^{13}C NMR δ 141.79, 136.87, 30.14, 29.44, 7.50, 3.22; ^{29}Si NMR δ 1.99; IR ($CHCl_3$) ν 1597, 1450, 1410, 1230, 998 cm^{-1}. Elemental anal. Calcd for $C_{10}H_{20}Si$: C, 71.34; H, 11.97. Found: C, 70.87; H, 12.03.

Protodesilation of (*E*)-1,4-Poly[2-(triethylsilyl)-1,3-butadiene]. Five hundred milligrams of polymer was dissolved in 20 mL of methylene chloride in a 50-mL round-bottom flask equipped with a Teflon-covered magnetic stirring bar. To this was added 2 mL of a 47% solution of aqueous HI. The mixture was stirred vigorously at room temperature for 4 days. It was then diluted with ether and the organic phase washed with aqueous sodium bicarbonate and water. It was dried over anhydrous magnesium sulfate and filtered and the solvent removed by evaporation under reduced pressure. The (*Z*)-1,4-polybutadiene obtained had the following spectral properties: ^1H NMR δ 5.376 (br s, 2 H), 2.07 (br s, 4 H); ^{13}C NMR δ 129.60, 27.38; IR (film) ν 1650, 1440, 980, 725 cm^{-1}.[7]

Polymerization of I in THF was carried out as above except that the reaction temperature was maintained at −25 °C. The polymer isolated had the following properties: ^1H NMR δ 5.99 (br s, (*Z*)-CH═), 5.71 (br s, (*E*)-CH═), 2.10 (br s, 4 H), 0.89 (t, 9 H, J = 6.5 Hz), 0.60 (q, 6 H, J = 6.5 Hz); ^{13}C NMR δ 144.18, 143.69, 141.90, 141.79, 136.81, 136.64, 135.94, 135.51, 38.48, 33.9, 33.5, 32.63, 30.51, 30.14, 29.43, 28.57, 7.66, 7.50, 4.30, 3.27; ^{29}Si NMR δ 2.06, 1.96, 1.91, 1.89, 0.51, 0.38, 0.30; IR ($CHCl_3$) ν 1600, 1450, 1412, 1233, 997 cm^{-1}. Elemental anal. Calcd: C, 71.34; H, 11.97. Found: C, 70.88; H, 11.87.

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Registry No. I, 112348-69-3; $H_3C(CH_2)_3Li$, 109-72-8.

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Stoichiometry Effects on Rheology of Model Polyurethanes at the Gel Point

Recent rheological experiments on cross-linking polymers[1-4] lead to a new mechanical definition of the gel point (GP). The network at GP was shown to be characterized by power law stress relaxation and power law dynamic moduli over the entire experimental range. A linear constitutive equation for the stress at GP, the *gel equation*, was formulated[2,4]

$$\tau(t) = S\int_{-\infty}^{t}(t-t')^{-n}\dot{\gamma}(t')\,dt' \qquad 0 < n < 1 \qquad (1)$$

where τ is the stress tensor, $\dot{\gamma}$ is the rate of deformation tensor, and S and n are two material parameters.

In addition to the newly observed power law behavior, the gel equation also predicts the classical attributes of GP,[5] i.e., infinite steady shear viscosity and zero equilibrium modulus. These commonly used properties are actually poorly suited for determining the gel point since their measurement requires steady-state experiments which cannot be performed near the GP where the relaxation time of the polymer diverges. As a result the GP had to be determined by extrapolation. By contrast, eq 1 predicts a material behavior which can be easily and accurately measured with dynamic mechanical methods. The possible ranges of power law exponent, $0 < n < 1$, and of gel strength, S, allow us to distinguish between different gels.

Surprisingly the stoichiometric ratio, r, of the reactants was found to strongly affect the power law exponent.[4] An exponent value of $n = {}^1/_2$ was measured on a poly(dimethylsiloxane) (PDMS) gel prepared at balanced stoichiometry[1,2] whereas a greater exponent value, $n > {}^1/_2$, was obtained on a PDMS gel with cross-linker deficiency.[4] Three PU gels with *balanced* stoichiometry but with different molecular weight between cross-link points[3] also exhibited the ${}^1/_2$ exponent.

In this study the rheological behavior of PU gels with unbalanced stoichiometry is investigated. The variations of the two material parameters in eq 1, S and n, are followed over the entire range of stoichiometric ratios for which gelation can take place. Our long-term objective is to determine whether eq 1 can be universally used to describe the rheological behavior of cross-linking polymers at the GP. Even though PU and PDMS gels have a different chemistry and a different functionality of the cross-link points, universality principles would require that they respond similarly to variations of the same parameters and especially to variations of the stoichiometry.

Experimental Section. System and Sample Preparation. PU networks were synthesized by end-linking reaction of α,ω-dihydroxypoly(propylene oxide) (PPO) prepolymer with tris(4-isocyanatophenyl) thiophosphate (DRF) cross-linker. Details of the component characterization and of the sample preparation are reported elsewhere.[3,6-8]

In order to avoid the interference of vitrification with gelation and to obtain some reasonably fast reaction rates, PPO1000 was selected as a prepolymer.[3] Its number-average molecular weight and its polydispersity were found to be M_n = 965 and M_w/M_n = 1.007 as measured by VPO and GPC, respectively. The hydroxyl content was determined by an acetyl chloride titration method. PPO functionality was found to be 1.88. The DRF cross-linker was purified by recrystallization from dry benzene.[8] The isocyanate purity was determined by titration[9] and was found to be 98%.

The stoichiometric ratio, r, of the system is defined here as the initial ratio of isocyanate to hydroxyl groups, [NCO]/[OH]. From Flory's theory of gelation,[5] and assuming an ideal cross-linking process, the PU system is expected to reach gelation for stoichiometric ratios ranging from ${}^1/_2 < r < 2$. The quasi-ideality of this cross-linking reaction at the temperatures of interest (below 90 °C) was verified by showing that the final network with the highest

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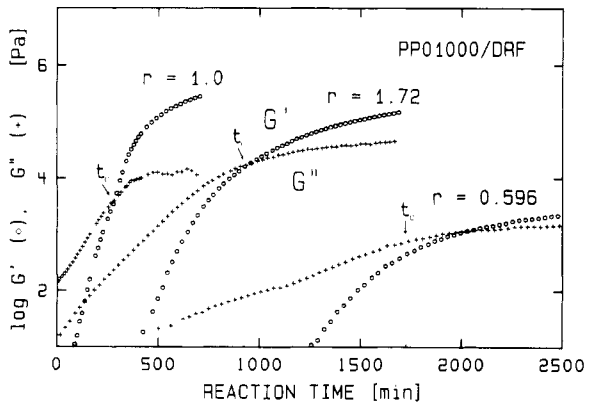

Figure 1. Curing curves of PPO1000/DRF networks with different stoichiometric ratios, r, of the reactants at $T = 30$ °C and $\omega = 0.5$ rad/s.

storage modulus is obtained for a composition very close to $r = 1$.[8]

Since the linear viscoelastic behavior of all the possible gel structures with $0.5 < r < 2$ is to be investigated, reaction mixtures with $r = 0.596$, 0.743, 1.43, and 1.72 were prepared (the gel with $r = 1.0$ was the topic of a previous study[3]). After mixing the desired quantities of PPO and DRF, for 5–10 min at 90 °C and under vacuum, the resulting curing samples were cooled to room temperature and quickly transferred to the rheometer. The cross-linking reaction was then continued at 30 °C and under a nitrogen atmosphere.

Rheological Experiments. The changes in dynamic storage, G', and loss, G'', moduli during isothermal cure were followed on a Rheometrics dynamic mechanical spectrometer using 25-mm diameter parallel disks. The experimental conditions were identical with those previously used with stoichiometrically balanced PU networks.[3]

The curing curves obtained with the two most extreme stoichiometric ratios, $r = 0.596$ and 1.72, are presented in Figure 1 where they are compared to the evolution with balanced stoichiometry, $r = 1.0$. $t = 0$ marks the beginning of the rheological experiment but not the beginning of the cross-linking process. However, direct comparison of the curing curves is possible since the differences in mixing times from one composition to another (no more than 5 min at 90 °C) are very small when compared to the total time for cross-linking (at least 24 h at 30 °C for $r = 1.0$). As expected, a strong dependence of the reaction rates upon the stoichiometric ratio is seen. With unbalanced stoichiometries the rate of cross-linking and the efficiency of the cross-link points decrease, resulting in a longer curing time, a lower elasticity (G' smaller), and a higher degree of imperfection ($\tan \delta = G''/G'$ smaller) of the final networks.[10,11]

Contrary to a widely held view,[12] previous studies with PDMS[1,2,4] led to the conclusion that gelation does not always occur at the instant of the crossover of G' and G'' on the curing curves, see Figure 1. Instead, gelation was found to occur before this point for a network with cross-linker deficiency.[4] In order to analyze the developing PU networks with unbalanced stoichiometry, frequency sweeps were rapidly performed at intermediate states of the cross-linking process. The curves obtained for the stoichiometric ratios $r = 0.596$ and 1.72 are presented in Figures 2 and 3, respectively. They are instant pictures of the frequency dependence of G' and G'' at different moments on the curing curves shown in Figure 1 and have been shifted by a factor A on the frequency scale to avoid overlap. From an initial low-frequency behavior with $G' \ll G''$ and with both moduli decreasing rapidly to zero each

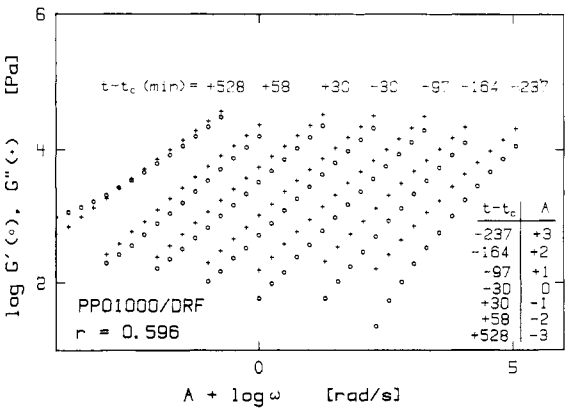

Figure 2. Storage and loss moduli at intermediate states of conversion for PPO1000/DRF with $r = 0.596$. t_c is not the instant of intersection (see Figure 1) of G' and G''.

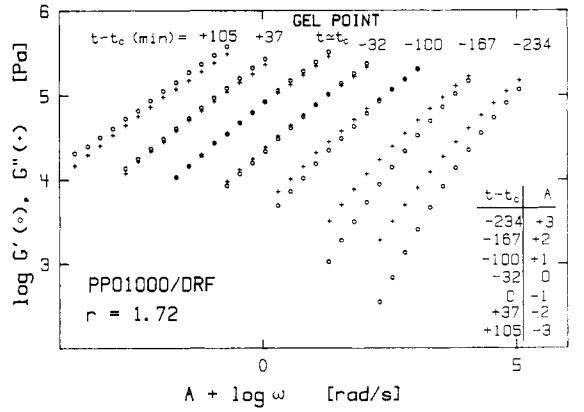

Figure 3. Storage and loss of moduli at intermediate states of conversion for PPO1000/DRF with $r = 1.72$. t_c is the instant of intersection (see Figure 1) of G' and G''.

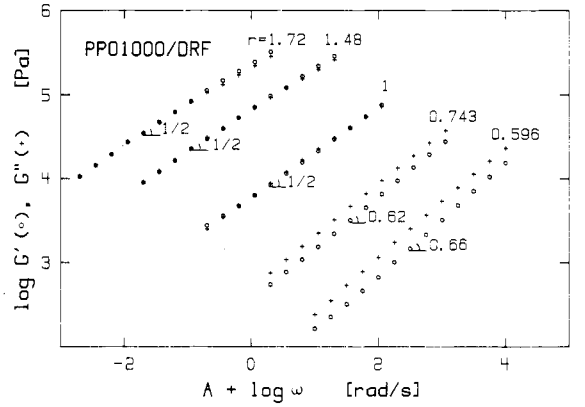

Figure 4. Storage and loss moduli at $t = t_c$ for PPO1000/DRF with $r = 0.596$, 0.743, 1.0, 1.48, 1.72. The respective shift factors in the graph are $A = -2, -1, 0, 1, 2$.

curing sample smoothly evolves toward a plateau value. Such evolutions are familiar and were shown to be characteristic of curing networks which undergo transition from the liquid to the solid state.[1,4] The remarkable common behavior, however, is the occurrence of a critical state at time t_c at which the dynamic moduli follow the power law dependence predicted by the gel equation, eq 1. The influence of the stoichiometric ratio upon this critical behavior is discussed in the following.

The solubility gave an independent test of the GP for a selected set of samples.[8] Before reaching the power law behavior, samples in a good solvent dissolved completely. Beyond the power law state, samples could not be dissolved any more.

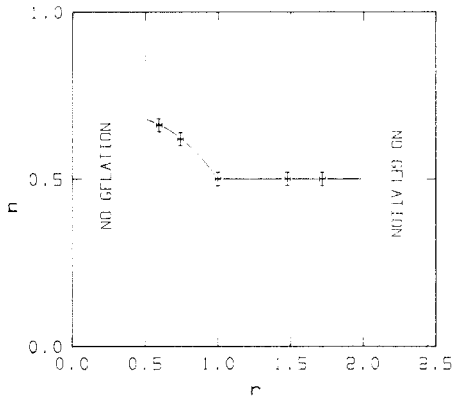

Figure 5. Measured power law exponent as a function of the stoichiometric ratio for PPO1000/DRF. The vertical lines indicate the theoretical limits of the compositions for which gelation is possible.

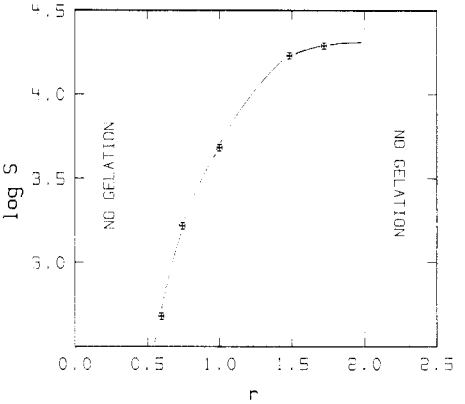

Figure 6. Measured gel strength as a function of the stoichiometric ratio for PPO1000/DRF.

Results and Discussion. The evolution of the rheological behavior at the GP as a function of the stoichiometric ratio, $0.5 < r < 2$, is presented in Figure 4. For gels with a deficiency of cross-linker, i.e., $r < 1$, the same variation as previously observed with PDMS[4] is seen. With decreasing values of r below stoichiometry, the slope of the power law increases above $n = {}^1/_2$ and G'' is greater than G' as predicted by the gel equation. Surprisingly, such an evolution of the power law exponent is not observed for gels with an excess of cross-linker. In this case not only is the exponent value $n = {}^1/_2$ conserved but it seems to be a limiting value. Consequently, for systems with an excess of cross-linker the instant of gelation can be easily determined from the crossover point of the loss and storage moduli on the curing curve, whereas this point is far away from the gel transition for $r = 0.596$ as seen in Figure 1.

The systematic error introduced by the fact that the curing reaction is not stopped, and that therefore the material is changing during the frequency sweep, was shown to be small in the case of networks with balanced stoichiometry.[3] With unbalanced stoichiometry this error is even smaller since the reaction rates are sensitively slower. We define the dimensionless *mutation number*

$$N_{mu} = t_{exp}\frac{1}{G}\frac{\partial G}{\partial t} \qquad (2)$$

for quantifying the change of property G during the frequency sweep (duration of experiment t_{exp}). The partial time derivative $\partial/\partial t$ indicates that the experimental conditions (frequency, temperature, pressure, etc.) are kept constant when evaluating the mutation number. G can be any typical property of interest; however, we are interested in the mechanical properties. With the storage modulus (and its gradient) at the gel point, the mutation number of our experiments was in the range 0.05–0.1, using data of Figure 1. This means that the storage modulus changed by 5–10% during the frequency sweep. Such a change might be considered significant but it is hardly visible on the log–log plot; i.e., it does not visibly alter the straight line of the power law near the gel point.

The power law exponent, n, and the gel strength, S, in eq 1 vary from one gel to another as summarized in Figures 5 and 6. The relaxation exponent has been directly related to the critical exponents of gelation.[13-15] This relation together with our experimental observation suggests that the critical exponents are not universal but that they depend on stoichiometry. Such finding is in agreement with percolation theory.[16] It should be noted that our findings disagree with the assumption[17] of a unique exponent n.

The observed rheological behavior at the GP is also in agreement with the predictions of recently derived fractal theory.[18,19] For instance, Muthukumar proposed that for a fractal cluster of dimension d_f the frequency dependence of the dynamic viscosity at intermediate frequency is given by[18]

$$\eta^*(\omega) \sim \omega^{-2/(d_f+2)} \qquad 0 < \omega \qquad (3)$$

From the gel equation, eq 1, the complex viscosity predicted at the GP is[4]

$$\eta^*(\omega) \sim \omega^{n-1} \qquad 0 < n < 1 \qquad 0 < \omega < \infty \qquad (4)$$

which leads to the fractal dimension at the GP as

$$d_f = 2n/(1-n) \qquad 0 < n < 1 \qquad (5)$$

Fractal dimensions between 1 and 3 would allow relaxation exponents in the range ${}^1/_3 \le n \le {}^3/_5$. A fractal dimension of 2 for gels with balanced stoichiometry was previously suggested.[20,21] This value is now seen to increase as the cross-linker proportion in the system is decreased below stoichiometry. The upper bound for the power law exponent of $n_{max} = 0.6$, as calculated from eq 4, is slightly lower than the highest experimental value measured, $n = 0.66$.

Equally interesting is the evolution of the gel strength, S. As seen in Figure 6, S is very sensitive to small variations of the stoichiometric ratio, and contrary to most of the final network properties, it does not go through a maximum at balanced stoichiometry. For networks with cross-linker deficiency a soft gel with low dynamic moduli and therefore a low strength is produced, whereas gels with cross-linker excess exhibit a higher strength. From these observations, it is speculated that gels with a deficiency of cross-linker lead to more highly branched molecules, many free ends, and consequently a higher fractal dimension. By contrast, gels with an excess of cross-linker would produce larger but less branched molecules able to form entanglements which result in a higher strength.

Conclusions. Rheological tests performed on cross-linking polyurethanes at the gel point confirmed the validity of the gel equation. For all the stoichiometric ratios of the reactants the frequency dependence of the dynamic moduli at the GP occurs in a power law. This behavior was previously found to be independent of the molecular weight between cross-links as well as of the nature of the system.

The power law exponent can be arbitrarily changed from 0.5 to about 0.7, depending on the stoichiometric ratio of the reactants. This suggests that there is not a unique molecular structure with a unique power law exponent corresponding to the gel state. Instead, two parameters

are needed to fully characterize a gel structure. These are the power law exponent and the gel strength.

It should again be emphasized that the above results apply at the gel point of model cross-linking polymers at temperatures far above vitrification. The prepolymers consisted of large bifunctional molecules, however, with an initial molecular weight well below the critical mass for entanglements, and of small trifunctional cross-linker molecules.

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Registry No. (PPO)(DRF) (block copolymer), 112320-36-2; DRF, 4151-51-3.

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Electron Nuclear Double Resonance from Paramagnetic Centers in Ionomers. Titanium(III) in Nafion

The presence of ions and of the polymer network in ionomers is believed to lead to segregation into polar and nonpolar regions and to ionic clustering.[1] Electron spin resonance (ESR) spectroscopy has been used in recent years in order to study the process of clustering of the ionic species in the polar phase of ionomers. In our studies[2] we have deduced the immediate environment, within about 0.3 nm, of the paramagnetic Cu(II) and Ti(III) in the perfluorinated ionomer membranes known as Nafion. We have been able to detect cations ligated to the oxygen atoms from the solvent and from the sulfonic groups of the polymer network. In addition, we have identified Cu(II)–Cu(II) and Ti(III)–Ti(III) dimers, based on the detection of the spin-forbidden half-field transition. The signal from the dimers appears even at low cation concentrations, compared with the concentration needed for complete neutralization of all the sulfonic groups in the ionomer. We have suggested that clusters are formed from the association of these dimeric species.

Determination of the cluster size is important for an accurate model of phase separation in ionomers. This implies measurement of the structure around the cation in the second solvation shell, to about 0.5 nm and even further, to the regions occupied by the organic network. At these distances the interactions of the nuclei with the paramagnetic centers are too weak to be measured by ESR, because the line widths detected in the solid state are inhomogeneously broadened and the signal is a convolution of many small interactions.

The resolution in magnetic resonance experiments is considerably enhanced by using multiple-resonance techniques. Of these techniques, electron nuclear double resonance (ENDOR) has increased resolution compared to ESR and increased sensitivity compared to NMR. The ENDOR signal is obtained by monitoring the change in the intensity of a partially saturated ESR signal while sweeping the nuclear transitions by an radiofrequency (rf) field which is typically in the range 2–50 MHz. The ENDOR effect is very sensitive to the relaxation paths in the spin system and it is usually difficult to predict the temperature corresponding to a maximum signal.[3]

In this paper we present the first application of ENDOR for the study of ionomers. ^1H and ^2H, and ^{19}F ENDOR signals were obtained in the temperature range 4–20 K in Nafion containing the paramagnetic cation Ti(III). To the best of our knowledge this is the first detection of ENDOR signals of these nuclei from a Ti(III) center surrounded by oxygen ligands.[4] The significance of the results and the information that can be obtained will be discussed. Extension of this method to other systems will be suggested.

Experimental Section. Nafion-H powder (Scientific Polymer Products) with an equivalent weight of 1100 g/mol of SO_3H was used without further purification. Methanol (Fisher) and deuteriated methanols (Norell Chemical Co.) were dehydrated by using molecular sieves Type 3A from Kodak. The deuterium enrichment of CH_3OD and CD_3OD was 99%. Methanol solutions of $TiCl_3$ from Aldrich, in the concentration range 0.04–0.10 M, were used to exchange 30–40% of the SO_3H groups of the ionomer, based on three sulfonate groups per Ti(III). More details on the experimental procedure have been published.[2c]

ESR and ENDOR spectra at X-band were measured with Bruker 200D SRC spectrometers in Detroit and Linkoping operating at 9.7 GHz. ESR spectra at 100 K were obtained by using the Bruker variable-temperature ER 4111 VT unit. ENDOR spectra were obtained in Linkoping with the Bruker ENDOR attachment equipped with the Aspect 2000 computer. The magnetic field was measured by using the Bruker ER 035 NMR Gaussmeter and the microwave frequency was measured with an EIP Model 548 A microwave frequency counter. The maximum rf power of the ENDOR unit is 100 W. In all ENDOR experiments helium was used as the coolant in a flow cryostat from Oxford Instruments.

Results and Discussion. The samples measured were Nafion containing Ti(III), swollen by CH_3OD and by CD_3OD. The samples are designated Ti/Nafion/CH_3OD and Ti/Nafion/CD_3OD, respectively.

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