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Rheological Characterization of the Gel Point: A New Interpretation

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ABSTRACT: Winter and Chambon have recently shown that the gel point can be precisely identified in a crosslinking process from rheological measurements on the reaction medium. The cross-linking reaction of poly(ethylene oxide) (PEO), carrying at both chain ends hydroxyl functions, with various pluriisocyanates was chosen to check the validity of this new method. The experimental setup included Fourier transform infrared (FTIR) spectroscopy to follow the conversion of the isocyanate functions with time and a rheometer to investigate the mechanical response of the reaction medium to oscillatory solicitations at various stages of the reaction. In stoichiometric systems at a given conversion, the storage modulus G' and the loss modulus G'' become congruent and proportional to $\omega^{1/2}$ over the entire frequency range. Simultaneously, the extent of reaction reaches the critical value p_c predicted by branching theory. This excellent agreement substantiates Winter's method and confirms its validity. This investigation has been extended to nonstoichiometric systems. When the end-standing hydroxyl functions of PEO are in excess, the rheological behavior observed at the gel point is quite different, and it was attempted to account for the phenomena observed.

Introduction

Dynamic viscoelastic properties of polymer solutions have been thoroughly investigated and are nowadays well understood.[1] Recently, the more complicated problem of the dynamic viscoelastic changes during a chemical process involving polymers has been addressed.[2] Considerable success has been achieved, in particular with respect to gel point (GP) determination in cross-linking reactions, although much remains to be understood. It has been shown by Winter and Chambon[2] that the gel point can be precisely identified and located by monitoring the dynamic viscoelastic parameters throughout the reaction. At the gel point the storage (G') and loss (G'') moduli are congruent over the whole spectrum of frequencies and proportional to the square root of the frequency.

This finding of Winter and Chambon is a major breakthrough if it is recalled that until recently the gel point was determined by extrapolation of equilibrium quantities such as the steady-state viscosity or the equilibrium modulus. Nevertheless, any method of characterization has to be checked by another independent technique to be considered valid. Several theories of gelation[3] (i.e., branching theories) predicting the extent of reaction at the gel point have been developed. Therefore if a correlation can be established between kinetic data—treated within the frame of the branching theory—and rheological measurements, Winter's method could be assessed and its relevance discussed.

This three-faceted approach, including rheology, kinetics, and gelation theory, is the purpose of the present paper. It is implemented by monitoring simultaneously the rheological changes in a mechanical spectrometer and the kinetics of reaction, followed by Fourier transform infrared spectroscopy (FTIR). The system studied is the end-linking reaction of poly(ethylene oxide) (PEO), carrying at both chain ends OH functions, with a pluriisocyanate cross-linker, either aromatic or aliphatic, in the presence of a solvent.

The influence of the reaction stoichiometry is investigated in the second part of the paper, and the results obtained are compared with Winter's.[2e] The rheological behavior of the reaction medium, especially the frequency dependence of the dynamic moduli, is shown to strongly depend upon the stoichiometry used: Rouse-like behavior (term used by analogy with the response of a concentrated polymer solution to high-frequency solicitations) characterizes the stoichiometric reaction medium at the gel point, whereas a Zimm-type regime prevails under stoichiometrically unbalanced conditions ($r = 0.7$). The occurrence of these two regimes is discussed and the interpretation given is based upon the analogy that exists with the concentration dependence of dynamic properties of polymers.[8]

General Considerations

The investigation of rheological changes occurring during a cross-linking reaction is rather novel.[4] Information on the viscosity increase of the medium (before GP) and on the equilibrium modulus of the material obtained (past GP), collected as a function of reaction time, is used to model cross-linking reactions of industrial importance. However, the gel point, characterizing the transition from liquid to solid, is poorly defined, since the parameters used to identify this precise stage of reaction (zero-shear viscosity and equilibrium modulus) are extrapolated values. Tung and Dynes[5] have made the first attempt to determine the gel point from dynamic viscoelastic data. They have found incidently that the crossover of the loss (G'') and storage (G') moduli occurs in the vicinity of the gel point. Similar crossovers are also observed in un-cross-linked polymers at the onset of the plateau zone, characterizing the presence of entanglements. To avoid any confusion between these two different phenomena (gel point and entanglements) Winter and Chambon have reconsidered the earlier method of Tung and Dynes and defined the conditions of its utilization. The reaction medium should be free of interferences that may arise either from the presence of entanglements in the earlier stages of the reaction or from phenomena such as crystallization or vitrification during reaction.

Under stoichiometric conditions, Winter and Chambon have established that loss and storage moduli are

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congruent at the gel point and proportional to $\omega^{1/2}$ over several orders of magnitude of the frequency.

The first part of this paper aims at testing the validity of Winter's method. The path adopted is based on the observation that in a cross-linking medium rheological changes are controlled by the reaction itself. Information on the reaction kinetics is used to convert the plots of G' and of G'' versus time, at any given frequency, into plots of G' and of G'' versus conversion p. The reaction time is the parameter common to both techniques. At the supposed gel point (using Winter's criteria) the conversion p_c experimentally measured is compared to that predicted by the branching theory.

The choice of α,ω-dihydroxypoly(ethylene oxide) as precursor is documented by its well-established functionality of 2, contrary to poly(propylene oxide), which exhibits an ill-defined functionality of 1.8. The molecular weight of the precursor is chosen below the threshold of physical entanglements. The presence of solvent (dioxane) is necessary because of the high tendency of PEO to crystallize when unsolvated.

Experimental Section

1. **Reactants.** The poly(ethylene oxide) samples were generously supplied by Hoechst Co. under designations which indicate their molecular weight. The number-average molecular weights were determined by size exclusion chromatography (GPC) (THF being the eluent) using a PEO calibration curve and by end-group analysis.[6] The values obtained, in close agreement with those given by Hoechst, are gathered in Table I.

The pluriisocyanates (Desmodur N 75 and Desmodur RF) were kindly provided by Bayer. Desmodur N 75 is a mixture of several aliphatic pluriisocyanates. It results from the reaction of a small amount of water with hexamethylene diisocyanate. Its number-average (f_n = 6.3) and weight-average (f_w = 10.1) functionalities have been determined previously.[10] Desmodur RF is a pure trifunctional aromatic compound: $S{=}P(O\text{-}p\text{-}C_6H_4N{=}C{=}O)_3$. The two cross-linking agents were used without further purification. They were titrated with di-n-butylamine.

Dioxane was distilled twice over sodium and kept under dry argon.

2. **Experimental Procedure.** Prior to its use, PEO was freeze-dried in the reaction vessel. Solvent (dioxane) and the pluriisocyanate cross-linker was subsequently introduced under dry argon. The weight fraction of polymer was set constantly to 0.33. The mixture was then transferred under an anhydrous atmosphere into the cell of the rheometer and into the FTIR cell. All reactions were carried out at 60 ± 0.1 °C.

The oscillatory shear experiments were performed under an argon atmosphere with a Rheometrics RMS-605 mechanical spectrometer equipped with a cone-and-cylinder cell. At given time intervals a frequency sweep extending from 100 to 0.1 rad/s was carried out. It took less than 10 min to measure the response to the constraint applied over the entire domain of frequencies covered. The times shown on the diagrams are true reaction times, obtained by interpolation, taking into account that the reaction proceeds during measurement. The storage (G') and loss (G'') moduli can thus be recorded as a function of both reaction time and frequency.

The kinetics of the reaction was monitored by FTIR. The extent of reaction p was obtained from the decay of the NCO peak at 2270 cm^{-1}:

$$p = \frac{[\mathrm{NCO}]_0 - [\mathrm{NCO}]_t}{[\mathrm{NCO}]_0}$$

The reaction between hydroxyl and isocyanate functions can be stopped at once by addition of butylamine, which is known to react readily with isocyanate functions. This procedure was of special interest to study samples very close to gelation.

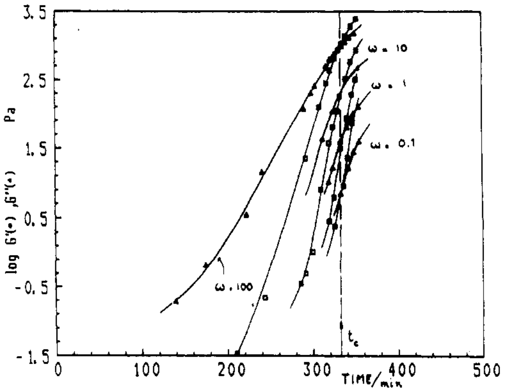

Figure 1. Plots of the storage and loss moduli, G' and G'', as a function of the reaction time t (in minutes). Each curve refers to a given frequency ω of the oscillatory shear applied (0.1 ~ 100 rad/s). System: PEO 1500/Desmodur RF; temperature 60 °C; solvent dioxane; concentration 33%; stoichiometric ratio r = [NCO]/[OH] = 1.

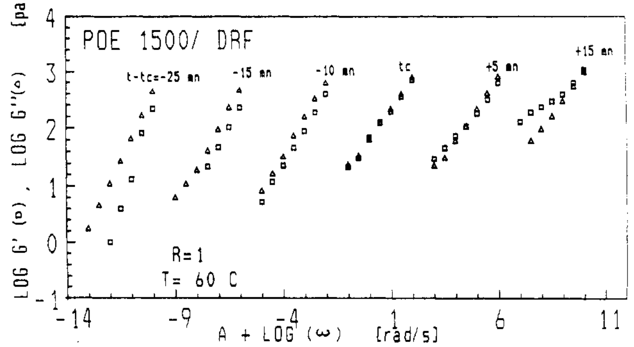

Figure 2. Dependence of the storage and loss moduli G' and G'' upon the frequency of the oscillatory shear applied at various times during the cross-linking reaction. t_c stands for the time at which gelation occurs. The numbers indicate the number of minutes before or after gelation. System: same as in Figure 1.

Table I
Determination of the Number-Average Molecular Weight of the PEO Samples

sample	M_n[a]	M_n[b]
PEO 1000 S	1010	950
PEO 1500 S	1450	1500

[a] By end-group analysis. [b] By GPC using PEO calibration.

Results and Discussion

(a) Stoichiometric Conditions. The dynamic moduli G' and G'' are plotted on Figure 1 as a function of reaction time, each curve corresponding to a given frequency (from 0.1 to 100 rad/s). The example shown refers to the cross-linking reaction of PEO 1500 by means of Desmodur RF. It can be seen that the crossover between G' and G'' takes place at the same critical reaction time t_c, independently of the frequency applied. In the initial part of the cross-linking reaction G'' is greater than G', pointing at the liquid nature of the medium. Beyond t_c, G' outweighs G'' and reaches a constant value at zero frequency, indicating that the material has become a viscoelastic solid.

The representation of log G' and log G'' versus log ω at different stages of the reaction is even more striking (Figure 2). At the gel point (t_c) the moduli not only are equal but they are also proportional to $\omega^{1/2}$ over the entire range of frequencies. The preexponential factor C has been determined to be equal to 63. According to Winter's definition, t_c is the time at which gelation occurs.

In addition to the rheological characterization, the degree of conversion is measured as a function of time

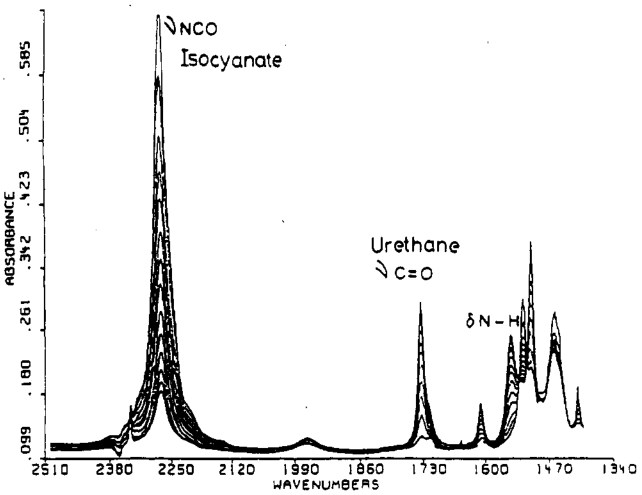

Figure 3. Infrared absorption diagrams recorded at various reaction times during cross-linking. System: PEO 1000/Desmodur RF in dioxane at a concentration of 33%; temperature 53 °C; $r = 1$. The isocyanate absorption decreases as the carbonyl band and the NH absorption increase.

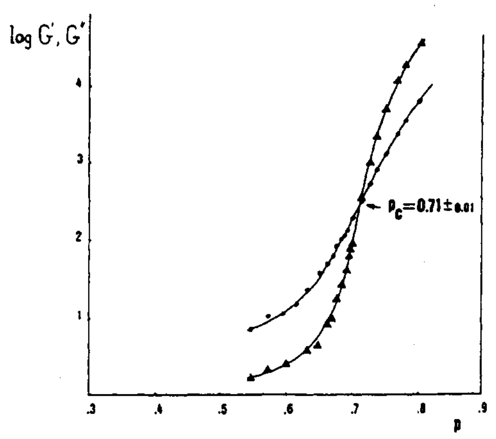

Figure 4. Variation of the storage and loss moduli at an oscillatory shear frequency $\omega = 63.1$ rad/s as a function of the conversion attained. p_c indicates the conversion at which gelation occurs. System: PEO 1000/Desmodur RF; concentration 33% in dioxane; temperature 53 °C; $r = 1$.

from the [NCO]-peak decay shown by the FTIR chart (Figure 3). The plots of G' and of G'' as a function of conversion can thus be drawn (Figure 4). p_c, the extent of reaction at the alleged gel point, is readily obtained from the crossover of G' and G'' and was found to be equal to 0.71.

The expression below arises from the branching theory and was used to calculate the critical conversion p_c at which gelation occurs:

$$rp_c^2 = 1/(f-1)(g-1)$$

It predicts for a stoichiometric system ($r = 1$) involving a difunctional precursor ($g = 2$) and a trifunctional cross-linker ($f = 3$) a conversion of 0.707 at the gel point. The excellent agreement between experiment and theory brings a staunch support to Winter's claims.

It would be unwise to draw a conclusion from experiments carried out on one single system. That is why another cross-linker (Desmodur N 75), different in many respects from Desmodur RF, was used in another set of experiments. As indicated in the Experimental Section, Desmodur N 75 is a mixture of various species, the weight-average functionality of which amounts to $f_w = 10.1$. The other parameters involved in the reaction (precursor PEO, stoichiometry, amount of solvent, temperature) were kept unchanged, as well as the procedure used to monitor the reaction. The rheological behavior of the medium throughout the reaction is identical with that described above (Figure 5). It is observed that at a given reaction stage the moduli become congruent, regardless of the frequency applied, and proportional to $\omega^{1/2}$. The extent of reaction at the crossing point of the two moduli is found to be equal to 0.32 (Figure 6). The value predicted by the expression given above, in which the weight-average functionality of the cross-linker should be used so as to take into account the distribution of functionalities, is found to be $p_c = 0.33$.

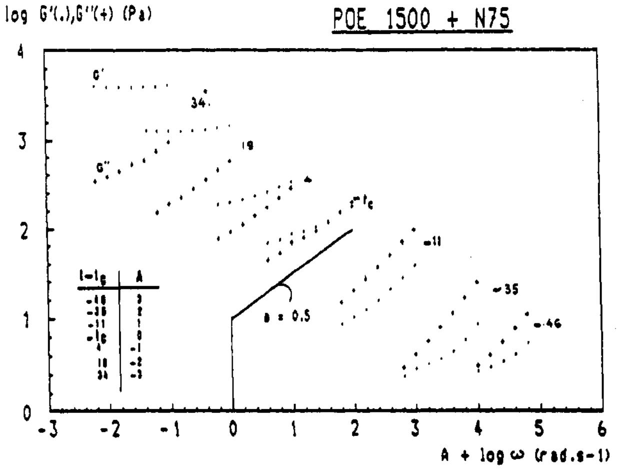

Figure 5. Variation of the storage and loss moduli as a function of the frequency ω of the oscillatory shear applied. System: PEO 1500/Desmodur N75; concentration 33% in dioxane; temperature 53 °C; $r = 1$.

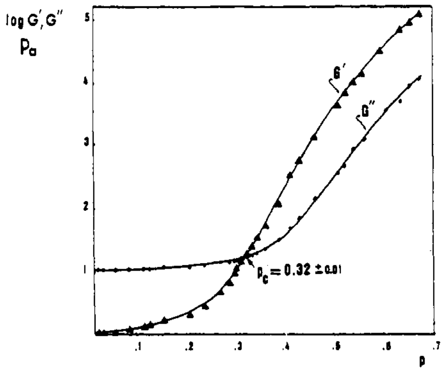

Figure 6. Variation of the storage and loss moduli at $\omega = 63.1$ rad/s as a function of the conversion p attained. System: PEO 1000/Desmodur N75; concentration 33% in dioxane; temperature 53 °C; $r = 1$.

The excellent agreement between the theoretical and experimental values of p_c, despite the nature of the cross-linker used, confirms Winter's statements on the gel point and demonstrates the relevance of the method. The problem of the accurate identification of the gel point, under stoichiometric conditions, can thus be considered settled. The behavior of the reaction medium at this precise stage of the cross-linking process remains to be understood. In an attempt to answer this question, it was considered necessary to achieve a thorough characterization of the reaction medium shortly before the gel point, which implies that the reaction be stopped.

This was done approximately 15 min before expected gelation by addition of a small quantity of n-butylamine. Frequency sweeps were carried out on this viscous solution at selected temperatures (from 30 to 70 °C) in order to broaden the frequency spectrum, applying the WLF

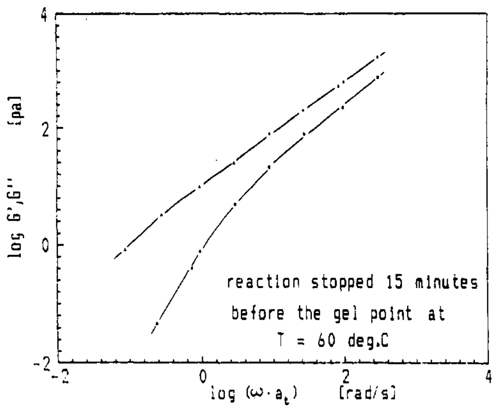

Figure 7. Master curves of the loss and storage moduli plotted on a logarithmic scale versus $a_T\omega$, for the system PEO 1500/Desmodur RF at a concentration of 33% in dioxane, the reaction having been stopped 15 min before the gel point was attained.

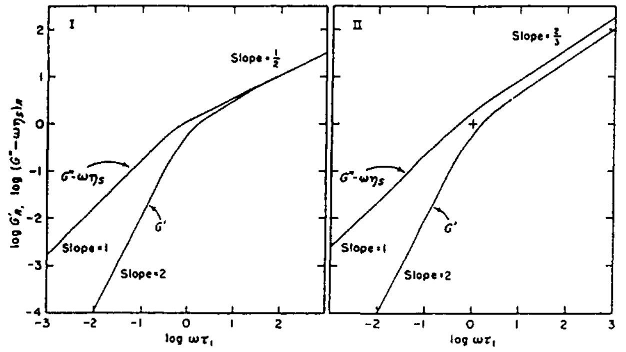

Figure 8. Logarithmic representation of the moduli G' and G'' (the latter corrected to take account of the viscosity of the solvent) of a concentrated solution of a high molecular weight polymer versus the frequency of the oscillatory shear ω. This figure is taken from: Ferry, J. D. *Viscoelastic Properties of Polymers*, 2nd ed.; Wiley & Sons: New York, 1970; p 213.

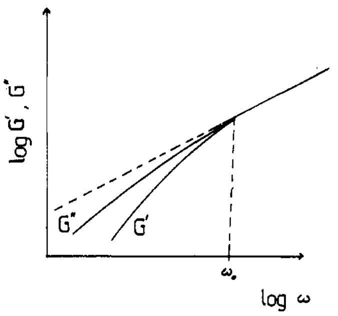

Figure 9. Schematic representation of the behavior of the reaction medium prior to gelation, showing the crossover frequency ω_0 at which G' and G'' are matching each other. This frequency ω_0 decreases as the reaction proceeds and eventually reaches 0 at the gel point.

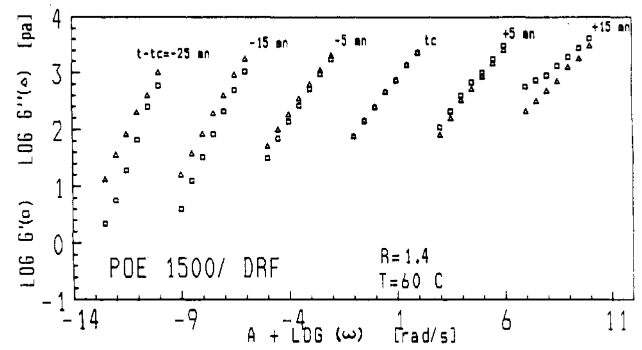

Figure 10. Variation of G' and G'' as a function of the frequency of the oscillatory shear applied at various reaction times before and after the gel point. System investigated: PEO 1500/Desmodur RF at 33% concentration in dioxane; temperature 60 °C; stoichiometric ratio r = [NCO]/[OH] = 1.4.

method. Temperatures lower than 30 °C and higher than 70 °C were avoided for two reasons: the high tendency of poly(ethylene oxide) to crystallize, and the instability of urethane linkages at high temperature. The data were processed to a WLF master curve by standard methods. The plots of log G' and log G'' versus log $a_T\omega$ are shown in Figure 7. Two regions can be distinguished: (i) at low frequencies, the classical liquid-type response is obtained ($G'(\omega) \simeq \omega^2$ and $G''(\omega) \simeq \omega$); (ii) at high frequencies, the moduli converge and tend toward the same frequency dependence.

Unfortunately, the difficulty of rheological measurements at high frequencies prevents accurate determination of the exponent n of the power laws, i.e., of the slopes of the plots of log G' and log G'' versus log ω. Nevertheless, there are some analogies between the behavior described here and that predicted by both the Rouse model and the Zimm model (for solutions of linear polymers):[1] Two regions, characterized by low-frequency slopes of 2 and 1, respectively, and a common high-frequency slope of $^1/_2$ are observed before gelation (Figure 8).

In cross-linking experiments, the "crossover frequency", defining the boundary between the two regions, tends toward zero as the reaction proceeds toward gelation (Figure 9). At the gel point, the pattern specific to the high-frequency region in the Rouse model extends throughout the frequency range: At low frequencies the medium behaves neither like a liquid ($G' \simeq \omega^2$, $G'' \simeq \omega$) nor like a typical elastomeric solid ($G' = G_\infty$ = constant and $G'' \simeq \omega$). From the analogy between a solution of linear macromolecules and a cross-linking medium, the transition from liquid to solid can be depicted as a stage at which the response of an infinite molecule over the whole frequency spectrum is limited to short-range motions (short with respect to the dimensions of the molecule). Just beyond the gel point, G' levels off as the frequency decreases, and G'' is found to be proportional to ω. At later stages of the reaction, the equilibrium modulus increases and G' and G'' depart from each other.

(b) Nonstoichiometric Conditions. It is of great importance to know whether the observations quoted above are general enough to apply to any type of cross-linking reaction, in particular to those carried out under nonstoichiometric conditions.

The same system (PEO 1500, Desmodur RF) and the same experimental conditions (temperature, concentration) have been chosen for this investigation. The parameter to be varied is the amount of cross-linking agent. Two stoichiometric ratios have been chosen, the first involving an excess of isocyanate (r = $[NCO]_0/[OH]_0$ = 1.4) and the second an excess of OH end groups (r = 0.7). Oscillatory shear experiments have been performed on these two reaction media, and the variation of G' and of G'' versus ω has been monitored throughout the reaction.

In the case of excess isocyanate, the plots of log G' and log G'' versus ω follow the same general pattern as observed under stoichiometric conditions. The moduli move closer as the reaction proceeds, and they are congruent and proportional to $\omega^{1/2}$ at the gel point. Beyond the gel point they depart again from each other (Figure 10). The gelation time t_c is obviously shorter than that measured for r = 1. Again, the crossover between G' and G'' is independent of the frequency applied.

When the stoichiometric ratio is in favor of OH functions (r = 0.7), the behavior exhibited by the reaction medium is quite different (Figure 11). The moduli still cross each

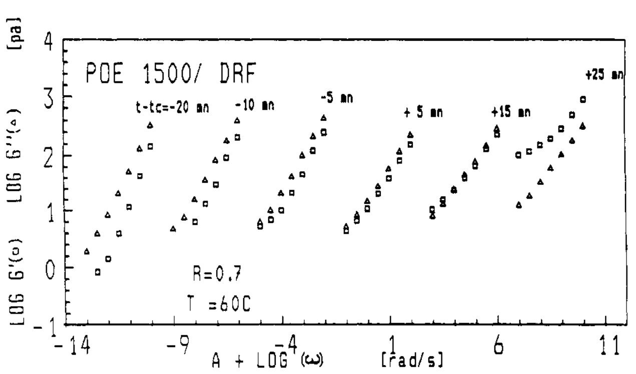

Figure 11. Same as Figure 10. The system investigated is the same except for the stoichiometric ratio: $r = 0.7$.

other as reaction proceeds, but the frequency independence of this crossing is no longer observed and cannot be used to characterize the gel point.

In a more accurate data analysis, it was established that there is a reaction stage at which both moduli (G' and G'') obey power laws with the same exponent n over the entire frequency spectrum. This common value of n is close to $^2/_3$, and the ratio of the moduli, G''/G', is of the order of $\sqrt{3}$. It turns out that this occurs precisely at the gel point, as has been established independently from a solubility test carried out after deactivation with n-butylamine. Similar nonstoichiometric systems (whether with $r > 1$ or with $r < 1$) have been investigated by Winter et al.[2e] Our results confirm their findings. It is shown in the Appendix that these observations ($G''/G' = \sqrt{3}$, and G' and G'' proportional to $\omega^{2/3}$) do not violate the Kramers–Kronig relations.[11]

The question is now to understand why the pattern described above takes place and, more specifically, why it only occurs when r is lower than unity. The fact that, at the gel point, the ratio of G'' to G' is equal to $\sqrt{3}$ and that both moduli are proportional to $\omega^{2/3}$ could be related to the predictions of the Zimm model[1] concerning the viscoelastic properties of linear polymer solutions. This model is in quantitative agreement with numerous experimental data on dilute polymer solutions, as it takes into account the hydrodynamic interactions between segments of the same molecule.[7] According to this model (Figure 8), G' and G'' should be proportional to $\omega^{2/3}$ and should differ by a factor $\sqrt{3}$ at high frequencies. In the domain of low frequencies the behavior expected from both the Zimm and the Rouse models are similar: a slope of 2 for log G' vs log ω and a slope of 1 for log G'' vs log ω. In a reaction medium that undergoes cross-linking it is now established that the boundary between these two regions is slowly shifted toward lower frequencies as the reaction proceeds (Figure 9). In the case of stoichiometric conditions the behavior of G' and G'' and the predictions arising from the Rouse model at high frequencies are in good agreement. Similarly, the values of the dynamic moduli found for $r < 1$ are in good agreement with the Zimm theory (at high frequencies). The change from Rouse-like to Zimm-like behavior could suggest that the tendency for the coils to overlap, which prevails under stoichiometric conditions, gets lower as the ratio r decreases. The hydrodynamic interactions between different portions of the same macromolecule then tend to overweigh the shielding that existed before.

This behavior can be accounted for if one remembers that a reaction medium with cross-linker deficiency will contain at the gel point a larger proportion of discrete macromolecules (including precursor chains) than under stoichiometric conditions. This might account for the higher value of the exponent n. In other words, the behavior at the gel point strongly depends on the surroundings of the infinite object that is just being formed.

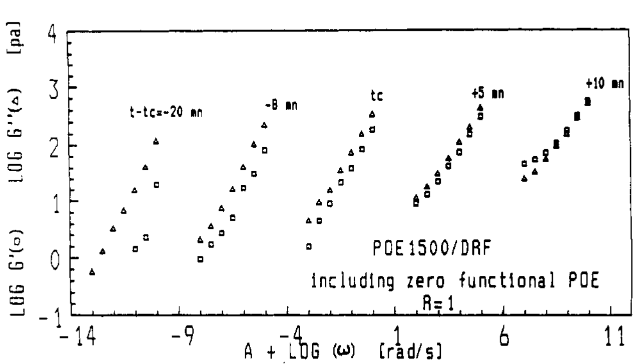

Figure 12. Same as Figure 10. System investiated: PEO 1500/ Desmodur RF under same conditions as in Figure 10, with a stoichiometric ratio $r = 1$ but in the presence of 14% of zero-functional PEO (which is unable to participate in the reaction). See text.

The transition from Zimm-like behavior to Rouse-like behavior occurs in polymer solutions as the concentration of the medium increases. The screening of hydrodynamic interactions is then balanced by the interchain interactions. The concentration dependence of this hydrodynamic screening is well established: predominance of Rouse-behavior at high concentrations, the Zimm-model providing a better description of polymer dynamics at low concentration.

Similarly, in cross-linking reactions the crossover from Zimm to Rouse regimes can also be accounted for in terms of the screening effect. As the stoichiometric ratio increases, the number of discrete macromolecules still present at the gel point keeps decreasing. If one speculates that these species play the same role as the solvent does in the case of polymer solutions, the situation is quite comparable: The concentration of the very large macromolecules determines the hydrodynamic screening, which in turn governs the overall behavior of the reaction medium at the gel point.

The following experiment supports this interpretation. The chemical system (PEO 1500, Desmodur RF, solvent, temperature) is kept identical and the reaction is conducted under stoichiometric conditions. In order to evidence the concentration effect, a given amount of zero-functional PEO α,ω-dimethyl ether (not involved in the reaction) is introduced. The reaction is monitored by the rheometer and the plots of log G'' and log G' versus log ω are displayed in Figure 12. The behavior found at the gel point is Zimm-like rather than Rouse-like. The moduli are proportional to $\omega^{2/3}$, and their ratio is close to 1.7.

Regardless of the stoichiometry used, the response of the "infinite" macromolecule—specifically its distribution of relaxation times—will depend upon its environment. Following these findings, a new definition of the gel point can be proposed (see Appendix), which is written as

$$G''/G' = \tan(n\pi/2)$$

n being the common exponent of the power laws at the gel point ($^1/_2 \leq n \leq {}^2/_3$). According to this definition, the Rouse-like and the Zimm-like regimes are the two limits exhibited by the relaxation spectrum (Table II).

The interpretation given above is based upon the analogy that has been found between the predictions of the molecular theories of viscoelasticity in the high-frequency range and the experimental data in the vicinity of the gel point.

Table II
Exponent of the Power Law at the Gel Point for Various Stoichiometric Ratios r of the Isocyanate to Hydroxy Functions

r	exponent n	G', Pa at $\omega = 1$ rad/s	G'', Pa at $\omega = 1$ rad/s
1	0.5	66	66
1.4	0.5	250	250
0.7	0.66	10	17

Recently, another approach of the dynamics of polymer solutions has been proposed, based upon the self-similar connectivity of branched macromolecules and upon a scaling theory of fractal correlations. According to this treatment, a power law is expected between the storage and loss moduli and the frequency of the applied shear.[13,14]

$$G' = G'' \simeq \omega^n \quad \text{with } {}^2/_3 \leqslant n \leqslant 1$$

However, the experimental results available so far for stoichiometric systems are not in agreement with this theoretical exponent: The values of n found are systematically lower and close to $^1/_2$.

Conclusion

Winter's method of gel point determination is assessed by means of an experimental setup including rheometric as well as kinetic measurements. The criteria given by Winter to define the gel point are in good agreement with the results arising from kinetics, treated within the context of the branching theory. The relevance of rheological dynamic characterization of the gel point is thus confirmed. Under nonstoichiometric conditions, especially when the amount of cross-linker is deficient with respect to stoichiometry ($r < 1$), the situation becomes more complicated. The relaxation time of a macromolecule approaching infinite dimensions depends upon its environment. Two types of behaviors, Zimm-like and Rouse-like, have been identified, exhibiting different distributions of relaxation times. The transition from Zimm-like to Rouse-like regimes is interpreted in terms of screening of the hydrodynamic interactions as the stoichiometric ratio r increases. A general rheological definition of the gel point is inferred from these observations.

It would be of interest to further investigate the gelation process for stiochiometries ranging between 0.7 and 1 and to check whether a continuous change from Zimm-like to Rouse-like behavior takes place, as suggested in Winter's recent paper.[2e] This would be indicative of an increasing contribution of hydrodynamic interactions to the rheological behavior of nascent networks as the stoichiometric ratio r decreases below unity.

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Appendix

If the frequency dependence of one dynamic modulus (either G' or G'') is known over the entire frequency range, the other modulus (G'' or G') can be calculated as a function of ω according to the Kronig–Kramers relations.[11] For a material with zero equilibrium modulus, these relations may be written

$$G''(\omega) = \frac{2\omega}{\pi}\int_0^\infty \frac{G'(x) - G'(\omega)}{x^2 - \omega^2}\,\mathrm{d}x \qquad \text{(A)}$$

$$G'(\omega) = \frac{2\omega^2}{\pi}\int_0^\infty \frac{G'(x)/x - G'(\omega)/\omega}{\omega^2 - x^2}\,\mathrm{d}x \qquad \text{(B)}$$

If the storage modulus follows a power law function of ω

$$G'(\omega) = k\omega^n \qquad (0 < n < 1) \qquad \text{(C)}$$

then eq A clearly shows that the loss modulus obeys the same frequency dependence. Introducing $u = x/\omega$

$$G''(\omega) = \frac{2k\omega^n}{\pi}\int_0^\infty \frac{u^n - 1}{u^2 - 1}\,\mathrm{d}u \qquad \text{(D)}$$

The integral in eq D being equal to $(\pi/2)\tan(n\pi/2)$ when $n < 1$,[2d,12] the (constant) ratio of $G''(\omega)/G'(\omega)$ is obtained:

$$G''(\omega)/G'(\omega) = \tan(n\pi/2) \qquad \text{(E)}$$

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