

# Studies on Isotactic Poly(phenyl glycidyl ether)-Modified Epoxy Resins. I. Physical Gels

ZHENG ZHANG, JIANJUN XU, YUNZHAO YU

Center for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

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**ABSTRACT:** Isotactic poly(phenyl glycidyl ether) (i-PPGE) was prepared using a Teysie catalyst. The polymer was dissolved in the epoxy resin at approximately 200°C and Gels were formed as the solutions cooled to room temperature. The gels were studied by rheological techniques, differential scanning calorimetry analysis, optical microscopy, and electron microscopy. The existence of a network in the gels was demonstrated by the nonlinear increase of the viscosity with i-PPGE concentration and by the significant storage modulus. A high isotacticity of the polymer was essential for gel formation. The thermal history of the system showed a great influence on the network structure and on the performance of the gel. The yield stresses of the physical gels increased with the concentration of i-PPGE. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1214–1222, 2002; DOI 10.1002/app.10444

**Key words:** physical gel; epoxy resin; poly(phenyl glycidyl ether); rheologic behavior

## INTRODUCTION

Gels represent solidified fluid systems in which the space is filled by a network. Many polymers can form physical networks in solutions above the critical concentration for gel formation and turn the fluid into a gel.<sup>1–6</sup> Physical gels of polymers have many applications in polymer processing; those in epoxy resin<sup>7–11</sup> are of particular interest because they can be used in the rheologic control of epoxy resins that are applied as structural adhesives, sag-resistant sealants, high-build-up coatings, and stereo lithographs.

Typical commercial rheology modifiers are fine minerals, such as fumed silica, which form a network structure through particle aggregation. These materials work well initially, but their effectiveness is lost gradually during storage as the aggregation breaks down through wetting by fluid

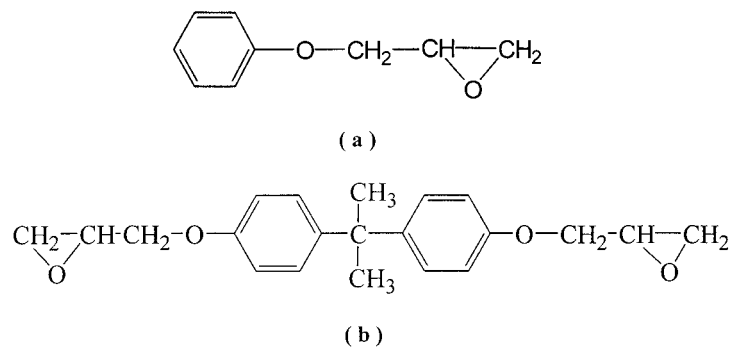
components. In contrast, networks based on polymer molecule assemblies are more stable. Therefore, epoxy systems of constant rheologic performance can be prepared through physical gels.<sup>10,11</sup>

For the preparation of physical gels, polymers are first dissolved in the liquid medium by heating. As the solution is cooled down, a network is formed through mechanisms of crystallization, phase separation, hydrogen bonding, ionic bonding, or chain entanglement.

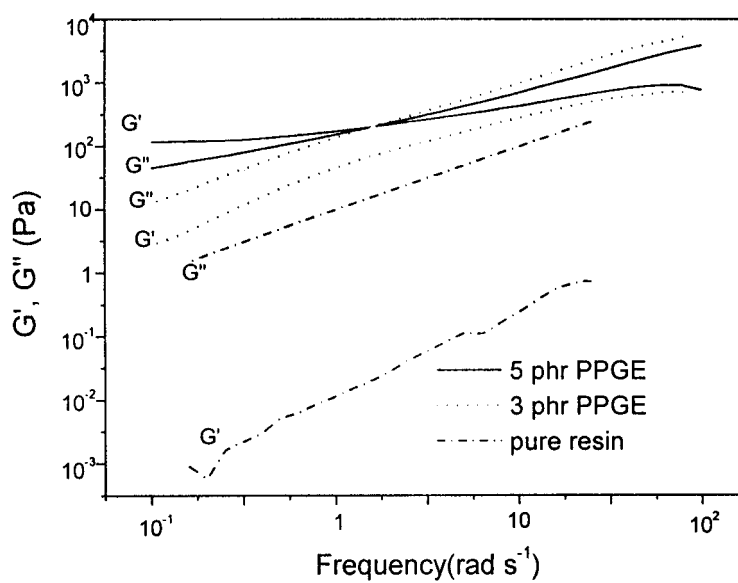
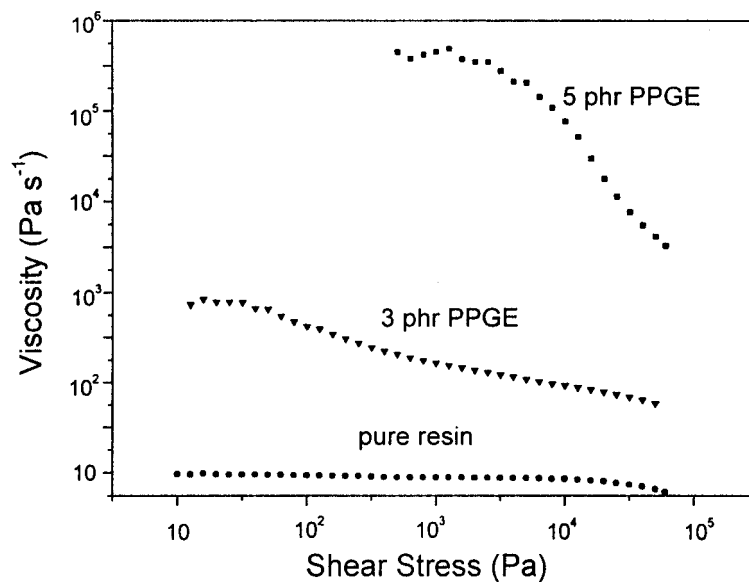
In our preliminary experiments, it has been found that isotactic poly(phenyl glycidyl ether) (i-PPGE) is useful for the preparation of physical gels in epoxy resins. In view of the chemical structure, phenyl glycidyl ether (PGE) can be looked at as a half of diglycidyl ether of bisphenol-A (DGEBA), a typical epoxy resin, as shown in Figure 1. Therefore, i-PPGE is well compatible with epoxy resins. However, i-PPGE is a crystalline polymer; it can form physical networks in epoxy resins easily. In this article, we report the preparation and characterization of physical gels of i-PPGE in the epoxy resin.

Correspondence to: Y. Yu, (yuyzh@95777.com).

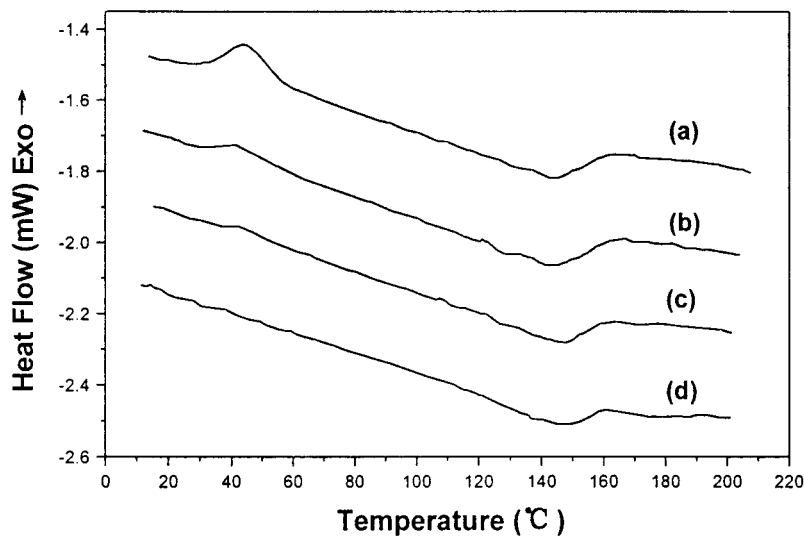
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**Figure 1** Structure formula of (a) phenyl glycidyl ether and (b) diglycidyl ether of bisphenol A ( $n = 0$ ).



**Figure 2** Rheologic behavior of epoxy resin and the resins containing 3 and 5 phr of isotactic poly(phenyl glycidyl ether) (a) viscosity versus shear stress and (b) dynamic modulus. PPGE = poly(phenyl glycidyl ether).



**Figure 3** Differential scanning calorimetry scans of transparent epoxy gels containing 5 phr of isotactic poly(phenyl glycidyl ether), aging time: (a) 15 min, (b) 40 min, (c) 90 min, (d) 24 h.

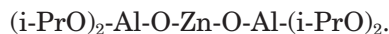
## EXPERIMENTAL

### Materials

The epoxy resin used in this study was DGEBA, EPON 828, provided by Shell Company (The Netherlands). PGE was obtained from the Yueyang Resins Factory (China). It was dried over calcium hydride for several days and distilled under reduced pressure. The distillate of 95–96°C /2 mm Hg was collected. Toluene used in the polymerization was dried over sodium and distilled before use.

### Preparation of Isotactic Poly(phenyl glycidyl ethers)

For the preparation of *i*-PPGE, PGE was polymerized using a Teyssie catalyst,<sup>12–15</sup> a bimetallic  $\mu$ -oxo-alkoxide of the following formula



The polymerization was carried out in strictly moisture-free conditions under the protection of high-purity nitrogen. For example, in a dried glass flask, 10 g of PGE and 30 ml Toluene were charged, and 0.25 g of the catalyst was introduced. The reaction mixture was heated for 3 h at 100°C in an oil bath under vigorous stirring. Then 10 ml of an HCl-ethanol solution was added to stop the reaction. The white product was filtered

out and washed with ethanol and deionized water to remove the catalyst. The polymer was dried at 140°C for 24 h in a vacuum oven.

The atactic fraction of the polymer was removed by extraction with acetone. The isotactic fraction (*i*-PPGE), yield approximately 75%, was a rigid polymer with a  $T_m$  ranging from 180° to 190°C, heat of fusion 47.7 J/g by differential scanning calorimetry (DSC). The intrinsic viscosity  $[\eta]$  was 0.65 dL/g, determined in tetrachloroethane solution at 30°C. The diad isotacticity was 82%, determined by <sup>13</sup>C-NMR analysis. This fraction was used in most studies in this work.

### Preparation of Physical Gels in the Epoxy Resin

The *i*-PPGE was dissolved in the DGEBA at temperatures in the range of 190° to 200°C. After complete dissolution, the solution was poured into a mold and cooled to room temperature to form a transparent gel. The specimens, if not specified, were transparent gels stored in a desiccator for more than 24 h before measurements.

### Characterization and Measurements

The tacticity of *i*-PPGE was determined by <sup>13</sup>C-NMR according to method given in Ronda et al.<sup>16</sup> TCE-d<sub>2</sub> was used as a solvent; the spectra were recorded at 77°C on a DMX 300M spectrometer with proton noise decoupling (Bruker Instruments, Ltd., USA). The molecular weight of *i*-

PPGE was determined by gel permeation chromatography using a PL-GPC210 instrument equipped with two PL gel Mixed B-10- $\mu\text{m}$  columns and a differential refractive index detector. The measurement was carried out at 160°C with orthodichlorobenzene as the eluant.

DSC analysis was carried out on a TA 2100 Modulated Differential Scanning Calorimeter at a heating rate of 10°C/min under nitrogen atmosphere.

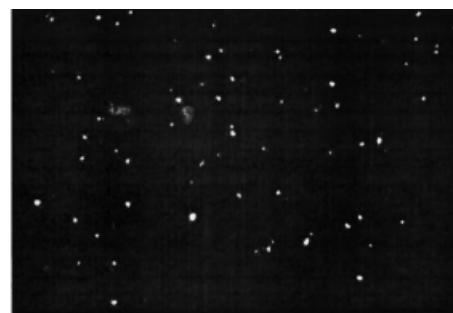
A Hitachi S-530 scanning electron microscope (SEM) and a Hitachi-800 transmission electron microscope (TEM) (Japan) were used in the study of the morphology of the physical gels. The fracture surfaces of the gel were studied using a Pt-C replica technique. Rheological measurements were carried out at 25°C on a dynamic stress rheometer, DSR200 (Rheometric Scientific, USA), using parallel plate geometry with  $\sim$  diameter of 25 mm and a gap of 0.5 mm.

## RESULTS AND DISCUSSION

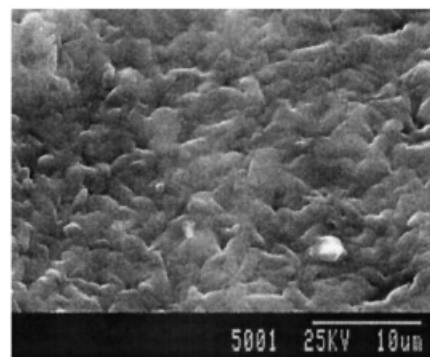
### Gels Formation of Isotactic Poly(phenyl glycidyl ethers) in Diglycidyl Ether of Bisphenol-A

The i-PPGE dissolves in the epoxy resin at approximately 200°C and crystallizes on cooling to room temperature. As the i-PPGE concentration exceeds a critical value, gels of i-PPGE in epoxy resin are formed. The critical gel concentration for i-PPGE is in the range of 1 to 5 phr, depending on the structure of i-PPGE and the thermal history of the system.

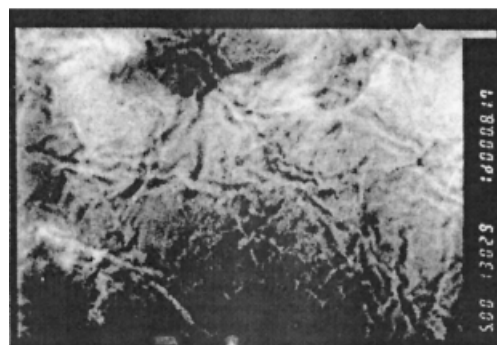
To study the behavior of i-PPGE/epoxy resin systems, rheologic measurements both in steady shear region and in dynamic region were carried out. A plot of apparent viscosity versus shear stress for the neat resin and the transparent gels, obtained by cooling the solution directly, is shown in Figure 2(a). It can be seen that the viscosity of DGEBA was low and less dependent on the shear stress. As 3 phr of i-PPGE was incorporated, the system became highly shear-thinning. The viscosity increased for two orders of magnitude at the low shear stresses compared with the neat resin. Even greater changes in the viscosity curves can be seen as the concentration of i-PPGE was increased from 3 to 5 phr. For the system containing 5 phr of i-PPGE, no viscosity data could be obtained at low shear stresses because the system showed a significant yield stress.



(a)



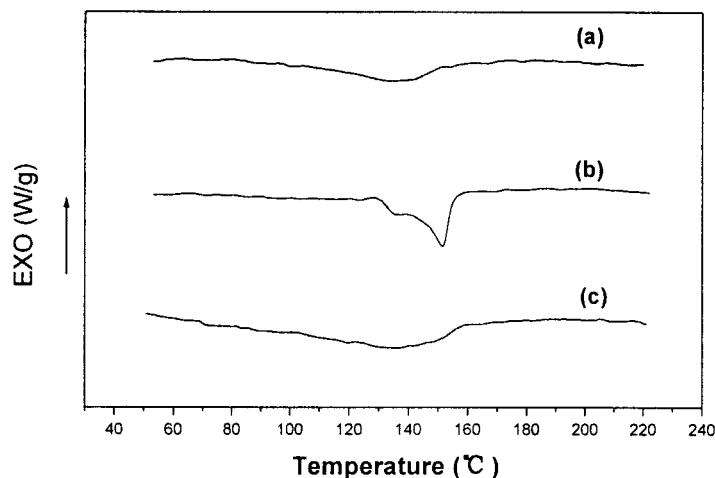
(b)



(c)

**Figure 4** Morphology of transparent isotactic-poly(phenyl glycidyl ether) (i-PPGE)/diglycidyl ether of bisphenol A gels. (a) Photographs of gels containing 4 phr i-PPGE taken with polarized light (200 $\times$ ), (b) scanning electron micrograph photo (4000 $\times$ ) of gels containing 5 phr i-PPGE after removal of the resin by extraction with toluene, (c) transmission electron micrograph photo (5000 $\times$ ) of a Pt-C replica of the fracture surface of gels containing 5 phr i-PPGE.

The frequency dependence of dynamic moduli is shown in Figure 2(b). The storage modulus  $G'$ , proportional to stress in phase with the strain,



**Figure 5** Differential scanning calorimetry scans of the epoxy resin containing 4 phr of isotactic poly(phenyl glycidyl ether): (a) the transparent gel, (b) the opaque gel, and (c) the opaque gel after dissolution at 200°C and quickly cooled to the room temperature.

provides information on the elasticity of the material. For the neat resin,  $G'$  was negligible. There was an increase for four orders of magnitude in  $G'$  as 3 phr of i-PPGE was incorporated. For the resin containing 5 phr of i-PPGE, there was a crossover in  $G'$  and  $G''$ . The intersection of the storage and loss moduli could be taken as a criterion of gelation.

The nonlinear increase of viscosity with the concentration of i-PPGE and the increase of elasticity indicate the existence of a network in the system.

### Mechanism of the Gel Formation

As a solution of i-PPGE in the epoxy resin was cooled quickly, it solidified very soon (within 2 min). The rapid gel formation may be the result of phase separation through spinodal decomposition. Similar process has been reported in gel formation for some systems.<sup>17–20</sup>

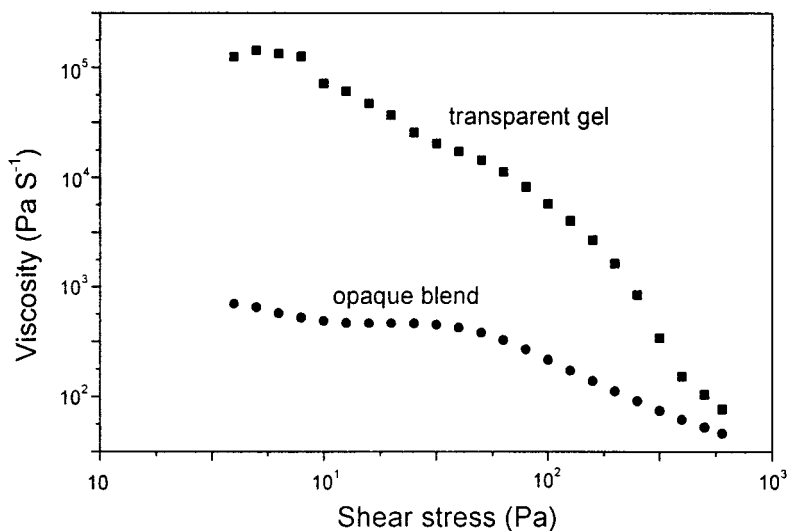
Liquid–liquid phase separation must be followed by the crystallization of i-PPGE, as demonstrated by DSC analyses. In the thermogram for the “fresh” gel, there was a significant exothermic peak at the vicinity of 45°C (Fig. 3), which was attributed to the crystallization of i-PPGE. The crystallites dissolved at approximately 140°C, as shown by the endothermic peak. The peak for the crystallization decreased with the aging of the gel at room temperature. Completion of crystallization was indicated by the disappearance of the

exothermic peak after 24 h. After that, the gel was stable: no change was found after staying at room temperature for months or at 100°–110°C for several days. We believe that the network in the gel was built of intertwined crystallites.

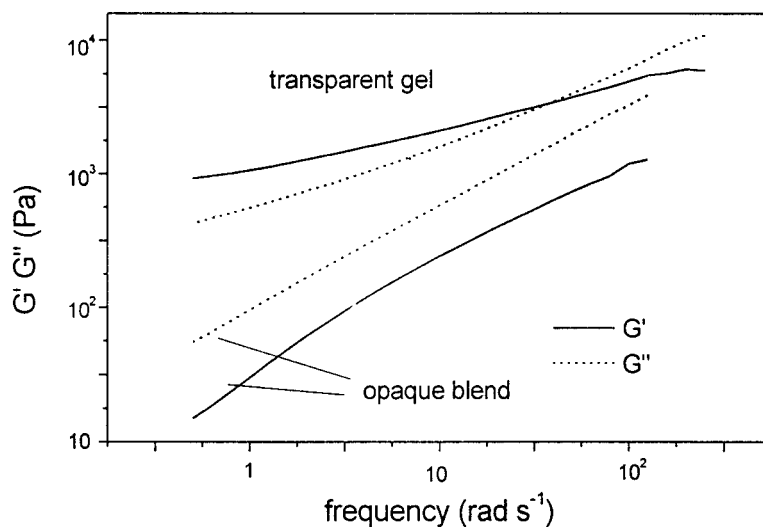
Crystallization took place both in the i-PPGE-rich phase and in the epoxy-rich phase. Crystallization in the DGEBA-rich phase was indicated by the lowering of the  $T_g$  for the epoxy resin.  $T_g$  for the neat DGEBA was  $-12.8^\circ\text{C}$ . It was  $-10.8^\circ\text{C}$  for the fresh gel because a fraction of i-PPGE was dissolved in the resin. After aging for 24 h, the gel's  $T_g$  was consistent with that of the neat DGEBA.

### Morphology Studies

In the polymer gels with large spherulites. Maltose crosses can be observed under an optical microscope with crossed polarizers.<sup>9–11</sup> However, for the gel of i-PPGE in epoxy resin, only a few bright specks could be seen on the dark background (Fig. 4[a]). The opaque gel of the i-PPGE/epoxy resin showed a brighter background with bright conglomerates. It is likely that the spherulites in the epoxy gel were too small for the optical microscope. To illustrate the network in the physical gels of i-PPGE in epoxy resin, a piece of the transparent gel with 5 phr of i-PPGE was soaked in toluene, a good solvent for the epoxy resin but a nonsolvent for i-PPGE. It was found that the contour of the test piece was not changed as the resin



(a)



(b)

**Figure 6** Rheologic behavior of epoxy gel containing 4 phr of isotactic poly(phenyl glycidyl ether) with different thermal history: (a) viscosity versus shear stress, (b) dynamic modulus.

was removed by attraction. Before study under SEM, the solvent was removed under vacuum. Although significant shrinkage took place on the removal of the solvent and although the feature in the SEM picture was severely distorted (Fig. 4[b]), the existence of a network was still conceivable.

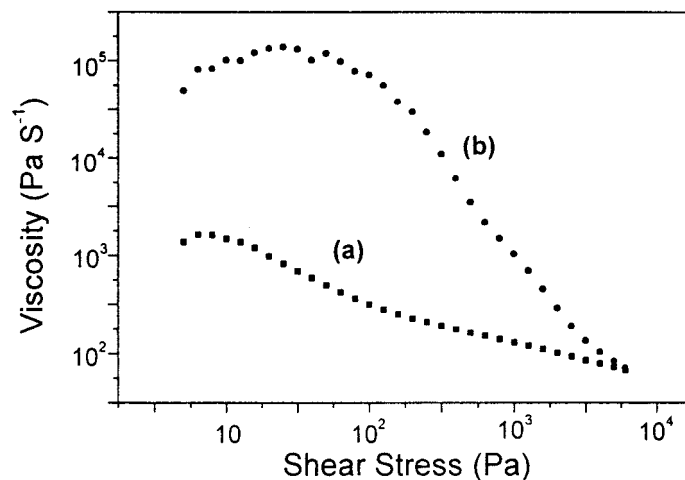
A replica technique was employed in the study of the morphology. Thus, a piece of the transparent gel was frozen in liquid nitrogen and fractured. The fracture surface was shadowed with

Pt-C by spattering. The resin on the coating was removed with solvent. Photographs of the Pt-C replica then were taken with a TEM. The skeleton of the network structure was clearly visible in the picture (Fig. 4[c]).

#### Effect of Thermal History

When the solution of i-PPGE in epoxy resin was cooled directly from 200°C to room temperature, the gel obtained was quite transparent, and





**Figure 7** Viscosity versus shear stress for epoxy gels containing 3 phr of isotactic poly(phenyl glycidyl ether): (a) diad isotacticity 58%,  $M_n$  26,000; (b) diad isotacticity 82%,  $M_n$  21,000.

therefore was termed a transparent gel. If the solution was annealed at 125°C for several hours and then cooled to room temperature, the obtained blend was milky white and opaque. It was therefore termed an opaque gel.

The change was reversible: As the opaque blend was heated to 200°C to dissolve the crystallites and then cooled quickly, a transparent gel was obtained again.

As opposed to the mechanism for the formation of transparent gels discussed in the previous section, solution crystallization played a significant role in the formation of the opaque gel. By annealing the solution at a temperature near the dissolution temperature, crystallites had more time to grow. Consequently, the size of the crystallites became large and fewer grew. Therefore, the network of intertwined crystallites in the opaque gel was looser. The solution-crystallization phase transformation is similar to the gel formation of poly(butylene terephthalate) in the DGEBA resin.<sup>10</sup>

This explanation was supported by the results of thermal analysis. In Figure 5, DSC thermograms for the gels containing 4 phr of *i*-PPGE are shown. The peak temperature for the dissolution of the transparent gel was found at approximately 140°C. The enthalpy of dissolution was 13.6 J/g-PPGE. It is reasonable that the opaque gel, with larger crystallites, had a higher peak temperature (~150°C) and a larger enthalpy of dissolution (37.4 J/g-PPGE) than the transparent gel. The rheologic performance of these gels was also quite different. It can be seen in Figure 6 that

the opaque gel was less elastic; that is, it had a weaker network.

#### Effect of Tacticity of Poly(phenyl glycidyl ether)

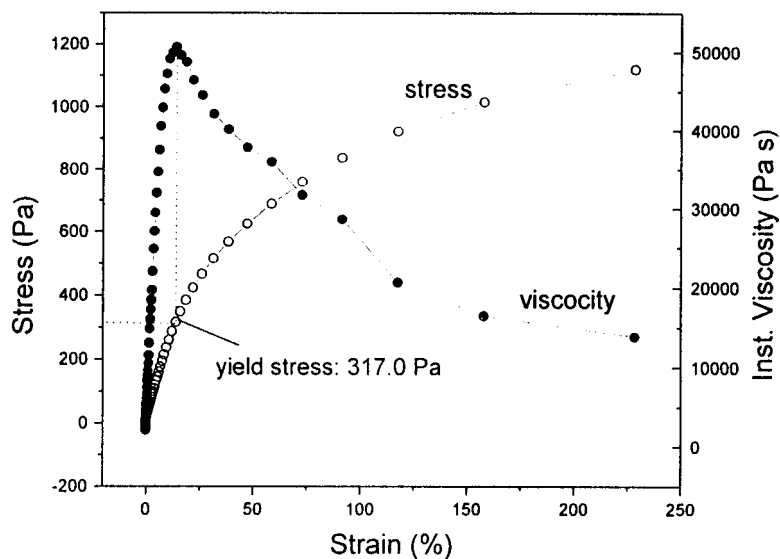
The isotacticity of PPGE is of critical importance for gel formation in epoxy resin. Atactic PPGE does not crystallize: It can dissolve in the epoxy resin at any ratio without gel formation.

PPGE of high isotacticity is preferable for the preparation of epoxy gels. For comparison, two transparent gels with 3 phr of PPGE were prepared in the identical conditions. The first gel contained PPGE of diad isotacticity 82% and  $M_n$  21 000; the second gel contained PPGE of diad isotacticity 58% and  $M_n$  26 000. The rheologic curves of these gels are given in Figure 7. It is seen that much stronger gels can be prepared by using a polymer of higher isotacticity at the same concentration.

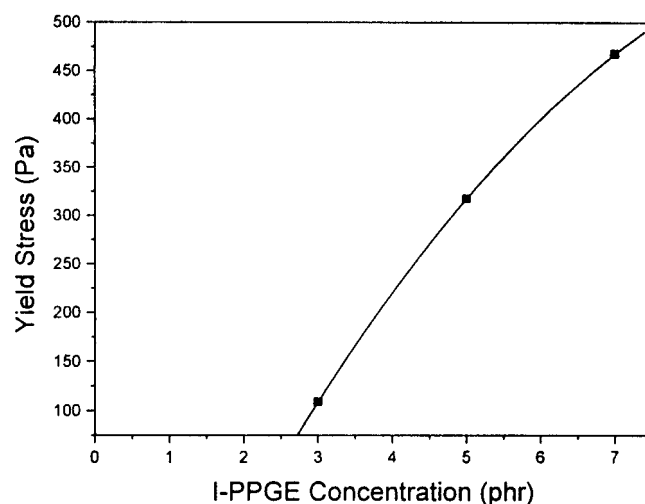
#### Yield Stress of Isotactic Poly(phenyl glycidyl ether)/Epoxy Gels

According to the values of the storage modulus of the gels, significant yield stresses can be expected. The yield stress of *i*-PPGE/epoxy gels is of practical interest for its applications in sag-resistant formulations.

To determine yield stress, a controlled stress rheometer was used. As the shear stress was increased from 0 to 1500 Pa in 100 steps, the strain was measured. Meanwhile, the apparent viscosity



(a)



(b)

**Figure 8** Yield stress of isotactic poly(phenyl glycidyl ether) (i-PPGE)/diglycidyl ether of bisphenol A gels: (a) determination of the gel containing 5 phr of i-PPGE, (b) yield stress of gels with different i-PPGE concentrations.

was calculated with the computer. The stress under which the viscosity began to fall off was taken as the yield stress. Figure 8(a) shows a diagram for the yield stress determination of an epoxy gel containing 5 phr of i-PPGE. The increase of yield stress with i-PPGE concentration is shown in Figure 8(b).

## CONCLUSION

i-PPGEs are soluble in epoxy resin above the melting temperature of the polymer. When the

concentration of the polymer exceeds the critical gel concentration, gels of i-PPGE in epoxy resin are formed. The networks in the gels are built of intertwined crystallites. A high isotacticity of the polymer is essential for the gel formation. When the solution is cooled quickly to room temperature, transparent gels with denser networks are formed. By annealing at a temperature near the dissolution temperature, the crystallites have more time to grow, and therefore, opaque gels with looser networks are obtained. Because of the



existence of a network, the gels are highly shear thinning. They have significant storage moduli and yield stresses.

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