

SYNTHESIS OF POLYBUTADIENE MACROINITIATOR AND POLY- BUTADIENE/POLYACRYLAMIDE BLOCK COPOLYMERS*

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ABSTRACT

An azo-group containing polybutadiene macroinitiator was prepared by Pinner synthesis and characterized by IR, NMR, GPC, viscosity and elemental measurements. The macroinitiator was further used to polymerize acrylamide (AAM) in benzene to form polybutadiene/polyacrylamide (PBD/PAAm) block copolymers. High conversion of AAM was obtained over a wide range of monomer/macroinitiator ratios. The PBD/PAAm block copolymers were found to have excellent solvent resistance.

INTRODUCTION

Most of commercially available block copolymers are manufactured by living anionic polymerization. Although this technique enables the preparation of block copolymers consisted of uniform lengths of segments, it requires strict elimination of moisture or oxygen. Furthermore, the kinds of monomers suitable for such anionic polymerization are rather limited.

Recently, free-radical polymerization has been widely used to synthesize block copolymers^[1-4]. The preparation of block copolymers by this mechanism may be accomplished by using a polymeric initiator, such as polyazoester, which is consecutively decomposed into two or more different kinds of monomers^[5-8], or simply in one step by using a polymeric initiator

* This work was supported by the National Natural Science Foundation of China (Grant 2907200)

Received February 26, 1994

containing blocks derived from telechelics^[2, 9-11]. Ethylene glycol, propylene glycol and telechelic polytetrahydrofuran have been used as the diol components in the syntheses of azo-containing macroinitiators^[1]. Free radical process is specially suitable for the syntheses of block-type amphiphilic polymers, since most of the water-soluble monomers are not anionically polymerizable.

We have synthesized polystyrene/poly (methacrylic acid)^[7] and polystyrene/polyacrylamide^[8] block copolymers by using a polyazoester as the initiator. In this work, an azo-containing polybutadiene macroinitiator was prepared by Pinner synthesis from telechelic polybutadiene with hydroxy ends, and the macroinitiator was further used to synthesize polybutadiene/polyacrylamide (PBD/PAAm) block copolymers.

EXPERIMENTAL

Materials

2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from benzene and dried under vacuum. The telechelic liquid polybutadiene with hydroxy end groups was kindly distributed by Jinzhou Petroleum Company. Its number average molecular weight was 1780 g/mol according to hydroxy-content analysis, and its 1,2-contents was 21.3 mol% according to ¹H NMR spectrum. Benzene was refluxed with CaH₂ overnight and distilled under nitrogen. Acrylamide (AAm) was recrystallized twice from acetone and dried in vacuum. Other chemicals used were all of reagent grade.

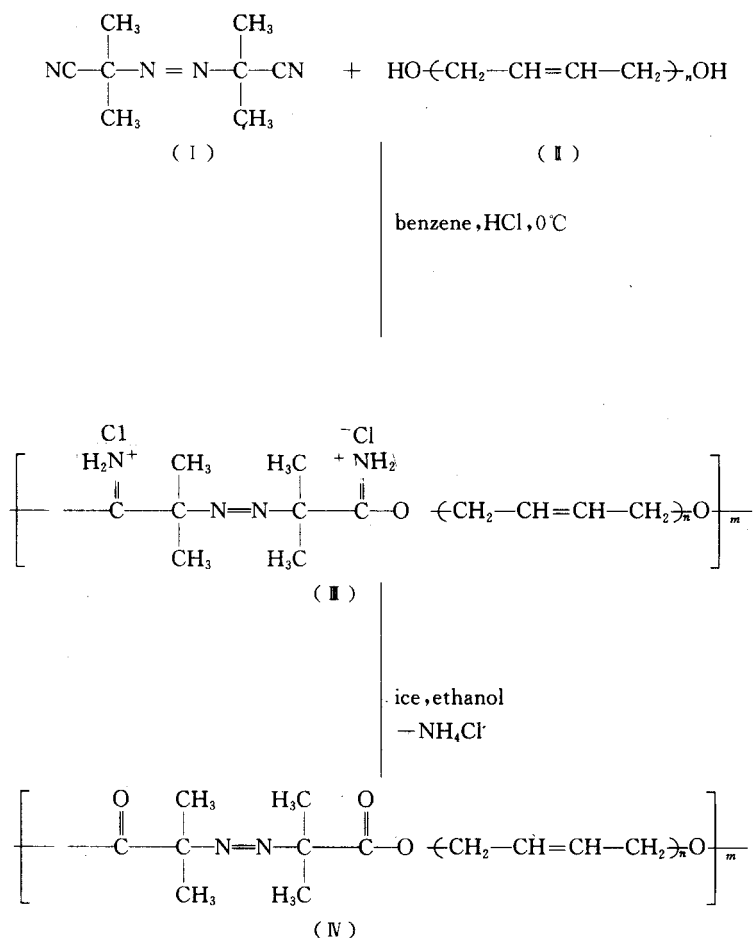
Measurements

Infrared spectrum was recorded on a Perkin-Elmer 580 B IR spectrometer. ¹H NMR spectra were taken on a JEOL FX 100 NMR spectrometer by using CDCl₃ as the solvent at room temperature. GPC measurements were carried out by means of a Shimadzu high-performance liquid chromatograph LC-6A with THF as solvent. The intrinsic viscosities were measured in benzene solution using an Ubbelohde capillary viscometer at 30.0 ± 0.1 °C. The total conversion of AAm was obtained by titrating the unreacted monomer, similar to Sigga's procedure for determination of unsaturated compounds^[12].

RESULTS AND DISCUSSION

Synthesis and characterization of polybutadiene macroinitiator

The azo-containing polybutadiene macroinitiator was synthesized by the Pinner synthesis from AIBN and telechelic polybutadiene with OH-endgroups, as shown in Scheme 1. Into a 500 ml three-necked round flask were added 140 g of liquid hydroxy-ended telechelic polybutadiene and 200 ml of benzene. The resulting solution was cooled down to 5–10 °C and then bubbled with dry HCl gas to saturation. A solution of 12.9 g of AIBN in 80 ml of benzene was then introduced, and the reaction mixture was further



Scheme 1

cooled to 0°C. The temperature was kept at 0°C while bubbling HCl gas.

As the reaction proceeded, the reaction mixture turned to a brown gel-like material, due to the interactive nature of the intermediate ionomer (III). After the reaction for 24h, 100 ml of pre-cooled ethanol and 100 g of crashed ice were then added under stirring. The mixture was transferred into a separating funnel, and washed succesively with water and ethanol 3—4 times to remove NH_4Cl and benzene. The recovered polybutadiene-based polyazoester was washed quickly with ethyl ether 1—2 times, and then dried in vacuum at room temperature.

Fig. 1 shows the IR spectrum of the azo-functionalized polybutadiene. The appearance of 1730 cm^{-1} band is in accordance with the structure of the polyazoester. ^1H NMR spectrum of the macroinitiator (Fig. 2) shows a new peak at 1.45 ppm, which can be attributed to the methyl protons came from AIBN units. The chemical shift of methyl protons of AIBN is 1.72 ppm, and the band shift from 1.72 to 1.54 ppm is in agreement with the substitution of nitrile groups with ester groups. According to the attribution of methyl protons of AIBN units in the ^1H NMR spectrum, we calculated that the molar ratio of AIBN unit/butadiene prepolymer was 1.06, which well agrees with the structure of the macroinitiator shown in Scheme 1.

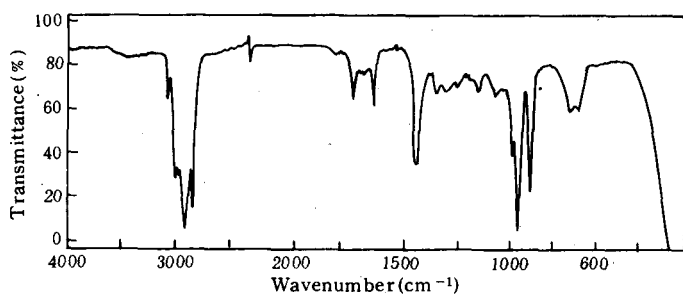


Fig. 1 Infrared spectrum of azo-containing polybutadiene macroinitiator

However, elemental analysis showed lower nitrogen content of the resulting macroinitiator, as listed below:

	C%	H%	N%
calculated	84.76	10.59	1.41
found	84.38	11.67	0.98

This phenomenon should be due to the difficulty of the second heterogeneous reaction between water and the gelled product, which resulted in partial thermal decomposition of the azo groups.

The GPC curves of the polybutadiene macroinitiator and the prepolymer are shown in Fig. 3. According to PSt standards, the M_w and M_n of the macroinitiator and the butadiene prepolymer are 41,000, 6,220, and 19,000, 3,910 g/mol, respectively. The intrinsic viscosity of the macroinitiator in benzene at 30°C was found to be 22.1 ml/g, being higher than 17.3 ml/g of the telechelic prepolymer. When ethylene glycol, propylene glycol or telechelic polytetrahydrofuran was used as the diol component in the Pinner synthesis, the degree of polymerization ($\overline{DP}$) was found to be in the range of 2–18, depending on the structure of the diol used^[1]. The estimated ($\overline{DP}$) value of the polybutadiene macroinitiator is about 2. The relatively lower ($\overline{DP}$) value is partly connected with the gelation in the first step shown in Scheme 1.

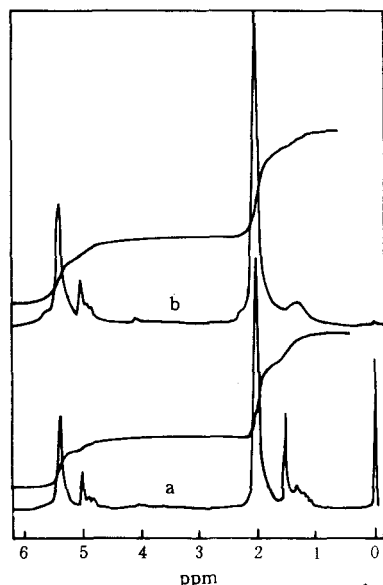


Fig. 2 ^1H NMR spectra of azo-containing polybutadiene macroinitiator (a) and butadiene prepolymer (b)

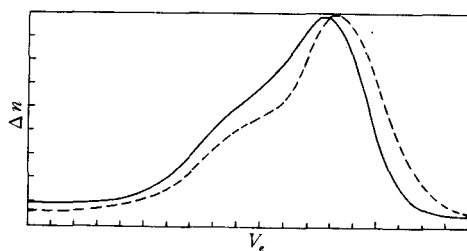
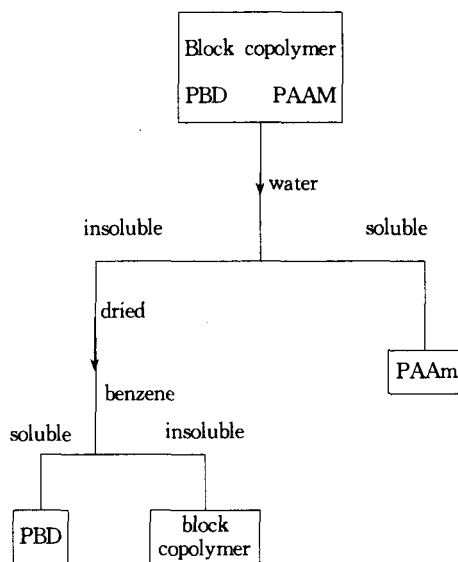


Fig. 3 GPC curves of azo-containing polybutadiene macroinitiator (solid line) and butadiene prepolymer (broken line)

Synthesis and purification of PBD/PAAm block copolymers

When the polybutadiene macroinitiator is used, the PBD/PAAm block copolymers can be prepared in one step. The synthesis was performed in a 500 ml three-necked flask with a stirrer, a reflux condenser and a nitrogen

inlet. The azogroup-containing polybutadiene macroinitiator, AAm and 100 ml of benzene were added to the flask. The reaction mixture was degassed by bubbling nitrogen for 30 min, and the polymerization was effected under a slight positive pressure of nitrogen in a thermostat kept at 80°C. AAm was quickly dissolved at the reaction temperature. As the polymerization proceeded, the reaction mixture became turbid and its viscosity increased apparently. After 6 hours of the reaction, the polymer was isolated by precipitation with ethanol and filtration, and then dried in vacuum at about 50 °C.



Scheme 2

As homopolymers were unavoidably produced together with the block copolymer in this process, the crude polymer was purified by selective solvent extraction at room temperature. The separation procedure is given in Scheme 2. The composition of both crude polymers and purified block copolymers were obtained by elemental analysis. Keeping in mind that amphiphilic polymers would absorb a certain amount of water, just like water-soluble polymers, the normalized data of nitrogen content were used in the following formula^[8]:

$$\text{PAAm wt \%} = \frac{71}{14} \text{ N \%} \quad (1)$$

The polymerization recipe and the results are listed in Table 1.

Oppenheimer and Heitz^[13] found that constant conversions were only obtained at a higher ratio of monomer to macroinitiator when azo-containing

polystyrene was used for polymerizing methyl methacrylate. It can be seen in Table 1 that AAm conversion was high over a wide range of monomer/macroinitiator ratio, and that the monomer conversion became somewhat lower when the ratio of monomer/macroinitiator was either very large or very small. These phenomena were also observed when azo-containing polystyrene was used for AAm polymerization^[8].

Table 1 Summarized data for synthesis and purification of PBD/PAAm block copolymers

Code	Polymerization recipe		Conversion	Crude polymer		Purified block copolymer		Homo-PBD/ pre-PBD	Homo-PAAM/ PAAM
	macro-initiator	AAm	of AAm	yield	PAAM content	weight	PAAM content		
	(g)	(g)	(%)	(g)	(wt %)	(g)	(wt %)	(%)	(%)
1	3	1.5	85.2	2.72	44.4	1.84	70.6	82.0	0
2	3	3.0	95.4	5.09	57.0	3.67	68.0	61.0	12.8
3	3	6.0	93.5	7.69	72.1	6.28	71.3	39.9	20.1
4	3	10.0	94.5	11.86	84.4	9.63	76.9	26.0	21.6
5	3	15.0	94.8	16.74	84.8	12.93	84.1	31.3	23.6
6	0.5	15.0	77.8	10.81					

According to the results of solvent extraction, the fraction of homopolymers can be calculated by the following equations:

$$\text{homo-PBD/pre-PBD (\%)} = \frac{W_p - W_b(1 - \text{PAAm wt \%})}{W_p} \quad (2)$$

$$\text{homo-PAAm/PAAm (\%)} = \frac{W_a C\% - W_b \text{PAAm wt \%}}{W_a C\%} \quad (3)$$

where W_p , W_a and W_b are the weight of pre-PBD, AAm and block copolymer, respectively, PAAm wt % is the weight percentage of PAAm in the block copolymer, and C % is the AAm conversion. As shown in Table 1, the content of homo-PBD decreased, while the content of homo-PAAm increased, with the increase of AAm/pre-PBD ratio in the feed. Since the block copolymer with short chain of PAAm segment had low molecular weight and was lost in the precipitation and purification procedures, block copolymers with lower PAAm content were not obtained. It can also be expected that the data of homo-PBD/pre-PBD in Table 1 are larger than the real values, especially in the case of lower AAm/pre-PBD ratio.

The most important characteristic of PBD/PAAm block copolymers is their behaviour of dissolution. Due to the great difference of polarity of the

two segments incorporated in a single chain, most common solvents, such as water, benzene, ethanol, THF and DMF, do not dissolve or disperse these block copolymers. This excellent solvent resistance is a good evidence for block structure of the prepared polymers.

Keywords:

Azo-containing polybutadiene macroinitiator; PBD/PAAm block copolymer; Amphiphilic polymer

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