

Characteristics of Polymer Light Conduits from Different Manufacturing Processes

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ABSTRACT: The characteristics of polymer light conduits (PLCs) prepared from three different processes are compared: (1) a bulk polymerization and melt spinning process (PLC1), (2) a thermal polymerization (PLC2), and (3) a UV curing photopolymerization (PLC3–PLC4) of a monomer mixture in a fluorinated ethylene propylene tube. PLC1 and PLC2 were obtained from Toray and Lumenyte, respectively. New PLCs, PLC3 and PLC4, were prepared from the monomer mixtures consisted of methyl methacrylate, 2-ethyl-hexyl acrylate, and the crosslinking agent polyethylglycol 200 diacrylate and diallyl phthalate, respectively. All four polymer light conduits contain the acrylic moiety. PLC2 may also contain the plasticizer additives, which resulted in an excellent flexibility but with a poor thermal stability. The flexibilities of PLC2 and PLC3 were significantly improved from that of PLC1 due to the insertion of a plasticizer and the long alkyl chain monomer 2-EHA, respectively. The much larger numerical apertures of PLC2–PLC4 than that of PLC1 suggest that PLC2–PLC4 can have a wide angle application. The transmitted distance of PLC1 is larger than those of PLC2–PLC4. However, the illumination intensity of PLC1 is worse than those of PLC2–PLC4. This result indicates that PLC1 is suitable for the applications as PLCs with the characteristics of long distance and low illumination intensity, while PLC2–PLC4 are suitable for short distance and high illumination intensity applications. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 2103–2109, 1997

Key words: polymer light conduits; thermal polymerization; UV curing polymerization

INTRODUCTION

Polymer optical fibers (POFs) are used in a wide variety of applications,^{1–4} for example, local area network, sensors, light guides, display, and illumination. They are composed of two parts: core (the inner part) and cladding (the outer part). The refractive index of the core is larger than that

of cladding. Hence, total internal reflection occurs when light transmits through the core–cladding boundary. Many efforts have been made to provide inexpensive, flexible, and durable light guides for general illumination applications. Polymer optical fibers have advantages over glass materials owing to their large diameters capable of transmitting large quantities of light under ordinary conditions. Furthermore, they are inexpensive, light weight, and have excellent flexibility for commercial applications.

Polymer light conduits (PLCs) or flexible light pipes (FLPs) are one kind of POF for illumination

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applications, which usually have a core diameter of at least 3 mm, heat resistance, illumination intensity, illumination distance, and excellent flexibility for a wide range of applications.⁵⁻⁷ Heat resistance of PLCs is required for using a high power light source. A metal halide lamp is commonly used as the light source for PLCs. According to the illumination intensity, PLCs can be cut to a various length for different applications. Since PLCs are used for lighting and decoration applications, flexibility is a very important property. Flexibility of PLCs is largely determined by the glass transition temperature (T_g) of the polymer core.⁶ For practical applications, T_g of the polymer core should be much lower than 100°C.

There are generally three different processes for preparing PLCs. The first kind is to use a bulk polymerization process for preparing a pure polymer, and then melt spinning to form a polymer core [e.g., poly(methyl methacrylate) (PMMA)]. In the following step, a polymer cladding (e.g., fluoropolymer), is extruded to adhere on the periphery of the polymer core. Hence, a PLC is produced.^{8,9} The PLCs produced by this kind of process can have a very low optical loss, which can transmit over long distances. However, they have two major drawbacks which limit their applications in luminescence. First, they are usually thermoplastic polymers which can only be used below 80°C. When used at a temperature higher than 80°C, their microstructures are deformed, which results in their use in only short distance applications and low illumination intensity. Furthermore, a high-power light source cannot be used in PLCs to generate enough illumination intensity. Second, the diameters of thermoplastic PLCs are usually < 3 mm. Hence, they cannot transmit large amounts of light. Although the amount of light transmitted can be increased by bundling a large number of small diameters of PLCs, they are too expensive for various commercial applications. The second process was invented by Lumenyte,¹¹ which filled the monomer mixtures in fluorinated ethylene propylene (FEP) copolymer tubes and then cured the monomers within the filled cladding by thermal copolymerization in a heating bath. The monomer mixtures contained methyl methacrylate, long alkyl chain acrylics, and a small amount (5–10%) of crosslinking agents (e.g., diallyl phthalate and 1,3-butylene dimethacrylates). This process can obtain PLCs with large diameters of 5–15 mm and high heat resistance due to the addition of the crosslinking agents. However, the low production

rate and the use of large, complicated manufacturing equipment significantly raise the cost of the prepared PLCs, thereby limiting their commercial applications. The third process for preparing PLCs is to use a photopolymerization process.¹⁵⁻¹⁸ Recently, we have successfully prepared step-index and gradient-index PLCs by UV curing photopolymerization processes. UV curing photopolymerization has the advantages of low cost, high production rate, environmental considerations, and excellent physical properties of the coated products. Therefore, it has potentials to be a commercial process for producing polymer light conduits.

Although UV curing photopolymerization has been successfully used in preparing PLCs, their characteristics from different processes with similar compositions have not been compared. In this article, the properties of PLCs from the above three different manufacturing processes will be characterized and compared. Thermoplastic PMMA polymer light conduit, PLC1, and thermoset polymer light conduit, PLC2, prepared from thermal polymerization were obtained from Toray and Lumenyte, respectively. New PLCs, PLC3 and PLC4, were prepared by UV curing photopolymerization, which have similar compositions of ($A_xB_yC_z$) with thermal polymerization reported by Lumenyte.¹¹ Here, A is the monomer controlling optical properties, B is the monomer controlling the flexibility, and C is the crosslinking agent controlling heat resistance. The adjustment of A, B, or C and x, y, or z will change the properties of PLCs. In this study, A, B, and C are methyl methacrylate (MMA), 2-ethyl-hexyl acrylate (2-EHA), and polyethyleneglycol 200 diacrylate (PEGDA) or diallyl phthalate (DAP). The molecular structures, thermal properties, solution properties, and optical properties of the PLCs from different processes will be studied to address the characteristics from different manufacturing processes.

EXPERIMENTAL

Materials

PLC1 (diameter 3 mm, PMMA optical fiber) was obtained from Toray, Japan (product code: PGR-FB3000). PLC2 (inner diameter = 8.8 mm, outer diameter = 10.2 mm, FEP cladding) was obtained from Lumenyte International Co. (Model number: WN400). PLC3 and PLC4 were prepared using

Table I The Formulations of the Reactant Mixtures of PLC3 and PLC4

Sample	A ^a (%)	B ^a (%)	C ^a (%)	D ^a (%)	E ^a (%)
PLC3	70	30	5 ^b	0.75 ^b	0.5 ^b
PLC4	70	30	5 ^b	0.75 ^b	0.5 ^b

^a A: methyl methacrylate, B: 2-ethyl-hexyl acrylate, C: polyethylene glycol 200 diacrylate (for sample PLC3), diallyl phthalate (for sample PLC4), D: 1-hydroxycyclohexyl phenyl ketone (HCPK), E: isoctyl 3-mercaptopropionate (IOMC).

^b Based on the weight percentage of monomers (A + B).

the chemicals described as the following. Methyl methacrylate (MMA, 99%, Janssen Chimica), 2-ethyl-hexyl acrylate (2-EHA, > 99%, TCI), and polyethyleneglycol 200 diacrylate (PEGDA, Monomer-Polymer & Dajac Lab., Inc.), Diallyl Phthalate (DAP, > 98%, TCI) were purified by vacuum distillation. 1-hydroxycyclohexyl phenyl ketone (HCPK, TCI) and isoctyl 3-mercaptopropionate (IOMC, 99%, Pfaltz and Bauner) were used without further purification. Heat-shrinkable FEP tubes (refractive index = 1.338, inner diameter = 9.4 mm, outer diameter = 9.7 mm, shrink ratio = 1.6 : 1) were purchased from Zeus Ind., USA.

Preparation of Polymer Light Conduits

The reaction mixture for preparing PLC3 and PLC4 are listed in Table I. The monomers A (MMA), B (2-EHA), and C (PEGDA for PLC3 and DAP for PLC4) were well mixed and then poured into a heat-shrinkable FEP tube. HCPK and IOMC were used as the photoinitiator (*D*) and the chain transfer agent (*E*), respectively. Next, both ends were sealed with a PMMA pellet. In order to prevent the bubble formation due to the volume shrinkage of monomers after the UV curing photopolymerization, a two-stage polymerization and a post-cure process were used in this study. The mixture inside the FEP tube was polymerized by four UV lamps of 250 W each first and then by three black lamps of 40 W each. Following that, the PLCs were post-cured for 24 h by a heater to further ensure the close contact of the core and the cladding.

Characterization

Infrared spectra of polymer thin films prepared from KBr pellet were recorded at room tempera-

ture using a Bio-Rao Digilab Division FTS-40 FTIR spectrophotometer. The elemental analysis of the prepared polymer cores was performed by using a Perkin–Elmer 2400-CHN elemental analyzer. The gel content of the polymer structure was estimated as described below. Five weight percent of the prepared polymer core was put into THF solvent in a beaker. Next, the undissolved polymer was filtered out from THF solution and dried in a vacuum oven. The gel content was calculated from the difference between the fresh sample and the extracted sample. Thermal analysis, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) were then performed under flowing nitrogen using a DuPont Model 950 thermogravimetric analyzer and a DuPont Model 910 differential scanning calorimeter, respectively. Indium (156.4°C) standard was used to calibrate the accuracy of the measured transition points. Next, the sample was sealed in DSC pans and run at 20°C/min under nitrogen atmosphere. TGA runs were performed at a heating rate of 10°C/min under nitrogen atmosphere. The refractive index profiles of the prepared polymer light conduits 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 optical transmission of the prepared PLCs was tested by the metal–halide light source with a power of 150 W (General Electric, Inc., USA).

RESULTS AND DISCUSSION

Figures 1 and 2 show the FTIR absorption spectra of the polymer cores of PLC1–PLC4. The important absorption bands of these four absorption spectra are listed in Table II. The strong absorption bands appearing at 1147–1148 cm^{-1} indicate the presence of the C—O—C stretching vibration band. The absorption bands at 1733–1748 cm^{-1} are assigned to the C=O stretching vibration band. The bands appearing between 2800 and 3000 cm^{-1} are attributed to the alkyl chain C—H stretching vibration bands. Furthermore, the strong absorption bands at 1387–1393 cm^{-1} indicate the presence of the C—H bending vibration.

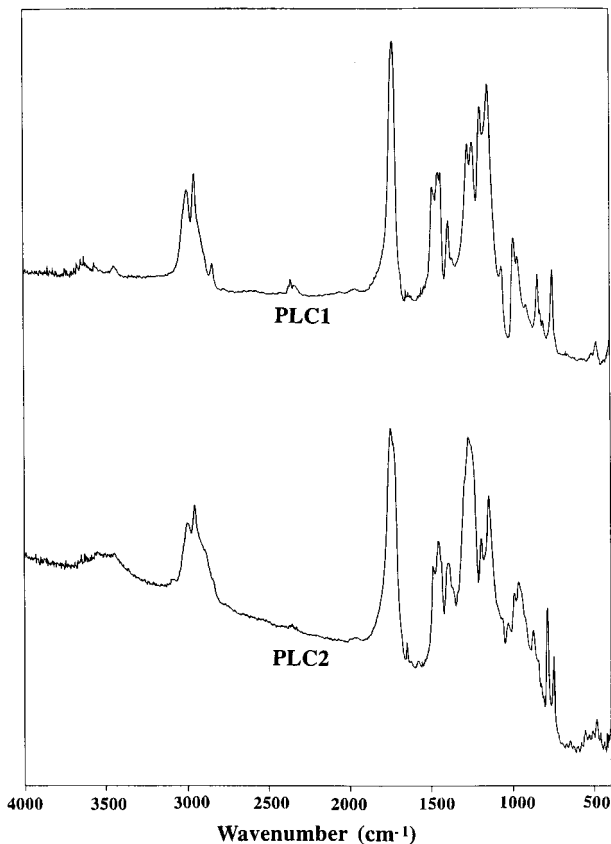


Figure 1 FTIR absorption spectra of PLC1 and PLC2.

The FTIR results shows the presence of the side chain of the methacrylic ester group. The elemental analysis results of the polymer cores of PLC1, PLC3, and PLC4 are in a fair agreement with the theoretical compositions, as shown in Table III. Furthermore, the polymer cores of PLC2 and PLC3 were only slightly soluble in various organic solvents such as acetone and THF. However, the polymer cores of PLC1 and PLC4 are completely soluble in THF. The estimated gel contents from the polymer cores of PLC1–PLC4 are 0%, 83%, 87%, and 0%, respectively, as shown in Table IV. This result implies the presence of the highly crosslinked polymer structures in the polymer cores of PLC2 and PLC3. However, PLC1 and PLC4 contain negligible crosslinked structures. The results of FTIR spectra, elemental analysis, and gel contents demonstrate that the structures of the PLCs PLC1, PLC2, and PLC3 were as originally expected. Although the FTIR and elemental results of PLC4 seem to have the expected polymer structure, the negligible gel content suggests the failed crosslinking reaction by the UV curing photopolymerization.

Figure 3 shows the TGA curves of the polymer cores of PLC1–PLC4 obtained in a nitrogen atmosphere at a heating rate of 10°C/min. The onset decomposition temperatures of PLC1–PLC4 are 337°C, 318°C, 338°C, and 304°C, respectively. The earlier decomposition of PLC2 core below 200°C indicates the existence of a small molecule additive in PLC2 (e.g., plasticizer). The poorer thermal stability of PLC4 than those of PLC1 and PLC3 provides another evidence of the uncrosslinked polymer structure. Although the incorporation of the PEGDA segment into the PMMA backbone enhanced the thermal stability, the insertion of the 2-EHA segment decreased the thermal stability. Hence, PLC1 and PLC3 showed comparable thermal stability. Figure 4 shows the DSC curves of PLC1–PLC4 obtained in a nitrogen atmosphere at a heating rate of 20°C/min. The glass transition temperatures (T_g) of PLC1–PLC4 are 118°C, –25°C, 58°C, and 61°C, respectively. The comparison of the T_g between PLC1 and PLC3 suggests that the insertion of 30% of 2-EHA and 5% of PEGDA into the polymer backbone significantly reduced T_g from 118°C to 58°C. The broad

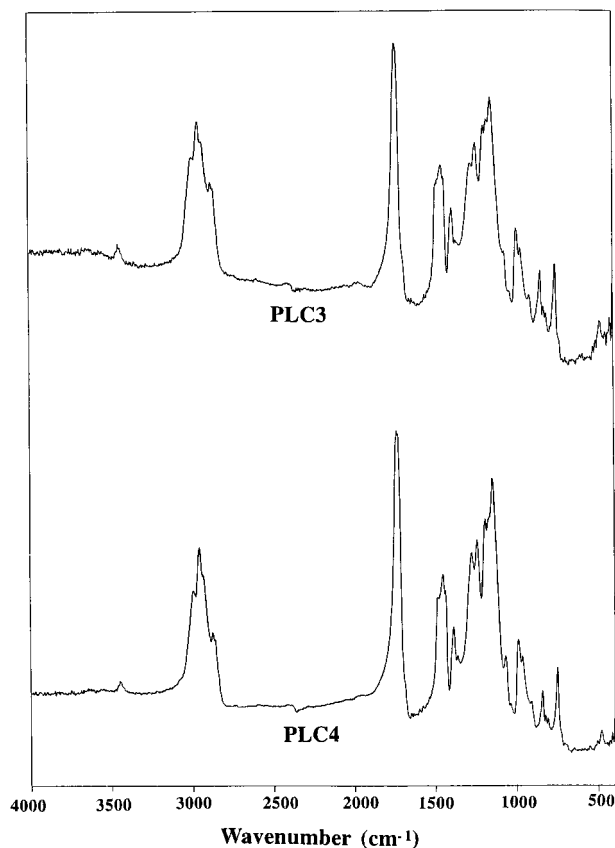


Figure 2 FTIR absorption spectra of PLC3 and PLC4.

Table II Assignment of the FTIR Spectra of PLC1-PLC4

Sample	C—O—C Stretching Vibration	C=O Stretching Vibration	C—H Bending Vibration	C—H Stretching Vibration
PLC1	1148	1733	1389	2843, 2952, 3000
PLC2	1148	1748	1393	2955, 3006
PLC3	1148	1735	1387	2877, 2956, 2991
PLC4	1147	1735	1388	2877, 2956, 2993

Data are in cm^{-1} .

thermal transition of PLC2 with T_g at -25°C provides another evidence of the small molecule additive (e.g., plasticizer), in this polymer core. The flexibility of the PLC is largely determined by the T_g of the polymer core. Hence, the order of the flexibility of the PLCs is $\text{PLC2} > \text{PLC3} > \text{PLC4} > \text{PLC1}$.

The refractive indices of the polymer cores of PLC1–PLC4 measured by the York P102 profile analyzer range from 1.490 to 1.498, as shown in Table IV. The NA of the PLCs calculated according to eq. (1) ranged between 0.444 and 0.674, as shown in Table IV. The much larger numerical apertures of PLC2–PLC4 than that of PLC1 indicate that PLC2–PLC4 can have wide angle applications. Furthermore, the optical properties of the polymer light conduits PLC1–PLC4 were further tested using the metal–halide light source with a power of 150 W at the one end of the polymer light conduit. From the visual inspection of the light illuminated from the core–cladding boundary, PLC1 can transmit more than 30 m but with low illumination intensity, since it has the smallest diameter of 3 mm. PLC2, PLC3, and PLC4 can transmit around 15 m, 12 m, and 10 m, respectively, with a high illumination intensity. PLC2 manufactured from the thermal polymerization have better optical characteristics as a PLC than PLC3 and PLC4. However, the complicated manufacturing equipment resulted in a much higher cost of PLC2 than those of PLC3 and PLC4 from

the UV curing photopolymerization. The adjustment of the reaction mixture composition and the process conditions might also enhance the optical properties of the PLCs prepared the UV curing photopolymerization.

DISCUSSION

Polymer Structures of Polymer Light Conduits Prepared by Different Manufacturing Processes

As expected, PLC1 prepared from the bulk polymerization and melt spinning processes is consisted mostly of methyl methacrylate as the polymer core. PLC2 contains the acrylic moiety from the FTIR spectrum and also has the crosslinked polymer structure from the solubility test. However, it may also contain the plasticizer additive from the TGA and DSC results, which increases the flexibility but decreases the thermal stability. The results of FTIR, elemental analysis, solubility, and thermal characterization show the successful preparation of PLC3 by UV curing photopolymerization. However, PLC4 does not have the crosslinked structure as expected. This suggests that the crosslinking agent poly(ethylene glycol) 200 diacrylate is more effective than diallyl phthalate under the current polymerization conditions. The adjustment of the composition of the monomer mixtures, the type and amount of the

Table III The Elemental Analysis Results of the Polymer Cores PLC1–PLC4

Sample	Theoretical Compositions	Experimental Compositions
PLC1	C : 59.98%, H : 8.05%	C : 58.17%, H : 7.79%
PLC2	—	C : 55.24%, H : 7.27%
PLC3	C : 63.12%, H : 8.84%	C : 63.11%, H : 8.85%
PLC4	C : 63.20%, H : 8.72%	C : 63.11%, H : 8.85%

Table IV The Properties of the Polymer Cores PLC1–PLC4

Sample	Gel Content (%)	T_d (°C)	T_g (°C)	n	NA
PLC1	0	337	118	1.490	0.444 ^a
PLC2	83	318	-25	1.498	0.674
PLC3	87	338	58	1.496	0.669
PLC4	0	304	61	1.497	0.671

^a Data taken from Toray catalog.

photoinitiator, the light intensity of the UV light, and the exposed time could lead to the successful crosslinking reaction using diallyl phthalate as the crosslinking agent. This will be future work since the objective of the present study is to compare the PLCs prepared from different manufacturing processes using similar compositions.

Applications of the Polymer Light Conduits PLC1–PLC4

The transmitted distance, the illumination intensity, the flexibility, and cost are the four major factors considered for the commercial applications of the PLCs. PLC1 can transmit the longest distance and have the lowest cost in the studied PLCs among PLC1–PLC4. However, it also has the properties of the poor illumination intensity and flexibility, which limit its application. PLC2 can be applied as a PLC with the characteristics of

medium transmitted distance, high illumination intensity, and excellent flexibility. However, it also has the disadvantages of the high cost and poor thermal stability. For the applications of PLC3 and PLC4, it can be applied as PLCs with the characteristics of low cost and high illumination intensity but within short distance and medium flexibility.

CONCLUSIONS

We have compared the polymer structures and properties of the polymer light conduits prepared from the bulk polymerization and melt spinning process (PLC1), the thermal polymerization (PLC2), and UV curing photopolymerization (PLC3–PLC4) of a monomer mixture in a FEP tube. New polymer light conduit PLC3 was successfully prepared by UV curing photopolymeriza-

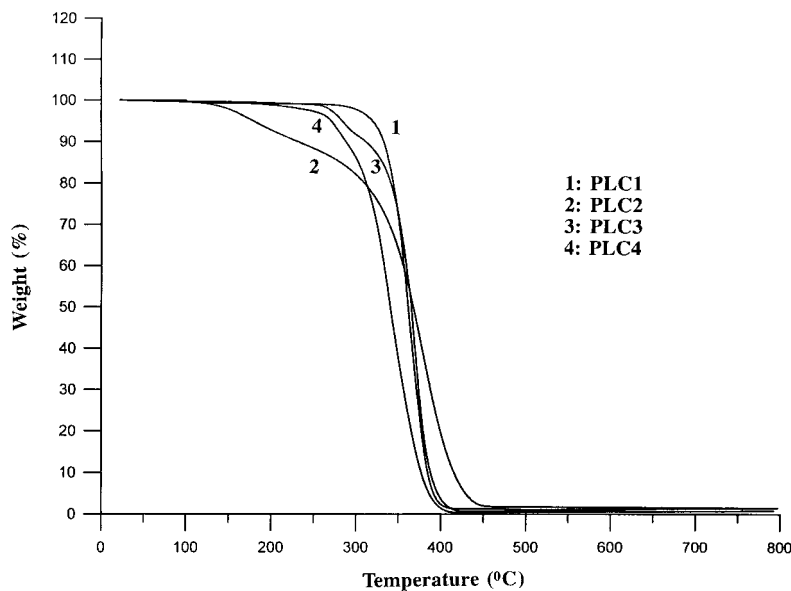


Figure 3 TGA curves of PLC1–PLC4 obtained in flowing N_2 at a heating rate of $10^\circ\text{C}/\text{min}$.

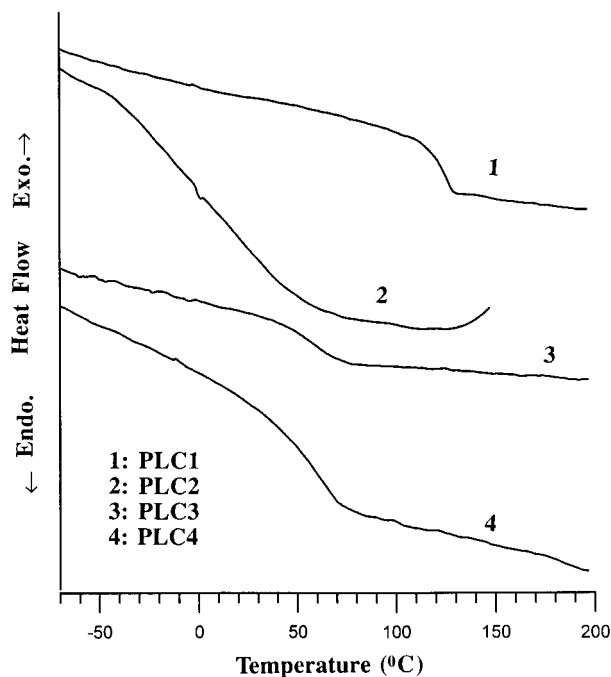


Figure 4 DSC curves of PLC1–PLC4 obtained in flowing N_2 at a heating rate of $20^\circ\text{C}/\text{min}$.

tion. All four PLCs contain acrylic moiety. The polymer core of PLC1 contains mostly methyl methacrylic moiety without the crosslinked structure. PLC2 and PLC3 have the crosslinked polymer structures as expected. However, PLC2 may contain the plasticizer additives, which resulted in excellent flexibility but poor thermal stability. Although the FTIR and elemental analysis results of PLC4 seem to have the expected polymer structure, the analysis of the solubility and thermal stability show the unsuccessful crosslinking reaction for diallyl phthalate under the present UV-photopolymerization process. The flexibilities of PLC2 and PLC3 are significantly improved from that of PLC1 due to the insertion of a plasticizer and the long alkyl chain monomer 2-EHA, respectively. The much larger numerical apertures of PLC2–PLC4 than that of PLC1 suggest that PLC2–PLC4 can have a wide angle application. The transmitted distance of PLC1 is larger than those of PLC2–PLC4. However, the illumination intensity of PLC1 is worse than those of PLC2–PLC4. This result indicates that PLC1 is suitable for the applications of PLCs with the characteristics of long distance and low illumination intensity, while PLC2–PLC4 are suitable for short dis-

tance and high illumination intensity applications.

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