Transparent Chiral Polymers for Optical Applications

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ABSTRACT: Optically active chiral polymers and copolymers of cholesteryl methacrylate have been studied for use in optical applications including plastic optical fibers. Homopolymers of chiral cholesteryl methacrylate with differing molecular weights and copolymers with methyl methacrylate were synthesized by free-radical copolymerization in tetrahydrofuran using azobisisobutyronitrile at 67°C for 26 h. All polymers were characterized for molecular weight, glass-transition temperature, optical rotation, transparency, and refractive index and solution blended to test for compatibility with poly(methyl methacrylate). Such chiral materials are of particular interest because they offer useful polarization properties without requiring bulk orientation of the molecules. This makes it possible to produce low cost optical elements such as circularly birefringent or circularly polarizing optical elements with potential applications in polarization manipulations and sensing. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 58–65, 2005

Key words: optically active; chiral; plastic optical fiber; cholesteryl methacrylate; poly(cholesteryl methacrylate); poly(cholesteryl methacrylate-*co*-methyl methacrylate)

INTRODUCTION

Optics plays an important role in applications as diverse as telecommunications, sensing, and displays.[1,2] Although polymers have not been the traditional materials of choice in optics because of their higher attenuation compared to glasses, they have significant advantages in terms of cost, weight, and flexibility. For example, there is an increasing move to miniaturized disposable devices in areas such as biomedical "lab on a chip" devices that are bringing polymers to prominence.

Another area where polymers have made an important impact is in the development of plastic optical fibers (POFs). POFs have attracted considerable interest because of their potential for high-speed short distance communications, such as within a car or an office or even from chip to chip. The renewed interest in POFs has seen the development of a new kind of polymer optical fiber, the microstructured polymer optical fiber (MPOF).[3] These fibers use a pattern of tiny air holes in the cladding to reduce the effective refractive index (RI). They also solve a number of other difficulties associated with conventional polymer fibers, such as the ease with which "single mode" operation can be produced. Single mode fibers are required for many specialty applications, including many sensing applications, and the difficulty in producing single mode POFs by traditional means has restricted their use in many applications. The fact that polymers can be doped with organic molecules also provides crucial advantages. Dye doped polymers have been used to construct scintillators for detection of high energy scintillation and in other fluorescent devices used to produce sensors, switches, and modulators.[4–11]

Although polycarbonates, polystyrene, and poly(vinyl chloride) have been used to make POFs, the most commonly chosen polymer has been poly(methyl methacrylate) (PMMA). The advantages of PMMA fibers are their comparatively low manufacturing costs; ease of use in making connections (connectors, splices); in the construction of branching and coupling elements; and their low sensitivity to external mechanical, physical, and environmental influences.[12] The transparency windows dictate that PMMA fibers are used in the visible, with the best transmission being at 650 nm and loss of 110 dB/km.[13a] At present POFs made of PMMA are employed especially in the field of machine control at low transmission rates, as well as in the fields of sensor technology, robotronics, simple illuminations systems, and local area network applications. Recent experimental work has shown that

transmission rates of 4.2 GB/s over 100 m is possible using PMMA graded index MPOFs.[13b]

Possible role of chirality in optical applications

Materials that rotate the electric field vector of an incident linear plane wave are known as optically active or circularly birefringent. This property is a characteristic of chiral materials.

Chirality thus has important optical implications relating to the polarization state of the light. Although superpositions of orthogonal circular and linear polarization *states* provide alternative means representing any polarization, circular and linear *birefringence* differ in important respects. Linear birefringence in materials requires a net molecular orientation, whereas circular birefringence is a property of the molecules themselves and will occur even in solutions. This restricts the applications of circular birefringence. Different orientations of linearly birefringent materials can be used to generate arbitrary polarization states, but the fact that circular birefringence is independent of orientation means that it cannot be used in the same way. The distinction is formalized in the Poincaré sphere that is used to describe both polarization states and birefringence: pure linear birefringence is denoted by points on the equator of the sphere, whereas circular birefringence is denoted by the unique positions of the poles.[14]

However, this restriction brings some advantages. Linear birefringence is produced easily in polymers by stress and is frequently produced when polymers are processed, for example, by extrusion, injection molding, or drawing. The birefringence this produces is often inadvertent and subject to thermal relaxation. Annealing after processing can reduce the molecular orientation and hence the linear birefringence, even to the point where it is no longer present. By contrast, optical elements using circular birefringence do not require molecular orientation. This means that some useful optical elements could be conveniently made using films or fibers of chiral polymers.

Circular polarization is associated with important physical phenomena, including Faraday rotation, in which linearly polarized light is rotated by the application of a magnetic field. Many biologically important molecules are optically active. This means that for a variety of important applications relating to sensing, circular birefringence offers the most appropriate optical route. For example, optical electrical current sensors employing the Faraday effect may use interferometric approaches based on circularly polarized light.[15] Circular birefringence offers a route to making optical fibers that are *polarization maintaining*, but circularly *polarizing* fibers (which allow only one handedness of light to be transmitted) require the other handedness to be lost. This may happen either because

of circular dichroism or by the appropriate choice of fiber design.

Pelet and Engheta[16] have also suggested the use of optically active materials in guided-wave structures to produce chiral waveguides for integrated optical devices, telecommunication electronic systems, printed circuit elements, and optoelectronic devices. Patents also report the use of chiral optical material in information storage material[17] and optical modular devices.[18] The glass-transition temperature determines the thermal stability of any device produced from that material. The thermal stability of polymer waveguides is enhanced by an increase in the glass-transition temperatures of the constituent polymers. Synthesis of high glass-transition temperature chiral polymers would be of great interest in this regard.

Chiral polymeric materials

Cholesterol and its derivatives are known for liquid crystallinity and as optically active compounds. Cholesterol is a steroid that has an unusual helical supermolecular structure, which is responsible for showing extreme optical activity and selective reflection of different wavelength ranges. These properties are used in cholesteric polymers, which show a liquid crystalline nature.[19]

This article relates to novel chiral materials for POFs and other optical applications. We synthesized homopolymers and copolymers of cholesteryl methacrylate (ChMA). The polymers were characterized for optical properties, molecular weights, glass-transition temperatures, and RIs. The polymers were particularly evaluated for compatibility or mutual solubility with PMMA. The blends were characterized for compatibility and glass-transition temperatures.

EXPERIMENTAL

Materials

Analytical grade cholesterol, methacrylic acid (MA), dimethyl formamide (DMF), *p*-toluene sulfonic acid (PTSA), and hydroquinone (Aldrich Chemical Co.) were used as received. Analytical grade toluene, chloroform, carbon tetrachloride, methyl ethyl ketone (MEK), thionyl chloride, methanol, and *N*,*N*-dimethyl aniline (Merck) were distilled 2 times before use. Azobisisobutyronitrile (AIBN, M/S SISCO) was recrystalized in methanol before use. Atactic PMMA suitable for making POFs was supplied by Vink Export.

Synthesis

Cholesterol MA (method 1)

Direct esterification. Cholesterol (0.02 mol, 6.66 g) was mixed with an excess of MA (0.05 mol, 5.0 g), hydro-

TABLE I
Synthesis of Poly(cholesteryl methacrylate)s

Code no.	ChMA		Solvent (mL)	AIBN		Chain transfer agent (mol %)	Remark
	mol	g		mol %	g		
H1	0.0044	2.0	THF (5)	1	0.0072	0.0	70% Yield
H2	0.0044	2.0	THF (5)	1	0.0072	0.1	68% Yield
H3	0.0044	2.0	THF (5)	1	0.0072	0.5	70% Yield
H4	0.0044	2.0	THF (5)	1	0.0072	1.0	65% Yield
H5	0.0044	2.0	THF (5)	1	0.0072	2.0	57% Yield
H6	0.0044	2.0	MEK[a] (5)	1	0.0072	0.0	Precipitation polymerization
D1	0.0044	2.0	DMF[a] (5)	1	0.0072	0.0	Precipitation polymerization
T1	0.0044	2.0	Toluene[a] (5)	1	0.0072	0.0	No polymerization

Reaction temperature = 67°C; reaction time = 26 h; ChMA, cholesteryl methacrylate; chain transfer agent; carbon tetrachloride; THF, tetrahydrofuran; MEK, methyl ethyl ketone; DMF, dimethyl formamide; AIBN, azobisisobutyronitrile.
[a] At the boiling temperature of the respective solvents.

quinone inhibitor (100 ppm), and PTSA catalyst (0.1 g). The reaction mixture was refluxed for 26 h at 82°C using a Dean–Stark apparatus (azeotropic distillation). MEK was used as a solvent. Thin layer chromatography (TLC) was performed at regular intervals. The obtained product was purified by repetitive precipitation in toluene using methanol. Three reactions were carried out, changing the solvents and catalyst (sulfuric acid).

Synthesis using dry hydrochloric gas. Dry hydrogen chloride gas was passed through a solution of cholesterol (0.02 mol, 6.66 g) and MA (0.05 mol, 5.0 g) in acetone and refluxed for 26 h. The product (mp 148°C) did not precipitate in either methanol or acetone but phase separated in water.

Methacryloyl chloride

MA (0.20 mol, 17.2 g) was charged in a three-necked round-bottomed flask equipped with a water condenser and traps containing sodium hydroxide solution in a water bath, and 0.5 mL of DMF was added. Thionyl chloride (0.20 mol, 23.8 g) was added dropwise over 60–70 min. The temperature was kept between 45 and 55°C. After the bubbling in the sodium hydroxide solution traps stopped, the reaction was continued for an additional 60 min. The methacryloyl chloride that was formed was purified by distillation.

ChMA (method 2)

ChMA was synthesized by reacting cholesterol and methacryloyl chloride in a mole ratio of 1:2. Cholesterol (0.0775 mol, 30 g), methacryloyl chloride (0.155 mol, 15.06 mL), *N,N*-dimethyl aniline (0.0775 mol, 9.14 g), hydroquinone (0.1 mol % cholesterol), and MEK (solvent, 30 mL) were refluxed in a three-necked round-bottomed flask for 26 h at 83°C. The reaction

was monitored by TLC. After 26 h, the reaction medium was cooled and poured into methanol. The precipitated product was filtered and washed several times with methanol. It was further purified by dissolving in MEK followed by precipitation in methanol. Repetitive precipitation of the product yielded white needlelike crystals. The monomer was characterized for melting point, IR, and ^{1}H-NMR. Two more batches were synthesized to check the reproducibility.

Poly(chMA)(PChMA)

PChMA may be synthesized by both bulk polymerization and solution polymerization.[20–22] Our methodology involves solution and precipitation polymerization.

Solution polymerization. ChMA (0.0044 mol, 2 g) was dissolved in tetrahydrofuran (THF), AIBN (1 mol %, 0.007 g) was added, and the reaction was carried out at 67°C for 26 h. The PChMA that was formed was precipitated in MEK. It was dried, ground, and further purified by repetitive precipitation in MEK. The product was dried and the yield was recorded. Four additional reactions were conducted to prepare PChMAs of differing molecular weights using different concentrations of chain transfer agent (carbon tetrachloride; Table I).

Precipitation polymerization. In a single-necked round-bottomed flask equipped with a condenser, ChMA (0.0044 mol, 2 g), MEK (5 mL), and AIBN (1 mol %, 0.007 g) were added and the reaction was carried out at 83°C for 26 h. MEK, which is a nonsolvent for PChMA, precipitated the polymer as it formed. The product was filtered, dissolved in chloroform, and precipitated in MEK. It was further purified by repetitive precipitation in MEK. The product was dried and the yield was recorded. Two additional reactions were

TABLE II
Synthesis of Poly(cholesteryl methacrylate-*co*-methyl methacrylate)s with differing compositions

Code no.	Mol ratio M_1/M_2	M_1 (mol)	M_2 (mol)	Monomer feed		Copolymer (g)
				M_1 (g)	M_2 (g)	
C1	0.9:0.1	0.0053	0.0006	2.440	0.060	1.86
C2	0.7:0.3	0.0050	0.0022	2.284	0.215	1.80
C3	0.5:0.5	0.0045	0.0045	2.047	0.450	2.08
C4	0.3:0.7	0.0036	0.0085	1.651	0.847	2.10
C5	0.1:0.9	0.0018	0.0166	0.839	1.660	2.12

Solvent, 5 mL of tetrahydrofuran; Initiator, 1 mol % AIBN; reaction temperature = 67°C; reaction time = 26 h; M_1, cholesteryl methacrylate; M_2, methyl methacrylate.

carried out to evaluate the effect of differing solvents (DMF or toluene; Table I).

Poly(ChMA-*co*-MMA) (PChMA-*co*-MMA)

ChMA (0.0053 mol, 2.44 g) and MMA (0.0006 mol, 0.060 g) in a 9:1 mol/mol ratio were dissolved in THF in a single-necked round-bottomed flask equipped with a water condenser. AIBN (1 mol %, 0.0096 g) was added and the reaction was carried out at 67°C for 26 h. The product was purified repeatedly by dissolution in chloroform, followed by precipitation in MEK. It was then dried and the yield was recorded. Four additional copolymers were synthesized by varying the mole ratio of ChMA to MMA. The data are presented in Table II.

Two additional batches of all homo- and copolymers were synthesized to check the reproducibility.

Solution blending

PChMA with the highest molecular weight and prepared without chain transfer agent (polymer H1), and PMMA in a ratio of 1:9 (w/w) were dissolved in chloroform and precipitated in MEK. The blend was dried and differential scanning calorimetry (DSC) was run. Similarly, two more blends were made in weight/weight ratios of 3:7 and 5:5.

PChMA-*co*-MMA (polymer C3) and PMMA in a ratio of 1:9 (w/w) were dissolved in chloroform and precipitated in MEK. The blend was dried and DSC was run to check the compatibility. Similarly, two more blends were made with ratios of 3:7 and 5:5.

Measurements

IR spectra

The IR spectra of the samples were taken on a Shimadzu model 470 spectrometer. The samples were run in KBr pellets. The sample was milled (2 mg), mixed with potassium bromide (100 mg), and pressed into a solid 1.2-cm diameter disk prior to the IR measurement.

UV–visible spectra

Solutions of polymers and copolymers (5 wt %) were prepared in chloroform, and the absorbance spectrum was recorded on a UV absorption spectrophotometer (Shimadzu 160). Samples were run in a wavelength range of 200–800 nm. The results are shown in Figure 1.

DSC analysis

The DSC analysis of the polymer samples was conducted using a Mettler V 2.5 F thermal analyzer coupled to a DSC-2920 MDSC cell. The sample mass was between 10 and 12 mg. Empty pans were weighed to match within a deviation of ±0.002 mg. All samples were heated to 300°C at 20°C/min in order to erase the previous thermal history. The samples were reheated at 3°C/min up to the decomposition temperature.

The temperature calibration was made by using an indium–lead–zinc standard and the heat flow was measured by using an indium standard. The thermal transitions were reported as the maxima and minima of their endothermic or exothermic peaks, respectively.

NMR spectra

A Bruker DRX-500 500-MHz spectrophotometer (a supercon magnet) was used to record the ^{1}H spectra. Five percent solutions of homo- and copolymers were made in deuterated chloroform to run the NMR.

Gel permeation chromatography (GPC)

The sample (10–12 mg) was dissolved in chloroform (5 mL) and GPC data were collected on a Waters 2690 apparatus with polystyrene standards.
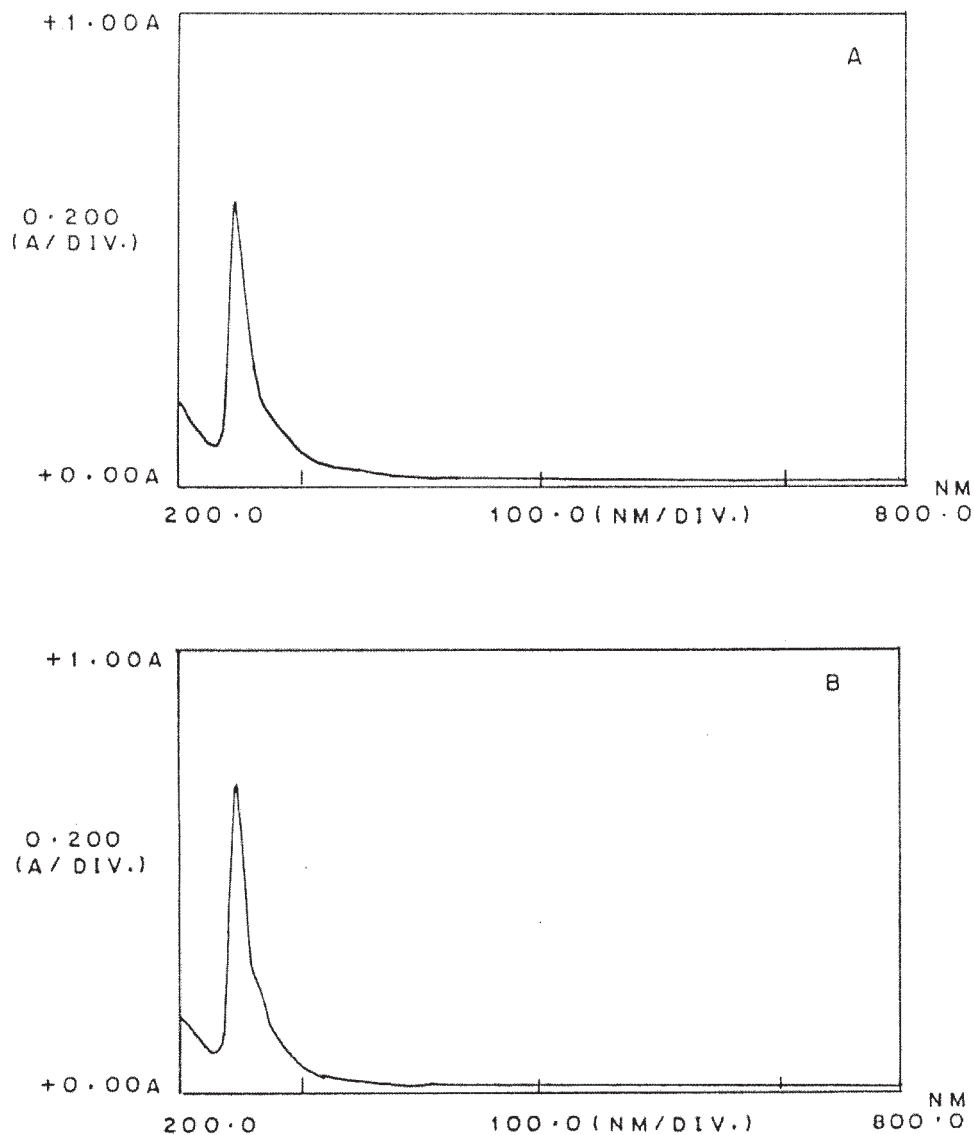
Figure 1 The UV–visible spectra of (A) homopolymer poly(cholesteryl methacrylate) (polymer H1) and (B) copolymer poly(cholesteryl methacrylate-*co*-methyl methacrylate) (polymer C3) in 5 wt % chloroform. In both spectra, $\lambda_{max} = 245$ nm.

Optical polarimetry

The specific rotation of all polymers was measured on a Jasco P 1020 polarimeter at 589 nm using a 1 wt % solution in chloroform at $26 \pm 0.5°C$ with a 1-cm length cell. All solutions were filtered before measurement.

Refractometer

A Mark II Plus (Leica) refractometer was used to measure the RIs of the polymers. The refractometer was calibrated with water before taking the RI. Sodium yellow light of 589 nm was passed through the solution of the 1 wt % sample in chloroform.

RESULTS

Cholesteric —OH is strongly hindered by six-membered rings, so even after using strong catalysts like

para-toluene sulfonic acid or sulfuric acid, the direct esterification of cholesterol with MA failed. ChMA synthesized from cholesterol and methacryloyl chloride was characterized by the melting point (Table III), IR spectroscopy (Table IV), and NMR spectroscopy. White, needlelike crystals of ChMA melted sharply at 107–108°C. ChMA was soluble in toluene, benzene, acetone, MEK, and chloroform. The ^{1}H-NMR peaks

TABLE III
Melting Points of Monomers

Product/reactant	Temperature (°C)	
	Reported	Observed
Cholesterol	147–152	148
Methacryloyl chloride	99	100
ChMA	107–109	107–108

TABLE IV
IR Spectra of Cholesterol and Cholesteryl Methacrylate

IR peaks	Cholesterol (cm^{-1})	ChMA (cm^{-1})
C—OH	3400	—
C=O	—	1709
C—O—C	—	1291
C—O	1050	1165
	1019	1026
	1005	—
C=C	1667	1671
	804	839
C—H	806	810
C=C	—	1632
C—H	—	937

TABLE VI
DSC Data of Solution Blending

Code no.	PChMA (H1)/PMMA ratio (w/w)	Copolymer (C3)/PMMA ratio (w/w)	T_g (°C)
B1	1:9	—	—
B2	3:7	—	130.8
B3	5:5	—	122.2
B4	—	1:9	—
B5	—	3:7	154.1
B6	—	5:5	145.6

were assigned and confirmed as reported by Shoji et al.[21]

The IR spectra indicate that the ring double bond in the cholesteryl pendent group (1671 cm^{-1}) did not participate in the polymerization. In addition, the disappearance of the C=C of vinyl carbon confirms homo- and copolymerization (Table IV). Both homo- and copolymers showed strong absorption at 245 nm in the UV spectrum (Fig. 1).

The GPC data of the homo- and copolymers are presented in Table V. The weight-average molecular weights (M_w) of the homopolymers ranged from 22,389 to 152,000, indicating an increase with a decrease in the concentration of the chain transfer agent (Table I), carbon tetrachloride. Precipitation polymerization also yielded low molecular weight because polymer chains precipitated before reaching the lengths dictated by the kinetic chain length. In addition, a solvent may act as a chain transfer agent for polymerization. The obtained copolymers had M_w values in the range of 85,455–152,920, depending upon

the polymerization conditions (Table II). No trend in the molecular weights relative to the copolymer composition was observed.

When heated under modulated conditions (3°C/min heating rate), the homopolymers (all samples) showed glass transitions in the range of 197–227°C (Table VI). Copolymers showed two glass transitions. The first ranged from 138 to 196°C and the second ranged from 176 to 249°C (Table VI). The homopolymers (PchMA, H1) and copolymer (polymer C3) were blended with PMMA to check for compatibility. The DSC thermograms of the blends (Table VI) showed no transition at 107.2°C because of the glass-transition temperature of PMMA. This indicates the absence of macrophase separation of either the homo- or copolymer with PMMA. The blends are compatible in all proportions with PMMA. The homopolymer blends show transitions at 131°C for the first transition and at 214°C for the second transition. Copolymers also show transitions in the same range, namely, at 154°C for the first transition and at 215°C for the second transition. All of the polymers show glass-transition temperatures in excess of PMMA. However, the result also implies that optical fibers using these materials as the core and PMMA as the cladding are not feasible, be-

TABLE V
DSC and GPC Data of Poly(cholesteryl methacrylate) and Poly(cholesteryl methacrylate-*co*-methyl methacrylate)

Code no.	DSC data T_g (°C)	GPC data M_n	M_w	PDI
H1	212.5	47,550	1,22,620	3.00
H2	197	31,125	1,05,780	3.30
H3	196	22,310	62,350	2.80
H4	227	29,885	56,215	2.17
H5	222	30,630	52,905	1.64
H6	208	13,879	22,389	1.61
D1	198.5	14,857	26,854	1.67
C1	163.5; 249	49,995	1,52,920	2.60
C2	162.5; 221	41,615	1,38,200	3.40
C3	138	50,930	1,46,480	2.80
C4	143; 176	47,500	1,03,380	1.90
C5	196	36,401	85,455	1.72

PDI, polydispersity index; T_g, glass-transition temperature; M_n, number-average molecular weight; M_w, weight-average molecular weight.

TABLE VII
Optical Rotation of Homo-
and Copolymers of ChMA

Code no.	$[\alpha]_D$ (°)
H1	−25.86
H2	−31.79
H3	−30.72
H4	−30.83
H5	−29.91
H6	−21.68
C1	−42.10
C2	−38.61
C3	−31.20
C4	−21.22
C5	−16.16
ChMA	−46.94
Cholesterol	−46.33

Specific rotation ($[\alpha]_D$) of individual polymer or copolymer was measured at a wave length of 589 nm in 1 a wt % solution of chloroform at 26 ± 0.5 °C. The cell was 1 cm long.

cause of the large difference in their thermal properties, which would make drawing them together problematic. It is fortunate therefore that the use of microstructures to produce the RI profile allows the entire fiber be made from a single material. This is clearly an advantage particular to MPOFs.

The optical data of homopolymers (PChMA) and copolymers (PChMA-*co*-MMA) is presented in Table VII. The homopolymers and copolymers are optically active and are levorotatory. In copolymers, the degree of rotation decreases with a decrease in ChMA content as the concentration of chiral centers is reduced. The value of this specific rotation of all polymers lies between −16 and −42°. The RI of all samples was 1.44. Polymers were made transparent by casting a film.

DISCUSSION

Although polymers have been used for optical applications for many years, the advent of new technologies, such as MPOFs and the "lab on a chip" concept, has brought renewed interest in tailoring polymer properties for particular applications.

POFs have traditionally been used in data transmission, where low attenuation is the dominant requirement, but there are other applications, such as sensors, for which other characteristics are critical. They can be employed to detect a large variety of parameters, including temperature, humidity, pressure, electric current and voltage, the presence of organic and inorganic compounds, wind speed, and RI. The mechanisms allowing detection of physical parameters by using POFs are very diverse, although most of them are based on light intensity modulation.

Although there are many advantages to using POFs, silica fibers can be used in temperature environments

that far exceed those in which conventional polymers are stable. It is of great interest to identify existing polymers and to design new polymers for use in high temperature environments. Two extensively reported main strategies for designing high temperature waveguides systems are the synthesis of new, high glass-transition temperature polymers and crosslinking of conventional polymer systems. The glass-transition temperature of a given series of polymers can be increased by incorporating stiff structures such as aromatic rings and by increasing hydrogen bonding and other dipole interactions.[23,24] Halogenation (particularly fluorination) of acrylates and MAs is known to increase the glass transition considerably.[1,25–27] Crosslinked acrylics, polycarbonates, and polycarbosiloxane network core materials[1,24,28] are also known to increase the glass-transition temperature. In our study a wide range of polymers were synthesized and all homo- and copolymers as well as blends were found to increase high glass-transition temperatures, which is desirable for producing high thermal waveguides for the above-mentioned applications.

Adhesion and compatibility of PChMMA with PMMA is a primary requirement for some applications; homopolymers as well as copolymers of ChMA are compatible with PMMA in all proportions. Representative samples showed a higher glass-transition temperature for the blend than PMMA, indicating that macrophase separation does not occur. The RI of the materials was less than that of PMMA in all cases.

Polymers for use in POF applications must possess transparency and a suitable molecular weight range to draw a fiber. Although our synthesis method includes solution polymerization followed by precipitation in a nonsolvent to form opaque polymers, transparency was obtained by casting the polymer solution as a film. The polymers are transparent and are in the molecular weight range that is suitable for fiber drawing.

Conventional waveguides such as optical fibers produce confinement of the light in the higher RI region (guidance in lower RI regions is possible using photonic bandgap effects). Thus, the relatively low RI of the chiral materials studied in this work mean that they could not be used as the core region of a standard PMMA-based POF. This restriction does not apply to MPOFs, however, where the microstructure in the cladding region can substantially lower the effective RI.

Both the RI and the glass-transition temperature of the synthesized materials make them unsuitable for use in conventional optical fibers. However, they are suitable for use in MPOFs, a fact that emphasizes the advantages this kind of fiber brings in allowing a much larger range of material properties to be used.

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