

Preparation and Characterization of Amphiphilic Block Copolymer of Polyacrylonitrile-*block*-Poly(ethylene oxide)

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ABSTRACT: The synthesis of polyacrylonitrile-*block*-poly(ethylene oxide) (PAN-*b*-PEO) diblock copolymers is conducted by sequential initiation and Ce(IV) redox polymerization using amino-alcohol as the parent compound. In the first step, amino-alcohol potassium with a protected amine group initiates the polymerization of ethylene oxide (EO) to yield poly(ethylene oxide) (PEO) with an amine end group (PEO-NH₂), which is used to synthesize a PAN-*b*-PEO diblock copolymer with Ce(IV) that takes place in the redox initiation system. A PAN-poly(ethylene glycol)-PAN (PAN-

PEG-PAN) triblock copolymer is prepared by the same redox system consisting of ceric ions and PEG in an aqueous medium. The structure of the copolymer is characterized in detail by GPC, IR, ¹H-NMR, DSC, and X-ray diffraction. The propagation of the PAN chain is dependent on the molecular weight and concentration of the PEO prepolymer. The crystallization of the PAN and PEO block is discussed. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1753–1759, 2003

Key words: anion; ethylene oxide; block copolymer

INTRODUCTION

The synthesis of block copolymers is one of the prospective trends in polymer modification. This process allows for the preparation of polymeric products with macromolecules containing segments of various chemical compositions and physicochemical properties. Polyacrylonitrile (PAN) fibers have many valuable properties and some drawbacks. These disadvantages include high susceptibility to static electrification, low abrasion resistance, and low moisture content. The synthesis of block copolymers of PAN and poly(ethylene oxide) (PEO) may remedy the situation.

Several research groups^{1–3} obtained PAN-*block*-poly(ethylene glycol) (PAN-*b*-PEG) block copolymers, using Ce(IV) salts as oxidizing agents. The product was either a bi-, tri-, or multisegment block copolymer of PAN-*b*-PEG, and even some crosslink polymer, depending on the number of functional —OH groups. Wodka^{4,5} synthesized a PAN-*b*-PEO block copolymer using a PEO prepolymer containing a xanthate group and an azo group, but the chromatograms of the block copolymers showed a multiblock distribution.

Ce(IV) salts in aqueous acidic solution either by themselves⁶ or in combination with reducing agents⁷ are well-known initiators for vinyl polymerization. The reducing agent may be alcohols,⁸ polyols,⁹ ketones,¹⁰ amino acids,¹¹ amines,¹² and so forth. The resulting polymers were suggested to have chain ends of a corresponding reducing agent moiety. This method was used for the preparation of graft and block copolymers. Compared to other methods of block copolymerization, this type of redox polymerization possesses a number of technical and theoretical advantages. Because of its applicability at low temperatures, side reactions can be minimized.

In the present work, we use anion polymerization to obtain a PEO-NH₂ prepolymer that contains only one functional —NH₂ group at first. Then the two block copolymers (PAN-*b*-PEO) are obtained through redox polymerization of the monomers by using PEO-NH₂ as the reducing agent and Ce(IV) as the oxidant in an aqueous medium. We also study the difference of polymerizations between the PEG and PEO-NH₂ as the reducing agents in the same redox system and the difference in the PEO crystallinity in PAN-PEG-PAN triblock and PAN-*b*-PEO diblock copolymers.

EXPERIMENTAL

The procured EO (Shanghai Gaoqiao Third Chemical Factory) was dried with calcium hydrate; the AN (Shanghai First Chemical Reagent Factory) was distilled under an N₂ atmosphere before use. Amino-alcohol from Shanghai Gaoqiao Third Chemical Fac-

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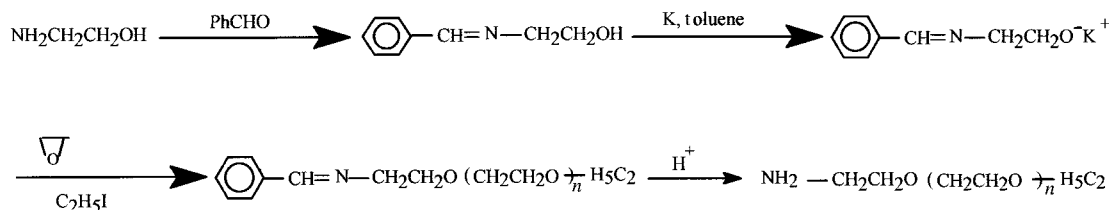
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tory was utilized. All other solvents were purified by conventional drying and distillation procedures.

Fluka PEG with a molecular weight of 2000 was used. Ceric ammonium nitrate (AR, Shanghai First Chemical Reagent Factory) was oven dried at 105°C for 1 h and then desiccator dried over phosphorous pentoxide prior to use.

Protection of amino group of amino-alcohol

We introduced 106 g (1 mol) of benzaldehyde into a three-neck flask fitted with a stirrer and 61.1 g (1 mol)



Preparation of PAN-*b*-PEO and PAN-PEG-PAN

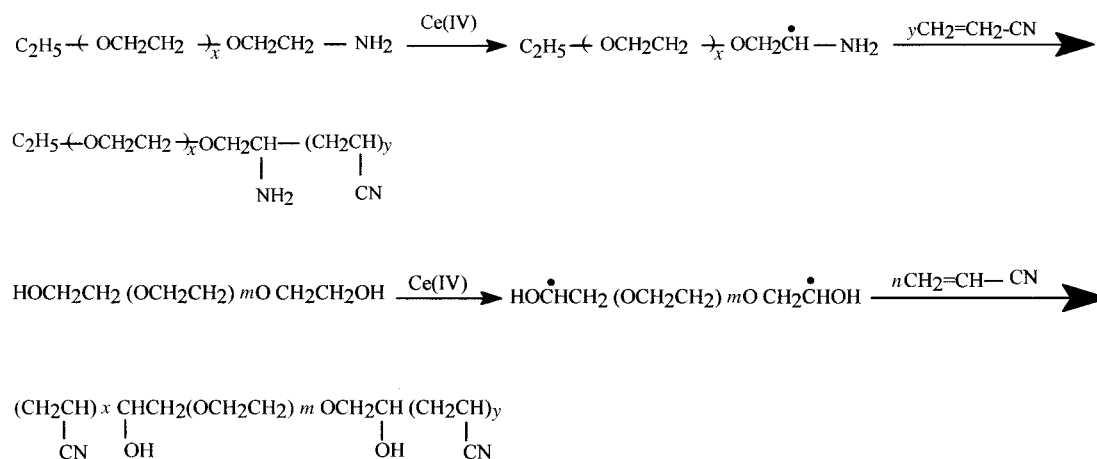
The synthesis of the block copolymers was carried out in an aqueous medium. A three-necked flask equipped with a stirrer, a reflux condenser, and a capillary supplying nitrogen was used for all the polymerization experiments. The AN, PEG, or PEO-NH₂ were placed in the flask. The system was thermostated at 40°C. The ceric ammonium nitrate in 1M nitric acid

of amino-alcohol was added dropwise from a funnel in a nitrogen atmosphere. The reaction was stirred for 12 h at ambient temperature. Then the product was distilled at low pressure.

Preparation of PEO with amine end group

The anionic polymerization of EO using protected amino-alcohol potassium as an initiator was similar to that described by Huang,¹³ which is presented here briefly:

was then added dropwise to the reaction mixture, and the polymerization was allowed to proceed with stirring in the dark for 2 h. The precipitated polymer was thoroughly washed first with water and then with methanol to removed unreacted PEG if present and dried at 60°C in a vacuum. The block copolymers thus synthesized were dissolved in DMF and reprecipitated with methanol. The mechanism is as follows^{14,15}:



Characterization

The IR spectra were obtained on a Nicolet Nexus 470 FTIR spectra spectrometer. The ¹H-NMR was recorded on a Bruker Avance 500 NMR spectrometer with TMS as the internal standard and DMSO as the solvent. The UV spectra were scanned on a Beckman DU-7 spectrometer. DSC studies were conducted with a Netzsch 204 in a nitrogen atmosphere at a heating rate of 10°C/min. Elemental analysis was carried out with a PE series two-

element analyzer. X-ray diffraction analysis was made with a DMAX/RB X-ray diffraction instrument.

The number-average molecular weight of the polymer was derived with a Perkin-Elmer 200 GPC chromatograph under the following conditions: 1.2-m column length, crosslinked polystyrene gel filler, 0.1-mL injection volume (0.1 g/mL concentration), DMF as the solvent and eluent, 1.2 mL/min flow rate, and 60 kg/cm² pump pressure. The chro-

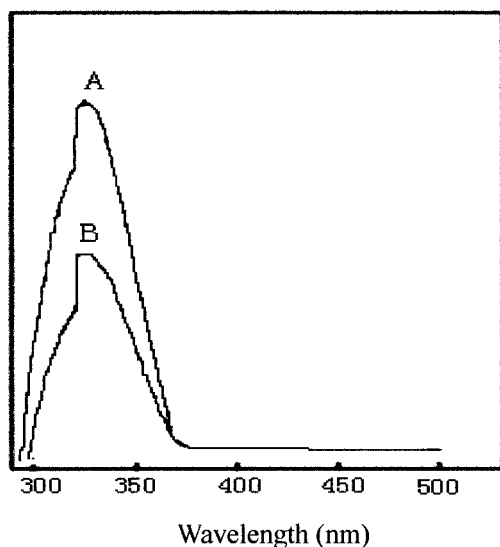


Figure 1 The UV spectra of a mixture of TCNE with aminoalcohol (curve A) and a mixture of TCNE with PEO-NH₂ prepolymer (curve B) with a ratio of 1:1 mol/mol (CH₂Cl₂ as solvent, concentration = 1.0×10^{-4} mol/L).

matograph was calibrated with standard polystyrene samples.

The molecular weights (M_w) of the copolymers were calculated from a single-point viscosity measurement at 25°C using a DMF solution for block copolymers and making use of the following equation¹⁶:

$$[\eta] = 2.33 \times 10^{-4} \times M_w^{0.75}$$

RESULTS AND DISCUSSION

Characterization of PEO-NH₂ prepolymer

The presence of the recovered amino group could be established by the UV spectra of the complex formed

with tetracyanoethylene (TCNE) and PEO-NH₂ as shown in Figure 1.

In Figure 1 shows the UV absorbance spectra of a small amine and PEO-NH₂ with a TCNE mixture. Their maximum absorbance peaks were located at 326 nm. This was attributed to the formation of a complex between TCNE and the amine end group of PEO-NH₂ through charge transfer. This is a very sensitive method to check whether the amine group existed in a molecule.¹⁷ The UV absorbance spectra of TCNE mixed with the various substituted amine groups have a characteristic absorbance in different wavelength areas, so they can be used to decide the substitution pattern of amine groups.¹⁸ With the measurement of the UV absorbance spectra, we may find that various substituted amine end groups of the PEO prepolymer would be obtained by using THF as the solvent in anion polymerization, but a similar phenomenon could not occur when using toluene as the solvent; that is, there is only the PEO-NH₂ prepolymer with a primary amine end group. The reason is under study now.

Determination of PAN-*b*-PEO

The purified PAN-*b*-PEO was characterized in detail by IR, NMR, and GPC. Figure 2 shows its IR spectrum. The strong band at 1101.17 cm^{-1} corresponding to the (C—O—C) stretching vibration of PEO-NH₂ and the other one at 2244.7 cm^{-1} (—CN stretching vibration) attributed to PAN confirm the formation of PAN-*b*-PEO. From the ¹H-NMR spectrum (Fig. 3), the chemical shift values at 2.08 (—CH₂) and 3.15 ppm (—CH) for PAN and 3.53 ppm (—CH₂CH₂O—) for PEO also establish the existence of PAN-*b*-PEO. In Figure 4 the GPC curves for PAN-*b*-PEO show the retention volume of the block copolymer; its molecular weight is

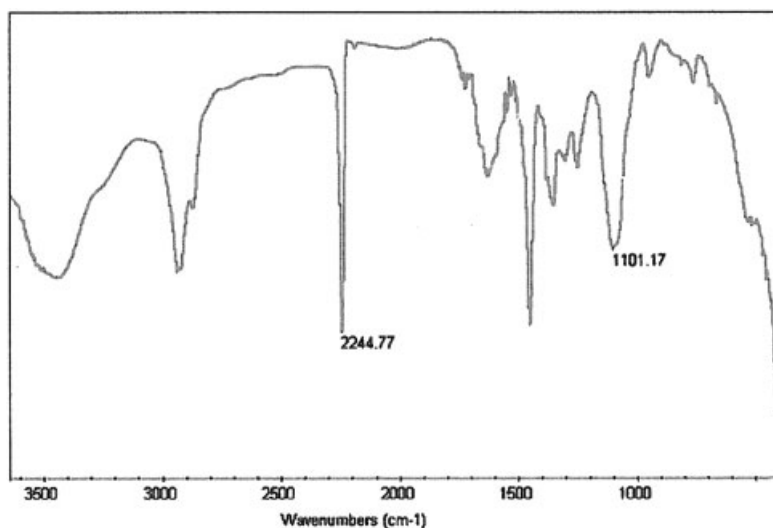


Figure 2 The IR spectrum of PAN-*b*-PEO.

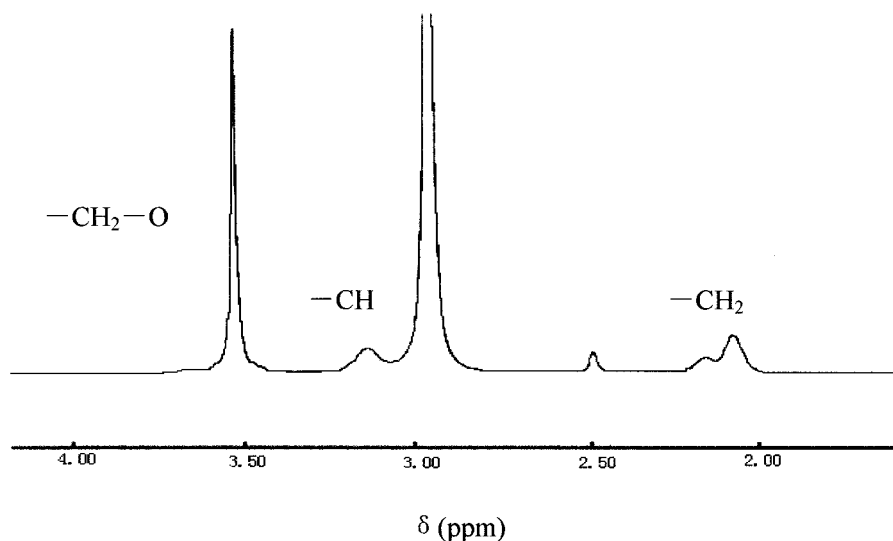


Figure 3 The $^1\text{H-NMR}$ spectrum of PAN-*b*-PEO.

about 6.79×10^4 , and the molecular weight distribution is 1.96. Moreover, there is only one peak for the block copolymer sample. Therefore, we may conclude that PAN-*b*-PEO was prepared by sequential initiation of anionic and redox copolymerizations.

Effect of concentration of PEO-NH₂ on block copolymerization

Figure 5 shows the dependence of the yield, composition, and molecular weight of the block copolymer on the prepolymer content in the reaction mixture. The yield curve shows a parabolic shape initially and then it decreases. This is an unusual phenomenon because the increase of the prepolymer content in the reaction mixture should bring about a higher yield and increased PEO-NH₂ quantity in the prepolymer thus obtained. The three possible reasons responsible for this phenomenon follow.

First, in the water, part of the amino groups would be enveloped because of the entanglement of PEO-NH₂ chains, so the efficient concentration of amino groups is decreased. As is well known, the entanglement density of the polymer chain is dependent on the molecular weight and concentration of macromole-

cules. When the concentration of PEO-NH₂ in the reaction mixture is low, the entanglement density of PEO-NH₂ in a dilute solution is rather small, the amino end groups are laid bare, and the behavior of PEO-NH₂ in the polymerization of AN in this case is very similar to that of a small amine molecule. After that the entanglement density is gradually raised with the increase in the concentration of PEO-NH₂; however, only when the concentration of PEO-NH₂ approaches a critical value are the amino end groups really covered, and thus the rate of polymerization starts to decrease.

Second, when the concentration of PEO-NH₂ is greater than the critical value, hydrogen bonds of the intra- or intermacromolecules, which are due to the interaction between the oxygen atoms of PEO-NH₂ and the hydrogen atoms of the amino end groups,

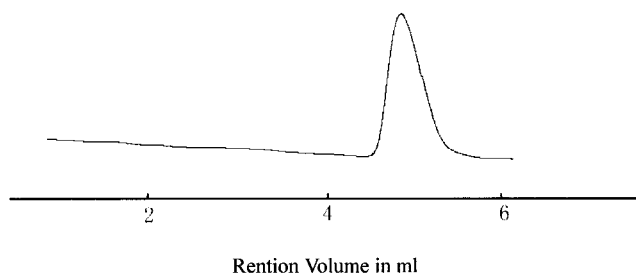


Figure 4 The GPC measurement of PAN-*b*-PEO.

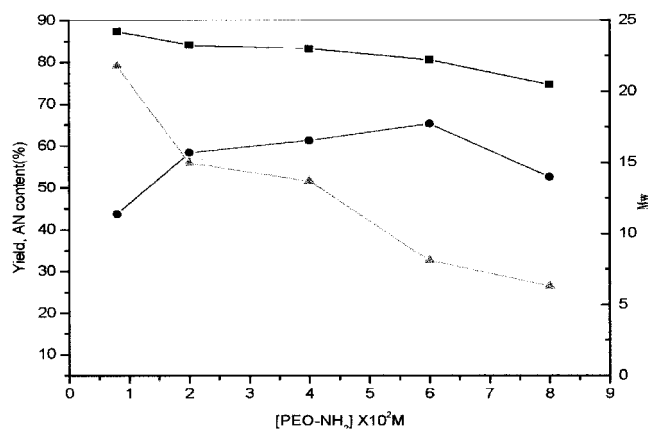


Figure 5 The effect of the PEO-NH₂ concentration on the yield, composition, and molecular weight of the block copolymer: [AN] = 0.8M, [Ce(IV)] = 0.06M, $t = 2$ h, $T = 40^\circ\text{C}$; (●) yield, (■) AN content, (▲) molecular weight ($\times 10^{-4}$).

TABLE I
Effect of Molecular Weight and Type of Macromonomer on Polymerization of Block Copolymers

Monomer	Yield (%)	PAN Content in Copolymer (%)	M_w ($\times 10^{-4}$)
PEG2000	81.9	78.9	6.4
PEO-NH ₂ 2000	65.3	80.5	8.1
PEO-NH ₂ 5000	48.9	67.7	12.9

may be formed and the initiation of PEO-NH₂ may be difficult, so the concentration of radicals decreases, leading to the drop of the polymerization rate.¹⁹

Third, it should be pointed out that the PEO-NH₂ segment in the PAN-*b*-PEO block copolymers is soluble in water. The increase of the concentration of PEO-NH₂ in the reaction mixture brings about the appearance of greater numbers of active centers. That would lead to the formation of block copolymers with very short PAN blocks. Such block copolymers can contain a small amount of macromolecule fractions of short PAN blocks that cannot be precipitated from the reaction mixture, and they can be removed when washing the products with water and methanol.

The increased concentration of PEO-NH₂ prepolymer leads to the formation of a higher number of free radicals. For this reason, more growing macromolecules are formed in the reaction system; but they have shorter PAN segments, so the molecular weight of the block copolymer shows a decreasing inclination.

Effect of molecular weight of PEO-NH₂ prepolymer on polymerization

When keeping the same polymerization conditions, the yield of the product would be decreased by increasing the PEO-NH₂ molecular weight as shown in Table I. This could also be explained from the viewpoint of the entanglement of macromolecule chains as mentioned above. The entanglement density of the long chains is certainly greater than the short ones and it is closely related to the decrease of the radical concentration.

As can be seen from Table I, the molecular weight of the PAN-*b*-PEO block copolymers increases with the increasing of PEO-NH₂ molecular weight.

Effect of monomer of PEG or PEO-NH₂ on polymerization

Table I also gives data related to yield, composition, and molecular weight of block copolymers with different macromonomers. Some interesting results were derived; that is, in similar conditions, the yield of the block copolymer obtained by using PEO-NH₂ as the monomer is lower than that by using PEG; conversely, the AN contents and the molecular weight of the block

copolymer are higher. From the experimental results we observed that the polymerization by using PEO-NH₂ as the monomer has an induction period. Considering the radical polymerization, the initiation reaction is the key to deciding the polymerization rate, so the rate of polymerization by using PEO-NH₂ as the monomer is slower than that with PEG and the radical concentration of PEO-NH₂ is decreased. Thus, the molecular weight of the block copolymer and the composition of AN increase because of the inverse dependence of the molecular weight on the concentration of radicals in radical polymerization, although the conversion of AN decreases. An investigation of the kinetics and mechanism of polymerization with PEO-NH₂ as the monomer in the Ce(IV) system is in progress.

Crystalline properties of two types of block copolymers

Figure 6 shows the DSC measurement results for PAN-*b*-PEO. For the common block copolymers composed of two immiscible systems, we might expect two glass-transition temperatures (T_g) to appear in the DSC curve. From curve 2, we found two T_g values: the T_g of the PEO chain segment was about -46.4°C , but the glass transformation is not very strong. It may be attributed to the higher crystallinity and faster crystallization rate of the PEO chain segment in common conditions; thus, the contents of the amorphous sections in PEO are very small. At the same time, the crystal melting temperature of the PEO segment is shifted from 69°C for the pure PEO homopolymer to

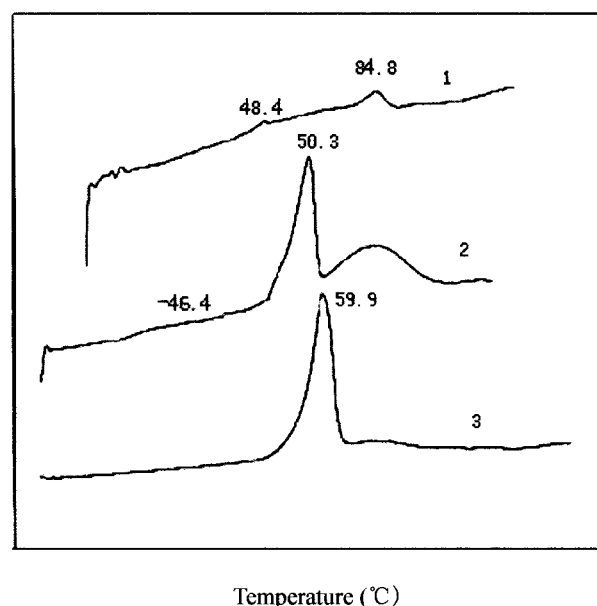


Figure 6 The DSC measurement of PAN-*b*-PEO. Content of PEO in the copolymer (%): 12.6 (curve 1), 32.3 (curve 2), and 50.3 (curve 3). Note: The curve is a different scale.

TABLE II
Effect of PEO Content on Crystallinity of
Block Copolymers

Sample	PEO (%)	T_{m1} (°C)	H_m (J/g)	T_g (°C)
PAN-PEG-PAN	35.2	48.1	26.97	124.9
PAN-PEO 1	32.3	50.3	29.21	134.8
PAN-PEO 2	19.5	48.2	5.57	122.3

50.3°C for the block copolymer. This shift in temperature is indicative of block copolymer formation. If the sample were simply a physical mixture of the two homopolymers, there would be no shift in the melting peak. In addition, the peak of the melt was wide, indicating that the crystallization of PEO is imperfect. This difference may be caused by the decrease in the packing density of PEO chains due to the insertion of PAN chain segments. The glass transition of the PAN block is similar to that of the PAN homopolymer.

Moreover, the DSC experiments in Figure 6 (curve 2) show that there are two melting peaks. The first melting is at 50.3°C, and the second one is at 88.4°C. This phenomenon about the PAN-*b*-PEO block copolymer has not been reported previously. It is worthwhile to point out that Nagarajan and Srinivasan²⁰ illustrated that the PAN-*b*-PEO block copolymer showed a shift in the melting peak of PEO to 80°C. However, theories^{21,22} on crystals consider that for a diblock copolymer consisting of PEO and an amorphous block, the longer the amorphous block, the thinner the lamellae of the PEO. Thus, the melting temperature of crystals of the PEO block would be decreased with the lamellar thickness (i.e., it decreases with the increase of the length of the PAN blocks). Similarly, the melting temperature of the PEO seg-

ment in PAN-*b*-PEO block copolymers should be lower than that of the PEO homopolymer. Therefore, we may consider the first peak at about 50°C as the real melting peak of the PEO segment crystal. The higher melting temperature at 80°C may be caused by the fractional or secondary crystallization of imperfect crystals of PEO, and further works confirmed this opinion. From curve 1 in Figure 6 we can see that with the lower PEO content in the block copolymer, the melting peak of the PEO segment at 48.4°C is too weak to be detectable. On the contrary, when the secondary crystallization change is the dominant part, the crystallization temperature is at 84.8°C. We could infer from crystallization theory that the higher the content of PEO segments in the copolymer, the more perfect is the crystallization of PEO chain occurring. Thus, the secondary crystallization of the PEO segment would first decrease and then disappear. This is confirmed by curve 3 in Figure 6. Further works are in progress.

The experimental results shown in Table II indicate that the crystallization of PEO segments would increase with the PEO content and decrease in the following order: PAN-*b*-PEO > PAN-PEG-PAN. Perhaps in the PAN-PEG-PAN triblock copolymer, the PAN blocks at the end of the PEG block limit the folding of the latter. In the PAN-*b*-PEO copolymer, however, the PEO blocks situated at the ends of the chains can be folded more freely and easily; thus, crystalline structures can be formed completely.

From the above-mentioned phenomena, we can conclude that the PAN block would have great influence on the crystallization of the PEO block. However, the reverse effect of PEO segments on the PAN block should be explained. It is well known that homopolymer PAN is a semicrystalline polymer. X-ray diffrac-

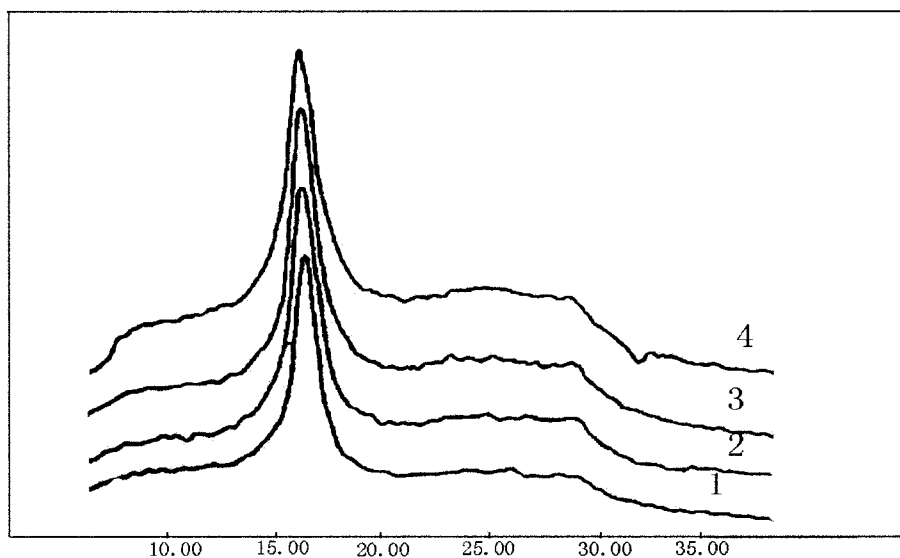


Figure 7 The X-ray diffraction of PAN-*b*-PEO. Content of AN in the copolymer (%): 96.4 (curve 1), 90.4 (curve 2), 87.4 (curve 3), and 85.2 (curve 4).

tion measurements (Fig. 7) show that the crystals of PAN would be affected by the insertion of PEO. The crystallinity of PAN will be increased with the longer block length of PEO chain segments. DSC data also confirmed these results as shown in Table II; the T_g of the crystal area of PAN becomes higher with the increasing length of PEO chain segments. This is because the PEO chains would stretch PAN when the PEO block in the copolymer packed and folded to crystallize. Consequently, this leads to the increase of the crystallinity of PAN.

CONCLUSION

In this study, a diblock copolymer composed of hydrophilic PEO and hydrophobic PAN was prepared successfully by a combination of anionic polymerization and Ce(IV) redox polymerization using aminoalcohol as the parent compound. The formation of the second block chain of AN is dependent on the concentration and molecular weight of the PEO-NH₂ prepolymer containing a —NH₂ end group. From a comparison of the polymerization with PEO-NH₂ or PEG as the macromonomer, we can conclude that the yield of the block copolymer is lower but the molecular weight is higher using PEO-NH₂ as the monomer than with PEG.

Some unusual crystalline properties of the PAN-*b*-PEO block copolymer are also observed. The PEO and PAN blocks have influence on the crystallization in the presence of the other one. The crystallinity of the PEO chain segments in the PAN-*b*-PEO diblock copolymer is higher than the PAN-PEG-PAN triblock copolymer with the same PEO content. The PEO segments have secondary crystallization phenomena that are dependent on the PEO content in the block copolymer.

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