

THE EVOLUTION OF VISCOELASTICITY NEAR THE GEL POINT OF END-LINKING POLY(DIMETHYLSILOXANE)S

James C. Scanlan and H. Henning Winter\*

Department of Chemical Engineering, University of Massachusetts, Amherst, MA 01003, USA

**Abstract:** The linear viscoelasticity of polymers near the gel point can be described by two scaling laws. The material at the gel point has a power-law linear viscoelastic relaxation modulus, and the relaxation exponent has been found to vary with the composition of the precursor materials, i.e., it is not universal for gelation. A second scaling law describes the evolution of the linear viscoelastic properties through the gel point. The rate of change of the dynamic mechanical modulus/viscosity is observed to scale as a power-law function of frequency. This power-law function defines a dynamic critical exponent, and this has been found to be independent of precursor composition for end-linking poly(dimethylsiloxane) polymers and equal to  $\kappa = 0.21 \pm 0.02$ . This exponent may be a universal measure of gelation. The technique of Time Resolved Mechanical Spectroscopy is used to observe the evolution of linear viscoelastic properties of crosslinking polymers *in situ* in the rheometer. A stretched exponential relaxation modulus describes the evolution of mechanical properties in the vicinity of the gel point very well. The exponents which characterize the divergence of the zero-shear viscosity and the equilibrium modulus are not universal, since they are related to the relaxation exponent and the dynamic critical exponent.

#### INTRODUCTION

The crosslinking of polymers is distinguished by the occurrence of gelation, which is a liquid-solid phase transition exhibiting critical behavior. The critical point is termed the gel point, and the material at the gel point is termed a critical gel. Rheological properties provide one of the most convenient measures of the evolution of crosslinking. Traditionally, a material was said to be at the gel point if simultaneously the zero-shear viscosity was infinite and the equilibrium modulus was zero. More recently, Chambon and Winter [1, 2, 3] arrived at a new mechanical definition of the gel point based on the observation that the entire relaxation spectrum is affected by the gelation transition. At the gel point, the relaxation time spectrum follows the relation

$$H(\lambda) = H_0 \lambda^{-n} \quad (1)$$

and as a consequence the relaxation modulus is a power-law (with  $H_0 = S/\Gamma(n)$ ):

$$G(t) = S t^{-n} \quad (2)$$

with just two material properties, the relaxation exponent,  $n$ , which is restricted between  $0 < n < 1$ , and the gel strength  $S$ . Each of these properties was found to depend on the composition

of the precursor materials [4]. Deviations from this scaling behavior are expected at very short times where different polymer dynamics dominate, i.e. equations 1-2 are valid above a characteristic shortest relaxation time,  $\lambda_0$ , which is dependent on the precursor material [4].

The gel point is difficult to determine precisely by measurement of the equilibrium rheological properties because these diverge at the gel point. The zero-shear viscosity evolves as

$$\eta_0 \sim (p_c - p)^{-s} \text{ (for } p < p_c) \quad (3)$$

and the equilibrium modulus grows as

$$G_e \sim (p - p_c)^z \text{ (for } p > p_c) \quad (4)$$

where  $p$  is the extent of reaction and  $p_c$  is the critical extent of reaction. The equilibrium properties must be measured at very low frequencies since the longest relaxation time also diverges at the gel point. The equilibrium properties are also difficult to measure because they require large strains, and these have been shown to alter the structure and properties of polymers near the gel point [5]. Dynamic mechanical techniques alleviate both of these complications as the properties at intermediate frequencies evolve continuously and only small strains are used to probe the material. The determination of the critical exponents is further complicated by experimental uncertainty of the critical extent of reaction.

It is expected that the critical exponents  $s$  and  $z$  are related to the evolution of the rheological properties on intermediate time scales because of the existence of mechanical self-similarity at the gel point (eq. 2). This paper describes this relation and a method for determining the critical exponents characterizing the evolution of rheological properties during gelation. The results suggest that a simple "stretched" exponential constitutive equation can describe the linear viscoelasticity of crosslinking polymers over a wide range of time and extent of reaction.

#### EXPERIMENTAL PART

We have previously described the technique of Time Resolved Mechanical Spectroscopy for characterizing the crosslinking material at intermediate frequencies *in situ* without stopping the reaction [6]. Small strain oscillatory shear is used to obtain the spectrum of linear viscoelastic properties over a finite window of frequency. Sample mutation, defined by

$$N_{mu} = \Delta t_r \frac{1}{G} \frac{\partial G}{\partial t_r} \ll 1 \quad (5)$$

is accounted for during the measurement of some property  $G$  over the duration of measurement  $\Delta t_r$ . Here  $t_r$  denotes the reaction time which is to be distinguished from the independent variable  $t$  of a rheological constitutive equation. Since  $N_{mu}$  ( $\sim \omega^{-(1+\kappa)}$ , see eq.8) increases with decreasing frequency in the vicinity of the gel point, this technique is necessarily restricted to a finite range of frequency.

Poly(dimethylsiloxane) (PDMS) was crosslinked by an end-linking reaction between

the pre-polymer ends and a multifunctional crosslinker molecule. Several different precursor compositions were prepared with two different pre-polymers, one a  $M_n \sim 10,000$  ( $\eta_0 = 0.5$  Pa s) pre-polymer (HULS-Petrarch PS442), and the other a  $M_n \sim 54,000$  ( $\eta_0 = 65$  Pa s) pre-polymer (HULS-Petrarch PS448). Some samples were modified by the addition of a diluent (an inert PDMS with  $M_n \sim 10,000$ ,  $\eta_0 = 0.5$  Pa s, HULS-Petrarch PS042). Several stoichiometries were studied by controlling the concentration of a four functional crosslinker (HULS-Petrarch T1915). More complete details of the sample preparation and rheological characterization can be found in [4].

## RESULTS

The evolution of the dynamic mechanical properties is shown in figure 1 for the  $M_n \sim 10,000$  pre-polymer with the four functional crosslinker [4]. Data for five different frequencies are shown. The properties at these intermediate frequencies evolve continuously through the gel point. The gel point at approximately 62 minutes was identified as the instant when the dynamic modulus became a power-law function of frequency:

$$G' \sim G'' \sim \omega^n \quad (6)$$

and the phase angle between stress and strain was independent of frequency:

$$\delta(\omega) = \text{constant} = n\pi/2 \quad (7)$$

There is no sharp change of slope in the evolution of these intermediate frequency properties near the gel point.

The *in situ* characterization of rheological properties provides important information about the kinetics of gelation. A sketch of the evolution of the dynamic mechanical properties is shown in figure 2. The dynamic modulus at zero frequency diverges from zero to a finite value at the gel point (see eq. 4), but intermediate frequencies evolve continuously through the gel point, and the rate of change of the dynamic moduli ( $\partial G^*/\partial t_r$ ) increases with decreasing frequency. The data from figure 1 are used to calculate the rate of change of the dynamic moduli as a function of frequency at the gel point as shown in figure 3. Also shown are the rates of change of the dynamic loss and storage moduli  $G'$  and  $G''$ . We find that the first p-derivative of the dynamic modulus scales as a power-law:

$$\frac{\partial \log G^*}{\partial p} \sim \frac{\partial \log G^*}{\partial t_r} \sim \omega^{-\kappa} \quad (\text{for } p \sim p_c) \quad (8a)$$

This scaling would be evidenced in the time domain as

$$\frac{\partial \log G(t)}{\partial p} \sim t^\kappa \quad (\text{for } p \sim p_c) \quad (8b)$$

The slope of the lines in figure 3 is the value of the exponent  $\kappa$ , which we term the dynamic critical exponent. We expect this relation to be valid between a shortest and longest relaxation time,  $\lambda_0 < t < \lambda_{\text{max}}$ , or in the frequency domain,  $1/\lambda_{\text{max}} < \omega < 1/\lambda_0$ . This exponent thus dictates the evolution of properties on all time scales including the equilibrium or zero-frequency properties. Precise knowledge of the critical point is not required to determine  $\kappa$

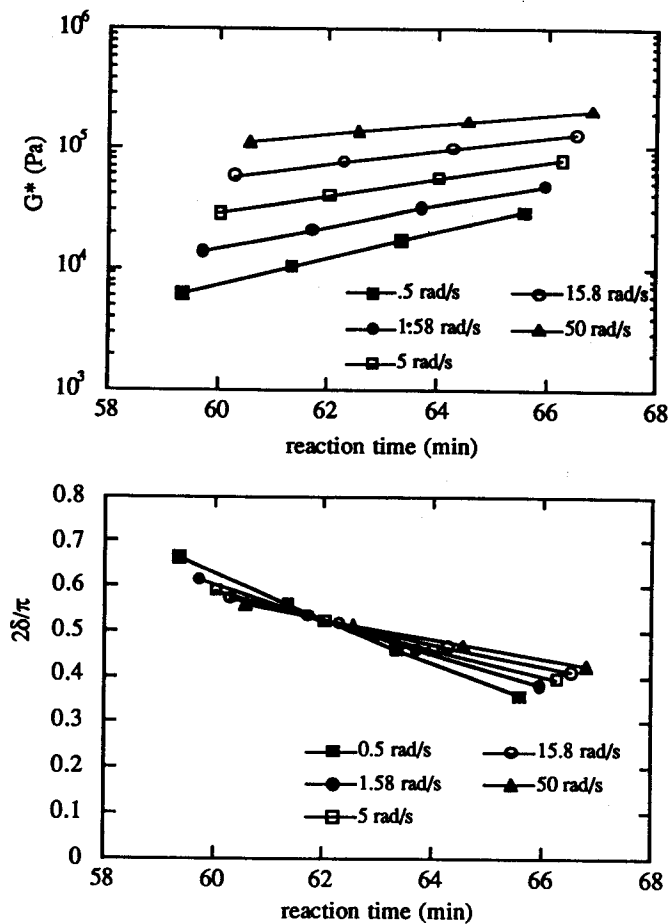


Figure 1a-b. Evolution of the dynamic modulus and normalized phase angle as a function of reaction time at five frequencies for the crosslinking reaction between a  $M_n \sim 10,000$  prepolymer and a four functional crosslinker molecule. The gel point occurs close to 62 minutes.

because the scaling of equation 8 should hold over a finite range of extent of reaction. The independent variable  $p$  can be substituted by the reaction time,  $t_r$ , as long as the derivative is evaluated over a narrow range of reaction time where

$$\Delta p \sim \Delta t_r \quad (9)$$

The value of the exponent determined from the data in figure 3 is  $\kappa = 0.21 \pm 0.01$ . The scaling observation appears to be valid over the range of frequency studied, and the exponent  $\kappa$  is constant over the time of the experiment reported in figure 1, although the range of extent of reaction was not determined.

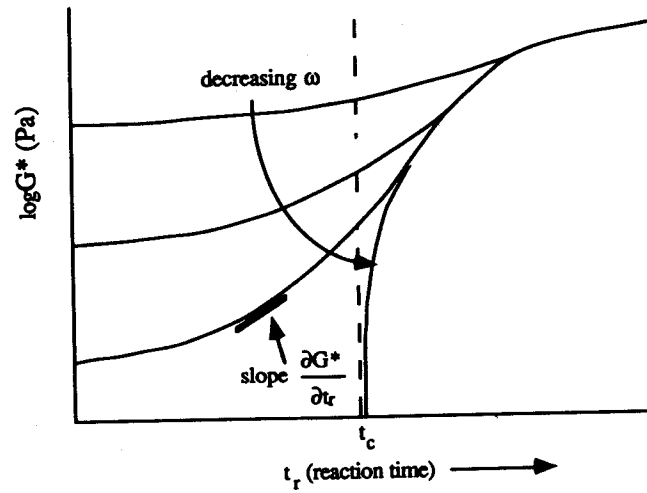


Figure 2. Schematic of the frequency dependence of the dynamic moduli near the gel point. The rate of change of the dynamic moduli ( $\partial G^*/\partial t_r$ ) increases with decreasing frequency near the gel point. The gel point occurs at time  $t_c$ .

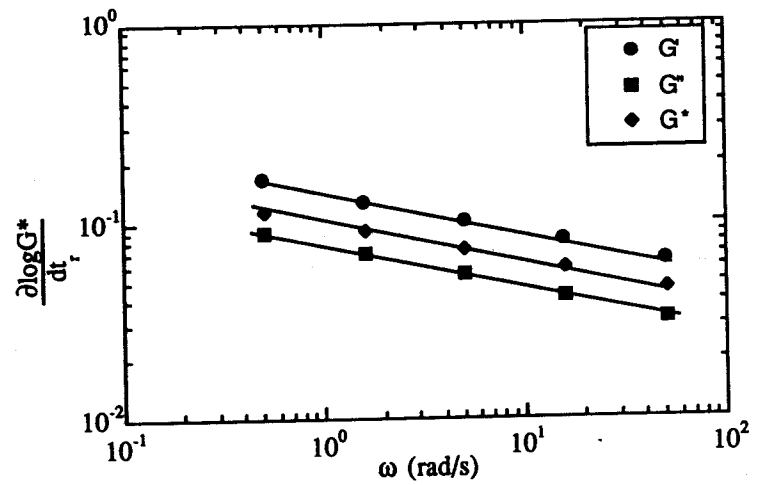


Figure 3. The rate of change of the dynamic moduli,  $G^*$ ,  $G'$ , and  $G''$ , at the gel point. Rates of change are calculated from the data in figure 1. A least squares fit provides  $\kappa = 0.21 \pm 0.01$ .

This experiment has been repeated on over thirty different pre-polymer compositions. The composition was varied by changing the stoichiometry, chain length and concentration of the precursor materials [4]. Although the relaxation exponent and gel strength varied over a wide range ( $0.2 \leq n \leq 0.9$ ,  $1 \leq S \leq 10^5$  (Pa s<sup>n</sup>)),  $\kappa$  takes on a constant value within experimental error: the average value of 30 experiments is

$$\kappa = 0.21 \pm 0.02 \quad (10)$$

#### GELATION THEORY

An observation such as equation 8 suggests a simple model for the evolution of linear viscoelasticity during crosslinking. Further, we expect that the exponent  $\kappa$  should be related to exponents which characterize the evolution of structure. Theories of gelation describe the evolution of cluster growth by statistical methods. They predict a critical point at which an infinite cluster first appears. There are two established theories: the first is termed classical theory [7, 8], and the second is termed percolation theory [9, 10]. These theories can be distinguished by their predictions of the critical exponents which describe the structure of the clusters. The cluster number distribution function  $N_M$  is expected to be a power-law of mass  $M$  at the gel point [10]:

$$N_M \sim M^{-\tau} \text{ (for } p = p_c) \quad (11)$$

The exponent  $\tau$  is termed the polydispersity index. Similarly, the cluster radius  $R_M$  should be a power-law of mass  $M$ :

$$R_M \sim M^{1/d_f} \text{ (for } p = p_c) \quad (12)$$

The exponent  $d_f$  is termed the fractal dimension.

Scaling theory attempts to describe the evolution of clusters for all extents of reaction. The scaling equation is [10]

$$N_M(p, M) \sim M^{-\tau} \cdot f\left[\frac{M}{M_{\max}}\right] \quad (13)$$

where  $f$  is a cutoff function, and  $M_{\max}$  is the molecular weight of the largest cluster.  $M_{\max}$  diverges defining a critical exponent  $\sigma$  that describes the evolution of cluster sizes in the vicinity of the gel point:

$$M_{\max} \sim |p - p_c|^{-1/\sigma} \quad (14)$$

It is common to write the cutoff function in terms of  $x = (M/M_{\max})^\sigma$  rather than  $x = M/M_{\max}$  to avoid divergences of  $p$ -derivatives of  $N_M$  at  $p_c$ , and so:

$$N_M(p) \sim M^{-\tau} \cdot f[(p - p_c)M^\sigma] \quad (15)$$

There are two independent exponents,  $\tau$  and  $d_f$ , which describe the structure of the critical gel, and one,  $\sigma$ , which describes the evolution of the structure in the critical region.

We expect a similarity between the evolution of static structure and the dynamic properties, so it is natural to write [11, 12, 13]:

$$G(t,p) = G(t,p_c) \cdot f\left[\frac{t}{\lambda_{\max}}\right] \quad (16)$$

where  $f$  is a cutoff function and  $\lambda_{\max}$  is the longest relaxation time of the material which diverges in the gelation threshold defining the dynamic critical exponent  $\kappa$ :

$$\lambda_{\max} \sim |p - p_c|^{-1/\kappa} \quad (17)$$

where an assumption is made that the critical exponent  $\kappa$  has the same value before and after the critical point. The data in figure 1 support this assumption since the intermediate frequency properties evolve smoothly through the gel point. The form of the cutoff function for all extents of reaction has to be determined by experiment, however, a stretched exponential function similar to that used to describe the evolution of structure may describe the behavior in the immediate vicinity of the gel point:

$$G(t, p) = S t^{-n} \exp\left(-\left(\frac{t}{\lambda_{\max}}\right)^\kappa\right) \quad (\text{for } p < p_c) \quad (18a)$$

and applying equation 17,

$$G(t, p) = S t^{-n} \exp(-c(p_c - p)t^\kappa) \quad (\text{for } p < p_c) \quad (18b)$$

where  $c$  is a material parameter which only depends on temperature.

The proper form of  $G(t)$  for the post-gel is not yet established. The stretched exponential equation diverges as  $t \rightarrow \infty$  for a positive argument in the exponential term, however, it may describe some of the intermediate time scale behavior,  $t < \lambda_{\max}$ .

#### DISCUSSION

We find that the evolution of rheological properties near the gel point can be described by two critical exponents, one for the rheological behavior at the critical point, and a second one for the evolution through the critical point. The dynamic critical exponent  $\kappa$  seems to adopt a universal value for gelation, while the relaxation exponent,  $n$ , the critical exponent of the relaxation spectrum at the critical point, is not universal but instead depends on precursor composition. Winter [14] showed that the exponents  $s$  and  $z$  describing the equilibrium properties are related to  $n$  and  $\kappa$  by

$$s = \frac{1-n}{\kappa} \quad (19)$$

$$z = \frac{n}{\kappa} \quad (20)$$

and thus these exponents are also not universal.

Table 1. Predictions of the dynamic critical exponents.

Research Group	s	z	n	$\kappa$
de Gennes [15, 16]	0.7	1.7	0.7	0.4
Martin et al. [12, 17] (percolation theory)	$(8-2\tau)/6\sigma$ 4/3	$(\tau-1)/\sigma$ 8/3	$3(\tau-1)/(2\tau+1)$ 2/3	$3\sigma/(2\tau+1)$ 1/4
this work (experiments)	$(1-n)/\kappa$ $0 < s < 5$	$n/\kappa$ $0 < z < 5$	$0 < n < 1$	0.21

There have been several predictions of the critical exponents  $s$  and  $z$ . De Gennes [15, 16] proposed analogies between the divergence of mechanical properties during gelation and other critical phase transitions and predicted  $s = 0.7$  and  $z = 1.7$  (equivalent to stating  $n = 0.7$  and  $\kappa = 0.4$ ). Martin et al. [12, 17] related  $s$  and  $z$  to static structure exponents, and using percolation predictions, proposed  $s = 4/3$  and  $z = 8/3$  (equivalent to  $n = 2/3$  and  $\kappa = 1/4$ ). A summary of these predictions is given in table 1. Measurements of  $s$  and  $z$  are scarce in the literature. Adolf et al. [18] recently studied an epoxy resin and measured  $s = 1.4 \pm 0.2$ . Adam et al. [19] studied a polyurethane system and reported values over a range  $0.6 \leq s \leq 0.9$  and  $1.8 \leq z \leq 3.9$ . The limited number of experimental studies reporting these quantities support the conclusion that these exponents are not universal. In our experiments, the calculated values of the exponents  $s$  and  $z$  vary from about 1 to 4. If  $\kappa$  is indeed a universal value of 0.2, then  $s$  and  $z$  are limited to  $0 < s, z < 5$ .

The longest relaxation time and the characteristic molecular weight should be related by a scaling relation:

$$\lambda_{\max} \sim (M_{\max})^A \quad (21)$$

where  $A$  is a scaling exponent. The reptation theory for narrow-distribution entangled linear polymers predicts  $A = 3$ , while for the Rouse model of unentangled polymers predicts  $A = 1$ . According to the scaling equation,  $\kappa$  is related to  $\sigma$ , the exponent characterizing the largest molecular weight, by

$$\kappa = \sigma/A \quad (22)$$

The experimental value of  $\sigma$  appears to be close to the percolation prediction of  $\sigma = 0.46$  and the classical theory prediction  $\sigma = 0.5$  [20, 21]. Using our result for  $\kappa$  together with the percolation theory yields  $A = 2.15$ , while the classical theory yields  $A = 2.34$ . In either case, this scaling exponent for branched polymers is intermediate between Rouse and reptation theories.

Because of the similarity of the cluster growth process, we speculate that the stretched exponential may be valid above the gel point as well. In fact, the data suggest a symmetry about the critical point. That is,  $\log[G(t)]$  as a function of  $\log[t]$  appears to be symmetric about the function  $G(t; p_c)$  on time scales  $t < \lambda_{\max}$ . In order to apply the stretched exponential, the



divergence at long times must be accommodated. One approach is to separate the relaxation modulus into a constant and a transient part. The stretched exponential would take on the form

$$G(t, p) = G_e(p) + S t^{-n} \exp[-c|p_c - p|t^\kappa] \quad (\text{for all } p) \quad (24)$$

and here the transient part decreases and the constant increases with increasing  $p$  beyond the gel point. However, such an approach cannot describe our observations with PDMS networks over a wide frequency window without making the material properties,  $S$ ,  $n$ , and  $\kappa$ , functions of the extent of reaction instead of constants.

We have applied the stretched exponential constitutive equation (equation 18) to the data of Chambon and Winter [1], who determined the mechanical properties of material close to the gel point over five decades of frequency by using quenched samples. A fit of their data at several different extents of reaction is shown in figure 4 using the critical gel properties  $S$  and  $n$  and the "universal" value of  $\kappa = 0.2$ . The stretched exponential (equation 18) can describe the transient response ( $t < \lambda_{\max}$ ) of the solid (gel) at least close to the gel point, but fails far from the gel point. There is only one fitting parameter in figure 4, the extent of reaction, since it was not measured during these experiments. Future experiments that simultaneously measure  $p$  and the rheological properties will be a more complete test of the constitutive equation. The proposed constitutive equation is not expected to describe all extents of reaction; instead it will have to be more general to be able to describe the limits of the Newtonian fluid and the Hookean solid.

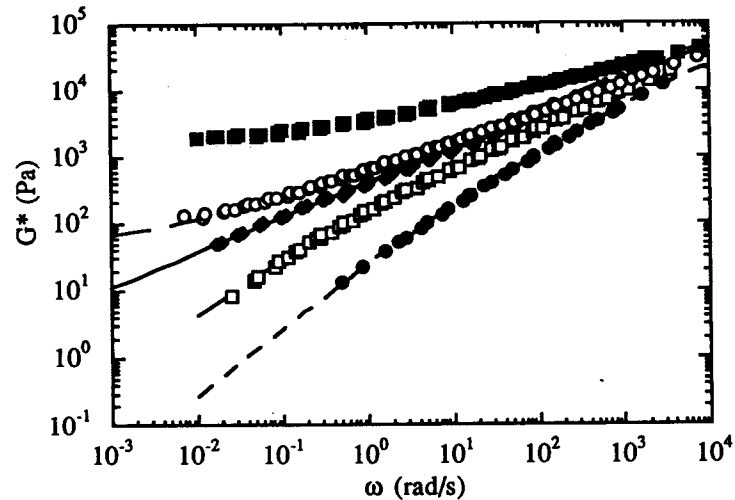


Figure 4. Comparison of the dynamic moduli reported by Chambon and Winter [1] with a stretched exponential function (equation 18) for various extent of reaction. The fit has only one fitting parameter, the value of  $c(p_c - p)$ , since the extent of reaction was not measured during the experiment. Constants for the fit are  $S = 230 \text{ Pa s}^n$ ,  $n = 0.52$ , and  $\kappa = 0.20$ . The values of  $c(p_c - p)$  are  $-5$ ,  $-1.45$ ,  $0$ , and  $0.45$ .

### CONCLUSIONS

The dynamic modulus  $G^*(\omega)$  grows monotonously through the gel point. No change in slope is observed near the gel point at intermediate frequencies. A discontinuity is only expected for the limit of zero frequency which cannot be measured. The rate of change of the linear viscoelastic properties follows a power-law dependence of frequency near the gel point. The self-similarity of linear viscoelasticity in the vicinity of the gel point permits the determination of the dynamic critical exponent without probing at zero-frequency and without having to determine the extent of reaction. Many experiments on poly(dimethylsiloxane) polymers with widely varying precursor composition indicate that the dynamic critical exponent takes on a universal value of  $\kappa = 0.21 \pm 0.02$ . Because the critical exponent characterizing the critical point relaxation is composition dependent, the exponents characterizing the evolution of the zero-shear viscosity and equilibrium modulus are also composition dependent, and not universal. Our observations suggest that the linear viscoelasticity of polymers near the gel point can be described by a stretched exponential relaxation modulus over a wide range of time and extent of reaction.

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