(14) (a) DeSantis, P.; Giglio, E.; Liquori, A. M.; Repanonti, A. *J. Polym. Sci., Part A* **1963**, *1*, 1383. (b) Magnasco, V.; Gay, G.; Nicora, C. *Il Nuovo Cim.* **1964**, *34*, 1263. (c) McCullogh, R. L.; McMahon, P. E. *Trans. Faraday Soc.* **1969**, 69.

(15) Otto, P.; Ladik, J. J.; Förner, W. *Chem. Phys.* **1985**, *95*, 365.

(16) Brown, D. E.; Beagley, B. *J. Mol. Struct.* **1977**, *38*, 167.

(17) (a) Tourillon, G.; Garnier, F. *J. Electroanal. Chem.* **1984**, *161*, 51. (b) Cui, C. X.; Kertesz, M. *Phys. Rev. B* **1989**, *40*, 9661.

(18) (a) Pulay, P.; Fogarasi, G.; Dang, F.; Boggs, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 2550. (b) Pulay, P.; Fogarasi, G.; Pongor, G.; Boggs, J. E.; Vargha, A. *J. Am. Chem. Soc.* **1983**, *105*, 7037.

(19) (a) Piseri, L.; Zerbi, G. *J. Mol. Spectrosc.* **1968**, *26*, 254. (b) Decius, J. C.; Hexter, R. M. *Molecular Vibrations in Crystals*; McGraw-Hill: New York, 1977. (c) Cui, C. X.; Kertesz, M., to be published.

(20) (a) Durig, J. R.; Church, J. S. *J. Chem. Phys.* **1980**, *73*, 4784. (b) Feher, F.; Fisher, H. *Naturwissenschaften* **1969**, *51*, 461.

(21) Vora, P.; Solin, S. A.; John, P. *Phys. Rev. B* **1984**, *29*, 3423.

(22) (a) John, P.; Odeh, I. M.; Thomas, M. J. K.; Wilson, J. I. B. *J. Phys. (Paris)* **1981**, *4*, C651. (b) Furukawa, S.; Matsumoto, N.; Toriyama, T.; Yabumoto, N. *J. Appl. Phys.* **1985**, *58*, 4658.

(23) (a) Higgs, P. W. *Proc. R. Soc. London* **1953**, *A220*, 472. (b) Liang, C. Y. *J. Mol. Spectrosc.* **1957**, *1*, 61.

Registry No. $(SiF_2)_n$ (SRU), 31801-01-1; $(GeH_2)_n$, 32028-94-7; Si_2H_6, 1590-87-0; Si_7H_{16}, 14693-65-3; polysilane, 32028-95-8; polyethylene, 9002-88-4; poly(tetrafluoroethylene), 9002-84-0; poly(methylsilane), 110477-49-1; poly(dimethylsilane), 28883-63-8; poly(diethylsilane), 125457-34-3.

Rubberlike Network Structure from Tensile Tests on Swollen Samples According to Flory's Last Theory and Application to Polyurethanes

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ABSTRACT: It is shown that Flory's last elasticity theory allows calculation of the limit values for the network chain molecular weight starting from mechanical equilibrium measurements of the modulus $|f^*|$. For any case it is possible to evaluate the upper limit M_a corresponding to affine behavior. However, it is not always possible to evaluate the lowest limit: when M is known and the synthesis conditions are controlled, the lowest limit is M_s, which is the chain stoichiometric molecular weight; otherwise, the lowest limit becomes M_{ph}, corresponding to phantom behavior, which, however, can be calculated only when the effective functionality ϕ of the network cross-links is known. It is also shown that imperfections of the cross-linking reactions can be estimated by comparing the experimental modulus with that of the perfect phantom network characterized by the stoichiometric M_s and ϕ_s (eq 15). A practical example of this analysis is proposed for two classes of polyurethanes, polyether diols reacted with toluenediyl diisocyanate (TDI) and polyester diols reacted with TDI. The demonstrations and the applications are made in the case of a swollen system; however, they can be extended to dry systems simply by putting $v_2 = 1$ in the formulas.

General Considerations

Tensile testing of swollen samples has been employed for a long time as a method to evaluate the effective elastic chain density in rubber networks. The difficulty in properly modeling the network behavior has been responsible for the growth of different theories for describing the mechanical properties in relation to the chemical–physical structure of these materials.[1–3]

The more recent theory of Flory[4–7] has led to complex analytical expressions. Referring to a network deformed by an applied tensile force f corresponding to an elongation ratio α, one can write the following constitutive equation:[4,5]

$$f = \frac{\xi KT}{L_0}\left(\frac{V}{V_0}\right)^{1/3}(\alpha - \alpha^{-2})\left(1 + \frac{f_c}{f_{ph}}\right) = f_{ph}\left(1 + \frac{f_c}{f_{ph}}\right) \qquad (1)$$

where f_{ph} is the tensile response the network would give if deformed following the "phantom" model, which was originally proposed by James and Guth.[2] f_c is given by constraints acting on the fluctuating junctions due to the presence of "entanglements".[4–7] Equation 1 refers to a network at temperature T and volume V. ξ is defined as the cycle rank of the network, i.e., the number of independent circuits therein, K is the Boltzmann constant, and L_0 is the sample length at the reference volume V_0, which is defined as the volume at which the mean square end-to-end distance of the chains in the network is equal to that of the same chains in the free, un-cross-linked state. The reference volume V_0 is assumed to be the volume of the network at the moment of its formation at the same temperature T. In a previous theory[1,3] referring to a model where the relative displacement of junctions was assumed to be affine in the strain, the number ν of elastically effective chains was considered in place of the term $\xi(1 + f_c/f_{ph})$. The extent of entanglement constraints on junction fluctuations is, in general, dependent on the network deformation, so f_c is a function of α and V/V_0. Reasonable estimates of f_c/f_{ph}, supported by experiments,[7] show that f_c is usually positive, although it may present negative values at very high swelling ratios ($V/V_0 > 3.5$–4).

Let us examine a network initially formed at a volume V_0, for example, in solution, which is dried so that its

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volume becomes V_n and then is swollen in a solvent to a volume V. Letting A^* represent the area of the dry unswollen sample (of volume V_n) and taking into account that $L_0 = L_n \upsilon_{2c}^{-1/3}$, we obtain from eq 1

$$\sigma = \frac{f}{A^*} = \frac{F}{V_n} KT \upsilon_{2c}^{1/3} \left(\frac{V}{V_0}\right)^{1/3} (\alpha - \alpha^{-2}) \qquad (2)$$

where υ_{2c} represents the volume fraction of the dry network with respect to the reference volume ($\upsilon_{2c} = V_n/V_0$) and F is a coefficient that collects the other coefficients of eq 1 and accounts for the network structure and its deformation. It is convenient to substitute the term V/V_0 with the ratio $VV_n/V_nV_0 = \upsilon_2^{-1}\upsilon_{2c}$, in which υ_2 is the volume fraction of the polymer in the swollen system. Equation 2 therefore becomes

$$\sigma = \frac{FKT}{V_n} \upsilon_{2c}^{2/3} \upsilon_2^{-1/3} (\alpha - \alpha^{-2}) \qquad (3)$$

Following many authors, we define the modulus $|f^*|$ as

$$|f^*| = \frac{\sigma \upsilon_2^{1/3}}{\alpha - \alpha^{-2}} = \frac{FKT \upsilon_{2c}^{2/3}}{V_n} \qquad (4)$$

The modulus was defined in a slightly different way by Erman and Flory:[7] $|f^*|_F = f/[A_0 \upsilon_{2c}^{1/3}(\alpha - \alpha^{-2})]$. $|f^*|_F$ is related to $|f^*|$ by the relationship $|f^*|_F = |f^*|\upsilon_{2c}^{1/3}$.

The term F can be experimentally evaluated by using the results of tensile tests in eq 4, and its value is an index for the network structure and behavior characterization: $F = \nu$ for a perfect affine network, and $F = \xi$ for a perfect phantom network ($f_c = 0$).[2] According to Flory's theory, we obtain (cf. eqs 1 and 2)

$$F = \xi(1 + f_c/f_{ph}) \qquad (5)$$

Moreover, when the network is perfect,[4] i.e., when no unreacted functional groups are present

$$\xi = \nu(1 - 2/\phi) \qquad (6)$$

where ϕ is the cross-link functionality. For instance, when $\phi = 4$, a phantom network would have an elastic reaction that is half that of an affine network having the same chain number ν. The relationship between the number of chains ν in the network and their molecular weight M_s can be easily derived in an ideal network:

$$\frac{\nu}{V_n} = \frac{\rho}{M_s} N_A \qquad (7)$$

where ρ is the density of the unswollen network and N_A is Avogadro's number. M_s refers to the stoichiometric chain length between two following junctions.

In Figure 1 the modulus $|f^*|$ is plotted as a function of ρ/M. In this graph, curves representing eq 4 with values corresponding to affine ($F = \nu$) and to phantom ($F = \xi$) behavior are represented by straight lines with slopes, respectively, equal to

$$A_a = \upsilon_{2c}^{2/3} RT \quad \text{(line a)} \qquad (8a)$$

$$A_{ph} = (1 - 2/\phi) \upsilon_{2c}^{2/3} RT \quad \text{(line b)} \qquad (8b)$$

where R is the gas constant. These lines have a general meaning since they describe the limit cases of the behaviors of rubbers endowed with pure entropic elasticity. In an ideal network the chain molecular weight coincides with M_s, ϕ is known, and $|f^*|_s$ will fall between lines a and b, if $f_c > 0$, in correspondence with abscissa ρ/M_s (Figure 1). In the case of high swelling only, when $f_c < 0$, $|f^*|$ is found below line b. Employing eqs 4–6, it is possible to determine the corresponding f_c/f_{ph} ratio that completely describes the deformation behavior of the network for the chosen α:

$$\frac{f_c}{f_{ph}} = \frac{|f^*|_c}{|f^*|_{ph}} = \frac{|f^*|_s - |f^*|_{ph}}{|f^*|_{ph}} = \frac{\overline{\overline{BS}}}{\overline{BO}} \qquad (9)$$

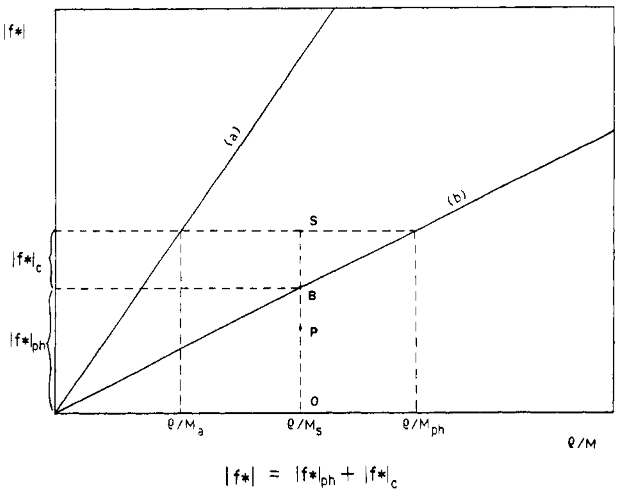

Figure 1. Schematic of modulus $|f^*|$ vs ρ/M diagrams. Lines a and b refer respectively to the affine model and the phantom model.

Table I
Properties of the Reagents

Poly(propylene oxide) Diols

reagent	mol wt	T_g, °C	trade name and producer
VR 400	430	−72	Voranol 4, Dow Chemical
VR 1200	1230	−68	Voranol 12, Dow Chemical
VR 2000	2180	−67	Voranol 20, Dow Chemical

Poly(tetramethylene adipate) Diols

reagent	mol wt	T_g, T_m, °C	trade name and producer
PTMA 600	575	−138.1, 41.1	Diexter SL 122, COIM
PTMA 1000	1035	−73.5, 47	Diexter G 215, COIM
PTMA 2200	2205	−34.1, 53.4	Diexter G 214, COIM
PTMA 3000	2980	—, 55.6	Diexter G 216, COIM

Cross-Linking Agents (Polyfunctional Amines)

cross-linker	functionality	mol wt
TIPA	3	191
EDA	4	350
DETA	5	392

Experimental Section

Two different classes of polyurethane networks, polyether based and polyester based, were prepared in solution according to a procedure reported in detail elsewhere.[8] NCO-terminated prepolymers were obtained by first reacting at 80 °C toluenediyl diisocyanate (TDI) with linear OH-terminated polymers consisting of (Table I) (a) poly(propylene oxide) diols (PE) of different molecular weight and (b) poly(tetramethylene adipate) diols (PES) of different molecular weight. The PE prepolymers were then cross-linked at ca. 30 °C by three-, four-, or five-functional cross-linking agents (CA): tri-2-propanol monoamine (TIPA), tetrapropanol diethylenediamine (EDA), and pentapropanol diethylenetriamine (DETA). The PES prepolymers were cross-linked with TIPA only at ca. 40 °C. Stannous octoate was used as a catalyst. The cross-linking reactions were carried out in ethyl acetate solvent (EA) (50% by weight), which was then evaporated. In this way good-quality, homogeneous polymer films of constant thickness (0.15–0.4 mm) were obtained from which strips ca. 70 mm long, 11 mm wide, and 0.3–0.4 mm thick were cut.

Tensile tests on swollen samples were performed by means of a dynamometer of our own design. The load was measured by a Mettler electronic balance (sensitivity 0.01 g) through an

Table II
Network Properties

	density, g/cm^3	v_2	v_{2c}	M_s	M_a	M_{ph}
			PE–PU Networks			
VR 400						
TIPA	1.18	0.502	0.414	905	4080	(1360)
EDA	1.17	0.651	0.417	950	2590	(1290)
DETA	1.18	0.662	0.409	935	1840	(1100)
VR 1200						
TIPA	1.10	0.373	0.420^a	1705	3660	1220
EDA	1.10	0.339	0.427	1750	3160	1580
DETA	1.10	0.641	0.434	1735	1950	1170
VR 2000						
TIPA	1.08	0.191	0.428	2655	6230	2060
EDA	1.06	0.190	0.403	2700	6900	(3450)
DETA	1.07	0.285	0.431	2685	4170	2500
			PES–PU Networks			
PTMA 600^b	1.20	0.694	0.420^a	1050	2450	810
PTMA 1000^b	1.19	0.592	0.420^a	1510	2140	710
PTMA 2200^b	1.18	0.485	0.423	2680	2760	910

^{a} Estimated values. ^{b} Cross-linked with TIPA.

inextensible wire fastened to the upper clamp, whose position was controlled by a cathetometer, accurate to 0.01 mm. The elongations were imposed by moving the lower clamp, which was rigidly connected to a micrometric screw rotating in a stationary housing. The lower clamp displacement was read by a dial gauge, accurate to 0.005 mm. After the sample was inserted in the clamps, a cylinder, which housed the sample and the clamps, was filled with toluene at room temperature, and the sample was allowed to swell to equilibrium. The length L_{0s} of the swollen sample was measured: it was practically the length at which the minimum load (0.01 g) could be detected. Then the preset strain was applied and after the relaxation phenomena completely subsided (generally after at least 60 min), the corresponding equilibrium force was measured. The hysteretic behavior was sometimes checked to be sure that equilibrium conditions prevailed. After the measurements the surface of the samples was dried with blotting paper, and the samples were rapidly weighed and then reweighed after the toluene was completely evaporated under vacuum. The volume fraction v_2 of the polymer in the swollen system was calculated as $v_2 = (W_{pd}/\rho_p)/(W_{pd}/\rho_p + W_t/\rho_t)$, where W and ρ indicate weight and density and the indices pd and t refer to polymer dried after immersion in toluene and to toluene solvent. The volume fraction v_{2c} of the polymer effectively embedded in the network was evaluated as $v_{2c} = (W_{pd}/\rho_p)/(W_{pi}/\rho_p + W_{ea}/\rho_{ea})$, where index pi refers to dry polymer before immersion in toluene and ea refers to ethyl acetate solvent used in the synthesis. The difference $W_{pi} - W_{pd}$ represents the amount of extracted polymer not incorporated in the network. In the calculations no correction was made of the V_0 change for the temperature used at the network formation. The values of v_2 and v_{2c} calculated for the tested networks are reported in Table II. Differential scanning calorimetry (DSC) analyses were performed on the initial polyols and on the prepared networks at a scanning rate of 10 °C/min over a temperature range of −150 to +250 °C. Number-average molecular weights M_p of the starting chains (diols) were determined by measuring the number of OH groups in the polydiols.[9] M_s was calculated by

$$M_s = M_p + 2M_{ca}/\phi_s + 2M_{tdi} \qquad (10)$$

where M_{ca} and M_{tdi} are the molecular weights of the cross-linking agent and toluenediyl diisocyanate.

Results

Figure 2 shows the glass transition temperatures (T_g's) as a function of M_s of PE–PU networks obtained with three-, four-, and five-functional cross-linking agents and the T_g's of PES–PU networks obtained with the trifunctional cross-linking agent. We observe that the T_g's depend on M_s, which is consistent with the fact that the cross-link density is higher in the case of short polyols, and, moreover, that the hard-segment density due to urethane groups decreases with increasing chain length of the polyols, so reducing the interchain attraction. The T_g is higher for PES–PU due to the lower chain flexibility of PES diols. We found that the cross-linking agent functionality is important in determining T_g only for the lower molecular weight networks. In this case we observed also that the T_g's are higher that those shown in Figure 2 when the NCO-terminated prepolymers are prepared at room temperature. According to the thermal analysis, all PE–PU are amorphous whereas the PES–PU synthesized from PES diols having M_w = 3000 are crystalline, showing melting points >50 °C, and were not examined in this work. The networks from PES diols having M_w = 2200 crystallized only some time after their preparation and were examined before this event. The lower molecular weight PES–PU are amorphous. We observe that the T_g's were lower than those shown in Figure 2 when the samples were swollen: all the mechanical data presented here refer to swollen samples in the elastomeric physical state since their T_g's were below room temperature.

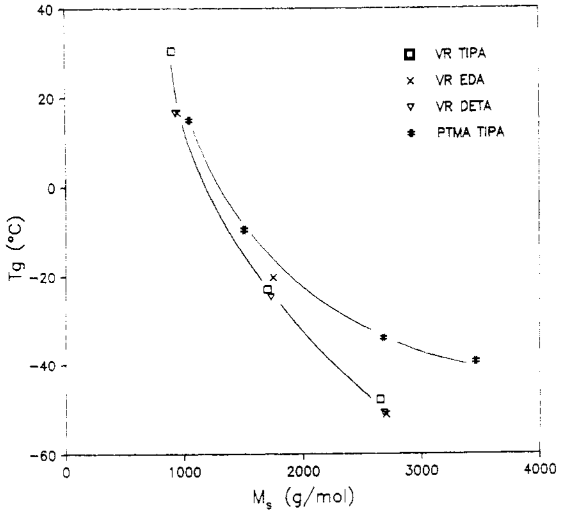

Figure 2. Glass transition temperatures of rubbery polyurethane networks (PE–PU and PES–PU) as a function of the stoichiometric molecular weight of chains.

Mechanical Properties. Figures 3 and 4 are plots of $\sigma v_2^{1/3}$ vs $(\alpha - \alpha^{-2})$ for PE–PU networks of different M_s (VR 400 and VR 1200) and different CA functionalities. Analogous data were obtained for VR 2000. Figure 5 shows data for PES–PU with TIPA cross-linking agent. The slopes of the $\sigma v_2^{1/3}$ vs $(\alpha - \alpha^{-2})$ regression lines give quan-

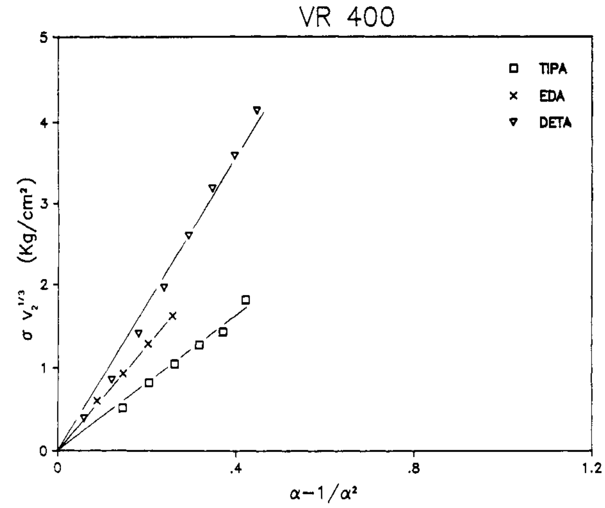

Figure 3. Experimental $\sigma v_2^{1/3}$ vs $(\alpha - \alpha^{-2})$ data and regression lines of VR 400 based polyurethane networks with different junction functionalities.

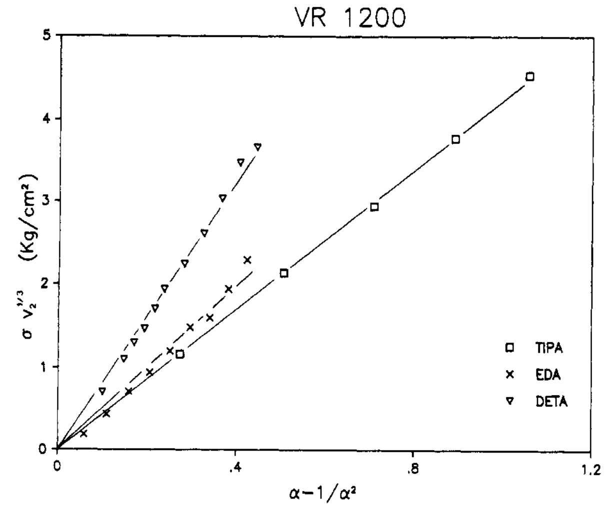

Figure 4. Experimental $\sigma v_2^{1/3}$ vs $(\alpha - \alpha^{-2})$ data and regression lines of VR 1200 based polyurethane networks with different junction functionalities.

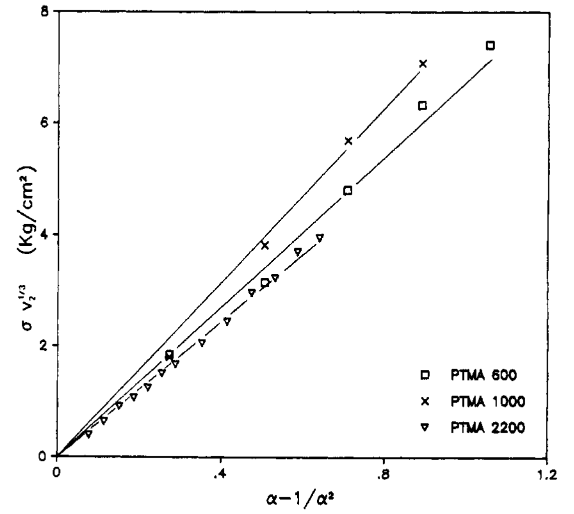

Figure 5. Experimental $\sigma v_2^{1/3}$ vs $(\alpha - \alpha^{-2})$ data and regression lines of polyester-based networks of different chain lengths cross-linked with trifunctional cross-linking agent (TIPA).

titative indications on the structural parameter F of each network. In the range of the experimental α the slope of $\sigma v_2^{1/3}$ is practically constant with $(\alpha - \alpha^{-2})$: the extensibility is not very large since the networks break at low strains, and our $|f^*|$ values correspond therefore to $|f^*|_{\alpha\to 1}$.

Discussion

When a network is mechanically tested, the experimenter may be in a position to know the conditions of its synthesis. However, even if the reagents are perfectly known, it may be that not all of the cross-linking functional groups react so that the mean functionality is lowered and the mean molecular weight becomes higher than the theoretical value. Looking at a given cross-link, if, for example, $\phi = 3$ and one functional group fails, the given points become part of one chain that takes a length $2M_s$. These facts increase the difficulty of application of Flory's theory and limit the possibility of knowing exactly the physical structure of the network starting from mechanical properties only.

In real cases the network is, in general, not perfect, but the Flory equation can still be used in referring to the mean values of the constitutive parameters of the network itself (ξ, ϕ, M, ν), of which only two are independent. Once $|f^*|$ is measured, different interpretations of the real network are possible according to the auxiliary information available. If the fundamental stoichiometric unit M_s is known, the true M depends on the synthesis conditions[10,11] and is, in general, unknown; the true ϕ is also unknown. We observe, however, that the mean molecular weight of chains between junctions cannot be lower than the value M_s calculated from stoichiometry. M_s represents therefore the lowest possible molecular weight of chains so that $M_s < M < M_a$. M_a is the maximum molecular weight possible for a given $|f^*|$. In fact, with reference to Figure 1, no experimental points ($|f^*|$, ρ/M_s) should be found to the left of line a. The molecular weight corresponding to the affine model is expressed by

$$M_a = \rho RT v_{2c}^{2/3}/|f^*| \tag{11}$$

In conclusion, in the case of a real network synthesized with known reagents, there is for each experimental $|f^*|$ value a corresponding average molecular weight $M_a > M > M_s$, which, however, cannot be precisely determined. The mean functionality ϕ is also not known. If one does not know M_s but can make reasonable estimates of ϕ only, wider limits of M can be foreseen. In fact, the actual mean molecular weight M of the network chains should be in the range $M_{ph} < M < M_a$. ρ/M_a and ρ/M_{ph} are found at the intersection of the straight lines a and b with the ordinate $|f^*|$ (Figure 1). The limit M_{ph} is given by $M_{ph} = (\rho/|f^*|)RTv_2^{2/3}(1 - 2/\phi)$. Finally, if no information at all is available on the network parameters, only the limit M_a can be evaluated (eq 11). Some interesting limit considerations can be made concerning the cycle rank ξ. Using eq 4, which is still valid, and taking into account eqs 1 and 2, we obtain

$$\frac{f_c}{f_{ph}} = \frac{F}{\xi} - 1 = \frac{|f^*|V_n}{\xi KT v_{2c}^{2/3}} - 1 \tag{12}$$

which gives a correlation between the true f_c/f_{ph} and the real cycle rank density ξ/V_n, which is, unfortunately, not sufficient to describe the network. However, the following considerations can be made. In an imperfect network $\xi < \nu_s(1 - 2/\phi_s)$, where ν_s is the total theoretical number of chains and ϕ_s is the stoichiometric functionality. Therefore a lower $|f^*|$ results than for the equivalent perfect network ($|f^*|_s$). If one compares the real network behavior to that of a perfect network in its phantom state having a molecular weight of chains equal to the stoichiometric molecular weight (M_s), it is possible

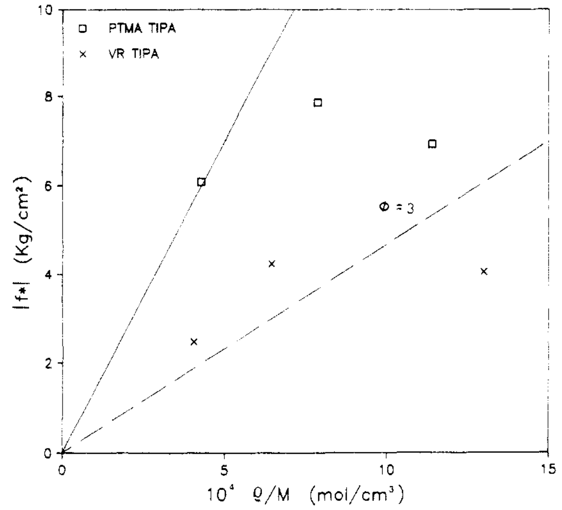

Figure 6. Modulus $|f^*|$ vs ρ/M of PE–PU and PES–PU cross-linked with trifunctional cross-linking agent (TIPA). The theoretical lines corresponding to the affine model (—) and the phantom model (- - -) are shown.

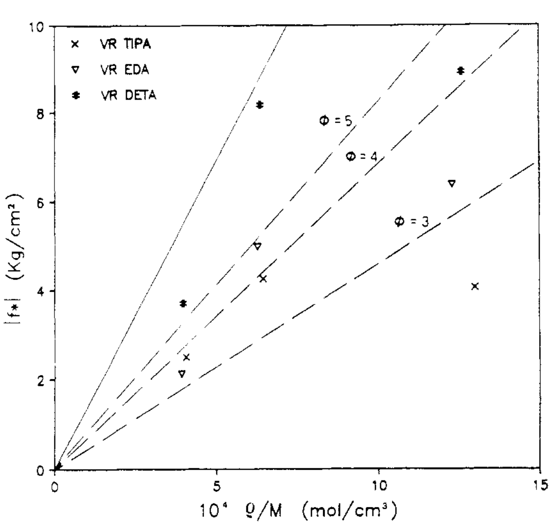

Figure 7. Modulus $|f^*|$ vs ρ/M of polyether-based polyurethanes cross-linked with different cross-linking agents. The theoretical lines corresponding to the affine model (—) and to phantom model for different junction functionalities ϕ (- - -) are shown.

to obtain a useful expression for $\bar{\xi}$. The ratio of the moduli in the two situations is

$$\frac{|f^*|}{|f^*|_{\mathrm{ph,s}}} = \frac{\bar{\xi}(1 + f_c/f_{\mathrm{ph}})}{\xi_s} \tag{13}$$

and using also eq 6 for ξ_s (stoichiometric cycle rank), we can write

$$\bar{\xi} = \frac{|f^*|}{|f^*|_{\mathrm{ph,s}}}\nu_s\left(1 - \frac{2}{\phi_s}\right)\frac{1}{1 + f_c/f_{\mathrm{ph}}} \tag{14}$$

In the case of not very large swelling ratios, when $f_c > 0$

$$\bar{\xi} < \frac{|f^*|}{|f^*|_{\mathrm{ph,s}}}\frac{\rho V_n}{M_s}N_A\left(1 - \frac{2}{\phi_s}\right) < \frac{|f^*|}{|f^*|_{\mathrm{ph,s}}}\xi_s \tag{15}$$

This disequation will be used in the applications. The solution to the problem of finding the true, mean molecular weight by using tensile tests remains therefore indeterminate. This is an important difference from what was accepted in the past when only the affine model was considered.[1] This approach has been used for a long time for the analysis of the cross-linking efficiency.[12]

Application. From our experimental data we can easily find $|f^*|$ and the corresponding F parameter (eq 4) valid in the range of short elongations ($\alpha \rightarrow 1$). In real situations, however, we cannot apply eq 5 to determine the ξ value that describes the network due to a lack of information on f_c/f_{ph}. In Figures 6 and 7 the theoretical frame line a–line b is reported for different cross-linking functionalities. Line a (affine model) is common to all of the graphs, since v_{2c} is practically equal for all of the cases, while the dotted lines b (phantom model) have slopes corresponding to the theoretical ϕ values ($\phi = 3$, $\phi = 4$, $\phi = 5$). Figure 6 shows the experimental points ($|f^*|$, ρ/M_s) of our PE–PU networks, while in Figure 7 the PES–PU experimental data are reported and compared with the trifunctional PE–PU. Figures 6 and 7 show that the experimental $|f^*|$ depends on the polyol chain length: in most cases a decrease of $|f^*|$ is observed for the highest molecular weight. In the case of PES–PU networks, moduli are higher than in the case of PE–PU networks of similar chain lengths reacted with the same cross-linking agent (TIPA). Comparing PE–PU and PES–PU of similar M_s, we see that PES–PU is closer to affine behavior than the corresponding PE–PU. For PE–PU we observe that the functionality influences the behavior of the network. Figures 6 and 7 show, in fact, that $|f^*|$, at equal M_s, decreases with decreasing functionality, moving far below the affine (a) line. This appears to be in agreement with the base hypothesis of Flory since an increasing number of chains connected to a network cross-link enhances the constraints on the junction fluctuations. Moreover, it is confirmed that even at $\alpha \rightarrow 1$ the network behavior is not affine.

In general, we did not find ($|f^*|$, ρ/M_s) points above line a, whereas we sometimes found points below line b. The graphs show that in all cases the PE–PU with the lowest molecular weight (VR 400) present moduli lower than those indicated by the theoretical line b, evaluated according to stoichiometric ϕ. We suggest as one of the possible reasons a much faster reaction of the network formation[13] in the case of shorter chains since the concentration of reactive groups is inversely proportional to M_p and the addition reaction of OH and NCO is kinetically of second order: we found experimentally that the increase of viscosity is much faster, and we believe that some chains may not find the chance to react in the way necessary to form the network even if they chemically join to the system (branching). In other words, the high reaction rate lowers the chance of using all of the cross-linking agent functionalities to build up the networks. The corresponding lowering of ϕ causes a decrease of the slope A_{ph} of the curve $|f^*|$ vs ρ/M. In the case of highly swollen networks ($f_c < 0$) a position below line b is possible in principle even in perfect systems. However, in our case, points below line b were obtained at $V/V_0 \lesssim 2.1$, i.e., when a reasonable estimate of the k and ζ parameters of Flory's model[7] indicates that f_c should be positive. Therefore in our case the position of experimental points ($|f^*|$, ρ/M_s) below line b indicates very probably that network imperfections are present. This fact could be analyzed by using eq 15, which can be employed when M and ϕ are known and which is easily interpreted in Figure 1, comparing the position of point P ($|f^*|$, ρ/M_s) with that of the corresponding point B (($|f^*|_{\mathrm{ph}}$, ρ/M_s), where $|f^*|_{\mathrm{ph}} = \xi K T v_{2c}^{2/3}/V_n$). In our case (eq 15) we obtained $\bar{\xi}/V_n \leq 2.89 \times 10^{-4}$ mol/cm³, $\bar{\xi}/V_n \leq 4.58 \times 10^{-4}$ mol/cm³, and $\bar{\xi}/V_n \leq 6.41 \times 10^{-4}$ mol/cm³, corresponding to PE–PU of low molecular weight (VR 400) respectively cross-linked with TIPA, EDA, and DETA. Should the experimenter get no information at all about M_s and ϕ_s, he could obtain the upper molecular weight limit only: M_a is calculated according to eq 11 (in our case, see column 6 of Table II). On the contrary, if one knows M_s, the uncertainty limits are in between M_s and M_a (columns 5 and 6). Table II also shows the limit values M_a and M_{ph} of the molecular weight corresponding to the experimental $|f^*|$ that should be considered in the case (columns 6 and 7) when M_s is not known but ϕ could be evaluated. The values of column 7 in parentheses refer to points that are below the theoretical line b. These points are characterized by $\phi < \phi_s$ due to synthesis imperfections, and therefore the corresponding M_{ph} values must not be considered.

As a final remark we observe that tensile tests of swollen networks have the advantage, compared to those of dry materials, of allowing the equilibrium to be reached more quickly, which makes the experimental work easier. Moreover, they allow one to examine also some glassy polymers when their T_g's in the swollen state become lower than room temperature, at which tensile tests are performed. All the above considerations can be extended to dry networks by putting $v_2 = 1$.

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References and Notes

(1) Flory, P. J. In *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(2) James, H. M.; Guth, E. *J. Chem. Phys.* **1953**, *21*, 1039.
(3) Treloar, L. R. G. In *The Physics of Rubber Elasticity*, 2nd ed.; Clarendon Press: Oxford, 1958.
(4) Flory, P. J. *J. Chem. Phys.* **1977**, *66*, 5720.
(5) Flory, P. J. *Polymer* **1979**, *20*, 1317.
(6) Flory, P. J. *Macromolecules* **1979**, *12*, 119.
(7) Erman, B.; Flory, P. J. *Macromolecules* **1982**, *15*, 800.
(8) Pegoraro, M.; Penati, A.; Zanderighi, L. XVIII FATIPEC Congress, Italy, Venice, 1986; Vol. 3, p 203.
(9) David, D. J.; Staley, H. B. In *Analytical Chemistry of the Polyurethanes*; Wiley: New York, 1969; Part 3, p 289.
(10) Flory, P. J. *J. Am. Chem. Soc.* **1936**, *58*, 1877.
(11) Esposito, P.; Pagliarani, L. Thesis, Polytechnic of Milan, Italy, 1982–1983.
(12) Zamboni, V.; Flisi, U.; Giunchi, G. *Rubber Chem. Technol.* **1971**, *44*, 1109.
(13) Minutillo, A. Thesis, Specialization School in Polymer Science, Polytechnic of Milan, Italy, 1986–1987.

Viscoelastic Properties of Telechelic Ionomers. 2. Complexed α,ω-Diamino Polydienes

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ABSTRACT: Complexation of the end groups of amino telechelic polydienes strongly affects the viscoelastic behavior. This is shown in the thermal dependence of the isochronous torsion modulus of a liquid polybutadiene selectively end-capped by a piperazine unit at both extremities. A rubbery plateau emerges when the telechelic polymer is coordinated to copper(II) or iron(III) chlorides. The rubbery plateau extends over a temperature range that depends on the molar ratio of the transition metal to the amine end group. Similar observations have been reported when the dynamic mechanical properties of an α,ω-bis(dimethylamino) telechelic polyisoprene have been investigated over the full range of temperature from the glassy plateau to the viscous flow. Upon complexation of the end groups, a rubberlike plateau is observed, which does not exist for the uncomplexed polymer. Furthermore, a secondary relaxation, attributed to the aggregation of the complexed amine end groups, occurs above T_g. The temperature at which the maximum of this relaxation is observed and the distribution of the relaxation times depend on the metal to amine end-group molar ratio. At a ratio of 1, $FeCl_3$ endows the chain network with higher cross-link density than $CuCl_2$ does. However, at the same time the temperature width of the rubbery plateau is much shorter for the former than for the latter polymer, indicating a relative thermal instability of the Fe–amine complexes.

Introduction

Thermomechanical properties of hydrophobic polymers are known to be modified by ionic groups randomly distributed along a polymeric backbone.[1,2] Interest in ionomers has to be found in the potential of cross-linking macromolecules in a thermoreversible manner. Alternative modifications of traditional polymers consist in replacing the ionic groups by other types of interacting groups. Examples have been described in which ligands have been attached onto polymeric chains and engaged in coordination reactions with metal salts.[3-5] Although many ligands can be used, this work focalizes on amino groups, which are one of the most studied groups both in solution and in solid state.[3-6] As recent papers indicate, there is plenty of interest in these systems.[7-15]

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