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Dynamic exponent of PDMS networks at the sol–gel transition

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Abstract

Five model polydimethylsiloxane (PDMS) networks were obtained by hydrosilation of a difunctional vinyl-terminated PDMS prepolymer with a SiH containing crosslinker. Viscoelastic experiments were performed in order to study the influence of molecular parameters on the dynamic properties at the sol–gel threshold. The results suggest that the critical exponents are not universal and depend on the chemical structure of the incipient gels. They show that the fractal dimension calculated from the rheological data in the framework of the viscoelastic mean field theory, is a decreasing function of the ratio functionality/molecular weight of the crosslinker.

Keywords: Sol–gel transition; Rouse dynamics; Polymers fractals

1. Introduction

The percolation theory largely described by Stauffer and Aharony [1] has been quite successful in predicting the static properties such as the distribution of masses and sizes of polymers around the sol–gel transition [2–5]. The later is a critical phenomenon that occurs during the formation of chemical gels. The relevant of the percolation theory to describe the sol–gel transition is due to the fact that theory takes into account loops and dangling ends. In this way, gelation is modelized independently of chemical structure as a percolation transition [1,6]. On the other hand the dynamic properties around the sol–gel transition is dependent of the chemical structure but relations between the structure and the dynamics properties remain misunderstood [3–5]. Near the gelation threshold, polymer clusters are fractal with a mass scaling as a power of their radius $R: M \propto R^{D_\mathrm{f}}$ where D_f is the fractal dimension of the clusters. The number of clusters of molecular weight M, $n(M)$, also obeys a scaling relation:

$$n(M) \propto M^{-\tau} f(M/M^*) \quad (1)$$

where $f(M/M^*)$ is the cutoff function indicating that there is no mass larger than M^* in the system. The mass M^* of the largest cluster is related to the characteristic correlation length ξ by the following relationship $M^* \propto \xi^{D_\mathrm{f}}$. In the three-dimensional percolation, the theoretical fractal dimension is $D_\mathrm{f} = 2.53$ [1,4]. For the chemical gelation of polymers, the degree of connectivity of clusters is a function of the extent of reaction. If p is the fraction of reacted bonds and p_c its value at the gel point, the relative distance to the threshold is

$$\varepsilon = \left|\frac{p - p_\mathrm{c}}{p_\mathrm{c}}\right|.$$

During the sol–gel transition, the viscoelastic properties of the material are function of ε [7]: for $p < p_\mathrm{c}$, the polymer is a viscoelastic liquid characterized by a zero frequency viscosity η, which diverges as one approaches the threshold: $\eta = \eta_0 \varepsilon^{-s}$. For $p > p_\mathrm{c}$, the polymer is a viscoelastic solid with a zero frequency elastic modulus G, which increases above the gel point: $G = G_0 \varepsilon^t$.

The zero frequency properties are related to the low frequency dependence of the complex modulus $G^*(\omega)$:

$$\eta = \lim_{\omega \to 0} \frac{G^*(\omega)}{\mathrm{i}\omega} \quad \text{and} \quad G = \lim_{\omega \to 0} G^*(\omega)$$

The complex modulus follows a power law at the sol–gel transition: $G' \propto G'' \propto \omega^u$ [8–10]. The relationship between the dynamic exponent u and the zero frequency exponents s and t is obtained from the scaling laws:

$$u = \frac{t}{s + t} \quad (2)$$

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The viscoelastic properties are complex around the threshold:

For $p < p_c$ and for frequencies lower than ω^*, the characteristic frequency of the largest cluster of mass M^*, the rheological behavior is liquid like; for $\omega \geq \omega^*$ the complex modulus obeys the power law $G^* \propto \omega^u$.

For $p > p_c$ and $\omega < \omega^*$, the viscoelastic behavior of the incipient gel is the one of a solid, whereas for $\omega \geq \omega^*$, the material follows the previous scaling law.

To take into account that the dynamic behavior near the threshold is governed by the characteristic frequency ω^*, the complex modulus can be expressed by the general expression [8,11,12]:

$$G^* = G_0 \varepsilon^t f\left(\frac{i\omega}{\omega^*}\right) \text{ with } \omega^* = \omega_0 \varepsilon^{s+t} \text{ and } f\left(\frac{i\omega}{\omega^*}\right) \propto \omega^u \quad (3)$$

$\omega_0 \approx 1/\tau_0$ where τ_0 is the relaxation time of the shortest fractal cluster and corresponds to the crossover relaxation time between Rouse fractal and Rouse normal viscoelastic behaviors. One important consequence of the self-similarity of the viscoelastic behavior is that G' and G'' are independent of ε for $\omega_0 > \omega > \omega^*$. At the sol–gel transition, the viscoelastic properties are modelized by the Rouse model applied to fractal polymers, called self-similar Brownian dynamics [13]. In this framework, the storage and the loss modulus are expressed by:

$$G'(\omega) = G_\infty (\omega\tau_0)^u \frac{u\pi}{2\sin\left(\frac{u\pi}{2}\right)} \quad (4)$$

$$G''(\omega) = G_\infty (\omega\tau_0)^u \frac{u\pi}{2\cos\left(\frac{u\pi}{2}\right)} \quad (5)$$

where G_∞ is the characteristic modulus of the incipient gel and the expression of the loss angle $\delta = \arctan\left(\frac{G''}{G'}\right) = \frac{u\pi}{2}$ is conform to experimental results. Chambon and Winter [14] have observed that $G'(\omega) \equiv G''(\omega)$ when $u = 0.5$ and $G'' > G'$ when $u > 0.5$, in agreement with the previous relations (Eq. (4) and (5)). By a Fourier transform, the relaxation modulus $G(t)$ can be calculated from the expression of the storage modulus (Eq. (4)) or of the loss modulus (Eq. (5)) leading to:

$$G(t) = G_\infty \left(\frac{\tau_0}{t}\right)^u u\Gamma(u) \quad (6)$$

Thus, as previously reported [14–17], $G(t)$ scales as t^{-u}.

In the tridimensional percolation model, the theoretical fractal dimension $D_f = 2.53$ is given by the percolation theory and is related to the critical exponent τ of Eq. (1) by the hyperscaling law $D_f(\tau - 1) = 3$ [1,4,18]. Here, the fractal dimension is a constant, which means that the gelation is considered from a physical point of view independently of the chemical structure.

In the mean field theory, the relation between the frequency exponent u and the fractal dimension is obtained [13,18–20]:

$$u = \frac{d}{\overline{D_f} + 2} \quad (7)$$

where d is the space dimension and $\overline{D_f}$ is the fractal dimension of the polymer with fully screened hydrodynamic interactions (Rouse fractal viscoelastic behavior).

The aim of this study is to understand the influence of the chemical structure of model networks on the viscoelastic behavior at the sol–gel threshold.

We have studied a structural series of five PDMS networks based on a difunctional vinyl prepolymer reacted with a SiH containing crosslinker of different functionality and molecular weight.

In Section 2, we describe the chemical structure of our prepolymers and crosslinkers, the reaction conditions and the experimental procedures of viscoelastic measurements. In Section 3, we present and discuss our experimental results.

2. Experimental

2.1. Chemical synthesis

The PDMS networks of crosslinked polymers used in this study are obtained by reaction between a vinyl-terminated linear polydimethyl siloxane prepolymer and a crosslinker containing Si–H functions. The crosslinker is either a tetrakis(dimethylsiloxy)silane (TDS) or a copolymer poly (dimethylsiloxane-co-methylhydrogenosiloxane). These reagents were obtained from Gelest and were used as received. The chemical structure and the functionality of the prepolymers and crosslinkers were determined by ^{29}Si and ^{1}H NMR in $CDCl_3$ with a Brucker Avance DPX 200 spectrometer. For ^{29}Si NMR spectra, $Cr(Acac)_3$ was added as a relaxation reagent and gated decoupling, with a 45° flip angle and a 5 s recycle delay, was used as described by Williams et al. [21] for obtaining quantitative data.

Five PDMS networks have been prepared from different starting products; we have disposed of two vinyl terminated PDMS prepolymers and four SiH crossinkers of different functionality and molecular weight.

The first vinyl-terminated PDMS called prepolymer A has the following structure:

$CH_2=CH\text{–}Si(CH_3)_2\text{–}O\text{–}[Si(CH_3)_2O]_n\text{–}Si(CH_3)_2CH{=}CH_2$

with $n = 114 \pm 10$.

The second vinyl-terminated PDMS called prepolymer B has the same chemical structure as prepolymer A but with $n = 200 \pm 20$.

Crosslinker 1 (TDS) is a four functional silane crosslinker with the following structure:

$(HSi(CH_3)_2O)_4Si$

Table 1

Starting products of the five model PDMS networks called polymer 1–5 characterized by number average molecular weight M_n (g/mol), functionality f and density d of prepolymers and crosslinkers. M_n and functionality f are determined by NMR, except for Crosslinker 1 (calculated from the chemical formula)

Reactants	Crosslinker 1, $M_n = 328.73$, $f = 4$, $d = 0.886$	Crosslinker 2, $M_n = 2250 \pm 250$, $f = 4 \pm 1$, $d = 0.970$	Crosslinker 3, $M_n = 2600 \pm 300$, 11 ± 1, $d = 0.980$	Crosslinker 4, $M_n = 6500 \pm 600$, $f = 7 \pm 1$, $d = 0.970$
Prepolymer A, $M_n = 8600 \pm 700$, $f = 2$, $d = 0.970$	Polymer 1	Polymer 2	Polymer 3	Polymer 4
Prepolymer B, $M_n = 15\,000 \pm 1400$, $f = 2$, $d = 0.970$		Polymer 5		

Crosslinker 2 is a Si–H containing random copolymer with a mean functionality of 5:

$$(CH_3)_3Si-O-[Si(HCH_3)-O]_x-[Si(CH_3)_2-O]_y-Si(CH_3)_3$$

with $x = 5 \pm 1$ and $y = 24 \pm 3$.The crosslinkers 3 and 4 has the same chemical structure as crosslinker 2 but with a functionality of 11 with $x = 11 \pm 1$ and $y = 24 \pm 3$ and with a functionality of 7 with $x = 7 \pm 1$ and $y = 100 \pm 10$, respectively.

Selected characteristics of the reagents are summarized in Table 1

The crosslinking was performed in bulk by hydrosilation with a platinum catalyst (solution of platinum (13 wt%) in divinyltetramethyldisiloxane) [22,23]:

$$\equiv Si-CH{=}CH_2 + HSi{\equiv} \xrightarrow{Pt} {\equiv}Si-CH_2-CH_2-Si{\equiv}$$

The reacted components of the five PDMS networks, called polymers 1–5, are presented in Table 1

For all of the samples, 0.5 μl of catalyst was introduced in 6 g of the blend of prepolymers and crosslinkers. In all cases, the concentration of the vinyl functions originating from the catalyst was negligible (at least 140 times lower than the concentration of vinyl originating from the prepolymers). The composition of the starting mixture is defined by the stoichiometric ratio r equal to the ratio of the concentration of initial silane functions to that of initial vinyl functions:

$$r = \frac{[SiH]_0}{[Vinyl]_0} = \frac{m_{SiH} f_{SiH} M_{Vinyl}}{m_{Vinyl} f_{Vinyl} M_{SiH}} \tag{8}$$

Here SiH and Vinyl indices refer to the SiH containing crosslinkers and the vinyl prepolymer, respectively. f, m, M are the functionality, the weight and the number average molecular weight of the reagents. f and M were derived from NMR data; m was measured using a high sensitivity balance (10^{-4} g). Several samples were prepared for different r ratios in order to determine the critical stoichiometric ratio r_c corresponding to the sol–gel transition. The experimental procedure consists in a first step to blend the prepolymer and the crosslinker for a given ratio r. Then, the catalyst is added under stirring and the crosslinking reaction begins. Prior to viscoelastic measurements, the samples are sonicated to eliminate bubbles.

2.2. Viscoelastic measurements

The viscoelastic measurements were performed at a temperature of 21 ± 0.5 °C using Rheometrics ARES and RFS III rheometers with parallel disks geometry. These rheometers have transducers of 2000 and 100 g. cm. allowing measurements of moduli above about 1 and 0.1 Pa, respectively. Measurements have been conducted in two stages:

In the first stage, the evolution of G' and G'' during the crosslinking reaction was measured at 10 rad/s for various r values. Fig. 1 shows an example of the gelation kinetics of polymer 1 for $r = r_{c1} = 0.44 \pm 0.01$. After 48 h at room temperature, the reaction is usually completed (G' and G'' constant in time), which is confirmed by the disappearance of the resonance corresponding to Si–H hydrogens in the ^{1}H NMR spectra of the samples.

In the second stage, after completion of the crosslinking, the dynamic properties of the samples have been measured. The frequency domain investigated was 10^{-3} to 10^2 rad/s. At the gelation threshold, the critical stoichiometric ratio r_c is the value for which both G' and G'' obey a power law ω^u. Each dynamic curve was analyzed as a function of the

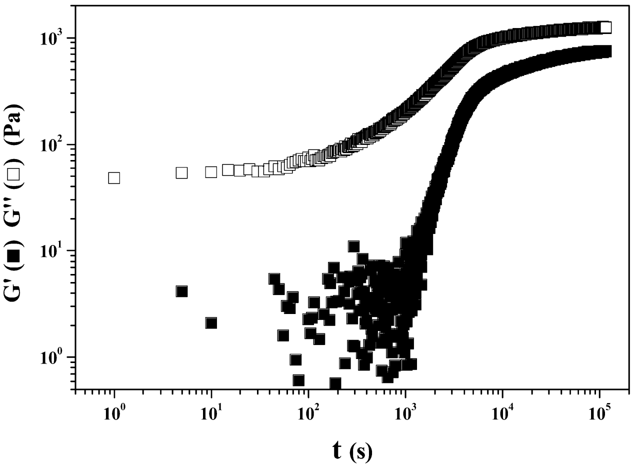

Fig. 1. Evolution of the viscoelastic properties (G' and G'' at $\omega = 10$ rad/s) with the time of reaction of polymer 1 at $r = 0.44 \pm 0.01$.

relative distance from the threshold [7,12]:

$$\varepsilon = \left| \frac{r - r_c}{r_c} \right| \tag{9}$$

Above the gel point, the zero frequency modulus G and the crossover frequency value ω^* defined as the frequency where $G'(\omega^*) = G''(\omega^*)$ are obtained. The curves $G \propto \omega^{*u}$ allow to verify the u values measured at r_c.

3. Results and discussion

The viscoelastic properties at the sol–gel threshold for polymers 1–5 are presented in Figs. 2–4. For polymer 1, the critical stoichiometric ratio at the percolation threshold $r_{c1} = 0.44 \pm 0.01$. The slope of the curves $G'(\omega)$ and $G''(\omega)$ from Figs. 2 and 3 gives the power exponent $u_1 = 0.69 \pm 0.01$. The phase angle δ is nearly independent of frequency and is given by $\delta = \arctan(G''/G') = u_1\pi/2$. Similar results are obtained for polymers 2, 4, 5 (Figs. 2 and 3) and one finds $r_{c2} = 0.26 \pm 0.01$, $r_{c4} = 0.30 \pm 0.01$, and $r_{c5} = 0.29 \pm 0.01$ and $u_2 = 0.76 \pm 0.01$, $u_4 = 0.77 \pm 0.01$, and $u_5 = 0.76 \pm 0.01$.

In the case of polymer 3, we were not able to measure the viscoelastic behavior at the sol–gel threshold. Due to the very high functionality ($f = 11$) of the crosslinker, a very small variation of the r value induced a large change in the viscoelastic behavior. Actually, our experimental precision on r is not high enough to prepare a sample with r exactly equal to r_c. Nevertheless r_c has been estimated from the rheological curves for which $\tan(\delta)$ is nearly constant for the largest frequency domain: $r_{c3} = 0.23 \pm 0.01$. The u exponent was obtained from the asymptotic value of $\tan(\delta)$ at high frequency: $u_3 = 0.75 \pm 0.03$ (Fig. 4).

From the rheological curves above the gel point, one can plot $G \propto \omega^{*u}$ for the five polymers (Fig. 5). This allowed us to obtain the same u values as found previously, independently of the r_c values but with a lower accuracy.

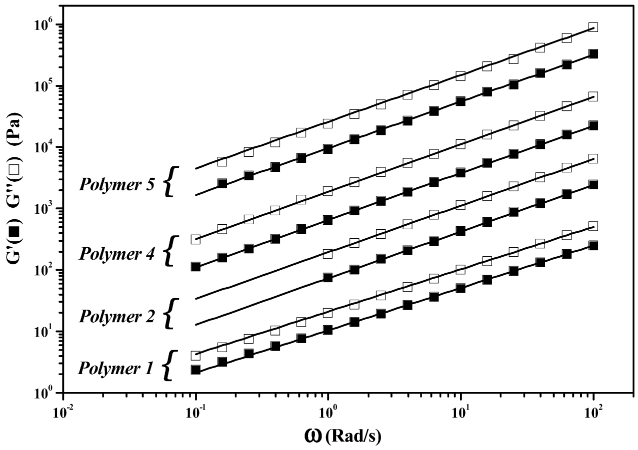

Fig. 2. Power law viscoelastic behavior of polymers 1, 2, 4 and 5 at the gelation threshold $r_{c1} = 0.44 \pm 0.01$, $r_{c2} = 0.26 \pm 0.01$, $r_{c4} = 0.30 \pm 0.01$ and $r_{c5} = 0.29 \pm 0.01$, respectively. $G^{*(\omega)}$ of polymers 2, 4 and 5 are multiplied by 30, 100, 2000, respectively. The slope of the log–log curves of the frequency dependence of G' and G'' are: $u_1 = 0.69 \pm 0.01$, $u_2 = 0.76 \pm 0.01$, $u_4 = 0.77 \pm 0.01$ and $u_5 = 0.76 \pm 0.01$, respectively.

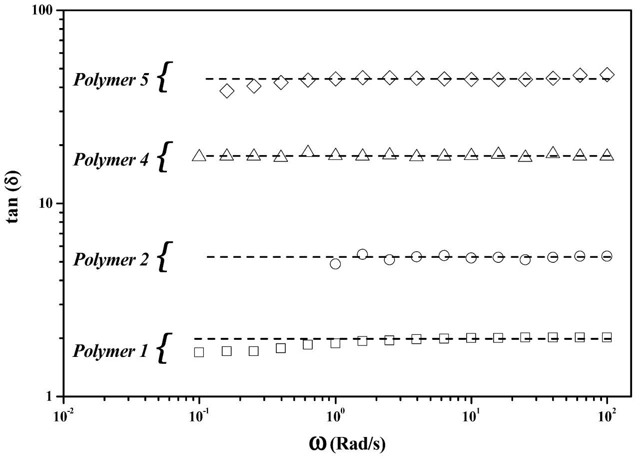

Fig. 3. tan(δ) for polymers 1, 2, 4 and 5 at the gelation threshold. tan$\delta(\omega)$ of polymers 2, 4 and 5 are multiplied by 2, 6, 17, respectively.

The fractal dimension $\overline{D_f}$ can be calculated from Eq. (7). The fractal dimension obtained for polymers 1–5 varies between 1.90 and 2.35 whereas the percolation theory predicts a fractal dimension of $\overline{D_f} = 2.53$, independently of the structure.

Table 2 reports the experimental values of r_c and u and $\overline{D_f}$. As expected, an increase of the functionality of the crosslinker involves a decrease of the critical stoichiometric ratio. The discrepancy between the r_c values of polymers 2 and 5 can be explained by the fact that a small variation of the molecular weight or functionality induces a consequent change of the r_c value. Moreover, the theoretical r_c value can be calculated more precisely using the weight functionality of the reagents [24,25]. Unfortunately, the NMR measurements used in this study give only the number

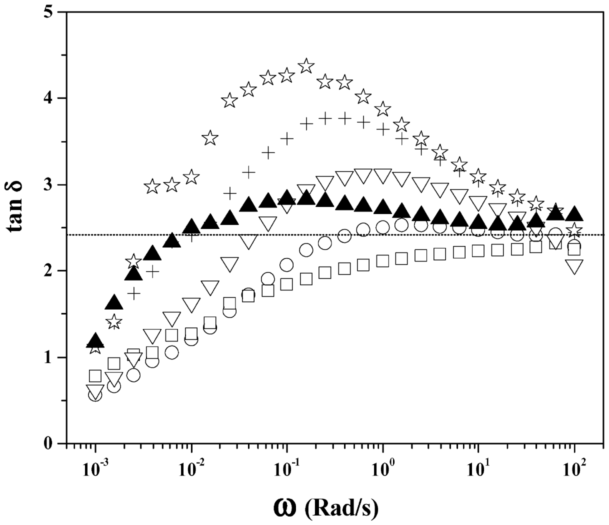

Fig. 4. Frequency dependence for several polymer 3 samples with $r \simeq r_{c3} = 0.23 \pm 0.01$ and the line corresponds to the mean value of tan(δ) leading to $u_3 = 0.75$.

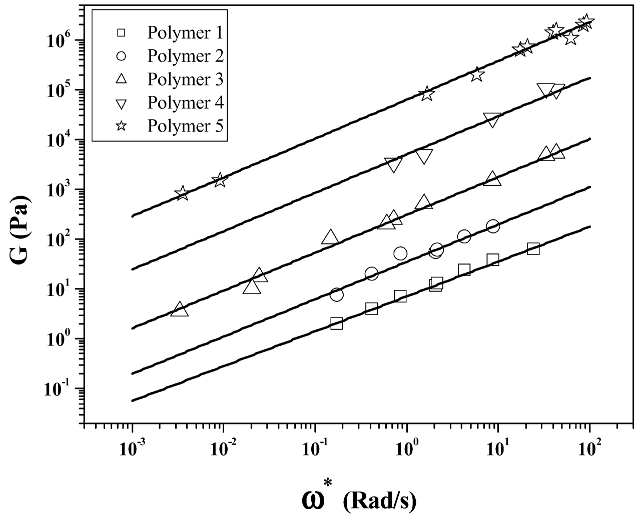

Fig. 5. Representation of the zero frequency modulus G_1, $G_2 \times 10^1$, $G_3 \times 10^2$, $G_4 \times 2 \times 10^2$, $G_5 \times 10^4$ versus ω^*. From the scaling relation $G \propto \omega^{*u}$, $u_1 = 0.70 \pm 0.02$, $u_2 = 0.75 \pm 0.02$, $u_3 = 0.76 \pm 0.02$, $u_4 = 0.77 \pm 0.02$ and $u_5 = 0.77 \pm 0.02$.

functionality of chemical products. Comparison of the critical exponent u and $\overline{D_f}$ shows that for polymer 1 they are significantly different from those obtained for the other polymers.

In the literature, we found only one study from Adam et al. [26] which can be compared to our five PDMS polymers. In this work, the PDMS network has been synthesized from the TDS crosslinker and a divinyl PDMS prepolymer with $M_n = 4900$ g/mol. The functionality and the molecular weight of the TDS were measured by GC/MS analysis: $f = 3.87$ and $M_n = 342$ g/mol. One can note that the functionality and the molecular weight of our TDS measured by NMR are slightly different and closed to those calculated from the chemical structure ($f = 4$ and $M_n = 328.73$ g/mol). The r_c and u values characteristic of the PDMS network of Ref. [26] are 0.335 ± 0.010 and 0.690 ± 0.005, respectively. u and $\overline{D_f}$ comparisons between polymers 2 and 5 and polymer 1 and of Ref. [26] show that the molecular weight of the vinyl prepolymer does not change the fractal dimension and the rheological behavior at the sol–gel transition. Then, the structural differences between polymers seem to arise mainly from the functionality f and the average molecular weight M_n of the crosslinker. According to this idea, the curves displayed in Fig. 6 show that both u and $\overline{D_f}$ vary linearly with the ratio f/M_n. This suggests that the fractal dimension increases with the crosslinker functionality and decreases with the crosslinker molecular weight. The ratio f/M_n could be understood as a branching rate that governs the local fractal structure of polymers.

Table 2
Critical values of polymers 1–5. $\overline{D_f}$ is derived using Eq. (7)

Critical values	r_c	u	$\overline{D_f}$
Polymer 1	0.44 ± 0.01	0.69 ± 0.01	2.35 ± 0.06
Polymer 2	0.26 ± 0.01	0.76 ± 0.01	1.95 ± 0.05
Polymer 3	0.23 ± 0.01	0.75 ± 0.03	2.00 ± 0.16
Polymer 4	0.30 ± 0.01	0.77 ± 0.01	1.90 ± 0.05
Polymer 5	0.29 ± 0.01	0.76 ± 0.01	1.95 ± 0.05

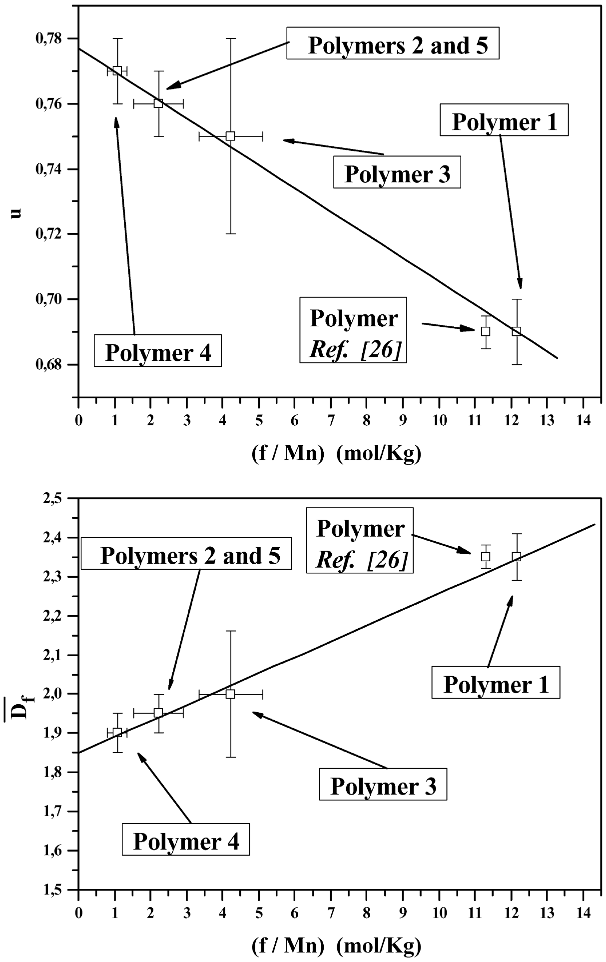

Fig. 6. (a) Critical exponent u and (b) fractal dimension $\overline{D_f}$ of polymers 1–5 versus the ratio (f/M_n) characteristic of the crosslinkers.

4. Conclusion

A structural series of PDMS networks was obtained by hydrosilation of a difunctional vinyl prepolymer with crosslinkers having different molecular weight and functionality.

The critical parameters r_c and u were obtained from dynamic rheological experiments at and above the sol–gel threshold.

The results point out that u and $\overline{D_f}$ appear to be independent of the vinyl prepolymer molecular weight and vary linearly with the ratio f/M_n characteristic of the crosslinkers. Thus, the dynamic exponent u and the fractal dimension (derived from u) are not universal and depend on the chemical structure of the reagents.

It would be interesting to compare the fractal dimensions obtained from rheological data to those measured by light scattering. Furthermore, the cluster molecular weight distribution could be determined by size exclusion chromatography (SEC). Only the determination of τ (polydispersity exponent measured by SEC) and $\overline{D_f}$ allow to verify the hyperscaling law which gives an image of the gel structure as a 'russian dolls' model. Finally, we could see if the influence of the chemical structure of the incipient network on the fractal dimension is also observed for the other systems.

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