

AN EPOXY/(METHYL METHACRYLATE) INTERPENETRATING POLYMER NETWORK FOR NONLINEAR OPTICS*

Ling-zhi Zhang^{a**}, Zhi-gang Cai^b, Quan-dong Ying^b and Zhao-xi Liang^a

^a Institute of Polymer Science, Zhongshan University, Guangzhou 510275, China

^b State Key Lab of Ultrafast Laser Spectroscopy, Zhongshan University, Guangzhou 510275, China

Abstract An interpenetrating polymer networks (IPN) consisting of an epoxy-based polymer network and a polymethyl methacrylate network were synthesized and characterized. The IPN showed only one T_g , and hence a homogeneous-phase morphology was suggested. The second-order nonlinear optical coefficient (d_{33}) of the IPN was measured to be 1.72×10^{-7} esu. The study of NLO temporal stability at room temperature and elevated temperature (100°C) indicated that the IPN exhibits a high stability in the dipole orientation due to the permanent entanglements of two component networks in the IPN system. Long-term stability of second harmonic coefficients was observed at room temperature for more than 1000 h.

Keywords Interpenetrating polymer networks, Second-order optical nonlinearity, Epoxy-based polymer, Polymethyl methacrylate

INTRODUCTION

In the last decade, an extensive effort has been dedicated to develop second-order nonlinear optical polymer materials for potential applications especially in electrooptic modulation and frequency conversion. Compared with their inorganic counterparts, polymers offer the advantages of large susceptibilities, high laser damage threshold, faster response time and infinite potential for molecular structure modifications. Polymers that exhibit second-order NLO properties require a noncentrosymmetric arrangement of the NLO chromophores. This can be obtained by poling the chromophores with a commonly used corona electric field. And other methods such as all-optical poling^[1, 2] and photo-assisted poling^[3] were also reported to achieve the orientation of chromophores. But the dipole orientation of chromophores will relax over time or at elevated temperatures. Therefore, the NLO polymers adopted for devices must have a stable and high second-order NLO response. Many researches have focused on improving the NLO stability by synthesizing high T_g polymers, such as NLO polyimides^[4, 5] or by creating a thermally crosslinked^[6] or photocrosslinked^[7, 8] polymer networks while poling.

The interpenetrating polymer networks (IPN) is known to be able to suppress the creep and flow phenomena in polymers^[9]. The motion of each polymer in the IPN is reduced by the entanglements between the networks. Second-order NLO IPNs have been developed to improve the stability of chromophore orientation^[10, 11].

* This work was supported by the Natural Science Foundation of Guangdong Province (980279, 980346) and the National Natural Science Foundation of China (19604015).

** Corresponding author: Ling-zhi Zhang (张立志), E-mail: stils02@zsu.edu.cn

Received June 10, 1998

In this paper, an IPN consisting of thermally crosslinked epoxy-based polymer incorporating acryloyl groups and polymethyl methacrylate formed by TDI/methyl methacrylate with hydroxyl groups in the side chain was designed to improve the stability of dipolar orientation after poling. The synthesis and characterization of the thermal and NLO properties of the IPN were also described.

EXPERIMENTAL

Materials

Toluene diisocyanate (TDI; 80, 20 mixture of 2, 4 and 2, 6 isomers) and glycidyl methacrylate (GMA, Aldrich) were used as obtained. 4-Nitro-4'-hydroxyl azobenzene (NHA) and the epoxy-based polymer (PENAA) were synthesized by the procedure described previously^[12, 13]. All the solvents, CHCl_3 , tetrahydrofuran (THF), 1,4-dioxane (DOX) were purified before use.

Synthesis of Monomer MAZ

GMA (8.4 g, 0.059 mol) and NHA (10 g, 0.041 mol) were dissolved in 40 mL of THF/DOX ($V/V = 1/1$). Then 2 mL Et_3N and 0.1 g 2,6-di-*tert*-butyl-4-methylphenol were added into the solution. The mixture was stirred for 2 days at 70 °C. The solution was concentrated and diluted with methanol. The orange solid was precipitated from water and recrystallized from 95% ethanol to yield monomer MAZ: 11.7 g, 75%; m.p. 136~137 °C.

$^1\text{H-NMR}$ (acetone) δ : 8.37 (*d*, 2H, aromatic, *ortho* to NO_2), 7.99 (*m*, 4H, on the benzene ring, *ortho* to $-\text{N}=\text{N}-$), 7.06 (*t*, 2H, aromatic, *ortho* to the O), 5.65 (*s*, 1H, $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CO}_2-$, *cis* to $-\text{CH}_3$), 6.18 (*s*, 1H, $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CO}_2-$, *trans* to $-\text{CH}_3$), 4.42 (*t*, 2H, $-\text{CH}_2\text{O}$), 4.37 (*t*, 1H, $-\text{CH}-$), 4.17 (*t*, 2H, $-\text{CH}_2\text{O}_2\text{C}(\text{CH}_3)=\text{CH}_2$), 1.98 (*s*, 3H, $-\text{CH}_3$), 1.64 (*s*, 1H, $-\text{OH}$).

IR (KBr): 3479 cm^{-1} ($-\text{OH}$), 1693 cm^{-1} ($-\text{C}=\text{O}$), 1630 cm^{-1} ($-\text{C}=\text{C}-$), 1518, 1342 cm^{-1} ($-\text{NO}_2$).

Elementary anal.: Calc. for $(\text{C}_{19}\text{H}_{18}\text{N}_3\text{O}_6)$ %: C 59.37, H 4.72, N 10.93, Found: C 58.80, H 4.86, N 10.42.

Synthesis of Copolymer P(MMA-co-MAZ)

The monomer MAZ (3.22 g, 8.39 mmol) was dissolved in 15 mL chlorobenzene/acetophenone ($V/V = 1/2$). The solution was heated to 70 °C under argon atmosphere. Methyl methacrylate (0.4 g, 4.0 mmol) solution of 1,4-dioxane was injected into the solution. 4 mL acetophenone/chlorobenzene ($V/V = 1/1$) solution of 0.1 g AIBN was then injected into the above solution four times within 2 h. The mixture was stirred for another 20 h. The polymer was isolated by precipitating into petroleum ether, and reprecipitated twice from CH_2Cl_2 solution into petroleum ether/ethyl ether ($V/V = 3/1$) to yield red orange solid P(MMA-co-MAZ): 2.1 g, 58%; $T_g = 111$ °C, $T_d = 285$ °C, $\lambda_{\text{max}} = 368$ nm.

$^1\text{H-NMR}$ (CDCl_3) δ : 8.296 (*s*, aromatic, *ortho* to NO_2), 7.897 (*s*, on the benzene ring, *ortho* to $-\text{N}=\text{N}-$), 7.017 (*s*, aromatic, *ortho* to the O), 4.316~4.125 (*m*, $-\text{CH}-\text{CH}_2\text{OOC}-$ and $-\text{OCH}_3$ of MMA), 3.579 (*s*, $-\text{CH}_2-\text{O}-\text{Ar}$), 1.923 (*s*, $-\text{OH}$ and $-\text{CH}_2-\text{C}(\text{CH}_3)-\text{C}=\text{O}$), 1.254~0.856 (*m*, $-\text{CH}_2-\text{C}(\text{CH}_3)-\text{C}=\text{O}$).

IR (KBr): 3465 cm^{-1} ($-\text{OH}$), 1728 cm^{-1} ($-\text{C}=\text{O}$), 1525 and 1342 cm^{-1} ($-\text{NO}_2$), 1250 cm^{-1} ($\text{C}-\text{O}$).

Elemental anal.: Calc. for $[(\text{C}_5\text{H}_8\text{O}_2)_{0.5}(\text{C}_{19}\text{H}_{18}\text{N}_3\text{O}_6)_{0.5}]$ (%): C 59.50, H 5.41, N 8.70, Found: C 58.71, H 5.45, N 8.67.

GPC: $M_n = 3738$, $M_w = 6920$.

Instrumentation

$^1\text{H-NMR}$ spectra were obtained on a Varian Unity INOVA 500 NB NMR spectrometer. IR spectra were recorded on a Nicolet 205 FTIR Spectrometer. Ultraviolet-visible spectra were taken on a

Shimadzu 240 Spectrophotometer. Elementary analysis was performed with a Perkin-Elmer 240 Elementary Analyzer. The number and weight average molecular weights of the polymer were determined with a Waters 208LC using THF as eluent. The GPC was calibrated with polystyrene standards. T_g was measured from differential scanning calorimeter (DSC) using a Perkin-Elmer DSC-7c at a heating rate of 10°C/min under nitrogen. The thermal degradation was measured on a TA instrument TGA with a heating rate of 10°C/min.

Film Preparation

The IPN was prepared by dissolving P(MMA-*co*-MAZ) (40 wt%), PENAA (60 wt%) and Et₃N (3 wt%) in DOX solvent. TDI (3.19 mmol, 4.5 mL) was then added (molar ratio of NCO/OH = 1.13/1). The final solution was then filtered through a 0.2 μm filter and spincoated onto the transparent glass, quartz and sodium chloride plates, respectively. The films were dried at 60°C under vacuum for 6 h. The typical thickness of the IPN films was 15 μm.

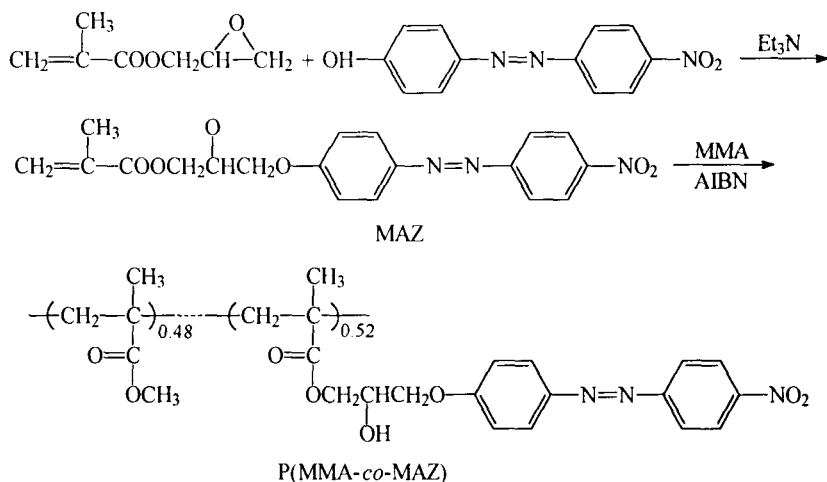
Poling and SHG Measurement

The poling was performed in a corona poling field at 8 kV. The distance between film surface and poling electrode was 1 cm. The temperature of polymer film was raised from ambient temperature to 160°C for 1 h, then the poled film was gradually cooled to 30°C to freeze the orientation. After 15 min, the SHG signal of the polymer film was measured relative to a quartz crystal. A mode-locked Nd:YAG laser beam (1064 nm) was used as basic light source. The polymer film was held at an angle of 45° to the incident laser beam, the output light was passed through a 532 nm filter and a IR cut filter and detected by a photo-multiplier. The experimental set-up was shown in our previous paper^[14].

RESULTS AND DISCUSSION

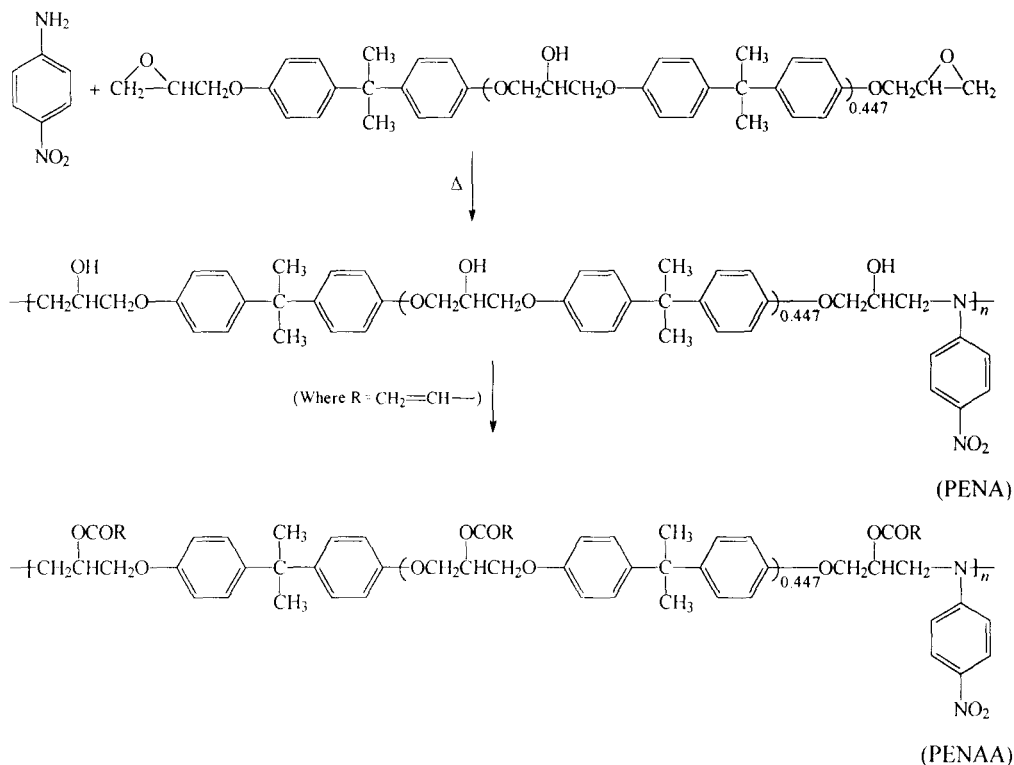
Synthesis of Functionalized Polymers

The monomer MAZ and the copolymer P(MMA-*co*-MAZ) were synthesized according to Scheme 1. The vinyl monomer carrying chromophores with —NO₂ like MAZ are rather difficult to undergo free radical polymerization because of the inhibiting effect of the —NO₂ group. When 4 mL acetophenone/chlorobenzene (v/v = 1/1) solution of 0.1 g AIBN was added in batches at 30 min intervals, MAZ and MMA underwent copolymerization much more easily. The chromophore content of P(MMA-*co*-MAZ) determined by ¹H-NMR is 52 mol%, which coincides well with the value calculated from elementary analysis.



Scheme 1

The synthesis of acryloyl functionalized epoxy-based polymer PENAA involved two steps (Scheme 2). In the first step, the nucleophilic 4-nitroaniline initiated the ring opening polymerization of E₄₄ epoxy resin. The second step involved the attachment of the crosslinkable acryloyl groups through esterification of the hydroxyl groups of epoxy polymer PENA. PENAA has a T_g of 83 °C.



Formation and Characterization of IPNs

In order to select the optimum crosslinking temperature, the crosslinking of the IPN film was monitored by DSC scans. The thermogram of the IPN revealed a strong exothermic peak at 104–175 °C (Fig. 1). Therefore, a temperature of 160 °C was selected as the poling and crosslinking temperature. After poling and curing were performed simultaneously at 160 °C for 1 h, IPN was formed. The DSC scan of the poled/cured samples are also shown in Fig. 1, which indicates that IPN has only one T_g appeared at 115 °C.

FTIR spectra provided further evidence for the IPN formation, as shown in Fig. 2. After curing at 160 °C for 1 h, the absorption of the isocyanate groups at 2270 cm⁻¹ completely disappeared, indicating the formation of the polymethyl methacrylate network and the epoxy-based polymer network simultaneously through a free radical polymerization of the acryloyl groups. Although the absorption band of acryloyl double bond at 1630 cm⁻¹ overlaps with the absorption of benzene groups in the polymer structure, a shift of C=O stretching frequency to higher wave-number is consistent with a loss in conjugation due to the reaction of the double bond^[15]. The IR spectral results indicate that IPN is formed through different reaction mechanisms upon heating. The microscopic observation reveals that the poled/cured IPN samples have excellent optical quality. The homogeneity of the samples is also suggested by the single T_g observed from DSC scan.

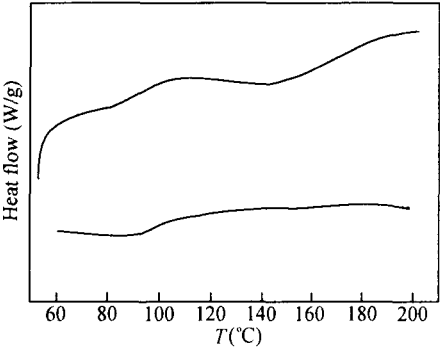


Fig. 1 DSC cures of the IPN samples before (top) and after (bottom) curing

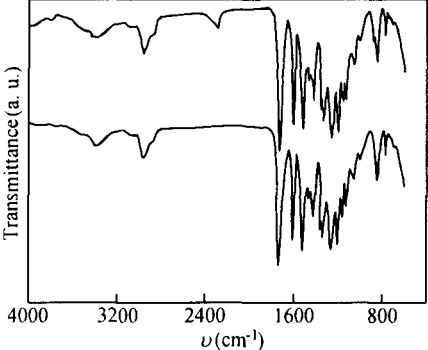


Fig. 2 IR spectra of the IPN samples before (top) and after (bottom) curing

Before and after poling/curing of the IPN, their UV-vis spectra show an absorption peak existing at $\lambda_{\text{max}} \approx 370 \text{ nm}$ (Fig. 3). However, the decrease of absorbance after poling is attributed to the chromophore alignment along the field direction during poling, causing the decrease of absorbance of the incident light perpendicular to the film. The order parameter (ϕ) is defined by $\phi = 1 - A_p/A_o$, where A_p and A_o are the absorbance of the poled and unpoled films, respectively. From Fig. 3, ϕ of the poled/cured IPN film was found to be 0.32.

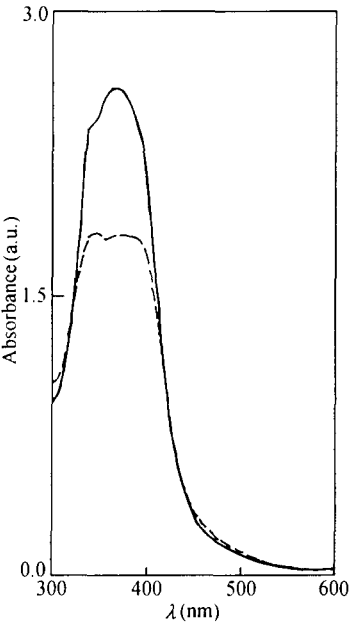


Fig. 3 Absorption spectra of the IPN sample (—) pristine, (---) poled and cured

SHG Measurements

The SHG measurements resulted in a d_{33} value of 1.72×10^{-7} esu for the poled/cured IPN films. The temporal stability of SHG signal for the IPN system was studied by plotting $d_{33}(t)/d_{33}(0)$ as a function of time at room temperature and elevated temperature (100 °C) as shown in Fig. 4. About 94% and 61% of the initial d_{33} value still remained after 1000 h and 350 min at room temperature and 100 °C, respectively.

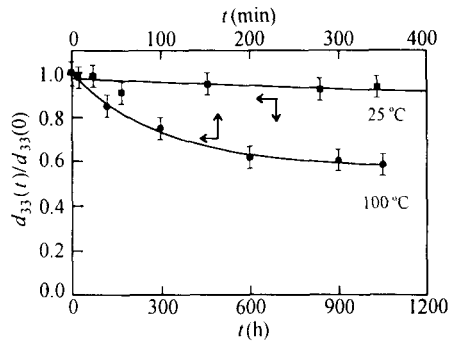


Fig. 4 SHG decay of the poled/cured IPN samples at ambient temperature

CONCLUSIONS

An NLO active methyl methacrylate copolymer and a functionalized NLO epoxy-based polymer with thermally crosslinkable acryloyl groups were synthesized, with which an IPN was developed for second-order nonlinear optics. The poled/cured IPN shows only one T_g , and is transparent and homogeneous. The IPN system has a larger second-order nonlinear optical coefficient and rather good temporal stability. A d_{33} value of 1.72×10^{-7} esu was found in the IPN sample. And the IPN shows a long-term stability of d_{33} value at 25 °C for more than 1000 h.

REFERENCES

- 1 Sekkat, Z., Wood, J., Knoll, W., Volksen, W., Miller, R.D. and Knoesen, A., J. Opt. Soc. Am. B, 1997, 14(4): 829
- 2 Si, J.H., Xu, G., Liu, X.C., Yang, Q.G. and Ye, P.X., Opt. Commun., 1997, 142: 71
- 3 Sekkat, Z. and Dumont, M., Appl. Phys. B, 1992, 54: 486
- 4 Miller, R.D. and Burland, D.M., Macromolecules, 1995, 28(14): 4970
- 5 Chen, T.A., Jen, A. and Cai, Y.M., J Am. Chem. Soc., 1995, 117: 7295
- 6 Jen, R.J., Chen, Y.M., Kummar, J. and Tripathy, S. K., J.M.S. Pure Appl. Chem.A. 1992, 29(12): 1115
- 7 Hanemann, T., Noel, C. and Haase, W., Adv. Mater., 1995, 7(5): 465
- 8 Masse, C.E., Conroy, J.C. and Cazeca, M., J. Appl. Polym. Sci., 1996, 60: 513
- 9 Klempner, D., Berkowski, L., "Encyclopedia of Polymer Science and Engineering", 2nd ed., Wiley, New York, 1986, Vol.8, p.279
- 10 Srikanth Sharma, P.R., Zhou, P.G. and Fish, H.L., J. Polym. Sci., Part A: Polym. Chem., 1996, 34: 1049
- 11 Xie, H.Q., Huang, X.D. and Guo, J.S., J. Appl. Polym. Sci., 1996, 60: 537
- 12 Zhang, L.Z., Cai, Z.G., Yu, Q.S. and Liang, Z.X., J. Appl. Polym. Sci., 1999, 71: 1081
- 13 Zhang, L.Z., Li, Y., Liang, Z.X., Yu, Q.S. and Cai, Z.G., React. Funct. Polym., in press
- 14 Liang, Z.X., Yan, X.Z., Chen, Y.L., Cai, Z.G., Yang, P.Q. and Xu, Z.L., React. Funct. Polym., 1997, 32: 75
- 15 Masse, C.E., Conroy, J.L., Cazeca, M., Jiang, X.L., Sandman, D.J., Kumar, J. and Tripathy, S.K., J. Appl. Polym. Sci., 1996, 60: 513