N,N-dimethylformamide, are unable to dissolve or disperse the obtained block copolymer due to the great difference of polarity of the two segments in the same chain.

The polymerization was also carried out in vials with different diameters under the same conditions given in Table I. The amount of the obtained polymer that dissolved neither in water nor in benzene increases with increasing the interface area. This means that the copolymer was really generated at the interface and supports the proposed free radical interfacial copolymerization mechanism.

The copolymer molecule at the interface should be affected by the two following drawing forces: one is from the oil phase, caused by the cooperative operation between oil soluble block and oil phase; the other one is from the water phase, caused by the cooperative operation between water-soluble block and the water phase. If one block (or propagating chain) is too long and another block (or propagating chain) in the same copolymer molecule is too short, the copolymer molecule could be drawn from the interface into the phase

Table II   Results of Free Radical Interfacial Copolymerization of Acrylamide with Styrene for 10 h According to the Recipe in Table I

| Crude Polymer Yield (g) | Separation by Solvent Extraction | | | Acrylamide in block (wt %) |
	PAM (g)	PS (g)	Block (g)	
7.80	3.78	3.20	0.82	92.2

Table III   Effect of Styrene Concentration in the Oil Phase on the Generated Polymers[a]

No.	Styrene in Oil Phase (g)	PAM Generated in Water Phase (g)	M_W of PAM (10^6 g/mol)	PS Generated in Oil Phase (g)	M_W of PS (10^5 g/mol)	Copolymer (g)
1	2.50	5.17	4.69	0.41	0.48	0.25
2	5.00	4.73	4.27	1.23	1.35	0.65
3	10.00	3.78	4.11	3.20	2.41	0.82
4	15.00	3.70	3.62	4.20	3.83	0.96
5	26.65	3.64	3.46	4.94	4.56	1.10

[a] The polymerization condition is same as that given in Table I; only the added amount of styrene in the oil phase was changed under a constant oil phase volume of 25 mL. In the experiment 5, pure styrene was used (no solvent in the oil phase).

containing the long block. In general, the propagation rate of acrylamide is much greater than that of styrene; therefore, in the case of low styrene concentration in the oil phase, the copolymer molecules with a very short polystyrene block and a long polyacrylamide block could be generated and are possibly drawn into the water phase. To study this migration effect of the copolymer molecules, the interfacial copolymerization was also carried out with different styrene concentrations. For these experiments, the polymerization conditions were kept constant, as given in Table I. Only the added amount of styrene in the oil phase was changed under the constant oil phase volume of 25 mL. The experimental results are given in Table III. It can be seen from experiment 1 in Table III that the amount of polyacrylamide generated in the water phase is more than the amount of acrylamide originally added to the water phase at very low styrene concentration. This is because in the case of very low styrene concentration in the oil phase, some copolymer molecules with short polystyrene block could be formed at the interface and drawn into the water phase, leading to the increase of the obtained amount of polyacrylamide. The absorption bands at 1495, 760, and 700 cm^{-1} in the IR spectra of the in-water-phase-generated PAM in experiment 1 confirm the existence of the PS block in the generated PAM chains in experiment 1 and is good evidence for the migration of some copolymer molecules with short block of polystyrene from the interface into the water phase. Because the propagation rate of polystyrene block increases with increasing styrene concentration, the tendency of this migration of copolymer molecules from the interface into the water phase will decrease with increasing styrene concentration in the oil phase; and, finally, at a high styrene concentration, the migration of co-

polymers can be neglected to give a constant amount of polyacrylamide generated in the water phase, as can be seen from experiments 3 to 5 in Table III.

According to the proposed mechanism, the molecular weight of polyacrylamide generated in the water phase should be independent of the styrene concentration in the oil phase, but it is observed that the molecular weight of the polyacrylamide generated in the water phase at low styrene concentration is greater than that at high styrene concentration (Table III). This is possibly due to the fact that the polyacrylamide generated at low styrene concentration contains some copolymers with a short polystyrene block, which was drawn from the interface into the water phase; and, in the state of aqueous solution, the hydrophobic association of these short polystyrene blocks can lead to the increase of the apparent molecular weight of polyacrylamide.[9] Because the tendency of the migration of copolymer molecules decreases with an increase in the styrene concentration, the molecular weight of polyacrylamide should decrease with increasing styrene concentration and finally be constant at a high styrene concentration. This can be seen from experiments 4 and 5 in Table III. This dependence of molecular weight of polyacrylamide generated in the water phase on the styrene concentration in the oil phase is also an evidence of the migration of copolymer molecules and supports the proposed mechanism for this interfacial radical copolymerization.

CONCLUSION

The molecules of a synthesized amphiphilic bifunctional initiator, which have not only a hydrophilic and a hydrophobic group but also two func-

tional groups generating radicals in both ends of the molecules, can preferentially orient at the interface between the water phase containing a water-soluble monomer and the oil phase containing an oil-soluble monomer to initiate an interfacial copolymerization. An amphiphilic block copolymer of acrylamide with styrene can be synthesized by this novel free radical interfacial copolymerization. Under certain conditions, the at-the-interface-generated copolymer molecules can be drawn from the interface into the water phase.

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