Effects of Fluorinated Substituents on the Refractive Index and Optical Radiation Resistance of Methacrylates

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SYNOPSIS

Novel fluorinated methacrylate polymers were synthesized. The purpose was to produce polymers with low refractive indices and increased resistance to optical radiation damage. Six different fluorinated substituents were appended on the monomer before polymerization. Optical-quality samples were prepared, and their transmission spectra, through 0.8 cm thick samples, were obtained. Each sample was tested for refractive index and glass transition temperature. The samples absorbed 10 MRad gamma radiation from a ^{60}Co source in an air environment; their transmission spectra were recorded immediately after irradiation and again after seven days had elapsed. As expected, increasing the fluorine content in the side chains resulted in decreased refractive indices. Fluorine content also influenced optical radiation stability. One polymer, poly(1H,1H-heptafluorobutyl methacrylate) retained superior UV/visible transmission after irradiation. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

As high-energy particle accelerators become more powerful and intense, superior performance is required of the detectors surrounding the collision sites. One method of tracking particles involves large numbers of plastic optical fibers, doped with organic fluors, offering both high temporal and high spatial resolution.[1] We are investigating polymers used to clad or coat these optical fibers.

Clad optical fibers consist of a transparent, high refractive index polymer core, surrounded by a transparent, low refractive index cladding. Light is produced in the core when high-energy charged particles pass through the fiber. The aromatic rings in the core are excited by the passing particles and deexcite via photon emission. These photons will be emitted in random directions. In addition, the core may be doped with organic fluors that increase the wavelength of the light emitted.

When light inside the core strikes the interface between the core and cladding, some of the light will be reflected back into the core. In this way, light propagates along the fiber. The percentage of randomly emitted light, propagated in the forward direction, L_{prop}, is given by[2]:

$$L_{prop} = [(n_{core} - n_{cladding})/n_{core}] \times 100 \quad (1)$$

where n is the refractive index.

Equation (1) implies that it is advantageous to decrease the refractive index of the cladding material. Conventional cladding material, poly(methyl methacrylate) (PMMA), has a refractive index of 1.49. By adding fluorinated functional groups to the methacrylate molecule, it is possible to decrease significantly the refractive index.[3] This is the objective of this research.

In order to achieve reliable high performance from a doped optical fiber in a high-energy, high-intensity radiation environment, the fiber must be transparent to the light emitted by the organic dyes with which it is doped. Most such commercial fibers emit at wavelengths between 300–500 nm. PMMA absorbs strongly in the blue and green regions (400–580 nm), after absorbing 10 MRad gamma irradiation.[4] This discoloration slowly fades with time. This means that the detection efficiency of a PMMA-clad fiber would not be constant if it were continually being exposed to high-energy radiation. Similarly,

other optical polymers, such as polystyrene and poly(4-methyl styrene), show radiation-induced absorption, which dissipate or anneal with time.[5] Polystyrene is the most commonly used core material.

Another aim of this research was to identify cladding polymers that exhibit minimal losses in transmission upon exposure to ionizing radiation. We identified fluorinated methacrylates that are superior to PMMA in radiation resistance in this article.

EXPERIMENTAL

Materials and Sample Preparation

PCR Industries (Gainesville, Florida) supplied the following monomers: trifluoro(ethyl methacrylate); 2,2,3,3-tetrafluoro(propyl methacrylate); 1H-1H-pentafluoro(propyl methacrylate); hexafluoro(isopropyl methacrylate); 1H-1H-hepatafluoro(butyl methacrylate); and 1H,1H,5H-octafluoro(pentyl methacrylate). Methyl methacrylate was obtained from Aldrich Chemical. The monomers were inhibited with 0.01% weight hydroquinone. Each was washed seven times in a separatory funnel with a 10% weight solution of NaOH in water to remove the inhibitor. Two tenths% weight 2,2'-azobis(2,4-dimethyl valeronitrile), a catalyst from Du Pont known as Vazo 52, was added to each sample. The polymerization was carried out in polyethylene tubes in an N_2 environment. The reaction tubes were incubated at 30°C for 30 h and were postcured at

100°C for 3 h. The polymerization temperature was optimized to reduce the reaction exotherm in order to minimize the formation of bubbles and optical defects. Samples were slow cooled and were removed from the reaction tubes.

The structures of the polymers are listed in Table I.

Molecular weights were not determined, due to the limited solubility of the fluoromethacrylate polymers in common organic solvents.

Three gram samples were weighed and were compression molded between 1.25 cm diameter glass disks, compressed at two metric tons and 140°C for 6 h and slow cooled. These samples were 0.8 cm thick.

Instrumentation

UV/Visible transmission spectra were recorded on a Hewlett-Packard Model 8452A Spectrophotometer.

A Du Pont 2910 Differential Scanning Calorimeter, equipped with a cooling unit, was used to determine glass transition temperatures. Samples were scanned in a nitrogen environment at a heating rate of 10°C/min.

Refractive indices were measured on molded polymers with an Abbe refractometer (Fisher Scientific), illuminated with 590 nm light. Poly(dimethyl siloxane) oil was used to provide optical contact.

Samples were irradiated at a dose rate of 41 KRad/h with a ^{60}Co gamma source. The character-

Table I

$$\left(-CH_2-\overset{\overset{\displaystyle CH_3}{\vert}}{\underset{\underset{\displaystyle X}{\vert}}{\underset{\vert}{\overset{\vert}{C}}}}-\right)_n$$
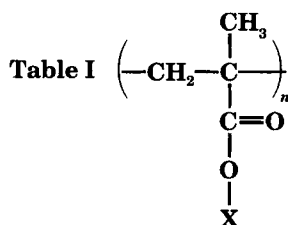
Monomer	X	T_g (°C)
A. Methyl methacrylate	$-CH_3$	105
B. Trifluoroethyl methacrylate	$-CH_2-CF_3$	69
C. 2,2,3,3,-Tetrafluoropropyl methacrylate	$-CH_2-CF_2-CF_2-H$	68
D. 1H,1H-Pentafluoropropyl methacrylate	$-CH_2-CF_2-CF_3$	70
E. Hexafluoroisopropyl methacrylate	$-CH\overset{\diagup CF_3}{\diagdown CF_3}$	56
F. 1H,1H-Heptafluorobutyl methacrylate	$-CH_2-CF_2-CF_2-CF_3$	65
G. 1H,1H,5H-Octafluoropentyl methacrylate	$-CH_2-CF_2-CF_2-CF_2-CF_2-H$	35

istic emission energies of this source were 1.17 and 1.33 MeV. At this low dose rate, there was no significant temperature increase in the samples during irradiation.

Spectrum Analysis

In order to quantify the optical damage sustained by the polymers, the following method was applied:

1. The spectrum of each sample was normalized such that it showed a 96% transmission for 800 nm light, which assumes that any loss in transmission at this frequency is due to surface scattering or other wavelength-independent mechanisms. This seems reasonable, since the transmission for all the samples seemed to be wavelength independent above about 600 nm.
2. The area under the transmission curve was integrated throughout the visible region, which was assumed to be 400 to 700 nm. This number is called the total transmission. Thus far, all fibers proposed for use at high-energy accelerators emit within this frequency range.
3. After irradiation, the spectra were retaken. They were normalized and were integrated in the same manner as the unirradiated fibers. This number was called the total transmission after irradiation. The difference between the total transmission and the total transmission after irradiation is called δ transmission.
4. After recovering for seven days, the spectra were retaken, were normalized, and were integrated as before. This number, subtracted from the total transmission, was called (δ + 7) transmission.
5. The difference between δ transmission and (δ + 7) transmission is called the integrated seven day recovery.
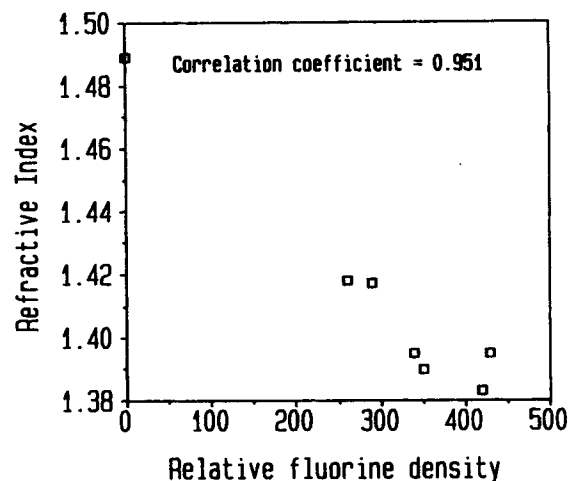

Figure 1 Refractive index vs. relative fluorine density for methacrylate polymers.

RESULTS AND DISCUSSION

Refractive Index

The commercially available PMMA had a refractive index of 1.489. The addition of fluorinated side groups to the methacrylate monomer should decrease the refractive index of the polymer by an amount proportional to the density of fluorine.[6] Table II lists the refractive indices of the polymers. In Figure 1, the refractive indices are plotted as a function of the fluorine densities. The correlation between the refractive index and fluorine density, R^2, is 0.951. More important, the refractive index was decreased from 1.489 for PMMA to 1.383 for poly(heptafluorobutyl methacrylate). The significance of this decrease will be discussed in the following paragraphs.

The amount of randomly-emitted light that will propagate in a fiber is related to the refractive indices of the core and cladding materials. Light, which strikes the interface at an angle (relative to a line

Table II   Optical Properties of Methacrylate Polymers

| Polymer	Refractive Index	Numerical Aperature	Critical Angle (Degrees)	Light Trapped (%)
Poly(methy methacrylate)	1.489	0.558	69.6	6.2
Poly(trifluoroethyl methacrylate)	1.418	0.719	63.1	10.8
Poly(tetrafluoropropyl methacrylate)	1.417	0.721	63.0	10.9
Poly(pentafluoropropyl methacrylate)	1.395	0.763	61.3	12.3
Poly(hexafluoroisopropyl methacrylate)	1.390	0.772	61.0	12.6
Poly(heptafluorobutyl methacrylate)	1.383	0.784	60.4	13.0
Poly(octafluoropentyl methacrylate)	1.395	0.763	61.3	12.3
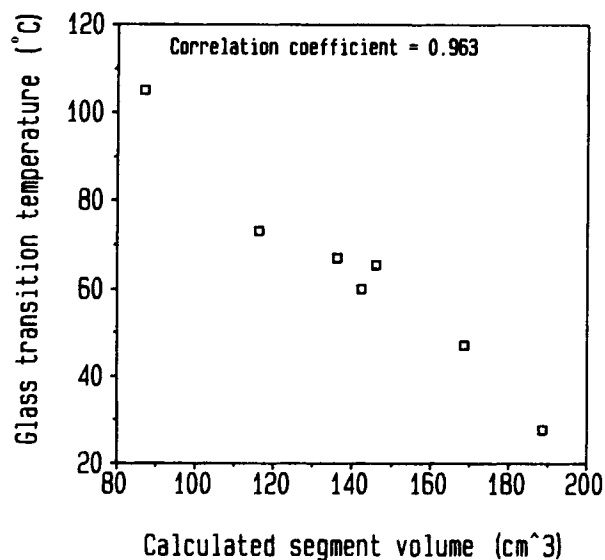
Figure 2 Glass transition temperature vs. calculated segment volume.

normal to the interface) greater than the critical angle, Θ_{crit}, will reflect back into the fiber, while the rest is scattered out. Angle Θ_{crit} is given by.[7]

$$\Theta_{crit} = \sin^{-1}(n_{clad}/n_{core}) \qquad (2)$$

The critical angle is determined solely by the refractive indices of the materials at the interface.

Another measure of light trapping in a fiber is the numerical aperature, N_A,[7] where:

$$N_A = (n_{core}^2 - n_{clad}^2)^{0.5} \qquad (3)$$

Table II lists the percent light trapped, Θ_{crit}, and the N_A for fibers with a polystyrene core and the given polymer as a cladding. The refractive index of polystyrene is 1.59. PMMA will trap 6.2% of randomly emitted light, while poly(heptafluorobutyl methacrylate), with a refractive index of 1.383, traps 13.6%. This is an increase of 202%.

Glass Transition Temperature

The glass transition temperature of the polymers are listed in Table I.

It is well documented that the glass transition temperature first decreases with the number of carbons in the ester group, passes through a minimum, and then increases in nonfluorinated methacrylate polymers.[8] The initial decrease is due to the increased bulk of the side chain, which increases the free volume of the molecules and decreases the mo-

lecular interaction.[9] The increase that follows is attributed to entanglements that accompany long chain lengths. The fluorinated side chains display the initial decrease. However, the side groups in this study are not of only different lengths, but of different shapes. Therefore, the glass transition temperatures are plotted as a function of the calculated monomer volume[6] in Figure 2. The glass transition temperature reflects the molar volume of the segments. Note that fluorinated esters result in methacrylate polymers with higher glass transition temperatures than nonfluorinated polymers. Poly(ethyl methacrylate), for example, has a T_g of 66°C, while poly(trifluoroethyl methacrylate) has a T_g of 73.7°C.

Radiation Effects on Transparency

Light in a fiber propagates by repeated reflection at the core/cladding interface. The average number of reflections along a fiber is calculated from[9]:

$$N = [L \sin \Theta_i / D (n_{core}^2 - \sin^2\Theta_i)^{0.5}] \pm 1$$

where N is the number of reflections, L is the length of the fiber, n_{core} is the refractive index of the core, D is the diameter of the fiber, and Θ_i is the angle of propagation. We assume that the average angle of propagation is halfway between the critical angle and the angle parallel to the interface. For a 1-meter long, 1-mm thick polystyrene core fiber, clad with poly(heptafluorobutyl methacrylate), $\Theta_i = 79°$, $n_{core} = 1.59$, and the beam reflects at the interface 786 times/meter.

With so many reflections, even slight absorption by the cladding will result in significant light loss over a meter of fiber. An effective cladding material is one that is completely transparent at the emission frequency of the fluorescent dyes in the core, even after prolonged exposure to high energy radiation.

It is well known that PMMA loses transparency upon exposure to high energy radiation. The optical radiation resistance of the fluorinated methacrylate polymers varied widely. Figures 3–9 compare the transmission spectra of the unirradiated polymers with the spectra after 10 MRad. Also included in Figures 3–9 are the spectra for the samples after seven days recovery at room temperature.

Poly(octafluoropentyl methacrylate) has a T_g of 28°C; consequently, the sample suffered mechanical creep during irradiation. As a result, the spectra after irradiation of this polymer were taken through a sample with uneven surfaces, resulting in scattering. The actual transmission of the polymer is better than reported here.
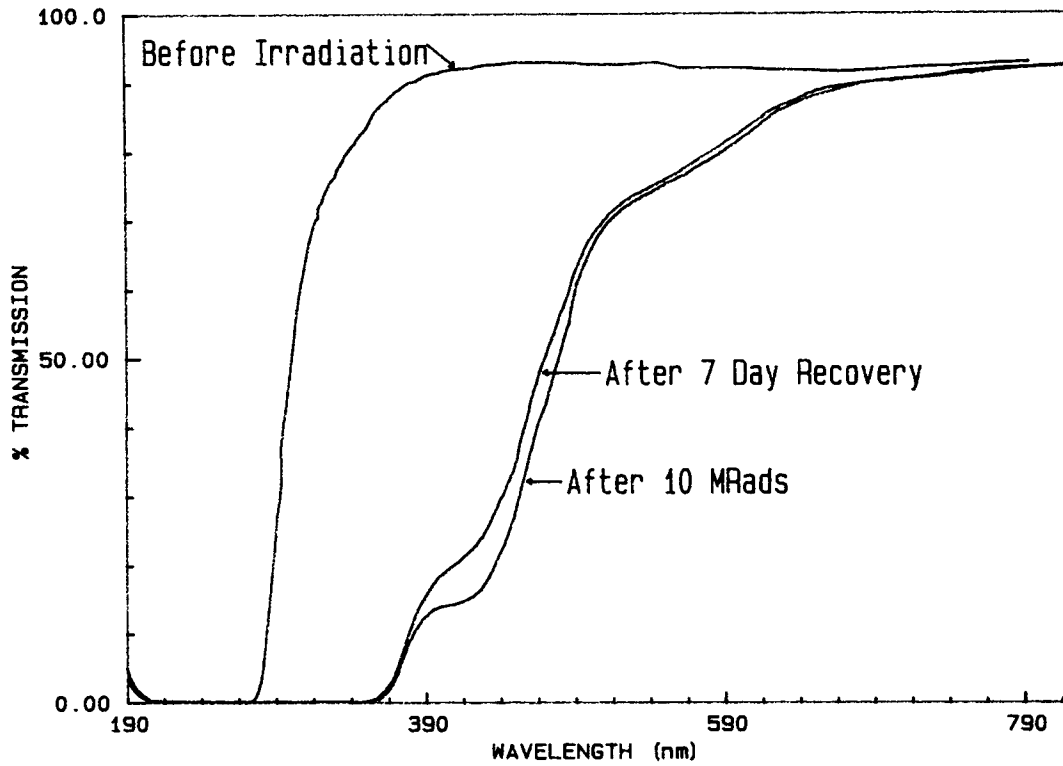
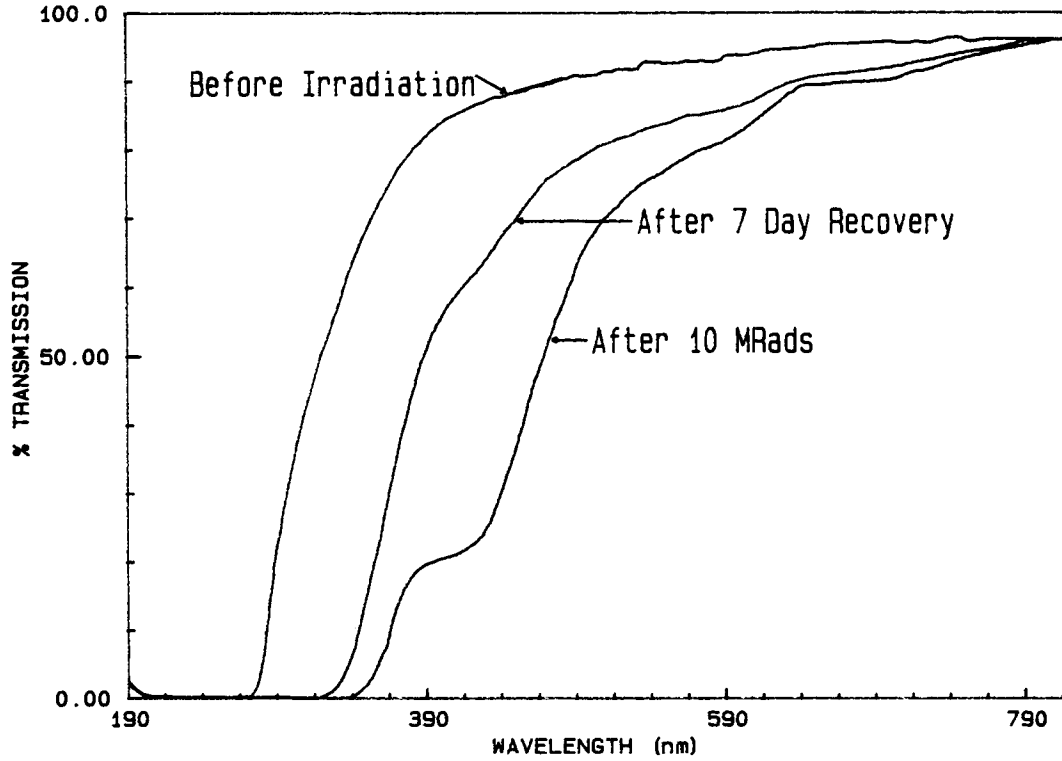**Figure 3** Poly (methyl methacrylate) before 10 MRad exposure, immediately after and after 7 days annealing.

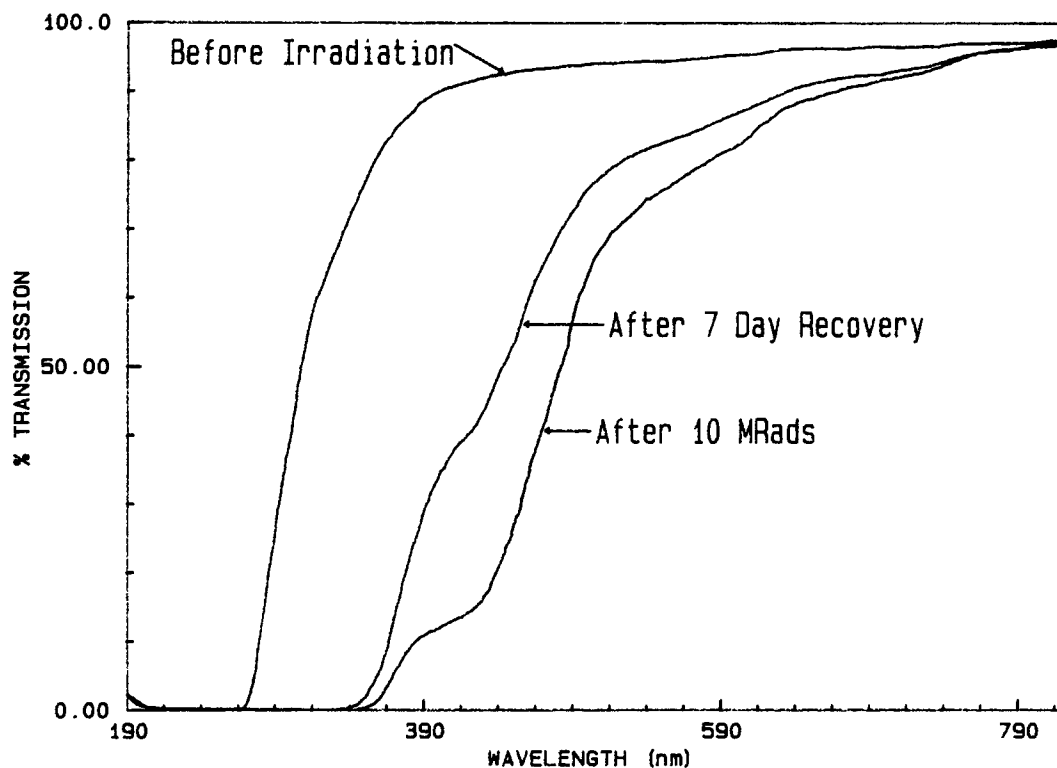**Figure 4** Polytrifluoro (ethyl methacrylate) before 10 MRad exposure, immediately after and after 7 days annealing.

Figure 5 Poly-2,2,3,3-tetrafluoro(propyl methacrylate) before 10 MRad exposure, immediately after and after 7 days annealing.
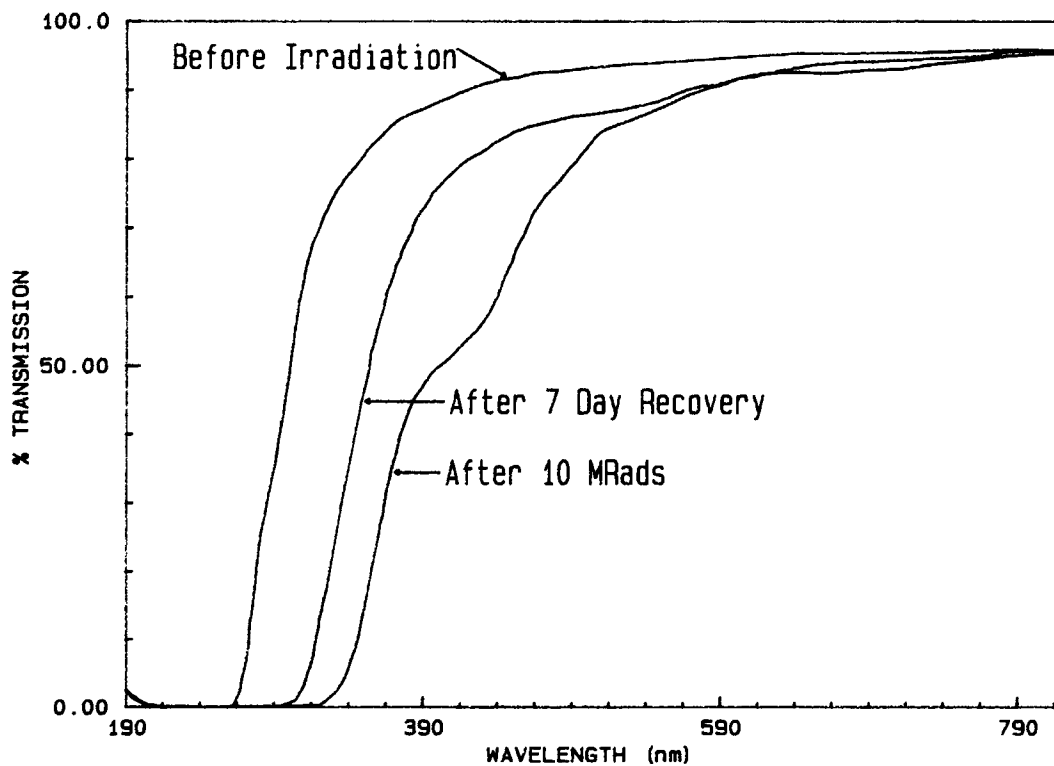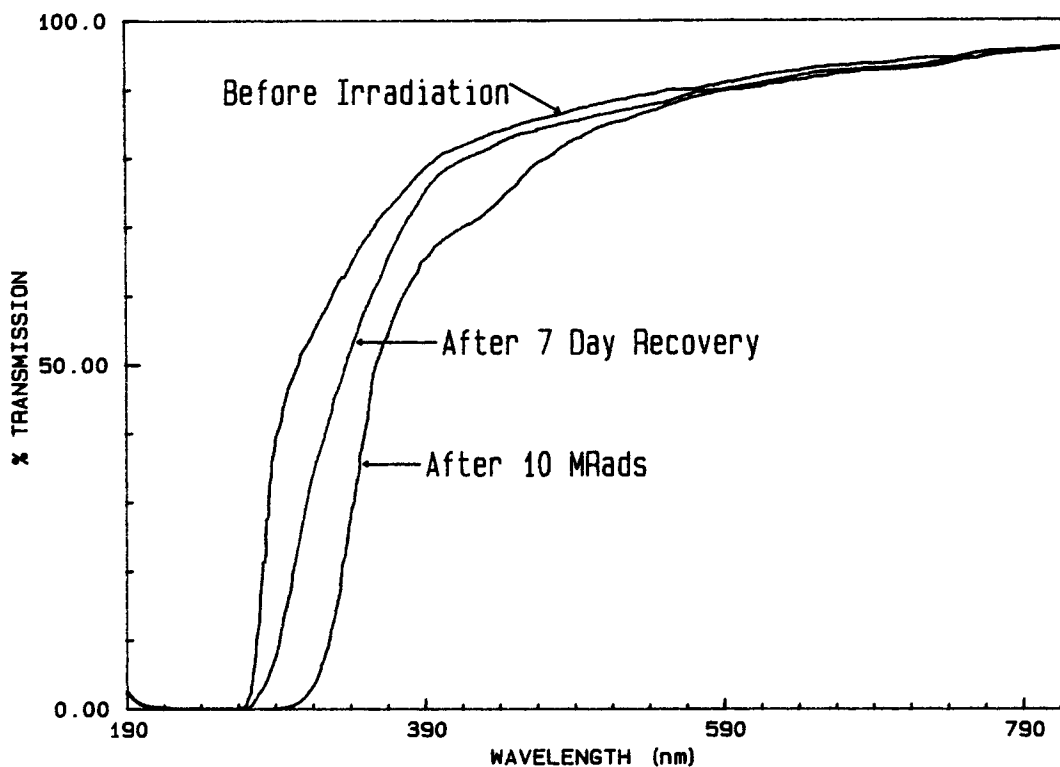

Figure 6 Poly-1H,1H-pentafluoro(propyl methacrylate) before 10 MRad exposure, immediately after and after 7 days annealing.

Figure 7   Polyhexafluoro(isopropyl methacrylate) before 10 MRad exposure, immediately after and after 7 days annealing.
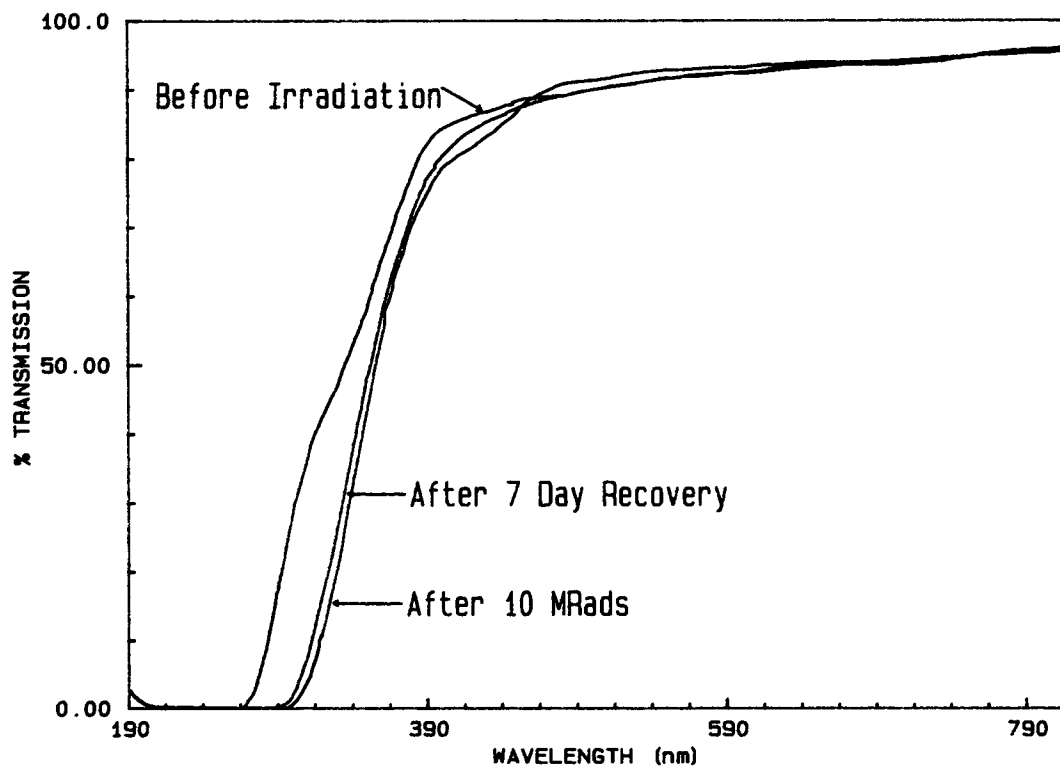

Figure 8   Poly-1H,1H-heptafluoro(butyl methacrylate) before 10 MRad exposure, immediately after and after 7 days annealing.
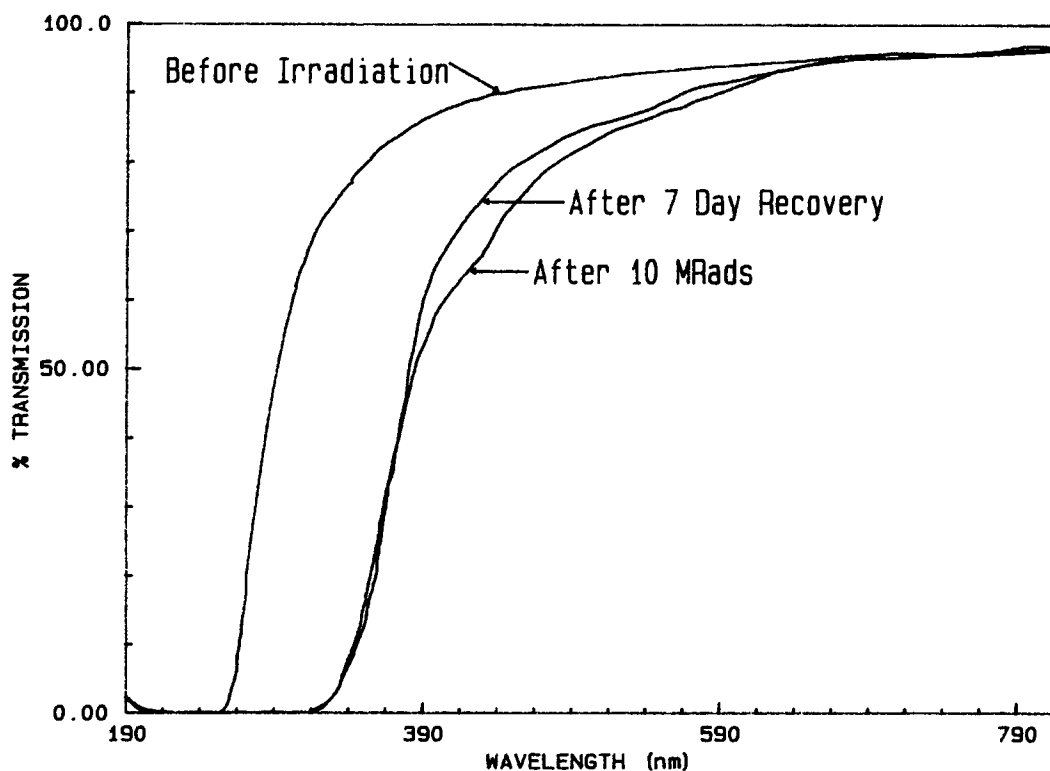
Figure 9 Poly-1H,1H,5H-octafluoro(pentyl methacrylate) before 10 MRad exposure, immediately after and after 7 days annealing.

One polymer, poly(hepatfluorobutyl methacrylate), showed superior radiation resistance.

In an effort to explain further the spectra, transmission data were compared to glass transition temperatures.

In the past, we have shown that decreasing the glass transition temperature of a homologous series of polymers has resulted in decreased radiation-induced optical damage and increased recovery rates.[10] In Figure 10, the total transmission after irradiation is plotted vs. T_g. There is a general trend that indicates that transmission is maximized in low T_g polymers. However, T_g seems not to be the most important factor in radiation resistance. Figure 11 plots the integrated 7-day recovery vs. T_g. Again, recovery seems to be less affected by T_g in the fluorinated polymethacrylates than it was in previously studied polymers.

The transient color centers are free radicals, which are formed during irradiation. These free radicals recover by recombination or by oxygen quenching.[11] The glass transition temperature and segmental mobility have a profound effect on both recovery mechanisms. We have shown that methacrylates with glass transition temperatures below the irradiation temperature, exhibit instantaneous

recovery.[12] Also, samples irradiated below T_g recover immediately when the temperature is raised above T_g. The polymers studied here were irradiated and recovered below the glass transition temperatures. Below T_g, the oxygen quenching mechanism dom-
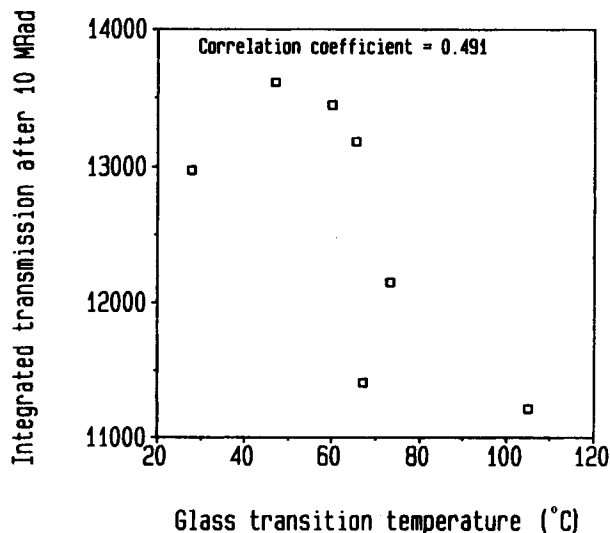

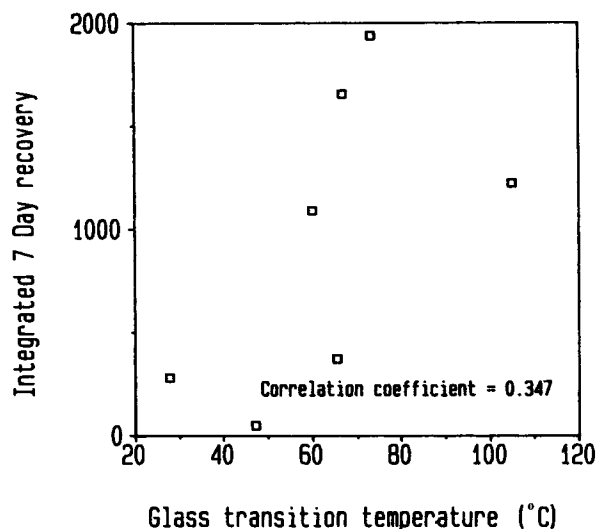**Figure 10** Integrated transmission after 10 MRad vs. glass transition temperature.

Figure 11 Integrated 7 day recovery vs. glass transition temperature.

inates recovery. Samples stored in the absence of oxygen recover at extremely slow rates. Our future research is aimed at monitoring the oxygen permeability of samples in an attempt to correlate permeability to optical radiation hardness and recovery.

CONCLUSIONS

As expected, the refractive index of the methacrylate polymers decreased as the fluorine content increased. Polymers with fluorinated ester groups have higher glass transition temperatures than polymers with nonfluorinated alkyl groups of the same carbon chain length. The glass transition temperatures of the fluorinated ester polymers correlate to the molar volume of the monomer. Exceptional optical radiation resistance is noted in poly(heptafluorobutyl methacrylate). This radiation resistance, combined with the low refractive index of the polymer, makes

it an ideal material for cladding radiation resistant optical fibers.

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