

Synthesis and characterization of large diameter acrylic polymer light conduits

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In this study, both thermosetting and thermoplastic acrylic polymer light conduits (PLCs) with a diameter of around 8 mm were synthesized in a FEP tube by a thermal polymerization. The composition of $A_xB_yC_z$ was used for the preparation of the polymer core. Here, methyl methacrylate (MMA) and butyl acrylate (BA) were used as the A and B components, respectively, while poly(ethylene glycol 400 diacrylate) (PEGDA-400) or isobornyl methacrylate (IBMA) was used for the C component. The glass transition temperatures of the prepared PLC cores are in the range of -33 to 118°C by the adjustment of polymer composition. The numerical apertures of the prepared PLCs can be as high as 0.678. The scattering loss due to structural imperfections probably accounted for most of the optical loss in the prepared large diameter PLCs. The peak maxima of the optical loss spectra in the wavelength range of 450–780 nm are in satisfactory agreement with the theoretical calculation from the FTIR spectra. They are due to the fifth harmonic and sixth harmonics of the C–H stretching vibration band. The peak maximum shifts to a higher wavelength on increasing the BA composition in PLCs. The optical loss at peak maxima can be correlated with the C–H bonding density. Hence, the optical windows of the prepared PLCs can be adjusted by polymer compositions. The thermal stability of the prepared thermosetting PLCs was much better than that of the thermoplastic PLCs for optical applications.

Introduction

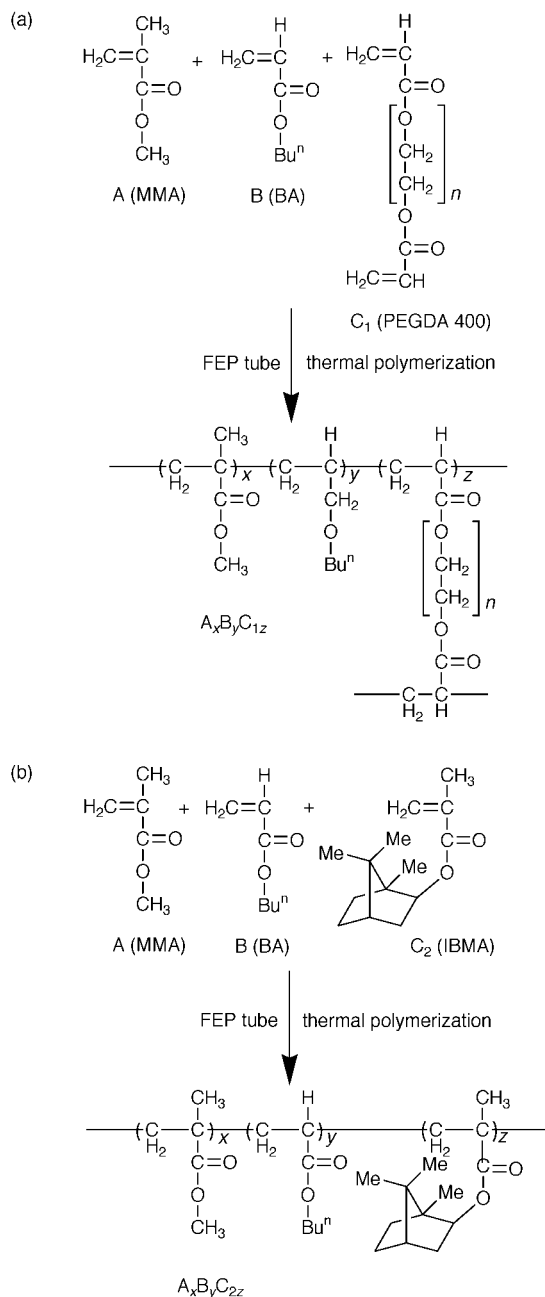
Polymer optical fibers (POFs) have been widely studied recently^{1,2} because of their potential applications in local area networks, sensors, illumination, light guides, and displays. They have advantages over glass materials of light weight, excellent flexibility, low cost, and large diameters capable of transmitting large quantities of light. Polymer light conduits (PLCs) are one kind of POFs for illumination and light-guiding applications. The basic structure of a PLC is composed of two parts: core and cladding, in which the core diameter is generally larger than 3 mm in order to obtain a high illumination intensity. Furthermore, the refractive index of the PLC core is larger than that of the cladding. Hence, total internal reflection occurs when light transmits through the core-cladding boundary.

The fundamental requirements of a polymer light conduit are low optical loss, excellent flexibility, and good heat resistance for using a high power light source to obtain a large illumination intensity. The extrusion method for preparing small diameter PMMA optical fibers cannot be easily used to prepare such large diameter PLCs. Therefore, several new approaches^{3–6} have been developed to prepare large diameter (> 3 mm) PLCs. Ishiharada *et al.*³ used a flexible PLC made of an organic liquid core and a fluoro-polymer cladding. The optical loss of the prepared liquid core PLC was as low as 120 dB km^{-1} at the wavelength of 580 nm. Furthermore, the manufacturing cost was low. However, the inconvenience of cutting into various lengths and the large optical loss incurred with bending limited the applications of the liquid core PLC. Zarian and Robbins⁴ invented large diameter thermosetting PLCs, in which first a crosslinkable monomer mixture was filled into a fluorinated ethylene propylene (FEP) copolymer tube and then the monomer was cured in a heating bath. The monomer mixture contained acrylic monomers, a small amount (5–10%) of crosslinking agents (*e.g.*, diallyl phthalate and 1,3-butylendimethacrylates), and other addi-

tions. This process obtained flexible PLCs with large diameters of 5–15 mm and a high illumination intensity. We recently investigated the thermal stability of one kind of Lumenyte PLCs and found out that a plasticizer additive was probably added into the reaction mixture.^{5a} Although the additive could improve the flexibility of the prepared PLC, it also significantly affected the thermal stability of PLC and thus limited the usable temperature range. We also used a UV curing photopolymerization to prepare a thermosetting PLC.^{5b} However, the optical transmission was poor compared with Lumenyte PLC. Flipsen⁶ prepared novel densely crosslinking polycarbosiloxanes, in which a single component prepolymer was synthesized first and then polymerized in a FEP tube. The Lumenyte scheme can use commercially available monomers to obtain the desired PLCs while the advantage of the Flipsen scheme is to produce a PLC with specially designed properties.

Fundamental understanding of the molecular structure factors on the PLC properties is very important for high quality PLCs for commercial applications. For a small diameter POF composed of one or two components, the structure-properties relationships have been addressed in the literature. Groh⁷ and Takezawa *et al.*^{8a} showed the importance of high harmonics of molecular vibration on the optical loss of POF. Takezawa *et al.*^{8b} and Koike *et al.*⁹ demonstrated the effects of the structural inhomogeneity on the light scattering loss of POF. Takezawa *et al.*¹⁰ identified the major attenuation loss of POFs at high temperature due to electronic transition loss. However, the molecular structural effects on the properties of three component large diameter (~ 8 mm) PLCs prepared by the thermal batch process have not been fully explored yet.

In this study, both thermosetting and thermoplastic PLCs with the composition $A_xB_yC_z$ were prepared and characterized. Here, A is the monomer controlling optical properties, B is the monomer controlling flexibility, and C is for controlling heat-resistance. The adjustment of A, B, or C and x , y , or z changes



Scheme 1 Synthetic scheme for preparing polymer light conduits (a) thermosetting PLCs, and (b) thermoplastic PLCs.

the properties of PLCs. In this study, A, B, and C were methyl methacrylate (MMA), butyl acrylate (BA), and poly(ethylene glycol 400 diacrylate) (PEGDA-400) and isobornyl methacrylate (IBMA), respectively. Poly(isobornyl methacrylate)¹¹ optical fiber was shown to have a high thermal stability. Here, IBMA was used as the heat-resisting monomer for preparing thermoplastic PLCs while PEGDA-400 was for preparing thermosetting PLCs. A large diameter (~ 8 mm) FEP tube was used as the cladding for preparing PLCs. Scheme 1 shows the synthetic routes for the preparation of both thermosetting and thermoplastic PLCs. The structure-property relationship in the prepared PLCs was studied by varying the composition of the MMA, BA, PEGDA, or, IBMA. On the other hand, the single component PLCs were prepared for comparing with the three component PLCs. Also, the comparison between the thermosetting and thermoplastic PLCs provides the effects of polymer morphology on the properties of PLCs.

Experimental

Materials

Methyl methacrylate (MMA, 99.8%, TCI), butyl acrylate (BA, 99+%, Acros), isobornyl methacrylate (IBMA, Aldrich) and poly(ethylene glycol 400 diacrylate) (PEGDA-400, Aldrich) 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 Ind., USA. 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 1. The bi-functional monomer PEGDA was composed of 4.8 wt% of the total mixture. The reaction mixtures were well mixed under a nitrogen atmosphere and then poured into a FEP tube vary slowly. Both ends of the FEP tube were sealed by Teflon plugs. In order to prevent bubble defects due to the volume shrinkage of monomers after polymerization, the monomer-filled FEP tube was polymerized thermally in an oil bath at a constant temperature of 80 °C for 6 hours first. Then, it was cured in an oven at 150 °C for 2 hours 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.

Characterization

Infrared spectra of polymer cores were prepared by grinding with KBr to form pellets and then recorded at room temperature using a Bio-Rad Digilab Division FTS-40 FTIR spectrophotometer. ¹H NMR spectra of the prepared thermoplastic PLCs were determined by a solution using a nuclear magnetic resonance spectroscope (JNM-EX-400, JEOL) at 400 MHz. The elemental analysis results of the prepared polymer cores were obtained by using a Perkin-Elmer 2400-CHN elemental analyzer. The molecular weight distribution of the prepared thermoplastic PLCs were determined by a gel permeation chromatographer (GPC) with a solvent delivery system (Spectroflow 400, ABI), a refractive index detector (RI-71, Shodex), and a GPC column (PL_{gel} 5 μ m MIXED-C, Polymer Laboratories). Thermal analysis, differential scanning calorimetry (DSC), was performed using a DuPont Model 910S differential scanning calorimeter with a heating rate of 10 °C min⁻¹ 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

Table 1 The compositions of the reaction mixtures^a for preparing large diameter acrylic PLCs

PLC	MMA (%)	BA (%)	PEGDA (%)	IBMA (%)
PLC1	100	0	0	0
PLC2 ^b	0	100	0	0
PLC3	0	0	100	0
PLC4	0	0	0	100
PLC5	85.7	9.5	4.8	0
PLC6	76.2	19.0	4.8	0
PLC7	66.7	28.6	4.8	0
PLC8	80	0	0	20
PLC9	60	20	0	20
PLC10	40	40	0	20

^aAll the reaction mixtures contained 0.1 wt% BPO based on the total weight of the monomers as the polymerization initiator. ^bThe preparation of PLC2 was not successful under the current preparation method.

aperture (NA) was calculated according to eqn. (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 Center for Measurement Standards, Industrial Technology Research Institute (Hsinchu, Taiwan). The wavelength range of the optical loss measurement was in the range of 450–80 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^{-1}) of the prepared PLC was calculated according to eqn. (2):

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

The thermal stability of the optical loss of the prepared PLCs was studied by heating these PLCs in an oven at the constant temperature of 100 °C for 200 hours. Then, the optical loss of heated PLCs was measured again in the same wavelength range.

The absorption maximum from the optical loss spectrum can be also determined theoretically by eqn. (3):⁷

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

in which μ_1 is the fundamental vibration wavenumber from the FTIR spectrum of the studied PLC, μ_n is the n th harmonic wavenumber, and χ is the anharmonicity constant. For the C–H vibration, χ is 0.019.⁷ Hence, the comparison between the absorption maximum determined from theoretical calculation by eqn. (3) and experimental results from the optical loss measurement can be obtained.

Results and discussion

Synthesis

The reaction mixtures in Table 1 except PLC2–PLC4 after polymerization yielded transparent polymer light conduits. The incomplete polymerization of PLC2 and PLC4 is probably due to the steric hindrance resulting from the bulky side groups. The fast polymerization of the PEGDA-400 monomer resulted in quick volume shrinkage. Hence, microvoids and an imperfect core-cladding boundary were obtained in the case of PLC3. Therefore, PLC3 had a poor optical quality and was unable to be measured accurately by the optical loss system. Furthermore, if there was more than 5 wt% of the PEGDA-400 used in the preparation of PLCs, it resulted in fast volume shrinkage or poor flexibility. Hence, 4.8 wt% of PEGDA-400 was chosen for the preparation of PLC5–PLC7. For thermoplastic PLCs, it might lead to the incomplete polymerization of IBMA if more than 20% IBMA was added into the reaction mixture. Hence, 20% of IBMA was used for the preparation of PLC8–PLC10.

Polymer structure

Fig. 1 shows the FTIR transmission spectra of the polymer cores of thermoplastic PLC1, PLC4, and PLC9. The characteristic absorption bands of the C–O–C, C=O, and C–H bands are shown at 1150 cm^{-1} , 1730 cm^{-1} , and 2880–3000 cm^{-1} , respectively, in these three spectra. However, a weak absorption band at 1638 cm^{-1} in the spectrum of PLC4 is probably due to the C=C absorption band of the unreacted IBMA monomer. This result indicates that the bulky side group of IBMA may lead to steric hindrance and thus incomplete polymerization. On the other hand, similar absorption bands at 1638 cm^{-1} are not observed in the

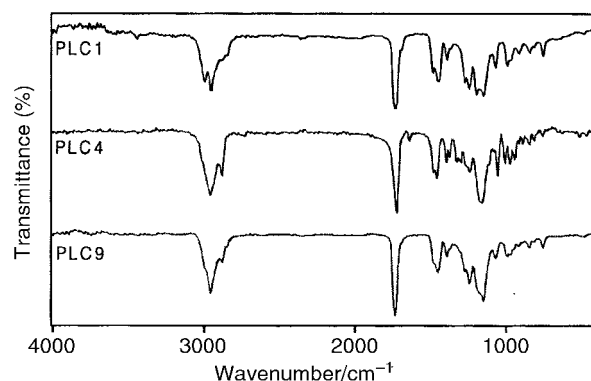


Fig. 1 The FTIR transmission spectra of the polymer cores of PLC1, PLC4 and PLC9.

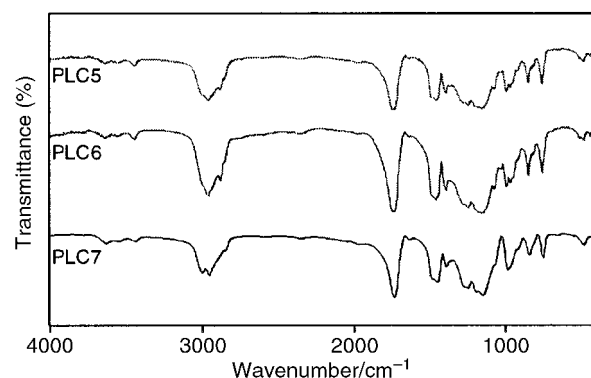


Fig. 2 The FTIR transmission spectra of the polymer cores of PLC5, PLC6 and PLC7.

prepared PLC8–PLC10. Fig. 2 illustrates the FTIR transmission spectra of the polymer cores of thermosetting PLC5–PLC7. The characteristic absorption bands of the C–O–C, C=O, and C–H of acrylic polymers are also observed in the spectra. An interesting characteristic of the C–H stretching band between PLC1 and the other PLCs is the absorption band around 2880 cm^{-1} . This band arises from the C–H stretching vibration band attached to the carbon atom while that attached to the oxygen atom is observed at 2993 cm^{-1} . Hence, the band around 2880 cm^{-1} increases its intensity when the composition of BA or IBMA moiety increases in the PLCs. This explains why the absorption band around 2880 cm^{-1} is found in the FTIR spectra of PLC2–PLC10 but not exhibited in PLC1.¹² The effect of the absorption band around 2880 cm^{-1} can further cause the shift of the peak maximum in the optical loss spectra, which will be discussed in the optical property section.

The ^1H NMR spectra of the PLC3 and PLC5–7 cores could not be obtained because of the insolubility of the thermosetting PLCs. Fig. 3a and Fig. 3b show the ^1H NMR spectra of the polymer cores of PLC4 and PLC9 in CDCl_3 , respectively. The assignments of the different CH, CH_2 , and CH_3 proton resonances are shown in the figures. The theoretical mole ratio of the MMA:BA:IBMA composition of PLC9 calculated from the reaction mixture is 0.71:0.18:0.11 MMA:BA:IBMA. This result is identical to that obtained from the ^1H NMR spectrum. The ^1H NMR results of PLC8 and PLC10 cores also show identical compositions with the theoretical results. However, unexpected proton resonance peaks at 5.5 ppm and 6.5 ppm are found in the spectrum of the PLC4 core, as shown in Fig. 3b. These peaks are assigned to the proton resonances on the C=C bond of the unreacted monomer, IBMA. Hence, Fig. 3b shows incomplete polymerization of PLC4, which is probably due to steric hindrance from the alicyclic side group. The incomplete polymerization of

Table 4 The fifth and sixth harmonics of the C–H stretching vibration band calculated from the FTIR spectra of the studied PLCs combined with eqn. (3)

	C–H stretching from FTIR spectrum ($\mu\text{l}/\text{cm}^{-1}$)	λ_5/nm^a	λ_6/nm^a
PLC1	2951, 2993	736, 726	627, 618
PLC3	—	—	—
PLC4	2880, 2957	754, 734	625, 642
PLC5	2885, 2955, 2996	753, 735, 725	641, 626, 617
PLC6	2884, 2956, 2992	753, 735, 726	641, 626, 618
PLC7	2882, 2956	753, 734	642, 618
PLC8	2881, 2953, 2991	735, 726, 754	642, 618, 626
PLC9	2878, 2954	755, 735	643, 626
PLC10	2876, 2957	755, 734	643, 625

^aCalculated from eqn. (3) and converted to the wavelength by the following equation: $\lambda = (1/\mu)$.

736 nm and 726 nm, 627 nm and 618 nm, respectively. The combination of the bands at 736 nm and 726 nm might form the band at 735 nm shown in Fig. 4. On the other hand, the band at 625 nm probably arises from the combination of the bands at 627 nm and 618 nm. Hence, the characteristic peaks at 735 nm and 625 nm in the optical loss spectrum of PLC1 are probably due to the λ_5 and λ_6 bands of the C–H stretching vibration band, respectively. In the case of PLC4, the 13% IBMA monomer residue and structure imperfection as described in PLC1 might be responsible for the large optical loss observed in Fig. 4. An interesting characteristic is the shift of λ_{max} from 735 nm of PLC1 to 745 nm of PLC4 as shown in Fig. 4. The band at 745 nm is probably due to the combination of the bands at 734 nm and 754 nm. The FTIR spectrum of PLC4 has a strong peak at 2880 cm^{-1} , which corresponds to the λ_5 band at 754 nm. This band is not observed in the FTIR spectrum of PLC1. This result explains the shift of the peak maximum between PLC1 and PLC4. Both PLC1 and PLC4 exhibited a large increase in optical loss after heating at 100 °C for 200 hours. This result implies that the scattering loss due to structural imperfection is probably enhanced after heating. Another possible reason is the heating temperature was close to the T_g s of PLC1 and PLC4. Hence, the microstructures of both PLCs could be damaged after heating for a long time and this could result in a large optical loss.

Fig. 5 and Fig. 6 exhibit the optical loss spectra of thermosetting PLC5–PLC7 in the wavelength range of 450–780 nm before heating and after heating at 100 °C for 200 hours, respectively. The optical losses of these three PLCs are in the range 1.0–5.0 dB m^{-1} for the studied wavelength range. As discussed above, the large optical loss is probably due to extrinsic scattering loss and the high harmonics of the C–H stretching vibration band. The λ_{max} of the optical loss spectra for PLC5, PLC6, and PLC7 are 735 nm, 737 nm, and 740 nm, respectively. It shifts from 735 nm to 740 nm as the BA composition increases from 9.5% to 28.6%. As observed from Fig. 2, the increasing composition of the BA moiety from PLC5

to PLC7 enhances the intensity of the vibration band around 2880 cm^{-1} and decreases the intensity of the vibration band around 2990 cm^{-1} . Hence, the red shift of λ_{max} with increasing BA composition is observed in the spectrum. This result suggests that the optical windows of the prepared PLCs can be tuned from their polymer structures. The small peak around 625 nm in Fig. 4 is probably due to the sixth harmonic of the vibration band as shown in Table 4. The optical losses of PLC5, PLC6, PLC7 at λ_{max} are 3.8, 3.9, and 4.4 dB m^{-1} , respectively. It is assumed the scattering loss is the same for PLC5–PLC7. The C–H bonding density of the BA moiety is higher than that of the MMA moiety and thus this results in a higher vibration absorption loss. Hence, the trend of the above optical loss is probably due to the increase of the BA moiety from 9.5 wt% of PLC5 to 28.6% of PLC7 along with decreasing the MMA moiety. The optical loss spectra of PLC5–PLC7 exhibit an insignificant change after heating in the wavelength range of 500–780 nm. However, it increases strongly in the wavelength range of 450–500 nm, which is probably due to the electronic absorption loss from the thermal oxidation reaction of the PLC core as reported in the literature.¹⁴ A further test of the thermal stability of PLC5–PLC7 at 120 °C showed a similar spectrum to that at 100 °C. This result suggests that the prepared thermosetting PLCs have superior thermal stability to PLC1 and PLC4.

Fig. 7 and Fig. 8 illustrate the optical loss spectra of thermoplastic PLCs, PLC8–PLC10, in the wavelength range of 400–780 nm before heating and after heating at 100 °C for 200 hours, respectively. The optical losses of these three PLCs are in the range 4.0–28.0 dB m^{-1} for the studied wavelength range. Hence, the structural imperfection due to scattering loss might be the major optical loss factor. The λ_{max} shows a red shift from 735 nm for PLC8, to 740 nm for PLC9, and then to 745 nm for PLC10, as the BA composition increases from 0% to 40%. This result can also be explained from the theoretical calculation of the λ_5 band of the corresponding FTIR spectra.

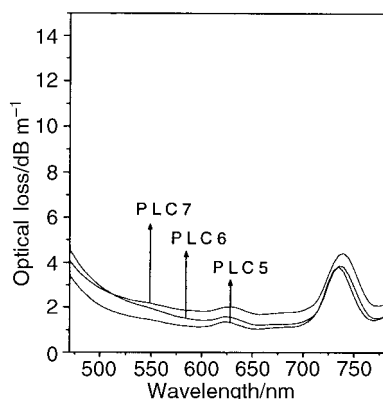


Fig. 5 The optical loss spectra (dB m^{-1}) of the thermosetting PLCs, PLC5–PLC7, in the wavelength range of 450–780 nm (before heating).

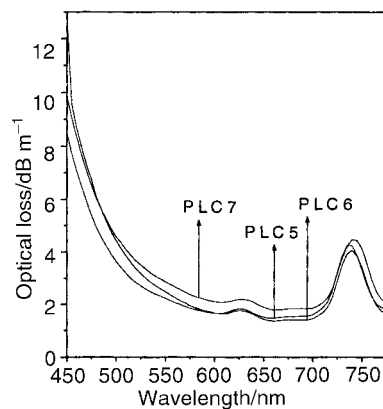


Fig. 6 The optical loss spectra (dB m^{-1}) of thermosetting PLC5–PLC7 in the wavelength range of 450–780 nm (after heating at 100 °C for 200 h).

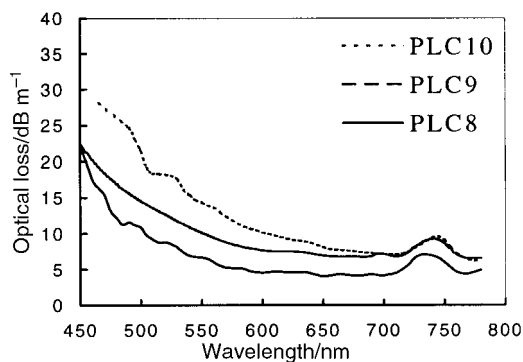


Fig. 7 The optical loss spectra (dB m^{-1}) of the thermoplastic PLCs, PLC8–PLC10 in the wavelength range of 450–780 nm (before heating).

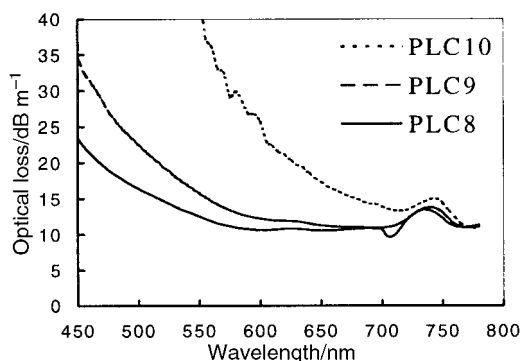


Fig. 8 The optical loss spectra (dB m^{-1}) of the thermoplastic PLCs, PLC8–PLC10 in the wavelength range of 450–780 nm (after heating at $100\text{ }^{\circ}\text{C}$ for 200 h).

The optical losses of PLC8, PLC9, and PLC10 at λ_{max} before heating are 7.1, 9.2, and 9.6 dB m^{-1} , respectively. This result again shows the effect of the high C–H bonding density of the BA moiety as previously discussed in the case of PLC5–PLC7. The optical losses shown in Fig. 7 are much larger than those of the thermosetting PLC5–PLC7. Besides the scattering loss due to the structural imperfection, the large C–H bonding density of the IBMA and BA moiety and the miscibility of the monomer composition probably account for the large optical loss. Also, the optical losses of the thermoplastic PLCs, PLC8–PLC10 enhanced significantly after heating as shown in Fig. 8. It is probably because the thermoplastic structure with low dimensional stability caused poor thermal stability. This result shows the significance of polymer morphology on the optical loss. Since a low T_g was required for achieving flexibility in the PLC application, both thermoplastic and thermosetting polymers have the flexible segment BA in their composition, which might reduce thermal stability. However, the dimensional stability of the thermosetting structure provides the microstructure rarely changed by heating. Hence, good thermal stability can be achieved in thermosetting PLCs. For example, PLC7 has a similar T_g to PLC10. However, the increase of optical loss after heating is insignificant as compared with that of PLC10.

Conclusions

In this study, both thermosetting and thermoplastic acrylic PLCs were synthesized and characterized in a FEP tube by a thermal polymerization. The T_g s of the prepared PLC cores are in the range of $-33\text{ }^{\circ}\text{C}$ to $118\text{ }^{\circ}\text{C}$ by the adjustment of polymer composition, which governs the flexibility of PLCs. The numerical apertures of the prepared PLCs are in the range of 0.652 to 0.678 and thus can be potentially used for high

illumination applications. The optical losses of the prepared PLCs are mostly due to scattering loss and the high harmonics of the C–H stretching vibration band. The peak maxima 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. The maximum shifts from 735 nm to 745 nm by adjusting the BA composition in PLCs. The optical loss at peak maxima can be correlated with the C–H bonding density. This result suggests that the optical windows of the prepared PLCs can be adjusted by molecular composition. The prepared thermosetting PLCs showed superior thermal stability to the thermoplastic PLCs.

Acknowledgements

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