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Rheology of Model Polyurethanes at the Gel Point

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ABSTRACT: The universality of the gel equation, a recently suggested rheological equation for polymers at the gel point, was tested on three well-defined cross-linking polyurethanes (PU). Stoichiometric amounts of triisocyanate cross-linker (DRF) were mixed with α,ω -dihydroxypoly(propylene oxides) (PPO) of nominal molecular weights 425, 1000, and 2000. As the cross-linking reaction progressed at 30 °C the evolution of the viscoelastic properties was measured. At the gel point, the storage modulus G' and the loss modulus G'' were found to be congruent and proportional to $\omega^{1/2}$, where ω is the frequency of the oscillatory shear experiment. The same behavior was previously observed with an end-linking poly(dimethylsiloxane), however, with tetrafunctional cross-linking points.^{1,2} This suggests universal validity of the rheological equation for stoichiometrically balanced end-linking polymers.

Introduction

The gel point (GP) in network polymers is known to manifest itself by an infinite steady-shear viscosity and a zero equilibrium modulus.³ In addition to that, Chambon and Winter^{1,2} observed that a cross-linking poly(dimethylsiloxane) (PDMS) system at GP exhibits congruent moduli

$$G'(\omega) \sim \omega^{1/2} \sim G''(\omega) \quad (1)$$

and stress relaxation in a power law

$$G(t) \sim t^{-1/2} \quad (2)$$

These phenomena, including infinite steady-shear viscosity and zero equilibrium modulus, are described by the *gel equation*, which is a linear viscoelastic constitutive equation for the stress²

$$\tau(t) = S \int_{-\infty}^t (t-t')^{-1/2} \dot{\gamma}(t') dt' \quad (3)$$

where $\dot{\gamma}$ is the rate of deformation of the sample at GP. The only material parameter in the equation is the gel strength S .

The apparent simplicity and clarity of the gel equation suggests its universal validity for end-linking polymers with balanced stoichiometry. We therefore selected three polyurethanes (PU) and studied their rheology in the vicinity of GP. Similarly to the PDMS system which was used in the earlier experiments, these PU networks are also formed by an end-linking reaction of stoichiometrically balanced chemical species. However, the cross-linking process occurs by a different reaction and the cross-link functionality was chosen to be 3 instead of 4 for the PDMS. Nevertheless they are found to exhibit the same rheological behavior at GP as PDMS. This will be shown in the following.

Experimental Section

System. The constituents of the system are α,ω -dihydroxypoly(propylene oxide) (PPO) of nominal molecular weight 425,

Table I
 α,ω -Dihydroxypoly(propylene oxide) (PPO)
Characterization

sample	PPO425	PPO1000	PPO2000
\bar{M}_n (VPO)	454	965	2018
\bar{M}_w/\bar{M}_n (GPC)	1.013	1.007	1.006
functionality	1.93	1.88	1.94

1000, and 2000 and tris(4-isocyanatophenyl) thiophosphate (DRF), for which structural formulas are shown in Figure 1. The nominal molecular weight of the prepolymer was chosen far below the critical value for physical entanglements. Advantages of this system are that (i) the initial compounds are well characterized and can be readily obtained with a high degree of purity, (ii) the linear PPO component is available at different molecular weights with narrow polydispersity, (iii) the well-defined chemistry of the cross-linking process^{4,5} makes it possible to form practically perfect networks, and (iv) the reaction kinetics at room temperature are slow.

Material Preparation and Characterization. Recent reports give details of sample preparation,⁴ of curing kinetics, and of the properties of the final networks.⁴⁻⁶

PPO prepolymers (Aldrich Chemical Co.) were dried prior to use by azeotropic distillation with added benzene. The number-average molecular weights and the molecular weight distributions were measured⁶ by VPO and GPC (Table I). The number of OH groups was determined by titration. In all three systems, the PPO prepolymers were found to be quasi-monodisperse ($\bar{M}_w/\bar{M}_n < 1.02$) and their functionality was very close to 2 (Table I).

The triisocyanate cross-linker was obtained from Mobay Chemical Co. in the form of a 20% solution in methyl chloride. After purification by recrystallization the NCO content was found to correspond to the expected theoretical value⁶ of 27.1%.

The curing samples were prepared by mixing stoichiometric amounts of PPO and triisocyanate at 90 °C and under vacuum. After 5–10 minutes of mixing, the reacting samples were cooled to room temperature and transferred into the rheometer.

Rheological Experiments. Small strain oscillatory shear experiments were performed with a Rheometrics dynamic mechanical spectrometer using 25-mm-diameter parallel disks and a nitrogen atmosphere. All the samples were reacted isothermally at 30 °C. The evolution of the storage (G') and loss (G'') moduli

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SYSTEM

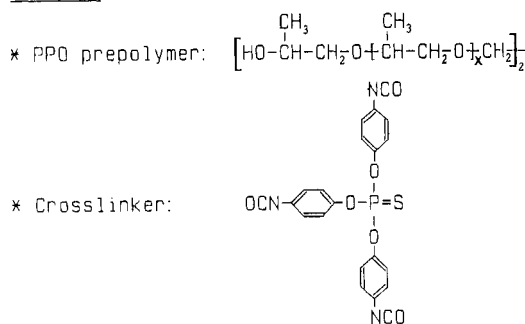


Figure 1. (a) α,ω -dihydroxypoly(propylene oxide) (PPO); (b) tris(4-isocyanatophenyl) thiophosphate (DRF).

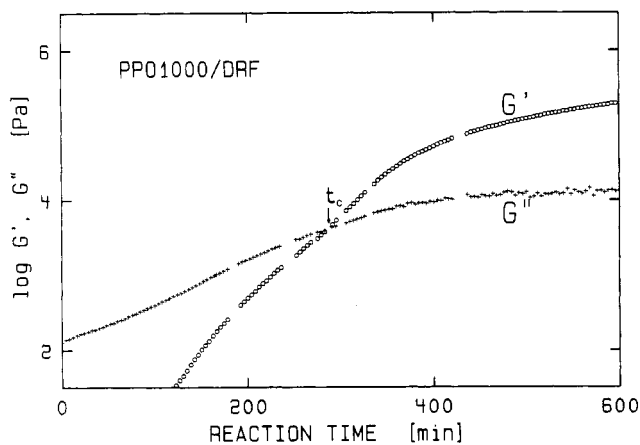


Figure 2. Evolution of the storage modulus G' and the loss modulus G'' during the cross-linking reaction of PPO1000/DRF at $T = 30^\circ\text{C}$ and $\omega = 0.5 \text{ rad/s}$. $t = 0$ marks the beginning of the isothermal rheological experiment but not the beginning of the cross-linking process. The isothermal gel time t_c is estimated from kinetics data⁵ to be 530 min.

at constant frequency was recorded as a function of the reaction time (time sweep). At chosen stages of the cross-linking process, the time sweep experiments were interrupted to measure the frequency dependence of G' and G'' (frequency sweep). Both types of experiments could be performed on the same reacting sample since the duration of a frequency sweep (about 6 min) was always very short compared to the total curing time (at least 15 h with PPO425). Thus the samples could be regarded as unchanged during the short frequency sweep, and the evolving viscoelastic response of the partially cured network could be analyzed.

Results and Discussion

Time Sweep Measurements. Figure 2 shows the isothermal evolution of G' and G'' vs. reaction time for the network synthesized with PPO1000. Only the most interesting part of the curing curve is presented since the complete leveling off of both moduli required more than 24 h at 30°C in this case. In a typical curing curve, the viscous behavior dominates the initial part of the experiment ($G'' \gg G'$) and the elastic behavior dominates the end of the experiment ($G' \gg G''$). Both moduli increase as a result of the increasing cross-link density, but the elastic component rises more sharply than the viscous component. Such an evolution of the dynamic storage and loss moduli is characteristic for networks formed by end-linking reaction with balanced stoichiometry. The same general behavior is observed for the networks prepared with PPO425 and PPO2000, the main differences being the magnitude of the moduli and the reaction rates.

The time-sweep curve, Figure 2, has been interrupted repeatedly. Sections of missing data points mark the intervals of time during which the viscoelastic properties of

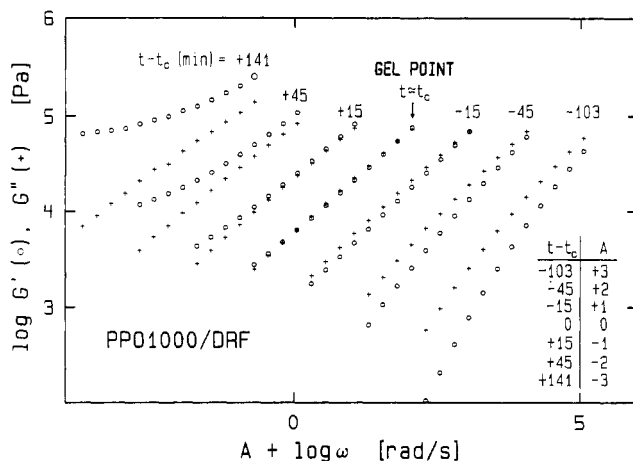


Figure 3. G' and G'' vs. frequency for PPO1000/DRF at 30°C and at different stages of network formation. Parameter is the reaction time. The curves have been shifted horizontally by a factor A of the value listed in the insert. t corresponds to the middle of the frequency sweep.

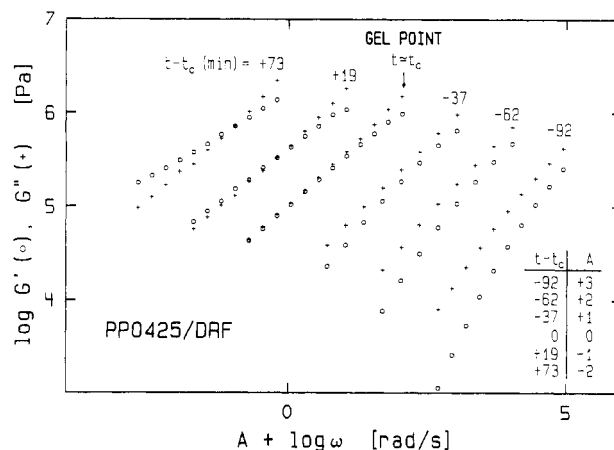


Figure 4. G' and G'' vs. frequency for PP0425/DRF at 30°C and at different stages of network formation.

the partially cured networks have been studied by frequency-sweep experiments.

Frequency Sweep Measurements. Frequency sweeps were performed in the vicinity of GP and are first discussed for the network synthesized with PPO1000, Figure 3. The curves have been purposely shifted horizontally by a factor A (see insert in Figure 3) for easier comparison. Analysis of these data indicates that, as previously observed for the PDMS system,^{1,2} the crossover of G' and G'' on the curing curve occurs at the instant of gelation t_c , Figure 2. Shortly before t_c , the material is still a liquid and so both moduli decrease to zero at low frequency. Shortly after t_c , the storage modulus G' tends toward a limiting value at low frequency, demonstrating the existence of permanent elasticity characteristic of a solid material. The shapes of both $G'(\omega)$ and $G''(\omega)$ change smoothly as the reaction proceeds; i.e., G' and G'' approach each other, superimpose, and pass each other in a continuous fashion.

For additional information, a sample at t_c was plunged into a mixture of methanol and toluene. The initial disklike shape of the sample dissociated almost instantaneously into numerous small clusters, revealing a lack of connectivity throughout the sample and indicating a macroscopic heterogeneity in the gelation process. Shortly after t_c , a sample could not be dissolved anymore. These experiments confirm that the crossover in Figure 2 occurs at the instant of gelation and that rheological experiments can provide a very sensitive tool to accurately localize GP.

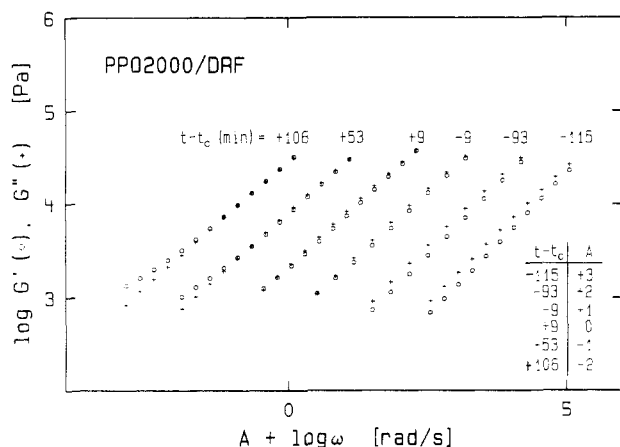


Figure 5. G' and G'' vs. frequency for PPO2000/DRF at 30 °C and at different stages of network formation.

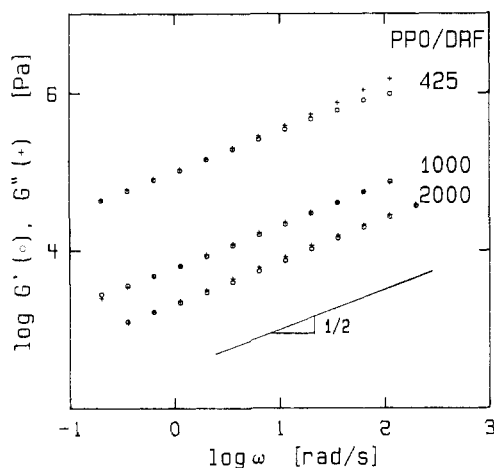


Figure 6. G' and G'' vs. frequency at the gel point for PPO425/DRF, PPO1000/DRF, and PPO2000/DRF.

The same general evolution of the rheological properties is observed for the samples prepared with PPO425 and PPO2000. However, with PPO425, Figure 4, the determination of GP is not as straightforward. In this case, vitrification interferes with gelation and causes a deviation from the predicted behavior at high frequency. This effect is discussed in more detail in a separate section below. With PPO2000, Figure 5, the reaction kinetics are very slow at 30 °C and the exact instant of gelation is difficult to determine from the available range of measurements. In this case, t_c has been determined from the crossover of G' and G'' on the curing curve (time-sweep experiment). However, two states, $t_c - 9$ min and $t_c + 9$ min in Figure 5, are asymptotically close to GP and exhibit the moduli congruency predicted by eq 3.

The cross-linking reaction continues during the frequency sweeps, which require about 6 min. The augmentation of G' and G'' during that time can be estimated with the slope of the curves in Figure 2. At the gel point, G' increases by about 15% and G'' by about 7% at 0.5 rad/s. Increases of less than 17% and 3% were found for G' at the gel point of PPO425 and PPO2000, respectively. This systematic error is small and can be detected in Figure 6 as a very slight increase in slope beyond the expected value of $1/2$.

For PPO1000 near the gel point, the 6-min time interval corresponds to an increase of the extent of reaction of about 0.2% as indicated by Feger and MacKnight,⁵ who studied the curing kinetics of a similar material. From their eq 7 and with a critical extent of reaction as given

Table II
Glass Temperature of the Fully Cured Networks

sample	PPO425/ DRF	PPO1000/ DRF	PPO2000/ DRF
T_g (midpoint), °C	+33	-20	-50

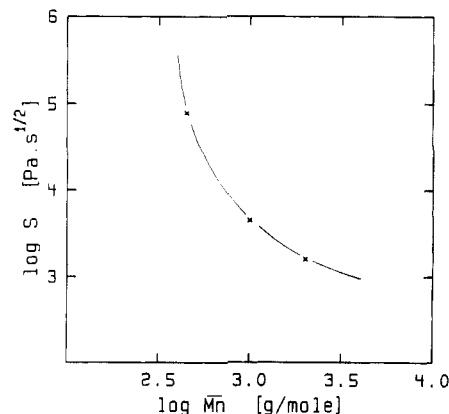


Figure 7. Measured gel strength S as a function of the strand length between cross-linking points.

by Flory's theory, the isothermal gel time t_c of PPO1000 at 30 °C is calculated to be 530 min. The relative length of the frequency sweep is therefore $\Delta t/t_c = 6/530 = 0.011$. Comparison with data of Adam et al.⁹ for the same value of $\Delta t/t_c$ indicates that our samples exhibited considerably smaller changes of the measured rheological parameters. This can be explained by the different range of shear rates used for the two experiments.

The range of measurements is limited to only 3 decades of frequency. Time-temperature superposition⁵ could not be applied at intermediate stages of the cross-linking process since the curing reaction of the PU had not been stopped. However, this limited range is sufficient to show that $G'(\omega)$ and $G''(\omega)$ grow together at $t = t_c$ and that they follow a power law with an exponent of $1/2$ at that instant. The behavior that had been observed with a PDMS^{1,2} system over nearly 6 decades of frequency is now observed with the PU system, Figures 3, 4, and 5. This result is highly significant since the functionalities of the two systems are fundamentally different (i.e., PU with $f = 3$ and PDMS with $f = 4$).

Effect of the Strand Length between Cross-Links on the Rheological Properties at GP. The complex modulus of GP networks with different strand lengths between cross-links is compared in Figure 6. Congruent moduli, $G'(\omega) = G''(\omega)$, and frequency dependence proportional to $\omega^{1/2}$ are observed for the networks prepared with PPO1000 and PPO2000. With PPO425 the congruent behavior is only observed at low frequency. The deviation at high frequency is attributed to the interference of vitrification with gelation. DSC measurements performed on fully cured networks,⁶ Table II, suggest that the temperature of vitrification of the gel (T_{gg}) prepared with PPO425 must be relatively close to $T = 30$ °C. This results in a sharper rise of $G''(\omega)$ at frequencies above 10 rad/s while $G'(\omega)$ still exhibits a slope of $1/2$. The same phenomenon may explain the results of Tung and Dynes,⁹ who observed a frequency dependence for the reaction time needed to reach the crossover point of G' and G'' .

The material parameter S appears to be extremely sensitive to changes of the strand length between cross-links, Figure 7. When the strand length is increased, the cross-link density is decreased, thus resulting in a softer gel characterized by a lower value of S . The glass transition temperature of the gel, T_{gg} , is also lowered with lower

cross-link density and so a gel with a lower value of S should exhibit a broader frequency range in which moduli are congruent.

Conclusions

The constitutive equation, eq 3, which was previously found to describe the viscoelastic properties of a PDMS network at GP, is also valid for a PU system. $G'(\omega)$ and $G''(\omega)$ have been found to be congruent and proportional to $\omega^{1/2}$ at GP, independent of the strand length between cross-links or the functionality of the cross-linker. The gel strength S strongly increases as the strand length between cross-links is decreased.

It has been shown that the crossover time of G' and G'' , as measured during the cross-linking reaction, corresponds to the exact instant of gelation. However, this result remains only valid if the frequency of the experiment is sufficiently low or if the experimental temperature is sufficiently far from the temperature of vitrification of the gel.

Finally it is important to recall that the present analysis is restricted to irreversible gels formed by end-linking reaction of stoichiometrically balanced chemical species.

Experiments at different stoichiometric ratios will be reported in a followup article.

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Hydrogen Bonding in Polymers. 4. Infrared Temperature Studies of a Simple Polyurethane

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ABSTRACT: Fourier transform infrared temperature studies of a simple linear semicrystalline aliphatic polyurethane, poly(1,4-butylene hexamethylenecarbamate), are presented. The main thrust of the work concerns the interpretation of the infrared spectral changes associated with hydrogen bonding and a comparison with our recently published studies of semicrystalline polyamides.

Introduction

We have recently published three papers pertaining to the interpretation of the infrared spectra of polyamides.¹⁻³ Specifically, infrared temperature studies were reported for a completely amorphous polyamide (commonly denoted nylon 6I/6T) and three semicrystalline polyamides; nylon 11, nylon 12, and a structurally irregular terpolyamide (denoted nylon 6/66/610). Three major normal modes associated with the amide group were emphasized in our studies which yield different, but complementary, information.

It is well recognized that the band envelope encompassing the N-H stretching mode is composed of two main contributions, attributed to "free" (non-hydrogen bonded) and hydrogen bonded N-H groups. The latter is primarily a reflection of the distribution of the strength of the hydrogen bonds (although there is also a degree of broadening due to anharmonicity). The mean strength of the hydrogen bonds diminishes with increasing temperature. Concurrently, there is a reduction in the area of the hydrogen bonded N-H band that is the result of two primary factors. First, a fraction of the bonded N-H groups transform to "free" N-H groups as dictated by equilibrium considerations. Second, and more importantly in the case of simple polyamides, the absorptivity coefficient is a strong function

of the strength of the hydrogen bond and varies significantly as the band shifts in frequency.¹ Without a knowledge of the variation of absorptivity coefficient with hydrogen bond strength, measurements of the concentration of "free" and hydrogen bonded N-H groups are subject to large errors. As we have pointed out previously, this has serious ramifications if infrared data obtained from the N-H stretching region are to be used for the estimation of thermodynamic parameters associated with hydrogen bonding.¹⁻³ The hydrogen bonded N-H mode is conformationally insensitive and the presence of order ("crystallinity") is reflected only in a reduction in the relative breadth of the band, which implies a narrower distribution of hydrogen bonded strengths.^{2,3}

The amide I mode (which may be considered, in simple terms, as the carbonyl stretching vibration) is, however, sensitive to order. Contributions to the amide I band envelope assigned to "free" (non-hydrogen bonded) carbonyl groups together with ordered and disordered hydrogen bonded carbonyl groups are readily discerned. This conformational sensitivity is not due principally to mechanical coupling to the main chain but rather to dipole-dipole coupling of the carbonyl groups. In addition, unlike the N-H stretching mode, the three different contributions comprising the amide I mode have absorptivity coefficients