

A New Class of Transparent Polymeric Materials. II. Synthesis and Properties of Poly(*N*-cyclohexylmaleimide-*alt*-isobutene) Modified with Lauryl Methacrylate

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SYNOPSIS

Transparent polymeric materials with high heat resistance and low water absorption were designed based on the alternating copolymers of *N*-substituted maleimide (RMI) with isobutene (IB). The *N*-substituent of the maleimide significantly affected the glass transition temperature (T_g) and water absorption of the copolymers. Poly(*N*-cyclohexylmaleimide-*alt*-IB) [poly(CHMI-IB)] showed a T_g value as high as 192°C and relatively low water absorption. Furthermore, the incorporation of a small amount of lauryl methacrylate in the copolymers was confirmed to reduce the water absorption of the copolymer drastically, although it decreased the T_g of the copolymers at the same time. Poly(CHMI-IB), containing 4 mol % lauryl methacrylate, showed a good balance of excellent transparency, high heat resistance, acceptable mechanical properties, and low water absorption. The heat deflection temperature was as high as 141°C. The water absorption at 23°C after immersion for 14 days was 0.56% and the dimensional change after 7 days was 0.06%. They are half and one-quarter of those of poly(methyl methacrylate), respectively. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The radical copolymerization of maleimides including *N*-phenylmaleimide and *N*-cyclohexylmaleimide with various vinyl monomers has been examined to improve the thermal properties of vinyl polymers.¹⁻⁸ The mechanical and optical properties of the copolymers of methyl methacrylate were also reported.^{9,10} However, the incorporation of a maleimide unit into the backbone of the vinyl polymers caused problems of brittleness and discoloration of the polymers. In previous articles¹¹⁻¹³ we reported the radical copolymerization of a series of *N*-substituted maleimides (RMIs) with isobutene (IB) and the properties of the resulting alternating copolymers. Especially, poly(*N*-methylmaleimide-*alt*-isobutene) [poly(MeMI-IB)] was found to have a unique bal-

ance of optical, thermal, and mechanical properties.¹³ The visible light transmittance was more than 90%, and it produced moldings with low birefringence. The heat deflection temperature was as high as 157°C, and the flexural modulus was the highest among typical amorphous polymers. However, the water absorption of poly(MeMI-IB) was relatively high, 2.0%, in water at 23°C after immersion for 14 days. Water absorption of the polymeric materials results in lowering of the dimensional stability, which is a serious problem, especially in optical uses such as optical lenses and compact discs. In fact, the large water absorption of poly(methyl methacrylate) (PMMA), as well as its low heat resistance, often limits its uses in spite of the excellent optical properties such as high transparency, large Abbe's number, and low birefringence. Because the large water absorption of poly(MeMI-IB) is an intrinsic characteristic depending on the chemical structure of the polymers, it would be modified by the design of the *N*-substituents of the maleimide unit. In this

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Table I Radical Copolymerization of RMI with IB

RMI	Yield ^a (%)	RMI in Copolymer (mol %)	$M_w \times 10^{-5}$	M_w/M_n	T_g (°C)	T_d (°C)
MeMI	96	50.3	2.0	2.4	157	389
iPMI	96	50.2	1.6	2.3	145	388
nBuMI	93	50.0	1.5	2.1	80	387
CHMI	94	50.0	1.7	2.1	192	396
PhMI	92	50.6	3.8	2.3	188	440

Copolymerization conditions: [RMI] = 0.9 mol/L, [IB] = 2.1 mol/L, [AIBN] = 5×10^{-3} mol/L, in dioxane at 60°C for 6 h.

^a Based on RMI.

study, we prepared a transparent polymeric material with high heat resistance and low water absorption based on the alternating copolymers of RMI and IB.

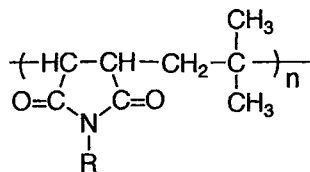
EXPERIMENTAL

Materials

N-Methylmaleimide (MeMI) and *N*-phenylmaleimide (PhMI), commercial products of Wako Chemical Industry, Ltd., were purified by recrystallization. Other RMIs, for instance, *N*-isopropylmaleimide (IPMI), *N*-*n*-butylmaleimide (nBuMI), and *N*-cyclohexylmaleimide (CHMI), were prepared from the reaction of maleic anhydride and the corresponding amines according to the method described in the previous article.¹¹ 2,2'-Azobis(isobutyronitrile)(AIBN) was purified by recrystallization. Dioxane, toluene, *n*-hexyl methacrylate, lauryl methacrylate, and stearyl methacrylate, commercial products of Tokyo Chemical Industry Co., Ltd., were purified by distillation before use. IB (Takahichi Trading Co., Ltd.) and perbutylneodecanoate (PBND) (Nippon Oil & Fats Co., Ltd.) were used without further purification. PMMA was a commercial product of Mitsubishi Rayon Co., Ltd.

Polymerization Procedures

RMI and a radical initiator in the solvent was placed into an autoclave provided with an agitator, nitrogen



Scheme 1

and isobutene inlet tubes, and a thermometer, and then the solution was purged with nitrogen several times. IB was weighed and introduced into the autoclave. Copolymerization was carried out at 60°C for a given time. After copolymerization, the polymerization mixture was poured into a large amount of methanol to precipitate the copolymer. The polymers were purified by repeating the reprecipitations. The copolymerization yield was determined by quantitative analysis of the residual RMI using gas chromatography. The composition of the copolymers was determined by elemental analysis and NMR spectroscopy.

Measurements

The number average molecular weight (M_n) and the molecular weight distribution (M_w/M_n) of the resulting polymers were determined by gel permeation chromatography calibrated with polystyrene stan-

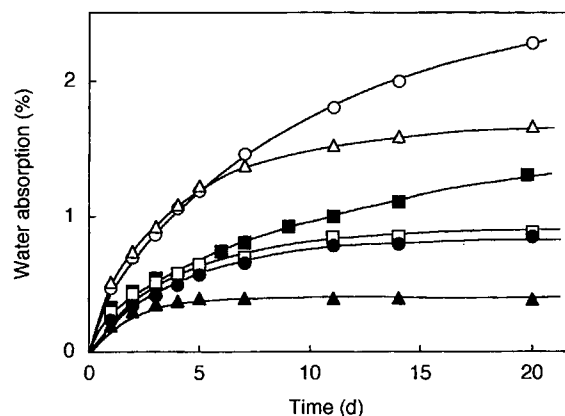


Figure 1 Relationships between the water absorption of the copolymers and the immersion time in water at 23°C. (○) Poly(MeMI-IB), (□) Poly(IPMI-IB), (▲) Poly(nBuMI-IB), (●) Poly(CHMI-IB), (△) Poly(PhMI-IB), (■) PMMA.

creased the T_g value of the resulting copolymers, while a linear alkyl substituent decreased it. The relationships between the water absorption of the copolymers and the immersion time in water at 23°C are shown in Figure 1. Poly(MeMI-IB) and poly(PhMI-IB) showed relatively large water absorption. The water absorption ability of the copolymers of RMI and IB decreased in the following order; poly(MeMI-IB) > poly(PhMI-IB) > poly(IPMI-IB) ≥ poly(CHMI-IB) > poly(nBuMI-IB). The water absorption of poly(nBuMI-IB) was the lowest among them and it was saturated within 5 days. The water absorption of poly(nBuMI-IB) after immersion for 14 days was 0.4%. It was one-third of that of PMMA (1.2%). However, the T_g value of poly(nBuMI-IB) was as low as 80°C. Poly(CHMI-IB) showed a good balance of high T_g value and low water absorption among the polymers. The T_g value was as high as 192°C and the water absorption was lower than that of PMMA.

Effect of the Incorporation of Alkyl Methacrylates into the Copolymer

As an attempt to improve the water absorption of PMMA, it was reported that the copolymerization of MMA with higher alkyl methacrylates reduced the water absorption of PMMA. However, it also lowered the heat resistance of PMMA to an impractical level.¹⁵ In this work, we tried to produce a copolymer with a good balance of high heat resistance and low water absorption based on poly(CHMI-IB) whose T_g value was the highest of that of the alternating copolymers with *N*-alkyl-

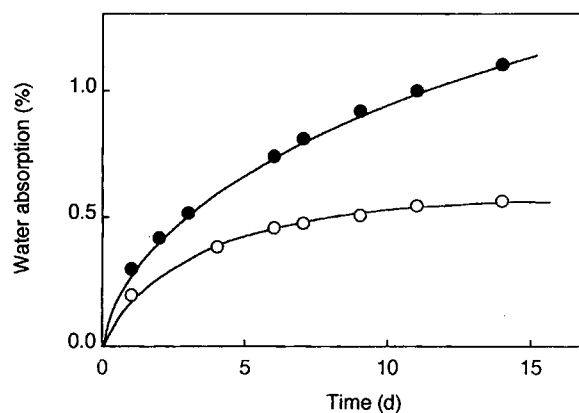


Figure 3 Relationships between the water absorption of the copolymers and the immersion time in water at 23°C. (○) *m*-Poly(CHMI-IB), (●) PMMA.

maleimide and IB. Terpolymerization of CHMI, IB, and a small amount of alkyl methacrylate was carried out for this purpose. Table II shows the T_g values and water absorption of the poly(CHMI-IB) modified with three kinds of alkyl methacrylates (RMA). The incorporation of a higher alkyl chain into the backbone of poly(CHMI-IB) was confirmed to reduce the water absorption drastically; however, it also lowered the T_g values at the same time. Poly(CHMI-IB) modified with lauryl methacrylate showed a good balance of a high T_g value and low water absorption among polymers. Figure 2 shows the effect of the lauryl methacrylate content in the copolymer on the water absorption and the T_g values of the resulting copolymers. Poly(CHMI-IB), con-

Table III Properties of Poly(CHMI-IB) Modified with Lauryl Methacrylate

Property	Unit	<i>m</i> -Poly(CHMI-IB)	PMMA
Transmittance	%	91	92
Refractive index		1.52	1.49
Abbe's number		52	53
Heat deflection temperature	°C	141	96
Thermal decomposition temperature	°C	393	303
Flexural strength	MPa	78	113
Flexural modulus	GPa	2.5	3.1
Izod impact strength (unnotched)	J/m	104	130
Water absorption			
1 day	%	0.19	0.26
14 days		0.56	1.21
Dimensional change			
1 day	%	0.02	0.04
7 days		0.06	0.23

Poly(CHMI-IB) contained 4 mol % lauryl methacrylate.

taining 4 mol % lauryl methacrylate, was found to show a good balance, for instance, T_g values as high as 148°C and a low water absorption of 0.56%.

Properties of Poly(CHMI-IB) Modified with Lauryl Methacrylate

Several properties, for instance, optical, thermal, and mechanical properties, and water absorption, of poly(CHMI-IB) containing 4 mol % lauryl methacrylate [*m*-poly(CHMI-IB)] were evaluated. The results are summarized in Table III compared with those of PMMA. The light transmittance of *m*-poly(CHMI-IB) was almost the same as that of PMMA and the refractive index was higher. The Abbe's number was as high as that of PMMA, indicating that the refractive index was less dependent on the wave number. *m*-Poly(CHMI-IB) showed excellent thermal stabilities, for instance, the heat deformation temperature and the thermal decomposition temperature were 45 and 90°C higher than those of PMMA, respectively. The flexural strength, modulus, and the Izod impact strength were lower than those of PMMA. However, these strength values may be acceptable in optical uses such as optical lenses. Figure 3 shows the dependence of immersion time on the water absorption of *m*-poly(CHMI-IB) and PMMA. The degree of water absorption of *m*-poly(CHMI-IB) was lower than that of PMMA, and it was almost saturated after 14 days. The amount of water absorption after immersion for 14 days was 0.56%, which was half of the value for PMMA at the same time (1.2%) and one-quarter of the saturated value (2.1%). The dimensional change after 7 days was 0.06%, and it was one-quarter of that of PMMA at the corresponding time.

CONCLUSIONS

A transparent polymeric material with high heat resistance and low water absorption was prepared based on poly(RMI-IB). Poly(CHMI-IB) modified with a small amount of lauryl methacrylate showed a good balance of optical, thermal, mechanical properties, and low water absorption. The optical properties were almost the same level as those of

PMMA, and the heat deformation temperature was 45°C higher than that of PMMA. This polymer has acceptable mechanical strengths, although they were not greater than those of PMMA. The water absorption and dimensional change of the copolymer were half and one-quarter of those of PMMA, respectively.

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