

SYNTHESIS OF STYRENE-METHYL METHACRYLATE BLOCK COPOLYMER BY POLYAZOAMIDE AS INITIATOR

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ABSTRACT

Polyazoamide(PAA) was used as initiator to prepare block copolymer P(MMA-b-St) by free radical polymerization. The fraction of block copolymer was about 50%. The structure of the block-copolymer was characterized by IR and the results of $^1\text{H-NMR}$ and GPC showed that the content of the block and the molecular weight ($\overline{M}_w$) of the prepolymer and block copolymer could be controlled by varying the mol ratio of styrene/PAA and MMA/prepolymer. DSC and TEM results revealed that the block copolymer has two separated glass transition temperatures and phase separation within the domain structure.

INTRODUCTION

The increasing importance of block copolymers stems from the fact that their chemical structures possess unusual physical properties which are related to their solid-state morphology. Phase separation occurs within domain structures depending on the composition and the block length.

Block copolymers prepared by using polyazoinitiator were first described by Furukawa^[1]. In this technique, polyazoamides were synthesized by reacting AIBN derivative with hexanediamine and block copolymers were obtained through two steps procedure (Smets procedure)^[2,3]. In the first step the polyazoinitiator was partially decomposed in the presence of a monomer to obtain an azo-groups-containing prepolymer. In the second step, decomposition of the remaining azo-groups in the presence of a second monomer resulted in the formation of block copolymers containing a fraction of homopolymers. In 1980's, polyazoesters, which were synthesized by reacting AIBN with diols in the presence of dry hydrochloride, were described by Heitz and his colleagues^[4,5,6] and were used to synthesize the block copolymers

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of P(MMA-*b*-St), P(MA-*b*-St) and P((St-co-Bd)-*b*-(St-co-AN)), etc.. Polyazoamide obtained by reacting AIBN with trioxane in the presence of concentrated sulfuric acid for preparing block copolymer has been reported by the authors^[7,8]. In the present paper, this polyazoamide is used to synthesize the block copolymer of P(MMA-*b*-St), and their structure has been characterized by IR and ¹H-NMR spectra. The molecular weight and T_g of the block copolymer have been measured by GPC and DSC, respectively. The results of TEM show that two phase separation occurs in the domain structure.

EXPERIMENTAL

1. Materials

Polyazoamide (PAA) was obtained by the methods described in the literature [7]. Styrene(St) and methyl methacrylate(MMA) were distilled under vacuum in N₂ atmosphere before use. DMF, benzene, methanol, cyclohexane, acetonitrile were purified by distillation.

2. Preparation of azogroups-containing prepolymer of polystyrene

50ml styrene, 150ml DMF and 0.462 g PAA were stirred for 21h at 80°C (20% decomposition of PAA) under N₂. The product was precipitated with methanol, dissolved in benzene and reprecipitated with methanol. 17.88 g prepolymer were obtained (Table 1).

Table 1 Solution polymerization of styrene at 80°C using PAA as initiator

No.	Styrene		Solvent		Initiator		Reaction time (min)	Yield (g)	Conversion of styrene (%)
	(ml)	(mol)	(ml)	(g)	(%, decomp.)				
20	50	0.463	150	0.462	20	1300	17.88	35.8	
21	50	0.463	150	0.616	20	1300	5.76	12.5	
22	50	0.463	200	0.932	20	1300	5.95	13.1	

3. Preparation of P(MMA-*b*-St) block copolymer

1.0 g prepolymer and 5.0ml MMA were dissolved in 50ml benzene and heated for 36 h at 80°C under N₂. The product was precipitated with methanol, dissolved in benzene and reprecipitated with methanol. 4.55 g product were obtained corresponding to 36.7% conversion of MMA (Table 2).

4. Purification

A Soxhlet apparatus fitted with a cooling jacket was used for extraction. PSt was extracted with cyclohexane while PMMA was extracted with acetonitrile. The solvents were removed and the polymers were dried under vacuum.

5. Measurement

The IR spectrum of block copolymer was measured by Nicolet MX-1 IR spectrometer and the different block contents of block copolymers were measured by $^1\text{H-NMR}$ on Varian-80A NMR instrument. The molecular weight of the prepolymers and block copolymers were determined by GPC in THF with Water-440 apparatus, and were calibrated against polystyrene standard. The glass transition temperature (T_g) of block copolymers were estimated from DSC. The domain structure observations were made by using JEM-100CX transmission electron microscopy (TEM).

Table 2 Conversion of MMA in the preparation of block copolymer by solution polymerization* and the composition of the reaction products

Block copolymer No.	MMA (ml)	Yield (g)	Conversion of MMA (%)	Fractionation PSt (%)	PMMA (%)	Block copolymer (%)	PMMA in block copolymer (%)
201	3.0	1.88	18.6	15	71	14	31.5
202	5.0	4.45	36.7	10	52	38	47.9
203	7.0	5.57	49.9	12	22	66	82.7
211	1.5	1.41	29.1	72	9	19	-
212	5.0	4.24	68.9	6	22	72	-
213	7.0	5.82	73.2	5	29	66	-
221	3.0	1.25	17.8	26	15	59	-
222	5.0	1.51	21.7	17	32	51	-
223	7.0	2.01	31.4	10	41	49	-

* Solution: benzene 50ml, prepolymer: 1.0g, reaction time: 36h, temperature: 80°C

RESULTS AND DISCUSSION

1. Preparation of P(MMA-*b*-St) block copolymer

The synthesis of block copolymer by free radical polymerization necessitates in the first formation of an azogroups-containing prepolymer by partial decomposition of the polyazo-initiator in the presence of a monomer A. This prepolymer is then polymerized with the second monomer B to form AB, ABA or $(\text{AB})_n$ type block copolymer. The architecture of the synthesized block copolymers is determined by the nature of the preferred termination reaction of the growing polymer chains and, thus, by the comonomer. The termination of PSt is predominantly a combination reaction, so the probability to form a PSt without azogroups is small. In the second step, the termination of PMMA is a disproportionation reaction, thus the structure of the block copolymer is PMMA-*b*-PSt (AB type). Therefore solution polymerization is a suitable technique in both steps.

The molecular weight of prepolymer was controlled by altering the feed ratio. The results showed that the molecular weight ($\overline{M}_w$) of prepolymer becomes higher

with increasing mol ratio of styrene/PAA (Fig.1). Because the $\overline{M}_w$ in low mol

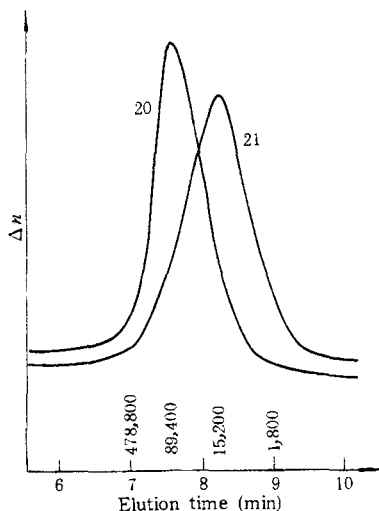


Fig. 1 The GPC curves of prepolymers sample No.20 and 21

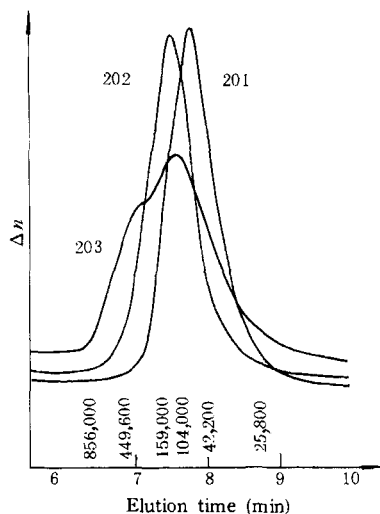


Fig. 2 The GPC curves of block copolymers sample No.201, 202, 203

ratio was about 10,000 (Fig. 1, sample No.21), some of the prepolymer was lost in the process of purification, so the conversion of styrene was low (Table 1). The block copolymers were prepared in the second step. The content of MMA block fraction is also controlled by changing the feed ratio of MMA/prepolymer, the higher the ratio the higher the $\overline{M}_w$ of block copolymer (Fig.2, Table 3) and the more PMMA block content in block copolymer (Table 2) will be. The conversion of MMA depends upon the prepolymer used. The results indicated that the conversion of MMA is higher by using prepolymer with low $\overline{M}_w$ because the efficiency of azogroups in such prepolymer is higher than the one in prepolymer with high $\overline{M}_w$.

Table 3 The average molecular weight and its distribution of prepolymer and block copolymers

Polymers sample No.	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
20	29,400	86,900	2.95
201	48,200	92,700	1.92
202	80,800	168,500	2.09
203	55,200	206,900	3.75

The fraction of PSt, PMMA in the block copolymer is affected by the prepolymer used and the mol ratio of MMA/prepolymer. The conversion of MMA and the MMA block content increased with increasing the mol ratio of MMA/prepolymer when the same amount of prepolymer was used, but the block copolymers containing low MMA block were lost in the process of extraction with cyclohexane, so the content

of PSt was higher. At the same mol ratio of MMA/prepolymer, since the azogroups in prepolymer with low $\overline{M}_w$ were more efficient, so the conversion of MMA and the MMA block content were higher. The block copolymers containing low content of PSt block were extracted by acetonitrile resulting in higher PMMA content and lower percent of block copolymers. All these results were listed in Table 2. Thus, 50% of the fraction of block copolymer was obtained using PAA through Smets procedure although the monomer conversion was about 15 ~ 50% and the initiator efficiency of PAA was about 15%^[9].

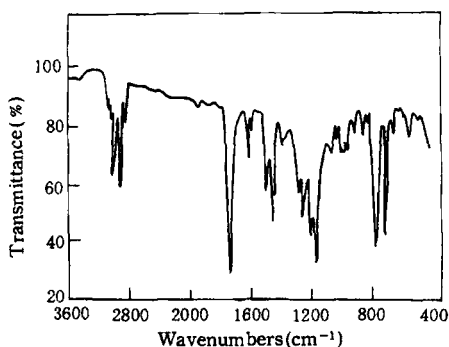


Fig. 3 IR spectrum of P(MMA-b-St)

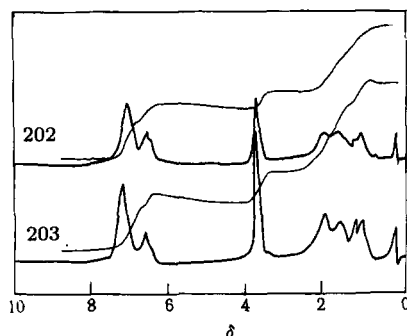


Fig. 4 ¹H-NMR spectra of P(MMA-b-St) samples No.202, 203 with different block contents

2. Characterization of P(MMA-b-St) block copolymer

The IR spectrum of the block copolymer prepared in this method is showed in Fig.3 in which absorption peaks at 1765cm⁻¹ correspond to carbonyl groups of PMMA block and 1490cm⁻¹, 1450cm⁻¹ correspond to phenyl groups of PSt block. The ¹H-NMR spectra (Fig.4) were used to calculate the composition using the expression:

$$\text{mol\% MMA} = \frac{I(\text{MMA})/3}{I(\text{MMA})/3 + I(\text{St})/5} \times 100$$

where $I(\text{MMA})$ is the integral area between 3.5 and 3.9 ppm and $I(\text{St})$ is the integral area between 6.65 and 7.15 ppm. The results are listed in Table 2.

Glass transition temperatures were measured by DSC for the block copolymers of sample No.201, 202 and 203. The two-phase nature of each sample was demonstrated by the presence of two T_g s, characteristic for each block (Fig.5). The T_g of the PMMA block increases with increasing the PMMA block content in the copolymer, this shift might reflect a small element of mixing the PSt block with the PMMA block in the interfacial regions of the domain structure. Typical data were recorded in Table 4. Investigation of domain structure with TEM was carried out with the pure block copolymer and in order to increase the contrast of the sliced bands the

sample was stored for 16 h over OsO_4 vapour. In Fig.6, the deep color reflects to the PSt block and the light color reflects to the PMMA block^[5]. The result of TEM revealed that the block copolymer has two-phase morphology in agreement with the demonstration of the two separated T_g s.

Table 4 Glass transition temperature of P(MMA-b-St) prepared with prepolymer No.20

Block copolymer	T_g of PMMA (°C)	T_g of PSt (°C)	Content of PMMA (%)
201	109	97	31.5
202	111	95	47.9
203	113	89	82.7

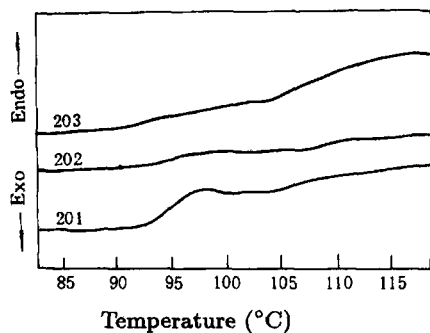


Fig. 5 DSC traces for P(MMA-b-St) of samples No.201, 202, 203

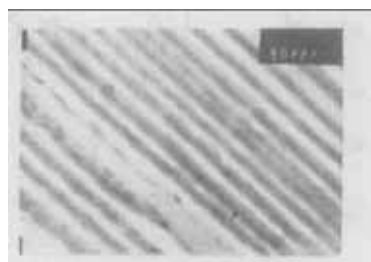


Fig. 6 The TEM photograph of P(MMA-b-St) No.203 shows the two-phase morphology

Keywords:

Polyazoamide; Free radical polymerization; Prepolymer; Block copolymer

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