

Analysis of Thermosetting Acrylic Polymer Light Conduits

W. C. CHEN, W. J. WANG

Department of Chemical Engineering, National Taiwan University, No. 1, Section 4, Roosevelt Road, Taipei, Taiwan, Republic of China

Received 29 July 1999; accepted 5 November 1999

ABSTRACT: In this study a series of thermosetting acrylic polymer light conduits (PLCs) with the composition of $A_xB_yC_z$ were synthesized to investigate the structure–property relationships. The A and B components were selected from methyl methacrylate (MMA), butyl acrylate (BA), or 2,2,3,3-tetrafluoropropyl methacrylate (TFPMA). Various bifunctional acrylics were used for the C component. High numerical aperture values were found in the prepared large-diameter PLCs. The peak maxima of the optical loss spectra vary from 735 nm to 745 nm, which satisfactorily agree with the theoretical calculation from the FTIR spectra. They are due to the fifth harmonic of the C—H stretching vibration band. The peak maximum and intensity can be adjusted by varying molecular composition. The peak intensity of the optical loss spectrum is proportional to the C—H bond density of the polymer core. The replacement of the MMA moiety by the TFPMA moiety in the three-component thermosetting PLCs reduces the peak intensity. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 2098–2104, 2000

Key words: light conduit; C—H bond density; optical loss

INTRODUCTION

Polymer light conduits (PLCs) are one type of polymer optical fiber (POF) used for illumination and light-guiding applications.^{1–3} The fundamental requirements of a polymer light conduit are large diameter (>3 mm), low optical loss, excellent flexibility, and good heat resistance for using a high-power light source to obtain large illumination intensity. For such kind of materials, multicomponent thermosetting polymers are usually used as the core material for PLC.^{4–7}

The extrusion method for preparing PMMA optical fibers is difficult to prepare using such large-diameter PLCs. Hence, several new approaches^{4–8} have been developed to prepare

large-diameter PLCs. Ishiharada et al.⁸ prepared a flexible PLC made of an organic liquid core and a fluoropolymer cladding. Zarian et al.⁴ discovered large-diameter multicomponent thermosetting PLCs in a heating bath. Our laboratories prepared thermosetting and thermoplastic PLCs with the composition of $A_xB_yC_z$ by both UV curing⁵ and thermal polymerization.^{6–7} It was shown that optical loss of multicomponent PLCs is due mainly to the extrinsic scattering loss. Furthermore, the peak maximum in the optical loss spectrum of the prepared large-diameter multicomponent acrylic PLCs can be attributed to the high harmonics of the C—H stretching vibration loss.⁷

The optical loss factors of single-component polymer optical fibers have been investigated both theoretically and experimentally. Groh⁹ and Takezawa et al.¹⁰ showed the importance of high harmonics of molecular vibration on the optical loss of POF. Takezawa et al.¹¹ and Koike et al.¹² demonstrated the effects of the structural inhomogeneity on the light-scattering loss of POF.

Correspondence to: W. C. Chen (chenwc@ms.cc.ntu.edu.tw).
Contract grant sponsor: National Science Council of Taiwan; contract grant number: NSC 87-2216-E002-019.

Journal of Applied Polymer Science, Vol. 76, 2098–2104 (2000)
© 2000 John Wiley & Sons, Inc.

Table I Composition for Preparing Polymer Light Conduits (wt %)

Composition Sample	MMA	BA	TFPMA	Bifunctional Acrylics
A	57.1	38.1	—	4.8 (HDMA)
B ^a	57.1	38.1	—	4.8 (PEGDA)
C	57.1	38.1	—	4.8 (EGDMA)
D ^a	66.7	28.5	—	4.8 (PEGDA)
E ^a	76.2	19.0	—	4.8 (PEGDA)
F	57.1	—	38.1	4.8 (PEGDA)
G	—	38.1	57.1	4.8 (PEGDA)

^a The same composition was prepared in reference 7.

Takezawa et al.^{13,14} identified the major attenuation loss of POFs at high temperatures due to the electronic transition loss. In a previous study⁷ the compositions of the prepared PLCs were limited to acrylic monomers with the C—H moiety. The effect of a fluoroalkyl acrylic moiety and the C—H bond density on the optical properties have not been addressed as yet.

In this study thermosetting PLCs with the composition of A_xB_yC_z were prepared and characterized. Here, A, B, and C moieties were used for controlling optical property, flexibility, and heat resistance. The compositions of the prepared PLCs are shown in Table I. The A and B components were selected from methyl methacrylate, butyl acrylate, or 2,2,3,3-tetrafluoropropyl methacrylate. On the other hand, the C component was 1,6-hexanediol dimethacrylate (HDMA), ethylene glycol dimethacrylate (EGDMA), and poly(ethylene glycol 400 diacrylate) (PEGDA). A large-diameter (~ 8 mm) FEP tube was used as the cladding for preparing PLCs. The effect of the C—H bond density on the peak intensity and position in the optical loss spectrum was studied. Theoretical calculation based on the FTIR spectrum of the prepared PLCs was used in order to correlate it with the peak maximum of the optical loss spectrum.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA, 99.8%, TCI, Tokyo), butyl acrylate (BA, 99+%, Acros, New Jersey), 2,2,3,3-tetrafluoropropyl methacrylate (TFPMA, 99%, Aldrich, Milwaukee, WI), 1,6-hexanediol dimethacrylate (HDMA, Aldrich), ethylene glycol dimethacrylate (EGDMA, 98%, Aldrich), and poly(ethylene glycol 400 diacrylate) (PEGDA, Al-

drich) were purified before preparation of PLCs. Heating shrinkable FEP tubes (refractive index = 1.338, inner diameter = 8.2 mm, outer diameter = 8.9 mm, shrinkable ratio = 1.2:1) were purchased from Zeus, Indiana. Benzyl peroxide (BPO, 98%, Osaka) was used as the polymerization initiator.

Preparation of Polymer Light Conduits

The compositions of the reaction mixtures for preparing large-diameter PLCs are listed in Table I. The preparation of the large-diameter PLC **B**, PLC **D**, and PLC **E** has been described previously.⁷ For the other PLCs the synthetic method was similar. It is described here briefly. The monomer-filled FEP tube was polymerized thermally in an oil bath at a constant temperature of 80°C for 6 h first. Then it was cured in an oven at 150°C for 2 h to complete the polymerization. The molecular structures and properties of the prepared PLCs remained unchanged even if it was polymerized in the oil bath for a longer time. The elemental analysis results of the cores of PLC **A**, PLC **C**, PLC **F**, and PLC **G** are listed as below: **A** (C_{cal} : 62.40%, H_{cal} : 8.55%; found— C_{exp} : 62.57%, H_{exp} : 9.01%); **B** (C_{cal} : 61.88%, H_{cal} : 8.52%; found— C_{exp} : 62.11%, H_{exp} : 8.94%); **C** (C_{cal} : 62.14%, H_{cal} : 8.48%; found— C_{exp} : 62.28%, H_{exp} : 8.88%); **F** (C_{cal} : 52.91%, H_{cal} : 6.49%; found— C_{exp} : 52.76%, H_{exp} : 6.35%); and **G** (C_{cal} : 51.60%, H_{cal} : 6.25%; found— C_{exp} : 51.91%, H_{exp} : 6.48%).

Characterization

Infrared spectra of polymer thin films prepared from the KBr pellet were recorded at room temperature using a Jasco model FTIR 410 spectrophotometer. The elemental analysis results of the prepared polymer cores were obtained by using a

Perkin–Elmer 2400-CHN elemental analyzer. Thermal analysis was done with differential scanning calorimetry (DSC), using a DuPont model 910S differential scanning calorimeter with a heating rate of 10°C/min under a nitrogen atmosphere. The refractive index profiles of the prepared PLCs were measured using a York P102 profile analyzer in which a matching oil with a refractive index of 1.458 was used as the reference. The numerical aperture (NA) was calculated according to eq. (1):

$$NA = (n_1^2 - n_2^2)^{1/2} \quad (1)$$

where n_1 and n_2 are the refractive indices of the polymer core and cladding, respectively. The PLC attenuation loss spectrum was measured by a cutback method using a halogen lamp and a grating monochromator. The measurement system was designed by the Center for Measurement Standards, Industrial Technology Research Institute (Hsinchu, Taiwan).⁷ The wavelength range of the optical loss measurement was in the range 450–780 nm. The output power I_1 of the PLC sample with a length of L_1 was measured first. Then it was cut to length L_2 , and the output power I_2 was measured. The optical loss, α (dB/m), of the prepared PLC was calculated according to the following formula:

$$\alpha = [10/(L_1 - L_2)] \log(I_2/I_1) \quad (2)$$

The absorption maximum from the optical loss spectrum can be also be determined theoretically by the following equation:⁹

$$\mu_n = (\mu_1 n - \mu_1 \chi n(n + 1)) \div (1 - 2\chi), \quad n = 2, 3, 4, \dots \quad (3)$$

in which μ_1 is the fundamental vibration wave number from the FTIR spectrum of the studied PLC, μ_n is the n th harmonic wave number, and χ is the anharmonicity constant. For the C–H vibration, χ is 0.019.⁹ Hence, a comparison was obtained between the absorption maximum determined from the theoretical calculation of eq. (3) and the experimental result from the optical loss measurement. The C–H bond density of the prepared PLCs was calculated by eq. (4)¹⁵ as shown below:

$$N = (\rho n_{C-H})/M_{ru} \quad (4)$$

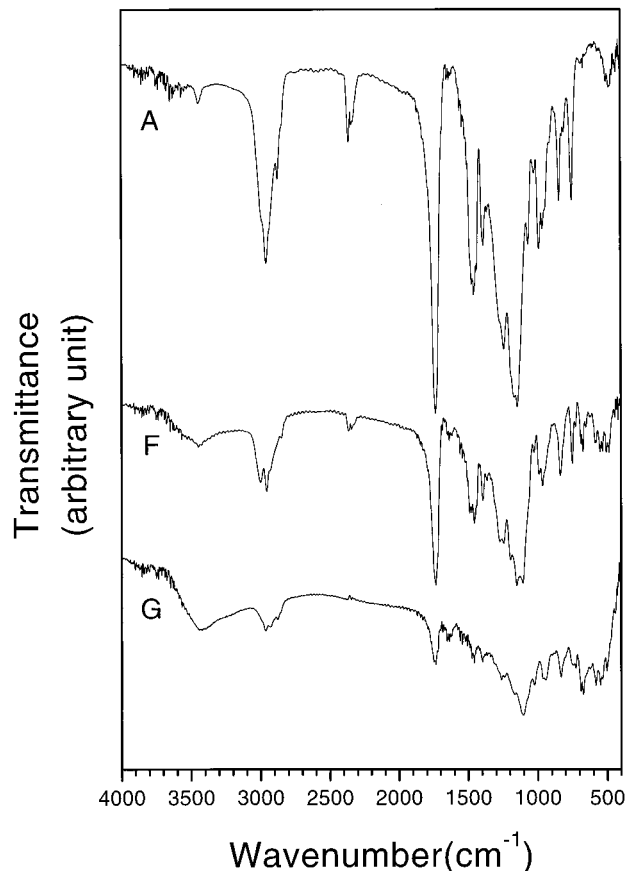


Figure 1 The FTIR transmission spectra of the polymer cores of PLC A, PLC F, and PLC G.

where N , ρn_{C-H} , and M_{ru} are the C–H bond density, the density of the PLC core, the C–H bond in the repeating unit of the PLC core, and the molecular weight of the repeating unit of the PLC core, respectively. The C–H bond density was used to correlate the peak intensity to elucidate the effect of molecular structure on the optical property.

RESULTS AND DISCUSSION

Figure 1 shows the FTIR transmission spectra of the polymer cores of PLC A, PLC F, and PLC G. The characteristic absorption bands of the C–O–C, C=O, and C–H bands are shown at 1140–1150 cm^{-1} , 1735 cm^{-1} , and 2880–3000 cm^{-1} , respectively, in these three spectra. These peaks are the characteristic absorption bands of an acrylic polymer. As presented previously,⁷ the high harmonics of the C–H stretching vibration result in the peak maximum of the optical loss

Table II C—H Stretching Vibration Band and Its Fifth and Sixth Overtone Positions

	C—H Band (cm^{-1})	λ_5 (nm)	λ_6 (nm)	$\lambda_{5,\text{exp}}$
A	2875, 2958	755, 734	643, 625	740
B ^a	2874, 2956	755, 734	643, 625	740
C	2876, 2959	755, 734	643, 625	740
D ^a	2875, 2956	755, 735	643, 626	740
E ^a	2876, 2953, 2993	755, 735, 726	643, 626, 618	735
F	2956, 3001	735, 724	626, 616	735
G	2878, 2965	754, 732	643, 624	745

^a Data from reference 7.

spectrum. Table II shows the C—H stretching vibration bands of the prepared PLCs and their fifth and sixth harmonic bands calculated from eq. (3). The theoretical peak maximum will be used to explain the experimental results, which will be discussed later. They can also be used to explain the difference in the peak position and intensity in the optical loss spectrum of the prepared PLCs. The elemental analysis results on the carbon and hydrogen contents of the prepared polymer cores satisfactorily agree with the theoretical calculation, as shown in the experimental section. The FTIR and elemental analysis results suggest that the molecular structures of the prepared polymer light conduits are as originally designed. The glass transition temperatures (T_g) of the prepared PLCs are in the range of -3°C to 91°C , as shown in Table III. The polymer structures of PLC **A–C** have a similar composition, except the 4.8% of the bifunctional acrylics, which results in a similar T_g value. PLC **F** has a high T_g value of 91°C because it does not have acrylic moiety with a long side chain. PLC **G** has the

moieties of both BA and TFPMA. Thus, it has the lowest T_g of -3°C among the studied PLCs. The glass transition temperature (T_g) of the PLC cores should be around room temperature to obtain sufficient flexibility for commercial applications. In view of the T_g value of the prepared PLCs, the studied PLCs, except PLC **F**, have suitable T_g values for commercial applications.

The refractive indices of the prepared polymer cores measured by York P104 are in the range of 1.466–1.494, which correspond to the NA values of 0.599 to 0.665 according to eq. (1), as shown in Table III. The NA values of the prepared PLCs are much larger than that of 0.14 for glass optical fibers. Furthermore, the diameter of the prepared PLCs is around 8 mm. Hence, they can transmit large quantity of light for high illumination applications.

Figure 2 exhibits the optical loss spectra of thermosetting PLC **A**, PLC **F**, and PLC **G** in the wavelength range of 450–780 nm. The optical loss factors of the PMMA optical fiber have been identified in the literature.^{3,9–14} In a similar

Table III Properties of Prepared Polymer Light Conduits

	T_g ($^\circ\text{C}$)	n	NA	C—H Bond Density	K^a (dB/m)
A	38	1.482	0.638	0.966	2.858
B ^b	33 ^b	1.492 ^b	0.658 ^b	0.965	2.912
C	38	1.481	0.634	0.963	2.750
D	41	1.488	0.651	0.955	2.619
E ^b	54 ^b	1.494 ^b	0.665 ^b	0.946	2.560
F ^b	91 ^b	1.482 ^b	0.638 ^b	0.843	2.106
G	-3	1.466	0.599	0.820	1.984

^a K (dB/m) = α_{740} (dB/m) - α_{695} (dB/m).^b Data from reference 7.

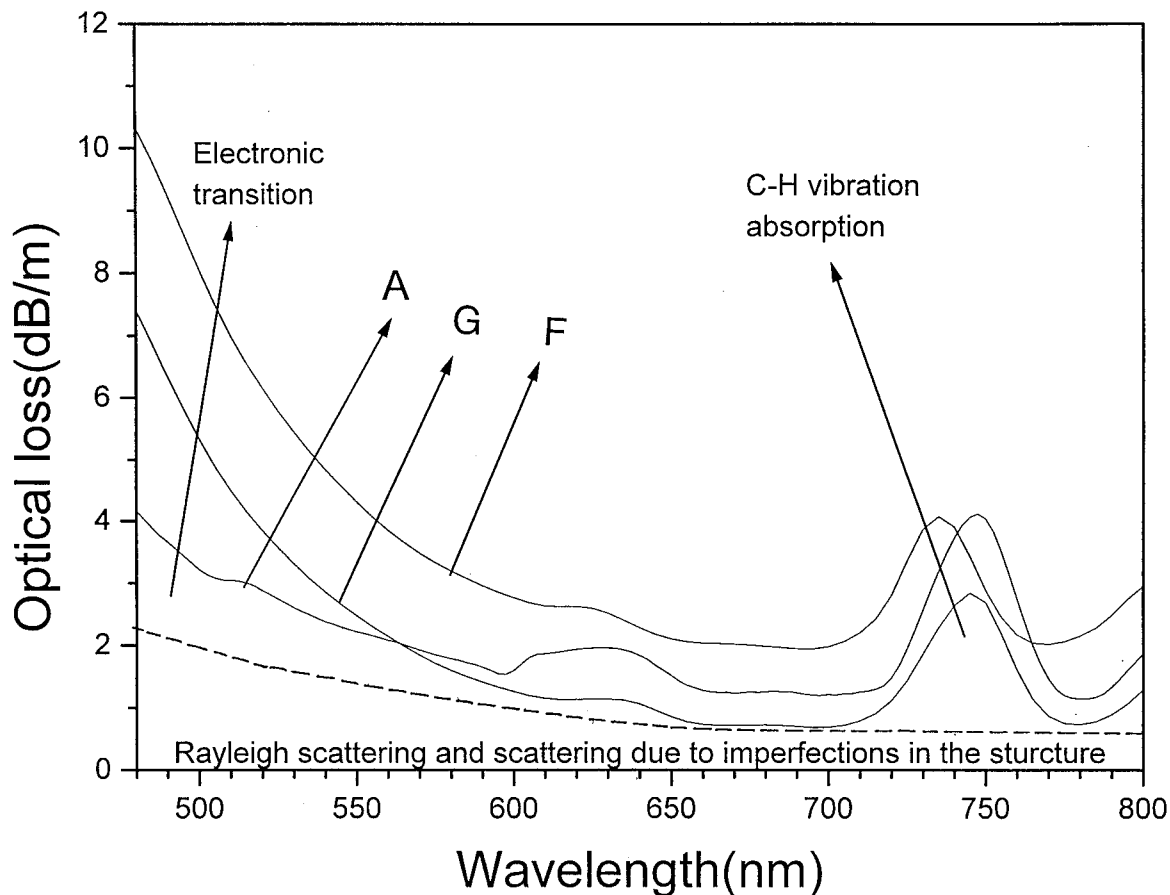


Figure 2 The optical loss spectra (dB/m) of PLC A, PLC F, and PLC G in the wavelength range of 450–780 nm.

way, the optical loss factors of the prepared three-component PLCs are identified in Figure 2. The scattering loss due to structure imperfection is the main loss for the prepared PLCs. The high harmonics of the C—H vibration loss and electronic transition loss are two other loss factors. The high harmonics of the C—H vibration loss can be observed from the peak maxima (λ_{\max}) around 740 nm and 625 nm in the optical loss spectrum, as discussed in a previous study.⁷ As shown in Table II, the 740-nm band from the experimental result can be attributed to the combination of the absorption bands around 755 nm and the 735-nm bands from the theoretical calculation. The band at 740 nm can be assigned as the fifth harmonic of the C—H stretching vibration band. In a similar way, the band around 625 nm is assigned to the sixth harmonic of the C—H stretching vibration band. In view of the peak maximum of prepared PLCs A–G, the theoretical calculation is in a

satisfactory agreement with the experimental results. The variation of the peak maximum, $\lambda_{5-\text{exp}}$, from 735 nm to 745 nm, a result of the different intensities of the C—H stretching vibration bands. Suppose the optical loss resulted from scattering can be approximated by the peak around 695 nm because it does not have the optical loss from C—H vibration loss. Hence, the peak intensity due to the fifth harmonic band of the C—H vibration can be approximated by the reduction of the optical loss around 740 nm from that at 695 nm, as shown in Table III. The C—H bond densities of the prepared polymer cores calculated from eq. (4) range from 0.082 to 0.0966, which are listed in Table III. Figure 3 shows the relationships between the peak intensity of the 740-nm band and the C—H bond density. A linear relationship can be obtained between the peak intensity and the electronic density. Hence, the optical loss of the three-component PLCs resulted from

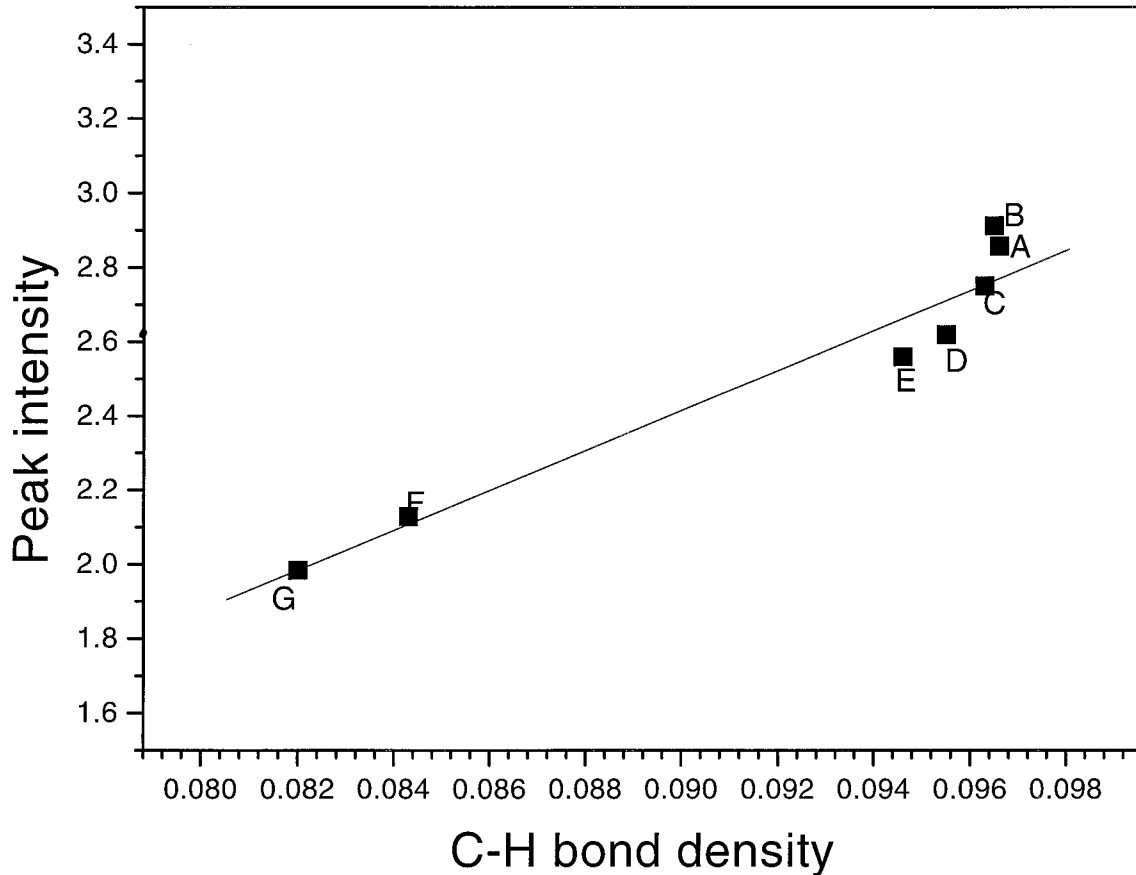


Figure 3 Variation of the peak intensity with the C—H bonding density for the prepared PLCs, A–G.

vibration loss can be controlled from their molecular structure. The replacement of the MMA moiety by the TFPMA moiety in the three-component thermosetting PLCs reduced the optical loss that had resulted from C—H vibration loss.

CONCLUSIONS

In this study a series of three-component acrylic PLCs were synthesized and characterized in a FEP tube by thermal polymerization. The T_g s of the prepared PLC cores except PLC **F** were around room temperature, and thus good flexibility can be probably achieved. The large numerical apertures along with large diameter of the prepared PLCs can be used potentially for high-illumination applications. The peak maximum in the optical loss spectra can be correlated with the theoretical calculation on the fifth and sixth harmonics of the C—H stretching vibration band. It can shift from 735 nm to 745 nm by adjusting the

molecular composition of the PLCs. The optical intensity of the peak maximum around 740 nm is proportional to the C—H bonding density. The experimental result clearly shows that replacement of the MMA moiety by the TFPMA moiety in the three-component thermosetting PLCs reduces the peak intensity.

The authors thank the National Science Council of Taiwan, Republic of China, for their financial support.

REFERENCES

1. Proceeding of POF '97 Conference, Kauai, Hawaii, September 22–25, 1997.
2. Proceeding of POF '98 Conference, Berlin, October 5–8, 1998.
3. Kaino, T. In *Polymers for Lightwave and Integrated Optics*; Hornak, L. A., Ed.; Marcel Dekker: New York, 1992; Chapter 1.
4. Zarian, J. J.; Robbins, J. A. (to Lumenyte International Co.) U.S. Pat. 5,225,166 (1993).
5. Chen, W. C.; Lin, H. Y. *Polym Bull* 1996, 36, 51.

6. Chen, W. C.; Chang, C. C.; Wang, N. H. *J Appl Polym Sci* 1997, 61, 2103.
7. Chen, W. C.; Chang, C. C. *J Mater Chem* 1999, 9, 2307.
8. Isliharada, M.; Naito, K.; Tanuma, I.; Matsumuro, Y.; Honda, T. In *Proceeding of the First Plastic Optical Fibres and Applications Conference*, June 22–23, 1992; p 49.
9. Groh, G. *Makromol Chem* 1988, 189, 2861.
10. Takezawa, Y.; Taketani, N.; Tanno, S.; Ohara, S. J. *Polym Sci Polym Phys* 1992, 30, 879.
11. Takezawa, Y.; Taketani, N.; Tanno, S.; Ohara, S. J. *Appl Polym Sci* 1992, 46, 2033.
12. Koike, Y.; Matsuoka, S.; Bair, H. E. *Macromolecules* 1992, 25, 4807.
13. Takezawa, Y.; Tanno, S.; Taketani, N.; Ohara, S.; Asano, H. *J Appl Polym Sci* 1991, 42, 2811.
14. Takezawa, Y.; Tanno, S.; Taketani, N.; Dhara, S.; Asano, H. *J Appl Polym Sci* 1991, 42, 3195.
15. Flipsen, T. A. C.; Steensam, R.; Penning, A. J.; Hadziioannou, G. *Adv Mater* 1996, 8, 45.