Equilibrium polymerization as an ordering transition

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We introduce a thermodynamic model of equilibrium polymerization capable of treating all physically important effects: monomer activation, growth of linear polymers, growth of ring polymers, excluded volume, (bi)functionality, *polymer rigidity*, and the effects of solution. We predict a possibility of both ordering and nonordering polymerization and a possibility of "reentrant" polymerization. The model may be used as a vehicle for studying liquid-crystal polymers.

A view of polymerization as a critical phenomenon has only recently been completed.[1] It was shown that equilibrium polymerization can be considered as nearly critical, criticality being pathological,[2] associated with an infinite binding energy or, equivalently, with the "ground state." Early chemical equilibrium theories of polymerization[3] already achieved a qualitative agreement with experiments by assuming polymerization to occur due to the competition between monomer activation (opening of S_8 rings) and fusing of two linear polymers into a larger one. The work of Ref. 1 went, at the same time, beyond the mean-field treatment of chemical equilibrium theories and beyond the treatments of statistics of long polymers[4] by considering in a full thermodynamic approach the same chemical species as chemical equilibrium theories and by accounting explicitly for the excluded volume and bifunctionality.[5] It emerged from such a description that polymerization is not an order-disorder–type transition and, thus, no experimentally observable domains should occur during polymerization.

Subsequent inclusion of ring polymers,[6] which did not change the above conclusions, required a price: Bifunctionality was replaced by a particular *finite* repulsion. This price might be too high for a realistic description of polymerization.

In order to unify previous treatments we will formulate below for the first time a model capable of considering all of the linear and ring polymers, bifunctionality of monomers, and the excluded volume. In addition, we will consider polymer rigidity on which effects our attention will be concentrated.

If polymers (monomers) were infinitely rigid they would tend to align, breaking the original rotational symmetry. Associated transition would be in this case of an order-disorder type, with the polymer phase being an ordered one. Therefore, depending on the rigidity, one expects to observe a crossover

from nonordering polymerization[1,3,6] to ordering polymerization which we will discuss here.

In order to make the above ideas more quantitative, we will first formulate a general thermodynamic model of equilibrium polymerization. For simplicity we treat the two-dimensional case. An extension to three dimensions is straightforward. Let us divide the space into simple square cells containing on the average one monomer unit. By assuming that in each cell there may be only one monomer unit and that through each face there may pass at most one polymer, the excluded volume is automatically taken into account. Furthermore, we assume that each monomer end may fuse to only one other monomer end (if they meet at the same face) and that each monomer has two ends. Thus, we include bifunctionality.

The allowed configurations (states) of a monomer in a single cell are shown in Fig. 1. Note that the allowed configurations are "average" and corresponding changes in enthalpy and entropy may contain a nonsingular temperature dependence.

We will assume that interaction energies depend only on the states in cells sharing a face. The biggest contribution will come from two polymer ends meeting at a face. This contribution is the fusing energy v
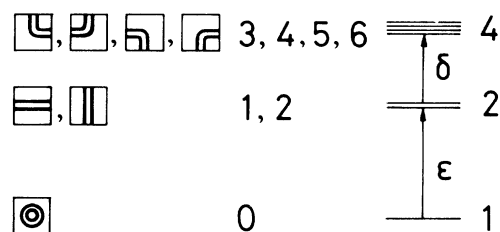

FIG. 1. Allowed single-site-monomer configurations, states (0 to 6), associated energies, and degeneracies.

of two polymers. Some of the possible configurations and their interaction energies are shown in Fig. 2. Clearly, the two polymer ends may come from two different linear polymers or from a single one. Therefore, we include a possibility of formation of ring polymers.

Various energies which we have introduced have a clear physical interpretation. The energy ϵ is the energy required to activate a monomer. Therefore, it is expected to be a positive decreasing function of temperature. The energy δ is associated with the rigidity of a single monomer. Therefore, it is related to the elastic energy of a monomer. The energy v is a fusing energy of two polymer ends. This energy is expected to be a negative increasing function of temperature. The energies $u_1, u_2, \ldots$ are similar to δ, associated with the stiffness of a polymer. They include interactions of a slightly longer range than these included in δ. When δ and u's are zero our model is equivalent to the one of Ref. 1, *except* that we include ring polymers, or to the one of Ref. 2, *except* that we account for bifunctionality.

Let us further associate with each cell $\vec{i}$ an occupation number $n_{\vec{i}}(l)$ of the state l. $n_{\vec{i}}(l) = 1$ or 0 depending on whether a monomer in cell $\vec{i}$ is or is not in the state l. By definition

$$\sum_{l=0}^{2S} n_{\vec{i}}(l) = 1 \quad \text{for all } \vec{i} , \tag{1}$$

where we assume a total of $2S + 1$ states of a monomer. Furthermore, we denote the configuration energy of a monomer in a state l by $\epsilon(l)$. Similarly, the interaction energy between two monomers, one at a site $\vec{i}$ in a state l and the other at a site $\vec{i} + \vec{e}$ in a state l', we denote by $v(l,l';\vec{e})$. In both cases we utilized the translational invariance of the energies.

Complete energy of our polymer system is given by

$$H = \sum_{\vec{i},l} n_{\vec{i}}(l) \left[\epsilon(l) + \frac{1}{2} \sum_{\vec{e},l'} v(l,l';\vec{e}) n_{\vec{i}+\vec{e}}(l') \right] , \tag{2}$$

where $\vec{i}$ runs over all lattice sites and $\vec{e}$ over all vectors connecting $\vec{i}$ to its nearest neighbors. The first term in the brackets comes from the single-site energies while the second term counts the two sites, interaction, energies. For example, in terms of Figs. (1) and (2) we have $\epsilon(1) = \epsilon$, $v(1,1;\hat{x}) = v$, etc.

The model Eq. (2) is very general and only some of its particular realizations such as the spin S Ising model and $(2S + 1)$ state Potts model have been studied. However, neither of the two models studied corresponds to polymerization and we expect that polymerization shows a complex critical behavior with possible crossovers from one universality class to another.
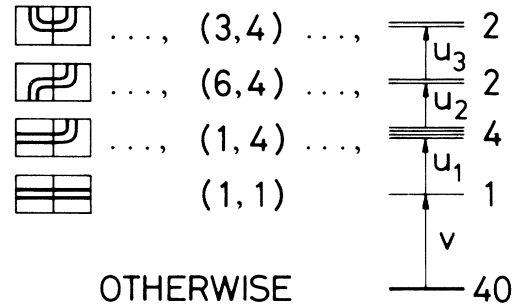

FIG. 2. Allowed two-site-monomer configurations, states, interaction energies, and degeneracies. Configurations related by symmetry are represented by a single configuration. The interaction is anisotropic.

Despite complexity of the general model Eq. (2) its mean-field equations are simple:

$$C_l = C_0 \exp[\bar{\epsilon}(0) - \bar{\epsilon}(l)]; \quad \sum_l C_l = 1 \tag{3}$$

with the effective energies

$$\bar{\epsilon}(l) = \epsilon(l) + \sum_{\vec{e},l'} v(l,l';\vec{e}) C_{l'} . \tag{4}$$

C_l is the thermodynamic average population of state l, which is to be determined self-consistently. (C_l is the concentration of monomers which are in state l.) We also assumed, for simplicity, a uniform state, which need not be the case in general.

The case of rigid polymers may be simulated, for example, by $\delta \gg 0$ or by $u_1, u_2, u_3 \gg 0$. We will consider the former case and $u_1 = u_2 = u_3 = 0$. By letting $\delta \to \infty$ the problem reduces to a three-state one: At each site there is either an unactivated monomer (a ring) or an activated monomer which may be either along $\hat{x}$ or $\hat{y}$ directions. This problem is analogous to an $S = 1$ spin system on a square lattice but it is different from the cases usually treated[7,8] in that our interaction $D_{\vec{e}} S_{\vec{i}} S_{\vec{i}+\vec{e}}$ is anisotropic $D_{\hat{x}} = -D_{\hat{y}}$.

Ground states of a rigid polymer system are indicated in Fig. 3. From the ground states it becomes immediately clear that polymerization will occur for sufficiently large fusing energy $(-v)$, depending on the size of binding energy (ϵ). The transition will be the ordering one characterized by symmetry breaking manifested in preferential population of one of the states $l = 1$ or $l = 2$ (the ground state is a doublet). Experimentally, this will be manifested by formation of boundels (domains) of parallel polymers.

In the mean-field approach, anisotropic interactions are averaged and our problem becomes identical, cf. $D_{\hat{x}} + D_{\hat{y}} = 0$, to the mean field of the Blume-Emery-Griffiths model.[9] Thus, we introduce the monomer
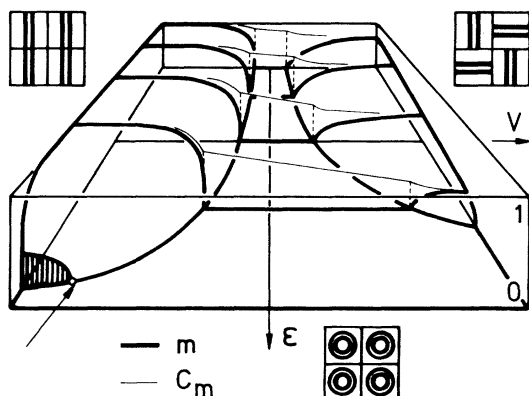
FIG. 3. A mean-field phase diagram and ground states of a two-dimensional polymerization. ϵ is the energy necessary to activate a monomer. $(-v)$ is the energy released by fusing of two monomers; $(-v) < 0$ corresponds to a repulsion between monomer ends which is not the case for polymerization. Corresponding checker-board ordering must be considered an artifact of the model. The continuous transition becomes, at tricritical point, a discontinuous one (shaded).

concentration

$$C_m = C_1 + C_2 = 1 - C_0 \tag{5}$$

and the *order parameter*

$$m = C_1 - C_2 \ . \tag{6}$$

Therefore, an order-disorder transition is characterized by $m \neq 0$ going to $m = 0$. The change in m will couple to C_m and produce a cusp in C_m. On the other hand, within the mean-field theory the average polymer length p is simply related to C_m and m:

$$p = 2C_m/[1 - m^2 - (1 - C_m)^2] \ . \tag{7}$$

Consequently, in the polymer state $m = 0$ and p increases as m and C_m are increased. These conclusions are confirmed by an explicit calculation.

The mean-field phase diagram is sketched in Fig. 3. An ordering above the upper critical line, $v = 1 + \frac{1}{2}\exp(\epsilon + 1)$, is not related to polymerization [m here refers to one sublattice and the sign of m^2 should be changed in Eq. (7)]. On the other hand, below the lower critical line, $v = -1 - \frac{1}{2}\exp(\epsilon - 1)$, the system orders *and* polymerizes. A characteristic of this transition is that m changes at T_c in a mean-field fashion, $m \sim |T - T_c|^{1/2}$, while C_m and p change as $|T - T_c|$, exhibiting only a finite discontinuity in the slope. The critical line ends at the tricritical point, $v = -\frac{5}{3}$, where the transition becomes discontinuous as indicated by shading in Fig. 3. At this first-order transition both m and C_m change discontinuously.

As an example, let us consider a physical system along a line indicated by an arrow in Fig. 3. In such
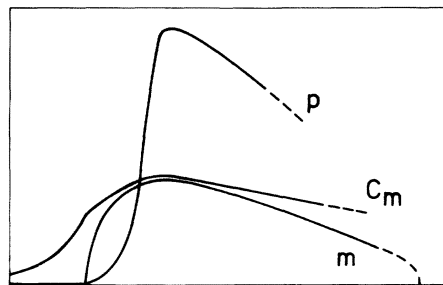

FIG. 4. Schematic, mean-field variation of the order parameter and relevant polymer variables, along a line indicated by an arrow in the phase diagram of Fig. 3.

a case both C_m and p would show a break in the slope at T_c but p would peak only after the transition (Fig. 4). Particularly interesting is a possibility of "reentrant" behavior. That is, at some higher temperature a second, continuous, order-disorder transition may occur at which polymerization is destroyed.[10]

Our analysis remains essentially valid for all $\delta > 0$ since the ground state stays the same.[11] Therefore, we expect that both nonordering $(\delta \leq 0)$ and ordering $(\delta > 0)$ polymerization may occur.[12] Experimentally, it is best to look for the ordering polymerization in solutions where the rigidity depends on solvent characteristics.[13]

In summary, we emphasize the new results which we find when treating all the relevant aspects of polymerization (i.e., monomer activation, growth of linear polymers, growth of *ring* polymers, bifunctionality, excluded volume, and polymer rigidity).

(i) Complementary to currently adopted views,[1,6] equilibrium polymerization may be an ordering transition $(\delta > 0)$.

(ii) Whereas other studies[1,6] find a single transition point, $v \rightarrow \infty$, $v - \epsilon = $ const, we find a transition line (in the $v\epsilon$ plane) along which a continuous transition occurs below the tricritical point and a discontinuous one occurs above the tricritical point.

(iii) In our model, C_m is nonzero on both sides of the transition, whereas elsewhere[1] C_m is found to be zero in the nonpolymer phase.

(iv) Finally, we find that both C_m and p have only a "mild" singularity at the transition ($|T - T_c|$ vs $|T - T_c|^{1/2}$, in a mean-field approach).

The above results, valid for $\delta > 0$, were exemplified here in the limit $\delta \rightarrow +\infty$.[11] We have treated only the two-dimensional case, but in three dimensions an additional, negative, isotropic interaction between parallel monomers is necessary to stabilize an ordered phase.[14]

The ordered phase is somewhat reminiscent of a polymeric liquid-crystal phase. An inclusion of the vacant sites into the model provides a vehicle for a more detailed study of polymeric liquid crystals. However, this will not be pursued here.

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[10] The last transition is analogous to nematic-isotropic or cholesteric-isotropic liquid-crystal transitions.

[11] A more detailed study of the whole region $\delta \in [-\infty, +\infty]$ will be given elsewhere.

[12] As δ is reduced a short-range ordering may be physically more realistic.

[13] See theoretical treatment by J. C. Wheeler and P. Pfeuty, Phys. Rev. Lett. 46, 1409 (1981) and references therein. In our model solvent effects may be partially accounted for in variation of δ. However, the model may be extended in a more rigorous fashion by including, for example, "no monomer" states and a constraint on the concentration (the chemical potential).

[14] If this interaction is positive, mechanically strong sheets consisting of crossed layers of ordered polymers may be formed. Such structures may be important in understanding the architecture in various biological systems.