

Synthesis and characterization of polymer light conduits

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Summary

Large diameter polymer light conduits are prepared for the first time by UV-curing. The polymer cores of the polymer light conduits are prepared from the copolymerization of various monomer mixtures in FEP tubes by UV curing, where FEP is used as the polymer cladding. The monomer mixtures consist of a multifunctional monomer for adjusting the heat resistance of the polymer cores and a monofunctional monomer for adjusting the flexibility. Experimental results indicate that the properties of the prepared polymer light conduits can be significantly modified by the formulations of the reactant mixtures. The onset thermal decomposition temperatures of the prepared polymer cores are 50°C to 79°C higher than that of the PMMA core. The glass transition temperatures and the refractive indices of the prepared polymer cores decrease from 78°C to -34°C and 1.490 to 1.474, respectively, when the contents of 2-ethyl-hexyl acrylate in the monomer mixtures increase from 0% to 70%. The prepared polymer light conduits conduits have large numerical apertures suitable for wide angle illumination applications.

Introduction

Light conduits are used in a wide variety of applications (1-9), e.g., local area network, light guides, display, and illumination. Many efforts have been made to provide inexpensive, flexible, and durable light guides for general illumination applications. Polymer light conduits have advantages over glass materials due to large diameters, light weights, excellent flexibilities, and capability to transmit large quantities of light under ordinary conditions.

A polymer light conduit consists of a polymer core and a polymer cladding, in which the refractive index of the cladding is 2-5% smaller than that of the core. Conventional polymer light conduits such as poly(methyl methacrylate) and polystyrene have a major limitation of poor heat resistance. The maximum temperature at which poly(methyl methacrylate) and polystyrene can be used is around 80°C. When used at a temperature higher than about 80°C, their microstructures are deformed. This deformity subsequently results in them to use only for short distance applications and low illumination intensity. Two methods used to improve the heat resistance of polymer light conduits are (a) the modification of the polymer core structures by inserting the heat-resisting segment (6,7), and (b) the improvement of the heat resistance of the polymer

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cladding(8). However, these approaches usually require preparing a special monomer or complicated synthetic scheme, thereby increasing the manufacturing cost. Thermal copolymerization of the monomer mixtures in FEP tubes is used to prepare large diameter polymer light conduits with high heat-resistance (9). However, the low production rate and high cost of the manufacturing process largely raise the cost of the prepared polymer light conduits and thereby limit their applications.

UV curing has been used extensively in surface coating due to the advantages of low cost, high production rate, environmental consideration, and excellent physical properties of the coated products. In this study, UV-curing is used to prepare large diameter polymer light conduits. To the best of our knowledge, this is the first time to use UV-curing for preparing polymer light conduits. The polymer cores of the polymer light conduit are prepared from a monomer mixture consisted of a multifunctional monomer, e.g., polyethyleneglycol 200 diacrylate (PEGDA), and monofunctional monomers, e.g., 2-ethyl-hexyl acrylate(2-EHA) while the polymer cladding is made of fluorinated ethylene propylene (FEP). The multifunctional monomer is polymerized to provide the crosslinked structure for enhancing the heat resistance. Simultaneously, the monofunctional monomer with a long alkyl chain is polymerized to improve the flexibilities of the prepared polymer light conduits. Hence, adjustment of the formulations of the multifunctional monomer and the monofunctional monomer subsequently produces a polymer light conduit with good heat resistance and flexibility. Furthermore, effects of the different compositions of MMA, 2-EHA, and PEGDA on the thermal stabilities, flexibilities, refractive indices, and numerical apertures of the prepared polymeric light conduits are also investigated in this study.

Experimental

Materials

Methyl methacrylate (MMA) (99%, Janssen Chimica), 2-ethyl-hexyl acrylate (2-EHA) (>99%, TCI), and polyethyleneglycol 200 diacrylate (Monomer-Polymer&Dajac Lab., Inc.) were purified by vacuum distillation. 1-hydroxycyclohexyl phenyl ketone (HCPK, TCI) and isooctyl 3-mercaptopropionate (IOMC, 99%, Pfaltz & Bauner) were used without further purification. The refractive indices of PMMA, Poly(PEGDA), and P(2-EHA) are 1.490, 1.509, and 1.467, respectively. 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

Different MMA, 2-EHA and PEGDA compositions were well mixed in a 3-neck reactor under nitrogen atmosphere. HCPK and IOMC were used as the photoinitiator and the chain transfer agent, respectively. The monomer mixture was then poured into a heat-shrinkable FEP tube under nitrogen atmosphere. Next, both ends were sealed with a PMMA pellet. The mixture inside the FEP tube was polymerized by two UV lamps of 60 W/cm each. The transfer speed of the tube was 3 m/hr. Following that, the polymer light conduits were post-cured at 120⁰C for 20 hours in an oven. The compositions of S1-S11 samples are listed in Table 1.

Table 1. The formulations of the reactant mixtures.

Sample	MMA (%)	2-EHA (%)	PEGDA (%)	HCPK (%)	IOMC (ppm)
S1	70	0	30	0.75	350
S2	60	10	30	0.75	350
S3	50	20	30	0.75	350
S4	40	30	30	0.75	350
S5	30	40	30	0.75	350
S6	20	50	30	0.75	350
S7	10	60	30	0.75	350
S8	0	70	30	0.75	350
S9(PMMA)	100	0	0	0.75	350
S10(poly(2-EHA))	0	100	0	0.75	350
S11(poly(PEGDA))	0	0	100	0.75	350

Characterization

Infrared spectra of polymer thin films prepared from KBr pellet were recorded at room temperature using a Bio-Rad Digilab Division FTS-60 FTIR spectrophotometer. The elemental analysis of the prepared polymer cores was performed by using Perkin-Elmer 2400-CHN elemental analyzer. The gel content of the polymer structure was estimated as described below. 1 wt% 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 951 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 10°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 equation (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 polymer light conduits was tested by the metal-halide light source with a power of 150 W (General Electric, Inc., USA).

Results and Discussion

Figure 1 shows the FTIR absorption spectrum of the polymer core S4. The strong absorption bands appearing at 1142 cm^{-1} and 1168 cm^{-1} indicate the presence of the C-O-C stretching vibration band of the PEGDA segment. The absorption band at

1736 cm^{-1} is assigned to the C=O stretching vibration band. The bands appearing at 2873 cm^{-1} and 2932 cm^{-1} are attributed to the alkyl chain C-H stretching vibration bands. The elemental analysis results of the prepared polymer cores correlated sufficiently with the theoretical compositions, as shown in Table 2. Furthermore, the prepared polymer cores S1-S8 were only slightly soluble in various organic solvents such as acetone and THF. The estimated gel contents from the prepared polymer cores S1-S8 and S11 ranged between 79% and 100%, as shown in Table 3. This result implies the presence of the highly crosslinked polymer structures in the prepared polymer cores. The results of FTIR spectrum, elemental analysis, and gel content demonstrate that the structures of the prepared polymer light conduits were as originally designed.

Figure 2 shows the TGA curves of the prepared polymer cores S4, and S9-S11 obtained in a nitrogen atmosphere at a heating rate of 10 $^{\circ}$ C/min. The onset decomposition temperatures of S4, S9 (PMMA), S10 (poly(2-EHA)), and S11 (poly(PEGDA)) are 329 $^{\circ}$ C, 272 $^{\circ}$ C, 308 $^{\circ}$ C, and 381 $^{\circ}$ C, respectively. Since poly(2-EHA) and poly(PEGDA) have higher onset decomposition temperatures than PMMA, the incorporation of 2-EHA and PEGDA into the PMMA backbone results in the higher onset decomposition temperature of S4 than that of PMMA. Moreover, the prepared polymer cores S1-S8 all have higher onset decomposition temperatures than PMMA, as shown in Table 3. This reveals that the incorporation of the crosslinked structure into the polymer backbone enhanced the thermal stability of PMMA core. The higher onset decomposition temperature of poly(2-EHA) than that of PMMA was probably due to the higher molecular weight of poly(2-EHA) ($M_w = 34 \times 10^4$, $M_n = 4.9 \times 10^4$) than that of PMMA ($M_w = 8.8 \times 10^4$, $M_n = 2 \times 10^4$). Figure 3 shows the DSC curves of S4, S9, S10, and S11 obtained in a nitrogen atmosphere at a heating rate of 10 $^{\circ}$ C/min. The glass transition temperatures (T_g) of S4, PMMA, poly(2-EHA), and poly(PEGDA) are 23 $^{\circ}$ C, 110 $^{\circ}$ C, -63 $^{\circ}$ C, and 31 $^{\circ}$ C, respectively. Poly(2-EHA) and poly(PEGDA) have a much lower T_g than S9. Hence, the insertion of 30% of 2-EHA and 30% of PEGDA into the polymer backbone significantly reduced T_g from 110 $^{\circ}$ C to 23 $^{\circ}$ C. Furthermore, the T_g of the S1-S8 decreased from 78 $^{\circ}$ C to -34 $^{\circ}$ C when the content of 2-EHA increased from 0% to 70%, as shown in Table 3. The significantly lower glass transition temperatures of the prepared polymer cores S1-S8 than that of PMMA indicate that the former has a superior flexibility to PMMA.

The refractive indices of the prepared polymer cores S1-S8 measured by York P102 profile analyzer range from 1.474 to 1.490, as shown in Table 3. The decrease of the refractive index with an increasing in the fraction of 2-EHA occurred because the poly(2-EHA) has a lower refractive index of 1.467 than that of PMMA ($n = 1.49$). This result implies that the refractive index of the polymer core can be adjusted through molecular design. The numerical apertures (NA) of the polymer light conduits calculated according to eq. (1) ranged between 0.602 and 0.698, as shown in Table 3. These NA values were significantly larger than those of glass light conduits, which normally range between 0.2 and 0.3. Furthermore, the optical transmission test of the prepared polymer light conduits S1-S8 showed that they maintained at 45% of the original light intensity after transmitted for 10 m. Hence, the prepared polymer light conduits have potential applications for wide-angle illumination.

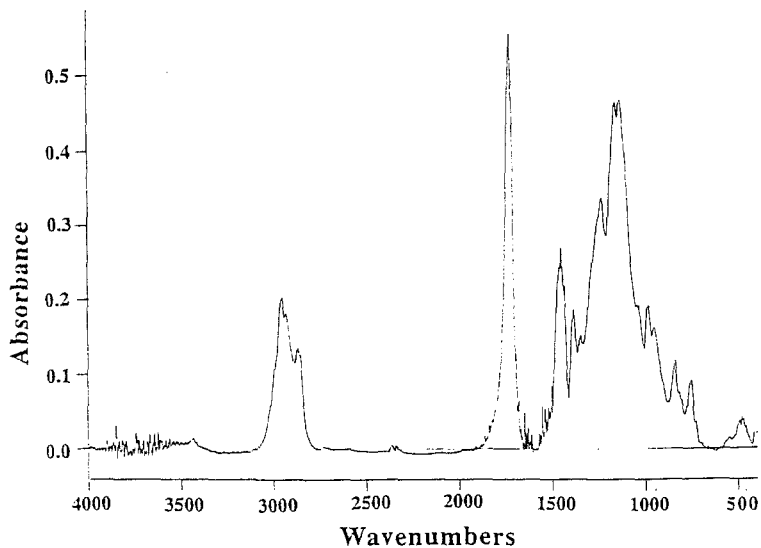


Figure 1. FTIR absorption spectrum of the prepared polymer core S4.

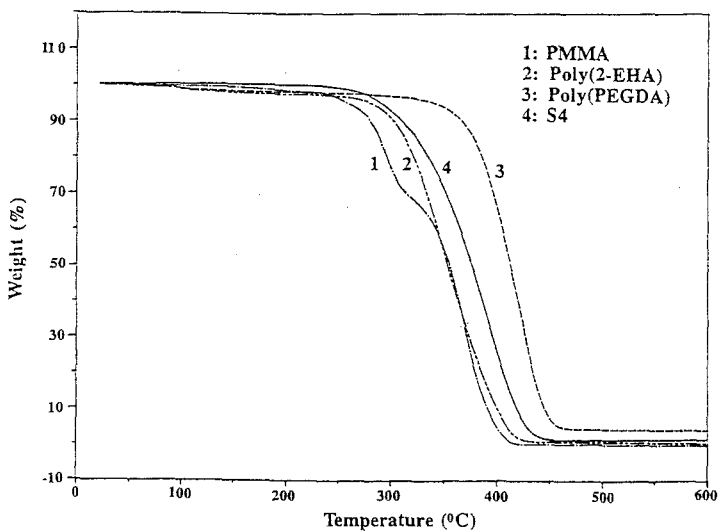


Figure 2. TGA curves of PMMA, poly(2-EHA), poly(PEGDA), and S4 obtained in flowing nitrogen at a heating rate of 10°C/min.

Table 2. The elemental analysis results of the prepared polymer cores S1-S8.

Sample	Theoretical Compositions	Experimental Compositions
S1	$[(C_5H_8O_2)_{0.7}(C_{14}H_{22}O_7)_{0.3}]$ C:57.52%, H:7.65%	C:58.27%, H:7.88%
S2	$[(C_5H_8O_2)_{0.6}(C_{11}H_{20}O_2)_{0.1}(C_{14}H_{22}O_7)_{0.3}]$ C:58.92%, H:7.98%	C:59.57%, H:8.22%
S3	$[(C_5H_8O_2)_{0.5}(C_{11}H_{20}O_2)_{0.2}(C_{14}H_{22}O_7)_{0.3}]$ C:60.19%, H:8.29%	C:60.74%, H:8.51%
S4	$[(C_5H_8O_2)_{0.4}(C_{11}H_{20}O_2)_{0.3}(C_{14}H_{22}O_7)_{0.3}]$ C:61.34%, H:8.56%	C:61.90%, H:8.79%
S5	$[(C_5H_8O_2)_{0.3}(C_{11}H_{20}O_2)_{0.4}(C_{14}H_{22}O_7)_{0.3}]$ C:62.39%, H:8.81%	C:62.84%, H:8.97%
S6	$[(C_5H_8O_2)_{0.2}(C_{11}H_{20}O_2)_{0.5}(C_{14}H_{22}O_7)_{0.3}]$ C:63.35%, H:9.04%	C:63.32%, H:9.28%
S7	$[(C_5H_8O_2)_{0.1}(C_{11}H_{20}O_2)_{0.6}(C_{14}H_{22}O_7)_{0.3}]$ C:64.24%, H:9.25%	C:65.28%, H:9.60%
S8	$[(C_{11}H_{20}O_2)_{0.7}(C_{14}H_{22}O_7)_{0.3}]$ C:65.06%, H:9.45%	C:66.16%, H:9.85%

Table 3. The properties of the prepared polymer cores

Sample	Gel Content (%)	T _d (°C)	T _g (°C)	n	NA
S1	83	325	78	1.490	0.656
S2	79	322	59	1.487	0.649
S3	85	331	30	1.485	0.644
S4	77	329	23	1.481	0.635
S5	82	348	20	1.480	0.630
S6	79	349	-14	1.478	0.629
S7	77	349	-27	1.475	0.620
S8	82	350	-34	1.474	0.618
S9	0	272	110	1.490	0.656
S10	0	308	-63	1.467	0.602
S11	100	381	31	1.509	0.698

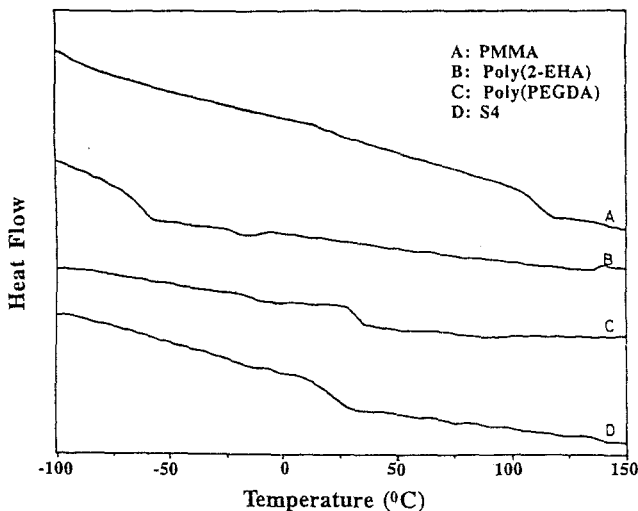


Figure 3. DSC curves of PMMA, poly(2-EHA), poly(PEGDA), and S4 obtained in flowing nitrogen at a heating rate of 10°C/min.

Conclusions

Polymer light conduits are successfully prepared for the first time from the copolymerization of the monomer mixtures in a FEP tube by UV-curing. The properties of the prepared polymer light conduits were significantly modified by the formulations of the reactant mixtures. The thermal stability and flexibility of the prepared polymer light conduits were largely enhanced by the incorporation of the crosslinked structure and the flexible segment into the polymer structure, respectively. Furthermore, the numerical apertures of the prepared polymer light conduits ranged from 0.602 to 0.698; which would be suitable for wide angle illumination applications.

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