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An Interpenetrating Polymer Network as a Stable Second-Order Nonlinear Optical Material

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Polymeric materials with second-order nonlinear optical (NLO) properties are of much interest for applications such as wave-guide electrooptic modulation and frequency-doubling devices.[1–7] The alignment of NLO chromophores in the poled polymers must be sufficiently stable at ambient temperature in order to use them in practical devices. Different approaches to improve the temporal stability have been reported by a number of investigators.[8–24] Cross-linking reactions have been employed to enhance the stability of second-order NLO properties in several poled polymer systems.[8,11,15–21] The resulting cross-linked network has a higher glass transition temperature (T_g) and a denser matrix, which reduce the mobility of the polymer chains. These features prevent the aligned NLO chromophores from relaxing to a random orientation. However, slow decay of second-order NLO properties at elevated temperatures was still observed in the polymers.

An interpenetrating polymer network (IPN) is a structure in which two or more networks are physically combined.[25,26] The IPN is known to be able to remarkably suppress the creep and flow phenomena in polymers. The motion of each polymer in the IPN is reduced by the entanglements between different networks. These properties of the IPN show a potential for restricting the mobility of the aligned NLO chromophores, which should greatly enhance the stability of the NLO properties. Figure 1 shows a schematic diagram of a full IPN consisting of two polymer networks.

In this paper, we present a novel approach to achieve a stable second-order NLO polymer by incorporating NLO moieties into a full IPN. This full IPN combines the network of an NLO-active epoxy-based polymer and the network of an NLO-active phenoxy–silicon polymer. The NLO properties and characterizations of these two cross-linked polymers have been reported earlier by us in refs 20 and 21, respectively. Each network can be formed simultaneously at 200 °C in a noninterfering manner. The epoxy prepolymer forms a network through acryloyl groups which is reactive at high temperature without the aid of any catalyst or initiator. The phenoxy–silicon polymer network is formed by a sol–gel process which consists of sequential hydrolysis and condensation reactions. The IPN shows excellent optical quality before and after simultaneous poling and curing. Characterizations of this IPN studied by means of FTIR and UV–vis spectroscopies, thermal analysis, scanning electron microscopy (SEM), and the stability of the NLO properties at 110 and 160 °C are also reported.

The NLO epoxy-based network is prepared from the epoxy prepolymer (BPAZO) based on the diglycidyl ether of bisphenol A and 4-(4′-nitrophenylazo)aniline functionalized with cross-linkable acryloyl groups.[20] The number average molecular weight of this prepolymer was determined to be 5200 g/mol by vapor pressure osmometry. The NLO phenoxy–silicon polymer is based on an alkoxysilane dye (ASD) of (3-glycidoxypropyl)trimethoxysilane and 4-(4′-nitrophenylazo)aniline, and the multifunctional phenoxyl molecule 1,1,1-tris(4-hydroxyphenyl)ethane (THPE). The syntheses of BPAZO and ASD were reported earlier.[20,22] Figure 2 shows the structures of BPAZO, ASD, and THPE.

To prepare a polymer solution for spin-coating, ASD and THPE with a molar ratio of 1.0:1.17 were dissolved in a mixed solvent (propylene glycol methyl ether acetate: 1,4-dioxane = 3:1 (v/v)) with a small amount of water and base catalyst. The details of the procedure were reported earlier.[21] BPAZO, which was dissolved in the same solvent was subsequently added to this solution. The resulting solution contains a weight ratio of 1:1 for BPAZO to ASD/THPE. The solution was then spin-coated onto glass microscope slides to form optical-quality thin films. The

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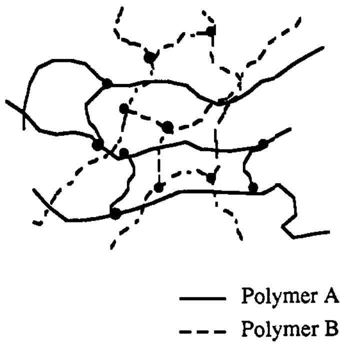
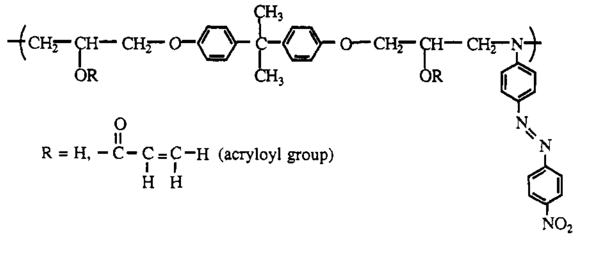
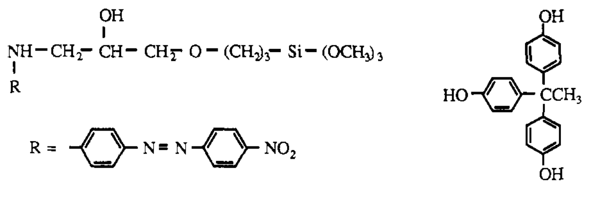


Figure 1. Structure of an interpenetrating polymer network.



(a) BPAZO



(b) ASD (c) THPE

Figure 2. Chemical structures of (a) BPAZO, (b) ASD, and (c) THPE.

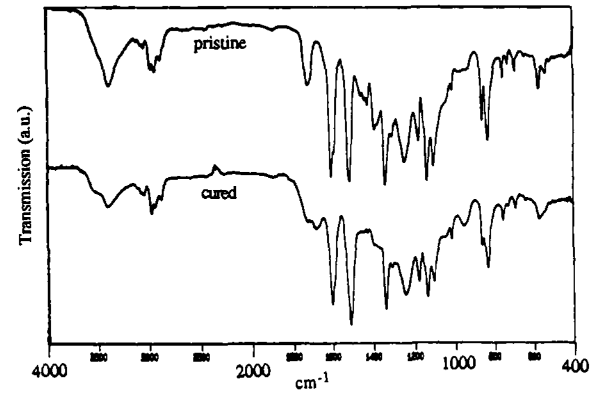


Figure 3. Infrared spectra of the IPN sample before and after curing.

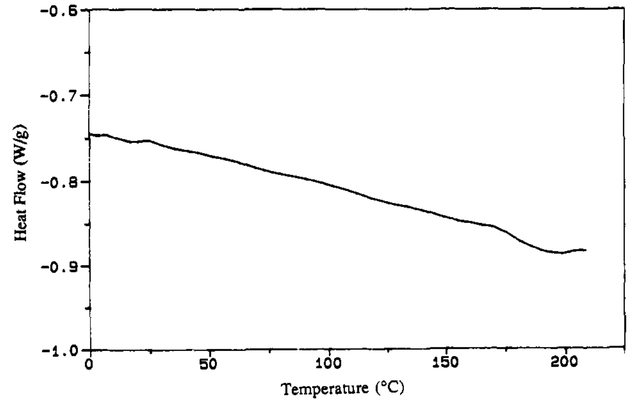


Figure 4. DSC thermogram of the cured IPN sample.

networks of BPAZO and ASD/THPE were formed simultaneously when the thin film was heated at 200 °C on a hot stage. The curing time was chosen to be 60 min to allow for sufficient cross-linking. The typical thickness of the cured films was approximately 0.6 μm. The reactions of both networks were monitored by FTIR (1760X, Perkin-Elmer). A differential scanning calorimeter (DSC 2910, T.A. Instrument Co.) was used to determine thermal properties of the samples. UV–vis spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. An ellipsometer (Rudolph Research) was used to measure the refractive index. An SEM (IC-130, International Scientific Instruments) was employed to study the morphology of the IPN film which was coated with a thin layer of gold.

The corona poling technique[3,8,20,21] was employed to align the NLO chromophores. The corona field was applied as the temperature was raised to 80 °C. The temperature was then increased to 200 °C with the corona field on. The corona current was maintained at 2 μA with a potential of 4 kV while the poling temperature was kept at 200 °C for 60 min. The formation of the networks and the molecular alignment for the poled order proceeded simultaneously during this period. The sample was then cooled slowly to room temperature before the corona field was discontinued.

The second-order NLO properties of the poled IPN samples were measured by second harmonic generation (SHG) from 1.064-μm laser radiation. The details of the SHG measurement were discussed elsewhere.[20,21] The relaxation behavior of the second-order NLO properties was studied by monitoring the decay of the second harmonic (SH) intensity as a function of time at 110 and 160 °C immediately after poling and curing.

Figure 3 shows the IR spectra of samples before and after curing at 200 °C. The THPE/ASD network was formed through a sol–gel process. After the sample was heated at 200 °C for 60 min, the hydroxyl absorption peak (3387 cm^{-1}) and the CH_3 bending peaks (1423 and 1391 cm^{-1}) decreased significantly due to the reaction of THPE with ASD. In addition, a new peak is observed at 951 cm^{-1} which confirms the formation of phenoxysilicon bonds.[21] The epoxy-based polymer network was formed through a free-radical polymerization. The reaction of BPAZO results in a shift of the carbonyl absorption peak (1724 cm^{-1}) to higher wavenumbers. The peak shift is due to the loss of conjugation by the reaction of the acryloyl group. In addition, an absorption peak was found at 1680 cm^{-1} which may be associated with intermolecular hydrogen bonding of the carbonyl group.[20] The results from the IR spectra indicate that these two polymers each form their own networks through different reaction mechanisms upon heating. However, the intensity of the absorption peaks from some functional groups such as nitro (1339, 1510 cm^{-1}) and phenyl (1602 cm^{-1}) were found to have slightly decreased. This indicates that some degree of thermal degradation has occurred during curing.

The poled and cured IPN sample showed excellent optical quality. Its refractive indexes at 532 and 1064 nm were determined to be 1.705 and 1.650, respectively. The homogeneity of this full IPN system is also suggested by the single T_g (176 °C) observed from the DSC thermogram with a 10 °C/min scanning rate (Figure 4). The T_g of the cured phenoxy–silicon[21] and BPAZO samples were determined to be 110 and 178 °C, respectively. The fact

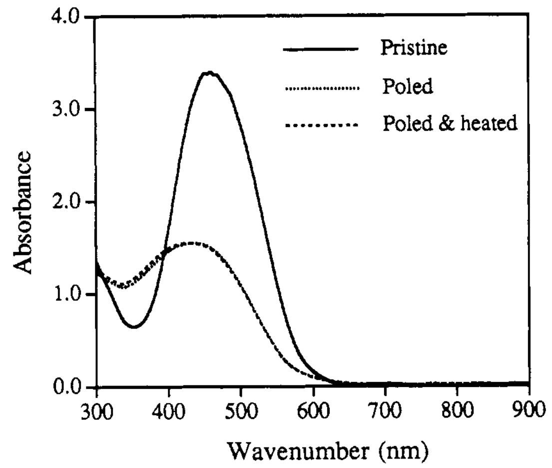


Figure 5. UV-vis absorption spectra of the IPN sample: (a) pristine, (b) right after poling and curing, and (c) poled/cured sample, after thermal treatment at 110 °C for 168 h.

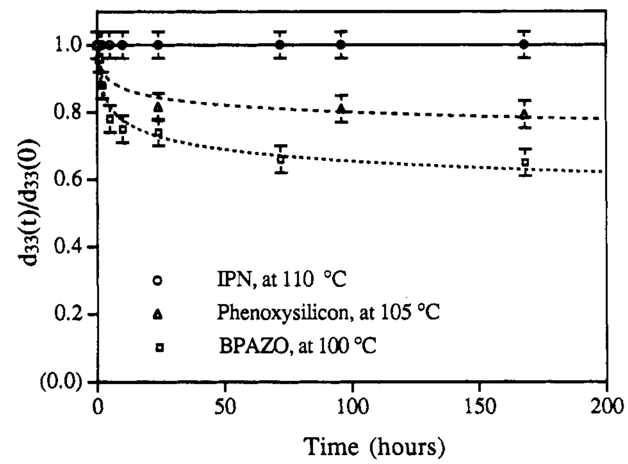


Figure 6. Time behavior of the second harmonic coefficient of different poled/cured samples.

that the T_g of the cross-linked phenoxy–silicon polymer did not manifest in the IPN sample implies that phase separation did not occur in this molecular composite. An extensive study of the relaxation phenomena of this IPN system will be performed using a dynamic mechanical analysis. The homogeneity of this IPN is further confirmed using SEM. No sign of any phase separation was observed when the magnification was increased upto 20 K. Optical microscopy reveals a clear transparent featureless film as well.

UV–vis absorption spectra of the IPN is shown in Figure 5. The pristine sample shows the absorption maximum of the disperse orange 3 at 458 nm. The absorption peak shifts to 436 nm, and the absorbance reduces right after poling and curing. The reduction of the absorbance and the peak shifting confirm the alignment of the chromophores as a result of poling.[15] However, some reduction of the absorbance also resulted from some sublimation or degradation caused during the curing and poling process. After the same sample was heated at 110 °C for 168 h, the absorption peak remained practically unchanged. This behavior implies that the chromophores did not degrade or sublime during this period of thermal treatment.

The temporal stability of second-order nonlinearity of the poled/cured IPN, BPAZO, and phenoxysilicon samples are shown in Figure 6. The IPN system shows no measurable decay of SH intensity after being heated at 110 °C for 168 h, whereas the BPAZO and the phenoxy–silicon samples show fast initial reduction of the SH intensity upon heating at 100 and 105 °C, respectively. The NLO coefficient, d_{33}, of the poled IPN sample was measured to be 33 pm/V despite the occurrence of some thermal degradation during sample processing. The d_{33} values of BPAZO and phenoxy–silicon samples were reported earlier to be 18 and 77 pm/V at 1.064 μm, respectively.[20,21,27] After the IPN sample was heated on a hot stage at 160 °C for 15 h, 50% retention of the d_{33} value was still observed. This stability of SH intensity for the IPN system is a result of the high T_g of polymers and the presence of a cross-linked network. In addition, permanent entanglements between the two networks further constrain the motion of aligned chromophores. Therefore, the mobility of the NLO chromophores is dramatically decreased which promotes the synergistic stability of the poled order. The excellent stability is ascribed to the novel interpenetrating crosslinked molecular structure of the IPN system.

In conclusion, a second-order NLO material with superb stability based on an IPN has been demonstrated. The poled polymer film exhibits a second order NLO coefficient d_{33} of 33 pm/V. The poled sample shows no change in its SH intensity after being heated at 110 °C for as long as the stability was monitored (168 h). Only 50% reduction of the d_{33} was observed as the sample was heated at the temperature close to its T_g for 15 h. The high rigidity of the polymer backbones and the interpenetrating structure of the polymer networks prevent the randomization of the aligned NLO chromophores. More detailed studies of the optical loss, and the relaxation behavior of the IPN system are in progress.

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(27) The corrected d_{33} values for the BPAZO and the phenoxy–silicon are 18 and 77 pm/V at 1.064 μm, respectively.