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Viscosity study in the reaction bath of the radical copolymerization of styrene divinylbenzene

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Résumé. — Nous mesurons la viscosité η , dans le bain de réaction d'une copolymérisation Divinylbenzène-Styrène. Nous présentons quelques résultats préliminaires obtenus au voisinage du point de gel. La variation de la viscosité η en fonction du temps de réaction est :

$$\eta \sim \left(\frac{t_c - t}{t_c} \right) - 0,78 \mp 0,1; \quad \text{si } \frac{t_c - t}{t_c} \leq 2 \times 10^{-2}$$

où t_c est le temps de réaction nécessaire pour que le point de gel apparaisse.

Nous pensons que le processus de gélification peut être analysé à l'aide de la théorie de percolation.

Abstract. — We report some preliminary viscosity measurements taken during the copolymerization of Styrene Divinylbenzene in the reaction bath, near the gel point.

The dependence of the viscosity η on the reaction time t is found to be :

$$\eta \sim \left(\frac{t_c - t}{t_c} \right) - 0.78 \mp 0.1; \quad \text{when } \frac{t_c - t}{t_c} \leq 2 \times 10^{-2}$$

where t_c is the reaction time at which the gelation occurs.

Thus the gelation process can be analyzed in terms of percolation theory.

The theory of gelation has been developed by Flory, Stockmayer and Gordon [1, 2] (F, S, G) using a Cayley tree model. This model does not take into account cyclization and excludes volume effects. The analogy between the gel process and percolation developed by Stauffer and de Gennes [3] enables cyclization and excluded volume effects to be taken into account.

Here we are concerned with the viscosity η of the sol near the gel point, measured *in situ*, in the reaction bath during the copolymerization. F, S, G did not attempt to predict the viscosity behaviour. However an analogy between the viscosity, η , in the reaction bath and the macroscopic conductance of a lattice composed of a mixture of super and normal conductors [4] has led to the prediction that the diver-

gence of the viscosity at the gel point follows a power law [5] :

$$\eta \sim \left(\frac{p_c - p}{p_c} \right)^{-s}$$

where p is the fraction of the reacted bond, and p_c its value at the gelation threshold. In the case of a mixture of super and normal conductors the exponent s has been determined by Monte Carlo simulation : $s = 0.7 \pm 0.07$ [6] while the *effective medium* approximation predicts $s = 1$ [7].

We have performed some preliminary experiments during the copolymerization of Styrene and Divinylbenzene (DVB) at 60 °C, using AZO-2,2' isobutyronitrile (AIBN) as initiator [8]. The composition of the sample was : styrene 4.01 mol/l, meta DVB 0.08 mol/l, AIBN 0.08 mol/l, and benzene was used as a solvent. The reactive elements were mixed in a glass tube, sealed after degassing under vacuum and then placed in the thermostat.

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The macroscopic viscosity in the reaction bath is determined by steady shear flow using a *magnetic sphere rheometer* [9], which is represented schematically in figure 1.

Fig. 1. — The magnetic sphere experiences a force created by a non-uniform magnetic field. By mean of a light source, S, and a lens, L, the sphere is imaged on the surface of the photodiodes P_1 P_2 . The differential current of the photodiodes P_1 P_2 , in the input of the monitor adjusts the current intensity, I , of the coil in such a way that the sphere remains at the same position in the cell, Sa , which contains the sol. $I \sim \eta a \delta$ where a ($a \approx 0.5$ mm) is the radius of the magnetic sphere and δ the velocity of the displacement of the sample. The displacement, δ , is measured by recording the output voltage of a displacement detector D.

[Un champ magnétique non uniforme exerce une force sur une sphère magnétique, immergée dans la cellule de mesure Sa . À l'aide d'une source lumineuse S et d'une lentille L, l'image de la sphère est projetée sur les photodiodes P_1 et P_2 . Un amplificateur différentiel ajuste l'intensité I de la bobine magnétique, à partir des courants de sortie des 2 photodiodes afin que la sphère soit maintenue en une position déterminée. $I \sim \eta a \delta$ où a est le rayon de la sphère ($\approx 0,5$ mm) et δ la vitesse de déplacement de la cellule Sa . Le déplacement δ est mesuré par l'enregistrement de la tension aux bornes d'un détecteur de déplacement D.]

In order to ascertain that the viscosity measured is Newtonian, we reduced the shear rate $\dot{\gamma}$ as the viscosity increased [10] ($0.1 \text{ s}^{-1} < \dot{\gamma} < 0.7 \text{ s}^{-1}$). The viscosity η can be measured every six seconds with an accuracy of 3%. This apparatus allows us to determine the viscosity up to the gel point, as a function of the reaction time. Time zero is the time at which the sample is introduced at 60°C ; it has been chosen arbitrarily, as it does not influence the following treatment.

We observe (fig. 2) that the viscosity increases rapidly only after a time of 8 h 35 min.

Knowing that the sample has a viscous behaviour at 9 h 04 min (3.264×10^4 s) and an elastic behaviour at 9 h 05 min (3.270×10^4 s), we can determine the gel time, t_c , as :

$$3.264 \times 10^4 \text{ s} < t_c < 3.270 \times 10^4 \text{ s}.$$

In figure 2 we present also the variation of the inverse of the viscosity with respect to time. We can see that :

— far from the gel point ($t < 3.14 \times 10^4$ s), the inverse of the viscosity is linear with time,

— near the gel point, a departure from the linear law is observed.

Since the conversion rate of each of the consti-

Fig. 2. — Variation of the viscosity with reaction time : ● viscosity measurements, + inverse of the viscosity, — linear behavior. η_r is a viscosity reference : $\eta_r \approx 30$ poises.

[Variation de la viscosité en fonction du temps de réaction : ● résultats expérimentaux, + inverse de la viscosité, — comportement linéaire. η_r viscosité de la solution de référence (≈ 30 poises).]

tutents is a smooth function of time and since the viscosity measurements were performed during a small time period ($t_c - t \lesssim 5 \times 10^{-2} t_c$), we can suppose that the fraction of reacted bond p varies linearly with time.

Supposing a power law variation :

$$\eta \sim \left(\frac{t_c - t}{t_c} \right)^{-s} \quad (1)$$

and using a least square fit for the whole time range

$$3.1086 \times 10^4 \text{ s} < t < 3.2628 \times 10^4 \text{ s}$$

we determine $s = 0.98 \pm 0.02$, $t_c = 3.275 \times 10^4$ s with a quality fit factor [11] $Q = 0.48$.

The departure from the linear law observed in figure 2 is confirmed by :

— The low Q value, which implies that the experimental points do not fit the theoretical law (1) (fig. 3b) :

— The time t_c determined by calculation is larger than the upper limit given by direct observation (3.27×10^4 s).

Consequently we fit the data by taking account separately the measurements done near the gel point and far from the gel point.

— Near the gel point

$$(3.2050 \times 10^4 \text{ s} < t < 3.2628 \times 10^4 \text{ s}),$$

we obtain using relation (1) :

$$s = 0.79 \mp 0.02,$$

$$t_c = 3.27 \times 10^4 \text{ s} \quad \text{and} \quad Q = 0.85.$$

This gel time corresponds to the upper limit obtained by direct observation.

— Far from the gel point

$$(3.1086 \times 10^4 \text{ s} < t < 3.1680 \times 10^4 \text{ s})$$

and $t_c = 3.27 \times 10^4 \text{ s}$ we obtain : $s = 1.05 \pm 0.04$ and $Q = 0.95$.

The high values of the quality factor Q indicate that this data processing is adequate (fig. 3a).

Fig. 3. — Variation of the deviation ε_i of the experimental to the theoretical value as a function of the time. a) Random distribution observed with the second fit. b) Non-random distribution observed with the first fit.

[Variation en fonction du temps des écarts ε_i des valeurs expérimentales par rapport aux valeurs théoriques. a) Distribution aléatoire obtenue lors du 2^e traitement. b) Distribution non aléatoire obtenue lors du 1^{er} traitement.]

In fact, the first value of s obtained by our method is strongly t_c dependent. Acceptable values for the quality factor (larger than 0.6) enforce a range of t_c values defined by :

$$|t_c - 3.27 \times 10^4 \text{ s}| \leq 20 \text{ s},$$

which leads to a corresponding range of acceptable values for s defined by :

$$|s - 0.78| \leq 0.08.$$

Figure 4 presents on a log-log scale variation of the

Fig. 4. — Log-Log plot of the viscosity as a function of the reduced time $(t_c - t)/t_c$.

[Variation de la viscosité en fonction de la variable réduite : $(t_c - t)/t_c$.]

viscosity as a function of reduced time $\left(\frac{t_c - t}{t_c}\right)$:

— near the gel point the exponent value found (0.78 ± 0.1) is in agreement with the Monte Carlo calculated value using a percolation type model,

— far from the gel point, the exponent value (1.05) is in agreement with experimental results given in ref. [12], and agrees well with the value given by the *effective medium* approximation.

This crossover from *effective medium behaviour* far from threshold to *critical exponent* behaviour near threshold is strikingly similar to what is found on the other side of the transition (above percolation threshold) for the conductance of a mixture of conducting and non-conducting materials [13].

On the whole, our results do suggest that gelation in the styrene DVB system can be analysed in terms of percolation theory.

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$$\eta = \left(\frac{p_c - p}{p_c}\right)^{-2\nu + \beta}, \quad \text{where } 2\nu - \beta = 1.2;$$

However the relation $s = 2\nu - \beta$ does not hold in the case $d = 3$ (d being the space dimensionality).

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 [10] The shear rate $\dot{\gamma}$ is defined as $\dot{\delta}/a$ where $\dot{\delta}$ is the velocity of the displacement and a (≈ 0.5 mm) is the radius of the magnetic sphere.
 [11] $Q = 1 - \frac{\left| \sum_{i=1}^{N-1} \varepsilon_i \varepsilon_{i+1} \right|}{\sum_{i=1}^N \varepsilon_i^2}$ where N is the number of experimental points considered. ε_i is the deviation of the i th experimental point from the i th theoretical point. $Q \rightarrow 1$ if ε_i is random.
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