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A novel free radical interfacial copolymerization

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SUMMARY

Free radical interfacial copolymerization which is carried out by means of an amphiphilic bifunctional initiator as a novel polymerization method was proposed for the first time. For utilizing the new polymerization method , an amphiphilic bifunctional initiator, palmitoyl (3-carboxy propionyl) sebacoyl diperoxide (PSD) , was synthesized and further used to initiate the free radical interfacial copolymerization of acrylamide (AM) with n-butyl methacrylate (n-BMA) which gave the amphiphilic PAM/PnBMA block copolymers. The resulting PAM/PnBMA block copolymers were purified by solvent extraction and characterized by elemental analysis, solubility, IR and DSC.

INTRODUCTION

In recent years, there has been considerable interest in amphiphilic block copolymers due to their potential applications as viscosifiers for enhanced oil recovery (EOR), as surface-active polymers for personal care products, as biocompatible materials in the biomedical field,[1] as moisture sensitive materials in the sensor technology, and for some other purposes. However, amphiphilic block copolymers can not easily be prepared because water-soluble and oil-soluble monomers have significantly different solubility characteristics. In general, four methods are used to synthesize these copolymers, i.e., (1) micellar copolymerization,[2] (2) homogeneous copolymerization,[3] namely, cosolvent method, (3) ultrasonic copolymerization, and (4) postpolymerization functionalization.[4] These methods have certain drawbacks, for example, copolymerization efficiency in method 1 is very low, method 2 and 3 lead to a statistical copolymer with extremely low molecular weight, and method 4 has limited uses owing to its special monomer selectivity.

In order to overcome these problems, we proposed a novel synthetic method in which an

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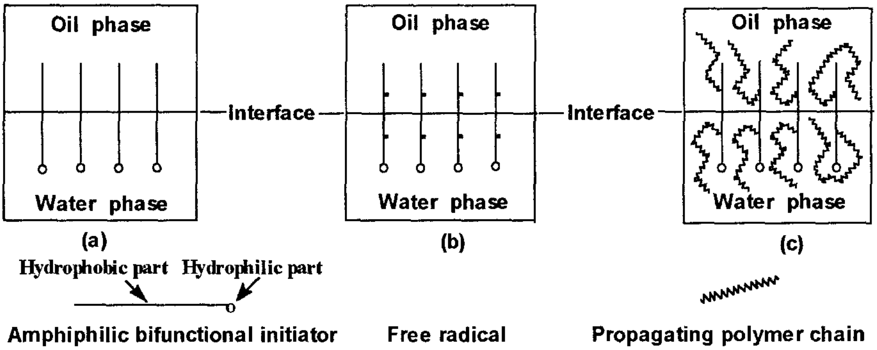
amphiphilic bifunctional initiator is used. The initiator carries not only hydrophilic and hydrophobic groups at both ends respectively but also two functional groups generating free radicals at both ends of the molecule .Therefore the initiator molecules can preferentially orient at the interface between water phase containing water-soluble monomers and oil phase containing oil-soluble monomers with the hydrophilic group drawing one functional group into the water phase and the hydrophobic group drawing the other functional group into the oil phase. Under certain conditions the two functional groups simultaneously generate free radicals to initiate the homopolymerization of the two types of monomers in their respective phase, as a result, amphiphilic block copolymers are formed at the oil-water interface. For this reason, the novel polymerization method which has not now been reported in the literature yet is called as free radical interfacial copolymerization. Its schematic representation of mechanism of polymerization was as follow :

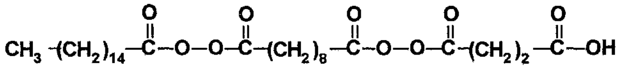


(a) : Hydrophilic and hydrophobic monomers are dissolved in water and oil phases respectively, the molecules of the amphiphilic bifunctional initiator orient at the oil-water interface.

(b) : The amphiphilic bifunctional initiator simultaneously generates free diradicals under certain conditions

(c) : The generating free diradicals simultaneously initiate homopolymerizations of hydrophilic and hydrophobic monomers at two phases respectively, as a result, amphiphilic block copolymers are formed at the oil-water interface.

For approaching this goal, an amphiphilic bifunctional initiator, palmitoyl (3-carboxy propionyl) sebacoyl diperoxide (PSD), was designed and synthesized, whose structure is shown below :



$$CH_3-(CH_2)_{14}-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-(CH_2)_2-\overset{O}{\overset{\|}{C}}-OH$$

which was further used for the synthesis of the amphiphilic acrylamide-n-butyl methacrylate (PAM/PnBMA) block copolymer. Subsequently, the block copolymer was characterized by solubility, IR, DSC and elemental analysis.

EXPERIMENTAL

Materials: n-butyl methacrylate was purified by distillation under reduced pressure before use, acrylamide (analytically pure), decane (chemically pure) and water (distilled water) were directly used without any further purification . The amphiphilic bifunctional initiator (PSD) was synthesized by the successive condensations of sebacoyl chloride with perpalmitic acid and monoperoxysuccinic acid.

Measurements: The IR spectra, as KBr disks, were recorded on Perkin-Elmer 1600 series infrared spectrophotometer. Elemental analysis to determine carbon, hydrogen and nitrogen content of the pure block copolymer was conducted by elemental analysis laboratory of Institute of Chemistry, Academia Sinica. DSC experiments were run on a Perkin-Elmer DSC-7 differential scanning calorimeter, DSC traces were taken from the scan at a heating rate of 10℃/min.

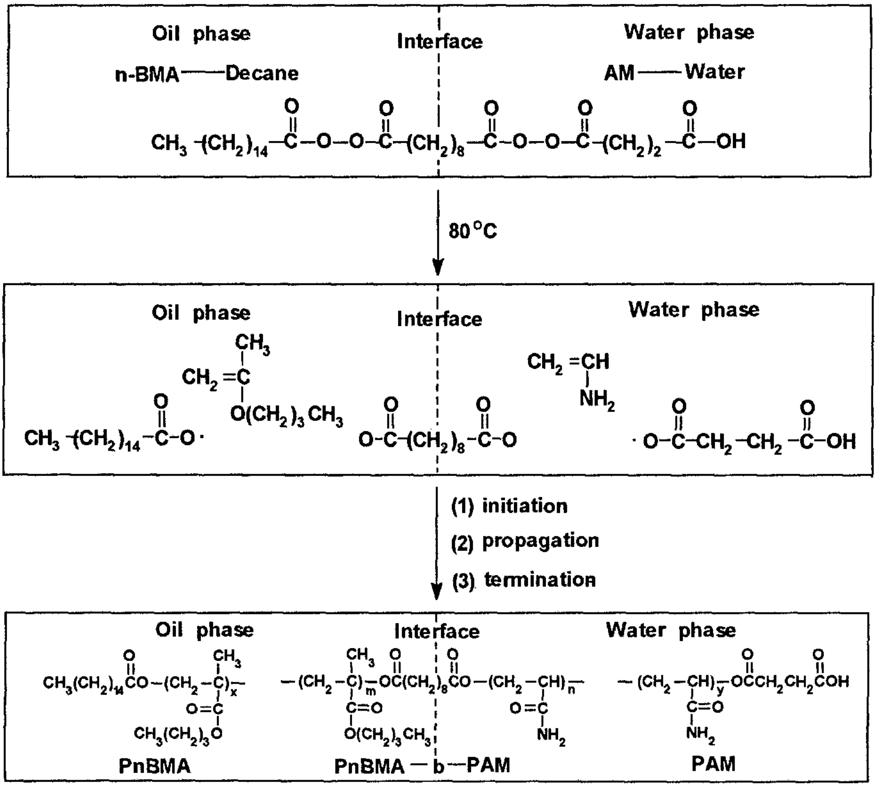
Free radical interfacial copolymerization : A water phase was obtained by acrylamide being dissolved in water, similarly, a oil-phase, n-butyl methacrylate, decane. The two phase were degassed in a continuous stream of nitrogen for 30 min. respectively. Under a nitrogen atmosphere, the water phase were first placed in a Pyrex phial, and the amphiphilic bifunctional initiator (PSD) was then added to the water phase , the oil phase was finally added. Subsequently the phial was quickly sealed with a rubber stopper equipped a thermometer. The reaction was allowed to proceed at 80 ℃ for 10h. The resulting polymers were precipitated from methanol, and washed with it several times. The precipitate was then filtered and dried in vacuum at room temperature. The crude polymers were purified by solvent extraction , using water to remove polyacrylamide homopolymer, acetone , poly (n-butyl methacrylate) homopolymer, respectively. At last, the polymer which dissolve in neither water nor acetone was obtained as a pure copolymer. The polymerization recipe is given in Tab.1.

Tab. 1. Recipe for free radical interfacial copolymerization of acrylamide with n-butyl methacrylate with PSD

Water phase	
Amount of acrylamide	5.00 g
Amount of water	20.65 g
Oil phase	
Amount of n-butyl methacrylate	10.00 g
Amount of decane	9.36 g
Amount of amphiphilic bifunctional initiator (PSD)	30.0 mg
Diameter of interface	3.50 cm
Temperature	80 ℃

RESULTS AND DISCUSSION

The water phase was formed by the water-soluble monomer acrylamide being dissolved in water , similarly the oil phase was formed by the oil-soluble monomer n-butyl methacrylate , which is not dissolved in water , being dissolved in decane. There is no doubt that there is a oil-water interface between the two phases. Because of its possessing structure analogous to surfactants, the amphiphilic bifunctional initiator (PSD) which initiated the free radical interfacial copolymerization of the two monomers , can preferentially orient at the interface with its hydrophilic group ($-\mathrm{COOH}$) drawing the functional group ($-\mathrm{C(O)OOC(O)}-$) near the hydrophilic group into the water phase and its hydrophobic group $(\mathrm{CH_3(CH_2)_{14}}-)$ drawing the functional group ($-\mathrm{C(O)OOC(O)}-$) near hydrophobic group into the oil phase. The initiator(PSD) simultaneously decomposed into radicals $\cdot\mathrm{OC(O)(CH_2)_8C(O)O}\cdot$, $\mathrm{CH_3(CH_2)_{14}C(O)O}\cdot$ and $\cdot\mathrm{OC(O)(CH_2)_2C(O)OH}$ at 80℃. The free diradicals $\cdot\mathrm{OC(O)(CH_2)_8C(O)}\cdot$ oriented at the interface and initiated the homopolymerization of the two monomers in their respective phase at the same time, as a result , the amphiphilic block copolymer PAM-b-PnBMA was formed at the oil-water interface . But the free radicals $\mathrm{CH_3(CH_2)_{14}C(O)O}\cdot$ and $\cdot\mathrm{OC(O)(CH_2)_2C(O)OH}$ resulted in the formations of the homopolymers of acrylamide and n-butyl methacrylate in the two phases respectively in this polymerization procedure. The proposed polymerization process is as follow.



Since formation of the homopolymers of acrylamide and n-butyl methacrylate together with the block copolymers PAM-b-PnBMA can not be avoided , separation procedures have to be carried out by solvent extraction, namely, the homopolymers of acrylamide and n-butyl methacrylate were removed by water and acetone respectively. The separation results are shown in Tab. 2.

Tab. 2. Results for free radical interfacial copolymerization of acrylamide with n-butyl methacrylate initiated with PSD for 10 h

Crude polymer yield	**Separation by solvent extraction**			**Elemental analysis (wt. %) of the block copolymer purified**			**Acrylamide in block**
	PAM	**PnBMA**	**Block**				
g	**g**	**g**	**g**	**C**	**H**	**N**	**(wt. %) a**
9.63	2.02	6.84	0.77	49.00	7.67	15.26	77.39

a) PAM (wt. %) = (71/14) × N %

The block copolymer is characterized itself in the dissolution behavior. Because of the great difference of polarity of the two segments incorporated in a same chain, most solvents such as toluene, THF, chloroform, ethanol, and DMF are unable to dissolve or disperse PAM-PnBMA block polymer. Up to now, the solvents for the block copolymer are not founded yet, which offers a good evidence to the nature of block structure.

The composition of the pure block copolymer calculated from results of elemental analysis is given in Tab. 2.

The block copolymer structure was elucidated by means of IR spectral measurement (figure 1). The absorption bands characteristic of polyacrylamide are at 3200, 1668, 1616, 1416 cm^{-1}, and of poly (n-butyl methacrylate) at 1731, 1243, 1178, 1150, 950 cm^{-1}.

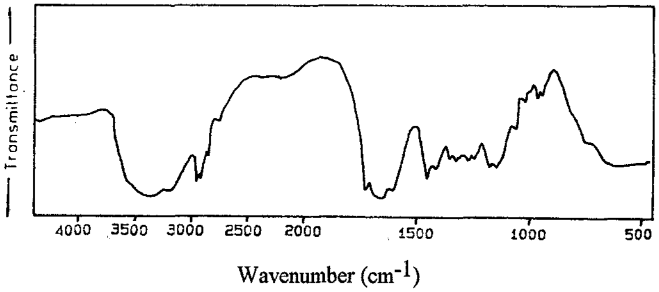
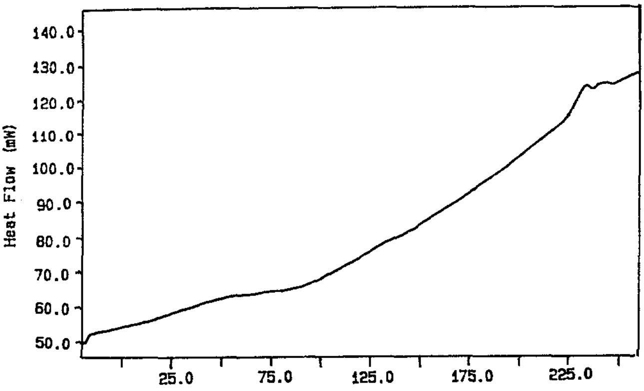


Fig. 1 IR spectrum of the poly (acrylamide-b-n-butyl methacrylate) block copolymer

The DSC curve of the block polymer was shown in figure 2. Two glass transition temperatures corresponding to PAM and PnBMA segments present at 225 ℃ and 35 ℃ respectively .The Tg for polyacrylamide under the same conditions was 222 ℃ ,and for poly(n-butyl methacrylate), 36.4℃.



Temperature (℃)

Fig.2 DSC curve of the poly (acrylamide-b-n-butyl methacrylate) block copolymer

Based on these findings, it is clear that amphiphilic block copolymers are able to be synthesized by our method.

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