

The effect of entanglements on the rheological behavior of polybutadiene critical gels

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Abstract: We investigated the stress relaxation behavior of critical gels originating from six nearly monodisperse, highly entangled polybutadiene melts of different molecular weight from 18 000 to 97 000 g/mole. The polymers were vulcanized by a hydrosilation reaction which takes place nearly exclusively at the pendant 1,2-vinyl sites distributed randomly along the polybutadiene chain. The BSW-spectrum represents the relaxation of the initial uncrosslinked precursor. A characteristic parameter is the longest relaxation time of the precursor. Crosslinking increases this longest time even further. Surprisingly, the relaxation spectrum of the precursor is not altered much by the crosslinking except for an additional long time behavior. At the gel point (critical gel), this long time behavior is self-similar. It follows the typical power law as described by the Chambon-Winter gel equation, $G(t) = St^{-n}$, in the terminal zone. The critical relaxation exponent was found to be close to $n = 0.5$ over a range of stoichiometric ratios and for all precursor molecular weights analyzed. A new scaling relationship was found between the gel stiffness, S , and the precursor molecular weight of the form: $S \sim M_w^{zn}$, where exponent z from the zero shear viscosity-molecular weight relationship, $\eta_0 \sim M_w^z$, is commonly found to be $z = 3.3-3.6$.

Key words: Gelation – critical gel – entanglement – relaxation time spectrum

1. Introduction

The molecular mobility of polymers is known to be reduced when the molecular weight exceeds a characteristic value M_c . The molecules form entanglements and at intermediate time scales the melt behaves like a rubber having a plateau modulus G_N^0 . Chemical crosslinking of such high molecular weight polymers increases the molecular weight even further. It results in a rheological behavior which somehow combines the elasticity of the entangled structure with the elasticity of the evolving chemical network during gelation.

The viscoelasticity of materials is generally defined by the relaxation time spectrum, $H(\lambda)$, for the transient part of the relaxation modulus (Ferry, 1980)

$$G(t) = \int_0^{\infty} H(\lambda) e^{-t/\lambda} \frac{d\lambda}{\lambda} + G_e, \quad (1)$$

where G_e is the equilibrium modulus. G_e is finite for viscoelastic solids and is zero for the liquid and for the

material at the gel point. The effect of entanglements on gelation can be investigated experimentally by mechanically probing molecularly well-defined samples and by searching for characteristic patterns in the relaxation time spectrum, $H(\lambda)$, as a function of increased extend of crosslinking, p .

As a starting point for the gelation process we chose a polymer melt with long linear flexible chains of nearly uniform length. For such a fluid, the effect of entanglements is well known (Ferry, 1980; Graessley, 1974; Doi and Edwards, 1986). Relaxation data may be expressed quantitatively by the empirical BSW-spectrum (Baumgaertel et al., 1990, 1992)

$$H(\lambda) = \begin{cases} n_e G_N^0 [(\lambda/\lambda_c)^{-n_g} + (\lambda/\lambda_{\max})^{n_e}] & \text{for } 0 < \lambda < \lambda_{\max} \\ 0 & \text{for } \lambda > \lambda_{\max} \end{cases} \quad (2)$$

The characteristic material parameters are the plateau modulus G_N^0 , the power law exponents n_g and n_e for

the glass transition and the entanglement region respectively, a crossover time λ_c for the onset of the glass transition and the longest relaxation time λ_{\max} .

It has also been established that polymers at the gel point (termed "critical gels") have a terminal relaxation spectrum which is self-similar (CW-spectrum) (Chambon and Winter, 1985, 1986, 1987). The empirical CW-spectrum has a power law distribution of relaxation times,

$$H(\lambda) = \frac{G_0}{\Gamma(n)} \left(\frac{\lambda}{\lambda_0} \right)^{-n}, \quad \lambda_0 < \lambda < \infty, \quad (3)$$

where n is the critical relaxation exponent, and Γ is Euler's gamma function. G_0 is a material characteristic modulus which, for endlinking systems, has a value near the modulus of the fully crosslinked material (Scanlan et al. 1991, Izuka et al. 1992). The lower limit, λ_0 , of the CW-spectrum depends on small scale details of the material. For the previously studied low molecular weight precursor materials having molecular weights around M_c or below, it marked the crossover to the glass transition. For high molecular weight materials, it marks the transition to the entanglement region as will be shown in this study.

A consequence of the critical gel having such a self-similar spectrum is that the transient part of the relaxation modulus scales as

$$G(t) = St^{-n}, \quad \lambda_0 < t < \infty, \quad (4)$$

where $S = G_0 \lambda_0^n$ is the gel stiffness. n is the critical relaxation exponent of Eq. (3). The dynamic moduli (G' , G'') scale with the frequency, ω , and are related to the gel strength and critical exponent as

$$G' = G'' / \tan \frac{n\pi}{2} = S \omega^n \Gamma(1-n) \cos \frac{n\pi}{2},$$

$$1/\lambda_0 > \omega > 0. \quad (5)$$

From Eq. (5) it follows that the phase angle (δ) between cyclic stress and strain is independent of frequency but proportional to n :

$$\delta = n\pi/2. \quad (6)$$

In this study, we wanted to explore the evolving spectrum, $H(\lambda)$, during gelation of entangled systems. More specifically, we needed to better understand how the spectrum makes the transition from Eq. (2) to Eq. (3) and how intermediate states of

crosslinking express themselves in a distribution of relaxation modes over a wide range of time scales. We also wanted to find out the molecular weight dependence of the scaling exponent, n , and the gel strength, S , for stoichiometrically balanced and imbalanced systems.

2. Experimental conditions

A system was chosen such that the precursor molecules were long enough to form entanglements, could be easily crosslinked, and could be synthesized with very narrow molar mass distribution. There was a choice of precursor polymers which could be crosslinked either at the chain ends or at sites along the chain. However, endlinking systems of very high molecular weight polymers prove to be problematic for such a study because the concentration of the reactive endgroups decreases as the molecular weight of the precursor is increased. Eventually, it would become nearly impossible to experimentally control the stoichiometry and to perform quantitative analysis on the endgroups. Therefore, in order for an endlinking system to have entanglements and be able to reach the gel point, it must have a very low M_c .

This inherent problem is overcome when crosslinking, not only at the molecular chain ends, but at sites along the backbone. For critical gels of this type, the molecular weight between crosslinks is random not only because the reactive sites are distributed randomly along the precursor chain, but also because the probability that a chemical reaction will take place at these sites is random.

Materials and characterization

Seven polybutadiene samples of different molecular weight and narrow molecular weight distribution were synthesized by Dr. Michael Masse (Shell Development Co.) using a standard anionic polymerization technique. GPC analysis and proton NMR were performed to determine molecular weights, polydispersity, and 1,2-vinyl content. The relative cis and trans content of the polybutadienes was measured by F.T. Raman spectroscopy in the laboratory of Dr. Shaw Ling Hsu. The glass transition temperatures were measured on a DuPont DSC instrument model 2910 at a heating rate of 20 K/min Table 1 gives a summary of the characterization. The details of synthesis and analysis are described in a previous paper on uncrosslinked polybutadienes (Baumgaertel et al., 1992).

Table 1. Characterization summary of polybutadiene precursor polymers

Sample	M_w	M_w/M_n	%cis	%trans	%vinyl	T_g (°C)
PBD 18	18100	1.03	41	52	7.30	-92
PBD 20	20700	1.04	39	53	8.19	-91
PBD 38	37900	1.05	41	51	7.70	-92
PBD 44	44100	1.04	39	53	8.11	-90
PBD 70	70200	1.02	43	50	7.30	-93
PBD 97	97000	1.07	41	51	8.04	-90
PBD 201	201000	1.27	44	48	7.88	-92

Rheological measurements

Storage and loss moduli (G' , G'') of the uncrosslinked polybutadiene melts were measured as a function of frequency using a Rheometrics Dynamic Spectrometer, RDS 7700, with 25 mm parallel plate geometry and gap settings between the plates of 0.6–1.5 mm. Cooled nitrogen was continuously circulated in the environmental chamber to obtain subambient temperatures. Measurements at temperatures in the range of -75° to 28°C extended the experimental frequency window through time-temperature superposition. The data were analyzed with the parsimonious model of Baumgaertel and Winter (1989, 1992).

Crosslinking reaction

A hydrosilation reaction is used to crosslink the polybutadiene chains at the 1,2-vinyl sites along the backbone with (p-bis(dimethylsilyl)benzene), a bifunctional silane crosslinker suggested by Aranguren and Macosko (1988). The crosslinker, as purchased from HULS America Inc., was found to be $>99.5\%$ pure by GC analysis. A platinum compound, cis-dichlorobis(diethyl sulfide) platinum II, catalyzed the reaction. The catalyst was synthesized according to the method suggested by Kauffman and Cowan (1960).

The hydrosilation reaction has an advantage over other crosslinking methods, such as peroxide or sulfur vulcanization, in that it takes place nearly exclusively at well defined sites on the chain, the 1,2-vinyl sites. The reactivity of the 1,2-vinyl sites has been found to be much higher than that of the 1,4-cis or trans units (Miron et al., 1973; Friedmann and Brossas, 1973; Aranguren and Macosko, 1988). A small level of conversion of the 1,4 units during the reaction has been reported to take place for stoichiometrically balanced systems ($r = 1$). It was observed that more 1,4 units react with silane when there is excess crosslinker (i.e., $r > 1$) (Aranguren and Macosko, 1988).

By using an aromatic silane as a crosslinker, the reaction is virtually free of side reactions (Aranguren and Macosko, 1988). Such undesired side reactions were always a concern when using siloxy silanes as crosslinkers at relatively high temperatures of 65° to 110°C . Side reactions of the silane could be as high as 20–30% (Aranguren and Macosko, 1988; Chambon, 1986; Macosko and Saam, 1985). However, side reactions were essentially avoided when crosslinking was carried out at lower temperatures (Fischer and Gottlieb, 1986) (e.g., 28°C) as was done in this work.

Sample preparation and measurements

Sample preparation started out by mixing 0.6 g of polybutadiene with 0.06 ml (~ 350 ppm) of catalyst solution (8.0×10^{-3} mol/l in toluene) for 10–12 min with a microspatula in a ceramic crucible. Vacuum stripping at 60°C for 2 h removed the toluene introduced with the catalyst solution. After letting the sample cool to room temperature, stoichiometrically balanced or imbalanced amounts of the crosslinker were added using a 0.1 ml Hamilton syringe. The stoichiometric ratio (r) of the system is defined here as the initial molar ratio of silane group to vinyl group $[\text{SiH}]/[\text{CH}=\text{CH}_2]$. Stoichiometric ratios ranged from 0.1 to 3.0. After mixing for 6–7 min, the reacting mixture was loaded into the RDS 7700 at 28°C .

The evolution of the dynamic moduli during crosslinking was measured at six frequencies from 1–316 rad/s by the consecutive frequency sweeps (CFS) technique (Scanlan and Winter, 1991; Izuka et al., 1992; Lairez et al., 1992). Data in the vicinity of the gel point were interpolated with the computer program "Gelpro" (Mours and Winter, 1994). The critical gel time (t_c) was easily determined by the self-similar relaxation pattern at the gel point (i.e., $\tan \delta$ is constant over the terminal frequency range).

Samples were allowed to cure for a total of 8–12 h at room temperature until the modulus did not change anymore, at which point the reaction was considered to have reached its highest possible conversion. A frequency sweep from 0.01 to 100 rad/s was performed on the fully cured samples at 28°C . The glass transition temperatures of fully cured samples with balanced stoichiometry were then measured at a heating rate of 20 K/min.

When using the CFS technique, some error is introduced due to the fact that the sample is changing while G' , G'' are being measured. A dimensionless parameter called the mutation number, N_{mu} , has been defined for specifying the limits of this technique (Winter et al., 1988; Scanlan and Winter, 1991):

$$N_{mu} = \Delta t \frac{1}{G} \frac{\partial G}{\partial t}, \quad (10)$$

where $\Delta t \approx 2\pi/\omega$ indicates the time for a single measurement at one frequency. A low frequency measurement requires a larger Δt and thus results in a large N_{mu} . Data can be accepted for $N_{mu} \ll 1$. In most of these experiments, N_{mu} for the lowest frequency of 1 rad/s was found to be in the range of 0.05 to 0.15. This means that the moduli changed by 5 to 15% during the measurement. The largest value of N_{mu} observed was 0.25 for PBD38 at $r = 3$. N_{mu} can be reduced by slowing the reaction down by lowering the temperature or using less catalyst. Samples reached the gel point in times ranging from 14 to 71 min. It was found that the rate of reaction increased with increasing precursor molecular weight and with increasing amount of crosslinker.

"Stopped" samples

Stopping of the crosslinking reaction at intermediate conversions has the advantage of giving stable samples. These are needed for extending the experimental frequency window through time-temperature superposition over a range of temperatures. For stopping the reaction, reacting mixtures at balanced stoichiometry were put onto a 25 mm disk fixture of the rheometer. An outer aluminum ring, set at about 0.6 mm depth, was used as a mold. The reacting sample was poured into the mold and allowed to cure at ambient temperature until the hydrosilation reaction was "stopped" by spraying <2 wt% of an 80% tetramethylethylenediamine (TMEDA) solution in toluene with an atomizer onto the sample surface. This "poison" rapidly diffused into the thin sample and deactivated the Pt catalyst at room temperature so that samples with well defined stages of crosslinking became available for detailed experiments.

3. Results

Polybutadiene precursor molecules: The dynamic viscosity (η^*) in the terminal zone, where η^* is independent of frequency, denotes the zero shear viscosity (η_0). Figure 1 shows the zero shear viscosity for samples PBD 18 through PBD 201 as a function of the weight average molecular weight. The slope of this scaling behavior was found to be 3.52 for all seven PBD samples which is slightly higher than the value of 3.4 commonly reported in the literature (Colby et al.,

1987; Ferry, 1980; Berry et al., 1968). 3.52 is reasonably close to 3.4 when experimental error is taken into consideration. The viscosities of the five highest molecular weights were found to scale with an exponent of 3.43. The two samples with the lowest molecular weights, PBD18 and PBD20, were found to have slightly lower viscosities than the 3.4 scaling relationship would predict.

Dynamic moduli (G' , G'') of the uncrosslinked bulk precursor samples have been reported in detail in other publications (Baumgaertel et al., 1992; Jackson et al., 1994).

Diluent effect of the crosslinker: It is a consequence of this two-component system, requiring small crosslinker molecules and long precursor molecules, that the added crosslinker increases the mobility of the precursor molecules. In this particular case, 12% by weight of crosslinker must be added in order to reach stoichiometrically balanced conditions. At this considerable amount, the crosslinker is fully compatible with the PBD. It acts as a plasticizer which lowers the zero shear viscosity (Fig. 1), but does not affect the molecular weight dependence for six diluted samples, PBD18 through PBD97. Figure 2 shows a comparison of the dynamic moduli of bulk PBD38 and PBD38 mixed with a stoichiometric amount of crosslinker. Dynamic data were taken for precursor molecules PBD 18 to PBD97 with a stoichiometrically balanced amount of crosslinker added (Fig. 3). The relaxation spectra, determined by the standard IRIS software, are shown in Fig. 4. Dilution also reduced the T_g by 3 K from that of the bulk precursors to -94°C . The dilution effect of the crosslinker on the relaxation behavior of polybutadiene is important to

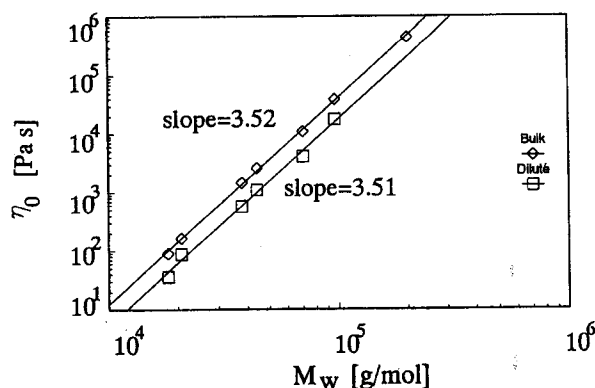


Fig. 1. Zero shear viscosity vs. weight average molecular weight for bulk PBD samples and samples diluted with stoichiometric amount of crosslinker. Scaling exponents are 3.52 and 3.51, respectively

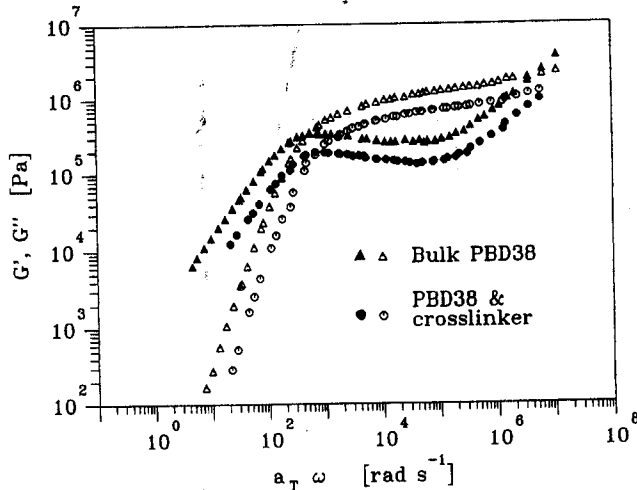


Fig. 2. Comparison of G' , G'' data of bulk PBD38 to PBD38 with stoichiometric amount of crosslinker. The plasticization effect of the crosslinker shifts the dynamic data down vertically and horizontally to higher frequencies. $T_{ref} = 28^\circ\text{C}$

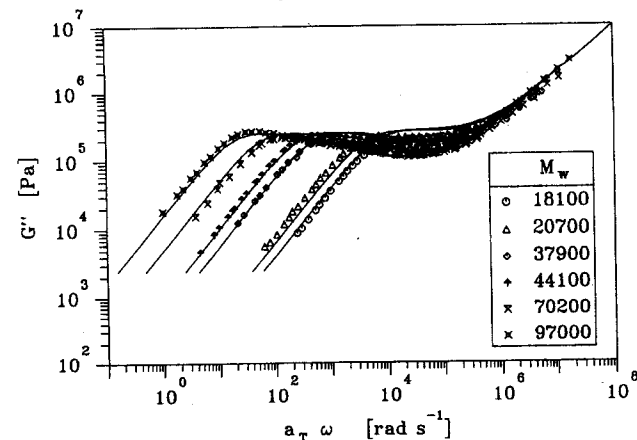
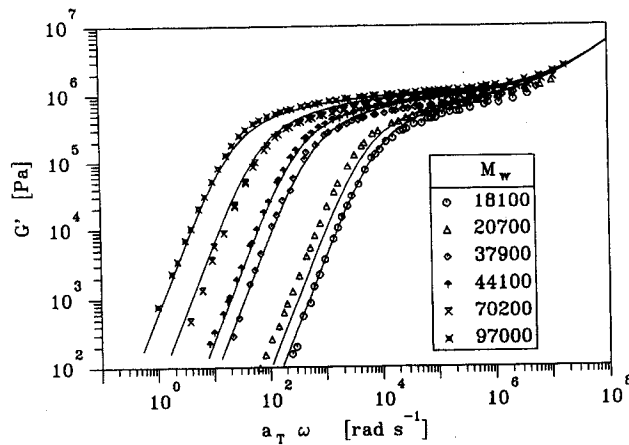


Fig. 3. a) Storage moduli (G') and b) loss moduli (G'') data of six PBD samples all diluted with stoichiometric amounts of crosslinker. The line indicates the BSW-model described in Eq. (21) with parameters in Table 4. $T_{ref} = 28^\circ\text{C}$

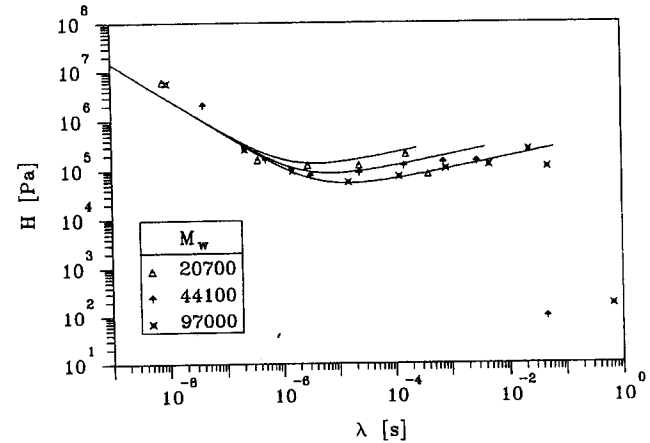
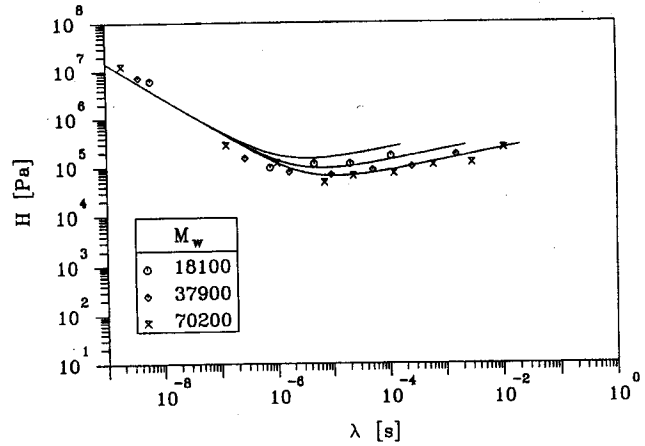


Fig. 4. Relaxation time spectra ($H(\lambda)$) for six diluted PBD samples shown in Fig. 3. Data points are from the IRIS calculation (parsimonious model). The lines represent the BSW-model described in Eq. (21)

include in the following considerations. The dynamic moduli of stopped samples at $r = 1$ must be compared to the dynamic data of the precursor mixed with a stoichiometric amount of crosslinker.

3.1 Fully crosslinked material ($p \rightarrow 1$)

The complex modulus (G^*) of five fully cured stoichiometrically balanced polybutadienes of different molecular weight is nearly independent of frequency when measured from 0.01 to 100 rad/s at 28°C , Fig. 5. The value of G^* at 0.01 rad/s was taken to be the equilibrium modulus (G_e). Off-balancing of stoichiometry reduced the dynamic modulus as shown for PBD18, Figs. 6 and 7. The T_g of fully cured samples at balanced stoichiometry, measured by DSC, increased by an average of 14 K (see Table 2) due to the fact that molecular motion is restricted by the chemical crosslinks (Ferry, 1980).

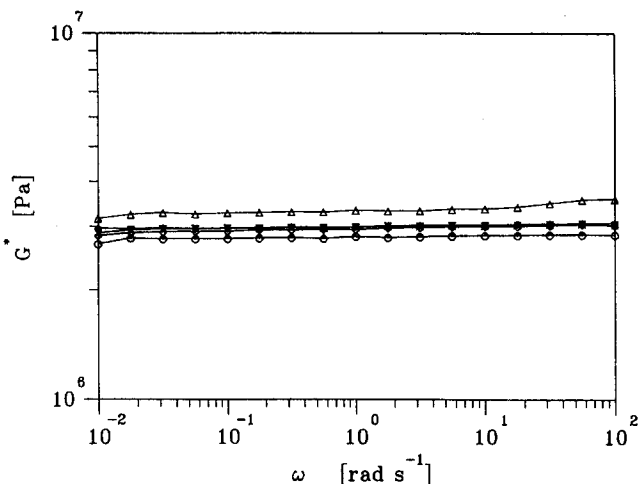


Fig. 5. Complex moduli (G^*) for fully cured PBD samples (\circ) PBD 18, (Δ) PBD 38, (\diamond) PBD 44, (\uparrow) PBD 70, (\bar{x}) PBD 97 at $r = 1$. $T_{ref} = 28^\circ\text{C}$

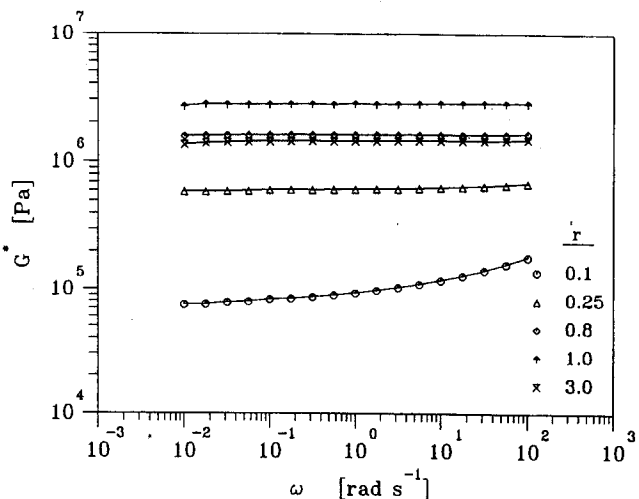


Fig. 6. Complex moduli (G^*) of fully cured PBD 18 at five different stoichiometric ratios. $T_{ref} = 28^\circ\text{C}$

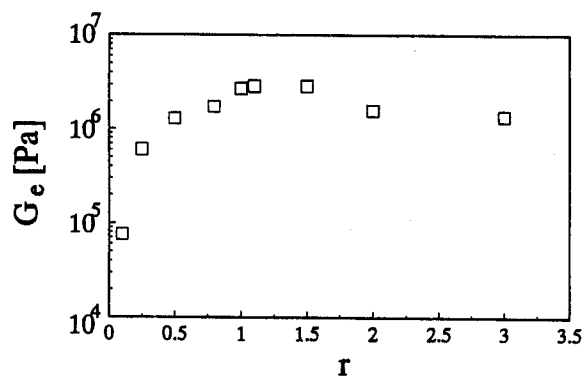


Fig. 7. Equilibrium moduli (G_e) of fully cured PBD 18 samples at ten different stoichiometric ratios. G_e was taken as the value of G^* at 0.01 rad/s and at 28°C

Table 2. Final network properties of fully cured samples with balanced stoichiometry ($r = 1$). G_e is taken as $G^*(\omega)$ at 0.01 rad/s. $G^*(\omega)$ measurements were made at 28°C

Fully cured sample	G_e [MPa]	T_g ($^\circ\text{C}$)
PBD 18	2.73	-81
PBD 38	3.24	-80
PBD 44	2.87	-80
PBD 70	2.96	-80
PBD 97	2.93	-79

Balanced stoichiometry ($r \approx 1$): Figure 5 shows G^* for fully cured samples at balanced stoichiometry of five different molecular weights. All of the samples have been found to have close to the same equilibrium modulus, G_e , and T_g within two degrees, see Table 2. The occurrence of the same equilibrium modulus suggests that all fully cured samples have the same crosslink density as shown by classical rubber elasticity theory (Ferry, 1980):

$$G_e = \frac{\rho RT}{M_{chem}}, \quad (10)$$

where ρ is the density of the crosslinked rubber and M_{chem} is the molecular weight between chemical crosslinks. Since all the precursors have the same concentration of reactive sites ($\sim 8\%$ vinyl units) per chain, it was to be expected that they all have the same crosslink density at full extend to reaction. This is typical for vulcanization reactions. This has to be compared to an endlinking process, where G_e and T_g would be expected to decrease with increasing precursor molecular weight since the molecular weight between crosslinks is dictated by the precursor molecular weight (Chambon et al., 1986; Izuka et al., 1992).

Imbalanced stoichiometry ($r \neq 1$): Figure 6 shows the complex modulus G^* for fully cured samples of PBD 18 at different values of r . The equilibrium modulus, shown in Fig. 7, of the samples is low for $r < 1$ and increases rapidly as r approaches 1. The maximum value of G_e was found to be at $r = 1.1$, which is slightly higher than the theoretical value of $r = 1$. This is attributed to the production of intramolecular loops and dangling ends at later stages of crosslinking where the polymer mobility is low. G_e decreases slightly as r approaches 3. The asymmetrical shape of G_e with r has been reported for other systems (Chambon and Winter, 1987; Aranguren and Macosko, 1988; Venkataraman et al., 1989; Izuka et al., 1992).

3.2 Transition through the gel point and critical gel behavior

The evolution of the dynamic moduli (G' , G'') was measured while a sample was crosslinking. Figure 8a shows $\tan \delta$ data for a crosslinking PBD18 sample at 28 °C at balanced stoichiometry. The intersect marks the critical gel time (t_c). The value of the gel stiffness (S) and the critical relaxation exponent (n) can be calculated from the interpolated dynamic data by using Eq. (6).

CFS has been found to have a limitation when measuring the gel point of precursors of exceedingly

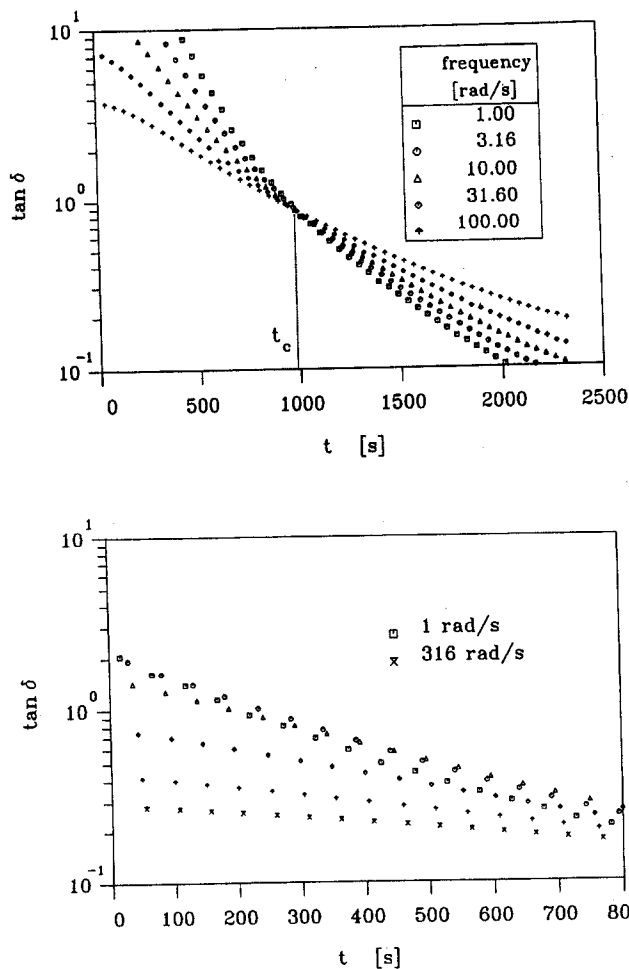


Fig. 8. a) CFS data showing $\tan \delta$ vs. time for a PBD18 sample with $r = 1$ curing at 28 °C. Five frequencies were scanned from 1 to 100 rad/s. The intersection point indicates the critical gel time (t_c). b) CFS data for a curing PBD97 sample at $r = 1$ at 28 °C. Six frequencies were scanned (\square) 1, (\circ) 3.16, (\triangle) 10, (\diamond) 31.6, (\uparrow) 100, (\bar{x}) 316 rad/s. Only the lowest three frequencies nearly intersect simultaneously at approximately 250 s

high molecular weight. Figure 8b shows CFS data for PBD97. $\tan \delta$ at the higher frequencies do not intersect with $\tan \delta$ at the lower frequencies. This phenomenon has been recently reported for this system for very high molecular weight precursors (> 70000 g/mole) (De Rosa and Winter, 1993). It is a purely experimental problem which is explained by the lack of low frequency data, see discussion section.

CFS measurements involved samples PBD18, PBD38, PBD44, and PBD70 over a range of stoichiometric ratios from 0.25 to 3.0. The value of S decreased slightly with r (Fig. 9a). The values of the relaxation exponent (Table 3) stayed in the narrow range from 0.41 to 0.53 and appeared to be insensitive to stoichiometric ratio (Fig. 9b) for the range of molecular weights which was studied here. The values of S and n are given in Table 3.

Stopped samples: G' and G'' master curves of PBD18 stopped at increasing extents of reaction are shown in Fig. 10. The initial uncured sample is a stoichiometric mixture of precursor and crosslinker. Figure 10a

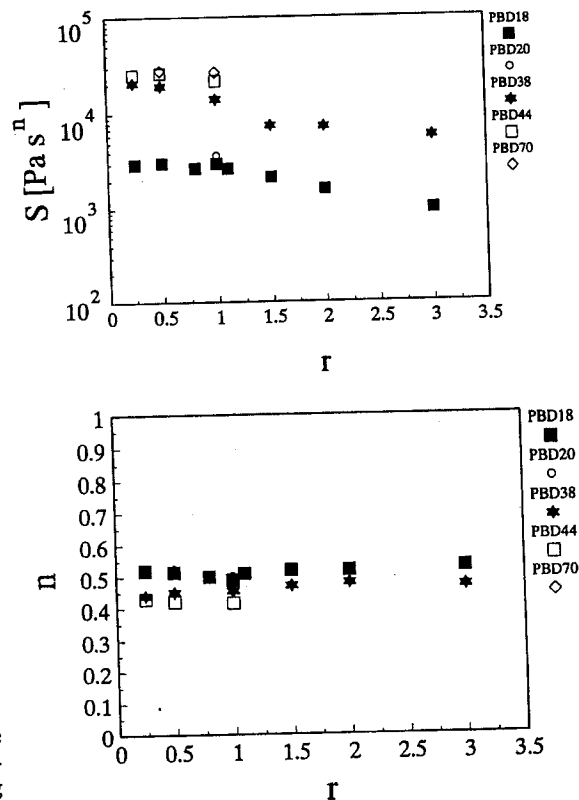


Fig. 9. a) Gel stiffness (S) and b) critical exponent (n) vs. stoichiometric ratio at 28 °C calculated from CFS data for samples PBD18 through PBD70

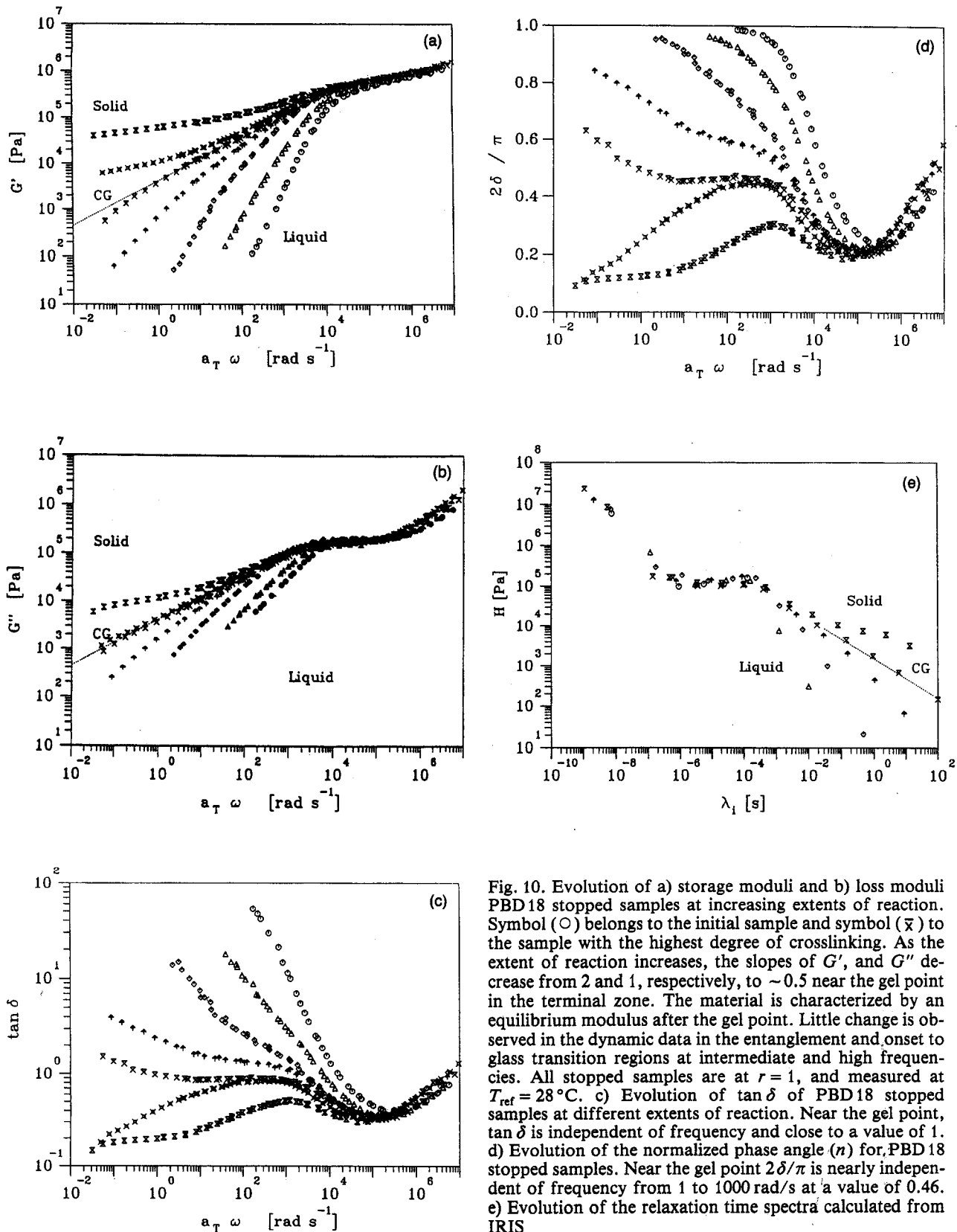


Fig. 10. Evolution of a) storage moduli and b) loss moduli PBD18 stopped samples at increasing extents of reaction. Symbol (\circ) belongs to the initial sample and symbol (\times) to the sample with the highest degree of crosslinking. As the extent of reaction increases, the slopes of G' , and G'' decrease from 2 and 1, respectively, to ~ 0.5 near the gel point in the terminal zone. The material is characterized by an equilibrium modulus after the gel point. Little change is observed in the dynamic data in the entanglement and onset to glass transition regions at intermediate and high frequencies. All stopped samples are at $r = 1$, and measured at $T_{ref} = 28^\circ\text{C}$. c) Evolution of $\tan \delta$ of PBD18 stopped samples at different extents of reaction. Near the gel point, $\tan \delta$ is independent of frequency and close to a value of 1. d) Evolution of the normalized phase angle (n) for PBD18 stopped samples. Near the gel point $2\delta/\pi$ is nearly independent of frequency from 1 to 1000 rad/s at a value of 0.46. e) Evolution of the relaxation time spectra calculated from IRIS

Table 3. Summary of critical gel stiffness, S , and critical relaxation exponent, n , for PBD gel samples for five precursor molecular weights at various stoichiometric ratios, r . All data were taken at 28°C:

Sample	r	S (Pa·s ^{n})	n
PBD 18	0.25	3000	0.52
	0.5	3100	0.51
	0.8	2700	0.50
	1.0	3000	0.49
	1.1	2700	0.51
	1.5	2200	0.52
	2.0	1600	0.52
	3.0	980	0.53
PBD 20	1.0	3700	0.50
PBD 38	0.25	20900	0.44
	0.5	19400	0.45
	1.0	13700	0.45
	1.5	7500	0.47
	2.0	7300	0.48
PBD 44	3.0	5700	0.47
	0.25	25300	0.43
	0.5	26200	0.42
	1.0	19900	0.42
PBD 70	0.5	27800	0.52
	1.0	24800	0.49

shows the evolution of the storage modulus (G') at increasing extents of reaction. As the crosslink density increases, the modulus extends to lower and lower frequencies until it straightens into a power law at the gel point with a slope of about 0.5. Beyond the gel point, an equilibrium modulus develops as an asymptote at low frequencies. The entanglement plateau and the onset to the glass transition are only slightly affected in shape by the addition of chemical crosslinks. Only at much higher crosslink density have the entanglement and glass transition region been observed to change shape.

Figure 10b shows the evolution of the loss modulus (G'') as the crosslink density increases. It is evident that the addition of chemical crosslinks has only very little effect on the onset to the glass transition region. However, crosslinking has the effect of lowering the slope of G'' in the entanglement region at intermediate frequencies.

Figure 10c shows the evolution of $\tan \delta$ for the data of Figs. 10a and b. Near the gel point, the low frequency $\tan \delta$ becomes independent of frequency and is close to a value of 1. The same data can be expressed as the normalized phase angle ($2\delta/\pi$), see Fig. 10d. At the gel point, ($2\delta/\pi$) is equal to the critical exponent n as described by Eq. (7). For the stopped sample near the gel point, a power law region for

nearly three decades (~ 1 to 1000 rad/s) gives a value of $n = 0.46$ which is close to 0.5.

The relaxation spectra ($H(\lambda)$) of the stopped samples were calculated with the standard IRIS software, see Fig. 10e.

We prepared critical gels by stopping the crosslinking reaction of stoichiometric mixtures of crosslinker with PBD 18, PBD 38, PBD 44, PBD 70, and PBD 97. Figure 11 compares the dynamic data of a stopped sample of PBD 44 near the critical gel point to the uncrosslinked mixture of PBD 44 precursor and crosslinker. The relaxation dynamics in the entanglement region and the onset of the glass transition remain virtually unaffected by the gelation process except for a slight decrease in the slope of G'' at intermediate frequencies. Figure 12a shows the dynamic moduli at the reference temperature of 28°C of samples PBD 18, PBD 44 and PBD 97 near the gel point. The power law behavior at the gel point only occurs in the terminal zone of the slope of the power law is close to 0.5. The corresponding relaxation time spectra, Fig. 12b, show three distinct regions of power law behavior: one power law is indicated at short times for the glass transition (not enough data to support any claim here), one at intermediate times for the entanglement region, and one in the terminal zone for the critical gel behavior.

The shift factors for all stopped samples (before, at, and after the gel point) were only slightly higher than those of the unreacted blend of precursor and crosslinker. They obey WLF behavior and are the same for all precursor molecular weights studied.

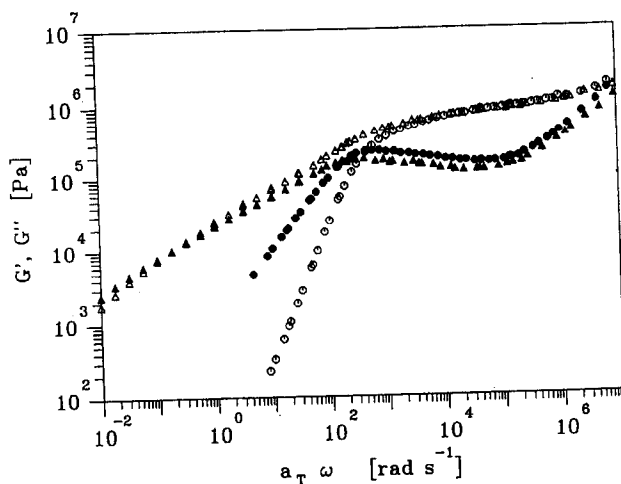


Fig. 11. Comparison of (Δ) stopped sample PBD44 near the gel point to (\circ) uncrosslinked diluted PBD44. The moduli were measured at temperatures from -75° to 28°C and shifted to 28°C

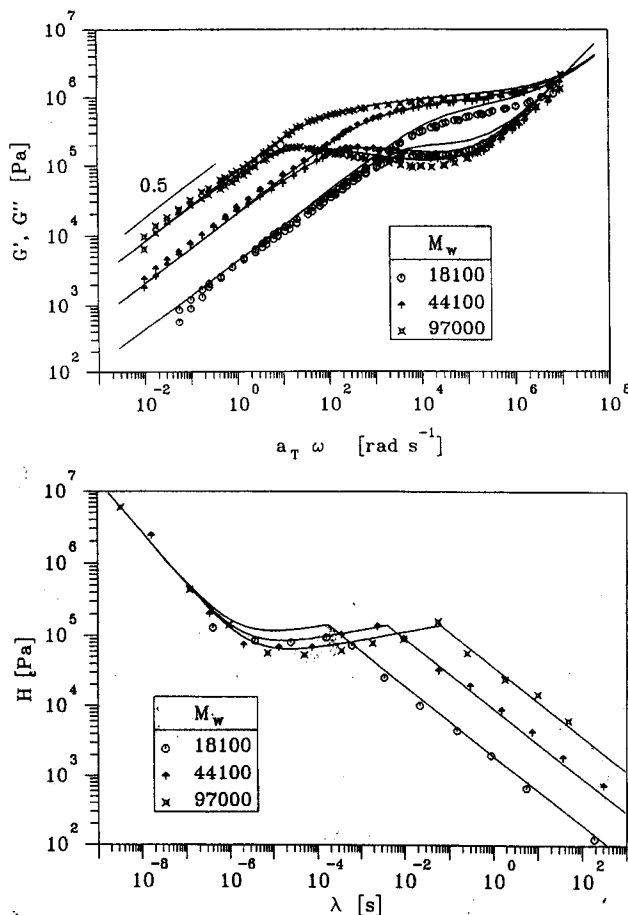


Fig. 12. a) Dynamic moduli of PBD18, PBD44, and PBD97 stopped samples near the critical gel point. The lines indicate the BSW-CW-model described in Eq. (23). b) Relaxation time spectra for stopped gel samples. The lines indicate the BSW-CW-model. Data are shifted to the reference temperature at 28 °C

4. Discussion

Relaxation spectrum of bulk precursor molecules

It has been previously reported that the relaxation time spectrum for linear flexible polymers of narrow molecular weight distribution can be represented by the BSW-spectrum (Baumgaertel et al., 1990). To rheologically characterize the bulk, i.e., uncrosslinked precursors, a BSW analysis was performed on each of the samples. The characteristic material parameters used for these data are given in Table 4.

For the undiluted precursors, the longest relaxation time scales with the molecular weight as

$$\lambda_{max} = \lambda_c \left(\frac{M}{M_c} \right)^z, \tag{11}$$

Table 4. BSW parameters for polybutadiene precursor polymers

BSW parameter	Parameter value
G_N^0 [Pa]	1.65 E + 6
n_e	0.23
n_g	0.73
λ_c [s]	4.04 E - 7
M_c [g/mole]	2714
z	3.52

where the exponent z is commonly found to be about 3.4 (Ferry, 1980), M is the molecular weight, M_c is the crossover molecular weight at which the scaling of the zero shear viscosity with M changes from the first to the 3.4th power, and λ_c is the crossover time. The details of the BSW analysis of the bulk polybutadiene samples has been recently reported (Jackson et al., 1994).

Relaxation spectra of diluted precursors molecules

The initial sample, before crosslinking, is actually a solution of precursor in the low molecular weight crosslinker. The crosslinker has a plasticizing effect which causes a vertical and horizontal shift of the data (see Fig. 2). Plasticization lowers the plateau modulus and shifts the value of λ_{max} and λ_c to shorter times due to the increased molecular mobility. This shifting must be taken into account to obtain BSW parameters for the diluted sample before crosslinking so that the crosslinked samples can be compared to the diluted initial state, not to the bulk precursors.

It was observed that the shape of the dynamic data and the relaxation spectra are not changed for samples with stoichiometrically balanced amounts of crosslinker in them. Thus, only a simple vertical and horizontal shift is applied to the data to account for the plasticization effect. Only at much lower concentrations of polymer (high solvent content) would the shape of the spectra be expected to change (Raju et al., 1981; Colby et al., 1991).

The vertical shift can be accounted for by examining the concentration dependence of the plateau modulus. The plateau modulus for bulk polymers is given as (Ferry, 1980)

$$G_N^0 = \frac{\rho RT}{M_e}, \tag{14}$$

where ρ is the density and M_e is the molecular weight between entanglements. Diluting the sample with solvent decreases the entanglement density. Consequently, M_e increases with increasing dilution. Therefore, for concentrated solutions, M_e should be proportional to ρ/c . The plateau modulus of the diluted polymer $G_{N,d}^0$ can be expressed in terms of the plateau modulus and molecular weight between entanglements of the bulk polymer (G_N^0 and M_e) as (Graessley, 1974; Ferry, 1980)

$$G_{N,d}^0 = \frac{c^2 RT}{M_e \rho} = v^2 G_N^0, \quad (15)$$

where the volume fraction $v = c/\rho$. This quadratic relation, v^2 , is very close to the proposal of deGennes (1976) who found that $G_{N,d}^0$ should be proportional to $c^{9/4}$. It has been found for concentrated solutions ($c > \sim 0.25$ g/ml) of several polymers that G_N^0 is closely proportional to c^2 (Nemoto et al., 1972; Masuda et al., 1972; Graessley, 1974). Several other systems have shown that the concentration dependence of G_N^0 is slightly higher with values from 2.2–2.3 (Riande et al., 1975; Isono et al., 1978). Further work needs to be done in this area. For this study, Eq. (15) was used to account for the shift in G_N^0 .

Like M_e , the crossover molecular weight also increases with dilution and is proportional to v^{-1} . Experimentally, the relationship between M_c of the diluted polymer ($M_{c,d}$) and the bulk polymer (M_c) has been found for several polymers to be (Nakagasu and Fox, 1960; Berry and Fox, 1968; Graessley, 1974):

$$M_{c,d} = \frac{M_c}{v}. \quad (16)$$

Combining this relationship with Eq. (11) reduces the longest relaxation time for the diluted sample as

$$\lambda_{\max,d} = \lambda_c \left(v \frac{M}{M_c} \right)^z, \quad (17)$$

and the crossover time shifts by the amount v^z to give

$$\lambda_{c,d} = \lambda_c v^z. \quad (18)$$

The shifting of the BSW-spectrum for the diluted samples can now be expressed as

$$H_d(\lambda) = n_e G_{N,d}^0 \left[\left(\frac{\lambda}{\lambda_{\max,d}} \right)^{n_e} + \left(\frac{\lambda}{\lambda_{c,d}} \right)^{-n_g} \right], \quad (19)$$

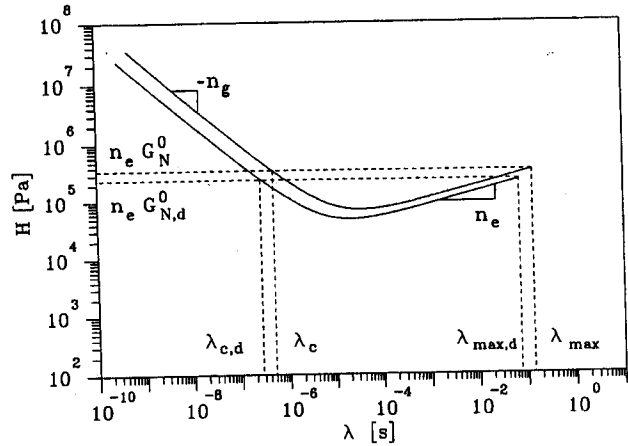


Fig. 13. Comparison of the schematic representations of the BSW-spectrum for the undiluted (upper curve) and diluted (lower curve) precursors. When the sample is diluted, λ_{\max} and λ_c are shifted to shorter times while G_N^0 is shifted downward. For high concentration of polymer, the shape is retained (i.e., n_e and n_g remain the same)

or in terms of the original parameters (before dilution) and the volume fraction v as

$$H_d(\lambda) = n_e v^2 G_N^0 \left[\left(\frac{\lambda}{v^z \lambda_{\max}} \right)^{n_e} + \left(\frac{\lambda}{v^z \lambda_c} \right)^{-n_g} \right]. \quad (20)$$

A schematic of the BSW spectrum for the diluted precursors compared to the undiluted precursor is shown in Fig. 13.

The BSW parameters for the diluted samples were determined by using the parameters for the bulk uncrosslinked samples (Jackson et al., 1994). The value of v shown in Eqs. (15) and (17) was optimized to fit the data. A value of v equal to 0.85 results in the best fit of the data. The value of v calculated from the amounts of crosslinker and precursor used was 0.87. The discrepancy between the two values of volume fraction is only 1.9%. Once the adjustments were made to the BSW parameters to account for the diluent, the single set of parameters was used for all of the diluted PBD samples. These values are given in Table 4. Figures 3 and 4 show a comparison of the BSW-spectrum for the diluted samples described in Eq. (19) and the data for six PBD precursors mixed with stoichiometric amounts of crosslinker.

Evolution of rheological properties during crosslinking

By adding chemical crosslinks, the longest relaxation time increases and the relaxation behavior in the

terminal zone slows down dramatically. Such an effect was observed by Valentine et al. (1968) for polybutadienes vulcanized with sulfur. The slopes of G' and G'' decrease (from 2 and 1, respectively) and approach 0.5 near the gel point, see Figs. 10a and b. Beyond the gel point, the storage modulus G' , levels off at low frequencies.

At increasing extents of reaction, the data sets show a small but systematic increase of the plateau modulus of G' and a small decrease in the slope of G'' in the entanglement regime. This phenomenon may be due to several factors. First, as the reaction proceeds, some of the crosslinker molecules attach to the PBD chains and lose their plasticizing effectiveness. Therefore, the effective solvent concentration of the solution decreases and according to Eq. (15), the plateau modulus increases. Second, the plateau modulus may increase due to trapped entanglements. In fully cured samples, chemical crosslinks add to the physical entanglements which results in an equilibrium modulus which is higher than the plateau modulus of the uncrosslinked material (Aranguren and Macosko, 1988; Dossin and Graessley, 1979). Experimental problems give rise to additional uncertainty since stopped samples past the gel point become difficult to load into the rheometer so that they completely fill the entire gap between the plates. Incomplete filling of the gap would result in an apparent lowering of the measured dynamic moduli.

The slope of G'' in the entanglement regime was observed to decrease from 0.23 to 0.12. The loss modulus in the onset to the glass transition region is primarily unaffected by chemical crosslinks up to and just past the gel point.

At the highest conversion of the reaction, it was observed that the equilibrium modulus was approximately 2 MPa higher than that of the plateau modulus of the uncrosslinked bulk precursors. Such results have also been reported by Aranguren and Macosko (1988). Figure 10e shows the evolution of the relaxation time spectrum, $H(\lambda)$, during crosslinking for PBD18 at increasing extents of reaction. The spectrum develops modes of relaxation at times longer than $\lambda_{\max,d}$ of the uncrosslinked precursor as the extent of reaction increases. This trend continues up to and through the gel point.

Effect of high precursor molecular weight on gel point detection

In order to observe the onset of gelation by CFS, the terminal zone of the precursor must fall within the experimental frequency window. For precursors of

low molecular weight (i.e., $M_w < M_c$) (Chambon and Winter, 1985, 1986, 1987; Adolf and Martin, 1990; Scanlan and Winter, 1991; Holly et al., 1988; Muller et al., 1991; Izuka et al., 1992; Lairez et al., 1992), detection of the gel point was easy because the terminal zone was readily accessible and no entanglement effect could interfere.

For gel point detection, each of the PBD samples appears to have an upper frequency limit depending on the molecular weight of the precursor denoted by $\omega_0 \sim 1/\lambda_0$ (Scanlan and Winter, 1991). This upper limit is approximately at the G' , G'' crossover point in the terminal zone for the unreacted precursor. Probing frequencies higher than this limiting value using CFS will result in data shown in Fig. 8b.

For PBD97, CFS is unable to detect the gel point because the lowest frequencies of this experiment are still above the limiting value which is 30 rad/s for PBD97 and crosslinker. The lower limit is determined by the limitations of the rheometer motor, sensitivity of the transducer at low frequencies, and the kinetics of the reaction. The terminal zone with the self-similar relaxation dynamics was not accessible. Samples with an exceedingly high initial molecular weight before crosslinking require experimental frequencies which are so low that the time for taking a single rheological data point would exceed the gel time. Here, the limiting molecular weight is about 70000 to 80000 g/mole. We have recently reported the effect of precursor molecular weight on gel point detection for this system (De Rosa and Winter, 1993).

The relaxation time spectrum at the gel point

The dynamic moduli of samples PBD18, PBD44, and PBD97, stopped close to the critical gel point, clearly show three regions of viscoelastic behavior, Fig. 12a. At long times, G' and G'' are nearly parallel and their slopes are close to 0.5. The same behavior was found for samples PBD38 and PBD70 stopped near the gel point.

The same three viscoelastic regions can be seen in $H(\lambda)$. Figure 12b shows $H(\lambda)$ for the dynamic data in Fig. 12a. From these data it is evident that the entire spectrum can be described by three power laws. The short and intermediate time represent the glass and entanglement region and the long time represents the critical gel behavior. It was surprising to see that the entanglement region changes so little during the initial crosslinking period.

Data obtained from stopped samples reveals something quite important about the rheological behavior of critical gels with entanglements. As the

molecules are crosslinked and become longer, one might expect that the plateau zone (entanglement region) may extend out to lower frequencies as it does for higher molecular weight precursors shown in Fig. 1. However, this does not occur and the entanglement regime remains approximately the same length even though the molecules are getting longer. This may be explained in the following manner.

A critical gel consists of many different species of molecular clusters: precursor molecules, dimers (two precursor molecules), trimer, tetramers, etc., and one largest cluster that spans the entire sample size with an infinite relaxation time and molecular weight. Flory (1953) and Stockmayer (1943) have reported statistical results for the weight fraction of each of these species at different extents of reaction or degrees of crosslinking. They have shown that as the gelation process proceeds, the weight fraction of the monomer is always greater than that of any one of the other species up to the gel point. Shortly after the gel point, the weight fraction of the infinite cluster rises sharply as crosslinking continues until it becomes larger than any other species in the sol. Therefore, at the gel point, the precursor molecules are still the most abundant species and they will ultimately dominate the rheological behavior. Thus, the length of the plateau region would be determined by the precursor molecule and thus remains approximately the same length.

A related molecular weight effect has been observed in a study by Watanabe and Kotaka (1984) with blends of entangled monodisperse polymers of different molecular weight. In the simplest case of binary blends of a 36000 g/mole polystyrene blended with smaller weight fractions of a 407000 g/mole polystyrene, they found that the dominating relaxation behavior came from the polymer with the highest weight fraction. The frequency range of the plateau in G' was found to be essentially the same length even when up to 20% of the high molecular weight polystyrene was blended in. The higher molecular weight polymer only affected the long relaxation time behavior well within the terminal zone of the small molecular weight polymer.

Effect of stoichiometry on S and n

The effect of stoichiometry on the critical gel properties has been reported for several endlinking systems. In each case the stoichiometric ratio, r , had a significant effect on the critical gel stiffness, S , and the relaxation exponent, n . Winter et al. (1988) reported for an endlinking polypropylene oxide that the

gel strength was sensitive to small variations in r . They reported that for $0.5 < r < 2.0$, S increased approximately by 1.5 decades from ≈ 500 to 20000 Pa s ^{n} . Scanlan and Winter (1991) observed for an endlinking PDMS that S varied by about 1 decade from ≈ 100 to 1000 Pa s ^{n} for a low molecular weight precursor and from ≈ 8000 to 50000 Pa s ^{n} for a higher molecular weight precursor above M_c for $0.5 < r < 3.0$. S appeared to be sensitive to a crosslinker deficiency (i.e., $r < 1$) and insensitive to an excess of crosslinker. Izuka et al. (1992) found that for an endlinking polycaprolactone that S ranged from about 100 to 19000 Pa s ^{n} for $0.61 < r < 1.76$.

In this study, we found that the gel stiffness is relatively insensitive to stoichiometric ratio. In Fig. 9, S is shown for PBD18 to vary from 980 to 3200 Pa s ^{n} over the range of $0.25 < r < 3.0$. S was found to decrease for an excess amount of crosslinker. For PBD38 S varied from 6000 to 21000 Pa s ^{n} over the same stoichiometric ratio range.

This type of effect of r on S is quite different from that observed for studies using endlinking systems where large changes in S were observed for relatively small changes in r . Interestingly, the effect of r on S found in this study resembles that of the effect of a diluent on S for gels. Scanlan and Winter (1991) studied S as a function of the concentration of inert medium-length and high-length PDMS chains mixed into crosslinking PDMS as diluents. Their results show that S decreases by less than one decade up to about 30 to 40% diluent at constant r .

Since our results show the same trend as those found for diluted PDMS, we may be experiencing the same type of diluting effect. The source of diluent in our system comes from the unreacted crosslinker at the gel point. Since the functionality of the precursors is so high, a significant amount of crosslinker must be added to reach conditions of $r \geq 1$. For $r = 1$, 12% by weight of crosslinker must be added. For $r = 3$, the amount of crosslinker needed was 28% by weight. Flory-Stockmayer theory (1953) shows that as functionality of the precursor increases, the percent conversion needed to reach the gel point decreases. For our samples at $r = 1$, only 10–20% of the silane needs to be converted to reach the gel point. Therefore, most of the crosslinker is still unreacted at the gel point and is acting as a diluent. This trend of results qualitatively resembles our data even though Scanlan used unreactive polymers as a diluent and our diluent is a small molecule.

Studies with endlinking systems have shown that the relaxation exponent, n , is sensitive to stoichiometry. Winter et al. (1988) found that for endlinking

polypropylene oxide that n was between $1/2$ and $2/3$ for a crosslinker deficiency ($r < 1$). For an excess of crosslinker ($r > 1$), n was found to be insensitive to r with a value of $1/2$. Scanlan and Winter (1991) found for an endlinking PDMS that n was also sensitive for $r < 1$. For a low molecular weight precursor they found $0.5 < n < 0.7$. For $r \geq 1$, n was observed to be about 0.5 . For a high molecular weight precursor, they found $0.2 < n < 0.4$ for $r < 1$. n was constant at 0.3 for $r > 1$. Recently, Izuka et al. (1992) found exponents in the range of $0.3 < n < 0.67$ over a stoichiometric range of $0.61 < r < 1.76$ for endlinking polycaprolactone with no constant value of n found for any stoichiometric range. Muller et al. (1991) reported $n = 0.5$ for $r \geq 1$ and $n = 2/3$ for $r < 1$ for endlinking polyethylene oxide.

The results of our study show that for five different precursor molecular weights crosslinked with stoichiometric ratios in the range of $0.25 < r < 3.0$ the relaxation exponent was found to be $0.41 < n < 0.52$. The values of n found are close to 0.5 as has been observed by others. However, we did not find n to be sensitive to the stoichiometric ratio. In fact, n was found to be quite constant over the stoichiometric range used.

The same insensitivity of n to r has also been observed in diluent studies of critical gels. Scanlan and Winter (1991) found that n is insensitive to the concentration of diluent of medium and long length chains up to some weight percent of diluent. For a medium length chain diluent, n remained close to 0.45 up to 30% diluent. For long length chain, n remained close to 0.35 up to 50% diluent. At higher concentrations of diluent, n was observed to increase approaching a value of 1 as the diluent approached 100% concentration.

Qualitatively, we see this type of trend in the exponent of our system. However, we did not observe any increase in n at higher concentrations of crosslinker. Though it appears that we used a wide range of stoichiometric ratios for our study, we did not examine samples over the entire possible range of stoichiometric ratios described by Flory (1953) for successfully reaching the gel point. Due to the high functionality of the precursor molecules the stoichiometric "window" is quite large, from 0.043 to 22.8 for PBD18 and from 0.007 to 133 for PBD97. Our values of r , used from 0.1 to 3 , are only a fraction of this large range and could be a reason why the critical exponent and the gel strength were close to being independent of r . It would be almost impossible to successfully measure samples with r much greater than 4 because the crosslinker concentration would be

so high that the viscosity of the mixture would be too low to measure with our rheometer.

Maybe this dilution effect can be avoided by using some other type of crosslinking mechanism such as peroxide or u. v. curing agent. In this case only a small amount of crosslinking agent would need to be introduced to crosslink the sample and the diluent effect could be removed. However, the control over stoichiometry would be lost.

Precursor molecular weight dependence of S

It has been reported that the precursor molecular weight influences the gel stiffness (Chambon et al., 1986; Scanlan and Winter, 1991; Izuka et al., 1992). Chambon et al. (1986) found that for three endlinking polypropylene oxide precursors of different molecular weight all below M_c , the gel strength decreased with increasing precursor molecular weight. It was proposed that this result was due to the fact that as the precursor molecular weight increases for an endlinking process, the crosslink density decreases. Thus, this would result in a softer gel and, consequently, a lower gel strength (Chambon et al., 1986). It should be noted that the experiments were performed near the glass transition temperature and that there might have been interference.

This trend was found to be just the opposite as the molecular weight of the precursors becomes high enough to contain physical entanglements. In the study by Scanlan and Winter (1991) one precursor molecular weight was below M_c and the other approximately $5 \times M_c$. They found that S for the higher molecular weight precursor was about 1 order of magnitude higher than that of the lower molecular weight precursor. Scanlan and Winter speculatively attributed this effect to the presence of physical entanglements (Scanlan and Winter, 1991).

A similar result was reported by Izuka et al. (1992) who studied gelation for five precursor molecular. Two were just below M_c , the other three were slightly above M_c .

For all precursors it was found that the gel strength increased with increasing molecular weight at constant r .

In this study, we have also found that the gel strength increases with increasing precursor molecular weight. Qualitatively, this trend agrees with those reported in the previous studies mentioned (Scanlan and Winter, 1991; Izuka et al. 1992). However, we have found that the value of S increases with the precursor molecular weight in a well behaved manner that can be described by a scaling relationship. Figure 17

shows the values of S determined by CFS and for stopped samples versus precursor molecular weight. The slope of these power laws have experimentally been found to be 1.76 and 1.81 for CFS and stopped sample data respectively by linear regression. A derivation of an expression has been worked out in the next section that describes this scaling relationship.

Empirical relaxation time spectrum for highly entangled critical gels

A change in notation has to be introduced at this time. The longest relaxation time of the precursor molecule (λ_{\max} in table 4) will be called λ_p and it will serve as a reference time scale for describing the evolving molecular dynamics during crosslinking. λ_p actually is the longest relaxation time at the onset of crosslinking, but the actual λ_{\max} of the crosslinking sample will exceed λ_p as the molecular weight increases. Much beyond the gel point the relaxation time will come down again and eventually will be lower than λ_p since more and more of the relaxing species will crosslink into the permanent network.

For the following data analysis, we propose a simple framework which captures the essential features of the observed spectra. More detailed analysis will have to follow. For getting started, we realize that the spectrum of the precursors is hardly changed at all by the crosslinking, but that a long time tail is added which follows the CW-spectrum characteristics. In the simplest case, we would add a Chambon-Winter spectrum to the BSW-spectrum of the diluted samples. This spectrum can be represented as

$$H(\lambda) = \begin{cases} n_e G_{N,d}^0 \left[\left(\frac{\lambda}{\lambda_{p,d}} \right)^{n_e} + \left(\frac{\lambda}{\lambda_{c,d}} \right)^{-n_g} \right] & \text{for } 0 < \lambda < \lambda_{p,d} \\ n_e G_{N,d}^0 \left(\frac{\lambda}{\lambda_{p,d}} \right)^{-n} & \text{for } \lambda_{p,d} < \lambda < \infty \end{cases} \quad (21)$$

Figure 14 shows a schematic representation of the spectrum in Eq. (21).

The short time limit for power law behavior denoted by λ_0 in Eq. (3) occurs at the onset of the rubbery regime for entangled polymers, $\lambda_0 \equiv \lambda_{p,d}$. For precursors of molecular weight below M_c , this value would indicate the time for the crossover to the glass transition since no physical entanglements are present. This effect has been discussed by Scanlan and Winter (1991) for an endlinking PDMS polymer. For

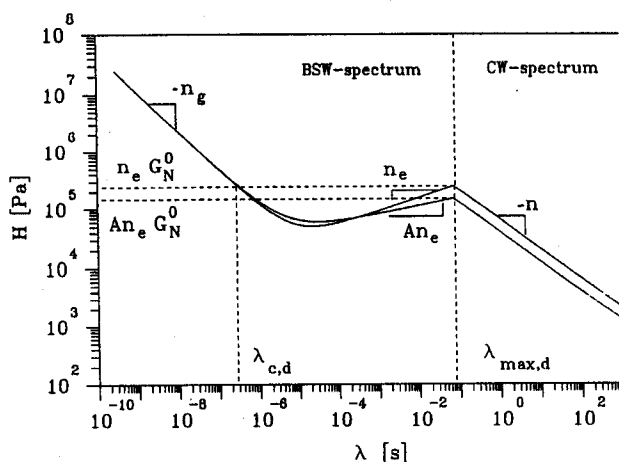


Fig. 14. Schematic representation of the gel spectra indicated by Eq. (21), with slope n_e at intermediate times, and Eq. (22), with slope An_e at intermediate times

entangled polymers, λ_0 is equal to the longest relaxation time of the precursor.

The simple framework, Eq. (21), allows us to analyze the entanglement region in greater detail, Fig. 15. The slope n_e actually decreases from 0.23 to 0.12 during the initial crosslinking period up to the gel point. The change in slope might be due to the broadening of the molecular weight distribution.

A better fit of the data can be achieved by accounting for the change in slope in Eq. (21). The form of the relaxation spectrum with entanglements can then be written as

$$H(\lambda) = \begin{cases} n_e G_{N,d}^0 \left[A \left(\frac{\lambda}{\lambda_{p,d}} \right)^{An_e} + \left(\frac{\lambda}{\lambda_{c,d}} \right)^{-n_g} \right] & \text{for } 0 < \lambda < \lambda_{p,d} \\ n_e G_{N,d}^0 A \left(\frac{\lambda}{\lambda_{p,d}} \right)^{-n} & \text{for } \infty > \lambda > \lambda_{p,d} \end{cases} \quad (22)$$

The slope of the entanglement regime is equal to An_e , where A is an empirical constant between 0 and 1. Here, we find a value of $A = 0.52$ fits best. For the uncrosslinked samples $A = 1$. Figure 14 shows a comparison of the schematic representation of the spectrum in Eq. (22) to the spectrum in Eq. (21). Figure 16 shows a comparison of the dynamic data of PBD97 stopped near the gel point to the model represented by Eq. (22). The parameters of the spectrum for the critical gel model are given in Table 5.

From Eq. (3) it has been found here for entangled gels that λ_0 is the longest relaxation time of the

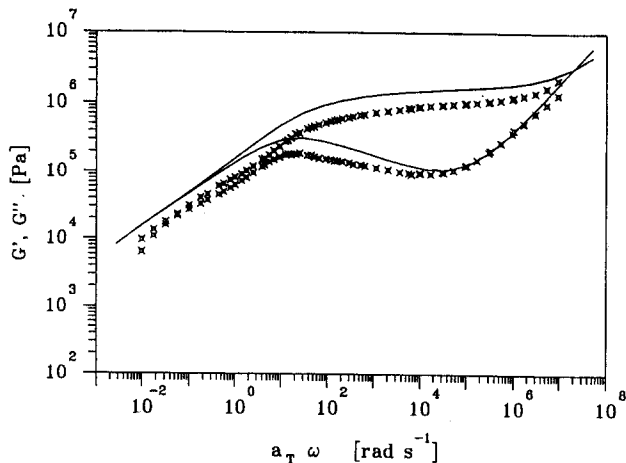


Fig. 15. Comparison of PBD97 critical gel dynamic data with BSW-CW-spectrum of Eq. (21). $T_{ref} = 28^\circ\text{C}$

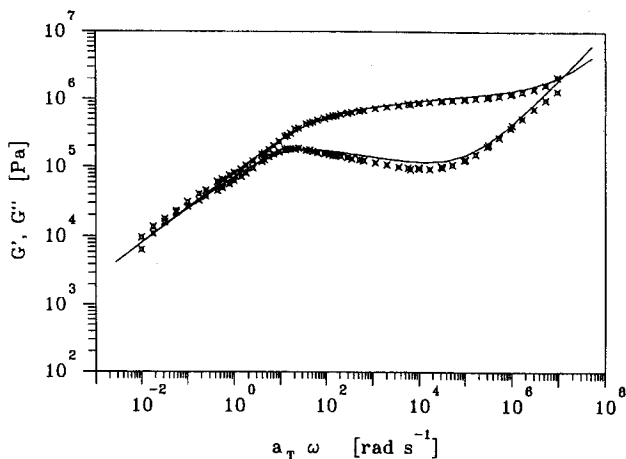


Fig. 16. Comparison of PBD97 critical gel dynamic data with BSW-CW-spectrum of Eq. (22). $T_{ref} = 28^\circ\text{C}$

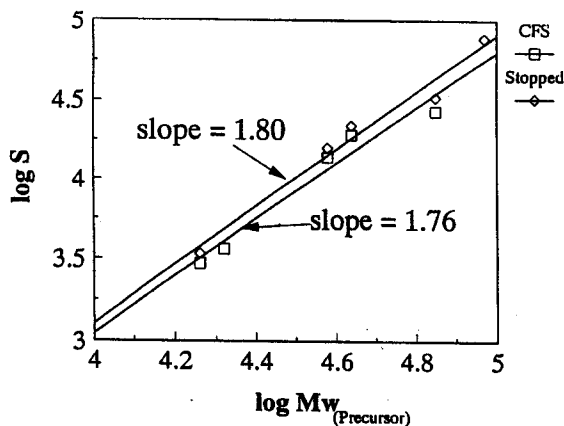


Fig. 17. Gel stiffness vs. precursor M_w relationship calculated from CFS and stopped sample data. The slopes of the fits give exponents of 1.76 and 1.81 respectively

Table 5. Parameters for the BSW-CW gel model

BSW-CW parameter	Parameter value
G_N^0 [Pa]	1.20 E+6
A	0.52
n_e	0.23
n_g	0.73
n	0.5
λ_c [s]	2.31 E-7
M_c [g/mole]	2714
z	3.51

diluted precursor ($\lambda_{p,d}$). By using Eq. (22), G_0 is given by

$$H = \frac{G_0}{\Gamma(n)} \left(\frac{\lambda}{\lambda_0} \right)^{-n} = A n_e G_N^0 \left(\frac{\lambda}{\lambda_{p,d}} \right)^{-n}, \quad (23)$$

which can be rearranged to give G_0 as

$$G_0 = A n_e G_N^0 \Gamma(n). \quad (24)$$

With the parameters in Table 5, G_0 is $2.55 \text{ E} + 5 \text{ Pa}$. It marks the upper limit of the power law of the gel at time $\lambda_{p,d}$.

The relaxation exponent n was found to be very close to 0.5 for all precursor molecular weights at all values of r studied. Therefore, as shown in Fig. 12 b, $H(\lambda)$ of the critical gels in the terminal zone will be a set of power law spectra with the same slope (i.e., n). From Eq. (21), we proposed that the CW-spectrum intersects the BSW-spectrum at λ_0 (i.e., $\lambda_{p,d}$). For critical gels of two different molecular weights, the value of H at the intersection point is the same

$$A n_e G_N^0 = H = \frac{S_1}{\Gamma(n)} \lambda_1^{-n}, \quad (25)$$

$$A n_e G_N^0 = H = \frac{S_2}{\Gamma(n)} \lambda_2^{-n}, \quad (26)$$

where λ_1 and λ_2 are $\lambda_{p,d}$ of precursors 1 and 2 of different molecular weights. The ratio of the S -value depends on the characteristic times

$$\frac{S_1}{S_2} = C \left(\frac{\lambda_1}{\lambda_2} \right)^n, \quad (27)$$

where C is a constant. The characteristic times grow with the z th power of molecular weights. This gives us the molecular weight dependence of the gel stiffness:

$$S \sim M^{zn} \quad (28)$$

A value of n equal to 0.5 and z equal to 3.51 will give a predicted exponent of 1.76 which is in excellent agreement with our experimental results found of 1.76 and 1.81 for CFS and stopped sample data, respectively.

5. Conclusions

The hydrosilation cure of monodisperse polybutadiene chains with a bifunctional silane crosslinker provides us with an ideal model system. By using precursors of narrow molar mass distribution, we are able to start out with the well known self-similar rheological behavior of the uncrosslinked material described by the BSW-spectrum. Added diluent in the form of the crosslinker must be taken into account to correct for the shift in the BSW-spectrum due to plasticization before crosslinking occurs. The parameters of the precursor and crosslinker BSW-spectrum can then serve as a reference for the critical gel behavior.

The typical self-similarity of the relaxation behavior in the terminal zone was observed for entangled polymers as was previously seen for several other systems without entanglements. It was found that the relaxation time spectrum of the critical gel with entanglements can be well-represented by a superposition of the BSW-spectrum and CW-spectrum with only minor modifications to be made in the entanglement region. The critical exponent, n , was found to be independent of precursor molecular weight over a range of stoichiometric ratios. The gel stiffness, S , was found to increase with the precursor molecular weight with a new scaling relationship.

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