Relations of Weight-Average Molecular Weights and the Thermal Properties of *N*-Cyclohexyl Maleimide–Methyl Methacrylate

DONG SHAOSHENG,[1] WANG QINGMIN,[2] WEI YUEZHEN,[1] ZHANG ZHIQIAN[1]

[1]Department of Applied Chemistry, Harbin Institute of Technology, P.O. Box 410, 150001, People's Republic of China

[2]Harbin Institute of Glass Fiber-Reinforced Plastics

Received 8 January 1998; accepted 6 April 1998

ABSTRACT: *N*-cyclohexyl maleimide (CHMI) was used to copolymerize with methyl methacrylate (MMA) by a suspension copolymerization method to produce heat-resistant poly(MMA) (PMMA) in this article. The copolymers were synthesized by changing the weight fractions of azobisisobutyronitrile (AIBN) and dodecanethiol (DDM), while the weight ratio of CHMI to MMA was defined. The effects of the weight fractions of AIBN and DDM on weight-average molecular weight (M_w) were studied. Meanwhile, relations between M_w and the glass transition temperature (T_g) and decomposition temperature (T_d) and M_w and the melt flow index (MFI) were described. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2001–2005, 1998

Key words: *N*-cyclohexyl maleimide; heat-resistant PMMA; weight-average molecular weight; thermal properties

INTRODUCTION

Poly(methyl methacrylate) (PMMA), as a kind of transparent polymeric material, has many excellent properties, including colorlessness, high light transmittancy, chemical resistance, and weathering corrosion resistance.[1] So PMMA is widely used for several applications, such as automobile parts, sign boards, carports, compact discs, lenses, and optical fibers.[2–3] Yet PMMA has a low heat resistance and its heat deflection temperature is as low as 96°C. The inferior property of PMMA greatly limits its use. The copolymerization of methyl methacrylate (MMA) and *N*-cyclohexyl maleimide (CHMI) has been taken as one of the best ways to produce heat-resistant PMMA.[4] The incorporation of rigid polar maleimide units in the backbone increases the rigidity and molecular interactions, so the heat resistance of PMMA increases. Moreover, mechanical properties can hardly be affected at all. Yet, the coloration of these copolymers has been proposed as the main difficulty. We found that by choosing the optimal weight fraction of CHMI to MMA and under proper copolymerization conditions, colorless heat-resistant PMMA could be produced for sure. What's more, the contents of azobisisobutyronitrile (AIBN) and dodecanethiol (DDM) greatly affected the properties of heat-resistant PMMA directly or indirectly, and the relations between weight-average molecular weights (M_w) and their thermal properties were studied.

Correspondence to: D. Shaosheng.

Journal of Applied Polymer Science, Vol. 70, 2001–2005 (1998)
 CCC 0021-8995/98/102001-05

Table I Copolymerization of MMA and CHMI: Reaction Compositions, M_ws and Thermal Properties of Heat-Resistant PMMA

No.	AIBN (g)	DDM (mL)	Melt Flow Index (g/min)	T_g (°C)	T_d (°C)	$\bar{M}_w$
1	0.16	0.34	3.1	119	329	82243
2	0.16	0.36	3.3	118	327	81169
3	0.16	0.40	4.1	106	330	77758
4	0.18	0.30	0.8	124	329	106980
5	0.18	0.36	3.5	117	324	80125
6	0.20	0.30	1.5	122	330	93639
7	0.20	0.34	2.1	116	334	79236
8	0.20	0.36	3.8	113	331	78035
9	0.20	0.40	4.4	104	328	72480
10	0.20	0.50	6.4	92	317	59320
11	0.20	0.60	9.1	63	310	47326

MMA:CHMI = 90 : 10.

EXPERIMENTAL

Materials

Methyl methacrylate (AR) 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.

CHMI was synthesized according to the literature[1] and recrystallized from chloroform, then dried under reduced pressure in a vacuum oven at room temperature for 4 h. AIBN was recrystallized from alcohol. DDM was distilled under reduced pressure. Poly(vinyl alcohol) 1788 (PVA1788) was used as a suspending agent.

Procedure

The copolymerization of MMA and CHMI was carried out by the suspension copolymerization method using AIBN as the initiator and DDM as the molecular weight moderator in nitrogen atmosphere. MMA (90 g) and CHMI (10 g) were firstly charged into a 4-necked round-bottom flask with a reflux condenser and a nitrogen gas inlet tube. The assembly was placed in a thermostated water bath and stirred by a mechanical stirrer. Nitrogen was passed through the reaction mixture continually, and different amounts of AIBN and DDM were added according to Table I. Finally, the suspending agent (200 mL; PVA, 0.02 wt %) was charged into the flask. The temperature was raised to 70°C for 1 h; 80°C for 1 h; 90°C for 1 h, and 100°C for 3 h. The copolymers were washed with distilled water until clean and dried in a vacuum oven at 90°C for 6 h to a constant weight.

Characterization

Melt Flow Index

The melt flow index (MFI) was recorded on a XRZ-400-1 Melt Flow Indexer (3.8 kg; 230°C).

Glass Transition Temperature (T_g) and Decomposition Temperature (T_d)

A thermomechanical analyzer (Perkin–Elmer Model TMS-2) and a thermogravimetric analyzer (Perkin–Elmer Model TGS-2) were used to record T_g and T_d curves, respectively, in a static air atmosphere at a heating rate of 10°C/min.

Weight-Average Molecular Weight

A gel permeation chromatograph (Waters Associated U.S.A.) equipped with Millinnium 2010 chromatography manager software system was used to determine M_ws of the copolymers.

Important components of the gel permeation chromatograph and the detailed conditions were as follows:

1. *Columns:* Styrene–divinylbenzene copolymer with the effective M_w range of 4–200 ×

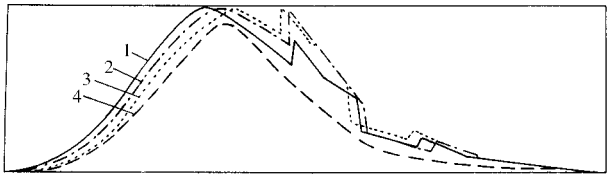

Figure 1 Three typical M_w curves of heat-resistant PMMA: (1) 106980; (2) 80639; (3) 72480; (4) 60830 [sample (4) was synthesized by the solution copolymerization method].

10^6, 10^5 Å, 10^4 Å, and 10^3 Å; 7.8 × 300 mm (Ultrastyragel, Waters Associates).

2. *Detector:* Waters Model 410 Differential Refractometer; detector temperature was 30°C.
3. *Standard:* TSK standard polystyrene (Tosoh Corp. 1-11-39, Akasaka Manato-Ku, Tokyo) with M_ws as follows (1) 5970, (2) 9100, (3) 18,100, (4) 37,900, (5) 96,400, and (6) 190,000.
4. *Solvent:* reagent-grade tetrahydrofuran (THF).
5. *Sample concentrations:* 0.1–0.5%.
6. *Flow rate:* 1 mL/min.
7. *Mobile Phrase:* reagent-grade THF.

RESULTS AND DISCUSSION

Experimental Results

In Table I, various contents of AIBN and DDM were shown, while the ratio of MMA to CHMI was a constant of 9 : 1. The weight-average molecular weights, T_g and T_d values, the melt flow indexes of heat-resistant PMMA were also summarized.

DISCUSSION

Effect of the Contents of AIBN and DDM on Weight-Average Molecular Weights

The molecular weight is a fundamental parameter of heat-resistant PMMA and affects almost all properties of the copolymers. When the reaction conditions and the amount of DDM are defined, M_w is defined firstly by the concentration of AIBN in the feeding.[5] As shown in Table I, with the increase of AIBN contents, M_ws decreased. For example, when the DDM content was 0.36 mL, M_ws were 81,169, 80,125, and 78,035, respectively, corresponding to the AIBN contents of 0.16, 0.18, and 0.20 g.

When the amount of AIBN was not changeable, we found that M_ws decreased with the increase of DDM contents. It was because the free radical chain transfer to DDM prevented the occurrences of too long polymeric chains. Meanwhile, free radicals of DDM could initiate the copolymerization continually and increased the number of reactive chains. The 3 typical M_w curves are depicted in Figure 1. The 3 curves showed that several peaks of the low-molecular-weight component did exist in all the 3 copolymers. These peaks suggested that the amount of the low-molecular-weight component was a little larger than the common curves of PMMA synthesized by the solution copolymerization method. Maybe these differences resulted from special polymerization methods and could not be changed radically.

Relation of M_w and the Melt Flow Index

The melt flow index is an important parameter defining the process procedures of heat-resistant PMMA moldings and directly affected by M_w.[6] In industry, it is often used to designate viscosities of the material melts. Figure 2 describes the relation of MFI and M_w.

With the increase of M_ws, MFIs obviously decreased. From Figure 2, the experience equa-

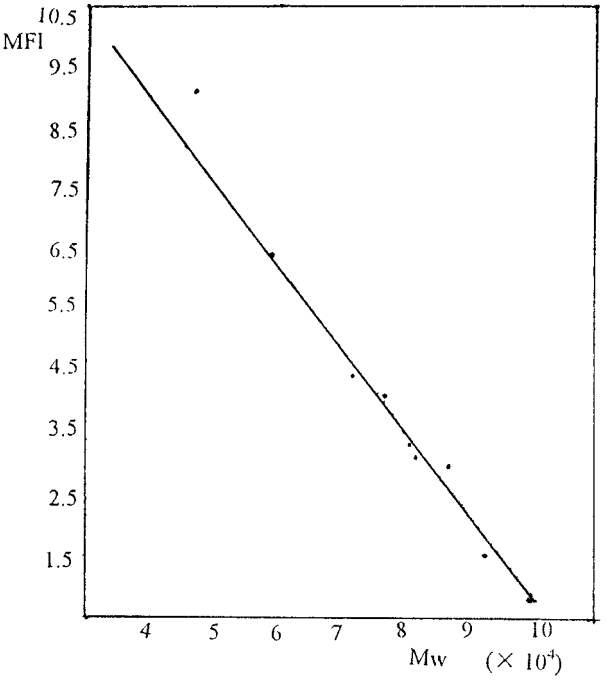

Figure 2 Relation chart of M_ws and MFIs.

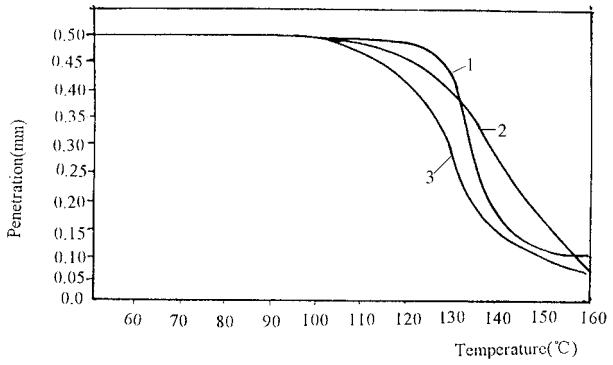

Figure 3 TMA curves of 3 different copolymers: (1) 124°C; (2) 118°C; (3) 106°C.

tion could be described as follows: MFI = 10.5–1.02 $M_w \times 10^{-4}$.

There are drawbacks of a long period and high cost in analyzing M_ws. This will put product analysis to an inconvenience in manufacturing. Now, according to this equation, we could detect M_w conveniently and quantitatively when the reaction conditions were defined.

Effect of M_ws on Thermal Properties of the Copolymers

Thermal properties are determined mainly according to the values of T_g and T_d because PMMA is a kind of amorphous polymer. T_g values of homopolymer of PMMA is 100°C and the T_d value 303°C. When 10% CHMI was added, T_g and T_d values of heat-resistant PMMA were 120 and 330°C, respectively. Thermomechanical analysis

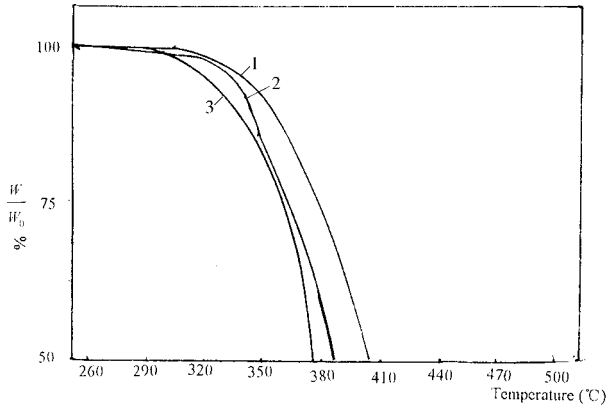

Figure 4 Three TG scans of 3 different copolymers: (1) 334°C; (2) 330°C; (3) 324°C. W is the residual weight of the sample; W_0 is the original weight of the sample.

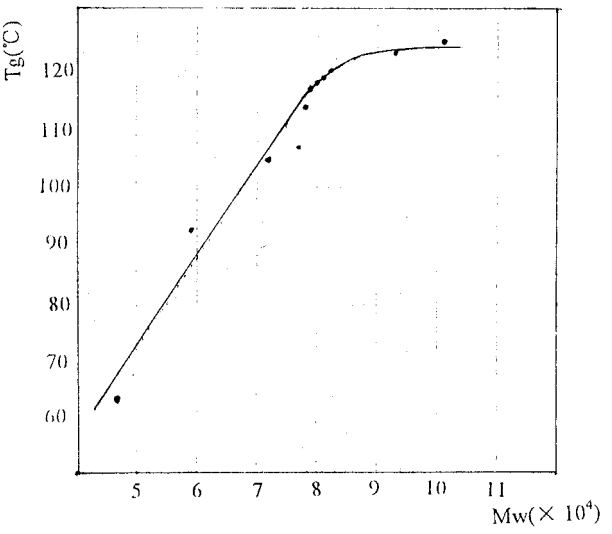

Figure 5 Effect of M_ws on T_g values of heat-resistant PMMA (CHMI content: 10%).

(TMA) curves and thermogravimetric (TG) scans of 3 samples are shown in Figures 3 and 4 correspondingly. The increase of T_g was due to the incorporation of rigid polar imide groups, which increased the rigidity and molecular interactions and made the rotation of the backbone more difficult. The relation of M_w and T_g is described in Figure 5. From Figure 5, we found that the critical M_w was about 8.5×10^4. When M_w was lower than the critical point, with the increase of M_w, T_g rose quickly in a linear relation. When M_w was beyond the critical point, T_g rose very slowly and became nearly constant. As known, mechanical properties of polymers, such as tensile strength and impact strength, will increase with the increase of M_w, even though M_w is far beyond the critical point on T_g. On the other hand, high M_w results in large melt viscosity of heat-resistant PMMA, which makes the injection molding very difficult or even impossible. Therefore, we must control the suitable M_w of 8.0–9.0 $\times 10^4$ to produce heat-resistant PMMA with excellent comprehensive properties.

T_d values showed little dependence on M_ws because they were affected mainly by the chain structure. As we know, in PMMA degradation, 3 stages will be found: (1) scission of head–head linkages (157–250°C), (2) chain-end-initiated decomposition (250–335°C), and (3) random main chain scission (335–427°C).[7] From Figure 4, we found the copolymers began to lose weight at the temperature of about 300°C.

This suggested that with the incorporation of CHMI, chain-end-initiated decomposition was effectively prevented, while random main chain scission was not stopped at all. So, T_d of heat-resistant PMMA was higher than PMMA by about 30°C.

CONCLUSION

With the increase of AIBN and DDM contents, M_w decreased and the relation was not linear. However, the relation of M_w and MFI was linear and with the increase of M_w, MFI decreased. When M_w was lower than 8.5×10^4, with the increase of M_w, T_g rose fast; when M_w was beyond 8.5×10^4, T_g rose much slowly and raising T_g by enhancing M_w was meaningless. The incorporation of 10% CHMI increased T_g of PMMA by 15–20°C, and T_d by 20–30°C.

REFERENCES

1. Yuichi Kita, *J. Appl. Polym. Sci.,* **63,** 363 (1997).
2. Toru Doi and Yoshihiko Sugiura, *J. Appl. Polym. Sci.,* **61,** 853 (1996).
3. Zhu Genyuan and Muxin, *New Chem. Mater.,* **5,** 3 (1995).
4. Li Yuesheng and Weng Zhixue, *New Chem. Mater.,* **5,** 20 (1994).
5. Pan Zhuren, *Polymer Chemistry,* Beijing, 1997.
6. He Manjun and Dong Xixia, *Polymer Physics,* Shanghai, 1993.
7. Veena Choudhary and Alpana Mishra. *J. Appl. Polym. Sci.* **62,** 707 (1996).