lowed by a "waiting time" should take $F(D)$ to its equilibrium value, and this trend is in fact indicated in Figure 3. A more quantitative consideration in terms of the generalized Van der Waals approach (P. Pincus, private communication) leads to a similar conclusion.

Finally, we note that our results contrast with the earlier study by Israelachvili and co-workers,[4] who used a similar method to measure $F(D)$ between mica surfaces in an aqueous solution of a commercial resin consisting mostly of highly polydispersed PEO[26] (Carbowax resin WSR N80, Union Carbide). The main difference is that their results indicated the continuous buildup with time of progressively thicker layers of surface-adsorbed material (up to 1000 nm over 24 h) and also complex short- and long-term hysteretic behavior suggestive of gellike material on the surfaces. This may be due to the polydisperse nature of the polymer as well as the possible presence of microgel or trace chemical impurities in the commercial material used in their experiments.

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Molecular Aspects of the Rubber Elasticity of Poly(diethylene glycol terephthalate) Networks

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ABSTRACT: Polymer networks were prepared by end-linking poly(diethylene glycol terephthalate) fractions of number-average molecular weight ranging from 7200 to 11 700 with an aromatic triisocyanate. Stress–strain isotherms carried out on the unswollen networks showed reversibility for elongation ratios α below 5; however, for values of $\alpha > 5$, the isotherms displayed a sharp increase or upturn in the reduced force $[f^*]$, which we attribute to maximum chain extensibility. In general, the networks exhibited a modulus significantly higher than would be expected on theoretical grounds. The theoretical analysis of the experimental results suggests that, for this particular system, there seems to be a high contribution to the elastic modulus from topological entanglements. According to this analysis, the molecular weight between entanglements lies in the vicinity of 2000. In order to get confirmatory evidence on the presence of entanglements in the fractions used in the preparation of the networks, dynamic viscoelastic measurements were carried out on un-cross-linked fractions lying in the range 4600–24 700. The time–temperature superposition principle was applied to the dynamic moduli to establish forms for the plateau and terminal responses, from which the relaxation spectra corresponding to these regions were determined. The presence of a minimum in the spectra separating the two sets of relaxation times corresponding to motions within entanglements and motions across entanglements loci suggests that relatively well-developed entanglements are already present in the low molecular weight fractions used in the preparation of the networks.

Introduction

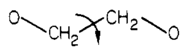
A controversial and important issue in the investigation of rubber elasticity that needs to be clarified is whether or not the topological entanglements contribute to the equilibrium elastic properties of amorphous polymer networks. In this regard, whereas some authors find a big

Table I
Characteristics of the PDET Networks

network	M_n	reaction time, days	r = [OH]/[NCO]	W_S, %	T, °C	α_r
A	7200	3	1.0	6.6	80	>4.5
B	7400	3	1.0	3.8	80	8
C-4	7400	26	1.0	3.4	70	
D	7400	9	0.984	3.7	70	
E	7400	18	0.90	3.4	100	
F	9100	3	1.0	3.6	80	>8
G	11700	3	1.0	7.4	80	8.2
H	11700	2	1.0	10.8	80	

contribution to the modulus from the entanglements, in some cases even much more important than the chemical cross-links, other workers find no need to invoke any contribution from entanglements to account for the modulus observed. Some of the most important studies on polymer elasticity were carried out on model poly(dimethylsiloxane) (PDMS) networks.[1-8] These networks, however, are not specially suitable to obtain information about the possible contribution of the entanglements to the modulus due to the low value of the plateau modulus, which suggests an unusually low density of interchain entanglements.[9] This problem was further investigated on other model networks prepared from polybutadiene,[10,11] ethylene–propylene copolymers,[12] polyurethanes,[13-16] and acrylic polymers.[17,18]

In order to get a better understanding of the molecular aspects of rubber elasticity it is necessary to examine the elastic behavior of a greater variety of polymer networks that differ significantly in the values of their plateau modulus. Within the family of aromatic polyesters, poly(diethylene glycol terephthalate) (PDET) is specially suitable for this purpose. PDET is soluble in common organic solvents, it does not crystallize from the bulk,[19] and its glass transition lies in the vicinity of room temperature.[20] Moreover, the conformational aspects of PDET chains have been thoroughly investigated.[21,22] The rotational isomeric state interpretation of the experimental dipole moments and the temperature coefficients of both the dipole moments and the unperturbed dimensions of PDET suggests that gauche states about CH_2–CH_2 bonds in these chains have an energy about 0.8 kcal/mol lower than the alternative trans states. These results were confirmed by ^{1}H NMR spectroscopic analysis[23] of PDET, which shows that the fraction of gauche states about these bonds is ca. 0.90. The great preference for gauche states about the moiety



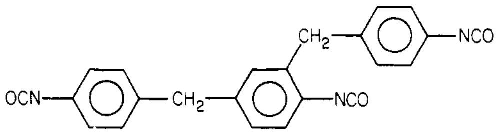
probably causes the chain to fold back on itself, so that these chains should be more coiled than initially suspected.[21] Therefore, the conformational characteristics of PDET should enhance the elastic properties of the networks prepared from these chains.

In a recent work,[22] preliminary results were reported regarding the equilibrium modulus of a model network prepared from unfractionated PDET. Although the results seemed to suggest that topological entanglements do not make significant contribution to the equilibrium elastic properties, they were not conclusive in this regard because they were limited to a single sample. It would be desirable to study the influence of the molecular weight on the elastic properties of model PDET networks in order to determine whether or not the interchain entanglements play an important role in the elastic properties of these networks. The purpose of this work is to investigate the equilibrium elastic properties of several of these networks differing in molecular weight. In order to gain deeper insight into the elastic properties of the networks, the viscoelastic behavior of un-cross-linked PDET in the plateau and terminal zones is also examined.

Experimental Section

Poly(diethylene glycol terephthalate) was prepared by the standard melt-phase procedure from dimethyl terephthalate and diethylene glycol, using tetraisopropyl titanate as catalyst. Additional details on the synthesis process are given elsewhere.[21] The polymer was fractionated at 30 °C by using chloroform–methanol as the solvent–nonsolvent system. Each fraction was redissolved, precipitated, and dried at 60 °C in vacuo. The number-average molecular weight of the fractions was determined with a Knauer vapor pressure osmometer.

Trifunctional model networks were prepared by end-linking hydroxyl-terminated poly(diethylene glycol terephthalate) with 2,4-bis(p-isocyanobenzyl)phenyl isocyanate.



The cross-linking agent was purified by crystallization in n-hexane immediately before use. In most experiments, stoichiometric equivalent amounts of polyester and isocyanate, both completely dried, were dissolved in a small amount of dried chloroform. The solution was cast into a Teflon mold, and the solvent was removed by evaporation in a dry atmosphere; then the homogeneous mixture of polymer and trifunctional cross-linking agent was kept at temperatures lying in the range 70–100 °C for different time intervals. The resulting networks were extracted in a Soxhlet with chloroform for 3 days. The amounts of soluble portions of the different networks are given in the fifth column of Table I.

Stress–strain isotherms were obtained on unswollen strips cut from the various network sheets, using standard techniques.[24] Since the thickness of the networks was very small (about 0.2 mm), precluding their direct measure, the cross-sectional area of the strips was obtained by weighing a perfectly cut sample of known width and length. The measurements were made at 70 °C using a sequence of increasing valus of the elongation ratios, α, with some inclusion of values out of sequence to test for reversibility. The elastic forces were recorded when they became sensibly constant (about 1 h being required in some cases), and the elongations were eventually increased to the rupture point of the network. Elastic experiments were also made on PDET networks swollen with m-tricresyl phosphate (MTCP), a completely nonvolatile solvent. The networks were first swollen in chloroform and then this solvent was interchanged by the diluent. In this way, networks with different degrees of swelling were prepared. The polymer volume fraction of the swollen network, v_{2S}, was calculated with the assumption of additivity of volumes. The densities of MTCP[25] and the polymer are

$$\rho(\mathrm{MTCP}) = 1.185 - 8.27 \times 10^{-4} T\ (°\mathrm{C})$$

$$\rho(\mathrm{PDET}) = 1.334 - 1.003 \times 10^{-3} T\ (°\mathrm{C})$$

The dynamic storage and loss moduli $G'(\omega)$ and $G''(\omega)$ were measured with a Rheometrics dynamic spectrometer on un-cross-linked PDET at temperatures lying in the range 40–90 °C. The values of the frequency ranged from 10^{-1} to 500 rad/s.

Table II
Influence of the Cross-Linking Reaction Time on the Characteristics of the Networks (T = 70 °C)

network	reaction time, days	W_S, %	$2C_1$	$2C_2$	$2C_2/2C_1$	A_3	A_3'
C-1	4	13					
C-2	11	6.5	0.183	0.331	1.81	0.38	1.06
C-3	14	4.7	0.202	0.400	2.0	0.41	1.25
C-4	26	3.4	0.261	0.563	2.17	0.54	1.69

Table III
Elastic Properties of the Extracted Unswollen PDET Networks

network	M_n	$2C_1$, N·mm^{-2}	$2C_2$, N·mm^{-2}	$2C_2/2C_1$	A_3	A_3'
A	7200	0.222	0.346	1.57	0.44	1.14
B	7400	0.299	0.761	2.54	0.61	2.16
C-4	7400	0.261	0.563	2.17	0.54	1.69
D	7400	0.272	0.688	2.53	0.56	1.97
E	7400	0.332	0.589	1.47	0.68	1.89
F	9100	0.275	0.719	2.61	0.70	2.50
G	11700	0.191	0.469	2.46	0.64	2.20
H	11700	0.108	0.463	4.26	0.37	1.94

Results and Discussion

Chemical Results. In order to prepare model networks with low sol fraction, one should use stoichiometric amounts of diol and isocyanate. However, to meet these requirements involves serious difficulties, owing to the fact that the number-average molecular weight of the chains is not always known with sufficient precision, at least for $M_n > 10\,000$; moreover, monofunctional chains and cycles can be present that alter the stoichiometry of the cross-linking reaction. It should be pointed out in this regard that the cyclic dimer is formed during polycondensation of PDET.[26] However, the high solubility of these cycles in comparison with that of the linear chains implies that the relatively high molecular weight fractions used in the preparation of the networks are cycle free.

The principal characteristics of the networks used in this study are shown in Table I. The cross-linking reactions were performed at temperatures lying in the range 70–100 °C and, in some cases, the ratio of the hydroxyl to the isocyanate groups was slightly different from unity. It can be observed that in spite of the variety of cross-linking conditions, networks with sol fractions lower than 3.4% were not obtained. In the second column of Table II is given, as an example, the variation of the sol fraction with time for network C. In general, at the beginning of the reaction, the sol fraction decreases rapidly as the reaction time increases, but in the final stages of the reaction the diffusion of the reacting groups is severely hindered and the cross-linking reaction proceeds very slowly. These qualitative results suggest, therefore, that completeness of the cross-linking reactions cannot be reached in a reasonable interval of time.

Elastic Results of PDET Networks. The elastic results were interpreted in terms of the "reduced stress" or modulus defined as[24]

$$[f^*] = v_{2S}^{1/3}f/[A(\alpha - \alpha^{-2})] \quad (1)$$

where v_{2S} is the volume fraction of polymer in the network, f is the elastic force at equilibrium, A is the cross-sectional area of the unstretched sample, and α is the elongation ratio (L/L_0). As usual, the reduced stress was plotted according to the Mooney–Rivlin formulation

$$[f^*] = 2C_1 + 2C_2\alpha^{-1} \quad (2)$$

where $2C_1$ and $2C_2$ are constants independent of the strain. In Figure 1 are shown stress–strain isotherms for some networks. The isotherms show an increase in the modulus or upturn for values of α larger than 5. The last column in Table I gives approximate values of the rupture elongations attained for some elastomers. It should be stressed that these data are only tentative because several tests would be necessary in order to get quantitative results. In any case the data show that the networks can reach very high extensions.

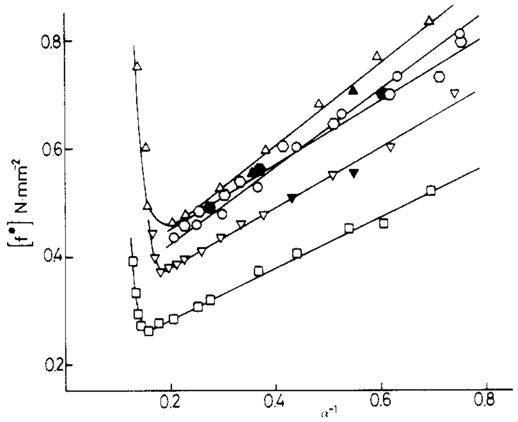


Figure 1. Representative stress–strain isotherms obtained on extracted samples at 70 °C: (△) network B; (▽) network C-4; (○) network E; (○) network F; (□) network G. Filled points are values taken out of sequence to test for reversibility before the upturn.

An important feature of the isotherms in Figure 1 concerns the reversibility. The isotherms are completely reversible in the region before the upturn, but the reversibility is lost in going back from a point in the upturn, hysteresis taking place. The hysteresis is probably caused by mechanical degradation at very high elongations. Values of $2C_1$ and $2C_2$ are shown in the third and fourth columns of Table III. It can be seen that for most networks the value of the ratio $2C_2/2C_1$ is somewhat higher than the upper bound of 2 predicted for trifunctional networks.

According to the Flory theory of rubberlike elasticity,[27-29] the modulus of a network at high and low deformations is given by

$$2C_1 = A_\phi \rho RT v_{2C}^{2/3} M_c^{-1} \quad (3)$$

$$2C_1 + 2C_2 = A_\phi' \rho RT v_{2C}^{2/3} M_c^{-1} \quad (4)$$

where ρ is the concentration (g/cm^3) of the PDET chains in the networks, v_{2C} is the volume fraction of the polymer during the cross-linking reaction, M_c is the molecular weight between cross-links, and A_ϕ and A_ϕ' are the so-called structure factors. For a trifunctional network ($\phi = 3$), $A_3 = 0.33$ and $A_3' = 1.0$; M_c is only equal to the original molecular weight (M_n) of the polymer prior cross-linking if the reaction is complete, being higher otherwise. The elasticity parameters for the networks of Table I are given in Table II. The values of A_3 and A_3', shown in columns six and seven of this table, were calculated with the assumption $M_c = M_n$. It can be observed that in most cases the values of the front factors are significantly higher than the theoretical ones, in some cases more than twice those values. The assumption $M_c = M_n$ is only valid in the case of completeness of the cross-linking reaction; however, as is clear from the data given in Table I, the reactions are far from being complete. Corrections for incomplete reactions would increase markedly the value of M_c and, therefore, those of A_3 and A_3'. It should be pointed out in this regard that as the sol fraction decreases, the differences between the experimental values of the front factors and those predicted by the theory increase, as can be seen in columns seven and eight of Table II, where the values of A_3 and A_3' are shown as a function of the sol fraction for C networks.

In order to investigate whether crystallinity vestiges were developed in the networks under strain, which might be responsible of the high value of the modulus, studies on the birefringence of the networks were recently made.[30] It was found that the stress-optical coefficient, C, decreases with increasing strain, suggesting that crystallinity is not developed in the strained networks. Moreover, the appearance of a downturn in the value of C for values of α at which an upturn in the plots of Figure 1 appears suggests that these upturns are not due to crystallinity but to maximum chain extensibility.

Elastic measurements were additionally performed at 70 °C on PDET networks swollen with tricresyl phosphate. Networks B, E, and H were used for this study. In the case of the swollen network H, the volume fraction of polymer in equilibrium $v_{2e} = 0.35$; however, for the much more perfect network E, $v_{2e} = 0.55$. The isotherms obtained are plotted in Figure 2. For high elongation ratios the isotherms exhibit an upturn which presumably is also due to maximum chain extensibility. Values of the elastic properties corresponding to the isotherms are given in Table V. As expected, the value of $2C_2$ decreases as v_{2S} decreases. A common characteristic of all the networks examined is that the value of $2C_1$, for each swollen network, is higher than that corresponding to the unswollen one. Moreover, the value of $2C_1$ increases as v_{2S} decreases. The changes in $2C_1$ with v_{2S} may be explained by considering that the Mooney–Rivlin plots are not linear but that they are S-shaped curves.[31,32] The higher is v_{2S}, the higher is the slope of the plots and, therefore, the more underestimated are the values of $2C_1$. Consequently, the values of both the modulus at infinite elongation and the front factors, shown in Table III, should be considered low bounds for these quantities.

Entanglement Contribution. Many authors[5,6,8,11,12,15,16,18] have postulated a large contribution to the modulus of polymer networks from topological entanglements. In this approach, the modulus at small elongations ($\alpha^{-1} \rightarrow 1$) is of interest, and an additional term in eq 4 is used to take into account the entanglement contribution

$$2C_1 + 2C_2 = A_\phi' RT v_{2C}^{2/3} M_c^{-1} + G_e^{\max} T_e \qquad (5)$$

In this equation the topological contribution to the modulus has been written as a product of a maximum possible modulus $G_e^{\max}$ and a trapping factor T_e, this last factor being the fraction of entanglements trapped when the network was formed. The value of $G_e^{\max}$ should be close to that of the plateau modulus obtained in stress-relaxation or dynamic experiments. It would be interesting to interpret our data by considering the contribution of the entanglements to the modulus. Equation 5 can be expressed in terms of the total density of cross-links (ν_t) by the expression

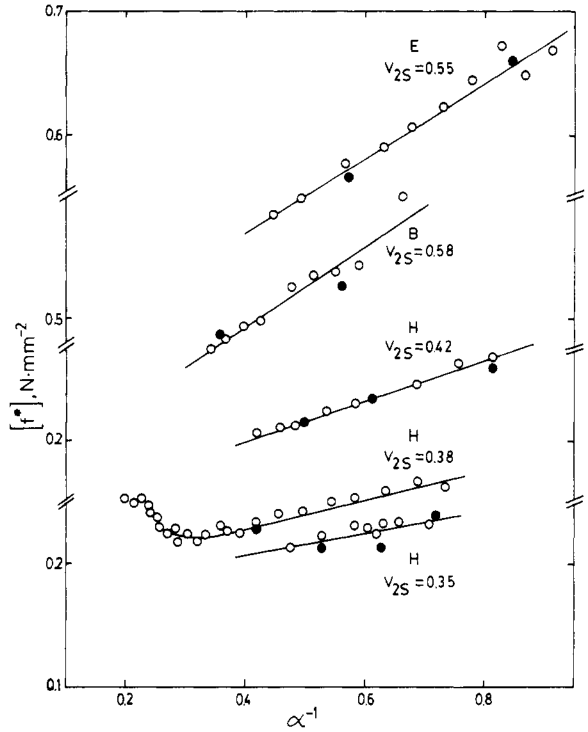


Figure 2. Stress–strain isotherms for the swollen networks at 70 °C.

$$\nu_t = \nu_c v_{2C}^{2/3} + \nu_e \qquad (6)$$

where ν_c and ν_e represent respectively the density of effective elastic chains corresponding to chemical cross-links and topological entanglements. In the present analysis, the density of elastic chains was obtained from the experimental value of the modulus

$$\nu_t = (2C_1 + 2C_2)/RT \qquad (7)$$

whereas the contribution of chemical cross-links was calculated from the sol fraction by using the Langley theory.[33] The pertinent equations for end-linked trifunctional networks are briefly described. The sol fraction (W_S) is related to the extent of the reaction, p, by means of the equation

$$W_S = W_X \left[\frac{1 - rp^2}{rp^2} \right]^3 + W_P \left[\frac{rp^3 - 2rp^2 + 1}{rp^3} \right]^2 \qquad (8)$$

where r is the stoichiometric ratio of hydroxyl to isocyanate groups and W_X and W_P are the weight fractions in the initial reaction mixture of cross-linking agent and polymer, respectively. The chemical and entanglement contributions are given by[34]

$$\nu_c = {}^3\!/_2 [X_3]_0 \left[\frac{2rp^2 - 1}{rp^2} \right]^3 \qquad (9)$$

$$\nu_e = \frac{\rho T_e}{M_e} = \frac{\rho}{M_e} \left[\frac{2rp^2 - 1}{rp^3} \right]^4 \qquad (10)$$

Table IV
Chemical Cross-Link and Entanglement Contribution to the Modulus of PDET Networks

network	M_n	$2C_1 + 2C_2$	$10^4\nu_t$, mol/cm³	$10^5\nu_c$, mol/cm³	$10^4\nu_e$, mol/cm³	ν_e/ν_t	$10^{-3}M_e$
A	7200	0.568	1.99	4.78	1.53	0.77	2.56
B	7400	1.060	3.72	6.38	3.10	0.83	1.84
C-1	7400						
C-2	7400	0.514	1.80	4.70	1.33	0.74	3.04
C-3	7400	0.602	2.11	5.70	1.54	0.73	3.20
C-4	7400	0.824	2.89	6.50	2.24	0.78	2.60
D	7400	0.960	3.35	6.20	2.75	0.82	2.00
E	7400	0.921	3.23	8.40	2.39	0.74	2.27
F	9100	0.994	3.48	5.54	2.94	0.84	1.98
G	11700	0.660	2.31	2.79	2.04	0.88	1.83
H	11700	0.571	2.00	2.06	1.81	0.90	1.43
						0.80 ± 0.06[a]	2.27 ± 0.50[a]

[a] Average values.

Table V
Chemical Cross-Link and Entanglement Contribution to the Modulus of Swollen PDET Networks

network	v_{2S}	$2C_1$, N·mm^{-2}	$2C_2$, N·mm^{-2}	$10^4\nu_t$, mol/cm³	$10^5\nu_c$, mol/cm³	$10^4\nu_e$, mol/cm³	$10^{-3}M_e$
B	0.58	0.363	0.326	2.42	4.44	1.99	2.86
E	0.55	0.397	0.307	2.46	5.64	1.89	2.73
H	0.42	0.134	0 166	1.05	1.15	0.94	2.75
H	0.42	0.150	0.113	0.92	1.15	0.81	3.19
H	0.38	0.182	0.118	1.05	1.09	0.95	2.73
H	0.35	0.172	0.090	0.92	1.03	0.82	3.14

where $[X_3]_0$ is the concentration of cross-linking agent and M_e is the molecular weight between entanglements. Values of ν_t, ν_c, ν_e, ν_e/ν_c, and M_e, obtained by the procedures indicated above, are shown in columns four through eight of Table IV. The results suggest a high contribution of the interchain entanglements to the modulus as large as about 80% of the total value. From the values given in the last column of this table, an average value of (2.3 ± 0.5) × 10^3 is obtained for M_e. These results are in opposition to preliminary ones[22] in which that contribution was not observed. It should be noted, however, that those preliminary results were obtained on samples extracted with chloroform at room temperature, and in these no sol fraction was detected. However, more careful extractions carried out during the course of this work (see experimental part) gave a sol fraction amounting to 6% on the same samples. This finding changes some of the conclusions of ref 22.

Values of ν_c, ν_e, and M_c were also obtained by the methods described above for the swollen networks. The results obtained are shown in Table V. As expected, the molecular weight between entanglements increases as the volume fraction of polymer in the network decreases.

Viscoelastic Behavior of Un-Cross-Linked PDET Chains. The analysis of the elastomeric properties of PDET networks suggests that the molecular weight between entanglements, M_e, is relatively small. It would be of importance, therefore, to determine, at least semiquantitatively, the value of the plateau modulus $G_N{}^\circ$ of un-cross-linked samples, which is related to M_e by the expression[35,36]

$$M_e = \rho RT/G_N{}^\circ \tag{11}$$

For this purpose, dynamic measurements were carried out at different temperatures, over a frequency range of more than 3 decades, on un-cross-linked fractions of number-average molecular weights 4600, 8000, 11700, and 24700. Examples of changes in the storage G' and loss G'' moduli with frequency are shown in Figures 3 and 4, respectively. By assuming that temperature superposition holds, all data at various temperatures were shifted on the curve at reference temperature 90 °C. The G'' master curves show the characteristic slope of 1 on the logarithmic plot in the terminal zone. That is[36]

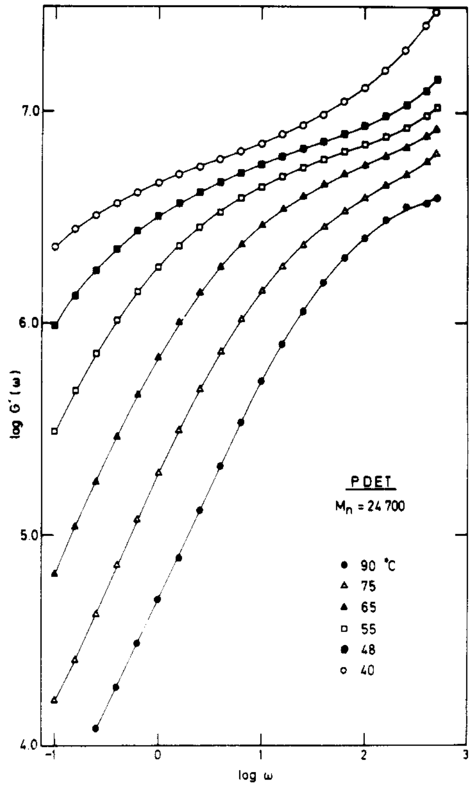


Figure 3. Storage modulus at several temperatures of un-cross-linked PDET chains (M_n = 24700). G' units are dyn/cm².

$$\lim_{\omega \to 0} [\mathrm{d} \log G''(\omega)/\mathrm{d} \log \omega = 1] \tag{12}$$

The G' master curve, on the contrary, extends to lower frequencies without attaining the limiting slope of 2 as required by linear viscoelasticity theory. This is characteristic of polymers with broad molecular weight distribution.

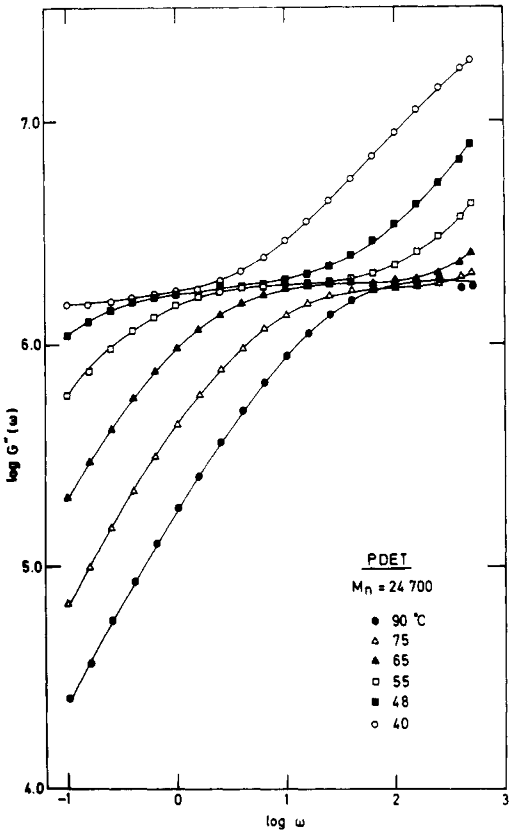


Figure 4. Loss modulus of un-cross-linked PDET chains (M_n = 24 000). G'' units are dyn/cm^2.

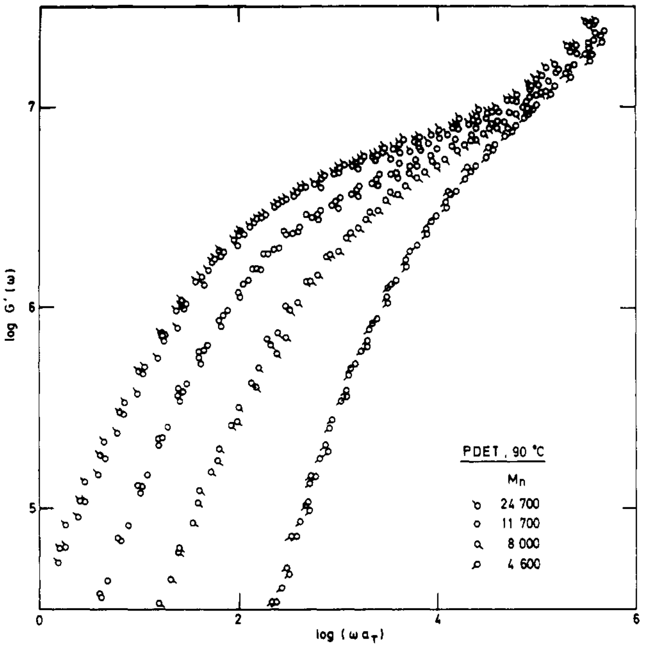


Figure 5. Storage modulus master curves for several samples of PDET of different molecular weight.

The temperature reduction of the data of Figures 3 and 4 results in curves G' and G'' that superimpose imperfectly in the plateau region. However, the general features of the plateau zone of linear viscoelastic behavior[36] are apparent in Figures 5 and 6 for the three samples of higher molecular weight. It can be observed that the width of the plateau zone increases as the molecular weight increases and the loss modulus becomes flat, so that the maximum and minimum which usually appear for this function in fractions of narrow molecular weight distribution[37] are not detected. For the lowest molecular weight fraction no plateau is observed, as expected.

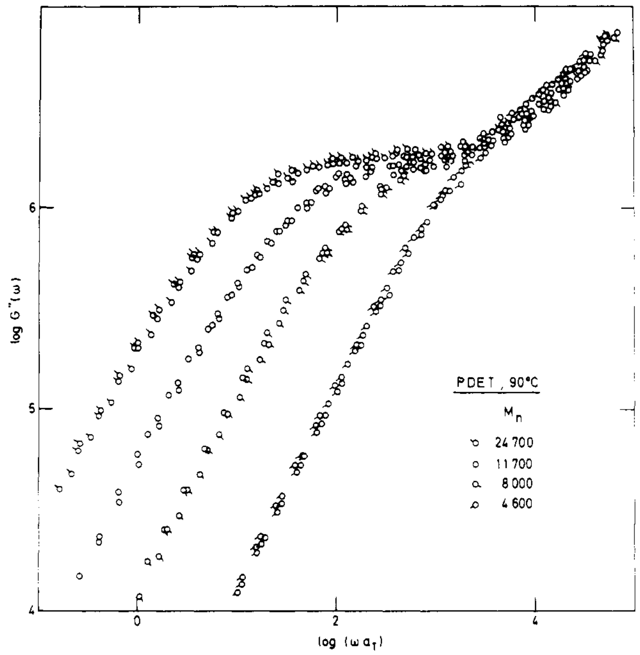


Figure 6. Loss modulus master curves for several samples of PDET of different molecular weight.

Usually, the plateau modulus of the entanglement network $G_N°$, which characterizes the rubbery plateau, is obtained from the equation[36]

$$G_N° = (2/\pi)\int_{-\infty}^{a} G''(\omega)\,\mathrm{d}\ln\omega = \int_{a'}^{\infty} H(\tau)\,\mathrm{d}\ln\tau \qquad (13)$$

where $H(\tau)$ represents the value of the relaxation spectrum at the relaxation time τ, and a and a' are taken to encompass the maximum of $G''(\omega)$ and $H(\tau)$, respectively. Since the minimum in the loss curves is blurred in all the cases, probably in part because of molecular weight heterogeneity, the value of $G_N°$ could not be obtained from the loss curves. Therefore, attempts were made to calculate this quantity from the relaxation spectrum. For fractions of sufficiently high molecular weight, the relaxation spectrum passes through a minimum in the plateau zone, separating the two sets of relaxation times corresponding to motions within entanglements and motions across entanglement loci. The relaxation spectra corresponding to the PDET fractions were obtained from G' by drawing smooth curves through the set of reduced data. The curves were fitted by spline functions, from which the second approximation to each of the relaxation spectra was calculated by using the Williams and Ferry second approximation.[38] Tschoegl's method[39] essentially yields the same spectra. Unfortunately, the values of $H(\tau)$ could not be further refined by the procedures described elsewhere[25,40,41] because of lack of experimental data in the high-frequency region. The spectra obtained (Figure 7) clearly show the existence of a minimum separating the two mechanisms indicated above in all the samples but that of M_n = 4600, where the minimum is not defined. The value of $G_N°$ was obtained from the spectra corresponding to the three fractions of higher molecular weight by using eq 13. The value of a' in this equation was defined by considering the peak symmetric with respect to the maximum. The average value obtained for the plateau modulus at 90 °C is ca. 6 × 10^6 dyn/cm^2, which corresponds to a value of 6400 for M_e. This result should only be considered semiquantitative in view of the uncertainties involved in the determination of the plateau relaxation peak. It should be stressed in this regard[42] that the viscosity at zero shear rate

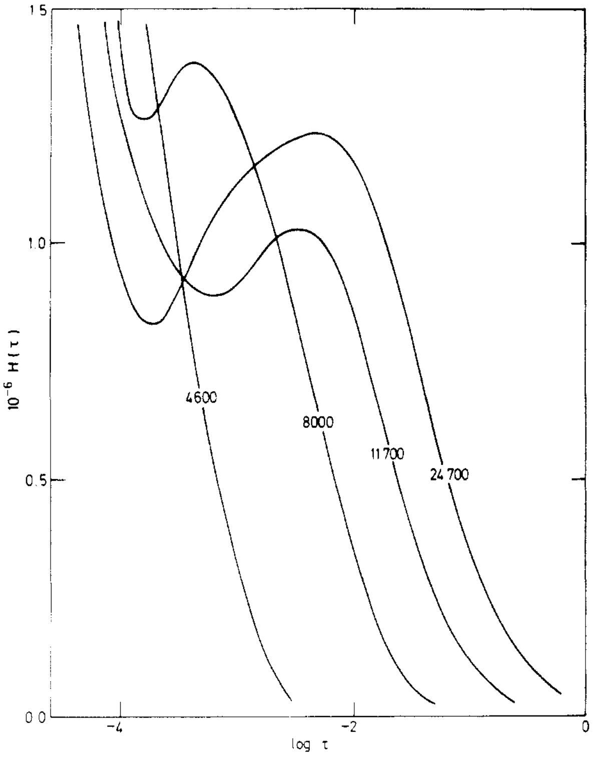


Figure 7. Relaxation spectra of several PDET samples of different molecular weight. H units are dyn/cm^2.

of fractions of molecular weight lying in the range 4800–23 000 is strongly dependent on M, suggesting that well-developed entanglements are actually present in relatively low molecular weight chains.

Concluding Remarks

The requirements of Langley's theory are difficult to meet because (a) the reactives should be of 100% purity, (b) the amount of polycycles and monofunctional chains in the sol fraction should be known, and (c) the value of ν_t, obtained from eq 7, is essentially overestimated because it has been shown[43] that the values of $2C_1 + 2C_2$ in the vicinity of $\alpha = 1$ are slightly lower than those obtained by linear extrapolation of the experimental data. For these reasons, the use of corrections for incomplete cross-linking, as estimated from sol fractions, may be in some cases misguided. It should be pointed out, however, that even considering that most if not all of the sol fraction consists of inert cycles and monofunctional chains rather than reactive chains, the most perfect networks exhibit equilibrium moduli much higher than those predicted by Flory's theory. It has been points out[44] that some networks may have exhibited artificially high moduli because of reinforcing effects from strain-induced crystallization. However, the facts that the isotherms are reversible for values of $\alpha^{-1} > 0.2$, the values of $2C_1$ increase with the degree of swelling, and besides that,the stress-optical coefficient departs from constancy at moderately high elongations ($\alpha^{-1} < 0.3$) in the sense that it decreases as the elongation ratio increases suggest that crystallinity cannot be considered responsible for the high modulus observed for PDET networks. Therefore, the only way of explaining the elastic behavior of these networks is to postulate that interchain entanglements contribute to the equilibrium modulus.

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