heterogeneous nucleation cannot, in principle, be discarded. The coexistence of all these phenomena make it, at the moment, impossible to give a quantitative explanation of the experimental data presented in this communication.

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Excluded volume effect on polymer films

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Using Monte Carlo methods we have investigated the excluded volume effect on polymer melts in two dimensions. Investigating chain lengths of up to $N=59$ at concentration $c=5/6$, our results strongly support predictions made recently by de Gennes: (1) end-to-end distance and gyration radius exhibit Gaussian behaviour $\propto\sqrt{N}$; (2) but their prefactors differ significantly from their random flight values; (3) in contrast to three-dimensional melts the chains are strongly segregated.

Keywords Polymers; film; melt; excluded volume; hard-sphere model; Monte Carlo simulation; segregation

In a dense system of long flexible polymers each chain is Gaussian and ideal. This was first understood by Flory[1] and has been shown quite convincingly by experiment[2-4], other theoretical argument[5] and computer simulations[6-9].

Recently, de Gennes[5] has put forward some arguments that the 'Flory theorem' does not hold strictly for polymer melts in two dimensions and he expects the chains to be 'not quite ideal and somewhat segregated'. These questions do not seem to have been probed by any method, whether by experiment or computer simulations.

In this communication, we present first Monte Carlo data which strongly support de Gennes' predictions.

As a model, we consider an ensemble of n chains each consisting of $N+1$ pointlike-beads joined together in two dimensions by N rigid links of length l. As an interaction between the beads, we choose a pure hard-core potential, i.e., one has n chains of $N+1$ hard spheres of diameter h each. From recent Monte Carlo renormalization calculations[10], we know that the single hard-sphere polymer chain exhibits the excluded-volume effect most effectively near the fixed point $(h/l)^* \simeq 0.6$. Therefore we choose for our present calculations $h=0.6\ l$. In order to simulate multiple chain systems at fixed concentrations we imposed periodic boundary conditions to our systems[11]. As volume V we choose a rectangular box $V=L^2$ and hence the concentration is defined by $c=nN/(L/l)^2$. Unlike for point-like atoms, any polymer chain will not usually be restricted to just the basic L^2-cell, but may typically extend over two (or more) neighbouring cells. In order to avoid any ambiguity of labelling, we concentrate on that 'image' of the chain for which one coordinate of a bead $\vec{r}_i$ lies within the basic cell. We then consider the interaction between $\vec{r}_i$ and all other beads of the same chain and other chains as well as all images (or parts thereof) of the chains inside the 8 neighbouring cells ('minimum image convention'[11,12]). For computing end-to-end distance and gyration radius of single chains, we have to use the chain not restricted to the basic cell (which then were 'cut into pieces' due to the periodic boundary condition). In order to generate ensembles of chain configurations we used the so-called (reptation dynamic' method for our Monte Carlo simulations[13]. There one first selects one of the ends of the chain at random and then removes the end link of the chain and adds it at the other end, specifying the orientation of the link by the randomly chosen angle φ, in the rante $-\pi<\varphi<\pi$. This mechanism, which corresponds to a movement of the chain along itself, produces an approach towards equilibrium.

Simulations have been performed at concentration $c=5/6$ for several chain lengths of up to $N=59$. In each case, the linear dimension L of the basic cell has been chosen to be $L \gg l\sqrt{N}$, for which the small size of the cell should not affect the chain conformations too much. *Table 1* summarizes our results for the mean-square end-to-end distance $\langle R_N^2\rangle = \langle(\vec{r}_1-\vec{r}_{N+1})^2\rangle$ and the mean-square of gyration $\langle S_N^2\rangle = \sum_{i=1}^{N}\sum_{j=i+1}^{N+1}\langle(\vec{r}_i-\vec{r}_j)^2\rangle/(N+1)^2$. An analysis of these data (*Figure 1*) shows convincingly that both $\langle R_N^2\rangle$ and $\langle S_N^2\rangle$ approach theif Gaussian behaviour $\propto N$ for $N \gtrsim 30$. However, this fact does not mean that the

Table 1 Normalized end-to-end distance and gyration radius at concentration c = 5/6 for various chain lengths and excluded volume ratio h/l = 0.6

$N+1$	n	L/l	R_N^2/l^2N	$\langle S_N^2\rangle/\langle S_N^2\rangle_0$
10	12	12.0	1.81 ± 0.02	1.77 ± 0.02
20	24	24.0	2.01 ± 0.02	1.94 ± 0.02
30	25	30.0	2.06 ± 0.02	2.08 ± 0.02
40	48	48.0	2.10 ± 0.02	2.12 ± 0.02
50	50	54.772	2.12 ± 0.03	2.12 ± 0.03
60	60	65.727	2.11 ± 0.04	2.13 ± 0.04

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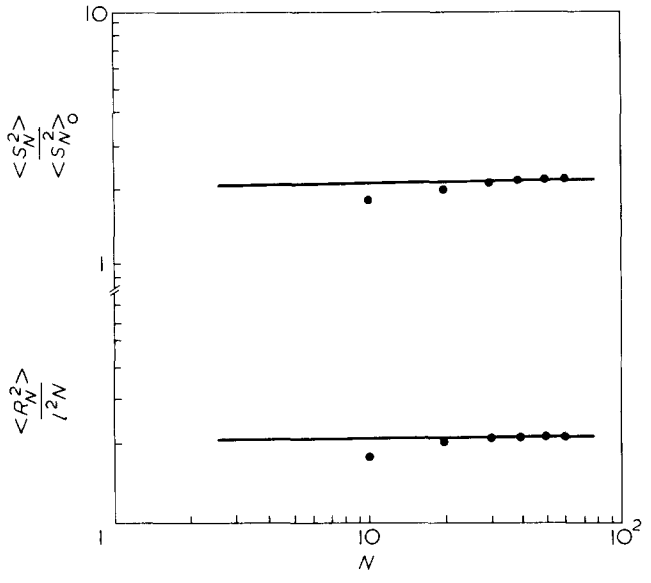

Figure 1 Log–log plot of the normalized end-to-end distance and the gyration radius as given in *Table 1*

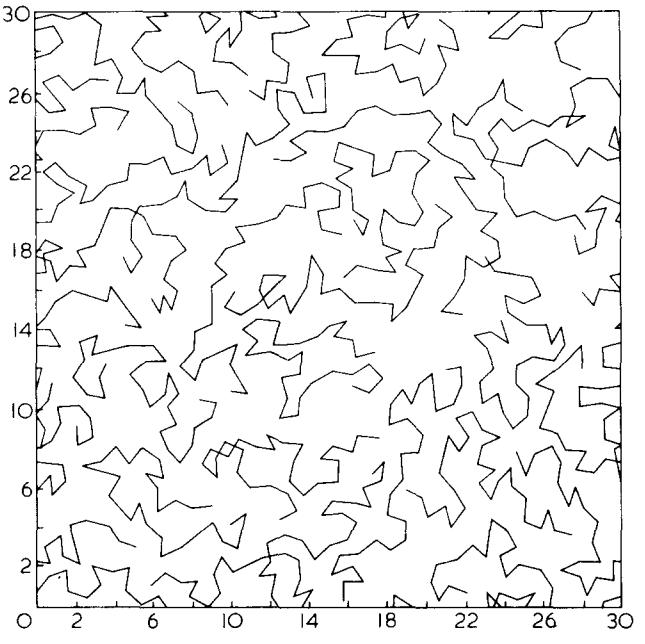

Figure 2 Snapshot picture of a typical configuration inside the basic cell for $N+1=30$, $n=25$, $L/l=30.0$

prefactors in the laws $\langle R_N^2\rangle \propto \langle S_N^2\rangle \propto N$ also assume their unperturbed values[14]: $\langle R_N^2\rangle_0 = l^2 N$, $\langle S_N^2\rangle_0 = l^2 N(N+2)/6(N+1)$. The chains are strongly swollen $\langle R_N^2\rangle/\langle R_N^2\rangle_0 \simeq \langle S_N^2\rangle/\langle S_N^2\rangle_0 \simeq 2.1 \pm 0.1$. A more detailed analysis of the dependence of the anomalous swelling factor on concentration and excluded volume h/l is under current investigation. It should be noted that comparing our previous calculations on the corresponding single chain model $(c=0)$[10], where $\langle R_N^2\rangle_{c=0} \propto N^{1.5}$ clearly for $N \gtrsim 8$, with our present results, we do not expect that the chains for $c \neq 0$ approach their single chain behaviour for $N \to \infty$.

Figure 2 sheds some light on de Gennes' second prediction: which is a typical example from the variety of melt configurations we have generated, directly supports the predicted segregation of the chains. Only few crossing of links can be seen. A more quantitative discussion of segregation effects will be published elsewhere.

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