Synthesis of poly[1,1,1,3,3,3-hexafluoro-2-(pentafluorophenyl)propan-2-yl methacrylate]: Thermal and optical properties of the copolymers with methyl methacrylate

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Abstract

Poly[1,1,1,3,3,3-hexafluoro-2-(pentafluorophenyl)propan-2-yl methacrylate (**I**)] was synthesized, and the copolymers of the monomer **I** with various compositions of methyl methacrylate (MMA) were prepared and characterized. The glass transition temperature values obtained for the copolymers were between 120 and 150 °C. The refractive indices of the copolymers were in the range of 1.4350–1.4872 at 532 nm. They were thermally stable (up to 297–323 °C), and their water absorptive properties were greatly decreased, compared with pure PMMA.
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1. Introduction

Poly(methyl methacrylate) (PMMA), a commercially available polymer, is produced in large quantities, demonstrates high light transmittance and provides excellent resistance to both chemical and weather corrosion [1]. These properties, coupled with low manufacturing cost and easy processing, make PMMA a valuable substitute for glass in optical device applications [2]. However, the major disadvantages of PMMA, such as its relatively low glass transition temperature (T_g) (around 100 °C) and high water absorption, limit its utility for optical electronic applications [3,4]. Since introducing fluorine atoms can dramatically improve the thermal and optical properties and water absorption of the polymer, Boutevin's group and our group have independently prepared fluorine-substituted phenyl methacrylates (**II**) and their polymers [5,6]. Because the refractive indices of MMA and the fluorine-substituted monomers are in a similar range, copolymers of these monomers may not have an increased light scattering [6].

The T_g-values of homopolymers of polyfluorinated phenyl methacrylates (**II**), such as pentafluorophenyl (**IIa**), tetrafluor-ophenyl (**IIb**), and *p*-trifluoromethyl perfluorophenyl (**IIc**) methacrylates (Fig. 1) were found to be 133, 125, and 135 °C, respectively. Although these fluorine-substituted phenyl methacrylates yield excellent random copolymers with various compositions of MMA, the T_g-values of the copolymers produced were in the range of 90–120 °C [6]. Generally, the T_g-values of alkyl and aryl methacrylates are higher than those of acrylates [7–10]. The T_g of poly(1,1,1,3,3,3-hexafluoro-2-(pentafluorophenyl)propan-2-yl acrylate was reported as 118 °C [11]. Accordingly the homopolymer's T_g of the methacrylate, having a 1,1,1,3,3,3-hexafluoro-2-(pentafluoro-phenyl)propan-2-yl group, would be expected to be higher than 118 °C. Therefore, in search of a good candidate for POF materials, we have synthesized methacrylate **I** (Fig. 1) and the T_g of the homopolymer was found to be 146 °C. Consequently, the thermal and optical properties of the homopolymer of **I** as well as the copolymers with various amount of MMA (Scheme 1) have been investigated.

2. Results and discussion

Using azobis(isobutyronitrile) (AIBN) as an initiator, homopolymerization of monomer **I** and its copolymerization with MMA were carried out in bulk. Without a chain transfer

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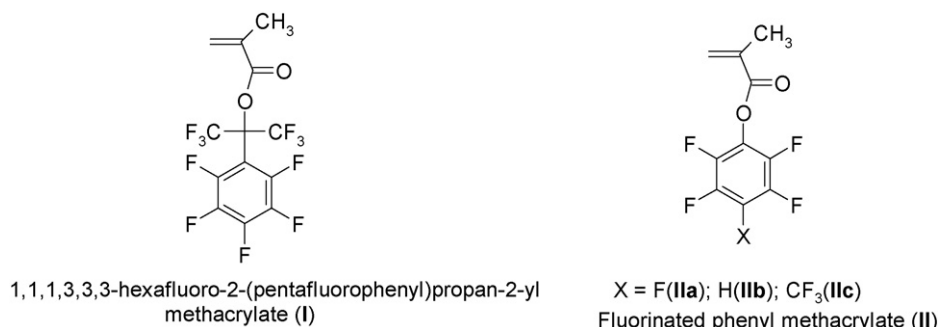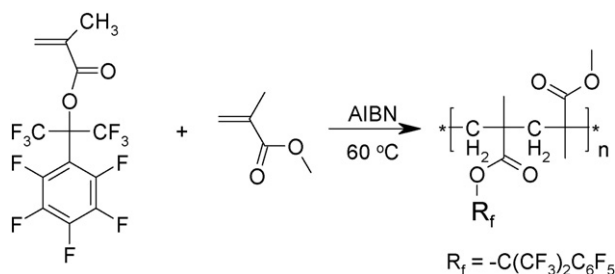 *E-mail address:* yokamoto@poly.edu (Y. Okamoto).

Fig. 1. Structures of fluorinated methacrylates.

Scheme 1. Copolymerization of I with methyl methacrylate.

Table 1
The effect of the chain transfer reagent (*n*-BuSH) on the M_n and M_w of the copolymers of **I** with MMA

Entry	Content of **I** in feed (mol%)	*n*-BuSH (mol%)	M_n ($\times 10^4$)	M_w ($\times 10^4$)
1	50	1.0	3.5	10.1
2	50	2.0	1.4	3.2
3	80	1.0	2.6	5.3
4	80	1.9	1.7	4.2

reagent, polymers obtained had too high a molecular weight and were not soluble in common organic solvents such as chloroform and THF. Therefore, *n*-BuSH was used to adjust the molecular weight of the polymers. As shown in Table 1, the chain transfer reagent, *n*-BuSH, effectively controls the molecular weights of the copolymers of **I** and MMA. Hence the high conversion (80–90%) copolymerization reactions of **I** and MMA were carried out with 1.0 mol% of *n*-BuSH at 60–80 °C. These results are summarized in Table 2. The polymers isolated, referred to as **P₁–P₆**, have only one T_g. When
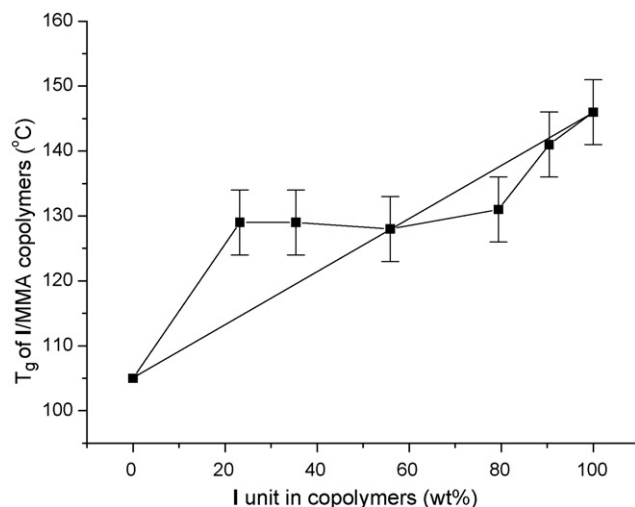

Fig. 2. Composition dependence of glass transition temperature (T_g) of I/MMA copolymers.

T_g-values of the copolymers were plotted versus the monomer compositions (Fig. 2), they were found to approximately fit with the Gordon–Taylor equation

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \qquad (1)$$

where w_1 and w_2 are weight fractions of the two monomeric units in the copolymer, T_{g1} and T_{g2} are T_g-values of related homopolymers, and k is generally considered a real fitting parameter. Depending on the actual value of k the T_g versus composition curves deviate from linearity defined by $k = 1$. For fitting the data it is convenient to linearize equation (1) as

Table 2
Results of copolymerization reaction of **I** with MMA

Entry[a,b]	Content of **I** in		Polymer	Conv. (%)	M_n ($\times 10^4$)	M_w ($\times 10^4$)	T_g (°C)
	Feed (wt%)	Polymer (wt%)					
1	17.6	18.3	**P₁**	90	2.3	3.5	121
2	31.3	31.9	**P₂**	88	2.6	4.0	123
3	49.4	50.3	**P₃**	90	3.3	7.8	124
4	78.6	78.0	**P₄**	83	3.5	10.1	132
5	93.1	92.6	**P₅**	82	2.3	4.4	140
6	100	100	**P₆**	80	2.4	4.6	146

[a] *n*-BuSH (1% mol) was used as a chain transfer reagent.
[b] The reaction was proceeded at 60 °C for 48 h and then heated at 80 °C for 12 h.

follows

$$T_g - T_{g1} = \frac{k(T_{g2} - T_g)W_2}{W_1} \qquad (2)$$

A plot of $T_g - T_{g1}$ versus $(T_{g2} - T_g)W_2/W_1$ yields k via linear regression [12,13]. In this case, when we set T_{g1} and T_{g2} as T_g-values of homopolymers of MMA and monomer **I**, respectively, the result was $k = 0.27$.

In the cases of the copolymerizations of **IIa** and **IIb** with MMA, the T_g-values were found to deviate positively from the Gordon–Taylor equation ($k = 1$). Since the fluorine substituted phenyl group is strongly electron-withdrawing, the ester group in **II** is highly polarized. Thus, there is a strong dipole–dipole interaction between the carbonyl group of MMA unit and the fluorine substituted phenyl ester group of **II** unit, resulting in an enhanced T_g and the positive deviation [6,14].

I also has a highly fluorinated ester group. However, the two trifluoromethyl groups on the methylene are much bulkier than those of **IIa** and **IIb**. This bulkier ester group inhibits the interaction between MMA and **I** unit, causing T_g to fit with the Gordon–Taylor equation ($k = 1$).

In order to calculate reactivity ratios of the monomers, the copolymerization reactions of **I** with various amounts of MMA were stopped at 16.8–34.7% monomer conversion. The reactivity ratios were found to be $r_1 = 0.53 \pm 0.01$ and $r_2 = 0.95 \pm 0.04$ for **I** and MMA, respectively. These data are summarized in Table 3.

The reactivity of **I** was lower than that of MMA. This may be due to the steric hindrance and the electro-withdrawing property of the 1,1,1,3,3,3-hexafluoro-2-(pentafluorophenyl)-propan-2-yl group. The reactivity ratios indicate that both of the monomers have good copolymerization properties and yield random copolymers.

The refractive indices of the copolymers of **I** with MMA were measured at 532, 633 and 839 nm. The data are cited in Table 4. Compared to the refractive index of pure PMMA, which is 1.4953, the refractive index of the homopolymer (**P₆**) of **I** is lower: 1.4350, both at 532 nm. The refractive indices of the copolymers exhibited a linear relationship with those of the monomer compositions as shown in Fig. 3.

All the copolymers obtained exhibited good thermal stability. The on-set decomposition temperatures of the copolymers are summarized in Table 4, and the TGA curves are shown in Fig. 4.

Table 3
Low conversion copolymerization reactions of **I** and MMA

Entry[a]	Content of **I** in		Time (h)	Conv. (%)	T_g (°C)
	Feed (wt%)	Polymer (wt%)			
1	17.6	23.2	1.0	16.8	129
2	31.3	35.4	3.0	32.9	129
3	49.4	55.9	4.0	34.7	128
4	78.6	79.4	5.6	21.5	131
5	93.1	90.4	18	31.4	141

[a] All the reactions were carried at 60 °C.

Table 4
The refractive indices and on-set decomposition temperatures of the copolymers

Polymer	T_d[a,b] (°C)	n_λ (nm)		
		532	633	839
P₁	297	1.4827	1.4788	1.4743
P₂	315	1.4749	1.4701	1.4655
P₃	317	1.4689	1.4642	1.4598
P₄	319	1.4483	1.4440	1.4393
P₅	323	1.4381	1.4328	1.4276
P₆	323	1.4350	1.4298	1.4253

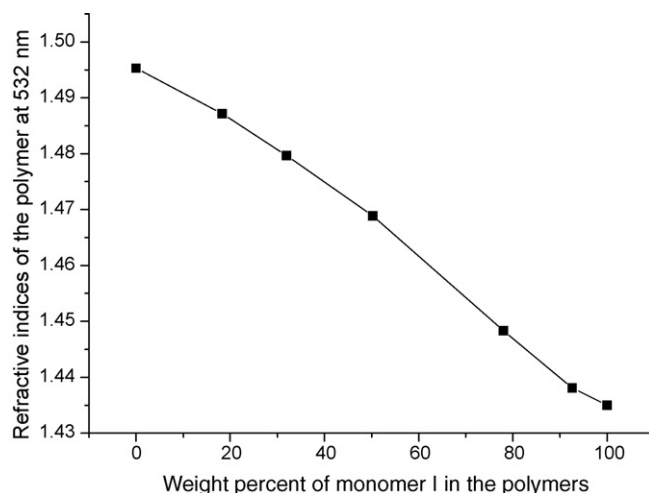[a] Under N_2 atmosphere.
[b] The T_d of PMMA is 300 °C.

Fig. 3. The influence of the weight percent of the fluorinated monomer I on the refractive indices of the polymers.

The water absorption of the copolymer was greatly decreased as compared to PMMA. An example of typical data was shown in Fig. 5.

Generally, flexibility is a very important character of plastic optical fiber (POF) materials. It was found that when the
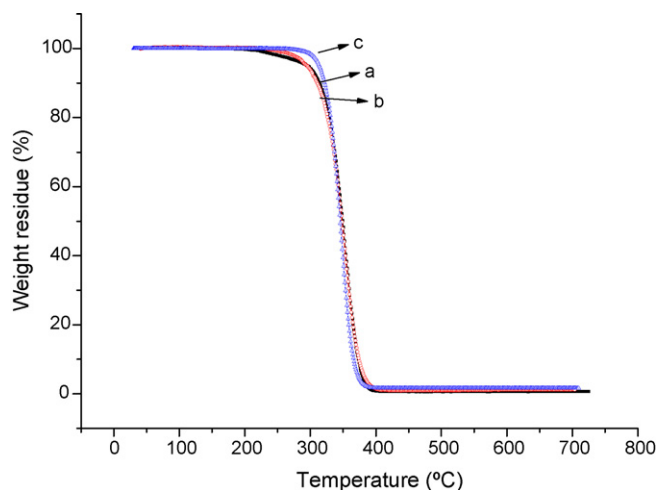

Fig. 4. The TGA curves of the polymers: (a) for **P₅**; (b) for **P₃**; (c) for homopolymer **P₆**.
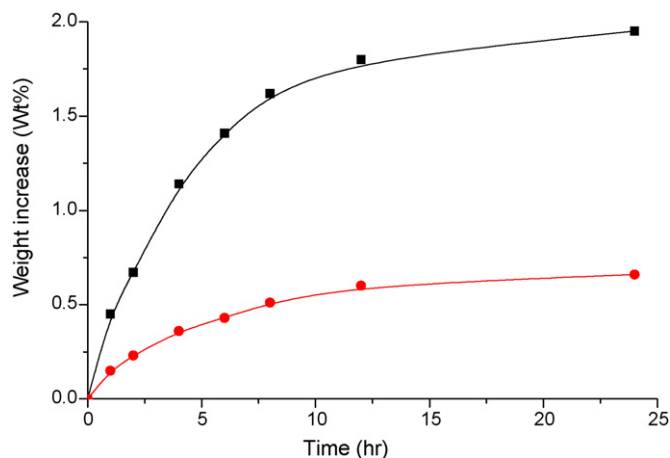
Fig. 5. The water absorptions of PMMA (■) and copolymer P$_2$ (●) at 60 °C, under 90% relative humidity (film, 30 mm × 20 mm × 2 mm).

amount of **I** increased to above 40 wt% the copolymers became a little brittle, while at below 40 wt% the films were flexible. This property combined with all the other properties mentioned above, indicate that copolymers with the percentages of monomer **I** lower than 40 wt% may be good candidates for POF materials.

3. Experimental

3.1. General

MMA, methacryloyl chloride, triethylamine, diethyl ether, chloroform and AIBN were purchased from Aldrich. Chloropentafluorobenzene, hexafluoroacetone were bought from SynQuest Co. Diethyl ether was distilled from sodium wire containing benzophenone, and the free radical initiator AIBN was purified by recrystallization from methanol. Monomers were purified with the traditional method. All the other chemicals were used directly without further purification. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were determined on a Brucker AC 300 spectrometer, at 300.1, 75.5 and 282.4 MHz, respectively, using CDCl$_3$ as a solvent. Chemical shifts are reported in δ (ppm) from internal TMS (^{1}H and ^{13}C) or from internal CFCl$_3$ (^{19}F).

3.2. Synthesis of monomer

3.2.1. Preparation of 1,1,1,3,3,3-hexafluoro-2-(pentafluorophenyl)propan-2-ol

To a 1 L three-necked flask, chloropentafluorobenzene (75 g, 0.37 mol) and diethyl ether (300 mL) were added under N$_2$ stream. The system was cooled to −78 °C, and *n*-BuLi (150 mL, 2.5 M, 0.375 mol) was added dropwise during 1 h. The reaction was subsequently stirred for 2 h. An excess of hexafluoroacetone (72 g, 0.43 mol) was added over 70 min. The resulting mixture was stirred for another 3 h, warmed up to room temperature, and poured into a 2 L beaker which contained 20 mL of H$_2$SO$_4$ and ice. The water phase was extracted with ether (3× 100 mL). The organic layers were

combined, washed with water and brine, and then dried over MgSO$_4$. Fractional distillation gave 110 g of colorless oil, bp 158–160 °C, yield 88%. ^{1}H NMR (CDCl$_3$): 4.08 (s, br., 1H); ^{19}F NMR (CDCl$_3$): 76.45 (m, 6F), 133.05 (s, br., 1F), 137.91 (w, br., 1F), 149.18 (m, 1F), 160.27 (m, 2F); MS (EI, 70 eV): *m/z* (%) = 334 (4.10) [*M*]$^+$, 265 (11.08), 195 (100), 167 (18.98), 117 (14.18), 69 (16.81).

3.2.2. Preparation of the monomer **I**

An ether (15 mL) solution of methacryloyl chloride (5.22 g, 50 mmol) was added dropwise into a mixture of 1,1,1,3,3,3-hexafluoro-2-(pentafluorophenyl)propan-2-ol (16.7 g, 50 mmol), triethyl amine (5.5 g, 54 mmol) and ether (45 mL) at 0 °C, under N$_2$ atmosphere. The resulting mixture was stirred at 0–25 °C for 6 h. Then the reaction was stopped. A white precipitate was filtered and washed with a small amount of ether. The combined ether solution was washed with 5% hydrochloric acid, 3% sodium bicarbonate, water, brine, and then dried over MgSO$_4$. After removing the ether with a rotary evaporator, the residue was distilled under vacuum to give a colorless oil at 79 °C/2 mmHg, yield 80%. IR (KBr): ν 1772 (C=O); ^{1}H NMR (CDCl$_3$): 2.02 (s, 3H), 5.85 (s, 1H), 6.32 (s, 1H); ^{19}F NMR (CDCl$_3$): 76.05 (t, *J* = 14.1 Hz, 6F), 133.28 (s, br., 1F), 140.34 (s, br., 1F), 148.84 (tt, *J* = 20.6 Hz, *J* = 5.1 Hz, 1F), 160.02 (m, 2F); ^{13}C NMR (CDCl$_3$): 18.3, 81.1, 103.5, 121.0, 133.2, 134.1, 138.4, 142.8, 145.8, 163.2; CIMS (M, %): 403 (*M* + 1, 100), 333 (25).

3.3. Polymerization

AIBN was employed as an initiator. *n*-BuSH was used as a chain transfer reagent. Polymerization reactions were carried out in bulk.

3.3.1. Low conversion copolymerization reactions

The monomer mixtures, including known amounts of comonomers, and initiator (1.0 mol%), were transferred into a glass polymerization tube. The tube was subjected to repeated freeze–pump–thaw cycles and sealed under vacuum. The polymerization reactions were proceeded at 60 °C. After the reaction mixture was in proper viscosity, the glass tube was opened and the contents were poured into a large amount of methanol with vigorous stirring to precipitate the polymer. After drying under vacuum at 50 °C for 24 h, polymer samples were reprecipitated from the chloroform solution into methanol. The purified polymer samples were dried under vacuum at 50 °C for 48 h.

3.3.2. High conversion copolymerization

The monomer mixtures, including known amounts of comonomers, chain transfer reagent (1.0 mol%) and initiator (1.0 mol%), were transferred into a glass polymerization tube. The tube was subjected to repeated freeze–pump–thaw cycles and sealed under vacuum. Then the polymerization reactions were proceeded at 60 °C for 48 h, and then at 80 °C for 12 h. The glass tube was opened and the contents were dissolved in small amount of chloroform. The chloroform solution were

poured into a large amount of methanol with vigorous stirring to precipitate the polymer. After drying under vacuum at 50 °C for 24 h, polymer samples were reprecipitated from the chloroform solution into methanol. The purified polymer samples were dried under vacuum at 50 °C for 48 h.

3.4. Measurements

Molecular weights were determined by gel permeation chromatography (GPC) (Waters 510) using chloroform as the eluent at a flow rate of 1.0 ml/min. The molecular weight calibration curve was obtained using polystyrene standards. The glass transition temperature (T_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_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. The polymer films (0.1–0.2 mm thick), fabricated by casting the polymers solutions on glass plates, were used to measure the refractive index on a prism coupler (Metricon, model 2010). The measurement accuracy was ±0.0005. The probe wavelengths in the prism were 532, 633 and 839 nm. A humidity oven having circulating air and maintaining 90 ± 3% humidity at 60 ± 2 °C was used to measure water absorption, and the sample sizes were 30 mm × 20 mm × 2 mm films.

4. Conclusion

The homopolymer (P_6) of I was thermally stable (up to 323 °C), and exhibited a T_g of 146 °C. I was randomly copolymerized with MMA. The T_g values of the copolymers, P_1, P_2 and P_3, containing 25–50 wt% of I, were found to be in the range of 120–125 °C. The refractive indices of these copolymers ranged from 1.4827 to 1.4689 at 532 nm. These copolymers were thermally stable (up to 297–323 °C), flexible, and displayed much less water absorption than PMMA. Thus, we suggest these copolymers may have various applications in the field of optical and electric devices.

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