

# Preparation and Properties of Methyl Methacrylate and Fluoroacrylate Copolymers for Plastic Optical Fiber Cladding

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**ABSTRACT:** Copolymers of methyl methacrylate (MMA) and fluoroacrylate (FA), with different FA content (0–100 wt %), were prepared by bulk polymerization. The chemical structure was identified by <sup>1</sup>H-NMR and other physical properties were measured by DSC, Abbé refractometer, X-ray diffractometry, polarized optical microscopy, and DMA. The copolymers were confirmed as random copolymers by Fineman–Ross analysis and first-order Markov statistics. Increasing the FA content from 0 to 100 wt % decreased the refractive index from 1.492 to

1.368. Copolymers with FA content higher than 70 wt % crystallized and led to low transparency and poor thermal properties. On the other hand, copolymers with FA content lower than 70 wt % was thermally stable ( $T_g$  was as high as 60°C) and transparent. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2082–2089, 2004

**Key words:** copolymerization; refractive index; crystallization; glass transition; transparency

## INTRODUCTION

Plastic optical fiber (POF) has been used in decorative displays or light-transmission systems, and it has recently been used in short-distance data transmission as well.<sup>1,2</sup> Compared with silica glass optical fibers, POF has many advantages, such as good ductility, light weight, low melting temperature, low cost, and large core diameter. Until now graded index POF (GIPOF) has been widely investigated for use in high data transmission.<sup>3</sup> The typical process for preparing GIPOF is as follows. Initially, the preform of the POF is produced by copolymerizing two or more monomers of different refractive indices in a tube made of polymer such as PMMA.<sup>4–9</sup> Then, the GIPOF is fabricated by thermally drawing the preform made by a batch process. The GIPOF is also prepared by continuous process.<sup>10–12</sup> However, it is difficult to obtain a refractive index profile by the continuous process. In contrast to GIPOF, the step index POF (SIPOF) is simply prepared by coextrusion of two components with different refractive indices, which is a more desirable method for commercial preparation.

SIPOF is composed of core and cladding polymers. Poly(methyl methacrylate) (PMMA) and polystyrene

(PS) are normally used as core materials because these polymers are easily purified at the monomer level to produce an exceedingly transparent polymer. The refractive index of the cladding materials should be less than that of the core materials by 2–5%. The cladding materials should be amorphous to give high transparency. PMMA and fluorinated polymers are used as the cladding materials for PS and PMMA core materials, respectively.<sup>13</sup> Cladding materials should have a lower refractive index than that of core materials to reflect light below a critical angle, which keeps the light transmitted down to the core. The critical angle is a factor of the difference of refractive index between core and cladding materials, referred to as the numerical aperture (N.A.).<sup>14</sup> All of the light from the transmitter does not enter POF because light loss occurs at the coupling interface between the transmitter and the fiber.<sup>15</sup> If the N.A. is small, a large fraction of incident light passes through the cladding, thus causing light leakage when the fiber is severely bended. Transparency of cladding materials also determines the extent of light loss. Opaque materials do not reflect light but absorb it, which causes a large optical loss. Cladding materials thus require low refractive index and high transparency.

Until now, several fluorinated polymers have been used for cladding materials. Among fluorine polymers, vinylidene–fluoride copolymers have low refractive index and good processability. Kobayashi et al.<sup>16</sup> reported an effective cladding material made

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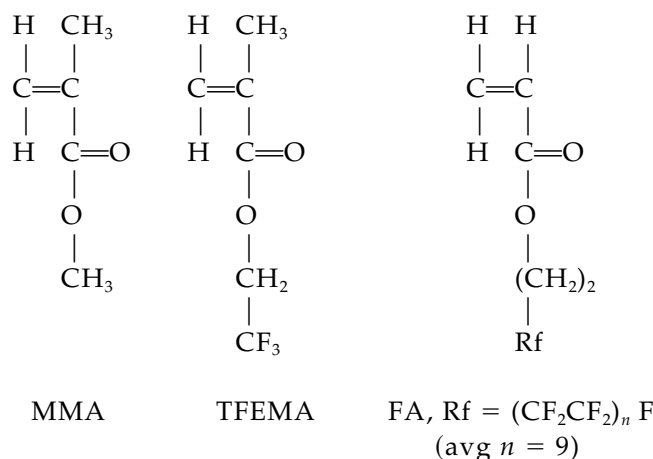
of a copolymer of vinylidene-fluoride, tetrafluoroethylene, and hexafluoropropylene. Pimbert et al.<sup>17</sup> first prepared a vinylidene-fluoride polymer and its copolymers with hexafluoropropene or trifluoroethylene, after which they blended the polymers with PMMA or MMA-trifluoroethyl methacrylate copolymers. Toshima et al.<sup>18</sup> used a copolymer of hexafluoropropene, tetrafluoroethylene, and vinylidene-fluoride as cladding materials, whose mol % ranged from 9/25 to 0/55 to 30/92. However, these cladding materials proved unsuccessful because of translucency and poor adhesion with the PMMA core resulting from high fluorine content. Fluoroacrylates and methacrylates have low refractive index, high transparency, and good copolymerizability with MMA.<sup>19-21</sup> Although vinylidene-fluoride copolymers are more widely used than fluoroacrylates and methacrylates for cladding materials, the use of fluoroacrylates and methacrylates will continue to increase because they have higher transparency and lower loss.

The structure of commercially available Zonyl<sup>®</sup> TA-N fluoroacrylate (FA) monomer is suitable for cladding materials because its long fluorinated alkyl side chains give low refractive index and a somewhat high glass-transition temperature ( $T_g$ ). FA should be copolymerized with MMA for high transparency, and a random copolymer structure is advantageous for obtaining a homogeneous refractive index. In this work, we investigated not only the structure and properties of MMA-FA copolymers prepared by bulk copolymerization but also their adaptability for POF cladding.

## EXPERIMENTAL

### Materials

As monomers, MMA (LG Chem, Seoul, Korea), 2,2,2-trifluoroethyl methacrylate (TFEMA), and Zonyl<sup>®</sup> TA-N fluoroacrylate (Dupont, Wilmington, DE) were used after purification by filtration through an inhibitor-remover column (Aldrich, Milwaukee, WI) to remove the hydroquinone inhibitor. The chemical structures of all monomers are shown below. The initiator V-601 (Wako Pure Chemicals, Osaka, Japan) was recrystallized from methanol. 1-Butyl mercaptane (Aldrich) was used as the chain-transfer agent without further purification. The polymers, such as PMMA, PFA, MMA-FA copolymer, and MMA-TFEMA copolymer, were prepared by bulk polymerization at 60°C for 24 h in a test tube in nitrogen atmosphere. The polymers thus prepared were postpolymerized at 100°C for 6 h to increase conversion.



### Optical properties

The refractive index was measured by Abbé refractometer. The sample (0.5 mm thick) was prepared by compression molding at 200°C. The sample was coated with bromobenzene (refractive index: 1.559) for optical contact. Transmittance was measured at 540 nm at a spectral bandwidth of 2 nm on a UV-vis spectrophotometer (Model V-530, Jasco, Tokyo, Japan).

### Thermal properties

The glass-transition temperature ( $T_g$ ) was determined from the second heat flow curve of DSC (Model 2910, TA Instruments, New Castle, DE). All the samples were scanned from 30 to 200°C in a dry nitrogen atmosphere at a heating rate of 20°C/min. Dynamic mechanical properties were measured by DMA (Rheometric Scientific, Piscataway, NJ) at a heating rate of 5°C/min and 10 Hz over the temperature range of -150 to 180°C. The sample [dimensions: 3 × 6 × 40 mm (thickness × width × length)] was prepared by compression molding (200°C at 1 atm).

### Chemical structure

The chemical structure of the sample was identified by <sup>1</sup>H-NMR (300 MHz; Varian Associates, Palo Alto, CA). The solvent was acetone-*d*<sub>6</sub> (Aldrich) at a concentration of 5–10 wt %.

### Crystalline structure

The crystal structure was examined by wide-angle X-ray diffractometer (D/MAX-2000, Rigaku Denki, Tokyo, Japan) with nickel-filtered Cu-K<sub>α</sub> radiation of 40 kV and 126 mA over the 2θ range of 5 to 45° at a scanning speed of 5°/min. The sample was prepared by filming and annealing at 80°C for 24 h. The crystal morphology was observed by optical microscope (Op-

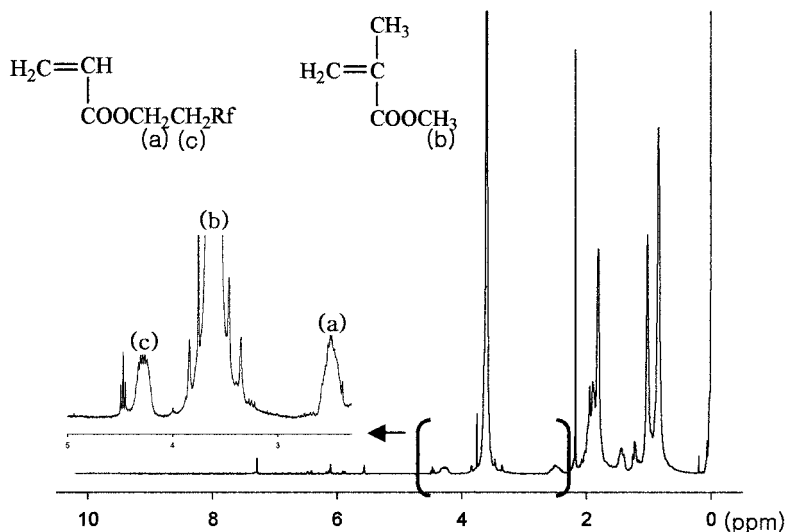


Figure 1 <sup>1</sup>H-NMR spectra of MMA-FA copolymer.

tiphot 2-pol, Nikon, Tokyo, Japan) in the transmitted-light mode. The samples was coated with poly(dimethyl siloxane), on which the cover glass was placed.

## RESULTS AND DISCUSSION

### Copolymer structure

The chemical structure of MMA-FA copolymers was identified by <sup>1</sup>H-NMR. In Figure 1, two peaks at 2.6 and 4.2 ppm represent the CH<sub>2</sub> group of FA in the side chain and the peak at 3.7 ppm represents the CH<sub>3</sub> group of MMA in methacrylate. The relationship between copolymer composition and feed composition shows good proportionality, as shown in Figure 2. However, these high conversion data may not inform one of the reactivity ratio of monomers and copolymer sequence.

To characterize the sequence of copolymers the reactivity ratio of monomers ( $r$ ) was determined by the Fineman-Ross expression<sup>22,23</sup>

$$\frac{x(1-y)}{y} = r_{FA} - r_{MMA} \frac{x^2}{y} \quad (1)$$

in which  $x$  and  $y$  are the molar ratio of MMA to FA in the copolymer and in the feed, respectively [i.e.,  $x = f_{MMA}/(1 - f_{MMA})$  and  $y = F_{MMA}/(1 - F_{MMA})$ ]. Figure 3 shows linear relationship between  $x(1-y)/y$  and  $x^2/y$ . According to the equation, the slope and intercept on the plot represent the reactivity ratio of MMA and FA, respectively. The reactivity ratios thus evaluated were 1.265 and 0.438 for MMA and FA, respectively.

The number-average sequence length ( $\langle l_{MMA} \rangle$  and  $\langle l_{FA} \rangle$ ) of each monomer in the copolymers and param-

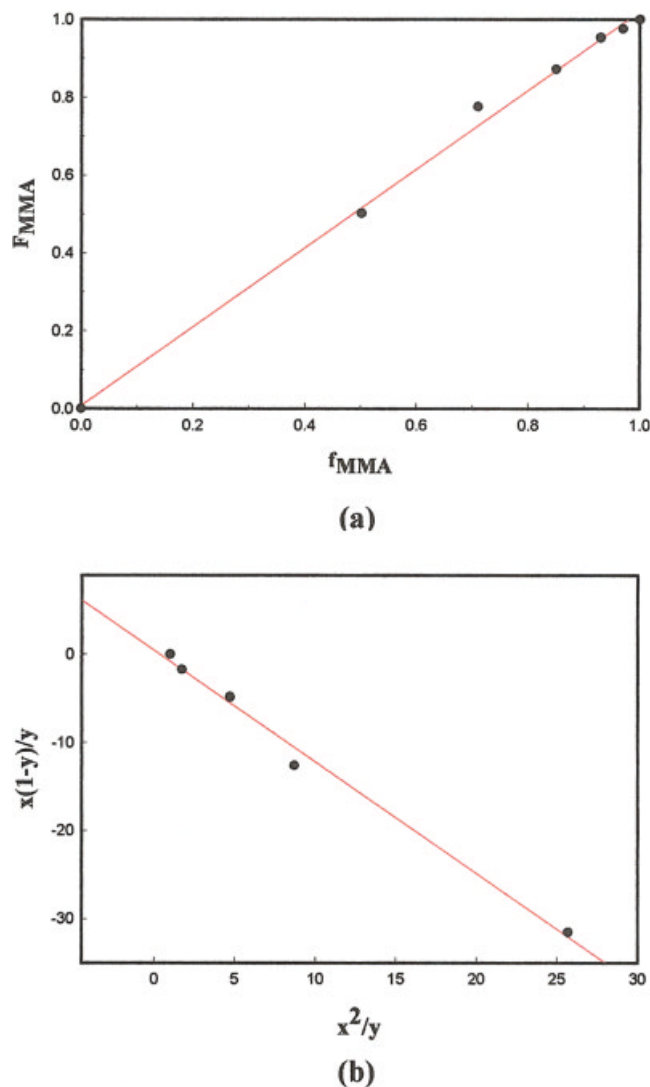
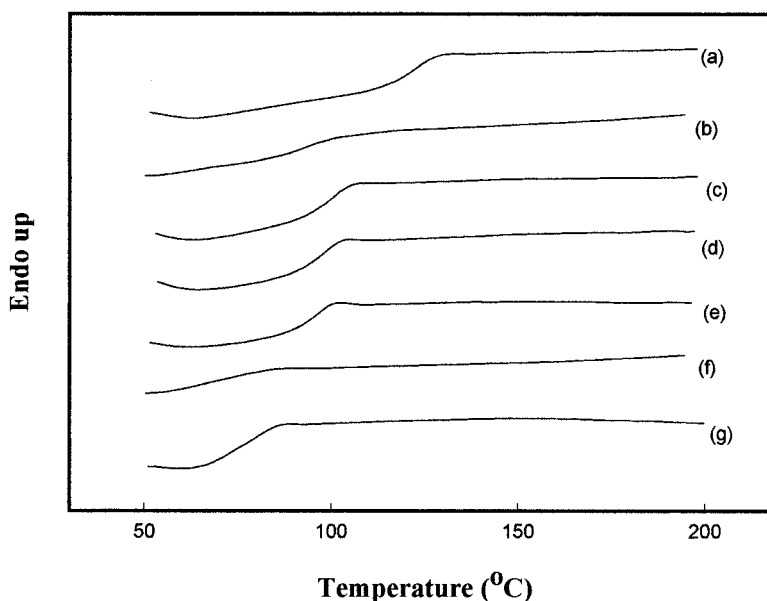


Figure 2 (a) MMA mole fraction in feeds ( $f_{MMA}$ ) and corresponding copolymers ( $F_{MMA}$ ). (b) Determination of reactivity ratios of MMA and FA by Fineman-Ross fitting given by  $x(1-y)/y = r_{FA} - r_{MMA}(x^2/y)$ .



**Figure 3** DSC heating thermograms of (a) PMMA; MMA-TFEMA (in wt %) (b) 85/15, (c) 70/30, (d) 50/50, (e) 30/70, (f) 15/85; and (g) P(TFEMA) at scanning rate of 20°C/min.

eter  $\chi$  can be calculated by first-order Markov statistics,<sup>22</sup> defined by the following equations:

$$\langle l_{\text{MMA}} \rangle = 1 + r_{\text{MMA}}\chi \quad (2a)$$

$$\langle l_{\text{FA}} \rangle = 1 + r_{\text{FA}}/x \quad (2b)$$

$$\chi = \frac{r_{\text{MMA}}X + 2 + r_{\text{FA}}/x}{r_{\text{MMA}}\chi + 1 + r_{\text{MMA}}r_{\text{FA}} + r_{\text{FA}}/x} \quad (3)$$

where  $\chi$  offers structural information of copolymers:  $\chi = 0$ ,  $\chi = 1$ , and  $\chi = 2$  represent block, random, and alternating copolymers, respectively.<sup>24</sup> Table I shows that the  $\chi$  values of the copolymers range from 1.011 to 1.137, which indicates that the copolymers are almost random copolymers.

Heterogeneity, characteristic of block copolymers, gives rise to substantial light leakage. Random copolymers are desirable for use in optical devices because they give optical homogeneity and transparency. Optical heterogeneity may make the refractive index and transparency vary from point to point within the material, which is the fatal disadvantage for POF cladding.<sup>25</sup> Some examples causing optical heterogeneity include phase separation in the polymer blends, phase separation in the block copolymers, and partial crystallization resulting from the long sequence of stereoregularity of polymers.

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### Crystallization behavior of the side chain of copolymers

Figure 3 shows the  $T_g$  values of MMA-TFEMA copolymers. As the content of TFEMA is increased, the  $T_g$  of the copolymer is decreased, which is attributed to the fluorinated side chain increasing the free volume of the molecules. Figure 4 shows DSC second heating and second cooling thermograms of MMA-FA copolymers. Pure PFA clearly exhibits both  $T_m$  and  $T_c$  peaks. However, the  $T_m$  peak disappears as the FA content is decreased.

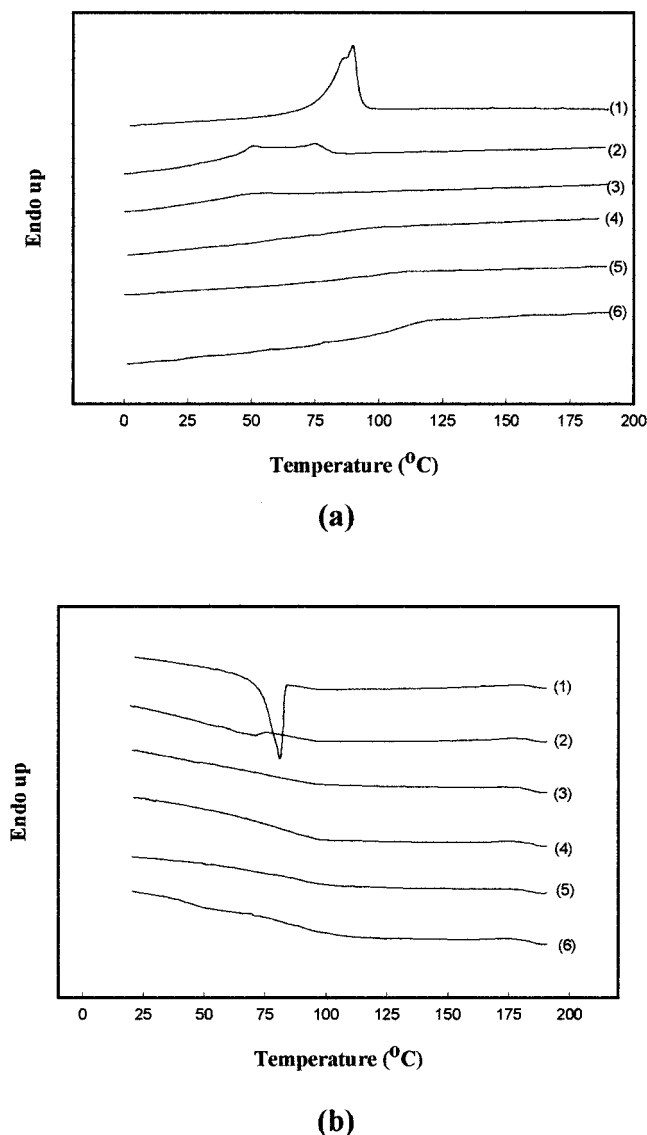
In Figure 4(a), the 15/85 (by wt) MMA-FA copolymer exhibits a very weak and broad peak over 50 to 80°C. To clarify this peak dynamic mechanical analysis was performed, and the result is given in Figure 5. As shown, the PFA/MMA-FA (15/85) (by wt) copolymer does not give any peak (or  $\alpha$ -transition) over the temperature range observed, although it does show melting behavior. This ascertains that the weak and broad peak on the DSC curve for MMA-FA (15/85) (by wt) copolymer is a melting peak. On the other

**TABLE I**  
Identification of Chemical Structure  
of MMA-FA Copolymers

MMA-FA content (wt %)	$\chi^a$	$l_{\text{MMA}}^b$	$l_{\text{FA}}^c$
85 : 15	1.011	41.901	1.014
70 : 30	1.024	17.807	1.033
50 : 50	1.051	8.169	1.077
30 : 70	1.092	4.097	1.179
15 : 85	1.137	2.275	1.435

<sup>a</sup> Randomness of copolymers ( $X = 1$ , random copolymer;  $\chi = 2$ , alternating copolymer).

<sup>b,c</sup> Number-average sequence length of MMA and FA, respectively.



**Figure 4** DSC heating (a) and cooling (b) thermograms of (1) PFA; MMA-FA (in wt %) (2) 15/85, (3) 30/70, (4) 50/50, (5) 70/30, and (6) 85/15 at scanning rate of 20°C/min.

hand, the other five copolymers clearly show  $\alpha$ -transition at the glass-transition temperature, which is increased with increasing MMA content.

From polarizing optical microscopy, shown in Figure 6, an ordered phase can be observed for PFA and MMA-FA 15/85 and 30/70 (by wt) copolymers. Figure 6(a) shows a grainy crystal structure of PFA, indicating that long side chains of FA are packed to form a crystal structure. Polymers, in which crystallizable long alkyl side chains are attached to the noncrystallizable main chain, can develop a layered structure with alternating crystalline side-chain region and amorphous main-chain region in the solid state.<sup>26</sup> The long side chains of FA in this study are composed of fluoro-alkyl groups. Because fluorinated alkyl chains are more rigid and linear than hydrocarbon chains,

PFA may readily crystallize. Bragg spacing ( $d$ ) of the long alkyl side chain is reported to be 4.2 Å.<sup>26</sup> However, the value of  $d$  of FA was measured to be 4.9 Å by X-ray diffraction, as shown in Figure 7. This originates from the bulkiness of fluorine when compared with hydrogen. As MMA content is increased, the crystal morphology of the FA component is changed.

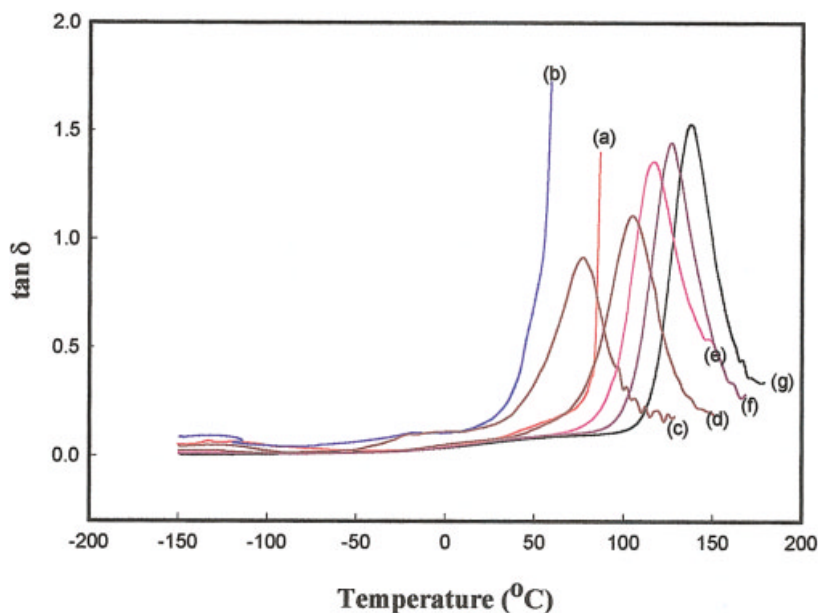
It is worth mentioning in Figure 6(b) that the uniformity of the crystalline morphology is substantially deteriorated if the MMA content is increased from 0 to 30 wt %. This suggests that an abundance of crystal defects may be formed in the bulk. That is, the amount of MMA copolymerized, 15 wt %, is equivalent to almost half of the polymer by mol fraction and MMA would interfere with crystallization of long side chains of FA. Thus, the resultant crystals would have a wide range of crystal sizes and less-perfect crystal structure. Consequently, the DSC heating thermogram of MMA-FA 15/85 (by wt) copolymer shows a broad range of melting temperatures from 50 to 80°C. At 15/85 (by wt) MMA-FA copolymer a small endothermic peak can be observed in Figure 4(a). WAXD patterns, shown in Figure 7(b), show a small ordered structure in MMA-FA 15/85 (by wt) copolymer. At 30/70 (by wt) MMA-FA copolymer shows a very weak peak in the WAXD pattern in Figure 7(c) but the crystalline morphology in Figure 6(c) suggests that the copolymer contains some crystals, although the crystal domains are not well defined. If the content of MMA exceeds in copolymerization, the copolymer obtained becomes absolutely amorphous. The dark image in Figure 6(d)-(g) clearly confirms this.

As can be imagined, the  $T_g$  of a plastic material is related to the service temperature of the material. In POF application the  $T_g$  is especially important and it should be higher than 60°C. As known, one should increase the fluorine content to diminish the refractive index, although this lowers the  $T_g$  of the raw material for POF. In the case of MMA-FA copolymer, the thermal properties would be enhanced by side-chain crystallization compared with those of MMA-TFEMA copolymers. Table II shows the  $T_g$  values and refractive indices of MMA-FA copolymers. However, crystallization reduces transparency, which is a crucial defect for POF cladding materials.

## Optical properties

### Refractive index

Figure 8(a) shows the refractive indices of the copolymers of MMA with FA and TFEMA. As the fluorine content is increased, the refractive index of the copolymers is decreased. Refractive index is reported to be dependent on the molar refraction and the density.<sup>27</sup> It increases with increasing intrinsic refractive power of a material, as quantified by its molar refraction. If two



**Figure 5** Variation of loss tangent ( $\tan \delta$ ) with temperature for (a) PFA; MMA-FA (in wt %) (b) 15/85, (c) 30/70, (d) 50/50, (e) 70/30, (f) 85/15; and (g) PMMA.

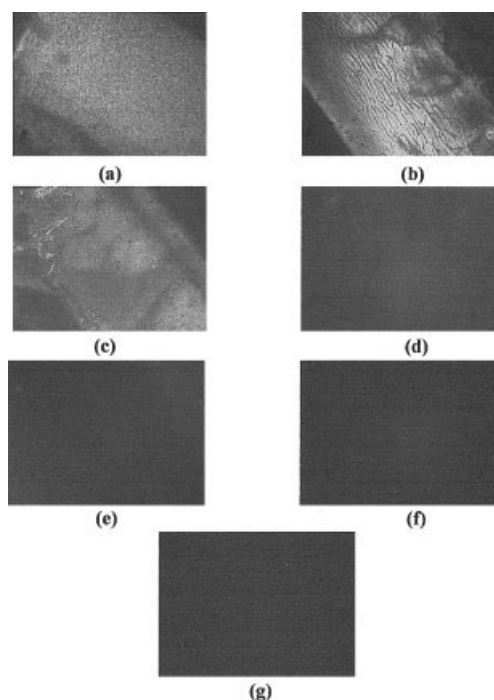
polymers have identical molar volume  $V$ , the polymer with the larger intrinsic refractive power will have a larger refractive index. The atoms act as "obstacles" to a beam of light traversing the material, and reduce the speed of the light beam. If two polymers have identical molar refraction, the polymer with the smaller  $V$

will produce a larger number of such obstacles per unit length of the beam of light, and will therefore have a larger refractive index. Thus intrinsic refractivity of the structural units and the density are the key factors determining the refractive index. Fluorinated polymers often have very high densities but very low intrinsic refractivities, which produce very low refractive indices. Figure 8(b) shows that refractive indices almost linearly decrease by increasing TFEMA mol fraction. That is, the copolymer MMA-TFEMA follows the rule of mixtures with respect to the refractive index. Thus, it is easy to control the copolymer's refractive index.

Particularly with the MMA-FA copolymer, replotting the refractive index against mole fraction instead of weight fraction gives a notable negative deviation from the rule of mixtures. The negative deviation over 0.5 mol fraction of FA seems to result from crystallization of the long side chain of FA, which decreases the molar volume of copolymers.

#### Transparency

Figure 9 shows transmittance of PFA, PMMA, and MMA-FA copolymers. As the MMA content is increased, transmittance of the copolymer is also increased. However, PFA and MMA-FA 15/85 and 30/70 (by wt) copolymers have low transmittance because of crystallization. The MMA-FA 15/85 (by wt) copolymer, in particular, has lower transmittance than that of PFA, which is the most crystalline among the tested materials. The difference of refractive index between PFA and PMMA is reasonably high. Thus a



**Figure 6** Polarized optical micrographs of (a) PFA; MMA-FA (in wt %) (b) 15/85, (c) 30/70, (d) 50/50, (e) 70/30, (f) 85/15; and (g) PMMA.

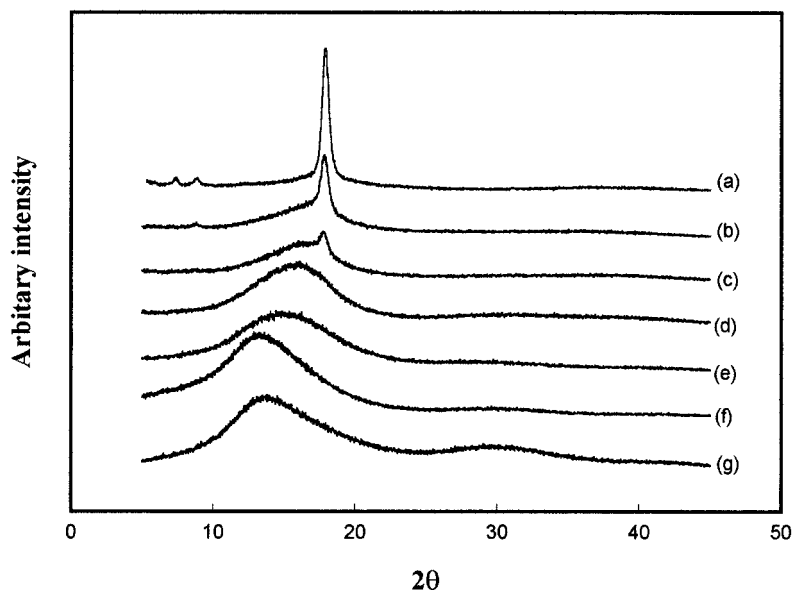


Figure 7 WAXD patterns of (a) PFA; MMA-FA (in wt %) (b) 15/85, (c) 30/70, (d) 50/50, (e) 70/30, (f) 85/15; and (g) PMMA.

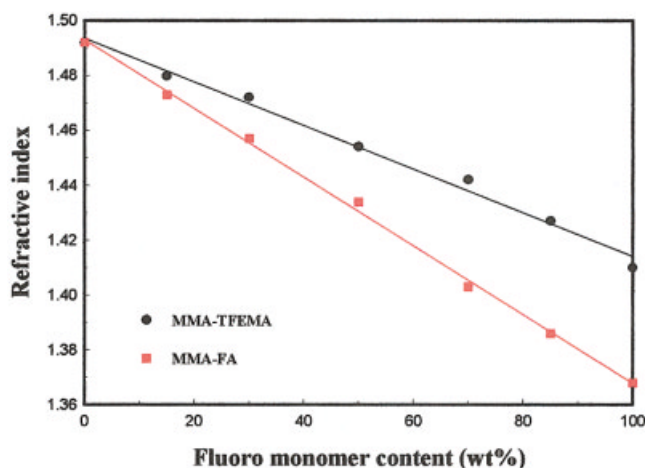
mismatch of refractive indices causes MMA-FA 15/85 (by wt) copolymer to be more translucent than PFA. Viewed microscopically, the refractive index fluctuates within the copolymers. Even random copolymers that have only one single refractive index unarguably contain a substructure, which leads to fluctuation of refractive index, causing some light scattering.<sup>28</sup> The 85 wt % of FA corresponds to 49.8 mol % of the copolymer in composition. This means that almost the same amount of FA and MMA molecules is included in the MMA-FA 15/85 (by wt) copolymer. Thus, a more notable fluctuation of refractive index occurs and the copolymer exhibits poorer transparency than that of the PFA polymer.

The translucent cladding material does not reflect light but absorbs it on the core-cladding boundary interface. Hence, PFA polymer and MMA/FA 85/15 (by wt) copolymer, which are somewhat translucent because of crystallization, cannot be applied for the cladding material. However, the MMA-FA copolymers containing FA content less than 70 wt % are recommended as the cladding material because of

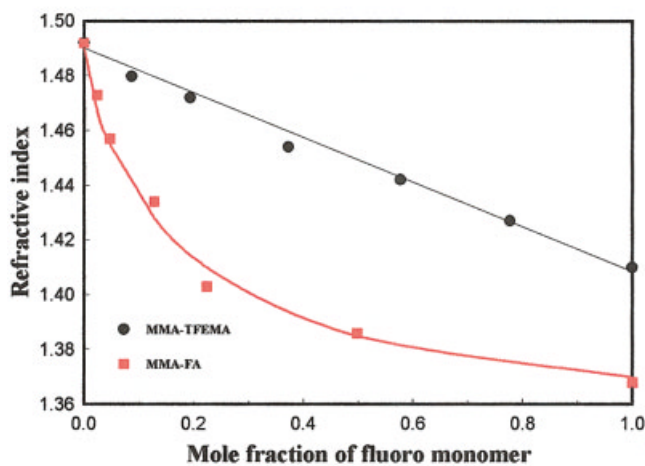
TABLE II  
Physical Properties of MMA-FA Copolymers

MMA-FA content (wt %)	Refractive index	$T_g$ (°C)
100/0	1.492	124
85/15	1.473	117
70/30	1.457	108
50/50	1.434	97
30/70	1.403	54 <sup>a</sup>
15/85	1.386	51 <sup>a</sup>
0/100	1.368	89 <sup>a</sup>

<sup>a</sup> Melting temperature.



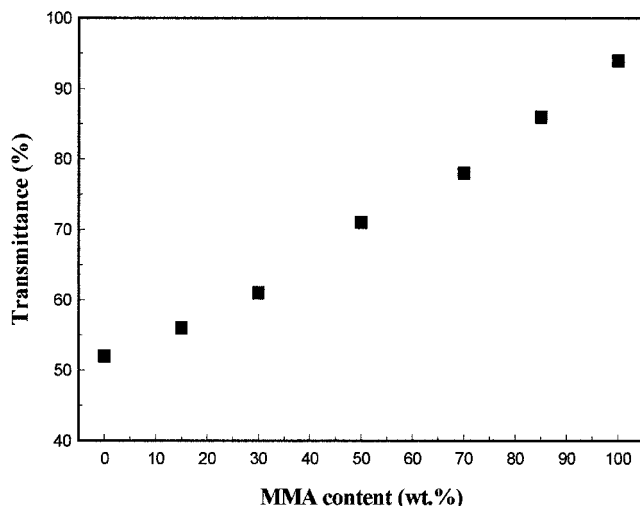
(a)



(b)

Figure 8 Variation of refractive index of MMA-TFEMA and MMA-FA copolymers with fluoro monomer content determined by (a) weight percentage and (b) mole fraction.





**Figure 9** Variation of transmittance of 0.5 mm thick copolymer sheets with MMA content measured at 540 nm at a spectral bandwidth of 2 nm.

good transparency together with low refractive index and reasonably high  $T_g$ .

### CONCLUSIONS

MMA-FA copolymers were investigated to verify their feasibility as materials for POF cladding. The synthesized copolymers proved to be random copolymers with one single refractive index and  $T_g$ . As expected, the refractive index of the copolymer was decreased as the fluorine content was increased. The MMA/FA copolymers with higher fluorine content had lower  $T_g$  than those with lower fluorine content. In choosing POF cladding material, a good balance of  $T_g$  and refractive index has been a problem to be solved. One solution to this problem is given here: use of a polymer that has substantially longer fluorinated side chains. The MMA-FA copolymers with FA content less than 70 wt % gave low refractive index along with high  $T_g$ . These copolymers may be used as the cladding materials for POF, and will find new applications in the field of optical devices.

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