Thermally Stable Interpenetrating Polymer Networks for Second-Order Nonlinear Optical Materials

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ABSTRACT: We report several kinds of interpenetrating polymer networks (IPNs) with nonlinear optical (NLO) properties. DMA spectra show that the two components of the IPNs have good compatibility with each other. The NLO materials have good optical transparency. The thermal stability of alignment was improved and the poled order remained very high. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 7–9, 1999

Key words: interpenetrating polymer networks; second-order nonlinear optical materials

INTRODUCTION

Recently nonlinear optical (NLO) materials were the focus of intense research for their potential application in optical signal processing, optical computing, and telecommunication.¹⁻⁴ Poled polymers were considered as the materials with the most potential. However, they suffered from decay in the second-order parameters with time due to the relaxation of active moieties in the polymer matrix.

Up to now, the most popular method to overcome the problem is doping NLO dye into a high glass transition temperature (T_g) polymeric matrix⁵ or bonding the dye into crosslinking systems.^{6,7} In high T_g systems, it is hard to pole the film because the very high poling temperature also increases the activity of the NLO dye. In addition, the dye is required to have high temperature stability. In crosslinked systems, a high degree of thermal stability was found. However, the second-order parameters were also found to be very small because the strong chemical bonds formed while crosslinking restrained the orientation of the NLO chromophores.

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Most recently some authors introduced semiinterpenetrating polymer network (IPN) technology into NLO materials.^{8–11} The IPN is known to be able to remarkably suppress the creep phenomenon in polymers. The motion of segments in the IPN is diminished by the entanglements between the networks. These properties of the IPN present the potential of restricting the mobility of the aligned NLO chromophores. Here we report several new kinds of IPNs. We dissolved the side chain NLO polymers into two kinds of crosslinkable polymers, then crosslinked them while poling. The thermal stability of the IPNs was good while the orientation orders were also very high.



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Figure 1 DMA spectrum of P1/PU(PHEMA).

EXPERIMENTAL

All the reagents were analytical. We synthesized crosslinkable poly(methyl methacrylate)-co-hydroxylethyl methacrylate [P(MMA-co-HEMA] [OH = 7.022×10^{-4} mol/g, number average molecular weight (M_n) of 7000] and polyepichlorohydrin (PECH) (OH = 6.388×10^{-3} mol/g, $M_n \approx 6000$). The synthesis of NLO polymers was described elsewhere.¹² DMA spectra were measured by a Rhevibron-DDV-II EA, and UV-vis spectra were recorded by a Varian Cary-2E.



To prepare the films, 50% (by weight) of the side chain NLO polymer was dissolved into P(MMA-co-HEMA) or PECH, then hexamethylene diisocyanate (—OH/—NCO = 1:1) was added (trimethylol propane was also needed for PECH). The solution was first filtered to remove



Figure 2 DMA spectrum of P2/PU(PECH).

particle impurities and then spun onto ITO glass. To remove the residual solvent, the film was then dried in a vacuum oven at room temperature for about 24 h. The thickness of the films was about $0.4-0.8 \ \mu m$.

The polymer film was poled by the corona poling technique. First it was poled at room temperature at 10 kV for 1 h. Then the temperature was raised to 100°C at the rate of 10°C/min, and poling was continued for 0.5 h. Finally the film was cooled to room temperature while the electric field was kept on.

RESULTS AND DISCUSSION

As we know, NLO materials must have good optical clarity. IPN-type NLO polymers must also



Figure 3 The relaxation behavior of polymer composites at 100°C for (\blacksquare) P1/PU(PHEMA) and (\blacktriangle) P1/PU-(PECH).



Figure 4 The relaxation behavior of polymer composites at 100°C for (\blacksquare) P2/PU(PHEMA) and (\blacktriangle) P2/PU-(PECH).

observe this rule. So the two components of the IPNs must have good compatibility with each other. If not, a phase separation would appear and the polymer would be opaque.

It is known theoretically that if the two components' solubility parameters are similar, the compatibility will be good. Because the chemical structure of P(MMA-co-HEMA) and our side chain NLO polymers are similar, their solubility parameters are about equal; this means the compatibility is good. The solubility parameters of PMMA and PECH are 19.0 and 19.2 $J^{1/2}/cm^{3/2}$, respectively.¹³ This implies that their compatibility will be good. The DMA proved that there was only one peak of the tan curve (Figs. 1, 2). This means the two components' compatibility was good. In fact, the IPN films were transparent.

We also used UV-vis spectra to study the relaxation behavior of the IPN-type NLO polymers. As we know, the poled order parameter can be expressed as the following equation^{14,15}:

$$\Phi = 1 - A_2 / A_1$$

where A_1 is the absorbance of the unpoled polymer films and A_2 is the absorbance of the poled polymer films. So we also used UV-vis spectra to

study the relaxation behavior of the poled polymer films. Figure 3 and Figure 4 show that they were stable at 100°C. After 240 h there was no decrease in the orientation order. This proved that the main chain of the NLO polymer was restrained by the crosslinked system. Additionally the orientation orders were relatively high. This may due to the fact that there was no chemical bond to restrain the orientation of the chromophores. This implies that the IPN system is superior to the common crosslinking system and high T_g system. This result agrees with the former works.⁸⁻¹¹

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