A New Class of Transparent Polymeric Materials. I. Production and Properties of an Alternating Copolymer of N-Methylmaleimide and Isobutene

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SYNOPSIS

An alternating copolymer of N-methylmaleimide and isobutene was produced by a radical precipitation polymerization method. The copolymer thus produced is a new class of transparent polymeric material that shows a unique balance of optical, thermal, and mechanical properties. The visible light transmittance was more than 90% and the stress optical coefficient was smaller than that of polycarbonate, leading to moldings with lower birefringence. The heat deflection temperature of the copolymer was as high as 157°C, and the thermal expansion coefficient was about 30% smaller than those of poly(methyl methacrylate) and polycarbonate. The copolymer showed excellent mechanical properties, specifically, the flexural modulus was the highest among the typical amorphous polymers. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Transparent polymeric materials, mainly poly(methyl methacrylate) (PMMA) and polycarbonate (PC), are widely used for many applications including signboards, carports, automobile parts, and sundries, as well as optical applications such as compact discs, optical lenses and fibers.[1] However, some inferior properties of these polymers often limit their use, for example, the low heat resistance of PMMA and the poor optical properties of PC. Consequently, the development of new types of amorphous polymers with excellent optical properties and high heat resistance is ernestly expected.

Maleimide and its derivatives such as N-phenylmaleimide are well known to polymerize to produce thermally stable polymers. The copolymerization with various vinyl monomers including methyl methacrylate and styrene has been also examined to improve the thermal properties of the vinyl polymers.[2–8] However, the incorporation of maleimide unit into vinyl polymers often causes problems of brittleness and discoloration.[9] In the previous article, we reported the radical copolymerization of a series of N-substituted maleimides with isobutene and the properties of the resulting alternating copolymers.[10] Among them, poly(N-methylmaleimide-alt-isobutene) [poly(MeMI-IB)] was found to have a unique balance of transparency, heat resistance, and mechanical strength. The establishment of the production method for poly(MeMI-IB) is an important subject for the industrialization. Suspension and emulsion polymerization methods that are generally used for vinyl polymerization are not applicable for the copolymerization of N-methylmaleimide with isobutene because N-methylmaleimide is a solid compound whose melting point is 96°C and the solubility in isobutene is quite low. Homogeneous solution polymerization also seems not to be available because the impurities such as residual N-methylmaleimide tend to cause discoloration of the resulting copolymer.[11] In this article, we deal with the production of poly(MeMI-IB) by a precipitation polymerization method, and the properties of the resulting copolymer are compared with those of PMMA and PC.

Table I   Results of Copolymerization of MeMI with IB in Various Solvent

Solvent (vol/vol)	Solubility Parameter[a] $(MPa)^{1/2}$	Yield[b] (%)	M_n $(\times 10^4)$	Remarks
Ethylbenzene	18.0	98	3.0	Particle
Toluene	18.2	99	8.0	Coagulation
Ethylacetate	18.6	98	6.0	Coagulation
Methylacetate	19.6	98	7.0	Coagulation
Toluene/Methanol (7/3)	—	99	13.0	Particle
Toluene/Methanol (5/5)	—	100	12.0	Particle
Methanol	29.7	98	13.0	Coagulation

Polymerization conditions: [MeMI] = 0.45 mol/L, [IB] = 4.05 mol/L, [BND] = 1 × 10⁻³ mol/L at 60°C for 5 h.
[a] Ref. 12.
[b] Based on MeMI.

EXPERIMENTAL

Materials

N-methylmaleimide was supplied from the Petrochemical Laboratory of Tosoh Corporation. t-Butylperoxyneodecanoate (BND), isobutene, and solvents were reagent grade commercial materials and were used without further purification. PMMA and PC were commercial products of Mitsubishi Rayon Co., Ltd., and Teijin Chemicals, Ltd., respectively.

Procedures

The copolymerization was carried out in 1 L and 50 L autoclaves provided with an agitator, nitrogen, and isobutene inlet tubes, and a thermometer. The typical procedures are as follows: N-methylmaleimide was dissolved in a toluene/methanol mixture in the 50 L autoclave; then BND as the radical initiator was added in the solution. After the solution was

Figure 1   ¹³C NMR spectrum of copolymer obtained in a toluene/methanol solvent.

purged with nitrogen several times, isobutene was weighed and introduced into the autoclave. The copolymerization was carried out at 60°C for 5 h. The polymer particles precipitated were separated by centrifugation and finally dried under reduced pressure at 80°C. The yield of the polymer particles was determined gravimetrically. The polymer, in part, was purified by repeated reprecipitations, followed by supercritical fluid extraction for the elemental analysis. The other measurements for determining the polymer properties were carried out without any purifications. The polymer particles obtained were extruded with a small amount of antioxidant into pellets using a twin-screw extruder by means of a Laboplastomil (Toyo Seiki K.K.). The test specimens were prepared by injection molding using a Minimat (Sumitomo Jukikikai Kogyo K.K.)

Measurements

The number average molecular weight (M_n) of the resulting polymers was determined by gel permeation chromatography calibrated with polystyrene standards using Tosoh RE-8000, RI-8000, and UV-8000 instruments equipped with TSK gel G-6000H, G-4000H, G-4000H, and G-2000H columns with
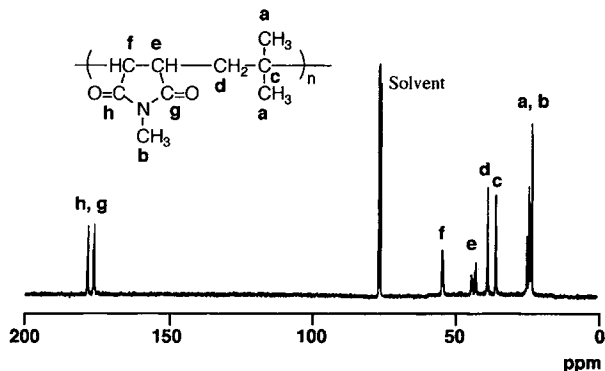
Table II   Optical Properties of Poly(MeMI-IB)

Property	Unit	Poly (MeMI-IB)	PMMA	PC
Light transmittance	%	91	92	88
Haze	%	1.5	1.3	1.7
Refractive Index		1.53	1.49	1.58
Abbe's number		51	53	29

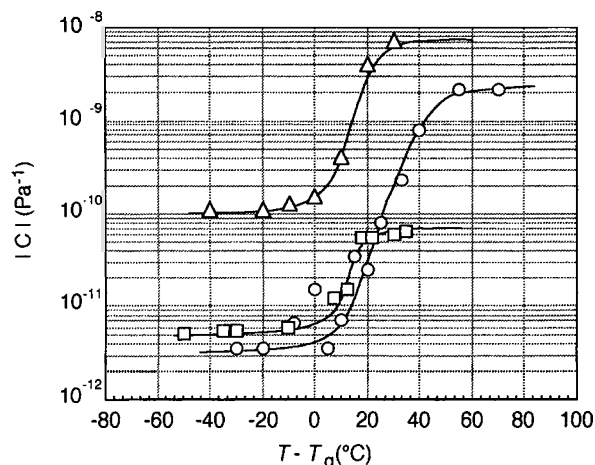**Figure 2** Absolute stress optical coefficient C vs. reduced temperature $T - T_g$. (○) poly(MeMI-IB), (□) PMMA, (△) PC.

$$\Delta n = C \cdot \sigma \qquad (2)$$

where Δn is the birefringence value, that is, the difference in refractive index between the extensional direction and the crossed direction, C is the stress optical coefficient, and σ is the applied stress. The coefficient was measured using an Optorheometer (model HRS-100: ORC Seisakusho) at a constant strain ratio of 1%/s and C was evaluated at 5% strain. The heat deflection temperature under a stated load of 1.8 MPa was measured by means of an H.D.T & V.P.S.T Tester (Toyo Seiki K.K.) Thermogravimetric analysis was carried out in a nitrogen stream at a heating ratio of 10°C/min by means of a Seiko TG/DTA200 to determine the onset temperature of the decomposition (T_d). The mechanical strength, modulus, and the Izod impact strengths were tested by means of a Tensilon UTM-2.5 (Toyo Baldwin Co., Ltd.) and an Izod impact tester (Toyo Seiki K.K.), respectively, according to ASTM standards.

chloroform as the eluent at 38°C. ^{13}C NMR spectra were taken by means of a JEOL GX-400 Spectrometer using deuterochloroform as the solvent. The light transmittance and haze were measured by means of a Color and Color Difference Meter using a model 1001 DP (Nippon Denshoku Kogyo Co., Ltd.). The refractive index and Abbe's number were determined by means of an Abbe refractometer (Atago Co., Ltd.). The Abbe's number (ν_D) is represented by the following equation:

$$\nu_D = \frac{n_D - 1}{n_F - n_C} \qquad (1)$$

where n_C, n_D, and n_F represent the refractive index at 656, 589, and 486 nm, respectively. The birefringence was evaluated as the stress optical coefficient using the following equation:

RESULTS AND DISCUSSION

Production of Poly(N-methylmaleimide-alt-isobutene)

Precipitation polymerization to produce the polymer in granular form using a solvent that dissolves the monomer and does not dissolve the resulting polymer is an attractive method for the production of the poly(MeMI-IB), because the problems described in introduction can be solved; for example, the impurities that dissolved in the solvent are easily separated by filtration, leading to the pure copolymers. The key point of this method is to find a suitable solvent. The results of the radical copolymerization of MeMI and IB in various solvents are summarized

Table III   Thermal Properties of Poly(MeMI-IB)

Property	Unit	Poly(MeMI-IB)	PMMA	PC
Heat deflection temperature				
Annealed	°C	157[a]	100[b]	140[a]
As molded	°C	142	95	136
Thermal decomposition temperature	°C	396	303	454
Coefficient of liner thermal expansion ($\times 10^{-5}$)	cm/(cm °C)	5.1	7.7	6.7

[a] Annealing at 120°C for 5 h.
[b] Annealing at 80°C for 5 h.

Table IV   Mechanical Properties of Poly(MeMI-IB)

Property	Unit	Poly(MeMI-IB)	PMMA	PC
Tensile strength	MPa	72.6	65.7	63.7
Flexural strength	MPa	129	113	92
Flexural modulus	GPa	4.81	3.14	2.16
Izod impact strength	J/m			
Notched		16	10	740
Unnotched		150	130	nonbreak

in Table I. All copolymerization produced the copolymers in high yields (98–100% based on MeMI). When using ethylbenzene or toluene/methanol mixtures as the copolymerization solvent, the precipitation polymerization proceeded feasibly to give the polymer particles without any dispersant, whereas coagulation was observed during the copolymerization in the other solvents. A clear relationship between the precipitation polymerization behavior and the solubility parameter of the solvent was not observed under these conditions. The relatively low molecular weight of the copolymer obtained in ethylbenzene was probably due to the high chain transfer constant of ethylbenzene. On the contrary, the molecular weight of the copolymer obtained in a toluene/methanol mixture (7 : 3 vol/vol) was high as 1.3×10^5, and its distribution value was 2.1, which was the same level as that of the copolymer obtained by the homogeneous polymerization of MeMI and IB in chloroform.[10] The resulting copolymer was confirmed to have an alternating structure of MeMI and IB units by elemental analysis (50.2 mol % of MeMI unit in the copolymer) and the ^{13}C NMR spectrum (Fig. 1). The resulting polymer particles had an average particle size of 250 μm and a bulk density of 0.31 g/cm^3.
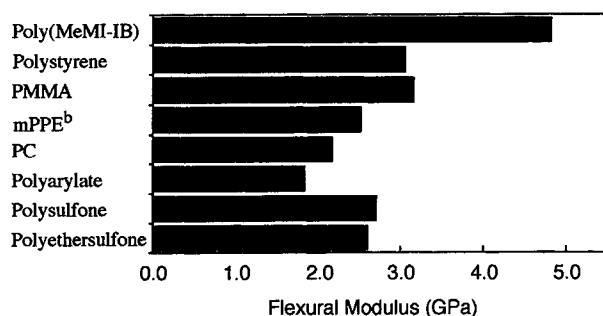

Figure 3   Flexural modulus of typical amorphous polymers. (a) Data from ref. 15 (b) Modified poly(phenylene ether).

Optical Property

The poly(MeMI-IB) produced above was found to give moldings with low yellowness index without further purification. The light transmittance, haze, refractive index, and Abbe's number of the poly(MeMI-IB) were evaluated and the results are summarized in Table II, together with those of PMMA and PC. The poly(MeMI-IB) shows excellent transparency as well as PMMA and was superior to PC. The refractive index was situated between those of PMMA and PC. The Abbe's number of the poly(MeMI-IB) was at the same level as that of PMMA, indicating that the refractive index was less dependent on the wave number compared with that of PC. The birefringence of the moldings is an important subject for transparent polymeric materials, especially in optical uses including optical lenses and discs. It results from the anisotropy of the moldings and relates to the polymer structure. It is well known that PC has a large stress optical coefficient and, therefore, moldings of PC have large birefringence even under small applied stress, thereby resulting in one of the serious disadvantages of PC.[1] Figure 2 shows the absolute C values for poly(MeMI-IB), PMMA, and PC plotted against the measured temperature reduced T_g for each polymer. Polymeric material always goes from a rubber-elastic state, through a transition state, and to a glassy state when it is processed into moldings, and so we evaluated the C values over a wide temperature range from T_g −50°C to T_g +50°C, assuming that eq. (2) is applicable for the small strain even in the glassy region for the time being. The sign of C of PMMA was negative, whereas that of PC was positive and

Table V   Surface Hardness of Poly(MeMI-IB)

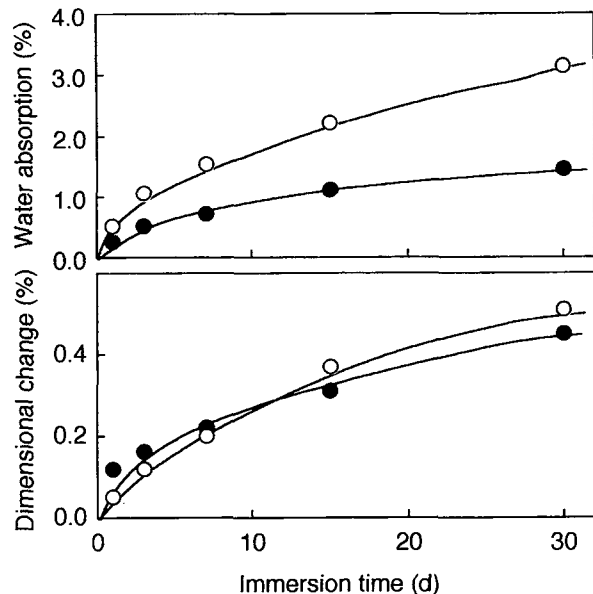| Property	Poly(MeMI-IB)	PMMA	PC
Pencil hardness	3H	3H	2B
Rockwell hardness	103	98	52

Figure 4 Dependence of immersion time on (a) water absorption and (b) dimensional change. (O) poly(MeMI-IB), (●) PMMA.

the C values of PMMA were much smaller than those of PC over whole range in agreement with the results reported.[13,14] The sign of C of poly(MeMI-IB) was found to be positive and the C values were much smaller than those of PC over the whole range and were at the same level as those of PMMA in the glassy region.

Thermal Property

The heat deflection temperature (HDT), the thermal decomposition temperature (T_d), and the coefficient of linear thermal expansion of the poly(MeMI-IB) are summarized in Table III. The HDT of the poly(MeMI-IB) after annealing was about 60 and 20°C higher than those of PMMA and PC, respectively. The T_d of the poly(MeMI-IB) was 90°C higher than that of PMMA. The coefficient of thermal expansion was about 30% smaller than those of PMMA and PC, indicating the excellent dimensional stability.

Mechanical Property

The mechanical properties of poly(MeMI-IB) are summarized in Table IV, compared with those of PMMA and PC. Poly(MeMI-IB) was found to have the highest tensile strength, flexural strength, and flexural modulus among them. Especially, the flexural modulus of the poly(MeMI-IB) was more than

twice that of PC. Figure 3 exhibits the flexural modulus of the typical amorphous polymers. It is noteworthy that the flexural modulus of poly(MeMI-IB) is the highest among those of the typical amorphous polymers. The Izod impact strength of the poly(MeMI-IB) was at the same level as that of PMMA and was inferior to that of PC.

Environmental Property

The low surface hardness, leading to the low scratch resistance, is one of the disadvantages of PC. The pencil hardness and Rockwell hardness of the poly(MeMI-IB) are represented in Table V, together with those of PMMA and PC. The surface hardness of the poly(MeMI-IB) was as high as that of PMMA and was superior to that of PC. Water absorption is an undesirable property for plastics, resulting in low dimensional stability. The time dependence of water absorption of the poly(MeMI-IB) and the dimensional change is shown in Figure 4. The water absorption of the poly(MeMI-IB) is higher than that of PMMA. However, because the expansion coefficient is half that of PMMA, the influence of the immersion time on the dimensional change was at the same level as that of PMMA. PC is well known
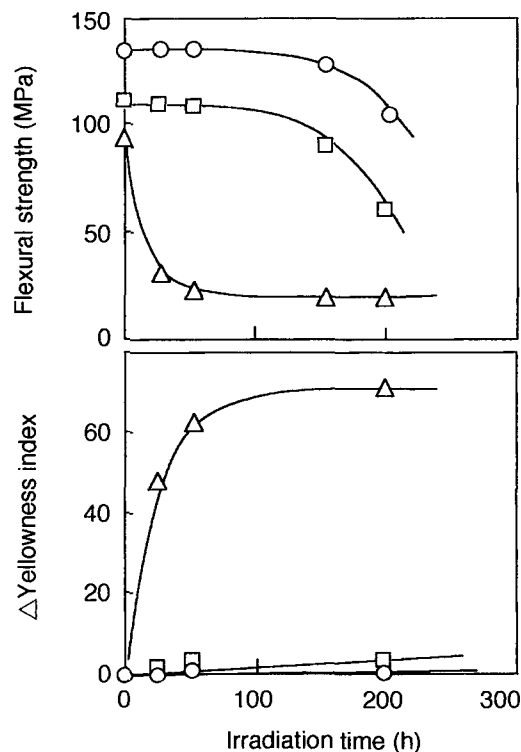

Figure 5 Dependence of UV irradiation time on flexural strength and Δ yellowness index. (O) poly(MeMI-IB), (□) PMMA, (Δ) PC.

to deteriorate in its properties, including mechanical strength and transparency on exposure to sunlight. The effects of UV irradiation time on the flexural strength and discoloration are shown in Figure 5. The flexural strength of PC was weakened drastically and the yellowness index increased on exposure to UV light. On the contrary, less deterioration of strength and only slight discoloration were observed for the poly(MeMI-IB), the same as those for PMMA.

CONCLUSIONS

Poly(MeMI-IB) produced by the radical precipitation polymerization method using a toluene/methanol mixture as the solvent is a new class of transparent polymeric material. The remarkable features of the polymer are (1) excellent optical properties, for example, high visible light transmittance and low stress optical coefficient; (2) excellent thermal stability, for instance, high heat resistance and low thermal expansion coefficient; (3) high modulus; and (4) good UV resistance.

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