

# High-Quality *N*-Substituted Maleimide for Heat-Resistant Methacrylic Resin

YUICHI KITA, KAZUO KISHINO, KOICHI NAKAGAWA

Nippon Shokubai Co., Ltd., Materials & Functions Research Laboratory, 992-1 Aza Nishioki Okihama, Aboshi-ku, Himeji-shi, 671-12, Japan

Received 4 March 1996; accepted 22 May 1996

**ABSTRACT:** A preparation procedure for colorless, transparent *N*-substituted maleimide of high quality which can provide heat-resistant transparent methacryl resins was developed. *N*-Alkylmaleimide, the alkyl substituent of which was composed of 2 to 4 carbons, is employed, giving a polymer with enhanced heat distortion temperature (HDT) because of the higher  $T_g$ . The advantages of relatively low melting points and high vapor pressure of *N*-alkylmaleimide can be used for the preparation of a high-quality product with purification of the monomer by distillation. *N*-Isopropylmaleimide (IPMI), which fulfills these requirements, is especially useful as a monomer for transparent resins. IPMI was synthesized in a high-yield using a mixture of orthophosphoric acid and orthophosphoric acid–isopropylamine salt as catalyst. IPMI, the purity of which is 99.9 wt % or above, contains 100–200 ppm of *N*-isopropylmaleamic acid, maleic anhydride, dimethylmaleic anhydride, solvent, and water. IPMI, which solidifies at 25.8°C, is obtained as a colorless liquid and is freely soluble in common monomers such as methyl methacrylate (MMA), styrene (St), and acrylonitrile (AN). The obtained IPMI showed excellent thermal stability, and no quality change was observed after heating for 100 h at 50°C. The copolymer of MMA and IPMI exhibited the same YI value as a measure of coloration, and almost the same transparency as the homopolymer of MMA. An increase in IPMI content in the copolymer by 1 mol % increased the polymer  $T_g$  by 0.8°C. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 1055–1062, 1997

**Key words:** high-quality—*N*-isopropyl maleimide—Heat-resistant resin

## INTRODUCTION

It is well known that incorporation of a rigid structural unit into a polymer backbone brings about enhancement of the glass transition temperature ( $T_g$ ).<sup>1,2</sup> Recently, copolymerization with *N*-substituted maleimide to elevate the  $T_g$  has been widely utilized to improve the heat distortion temperature (HDT). The most familiar example is the heat-resistant ABS resin (acrylonitrile–butadiene–styrene resin) which contains an *N*-phenylmaleimide (PMI) unit in the polymer backbone.<sup>3</sup>

The ABS resin modified by the PMI unit is known to exhibit higher HDT than that attained by copolymerization with  $\alpha$ -methylstyrene, which has been so far utilized for heat-resistant ABS resin. It is noteworthy that the HDT of the high heat-resistant ABS resin containing a PMI unit is as high as that of the modified polyphenylene oxide resin widely known as an engineering plastic.<sup>3,4</sup>

The methyl methacrylate resin produced by copolymerization of MMA with *N*-cyclohexylmaleimide (CHMI) has been known as a transparent heat-resistant resin.<sup>5,6</sup> A heat-resistant poly(vinyl chloride) resin has been produced by copolymerization of monomeric vinyl chloride with CHMI.<sup>7,8</sup> Preparation of a heat-resistant and transparent resin by copolymerization of an olefin with

Correspondence to: Yuichi Kita

© 1997 John Wiley & Sons, Inc. CCC 0021-8995/97/081055-08

*N*-substituted maleimide<sup>9</sup> has also been proposed. Consequently, *N*-substituted maleimide has drawn attention as a monomer which affords a heat-resistant resin by copolymerization without damaging the characteristics of the original homopolymer. Such an *N*-substituted maleimide is also utilized for improvement of transparent resins.<sup>10,11</sup> Generally, most of the *N*-substituted maleimides bearing an aryl group have been obtained as colored materials: commercial *N*-arylmaleimide is orange or yellow and use of the colored maleimide may result in the coloration of the copolymer. *N*-Substituted maleimide having an aliphatic or alicyclic group seems to be suitable for the transparent resins because the colorless products may yield colorless copolymers.

We have been investigating the mechanism of dehydration of *N*-substituted maleamic acid to *N*-substituted maleimide in an organic nonpolar solvent using an acid catalyst. A mixture of the acid and its amine salt has been found to provide an efficient catalyst for the dehydration reaction because the amine salt suppresses the hydrolysis of *N*-substituted maleamic acid, which is the major side reaction. Therefore, selectivity of the *N*-substituted maleimide from *N*-substituted maleamic acid is improved using this catalyst.<sup>12</sup> Furthermore, *N*-alkyl or alicyclic maleimides which are synthesized in a low yield, because the *N*-alkyl- or *N*-alicyclic maleamic acid precursor of the maleimide is readily hydrolyzed with the acid catalyst,<sup>12</sup> can be prepared using a mixture of the acid and the amine salt in good yield.

The present studies were undertaken to develop a synthetic procedure for IPMI which can be employed as heat-resistant transparent resins. The polymeric material containing the maleimide units was subjected to characterization.

## EXPERIMENTAL

### Materials and Methods

Maleic anhydride (MAN) and MMA were the products of Nippon Shokubai Co., Ltd. *o*-Xylene, isopropylamine (IPA), and orthophosphoric acid were reagents from Wako Pure Chemical Industries, Ltd.

### Preparation of IPMA

MAN was dissolved in *o*-xylene (6× the amount of MAN) at 55°C to prepare a homogeneous solution. An equimolar amount of IPA relative to MAN was charged into the MAN solution at the

same temperature and allowed to stand for 3 h to obtain the IPMA solution. This solution was used for the subsequent dehydration reaction without isolation of IPMA.

### Preparation of the Catalyst

A mixture of orthophosphoric acid and an orthophosphoric acid monoisopropylamine salt mixture in a 50/50 weight ratio was employed as the catalyst. The two-component catalyst was prepared by dropwise addition of IPA to orthophosphoric acid with stirring.

### Preparation of IPMI

A jacketed reactor equipped with a condenser with a water separator and a stirrer were employed for preparation of IPMI.<sup>12</sup> The catalyst and 200 ppm of copper dibutyldithiocarbamate were admitted to the IPMA solution. Dehydration of IPMA was conducted for 5 h at the reflux temperature of the reaction mixture. Water, formed during the reaction, was continuously removed.

### Purification of Product

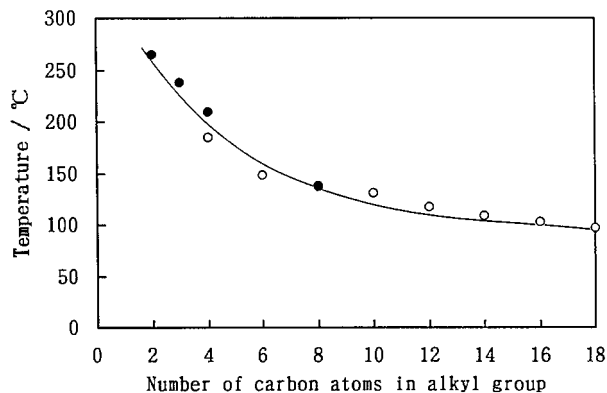
The organic layer, which was separated from the catalyst at 140°C after the dehydration reaction, was washed twice with water. The *o*-xylene was then evaporated from the organic layer, and the remaining IPMI in the flask was purified by distillation using Older–Shaw distillation equipment at 130–150°C at 10 torr. IPMI was liquid at 40°C in a receiver during distillation. *p*-Methoxyphenol (MEHQ) (50 ppm) was added to the distilled IPMI to prevent premature polymerization.

### Stability Test

IPMI, 50 g, in a test tube was heated at 50°C after introducing an air and nitrogen mixed gas containing 5 vol % oxygen into the purified IPMI. After storage at 50°C for 100 h, the amount of impurities in IPMI were analyzed using HPLC, and the IPMI appearance was examined by visual inspection.

### Measurement of Vapor Pressure

The vapor pressure was controlled by adjusting the temperature of the liquid sample after 65 mL of the IPMI sample was charged into the ebulliometer. After adjustment, the temperature and the

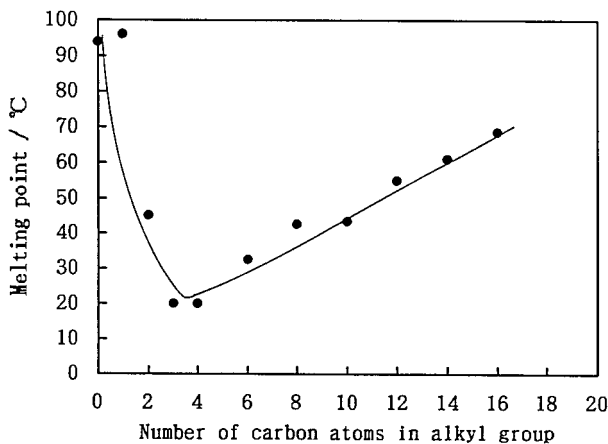


**Figure 1** Relationship between penetrometer softening points (●) (ref. 14) or  $T_g$  (○) (ref. 15) and number of carbon atoms in the alkyl group of *N*-alkylmaleimide. The isopropyl group is given by carbon number 3.

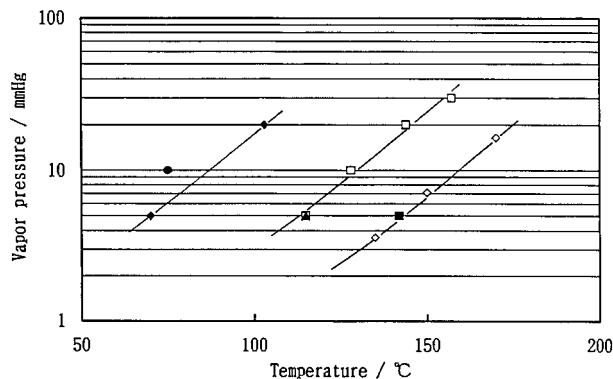
pressure were measured at the steady boiling state.

#### Preparation of Acrylic Sheets

Poly(vinyl chloride) tubes (4 mm $\phi$ ) were placed between two clean glass plates (240  $\times$  180  $\times$  5 mm) to create a space to be filled with the polymerization mixture, and the glass plates were fixed together with steel clamps. IPMI was dissolved in MMA, and this solution was degassed under 200 torr vacuum for 10 min. The monomer solution, containing benzoyl peroxide (0.2 wt %), was charged into the mold after saturation with nitrogen. The filled mold (with its opening closed) was placed in a water bath thermostatted at 60°C for 5 h. The copolymer sheet was removed from



**Figure 2** Relationship between melting point (refs. 14, 16–19) and number of carbon atoms in the alkyl group of *N*-alkylmaleimide.



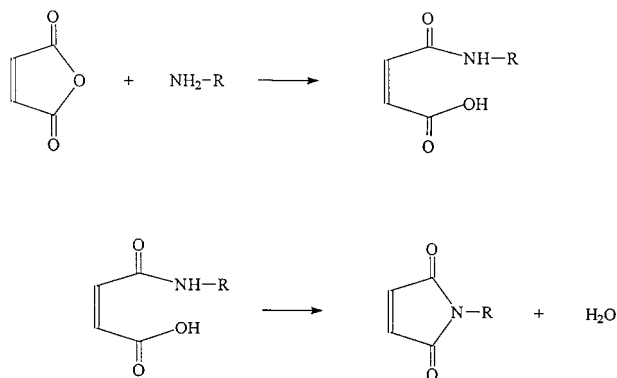
**Figure 3** Comparison of vapor pressure of *N*-substituted maleimide: PMI, ◇; CHMI, □; *N*-butylmaleimide, ◆ (ref. 14); *N*-isopropylmaleimide, ● (ref. 14); *N*-hexylmaleimide, ▲ (ref. 16); *N*-octylmaleimide, ■ (ref. 16).

the mold after polymerization, and the sheet was heated further in an oven at 120°C for 2 h to complete polymerization. Amounts of residual IPMI and MMA monomers were measured using GC.

After confirmation that the residual monomers were < 0.1 wt %, nitrogen content of the copolymer was determined by the elemental analysis using the Yanako CHNMT-3. The amount of IPMI unit in the copolymer was calculated from the nitrogen content. Transmittance and haze were measured using a Nippon Denshoku Kogyo ND-1. A part of the sheet was subjected to YI measurement.

#### Measurements

The purity of IPMI was measured using HPLC (Shimadzu LC-10A) under the following conditions: column, TSK-gel ODS-120T (4.6 mm $\phi$   $\times$  25 cm); mobilephase, a mixture of the aqueous solution of 0.02 mol/L potassium hydrogen phosphate and methanol (2 : 1 weight ratio adjusted



**Scheme 1**

**Table I** Synthesis of IPMI

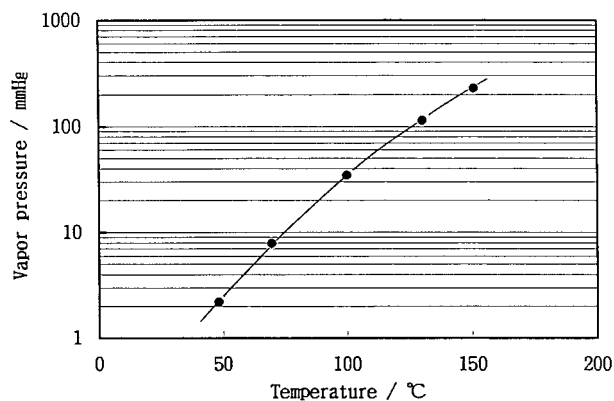
Run No.	Catalyst	(wt %)	Solvent	Temp. <sup>a</sup> (°C)	Time (h)	Yield Based	
						on IPA (mol %)	Foreign Material on the Boundary
1	Orthophosphoric acid	50	<i>o</i> -Xylene	149	3	47.5	Exist
2	Orthophosphoric acid/IPA salt <sup>b</sup>	50	<i>o</i> -Xylene	149	3	62.1	None
3	Orthophosphoric acid/IPA salt <sup>b</sup>	100	<i>o</i> -Xylene	149	3	69.1	None
4	Orthophosphoric acid/IPA salt <sup>b</sup>	100	<i>o</i> -Xylene	149	5	77.2	None
5	Orthophosphoric acid/IPA salt <sup>b</sup>	100	Mesitylene	169	5	85.3	None

<sup>a</sup> Maximum temperature.<sup>b</sup> [Orthophosphoric acid]/[IPA salt] = 1 : 1 (molar ratio).

at pH = 3.0 with orthophosphoric acid); column temperature, 40°C; flow rate, 0.8 mL/min; detector, 210 nm. Gas chromatography (Shimadzu GC9A) was performed using a capillary column of FS-WCOT Unisole-400 (50 m × 0.25φ) at a column temperature of 140°C. Absorbance of 450–820 nm was measured to determine the extent of coloration of monomer using a visible and ultraviolet spectrophotometer (Shimadzu UV-250) the path length of which is 50 mm, and the refractive index was measured using a refractometer (Erma Optical Works, Ltd). The water content was obtained with a water content analyzer (Mitsubishi-kagaku KF-05). The YI of the IPMI/MMA copolymer was determined using a Nippon Denshoku Kogyo Σ80. Specific gravity was measured with a pycnometer, and thermal analysis was performed using a DTA/DSC analyzer (Rigaku TG8110).

## RESULTS AND DISCUSSION

*N*-Substituted maleimide for the transparent resins has been previously investigated.<sup>5–9</sup> *N*-Alkyl-



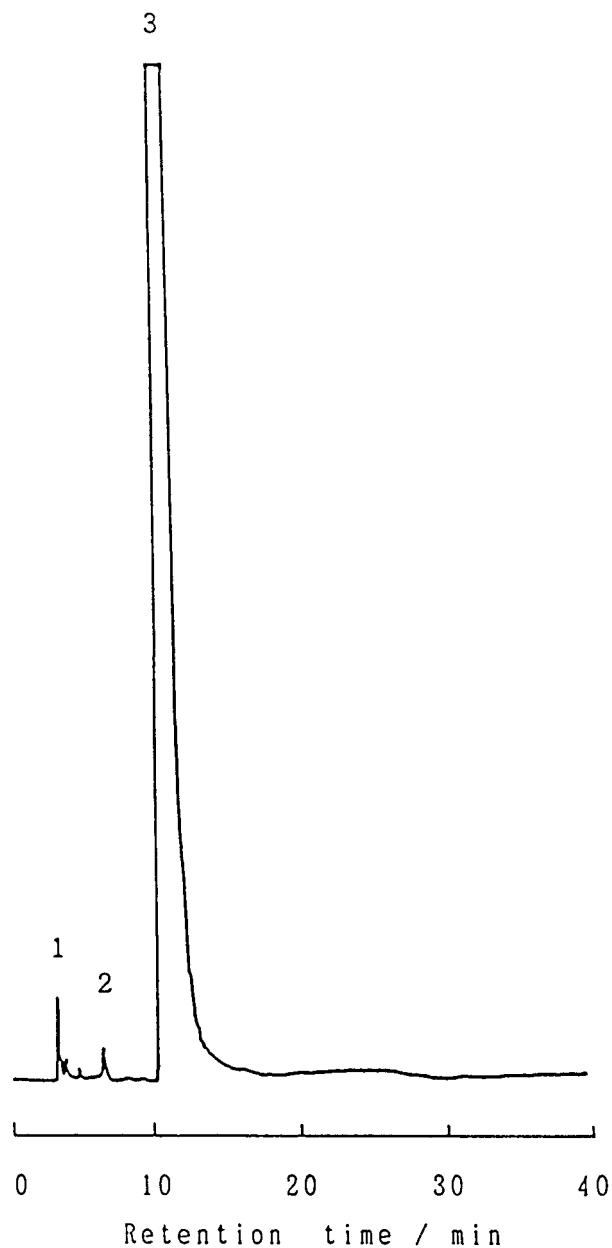
**Figure 4** Temperature dependence of vapor pressure of IPMI.

maleimide is expected to be suitable for transparent resins such as poly(methyl methacrylate), polystyrene, and polyolefin because the colorless maleimide does not induce coloration in the copolymer. The most important requirement for performance is enhancement in the HDT of the resin. This capability can be predicted from the  $T_g$  or softening point of the homopolymer of *N*-alkylmaleimide,<sup>13</sup> and the monomeric maleimide yielding a higher  $T_g$  homopolymer has been employed to improve the HDT of the copolymer resin.

Figure 1 illustrates the relationship between the  $T_g$  or softening point of the *N*-alkylmaleimide homopolymer and the number of carbon atoms in the alkyl substituent. The  $T_g$  and softening point increase considerably as the number of carbon atoms in the substituent decreases. It is expected that the *N*-alkylmaleimide having a substituent consisting of 1–4 carbons improves the HDT effectively.

Another important requirement for a transparent resin is high purity of the maleimide. A high yield and an extremely small amount of by-product during the production of the *N*-alkylmaleimide are required to prepare a high quality copolymer. The by-product and polymer or oligomer generated by thermal polymerization are expected to be undesirable materials contaminating IPMI. Accordingly, an *N*-alkylmaleimide with a lower melting point could attain higher purity because heat damage during production such as thermal degradation and polymerization may be reduced.

Figure 2 illustrates the relationship between the melting point and the number of carbons in the alkyl substituent. The maleimides bearing 2–10 carbons in the alkyl substituent exhibit a melting point below 50°C, and therefore the thermal damage during production can be minimized. Dis-



**Figure 5** HPLC chromatograms of IPMI (3) containing small amounts of MAN (1) and IPMA (2).

tillation seemed to be one of the most efficient methods to obtain a highly pure product.

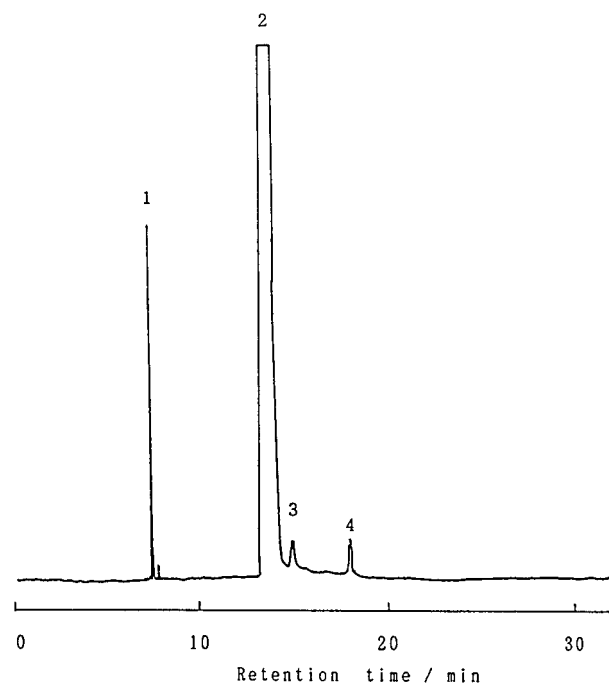
Figure 3 shows the relationship between the vapor pressure and the number of carbons in the alkyl substituent of the maleimides. The *N*-alkyl-maleimide having 3–4 carbons in the substituent is expected to be distilled conveniently. Based on the consideration of melting point and boiling point, we chose IPMI as one of the most suitable monomers for the heat-resistant transparent resins.

**Table II** Analytical Data of Refined IPMI

Item	Analytical value
Appearance <sup>a</sup>	20
Purity (wt %)	>99.9
<i>o</i> -Xylene (wt %)	0.020
MAN (wt %)	0.015
IPMA (wt %)	0.009
DMMA (wt %)	0.013
Water (wt %)	0.017
MEHQ (wt %)	0.004
Insoluble material	None
Solidification point (°C)	25.8

<sup>a</sup> Platinum–cobalt color standard, Ref. 20.

*N*-substituted maleimide is synthesized by dehydration of *N*-substituted maleamic acid, which is produced by a reaction of MAN and primary amine as shown in Scheme 1. In this dehydration reaction of *N*-substituted maleamic acid, maleic acid, which is produced by hydrolysis of *N*-substituted maleamic acid, converts to fumaric acid (FA).<sup>12</sup> This hydrolysis of the maleamic acid and its subsequent reaction is the main side reaction. Accordingly, hydrolysis of *N*-substituted maleamic acid must be suppressed to improve the yield

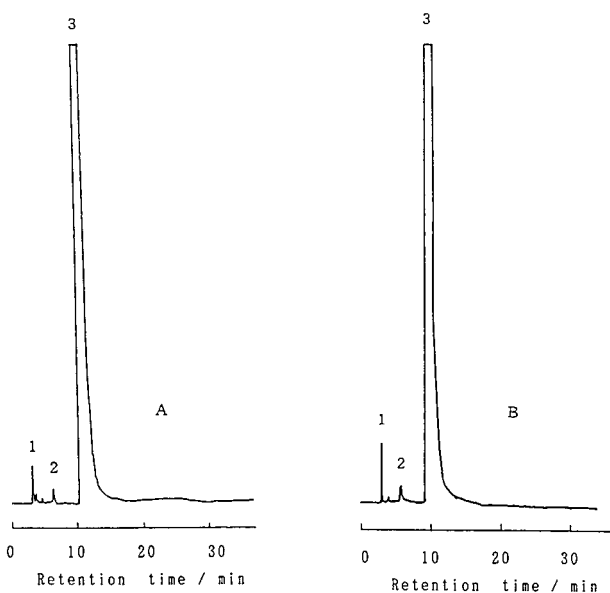


**Figure 6** GC chromatograms of IPMI (2) containing small amounts of *o*-xylene (1), DMMA (3), and unidentified impurity (4).

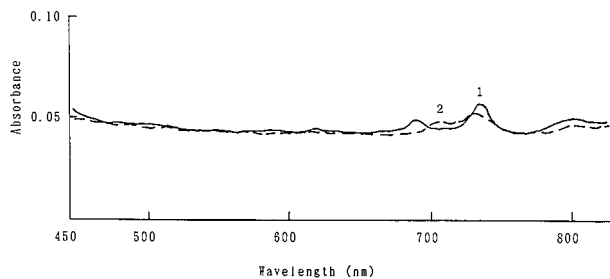
**Table III Heat Stability of Refined IPMI**

Item	Initial	After 100 h at 50°C
Purity (wt %)	>99.9	>99.9
MAN (wt %)	0.015	0.018
IPMA (wt %)	0.009	0.007
Insoluble material	None	None

of *N*-substituted maleimide. We have reported previously that the acid catalyzes the dehydration and hydrolysis of the maleamic acid and that the amine salt is expected to suppress the hydrolysis.<sup>12</sup> Therefore, the acid–amine salt combination exerts an excellent catalytic effect and suppression of hydrolysis simultaneously, and it was proved that this acid–amine salt is the best catalyst for the synthesis of *N*-substituted maleimide yet examined.<sup>12</sup> The dehydration of IPMA was performed under various conditions by changing the solvent, the amount of the catalyst, temperature, and reaction time. Table I summarizes these results. IPMI was obtained in a high yield employing the catalyst consisting of orthophosphoric acid and its amine salt. FA crystals existing at the boundary between the organic layer and the catalyst layer were not observed after the reaction with the two-component catalyst. The yield of IPMI was found to be improved by raising the



**Figure 7** HPLC chromatograms of IPMI (3) containing small amounts of MAN (1) and IPMA (2) before (A) and after (B) heating at 50°C for 100 h.



**Figure 8** Visible spectra of IPMI (1) and MMA (2).

reaction temperature in a solvent of higher boiling point. The reason why the yield of IPMI is improved at high temperature is considered to be that the hydrolysis of IPMA is suppressed at high temperature because the amount of water existing in the catalyst layer becomes smaller at higher reaction temperatures.

The relationship between the vapor pressure of IPMI and temperature is shown in Figure 4. The high vapor pressure of IPMI allows for efficient purification by distillation. The results of HPLC analysis of the purified IPMI are shown in Figure 5. Apparently, high quality IPMI was produced and small amounts of MAN and IPMA were detected as impurities (see Table II). The purified IPMI was also analyzed by GC as illustrated in Figure 6. Three peaks shown in Figure 6 were confirmed to be *o*-xylene, which was used as the solvent, dimethylmaleic anhydride (DMMA), and MAN by MS spectra of authentic samples.

Colorlessness and transparency, which are the most important requirements for the transparent resins, were examined by visual inspection. The color number of the purified IPMI was 20 on the platinum–cobalt color standard, which is indicated in the annual book of ASTM standards,<sup>20</sup> and any foreign material should not be found in the high quality IPMI. The quality of the refined IPMI is summarized in Table II. We could antici-

**Table IV Physical Properties of IPMI and Some Methacrylic Esters**

Monomer	$n_D^{25}$	Density (g/cm <sup>3</sup> ) at 25°C
IPMI	1.474	1.0826
MMA <sup>a</sup>	1.4120	0.939
Bornyl methacrylate <sup>a</sup>	1.4739	—
Cyclohexyl methacrylate <sup>a</sup>	1.4583	—

<sup>a</sup> Ref. 21.

**Table V Miscibility of IPMI, PMI and CHMI in Common Monomer at 25°C**

Monomer	Miscibility (g/100 g of monomer)		
	IPMI	PMI	CHMI
St	Freely	21	55
AN	Freely	100	68
MMA	Freely	—	41

pate that liquid IPMI can be purified to high quality by distillation. Furthermore, the high quality was expected to be maintained in the liquid state. The analytical data shown in Table II also indicate that the high purity of IPMI was attained as expected.

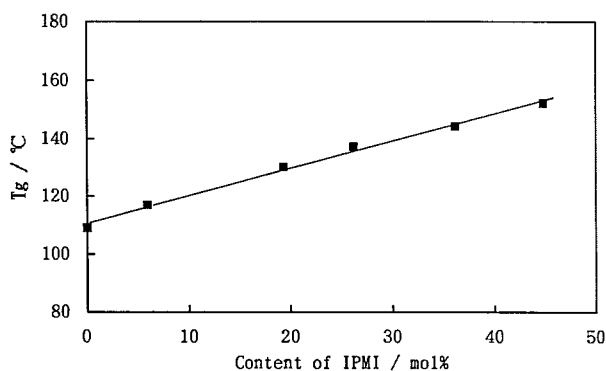
IPMI can be handled as a fluid at room temperature because its solidification temperature is 25.8°C. The stability of IPMI during storage is also an important requirement, and the results of a heat stability test are summarized in Table III. Moreover, HPLC chromatograms of IPMI before and after storage are shown in Figure 7. Actually, no change in purity and no impurity produced during storage at 50°C were seen, and the superior heat stability of IPMI was confirmed. Probably, a limited amount of water in IPMI reduces the hydrolysis rate, and efficient purification appears to suppress generation of radical species which could initiate polymerization of IPMI on heating.

IPMI for transparent resins is strictly required to be colorless. The visible spectrum of IPMI itself is shown in Figure 8 together with monomeric MMA, which is usually used for transparent resins. Absorption in the region from 690 to 740 nm is not observable except for a small absorption in comparison with the spectrum of MMA. It is proved that the refined IPMI has excellent transparency as well as MMA. The refractive index and

**Table VI Characterization of IPMI/MMA Copolymer and PMMA**

Item	IPMI/MMA copolymer	PMMA
Transmittance <sup>a</sup> (%)	92.9	93.0
Haze <sup>a</sup> (%)	0.4	0.4
YI	0.8	0.8
$T_g$ (°C)	117	109

<sup>a</sup> Ref. 23.

**Figure 9** Relationship between  $T_g$  and IPMI content of IPMI/MMA copolymer.

density of IPMI measured are listed in Table IV. The refractive index of IPMI is confirmed to be similar to that of methacrylic ester.

Miscibility of IPMI with various monomers is required for copolymerization over a wide range of comonomer composition. The miscibilities of IPMI with common monomers are shown in Table V and compared with those of PMI and CHMIs. Unlike IPMI, PMI and CHMI are solids at room temperature; the melting points of PMI and CHMI are 89.9°C and 90.0°C, respectively. IPMI was freely miscible with St, AN, and MMA, although PMI and CHMI exhibited limited solubilities. These findings indicate that IPMI can be copolymerized with these monomers in a homogeneous system. The monomer reactivity ratios for the copolymerization of MMA ( $M_1$ ) and IPMI ( $M_2$ ) have been evaluated:  $r_1 = 1.72$ , and  $r_2 = 0.17$ .<sup>22</sup> The  $r_1$  and  $r_2$  values show that a copolymer containing a significant amount of IPMI can be prepared. The copolymerization of IPMI over a wide comonomer composition range to yield a high heat-resistant resin is one of the important characteristics of IPMI.

The selected properties of the MMA/IPMI copolymer are summarized along with those of PMMA in Table VI. The MMA/IPMI copolymer exhibits almost the same YI, haze, and transparency as PMMA. Figure 9 indicates the relationship between  $T_g$  and the content of IPMI units incorporated in the copolymer. This figure shows that an increase in the IPMI content by 1 mol % (wt %) brings about an enhancement of  $T_g$  by 0.8°C (1°C).

## CONCLUSIONS

Highly refined colorless *N*-substituted maleimide having superior transparency is required for heat-

resistant transparent resins. *N*-Alkylmaleimides bearing a substituent consisting of 2 to 4 carbons were expected to be highly purified monomers because of the melting points and vapor pressures in desirable ranges for convenient production and purification. The superior ability for enhancement of the heat-resistant character of a resin is also expected for the *N*-alkylmaleimide based on the  $T_g$  and the softening point of the homopolymer, IPMI, which was chosen as one of the *N*-alkylmaleimides, was synthesized, and its application to heat-resistant resin was examined.

IPMI was synthesized in high yields using a 1 : 1 (wt/wt) mixture of orthophosphoric acid and orthophosphoric–isopropylamine salt as a catalyst in a nonpolar organic solvent, and the water formed was continuously removed from the reaction mixture by distillation. The IPMI was obtained in high purity,  $\geq 99.9$  wt %, containing 100–200 ppm of IPMA, MAN, DMMA, solvent, and water as contaminants. IPMI is a colorless liquid and exhibits good heat stability. Polymer formation was not observed on heating during storage. The solidification point of the IPMI was 25.8°C, and IPMI is freely miscible with St, AN, and MMA at room temperature. The refractive index of the IPMI was 1.474 at 25°C, which is similar to that of methacrylic ester. Copolymerization of MMA with IPMI yielded a heat-resistant methacrylic resin showing almost the same transparency, YI, and haze as well as MMA homopolymer. Incorporation of 1 mol % (wt %) of the IPMI units in the polymer chain was confirmed to enhance the heat resistance by 0.8 (1)°C.

## REFERENCES

- H. Aida, M. Kimura, A. Hukuoka, and T. Hirobe, *Kobunshi Kagaku*, **28**, 354 (1971).
- T. Doi, A. Akimoto, A. Matsumoto, and T. Otsu, *J. Polym. Sci., Part A: Polym. Chem.*, **34**, 367 (1996).
- E. Nield and J. B. Rose, U. S. Pat. 3,652,726 (1972).
- T. Saeki and K. Motomatsu, *PETEROTECH*, **8**, 1157 (1985).
- H. Sato, *Jpn. Kokai*, **87**, 156115 (1987).
- H. Sato and M. Matsuo, *Jpn. Kokai*, **89**, 62315 (1989).
- G. Kuhne and A. Neumaier, U. S. Pat. 3,756,991 (1973).
- S. Masuko, H. Takahara, and A. Yamamoto, *Jpn. Kokai*, **88**, 245413 (1988).
- T. Doi, *Jpn. Kokai*, **93**, 93082 (1993).
- K. Maeda and F. Fukajima, *Jpn. Kokai*, **86**, 252211 (1986).
- S. Adachi, K. Tanaka, and M. Maeda, *Jpn. Kokai*, **94**, 116331 (1994).
- Y. Kita, T. Kashitani, K. Kishino, and K. Nakagawa, *Nippon Kagaku kaishi*, **12**, 971 (1995).
- M. Sato, *Goseijusi*, **40**, 7 (1994).
- R. C. P. Cubbon, *Polymer*, **419** (1966).
- A. Matsumoto, Y. Oki, and T. Otsu, *Polym. J.*, **23**, 201 (1991).
- N. B. Mathta, A. P. Phillips, F. F. Lui, and R. E. Brooks, *J. Org. Chem.*, **25**, 1012 (1960).
- K. Hayakawa, H. Yamakita, and K. Kawase, *J. Polym. Sci.*, **8**, 1227 (1970).
- D. G. Smyth, A. Nagamatsu, and J. S. Fruton, *J. Am. Chem. Soc.*, **82**, 4600 (1960).
- J. G. Ramos, J. M. Barrales-Rienda, and M. S. Chaves, *Anales De Quimica*, **73**, 139 (1977).
- Annual Book of ASTM Standards*, Part 29, 156 (1981).
- B. B. Kine and R. W. Novak, *Encyclopedia of Polymer Science and Engineering*, vol. 1, p. 240, John Wiley & Sons, New York, 1989.
- I. Takase, S. Fukushima, H. Aida, and M. Yamada, *Kobunshi Kagaku*, **30**, 632 (1973).
- Annual book of ASTM Standards*, Sec. 8, 355 (1992).