

# Improvement of the Physical Properties of Poly(methyl methacrylate) by Copolymerization with Pentafluorophenyl Methacrylate

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**ABSTRACT:** Copolymers of methyl methacrylate (MMA) and pentafluorophenyl methacrylate (PFPMA) of various compositions were prepared with a free-radical initiator. When PFPMA was included in the copolymers, the glass-transition temperatures increased and showed a positive deviation from the Gordon–Taylor equation. A copolymer containing 20 wt % PFPMA exhibited almost zero orientational birefringence, and the photoelastic birefringence became zero when the copolymer contained 13 wt % PFPMA. When 20 wt % PFPMA was incorporated into the MMA copolymer, its water absorption decreased to

0.4 wt % versus 1.8 wt % for poly(methyl methacrylate) (PMMA) under the same condition. The flammability of the PFPMA/MMA copolymer was reduced in comparison with that of the MMA homopolymer. The refractive indices of the PFPMA/MMA copolymers were very close to that of PMMA, and the transmittances of the copolymers were slightly better than that of PMMA. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 4219–4224, 2007

**Key words:** copolymerization; fluoropolymers; transparency

## INTRODUCTION

Poly(methyl methacrylate) (PMMA) is a mass-produced, commercially available polymer that demonstrates high light transmittance and provides excellent resistance to both chemical and weather corrosion.<sup>1</sup> These properties, coupled with low manufacturing costs and easy processing, make PMMA a valuable substitute for glass in optical device applications.<sup>2</sup> Despite these advantages, PMMA is of limited use for optical electronics because of its relatively low glass-transition temperature ( $T_g$ ; ca. 100°C), high water absorption, and negative birefringence.<sup>3,4</sup> To increase  $T_g$  of PMMA, investigators have explored its copolymerization with a rigid or bulky monomer<sup>5,6</sup> and with monomers that can form hydrogen bonds through the carbonyl group of methyl methacrylate (MMA).<sup>7–10</sup> Unfortunately, both types of modifications tend to reduce the transparency or humidity resistance of the copolymers obtained.

In visible and near-IR spectrum regions, the intrinsic light losses of PMMA are dominated by combina-

tions of C–H overtone stretching and deformation vibrations. When hydrogen atoms of C–H bonds are replaced with fluorine atoms, there is a decrease in the band vibration energy, and thus the absorption band is minimized in the visible to near-IR spectrum region.<sup>11,12</sup> Bontevin et al.<sup>13</sup> prepared several fluorine-substituted methacrylate monomers, and their polymers exhibited high transparency. Among these fluorinated polymers, the refractive index of poly(pentafluorophenyl methacrylate) (PPFPMA) is similar to that of PMMA. This makes it possible to produce copolymers from the two monomers without high light scattering.

Pentafluorophenyl methacrylate (PFPMA) has a high dipole moment because of fluorine, which is most electronegative.<sup>14</sup> The dipole moment results in a dipole–dipole interaction between PFPMA and MMA units in their copolymers. On the other hand, perfluoro-substituted benzene is a highly electron-deficient molecule that tends to form complexes with electron-donating groups such as aromatic hydrocarbons and amines.<sup>15,16</sup> This provides the potential to form a weak complex between the pentafluorophenyl and ester moieties in copolymers of PFPMA and MMA. Complex formation may reduce the segmental mobility of the polymer chains and result in increases in  $T_g$  of these copolymers.

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Although PMMA displays a small negative birefringence,<sup>17</sup> PFPMA exhibits a positive birefringent character. Thus, when copolymers of MMA and PFPMA are prepared with adjusted compositions, these opposite birefringent properties can compensate for each other and result in zero birefringence. Fluoropolymers have also been shown to demonstrate low water absorption and flame retardancy.<sup>18,19</sup> When MMA is copolymerized with PFPMA, these properties, inherited with PMMA, may also be improved. Thus, we prepared copolymers of MMA and PFPMA with various compositions and investigated their physical properties in detail.

## EXPERIMENTAL

### Materials

MMA, methacryloyl chloride, phenol, pyridine, diethyl ether, tetrahydrofuran, chloroform, sodium hydroxide, anhydrous magnesium sulfate, di-*tert*-butyl peroxide, and 1-butanethiol were purchased from Sigma–Aldrich (Milwaukee, WI). Pentafluorophenol was purchased from SynQuest Laboratories, Inc. (Alachua, FL).

### Polymer preparation

The preparations of phenyl methacrylate (PMA) and PFPMA were modified from the literature.<sup>13,20</sup> All the monomers were washed with a 5% sodium hydroxide solution, dried over anhydrous magnesium sulfate, and distilled freshly before use. Monomer mixtures with di-*tert*-butyl peroxide as an initiator and 1-butanethiol as a chain-transfer agent were transferred into an ampule and subjected to three freeze–pump–thaw cycles, which were followed by sealing under a vacuum with flame. The polymerization was carried out in a heating bath at  $100 \pm 1^\circ\text{C}$  for 24 h. The content inside the ampule was dissolved in chloroform and precipitated from methanol. The obtained polymer samples were dried under a vacuum in an oven at  $50^\circ\text{C}$  for 48 h.

### Characterization

The molecular weights of the polymers were determined with a Waters 510 gel permeation chromatograph (Milford, MA) with chloroform as an eluent at a flow rate of 1.0 mL/min. The molecular weight calibration curve was obtained with polystyrene standards.  $T_g$  of the polymers was measured with a DSC 2920 module of the TA Instrument 5100 system (New Castle, DE) at a scan rate of  $10^\circ\text{C}/\text{min}$ .  $T_g$  was taken in the second heating scan as the midpoint of the heat capacity transition between the upper and lower points of deviation from the extrapolated liq-

uid and glass lines. The polymer films (0.1–0.2 mm thick), fabricated through the casting of the solutions onto glass plates, were used to measure the refractive index with a prism coupler (module 2010, Metri-con Corp., Ltd., Pennington, NJ). The measurement accuracy was  $\pm 0.0005$ . The probe wavelengths in the prism were 532 and 839 nm.

### Water absorption

A humidity oven having circulating air and maintaining  $90 \pm 3\%$  humidity at  $60 \pm 2^\circ\text{C}$  was used. The sample films were  $30 \times 20 \times 2 \text{ mm}^3$ .

### Flame retardancy

The flammability of the polymers was characterized with a horizontal burning test according to tests for the flammability of plastic materials (UL 94; July 29, 1997).<sup>21</sup> The polymer specimens were  $125 \times 12.7 \times 1.6 \text{ mm}^3$ . They were held at one end in a horizon position, and a flame was applied to the free end. The linear burning rate [ $V$  (mm/min)] was calculated as follows:

$$V = 60 L/t \quad (1)$$

where  $L$  is the burned length (mm) and  $t$  is the time (s).

### Birefringence

Optical heterodyne interferometry was employed with birefringence measurement equipment (ABR-10A, Uniopt Corp., Ltd., Shizuoka, Japan) at a wavelength of 633 nm during the application of a load in the diametrical parallel direction of the cylindrical polymers (diameter = 18 mm, length = 10 mm). In this measurement, the photoelastic birefringence ( $\Delta n$ ) caused along the central axis of the cylindrical polymers was measured. Principal stresses  $\sigma_1$  and  $\sigma_2$  occur at the central axis in the directions perpendicular and parallel to the load direction, respectively, when the load is applied.  $\sigma_1$  and  $\sigma_2$  indicate tensile stress when the sign is positive, and they indicate compression stress when the sign is negative.  $\Delta n$  is defined as follows:

$$\Delta n = C\Delta\sigma = C(\sigma_1 - \sigma_2)$$

where  $C$  is the photoelastic coefficient of the polymer and  $\Delta\sigma = \sigma_1 - \sigma_2$  is the principal stress difference. A positive polymer has  $C > 0$ , and a negative polymer has  $C < 0$ . The  $C$  values of the polymers were determined on the basis of the results for  $\Delta n$ .

For the orientational birefringence measurements, polymer films with a thickness of about 40  $\mu\text{m}$  were uniaxially drawn at  $130$ – $140^\circ\text{C}$  and a rate of 4–20 mm/min with a universal tensile testing machine

(Tensilon RTC-1210A, A&D Co., Ltd.). The orientation degrees of the main chains of the polymers were confirmed from an IR dichroic ratio measured by polarized Fourier transform infrared spectroscopy. The orientational birefringence of the uniaxially drawn films was measured at a wavelength of 633 nm by optical heterodyne interferometry with birefringence measurement equipment (ABR-10A, Uniopt).

### Transmittance

The polymer rods (diameter = 12 mm, length = 10 mm) were prepared through polymerization in bulk. The end faces of the polymer rods were polished for the transmittance spectrum measurements with a spectrophotometer (Hitachi Co., Tokyo, Japan). To correct the reflecting loss, the real transmittance value ( $T$ ) was calculated as follows:

$$T = X/(1 - R)^2 \quad (2)$$

where  $X$  is the measured transmittance value.  $R$  is the correction factor:

$$R = [(n_1 - n_2)/(n_1 + n_2)]^2$$

where  $n_1$  and  $n_2$  are the refractive indices of the polymer and air.  $n_1$  was measured with a model 2010 prism coupler (Metricon) and calibrated with the Sellmeire equation.<sup>22</sup>  $n_2$  was assigned a value of 1.0003.

## RESULTS AND DISCUSSION

### Characterization

The PFPMA/MMA copolymers were characterized as shown in Table I. The molecular weight of the copolymers decreased with an increasing amount of the PFPMA monomer, and this could be due to its faster termination reaction. Interestingly, the PFPMA and MMA homopolymers had very similar refractive

TABLE I  
Characterization of the PFPMA/MMA Copolymers

Run <sup>a</sup>	PFPMA in the copolymer (wt %)	$M_w (\times 10^4)^b$	$n_d^c$	
			532 nm	839 nm
1	0	—	1.4953	1.4852
2	31	13.4	1.4936	1.4835
3	54	11.8	1.4927	1.4827
4	80	9.3	1.4910	1.4809
5	100	—	1.4894	1.4763

<sup>a</sup> Di-*tert*-butyl peroxide (0.863 mol %) and 1-butanethiol (0.265 mol %).

<sup>b</sup> Weight-average molecular weight.

<sup>c</sup> Refractive index.

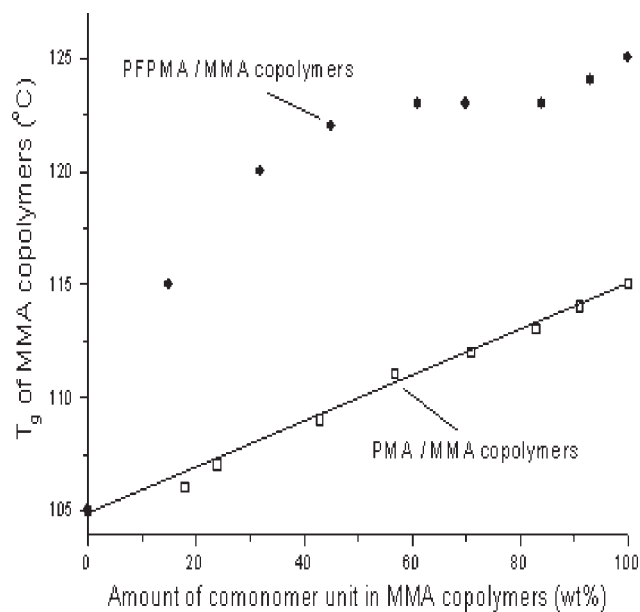
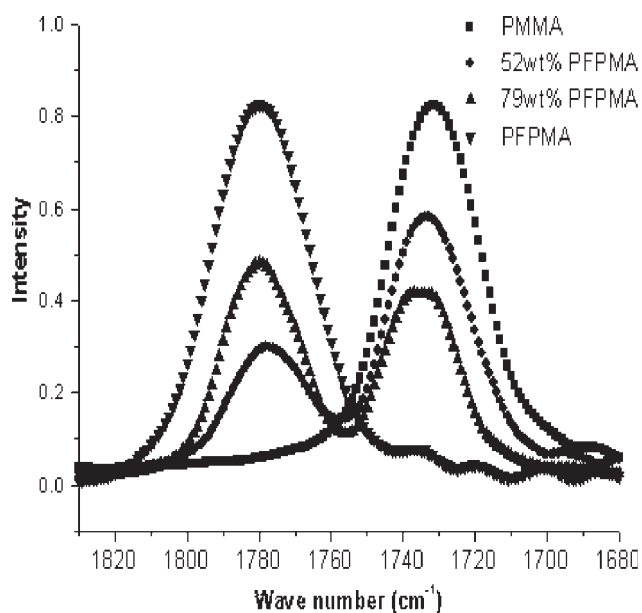


Figure 1 Effect of the composition of the MMA copolymer on  $T_g$ .

indices, and their copolymers had refractive indices between them. The similar refractive indices of the two repeating units in the copolymers minimized the possibility of light scattering.

### $T_g$

When 20–25 wt % PFPMA was in the copolymers with MMA, the  $T_g$  values of the copolymers increased to 115–120°C. The composition dependence of the copolymer  $T_g$  showed a positive deviation from the Gordon–Taylor equation. However, the  $T_g$  values of the copolymers of PMA and MMA were fitted with the Gordon–Taylor equation (Fig. 1).<sup>23</sup> This different tendency possibly occurred because the fluoro-substituted phenyl group was a little bulkier than the phenyl group on account of the fluorine atoms. However, when much bulkier 2,6-diphenylphenyl or 2-naphthyl methacrylates were copolymerized with MMA, the  $T_g$  values of the resulting copolymers did not show a positive deviation.<sup>9</sup> Thus, the enhancement of  $T_g$  of PMMA through copolymerization with PFPMA could involve some interaction between fluorinated phenyl and ester groups, which could be a weak charge-transfer complex or a dipole–dipole interaction, that reduced the segmental mobility of the polymer chains. IR spectra of the homopolymers of MMA and PFPMA and their copolymers are shown in Figure 2. The carbonyl peak for PMMA appears at 1730  $\text{cm}^{-1}$ , and because of strong electron drawing of the pentafluorophenyl group, the carbonyl peak for PFPMA

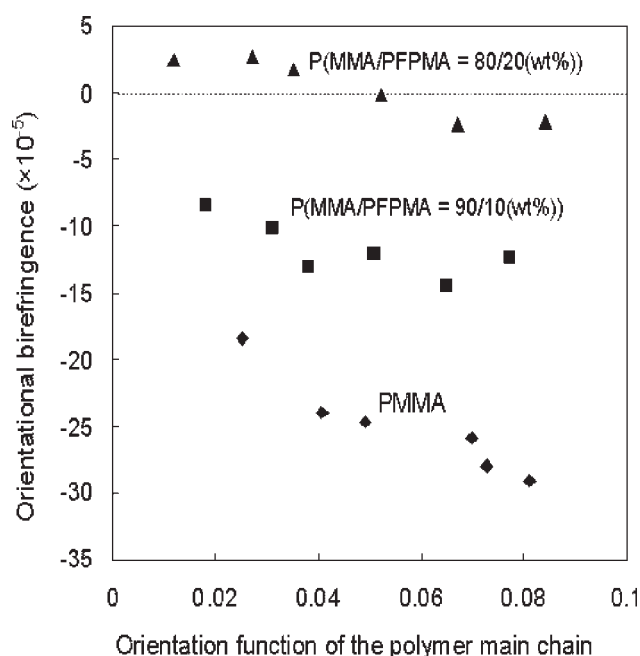


**Figure 2** IR spectra of PFPMA/MMA copolymer films (ca. 0.1 mm thick).

appears at a much higher wave number,  $1780\text{ cm}^{-1}$ . If a charge transfer from the carbonyl group of MMA to the pentafluorophenyl had occurred, the wave number corresponding to the carbonyl of MMA should have shifted to a lower wave number.<sup>11</sup> However, the carbonyl peaks of MMA in the copolymers appeared at a slightly higher wave number, and this may have been due to the electron-drawing property of PFPMA in the copolymer. Thus, the positive deviation of the  $T_g$  values of the copolymers of MMA and PFPMA was due to the dipole-dipole interaction between MMA and PFPMA, which resulted in a decrease in the segmental mobility of the polymer chains and the enhanced  $T_g$  values of the copolymers.<sup>24,25</sup>

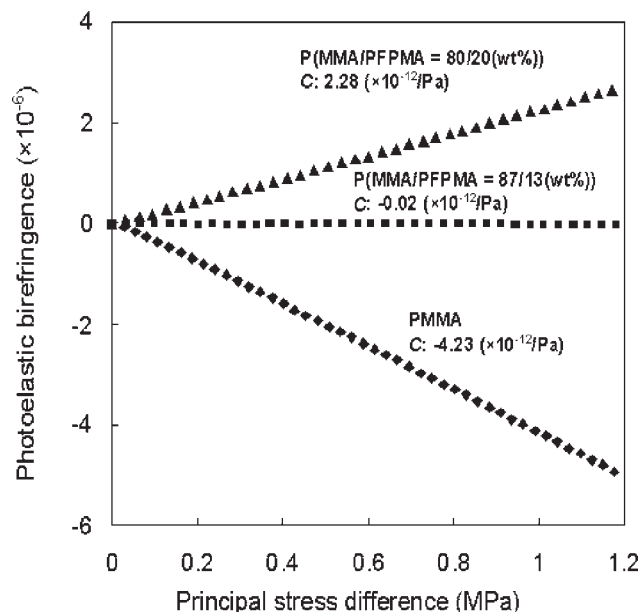
### Birefringence

The utilization of polymers for optical devices has one serious drawback: they exhibit birefringence. The major types of birefringence are orientational and photoelastic birefringence. Recently, some of us successfully demonstrated that a zero-birefringence optical polymer can be prepared with two different methods: a polymeric system doped with an organic compound or an inorganic crystal that has birefringence that is the opposite of that of the polymer used.<sup>26,27</sup> Figure 3 shows the orientational birefringence versus the orientation function of the polymer main chains. PMMA exhibited a negative orientational birefringence in the oriented state. Its birefringence was compensated by the copolymerization with PFPMA, which had a positive orientational birefringence, and became zero when the copolymer

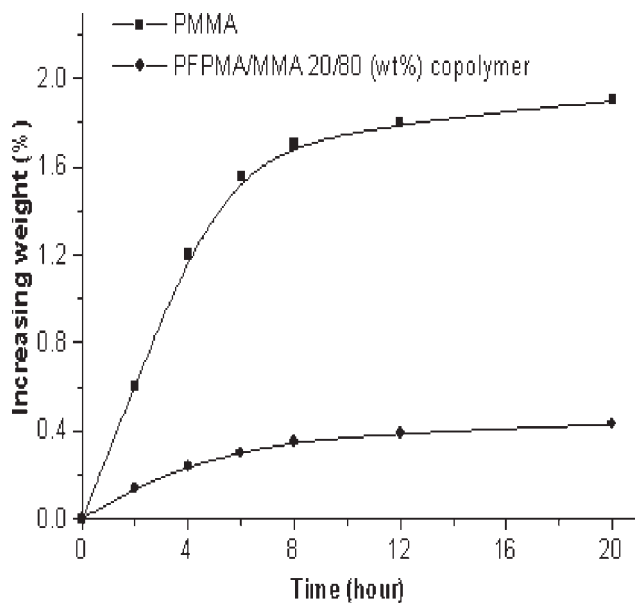


**Figure 3** Orientational birefringence of the MMA/PFPMA copolymers.

had a ratio of MMA/PFPMA = 80/20 (wt %). Figure 4 presents the photoelastic birefringence versus the principal stress difference of the polymers. PMMA exhibited negative photoelastic birefringence, and  $C$  was  $-4.23 \times 10^{-12}/\text{Pa}$ . Its negative birefringence was shifted to positive birefringence with an increase in PFPMA and was virtually eliminated with a ratio of MMA/PFPMA = 87/13 (wt %), for which  $C$  was  $-0.02 \times 10^{-12}/\text{Pa}$ .



**Figure 4** Photoelastic birefringence of the MMA/PFPMA copolymers.



**Figure 5** Humidity absorption of the PFPMA/MMA copolymer and PMMA ( $30 \times 20 \times 2 \text{ mm}^3$  sheet, 90% humidity,  $60^\circ\text{C}$ ).

### Water absorption

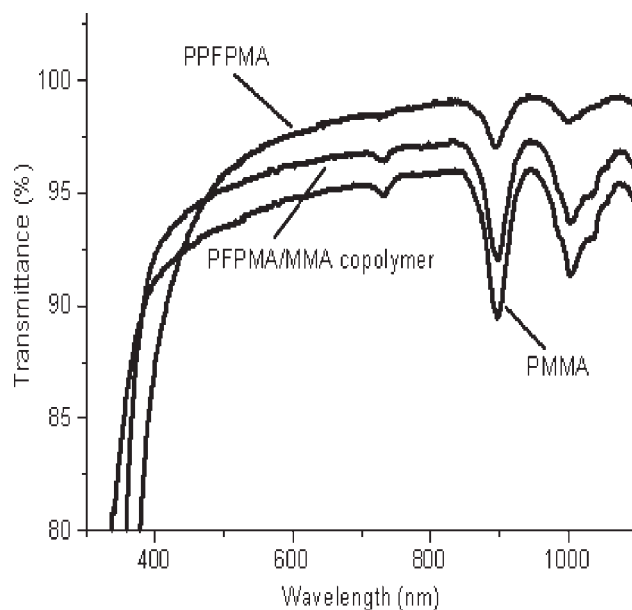
Among the unique properties of fluorinated polymers, fluoropolymers exhibit low water absorption. PMMA tends to absorb as much as 2.0 wt % water under 90% humidity. When MMA was copolymerized with PFPMA (20 wt %), the water absorption of the polymer decreased to 0.4 wt %, as shown in Figure 5. The decreased water absorption could have benefited from the hydrophobic surface and bulk of the copolymer materials containing fluorinated repeating units, and this is a common phenomenon for fluoropolymers.

### Flammability

As is well known, fluoropolymers have excellent flame retardancy.<sup>19</sup> The flammability of the MMA and PFPMA copolymers was measured according to the standard test for the flammability of plastic

**TABLE II**  
Results for the Horizontal Burning Tests of the PFPMA/MMA Copolymers

Sample	Burning time (s)	Linear burning rate (mm/min)	Burning atmosphere
PMMA	45	100	Smoke-free
MMA-co-PFPMA (49/51 wt %)	62	72.6	Little smoke
MMA-co-PFPMA (15/85 wt %)	75	60.0	Much smoke



**Figure 6** Transmittance of the PFPMA and MMA homopolymers and their copolymer (38/62 wt %).

materials (Table II).<sup>21</sup> These results showed that the copolymers of MMA and PFPMA required longer burning times and were less flammable in comparison with PMMA. The introduction of fluorinated comonomer PFPMA into the MMA polymers reduced their flammability.

### Transmittance

Transmittance measurements of the PFPMA homopolymer and its copolymer with MMA were carried out for comparison with the MMA homopolymer at wavelengths of 300–1100 nm. The results showed that the transmittance of the copolymer was slightly better than that of the PMMA homopolymer, as shown in Figure 6. The strong C—F bond and lower number of C—H bonds in the PFPMA/MMA copolymer in comparison with PMMA reduced the light absorption in the visible and near-IR region, and this was favorable for optical information processing.

## CONCLUSIONS

Various copolymers of MMA and PFPMA were prepared. The  $T_g$  values of the MMA copolymers were enhanced by the incorporation of the PFPMA monomer. The orientational and photoelastic birefringence of these copolymers could be adjusted to zero through the control of the copolymer composition. These copolymers also had much less water absorption and reduced flammability in comparison with PMMA. The refractive indices of the copolymers were very close to that of PMMA, and the transmit-

tances of the copolymers were slightly better than that of PMMA. These results indicated that various physical properties of MMA polymers were improved by the copolymerization with PFPMA, and this makes it possible to widely apply MMA polymers in the field of optical electronics.

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