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Water-soluble and amphiphilic polymers

5. Synthesis and characterization of styrene-methacrylic acid block polymers

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SUMMARY

Styrene-methacrylic acid block polymers were prepared by radical polymerization by using a polyazoester as initiator. Its partial decomposition in the presence of styrene resulted in an azogroup-containing styrene prepolymer, which was further used to polymerize methacrylic acid to form new PSt-PMAA block polymers. It was found that the conversion of MAA and the content of homo-PSt increased, while the content of homo-PMAA decreased, with the increase of pre-PSt/MAA ratio in the feed of the second step. The nature of the block structure of the purified block polymers was proved by their solubility and micellization. The results of DSC and dynamic mechanical analysis showed that the PMAA segments were partially crystalline with $T_m = \sim 234$℃, $T_{g1} = 41$--47℃, and $T_{g2} = \sim 185$℃. An outstanding feature of PSt-PMAA block polymers was their rather high tan δ values over a broad temperature range.

INTRODUCTION

Although many synthetic methods have been developed for preparation of block polymers, a growing interest has recently been focused on exploitation of free radical polymerization process (1-8) . The synthesis of block polymers may be conveniently accomplished by using a polymeric initiator which is consecutively decomposed in two different monomers (6-8) or a polymeric initiator containing blocks derived from polydiols and telechelics (5). This way of synthesis is extremely flexible and allows combination of hard and soft blocks, or of hydrophilic and hydrophobic segments.

Amphiphilic polymers, which consist of both hydrophilic and hydrophobic segments are special among block and graft polymers from both the theoretical and practical points of view. As far

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*To whom correspondence should be addressed as the authors are aware, styrene-methacrylic acid block polymers (PSt-PMAA) have not yet been prepared. In this work, PSt-PMAA block polymers with different compositions were synthesized by using a polyazoester as initiator and characterized by solubility and micellization, viscometry, ^{1}H-NMR, DSC and dynamic mechanical analysis.

EXPERIMENTAL

Materials--Azoisobutyronitrile (AIBN) was recrystallized from methanol and dried over P_2O_5. Diethylene glycol, styrene and methacrylic acid were purified by distillation in vacuum. Methanol was dried by Mg and distilled. Benzene was refluxed with CaH_2 overnight and distilled.

Measurements -- ^{1}H-NMR spectra were taken on a JEOL FX100 NMR spectrometer using d-DMF as solvent. The peak area ratio of benzene ring protons over total protons of methyl, methylene and methine was used to calculate the composition of block polymers. Viscosity measurements were carried out in DMF solutions using an Ubbelohde viscometer at 30.0± 0.1℃. Huggins constants were calculated as usual from the plots of reduced viscosity η_{sp}/C against concentration C. DSC experiments were run on a Perkin-Elmer DSC-7 differential scanning calorimeter. Samples were first heated at a high rate (~200℃/min) to 150℃ and kept at this temperature for certain time in order to remove possibly contaminated water. After cooling, DSC traces were taken from the second scan at a heating rate of 10℃ /min. Dynamic mechanical data at 3.5 Hz were obtained on a Rheovibron DDV-II-EA between ambient temperature and +200℃ with a heating rate of 3.0℃/min.

RESULTS AND DISCUSSION

A polyazoester initiator was prepared by reacting AIBN with diethylene glycol according to the procedure described by C. Oppenheimer and W. Heitz (6). The polyazoester was a viscous, pale yellow oil, and the results of its elemental analysis were very close to the calculated values and that found by Oppenheimer and Heitz,

Calcd.	C	52.9;	H	7.4;	N	10.3
Found	C	51.6;	H	7.4;	N	9.6
Data of Oppenheimer and Heitz	C	52.3;	H	7.4;	N	8.6

An azogroup-containing polystyrene prepolymer was synthesized by precipitation polymerization in methanol with the polyazoester as initiator. Styrene (300 ml), methanol (408 ml), and the polyazoester (4.9 g) were mixed in a three-necked flask under N_2 and heated to 64℃ in a preheated thermostat. The polymerization was continued for 6 hrs (30% decomposition of the initiator) , and the reaction mixture was quenched. The product was removed by filtration, dissolved in benzene, precipitated with methanol and dried at room temperature in vacuum. Molecular weight and molecular weight distribution of the prepolystyrene were measured by GPC (Water 150C, THF, 30.0℃) as given in Figure 1, Mn, Mw and Mw/Mn being 3.40×10^4, 1.21×10^5 and 3.55, respectively.

The synthesis of block polymers was performed in a 500 ml three-necked flask with stirrer, reflux condenser and nitrogen inlet. Azogroup-containing polystyrene prepolymer and methacrylic acid were dissolved in 100 ml benzene. The reaction mixture was degassed by bubbling nitrogen for about 30 minutes. Polymerization was effected at 80℃. The reaction mixture became turbid in about 15 minutes, indicating the formation of block polymers. After 6 hours reaction, the reaction mixture was cooled down ,the polymer was isolated by precipitation with petroleum ether and filtration, and then dried in vacuum at about 50℃. As all know, homopolymers were unavoidably produced together with block polymers in this process. The crude polymer was purified by solvent extraction, using ethanol to remove poly(methacrylic acid) homopolymer, cyclohexane (39℃--40℃) polystrene homopolymer, respectively.

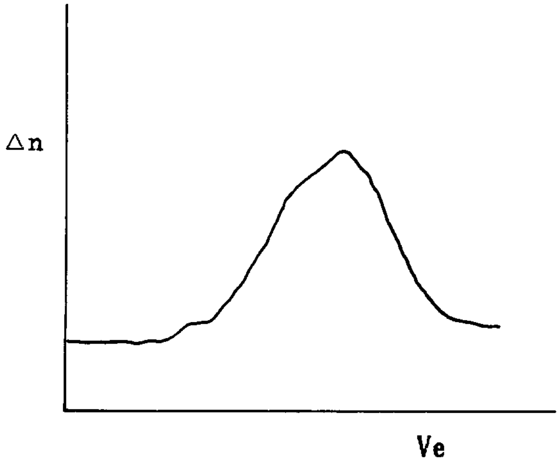

Fig. 1. GPC of the azogroup-containing prepolystyrene

Table 1 Conversion of MAA and composition of the reaction product in the preparation of block polymers

feed		yield	conversion	fractionation		
pre-PSt (g)	MAA (g)	(g)	of MAA (%)	homo-PSt (%)	homo-PMAA (%)	block polymer (%)
1.5	8.5	6.3	56.5	3.2	47.6	49.2
3.0	7.0	10.0	100	6.0	33.0	61.0
5.0	5.0	10.0	100	11.0	28.0	61.0
7.0	3.0	10.0	100	32.4	14.8	52.8
8.5	1.5	9.9	93.3	43.5	4.0	52.5

As shown in Table 1, the conversion of MAA and content of homo-PSt increased, while the content of homo-PMAA decreased, with the increase of pre-PSt/MAA ratio in the feed. The results are reasonable, although Oppenheimer and Heitz (6) have found that higher conversions of methyl methacrylate (MMA) in the presence of prepolystyrene were only obtained at a higher ratio of monomer to polymer with an explanation of lower initiation efficiency at lower monomer concentrations.

The most important characteristic of the block polymers is their behavior of dissolution. Because of the great difference of polarity of the two segments incorperated in a single chain, most solvents, such as toluene, THF, cyclohexane and ethanol do not dissolve or disperse PSt-PMAA block polymers. As far as we know till now, these block polymers are soluble only in dimethyl formamide (DMF). It also seems that DMF is becoming a poor solvent with the increase of PMAA content. Introducing the DMF solutions into water (a selective solvent for PMAA) or benzene (a selective solvent for PSt) resulted in formation of micell emulsions, which is a good evidence for the nature of block structure.

^{1}H-NMR and acid-base titration were used for determination of the compositions of the PSt-PMAA block polymers. It can be seen from Table 2 that the agreement of the results from the two methods is rather good.

The value of intrinsic viscosity $[\eta]$ of the block polymers in DMF increased with the MAA/pre-PSt ratio in the feed, indicating the increase of the length of PMAA segment.

It is of interest to note the dependence upon PMAA content of the Huggins parameter K′ for these block polymers. The value

Table 2 Main Characteristics of PSt-PMAA Block Polymers

Sample		BP-1	BP-2	BP-3	BP-4	BP-5
Feed (pre-PSt/MAA)		15/85	30/70	50/50	70/30	85/15
PMAA (wt%)	titration		57.5	37.1	28.7	19.2
	H-NMR		58.5	35.9	27.7	
visco-metry	[η] (ml/g)		167	116	92	53
	K′		0.314	0.386	0.343	0.338
DSC	T peak (℃)	235.7	234.7	233.9	233.3	233.8
	ΔH (J/g)	260.3	184.1	120.8	76.6	98.1
	Tg (℃)	102.5	97.9	106.3	106.6	103.6

of K′ rises with PMAA content, reaches a maximum at PMAA content $\sim$ 36% ,and then falls off, as can be seen in Table 2. The fact that K′ increases with PMAA content in lower PMAA content range would be expected for systems where the solvent is becoming an increasingly poor one. The decrease of K′ with further increase of PMAA content is probably connected with possibly occuring of intermolecular association.

Figure 2 shows the trace of differential scanning calorimetry (DSC) for sample BP-3. An apparent endothermic peak can been seen at 233.9℃. From DSC trace, only one glass transition temperature corresponding to PSt segments was detected. The results of DSC experiments are summarized in Table 2. It has been known that so-called "conventional" types of PMAA (cv-PMAA) produced by free radial mechanisms, are somewhat syndiotactic rather than being purely atactic (9). A PMAA sample prepared by AIBN initiated polymerization showed an endothermic peak at 234. 3℃, ΔH being 373.7 J/g. Obviously, the PMAA segments of PSt-PMAA block polymers synthesized by azogroup-containing styrene prepolymer have the similar stereoregularity as PMAA produced by azo-initiated free radical polymerization.

There is still some controversy as to the glass transition temperature Tg and melting temperature Tm of PMAA in literature. Aylward (10) has studied an isotactic sample of PMAA by

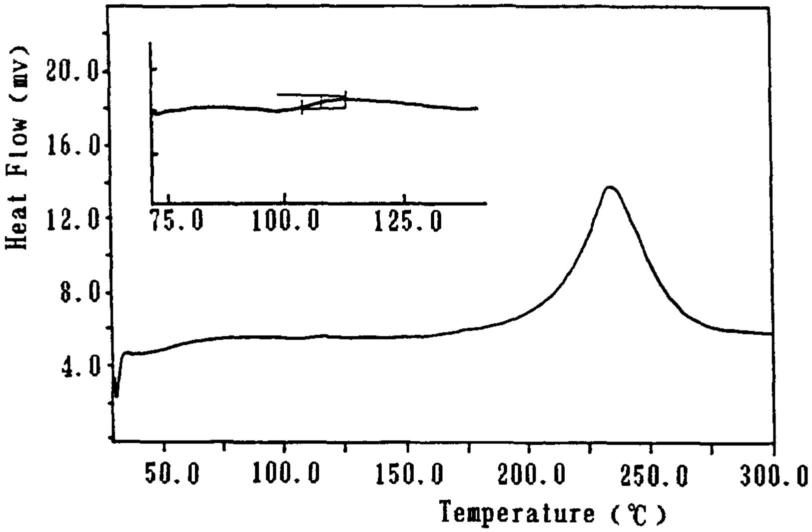

Fig. 2 DSC trace of sample BP-3

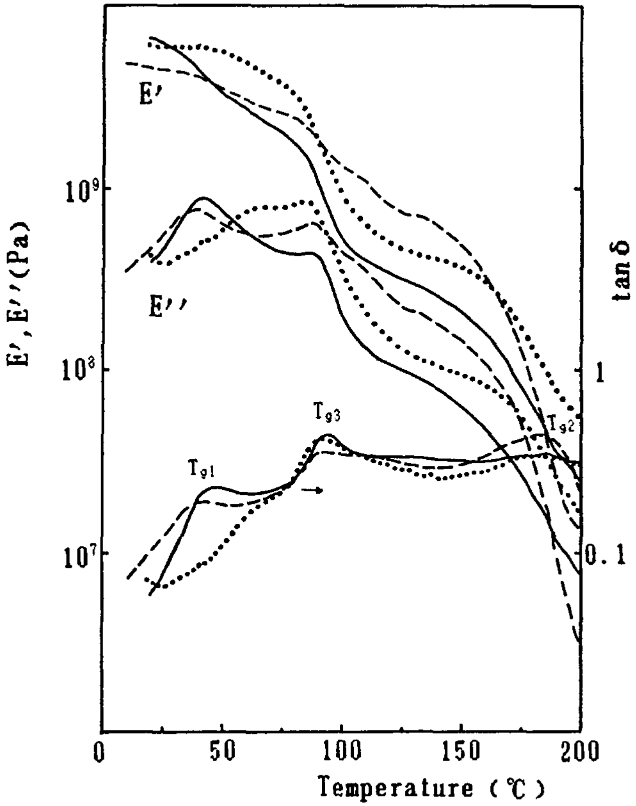

Fig. 3 Dynamic mechanical spectroscopies of PSt-PMAA block polymers

------ BP-2 ——— BP-3 ·········· BP-4

differential thermal analysis (DTA), observing endothermic transitions at 68 and 183℃, which were assigned by him to Tg and Tm, respectively. However, the glass transition temperature of PMAA was found by Fitzgerald and Nielsen (11) to be Tg=185℃, and it was also stated that this value may be too low since the polymer sample was believed to contain at least 5% water. The discrepancy may stem both from the different sources of PMAA samples and from incorrect assignment of the experimental results. We now believe that the endothermic transition appeared at 233.3-235.7℃ should be assigned to Tm of partial syndiotactic PMAA segments.

In order to get more information about glass transition temperatures of PSt-PMAA block polymers, the dynamic mechanical properties of three block polymer samples were studied from room temperature up to 200℃. The temperature dependence of storage modulus E′ , loss modulus E′′, and loss tangent tan δ of PSt-PMAA block polymers is illustrated on Figure 3. According to the dynamic mechanical data, PSt-PMAA block polymers with a higher PMAA content display three tan δ peaks. Clearly, Tg_3 (~97℃) should be assigned to PSt sgments, while Tg_1 (41-47℃) and Tg_2 (~185℃) are due to the contribution of PMAA segments. It is also of interest to note that the dynamic mechanical spectra of PSt-PMAA block polymers exhibit very broadened glass transition regions with rather high values of tan δ, which suggest that the PSt and PMAA segments are partially miscible in certain extent.

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