### Copolymers of Methyl Methacrylate with *N*-Trifluorophenyl Maleimides: High Glass Transition Temperature and Low Birefringence Polymers

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**ABSTRACT**: Copolymers of methyl methacrylate (MMA) with 2,3,4- and 2,4,6-trifluorophenyl maleimides (TFPMIs) were synthesized by a free radical initiator, azobisisobutyronitrile, in 1,4-dioxane and also in bulk. The refractive indexes of the copolymers were in the range of 1.49–1.52 at 532 nm. The  $T_{\rm g}$ s were 133–195 °C depending on copolymer compositions. In addition, the copolymers were thermally stable,  $T_{\rm d} > 350$  °C. The orientational and photoelastic birefringence of the copolymers were also investigated. As both of the orientational and photoelastic birefringences of PMMA are negative, whereas those of poly(TFPMI)s are positive, we could obtain nearly zero orientational and

INTRODUCTION Maleimide and its derivatives are well known to give thermally stable polymers and the copolymers with various vinyl monomers such as methyl methacrylate (MMA) and styrene.<sup>1-7</sup> N-Pentafluorophenyl maleimide (PFPMI) was colorless, and it was readily copolymerized with MMA by a free radical initiator such as azobisisobutyronitrile (AIBN) in solution and also in bulk. The copolymers obtained were thermally stable up to 370 °C, and the water absorption of these copolymers was greatly reduced because of the highly hydrophobic nature of the fluorine-substituted aromatic ring. The refractive index of poly(PFPMI) was almost the same as that of PMMA, which were 1.4989 and 1.4953 for poly(PFPMI) and PMMA at 532 nm, respectively. Thus, the refractive indexes of the copolymers (MMA-co-PFPMI) remained nearly constant (1.4965-1.4970 at 532 nm) regardless of the content of PFPMI in the copolymers, which minimized light scattering of the copolymers. The glass transition temperatures  $(T_g)$  of the PFPMI-co-MMA were in the range of 140-180 °C with the PFPMI content from 18.8 to 65 mol %.8

2,3,4-Trifluorophenyl maleimide (2,3,4-TFPMI) was also colorless, and the refractive index of poly(2,3,4-TFPMI) was a little higher than that of poly(PFPMI); 1.5505 vs. 1.4965 at photoelastic birefringence polymers when the ratios of 2,3,4-TFPMI/MMA were 15/85 and 5/95 mol %, respectively. For 2,4,6-TFPMI, zero orientational and photoelastic birefringences could be obtained when the ratios of 2,4,6-TFPMI/MMA were 12/88 and 3/97 mol %, respectively. The  $T_{\rm g}$ s of those copolymers with zero birefringences were in the range of 135–140 °C. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 000: 000–000, 2012

**KEYWORDS**: copolymerization; fluoropolymers; methyl methacrylate; *N*-trifluorophenyl maleimides; orientational and photoelastic birefringence; thermal properties

532 nm, respectively. However, the starting compound for the preparation of 2,3,4-TFPMI, 2,3,4-trifluoroaniline is much cheaper than that of 2,3,4,5,6-pentafluoroaniline and it is more reactive in the preparation of the maleimide. Thus, we have prepared 2,3,4-TFPMI, and for comparison, the isomer 2,4,6-TFPMI was also prepared. The  $T_{\rm g}$ s of homopolymers of 2,3,4-TFPMI and 2,4,6-TFPMI were more than 230 °C.

The utilization of polymers for optical application has one serious drawback. They exhibit birefringence. The major types of birefringence are orientational and photoelastic birefringences. Orientational birefringence is defined as birefringence caused by orientation of the polymer main chains, which tends to be caused in processes such as injection molding, extrusion, and heat drawing, in which polymer main chains are oriented in the molten state and solidify in the oriented state during the following cooling process to room temperature because they are generally not relaxed completely in the process. Photoelastic birefringence is defined as birefringence caused by elastic deformation below the  $T_{\rm g}$ . Photoelastic birefringence tends to be caused during the use of optical polymer devices.<sup>9</sup> Several methods have been investigated to eliminate the birefringence phenomena. They are the random copolymerization,<sup>10,11</sup> the anisotropic

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### 2,4,6-trifluorophenyl maleimide 2,4,6-TFPMI R1, R3 R5 = F R2, R4 = H

SCHEME 1 Synthesis of 2,3,4-TFPMI and 2,4,6-TFPMI.

molecule dopant,<sup>12,13</sup> the birefringent crystal dopant,<sup>14,15</sup> and the polymer blending methods.<sup>16</sup> In the random copolymerization method, positive and negative birefringent monomers that compose positive and negative birefringent homopolymers are randomly copolymerized. As a result, birefringence is mutually canceled at a specified monomer ratio.

PMMA exhibits both negative orientational and photoelastic birefringences, whereas poly(PFPMI) shows both birefringences positive. Thus, we have obtained the polymer with zero orientational and photoelastic birefringences by adjusting the amount of the MMA and PFPMI, MMA/PFPMI 88.9/11.1 mol % and 93.8/6.2 mol %, respectively. The  $T_{\rm g}$ s of these copolymers were estimated to be about 128 and 122 °C, respectively.<sup>17</sup> As poly(TFPMI)s also exhibit both positive orientational and photoelastic birefringences, TFPMIs were copolymerized with MMA. Thus, to obtain high  $T_{\rm g}$  and zero birefringence polymers, we have prepared the copolymers of TFPMI with MMA of different compositions (Scheme 1), and we report here the physical and optical properties of these copolymers.

#### **EXPERIMENTAL**

#### **Materials**

Zinc chloride, hexamethyldisilazane (HMDS), MMA, maleic anhydride, AIBN, and solvents were purchased from Aldrich. 2,3,4-Trifluoroaniline and 2,4,6-trifluoroaniline were purchased from SynQuest Laboratory.

# Synthesis of Fluorinated Phenyl Maleimides: 2,3,4-TFPMI and 2,4,6-TFPMI

2,3,4-TFPMI and 2,4,6-TFPMI were synthesized according to reported method with some modifications.<sup>18,19</sup> In a 500-mL three-necked flask provided with a stirrer, a reflux condenser, and a dropping funnel, 26.8 g (0.27 mol) of maleic anhydride and 140 mL of 1,4-dioxane were placed. The 1,4-dioxane solution (90 mL) of 40 g of 2,3,4-trifluoroaniline (0.27 mol) was added to the flask using a dropping funnel for 1 h at ambient temperature. The reaction was completed in 5 h at room temperature. The precipitate formed was

filtered and dried, which was used in the next step without purification (yield 80%, 53.4 g). The obtained product and 29.3 g (0.22 mol) of anhydrous zinc chloride (ZnCl<sub>2</sub>) were dissolved in 200 mL of anhydrous tetrahydrofuran (THF) in a three-necked flask fitted with a thermometer. The mixture was heated up to 45–50 °C, and then into the resulting solution, 66.7 mL (0.32 mol) of HMDS in 60 mL of anhydrous THF was added dropwise over a period of 0.5 h. After stirring at 45–50 °C for 5 h, the reaction mixture was cooled and filtered to remove the residue. The pure compound was obtained by column chromatography on silica gel [eluent, hexane/THF = 3:1 (v/v); yield 58.5%; m.p. 110–111 °C].

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  (s, 2H, CH=CH), (m, 2H, Ph-H).

2,4,6-TFPMI was prepared by similar method as 2,3,4-TFPMI. The yield of 2,4,6-TFPMI was a little higher than its aforementioned analog (yield 64.6%; m.p. 105  $^{\circ}$ C).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  (s, 2H, CH=CH), (m, 2H, Ph-H).

## Homopolymerization and Copolymerization of 2,3,4-TFPMI and 2,4,6-TFPMI with MMA

The homopolymerizations of 2,3,4-TFPMI and 2,4,6-TFPMI were carried out at 60 °C for 72 h using AIBN as the initiator. Copolymerizations of 2,3,4-TFPMI and 2,4,6-TFPMI with MMA were carried out in 1,4-dioxane solutions and also in bulk with AIBN as the initiator. Monomer solutions and initiator were transferred into a glass tube and subjected to three freeze-pump-thaw cycles, which were followed by sealing under vacuum. The copolymers were purified by repeated precipitation from THF solution into a large amount of methanol. For the bulk copolymerization, after polymerizing at 60–80 °C for 24 h, the polymer produced was purified by the precipitation from THF solution into a large amount of methanol. The polymer collected was dried under vacuum at 60 °C for 48 h. The monomer conversions were in the range of 85–90%.

#### Characterization

<sup>1</sup>H NMR spectra were determined on a Brucker AC 300 spectrometer, at 300 MHz, using CDCl<sub>3</sub> as a solvent. Chemical

#### TABLE 1 Copolymerization of 2,4,6-TFPMI with MMA in 1,4-Dioxane<sup>a</sup>

	Mole Fraction of 2,4,6-TFPMI							Refractive Index	
Sample	Feed (mol %)	Copolymer (mol %) <sup>c</sup>	Conversion (%)	<i>M</i> <sub>n</sub> <sup>b</sup> (×10 <sup>4</sup> )	PDI <sup>b</sup>	<i>T</i> g (°C)	<i>T</i> <sub>d</sub> (°C)	532 nm	839 nm
2,4,6-TFPMI- <i>co</i> -MMA-1	20	17.8	92.5	3.0	2.62	148	344	1.5095	1.4985
2,4,6-TFPMI- <i>co</i> -MMA-2	40	33	83.6	3.2	2.80	165	350	1.5105	1.5000
2,4,6-TFPMI- <i>co</i> -MMA-3	60	46.5	65.7	2.35	3.78	181	360	1.5140	1.5015
2,4,6-TFPMI- <i>co</i> -MMA-4	80	60	43.0	0.98	4.56	200	370	1.5220	1.5080

 $^{\rm a}$  All the copolymerizations were carried out at 60  $^\circ\text{C},$  using AIBN as initiator.

<sup>b</sup> Determined by GPC, using THF as eluent.

<sup>c</sup> Calculated by <sup>1</sup>H NMR.

shifts were reported in  $\delta$  (ppm) from internal tetramethylsilane (TMS). The refractive indexes of the polymers were measured using a Metricon model 2010 prism coupler. The measurement accuracy was  $\pm 0.0005.$ The probe wavelengths in the prism were 532, 633, and 839 nm. Molecular weights were determined by gel permeation chromatography (GPC; Waters 510) using THF as the eluent at a flow rate of 1.0 mL/min. The molecular calibration curves were obtained using polystyrene standards. The  $T_{\rm g}$  of polymers was measured using a DSC 2920 module with the TA Instrument 5100 system, with a scan rate of 10 °C/min. The  $T_{\rm g}$  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 liquid and glass lines.

#### **Birefringence Measurement**

Birefringence of polymer was measured on thin films.<sup>20</sup> The THF solutions were spread onto a glass plate using a knife coater, then dried at room temperature for 1 h followed by drying at 90 °C under reduced pressure for 24 h. The sample polymer films were cut into a dumbbell shape. For the orientational birefringence measurements, polymer films with a thickness of about 40  $\mu$ m were uniaxially drawn above  $\mathit{T}_{\rm g}$  temperature at  ${\sim}157$   $^{\circ}\text{C}$  and a rate of 4-20 mm/min with a universal tensile testing machine (Tensile RTC-1210A, A&D). The orientational degrees of the main chains of the polymers f were confirmed from an IR dichroic ratio measured by polarized Fourier transform infrared spectroscopy. The orientational birefringence  $\Delta n_{\rm or}$  of the uniaxially drawn films was measured at a wavelength of 633 nm by optical heterodyne interferometry with birefringence measurement equipment (ABR-10A, Uniopt Corp., Japan). The photoelastic birefringence  $\Delta n_{\rm ph}$  was measured by using the same equipment with adding stress. The photoelastic birefringence  $\Delta n_{\rm ph}$  is expressed as follows:

$$\Delta n_{ph} = C\sigma,\tag{1}$$

where *C* is the photoelastic coefficient of the polymer and  $\sigma$  is the stress. 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  $\Delta n$ .

#### **RESULTS AND DISCUSSION**

#### Homopolymerization of 2,3,4-TFPMI and 2,4,6-TFPMI and Their Copolymerizations with MMA in Solution

2,3,4-TFPMI was polymerized in benzene at 60 °C using AIBN as initiator, and the polymer produced was rather insoluble in benzene and precipitated.<sup>21</sup> On the other hand, under similar conditions, 2,4,6-TFPMI was polymerized without precipitation. The copolymerization of 2,3,4-TFPMI and 2,4,6-TFPMI with MMA were carried out in 1,4-dioxane solution using AIBN as the initiator at 60 °C. The results of copolymerizations are summarized in Tables 1 and 2. The feed ratios of TFPMIs were in the range of 0.2-0.8. As is shown in Tables 1 and 2, the number-average molecular weights of the copolymers decreased, whereas the polydispersity of copolymers increased with increase in the amount of TFPMIs added, which was due to the low reactivity of TFPMIs when compared with that of MMA. As shown in Tables 1 and 2, the monomer conversion and the molecular weights of 2,4,6-TFPMI copolymers were slightly higher than that of copolymers of asymmetrically substituted TFPMIs, which indicated that 2,4,6-TFPMI was more reactive than its analogs.

The compositions of copolymers produced were calculated from the characteristic proton resonance signals of TFPMIs and MMA repeat units in <sup>1</sup>H NMR spectra of TFPMI-*co*-MMAs (Figs. 1 and 2), which were the protons from phenyl ring ( $\delta = 6.75$ -7.0 ppm for 2,4,6-TFPMI and 6.9-7.2 ppm for 2,3,4-TFPMI, respectively) and methoxy groups in the side chains of MMA ( $\delta = 3.43$ -3.87 for MMA), respectively. In addition, as shown in Figures 1 and 2, the signal of phenyl ring protons in both of the TFPMI are shifted to higher field, and the methoxy group of MMA first splits into two peaks and then shifts to downfield when the content of TFPMI in copolymers increases, which may be due to the interaction between the electron-deficient trifluorophenyl group of TFPMI and carbonyl group of MMA in the solution.

To obtain the monomer reactivity, the copolymerization was terminated at low conversion (<10%). The monomer reactivity ratios were calculated using Fineman-Ross method.<sup>21</sup> For 2,4,6-TFPMI-*co*-MMA, the values of  $r_1$  (2,4,6-TFPMI) and  $r_2$  (MMA) were 0.26 and 0.95, and for 2,3,4-TFPMI-*co*-MMA, the values were 0.37 ( $r_1$ , 2,3,4-TFPMI) and 0.97 ( $r_2$ , MMA),



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TABLE 2 Copolyr	nerization	of 2,3,4-	TFPMI v	vith MN	/IA in ′	1,4-Dioxane <sup>®</sup>
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	Mole Fraction of 2,4,6-TFPMI							Refractive Index	
Sample	Feed (mol %)	Copolymer (mol %) <sup>c</sup>	Conversion (%)	<i>М</i> <sub>n</sub> <sup>b</sup> (×10 <sup>4</sup> )	PDI <sup>b</sup>	<i>T</i> g (°C)	<i>T</i> d (°C)	532 nm	839 nm
2,3,4-TFPMI- <i>co</i> -MMA-1	20	18.0	87.7	2.4	3.0	146	352	1.5030	1.4990
2,3,4-TFPMI- <i>co</i> -MMA-2	40	39.3	71.6	2.7	2.82	164	360	1.5125	1.5020
2,3,4-TFPMI- <i>co</i> -MMA-3	60	48.6	56.7	1.3	3.69	176	374	1.5190	1.5080
2,3,4-TFPMI- <i>co</i> -MMA-4	80	63.8	30.0	0.8	4.52	195	378	1.5260	1.5145

 $^{\rm a}$  All the copolymerizations were carried out at 60  $^\circ\text{C},$  using AIBN as initiator.

<sup>b</sup> Determined by GPC, using THF as eluent.

<sup>c</sup> Calculated by <sup>1</sup>H NMR.

respectively. The Q and e values for both of fluoro-substituted phenyl maleimide were also calculated using the Alfrey-Price equation.<sup>22</sup> The  $Q_2$  and  $e_2$  values for MMA were taken from the literature.<sup>23</sup> The results were found to be 1.23 ( $Q_1$ ) and 1.58 ( $e_1$ ) for 2,4,6-TFPMI-*co*-MMA and 1.13 ( $Q_1$ ) and 1.40 ( $e_1$ ) for 2,3,4-TFPMI-*co*-MMA, respectively. The Q and e values of *N*-phenylmaleimide (PMI) were reported to be 1.29 and 1.54, respectively. The slightly lower Q and e values for TFPMI when compared with that of PMI are due to the electronwithdrawing property of pentafluorophenyl group.

# Thermal and Optical Properties of Copolymers of *N*-TFPMIs with MMA

Polymers of *N*-substituted maleimides were reported to have high  $T_{\rm g}$  and thermal stability. The  $T_{\rm g}$ s for 2,3,4 TFPMI-*co*-MMA and 2,4,6-TFPMI-*co*-MMA were measured, and their values are shown in Tables 1 and 2, respectively. The  $T_{\rm g}$ s of copolymers were found to increase linearly with the increasing amount of the TFPMIs in the copolymers, and the relationship between  $T_{\rm g}$  and the polymer composition fits the



**FIGURE 1** <sup>1</sup>H NMR spectra of 2,4,6-TFPMI-*co*-MMA containing 17.5 (A), 25.6 (B), 36.5 (C), and 50.0 mol % (D) of TFPMI.

Gordon-Taylor equation, which indicated that there was no significant interaction between the partially fluorinated phenyl rings and MMA moieties of the copolymers in the solid state. To investigate the effect of substituted fluorine in the molecular structures on their thermal properties, we plotted the  $T_{\rm g}$ s of 2,3,4-and 2,4,6-TFPMI with 2,3,4,5,6-PFPMI and nonfluorine-containing PMI-based copolymers versus their contents in corresponding copolymers in Figure 3. It is shown that the trifluorinated N-substituted phenyl maleimides exhibit the higher  $T_{\rm g}$ s than their perfluoro and nonfluoro N-substituted analogs, and the position of fluorine on phenyl ring has no effects on their  $T_{\rm g}$ .

Thermal stability of the copolymers was determined by thermogravimetric analysis in a nitrogen atmosphere. The results are also summarized in Table 1. It can be seen that introducing TFPMIs as comonomer significantly ameliorated the decomposition temperature of PMMA.<sup>24</sup>

In our previous study, it was found that the PFPMI homopolymer had almost the same refractive index with PMMA, as a result of which the refractive indexes of the copolymers



FIGURE 2 <sup>1</sup>H NMR spectra of 2,3,4-TFPMI-*co*-MMA containing 16.7 (A), 27.1 (B), 35.4 (C) and 43.5 mol % (D) of TFPMI.

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FIGURE 3  $T_{\rm g}$  of 2,3,4-TFPMI-, 2,4,6-TFPMI, PFPMI-, and PMI-co-MMA.

remained nearly constant regardless of the polymer composition. In this study, we have found that the refractive indexes of TFPMI-*co*-MMA are in between of those of the PFPMI and PMI and increase linearly with increase in the content of TFPMI in copolymers (Fig. 4). In addition, the asymmetrically substituted phenyl ring in poly(TFPMI) possesses slightly higher refractive

#### TABLE 3 Copolymerization of TFPMI with MMA in Bulk<sup>a</sup>

**FIGURE 4** Refractive indexes of 2,3,4-TFPMI-*co*-MMA, 2,4,6-TFPMI-*co*-MMA, PFPMI-*co*-MMA, and PMI-*co*-MMA.

indexes when compared with its symmetrically substituted analog at the same content of TFPMI in copolymers.

### **Physical Properties of the Copolymers Prepared in Bulk** To investigate the physical properties of TFPMI-co-MMA

polymer for the application in the optical devices, we prepared copolymers in bulk using AIBN as radical initiator. The copolymers obtained were purified by reprecipitation from

	Feed Ratio (mol %)	TFPMI Content in Copolymers (%) <sup>b</sup>	Conversion (%)		Refractive Index		
Sample				$T_{g}$ (°C)	532 nm	633 nm	839 nm
2,3,4-TFPMI- <i>co</i> -MMA-1	5	3.0	95.3	133	1.4970	1.4930	1.4880
2,3,4-TFPMI-MMA-2	10	9.0	90.4	137	1.5030	1.4980	1.4925
2,3,4-TFPMI-MMA-3	20	17.5	83.2	145	1.5080	1.5030	1.4965
2,4,6-TFPMI-MMA-1	5	3.0	93.4	134	1.4955	1.4910	1.4855
2,4,6-TFPMI-MMA-2	10	5.0	91.2	135	1.4975	1.4925	1.4870
2,4,6-TFPMI- <i>co</i> -MMA-3	20	17.3	85.8	147	1.5090	1.5025	1.4970

<sup>a</sup> All the copolymerizations were carried out at 60 °C, using AIBN as <sup>b</sup> Calculated from <sup>1</sup>H NMR spectra. initiator.

TABLE 4	Birefringence	Properties	of	Copoly	mers
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Polymer	Intrinsic Birefringence (10 <sup>-3</sup> )	Photoelastic Coefficient (TPa <sup>-1</sup> )
2,3,4-TFPMI- <i>co</i> -MMA (9.0/91.0 mol %)	-0.8	4.2
2,3,4-TFPMI- <i>co</i> -MMA (17.5/82.5 mol %)	0.2	12
Poly(2,3,4-TFPMI)	13 (calculated)	47 (calculated)
2,4,6-TFPMI- <i>co</i> -MMA (3.0/97.0 mol %)	-4.0	0.03
2,4,6-TFPMI- <i>co</i> -MMA (5.0/95.0 mol %)	-3.2	2.5
Poly(2,4,6-TFPMI)	17 (calculated)	69 (calculated)
PMMA	-5.7	-5.3



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**FIGURE 5** Orientational birefringence of TFPMI-*co*-MMA versus orientation degree of polymer chains.

the THF solution into a large amount of methanol and dried under vacuum oven at 60  $^{\circ}$ C. The physical properties of TFPMI-*co*-MMA are summarized in Table 3.

It is found that the conversions of copolymerization were generally more than 80%, and the number–average molecular weights of copolymers were higher than those produced in 1,4-dioxane solution. The thermal properties of PMMA were effectively improved by being copolymerized with TFPMI monomers. The  $T_{\rm g}$  of PMMA (~110 °C) was increased to 133 °C for copolymer containing 3 mol % of TFPMI.<sup>24</sup>



FIGURE 6 Photoelastic birefringence of TFPMI-*co*-MMA versus stress.

#### Birefringence

Figure 5 shows the orientational birefringence versus the orientation degree of the polymer chains. PMMA exhibits a negative orientational birefringence. Its birefringence is compensated by the copolymerization with TFPMI, which has a positive orientational birefringence effect. Orientational birefringence  $\Delta n_{\rm or}$  can be written as follows:

$$\Delta n_{or} = f \Delta n^0. \tag{2}$$

Here,  $\Delta n^0$  is intrinsic birefringence that means birefringence of polymer is in the completely oriented state (f = 1.0).



**FIGURE 7** Intrinsic birefringence and photoelastic coefficient of copolymers as a function of the composition of the copolymers: (a) 2,3,4-TFPMI-*co*-MMA and (b) 2,4,6-TFPMI-*co*-MMA.

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Based on this relation and experimental results, intrinsic birefringences of the polymers were obtained (Table 4).

The photoelastic birefringence versus the stress of the polymers is shown in Figure 6. PMMA exhibited negative photoelastic birefringence, and photoelastic birefringence constant *C* was approximately -5.3 (TPa<sup>-1</sup>). Its negative birefringence was shifted to positive birefringence with an increase of TFPMI content. Photoelastic coefficients of the copolymers are listed in Table 4.

Figure 7 shows intrinsic birefringence and photoelastic coefficient of TFPMI-*co*-MMA as a function of content of MMA unit in the copolymers. Those relations can be written as follows:

Poly(2,3,4-TFPMI-co-MMA):

$$\Delta n_{or} = -0.18 M_{MMA} + 13.13, \tag{3}$$

$$C = -0.53M_{MMA} + 47.43. \tag{4}$$

Poly(2,4,6-TFPMI-*co*-MMA):

$$\Delta n_{or} = -0.2M_{MMA} + 17.46, \tag{5}$$

$$C = -0.74M_{MMA} + 69.03. \tag{6}$$

Here,  $M_{\rm MMA}$  is the content of MMA unit in the copolymers.

The ratios of 2,3,4-TFPMI/MMA for zero orientational birefringence and zero photoelastic birefringence were calculated to be 15/85 mol % (28/72 wt %) and 5/95 mol % (10/90 wt %), respectively, by eqs 3 and 4. The intrinsic birefringence and the photoelastic birefringence of poly(2,3,4-TFPMI) were calculated to be  $13 \times 10^{-3}$  and 47 (TPa<sup>-1</sup>) (Table 4).

The ratios of 2,4,6-TFPMI/MMA for zero orientational birefringence and zero photoelastic birefringence were calculated to be 12/88 mol % (24/76 wt %) and 3/97 mol % (7/93 wt %), respectively, by eqs 5 and 6. The intrinsic birefringence and the photoelastic birefringence of poly(2,4,6-TFPMI) were calculated to be  $17 \times 10^{-3}$  and 69 (TPa<sup>-1</sup>) (Table 4).

These results show that 2,4,6-TFPMI unit exhibits higher orientational and photoelastic birefringence effects than those of 2,3,4-TFPMI.

#### CONCLUSIONS

2,3,4- and 2,4,6-TFPMIs were synthesized and copolymerized with MMA using AIBN as initiator in 1,4-dioxane or in bulk. The glass transition temperatures of the copolymers were high (133–195 °C) depending on copolymer compositions. The copolymers obtained were thermally stable. The orientational and photoelastic birefringences of copolymers of TFPMIs and MMA were measured. The copolymers of MMA/2,3,4-TFPMI would exhibit zero orientational and photoelastic birefringences when the ratio of 2,3,4-TFPMI/MMA were 15/85 and 5/95 mol %, respectively. For the copolymers of 2,4,6-TFPMI/MMA, the ratios of copolymers with zero orientational and photoelastic birefringences were determined to be 12/88 and 3/97 mol %, respectively. The  $T_{\rm g}$ s of these

copolymers with zero birefringence were in the range of 135–140  $^\circ\text{C}.$ 

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