

Verification of the Hyperscaling Law on Polymer Clusters by Neutron-Scattering Experiments

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Measurements of the small-angle neutron scattering by polymer clusters near the gelation threshold have been made possible, in the bulk state, using mixtures of deuterated and hydrogenated polyurethane samples. The exponent which links the scattered intensity to the transfer vector q is predicted to be $(3 - \tau)D_p$, where τ is the exponent which characterizes the mass distribution and D_p the fractal dimension of polymer clusters in the bulk state. This exponent is found to be equal to 2.00 ± 0.05 . Using this result and the τ value determined in a previous experiment on the same system, we verify the hyperscaling law and deduce $D_p = 2.50 \pm 0.06$.

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The hyperscaling relation links two exponents of a critical phenomenon [1] to the space dimension d and is of special importance in the gelation process. The gelation process is a critical phenomenon of connectivity which leads to polymer clusters having a continuous mass distribution [2]. In this case, the hyperscaling law can be expressed as

$$d/D_p = \tau - 1, \quad (1)$$

where D_p is the fractal dimension of polymer clusters and τ the exponent which characterizes the continuous mass distribution. At the gelation threshold the number n_i of polymer clusters having a mass M_i is proportional to $M_i^{-\tau}$. The hyperscaling law implies a double fractal nature of these polymer clusters. This means that each cluster occupies the space in a fractal manner, and in addition the cluster's distribution and its space organization are fractal: Clusters having the same size do not overlap, but smaller clusters are in such a proportion as to fill the inherent voids of larger ones [3].

Previous works performed on the polyurethane system allow us to determine the exponent τ mentioned above [4] and the exponent γ which describes the divergence of the second moment of the cluster mass distribution [5]. For this system, as well as for other chemical systems [6], both exponent values are found to be in good agreement with the percolation model ($d=3$). But, in order to prove that both these critical phenomena—gelation and percolation—belong to the same universality class, it is necessary either to determine a third exponent or to verify the validity of the hyperscaling law [7]. In this paper, we report a new experimental study which is used conjointly with previous work [4,5] to claim that, in this system, the hyperscaling law is valid and that percolation and gelation belong to the same universality class.

The polymer clusters investigated in this paper are

polyurethane samples. They result from a chemical reaction, called polycondensation, between two kinds of monomers. One carries two reactive groups (hexamethylene diisocyanate) and the other three reactive groups [poly(oxypropylene) trimethylol propane]. The degree of connectivity of the polymer cluster population is fixed by the initial hexamethylene diisocyanate ratio, which was chosen in order to obtain a polycondensation reaction completed near and before the gel point.

Small-angle neutron-scattering experiments were performed at the Laboratoire Léon Brillouin in Saclay on the PACE spectrometer. Hydrogenated polyurethane (PUH) and deuterated polyurethane (PUD) were prepared without solvent [8]. The latter was obtained using partially (65%) deuterated poly(oxypropylene) trimethylol propane.

PUD and PUH samples were characterized by light-scattering experiments performed in dilute dioxane solution. Their characteristics are given in Table I. Both samples have, within experimental accuracy, identical z -average radii of gyration (R_z). Thus both samples were elaborated at the same relative distance to the gel point ($\sim 2 \times 10^{-2}$). One has to note that polymers are swollen in dilute solutions; thus their radii of gyration are larger than in the bulk state.

In order to prepare a blended sample of PUH and

TABLE I. Characteristics of the polymers studied (measured in dilute solution by light scattering): PUH and PUD are hydrogenated and deuterated polyurethane, respectively, R_z the z -average radius of gyration, and M_w the weight-average molecular weight.

	R_z (Å)	$10^{-5}M_w$
PUH	610 ± 30	6.8 ± 0.1
PUD	630 ± 15	6.9 ± 0.1

PUD, hydrogenated and deuterated polymers were first dissolved in deuterated tetrahydrofuran (TDF) at a concentration of about 50%. From these two solutions, in different proportions, four samples were prepared. The samples were kept in an oven over vacuum at 70°C for several days. For each sample, the residual amount of solvent was measured. The various concentrations are listed in Table II.

The range of the transfer vector q investigated was $4 \times 10^{-3} < q < 3 \times 10^{-1} \text{ \AA}^{-1}$ ($q = 4\pi/\lambda \sin\theta/2$, λ and θ being the incident wavelength and the scattering angle, respectively). The incident wavelengths used were 4.53, 6.56, and 10.3 Å and the sample-to-detector distances were 1.36, 4.46, and 3.16 m, respectively. Spectra obtained from pure PUD samples allowed us to determine the numerical factor required to superimpose spectra obtained from the three different q ranges. For each sample the incoherent contribution (background) was determined by taking the mean value of the scattered intensity measured at high q . In this q range ($0.28 < q < 0.32 \text{ \AA}^{-1}$), the coherent scattering becomes much smaller than the incoherent contribution [9].

Theoretically and in a general manner [10] the scattered intensity per monomer (I/C) is given by

$$I/C \sim M_w f(qR_z), \quad (2)$$

where M_w is the weight-average molecular weight ($M_w = \sum n_i M_i^2 / \sum n_i M_i$), and R_z the z -average radius of gyration ($R_z^2 = \sum n_i M_i^2 R_i^2 / \sum n_i M_i^2$). The function $f(qR_z)$ is equal to 1 for $qR_z \ll 1$ and equal to $(qR_z)^x$ for $qR_z \gg 1$. If the polymer is probed at a scale length $1/q$ smaller than R_z the scattered intensity is insensitive to R_z .

Percolation theory [1] predicts that in the bulk state near the gelation threshold, the corresponding z -average radius of gyration, without swelling, is proportional to the connectivity correlation length ξ . This correlation length is defined as the size of the largest cluster whose mass is M^* . The fractal nature of this cluster leads to

$$M^* \sim \xi^{D_p}, \quad (3)$$

where D_p is the fractal dimension of polymer clusters in the bulk state. Moreover, masses M^* and M_w are linked by

$$M_w \sim M^{*(3-\tau)}. \quad (4)$$

TABLE II. Characteristics of the samples and experimental values of the exponent $Y = D_p(3 - \tau)$, where $C_i = (\text{weight of } i)/(\text{total weight})$.

Sample	$C = C_{\text{PUH}} (\%)$	$C_{\text{PUD}} (\%)$	$C_{\text{solvent}} (\%)$	Y
1	1.516	77.94	20.53	2.04
2	0.8865	76.76	22.35	2.03
3	0.380	72.54	27.07	1.93
4	44.91	49.81	5.27	1.99

Thus,

$$M_w \sim \xi^{D_p(3-\tau)}. \quad (5)$$

Inserting Eq. (5) into Eq. (2) for $q\xi \gg 1$, i.e., a q range inside which the scattered intensity is expected to be independent of ξ , we recover the result [4,11]

$$I/C \sim q^{-Y}, \quad (6)$$

with

$$Y = D_p(3 - \tau). \quad (7)$$

The exponent τ was measured for this polyurethane species and was found to be [4]

$$\tau = 2.20 \pm 0.04. \quad (8)$$

In a melt, which is incompressible, assuming perfect identity between deuterated and hydrogenated species interactions, it was theoretically expected (see Ref. [10], p. 67) and experimentally shown [12] that, whatever the volume fraction ϕ of labeled species, the scattered intensity is proportional to $\phi(1 - \phi)$. This allows one to perform experiments at high concentration while having access to the same information as at the zero-concentration limit. The exact densities of monomers being unknown, instead of ϕ we use the mass concentration C of labeled species given in Table II. In Fig. 1 is plotted on a log-log scale, as a function of the transfer vector q , the dependence of

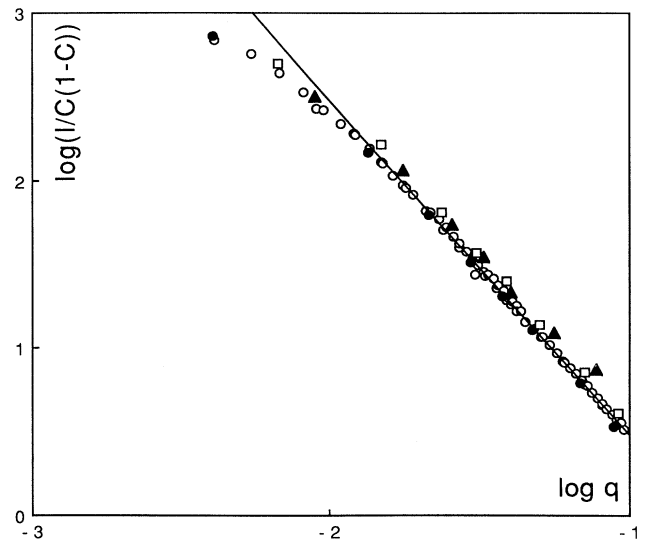


FIG. 1. Log-log plot of the ratio of the scattered intensity in arbitrary units to $C(1 - C)$ vs the transfer vector q (in \AA^{-1}), for the four samples. The straight line corresponds to the mean-square fit of data obtained on sample 4. Its slope, which corresponds to the exponent Y , is 2.00. For clarity's sake, we have kept only one out of nine points in the curves corresponding to samples 1, 2, and 3. ●, sample 1; □, sample 2; ▲, sample 3; ○, sample 4.

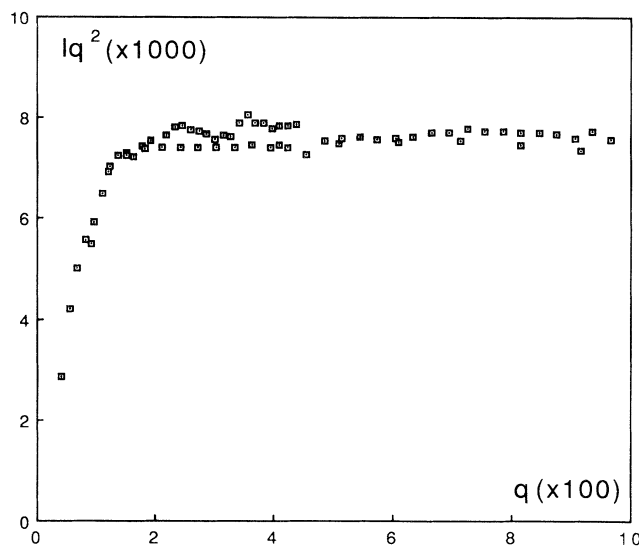


FIG. 2. Check of the q^{-2} dependence of the intensity (arbitrary units) scattered by sample 4 taken as an example.

the scattered intensity divided by $C(1-C)$. This ratio is actually independent of the concentration and q dependent. The slope of the straight line [13] at high q ($1.2 \times 10^{-2} < q < 0.1 \text{ \AA}^{-1}$) corresponds to the exponent $Y = D_p(3-\tau)$. The Y values obtained for the four different samples are given in Table II. The corresponding mean value is

$$Y = 2.00 \pm 0.05. \quad (9)$$

The curvature observed in Fig. 1 at low q ($4 \times 10^{-3} < q < 1.2 \times 10^{-2} \text{ \AA}^{-1}$) is due to the fact that experiments are sensitive to the size ξ of the largest polymer cluster [14].

A check of the q^{-2} dependence of the scattered intensity is given in Fig. 2 where Iq^2 is plotted as a function of the transfer vector q for one sample taken as an example. One can see that this quantity is a constant for $q > 1.2 \times 10^{-2} \text{ \AA}^{-1}$.

The hyperscaling law can be verified, using two independent experiments. Introducing in relation (1) the exponent Y , we obtain

$$d/Y = (\tau - 1)/(3 - \tau). \quad (10)$$

The left-hand side of Eq. (10) is given by the present experimental result performed at $d=3$,

$$d/Y = 1.50 \pm 0.04,$$

while the right-hand side can be derived from the earlier experimental result reported in Ref. [4] [see Eq. (8) of the present paper],

$$(\tau - 1)/(3 - \tau) = 1.50 \pm 0.12.$$

Therefore we conclude that, within the experimental

accuracy, the hyperscaling law is valid for the gelation process described here. This relation now established allows one to get rid of the τ inaccuracy. Combining Eqs. (1) and (7), the fractal dimension of polymer clusters in the bulk state can be written in terms of the exponent Y :

$$D_p = (Y + d)/2. \quad (11)$$

Using the measured value of Y , we find that

$$D_p = 2.50 \pm 0.06, \quad (12)$$

which is in good agreement with the fractal dimension of percolation clusters determined by computer simulations [15].

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