

Elasticity of urethane networks

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Various polymer networks have been prepared based on poly(propylene oxide) which has been linked either by urethane groups or ester groups. These networks have been examined by stress-strain measurements to find the degree of deviation from ideal rubber elasticity (as specified by the statistical theory) and by neutron scattering to find the mobility of the poly(propylene oxide) chain. The stress-strain results showed the urethane-linked networks to be identical to the ester-linked networks as long as there were no short chain polyols in the formulation. Networks containing short chain polyols have a greater deviation from ideal rubber elasticity. The neutron scattering results showed the ester-linked poly(propylene oxide) to have the same mobility as an uncrosslinked poly(propylene oxide), whereas urethane-linked networks have a lower mobility, similar to an analogous urethane-linked polymer. A small effect of crosslinking was observed. The results are explained in terms of some phase separation occurring in the polyurethanes only when short chain polyols are present. In the simple urethane-linked networks the poly(propylene oxide) chain mobility is reduced by hydrogen bonding to the urethane groups, but this has no effect on the equilibrium stress-strain properties.

INTRODUCTION

The various theories of rubber elasticity lead to a general expression for the free energy change for unit volume on deformation of a network:

$$\Delta F_{cl} = A \frac{\nu}{2} kT (\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) - B \nu kT \ln \lambda_x \lambda_y \lambda_z \quad (1)$$

where ν is the number of elastically effective chains per unit volume; k is the Boltzmann constant; T is the absolute temperature; λ_x , λ_y , λ_z are the deformation ratios in the directions specified by the x , y , and z axes; A and B are constants. The exact values of the constants are a matter of some contention.

For a network with tetrafunctional crosslinks the theory results in a value of G , the shear modulus, of

$$G = A \nu kT = 2AnkT = \frac{A \rho RT}{M_c} \quad (2)$$

where n is the effective number of crosslinks and ρ is the density.

The term including B in equation (1) has no effect unless there is a change in volume accompanying the deformation.

Real polymer networks do not generally obey the theories developed even qualitatively when an appreciable range of extension ratios ($\lambda_x = 1 \rightarrow 2$) is considered. Mooney² modified the expression by adding an extra term to give:

$$\Delta F = C_1 (\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) + C_2 \left(\frac{1}{\lambda_x^2} + \frac{1}{\lambda_y^2} + \frac{1}{\lambda_z^2} - 3 \right) \quad (3)$$

where C_1 and C_2 are constants and C_1 is often given as:

$$C_1 = A(\nu/2)kT \quad (4)$$

The modified equation extends the range of applicability though not to a very great extent and the physical significance of the extra term is uncertain; however, in the absence of any alternative, it has been usual to describe the deviation of networks from ideal behaviour in terms of the relative sizes of the constants C_1 and C_2 .

In the case of unidirectional extension substitution of $\lambda_y = \lambda_z = \lambda_x^{-1/2}$ in equation (3) and differentiation with respect to λ_x yields the force f . The analysis of data is conveniently carried out in terms of a reduced force f^* given by:

$$f^* = \frac{f}{A^*(\lambda_x - \lambda_x^{-2})} = 2C_1 + 2C_2 \lambda_x^{-1} \quad (5)$$

where A^* is the cross-sectional area of the undistorted sample. Thus a plot of f^* against λ_x^{-1} should give a straight line with slope $2C_2$ and intercept $2C_1$.

A review of experimental results of determinations of C_2 values, and theories of the origin of C_2 has been written fairly recently by Mark. A variety of experimental facts are clues to the origin of the term, for example³:

- (a) if a sample is tested in both extension and compression different C_2 values are found, the value found in compression usually being much lower;
 - (b) swollen samples show a much lower value of C_2 .
 - (c) samples prepared in the presence of a solvent and then dried show a lower value of C_2 ;
 - (d) much conflicting data exists concerning the dependence of C_2 on crosslink density and on temperature.
- Considering the inadequacies of the equation, an alternative expression has been suggested⁴:

$$f = \frac{2GA^*}{n} (\lambda^n - \lambda^{-n/2}) \quad (6)$$

which has the advantage of extending the region of fit, and working equally as well in compression as in extension. The constant 'n' is between 1 and 2 for most rubbers and is 2 for ideal rubber (i.e. one for which equation (1) holds).

Measurements of C_2 values have been made⁵ for a wide variety of polyurethane elastomers prepared from poly(propylene oxide) polyols crosslinked with diisocyanates. An increase in the ratio C_2/C_1 was found with increasing urethane group concentration in the chains. The results were explained in terms of intermolecular order in the networks.

Commercial polyurethanes containing short chain diols and high urethane concentrations have a 'blocky' nature and easily observable gross phase separation⁶ but this is not as easily demonstrable in networks containing no short chain polyols.

This paper describes the evaluation of C_2 terms of certain polyurethane networks and also networks in which the urethane crosslinks have been replaced by ester crosslinks which do not have the potential hydrogen bonding exhibited by a urethane. Results are also presented of neutron scattering experiments which have measured the mobility of the poly(propylene oxide) chain in the two types of network compared with that of a free poly(propylene oxide) chain. These results are part of a larger study of segmental motion in bulk polymers and networks (ref 10 and future publications by the same group).

EXPERIMENTAL

Preparation of networks

The polyurethane networks were similar to those used in a previous study⁷ prepared by the reaction of a trifunctional poly(propylene oxide) with diphenylmethane-4,4'-diisocyanate (MDI).

The poly(propylene oxide) had a nominal molecular weight of 3000 and hence an equivalent weight per hydroxyl group of 1000; the measured hydroxyl value was 57 mg KOH g⁻¹. The sample was dried under a stream of nitrogen at a reduced pressure while heating at 100°–110°C for 1 h. The MDI was distilled at 180°C under reduced pressure and used within a day of distillation. The reactants were mixed in a flask at about 40°C, degassed, and cooled to room temperature. A drop of dibutyltin dilaurate was added as a catalyst, the mixture stirred under vacuum for 1 min and poured into a mould. The mixture was then heated overnight at 60°C to complete the cure. The mould consisted of a rubber gasket between glass plates treated with a mould release agent, or preferably a PTFE gasket between PTFE plates. It was in the form of a 'dog-bone' to produce samples with a central portion of about 1 cm wide by 0.35 cm thick and 5 cm length, suitable for mechanical testing. A second mould was used to prepare thin sheets of the sample 0.2 mm thick, suitable for neutron scattering measurements.

The ester-linked networks were prepared by a method similar to that used by Stepto in studies of stress-strain curves in compression⁸.

Redistilled sebacoyl chloride was weighed into a dry flask and an equivalent amount of the dried poly(propylene oxide) as above was added and mixed. The mixture was heated at 50°–55°C for 20 min, cooled and degassed. It was then

poured into the moulds as above and heated at 60°C for 2 h followed by 85°–90°C for at least 48 h. The crosslinked samples were transferred to a vessel through which a slow current of nitrogen was passed for at least 2 days, to remove HCl produced in the reaction, before testing. Similar networks were also prepared by reacting a poly(propylene oxide) of 2000 mol wt, mixed with trimethylol propane and sebacoyl chloride. Such networks were analogous to polyurethane networks containing low molecular weight alcohols which have been reported as giving higher C_2 values⁵.

It is possible to measure the efficiency of the polyurethane-forming reaction by reacting the unreacted isocyanate groups with C-14 methanol as described in a previous paper⁷, and this efficiency is always found to be in excess of 99%. However, it was not possible to measure the efficiency of the ester-forming reaction in a similar manner, as the methanol undergoes ester interchange with the network under acid catalysis, the network completely breaking down after 2 days. It is therefore necessary to infer the extent of reaction from the known kinetics of the system⁸. The modulus of the samples formed, relative to that of the polyurethane can also be taken as an indication of the reaction efficiency.

Linear polymers were also prepared by reacting a linear poly(propylene oxide) of molecular weight 2000 with MDI and with sebacoyl chloride, respectively. These polymers were chemically identical to the networks described above but did not form a network. These were used for comparison in neutron scattering studies to separate the effect of crosslinking from the chemical effect of the crosslinking group.

Stress-strain measurements

Stress-strain curves were measured by holding the samples in a clamp and suspending a series of weights. The extension of the sample was found by measuring the distance between two marks on the central section of the dog-bone using a travelling microscope. The weights were increased until the sample broke. Plots of f^* against λ_x^{-1} allowed the constants C_1 and C_2 to be found graphically.

The results were also analysed by a computer method. The program was designed to include an error for each length measurement, and thus calculate an error in λ_x . Each point was loaded accordingly in the estimation of the best straight line and an overall error in the constants C_1 and C_2 calculated. For small deformations the length L is close to L_0 the original length, thus $\lambda_x (=L/L_0)$ is very close to 1 and the resultant error in the term $(\lambda_x - \lambda_x^{-2})$ is very large. These points are therefore given very little loading. The samples used (which can often be extended only slightly before breaking) thus give inaccurate C_1 and C_2 values and the errors quoted are hence quite large.

The computer program also calculated values of A and n from equation (6). However, this was found to be a more difficult equation to fit accurately, especially in view of the small extensibility of the samples. The values of n calculated thus have very large errors.

Neutron scattering measurements

These measurements were carried out using the INIO back-scattering spectrometer at the Institut Laue-Langevin, Grenoble.

The apparatus and its use in the study of backbone motion in polymer solutions and melts has been described in a number of references^{9–11}. Essentially, a highly mono-

Table 1 Results from stress-strain measurements

	$2 C_1$ (g/cm ²)	$2 C_2$ (g/cm ²)	C_2/C_1	n
(A) Trifunctional 3000 mol wt PPO plus sebacoyl chloride (polyester)	5230 ± 200	1564 ± 120	0.30 ± 0.03	1.49
	5520 ± 155	1780 ± 187	0.32 ± 0.04	1.39
	5700 ± 700	1900 ± 900	0.33 ± 0.17	1.31
	6000 ± 300	1560 ± 380	0.26 ± 0.07	1.43
	4580 ± 50	1544 ± 60	0.34 ± 0.01	1.42
Average	4650 ± 40	1374 ± 50	0.30 ± 0.01	1.56
			0.31	1.45
(B) Trifunctional 3000 mol wt PPO plus MDI (polyurethane)	4986 ± 100	1456 ± 90	0.29 ± 0.02	1.53
	5186 ± 300	1770 ± 350	0.34 ± 0.07	1.31
(C) Bifunctional 2000 mol wt PPO, TMP and sebacoyl chloride (polyester)	2532 ± 15	814 ± 20	0.32 ± 0.01	1.56
	2523 ± 62	849 ± 77	0.34 ± 0.03	1.43
(D) Trifunctional 4000 mol wt PPO plus sebacoyl chloride	3036 ± 60	1061 ± 82	0.35 ± 0.03	1.54
	2850 ± 33	1036 ± 45	0.36 ± 0.02	1.50
(E) Bifunctional 2000 mol wt PPO plus TMP and MDI (polyurethane)	2260	1210	0.54	—
	2190	1210	0.55	—

chromatic beam of neutrons is scattered from the polymer sample. Small increases in the energy spread of the incident beam are measured and related to the relatively slow motion of the polymer as it explores the millions of configurations available to it in a solution or a melt.

The variation of the observed energy broadening as a function of scattering angle is related to the details of the type of motion observed. For example Fickian diffusion leads to broadening of the scattered energy spread which increases as the square of the sine of half the scattering angle. More precisely $\Delta\epsilon = 2hDK^2$ where D is the macroscopic diffusion coefficient and $K = (4\pi/\lambda) \sin(\theta/2)$.

For convenience, the data is presented on logarithmic scales as $\Delta\epsilon$, the full width at half maximum of the scattered energy profile (resolution effects having been removed) versus K where K is the wave vector change on scattering ($= (4\pi/\lambda) \sin(\theta/2)$ where θ is the scattering angle).

A shift of the data up the vertical axis is then an indication of an increase in the frequency of the motion being observed, while a change of slope indicates a change in the type of motion being observed.

All experiments on networks and melts were performed on thin films (0.2 mm thick, 20 cm² area) at 70°C. Experiments on solutions were at room temperature and samples were prepared at thicknesses corresponding to the same weight per unit area of the polymer as the thin films. Samples were held in thin-walled aluminium cans. The scattering from an empty can, or a can containing solvent only, where relevant, was subtracted before the broadening was analysed.

RESULTS AND DISCUSSION

Stress-strain results

Values of C_1 and C_2 measured for various samples are given in Table 1 along with the ratio C_2/C_1 and a value of n from equation (6). It can be seen that the values of C_2/C_1 for the polyester prepared from a trifunctional PPO (A) and the values for the corresponding polyurethane (B) are identical within experimental error.

Samples prepared using a bifunctional PPO with trimethylol propane and sebacoyl chloride (C) show a lower modulus, possibly due to a greater probability of closed loop forma-

tion during network formation. The values of C_2/C_1 are, however, identical to those for samples prepared from the trifunctional PPO (A). The corresponding urethanes (E) show higher C_2/C_1 values in agreement with the results of Prins⁵.

Ester-linked networks from 4000 MW PPO (D) also give a lower modulus, as expected, but a similar value for C_2/C_1 . Prins⁵ found, for a series of polyurethanes, that C_2/C_1 was independent of molecular weight between crosslinks. These results suggest that although the value of C_2/C_1 , for polyurethane networks made containing low molecular weight alcohols, increases with increasing percentage of urethane groups, the residual value of C_2/C_1 , found for networks containing no low molecular weight alcohols is not due in any way to the urethane groups. It is probably an inherent property of the poly(propylene oxide) networks themselves and is directly comparable with C_2/C_1 values found for other polymer network systems.

One could conjecture that the increased values of C_2/C_1 for polyurethanes containing short chain polyols may be due to phase separation in polyurethane systems and that networks prepared only from long chain polyols are not subject to phase separation.

Neutron scattering

Results in Figures 1, 2, 3 and 4 are plotted logarithmically as $\Delta\epsilon$ (full width at half maximum of the broadening of the incident energy spread) versus K where $K = (4\pi/\lambda) \sin(\theta/2)$.

The shift to lower values of $\Delta\epsilon$ for corresponding K values observed for the urethane network data in Figure 1, indicates, as might be expected, that the chain motion in the networks is slowed down relative to the free polymer. However, the linear 3000 polymer, which contains urethane groups at the same wt %P as the 300 network is also considerably slowed down. The possibility that the urethane groups are stiffening the local mechanics of the individual chains is eliminated when results on dilute solutions — shown in Figure 2 — are inspected. In solution, the rate of motion is unaffected by the presence of the urethane segments. Clearly there is a chain-chain effect arising from the urethane groups themselves.

The specific effect of the urethane segments in slowing down the chain motion in bulk is further underlined by the observation in Figure 3 that a linear poly(propylene oxide)

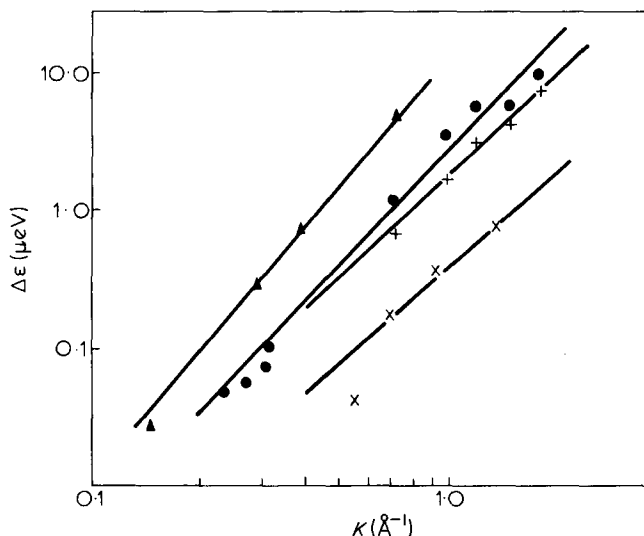


Figure 1 Double logarithmic plot of full width at half maximum $\Delta\epsilon$ (μeV) of broadening of incident spectrum observed for: \blacktriangle , poly(propylene oxide); \bullet , linear urethane-linked poly(propylene oxide); +, urethane-linked poly(propylene oxide) 3000 network; x, urethane-linked poly(propylene oxide) 1500 network against wave vector κ (\AA^{-1}), All at 67°C

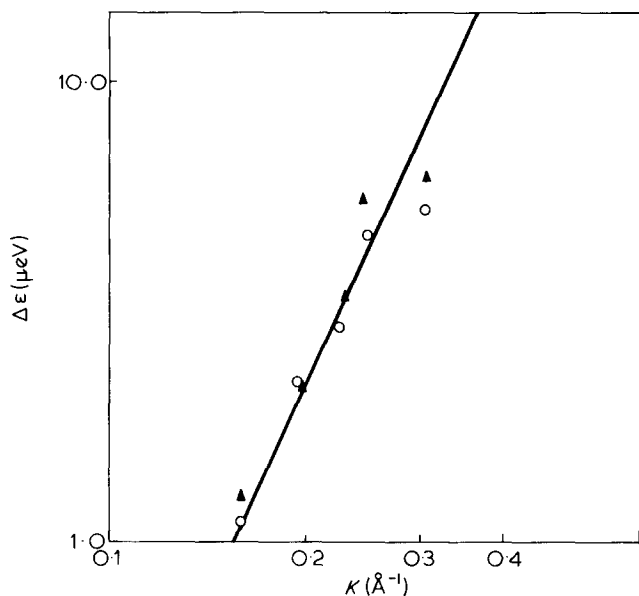


Figure 2 Double logarithmic plot as Figure 1. \blacktriangle , Poly(propylene oxide); \circ , linear urethane linked poly(propylene oxide) both in C_6D_6 solution

is essentially indistinguishable from ester-linked poly(propylene oxide).

Figure 4 compares the motion of a linear ester-linked poly(propylene oxide) with the ester-linked (sebacate) poly(propylene oxide) networks. Comparison with Figure 1 indicates that the effect of the crosslinking on the freedom of motion is very much reduced when urethane units are replaced by esters. This suggests that there are two mechanisms causing reduction in chain mobility on the time scale of the neutron experiment. The first is the purely mechanical effect of the increased crosslink density which would be expected to be similar for the two types of networks. Figure 4 shows this effect to be rather small even when crosslinks are only 10 monomer units apart. The second mechanism which comes into play in the urethanes is likely

to be hydrogen bonding of the urethane groups either to other urethane groups or to the poly(propylene oxide) chain.

Since urethane-urethane interaction would act essentially as extra crosslinks, and the effect of crosslinks on the chain mobility has been shown to be small, (see Figure 4), the major effect is probably due to urethane-poly(propylene oxide) interaction. For this to occur there cannot be a complete phase separation of urethane and poly(propylene oxide) in the networks.

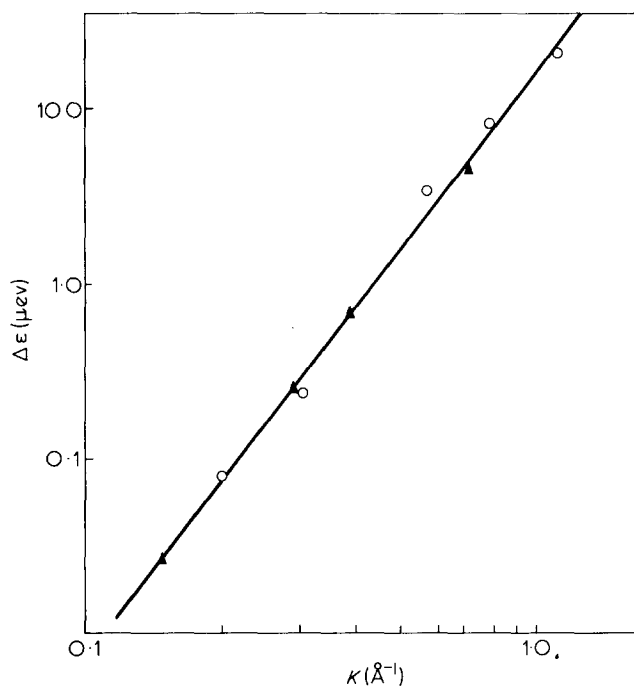


Figure 3 Double logarithmic plot as Figure 1. \blacktriangle , Poly(propylene oxide); \circ , linear ester linked poly(propylene oxide)

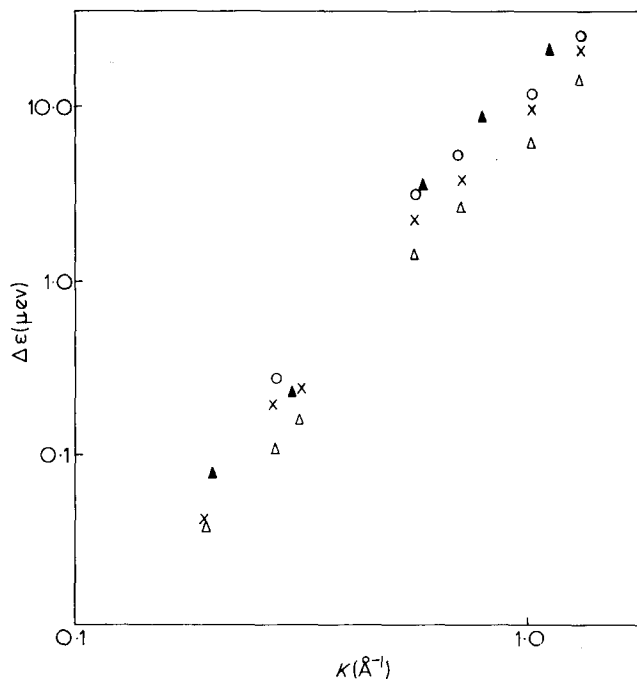


Figure 4 Double logarithmic plot as Figure 1. \blacktriangle , linear ester-linked poly(propylene oxide); \circ , ester-linked poly(propylene oxide) 3000 network; x, ester-linked poly(propylene oxide) 1500 network; Δ , ester-linked poly(propylene oxide) 1000 network. All at 67°C

CONCLUSION

The results from neutron scattering measurements show a reduction in poly(propylene oxide) chain mobility in the presence of urethane groups. This effect is separate from any effect of chain crosslinking and can be removed by replacing the urethanes by ester groups in the network. The effect has been attributed to hydrogen bonding and suggests that the urethane groups are in intimate contact with the poly(propylene oxide) chain.

The stress-strain measurements show that the deviations from ideal rubber elasticity are independent of the presence or absence of urethane groups in a network if that network contains no short chain diols. This might be expected for an equilibrium property rather than a kinetic property of the network. This suggests again that these are simple networks with none of the two phase structure often associated with polyurethanes. Deviations from ideal rubber elasticity are larger for networks containing short chain diols which are known to exhibit phase separation. The residual deviation is probably a property of the poly(propylene oxide) network itself.

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