

# Physicomechanical Properties of Poly(methyl methacrylate-co-*N*-arylmaleimides)

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## SYNOPSIS

The article describes the effect of incorporating low mol fractions of *N*-*o*-tolylmaleimide (MO)/*N*-*p*-tolylmaleimide (MP) in poly(methyl methacrylate) (PMMA) on  $T_g$ , thermal behavior, mechanical, and optical properties. The glass transition temperature ( $T_g$ ) of PMMA increased by 10–12°C upon incorporation of an  $\sim 0.026$  mol fraction of *N*-arylmaleimides. A further increase of *N*-arylmaleimide content up to 0.1 mol fraction in the copolymers resulted in a further  $\sim 10^\circ\text{C}$  increase in  $T_g$ . The tensile strength and % elongation decreased, whereas modulus increased with increasing maleimide content. The solar transmittance and % transmittance at higher wavelengths of the copolymer sheets having a low mol fraction of *N*-arylmaleimides (i.e., 0.026–0.05) were comparable to PMMA.

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## INTRODUCTION

To extend the application areas of poly(methyl methacrylate) (PMMA) and its copolymers in solar energy collection devices, it is necessary to increase  $T_g$  without affecting its transparency, weatherability, and mechanical properties. The factors which affect the  $T_g$  of polymers are (a) molecular structure, (b) molecular weight, and (c) additives. A restriction to molecular motion leads to an increase in  $T_g$ . For example, polymers with a stiff backbone and rigidly held bulky side groups have high  $T_g$ . An increase in intermolecular forces of attraction also increases  $T_g$ .<sup>1,2</sup> However, the prediction of  $T_g$  from structural information alone is a bit difficult. Incorporation of a low mol fraction of *N*-arylmaleimide, a polar monomer with rigid side groups in PMMA, is expected to increase  $T_g$ . Copolymers of MMA with *N*-phenylmaleimide,<sup>3,4</sup> *N*-cyclohexylmaleimide,<sup>5,6</sup> *N*-(4-substituted phenyl)- $\alpha$ -chloromaleimide,<sup>7</sup> *N*-alkyl- $\alpha$ -chloromaleimide,<sup>8</sup> *N*-(4-substituted phenyl)citraconimide,<sup>9</sup> and *N*-alkylcitraconimide<sup>10</sup> have been reported in the literature. Polymer alloys based on MMA-*N*-phenylmaleimide copolymers and styrene-maleic anhydride/acrylonitrile have been described.<sup>11,12</sup>

However, the presence of imide groups in the PMMA backbone may also affect the optical and mechanical properties. Therefore, it was considered of interest to study the physicomechanical properties of copolymers of MMA and *N*-arylmaleimides. In our earlier articles,<sup>13,14</sup> we reported the solution copolymerization of *N*-arylmaleimides (mol fraction: 0.1–0.5) with MMA using a free-radical initiator. However, the copolymers thus obtained were of relatively low intrinsic viscosity. An increase in  $T_g$  and thermal stability was observed upon copolymerization. Copolymers of MMA with *N*-substituted maleimides prepared by group-transfer polymerization have also been reported to have low molecular weight.<sup>15,16</sup>

The present investigations were undertaken with an aim to investigate the incorporation of a low mol fraction (0.026–0.098) of *N*-*o*-tolylmaleimide (MO) and *N*-*p*-tolylmaleimide (MP) in PMMA on  $T_g$ , thermal behavior, transparency, and mechanical properties.

## EXPERIMENTAL

### Materials

Methyl methacrylate (MMA) (Fluka AG) was washed with a dilute solution of sodium hydroxide, followed by water, dried, and distilled under reduced

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pressure before use. *N*-*o*-tolylmaleimide (MO) and *N*-*p*-tolylmaleimide (MP) were prepared according to the method reported elsewhere.<sup>3</sup>

### Preparation of Prepolymer Syrup

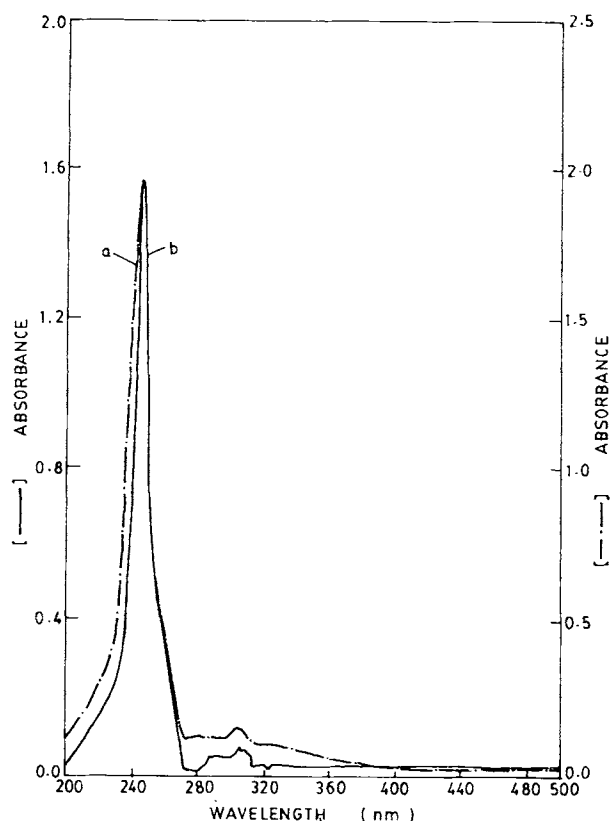
Requisite quantities of MMA and MO/MP were taken in a one-necked 250 mL round-bottomed flask fitted with a reflux condenser. Nitrogen gas was bubbled through the solution and then 1% (w/w) of azobisisobutyronitrile (AIBN) was added. The temperature was raised to 60°C. When the % conversion was around 15%, the flask was removed and the contents cooled using ice-cold water.

### Preparation of the Mold

Two toughened glass plates of 21.5 × 29.0 cm<sup>2</sup> were cleaned with chromic acid, water, and acetone and then dried. The glass plates were sprayed with a silicone-releasing agent and wiped using a tissue paper to get a thin uniform coating. A PVC gasket of diameter 2 mm was placed in between the plates which were held together using steel clamps. One side of the glass plate was kept open for pouring the prepolymer syrup.

### Fabrication of Polymer Sheets

Approximately 50 mL of prepolymer syrup was poured into the mold. Then, the opening of the mold was closed using a metal plate and clamps. The filled mold was placed in a preheated water bath and maintained at 60°C for 3 h. The assembly was then removed and placed in an air oven at 90–110°C for 3 h. Later, it was allowed to cool. The clamps were then removed and the sheet was taken out by passing a stream of water. The sheet was washed with water followed by wiping the excess water with a filter paper. Several copolymer sheets were prepared by



**Figure 1** Electronic spectra of MMA : MP copolymer (sample Z) recorded in chloroform solution: (a) original; (b) after precipitation.

varying the mol fraction of *N*-arylmaleimides in the initial feed (Table I).

### Characterization

The intrinsic viscosity of the copolymers was determined in chloroform at 30.0 ± 0.1°C using an Ubbelohde suspension-level viscometer. Glass transition temperatures were determined by recording

**Table I** Fabrication of Sheets of MMA and *N*-Arylmaleimides

Sample Designation	<i>N</i> -Arylmaleimide	Mol Fraction of <i>N</i> -Arylmaleimide	Thickness of Sheets (mm)	[ $\eta$ ] (dL/g)
PMMA	—	—	1.50	1.78
P	MO	0.026	1.10	2.22
Q	MO	0.050	1.15	2.44
R	MO	0.070	1.08	2.62
S	MO	0.098	1.15	2.75
X	MP	0.026	1.15	2.30
Y	MP	0.050	1.20	2.52
Z	MP	0.074	1.15	3.10

DSC scans using a DuPont 9900 thermal analyzer having a 910 DSC module. The weight of the sample was  $6.0 \pm 0.9$  mg and a heating rate of  $10^\circ\text{C}/\text{min}$  was used in each experiment. For recording DSC scans, powdered samples were obtained by dissolving small pieces of sheets in chloroform and precipitating the polymer by dropwise addition of this solution to an excess of methanol. To keep the thermal history of all the copolymers the same, the powdered samples were heated in a DSC pan to  $120^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$ , and this temperature was maintained for 2 min. The samples were allowed to cool and DSC traces were recorded in the second heating cycle. The endothermic transition region was characterized by determining the following temperatures:

- $T_0$ : temperature of first deviation from the base line
- $T_e$ : extrapolated onset temperature
- $T_g$ : midpoint temperature
- $T_f$ : extrapolated end set temperature.

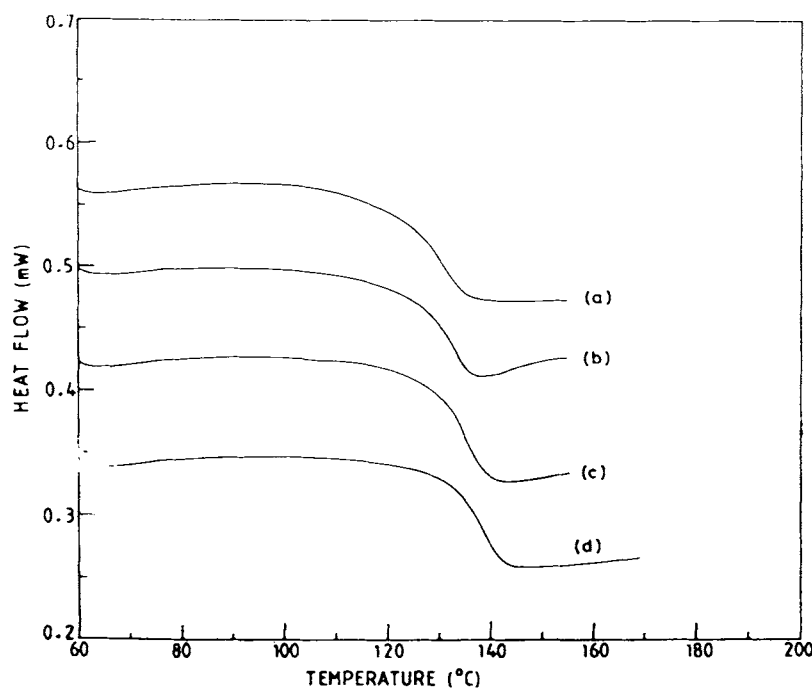
Thermal stability was determined using a DuPont 1090 thermal analyzer having a 951 TG module. A heating rate of  $10^\circ\text{C}/\text{min}$  and a sample size of  $10 \pm 1$  mg was used.

**Table II Results of DSC Scans of MMA : N-Arylmaleimide Copolymers**

Sample Designation	$T_0$ ( $^\circ\text{C}$ )	$T_e$ ( $^\circ\text{C}$ )	$T_g$ ( $^\circ\text{C}$ )	$T_f$ ( $^\circ\text{C}$ )
PMMA	105	112	118	125
P	111	124	128	135
Q	116	126	132	136
R	119	128	134	139
S	124	132	137	142
X	116	125	130	134
Y	120	127	133	137
Z	124	131	135	139

### Mechanical Properties

Tensile and flexural properties were determined according to ASTM D 638 and ASTM D 790-80, respectively, using an Instron tensile tester model 1121 at ambient conditions. For tensile testing, dumbbell-shaped specimens (length 165 mm, width of narrow section 12.5 mm, and thickness 1 mm) were used. A gauge length of 50 mm, full-scale load of 200 kg, chart speed of 100 mm/min, and crosshead speed of 1 mm/min were used. A minimum of five samples were tested for each composition and the average was taken. From the stress-strain curves, tensile



**Figure 2** DSC scans of MMA : MO copolymers (second heating cycle): (a) P; (b) Q; (c) R; (d) S (heating rate =  $10^\circ\text{C}/\text{min}$ ).

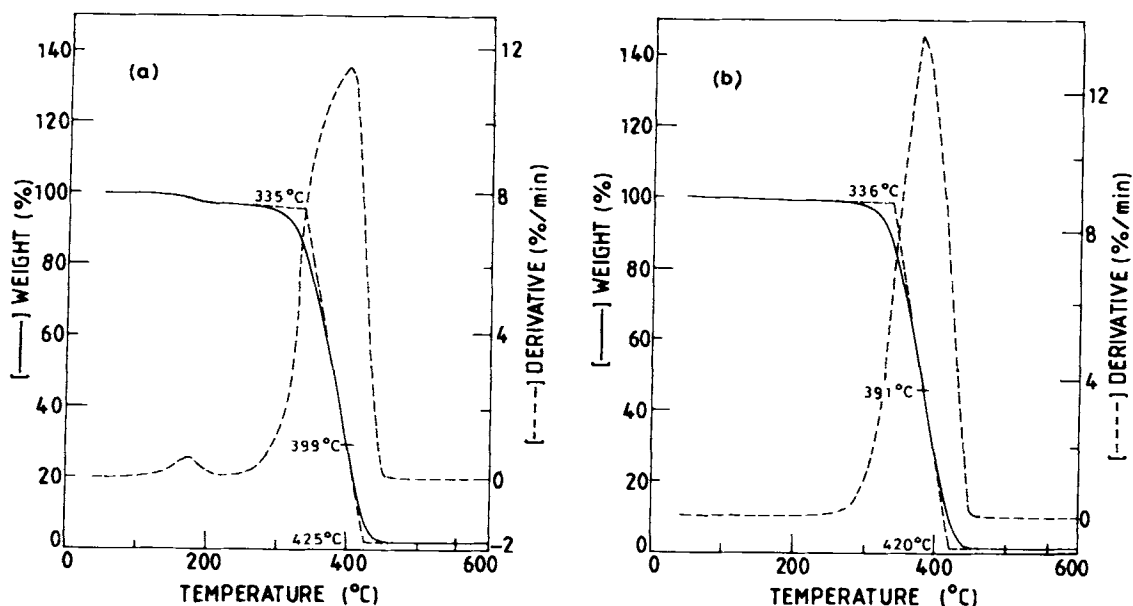


Figure 3 TG and DTG traces of MMA : MO copolymers in nitrogen atmosphere: (a) P; (b) Q; (heating rate = 10°C/min).

strength, percent elongation, and modulus were calculated.

For flexural testing, the distance between the support spans was 30 mm and the load was applied at the center of the sample. A strain rate of 1 mm/min was used. The flexural strength and flexural modulus were calculated by using the standard method.

### Transmittance

The D and S Alphotometer, which is a miniaturized pyranometer specially designed to enable routine

measurements of solar transmittance, was used to measure solar transmittance of the sheets. To determine the transmittance of a material, the amount of solar energy transmitted through the material was compared with the amount of incident solar energy. The measurement procedure consisted of facing the Alphotometer detector toward the sun to measure the incident energy and then placing the transmitting material (sheets of size 8 × 8 cm<sup>2</sup>) in front of

Table III Thermal Behavior of Copolymers

Sample Designation	$T_i$ (°C)	$T_{max}$ (°C)	$T_f$ (°C)	Weight Loss (%)
PMMA	157	189	250	21
	240	300	335	46
	335	395	427	34
P	335	399	425	95
Q	336	390	420	99
R	345	390	417	98
S	353	392	419	98
X	332	387	420	98
Y	345	386	419	98
Z	353	400	420	98

$T_{max}$ : temperature of maximum rate of weight loss, evaluated from differential thermogravimetric traces.  $T_i$  and  $T_f$ : initial and final decomposition temperatures.

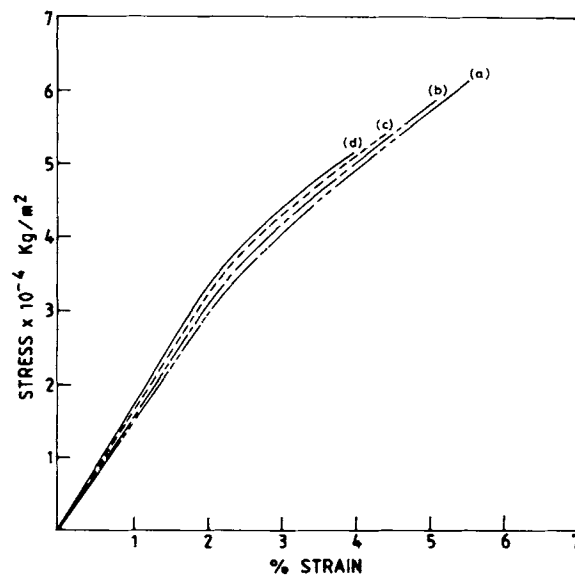
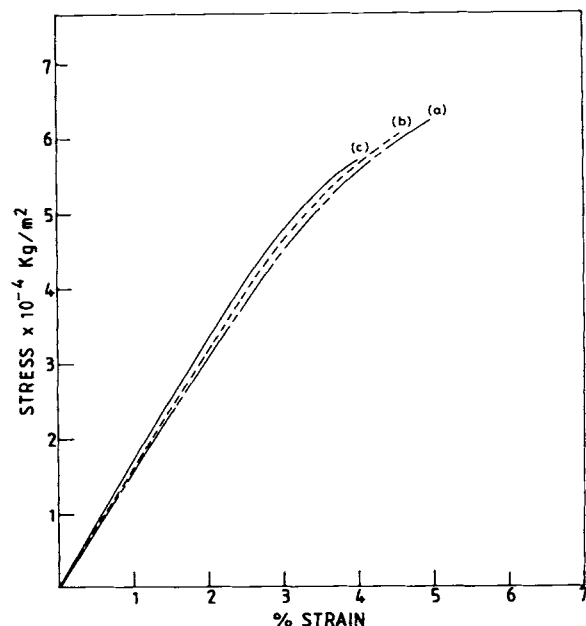


Figure 4 Stress-strain curves of MMA : MO copolymers: (a) P; (b) Q; (c) R; (d) S.



**Figure 5** Stress-strain curves of MMA : MP copolymers: (a) X; (b) Y; (c) Z.

the detector to measure the transmitted energy. The light transmittance of the sheets in the wavelength range of 300–800 nm was also measured using a Hitachi-330-UV-vis spectrophotometer.

### Turbidity

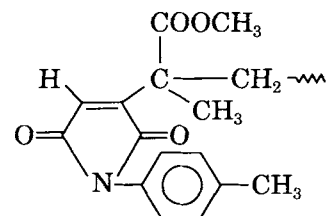
As the percent light transmittance depends on the thickness of the sample, the turbidity ( $\tau$ ) was therefore calculated using

$$\tau = -(1/x) \cdot \ln T$$

where  $x$  is the thickness of the sample, and  $T$ , the fraction of light transmitted by the sample.

## RESULTS AND DISCUSSION

The PMMA sheets were colorless and transparent. Introduction of even a low mol fraction of MP in the PMMA backbone resulted in a yellowish tinge. The yellow color deepened by an increase in the MP content in the copolymer. Since the monomer MP was yellow in color, the yellow tinge may therefore arise due to the presence of unreacted monomer or low molecular weight material (oligomer) having the following types of end groups:



To investigate this aspect, a portion of the sheet was dissolved in chloroform and precipitated in methanol. Colorless polymer powder was obtained by such a treatment, indicating thereby that by total precipitation the oligomers have been removed. The electronic spectra of the precipitated as well as the original copolymer sheets (recorded in chloroform) showed the presence of an absorption band with  $\lambda_{\max}$  at 240 nm (Fig. 1). This absorption band extended up to 400 nm in the case of original sheets, whereas in the precipitated copolymer, no absorption was observed above 320 nm. Copolymer sheets based on MMA : MO remained colorless even when the mol fraction of the comonomer was 0.1.

The intrinsic viscosity of the copolymers was in the range of 2.2–3.1 dL/g. An increase in MO/MP content in the copolymers resulted in an increase in intrinsic viscosity. The values of  $[\eta]$  are higher than are the values obtained for copolymers prepared using solution polymerization techniques and isolated

**Table IV** Mechanical Properties of Copolymer Sheets

Sample Designation	Tensile Stress ( $\text{kg}/\text{m}^2 \times 10^{-4}$ )	% Elongation	Modulus ( $\text{kg}/\text{m}^2 \times 10^{-6}$ )	Flexural Strength ( $\text{kg}/\text{m}^2 \times 10^{-6}$ )	Flexural Modulus ( $\text{kg}/\text{m}^2 \times 10^{-8}$ )
PMMA	635	6.5	145	10.4	7.65
P	615	5.44	153	11.5	10.16
Q	606	5.08	156	11.3	10.31
R	542	4.28	161	10.97	10.74
S	510	3.82	164	11.3	10.94
X	620	4.8	152	10.98	10.73
Y	598	4.52	158	10.9	10.96
Z	560	4.1	161	10.41	11.11

**Table V** Solar Transmittance and Turbidity of PMMA and MMA : *N*-Arylmaleimide Copolymer Sheets Measured at 45° Inclination at 12.00 Noon

Sample Designation	Solar Transmittance	Turbidity ( $\tau$ )
PMMA	0.92	0.056
P	0.92	0.076
Q	0.92	0.073
R	0.92	0.077
S	0.90	0.092
X	0.90	0.092
Y	0.89	0.097
Z	0.87	0.121

at low % conversion.<sup>14</sup> The sheet fabrication is a bulk polymerization process where the viscosity of the medium is much higher than that encountered in solution polymerization. A further gel effect above 15% conversion has been reported in MMA homopolymerization.<sup>17</sup> The observed high  $[\eta]$  values of the sheets can thus be easily explained.

The DSC scans of the copolymer sheet samples are shown in Figure 2 and the results are summarized in Table II. Incorporation of even a 0.026 mol fraction of MO/MP in the MMA backbone resulted in an increase of 10–12°C in  $T_g$ . The  $T_g$  increased as the mol fraction of the *N*-arylmaleimide increased in the copolymer sheets. The presence of a methyl substituent at the *ortho* or *para* position did not affect the  $T_g$  significantly.

Weight loss in three steps was observed in PMMA prepared by bulk polymerization. This behavior has been attributed to the onset of degradation at weak sites in the polymer (i.e., head-to-head linkages, end group-initiated degradation) and random scission of the polymer backbone.<sup>18–20</sup>

Only a single-step degradation was observed in the copolymers. The incorporation of even low mol fractions of MO/MP in PMMA resulted in an increase in the initial decomposition temperature ( $T_i$ ). As the *N*-arylmaleimide content increased in the copolymer sheets, an increase in  $T_i$  was observed (Fig. 3). The presence of the —CH<sub>3</sub> group at the *ortho* or *para* position in the benzene ring of *N*-arylmaleimide did not affect the degradation behavior (Table III).

The stress–strain curves of copolymer sheets of MMA : MO and MMA : MP are shown in Figures 4 and 5 and the results are summarized in Table IV. In all the copolymer sheets, tensile stress decreased as the *N*-arylmaleimide content increased. The decrease was only marginal up to a 0.05 mol fraction

**Table VI** % Transmittance of Copolymer Sheets of MMA and *N*-Arylmaleimides

Sample Designation	% Transmittance at Different Wavelengths (nm)			
	700	600	500	400
PMMA	89	88	88	83
P	86	85	84	74
Q	84	83	80	59
R	83	82	80	54
S	80	78	74	40
X	73	70	66	38
Y	63	60	56	19
Z	53	50	45	10

of *N*-arylmaleimide; however, it was significant at higher mol fractions (0.05–0.1 mol fractions). Elongation (%) decreased while modulus increased with an increase in the *N*-arylmaleimide mol fraction in the copolymers. Flexural stress and flexural modulus did not change with *N*-arylmaleimide content; it remained almost constant.

The solar transmittance of the copolymer sheets at an inclination of 45° were found to be comparable with that of PMMA (Table V). In case of MMA : MP sheets, the transmittance values were slightly lower. The turbidity of the sheets containing *N*-arylmaleimides were higher as compared to PMMA and the values were found to increase with an increase in the *N*-arylmaleimide content in the copolymer.

The % transmittance of the copolymer sheets at different wavelengths was also measured (Table VI). The % transmittance was low at lower wavelength (400 nm), indicating the absorption of light by the copolymer sheets, which is due to the presence of

**Table VII** Turbidity ( $\tau$ ) Values for Copolymer Sheets of MMA and *N*-Arylmaleimides

Sample Designation	Turbidity ( $\tau$ ) at $\lambda$ (nm)			
	700	600	500	400
PMMA	0.078	0.085	0.085	0.124
P	0.132	0.148	0.159	0.274
Q	0.152	0.162	0.194	0.459
R	0.173	0.184	0.207	0.571
S	0.194	0.210	0.262	0.797
X	0.274	0.310	0.355	0.830
Y	0.402	0.444	0.504	1.420
Z	0.552	0.603	0.694	1.960

an aromatic group of the *N*-arylmaleimides. The turbidity of the copolymers increased as the mol fraction of the *N*-arylmaleimide increased (Table VII). The turbidity values were higher at lower wavelengths. MMA : MP copolymer sheets showed higher values of turbidity as compared to MMA : MO copolymer sheets.

On the basis of the above studies, it can be concluded that the incorporation of up to a 0.05 mol fraction of *N*-*o*-tolylmaleimide or 0.026 mol fraction of *N*-*p*-tolylmaleimide increases the  $T_g$  of the copolymers by 10–15°C without impairing its useful optical properties.

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