Study on the Synthesis of Heat-Resistant PMMA

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ABSTRACT: *N*-cyclohexylmaleimide (CHMI) and styrene (St) were used to copolymerize with methyl methacrylate (MMA) to synthesize heat-resistant poly(methyl methacrylate) (PMMA) by a solution copolymerization method and a suspension copolymerization method. Residual CHMI concentrations in the copolymers were analyzed by gas chromatography. Effects of styrene on residual CHMI concentration, glass transition temperature (T_g), molecular weight, and molecular weight distribution were studied. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1335–1339, 1999

INTRODUCTION

Poly(methyl methacrylate) (PMMA) is a kind of important transparent polymeric material with high light transmittancy, colorlessness, chemical resistance, and weathering corrosion resistance. However, PMMA has low heat-resistance, and its heat deflection temperature is as low as 96°C. Recently, further improvement in the heat-resistant property has been strongly desired, and several attempts to improve the thermal property have been made for the PMMA resin. The copolymerization of N-cyclohexylmaleimide (CHMI) and methyl methacrylate (MMA) has been known as one of the optimum methods because the glass transition temperature (T_g) is effectively enhanced, and the copolymer exhibits higher thermal degradation temperature than PMMA.^{1,2} However, the coloration of this copolymer at high temperature has been pointed out as an undesirable characteristic because the residual CHMI in the copolymer tends to cause coloration. So residual CHMI concentration in the copolymer has to be decreased in order to produce heat-resistant PMMA without coloration at high temperature.

In this article, residual CHMI concentration was examined by gas chromatography (GC), and

Journal of Applied Polymer Science, Vol. 72, 1335–1339 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/101335-05 the effect of styrene (St) on residual CHMI concentration was studied. Meanwhile, the effects of St on glass transition temperature, molecular weight, and molecular weight distribution were also discussed.

EXPERIMENTAL

Materials

MMA (analytical reagent) was purified by washing with 5% NaOH solution, then with distilled water until neutral. The washed monomer was dried over anhydrous Na_2SO_4 , then distilled under reduced pressure. St was purified by the same method as MMA. CHMI was synthesized according to Yuichi Kita² and recrystallized from chloroform, then dried under reduced pressure in a vacuum oven at room temperature for 4 h. Azobisisobutyronitrile (AIBN) was recrystallized from alcohol. Dodecanethiol (DDM) was distilled under reduced pressure. Poly(vinyl alcohol) 1788 (PVA1788) was used as a suspending agent.

Procedures

Suspension Copolymerization

The copolymerization of CHMI, St, and MMA was carried out in a four-necked, round-bottom flask equipped with a reflux condenser, a nitrogen gas

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No.	Solution Copolymerization		Suspension Copolymerization							
	1	2	3	4	5	6	7	8	9	
MMA (mL)	90	80	95	95	90	80	85	85	78	
St (mL)	_	10	_	_	_	10	5		7	
CHMI (g)	10	10	5	5	10	10	10	15	15	
AIBN (g)	0.2	0.2	0.08	0.2	0.2	0.2	0.08	0.2	0.2	
DDM (mL)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	
PVA (0.02%, wt)	_		200	200	200	200	200	200	200	
Toluene (mL)	200	200	_	—	_	—	_	—	—	

 Table I
 Reaction Composition

inlet, and a thermometer. The assembly was placed in a thermostatted water bath and stirred by a mechanical stirrer. MMA, CHMI, St, AIBN, and DDM were charged into the flask according to Table I. Nitrogen was passed through the reaction mixture continually. Finally, the suspending agent solution (200 mL 0.02 wt %) was charged into the flask. The temperature was raised to 80° C for 4 h, then to 100° C for 2 h. The copolymers were washed with distilled water until clean and dried in a vacuum oven at 90° C for 6 h to constant weight.

Solution Copolymerization

Solution copolymerization was carried out in the same assembly as suspension copolymerization. MMA, CHMI, St, AIBN, DDM, and toluene were



Figure 1 Gas chromatography spectra of residual CHMI in the copolymers: (1) 0.45, (2) 0.36, (3) 0.60, (4) 0.40, (5) 0.47, (6) 0.45, (7) 0.76, (8) 0.44, and (9) 0.42%.

charged into the assembly according to Table I. Nitrogen was passed through the reaction mixture continually. The temperature was raised to 80°C for 6 h, then to 100°C for 4 h. Toluene in the copolymer was dried in a vacuum oven at 230°C for 20 min.

Characterization

Glass Transition Temperature

A thermomechanical analyzer (Perkin–Elmer Model TMS-2, Perkin–Elmer Corp., USA) was used to record T_g curves in a static air atmosphere at a heating rate of 10°C/min.

Molecular Weight and Molecular Weight Distribution

A gel permeation chromatograph (Waters Associates, USA) equipped with a Millinnium 2010 chromatography manager software system was used to determine molecular weights of the copolymers. Important components of the gel permeation chromatography, and the detailed conditions were as follows.

- 1. Columns: styrene–divinylbenzene copolymer with the effective M_w range of 200–4 $\times 10^6$, 10^5 , 10^4 , and 10^3 Å; 7.8 $\times 300$ mm (Ultrastvragel, Waters Associates).
- 2. Detector: Waters Model 410 Differential Refractometer; detector temperature, 30°C.
- 3. Standard: TSK standard polystyrene (TOSOH Corp., 1-11-39, Akasaka Manato-Ku Tokyo, Japan). M_w s: (1) 5970; (2) 9100; (3) 18,100; (4) 37,900; (5) 96,400; (6) 190,000.
- 4. Solvent: reagent-grade tetrahydrofuran (THF).

NT	1	0	0	4	~	0	-	0	0
No.	1	2	3	4	б	6	1	8	9
Color	colorless	colorless	light yellow	colorless	colorless	colorless	yellow	colorless	colorless

Table II The Color of Each Copolymer at 230°C

- 5. Sample concentrations: 0.1–0.5%.
- 6. Flow rate: 1 mL/min.
- 7. Mobile phrase: reagent-grade THF.

Gas Chromatography

PE (3920B) gas chromatograph was used to determine residual CHMI concentrations in the copolymers. Important components of gas chromatograph and detailed conditions were as follows.

- 1. Hydride flame-ionizing detector.
- 2. Recorder: 10 mV; response time is greater than 1 s.
- Chromatobar: 10% PEG 6000 Shimalite TPA 60-80; 1.5 m × 3 mm; 160°C.
- 4. Flame air: H₂, 30 mL/min.
- 5. Carrier gas: N₂, 38 mL/min.
- 6. Detector: 200°C.

RESULTS AND DISCUSSION

Effects of Copolymerization Methods and Reaction Compositions on Residual CHMI Concentration in the Copolymers

From Figure 1, we found that the contents of AIBN had an evident effect on the residual CHMI



Figure 2 Thermomechanical analysis curve of sample 6 (128°C).

concentrations. As to samples 3 and 4, only the AIBN contents were different, but the residual CHMI concentration of sample 3 was as high as 0.6%, while the residual CHMI concentration of sample 4 was 0.4%. That the AIBN content of sample 7 was 0.08% lead to the highest residual CHMI concentration of 0.76% in the copolymers. As is known, it is difficult for CHMI to copolymerize with MMA, so high AIBN contents in the feed were desired for full copolymerization of CHMI and MMA, and high AIBN contents resulted in low residual concentration in the copolymers.

In contrast to sample 1, 10 mL St was added to sample 2, while other reaction conditions and compositions were all the same. This leads to a lower residual CHMI concentration in sample 2 than that in sample 1 by 0.09%. To samples 8 and 9, the residual CHMI difference was 0.02%. It is suggested that the addition of St in the feed decreased residual CHMI concentration. Because of the polar effect of double bonds of St and CHMI, CHMI reacted with St easily. The addition of St in the reaction mixture made the copolymerization of CHMI and MMA less difficult, and more CHMI reacted with MMA. Meanwhile, we also found the effect of St was different in solution copolymerization and suspension copolymerization. The difference of residual CHMI concentration between samples 1 and 2 was 0.09%, and that of samples 5 and 6 was as low as 0.02%. In solution copolymerization, with the existence of toluene solvent, the viscosity of reaction mixture was small, and, thus, monomers moved freely, and St had more chances to collide with CHMI. Without the effective collision of St and CHMI, it was impossible for St and CHMI to react. While in suspension copolymerization, monomers moved freely at the beginning of the copolymerization but with the increase of the conversion percentage, the viscosity of the reaction mixture grew larger, and CHMI was enclosed in the polymeric chains. It was difficult for CHMI to collide with MMA. As a result, residual CHMI concentrations were high in the copolymers.

To samples 8 and 9, 15 g of CHMI was added, while residual CHMI concentrations in both co-

No.	1	2	3	4	5	6	7	8	9
T_g (°C)	115	112	123	119	130	_	129	135	130

 Table III
 Glass Transition Temperatures of the Copolymers

polymers were below 0.45%. It showed that residual CHMI concentration did not increase with CHMI content within a certain extent; and, according to this, PMMA with higher heat-resistance could be produced for sure.

The colors of the copolymers at 230°C are shown in Table II. Only samples 3 and 7 turned yellow. Normally speaking, when residual CHMI concentration was beyond 0.5%, the copolymer would grow yellow at 230°C. This was evidently suggested in Table II.

Effects of Copolymerization Methods and Reaction Compositions on Glass Transition Temperatures of the Copolymers

The thermogravimetric analysis (TMA) curve of sample 6 is shown in Figure 2, and other T_g s are summarized in Table III. It was suggested that

with the increase of CHMI content, the T_g rose correspondingly, such as in samples 4, 5, and 8, but the effect of per maleimide unit decreased. As to samples 4 and 5, the CHMI content difference of 5 g resulted in a T_g difference of 11°C; but to samples 5 and 8, the CHMI difference of 5 g leads to a T_g difference of 5°C.

From samples 1 and 2, samples 5, 6, 8, and 9, we found that with the addition of St, the T_g of the copolymer decreased somewhat. The reasons were as follows: (1) St with a benzene unit of large spatial bulk enlarged the free bulk of the copolymer according to the free bulk theory; (2) the incorporation of the benzene unit to side chains destroyed the physical crosslinking points and, thus, decreased the physical crosslinking point density. So the polymeric chains moved easily.

In Table III, the T_{g} s of samples 1 and 2 were lower than those of the samples synthesized by



Figure 3 Molecular weight and molecular weight distribution curves of samples 2 and 6.

No.	1	2	3	4	5	6	7	8	9
${M_n \over M_w/M_n}$	25,289 2.791817	2.528434	43,673 3.262325	38,067 3.031629	38,163 2.969895	2.949830	43,576 3.036725	38,357 2.955369	39,062 2.912325

Table IV M_n and M_w/M_n of the Copolymers

the suspension copolymerization method. This was because samples 1 and 2 were produced by the solution copolymerization method, and free radical chain transfer to toluene leads to the low molecular weight of samples 1 and 2. Low T_g s of samples 1 and 2 resulted from low molecular weight of other samples were summarized in Table IV.

Effects of Copolymerization Methods and Reaction Composition on Molecular Weight and Molecular Weight Distribution

Molecular weight and molecular weight distribution curves of samples 2 and 6 were shown in Figure 3. Number-average molecular weights and molecular weight distributions (M_w/M_n) , where M_w is the weight-average molecular weight) of other samples were summarized in Table IV.

It was found that M_w/M_n values of samples 1 and 2 were smaller than others. The reason was that in solution copolymerization, free radicals transferred to toluene, which resulted in low M_n and low M_w/M_n . From Figure 3 and Table IV, it was shown that with the addition of St, M_w/M_n decreased. Especially to samples 1 and 2, the decrease was 0.263383. The tendency of the M_w/M_n decrease was also shown by samples 5, 6, 8, and 9. Yet the reason should be studied further in the future.

CONCLUSION

Copolymers synthesized by a solution copolymerization method had lower M_n and M_w/M_n and lower residual CHMI concentrations than copolymers by the suspension copolymerization method. In both copolymerization methods, with the addition of St, the residual CHMI concentration decreased, and M_w/M_n grew smaller. T_g decreased somewhat. But the effect of St was larger in the solution copolymerization method than in the suspension copolymerization method.

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