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Terminal Relaxation of Model Poly(dimethylsiloxane) Networks with Pendant Chains

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ABSTRACT: Stress relaxation of model poly(dimethylsiloxane) networks with pendant chains and nearly constant cross-linking density was studied. The networks were obtained by end-linking a mixture of long chains bearing terminal reactive groups with a trifunctional cross-linker. Long poly(dimethylsiloxane) chains in the initial mixture contain 90 wt % of difunctional molecules with reactive groups at both ends and 10 wt % of monofunctional chains with a single reactive terminal group located in one of their ends. Difunctional chains will be mainly elastically active chains after cross-linking while monofunctional chains will remain as long pendant molecules. The fitting of the experimental stress relaxation values to the classic Chasset−Thirion equation shows a strong dependence of the exponent on the molecular mass distribution of the pendant chains. From these results, a new model for the terminal relaxation of elastomers is proposed, taking into account the molecular mass distribution of pendant chains. The dynamics of polymer networks in the terminal relaxation zone is modeled considering the reptation theory. In the terminal zone, the proposed model behaves similarly to the Chasset−Thirion equation. The model adequately describes the behavior of networks synthesized by end-linking. On the other hand, when applied to different networks, it leads to similar conclusions as previous theories developed for networks obtained by random cross-linking.

Introduction

It is well-known that chain branches, such as those present in star polymer melts and dangling chains in polymer networks, dramatically modify the classical reptation picture. For the kind of chains that we are considering, branching points prevent the reptation (motion along the confining tube). Star arms or pendant chains renew their configuration by retracting along their tube axes. The decrease in entropy can be explained by the diffusion of the chain end in a potential field. Since retraction is entropically unlikely, stress relaxation will be exponentially slower as the molecular weight of dangling chains or star arms increases.[1−3]

In the last few years, several models have been proposed in order to describe the relaxation of cross-linked polymer networks.[3−14] These models attribute the long time relaxation of elastomers to the slow diffusion of pendant chains by arm retraction. With these assumptions, a power law dependence with time is predicted at long relaxation times. However, current theories disagree in the dependence of the power law exponent on the degree of cross-linking.[12]

On the other hand, in the terminal zone, experimental data for the relaxation modulus can be represented by the empirical equation of Chasset and Thirion.[11]

$$G(t) = G_\infty\left[1 + \left(\frac{\tau_E}{t}\right)^m\right] \qquad (1)$$

In this equation, G_∞ is the equilibrium modulus, τ_E is a characteristic time, and m is a parameter which depends on the network structure. This equation was proposed by Chasset and Thirion in order to describe the behavior of networks obtained by random cross-linking. Experimentally, the dependence of m on the cross-linking density was studied by Ferry and Dickie.[13] In networks obtained by random cross-linking, the Chasset−Thirion exponent m was typically found to be a small number in the range 0.1−0.3. In these networks, stress relaxation rates are also known to strongly depend on cross-linking density.

It is important to emphasize that in random networks the power law relationship works well only over a limited time span and important deviations appear at long times in highly cross-linked polymer networks.[12] The modification in the dynamic behavior of random networks is not surprising, taking into account that both its structure and its content of defects change dramatically with the cross-linking density. While at low cross-linking densities the system contains long dangling chains and the effects of arm retraction and dynamic dilution[2] dominates the viscoelastic response, at high cross-linking densities the system contains principally short pendant chains and the dynamics is dominated by Rouse-like diffusion[1] and arm retraction in a fixed network.[6] On the other hand, some of the dynamic tests of previous works were carried out at temperatures not low enough to avoid thermal degradation.[11,13] In this case, the structure of the network could change continuously during the experiments. Then both changes in the dynamic behavior and changes in the structure could be responsible for a non-power-like behavior at long times.

Since networks obtained by random cross-linking result in a broad distribution of elastic and pendant chains, they are not very suitable for studies aiming to understand the relationships between the structure of pendant chains and the dynamic properties of polymer networks.[14] To study the influence of network defects

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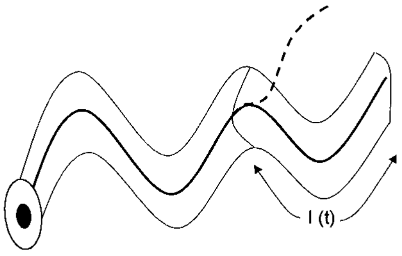

Figure 1. Schematic representation of the process of viscoelastic relaxation for a linear pendant chain in a network given by the diffusion of the chain free end.

on their properties, it is convenient to work with tailor-made systems that have a well-defined molecular structure. One of the most successful techniques to obtain networks with controlled amounts of defects is the end-linking technique.[16,17] With this procedure, by mixing long linear chains with reactive groups in one or both ends, it is possible to obtain networks with a controlled amount of linear pendant chains of uniform size. In particular, poly(dimethylsiloxane) networks offer thermal stability and a very good control of the molecular structure. By contrast with random networks, the end-linking system allows one to control both the amount and the length of pendant chains, while the cross-linking density remains constant.

According to de Gennes, the process of viscoelastic relaxation for a linear pendant chain in a network is given by the diffusion of the chain free end.[3] This process is accompanied by creation of a non-entangled loop. Estimating the probability of creation of an unentangled loop of N segments ($P(N)$), he found

$$P(N) = \exp(-\alpha N) \tag{2}$$

where α is a constant independent of the pendant chain length (N).

Then assuming that the time required to form the unentangled loop (τ_N) is inversely proportional to $P(N)$, de Gennes obtained

$$N \sim \frac{1}{\alpha} \ln\left(\frac{\tau_N}{\tau_0}\right) \tag{3}$$

where τ_0 is a characteristic time.

After a given time t, l segments, near the free end of the pendant chain, had been relaxed by diffusion (Figure 1). Then, for analogy with eq 3, the relationship between l and t is given by

$$l(t) \sim \frac{1}{\alpha} \ln\left(\frac{t}{\tau_0}\right) \tag{4}$$

Finally, de Gennes assumed that mechanical stress $\sigma_N(t)$ at time t is proportional to the number of segments that have not been retraced, given by $N - l(t)$:

$$\sigma_N(t) \sim N - l(t) = N - \frac{1}{\alpha} \ln\left(\frac{t}{\tau_0}\right) \tag{5}$$

From eq 5, it can be concluded that stress relaxes logarithmically in networks with long pendant chains.

On the other hand, several models have been proposed in order to explain the Chasset−Thirion behavior in networks obtained by random cross-linking. Considering the molecular mass distribution and a reptation mechanism for a pendant chain, those models show a power law form for stress relaxation experiments

Table 1. Molecular Characterization of the Linear Prepolymers and Other Reactants Used for the Preparation of Model PDMS Networks

polymer	M_n (Da) FTIR	M_n (Da) GPC	M_w (Da) LALLS	M_w (Da) GPC	M_w/M_n GPC
D_1	7900	7900		22 100	2.80
M_1	21 200	24 200	26 900	26 500	1.08
M_2	46 300	47 800	52 400	51 300	1.07
M_3	61 500	67 600	101 100	83 500	1.24
M_4	96 600	97 800	128 700	121 300	1.24
M_5		224 700	295 000	269 400	1.20

Cross-Linker: $(HSi(CH_3)_2O)_3Si\ C_6\ H_5$ (A_3)

Catalyst: *cis*-$(Pt((C_2H_5)_2S)_2Cl_2)$

$$\sigma_N(t) \sim t^{-m} \tag{6}$$

with $m \propto \mu^\delta$, where μ is the cross-linking density and δ depends on the model considered. For a randomly cross-linked network, using de Gennes analysis and taking into account the distribution of pendant chain lengths, Curro and Pincus[5] and Curro et al.[6] found $\delta = 1$. A later model, proposed by Thirion and Monnerie, found $\delta = {}^1/_3$.[7,8] In their model, Thirion and Monnerie modified the analysis of Curro−Pincus using the unentangled loop probability function calculated by Helfand and Pearson.[9] On the other hand, calculating the probability density for the maximum displacement of an one-dimensional continuous-time random walk with pausing-time distribution, Gaylord et al. found $\delta = 0$.[10,12] In this model, the exponent m is not explicitly related to the cross-linking density.

In this work, we analyze the terminal relaxation of PDMS model networks with pendant chains obtained by end-linking. First, we study the dependence of m with the average molecular mass of pendant chains and then a new model for the terminal relaxation is proposed.

Experimental Section

To clarify the dependence of m with network structure, model PDMS networks with controlled amounts of pendant chains were synthesized.

Model silicone networks were obtained by a hydrosilylation reaction. The reaction is based on the addition of hydrogen silanes from the cross-linker molecules to end vinyl groups present in the prepolymer molecules. A commercial difunctional prepolymer (D_2) and five nearly monodisperse monofunctional prepolymers (M_1 to M_5) were utilized.

The networks were prepared by reacting known amounts of the monodisperse linear molecules of different molecular weights bearing only one vinyl group at the chain end, a trifunctional cross-linker, and commercial difunctional prepolymer containing vinyl groups at both extremes of the chains.

Table 1 shows the results of the molecular weight characterization of the prepolymers, as well as a description of the other reactants used in the cross-linking reactions. In this table D_1 (United Chemical Technology Inc.) is the difunctional prepolymer and M_1−M_5 are the monofunctional prepolymers. Monofunctional molecules were synthesized by anionic polymerization using *n*-butyllitium as initiator and *n*-hexane as solvent.[15] Table 1 shows that the monofunctional prepolymers present a narrow molecular mass distribution. Phenyltris(dimethylsiloxy)silano (A_3) (Petrarch Systems, Inc.) was used as cross-linker and a Pt salt was employed as catalyst for the cross-linking reaction.

Table 2 shows the nomenclature and composition of the synthesized networks. In this table $M_{w_{B1}}$ and w_{B1} indicate the

Table 2. Nomenclature, Composition, Elastic Modulus at Low Frequency, and Chasset−Thirion Exponent Obtained from Fitting Experimental $G(t)$ Values

network	M_{wB1} (Da)	W_{B1}	r	$G'_{\omega\to 0}$ (MPa)	G_∞^f (MPa)	m
GP1F310	26 700	0.097	1.05	0.194	0.194 ± 0.01	0.77 ± 0.05
GP2F310	51 900	0.097	1.05	0.191	0.191 ± 0.01	0.46 ± 0.05
GP3F310	92 300	0.097	1.06	0.199	0.196 ± 0.01	0.16 ± 0.03
GP4F310	125 000	0.098	1.05	0.202	0.198 ± 0.01	0.12 ± 0.03
GP5F310	282 200	0.104	1.06	0.201	0.195 ± 0.02	0.05 ± 0.03

mass average molecular mass and the mass concentration of monofunctional chains (B_1) respectively, and r the stoichiometric imbalance (r = [A]/[B]).

Reactants were weighted in order to obtain stoichiometrically balanced mixtures, mixed with a mechanical stirrer and degassed under vacuum to eliminate bubbles. The reactive mixture was then placed between the plates of a Rheometrics Mechanical spectrometer. The cure reaction was carried out between the plates at 60 °C. After 24 h, final properties were measured. All measurements were carried out in simple shear dynamic and stress relaxation experiments with deformations of up to 10%, within the range of linear viscoelastic response. Details from sample preparations, network structure, characterization, and dynamic properties can be found in previous work.[16,17]

According to the modified rubber elasticity theory, the shear equilibrium modulus (G_∞) for networks prepared in bulk can be expressed as[18−20]

$$G_\infty = (\nu - h\mu)RT + G_e T_e \tag{7}$$

where ν is the density of elastically active chains, h an empirical parameter that can vary between 0 and 1, μ the density of cross-linking points, R the gas constant, and T the absolute temperature. T_e is the fraction of trapped entanglements in the network and G_e is the maximum contribution to the modulus due to trapped entanglements. It is expected that G_e should be close to G_N^0 (plateau modulus from experiments on linear chains). Theoretical calculations as well as experimental measurements indicate that $G_e \sim 0.8G_N^0$.[4,21]

Table 2 shows the elastic modulus in the low-frequency limit G_0' ($\omega \to 0$) at T = 273 K. This polymer system is rheologically simple and the time−temperature superposition principle was verified in the temperature range analyzed. Similar behavior was previously found in other poly(dimethylsiloxane) networks.[16]

The elastic modulus of the different networks was found to be nearly constant (the variations are smaller than 4%). Then, assuming that variations in ν, h, G_e, and T_e in the different networks are small, it is reasonable to suppose that μ is nearly constant.

Figure 2 shows master curves of stress relaxation modulus, $G(t)$, as a function of time at the reference temperature (273 K). Although more decades in time were analyzed, experimental values are not included in this study because at long times the signal becomes very noisy, probably as a consequence of baseline fluctuations. The networks prepared with almost constant cross-linking density exhibit relaxation times that rise with an increase in the molecular mass of monofunctional chains.

Figure 3 shows experimental values of relaxation modulus ($G(t)$) as a function of time (t) for the network labeled as GP2F310 and the fitting results corresponding to the Chasset−Thirion model (eq 1). In this figure we can see that experimental data are in good agreement with eq 1. Similar results were obtained for all the networks studied.

The Chasset−Thirion exponent m obtained by least-squares fit of experimental data are shown in the last column of Table 2. The value of m diminishes considerably with the increase in the average molecular mass of the monofunctional chains (pendant chains).

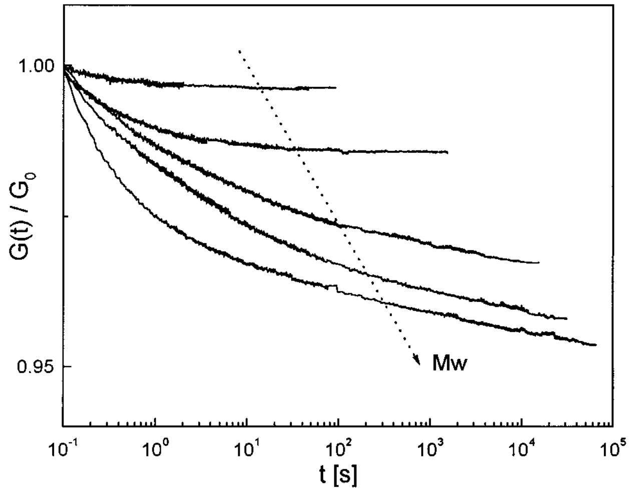

Figure 2. Master curves of stress relaxation modulus ($G(t)$) as a function of time at reference temperature (T_0 = 273 K). The parameter corresponds to the average molecular weight of monofunctional chains added to the networks.

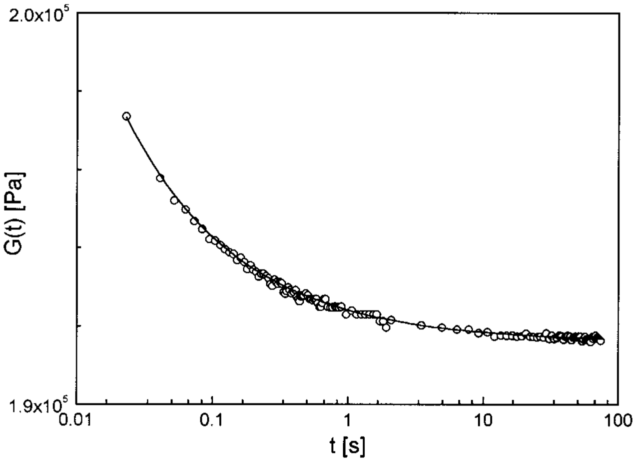

Figure 3. Experimental values of relaxation modulus ($G(t)$) as a function of time for the network labeled GP2F310 (open circles) and the fitting results corresponding to the Chasset−Thirion model (solid line).

The values of the equilibrium relaxation modulus obtained from the curve fitting procedure (G_∞^f) are also included in Table 2. Since the networks analyzed in this work have a content of pendant chains of approximately 10 wt %, the difference between the equilibrium modulus determined from the low-frequency limit of the dynamic experiments and G_∞^f is very small (less than 3%). When the molecular weight of the pendant chains increases, it is more difficult to precisely determine the exponent m. In this case, small variations of G_∞^f produce important changes in m values (approximately 40% for network GP5F310). McKenna and Gaylord[12] found similar results in random networks with $m \approx 0.1$, where the value of m obtained from the curve fitting was very sensitive to the values of G_∞^f. On the other hand, the relative error in the determination of the exponent m decreases when the molecular weight of the pendant chains decreases.

Theory

In this work, network dynamics is described by a new model based on tube renewal following the approach proposed by Curro and Pincus.[5] Although the initial model proposed by de Gennes neglects the effect of molecular weight on the factor τ_0, as it was shown by the theory of Pearson and Helfand, the dependence of τ_0 with the molecular weight is small (power law). Then, as a first approximation, we assume that τ_0 does not depend on the molecular weight of the pendant chains. The proposed model considers that eq 5 is valid only for times smaller than τ_N with a distribution of molecular mass of the pendant chains similar to the experimental one.

To analyze the dynamic of networks with pendant chains, we assume that the contribution of a pendant chain of N segments to the mechanical stress is given by eq 5 only for times smaller than τ_N ($t \leq \tau_N$). Then

$$f_N\,(t) \sim \begin{cases} N - (1/\alpha)\ln(t/\tau_0) & \text{for } t \leq \tau_N \\ 0 & \text{for } t > \tau_N \end{cases} \qquad (8)$$

or

$$f_N(t) \sim \left[N - \frac{1}{\alpha}\ln\left(\frac{t}{\tau_0}\right)\right]H(\tau_N - t) \qquad (9)$$

where τ_0 is a characteristic time of the system and $H(\tau_N - t)$ is the Heaviside function (step function).[22] For a lattice model, Pearson and Helfand found that α depends only on the lattice coordination number, q:[9]

$$\alpha = \frac{1}{2}\ln\left[\frac{q^2}{4(q-1)}\right] \qquad (10)$$

Equation 3 implies that the complete renewal time τ_N depends exponentially on the number of segments N

$$\tau_N = \tau_0 \exp(\alpha\, N) \qquad (11)$$

A network generally contains a distribution of pendant chain lengths. Then, to obtain the relaxation modulus, we must average over all pendant chain lengths

$$G(t) = G_\infty + (G_0 - G_\infty)\int_0^\infty f_N(t)\, P_N\, \mathrm{d}N \qquad (12)$$

where the constant $(G_0 - G_\infty)$ is assumed to be proportional to the mass fraction of pendant chains and P_N is the probability of having a pendant chain of N segments.

Generally, the distribution of pendant chain lengths cannot be determined. However, in model networks obtained by end-linking, it is possible to obtain a good control of network structure.[14] In a previous work, Villar et al. analyzed, by mean field theory, the structure of networks obtained by terpolymerization of a multifunctional cross-linker A_f and monofunctional and difunctional linear chains, B_1 and B_2, respectively.[23] For stoichiometrically balanced networks, at the maximum extent of reaction, pendant chains are constituted exclusively by the monofunctional linear chains B_1. On the other hand, at intermediate extents of reaction, a considerable amount of difunctional chains B_2 may be present in the pendant material.

Despite all the care taken in the preparation of the networks, a small fraction of the B_2 chains may remain as pendant chains due to incomplete reaction. The presence of these undesired chains in the networks may affect the relaxation experiments. However, as in this work the monofunctional B_1 chains have molecular weights much higher than the difunctional B_2, the contribution of the B_2 chains to the relaxation modulus at long times (terminal zone) will be negligible. The result of the relaxation measurements will reflect only the contribution of the longer B_1 chains to the relaxation modulus.

In this work, we assume that the distribution of pendant chain lengths is given by the distribution of molecular mass of monofunctional chains. In a previous work was shown that molecular mass distribution of anionic PDMS (B_1) can be described by the log-normal distribution[24]

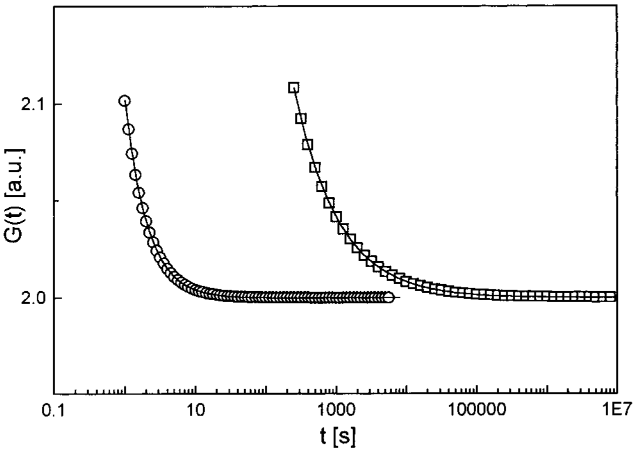

Figure 4. Numerical results from integration of eq 15, (○) $N_m = 5$ and (□) $N_m = 10$, and least-squares fit of numerical data to Chasset−Thirion equation (solid lines) for $M_w/M_n = 1.1$

$$P_N = \frac{A}{N}\exp\left[-\left(\frac{1}{z}\ln\left(\frac{N}{N_m}\right)\right)^2\right] \qquad (13)$$

where N_m represents the maximum of the distribution, A is a normalization constant, and z is a parameter related to the moments of the distribution which can be obtained from the following equation:[25]

$$\frac{M_w}{M_n} = \frac{M_z}{M_w} = \exp\left(\frac{z^2}{2}\right) \qquad (14)$$

M_n, M_w, and M_z are the number-average molecular mass, the mass-average molecular mass, and the z-average molecular mass, respectively.

Combining eqs 9, 12, and 13, we obtain for the relaxation modulus

$$G(t) = G_\infty + (G_0 - G_\infty)\int_0^\infty \left[N - \frac{1}{\alpha}\ln\left(\frac{t}{\tau_0}\right)\right]H(\tau_N - t)\frac{A}{N} \exp\left[-\left(\frac{1}{z}\ln\left(\frac{N}{N_m}\right)\right)^2\right]\mathrm{d}N \qquad (15)$$

Results and Discussion

Figure 4 shows numerical results from the integration of eq 15 (open symbols) for two different values of N_m (5 and 10). The integration of eq 15 was made considering a fixed polydispersity of 1.1, $\alpha = 0.6$ (corresponding to a coordination number $q = 12$),[6] and a characteristic time τ_0 arbitrary fixed in 0.01 s. A least-squares fit of numerical data to the Chasset−Thirion equation (solid lines) shows a very good agreement with theoretical values calculated using eq 15. Theoretical calculations were made using a log-normal distribution of pendant chains, but similar results were obtained for different distributions such as exponential or Schulz−Zimm, among others.

In networks obtained by random cross-linking, the distribution of pendant chain lengths is assumed to be geometric[5]

$$W(N) \sim p(p-1)^{N-1} \qquad (16)$$

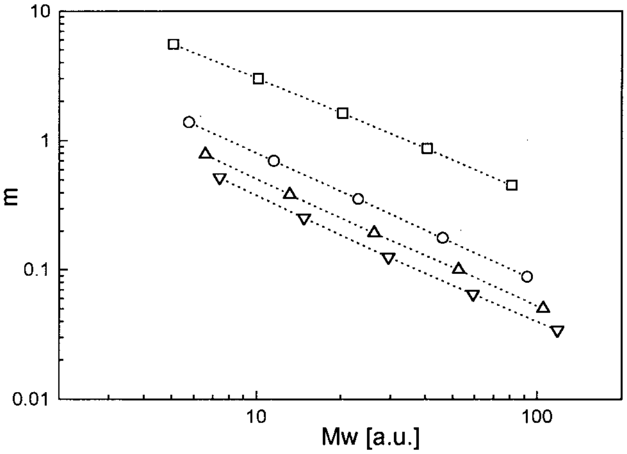

Figure 5. Chasset−Thirion exponent (m) as a function of mass average molecular mass of pendant chains M_w for different polydispersities values: (□) $M_w/M_n = 1.01$, (○) $M_w/M_n = 1.1$, (△) $M_w/M_n = 1.2$, and (▽) $M_w/M_n = 1.3$. Values of $\tau_0 = 0.01$ and $\alpha = 0.6$ were used.

where $W(N)$ represents the probability of having a pendant chain of N segments and p is the probability of having a cross-linked segment, which is given by the ratio of density of cross-linking points to segment density, $p = \mu/\rho$.

The moments and polydispersity (PD) in a geometric distribution are given by[26]

$$N_n = E(N) = \frac{1}{p} \tag{17}$$

$$N_n = \frac{E(N^2)}{E(N)} = \frac{2}{p} - 1 \tag{18}$$

$$\mathrm{PD} = 2 - p \tag{19}$$

Equation 19 is valid to describe the distribution of pendant chain lengths only if $p \ll 1$.[5] In this case, we have

$$N_n \approx \frac{N_w}{2} \propto \frac{1}{\mu} \tag{20}$$

$$\mathrm{PD} \approx 2 \tag{21}$$

According to the Curro and Pincus theory,[5] the Chasset−Thirion exponent for the terminal relaxation of networks obtained by random cross-linking results $m \propto \mu$. Then, from eq 20 with $\delta = 1$

$$m \propto \frac{1}{M_w} \approx \frac{1}{2M_n} \tag{22}$$

Figure 5 shows the behavior of the Chasset−Thirion exponent as a function of mass average molecular mass of pendant chains M_w for several narrow polydispersities. The Chasset−Thirion exponent was obtained by least-squares fit of the numerical data obtained from integration of eq 15. The value of m decreases with an increment in the mass average molecular mass of monofunctional chains added to the network. A power law dependence of the Chasset−Thirion exponent m with the mass average molecular mass of pendant chains was found

$$m = aM_w^{-b} \tag{23}$$

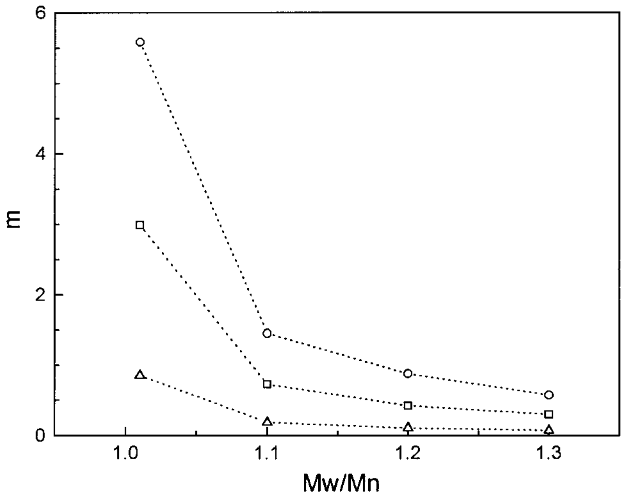

Figure 6. Chasset−Thirion exponent (m) as a function of the polydispersity of pendant chains. Symbols: (□) $M_n = 5$, (○) $M_n = 10$, and (△) $M_n = 40$.

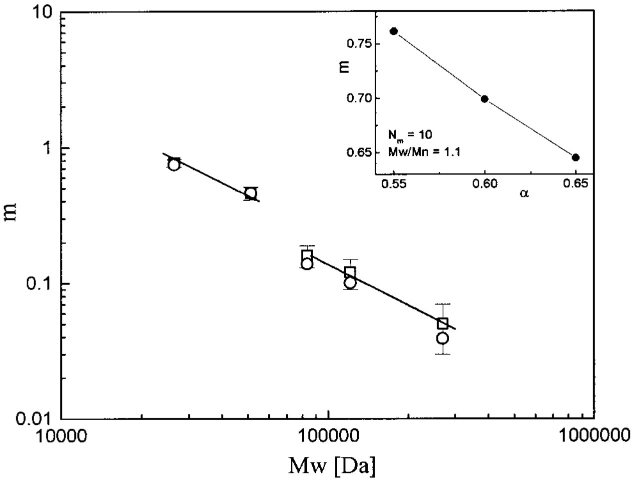

Figure 7. Chasset−Thirion exponent (m) obtained from least-squares fit of experimental data, as a function of the mass average molecular mass of the monofunctional chains (M_{wB1}) added. Symbols: (□) experimental values; (○) theoretical model. Values of $\tau_0 = 0.01$ and $\alpha = 0.6$ were used.

where a and b are constants. From these results, we observe that the exponent b is close to unity in the range of polydispersities studied in this work. This result is in good agreement with the value predicted by Curro and Pincus model (eq 22).

Figure 6 shows the evolution of the Chasset−Thirion exponent m as a function of the polydispersity of pendant chains; m values increase when polydispersity decreases. The increment is higher when the length of pendant chain decreases. On the other hand, when the polydispersity is increased, m becomes nearly independent of pendant chain length.

Figure 7 shows the exponent m (obtained from least-squaresd fit of experimental data shown in Table 2), as a function of the mass average molecular mass of the monofunctional chains added. The experimental results confirm that the exponent $b \approx 1$. The slope of m vs M_{wB1} in a log−log plot is −1 for the set of pendant chains with similar polydispersity, i.e., GP1F310 and GP2F310 ($M_w/M_n \approx 1.07$) and GP3F310, GP4F310, and GP5F310 ($M_w/M_n \approx 1.20$). Numerical results obtained from eq 15 were also included in Figure 7. Theoretical calculations were carried out considering $\alpha = 0.6$ and $\tau_0 = 0.01$ s. The polydispersity and average molecular mass of each particular monofunctional chain were also used in the calculations. It is possible to observe that *m* decreases when M_w increases with a good agreement between experimental and theoretical values, even when the theory underestimates the experimental values. The insert of Figure 7 shows that the theory predicts a nearly linear behavior of *m* vs α. Small changes in the value of α produces similar variations in the values of m; increasing α from 0.6 to 0.65 produces a 8% decrease in the value of *m*. Then the differences between theory and experimental values can be attributed to small variations in the exponent α, although other variables such as dynamic dilution or nonidealities in the network structure could be present.

On the other hand, in networks with pendant chains of high molecular weight the value of *m* presents the major uncertainty. Although in the range of molecular weight of pendant chains covered in this work the relaxation modulus has, at long times, a power law behavior, it is not clear from our experiments if this representation is still valid for networks with pendant chains of very high molecular weight. More experiments will be required in order to verify the dynamic behavior of networks containing pendant chains of higher molecular weight than those analyzed in the present work.

Conclusions

Terminal relaxation experiments gave a new insight on the influence of molecular mass distribution of pendant chains on the Chasset−Thirion exponent in model networks of PDMS with nearly constant cross-linking density and controlled amounts of linear pendant chains.

Using a modification to previous theories, we proposed a model for the terminal relaxation of elastomers. The model is in good agreement with experimental data obtained from end-linking model networks. It is also capable of reproducing values calculated with previous models for networks prepared by random cross-linking.

We want to emphasize the influence of molecular mass and distribution of molecular masses of pendant chains on the Chasset−Thirion exponent *m*.

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