polymer papers

Ultrasonic studies of polyurethane network formation

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The formation of polyurethane networks has been followed by measuring ultrasonic absorption and velocity as a function of time for discrete frequencies. In order to determine the relaxation spectra in the pre-gel phase, ultrasonic measurements were performed on quenched samples over the frequency range 5–1000 MHz. The data observed are discussed in terms of molecular motions and interactions.

(Keywords: ultrasonics; networks; polyurethanes; gelation; poly(oxypropylene triol))

INTRODUCTION

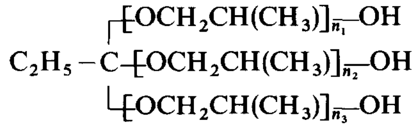
Ultrasonic propagation has traditionally been used for the characterization of the high frequency dynamic process which occurs in polymer solutions and solids[1,2]. The close connection between sound propagation and polymerization of reactive species in solution was first pointed out by Sokolov[3]. Subsequently, measurements have been reported on the use of ultrasonics for the monitoring of polymerization of polystyrene[4], poly(vinyl chloride)[5,6] and poly(vinyl acetate)[7,8].

The aim of this study was to gather quantitative information on the processes which occur during the formation of a polyurethane network structure. The observed changes in attenuation can be ascribed to a combination of rheological properties and changes of the dynamic spectrum generated as a consequence of the polymerization process.

EXPERIMENTAL

Synthesis of urethane networks

The polyurethane networks were formed by the condensation of poly(oxypropylene triol) with hexamethylene diisocyanate (HMDI). The polyols used in the study were propylene oxide adducts of trimethylolpropane with the structural formula:



$$C_2H_5-C\begin{cases}-[OCH_2CH(CH_3)]_{\bar{n}_1}-OH\\-[OCH_2CH(CH_3)]_{\bar{n}_2}-OH\\-[OCH_2CH(CH_3)]_{\bar{n}_3}-OH\end{cases}$$

where n_c is the average degree of polymerization of each of the arms. The polyols were dried for 2 h under reduced pressure (0.01 mbar) and the residual water content was determined by the Karl Fischer method to be less than 200 ppm. The hydroxyl content of the polyol was determined by acetylation and the molecular weight was determined by size exclusion chromatography. The effective functionality of the polyols was determined to be equal to three[9] and the characteristics of the polyols are summarized in *Table* 1.

The purity of the hexamethylene diisocyanate (HMDI) was assessed using size exclusion chromatography and ^1H n.m.r. spectroscopy and was determined to be better than 99%.

The networks were synthesized by mixing the dried triol with HMDI for various stoichiometric ratios of NCO and OH groups. The ratio of the concentration of NCO to OH was designated r, and reaction was achieved by the addition of 2×10^{-3} g dibutyl tin dilaurate catalyst for every gram of HMDI. Toluene was used as solvent for the reaction and the temperature was maintained at 313 K whilst the crosslinking process proceeded. The gel point was determined as the point at which the liquid reaction mixture ceased to flow in an inverted test tube. In order to determine the relaxation spectra in the pre-gel phase, ultrasonic measurements were performed on quenched samples. These samples were prepared by polycondensation of triols and HMDI with toluene until complete reaction of isocyanate groups with different initial stoichiometric ratios below r_0, the critical value to reach the gel point.

Table 1 Characteristics of the polyols used in this study

Code	Ugipol 3170	Ugipol 3180	Ugipol 1160
M_n (g mol^{-1})	695	1590	2540
M_W/M_n	1.03	1.05	1.04
Hydroxyl content (m mol g^{-1})	4.32	1.97	1.21

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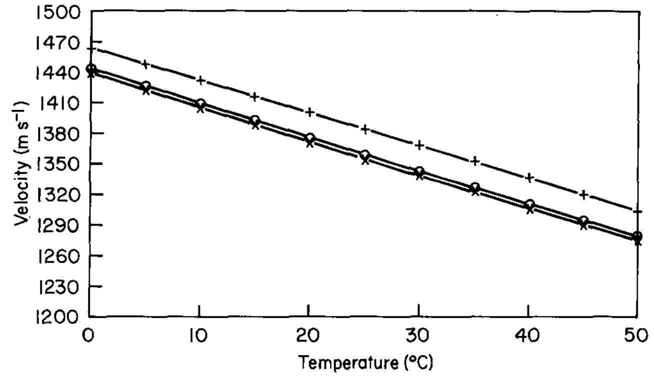

Figure 1 Temperature dependence of ultrasonic velocity for pure triols: +, 700 (Ugipol 3170); ○, 1500 (Ugipol 3180); ×, 2500 (Ugipol 1160)

Table 2 Temperature coefficients of triols

Coefficient (ms^{-1})	Triol 700 (Ugipol 3170)	Triol 1500 (Ugipol 3180)	Triol 2500 (Ugipol 1160)
C_0	1463.34	1443.20	1439.92
C_1	−3.223	−3.484	−3.680
C_2	26.72×10^{-4}	31.92×10^{-4}	112.1×10^{-4}
C_3	39.64×10^{-6}	24.211×10^{-6}	-71.14×10^{-6}
σ	0.18%	0.15%	0.17%

The polycondensation reaction was carried out at 313 K and the time required for complete reaction of all isocyanate groups was about 8 days.

Viscosity measurements

The viscosities of the triols and the various mixtures of toluene–triols and quenched samples were determined using an Ubbelohde suspended level viscometer thermostatically controlled to within about ±0.01 K and the flow times were measured electronically, yielding an overall precision of better than 1%.

Ultrasonic velocity

Velocity measurements were performed using an optical interferometer based on the Raman Nath diffractometer principle[10] and an acoustic beat technique[11]. The precision of measurements was estimated to be 10^{-4} with the first method and 10^{-3} with the second.

Acoustic absorption

Low frequency attenuation data were obtained using a conventional pulse apparatus operating over the frequency range 5–100 MHz[12]. High frequency data were obtained using a pulse method operating in the range 100–1000 MHz and using a lithium niobate transducer[13]. The precision of measurements of the absorption measurement was ±5% at low frequency (5 MHz) and to ±2% at high frequency (450 MHz).

RESULTS AND DISCUSSION

Ultrasonic velocity

The ultrasonic velocity for three pure triols measured over the temperature range 0–50°C showed behaviour typical of that observed in other hydrogen bonding liquids (*Figure 1*). In this region the velocity increases as the molecular weight decreases. The data may be fitted to a series approximation of the form:

$$C = C_0 + C_1T + C_2T^2 + C_3T^3 \qquad (1)$$

where T is the temperature in degrees Celsius. The temperature coefficients obtained together with the standard deviations are presented in *Table 2*.

Acoustic attenuation data

In order to interpret the ultrasonic attenuation data for the reaction mixtures, measurements were performed on the pure triols and their solutions in toluene at 27°C (*Figures 2* and *3*). It is apparent that it is not possible to describe the observed acoustic attenuation data in terms of a single relaxation and we have therefore assumed a double relaxation to be appropriate and have used the form:

$$\frac{\alpha}{f^2} = \frac{A_1}{[1+(f/f_1)^2]} + \frac{A_2}{[1+(f/f_2)^2]} + B \qquad (2)$$

where A_1 and A_2 are the amplitudes and f_1 and f_2 are the relaxation frequencies of the two processes. The constant B is associated with the classical Navier–Stokes contribution to sound attenuation and in the case of

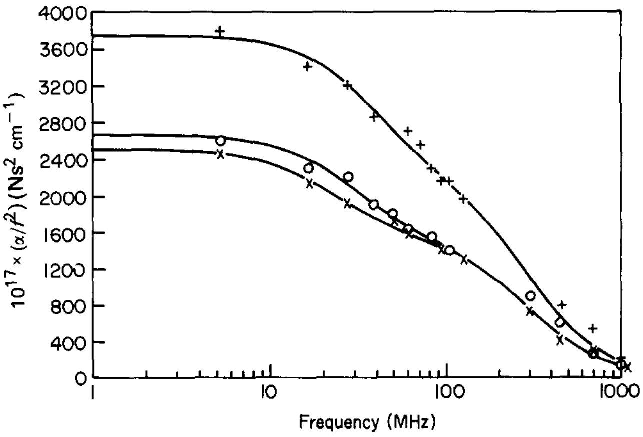

Figure 2 Variation with frequency of the acoustic attenuation of the triols at 27°C: +, 700; ○, 1500; ×, 2500

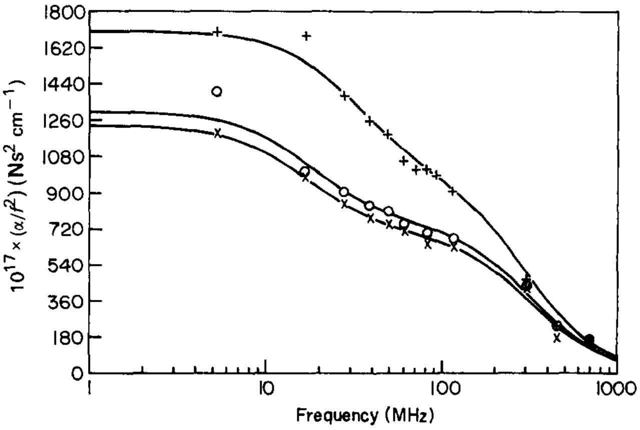

Figure 3 Variation with frequency of the acoustic attenuation for an 11% solution in toluene of the three triols at 27°C: +, 700; ○, 1500; ×, 2500

Table 3 Acoustic attenuation data

	A_1 ($\times 10^{17}$)	f_1 (MHz)	A_2 ($\times 10^{17}$)	f_2 (MHz)	σ %	c (ms^{-1})	v_s (Stokes)	(α/f^2) calc ($\times 10^{17}$)
Pure triols								
700	1600	39	2150	300	2.9	1377.5	3.02	2800
1500	1180	30	1480	300	2.3	1351.9	3.08	8270
2500	1000	23	1500	300	1.6	1347.3	4.33	4648
11% toluene								
700	700	32	1000	300	2.5	1356.6	0.79	833
1500	550	18	750	320	1.8	1339.2	0.86	953
2500	530	17	700	320	2.3	1332.8	1.20	1334
Triol 700								
Toluene 0%	1600	39	2150	300	2.9	1377.5	3.02	2800
11%	700	32	1000	300	2.5	1356.6	0.79	833
42%^{a}	150	30	200	300	2.9	1319.7	0.11	126
Triol 700 (42% toluene)								
$r=0^a$	150	30	200	300	2.9	1319.7	0.11	126
$r=0,20$	300	40	300	400	2.4	1338.8	0.20	224
$r=0,42$	500	15	450	400	2.5	1353.1	0.81	863
$r=0,50$	450	22	500	400	2.3	1357.2	1.93	2033
$r=0,57$	740	31	320	480	9.8	1361.3	10.5	10973
Triol 700 $r=0.2$								
Toluene 11%	2400	17	1800	320	3.6	1376.8	3.98	4018
25%	950	11	730	310	3.0	1343.7	0.65	707
42%	300	40	300	400	2.4	1338.8	0.20	224

A_1, A_2: N s^2 cm^{-1} ^{a} $B=100$

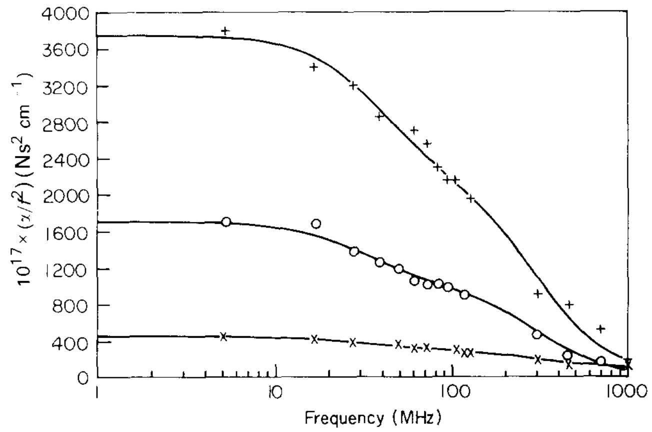

Figure 4 Influence of concentration on the acoustic attenuation for triol 700. Concentration: +, 0%; ○, 11%; ×, 42%

organic systems can be associated with a viscous contribution:

$$B = (\alpha/f^2)\text{observed} = 8\pi^2 v_s/3c^3 \qquad (3)$$

where c is the velocity of sound and v_s is the static shear viscosity of the medium. In the case of low molecular weight organic systems, the viscosity v_s does not exhibit a relaxational effect below 1000 MHz, and the attenuation predicted using equation (3) approximates closely to the observed value. However, in the case of polymer systems the viscosity can exhibit relaxational characteristics and will contribute to the relaxational behaviour. It has been shown in previous papers[1,2] that the effects of this contribution to the attenuation can be predicted on the basis of a modified Rouse model. In all systems studied equation (2) was shown to fit the data within the error in the parameters presented in *Table 3*.

Pure alcohols and their solutions in toluene

Before discussing the effects of the gelation process on the ultrasonic relaxation we will consider the spectrum exhibited by the pure triols and their solutions in toluene. The ultrasonic attenuation plots for the three triols are presented in *Figure 2*. An increase in molecular weight leads to a decrease in the amplitude of the process, and is consistent with the idea that the main contribution to the relaxation comes from hydrogen bonding interactions. It is not possible on the basis of these data to interpret the molecular relaxation processes in terms of specific motions. The high frequency process is essentially identical in the 1500 and 2500 systems and larger in the 700 system. It is probable that the spectrum is a mixture of rotational isomerization of the chains and of hydrogen bonds breaking and forming. In order to explore the nature of the relaxation, one of the triols was dissolved in toluene and the ultrasonic relaxation studied (*Figure 4*). The relaxation frequencies do not appear to change significantly with dilution; however, the amplitudes of the relaxations decrease markedly. This observation implies that the process that occurs is a relatively local relaxation process and does not involve collective motions of large groups of molecules. If the relaxation were a simple isomeric process then an approximately linear correlation of the amplitude with concentration might be anticipated. In fact, this is not observed, which indicates that the process giving rise to the relaxation probably involves both intra- and intermolecular interactions. It is not possible to extrapolate further the data to give more information on the detailed relaxation processes.

Quenched branched polyurethanes

Ultrasonic attenuation was measured for 42% solutions of the triol in toluene with isocyanate in stoichiometric ratios $r=0$, 0.2, 0.42, 0.50 and 0.57,

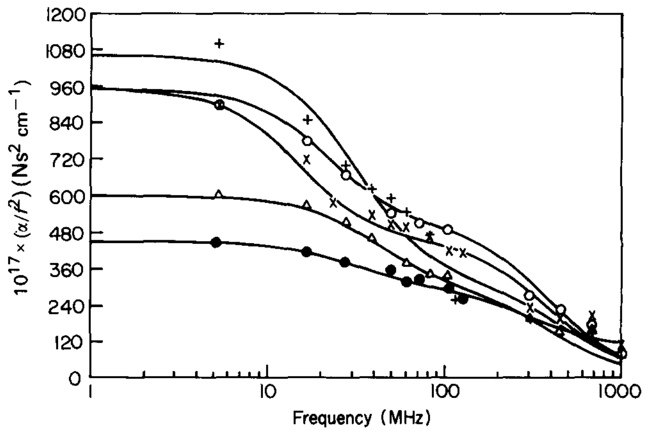

Figure 5 Acoustic attenuation of the triol 700–isocyanate reaction product obtained at 27°C for a 42% solution in toluene for various stoichiometric ratios. r: ●, 0; △, 0.2; ×, 0.42; ○, 50; +, 0.57

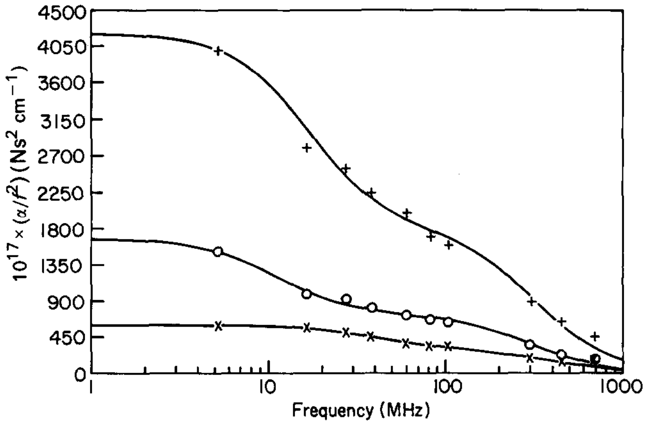

Figure 6 Acoustic attenuation of the triol 700–isocyanate reaction product ($r = 0.20$) obtained at 27°C diluted in toluene. Concentrations: +, 11%; ○, 25%; ×, 42%

gelation occurring at $r = 0.61$. The experimental data can also be fitted to a twin relaxation process. The interesting feature which emerges from these studies, as shown in *Figure 5*, is that as the reaction proceeds so the magnitude of the relaxation increases and there is also a change in the relaxation distribution. Increasing the molecular weight of a polymer will usually lead to the appearance of relaxations in the region below 10 MHz, due to viscoelastic effects.

As the length of a polymer chain increases so its longest mode relaxation time will move to lower frequency. Studies of narrow molecular weight polystyrene molecules in dilute solution in toluene are observed to exhibit relaxation processes associated with viscoelastic processes ranging from 100 MHz for $M_n = 600$ to 100 Hz for $M_n = 10$. The fact that the observed relaxation spectrum conforms closely to that expected on the basis of the hydrogen bonding processes implies that even in the sample with $r = 0.57$ the polymer network has not reached a sufficient size to give rise to a significant viscoelastic contribution to the relaxation in the MHz frequency region. Increases in the amplitude and changes in the relaxation spectra have recently been observed as a consequence of entanglements in linear polymer chains[15]. In the case of poly(dimethyl siloxane) a molecular weight of 12 000 is required before significant normal mode effects become evident.

In order to gain further insight into the origins of the relaxation, a sample prepared using $r = 0.2$ was further diluted with toluene. As the concentration of solvent is increased the extent of inter-chain interaction will decrease and this will result in both a change in the distribution of relaxation and in the amplitude (*Figure 6*). The effects observed can be explained on the basis that the triol forms a complex spatial structure to which are associated a number of normal modes and hydrogen bonding interactions. The topography of the systems is too complex to model in terms of a simple combination of collective normal mode processes and hydrogen bonding interactions. It should be noted that, again, the amplitude does not correlate with the concentration of the urethane, which is consistent with the concept of the complex process outlined above. The observed increase in the relaxation amplitude is in line with the presence of a contribution to the attenuation arising from normal mode relaxation (*Table 3*) and exhibiting a relaxation in the MHz frequency region.

Kinetics of gel formation

The course of the gelation reaction of a system constituting a triol ($M = 700$) and a diisocyanate with a stoichiometric ratio $r = 1$ in an 11% (w/v) solution in toluene was followed as a function of time. The ultrasonic cell used was composed of two pairs of transducers at a fixed distance, thermostatically controlled to within ±0.01°C. Ultrasonic velocity and absorption were determined by measurement of the phase and amplitude of the received signal during the course of the reaction.

Velocity

No change in velocity was observed during the period over which the reaction was monitored. However, there could be a small change in compressibility which is compensated for by the change of density which occurs during the reaction.

Acoustic attenuation

The amplitude of the signal is reduced as the reaction proceeds towards gelation and the diffractional attenuation is defined as:

$$\frac{\Delta\alpha}{f^2} = \frac{\alpha_1 - \alpha_2}{f^2} \qquad (4)$$

where α_1 is the initial attenuation and α_2 is the attenuation of the reacting system (*Figure 7*). Gelation of the sample occurs after ≈ 1 h and corresponds to a point

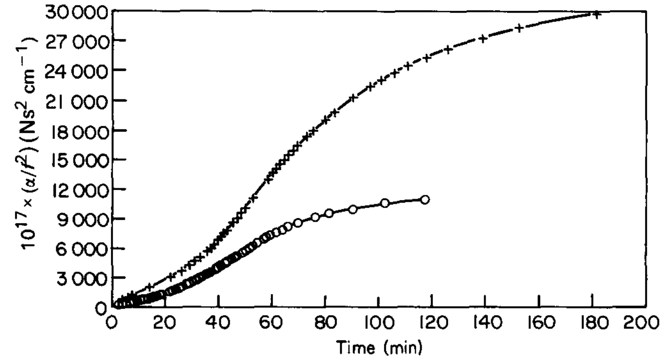

Figure 7 Variation of the acoustic attenuation as a function of time for the triol 700–isocyanate reaction ($r = 1$). Studies performed on an 11% solution at: +, 4 MHz; ○, 19 MHz

half way up the curves. Gelation is associated with the point at which sufficient structure has been generated for the solution not to flow. However, there is clearly a very significant extent of reaction still possible. Reaction continues for a further 2.5 h until no further changes in the matrix occur. Similar behaviour has been observed for the gelation of aqueous systems[14].

CONCLUSION

The study described indicates the potential of the ultrasonic method for the study of reacting systems. Unfortunately, the complexity of the relaxation spectrum makes it difficult to develop an analytical molecular model to analyse the data further. The results obtained so far encourage us to pursue this topic by examining other gelling systems in order to establish from the behaviour of each the general and relevant features, and to analyse the data from recent theoretical approaches of critical phenomena.

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