

SYNTHESIS AND CHARACTERIZATION OF BLOCK POLYMER OF ALTERNATING COPOLYMERS

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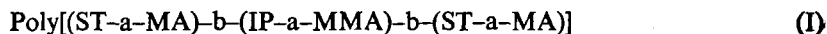
ABSTRACT

Block polymer of alternating copolymers, poly[(ST-a-MA)-b-(IP-a-MMA)-b-(ST-a-MA)] (I), has been synthesized in the presence of $\text{AlEt}_{1.5}\text{Cl}_{1.5}$ by using $\text{Mn}_2(\text{CO})_{10}/\text{CBr}_4$ initiation system. The GPC results indicate that there is no unreacted prepolymer in I purified by precipitation and fractionation.

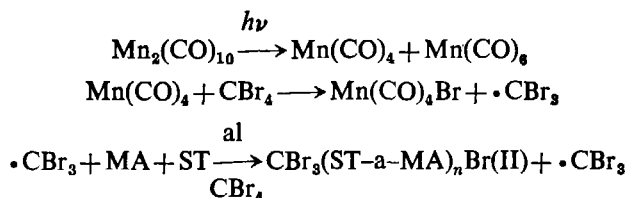
The study of NMR shows that every block of polymer I has alternating structure. The dynamic mechanical properties of I measured by torsional braid method indicate that the polymer has two T_g 's, being 38 and 75°C, respectively. The transmission electron micrographs of I show they have two phase structure and the domain size increases with increasing molecular weight of hard block.

INTRODUCTION

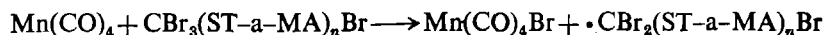
Bamford and Han^[1] have synthesized a novel type of polymer, block polymer of alternating copolymers, in which all blocks are alternating copolymers. $\text{Mn}_2(\text{CO})_{10}/\text{CBr}_4$ was used as initiator and $\text{AlEt}_{1.5}\text{Cl}_{1.5}$ (al) as complexing agent. The characterization of this polymer has not been studied in detail. In this work, block polymer I with different molecular weights of hard blocks have been synthesized and characterized, where MA, MMA, ST and IP represent methyl acrylate, methyl methacrylate, styrene and isoprene, respectively.



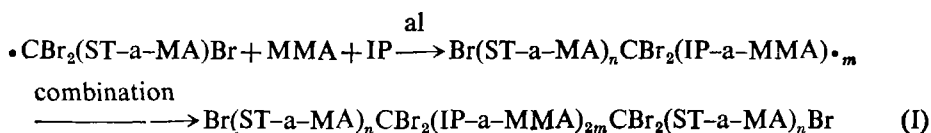
The principle of synthesizing this polymer is shown as follows:



Bromine-terminated prepolymer II is an alternating copolymer containing reactive bromine atom in the end, which will be able to react with $\text{Mn}(\text{CO})_4$ as a halogen containing compound to produce free radical.



The radical can initiate the copolymerization of IP and MMA in the presence of al to obtain block polymer of alternating copolymers.



EXPERIMENTAL

Materials

Monomers MA, MMA, ST and IP were washed with an aqueous solution of NaOH, dried over CaCl_2 and then CaH_2 and distilled before use.

$\text{AlEt}_{1.5}\text{Cl}_{1.5}$ was obtained by reaction of aluminium with chloroethane at 70–80°C. 25% toluene solution of it was used.

$\text{Mn}_2(\text{CO})_{10}$ (BDH reagent) was sublimed in vacuum at room temperature. CBr_4 was analytical reagent.

Toluene (A.R.) was dried over 4Å molecular sieve.

Apparatus and technique

1. Polymerization

$\text{Mn}_2(\text{CO})_{10}$, CBr_4 , toluene, al, MA and ST were added into a three-neck flask filled with a thermometer and an agitator. The reaction mixture was illuminated with a CYF 400 W reflective high pressure mercury lamp for 45 minutes and then poured into methanol. The bromine-terminated alternating copolymer II was precipitated and purified by reprecipitation two times.

$\text{Mn}_2(\text{CO})_{10}$, Prepolymer II, toluene, al, MMA and IP were added into a glass ampoule which was illuminated by a 200 W high pressure mercury lamp in a thermostat at 25±0.1°C for 45 minutes. The block polymer I was then precipitated from methanol.

2. Characterization

The unreacted prepolymer II in polymer I was measured with Waters 150C GPC instrument.

The ^1H - and ^{13}C -NMR spectra were recorded with JEOL FX-100 FT NMR spectrometer. The diameter of sample tube was 5 mm, and CDCl_3 was used as solvent.

The dynamic mechanical properties of I were measured with home-made torsional braid apparatus.

The transmission electron micrographs were taken from Hitachi H-500 electron microscope. The sample film used was made from 1% benzene solution and stained by OsO_4 .

RESULTS AND DISCUSSION

Synthesis of bromine-terminated alternating copolymer II

The polymerization reaction using $\text{Mn}_2(\text{CO})_{10}/\text{CBr}_4$ initiator system is of free radical type,

and CBr_4 is a strong chain transfer agent^[2], so that the products II with different molecular weight could be obtained by means of changing the concentration of initiator. Table 1 shows the prescription for synthesizing prepolymers II.

Table 1 The prescription for synthesizing II and their molecular weight*

	II-1	II-2	II-3
[ST] ($\text{mol} \cdot \text{dm}^{-3}$)	0.8	0.8	0.8
[MA] ($\text{mol} \cdot \text{dm}^{-3}$)	0.8	0.8	0.8
[al] ($\text{mol} \cdot \text{dm}^{-3}$)	0.1	0.1	0.1
$[\text{Mn}_2(\text{CO})_{10}]$ ($\text{mol} \cdot \text{dm}^{-3}$)	1.0×10^{-3}	1.0×10^{-3}	2.0×10^{-4}
$[\text{CBr}_4]$ ($\text{mol} \cdot \text{dm}^{-3}$)	1.6×10^{-2}	2.0×10^{-3}	2.0×10^{-3}
Molecular weight	7,000	8,000	13,000

* Reaction conditions: 25°C, 45 minutes.

Synthesis and purification of block polymer of alternating copolymers I

In order to obtain block polymers with different molecular weights of hard blocks, the polymerizations were carried out in the conditions described above. The concentrations of $\text{Mn}_2(\text{CO})_{10}$, al, IP, MMA and prepolymer II were 2×10^{-4} , 0.2, 0.8, 1.6 $\text{mol} \cdot \text{dm}^{-3}$ and 83 $\text{g} \cdot \text{dm}^{-3}$, respectively, and the total volume was 10 cm^3 . The polymers I obtained were precipitated from methanol, which molecular weights were in the range of 150,000 to 200,000.

The polymer I was purified by precipitating it from its 1% solution in methyl ethyl ketone with methanol^[1], GPC results of I and II showed that the unpurified sample has no obvious two peaks, which means bromine-terminated prepolymer II has reacted completely in 45 minutes, and the molecular weight distribution of purified polymer I changes to more narrow, which means that the portion with lower molecular weight has removed away essentially. It appears that polymer I is not a mixture and does not contain unreacted prepolymer II.

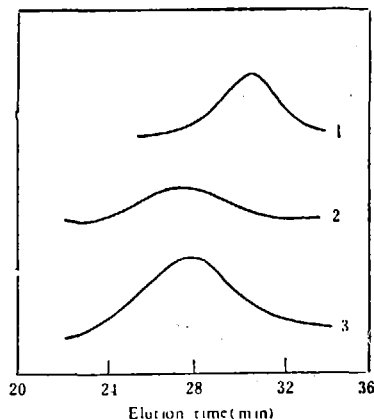


Fig. 1 GPC of polymers I and II
1. Polymer II; 2. Unpurified I; 3. Purified I.

Studies on NMR

As we know, NMR spectra can give the evidence for alternating structure of copolymers. Fig. 2 shows the ^1H -NMR spectra of polymer I, II and poly(IP-a-MMA) (III) obtained by the same method as is used for polymer II, which can be regarded as the middle block of

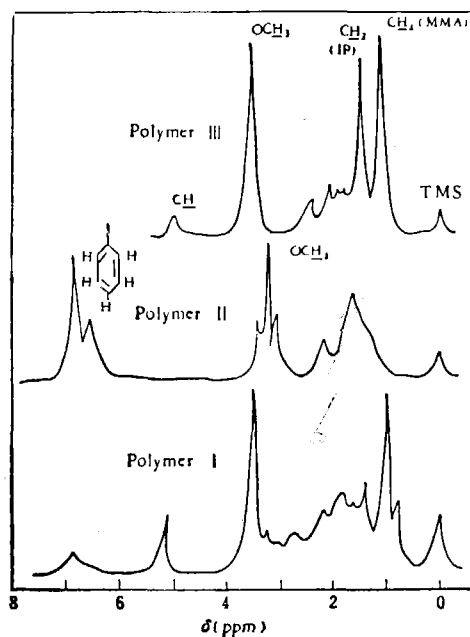


Fig. 2 ^1H -NMR spectra of polymer I, II and III

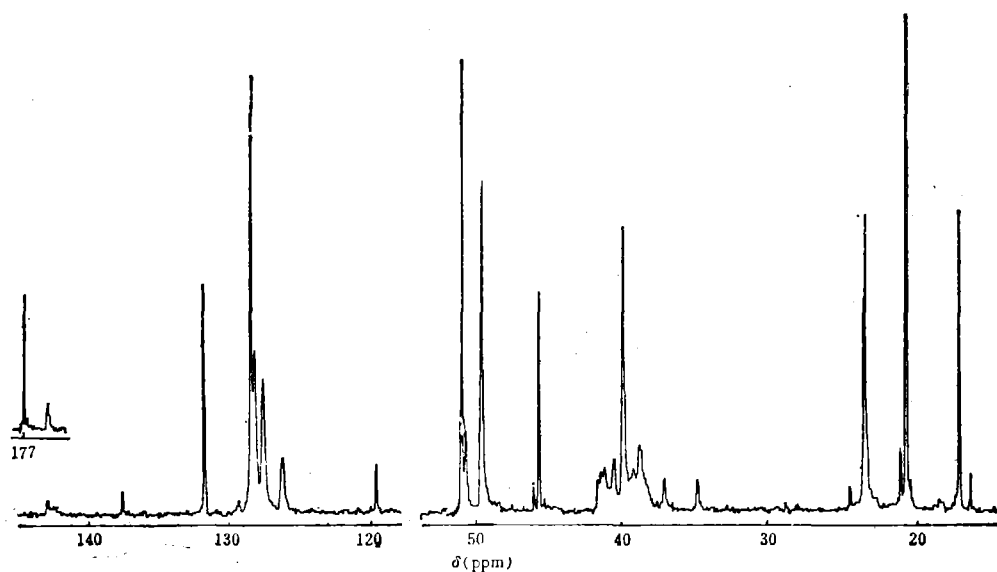


Fig. 3 ^{13}C -NMR spectrum of polymer I

polymer I. The ^1H -NMR spectrum of III is consistent with that of an alternating copolymer of IP and MMA reported in reference [3]. The peaks at 5.2 and 3.6 δ arise from $=\text{CH}-$ in IP and $-\text{OCH}_3$ in MMA, respectively, and there is no 2.0 δ peak arising from $-\text{CH}_2-\text{CH}_2-$ of IP-IP diads. The ^1H -NMR spectrum of II is consistent with that of Poly(ST-a-MA) obtained by Hirooka^[4]. The three peaks in the range of 3.0–3.5 arise from $-\text{OCH}_3$ in MA. The ^1H -NMR spectrum of I is just the sum of the spectra of polymer II and III, showing that every block of polymer I has alternating structure. The peaks of II in I is rather weaker because of the lower molecular weight of II than III.

The ^{13}C -NMR spectrum of I has been assigned^[5]. Ten strong peaks in Fig. 3 arise from ten carbons of Poly(IP-a-MMA). The IP units in I are predominately *trans*-1,4 configuration and connect to MMA in the form of "head to head". The other weak peaks are assigned to the carbons of polymer II. It is also proved that every block of polymer I has alternating structure.

Dynamic mechanical properties of polymer I

The logarithmic decrement and relative rigidity $1/P^2$ measured with torsional braid apparatus are shown in Fig. 4. It is obvious that polymer I has two damping peaks namely two T_g 's, being 38 and 75°C, respectively.

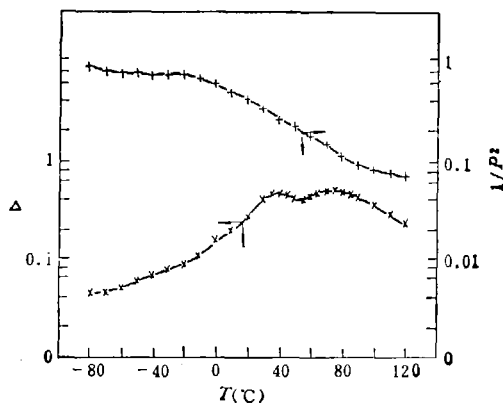


Fig. 4 Dynamic mechanical properties of polymer I

Morphology of polymer I

In order to indicate clearly the two phase structure of block polymer I, the morphology of which with different molecular weights of hard blocks was investigated by transmission electron microscopy, showing in Fig. 5. It can be seen that polymer II blocks form the separate phase and the domain size increases with increasing the molecular weight of II. The average diameters of domains are approximately 200, 250 and 400 Å respectively, in three samples with different molecular weights. It is also to be seen from the electron micrographs that there are some dark streaks in the domains and bright ones in the continuous phase. It may be due to the partial compatibility of MMA and MA contained in soft and hard blocks. We hope to report the results about the morphology of polymer I in detail.

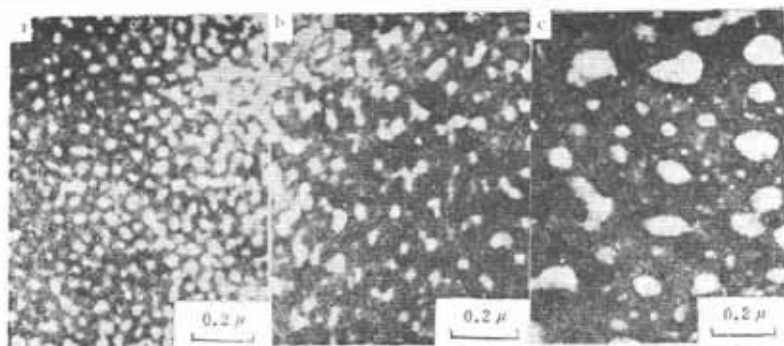


Fig. 5 Transmission electron micrographs of polymer I

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