Journal of Statistical Physics, Vol. 89, Nos. 1/2, 1997

Progressive Construction of an "Olympic" Gel

E. Raphaël,[1] C. Gay,[1] and P. G. de Gennes[1]

Received November 18, 1996; final April 9, 1997

We consider a melt of cyclic polymers (N monomers per chain) containing a small volume fraction ϕ of open cycles (P monomers per chain, with $P < N$) with reactive ends. The reaction leads to the formation of small P-rings. If these P-rings trap a sufficient number of N-rings, a macroscopic cluster ("Olympic" gel) will appear. Using a very primitive theory (where the statistics of knots is replaced by a statistics of proximity), we expect gelation to occur when $\phi > \max\{P^{1/2}/N, (1/N)\exp(\text{const}/P)\}$. Our study is restricted to N-rings that are small enough for their conformations to be Gaussian.

KEY WORDS: Polymer rings; gel; gelation.

1. INTRODUCTION

Some years ago, Clarson, Mark and Semlyen studied the trapping of polymer rings by a growing polymeric network.[1] In the present work, we address the following related problem, raised by S. J. Clarson.

Consider a melt of polymer rings (each with N monomers), all rings being non-concatenated. In recent years, much work was devoted to the statics (and dynamics) of such a melt of rings.[2,3] The radius of gyration of the rings is different from the usual extension $R \approx aN^{1/2}$ of linear chains in melts: although the matter is not entirely settled, the rings are considered to be more confined ($R \approx aN^{2/5}$ according to Cates and Deutsch,[2] $R \approx aN^{1/3}$ according to Khokhlov and Nechaev[3]). This effect, which is present for long rings, is due to interchain topological interactions; they exclude conformations in which different rings are concatenated. In the present work, to avoid these complications, we choose a melt of rings shorter than the usual entanglement length derived from elastic data in melts

---

[1] Collège de France, Physique de la Matière Condensée, URA 792 du CNRS, 75231 Paris cedex 05, France.

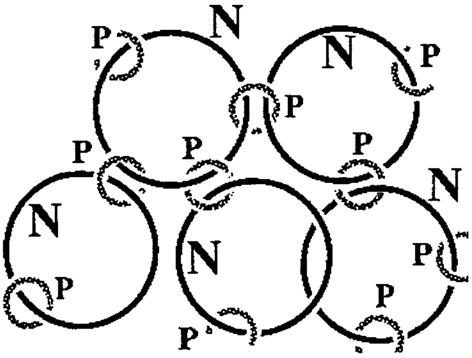

Fig. 1. Schematic representation of an "Olympic" gel: the closing reactions of the P-chains have led to the trapping of some surrounding N-rings.

($N < N_e$). As a result, the rings can be considered as Gaussian: $R_N \approx aN^{1/2}$. To this melt, we add a small volume fraction ϕ of linear chains (P), whose ends are reactive so that they can connect to form new small rings ($P < N$). Our aim is that the P-rings, once formed, connect a sufficient number of N-cycles for a macroscopic cluster to appear ("Olympic" gel, see Fig. 1).

The rather complex process described above, which involves N-rings and linear P-chains, is necessary. Indeed, if one wanted to construct the gel by using open N-rings with reactive ends and no P-chains, one would have to face the following dilemma. At low N-chain concentration (non-overlapping chains), the closing reaction would not build up a macroscopic network. On the other hand, at higher concentrations, chain ends would react non-selectively, (i.e., with chain ends from other chains) so that undesired objects such as long, linear chains or large rings would form. In the process considered in the present paper (which involves N-rings and linear P-chains), we choose $P < N$ for the same selectivity reasons.

It is impossible, in the present state of the art, to perform a good classification, and a good statistics of knots between chains. Here, we shall use the following quantities. Each N-ring is topologically connected to an average number ν_P of P-small rings. And each P-ring encircles on average ν_N larger N-rings. These quantities are necessary to determine the gelation point, as we discuss in Section II. We now give some naive estimates for both ν_p and ν_N.

A. Estimation of ν_p

Let us surround the N-chains of interest by a "tube" of diameter $aP^{1/2}$ equal to the average size of a P-chain (Fig. 2). We assume that all P-chains

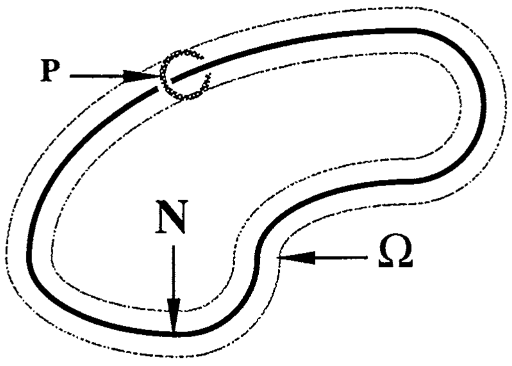

Fig. 2. All P-chains that may trap a given N-ring are located within a tube of diameter $aP^{1/2}$ and of volume $\Omega = NP^{1/2}a^3$.

that are not inside the tube cannot bind to the N-chain. On the other hand, we assume that any P-chain inside the tube has a fixed probability f of binding with the N-chain. The volume of the tube is:

$$\Omega = \frac{N}{P}(aP^{1/2})^3 = NP^{1/2}a^3 \tag{1}$$

and the average number of P-chains inside Ω is:

$$v_P^0 = \Omega \frac{\phi a^{-3}}{P} = NP^{-1/2}\phi \tag{2}$$

However, we must recognize that a P-chain suffers some entropy loss when it feels the constraint of circling around the N-chain. For instance, if the P-chain has to circle around a hard cylinder of radius r, it must have an extension $2\pi r$; the scaling law for its stretching energy is then given by:

$$\Delta F \cong kT\frac{(2\pi r)^2}{Pa^2} \tag{3}$$

Thus, among the v_P^0 available P-chains, the fraction f that will link is expected to be

$$f = \exp(-\Delta F/kT) = \exp\left[-\frac{(2\pi r)^2}{Pa^2}\right] \cong \exp\left(-\alpha\frac{N_0}{P}\right) \tag{4}$$

where $r \simeq aN_0^{1/2}$. Here, N_0 is the number of monomers required to encircle another strand (its value is briefly discussed in Section III). The numerical coefficient α is of order unity.[4] Finally, the average number of P-rings trapped by an N-chain is:

$$\nu_P = \nu_P^0 \cdot f = \frac{N\phi}{P^{1/2}} \exp\left(-\alpha \frac{N_0}{P}\right) \tag{5}$$

B. Estimation of ν_N

We consider one small P-cycle of radius $aP^{1/2}$ and of volume $a^3P^{3/2}$. Within this volume, we find a number ν_N^0 of distinct N-chains. Since each of these chains has about P monomers inside the volume of interest, we may put:

$$\nu_N^0 \simeq \frac{a^3 P^{3/2}}{Pa^3} = P^{1/2} \tag{6}$$

Again, we expect that only a fraction g of the ν_N^0 chains will be effectively linked, and for simplicity we assume $g = f$, where f is given by Eq. 4. Thus, we arrive at:

$$\nu_N = \nu_N^0 \cdot g = P^{1/2} \exp\left(-\alpha \frac{N_0}{P}\right) \tag{7}$$

II. GELATION IN A TREE APPROXIMATION

Since we assumed that each of the ν_P^0 small P-chains that surround a given N-ring have an equal and independent probability f of being linked to it, we can construct more general, binomial probabilities. The probability that any given N-ring is linked with p smaller P-rings $(O \leqslant p \leqslant \nu_P^0)$ is given by:

$$W_P = f^p (1-f)^{\nu_P^0 - p} \frac{\nu_P^0!}{p!\,(\nu_P^0 - P)!} \tag{8}$$

The average value of p (see also Eq. 5) is:

$$\begin{aligned} \nu_P = \langle p \rangle &= \frac{W_1 + 2W_2 + 3W_3 + \cdots}{W_0 + W_1 + W_2 + W_3 + \cdots} \\ &= W_1 + 2W_2 + 3W_3 + \cdots = \nu_P^0 \cdot f \end{aligned} \tag{9}$$

But to determine the gelation point, since those rings that are linked to no other rings play no role, we rather need conditional probabilities. Let $\tilde{W}_p$ be the probability that a given N-ring that is *already* linked to a P-ring, be connected to p *other* P-rings $(0 \leqslant p \leqslant \nu_P^0 - 1)$. Similarly to Eq. 8, we have:

$$\tilde{W}_p = f^p(1-f)^{\nu_P^0 - 1 - p} \frac{(\nu_P^0 - 1)!}{p!\,(\nu_P^0 - 1 - p)!} \tag{10}$$

The average number of other P-rings is now:

$$\tilde{\nu} = \frac{\tilde{W}_1 + 2\tilde{W}_2 + 3\tilde{W}_3 + \cdots}{\tilde{W}_0 + \tilde{W}_1 + \tilde{W}_2 + \tilde{W}_3 + \cdots} = (\nu_P^0 - 1) \cdot f \tag{11}$$

Similarly, if $\tilde{\nu}_N$ is the average number of *other* N-rings which are linked to the P-ring under consideration, once we already know that it is linked to *one, given* N-ring, we have:

$$\tilde{\nu}_N = (\nu_N^0 - 1) \cdot f \tag{12}$$

To see if the N-rings are connected together through smaller P-rings so as to form a macroscopic network, we may consider one particular N-ring, *already* connected to some other rings through one given P-ring, and look at how many *other* N-rings it is linked to, on average. This number is $\tilde{\nu}_P \cdot \tilde{\nu}_N$. If $\tilde{\nu}_P \cdot \tilde{\nu}_N > 1$, it will be linked to more than one other N-rings, which, in turn, will be linked to more than one other rings at the next generation, etc. We then expect gelation. On the opposite, if $\tilde{\nu}_P \cdot \tilde{\nu}_N < 1$, we expect to get only finite clusters. Thus, the criterion for gelation should be:

$$(\nu_P^0 - 1)(\nu_N^0 - 1)\, f^2 = \left(\frac{N\phi}{P^{1/2}} - 1\right)(P^{1/2} - 1) \exp\left(-2\alpha \frac{N_0}{P}\right) \geqslant 1 \tag{13}$$

More precisely, we can introduce the following probabilities. We define ω_l as the probability that a given N-ring belong to a cluster containing a total of l rings of both kinds, including the N-ring itself (see Fig. 3, F_0). $\tilde{\omega}_l$ is the probability that an N-ring which is *already* concatenated with a given P-ring, belong to a cluster containing l rings, including the N-ring, but ignoring the initial P-ring and all the branches that are attached to it (see Fig. 3, F_1). $\tilde{\omega}_m$ is the corresponding probability for a P-ring (see Fig. 3, H_1).

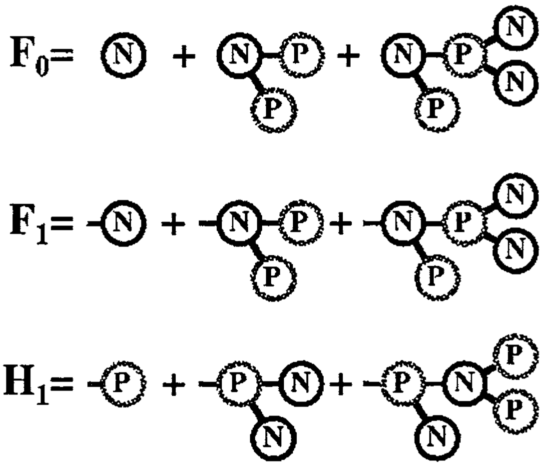

Fig. 3. Diagrammes of some cluster structures, with successive generations of neighbours (see Eqs. 14–17).

Following the approach of Gordon,[5] we can define the following generating functions for the probabilities ω_l, $\tilde{\omega}_l$ and $\tilde{\omega}_m$:

$$\begin{aligned} F_0(\theta, f) &\equiv \sum_l \omega_l(f)\, \theta^l \\ F_1(\theta, f) &\equiv \sum_l \tilde{\omega}_l(f)\, \theta^l \\ H_1(\theta, f) &\equiv \sum_m \tilde{\omega}_m(f)\, \theta^m \end{aligned} \tag{14}$$

These functions are linked through the coefficients W_p (Eq. 8) and similar coefficients, as can be seen from the diagrams of Fig. 3:

$$F_0(\theta, f) = \theta \sum_{p=0}^{\nu_P^0} W_p(f)\, H_1^p(\theta, f) = \theta(1 - f + fH_1)^{\nu_P^0} \tag{15}$$

$$F_1(\theta, f) = \theta \sum_{p=0}^{\nu_P^0 - 1} \tilde{W}_p(f)\, H_1^p(\theta, f) = \theta(1 - f + fH_1)^{\nu_P^0 - 1} \tag{16}$$

$$H_1(\theta, f) = \theta \sum_{n=0}^{\nu_N^0 - 1} \tilde{W}_n(f)\, F_1^n(\theta, f) = \theta(1 - f + fF_1)^{\nu_N^0 - 1} \tag{17}$$

where $\tilde{W}_p$ is given by Eq. 10, and where $\tilde{W}_n$ is the corresponding probability for an N-ring $(0 \leqslant n \leqslant \nu_N^0 - 1)$.

For $\theta = 1$, Eqs. 15–17 always have the trivial solution $F_0 = F_1 = H_1 = 1$. But there is another solution with F_0, F_1 and $H_1 < 1$, branching out at the gel point ($S_\infty(f) = 1 - F_0(1, f)$ is the gel fraction). Combining Eqs. 16 and 17 in the limit $F_1(1, f) \sim 1$ and $H_1(1, f) \sim 1$, one recovers the gelation criterion of Eq. 13.

In the above tree approach, we did not take into account the following point. Starting from one given ring, different other rings, at various "generations" in the tree, may in fact be the same ring. Thus, the gelation threshold may be slightly underestimated in our approach.

III. DISCUSSION

In order to be above the gel point $\phi = \phi_{\text{gel}}$ we need, according to Eq. 13, $\phi > P^{1/2}/N$ and $\phi > (1/N)\exp(2\alpha N_0/P)$. Hence:

$$\phi_{\text{gel}} \cong \max\left\{\frac{P^{1/2}}{N}, \frac{\exp(2\alpha N_0/P)}{N}\right\} \tag{18}$$

In practice, for chemical reasons, we prefer to have P not too large. We also choose $N < N_e$ to avoid the complications mentioned in the introduction about the statics of the rings in the melt. Assuming $N_0 \approx N_e$ and taking $N_e \approx 300$ (a plausible value for polystyrene), we can choose $N = 300$ and $P = 100$. Assuming $\alpha \approx 1/2$, we then have $\phi_{\text{gel}} \approx 0.07$, which is smaller than the overlap volume fraction for the P-chains, $\phi^* \approx 0.1$. The experiment may thus be feasible, although marginal, if we restrict ourselves to small values of N. For larger values ($N > N_e$), the expressions for v_P^0 and v_N^0 (Eqs. 2 and 6) would be altered, but the basic ideas should remain. Note that N_0 might be somehow related to the minimal number of monomers required to make a tight knot(6) and might thus be somewhat smaller than N_e. These two possibilities ($N > N_e$ and $N_0 < N_e$) could allow for a wider choice of molecular weights and concentrations.

Since the ends of the P-chains are reactive (and, therefore, chemically different from the other monomers in presence), one might worry about phase segregation between the N-chains and the P-chains before the cyclization reaction of the P-chains. However, one can show that, for any realistic value of the interaction parameter χ between the reactive and the non-reactive monomers, such a phase segregation does not occurs.(7)

Finally, we should emphasize again that the numerical coefficients in Eqs. 13 and 18 are uncertain, but the general structure of $\phi_{\text{gel}}(N, P)$ is interesting and would, hopefully, be measured experimentally in the future.

ACKNOWLEDGMENTS

The progressive construction of an "Olympic" gel was first raised (to our knowledge) in an informal discussion between Prof. S. J. Clarson and one of us (P. G. de Gennes). We thank the referee for useful comments.

REFERENCES

1. S. J. Clarson, J. E. Mark, and J. A. Semlyen, *Polym. Comm.* **27**:244–245 (1986).
2. M. E. Cates and J. M. Deutsch, *J. Physique* **47**:2121–2128 (1986).
3. A. R. Khokhlov and S. K. Nechaev, *J. Phys. II France* **6**: 1547–1555 (1996); *Phys. Lett.* **112A**:156–160 (1985).
4. Note that Eq. 4 might provide a crude approach for the modelization of experiments by Clarson, Mark and Semlyen on the trapping of cycles in networks (see Fig. 1 of ref. 1).
5. M. Gordon, *Proc. Roy. Soc. A London* **268**:240 (1962); P. G. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell University Press, NY, 4th. ed. (1985) Chapt. 5.
6. P. G. de Gennes, *Macromol.* **17**:703–704 (1984).
7. For simplicity reasons, let us first assume that the N-chains are linear rather than cyclic. The Flory–Huggins free energy of the system, F, is then given by $Fa^3/kT = (\phi/P)\log(\phi/P) + [(1-\phi)/N]\log[(1-\phi)/N] + \chi(\phi/P)(1-\phi/P)$, where ϕ is the volume fraction of the P-chains.$^{(8)}$ The Flory parameter χ characterises the interaction between reactive and non-reactive monomers, and the quantity ϕ/P in the interaction term is simply the concentration of reactive ends. From F, one can construct the Flory-Huggins free energy *of mixing*:$^{(8)}$ $F_{\text{mix}}a^3/kT = (\phi/P)\log\phi + [(1-\phi)/N]\log(1-\phi) + (\chi/P^2)\,\phi(1-\phi)$. The critical point (corresponding to the minimum value of χ on the spinodal curve)$^{(8)}$ is obtained when $\phi = \phi_c$, where $\phi_c = N^{1/2}/(P^{1/2}+N^{1/2})$. The critical value of χ is given by $\chi_c = (P/2N)(N^{1/2}+P^{1/2})^2$ (note that this value of χ_c is P^2 times larger than the usual value corresponding to the case where not only the ends but all the monomers of the P-chains are chemically different from the monomers of the N-chains). For $N \gg P$, the above formulae reduce to $\phi_c \cong 1$ and $\chi_c \cong P/2$. This last result indicates that, for any realistic value of the interaction parameter χ, the two types of chains are entirely compatible. In our problem, the N-chains are in fact cyclic (rather than linear): according to the recent study of Khokhlov and Nechaev$^{(3)}$ (see also the work by Cates and Deutsch,$^{(2)}$ this should enhance the compatibility of the two types of chains even further.
8. P. G. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell Univ. Press, Ithaca, 1979.