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Mechanical Measurements in the Reaction Bath during the Polycondensation Reaction, near the Gelation Threshold

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ABSTRACT: The evolution of the mechanical properties, as a function of time t, during the gelation process was studied by means of the sphere magnetorheometer near the gel point t_g. For the set of samples studied, the weight fraction of solvent and the mean molecular weight between two successive junctions points of the branched polymer were modified. As a function of the reduced time $1 - t/t_g$, the viscosity η and the shear elastic modulus G can be described by simple power laws only for samples that have the smallest mean molecular weight between two successive junction points. We find $\eta \sim (1 - t/t_g)^{-0.8\pm0.1}$ and $G \sim (t/t_g - 1)^{3.2\pm0.5}$. The exponent values are independent of the weight fraction of the solvent. Those results are in agreement with percolation theory and recent theoretical predictions.

Introduction

The evolution of the reaction during the gelation process is characterized by the conversion factor,[1] p; this parameter is equal to 0 and 1 at the beginning and at the end of the reaction, respectively. The mechanical properties are typical of the sol–gel transition; at the gel point, p_c, the reaction bath goes from a liquid medium to an elastic medium.[2] For $p < p_c$, there is a sol that is an assembly of polydisperse finite clusters. For $p > p_c$, there is a sol embedded in a gel that is an infinite cluster (i.e., it has the size of the vessel). Our aim is to study the mechanical properties near p_c because, according to percolation or classical theories, they must be universal whatever the structure of the gel in its final state ($p = 1$).

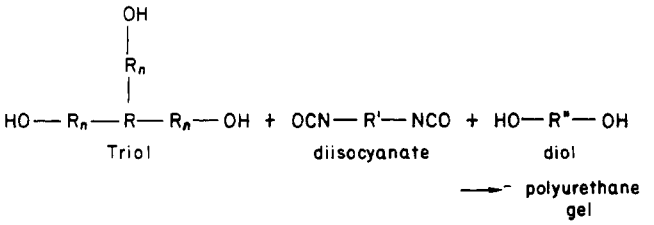
Previous[3,4] mechanical measurements were performed on radical copolymerization with solvent (polystyrene/divinylbenzene/benzene) and polycondensation without solvent (diisocyanate/triol). In both systems it was found that the viscosity η diverges at the gel point as $\eta \sim (p_c - p)^{-S}$ with $S = 0.78 \pm 0.05$. The increase of the elastic modulus was different in the two systems: we obtained $G \sim (p - p_c)^T$ with $T = 2.1 \pm 0.3$ for copolymerization and $T = 3.2 \pm 0.6$ for polycondensation. These measurements were done with a new apparatus, the sphere magnetorheometer, and the strong difference observed between the T exponent values could be assigned to experimental difficulties.[3] In order to validate the preliminary results we have performed experiments on several polycondensation samples, in which the hydroxyl groups and isocyanate groups have equal reactivities[5] and which present the following advantages: the gel time is a controllable quantity and can be chosen to be very long (132–500 h); well-defined "quenched samples" can be prepared.

In this way, it is possible to perform measurements at low shear rates and low shear deformations very near the gel point and to determine quantitatively the perturbation induced by mechanical measurements.

We have also changed the proportion of solvent and the mean molecular weight between two successive junction points in order to observe their influence on the mechanical properties. We already know that those parameters have a strong influence on the absolute value of p_c.[6,7]

Experimental Conditions

Samples and Materials. The polycondensation reaction studied is



The condensation occurs between the OH groups of the polyols and the NCO groups of the diisocyanate. The polycondensation was studied on four types of samples (I–IV) that differ by the weight fraction of diol, the weight fraction of solvent (toluene), and the molecular weight of the triol. The composition and the characteristics of the four types of polycondensation are given

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Table I
Composition and Characteristics of the Different Types of Polycondensations[a]

system	ρ	w	M_n, triol	M_n, diol	M_n, diisocyanate	r
I	1	0	715 or 695		168	1
II	1	40% ≤ w ≤ 60%	715 or 695		168	1
III	1	0	2970		168	1
IV	$^2/_3$	16% ≤ w ≤ 30%	2970	3900	168	1

[a] r is the stoichiometric ratio r = [NCO]/[OH]; w is the weight fraction of toluene; ρ is equal to [OH triol]/([OH triol] + [OH diol]).

Table II
Characteristics of the Polyols Used[a]

precursors polyols	LHT 240	UGIPOL 3170	LG56	PPG 4000
M_n	715	695	2970	3900
M_w/M_n	1.03	1.03	1.06	1.04
hydroxyl extent	4.20	4.32	1.01	0.51

[a] Amount of hydroxyl extent is expressed in mmol g^{-1}.

in Table I. In all the systems studied OH and NCO groups were present in equivalent quantities; the ratio of NCO to OH groups initially present was $r = 1.000 \pm 0.0005$. The complete reaction of isocyanate groups was checked by infrared spectroscopy. The homogeneity of the samples was checked by observing the intensity of the light scattered by the gel at different locations. The toluene used was freshly distilled. The purity of hexamethylene diisocyanate (HMDI) was controlled by size exclusion chromatography (SEC) and nuclear magnetic resonance (NMR) and was estimated to be 99%.

Four kinds of polyoxypropylene polyols were used: LG56, LHT 240, UGIPOl 3170, and PPG 4000. These polyols are propylene oxide adducts of glycerol (LG56), 1,2,6-hexanetriol (LHT 240), trimethylolpropane (UGIPOL 3170), and ethylene glycol (PPG 4000). In this way the chains of polyol are terminated by secondary hydroxyl groups. The polyols were dried for 2 h at reduced pressure (0.01 mbar), and the residual amount of water was smaller than 200 ppm (Karl Fisher method). The amount of hydroxyl groups was evaluated from acetylation, and the molecular weights of polyol samples were determined from SEC analysis. The characteristics of the polyols are given in Table II.

In the preparation of triol some dehydration reactions may occur that lead to units with a functionality smaller than 3. The narrow molecular weight distribution, $M_w/M_n \leq 1.06$, suggests that this is not the case. Moreover, in order to detect the presence of triol units that are not trifunctional we prepared polyurethane polymers by reaction of triol with an excess of *n*-octadecyl isocyanate. The SEC chromatograms of the resultant polymers exhibit only one peak, which confirms that the effective functionality of triol is 3.[8]

In order to study the mechanical properties during the polycondensation all the components plus a magnetic sphere were placed together in a tube which was sealed under argon. The kinetic rate of the reaction (or gelation time) was changed by varying the temperature (25–70 °C).

Mechanical Measurements. During the polycondensation reaction the viscosity or the elasticity of the reaction bath was measured with the sphere magnetorheometer. As a complete description has been given elsewhere,[9] we describe here only the principle of the apparatus (see Figure 1).

When the tube (T_u), which contains the reaction bath, is at rest in order to maintain the sphere (diameter $d \approx 1$ mm) in levitation, a voltage V_0 is applied to the coil. The magnetic force counterbalances the gravitational and the buoyancy forces. When a displacement of the tube is imposed, $\Delta(t)$, at a velocity $v(t)$, the sphere experiences an additional force $f(t)$. For a pure viscous liquid, $f(t)$ is proportional to the velocity $v(t)$ and to the viscosity η. For a pure elastic solid, $f(t)$ is proportional to the displacement $\Delta(t)$ and to the shear elastic modulus G.[10] In order to maintain

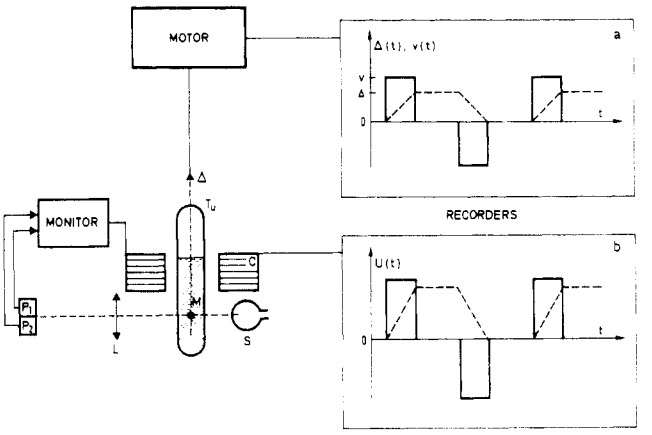

Figure 1. Schematic diagram of the sphere magnetorheometer. The ratio of the diameter of the magnetic sphere (M) to the internal diameter of the tube (T_u) is 0.1. The magnetic sphere experiences a force due to an external coil C. The sphere is imaged on two photodiodes (P_1, P_2) by means of an optical system ((S) light source and (L) lens). The differential photocurrent of the photodiodes is fed to the monitor which adjusts the voltage ($V(t) = V_0 + U(t)$) applied to the coil in such a way that the sphere remains at the same place. For viscoelastic measurements the tube T_u, containing the sample, is displaced by means of a stepping motor. In part a is represented a typical displacement as a function of time: the solid and broken lines correspond respectively to the displacement $\Delta(t)$ and to the velocity $v(t)$. In part b is represented as a function of time t the voltage U: solid and broken lines correspond respectively to a pure viscous and a pure elastic system.

the sphere at the same location an increment of voltage, $U(t) = V(t) - V_0$, proportional to the force $f(t)$ has to be applied to the coil: $U(t) = A\eta v(t)$ for a pure viscous liquid and $U(t) = AG\Delta(t)$ for a pure elastic solid. The factor A can be determined by a calibration on a standard oil.

During the gelation process the reaction bath has neither the properties of a pure viscous liquid nor the properties of a pure elastic solid. It is always a viscoelastic system, and we have[9]

$$U(t) = A \int_0^t G(t - t')v(t')\,dt'$$

$G(t)$ is the shear relaxation modulus of the reaction bath linked to the dynamical viscosity by[11]

$$\eta(t) = \int_0^t G(t')\,dt'$$

Typical viscoelastic liquid behavior observed before the gel point, i.e., in the sol, is given in Figure 2. At time t_0, within a period of time $t_1 - t_0$, a displacement of the tube with a constant velocity v is imposed. The voltage $U(t)$, in these conditions, is proportional to the dynamical viscosity: $U(t) = Av\eta(t - t_0)$. At short times (see Figure 2), $U(t)$ is an increasing function of time that is characterized by the mean longest viscoelastic relaxation time τ of the reaction bath. At long times $t - t_0 > 3\tau$, the voltage becomes a constant, U_S, that is proportional to the static viscosity η of the reaction bath: $U_S = Av\eta$. These statements are correct if the measurements are performed at low reduced shear rates: $v\tau/d$.

In order to determine the influence of the shear rate on the viscosity we performed measurements on a "quenched sample". We prepared a sample of type I (see Table I) but with a stoichiometric ratio $r = 0.5624$. After complete reaction of the isocyanate groups, the sample is a liquid ($r_g - r \approx 4 \times 10^{-3}$, where r_g is the stoichiometric ratio at which the gel phase appears). On this sample we found that the viscosity deduced at $v\tau/d \lesssim 3.5 \times 10^{-2}$ was independent of the velocity v within ±1% and thus independent of the shear rate (see Figure 3). During the study of gelation process all the measurements were made with $v\tau/d \lesssim 1.5 \times 10^{-2}$, so the measured viscosity represents the static viscosity of the sol.

Typical viscoelastic solid behavior observed after the gel point is reported in Figure 4a. During the time $t_1 - t_0$ the tube is

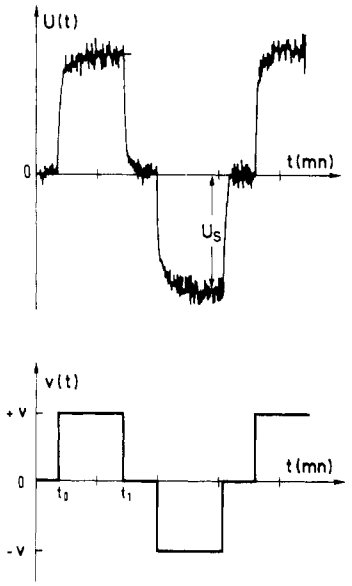

Figure 2. Typical behavior of the viscoelastic force ($\sim U(t)$) below the gel point ($|\epsilon| = 1 - t/t_g \approx 1.5 \times 10^{-2}$); one division on t axis represents 1 min. In this example the relaxation time τ is of the order of 6 s and the reduced shear rate $v\tau/d$ is about 10^{-2}. A steady viscoelastic force is reached after 36 s.

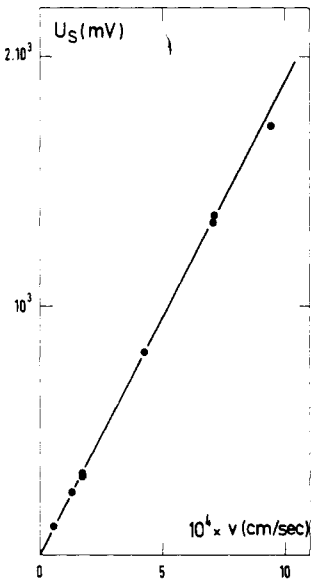

Figure 3. Check of the proportionality between the increment of voltage U_S (see Figure 2) and the velocity for the case of a "quenched sample" $r = 0.5624$ ($\Delta p \approx 4 \times 10^{-3}$). The reduced shear rate $v\tau/d$ is equal to 0.05 for $v = 10^{-3}$ cm/s.

displaced at a constant speed v; at time t_1 the motion is stopped, and thus the total displacement of the tube is $\Delta = v(t_1 - t_0)$. For $t > t_1$, the voltage $U(t)$ is a decreasing function of time with a characteristic time τ. For $t - t_1 > 3\tau$, $U(t)$ is a constant U_S proportional to the static shear modulus: $U_S = AG\Delta$. This statement is correct only for low shear deformations: Δ/d. In order to determine the influence of the shear deformation on the shear elastic modulus, measurements were performed on another quenched sample of type I (see Table I) with a stoichiometric ratio of 0.57 larger than r_g ($r - r_g \approx 10^{-2}$). One can see in Figure 4b that for $t_0 + 3\tau < t < t_0 + 10\tau$ the voltage $U(t)$ increases linearly with time. Thus $(1/v)(dU/dt)$ is a constant AG equal to 1.48×10^4 mV/cm. For $t > t_1 + 3\tau$, the voltage reaches a constant value U_S. A plot of U_S vs. Δ, see Figure 5, shows that U_S is proportional to Δ when the shear deformation $\Delta/d \lesssim 0.1$; this leads to $AG = 1.44 \times 10^4$ mV/cm. On this sample we find that the shear elastic modulus, determined from the voltage U_S at 3τ after stopping the displacement, is to within 5% equal to the value obtained from the slope of the voltage at 10τ after the beginning of the

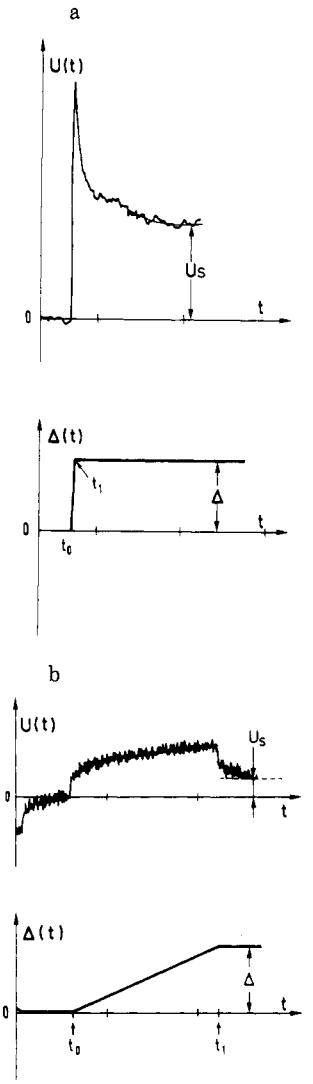

Figure 4. (a) Example of the behavior of the voltage $U(t)$ above the gel point ($\epsilon = t/t_g - 1 \approx 1.6 \times 10^{-2}$). One division on t axis represents 1 min. The period $t_0 - t_1$ where the sample was displaced by Δ was very short in order to reduce the time needed for each measurement. (b) Typical viscoelastic solid behavior obtained with a "quenched sample" above the gel point $r = 0.57$ ($\Delta p \approx 10^{-2}$). One division on t axis represents 6 min. The relaxation time τ is estimated to be of the order of 50 s.

displacement. During the study of the gelation process, as a function of time, the measurements were performed at shear deformations smaller than 0.1 and the shear elastic modulus was obtained from the steady voltage U_S at 3τ after stopping the displacement. Thus we measured a static shear elastic modulus.

One must note that the four typical behaviors of the viscosity and the elastic modulus presented in Figure 6 are the result of about 20 experiments, which allowed us to control the influence of the different experimental parameters. In particular, it was observed that the number of measurements per hour does not influence the viscosity and elastic behaviors. This observation shows that our mechanical measurements do not perturb the system.

Determination of the Gel Time. The gel time corresponds to the time t_g when the static viscosity goes to infinity and the static elastic modulus begins to be different from zero. Direct observation of the behavior of the voltage $U(t)$ allows us to determine a time interval, $[t_v, t_e]$, where t_g is located. For times smaller than t_v and larger than t_e the voltages are typically those given in Figure 2 and Figure 4a, respectively. In the time domain $[t_v, t_e]$ reliable measurements are not possible because the voltage does not reach a constant value U_S either during the displacement of the tube or after the displacement of the tube. This can be due to a rapid increase of η or G during the time of the measurements or to a relaxation time τ which becomes of the order

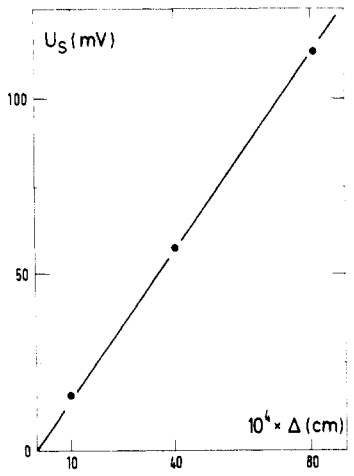

Figure 5. Check of the proportionality between the voltage U_S, measured at 3τ after stopping the displacement, and the total displacement Δ of the sample in the case of the "quenched sample" corresponding to Figure 4b. The shear deformation Δ/d is of the order of 0.1 for $\Delta = 10^{-2}$ cm.

of the time of the measurements. In contrast, if $G \lesssim 0.25$ dyn/cm^2, the fluctuations of U_S are larger than the mean value and G cannot be measured.

If the measurements done in the vicinity of t_v and t_e are extrapolated, we determine the time t_g where the viscosity is infinite and the shear elastic modulus is equal to zero. The extrapolation is done with a nonlinear fitting program[12] which assumes that the viscosity and the shear elastic modulus depend on powers of $t - t_g$ with the constraint that $t_v \leq t_g \leq t_e$. Typical examples for the accuracy of t_g are given under Figure 6.

Experimental Results and Discussion

The experiments were performed in a time domain close to the gel point $5 \times 10^{-3} \lesssim |t - t_g|/t_g \lesssim 5 \times 10^{-2}$. Typical experimental data obtained with the four kinds of polycondensation are given in Figure 6 where the variation of the viscosity and the shear elastic modulus are plotted in a log–log representation as a function of the reduced time $\epsilon = (t - t_g)/t_g$.

The increase of the viscosity and of the shear elastic modulus can be reasonably described, in this representation, by a linear behavior only for polycondensation systems I and II. From least-square fits we obtain the following slopes for the viscosity (S) and the elasticity (T): $S = 0.82$, $T = 3.6$ (case I) and $S = 0.93$, $T = 3.55$ (case II).

For polycondensation of type III the increase of the viscosity and of the shear elastic modulus are less rapid than those observed in the former cases: $d\eta/\eta < 0.7|d\epsilon/\epsilon|$ and $dG/G \leq 2d\epsilon/\epsilon$. One must note that log η and log G are linear functions of ϵ.

For polycondensation of type IV the increase of the viscosity is much more rapid far from the gel point ($d\eta/\eta \approx |d\epsilon/\epsilon|$ for $|\epsilon| > 10^{-2}$) than near the gel point ($d\eta/\eta \approx 0.3|d\epsilon/\epsilon|$ for $|\epsilon| \approx 5 \times 10^{-3}$). In the sample given in Figure 6IV, it appears that in the time domain $\epsilon > 10^{-2}$ the shear elastic modulus has a linear behavior ($dG/G \approx 3.8\, d\epsilon/\epsilon$). But one must not accord any importance to the 3.8 slope value because on the same kind of polycondensation sample[13] $(dG/G)/(d\epsilon/\epsilon)$ is an increasing function of ϵ.

The behaviors of the viscosity and of the shear elastic modulus as a function of the reduced time ϵ are only meaningful if the gel time is determined accurately. If the location of the gel point within the error bar (see figure caption 6) is shifted, we find that for cases I and II the viscosity and the shear elastic modulus can always be described by a linear behavior in log–log representation and for cases III and IV viscosity and elasticity can never be linearized simultaneously.

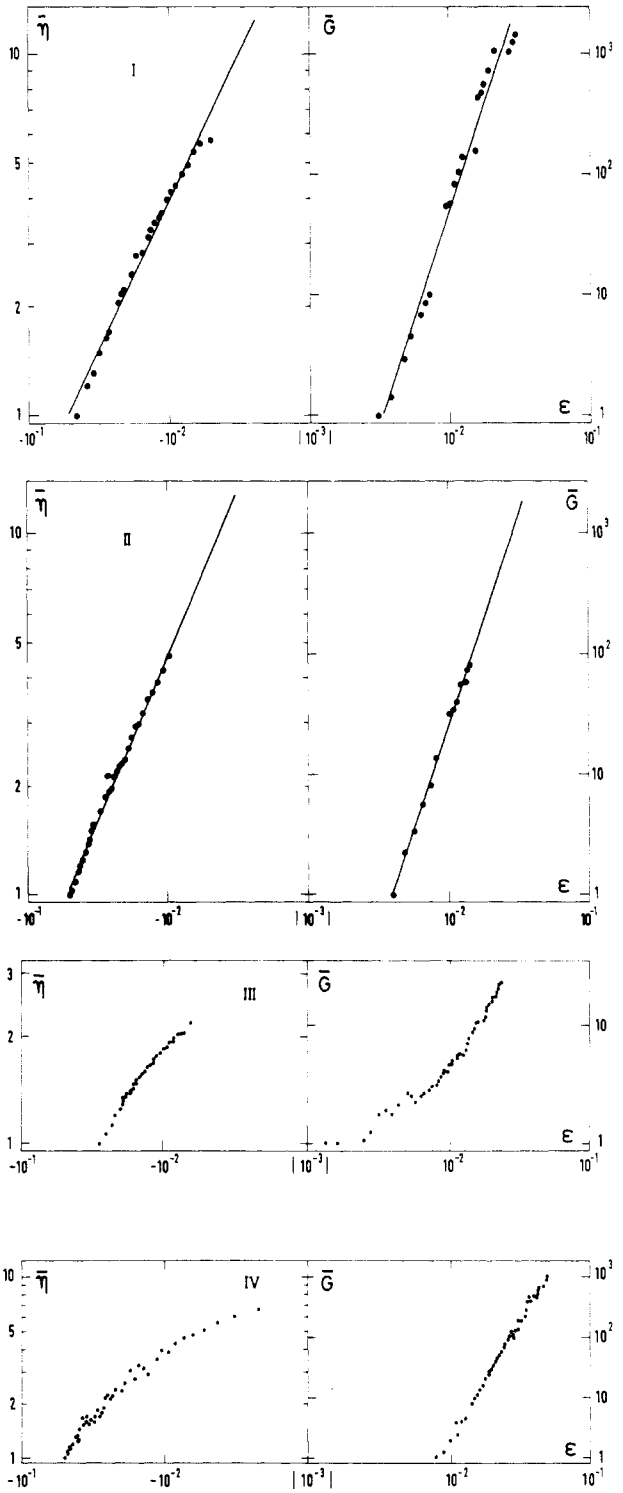

Figure 6. Example of the increase of the viscosity and of the elastic modulus near the gel point. On the abscissa is plotted $\epsilon/|\epsilon|$ log $|\epsilon|$ and on the ordinate log $\bar{\eta}$ or log $\bar{G}$. $\bar{\eta}$ and $\bar{G}$ are the viscosity or the shear elastic modulus normalized to the viscosity or the elastic modulus of the first experimental point. (I) Polycondensation of type I at 60 °C; the gel time is t_g (min) = 2100 ± 2. (II) Polycondensation of type II (40% toluene) at 25 °C; the gel time is t_g (min) = 9422 ± 28. (III) Polycondensation of type III at 70 °C; the gel time is t_g (min) = 7195 ± 36. (IV) Polycondensation of type IV (30% toluene) at 70 °C; the gel time is t_g (min) = 29808 ± 90.

We must note that in the example of Figure 6, part III, the accuracy of the t_g value is very poor. This is due to the fact that the shear elastic modulus and the viscosity do not increase near the gel point.[14]

In order to compare the experimental results with theory[15-19] the fraction p of OH groups that have reacted must be determined. Assuming, as a first approximation, that the rate of formation of urethane is first order with respect to the concentration of hydroxyl and isocyanate groups,[20] we have

$$\Delta p = p - p_c = p_c \frac{1 - p_c}{1 + p_c\epsilon}\epsilon$$

where p_c is the fraction of OH groups that have reacted at time t_g. Since the experiments were performed close to the gel point ($|\epsilon| \leq 5 \times 10^{-2}$), the two quantities Δp and ϵ can be considered as being proportional:[21]

$$\Delta p = p_c(1 - p_c)\epsilon$$

The relative error due to the linearization is always smaller than ϵ. Thus the use of ϵ instead of Δp, in Figure 6, does not introduce any distortion.

At the present time, in the case of polycondensation of types III and IV, we have no explanation for the behavior of η and G near the gel point. Further experiments are needed in order to understand the gelation process of these systems.

Now let us discuss the results obtained in the systems I and II. It is well-known[22] that the presence of a solvent favors the formation of cyclic structures of small size. From the experimental results where it has been found that the S and T values are independent of the weight fraction of solvent, we can deduce that the presence of small cyclic structures does not influence the mechanical properties (η and G) near the gel point. This conclusion is similar to that obtained by numerical simulation[23,24] for the degree of polymerization. Since Δp is proportional to ϵ, the slopes S and T can be identified with the exponents S and T defined in the introduction. Five experiments performed on polycondensation systems of types I and II show that S lies between 0.7 and 0.9 and T lies between 2.7 and 3.7.

The viscosity exponent S is in agreement with previous values obtained on radical copolymerization and polycondensation.[3,4] It is also identical (within experimental reproducibility) with the exponent, s, of the superconductivity of a percolating random network of superconducting and normal bonds.[17] From numerical calculations one obtains $s = 0.75 \pm 0.04$[25] and from experiments $s = 0.73 \pm 0.07$.[26] The present experimental result would mean that gelation is described by percolation[15] and supports the de Gennes analogy between the viscosity of the gelation bath and percolating superconductivity.

The exponent value T of the shear elastic modulus is in agreement with our previous[3] experiments and with the results of Gordon on triacetic acid decamethylene glycol/benzene polycondensation.[27] The T value is close to but larger than the value predicted by graph theory[3,18] and differs by a factor of 1.6 with the exponent value t predicted if an analogy is made between the elastic modulus and the electrical condutivity[16] of a random network of insulator and conductor bonds ($t = 1.94$).[28]

The striking fact is that the exponent value of the shear elastic modulus agrees with graph theory, whereas the exponent value of the viscosity agrees with percolation theory in the same range of ϵ. One way to explain this result is to invoke a critical domain (where percolation exponent values hold) broader below p_c ($\Delta p_-{}^*$) than above p_c ($\Delta p_+{}^*$). From Figure 6, parts I and II, we find that if a critical domain exists above p_c, it will occur at $\epsilon_+{}^* < 3 \times 10^{-3}$. In contrast, below p_c we find a percolation exponent value on the whole range of ϵ investigated, thus $\epsilon_-{}^* > 5 \times 10^{-2}$. This means that $\Delta p_+{}^*/\Delta p_-{}^* < 6 \times 10^{-2}$. This result must be compared with numerical simulation of the weight-average degree of polymerization[29] and the conduction of hierarchic networks.[30] Actually, the two simulations lead respectively to $\Delta p_+{}^*/\Delta p_-{}^* = 0.5$ and $\Delta p_+{}^*/\Delta p_-{}^* = 0.2$. The critical domain seems indeed to be broader below p_c than above, but the experimental assymetry would be much bigger (by a factor 10) than that found by calculation.

The preceding discussion implies that the de Gennes analogy between conductivity and elasticity is valid. Recent theoretical work[31,32] shows that T is larger than the conductivity exponent t whatever the space dimensionality D and $2.85 < T < 3.55$ in $D = 3$. This has been verified experimentally[33] (for $D = 2$) on a percolating system made of metal and voids where the conductivity and the elasticity exponents were measured simultaneously. The difference between t and T could explain our experimental results. But one must be cautious in drawing conclusions because those two explanations ($t \neq T$ and $\Delta p_+{}^*/\Delta p_-{}^* < 6 \times 10^{-2}$) are opposed to the experimental fact that for radical copolymerization[34] as well as for gelatin[35] it was found that $t = T$.

Summary and Conclusions

The mechanical measurements performed in the reaction bath during the polycondensation gelation process, as a function of reaction time, are reproducible for a great number of samples.

Even very near the gel point ($|\epsilon| = |t - t_g|/t_g = 3 \times 10^{-3}$) the measurements are static measurements: the viscosity is independent of the shear rate, and the shear elastic modulus is independent of the shear deformation.

In the set of polycondensation samples studied, two kinds of results exist: (a) results obtained with samples having a high molecular weight between junction points (samples III and IV), for which η and G increase slowly near t_g—no exponent values can be deduced from those experiments; (b) results obtained with samples having a low molecular weight between junction points (samples I and II), for which η and G increase strongly near t_g.

For the latter system, the viscosity diverges at t_g following a power law in ϵ with an exponent value of 0.8 ± 0.1, identical with that determined for a radical copolymerization. This result supports the de Gennes and the Stauffer analogies. The shear elastic modulus increases above t_g with a power law with an exponent 3.2 ± 0.5, larger than the experimental value (2.2) determined in different systems (gelatin and radical copolymerization).

Graph or percolation theories lead to exponent values for the mechanical properties near the gel point that must be independent of the gelation process studied; this is called universality. Graph theory leads to a set of exponents that are different from those predicted by percolation theory. The present experimental results and their comparison with experimental results obtained in other different systems show that mechanical properties are not universal. This lack of universality may be due to the extent of the critical domain, which may depend on the system studied. Indeed, it has been proposed that the extent of critical domain depends on molecular parameters and on the cross-linking process.[36] In contrast, recent theoretical work suggests that the elasticity exponent value is strongly dependent on the stiffness of the chain between two junction points. Thus mechanical properties are not universal. This has to be compared to the well-known fact that two second-order phase transitions may have static properties which belong to the same universality class, whereas their dynamical properties belong to different classes.

If the stiffness of chains has an importance, the results obtained here indicate that small cycle structures are irrelevant quantities for the variation of the mechanical properties near the gel point. Actually the S and T exponent values are independent of the weight fraction of solvent.

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Registry No. (HMDI)·(LHT 240) (copolymer), 53479-43-9; (HMDI)·(UGIPOL 3170) (copolymer), 57596-47-1; (HMDI)·(LG 56) (copolymer), 58450-56-9; (HMDI)·(LG 56)·(PPG 4000) (copolymer), 98527-37-8.

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Small-Angle X-ray Scattering from Semidilute Polymer Solutions. 1. Polystyrene in Toluene

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ABSTRACT: Small-angle X-ray scattering has been measured on solutions of polystyrene in toluene at various concentrations covering from the dilute to semidilute regions. The correlation length ξ for the monomer-density distribution and the number of monomeric units g_m involved within this range have been determined as a function of the concentration and the molecular weight of the polymer. The results of ξ and g_m agree with the scaling predictions for the semidilute–good region and with the blob hypothesis when the molecular weight is higher than 1.1×10^5 and ξ is not very small ($\gtrsim$20 Å). On the other hand, for lower molecular weights and smaller values of ξ, the results are in agreement with Moore's mean-field theory proposed for poor solvents. The value of the binary cluster integral B_1 has been estimated by Moore's theory and is in good agreement with those estimated at infinite dilution.

Introduction

Since a scaling theory for polymer solutions was first proposed by de Gennes,[1] various studies have been performed on the properties of semidilute polymer solutions.[2-6] In particular small-angle neutron scattering[2,3] has provided experimental evidence for the theory, and the features of the semidilute region distinguishable from the dilute and concentrated regions have been established.

The semidilute region is defined as a concentration range in which the number density of polymer chains is large enough to enable individual chains to overlap, while still ensuring diluteness of the local number density of the segments. The mass concentration c^* at the overlap threshold between the dilute and semidilute regions is usually given by

$$c^* = M/N_A\langle S^2\rangle^{3/2} \quad (1)$$

where M is the molecular weight of the polymer, N_A is Avogadro's number, and $\langle S^2\rangle$ is the mean square radius of gyration of a single chain.

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