

Brillouin scattering from polyurethane gels†

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The hypersonic sound speed and attenuation in a series of PPO polyurethane gels show a strong crosslink dependence in highly crosslinked samples. The temperature of maximum loss for the α -relaxation is raised from ~ 370 K to ~ 400 K in a highly crosslinked gel whilst the β -loss maximum is unaffected. This result indicates cooperative motion at the transition with a rearranging unit which appears to involve some 3 or 4 monomer units. The hypersonic properties were also found to depend upon the relative proportions of polymer and solvent in the gel. In the dry network hydrogen bonding between the urethane links and the interposed PPO dominates the dynamics. As the proportion of solvent increases, the effect of this hydrogen bonding is reduced, lowering the relaxation temperatures.

Keywords Brillouin scattering; polymer gels; crosslinking; solvent concentration; relaxations; relaxation temperatures

INTRODUCTION

Brillouin scattering has been widely used to study mechanical relaxations in polymers at high frequencies; much of this work is contained in a recent review¹. There have been, however, few investigations into Brillouin scattering from polymer networks or gels²⁻⁵. Such investigations, we believe, are useful in understanding these very fast motions in polymers. The comprehension of these motions may lead us to an understanding of the glass transition. Most models of the glass transition invoke some form of cooperative model of motion about the glass transition temperature, T_g , to account for the variable activation energy observed for this process. The degree of cooperativity decreases as T_g becomes more distant. To date there have been no useful Brillouin scattering experiments reported in the literature where the cooperative nature of the high frequency glass transition (α -relaxation) has been studied.

The only other comprehensive Brillouin scattering study of a gel, gelatin, by Bedborough and Jackson³ that has been reported offered no investigation into the cooperative α -relaxation. Instead, these authors found that the scattering arose from structure associated with the collagen helices. In dry networks where one would expect to observe such structural scattering about the analogous crosslinks, this is not observed.

In this paper we report our measurements of the hypersonic properties of some end-linked poly(propylene oxide) polyurethane gels. They are model gels, of good optical quality and relatively well characterized. Importantly, high crosslink densities were attained and a range of different concentrations were available. The pure polymer liquid, PPO, is well characterized in this frequency range⁶. They appear to be ideal samples in

which to investigate cooperativity through the crosslink dependence of the hypersonic acoustic properties.

THEORY

In Brillouin scattering experiments a visible photon is inelastically scattered from a thermal phonon and undergoes a frequency shift, ν_B , the Brillouin shift. Conservation of energy and momentum require that the sound speed, v_s , be related to ν_B by:

$$v_s = \frac{\nu_B \lambda_0}{2n \sin(\theta/2)} \quad (1)$$

where λ_0 is the photon wavelength in vacuum, n the refractive index of the scattering medium and θ is the angle through which the incident light is scattered. This inelastically scattered light is broadened above the incident width by the phonon spectral width due to damping. The resultant Brillouin linewidth, Γ , is related to the mechanical loss tangent by:

$$\tan \delta = \frac{\Gamma}{\nu_B} \quad (2)$$

Near a relaxation frequency the spectrum becomes asymmetrical and $\tan \delta$ may be extracted by using the following approximate relationship⁷:

$$\tan \delta \approx \frac{2\Gamma^+}{\nu_B} \left\{ 1 + \frac{\Gamma^+}{2\nu_B} \right\} \quad (3)$$

where Γ^+ is the half width at half height measured on the high frequency side of the peak. The observed damping corresponds to fluctuations in the dielectric tensor which are averaged over a volume, the cube of the phonon wavelength. Many processes can contribute to the phonon linewidth and in most cases there is no simple way

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Table 1

| Sample | % Polymer | G (10^5 N m^{-2}) | $\langle n_c \rangle$ |
|--------|-----------|---------------------------------|-----------------------|
| 1 | 50 | 6.77 | 13 |
| 2 | 50 | 6.00 | 19 |
| 3 | 50 | 3.64 | 43 |
| 4 | 50 | 2.41 | 49 |
| 5 | 50 | 0.64 | 110 |
| 6 | 90 | 5.83 | 35 |
| 7 | 70 | 4.90 | 35 |
| 8 | 60 | 3.64 | 35 |
| 9 | 40 | 0.96 | 35 |

of obtaining direct relationships between the relaxation times of such processes and the width¹. It is common in Brillouin scattering that at the temperature where the loss tangent is a maximum the loss process is occurring at some characteristic rate taken as the inverse of the Brillouin shift at this temperature. Whilst this argument is necessarily crude it is, however, useful for discussing processes for which the current understanding only allows interpretation to 'order of magnitude' precision. Because there is not a microscopic theory of Brillouin scattering from relaxing polymer materials, with certain assumptions, it is always possible to relate the measured quantities (v_s and $\tan \delta$) to relaxation times^{2,7}.

EXPERIMENTAL

Polyurethane gels

The poly(propylene oxide) polyurethane gels were made by reacting PPO polyols with 4-4' diphenylmethane diisocyanate in dibutyl phthalate (DBP). Three different PPO polyols were used⁸, two trifunctional and one bifunctional. The trifunctional units, had average molecular weights (M_n) of ~ 1000 and ~ 3000 respectively. The bifunctional unit has a molecular weight of ~ 2000 . In this preparation technique the network component is made by crosslinking at chain ends and by varying the proportions of these three polyols, networks of differing crosslink density are produced. The crosslink density may be obtained from the chemical composition with the assumption that all reactive end groups are totally incorporated into the network, that the reaction has an efficiency of 100% and that closed loops are ignored⁸. If these assumptions are accepted the value of $\langle n_c \rangle$, the number of PPO monomer units between crosslinks, will serve as a lower limit in each case. The study of somewhat similar gels made by Allen *et al.*⁹ indicated that closed loops were found to be important only in the networks containing a sizable proportion of the chain extender. The details of our gels are shown in Table 1 where we also list the static shear modulus, G . This was measured by Egerton¹⁰, who also prepared these gels, by using the technique of ball-bearing indentation. The refractive index of these gels has been measured and found to be ~ 1.54 at room temperature.

Light scattering technique

The Brillouin spectra were obtained using a triple-pass Fabry-Perot spectrometer¹¹. Some 100 mW of single mode 514.5 nm light was incident upon the sample; no local heating of the sample was apparent. Experiments were carried out as a function of both scattering angle and temperature. The temperature of the sample was

measured using a thermocouple thermometer inserted into the gel close to the scattering volume. The gels were allowed to attain thermal equilibrium before any data were collected. The highest temperatures studied were generally $\sim 420 \text{ K}$; temperatures in excess of this caused some discolouration of the sample as it degraded.

The spectrometer was always operated at an optimized free spectral range, generally $3\nu_B$, to reduce any effect of shrinkage of the Brillouin lines due to the proximity of the strong Rayleigh peak¹². The parasitic broadening of the Brillouin linewidth by the spectrometer arises principally from two effects; the finite collection aperture which allows light from a spread in wavevector to be analysed and the finite resolution of the Fabry-Perot etalon. The aperture effect was corrected using the data of Danielmeyer¹³ and the Fabry-Perot broadening by the deconvolution technique of Lindsay *et al.*¹⁴. Each experimental point presented is the mean value obtained from at least six good quality Brillouin spectra. The error in the sound speed is less than 1%, and in the loss tangent is $\sim 8\%$.

RESULTS

In Figure 1 the room temperature values of the sound speed, v_s , and the loss tangent in a series of 50% gels with different degrees of crosslinking are shown, the data relating to a scattering angle of 124° . Data were also recorded at 56° scattering angle. The sound speed is raised overall and the loss tangent lowered with increasing phonon frequency. The increase in v_s with frequency at a given crosslink density is consistent with the frequency dependence of the longitudinal modulus previously measured for pure poly(propylene glycol)². At the highest crosslink densities the sound speed increases markedly

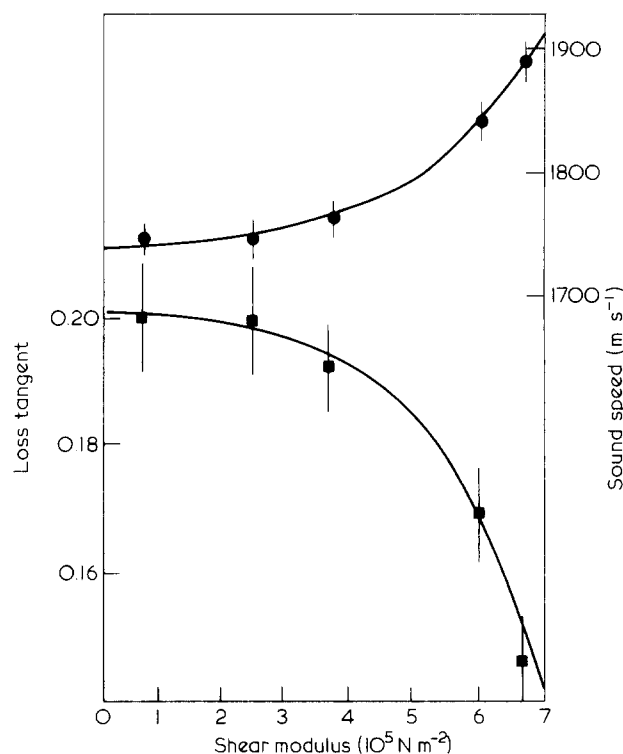


Figure 1 Room temperature measurements of the sound speed (●) and loss tangent (■) as a function of shear modulus in a series of 50% gels at a scattering angle of 124°

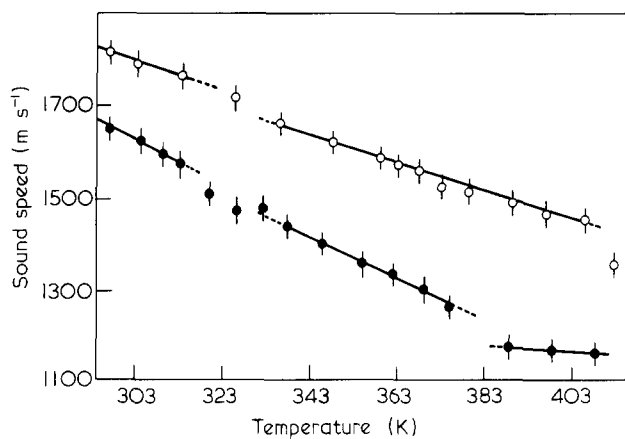


Figure 2 The temperature dependence of sound speed in two gels, 1 (O) and 4 (●) at a scattering angle of 56°

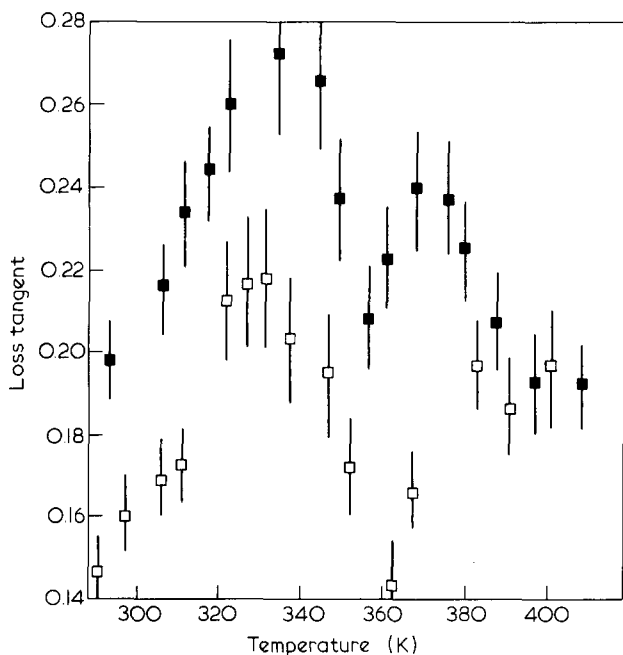


Figure 3 The temperature dependence of the loss tangent in gel 1 (□) and gel 4 (■) at a scattering angle of 56°

(the solid line is purely a schematic fit to the data). A marked fall in $\tan \delta$ is evident at the highest crosslink densities; this correlates with the decrease in compressibility indicated by the sound speed data. In Figures 2 and 3 we show v_s and $\tan \delta$ at a scattering angle of 56° for two differently crosslinked gels, numbers 1 and 4. In the case of the lightly crosslinked gel (4) two inflexions are visible in the sound speed data at ~ 370 K and ~ 330 K corresponding to loss maxima observed at these temperatures. These maxima correspond to the α and β loss maximum temperatures observed in the pure PPO by Patterson *et al.*⁶ at these frequencies. In the highly crosslinked sample the β relaxation appears to be unaffected in form although the sound speed is higher and the loss tangent lower overall. The α -relaxation is clearly shifted to higher temperatures though the data are limited to temperatures below 410 K. However, both sets of data (v_s and $\tan \delta$) together suggest that the loss maximum is now located near 400 K. In Figure 4 we show the sound speed and loss tangent in a series of gels at 290 K. All these gels have an identically crosslinked polymer component

but have varying polymer concentrations. As the polymer concentration in the gel increases the sound speed also increases but the loss tangent falls.

DISCUSSION

The data shown in Figures 1–4 illustrate that the hypersonic properties of these gels depend on both the crosslink density (i.e. the shear modulus) of the network component and the concentration of polymer within the gel. The qualitative agreement between the data presented here with that obtained by Patterson⁶ from the pure polymer fluid would support the view that the Brillouin spectrum originates from the polymer component of the gel. We do not, however, rule out any contribution from the solvent but would argue that this would represent only a small effect. Indeed the work of Moore *et al.*¹⁵ would appear to rule out any relaxational behaviour in dibutyl phthalate at the frequencies and temperatures encompassed within this study.

Separate from the two main dependences of the data, it is clear that there exists some broad background contribution to the linewidth in Figures 1 and 3. It has not been possible within the scope of this present series of experiments to isolate this background to any one or collection of causes. One could envisage a number of mechanisms being responsible for such an effect; structural relaxation, relaxation of the specific heat, relaxation in the solvent at distant temperatures or small particle scattering. We are able to discount the latter possibility in relation to scattering from the crosslink

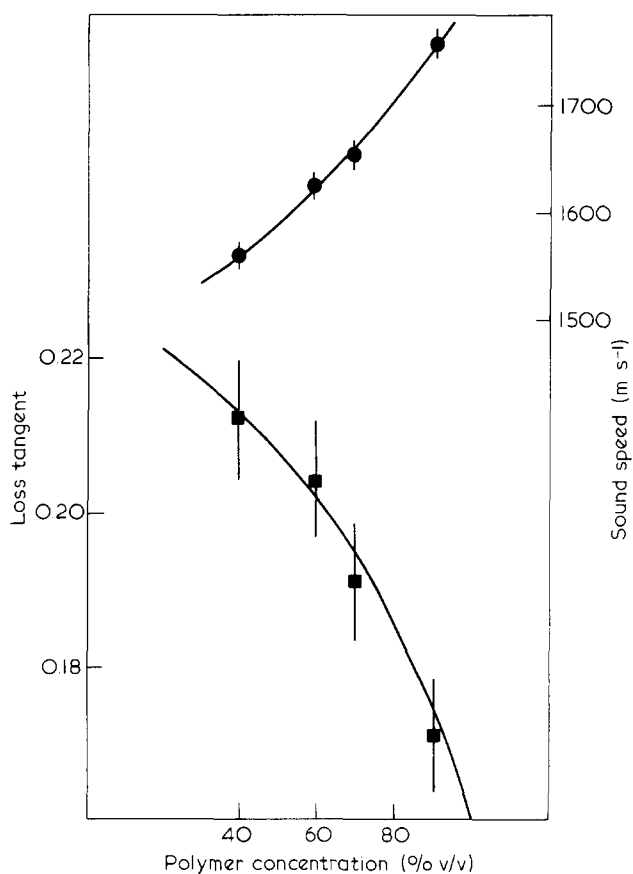


Figure 4 The sound speed (●) and the loss tangent (■) in a series of gels with identical dry crosslink density composition. The data were taken at room temperature and at 56° scattering angle

points (the dominant mechanism in the data of Bedborough and Jackson³ since this would increase the loss tangent at higher crosslink densities, in contradiction to our data.

Whilst it is impossible to completely divorce any discussion on the effects due to pure crosslinking and to polymer concentration we shall initially consider them separately. This is not such heresy since the data presented in *Figures 1-3* were carried out in gels having the same polymer concentration; effects due to concentration are likely to be little different between these samples.

Crosslink effects upon the α and β -relaxations

The observed insensitivity of the β -relaxation to crosslinking, *Figure 3*, would indicate that the corresponding relaxational behaviour is essentially localized. This would support the interpretation of Saba *et al.*¹⁶ that the β -relaxation in PPO involves only a small number of monomer units. Conversely the movement of the α -relaxation loss peak in the highly crosslinked gel would suggest that the mechanism responsible has a longer range, with the rearrangement at room temperature having a correlation length comparable to the intercrosslink distance in the highly crosslinked samples. We believe this indicates that the relaxations are of a cooperative nature with the size of the cooperatively rearranging unit approaching that of the intercrosslink distance. Leaving the question of what is meant by the distance between crosslinks we can gain an idea (albeit rather crude) of the size of the cooperative regions and the effect of crosslinking upon them. Although we could obtain similar estimates from other cooperative models we shall consider these data in terms of the Adam and Gibbs¹⁷ model. Following Adam and Gibbs we can write an average relaxation rate for the process as:

$$W(T) = \bar{A} \exp(-z^* \Delta\mu/RT), \quad (4)$$

where \bar{A} is a constant in that it is only weakly dependent on temperature, T , $\Delta\mu$ is the barrier to motion for one monomer unit and z^* the number of monomers which rearrange simultaneously at a given temperature. Since the configurational entropy of a chain will fall in proportion to the crosslink density and because z^* varies inversely with the configurational entropy, S_c ¹⁷, a simple approach is to write the value of z^* at some crosslink density, ρ , as:

$$z^*(\rho) = z^*(0) + B\rho \quad (5)$$

where B is a constant, in effect a correlation length associated with each crosslink expressed in terms of monomer units per crosslink.

With an activation energy for the α -relaxation of ~ 7 kcal mol⁻¹ in this frequency range (where Arrhenius behaviour is observed)¹⁸ and taking $\Delta\mu \sim 2$ kcal mol⁻¹, the activation energy for rotation about the C-C bond¹⁹, $z^*(0) \sim 3$ or 4 monomer units. One would not, therefore, expect to observe much effect upon relaxation rates until the intercrosslink distance was about twice this value. A recent series of neutron scattering experiments on chemically identical polyurethane networks by Walsh *et al.*²⁰ have indicated the importance of hydrogen bonding between the urethane groups and the PPO chain. These

workers found that the mobility of the polymer chains, whilst being slightly reduced with an increasing crosslink density, were greatly reduced by the presence of this hydrogen bonding. It would appear that these hydrogen bonds behaved like extra crosslinks in these networks at neutron scattering frequencies.

We have no reason to dismiss this effect within the network component of the gels we have studied. For this reason the value of $\langle n_c \rangle$ quoted in *Table 1* must be regarded as an approximate value; the actual value is expected to be smaller. The movement of the α -relaxation temperature and the difference in room temperature properties occur for heavily crosslinked gels with values for $\langle n_c \rangle$ of 13 and 19. The additional crosslinking produced by the hydrogen bonding would result in better agreement with the Adam and Gibbs theory.

Our data do not indicate whether it is the chain length between crosslinks or the physical separation of the crosslinks which matters. This discussion has leaned heavily towards the former, that is intrachain rather than interchain processes dominate the relaxation mechanisms. We would wish to point out that with such short chain lengths the difference is not great. However, the distinction is important in view of the similarity of the relaxational behaviour of molecular liquids, and particularly significant at lower temperatures where z^* becomes large.

Effect of the gel liquid

Whilst the previous section dealt with the effect of crosslink density upon the hypersonic dynamics of the polymer component, any discussion of the influence of the gel liquid was ignored. Further, the arguments presented relied upon the earlier work of Walsh *et al.*²⁰ on the hydrogen bonding present in the dry network. Whilst in the networks this dominates the polymer dynamics we believe that the presence of the gel liquid reduces this effect. Dibutyl phthalate, an aromatic solvent, will tend to reduce effects of hydrogen bonding by becoming hydrogen bonded itself from its carbonyl oxygen. The data shown in *Figure 4* shows that the hypersonic properties are influenced by the presence of DBP. As the concentration of DBP is increased the loss tangent increases whilst the sound speed falls. The increase in the loss tangent (the energy absorption per cycle²) would indicate that the relaxation spectrum is altered. This phenomenon is not unique. Two separate Brillouin scattering studies by Wang and co-workers^{21,22} have identified such an effect. In the study of poly(propylene glycol) in solution with methyl-cyclohexane the β -relaxation loss peak of the PPG was shifted to lower temperatures as the proportion of solvent was increased. The effect of increased cyclohexane concentration in polystyrene solutions on the loss tangent can be obtained from the data of Lempert and Wang²². At 290 K the loss tangent is a maximum for a 50% solution which has an hypersonic relaxation at this temperature; at higher and lower concentrations the loss tangent falls as this relaxation moves away from this temperature. For greater solvent concentrations the relaxation temperature is depressed below 290 K. These observations would correlate well with the hypersonic properties we have recorded in the polyurethane gels.

Whilst Lempert and Wang²² in their paper used a model based upon structural relaxation to explain the

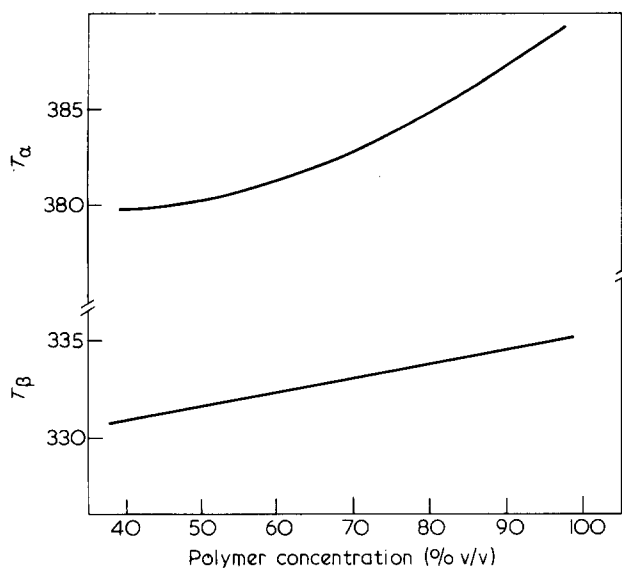


Figure 5 Theoretical temperature dependence of the hypersonic α and β relaxation temperatures due to solvent softening

results, in this paper, we put forward an explanation which embodies the hydrogen bonding present in these polyurethanes. We propose that, as the concentration of DBP in these gels increases, the hydrogen bonding observed in the network component is reduced. This is supported by the Raman spectra of the gels. In the Raman spectrum of pure DBP a doublet is observed at 1584 cm^{-1} and 1602 cm^{-1} whilst a third higher energy mode is apparent in the 40% polymer concentration gel at 1612 cm^{-1} ; no Raman lines were found in this frequency region for the pure polymer. Whilst the third line has not yet been assigned, its position is characteristic of hydrogen bonding in these materials²³.

The reduction in the density of hydrogen bonding by the DBP will increase the mobility of the polymer between the crosslinks as the gel becomes more dilute. This would lead to a reduction in the relaxation temperatures. To gain some appreciation of the magnitude of this effect we assume that the hydrogen bonds increase the activation energy (ΔH) of the hypersonic relaxations. We can write this crudely in the following form:

$$\Delta H(\Phi) = \Delta H(0) - K\Phi \quad (6)$$

where $\Delta H(0)$ is the activation energy in the network and Φ is the normalized concentration of the solvent. K is a constant that can be considered to be a mobility indicator. To study the effect of solvent softening we have assumed that the activation energy in the 50% gel is identical to that in the pure liquid polymer and that the temperatures of α and β relaxations are those found for pure PPO liquid. The physical validity of such an assumption is reasonable, the effect of gel liquid and crosslinking are competitive, but we shall only use it to gain some rough quantitative idea of a temperature spread. Using the well known single relaxation time expressions for the loss tangent¹⁸ we have

calculated independently the temperatures of maximum loss for the α and β relaxations in gels of differing concentrations having activation energies given by equation 6. These data are shown schematically in Figure 5. In the region of interest it can be seen that the α -relaxation varies over a temperature range of $\sim 6^\circ$ whilst the β -relaxation varies by $\sim 5^\circ$.

In the gels most crosslinked, discussed in the previous section, we found that whilst the Adam and Gibbs theory predicted that cooperative rearrangement occurred for oligomers of length 3 or 4 monomer units, we have reported temperature shifts for network components of ($\langle n_c \rangle$) 13 and 19 monomer units in length. The number of monomer units between crosslinks, $\langle n_c \rangle$, was calculated subject to the usual restrictions, from the composition of the network component. Such a calculation will not include the extra contribution to the crosslink density from the hydrogen bonds. Since Walsh *et al.*²⁰ believed that these hydrogen bonds in networks dominated the dynamics over the crosslinks we can expect the number of monomer units between crosslinks to be reduced below $\langle n_c \rangle$ even in the 50% samples. To obtain good agreement between the quantitative application of the cooperative theory and our data only one hydrogen bonded crosslink need be present between each pair of urethane crosslinks, on average; this would appear to be physically reasonable.

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