Optical properties of cyclic olefin copolymers

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Abstract. The optical properties of a cyclic olefin copolymer, Topas™, made by Celanese AG, are presented. This class of materials is attractive on account of their high use temperature, excellent optical transmission, low birefringence, and low moisture uptake. These materials are compared with other commonly used thermoplastics, namely, polycarbonate and polymethyl methacrylate. Finally, Topas™ is compared with a number of other optical polymers being studied for optical waveguiding applications. It is found that at 830 nm Topas™ has low losses (less than 0.5 dB/cm), so that it may be useful for datacom applications. At the telecommunication wavelength of 1550 nm the losses are in the range of 0.7 dB/cm.
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1 Introduction

Optical plastics[1] are an important article of commerce and are used widely to make substrates for optical storage devices such as compact discs (CDs) and digital videodiscs (DVDs),[2] lenses for cameras and projection displays,[3] optical fiber,[4] sheet products for glazing and displays, and most recently, diffractive optical lenses.[5] The advantages of optical plastics over glass are many: mechanical toughness together with high optical transmission, the ability to mold aspherical shapes and to mold or emboss submicron features such as pits and grooves in a CD or in a diffractive optic lens, and, finally, the ability to design additional mechanical features around a lens so that it can easily be incorporated into a larger design. These advantages outweigh some of the obvious disadvantages of optical plastics compared to glass, namely, lower chemical and moisture resistance, greater thermal expansion coefficient, and smaller Abbe number. Glass is still the preferred material wherever high thermal and chemical stability are required.

The two most widely used optical plastics are polycarbonate (PC) and polymethylmethacrylate (PMMA). PC is widely used in optical storage because of a unique combination of properties: optical clarity and mechanical toughness, together with a low melt viscosity at high processing temperatures that enables CDs to be molded with a short cycle time. PMMA is widely used as a sheet glazing material and for optical lenses because of its optical clarity and UV resistance. However, these materials have a number of deficiencies. PC usually has a high birefringence unless special processing equipment and conditions are used, and it has a low Abbe number, precluding it from certain lens designs. PMMA on the other hand is brittle; has high moisture uptake, causing swelling; has lower heat deflection than PC; and cannot easily be metallized for CD applications. For these reasons there are ongoing developments of new optical plastics to circumvent the deficiencies of PC and PMMA.

More recently, polymers and plastics have found increasing use in optical components and devices such as waveguided integrated optics. The materials for those applications must satisfy many requirements, of which the foremost are high use temperature, high optical transmission in the near infrared (NIR) region of the optical spectrum, low moisture absorption, low birefringence, and, in certain application, a large thermo-optic coefficient.[6]

Cyclic olefin copolymers (COCs) are a new class of optical thermoplastics that have a number of attractive properties, namely, low moisture uptake, high water barrier, low birefringence, high optical transmission, large Abbe number, chemical resistance to common solvents such as acetone, and high heat deflection temperature. They are copolymers of ethylene and a cyclic olefin such as norbornene or cyclopentene.[7] The different types of injection moldable COCs available commercially are Zeonex (Nippon Zeon, Japan), Arton (Japan Synthetic and Rubber, Japan), Apel (Mitsui, Japan), and most recently Topas™ COC (Ticona division of Celanese AG, Summit, USA, and Frankfurt, Germany). BF Goodrich has also recently developed a new class of norbornene-based optical polymers that are crosslinked thermally, which are useful as plastic substrates for displays, low-K dielectrics, and optical waveguides.[8]

The purpose of this paper is to describe the optical properties of COC thermoplastics and to compare them with existing optical plastics such as PMMA and PC. We use Topas™ as the latest example of that family of thermoplastic optical polymers. It is a copolymer of ethylene and norbornene that is commercially available in a range of heat deflection temperatures from 80 to 180°C, depending on the amount of norbornene in the copolymer. It is polymerized by metallocene catalysts,[7] in contrast to the more conventional methods used to make other COC plastics. Some

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Table 1 Refractive index, Sellmeier fitting parameters, and Abbe number of Topas™ COC 5013.

Quantity	Wavelength (μm)	Value			
		$T=15$	25	50	75°C
n	0.4358	1.5465	1.5455	1.5428	1.5403
	0.4861	1.5411	1.5400	1.5374	1.5350
	0.5461	1.5367	1.5354	1.5331	1.5305
	0.5876	1.5344	1.5333	1.5308	1.5283
	0.6563	1.5315	1.5305	1.5280	1.5255
	0.7065	1.5302	1.5289	1.5263	1.5238
	0.7682	1.5285	1.5275	1.5250	1.5225
	1.014	1.5253	1.5240	1.5218	1.5191
A_1		2.043	2.045	2.042	2.034
A_2		0.2733	0.266	0.2634	0.2629
A_3		0.202	0.206	0.2058	0.2062
Abbe no.		55.7	56.4	55.3	54.7

of the optical properties of Topas™ and their applications to diffractive optic lenses have been presented earlier.[9–11]

2 Materials and Methods

Topas™ COC was obtained from Ticona. The samples had glass transition temperatures T_g of 80, 140, 160, and 180°C. An experimental sample with $T_g=225$°C was also obtained and characterized. Most of the measurements reported in this paper are on the $T_g=140$°C grade.

The thermoplastic pellets were compression-molded with a TMP press (Technical Machine Products, Cleveland, Ohio) into films and disks for optical transmission and refractive index measurements. Care was taken not to induce birefringence in the samples. The pellets were also injection-molded into tensile bars and disks for mechanical and birefringence measurements. The injection molding was carried out with an Arburg Allrounder 25-ton machine (Arburg, Germany). The refractive indices were measured by two methods. Firstly, the compression-molded films were measured by a Metricon thin-film index instrument (Metricon model 2010, Pennington, NJ) at the three wavelengths 543, 633, and 780 nm. Secondly, Eastman Kodak (Rochester, NY) molded prisms and measured indices by a beam deflection technique at several different wavelengths (see Table 1). The optical transmission through the disks was measured with a UV-visible-NIR spectrometer (Perkin Elmer, Lambda 9). The stress optic coefficient was measured in the melt state by Professor G. Fuller of Stanford University using the techniques described in Ref. 12. The thermal conductivity was measured by AC Technology (Ithaca, NY).

3 Results and Discussion

3.1 *Structure and Glass Transition Temperatures*

The structure of Topas™ COC copolymers is shown in Fig. 1. It is a random copolymer of ethylene and norbornene. The presence of norbornene in polyethylene does two things: it raises the glass transition temperature T_g and reduces crystallinity, so that when norbornene is present in large amounts the copolymer is amorphous. DSC studies showed one melt endotherm corresponding to the glass transition only, and no evidence was found for crystals in the polymers studied here. Figure 2 shows the increase of T_g with mole percentage of norbornene in the copolymer. One can see that it is possible to obtain a very high T_g of 250°C. Topas™ COC can be used in many applications, ranging from packaging where a moisture barrier is important, and medical containers where steam sterilization is important, to precision optical lens applications where low birefringence and low moisture uptake are important.

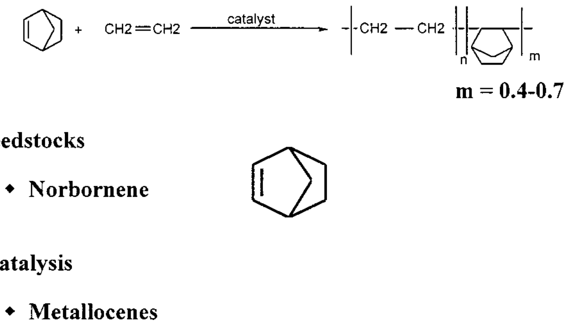

Fig. 1 Chemical structure of Topas® COC.

3.2 *Optical Transmission and Loss*

Figures 3 and 4 show the optical transmission of two grades of Topas™ COC, one with a standard processing stabilization package (grade 5013) and another with no additives (grade 6015). The latter grade has a higher optical transmission in the near UV region, which is of interest for applications using 200- to 350-nm light, such as in fluorescence diagnostic techniques. The transmission scans are given for different thicknesses. They were fitted to the equation below to yield the loss in decibels per centimeter:

$$\text{loss}=-\frac{10}{L}\log T, \tag{1}$$

where L is the thickness of the sample and T is the transmission. Figure 5 is a plot of the loss versus wavelength. One can see that the optical losses are of the order of 1.0

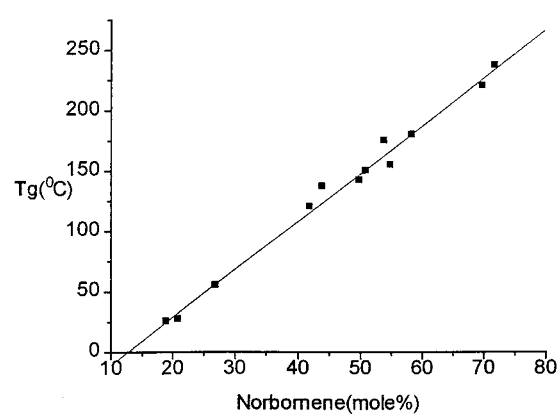

Fig. 2 Glass transition temperature T_g versus norbornene content.

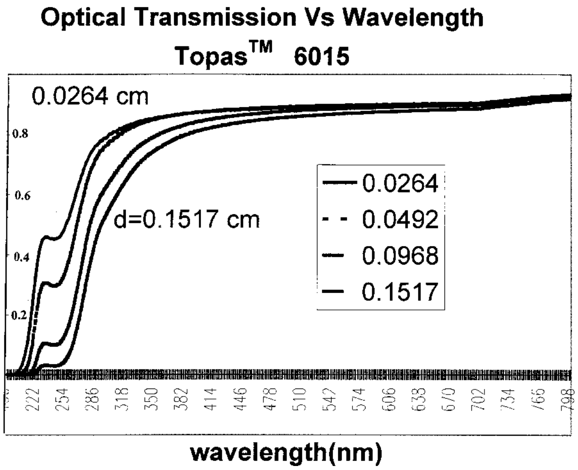

Fig. 3 Optical transmission of Topas™ COC 6015 without heat stabilization additives, for different film thicknesses. Thickness values are in centimeters.

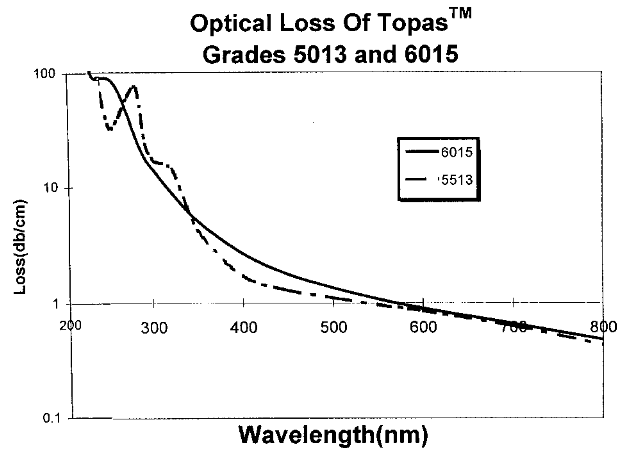

Fig. 5 Optical loss of Topas™ COC 6015 and 5013 versus wavelength.

dB/cm when the wavelength is greater than 500 nm. The loss is about 0.5 dB/cm near the important laser wavelength of 800 nm.

Figure 6 shows the optical transmission of Topas™ COC (grade 5013) in the visible and NIR region. It shows that it has optical windows at the important laser wavelengths of 1.06, 1.3, and 1.5 μm. The optical loss has been expressed in decibels per centimeter in Fig. 7 using the following procedure. The transmission through a substrate of plastic is given by

$$\dot{T}=\langle \mathrm{Fr}\rangle e^{-\alpha L}, \tag{2}$$

where L is the thickness, α is the absorption coefficient, and the average Fresnel coefficient for incoherent radiation is given by[13]

$$\langle \mathrm{Fr}\rangle=\frac{2n}{1+n^2}, \tag{3}$$

where n is the refractive index of the substrate. Since the index of refraction as a function of wavelength has been measured and the thickness is known, it is possible to compute α from the experimental transmission data and then to calculate the loss. The results in Fig. 7 show that the losses are about 0.5 dB/cm near 1300 nm and 0.7 dB/cm near 1550 nm. Therefore, these materials could have utility for fabricating short waveguides. Recently, a number of workers have reported waveguides made from Topas™ by compression molding of sheets or spin coating from a solvent.[14,15]

3.3 *Refractive Indices*

Table 1 summarizes the refractive indices of Topas™ COC grade 5013. The data were fitted with a Sellmeir equation of the form

$$n^2=A_1+\frac{A_2\lambda^2}{\lambda^2-A_3^2}, \tag{4}$$

where n is the refractive index, λ is the wavelength in micrometers, and $A_{1,2,3}$ are fitting parameters. Table 1 also

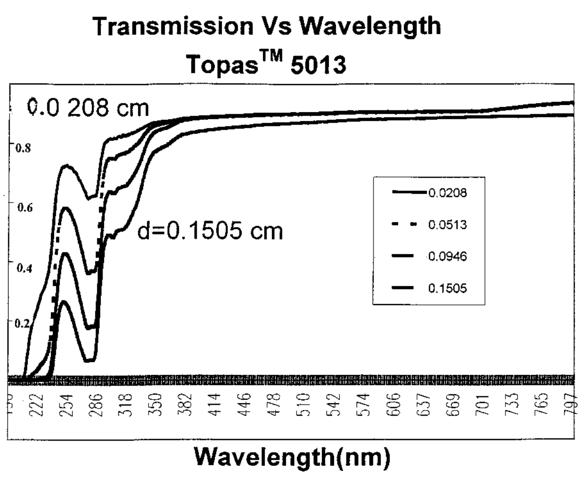

Fig. 4 Optical transmission of Topas™ COC 5013 with heat stabilization additives, for different film thicknesses. Thickness values are in centimeters.

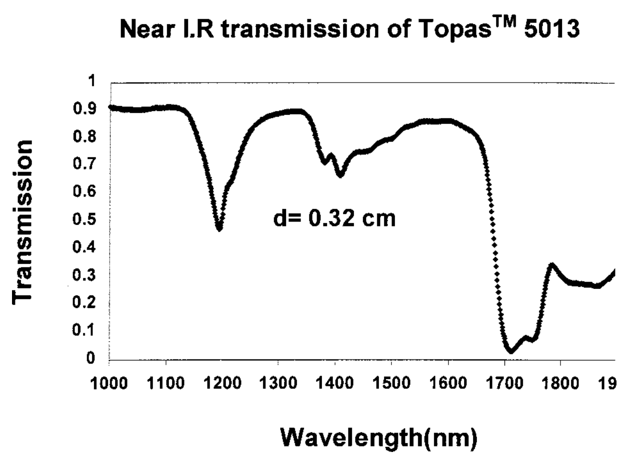

Fig. 6 NIR transmission of Topas™ COC 5013. Sample thickness is 0.32 cm.

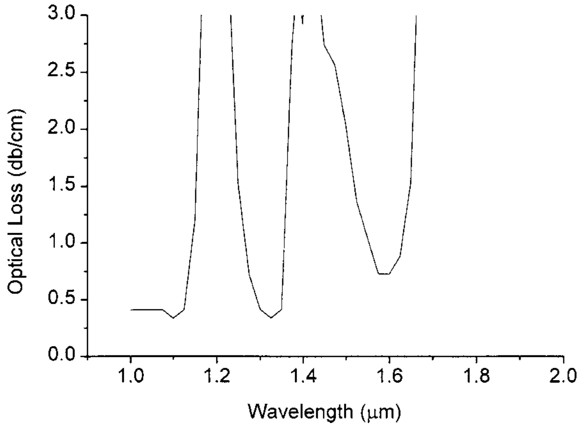

Fig. 7 Optical loss of Topas™ 5013 in the NIR region.

gives the calculated Abbe parameters as a function of temperature, which show very little variation with composition. Figure 8 shows the temperature dependence of the refractive index at 656 nm. It has the form

$$n=1.533-10^{-4}T, \quad (5)$$

where T is the Celsius temperature. The slope dn/dT is independent of wavelength over the range reported here.

Table 2 contains the refractive indices of the different Topas™ COC grades with different T_g values. One sees that the refractive index increases rapidly from polyethylene to Topas™ up to $T_g=140°C$. Then it stays fairly independent of T_g up to the highest measured value, 225°C.

3.4 *Stress Optic Coefficient and Birefringence of Molded Parts*

The stress optic coefficient (SOC) of Topas™ COC grade 5013 ($T_g=140°C$) was measured by Prof. G. Fuller of Stanford University[12] in the melt state and was found to be 100×10^{-12} to $400\times10^{-12}\,Pa^{-1}$. This value is much less than those for PC and polystyrene (PS) (see Table 3). The origin of the low SOC is the aliphatic spherically shaped norbornene group, which makes the polymer more isotropic than PC and PS.

We also measured the birefringence of injection-molded tensile bars made from COC with different T_g. The birefringence of molded parts depends on the shear, tempera-

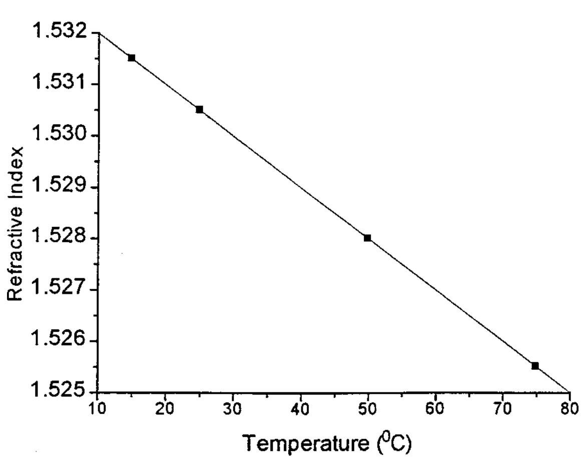

Fig. 8 Change of refractive index with temperature at a wavelength of 656 nm.

Table 2 Refractive indices of Topas™ COC grades versus T_g at 633 nm.

Glass transition temp. T_g (°C)	Refractive index
−20 (polyethylene)	1.49
80	1.5361
120	1.5317
135	1.5319
150	1.5320
180	1.5309
220	1.5311

Table 3 Comparison of the optical and physical properties of Topas™ COC 5013 with polycarbonate (PC), polymethylmethacrylate (PMMA), and polystyrene (PS). The thermal diffusivity of Topas COC was measured by AC Technology, Ithaca, NY. The SOC of Topas™ was measured by Prof. G. Fuller, Stanford Univ.

	Value			
Property	Topas™ COC	PMMA	PC	PS
n (589 nm)[1,16]	1.533	1.491	1.586	1.590
Abbe number[1,16]	56.4	57.2	29.8	30.9
$dn/dT(10^{-5}\,°C^{-1})$[1,16]	−10	−8.5	−14.3	−12
SOC ($10^{-12}\,Pa^{-1}$):				
$<T_g$, solid[17]	−4	−4.6	68	5
$>T_g$, melt[12,18]	100–470	−150	3500–5500	−4400
Transmission (%),[16] thickness 3 mm	>92	>92	>89	>88
Density (g/cm^3)	1.02	1.19	1.2	1.1
Heat deflection temp. (°C)[17] at 264 psi	120	85	120	80
Modulus of elasticity (MPsi)[2,16,17]	0.45	0.45	0.34	0.43
Elongation (%) at break	3	4	80	2
Coeff. of thermal expansion ($10^{-5}\,°C^{-1}$)[1,16]	6	6.5	7	7
Water absorption (%)[17]	<0.01	0.3	0.15	0.2
Thermal diffusivity ($10^{-8}\,m^2/s$)[19]:				
50°C	9	11.8	14.5	11.1
250°C	7.5	NA	11	NA

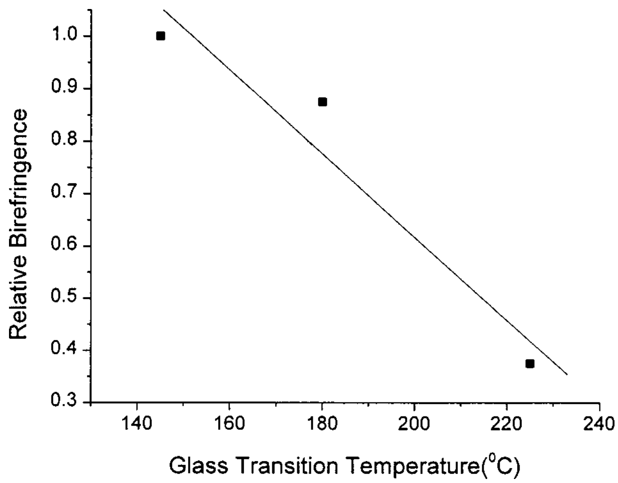

Fig. 9 Change of relative birefringence of molded parts with increase of glass transition temperature and norbornene content.

ture, and molecular weight of the polymers. The polymers used in this work all had comparable molecular weights. We tried to minimize differences between molded samples by keeping the injection pressure the same. We increased the processing temperature T_p of the injection molding machine for the different COC polymers with increasing T_g so that $T_p - T_g$ was constant. That way the melt viscosities would be comparable for the different copolymers used here. We also measured the birefringence on the tensile bar at the same distance from the gate where the molten plastic entered the mold. We report here the relative birefringence of Topas™ COC of different T_g.

Figure 9 is a plot of the relative birefringence for the different T_g polymers studied, normalized to the birefringence of Topas™ COC ($T_g = 140°C$). We see that as the T_g (and also the norbornene content) increases, the birefringence drops steeply. The reason is that the incorporation of the spherically shaped norbornene group makes the polymer less birefringent.

3.5 *Comparison with Other Optical Plastics*

Table 3 is a comparison of the optical and other physical properties of Topas™ COC with PMMA, PC, and PS. COC has a number of attractive features compared to other optical plastics, including a large Abbe number, moderately high refractive index, low birefringence, and high optical transmission. In addition it is very stiff, so that molded parts retain their shape, and it has a high glass transition temperature to withstand high-temperature use. It absorbs little water, which helps in the retention of the molded shape and optical properties.

COC also has a number of disadvantages in comparison with other plastics. It does not have the toughness of PC which is important in certain molding processes, or its heat diffusivity, which is important when fast cooling is important.

3.6 *Polymers for Communication Applications*

Optical polymers are finding increasing use in optical components, whether they be in injection molded lenses or waveguides for integrated optics. Many requirements have

Table 4 Comparison of Topas™ with other optical polymers for communication application. CWM, channel waveguide measurement; OFM, optical fiber measurement.

Polymer	T_g (°C)	Loss (dB/cm) [at λ (nm)]	n [at λ (nm)]	dn/dT (10^{-4}°C^{-1})	Birefring. Δn	Moisture absorption (%)
Topas™ (Ticona)	140–180	0.5 [820] 0.5 [1300] 0.7 [1550]	1.5319 [633] 1.5259 [830] 1.5217 [1550]	−1	Low	<0.01
BF Goodrich[8]	Crosslink >280	<0.1 (CWM)	1.538 [820] 1.532 [1550]	−2.45	10^{-3}–10^{-5}	<0.1
Allied Signal:						
Acrylate[6]	Crosslink 25	0.02 [840] 0.5 [1550] (CWM)	1.45–1.49	−2 to −3	2×10^{-4}	No change in optical prop. at 85°C, 85% RH
Halogenated acrylate[6,23]	crosslink −50	0.07 [1550] 0.24[23] (CWM)	1.4[23]	−3[23]	0–0.007	Same as above
Dow[6,20,22] Cyclotene	>350	0.51 [633] 0.8 [1330] (CWM) 1.5 [1550]	1.57 [633] 1.56 [1550]			
Asahi Glass Cytop[20,21]	108	0.0005 [830] (OFM) 0.003 [1550]	1.354 [830] 1.35 [1550]			
PMMA[20,24]	95–105	0.002 [650] (OFM) 0.65 [633] (CWM) 2 [820] (OFM)	1.49	−0.85	Low	0.3

to be met, including high use temperature, low moisture absorption and birefringence, high optical transmission at 850 and 1550 nm, and amenability to polymer processing techniques such as injection molding and spin coating from solution. A number of polymer systems have been proposed, including fluoropolymers [such as Cytop[20,21] (Asahi Glass)], benzocyclobutene[22] (Dow Chemical), UV-curable partially fluorinated acrylates[6] (Allied Signal), and norbornene-containing heat-curable crosslinked polymers[8] (BF Goodrich). Topas™ also appears to satisfy most of the requirements for short-distance datacom applications, based on the results reported here and elsewhere.[14,15]

Table 4 gives a detailed comparison of a number of polymer systems recently presented in the literature. We focus on a number of key properties such as the use temperature, optical loss, refractive index, thermo-optic coefficient, birefringence, and moisture uptake. Topas™ has fairly low loss at 820 nm, which is useful for datacom applications; however, the losses at 1550 nm are somewhat higher, making this material less useful for telecommunication devices. The thermo-optic coefficient is not as large as for some of the crosslinked materials such as those from BF Goodrich and Allied Signal; therefore it may be useful as a cladding material to ''tune'' the optical properties of waveguides. The glass transition temperature is fairly high and should be able to withstand environmental testing at 85°C and 85% relative humidity. The refractive index is rather high; ideally one would like a polymer to match the index of glass fiber to decrease Fresnel back reflection.

4 Conclusions

COC is an interesting new class of optical polymers that has a number of attractive features, such as low moisture absorption and low shrinkage, which help maintain lens figures; high optical transmission; high Abbe number and low birefringence to minimize aberration and distortion in optical systems; and high use temperature for demanding applications. It also has a number of potential disadvantages, such as brittleness and low heat diffusivity, which may limit its use in some applications. Topas™ may also have interesting applications in integrated optics and optical interconnects; however, more work needs to be done to characterize accurately its optical losses at the wavelengths of 850, 1300, and 1550 nm.

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