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Scaling Behavior of Pregel Sols Obtained by End-Linking of Linear Chains

The sol–gel transition has been the subject of many theoretical and experimental studies in the last 50 years.[1-5] From a fundamental point of view, the universal features related to the transformation of the viscous reaction bath into an elastic solid are quite fascinating. From a more practical point of view, these universal features seem to be very useful to explain some of the properties of the final gel.[6]

To describe the sol phase before the gel point, the fundamental quantity is the size distribution function (SDF) of the species in the reaction bath.[1,3,7] It has been shown recently that size-exclusion chromatography (SEC) experiments provide a direct measurement of this function.[8-10]

Up to now, two different gelling reactions have been investigated with this technique: irradiation-induced random cross-linking of linear polystyrene (PS) solutions in θ conditions[8,9] and bulk condensation polymerization leading to a polyester network.[10] Although the two systems are quite different, the characterization of their sol phase before the gel point gave similar results. In both cases the experimental distribution functions are found to obey a scaling form. Also the values of the exponent τ, that characterizes the decay of the SDF at the gel point, are in good agreement with each other.

The purpose of this note is to describe preliminary results obtained with the SEC technique on a third and different system: end-linking of poly(dimethylsiloxane) (PDMS) chains in the melt. The results are shown to be consistent with those obtained with the two previous systems.

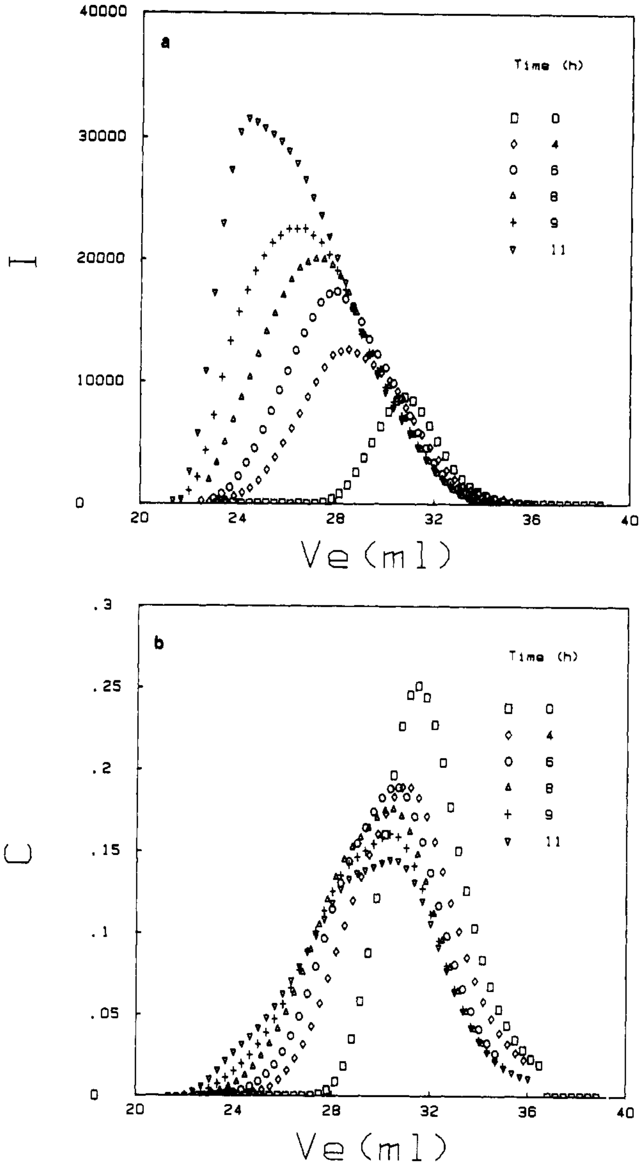

Figure 1. (a) Refractometry chromatograms for samples with different reaction times. The curves are normalized to a unit area. (b) Light-scattering chromatograms of the samples in (a). The curves are normalized so that the area is proportional to the weight-average molecular weight of the samples.

The precursor α,ω-functional linear chains are PDMS chains ($M_{w,0} \simeq 27000$) with dimethylsilyl groups at the ends. These chains are heated at 70 °C with tetrakis(allyloxy)ethane at a 1/1 stoichiometric ratio of dimethylsilyl to unsaturated functions, in the presence of chloroplatinic catalyst.[11] Samples are removed from the reaction bath at different reaction times and the reaction is stopped by using Rosenmund's poison.[12] Under these experimental conditions, we expect that the main reaction is the end-linking of the preexisting chains by the tetrafunctional units, with no influence of side reactions.[11] Thus branched molecules are obtained with a fixed length between cross-linking points.

Once the reaction is stopped, the samples are diluted in toluene and characterized by SEC coupled on line with a SHODEX SE11 refractometer and a home-built light-scattering apparatus.[13] The light source is a He–Ne laser and the scattering angle is 90°.

Figure 1 shows the evolution of the refractometry (a) and light-scattering signals (b) as the reaction time increases.

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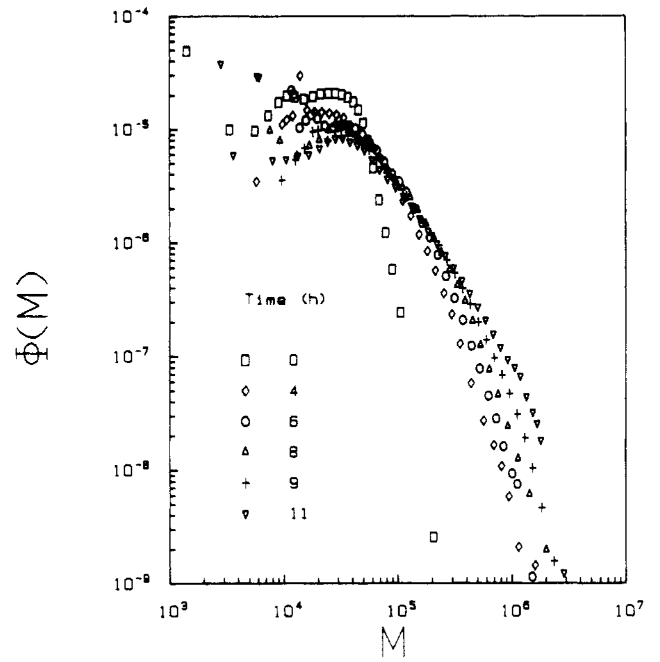

Figure 2. Size distribution functions of the samples in Figure 1, calculated as described in ref 8 and 9.

It can be seen that the concentration of small linear chains decreases progressively as larger branched molecules are formed. Although their concentration is rather small, these large molecules are responsible for a large increase of the scattered light intensity.

Usually the weight-average molecular weight M_i of the molecules in a given fraction i is simply calculated as

$$M_i = K\frac{I_i}{C_i} \tag{1}$$

where I_i is the intensity scattered by the molecules in this fraction, C_i is their concentration, and K is a known apparatus constant. In writing (1) we have ignored concentration effects and angular dependence, both of which affect the scattered intensity. Neglecting concentration effects is usually a good approximation, since the concentrations in the fractions are less than 10^{-5} g/cm^3. Our light-scattering setup, ignoring the angular dependence from the scattered intensity, introduces an error smaller than 5% for molecules with radii of gyration smaller than 180 Å. We can use a blob model[14] to estimate the corresponding molecular weight of the branched molecules. We write

$$R \simeq [M_w/M_{w,0}]^{1/2}R_0$$

where $R_0 = 0.12\ M_{w,0}{}^{0.59}$ is the radius of gyration of the linear precursor chains in toluene.[15] Thus we can estimate the upper limit of the molecular weight of branched molecules that we can measure with an error less than 5%. This limit is roughly 4×10^5, which corresponds to molecules built up with 15–20 linear chains. The molecular weights of larger molecules are progressively more underestimated as the molecular weight increases.

To characterize the sol phase, the useful quantity is the size distribution function $\varphi(M, \epsilon)$, defined so that $\varphi(M, \epsilon)$ dM is the weight fraction of monomers belonging to molecules with molecular weight between M and M + dM. Here $\epsilon = 1 - p/p_c$, where p is the extent of the reaction and p_c is the p value at the gel point. Figure 2 shows the evolution of the SDF of the samples with different reaction times. The SDFs are calculated from the experimental data as described in previous papers.[8,9] They show the expected increase of the weight fraction of high molecular weight species as the reaction time increases. In Figure 2 we have kept the points corresponding to molecular weights larger than 4×10^5 in order to give a better qualitative illustration of the spreading of the SDF as the gel point is approached. In the following these points will be ignored for the quantitative analysis.

Classical theories as well as percolation theory predict a scaling form for the SDF of the high molecular weight species near the gel point. This can be written as

$$\varphi(M,\epsilon) \simeq M^{-\tau+1}f(M/M^*(\epsilon)) \tag{2}$$

Here f is a cutoff function ($f(x) \simeq 1$ for $x < 1$ and $f(x) \to 0$ for $x > 1$) and $M^*(\epsilon)$ is a cutoff molecular weight that diverges at the gel point as

$$M^* \simeq \epsilon^{-1/\sigma} \tag{3}$$

The two critical exponents τ and σ have different values in classical theory ($\tau = {}^5/_2$, $\sigma = {}^1/_2$) and in percolation theory ($\tau \simeq 2.2$, $\sigma \simeq 0.46$). Equations 2 and 3 imply that the SDF has a simple decreasing power-law behavior at the gel point. The scaling form (2) gives a very simple relationship between M^* and the kth moment $\langle M^k\rangle$ of the SDF. We have

$$\langle M^k\rangle = \int M^k\varphi(M,\epsilon)\ \mathrm{d}M \simeq M^{*k+2-\tau}, \qquad k > 1 \tag{4}$$

In particular, the weight-average molecular weight M_w, defined as $M_w = \langle M^1\rangle/\langle M^0\rangle$, scales like

$$M_w \simeq M^{*3-\tau} \tag{5}$$

The experimental determination of the cutoff molecular weight M^* can be done in different ways. It has been proposed[8,9] to identify M^* to the molecular weight M_{max} of the molecules that gives a maximum contribution in the light-scattering curves (Figure 1b). This definition is based on the fact that the cutoff molecular weight M^* gives the dominant contribution in terms like $M^k\varphi(M)$ ($k > 1$). In fact it has been shown[8,9] that due to the separation process in the SEC columns, the light-scattering signal is proportional to $M^2\varphi(M)$. Another way to measure the cutoff molecular weight would be to directly fit the experimental SDF with eq 2, assuming a specific analytic form for the cutoff function. Patton et al.[10] recently used this approach with an exponential form for $f(x)$. Their data are well described with this choice. They found that the cutoff molecular weights M_{char}, determined in this way, are proportional to the values M_{max} corresponding to the maximum contribution in the light-scattering curve.

Here we prefer to use M_{max} as a measurement of the cutoff molecular weight because this method does not involve any fitting procedure. Figure 3 shows the variation of M_w as a function of the cutoff molecular weight M_{max}. Since $M^* \simeq M_{max} \simeq M_{char}$, from relation 5 we obtain the value $\tau \simeq 2.27 \pm 0.04$ for this system.

This is very close to the value $\tau \simeq 2.3 \pm 0.1$ found in the PS system[8,9] and $\tau \simeq 2.28 \pm 0.03$ found in a polyester system.[10]

It has been argued[8,9] on the basis of eq 2 that the function $G(M/M^*) = M^{*\tau-1}(\epsilon)\varphi(M,\epsilon)$ should be independent of the advancement of the reaction. This representation is used in Figure 4 for the experimental points corresponding to molecular weight between 1×10^5 and 4×10^5. As for the two previous systems,[8,10] a good collapse of the data points is observed, although in this case the light-scattering apparatus used covers too restricted a molecular weight range to permit a definitive conclusion.

The continuous and the dashed lines in Figure 4 correspond to the experimental points obtained in this rep-

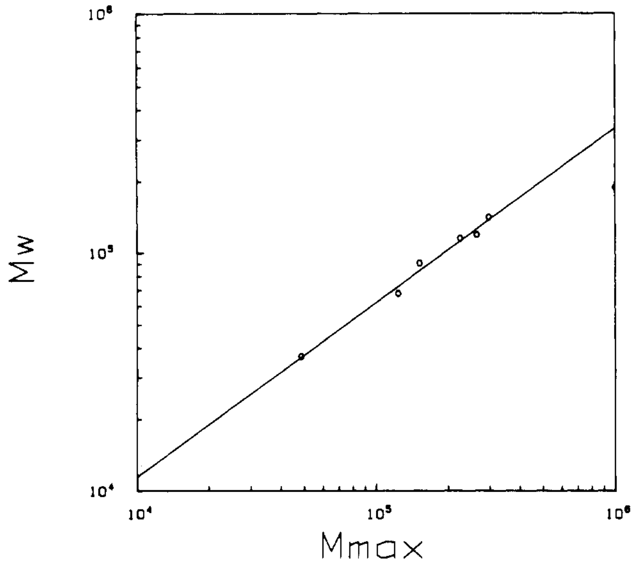

Figure 3. Evolution of the weight-average molecular weight M_w of the samples as a function of the characteristic molecular weight M_{max}. The slope corresponds to $3 - \tau = 0.73 \pm 0.04$. The highest molecular weight sample is not taken into account, since at 90° scattering angle, the M_w and the M_{max} values are underestimated for this sample (see text).

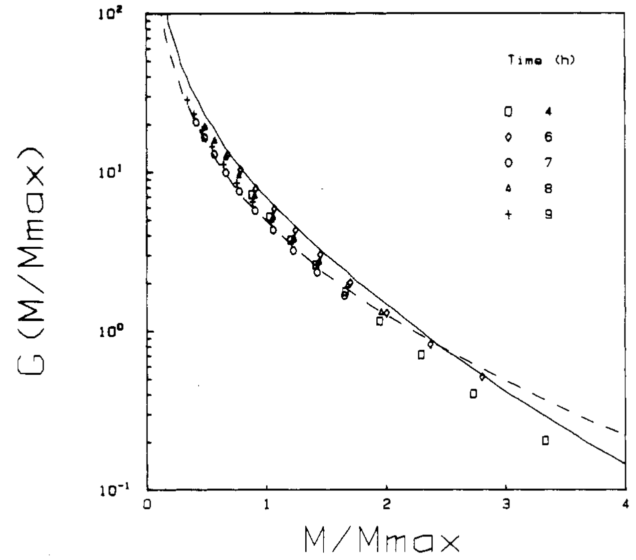

Figure 4. Plot of the renormalized size distribution function $G(M/M_{max}) = M_{max}^{\tau-1}\varphi(M,\epsilon)$ for some samples. Experimental points correspond to molecular weights between 1×10^5 and 4×10^5 g/mol. Continuous and dashed lines sum up the experimental results obtained for the PS system[8,9] and the polyester system,[10] respectively (see text).

resentation with the PS system and the polyester system, respectively. Since we use M_{max} instead of M_{char}, the experimental $G(M/M_{char})$ reported by Patton et al. has been corrected to take into account the proportionnality constant between the two quantities. If we call α the ratio M_{char}/M_{max}, then $G(M/M_{char}) = \alpha^{\tau-1}G(\alpha M/M_{max})$. From Figure 14 in ref 10, we estimated that α is close to the value $\alpha = 2$. Data in Figure 4 show that the renormalized function G gives a good description of the three systems without any fitting parameter. Small deviations between the different systems are observed for high values of M/M_{max}. It is not clear if this should be attributed to different cutoff functions in the three systems or to a lack of accuracy in the experimental data. In fact high values of M/M_{max} correspond to a strong decrease in the concentration of the corresponding branched molecules. Also the graphical estimation of α is not precise. More work is needed to clarify this point. It may be useful in the future to use a unique definition for the cutoff molecular weight. Perhaps the z-average molecular weight $\langle M^2\rangle/\langle M^1\rangle$ suggested earlier[4] is a good experimental definition for M^*.

In conclusion we have reported in this paper preliminary results on pregel samples obtained by end-linking of PDMS chains in the melt. The size distribution function of the samples exhibits a scaling form as in previously studied systems. The measured value $\tau \simeq 2.27 \pm 0.04$ is very close to the value found in the PS and the polyester systems. Patton et al. have pointed out[10] that the PS and polyesters systems are perhaps not so different since both have widely spaced cross-linkings. This is also true for the PDMS system. This feature may explain the similar behavior of the three systems and the measured value of τ that is in between the percolation value and the Flory–Stockmayer value.[10] Current work on still different systems is in progress to clarify this point.

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