

Copolymerization of Methyl Methacrylate and *N*-Alkyl Methacrylamide

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ABSTRACT: A new approach to the preparation of colorless and high transparent methacrylic resins was described. *N*-Alkyl methacrylamide, the alkyl substituent of which was methyl, cyclohexyl, or isobornyl, was employed to copolymerize with methyl methacrylate, giving the copolymer with enhanced glass transition temperature around 10–15°C higher than that of homo-poly(methyl methacrylate). The comonomers, *N*-cyclohexyl methacrylamide and *N*-isobornyl methacrylamide, were prepared by reaction of methacrylonitrile with cyclohexene and camphene, respectively. All the three kinds of copolymers showed the water absorption similar to that of homo-poly(methyl methacrylate) after the samples were immersed in water for 2–8 days. The copolymers also showed high weather resistance toward sunshine in atmosphere for 16 months. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 400–405, 2001

Key words: methyl methacrylate; *N*-alkyl methacrylamide; copolymerization; heat-resistance; weather-resistance

INTRODUCTION

Poly(methyl methacrylate) (PMMA) is the most popular commercial polymer in the acrylic industry at present. The relatively high clarity and excellent light transmission of PMMA (i.e., transparency) coupled with its resistance to sunlight and low density make this polymer ideally suited to the production of automobile taillight lenses, dial covers, lighting fixtures, and other related articles. PMMA has excellent weather resistance and durability and is pleasing in appearance when formulated into relatively thick sections. However, the glass transition temperature (T_g) of PMMA is generally between 85 and 105°C. For relatively long time periods or for lighting sys-

tems in which relatively great amounts of heat are produced by the lamps, the T_g of PMMA is unsatisfactorily low.

To obtain specifically optimized physical properties for acrylics, it is well known that the copolymerization of different monomers is a useful method.^{1–5} The copolymerization of methyl methacrylate (MMA) and methacrylamide (MAD) was studied in our laboratory. The copolymer offered enhanced thermal and mechanical properties compared with homo-PMMA, and the high transparency was basically maintained. However, its durability was poor owing to the absorption of moisture by the polar amide groups.⁶ The polarity of *N*-aryl-substituted MAD is much lower than unsubstituted MAD, and the copolymer of MMA with *N*-phenyl or *N*-tolyl MAD showed much less absorption of moisture with high thermal and mechanical properties, but the transparency of copolymer deteriorated by introducing the aromatic groups into chains.^{7,8} Thus, we synthe-

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sized three *N*-alkyl-substituted MAD, prepared their copolymers with MMA, and characterized the optical, thermal, absorption of moisture, and weatherability properties.

EXPERIMENTAL

Materials

MMA (AR grade) was distilled under reduced pressure after being washed by sodium hydroxide solution and dried. Azobisisobutyronitrile (AIBN, AR grade), benzoyl peroxide (BPO, AR grade), and camphene (CP grade) were recrystallized, and cyclohexene (CP grade) was distilled. Methacrylonitrile (AR grade, from Acros Inc.) and *t*-butyl perbenzoate (BPB, AR grade, from Acros Inc.) were used as purchased without further purification. Methacryloyl chloride was prepared from methacrylic acid and benzoyl chloride in a procedure similar to the one described for the preparation of acryloyl chloride.⁹ Methylamine hydrochloride was prepared from methylamine-water solution (CP grade) and concentrated hydrochloride. All other reagents of AR grade were used without further purification.

Synthesis of *N*-Methyl Methacrylamide (MMAm)

The synthetic procedure of MMAm was similar to that for synthesis of 1,2-dimethyl hydrazine dimethacrylamide.¹⁰

A mixture of 0.19 mol NaOH in 50 mL water and 0.19 mol CH₃NH₂·HCl in 200 mL chloroform was introduced into an ice-salt cooled four-necked flask equipped with a mechanical stirrer and a thermometer. Measures of 0.19 mol methacryloyl chloride in 75 mL chloroform and 0.19 mol NaOH in 25 mL water were added simultaneously into the flask with stirring at 0°C. After isolating the chloroform phase and evaporating the chloroform off, the residual liquid was dried with sodium sulfate and distilled under reduced pressure using CuCl as inhibitor.

Yield: 51.0%. bp: 70.5–71.0/0.5 mmHg (lit.¹¹ bp: 108–110/10 mmHg). $n_D^{20} = 1.4738$. ¹H-NMR (CDCl₃, ppm): 6.41 (1 h), 5.71 (s. 1 h), 5.31 (S. 1 h), 2.87 (D. 3 h), 1.97 (s. 3 h). Elementary analysis for C₅H₉NO: C, 60.58%; H, 9.15%; N, 14.13%; O, 16.14%. Found: C, 59.00%; H, 9.43%; N, 14.61%; O, 16.96%.

Synthesis of *N*-Isobornyl Methacrylamide (IMAm)

The synthetic procedure of IMAm was similar to the procedure described for the preparation of *N*-isobornyl acrylamide by Ritter reaction.¹²

A mixture of 0.02 mol methacrylonitrile and 0.03 mol camphene was slowly added to an ice-cooled mixture of 0.04 mol concentrated sulfuric acid and 6 mL glacial acetic acid with stirring. Then the temperature was increased to 40°C, and the mixture was stirred for 5 h. The product was poured into ice water (200 g), decolorized with active carbon, and recrystallized from *n*-hexane. A white needlelike crystal was obtained. To assure the purity of the product, a small amount of product was dissolved in chloroform. If the solution was not colorless, the product had to be decolorized again.

Yield: 56.0%. m.p. 81–83°C. ¹H-NMR (CDCl₃, ppm): 5.76 (s. 1 h), 5.64 (s. 1 h), 5.30 (s. 1 h), 3.95 (m. 1 h), 1.95 (s. 3 h), 1.89–0.85 (m. 16 h). Elementary analysis for C₁₄H₂₃NO: C, 75.97%; H, 10.47%; N, 6.33%; O, 7.23%. Found: C, 75.64%; H, 10.86%; N, 6.42%; O, 7.08%.

Synthesis of *N*-Cyclohexyl Methacrylamide (CMAm)

The synthetic procedure of CMAm was similar to that of IMAm.

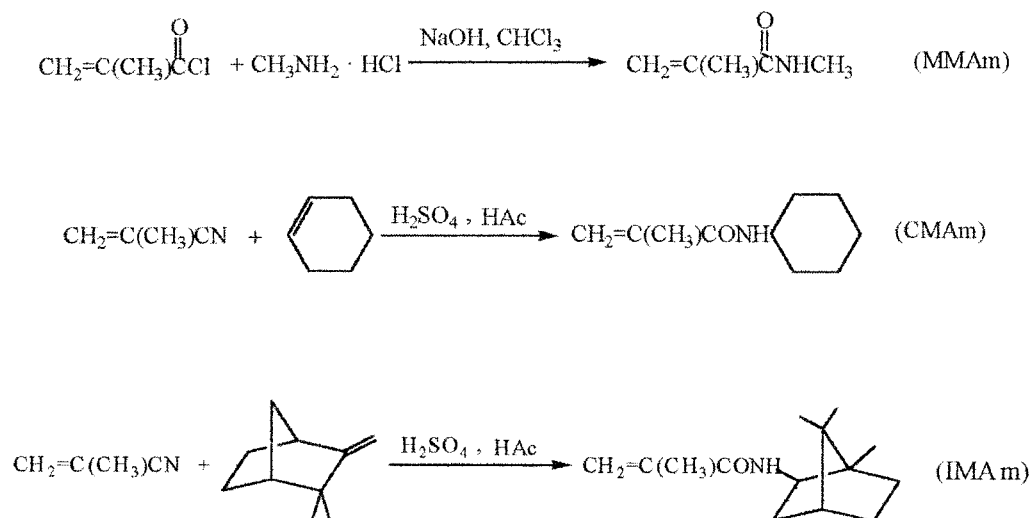
Yield: 40.7%. m.p.: 112–114°C. ¹H-NMR (in CDCl₃, ppm): 5.65 (s. 2 h), 5.30 (s. 1 h), 3.80 (m. 1 h), 1.95 (s. 3 h), 1.95–1.14 (m. 10 h). Elementary analysis for C₁₀H₁₇NO: C, 71.81%; H, 10.25%; N, 8.38%; O, 9.57%. Found: C, 71.22%; H, 10.72%; N, 8.61%; O, 9.46%.

Polymerization in Sealed Tubes

N-alkyl methacrylamide was introduced into the ice-cooled tube containing MMA, AIBN, or BPO (0.1 wt % of MMA) and BPB (0.05 wt % of MMA) and degassed in a vacuum for 10 min. Then the tube was sealed and heated at 85–90°C. When the viscosity of the solution in the tube increased and reached near to that of glycerol, the tube was cooled to room temperature and then heated in an oven at 65–70°C for 24 h. Finally, the temperature of the oven was increased gradually until 130°C and kept at 130°C for 6 h.

Preparation of Sheet of Polymer

N-alkyl methacrylamide was dissolved in MMA containing AIBN or BPO (0.1 wt % of MMA) and BPB (0.05 wt % of MMA), degassed in vacuum, and charged with nitrogen. Then it was heated at 85–90°C until the viscosity of the reaction mixture reached near to that of glycerol, cooled to room temperature, and then introduced into a cell comprising two paralleled glass plates (80 × 60



Scheme 1 Synthetic reactions of *N*-alkyl methacrylamides.

× 4 mm), provided with a separating polyethylene tubing (4 mmϕ) around the edges and three edges were sealed with cellophane. As the cell almost completely filled with syrup, the free end of the tubing was sealed up with cellophane. Then the cell was heated in an oven at 65–70°C for 24 h, keeping the sealed free end upward. The temperature of the oven was increased gradually until 130°C and kept at 130°C for 6 h.

Analysis

The elementary analysis was measured on a Vario EL instrument (Germany).

¹H-NMR spectra were recorded at room temperature on a Bruker (Billerica, MA) ARX-400 NMR spectrometer (measured at 400 MHz) with CDCl₃ as solvent.

The *T_g* of the copolymer was measured on a TA Instruments differential scanning calorimeter (Model 2010; New Castle, DE) at a temperature elevation speed of 10°C/min.

The transmittance of the sheet was measured on a UV-Vis recording spectrophotometer (Model UV250; Japan) and calculated according to eq. (1).

The water absorption of the polymers were tested by immersing samples (0.5–0.8 g) into water at 25–30°C; the weight changes were observed after every desired period.

The weatherability of the polymers was tested by hanging polymer samples outside the window toward the south. Then the transmittance values during the aging test were measured.

RESULTS AND DISCUSSION

Syntheses of Comonomers

Among the *N*-alkyl-monosubstituted MAD compounds, we prepared the simplest one, MMAm, the simplest alicyclic substituted one, CMAm, and the more complicated alicyclic substituted one, IMAm. The preparation of the first two compounds were explained in the literature.^{13–17} However, the physical properties of CMAm, such as melting point, were not reported. The last one, IMAm, could not be found in the literature. We prepared the three comonomers according to the reactions displayed in Scheme 1.

Copolymerization in Sealed Tubes

It is well known that the enhancement of intermolecular force or the presence of a rigid, bulky substituent in chains may increase the *T_g* of PMMA.^{6–8} In this article, each of the three comonomers (MMAm, CMAm, and IMAm) has a hydrogen atom in the amide group. When they copolymerized with MMA, the intermolecular force of chains will become large because of the formation of hydrogen bonds. In addition, when CMAm or IMAm copolymerized with MMA, the bulky substituted amide group will also influence the *T_g* value of the copolymer. From Table I, we can see that by incorporating either of such comonomer moieties into chains, the *T_g* value increased around 10–15°C and the copolymers were colorless and highly transparent. While the feed

Table I Properties of Copolymer

Ingredient (by wt)	Properties of Copolymer	
	Appearance	T_g (°C)
MMA : MMAM		
100 : 0	Colorless, transparent	107
100 : 5	Colorless, transparent	112
100 : 10	Colorless, transparent	115
100 : 15	Colorless, transparent	117
100 : 20	Colorless, transparent	120
MMA : CMAM		
100 : 0	Colorless, transparent	105–110
100 : 10	Colorless, transparent	122
100 : 15	Colorless, transparent	122
100 : 20	Colorless, transparent	123
MMA : IMAM		
100 : 10	Colorless, transparent	120

amount of comonomer was the same, the T_g of copolymer formed by MMA with CMAM or IMAM is higher than that of copolymer formed by MMA with MMAM, which must be due to the bulky substituent in CMAM or IMAM.

Water Absorption of the Copolymers

When moieties of unsubstituted MAD were incorporated into the PMMA chains, the properties of copolymer were significantly improved.⁶ However, for the strong polarity of MAD units, the copolymers absorbed the moisture more easily than homo-PMMA, decreasing gradually the properties of copolymers, and showed poor durability. In this article, one of the hydrogens in amide group was replaced by an alkyl radical. Compared with unsubstituted MAD, the new comonomer moieties show less hydrophilicity, maintain the ability of formation of hydrogen bonds, and result in similar water absorption of copolymers to that of homo-PMMA (Table II).

Copolymer Sheets and Their Transmittance

We prepared the copolymer sheets and determined the transmittance values. The transmission curves of copolymer sheets in the visible region of light is shown in Figure 1. The average transmittance was determined in the wavelength range of 400–700 nm for every 10 nm as $T_{400+10n}$, where $n = 0-30$ by eq. (1):

$$\text{Transmittance} = \left(\sum_{n=0}^{30} T_{400+10n} \right) / 31 \quad (1)$$

The average transmittance of the copolymer of MMA with either one of the three comonomers is close to that of homo-PMMA (Table III). The average transmittance of copolymer of MMA with 10% IMAM is even slightly higher than that of homo-PMMA.

Weatherability Test

To verify whether the hydrogen atom in the amide group (—CONH—) is unstable toward sunshine in atmosphere, the aging test was carried out. A copolymer sample of MMA and IMAM (IMAM/MMA = 0.05 by weight), prepared in the earlier stage of our research work with slightly lower transmittance (92.0%), was hung outside the window toward the south and the change of transmittance values during the aging test was shown in Figure 2.

After 9.5–16 months of the aging test, the transmittance decreased in a similar extent both for the copolymer and for the PMMA, and the transmittance of copolymer still remained high around 90%. Therefore, the oxidation of the hydrogen atom in amide group (—CONH—) of copolymer, resulting in deepening the color and decreasing the transmittance, is not serious.

CONCLUSIONS

1. MMA copolymers with *N*-alkyl monosubstituted methacrylamide, such as MMAM, CMAM,

Table II Test of Water Absorption of Copolymers

Ingredient (by wt)	Water Absorption (%)	
	After 3 days	After 8 days
MMA : MMAM ^a		
100 : 0	0.25	0.46
100 : 15	0.31	0.52
MMA : CMAM ^b	After 2 days	After 4 days
100 : 0	0.57	0.74
100 : 10	0.47	0.66
100 : 20	0.59	0.81
MMA : IMAM ^b		
100 : 10	0.48	0.65
100 : 15	0.50	0.58
100 : 20	0.53	0.75

^a At 20°C.

^b At 30°C.

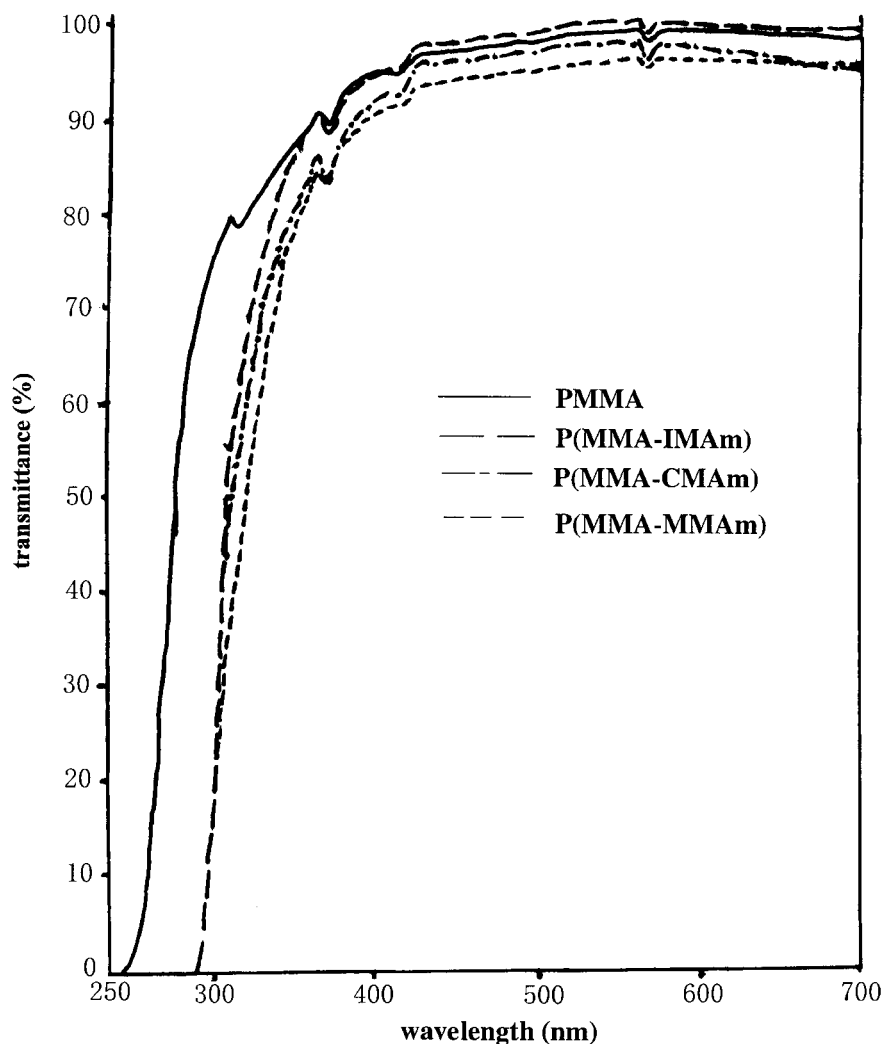


Figure 1 Transmission curve of copolymer sheets in the visible region.

or IMAm, offered the enhanced T_g , around 10–15°C higher than that of homo-PMMA.

2. Among the *N*-alkyl monosubstituted methacrylamide comonomers, CMAm and IMAm

gave copolymers with higher T_g than that of MMAm for the same feed amount of comonomer.

3. All three kinds of copolymers showed similar water absorption compared with that of homo-

Table III The Average Transmittance of Copolymers

Ingredient (by wt)	Thickness of Sample (mm)	Transmittance (%)
MMA : MMAm		
100 : 0	3.0	97.7
100 : 10	2.16	94.0
100 : 15	1.9	95.0
MMA : CMAm		
100 : 15	2.3	96.3
100 : 18	2.6	95.3
MMA : IMAm		
100 : 10	3.0	99.3

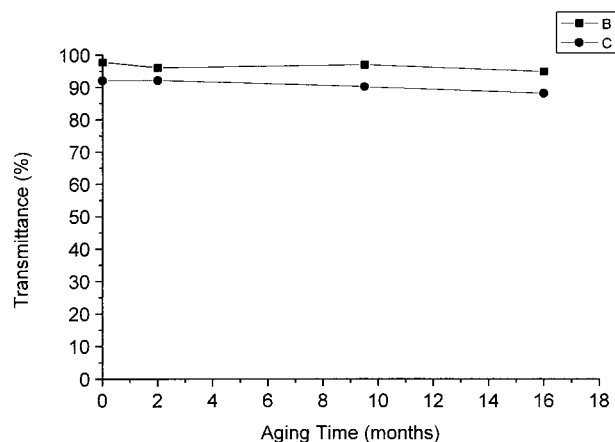


Figure 2 The aging curves of PMMA and a copolymer. B: PMMA, 3.0 mm thickness; C: Copolymer of MMA and 5% W_{MMA} of *N*-isobornyl methacrylamide, 3.6 mm thickness.

PMMA under the same immersion in the water condition.

4. The transmittance of MMA copolymer with IMAM decreased in a similar extent compared with that of homo-PMMA during the 16-month aging test, and the transmittance of copolymer still remained around 90%.

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