Local dynamics of cross-linked polymer chains
A. Lapp, T. Csiba, B. Farago, M. Daoud

To cite this version:

HAL Id: jpa-00247746
https://hal.archives-ouvertes.fr/jpa-00247746
Submitted on 1 Jan 1992

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Short Communication

Local dynamics of cross-linked polymer chains

A. Lapp (1), T. Csiba (2), B. Farago (3) and M. Daoud (1)

(1) Laboratoire Léon Brillouin (C.E.A.-C.N.R.S.) C.E.N. Saclay, 91191 Gif/Yvette cedex, France
(2) Central Research Institute for Physics, P.O. Box 49, 1525 Budapest, Hongrie
(3) Institut Laue Langevin, 156 X Centre de tri, 38042 Grenoble cedex, France

(Received 24 March 1992, accepted in final form 18 June 1992)

Abstract. — We report neutron spin echo measurements of the dynamic correlation function of cross-linked polydimethylsiloxane dissolved in toluene. The experiments were performed on semi-dilute solutions. The main result is that at the frequencies probed by the spectrometer, there is no difference between the dynamics of cross-linked and uncrosslinked polymers. The dynamics is Zimm like and includes hydrodynamic interactions. Using a reduced time variable, it is possible to plot all the experimental data for both concentrations we studied on the same mastercurve. Moreover, previous results by Csiba et al. on uncross-linked PDMS are also located on the same curve. This shows that cross-linking has no dramatic effect on the local dynamics of the linear chains.

1. Introduction.

The hydrodynamic properties of polymer chains have been under constant study for a long time [1, 2]. The reasons for this are the fact that they were poorly understood, and that rheological [3] properties are the basis for many applications. Until rather recently, only large scale observations were possible, such as diffusion coefficients and viscosity. More recently, the quasi elastic light scattering [4] and neutron spin echo techniques made possible the study of much more detailed properties, and it became possible to test on a local scale the validity of the hydrodynamic assumptions. This was done on various polymers in different conditions [5-7], including dilute solutions in good or theta solvents, semi-dilute solutions and melts with some labelled chains in a deuterated matrix. It was shown among others that the hydrodynamic interactions are present both in a dilute solution and for the cooperative motions in the semi-dilute case. The Dubois-Violette and de Gennes [8] predictions were tested, and it was shown that their function, to be discussed below, was in very good agreement with the experimental results [9] for the scattered intensity $S(q, t)$, where $q$ is the momentum transfer, and $t$ is the time. More recently, there was a growing interest in the properties of randomly branched polymers.
The static properties were studied by various techniques, including light \[10, 11\] and neutron \[12\] scattering. It was clearly shown that these branched macromolecules are fractal. It was also realized that their fractal dimension is not obtainable by a single experiment because of the existence of an extremely large polydispersity \[13, 14\]. The latter implied that the average values that are measured lead to an effective dimension that is different from the actual one. These polydispersity effects are also important for the dynamical properties, because they result in a wide distribution of relaxation times \[15-17\]. The latter implies non exponential, such as power law, or stretched exponential relaxations. A special case of branched polymers is when one cross-links linear chains. This corresponds to vulcanization, and is of important practical interest. These macromolecules have very long relaxation times that were studied recently by Rubinstein et al. \[18\], and also present a continuous distribution of times. Therefore, their study has both a fundamental and a practical interest. But before going into the study of such complicated structures, it is important to check the changes that occur in the dynamics of the linear constituents once they are cross-linked, and are part of a larger structure. It is usually assumed in most studies that the cross-linking procedure does not change the local dynamics of the chains, but, to our knowledge, this was not checked experimentally so far. It is the purpose of this paper to address this question and to see the possible differences in the dynamical behavior of linear chains in the free state, and in a cross-linked state. In order to do this, we studied with the IN11 Neutron spin echo spectrometer of the I.L.L. the scattered intensity by solutions of polydimethylsiloxane (PDMS) in toluene. Such linear chains were previously studied with the same technique both in dilute and semi-dilute solutions. Therefore, it was possible to compare directly their results to those we obtained on the same material that was end linked prior to our experiments. As we will see, there is basically no difference between the two sets of experiments, and one may conclude that the assumption that cross-linking does not change the local dynamics is satisfied. In the next part, we recall the previous results on the scattered intensities by linear and branched polymers. Section 3 deals with the synthesis of the branched PDMS, and section 4 with the spin echo technique. Our results and their treatment are given in the last section. It is also shown in this section that universal coordinates are possible, that include both our results and the previous ones.

2. Hydrodynamics of macromolecules.

In this section, we recall briefly the results we need about the hydrodynamics of both linear and branched polymers. This was considered earlier by Dubois-Violette and de Gennes (DVG) \[8\] for a dilute solution of linear chains. The most realistic assumption is that hydrodynamic interactions are present and that a Zimm dynamics is valid. This implies for instance that the diffusion coefficient \(D_0\) is inversely proportional to the radius of gyration \(R\) of a chain:

\[
D_0 \sim R^{-1}
\]

(1)

a relation that was checked experimentally by quasi elastic light scattering \[4, 19b\]. DVG considered the problem at a more microscopic level \[8\]. The equation of motion may be written as

\[
\frac{d r_n}{dt} = W \left\{ a_n - a_{n-1} + \zeta \sum_{m \neq n} |m-n|^{-1/2} [a_m - a_{m-1}] \right\}
\]

(2)

with \(W\) a microscopic frequency, \(\zeta\) a constant, \(r_n\) the position of monomer \(n\), \(a_n(t) = r_n(t) - r_{n-1}(t)\) is the location of link \(n\) along the chain at time \(t\), and where the first term corresponds
to the elastic contribution and the second one is related to the Oseen tensor and represents the hydrodynamic interactions. For an infinite chain, it is possible to look for eigenmodes of the form

$$r_n = K \exp \{ipn - t/\tau_p\}$$

where the relaxation times $\tau_p$ are given by

$$\frac{1}{W\tau_p} = 2(1 - \cos p) + 4\zeta \sum_{s=1}^{\infty} s^{-1/2} \cos(ps)(1 - \cos p)$$

It is then possible to derive the time dependent scattered intensity $S(q,t)$, where $q$ and $t$ are respectively the scattering vector and time.

$$S(q,t) = \sum_{ij=1}^{N} \langle \exp \{iq[r_i(0) - r_j(t)]\} \rangle$$

where $i$ and $j$ are monomers along the chain.

Relation (5) was calculated by DVG, who found for the coherent scattering and a Gaussian chain

$$S(q,t) \sim \frac{2}{\varepsilon} N f(\theta)$$

with

$$\varepsilon = q^2 b^2 / 6$$

and

$$\theta = \varepsilon^{3/2} W |t|$$

with $W = \sqrt{2\pi\zeta W}$ and $f(x)$ is a complicated function that was calculated exactly by DVG for the Gaussian case; $b$ is the step length, and $W$ a macroscopic frequency.

These results may be summarized in the following way:

One way define a characteristic frequency $\Omega$ that is for instance the half width for the decay of $S(q,t)$. This is

$$\Omega \sim \alpha q^3 \quad (qR \gg 1)$$

and

$$\Omega \sim D_q^2 \quad (qR \ll 1)$$

Note also that equation (6) may be written in a scaled form:

$$S(q,t) \sim S(q,0) f \left( qt^{1/3} \right)$$

The above results were recently checked experimentally by neutron spin echo by Csiba et al. [9], Richter et al. [26], and by Nicholson et al. [7]. The above analysis was extended to semi dilute solutions, where the results are basically the same when one considers the local dynamics, that is the collective motions related to the concentration blobs. The main difference comes from the diffusion coefficient that is dependent on concentration only. Instead of equation (1), one has

$$D_c \sim \xi^{-1}$$

where $\xi$ is the size of the blob.
The same kind of calculations were done more recently [20] on randomly branched polymers, following the same lines as above. The main difference comes from the fact that polydispersity effects are very important, and this affects the diffusion coefficient for instance. In a dilute solution, it was found that

$$D \sim R_s^{-1} \sim N_w^{-5/8}$$

Relation (12) was checked experimentally by Candau et al. [11] by quasi-elastic light scattering (QELS). Similarly, the $q^3$ variation of the characteristic frequency was recently observed on branched structure by QELS by Delsanti and Munch [27]. Because the hydrodynamic assumption is the same, a similar scaled form for the scattered intensity was found. However, the scaling functions are different for a linear and branched polymer. A special case of randomly branched polymers corresponds to vulcanization. This is the case when linear chains are cross-linked in order to get branched structures, and eventually a gel. Cross linked rubbers belong to this class. It was shown that this case is more interesting because the width of the critical region depends on the mass of the initial chains [21-23]. The dynamics was also considered by Rubinstein et al. [18], who showed that there exists exponentially long times in this case. However, all the above analysis assumed that the basic object one has to consider is the chain itself. Therefore, it was implicitly assumed that the size of a chain does not change dramatically when it is part of a larger structure. Similarly, for the dynamics, it was assumed that the basic time is the time for a free chain, and does not change when it is cross-linked to other. This is precisely what we tested in our study of cross-linked PDMS. Dilute and semi-dilute solutions of free chains were studied earlier, and it was possible to synthesize cross-linked chains of the same material and to study their dynamics by spin echo, in similar conditions, looking for deviations with regard to the previous results on uncross-linked chains. This is what is discussed below.

3. Experimental.

3.1 Sample Preparation. — The polymer sample is poly(dimethylsiloxane) [PDMS] with dimethylsilyl units at both ends and was prepared in bulk by cationic ring-opening polymerization of octamethylcyclotetrasiloxane (D₄) in the presence of tetramethylcyclotetrasiloxane, acting as a transfer agent.

The gelling reaction was made in the following way: the precursor linear chains, previously degassed under vacuum, are heated at 70 °C with the tetrakis(allyloxy)ethane at a 1/1 stoichiometric ratio of dimethylsilyl to unsaturated functions in the presence of $5 \times 10^{-4}$ mole of chloroplatinic acid per mole of PDMS [24]. The hydrosilylation reaction was stopped, before the gel point, after 6 h by using Rosenmund's poison [25].

The precursor linear PDMS chains and the branched molecules were characterized by size exclusion chromatography (SEC) coupled on line with a differential refractometer (Shimadzu RID-6A) and a low angle laser light scattering (LALLS) photometer (Chromatix CMX-100). Toluene, a good solvent for PDMS, was used as elution solvent at a flow rate of 1 cm³.min⁻¹.

The experimental results are listed in Table I.

Table I. — Molecular characteristics of sample.

<table>
<thead>
<tr>
<th></th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear Precursor</td>
<td>18900</td>
<td>29500</td>
<td>1,6</td>
</tr>
<tr>
<td>Branched Molecule</td>
<td>36500</td>
<td>656000</td>
<td>18</td>
</tr>
</tbody>
</table>
The samples we used were polymer solutions made of branched (hydrogenated) PDMS dissolved in deuterated toluene at two concentrations: 5% and 20%. The overlap concentration $C^*$ was determined by small angle neutron scattering [30] to be approximately 2%. The solutions were held in quartz cans of optical path 4 mm for the 5% solution and 2 mm for the other one. In a dilute solution, the radius of gyration of the branched polymer was measured by light scattering [30] and is 674 Å. The screening length in the more concentrated solution [30] is approximately 30 Å, and is smaller than the radius of the linear precursor. The latter is [30] $R_L \approx 60$ Å.

3.2 NEUTRON SPIN-ECHO. — The experiments were carried out at the spin-echo spectrometer IN-11 at the Institut Laue Langevin (Grenoble, France). For a detailed description of the technique, the reader is referred to Mezei’s book [28]. The wavelength of the incident neutrons was 11.25 Å and the domain of scattering angle was $2^\circ \leq \theta \leq 8^\circ$ covering a wave vector transfer range $q$ ($q = (4\pi/\lambda)\sin \theta/2$), $1.95 \times 10^{-2} \leq q (\text{Å}^{-1}) \leq 7.79 \times 10^{-2}$. After subtraction of the background scattering functions and normalization by the resolution function of the instrument, the intermediate scattering functions $S(q,t)$ were analyzed in the time range $0.40 \leq t (\text{ns}) \leq 36.78$.

4. Results and comments.

Both branched polymer solutions are semi-dilute, and their dynamics may be fitted by a stretched exponential function

$$\frac{S(q,t)}{Q(q,0)} = \exp \left[ \left( \frac{-t}{\tau} \right)^n \right]$$ (13)

where $\tau$ is the relaxation time, and $n$ depends, in principle, on the observation range:

For $q\xi \gg 1$, with $\xi$ the screening length, the dynamics should be described by a Zimm model with $n = 2/3$.

For $q\xi \ll 1$, and $qa \gg 1$, where $a$ is the diameter of the tube, the hydrodynamic interactions should be screened, and the dynamics follows a Rouse model, with $n = 1/2$.

Finally, for still smaller values of $q$, reptation takes over in the uncross-linked case. In the cross-linked case, larger scale very slow motions occur for distances larger than the radius of individual chains, as dicussed by Rubinstein et al. [18].

In order to determine the exponent $n$ experimentally, we plotted $\ln(-\ln(S(q,t)/S(q,0)))$ as a function of $\ln t$. This way, we obtained an average value $n = 0.69 \pm 0.09$, in good agreement with the Zimm value. In what follows, we will use the latter value. In order to provide a visualization of this value, figure 1 shows a plot of the experimental [29] $S(q,t)/S(q,0)$ together with the best fit by a stretched exponential like equation (13) with $n = 0.67$. We also tried a fit with a simple exponential, but the results were in much better agreement with the Zimm value.

Finally, it is possible to introduce a characteristic frequency $\Omega$, ar. 1 to write relation (13) in the following form

$$\frac{S(q,t)}{S(q,0)} = \exp \left[ -(\Omega t)^{2/3} \right]$$ (14)

Using the latter relation, we checked the proportionality of the characteristic frequency to $q^3$, equation (12a). We get

$$\frac{\Omega_{5\%}}{q^3} = (2.01 \pm 0.06) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$$
Fig. 1. — The reduced scattered intensity $S(q, t)/S(q, 0)$ as a function of time for various values of the scattering vector $q$. The curves correspond to a best fit with a stretched exponential with exponent 0.67. (1a) corresponds to a concentration of 5 %, and (1b) to 20 %. (See also Ref. [28]). Symbols correspond to different angles: ($\times$) 2°; (+) 3°; (o) 4°; (□) 5°; (φ) 8°.

These results clearly show that for both solutions, we are probing the internal modes of the polymers, and that $q\xi \gg 1$. They are also in agreement with those obtained recently on free linear PDMS chains [19a], and to those of Csiba et al. [9]. The difference that is observed between the coefficients for both concentrations, although statistically significant, does not allow us to conclude that this coefficient varies with concentration.

Relation (14) may be obtained directly from relation (5) by the following simple argument: for large times compared with the longest (Zimm) time, the scattered intensity assumed a
Gaussian behaviour,

\[ S(q, t) \sim \exp \{-D^2_q t\} \quad (t \gg T_2) \quad (15) \]

where \( D \) is the diffusion coefficient. For shorter times, when one considers the internal modes, it is possible to assume that the diffusion coefficient is no longer a constant, but is time dependent. This may be related to the fact that one is considering the motion of a part of the chain that depends on the observation time. This implies a stretched exponential behavior. The exponent 2/3 is obtained by matching the latter dependence with relation (15) for \( t \sim T_2 \sim N^{3/2} \). Note that for \( q \xi \gg 1 \), this result also holds for large times. Note also that this implies a diffusive behavior in the sense that there is still a \( q^2 \) in the argument of the exponential.

Finally, equation (14) tells us that the relevant variable is not \( t \) itself, but rather the product \( \Omega t \). Using the latter variable, we may plot on a single-universal curve all the experimental results corresponding to the different values of \( q \), and both concentrations that were considered. This is shown in figure 2, which clearly exhibits a universal fit to the various parameters we used. In order to see how the Csiba et al. results were placed in such a representation, we used their experimental data at a concentration of 20%, similar to the ones we used. Within experimental accuracy, these points also fitted on the same curve. Such universality is strongly in favor of the fact that for semi-dilute solutions, and in the observation range that we used, the behavior of the linear chains which are part of a branched structure is identical to the one of free linear chains. We would like to stress that although the effective time range that is attainable with the spin echo spectrometer is relatively modest, this representation allows us to scan a considerably larger reduced time range, four orders of magnitude being considered in this plot. Such a result, although extremely interesting, is not really surprising: such large time intervals are already studied for instance in the glass transition with the W.L.F. equation [3].

---

Fig. 2. — Mastercurve for the various data in figure 1. The (x), (+) and (o) symbols correspond to our results for the 5% and 20% cross-linked samples, and to the results of Csiba et al. for uncross-linked PDMS with concentration of 20%, respectively. These latter points are undistinguishable from those of the cross-linked samples.
5. Conclusion.

We studied the dynamics of end linked PDMS chains with the neutron spin echo technique. For this purpose, two solutions of PDMS in deuterated toluene were used, at 5 and 20% respectively. The overlap concentration $C^*$ was determined by Small angle neutron scattering [30], and is approximately 2%. The experimental results could be fitted with a Kohlrausch stretched exponential law, with an exponent 2/3, indicating a Zimm dynamics. It was possible to determine a characteristic frequency $\Omega$ for the decay of the scattered intensity. As a function of the wavevector $q$, this varies as $q^3$, again indicating the presence of hydrodynamic interactions. Finally, we showed that it is possible to define universal coordinates and to plot the ratio $S(q,t)/S(q,0)$ as a function of the product $\Omega t$. This choice of coordinates provides a mastercurve for both concentrations we used and for the various values of $q$ that are available with the IN11 spectrometer of the I.L.L. Moreover, the experimental results of Csiba et al., concerning free (uncrosslinked) PDMS at similar concentrations could also be placed on the same mastercurve. This shows that the usual assumption that cross-linking does not affect dramatically the dynamics of the chains at a local scale is sound.

Acknowledgements.

The authors are much indebted to M. Delsanti and G. Jannink for many discussions.

References

[29] The scattering curves at angle 4° for the solution at 5 % were eliminated because of the poor statistics we had. Similarly, the curves for angle 2° for the solution at 20 % were also discarded because of its pollution by the central beam.