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Single-phase bicomponent network by random crosslinking of hydroxyl-terminated polyisobutylene/polytetrahydrofuran mixtures

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Summary

Random bicomponent networks were prepared from 50/50 wt % mixtures of hydroxyl-terminated polyisobutylene (HO-PIB-OH) and polytetrahydrofuran (HO-PTHF-OH) by the use of triphenylmethane triisocyanate (TTI) endlinking agent. Differential scanning calorimetry (DSC) and dynamic mechanical techniques were employed to study the networks. The glass transition temperature (T_g) of HO-PIB-OH was found to increase upon network formation. This T_g increment was used to estimate the molecular weight between crosslinking points ($\overline{M}_c$). HO-PIB-OH/HO-PTHF-OH mixtures are immiscible and exhibit an upper critical solution temperature, however, the 50/50 network in a two-phase regime for the precursors gives a single T_g situated between the T_gs of the component networks. The single-phase network may be due to rapid nondiscriminatory endlinking and to an increase of the single-phase region of the phase diagram because of crosslinking.

Introduction

In the course of our studies on the preparation and characterization of novel multicomponent networks, we became aware of the significance of miscibility of the precursors on the morphology of such networks (1,2). Depending on the relative rates of crosslinking and phase separation, phase-separated or single-phase networks may arise which would exhibit significantly different network characteristics. In our previous paper (2), we have defined a phase diagram for HO-PIB-OH/HO-PTHF-OH mixtures and have found an upper critical solution temperature. Subsequently, the kinetics of phase separation was explored to gain better insight of the network structure.

This paper concerns bicomponent networks prepared by crosslinking 50/50 HO-PIB-OH/HO-PTHF-OH mixtures with stoichiometric amounts of TTI, and their characterization by DSC and dynamic mechanical methods. The molecular weight between crosslinking points are estimated by Nielsen's empirical equation (3). The effects of crosslinking on the miscibility phase diagram and on the resulting network structure are discussed.

Experimental

Polytetrahydrofuran (HO-PTHF-OH) with $\overline{M}_n$ = 2,000, i.e., $\overline{DP}_n \sim 28$, was purchased from Scientific Polymer Product Co. Hydroxyl-terminated polyisobutylene (HO-PIB-OH) was synthesized by living cationic polymerization and subsequent functionalization (4-6); $\overline{M}_n$ = 1,500, i.e., $\overline{DP}_n \sim 27$, $\overline{M}_w/\overline{M}_n = 1.16$, and number average terminal functionality $\overline{F}_n = 2 \pm 0.1$. Triphenylmethane triisocyanate (TTI, Desmodur R) was obtained from Mobay Chemical Co.

The bicomponent networks were prepared under a dry N_2 atmosphere in a dry box. Preweighed mixtures of HO-PIB-OH and HO-PTHF-OH were prepared in 125 ml erlenmeyer flask and dried in a vacuum oven at 50 °C until weight constancy. A stoichiometric quantity of TTI relative to the total hydroxyl content was added to the diol mixture and the system was diluted with tetrahydrofuran (THF) to 30-35 wt % solid content. The system was stirred manually by rotating the flask until it reached a honey like viscosity (30-45 min). The viscous liquid was poured into the cavity of an open Teflon mold (10 x 10 x 0.5 cm). The bicomponent network films were allowed to cure for one day at room temperature in the dry box, then for one day at ambient temperature in a vacuum oven, and finally for 3-4 days at 60 °C in a vacuum oven. The amount of soluble (sol) fractions were determined by extraction of two samples each with benzene and THF, both good solvents for HO-PIB-OH and HO-PTHF-OH. Thus two preweighed samples of known dimensions (~1.0 x 0.5 x 0.04 cm) were immersed in benzene or THF at room temperature and the swollen samples were blot dried and weighed every 24 hrs until weight constancy was reached. Then the samples were dried in a vacuum oven at ambient temperature (weight constancy in about 2 days) and their dry weights were determined. Sol fractions for both solvents were less than 2 %.

DSC thermograms were obtained on a Du Pont 9900 Thermal Analyzer in the -120 to 100 °C range. An indium standard was used for temperature calibration. The samples were preheated to 100°C for a few minutes to remove thermal history. The heating rate was 20 °C/min. Dynamic mechanical experiments were conducted on a Dynamic Mechanical Thermal Analyzer (DMTA, Polymer Laboratories Inc.) in the -120 to 100 °C range at a heating rate of 1°C/min. The specimens were 10 mm long, 3 mm wide, and 500 μm thick.

Results and Discussion

A commonly used criterion to characterize blend miscibility is the glass transition temperature of the mixtures (7). Immiscible mixtures

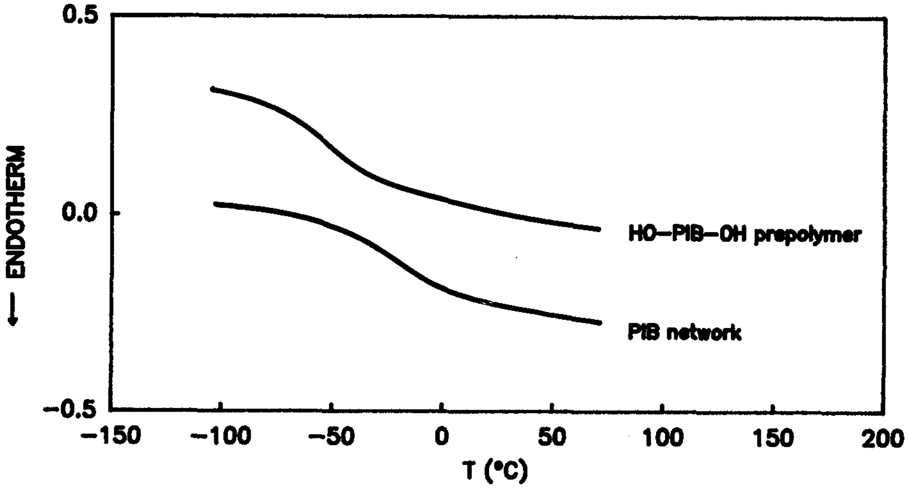

Fig. 1. DSC thermograms of HO-PIB-OH and PIB network.

usually exhibit two T_gs, whereas miscible systems yield a single T_g. This criterion is valid only if the T_gs of the components are sufficiently separate. Figure 1 shows the thermograms of HO-PIB-OH and the network prepared from it. While the T_g of the HO-PIB-OH appears at ~ -47°C, it moves to ~ -19°C upon crosslinking. This increase in T_g is due to the restricted mobility of HO-PIB-OH chain ends upon network formation. Intuitively, the increase of T_g is expected to be larger for shorter precursors than with longer ones. According to Nielsen (3) this T_g shift is inversely proportional to the molecular weight between junction points, i.e., the larger the chain length, the lesser effect of crosslinking on the T_g increment,

$$T_g - T_g^{o} = K/\overline{M}_c \qquad (1)$$

where T_g^{o} and T_g represent the glass transition temperatures of uncrosslinked and crosslinked networks, respectively, and $\overline{M}_c$ is the molecular weight between crosslinks. This equation with an empirical value of $K = 3.9 \times 10^4$ was found to be valid for a number of thermosets (3). The data for Figure 1, and Nielsen's equation with the above constant, give $\overline{M}_c$ of the PIB network. This value is very close to the $\overline{M}_n = 1{,}500$ for the HO-PIB-OH precursor, which suggests that endlinking was virtually complete, i.e., $\overline{M}_n \cong \overline{M}_c$. Obviously, the network cannot be perfect because it must contain some dangling chains which do not contribute to the T_g increase and the contribution of the endlinking agent TTI was neglected. Chain entanglement is expected to be absent because the $\overline{M}_n$ of HO-PIB-OH precursor is appreciably lower than ~ 8,000, the critical entanglement molecular weight of PIB networks (8). Hence, the observed T_g enhancement is attributed to crosslinking.

Similar observations have been made with the PTHF system: whereas the T_g of the HO-PTHF-OH was ~ -80 °C, that of the PTHF network increased to ~ -65 °C. This T_g increment is less dramatic than that measured with the PIB system, possibly because of the higher molecular weight of the

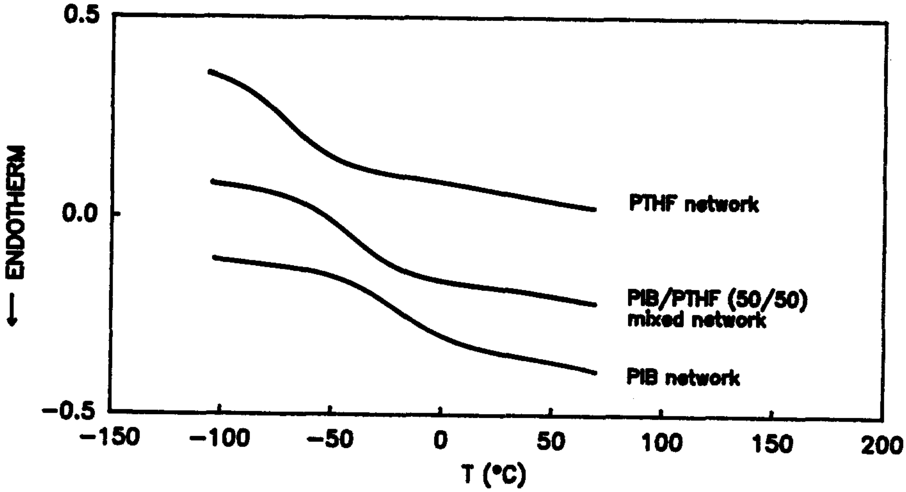

Fig. 2. DSC thermograms of PIB network, PTHF network, and 50/50 bicomponent network.

PTHF. Figure 2 contrasts DSC traces of PIB, PTHF homogeneous networks, and 50/50 bicomponent network. Interestingly the bicomponent network exhibits a single T_g in between those of the homogeneous networks, although the uncrosslinked HO-PIB-OH/HO-PTHF-OH mixture is immiscible at room temperature (2).

The presence of a single phase bicomponent network was further confirmed by dynamic mechanical studies. According to the data in Figure 3, the 50/50 bicomponent network shows a single loss tangent intermediate between those of the homogeneous networks. The formation of single-phase 50/50 PIB/PTHF network is due to rapid random endlinking of HO-PIB-OH/HO-PTHF-OH mixtures by TTI in homogeneous THF solution. Evidently the triisocyanate is nondiscriminatory and sufficiently reactive with the primary hydroxyl groups ($-CH_2OH$) of either precursors to cause random endlinking.

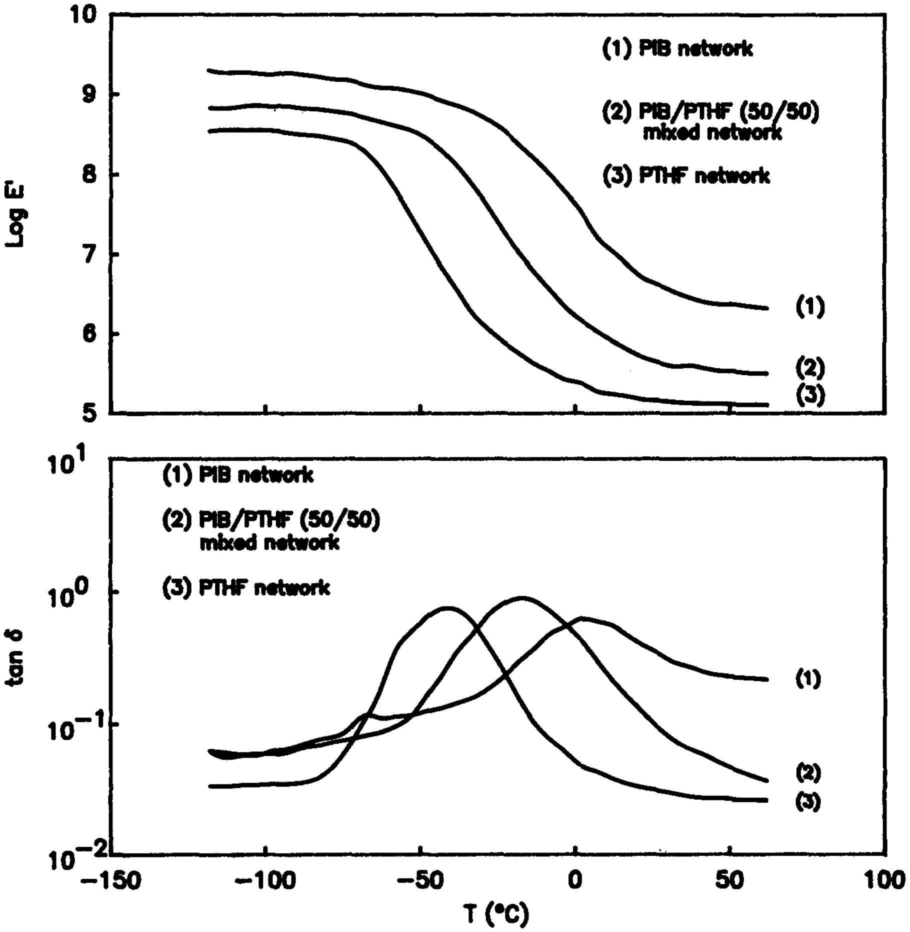

Fig. 3. Storage moduli and loss tangents as a function of temperature for PIB network, PTHF network, and 50/50 bicomponent network.

Single-phase bicomponent network formation can also be explained by the effect of crosslinking on the phase diagram. In the context of mean field approximation, de Gennes (9) predicted that the Flory-Huggins interaction parameter at spinodal (χ_s) is inversely proportional to the degree of polymerization between crosslinks (N_c). The mean field assumption gives $\chi \sim 1/T$; thus, decreasing the chain length between crosslinks widens the miscibility window, i.e., the single-phase region of the phase diagram increases. This prediction was recently confirmed by Briber and Bauer (10) who studied the effect of radiation crosslinking on the miscibility phase diagram of polystyrene/poly (vinyl methyl ether) blends. As predicted by de Gennes (9), the authors found that the spinodal temperature varies inversely with the radiation dose and N_c, which results in a large increase in the single phase region. The shift of the lower critical solution temperature curve to higher values was attributed to radiation crosslinking between dissimilar chains. These findings are in good agreement with our observation of single-phase network formation upon cross-linking which in turn may be due to the widening of the miscibility window of HO-PIB-OH/HO-PTHF-OH mixtures.

Conclusion

A single-phase random bicomponent network was obtained upon crosslinking 50/50 HO-PIB-OH/HO-PTHF-OH with TTI at ambient temperature. The temperature of crosslinking was within the two-phase region of the phase diagram of the uncrosslinked precursor mixture. As predicted by de Gennes crosslinking causes an increase in the single-phase region.

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