

MECHANICAL PROPERTIES NEAR GELATION THRESHOLD, COMPARISON WITH CLASSICAL  
AND 3d PERCOLATION THEORIES

M. Adam<sup>+</sup>, M. Delsanti<sup>+</sup>, D. Durand<sup>++</sup>, G. Hild<sup>+++</sup> and J.P. Munch<sup>\*</sup>

DPh-G/SRM, CEN Saclay, BP n°2, 91190 Gif-sur-Yvette, France

Abstract - Mechanical measurements done in the reaction bath, near gelation threshold, lead to the following results:

- An elastic behaviour,  $E \sim \Delta p^t$ , with  $t=3.2$  for polycondensation and  $t=2.1$  for radical copolymerization. Both  $t$  values are higher than the one predicted by 3d percolation theory.

- On both systems a viscosity behaviour,  $\eta \sim \Delta p^{-s}$ , with  $s=0.78$  in agreement with 3d percolation theory.

INTRODUCTION

A competition exists between classical and 3 dimensional (3d) percolation theories concerning the gelation transition. Here, we try to test the validity of both theories on mechanical behaviour at the sol gel transition. We present recent mechanical measurements, done in the reaction bath, during the gelation process, near its threshold.

We shall recall the theoretical framework mentioned by Stauffer (1), then go into details of the experimental procedure and present the results obtained on radical copolymerization and on polycondensation samples.

I. COMPARISON BETWEEN THEORIES

We shall not enter into details of both theories, but we should like to point out their main approximations, considering that both theories predict what happens near the gel point.

Classical theory is a percolation on a Bethe lattice, which can be embedded only in a space of infinite dimension. Thus steric hindrances could not be taken into account. Restricted to a 3d space, a fraction of monomers should occupy the same spatial position. This approximation seems to us more drastic than the absence of cyclic bonds.

By introduction of a fictitious lattice, 3d percolation theory takes into account steric hindrance effect - but neglects diffusion processes (2) and substitutes the real growth process by a uniform random bond drawing. This last approximation can be serious in the case of radical copolymerization where all the monomers are not equivalent. Indeed, Monte Carlo simulation indicates (3) that the cluster structures in radical copolymerization are different from the simple 3d case.

Percolation theory shows that classical exponents values are invalid for a space dimensionality smaller than 6 (4) ; on the other hand, the analogy between standard 3d percolation and gelation is not obvious.

Now let us recall what are the theoretical predictions on mechanical properties of both theories.

Classical theory

There is no theoretical prediction on viscosity  $\eta$  behaviour. This theory does take into account neither spatial, nor dynamical interactions between the clusters, so it cannot predict the divergence of the viscosity at the gel point.

-----  
<sup>+</sup> Authors to whom requests for reprints should be addressed.

<sup>++</sup> Laboratoire de Physico-chimie Macromoléculaire de la Faculté des Sciences du Mans, route de Laval, 72017 le Mans Cedex.

<sup>+++</sup> Centre de Recherches sur les Macromolécules, 6 rue Boussingault, 67083 Strasbourg Cedex.

<sup>\*</sup> Laboratoire d'Acoustique Moléculaire, Université Louis Pasteur, 4 rue Blaise-Pascal 67070 Strasbourg Cedex.

A calculation of the elasticity  $E$  due to Gordon (5) leads to

$$E \sim \Delta p^t \quad \text{where } t = 3$$

and

$$\Delta p = p - p_c, \quad \text{where } p,$$

the degree of advancement of the reaction in the gelation process, is identified with bond probability in percolation ( $p_c$  is the  $p$  value at the gel point).

### 3d percolation

There is no direct calculation of  $\eta$  (see note a) and  $E$ , during the gelation process but analogies between :

- viscosity of the sol, in the reaction bath and the electric conductance of a random network of super- and normal- conductors (7),

- elasticity of the gel phase and the electric conductance of a random resistor network (8).

Using Monte Carlo simulations on 3d percolation models it has been found that :

$$\eta \sim \Delta p^{-s} \quad s = 0.7 \pm 0.07 \quad (9)$$

$$\text{and} \quad E \sim \Delta p^t \quad t = 1.62 \pm 0.05 \quad (10).$$

De Gennes (8) introduced a relation between  $t$  and  $\nu$  :

$$t = 1 + (d-2)\nu,$$

where  $\nu$  is the exponent characteristic of the size  $\xi$  of the largest cluster ( $\xi \sim \Delta p^{-\nu}$ ). In 3d percolation theory, exponent values are in rather good agreement with the preceding relation ( $\nu=0.8$ ). But, in classical theory ( $\nu=0.5$ ), this relation is fulfilled only for  $d=6$ .

TABLE 1. Theoretical exponent values

Classical theory		3d percolation
$s$	-	0.7
$t$	3	1.62

One can see, from a theoretical point of view, that only elastic measurements can allow us to choose between both theories. Unfortunately, experimentally, if viscosity is a well defined and measurable quantity, measurements of elasticity are less reliable as we shall see later.

## II. VISCOSITY AND ELASTICITY MEASUREMENTS

### A. Instrumentation

The magnetic sphere viscosimeter has been realized by P. Pieranski and B. Meyer (11) following an original idea of M. Gordon (12). A magnetic sphere is introduced with each sample ( $5 \text{ cm}^3$ ) into a glass tube which is then sealed. The magnetic sphere experiences a force  $F$  due to a non uniform magnetic field created by an external coil  $C$ . One images the sphere on two photodiodes by an optical system (Fig.1). The differential photo current of  $P_1$ - $P_2$  is fed to the monitor which adjusts the voltage  $V$  applied to the magnetic coil in such a way that the sphere remains at the same spatial position on the coil axis. Thus, the force  $F$  acting on the magnetic sphere is proportional to the voltage  $V$ . Measuring  $V$ , one has a knowledge of the magnetic force which counteracts viscous or elastic force.

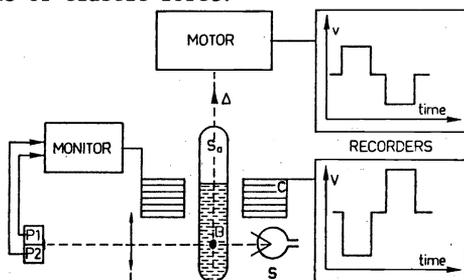


Fig.1. Schematic diagram of the apparatus : S light source, L lens, B magnetic sphere,  $\Delta$  displacement of the sample  $S_a$ , C coil.

Note a. All theoretical attempts (6, 7) to calculate the divergence of the viscosity, near  $p_c$ , have failed because the influence of hydrodynamic interactions has been underestimated.

For a viscous fluid, the cell is moved at a velocity  $v$ , in the direction of the coil axis. The force acting on the sphere is :

$$f = 6 \pi \eta r v$$

where  $r$  is the radius of the sphere. For an elastic system, the cell is displaced by  $\Delta$ , the force acting on the sphere is

$$f = 6 \pi r E \Delta$$

thus we have :

$$V = A v \eta \quad \text{or} \quad V = A \Delta E$$

where  $A$  is a numerical factor, determined by calibration.

The displacement of the cell is realized by a step motor (steps of  $0.1 \mu\text{m}$ ) which allows to have velocities down to  $5 \times 10^{-6} \text{cm s}^{-1}$  with an accuracy of  $2 \times 10^{-3}$ .

Typically, measurements of a silicon oil of  $\eta = 50$  poises, with a sphere of  $0.1 \text{cm}$  diameter lead to  $V/v = 1.6 \times 10^4 \text{mV cm}^{-1} \text{s}$  with a precision better than  $10^{-2}$ . In this case  $A = 320 \text{mV.cm}^{-1} \text{s.p}^{-1}$

#### B. Drawbacks and advantages of the procedure

In order to have reliable measurements of  $\eta$  and  $E$ , one must verify that, for a given  $p$  :

$$\text{when } p < p_c \quad , \quad \eta = \frac{V}{A v} = \text{const} \quad \text{and}$$

$$\text{when } p > p_c \quad , \quad E = \frac{V}{A \Delta} = \text{const.}$$

If measurements are done during polymerization, these laws can hardly be verified near the gel point because  $\eta$  and  $E$  increase during one measurement. In this case the measurements are done at very low shear rate, when  $p < p_c$  (typically  $v/r = 4 \times 10^{-4} \text{s}^{-1}$ ) and at small shear deformation ( $\Delta/r = 4 \times 10^{-2}$ ), when  $p > p_c$ .

On polycondensation samples, the apparition of a time response, near the gel point, which can be even longer than the displacement time, makes difficult the measurement of the steady force (see note b).

In order to be free of those two problems we plan to realize an experiment on a quenched sample, viscosity and elasticity measurements will be done at  $25^\circ\text{C}$ , where chemical reaction is stopped, polycondensation will be performed, as usual, at high temperature.

Those difficulties are counterbalanced by the following advantages :

- measurements can be performed, during the gelation process, without any chemical intervention and very close to the gel point,

- sol and gel phases are submitted to very small deformations which can prevent all destructions of the fragile gel structure, near  $p_c$ .

#### C. Polymeric systems

Two types of polymerization have been studied (note c) :

- radical copolymerization (13) of styrene (4 mol/l) - meta divinyl benzene (0.08 mol/l). Azo-2-2' isobutyro nitrile is used as initiator (0.08 mol/l) and benzene as solvent. Polymerization is done at  $60^\circ\text{C}$  and the time required for gelation about 9 hours,

- polycondensation (14) : hexamethyl di-isocyanate is mixed with Niax triol LHT240 (manufactured by Union Carbide Corporation - propylene oxide adducts of 1,2,6-hexane triol) in order to obtain an equal number of sites OH and NCO. The gelation time is about 32 hours at  $60^\circ\text{C}$ .

#### D. Evaluation of the degree of advancement of the reaction $p$

Since  $p$  is a smooth and slowly varying function of the time of reaction  $T$  and since our measurements are done at  $10^{-3} < \Delta T/T_c < 5 \times 10^{-2}$  around  $T_c$ , we can use  $T$  as a variable.

Note b. This might be due to the presence of entanglements between clusters. The time constant comes from the reorganization of the system around the moving sphere.

Note c. Styrene DVB samples are prepared in Strasbourg (G. Hild - R. Okasha) and polycondensation samples in le Mans (D. Durand). Inquiries concerning details on the chemical procedure should be addressed to them.

This approximation has been verified recently by Burchard (15) on radical copolymerization and can be estimated from a kinetic calculation of polycondensation. The relative error on the exponents values, induced by the approximation  $\Delta p/p_c \sim \Delta T/T_c$ , for a second order reaction is smaller than the range of  $\Delta T/T_c$  ( $15 \times 10^{-2}$ ), if the reaction rate is a constant around  $T_c$ .

#### E. Fit of the experimental data

One must compare the experimental results with the functions

$$\eta = B (T_c - T)^{-s}$$

$$E = C (T - T_c)^t.$$

Thus we have to determine five variables with about 40 points. Using a fit program (16), we obtain  $B, s, T_c, C, t$ . The  $T_c$  estimated value must be between the two limits :

$$T_v < T_c < T_E$$

where  $T_v$  and  $T_E$  are the reaction times where the last viscosity and the first elasticity measurements were performed, respectively.

We reject all data which gives a poor quality factor (17) and a poor accuracy of the exponent values.

### III. EXPERIMENTAL RESULTS

The estimated values of  $t, s, T_c$  for experiments done on radical copolymerization and on polycondensation samples are given in table 2.

TABLE 2. Experimental values of  $s, t$  and  $T_c$

Type of polymerization	$T_c$ hours	$s$	$t$
polycondensation	$30.673 \pm 0.02$	$0.77 \pm 0.04$	$3.23 \pm 0.2$
	$32.352 \pm 0.002$	$0.74 \pm 0.04$	$2.62 \pm 0.1$
	$32.713 \pm 0.003$	$0.61 \pm 0.04$	$3.25 \pm 0.01$
	$35.017 \pm 0.03$	$0.85 \pm 0.07$	$3.88 \pm 0.6$
radical copolymerization	$9.083 \pm 0.005$	$0.79 \pm 0.02$	$2.4 \pm 0.2$
	$10 \pm 0.001$	$0.9 \pm 0.06$	$1.8 \pm 0.1$

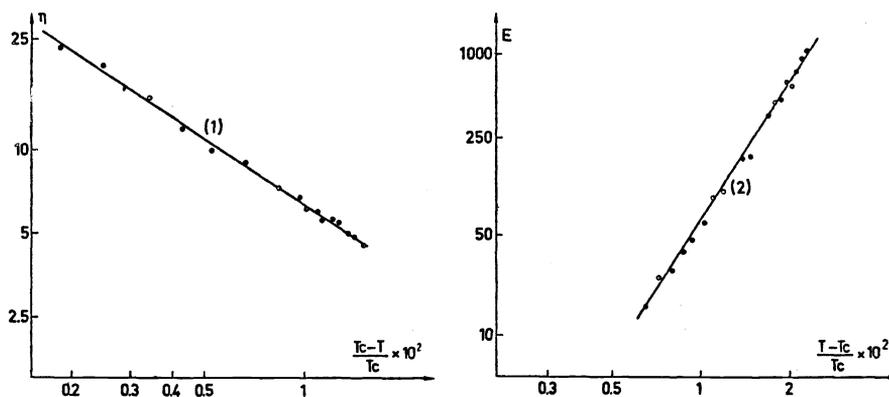


Fig.2. Examples of mechanical behaviour : curve 1, viscosity from radical copolymerization,  $\eta$  is expressed in poise; curve 2, elasticity from polycondensation,  $E$  is expressed in dyne/cm<sup>2</sup>.

The  $s$  values are, within experimental accuracy, identical for both systems. Their mean value is :

$$s = 0.78 \pm 0.05$$

definitively smaller, near the gel point, than the value predicted by effective medium theory ( $s=1$ ) (18). This is well confirmed by the fact that, if one plots the inverse of the viscosity as a function of time, one finds a time where  $1/\eta \rightarrow 0$  which is systematically shorter than  $T_c$ .

This experimental  $s$  value is in good agreement with percolation predictions (0.7).

The mean  $t$  values obtained on each system are :

- for polycondensation samples  $t = 3.2$  which corresponds to the classical value
- for copolymerization samples  $t = 2.1$ .

Both  $t$  values are significantly higher than the  $t$  value (1.62) estimated by Monte Carlo technique using 3d percolation model. This can be explained by :

i) a very narrow critical domain in  $\Delta T/T_c$ , where 3d percolation theory is valid ; but this would imply very different extents of the critical domain above and below  $T_c$ .

ii) The structure of the clusters are very different in gelation and in standard 3d percolation case. In the radical copolymerization samples,  $t$  value corresponds to :

$$\nu = \frac{t-1}{d-2} = 1.1,$$

higher than classical value ( $\nu = 0.5$ ) and 3d percolation value ( $\nu = 0.8$ ). This is confirmed by Monte Carlo simulations on radical copolymerization on 3d percolation model (3).

iii) The presence of trapped entanglements between clusters which are not taken into account in both theories.

The important scattering of the  $t$  values can be explained by experimental difficulties - one of our problems is to determine the steady force, near  $T_c$ , when a long time constant appears in the case of polymerization by polycondensation. The difficulties encountered by other recent experiments (15,19) do not allow us to give a definite answer concerning to the gelation problem.

We think that an experiment done on quenched samples will help us to clarify the problem of the elastic critical behaviour of the gel phase.

The theoretical effort must be maintained in order to confirm the difference between standard 3d percolation model and gelation on radical copolymerization.

Acknowledgements - Two of us (M.A. and M.D.) wish to thank P. Manneville and L. de Seze for helpful discussions.

#### REFERENCES

1. D. Stauffer, This conference proceedings.
2. D. Stauffer, Physics reports 54, 1 (1979).
3. P. Manneville and L. de Seze, to be published in Springer Series in synergetics : coll. sur les méthodes de calcul pour l'étude des phénomènes critiques, Carry-le-Rouet (1980).
4. P.G. de Gennes, Scaling concept in polymer physics, Cornell University Press - Ithaca and London (1979).
5. M. Gordon and S.B. Ross - Murphy, Pure and Applied Chem. 43, 1 (1975).
6. D. Sievers, Submitted to J. de Phys. L.
7. P.G. de Gennes, C.R. Hebd. Séan. Acad. Sc. B 286, 131 (1978).
8. P.G. de Gennes, J. de Phys. L 37, 1 (1976).
9. J. Bernasconi, J. Phys. Rev. B18, 2185 (1978).
10. S. Kirkpatrick, Ill-condensed matter, p.366, Les Houches, North-Holland (1973).
11. R. Meyer and P. Pieranski, Preprint (P. Pieranski Bât.510, Université de Paris-Sud, F 91405 Orsay-Cedex).
12. M. Gordon, S.C. Hunter, J.A. Loue and T.C. Ward, Nature 217, 735 (1968).
13. R. Okasha, G. Hild and P. Rempp, European Polym. J.15, 975 (1979).
14. W. Hopkins, R.H. Peters and R.S.T. Stepto, Polymer J. 15, 315 (1974).
15. R.S. Witney and W. Burchard, Makromol. Chem. 181, 869 (1980).
16. M. Tournarie, J. de Phys. 30, 737 (1969).
17. M. Adam, M. Delsanti, R. Okasha and G. Hild, J. de Phys. L 40, L539 (1979).
18. J.P. Straley, J. de Phys. Colloq. 37. C9. 783 (1976).

19. M. Schmidt and W. Burchard, Submitted to Macromolecules.  
J.C. Bacri, J.M. Courdille, J. Dumas and R. Rajaonarison, J. de Phys. L.41, L 369 (1980).  
J. Dumas and J.C. Bacri, J. de Phys. L.41, L 279 (1980).  
B. Gauthier-Manuel and E. Guyon, C.R. Hebd. Sean. Acad. Sc. B290, 465 (1980).