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# GELATION AND PERCOLATION : SWELLING EFFECT

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#### Résumé

Des mesures de diffusion de neutrons aux petits angles ont été réalisées sur des polymères were performed on Polyurethane branched polymers branchés de Polyuréthanne synthétisés par polycondensation au voisinage du seuil de gélification. nent  $\tau$  of the size distribution function is measu-Nous trouvons que l'exposant  $\tau$  de la distribution red, on a system cross-linked by polycondensation. en nombre des tailles est égal à 2,2  $\pm$  0,04. Il en We find  $\tau$  = 2.2  $\pm$  0.04. This leads to a fractal résulte une dimension fractale des polymères dans dimension for the polymers in the reaction bath le bain de réaction  $D_p = 2.5 \pm 0.09$ , en accord avec  $D_p = 2.5 \pm 0.09$ , in agreement with percolation le modèle de percolation. En solution diluée, la model. In the dilute state, the fractal dimension dimension fractale est D = 1,98  $\pm$  0,03 également en is D = 1.98  $\pm$  0.03, in agreement with recent preaccord avec des prédictions récentes. Donc les plus dictions. Thus the largest branched polymers are grands polymères gonflent par dilution.

### Abstract

Small angle neutron scattering experiments synthetized near the gelation threshold. The exposwollen by dilution, and behave as lattice animals.

De Gennes<sup>[1]</sup> and Stauffer<sup>[2]</sup> pointed out some years ago that the Sol-Gel transition may be modelled by percolation. This was followed by a rather controversial discussion about whether cri- very large branched polymers, exhibits a lattice tical or mean field exponents should be observed animal behavior in the dilute regime. near the gelation threshold. More recently, it was argued on the basis of a Flory theory that the branched polymers, in a very diluted solution, should swell as lattice animals<sup>[3]</sup>.

The purpose of this letter is to show, on a sol obtained by chemical cross-linking, that:

(i) the number size distribution [4] at the threshold decreases as

 $n(s) \sim s^{-\tau}$ 

where  $\tau$  is the percolation rather than the mean field exponent

(ii) a fraction of the sol, containing only

The experiments were performed by small angle neutron scattering on the PACE spectrometer in Saclay<sup>[5]</sup>. Two wavelengths,  $\lambda = 7$  Å and 15 Å, were used. The distance from sample to detector was 2.5 m. The corresponding range of investigated scattering vector is

$$5 \times 10^{-3} \leq q(A^{-1}) \leq 1.1 \times 10^{-1}$$

where  $q = \frac{4\pi}{\lambda} \sin \theta/2$ ,  $\theta$  being the scattering angle.

Hydrogenated polyurethane is prepared [6] without solvent by chemical cross-linking (polycon-

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densation) of poly [oxypropylene] - triol (trifunctional unit) with molecular weight of 700 and hexamethylene diisocyanate (bifunctional unit) with molecular weight of 168. The chemical reaction is "quenched"<sup>[6]</sup> below the gelation threshold ( $p_c$ ) at a distance ( $\epsilon = p_c$ -p) smaller than 10<sup>-2</sup>. Part of the sol obtained this way was directly diluted in deuterated tetrahydrofurane (TDF). The other part was fractionated by size exclusion chromatography. The fraction that was investigated contained less than 10% of the total distribution and corresponds to the largest molecular weights. This fraction was subsequently diluted in TDF.

Both unfractionated and fractionated samples were studied by intensity light scattering<sup>[7]</sup>. The main results, summarized in table I, are:

. The Z average radius of gyration  $\rm R_{_Z}$  decreases when concentration increases, values given in table I are extrapolations to zero concentration.

. The scattered intensity at zero q vector has a maximum at  $\tilde{c}$ .

. The concentration dependence of the inverse of the scattered intensity at zero q vector,  $\mathbf{I}_{q\mapsto 0}$  :

$$\frac{c}{I_{q \mapsto 0}} = \frac{K}{M_{w}} (1 + 2Bc)$$

provides the interaction parameter B and the weight average molecular weight  $M_w$ , K being a measurable optical constant.

Details on intensity light scattering experiments will be given elsewhere.

## **Polydisperse Samples**

In the first series of experiments, all the sol was used. Near the gelation threshold, we assume the Stauffer distribution<sup>[8]</sup>: the probability  $n(s,\epsilon)$  of having a polymer with size s at a distance  $\epsilon$  from the threshold is

$$n(s,\epsilon) \sim s^{-\tau} f(\epsilon s^{\sigma}) \tag{1}$$

where  $\tau$  and  $\sigma$  are the usual exponents<sup>[8]</sup> and f(x) is an exponentially decreasing function.

The intensity scattered by a single polymer with size s is proportional to the Fourier transform of its pair correlation function,  $r^{D-d} g\left[\frac{r}{R(s)}\right]$ 

$$I_{g}(q) \sim \int d\underline{r} e^{i\underline{q}\underline{r}} \frac{1}{r^{d-D}} g\left[\frac{r}{R(s)}\right]$$
 (2)

where D is the fractal dimension [9] of the polymer and R(s) its radius of gyration

$$\mathbf{s} \sim \mathbf{R}^{\mathbf{D}}(\mathbf{s})$$
 (3)

The intensity scattered at infinite dilution is the averaged sum of the intensities scattered by all the polymers present in the solution

$$I(q) = \int ds \ s \ n(s,\epsilon) \ I_{s}(q)$$
(4)

with the normalization condition below p

$$\int ds \ s \ n(s,\epsilon) = 1$$

Using relations (1) to (4) we get

$$I(q) \sim q^{-D(3-\tau)} h(qR_{-})$$
 (5)

where

$$R_{z}^{2} = \frac{\int ds \ s^{2} \ n(s,\epsilon) R^{2}(s)}{\int ds \ s^{2} \ n(s,\epsilon)} \sim \epsilon^{-2/\sigma_{D}}$$
(6)

and h(x) is a function with asymptotic behaviors

$$h(x \gg 1) \sim 1$$
 (7a)

$$h(x \ll 1) \sim x^{D(3-\tau)} (1-x^2)$$
 (7b)

From (7b) one can show that the intensity for zero scattering vector is

$$I(\mathbf{q} \mapsto \mathbf{0}) \sim \mathbf{M}_{\omega} \sim \epsilon^{-\Upsilon}$$
 (8)

Equation (5) was already derived by Martin and Ackerson<sup>[10]</sup> with the same approach. Note however that they neglected the interactions and the swelling of the polymers. Their result, Eq.(5), is however very general, whatever the fractal dimension D of the polymers.

We have measured the q dependence of the intensity scattered by diluted samples

 $(0.1\ c < c < 0.3\ c)$ . We find that, for the 7 A incident wavelength and for a range of q extending from  $10^{-2}A^{-1}$  to  $8\times10^{-2}A^{-1}$ , the scattered intensity may be described by a power law, with an exponent dependent slightly on concentration<sup>[11]</sup>: for  $c = 2.8\times10^{-3}$  g/cm<sup>3</sup> and  $c = 8.3\times10^{-4}$  g/cm<sup>3</sup> the exponent values are  $1.51 \mp 0.02$  and  $1.59 \mp 0.07$ , respectively.

A linear extrapolation to zero concentration leads to an exponent value  $1.62 \pm 0.02$ .

In Figure 1 we show, on a log-log plot, the scattered intensity for the sample with lowest concentration (c  $\approx 0.1$   $\tilde{c}$ ) as a function of q. The range of q here goes from  $5 \times 10^{-3} A^{-1}$  to  $8 \times 10^{-2} A^{-1}$ .

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Fig.1 : Scattered intensity in arbitrary units, as a function of the scattering vector in log-log the polydisperse scales for sample at  $c = 8.2 \times 10^{-4} \text{g/cm}^3$ . The full line corresponds to  $q^{-1.59}$  dependence. The investigated  $qR_{r}$  range lies between 3 and 40. In the insert is represented in linear representation the intensity multiplied by  $q^{1.59}$  versus q. • and  $\circ$  are measurements performed at  $\lambda = 7$  Å and  $\lambda = 15$  Å, respectively. In this figure we have kept only the points which correspond to a ratio of the total intensity (I+B) divided by the incoherent intensity (B) bigger than 1.1, because the incoherent intensity is known with a precision of 10%.

The observed linear behavior is in good agreement with the power law obtained from relations (5) and (7a). This implies

$$D(3-\tau) = 1.59 \pm 0.05$$
 (9)

in good agreement with the zero concentration value. In this relation (9),  $\tau$  is the exponent of the number size distribution of the sol and D the fractal dimension of an individual polymer in the dilute solution.

Equation (9), is in good agreement with previous light scattering results by Schosseler and Leibler<sup>[12]</sup> and Candau et al<sup>[13]</sup> on different systems.

#### Large Fractions

In order to obtain both D and  $\tau$ , a second set of experiments was performed with the fraction made of the largest molecular weights distribution (see Table I). As in last section, dilute solutions were used. Now the distribution is

$$n_{f}(s,\epsilon) = s^{-\tau} f\left(\frac{s}{m}, \epsilon s^{\sigma}\right) \qquad (1')$$

TABLE I

Characteristics of the two different samples used, determined by intensity light scattering.  $R_{_2}$ ,  $M_{_W}$ ,

B,  $\tilde{c}$  are defined in the text.

	R <sub>2</sub> (Å)	Mw	B(cm <sup>3</sup> /g)	c̃(g∕cm³)
fractionated sample	1000	10 <sup>7</sup>	400	4×10 <sup>-3</sup>
polydisperse sample	600	5×10 <sup>5</sup>	15	10 <sup>-2</sup>

where a minimum size m is introduced. The total scattered intensity is

$$I_{f}(q) = \int ds \ s^{1-\tau} f\left(\frac{s}{m}, \ \epsilon \ s^{\sigma}\right) \int d\underline{r} \ \frac{e^{i\underline{q}\cdot\underline{r}}}{r^{d-D}} \ g\left(\frac{r}{R(s)}\right) (2'a)$$
$$I_{f}(q) \sim q^{-D} \int g\left(qs^{1/D}\right) \ s^{1-\tau} \ f\left(\frac{s}{m}, \ \epsilon \ s^{\sigma}\right) ds \ (2'b)$$

When the scattering vector range is such that  $qR_{m} \gg 1$ , where  $R_{m}$  is the radius of gyration of the smallest polymers present in the solution,  $g(qR_{z} \gg 1)$  is independent of x, and thus

$$I_{c}(q) \sim q^{-D} m^{2-\tau}$$
 (10)

(10')

More generally, for  $qR_2 > 1$ , from (2b) we get

$$I_{f}(q) \sim q^{-D(3-\tau)} S(qR_{n})$$

 $S(x \gg 1) \sim x^{(2-\tau)D}$ 

with and

leading to (10) and (5, 7a) in each of these regimes, respectively.

Experiments with the fractionated sample were performed with dilute solutions in TDF  $(0.5\ c\ s,\ c\ s,\ c\)$ . With the 7 A incident wavelength and q ranging from  $1.1\times10^{-2}$  to  $1.1\times10^{-1}$  A<sup>-1</sup>, the scattered intensity can be described by a power law in q with an exponent independent of concentration<sup>[11]</sup>, within experimental accuracy. For instance, the exponent values are  $1.97\pm0.1$ and  $2.05\pm0.04$  for  $c = 2.0\times10^{-3}$  g cm<sup>-3</sup> and  $2.7\times10^{-3}$  g cm<sup>-3</sup>, respectively.

On Figure 2 is displayed in a logarithmic representation the scattering intensity as a function of q  $(5 \times 10^{-3} < q(A^{-1}) < 1.1 \times 10^{-1})$ , with incident wavelengths 7 Å and 15 Å, for the sample

with  $c = 2 \times 10^{-3} \text{g/cm}^3$ . The linear behavior in this plot corresponds to an exponent value 1.98 ± 0.03, independent of the range of q where the neutron experiments are performed. By intensity light scattering, both with the polydisperse and with the fractionated samples, the same limiting slope  $\left(\frac{d \log I}{d \log q}\right)_{q}$  = 1.5 ± 0.1 is found. Then from

light scattering experiments together with (10'), we get

and from neutron scattering experiments together with (10), we get

R\_ 2 200 Å

q\_1 R\_之1



Thus, we identify, the exponent measured by neutron scattering on the fractionated sample, with the fractal dimension of very large branched polymers in a dilute solution

$$D = 1.98 \pm 0.03$$
 (11)

Relations (9) and (11) lead to

$$\tau = 2.2 \pm 0.04 \tag{12}$$

for the exponent of the distribution of sizes near the threshold.

This result is very similar to those obtained previously by gel permeation chromotography on a different system by Schosseler and Leibler [14].

This is in favour of percolation for being, at least, a universality class for the connectivity properties of branched polymers near the sol-gel transition.

The fractal dimension D measured in dilute solution is different from percolation fractal dimension D<sub>p</sub> for the same branched polymers in the reaction bath, without any fractionation nor solvent. Actually, D<sub>p</sub> is related to  $\tau$  by

$$D_{p} = \frac{3}{\tau - 1} \tag{13a}$$

Equations (12) and (13a) lead to

 $D_p = 2.50 \pm 0.09$  (13b)

in excellent agreement with best numerical estimates for percolation<sup>[15]</sup>.

Thus branched polymers in dilute solutions swell and have the same fractal dimension as lattice animals  $(D=2)^{[3]}$ . Such animal like behavior was observed by Schaefer and Keefer<sup>[16]</sup> on Silica condensation polymers. Their system however is very different from the present system, because they do not observe any swelling upon dilution whereas we do.

The small angle neutron scattering experiments on branched polyurethane prepared by polycondensation close to the gelation threshold enable us to draw the following conclusions:

(i) In dilute solutions, very large branched polymers obtained by fractionating a sol have the same fractal behavior as lattice animals. This shows that the swelling of these polymers is rather insensitive to the presence of large loops.

(ii) At the threshold, the exponent  $\tau$  of the size distribution is equal to  $2.2 \pm 0.04$ . This implies a fractal dimension for the branched polymers in the reaction bath  $D_p = 2.50 \pm 0.09$ , in very good agreement with numerical simulations<sup>[10]</sup> of percolation. Thus the connectivity properties of the sol-gel transition in polyurethane seem to be described by percolation with critical rather than mean-field exponents.

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