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THERMAL ANALYSIS OF POLY(AN–co–St) AND POLY(AN–St–MMA)

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Abstract

Poly(AN–co–St) (PAS) and poly(AN–St–MMA) (PASM) were synthetized by emulsion polymerisation. The glass transition temperatures (T_g) of the copolymers and the relationship between T_g and the components of the copolymers were investigated by differential scanning calorimetry. The results show that T_g for the AN–St bipolymers has a peak value in the range 115–118°C at a content of 50 mass% St. When methyl methacrylate was added, the T_g of the terpolymer was decreased by about 2–6°C. The thermostability and the activation energy E of degradation were determined by thermogravimetric analysis.

Keywords: acrylonitrile, copolymer, methyl methacrylate, styrene, thermostability

Introduction

The bipolymer PAS formed from styrene (St) and acrylonitrile (AN) is a thermoplastic engineering plastic. It has higher mechanical properties than those of polystyrene, (PSt) and can be used for injection and extrusion molding to make many kinds of plastic products. PAS resin can be blended with chlorinated polyethylene to make ACS resin [1, 2].

The thermostabilities of the homopolymers polymethyl methacrylate and polyacrylonitrile (PMMA and PAN) and copolymer (PAS) have been determined [3–6], but studies on the thermostability of the terpolymer formed from St, AN and methyl methacrylate (MMA) have been lacking until now. The glass transition temperatures (T_g) of PSt, PMMA and PAN had been reported [7, 8], but reports on the relationship between T_g and the components of the copolymers PAS and PASM have been lacking until now. In the present paper, T_g and the relationship between T_g and the components of the bipolymer and terpolymer are investigated. The thermostabilities and activation energies of degradation of these homopolymers and copolymers were investigated by thermogravimetric analysis (TG) and the results are discussed.

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Experimental

Material

The monomers AN, St and MMA were supplied by Beijing Chemical Reagent Co. Sodium dodecylsulfate (SDS), potassium persulfate ($K_2S_2O_8$), $Al_2(SO_4)_3 \cdot 18H_2O$ and Na_3PO_4 were all of analytically pure grade, and were supplied by Tianjin Chemical Reagent Co.

Synthesis of PAS bipolymer and PASM terpolymer

The bipolymers of AN and St were synthetized by emulsion polymerisation. The monomers AN and St were freshly distilled. SDS was used as emulsifier, and $K_2S_2O_8$ as initiator. Distilled deionised water (DIW) was used in all polymerisations. All components were purged under N_2 for 20 min. The SDS and DIW were charged into a four-necked glass flask. The reaction vessel was then heated to 80°C, and at the same time the mixture was stirred. The monomer mixture and $K_2S_2O_8$ were added over the course of 1.5 h under a N_2 atmosphere. The reaction temperature was next held at 85°C for an additional 2 h. The copolymer was precipitated with $Al_2(SO_4)_3$ solution, purified by washing with warm DIW, and then dried in vacuum. The copolymer was purified by extraction, using a Soxhlet extractor [9]. Cyclohexane was used as volatile extraction solvent. The homopolymer of AN can not be formed under these conditions according to the reactivity ratio in radical polymerisation [10]. The conversion of the monomers was usually 95–98%. The molecular mass was determined by the method of gel permeation chromatography (GPC); it was usually $1.35 \cdot 10^5$.

The terpolymer PASM was synthetized by the same method.

Characterization of thermoproperties

T_g was measured with a Shimadzu DT-40 differential scanning calorimeter (DSC) operating in N_2 atmosphere. The DSC instrument was calibrated with an indium standard. α-Al_2O_3 was used as reference material. A sample of about 4–6 mg was scanned at a heating rate of 20°C min^{-1}. T_g was taken at the midpoint of the heat capacity change (ΔC_p) [11, 12].

The thermostability was tested by TG with a Shimadzu DT-40 instrument in static air atmosphere. About 10 mg of sample was placed in a platinum cell which was transferred to the detector plate, and the furnace was then heated at a rate of 10°C min^{-1}.

Results and discussion

T_g of bipolymer and terpolymer

The monomer reactivity ratio in the radical copolymerisation of AN and St is r=0.04 and r_2=0.4, respectively [10]. This shows that alternating copolymerisation of AN and St is more generally accepted than homopolymerization. The extraction experiment revealed that the homopolymer of St is not formed. T_g is a significant parameter for the polymer. T_g for copolymers depends on the components. DSC was used to determine T_g for PAS and PASM. The sample was scanned at a heating rate of 20°C min^{-1}. T_g was taken at the midpoint of the heat capacity change. T_g for the copolymers PAS and PASM changes with change of the component, as shown in Figs 1 and 2.

Figure 1 demonstrates that T_g for PAS has a peak at 50 mass% St. AN is a polar molecule and can increase the interaction force between molecules or chain segments. Consequently, the conformational energy of the bonds increases, and the mobility of the chain segments decreases. Since T_g depends on the chain flexibility before the content of AN reaches 50 mass% St, T_g rises.

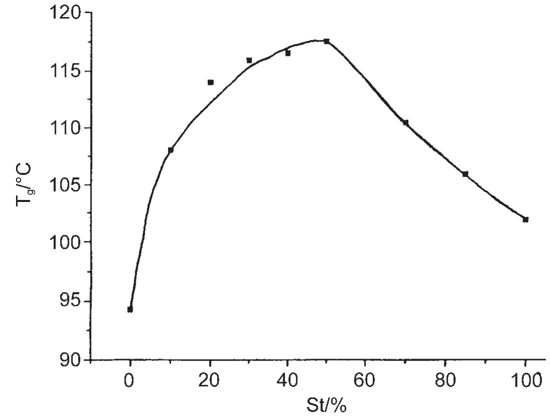

Fig. 1 Curve of T_g of poly(AN-co-St) at different St contents

The alternating copolymerisation of AN and St can increase the steric hindrance of conformational change and rotational potential, and the mobility of the chain segments decreases. As the stiffness of the molecular chain increases, T_g rises. When the

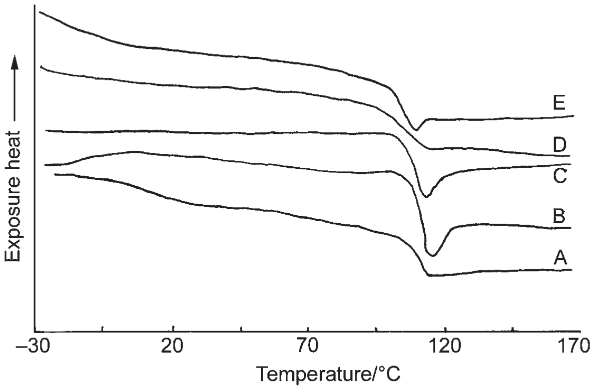

Fig. 2 DSC graphs of copolymers (specimens A, B, C, D and E); A – 0% MMA; B – 6.5% MMA; C – 13% MMA; D – 20% MMA and E – 26.5% MMA

St content is lower, the steric hindrance of the conformational change decreases, and the flexibility of the molecular chain increases; T_g becomes lower again.

T_g for the terpolymers is decreased by about 2–6°C (Table 1). Figure 2 depicts DSC traces of the copolymers.

Table 1 Relationship between T_g and MMA content in terpolymer

AN:St:MMA	6.7:13.3:0	6.7:12:1.3	6.7:10.7:2.6	6.7:9.3:4	6.7:8:5.3
T_g/°C	110.9	112.8	106.9	108.5	103.6

Thermostability of copolymers

In order to determine the thermal stability of the bipolymer PAS and the terpolymer PASM, TG was used. Thermal degradation data on these copolymers are presented in Table 2, and some thermogravimetric curves of the copolymers in Fig. 3.

Table 2 Thermal degradation data on copolymers

Component ratio/mass	Temperature/°C	
	initial mass loss	half mass loss
AN:St		
1:0	310.3	390.0
1:1	351.9	396.4
1:1.5	343.2	386.4
1:2	335.3	384.5
1:2.5	330.1	380.4
1:3	328.4	378.2
0:1	269.3	329.3
AN:St:MMa		
0:0:1	264.8	307.3
6.7:13.3:0	335.3	384.5
6.7:12:1.3	310.6	382.1
6.7:10.7:2.6	304.8	386.4
6.7:3:4	293.6	382.2

As may be seen from Table 2, the thermal decomposition temperature of the bipolymer PAS decreased with increasing content of St, but the decomposition temperature of the bipolymer was higher than those of PAN and PSt. The results demonstrate that copolymerisation can increase the thermostability. In the terpolymer, the decomposition temperature decreased with increasing MMA content. The starting decomposition temperatures of the bipolymer are in the range 328–350°C, and those of the terpolymer are in the range 293–318°C. The temperatures of 50% mass loss (T_{d50}) for the bipolymer are in the range 378–396°C, and those for the terpolymers are

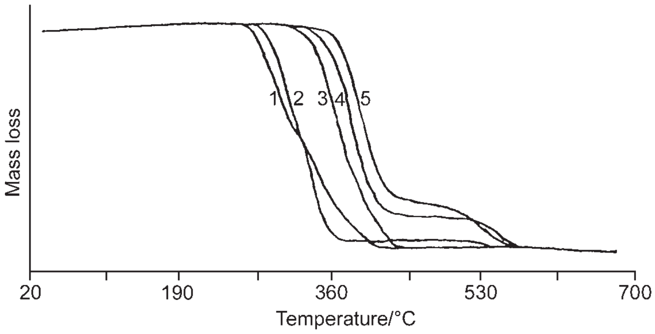

Fig. 3 Dynamic TG curves of copolymers (specimens 1, 2, 3, 4 and 5); 1 – PMMA; 2 – PSt; 3 – PAN; 4 – terpolymer (13% MMA) and 5 – bipolymer (AN/St=1/2)

in the range 307–386°C. This shows that MMA decreases the decomposition temperature of the copolymer, because MMA has a lower degradation temperature.

The following kinetic equation was assumed to hold for these thermal degradation reactions [13]. When the reaction order is n=1:

$$\ln\left(-\frac{\ln c}{T^2}\right)=\ln\left[\frac{AR}{\phi E}\left(1-\frac{2RT}{E}\right)\right]-\frac{E}{RT} \tag{1}$$

where $c=W/W_0$, W=residual mass, W_0=total mass, A=frequency factor, ϕ=heating rate, R=ideal gas constant and E=activation energy. Plots of $\ln(-c/T^2)$ *vs.* $1/T$ according to Eq. (1) are shown in Fig. 4.

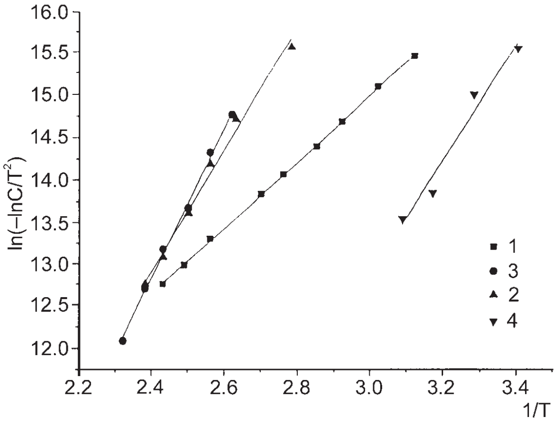

Fig. 4 Thermogravimetric analysis plot of $\ln(c/T^2)$ *vs.* $1/T$; 1 – PSt; 2 – PAS; 3 – PASM; 4 – PAN

We can obtain the activation energies of thermal degradation for these polymers. The data in Table 3 illustrate that the activation energies of thermal degradation of the copolymers are higher than those of PSt and PAN. Thus, the resistance to heat of the copolymers is better than that of the homopolymers PSt and PAN.

Table 3 Activation energy E of thermal degradation of the polymers in air atmosphere

Polymer	PSt	PAS	PASM	PAN
E/kJ mol^{-1}	32.57	60.18	74.07	56.77
r	0.9998	0.9960	0.9985	0.9830

r – linear correlation coefficient

Conclusions

1. T_g for the AN/St bipolymer peaks at a content of 50 mass% St. T_g for the terpolymer drops with increasing content of MMA as compared with that of the bipolymer. When the MMA content is 6.5% in mass, T_g is 112.8°C.
2. The thermostability of the copolymer is better than those of the homopolymers of PSt and PAN. MMA has some effect on the decomposition temperature of the terpolymer. The temperature of initial mass loss of the bipolymer is in the range 328–350°C, and that of the terpolymer is in the range 293–318°C.

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