Synthesis of *N*-Cyclohexylmaleimide for Heat-Resistant Transparent Methacrylic Resin

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SYNOPSIS

N-Cyclohexylmaleimide (CHMI) was synthesized in high yield by dehydration and ring closure of *N*-cyclohexylmaleamic acid (CHMA) in an organic nonpolar solvent that is immiscible with water in the presence of a catalyst consisting of a mixture of acid and its amine salt. The optimal molar ratio of the acid to the amine is in the range of 1/0.65–1/0.8. *N*-Cyclohexylaminosuccinic anhydride (CASA), which is a major by-product, was found to induce coloration of the methyl methacrylate/CHMI copolymer. The CASA content could be decreased by distillation under reduced pressure. CHMI contaminated with less than 0.9 wt % of CASA can be used for heat-resistant poly-(methyl methacrylate) resin (MMA/CHMI copolymer) free from coloration, as well as for methyl methacrylate homopolymer. © 1997 John Wiley & Sons, Inc.

INTRODUCTION

Poly(methyl methacrylate) (PMMA) has been used as the raw material for glazing and optical applications such as lighting and decorative material, lens, and optical fibers because PMMA has many advantages such as weather resistance, high light transmittancy, chemical resistance, light weight, and dimensional stability.[1]

Recently, further improvement in the heat-resistant property has been strongly desired, and various attempts to improve the thermal property have also been made for the PMMA resin.[2] Heat-resistant PMMA produced by copolymerizing with monomers having enhanced heat resistance, such as α-methylstyrene[3] and maleic anhydride (MAN),[4] has been found. However, these copolymers have some problems such as limiting of the heat distortion temperature and coloration due to residual MAN arising from the low copolymerization ability with MMA.[2] Although heat-resistant PMMA crosslinked with a multifunctional monomer such

as dimethylolpropane diacrylate has also been found,[5] difficulty in the molding of this polymer limits its application.

The copolymer of methyl methacrylate (MMA) with *N*-substituted maleimide has been known as one of the most superior resins among the above-mentioned resins because the heat distortion temperature is effectively enhanced by the incorporated *N*-substituted maleimide unit, and because the copolymer also exhibits a higher thermal degradation temperature than PMMA. The transparent heat-resistant PMMA could be used for various applications in glazing and optical uses. The thermal properties of the copolymers of MMA with *N*-substituted maleimide having various types of substituents including *N*-aryl maleimide have been reported.[6–10] However, the coloration of these copolymers has been pointed out as an undesirable characteristic because the monomeric maleimide used tends to cause coloration. Furthermore, *N*-aryl-substituted maleimide has not been used for the heat-resistant PMMA because of the inferior transparency of the resulting polymer. *N*-Substituted maleimide having aliphatic or alicyclic groups such as *N*-butylmaleimide or *N*-cyclohexylmaleimide (CHMI) are colorless materials, and copolymerization with MMA provides a resin without coloration.

The *N*-substituted maleimide having an aliphatic or alicyclic substituent has not been synthesized in sufficiently high yields, although the aryl maleimide can be produced in a substantially high yield. Accordingly, CHMI have rarely been used for the production of the heat-resistant PMMA resin because by-products relating to a low yield of CHMI seem to induce coloration of the resultant resin. So far, the synthesis of CHMI in a high yield has not been developed.

Several synthetic procedures of *N*-substituted maleimide, which are divided into two types, have been proposed. One involves the ring closure of maleamic acid to maleimide through dehydration with a carboxylic anhydride such as acetic anhydride.[11] This method was developed by Seale[11] in the 1940s and has been subsequently modified. However, because the dehydration requires an equimolar amount of acetic anhydride to maleamic acid, the same amount of acetic acid, which should be disposed, may be produced. Accordingly, the relatively high cost limits wide application of this method.

One of the syntheses classified as the second type involves the dehydration of maleamic acid in the presence of an acid catalyst under reduced pressure at high temperature; maleimide is produced by continuous distillation from the reactor.[12] The dehydration has been performed after the adduct formation of maleamic acid with a diene such as furan.[13] The acid-catalyzed dehydration of maleamic acid is also carried out in organic solvent while the water produced is expelled from the reaction mixture.[14] The preparation of maleimide catalyzed with acid accomplished by the continuous removal of water is considered to be the best method from a safety and economical point of view. However, *N*-substituted maleimide having an aliphatic or alicyclic substituent, unlike the arylmaleimide, cannot be synthesized in high yield by the method involving the continuous removal of water.

We have been investigating the dehydration mechanism of *N*-substituted maleamic acid yielding *N*-substituted maleimide in an organic nonpolar solvent that is immiscible with water. The catalyst effective for the synthesis of the maleimide bearing an aliphatic or alicyclic substituent in addition to an aromatic substituent has been developed.[15]

These studies were undertaken to synthesize a high-quality CHMI useful for the transparent polymer material. The structure of the by-products were revealed, and the influence of the con-

Table I   Quality of the Monomeric MMA

Item	Criterion
Appearance	Colorless/transparent
Color no.[a]	<5
Water (wt %)	<0.05
Acidity	<0.05
Inhibitor	Topanol-A, 5 ppm
Assay (wt %)	>99.8

[a] Color standard number of platinum-cobalt color standards, ASTM D 1209.

taminants on the coloration of the copolymer of MMA/CHMI was examined.

EXPERIMENTAL

Materials

MAN and MMA, the qualities of which are shown in Table I, were products of Nippon Shokubai Co., Ltd. *o*-Xylene and cyclohexylamine (CHA) were reagents from Wako Pure Chemical Industries, Ltd.

Preparation of *N*-Cyclohexylmaleamic Acid

MAN was dissolved in *o*-xylene (5 times wt % MAN) at 55°C in order to prepare a homogeneous solution. A solution of CHA containing an equimolar amount of MAN in *o*-xylene, which was the same weight as MAN, was prepared. The CHA solution was charged into the MAN solution at the same temperature for 0.5 h and allowed to stand for 3 h to attain a slurry of *N*-cyclohexylmaleamic acid (CHMA).

Preparation of CHMI

The dehydration of CHMA was conducted for 5 h at reflux temperature. The formed water was continuously removed after the addition of the catalyst and 200 ppm copper dibutyldithiocarbamate to the CHMA slurry.

Purification of Product

After the reaction, the organic layer, which was separated from the catalyst at 140°C, was washed twice with water. *o*-Xylene was distilled off from the organic layer under 30 torr. CHMI remaining in the flask was purified by distillation at 130–

Table II   Effect of Amine Salt on CHMI Yield

Run No.	Acid Catalyst	[Acid]/[CHA] in the Catalyst (Molar Ratio)	Yield of CHMI Based on CHA (mol %)
1	Sulfuric acid	1/0	19.5
2	Sulfuric acid	1/0.6	46.2
3	Sulfuric acid	1/1	59.2
4	Sulfuric acid	1/1.2	59.4
5	Sulfuric acid	1/1.5	55.1
6	Sulfuric acid	1/2	37.9
7	Orthophosphoric acid	1/0	55.6
8	Orthophosphoric acid	1/0.2	63.2
9	Orthophosphoric acid	1/0.4	71.3
10	Orthophosphoric acid	1/0.65	78.9
11	Orthophosphoric acid	1/0.8	75.9
12	Orthophosphoric acid	1/1	70.3

150°C under 10 torr. CHMI was further purified by recrystallization from toluene.

The by-products in CHMI were separated by high-performance liquid chromatography (HPLC). The by-products dissolved in an eluent were dried with a vacuum dryer at 30°C, and the isolated by-products were purified by recrystallization from chloroform/hexane.

Preparation of Acrylic Sheets

Four-millimeter-diameter polyvinyl chloride tubes were placed between two clean glass plates (240 × 180 × 5 mm) and fixed together with steel clamps. CHMI was dissolved in MMA to prepare a 20 wt % CHMI solution. This solution was degassed under 200 torr for 10 min, and lauroyl peroxide (0.4 wt %) was then added to this monomer solution. The monomer solution containing the initiator was charged into the mold after saturation with nitrogen. The filled mold with its opening closed was placed in a water bath thermostated at 55°C for 20 h. After polymerization, the copolymer sheet was removed from the mold, and a part of the sheet was subjected to yellow index (YI) measurement.

Measurements

The purity of CHMI was examined by the use of HPLC (Shimadzu LC-10A), and the following conditions were used for this measurement—column, Zorbax ODS (4.6 mmϕ × 25 cm); mobile phase, a mixture of the aqueous solution of 0.005 mol/L potassium hydrogen phosphate and methanol, of which the weight ratio was 1 : 0.818; column temperature, 45°C; flow rate, 0.8 mL/min; detector, 220 nm. IR, [1]H-nuclear magnetic resonance (NMR) and ^{13}C-NMR, and mass spectra were recorded with Japan Biorat SPC-3200, Varian VXR-300S, and JEOL JMS-AX505WA spectrometers, respectively. The melting point was measured with a Buch 501K. Elemental analysis was performed with a Yanako CHN MT-3. The YI of the CHMI/MMA copolymer was determined with a Nippon Denshoku Kogyo Σ 80.

RESULTS AND DISCUSSION

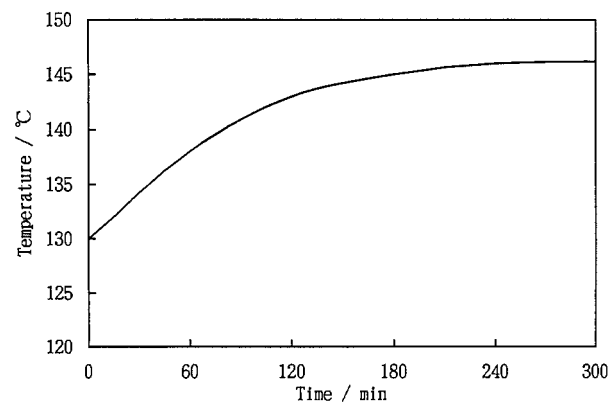We have reported the synthesis of N-butylmaleimide in high yield by the dehydration of N-butyl-

Figure 1   Changes in temperature during the dehydration of CHMA catalyzed with a mixture of orthophospheric acid and CHA.

Table III   Effect of Temperature on CHMI Yield

Run No.	Solvent	Boiling Point[a] (°C)	Temperature[b] (°C)	Yield (mol %)
13	o-Xylene	144.4	148	78.9
14	Cumene	152.7	157	84.4
15	Mesitylene	164.7	168	87.3
16	Pseudocumene	169.4	173	87.1
17	p-Cymene	175	179	72.8

A mixture of orthophosphoric acid and CHA (1/0.65 mol/mol) was used as a catalyst.

[a] From *Encyclopedia Chimica,* Kyoritu Shuppar Co., Ltd.

[b] Maximum temperature.

maleamic acid (BMA) in the presence of a mixture of acid and an amine salt as the catalyst. The hydrolysis of BMA as a side reaction was effectively suppressed with the two-component catalyst.[15] Dehydrations of BMA were performed with different acids at various [acid]/[amine] molar ratios. Table II summarizes the effect of the catalyst, indicating that a mixture of the acid and the amine salt is advantageous over the single-component acid catalyst such as sulfuric and orthophosphoric acids. It has been found that orthophosphoric acid functions more effectively than sulfuric acid. The optimal range of [acid]/[amine] molar ratio for the catalyst activity depends on the type of acid component. The acid component catalyzes the dehydration and hydrolysis of maleimide, and the amine salt is expected to suppress the hydrolysis. Therefore, the acid-amine salt combination simultaneously exerts these functions.

Figure 1 illustrates typical changes in temperature during the ring-closure reaction of CHMA. The temperature of the reaction mixture approached the boiling temperature of the solvent as the reaction proceeded because water formation accompanied by the dehydration of CHMA is reduced with an increase in conversion. The results of the CHMI synthesis in inert solvents having different boiling points are shown in Table III. A high yield of CHMI was attained at a higher temperature when a solvent of higher boiling point was used. This tendency implies that selectivity during the conversion of CHMA to CHMI relative to the dehydration yielding the by-product increases at higher temperatures.

HPLC chromatograms of the purified CHMI after distillation and recrystallization are depicted in Figure 2. A large peak and three small peaks are observed. One of the by-products separated by HPLC had its structure confirmed by mass, ^{1}H-NMR, ^{13}C-NMR, and IR spectroscopies and by elemental analysis, as summarized in Table IV. All of the spectra are also shown in Figures 3–5. Mass spectroscopic inspection and elemental analysis reveal that the chemical composition of the main component of the by-products is $C_{10}H_{15}O_3N$. The ^{13}C-NMR spectrum in Figure 3 exhibits the resonances assignable to the carbonyl carbons of the cyclic acid anhydride (174.8 and 178.3 ppm), methine bound to the amino group (65.8 ppm), and methylene (24.9 ppm) and to the methine carbon of the cyclohexyl ring (50.4 ppm) and methylene (37.6, 28.6, 28.3, and 25.4 ppm).
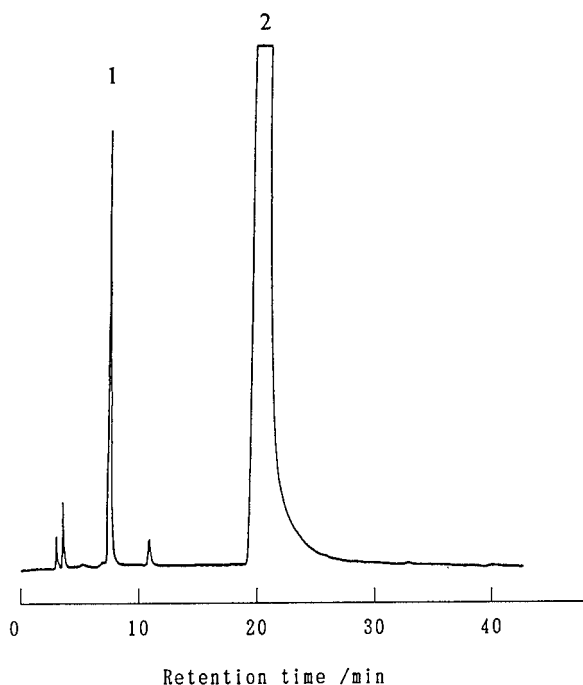

Figure 2   HPLC chromatograms of CHMI product. (1) CHMI, (2) CASA.

Table IV   Analytical Data of Main By-Product

Measurement	Observation
mp (°C)	155.5–156.5
Mass Spectrum m/z (M+)	197 (M+)
Elemental analysis (wt %)	Found: C, 60.5; H, 7.9, N, 6.9, 0, 24.7, Calcd.: C, 60.9, H, 7.67, N, 7.10, 0, 24.33.
Molecular formula	$C_{10}H_{15}O_3N$
IR/KBr ν (cm^{-1})	3,400 s, 2,930 s, 1,695 vs, 1,390 s, 1,195 s, 735 m, 590 m
^{1}H-NMR δ (ppm)	6.05 (1H, d), 4.40 (1H, m), 3.80 (1H, m), 2.95 (1H, dd), 2.40 (1H, dd), 2.00 (2H, q), 1.80 (2H, d), 1.60 (H, m), 1.20 (3H, m)
^{13}C-NMR δ (ppm)	178.3 (1C), 174.8 (1C), 65.8 (1C), 50.4 (1C), 37.6 (1C), 28.6 (1C), 28.3 (1C), 25.4 (2C), 24.9 (1C)

s, strong; vs, very strong; m, medium; d, doublet; dd, double doublet; m, multiplet; q, quartet.

The proton of the amino group (6.05 ppm), methine (4.40 and 3.80 ppm), methylene (2.95 and 2.40 ppm), and the cyclohexyl group (2.00–1.20 ppm) appear in the ^{1}H-NMR spectrum shown in Figure 4. The absorption band of the secondary amine, alkene, and cyclic acid anhydride appear in the IR spectrum illustrated in Figure 5 at 3,400, 2,930, 1,695, and 1,390 cm^{-1}, respectively. The main by-product was confirmed to be *N*-cyclohexyl aminosuccinic anhydride (CASA), on the basis of spectral and elemental analyses. CASA may be produced by hydrolysis and dehydration of the reaction product of CHMI and CHA, as shown in Scheme 1. Three types of minor by-products were confirmed to be MAN, CHMA, and FA on the basis of the comparison of the respective retention times of HPLC with authentic samples.

The No. 10 sample in Table II was used as the crude material for this purification, and the extent of purification was varied by the ratio of [distillate]/[feed] during the distillation. The quality of the purified CHMI after recrystallization of the distilled CHMI is also listed in Table V. CHMI of different purities were submitted for copolymerization with MMA in the mold, and the YI of the sheets were evaluated with a color meter. The YI values are also given in Table V. Apparently, the finding that the YI value increases with an increase in the content of CASA in CHMI manifesting that contamination with CASA is one of the main causes for changes in color. However, the YI value of the copolymer of CHMI containing 0.9% CASA was estimated to be 0.8, as was the YI value of the PMMA homopolymer. The boundary between coloration and no color change in PMMA seems to be present in the range of a CASA content of 0.9% or more.

CONCLUSIONS

CHMI was synthesized by the dehydration and ring closure of CHMA with a mixture of acid and
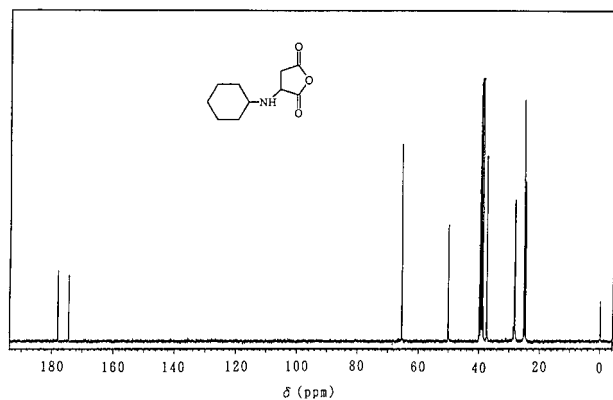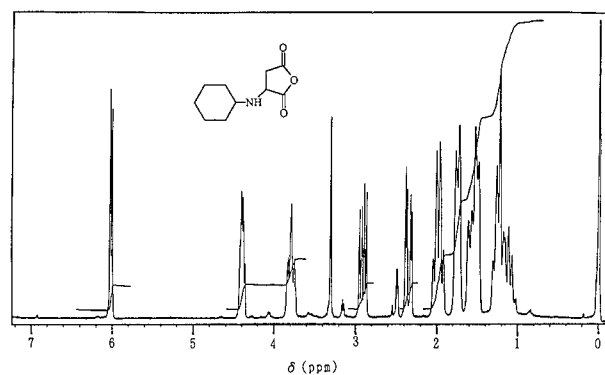

Figure 3   Carbon NMR spectrum of CASA.
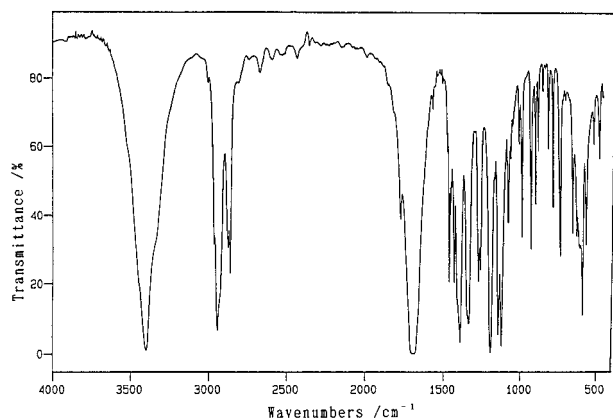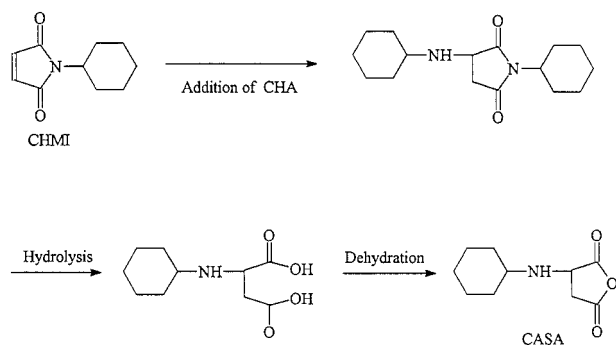

Figure 4   Proton NMR spectrum of CASA.

Figure 5 IR spectrum of CASA.

Table V Characteristics of CHMI and YI Value of Copolymer with MMA

Product[a]	mp (°C)	Purity (wt %)	Impurity (wt %)			YI[b]
			MAN	FA	CASA	
1	87.6	97.4	0.01	<0.01	2.5	4.0
2	88.3	98.2	0.01	<0.01	1.8	2.4
3	89.1	99.1	0.01	<0.01	0.9	0.8
4[c]	90.2	>99.5	0.01	<0.01	<0.01	0.8

[a] Contained Topanol-A (100 ppm) as a stabilizer.
[b] The YI value for the MMA homopolymer was 0.8 by out measurement.
[c] Purified by recrystallization.

its amine salt in an organic nonpolar solvent that is immiscible with water. The optimal region of the molar ratio of [acid]/[amine] was observed to be 1/0.68−1/0.8 for orthophosphoric acid and CHA. It is considered that this two-component catalyst has the ability of dehydration and inhibits the hydrolysis of CHMA. CASA, which was confirmed as the major by-product, can be eliminated by distillation. CHMI contaminated with various amounts of CASA were copolymerized with MMA in the mold to evaluate the YI of the respective copolymers. As a result, it was proved that an increase in the CASA content in CHMI increased the YI of the copolymer, and the influence of CASA was observed in the range of a CASA content higher than 0.9%. CHMI contaminated by less than 0.9% of CASA can be used for the heat-resistant MMA resin free from coloration as well as for the MMA homopolymer.

Scheme 1.

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