Chain radius dependence on concentration in a 2D living polymer system

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Abstract. A living polymer system is used to study the effect of concentration on a broad, polydisperse two-dimensional polymer system. It is found that the mean squared end-to-end radius of a chain of L monomers does not decrease by following a simple power law of the concentration but by a function of the form $R^2(L,\phi) = R^2(L,0)(1 - cL^\varepsilon\phi)$. An origin for such a behaviour is proposed.

PACS. 02.70.Lq Monte-Carlo and statistical methods – 64.75.+g Solubility, segregation, and mixing; phase separation – 82.35.+t Polymer reactions and polymerization

Introduction

The effect of concentration on the polymer chain dimension has been studied by computer simulation [1–6], and power-law dependencies using scaling argument have been given [7].

A single, two-dimensional, self avoiding walk chain made of L monomers has a mean squared end to end distance of the form $R^2(L) \sim (L-1)^{1.5}$. In a two-dimensional, monodisperse melt, where the mutual chain avoidance plays a major role, the chains are globular with a mean end-to-end square distance $R^2(L)$ scaling like L. It follows in this last case that the local density $\phi_l = L/R^2(L)$ is therefore constant. This means also that only one chain can be found in the space explored by a given chain. In other words, the chains cannot penetrate each other. Hence, in a two-dimensional system, a transition from a fully swollen to a globular states occurs by increasing the local density. In three dimension, the case is different: the local density is always a decreasing power law function of L. This allows, whatever the concentration, the presence of monomers of other chains in the space explored by one chain. Hence chain in the melt are not globular. Strictly speaking, the interpenetrating of chains in three dimensions does not happen in the dilute regime. They are first separated from each other at dilute concentration and penetrate each other with increasing density [8]. In two dimension, dilute chains are also separated but, unlike in three dimensions, they do not seem to penetrate each other with increasing concentration and the chains are segregated at high concentration [3,7]. Otherwise, it would mean that they first penetrate each others with increasing concentration and then separate at higher concentration in order to reach the globular state.

Considering that chains are non-interpenetrating in two dimensions, the two-dimensional blob picture cannot be like it is in three dimensions. In three dimensions, a blob is defined as a part of the chain with correlations of the excluded volume type. A dilute SAW is a chain made of one blob. As the density increases, not only does a compression of the chain at the chain border by other chains occur, but the monomers of the other chains penetrating the coil screen the excluded-volume interaction of the monomers belonging to the same chain. This last effect allows a transition from a chain of N monomers made of one blob of size N to a chain of N blobs of size one. In two dimensions, the screening of intra-chain excluded volume interaction by monomers belonging to other chains does not exist.

In a three-dimensional melt or semi-dilute system of polydisperse chains, the chains also interpenetrate each other. In case of a long chain of contour length N in a melt of short chains of contour length P, the long chain is swollen under the condition $P < N^{1/2}$ [7].

In two dimensions, it is not obvious that for broad chain-size distributions a swelling of the greatest chains by the shortest occurs. The recent development of the study of equilibrium polymerization [9] by computer simulation [10–13] can be used as a model for a highly polydisperse system of polymers, with an exponentially decaying distribution of chain length $C(L)$.

The chain distribution $C(L)$ is so far not available experimentally but $C(L)$ has been recently accurately studied by computer simulation [14].

$$\langle L \rangle = \phi^\alpha e^{E/2kT} \qquad 0.5 \leq \alpha \leq 0.84 \text{ (in 2D)}$$

$$C(L) \propto \left(\frac{L}{\langle L \rangle}\right)^{\gamma-1} e^{-L/\langle L \rangle} \quad \gamma - 1 < 0.34 = \gamma_{2d} - 1 \quad (1)$$
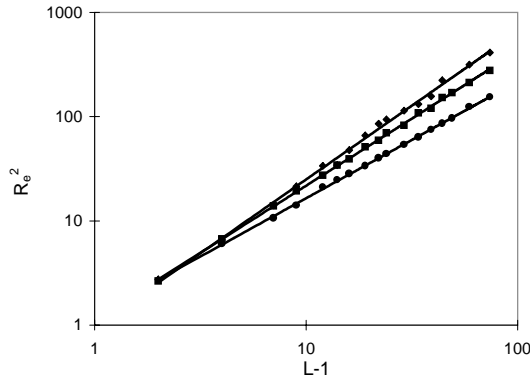
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Fig. 1. Scaling plot of $\langle R_e^2 \rangle$ *versus* $\langle L - 1 \rangle$ at various density: $\phi = 0.25$ (diamonds), $\phi = 0.49$ (squares), $\phi = 0.9025$ (circles).

where L is the degree of polymerization, E the energy of binding between two monomers in a chain and $\phi = \sum_l LC(L)$ is the total concentration in monomers.

This case is very favourable for chain swelling with a few long chains among many small chains.

Computer simulations of monodisperse dense systems in two dimensions have clearly shown non interpenetrating segregated chains [3] with chains packed in a hexagonal array. Some doubts about the effective expansion of the longer chains due to the presence of the short chains in a polydisperse two-dimensional system have been cast recently [12] in a computer simulation. These doubts were already mentioned in an older work [15] on equilibrium polymerization. The swelling can only be seen if the smaller chains do really penetrate the longer chains.

Brief summary of the simulation procedure

The simulations in this work were conducted with the same parameters as in [12]; where an extensive description of the simulation procedure can be found. The mean end-to-end square distance $R^2(L)$ is given as usual in unit of lattice spacing.

In the present study, the ends of a given polymer chain are not allowed to bind together. This last condition avoids the formation of rings [13,16] which gives a different length distribution for even and odd chain length (in monomer units) with temperature.

This is not really a constraint if we consider micellar systems in which rings are not likely to occur [9].

The breaking of the chain reduces the non-ergodicity of the algorithm [6]. In fact, it should suppress it completely; it has been proved [17] that the slithering snake algorithm with a non-L conserving algorithm is ergodic.

Results and discussion

Figure 1 displays the mean end to end square radius as a function of L for three different values of the concentration ϕ. Although the range of chain size is broad, only a single
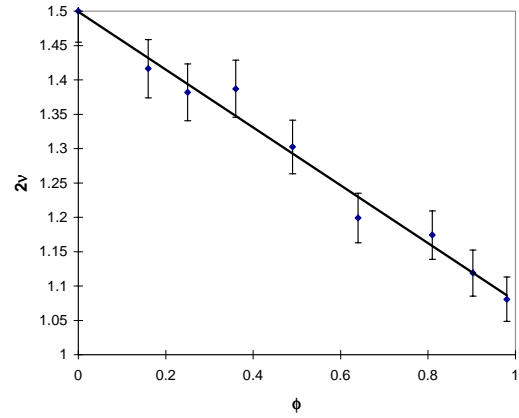

Fig. 2. Plot of the apparent exponent ν *versus* concentration ϕ.
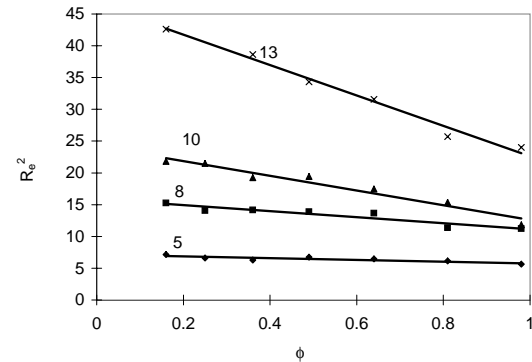

Fig. 3. Plot of $R_e^2(L)$ *versus* concentration ϕ for $L = 5$ (diamonds), $L = 8$ (squares), $L = 10$ (triangles), $L = 13$ (crosses).

regime is observed. This witnesses that the shorter chains do not swell the greater one whatever the value of ϕ for the range of contour length L investigated.

The exponent ν has been extracted using the dependence of $R^2(L)$ on $L-1$ for various concentrations. The values of ν clearly interpolates almost linearly between the value for a SAW ($\nu = 3/4$) to a value slightly above the globular state, $\nu = 1/2$ (Fig. 2). Figures 3 and 4 show the decrease of $R^2(L)$ with increasing concentration ϕ at some given values of L.

According to reference [1], the mean end to end square radius behaves as given by a non reversal walk by approaching the melt density. It means that the chain behaves as if immediate step reversal is forbidden but double occupancies with monomers other than the nearest are allowed. We note that the explanation of reference [1] was given for relatively short chains (typically eight-link self avoiding walks).

In the following, a more general explanation than the one proposed in [1] is developed. The decrease of $R^2(L)$ is a linear function of ϕ and can be written

$$R^2(L, \phi) = A - B\phi \qquad (2)$$

which is qualitatively different than the power law seen in 3D. This expression is also different than what would be expexted from a blob picture. The coefficients A and B
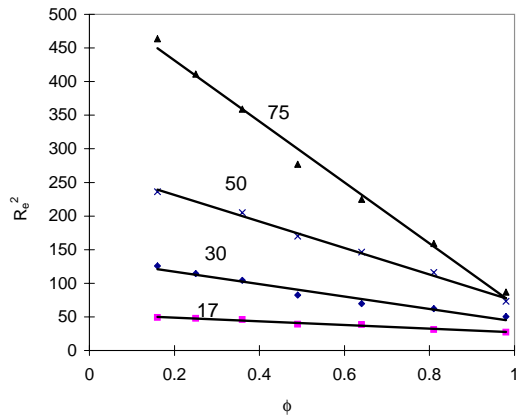
Fig. 4. Plot of $R_e^2(L)$ *versus* concentration ϕ for $L = 17$ (squares), $L = 30$ (diamonds), $L = 50$ (crosses), $L = 75$ (triangles).
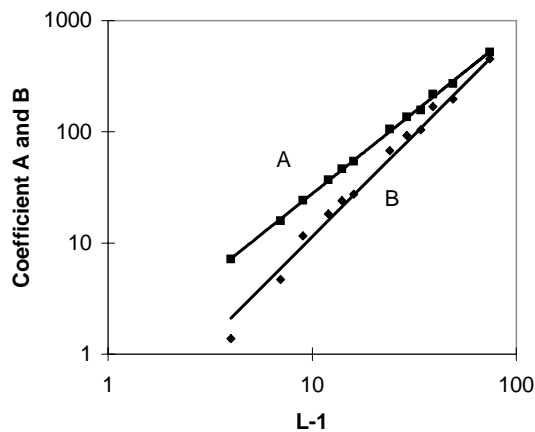

Fig. 5. Scaling plot of the coefficients A (squares) and B (diamonds) as a function of $L - 1$.

are given, however, by power-law functions of L (Fig. 5):

$$A = aL^{1.5},$$
$$B = bL^{1.83}. \tag{3}$$

The coefficient A is clearly the value $R^2(L)$ at $\phi \to 0$ and scales with L as expected with the exponent 1.5.

Equation (2) can be rewritten

$$R^2(L, \phi) = R^2(L, 0)(1 - cL^\varepsilon \phi) \tag{4}$$

where $c = 0.21$ numerically.

The value of 0.33 for the exponent ε is very near the value of $\gamma_{2d} - 1 = 0.34$. It is not ruled out that this value comes from the number of possible way of forming a self-avoiding walk on N steps:

$$\Re(N) \approx \overline{N}^L N^{\gamma - 1} \tag{5}$$

in the limit $N \to \infty$.

It simply means that the more extended chain configurations are gradually forbidden with increasing concentration. Moreover, this rate is directly proportional to the expanding factor $L^{\gamma - 1}$. The data and explanations of the authors of reference [1] can be seen as a particular situation of the present case for short chains, for which equation (5), only asymptotically correct, ceases to be valid. Indeed, the value of B for chains of length $L < 10$ does not fall on the scaling curve (Fig. 5). In reference [1], although the 20-link chain shows a clear linear decrease with ϕ, the decrease for 8-link chains is of poorer quality. This is also observed in our case: the quality of the linear fit is only very good for chains of more than 10 monomers. The origin of this phenomenon and the interpretation of the results of reference [1] are the following: short chains behave essentially as non-reversal step chains. Indeed, the excluded volume interaction comes essentially from the nearest neighbour and not from the other monomers; the chains are too short to allow the monomer of one end to explore, for example, the same environment as the other end. An excluded volume interaction between both end of a short oligomer is therefore impossible. As a consequence, there is for short chains hardly a distinction between SAW and non reversal step behaviour.

Equation (4) has only a physical meaning provided that $cL^\varepsilon \phi < 1$. Long chains at high concentration can not follow equation (4). It is expected that the longer chains are in fact swollen in a dense living polymer system [21]. Although this has been theoretically established in 3D, the same appears to be true in 2D. A molecular dynamics simulation has shown that the presence of large disk-like solvent molecules in a system of 2D chains induces a swelling of the chain [22]. However, this swelling does not imply the penetration of the solvent molecule in the coil. On the contrary, the chain is squeezed and fills the space left between the solvent molecules. The smaller chains with a globular conformation in the present system behave as the disk-like solvent molecules.

Conclusion

The mean end to end square distance of a polymer chain in a living polymer system as a function of the concentration is not a power law function of the concentration. The function determined by analysing the numerical results shows that the mean end to end square distance decrease is directly bound to the critical exponent γ. This function ceases to be valid for very long chains since their behaviour is strongly influenced by the smaller ones. The similar behaviour of monodisperse chains found in the literature and the present polydisperse system for the chains of contour length $L < 10$ is attributed to artifacts.

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