# Phase Transition of Cubic-Lattice Polymer Systems

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ABSTRACT: Monte Carlo simulations of a lattice polymer system of chains of 20 segments each, comprising a total of 441 chains on a 21 × 21 × 21 cubic lattice (and hence filling ca. 95.2% of the total volume), are performed to study the details of the disordered vs. the ordered states of bulk polymers of great length as a function of chain flexibility. Assuming an energy $\epsilon > 0$ for each transverse ("gauche") bond connection over that of a collinear ("trans") bond, we find a definite first-order phase transition to a nearly perfectly ordered state upon cooling the system from a disordered state stable at high reduced temperatures $\tilde{T}$ ($=k_BT/\epsilon$), as demonstrated by discontinuities in the internal energy (conformational order) and the macroscopic orientational order parameter. The appearance of hysteresis in the transition upon heating from the ordered state further confirms the first-order character of this transition. The key features of the Monte Carlo results are matched closely by the predictions of mean-field theory, except that in disordered states close to the transition the chains exhibit appreciable conformational perturbations. This is manifested in enhancement of more extended conformers and significant local orientational correlations, the latter being limited primarily to near-neighbor segments. Relevance of these results to the molecular configurations and phase transitions of real polymers is discussed.

## Introduction

The statistical thermodynamics of polymers has generally been treated on the premise that the conformational characteristics of a polymer chain confer sufficient tortuosity or flexibility for the occurrence of random disorder in the bulk polymer. For example, in the original Flory–Huggins lattice treatments[1,2] the chain is allowed to bend freely at intervals approximating to the chain diameter. For many real polymers, however, the implicit assumption of complete chain flexibility is unwarranted as demonstrated by detailed studies of chain conformations;[3] quite often the persistence lengths of real chains greatly exceed the average chain diameter. The consequence of such limited flexibility, or semiflexibility, was first investigated by Flory[4] employing a lattice chain model wherein the collinear ("trans") connection of successive chain segments is preferred by an energy $\epsilon$ over each of the alternate ("gauche") conformations. Hence, the flexibility is expressed as the fraction, $g$, of gauche bonds of the unperturbed chain, which is in turn determined by the reduced temperature defined by

$$\tilde{T} = k_BT/\epsilon \tag{1}$$

for a given lattice. Adopting the mean-field approximation for the availability of unoccupied lattice sites, Flory showed that this flexibility, $g$ (or $\tilde{T}$), must exceed a critical value in order for the disordered state to remain stable at the high densities occurring in the undiluted polymer. Below this flexibility, the random configurations for the system of chains are virtually unavailable, reflecting the physical impossibility of packing rigid chains to high density in a disordered array. He therefore concluded that in a system at equilibrium, this situation must be arrested by a first-order transition to a highly ordered state. Hence, the concept of phase transition due solely to intramolecular forces was proposed.

Although the validity of this theory, especially the aspects of the mean-field approximation, has been questioned in a number of recent publications[5–9] employing various statistical mechanical models, the dominant feature of a first-order transition has been confirmed recently by a Monte Carlo simulation in a two-dimensional square-lattice system.[10] However, some important deviations were also observed, reflecting the shortcomings of the mean-field approximation of estimating the partition function of the system as a whole from the averages for near neighbors. This deficiency is most severe in two dimensions. Significant deviations occur in the fractions of gauche bonds (conformational order) and the macroscopic orientational order parameter in the ordered and the disordered states at the transition. Furthermore, the fractions of gauche bonds in the disordered states at the reduced temperatures even far above the transition (and, hence, for rather flexible chains) exhibit appreciable deviations from those of the unperturbed chains.

In this paper, we present the results of Monte Carlo simulations of a bulk polymer system on a cubic lattice. The three-dimensional nature of this system offers a better test of the mean-field approximation in describing real polymer systems. On the other hand, the cubic-lattice model is still deficient in representing the configurational characteristics of real chains, since the diversity of conformations accessible to real chains is poorly represented by this model. Hence, our main purpose is to explore the general characteristics of the bulk polymer systems as a function of chain flexibility and to test the applicability of mean-field theory.

## Monte Carlo and Analytical Procedures

**Monte Carlo Simulation.** Using the usual reptation sampling technique with periodic boundary conditions,[11] we simulate a lattice polymer system of chains of 20 segments each, comprising a total of 441 chains on a 21 × 21 × 21 cubic lattice. The system thus contains voids of ca. 4.8% in volume in order to apply the reptation sampling technique. Starting from an arbitrary configuration, one therefore selects at random one of the ends of a randomly selected chain and then removes this end link of the chain and adds it to the other end, specifying randomly the orientation of the link. This trial move provides a new state, which is accepted as a new one if the transition probability $W$ exceeds a random number between 0 and 1; otherwise, it is rejected and the old configuration is counted once more in the averaging. The sampling time is therefore counted as the number of Monte Carlo trials. The transition probability is constructed so that it satisfies detailed balance with the equilibrium distribution $P_0 \propto \exp(-E/k_BT)$, where $E$ is the total energy of the system: $W = 1$ for $\Delta E = E_{new} - E_{old} \leq 0$; $W = \exp(-\Delta E/k_BT)$ for $\Delta E > 0$. This is the well-known Metropolis method.[12] The collinear trans connection of consecutive chain segments is favored by a configurational energy $\epsilon$ over each of the four right-angled gauche bonds. The system therefore

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tends to equilibrium with respect to the reduced temperature $\tilde{T}$ defined by eq 1. Since the generation of each new configuration requires the movement of chain ends, this reptation sampling technique is not capable of accounting for the contributions of the "locked-in" configurations, wherein both chain ends are surrounded by the segments of the same chain. However, the number of such configurations is very small, and hence the error due to this limitation should be negligible.

No detectable change of the system within the sampling time of $\sim 3.5 \times 10^9$ Monte Carlo trials was taken as the criterion for a stable state at reduced temperatures near the transition. This long sampling time was taken to eliminate the long-lived metastable states as much as possible. When noticeable changes occur within this time interval, the Monte Carlo sampling was continued until the system reached a stable state. A minimum interval of $\Delta\tilde{T} = 0.0125$ was used near the transition, while larger intervals were chosen well away from the transition.

The system thus generated is characterized by two macroscopic order parameters: the internal energy (or conformational order) denoting the average fraction, $g$, of gauche bonds and the orientational order parameter $s$ ($=\langle 3\cos^2\phi - 1\rangle/2$), $\phi$ being the angle between a lattice bond and the macroscopic orientation axis. In the cubic lattice, the orientational order parameter $s$ is given by $(3f_z - 1)/2$, $f_z$ being the fraction of bonds aligned along the axis of macroscopic orientation. Since the sign of the value of $s$ for a given Monte Carlo sample can fluctuate in disordered states, its average over different Monte Carlo samples is carried out with its absolute value $|s|$.

Further details of molecular order are also characterized by evaluating the population, $f(h)$, of bonds within straight-chain sequences comprising $h$ bonds and the local orientational correlations $p_2(d)$ between pairs of segments belonging to different chains as a function of their separation distances $d$ (in units of the bond length). The values of $p_2(d)$ are computed here by averaging $(3\cos^2\phi' - 1)/2$, $\phi'$ being the angle between bonds attached to the two segments considered, for all pairs of segments whose separation distances fall between $d + 0.2$ and $d - 0.2$. Since each segment has two bonds connected to it, the orientational correlation between two segments actually involves averaging over four pairs of bonds; the two segments at the chain ends having only one attached bond each are not included in this calculation.

**Mean-Field Lattice Theory.** The configurational partition function $Z$ in the disordered state of a mixture formed from $n_1$ vacant sites (or solvent molecules) and $n_2$ chain molecules comprising $r$ segments each is given from the theory of thermodynamics of polymer solutions by

$$Z = \left(\frac{rn_2 + n_1}{n_2}\right)^{n_2}\left(\frac{rn_2 + n_1}{n_1}\right)^{n_1} q^{n_2} z_c^{(r-2)n_2} \times \left\{\frac{rn_2 + n_1}{[rn_2(1 - 2/q) + 2n_2/q + n_1]}\right\}^{rn_2(1-q/2)-n_2-n_1q/2} \quad (2)$$

where $q$ is the coordination number of the lattice and $z_c$ is the factor contributed to the intramolecular configurational partition function per segment; a more rigorous treatment of the a priori probability of finding a vacancy[2,13-15] is adopted here. Taking the energy associated with each of the $q - 2$ gauche placements to be $\epsilon$ relative to zero for the preferred collinear trans placement

$$z_c = 1 + (q - 2)\exp(-\tilde{T}^{-1}) \quad (3)$$

Assuming that in the ordered state the chains form the all-trans rodlike conformation and lie parallel to one another, the partition function $Z'$ in the ordered state is

$$Z' = [(n_1 + n_2)/n_1]^{n_1}[(n_1 + n_2)/n_2]^{n_2} \quad (4)$$

For the cubic-lattice system of Monte Carlo simulations, the transition is calculated by inserting $n_1 = n_2$, $r = 20$, and $q = 6$ in eq 2–4 and equating $Z = Z'$.

**Unperturbed Chain Statistics.** The fraction of gauche bonds is

$$g = (q - 2)\exp(-\tilde{T}^{-1})/[1 + (q - 2)\exp(-\tilde{T}^{-1})] \quad (5)$$

and the fraction of bonds in straight sequences comprising $h$ bonds is

$$f(h) = 2(1 - g)^{(h-1)}g + (r - 2 - h)(1 - g)^{(h-1)}g^2 \quad \text{for } h < r - 1 \quad (6a)$$

$$f(h) = (1 - g)^{(h-1)} \quad \text{for } h = r - 1 \quad (6b)$$

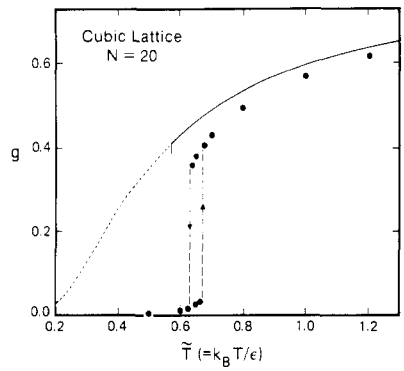


**Figure 1.** Average fractions of transverse "gauche" bonds of the cubic-lattice polymer system comprising chains of 20 segments each filled to ca. 95.2% ot the total volume plotted against the reduced temperature $\tilde{T}$ ($=k_BT/\epsilon$, $\epsilon$ being the energy of the gauche bond over that of the collinear "trans" bond). The filled circles represent the Monte Carlo results obtained by both heating and cooling the system, and the solid and the dotted lines represent the unperturbed chain above and below the transition calculated according to mean-field theory, respectively.

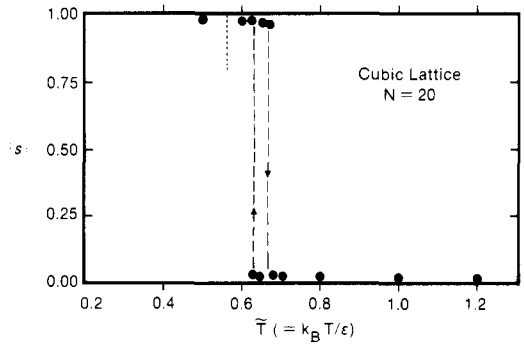


**Figure 2.** Monte Carlo results of the macroscopic orientational order parameter of the cubic-lattice polymer comprising chains of 20 segments each filled to ca. 95.2% of the total volume plotted against the reduced temperature $\tilde{T}$. The transition of the perfectly ordered to a completely disordered state which is calculated according to mean-field theory is denoted by the dotted line intersecting the upper horizontal abscissa.

## Numerical Results

Starting from a completely ordered system (i.e., $g = 0$ and $s = 1.0$), the changes in the average conformation and the orientational order parameter of the system with reduced temperature are shown in Figures 1 and 2, respectively. As $\tilde{T}$ is increased from 0, the system remains nearly perfectly ordered until $\tilde{T} = 0.6625$. At the next incremental increase to $\tilde{T} = 0.675$, the system undergoes an abrupt change in both conformation and orientation to a

disordered state. Further increase in $\tilde{T}$ causes a continuous change in the average conformation, whereas no change is observed in the macroscopic orientational order parameter. The discontinuities in both the conformational and the orientational order thus indicate a first-order phase transition.

As the system is cooled from the disordered state, the cooling curve exhibits a definite supercooling of $\Delta\tilde{T} = 0.0375$ in the transition temperature, compared with the heating curve. The supercooled disordered state, exhibiting no sign of change within the sampling time of $\sim 3.5 \times 10^9$ Monte Carlo trials, is thus indicative of the presence of persistent metastable states near the transition. The discontinuities of the transition and the appearance of the hysteresis in the transition temperatures thus demonstrate very clearly the first-order character of the order–disorder transition observed here.

While the average conformations in the ordered states obtained by cooling the disordered state are identical with those obtained by heating the perfectly ordered initial state, an interesting deviation is observed for the macroscopic orientational order parameter. In the ordered states obtained by cooling, the nearly rodlike chains lie parallel to one another within a given lattice layer of the cubic lattice, but the orientation axis of chains in a given layer can assume at random either of the two orthogonal axes in the plane in the layer. (This additional degree of freedom available to the ordered state of the cubic-lattice chain, however, is inconsequential in terms of the total partition function of the system.) Thus, the orientational order parameter in the ordered states refers to the chain segments within each such layer.

Also shown in Figure 1 are the fractions of gauche bonds of the unperturbed chain vs. $\tilde{T}$, which in the mean-field approximation can be equated with those of bulk polymers in disordered states. The transition from a completely disordered to a perfectly ordered state at $\tilde{T} \simeq 0.56$, calculated from eq 2 and 4 of mean-field lattice theory, is denoted by the demarcation of the solid line above and the dotted line below the transition. (This temperature is considerably lower than $\tilde{T} = 0.860$ calculated for the system of infinite chains containing no voids.) The results of Figure 1 thus show that mean-field theory predicts very closely all the essential features of the Monte Carlo simulations, namely, the first-order character of the transition, the critical degree of flexibility at the transition denoted by $g$ (or $\tilde{T}$), and the degree of the conformational and the orientational order in the ordered as well as in the disordered states.

One important point to be noted here is that although the fractions of gauche bonds in the disordered states evaluated by the two methods are in close agreement, the gauche fractions of the Monte Carlo results are always smaller than those of unperturbed chains regardless of $\tilde{T}$. At large values of $\tilde{T} > 1.2$, the relative difference is less than $\sim 3\%$. However, as $\tilde{T}$ is decreased (and thus the flexibility decreases), the difference increases continuously. The maximum deviation observed here, occurring in the disordered state just prior to the transition at $\tilde{T} = 0.6375$, is $\sim 20\%$. In other words, a considerable perturbation of chain conformations occurs to favor more extended conformations in the disordered states near the transition, wherein the chain flexibility, though sufficient to form a stable disordered state, is only marginal.

This conformational perturbation is indicated in detail by the bond distribution function $f(h)$, denoting the fraction of bonds in straight sequences of $h$ bonds, shown in Figure 3. At $\tilde{T} = \infty$, the bond distribution of the Monte

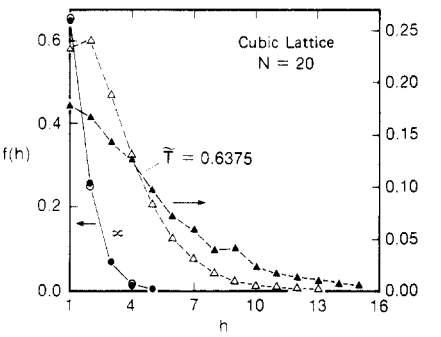


**Figure 3.** Bond distribution function $f(h)$ representing the fraction of bonds in straight sequences comprising $h$ bonds evaluated in the two disordered states at $\tilde{T} = \infty$ and 0.6375, respectively, by the Monte Carlo method and the unperturbed chain statistics. The Monte Carlo results are represented by closed circles and closed triangles, and those of unperturbed chains are shown by open circles and open triangles.

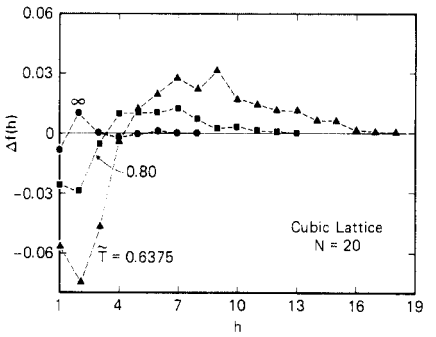


**Figure 4.** Deviations in the bond distribution function exhibited by the Monte Carlo results compared with those of the unperturbed chains in the disordered states at the indicated values of $\tilde{T}$.

**Table I**
**Conformational Perturbation and Nearest-Neighbor Orientational Correlations vs. Reduced Temperature and Transition Entropy of Monte Carlo Results**

| $\tilde{T}$ | $\sum\Delta f(h) > 0$ | $p_2(1)$ | $\Delta S/k_B$ (per segment) |
|---|---|---|---|
| $\infty$ | 0.01 | 0.03 | |
| 1.2 | 0.03 | 0.09 | |
| 0.8 | 0.08 | 0.14 | |
| 0.675 | 0.11 | 0.22 | 0.55[a] (0.72)[b] |
| 0.6375 | 0.18 | 0.27 | 0.53[c] |

[a] This is taken from the heating curve. [b] This is the value predicted by mean-field theory. [c] This is taken from the cooling curve.

Carlo simulations (closed circles) is virtually identical with that of the unperturbed chain (open circles). On the other hand, at $\tilde{T} = 0.6375$ Monte Carlo results (closed triangles) exhibit larger populations of highly extended conformers than those of the unperturbed chain (open triangles) with concomitant reduction in the fraction of short straight sequences. The deviations in bond distributions are plotted in Figure 4 as a function of sequence length at the three values of $\tilde{T}$ indicated therein. They show the fractions of chain segments involved to be very small in most cases; as the results listed in n Table I show, they comprise less than 3% at $\tilde{T} > 1.2$. In the region very close to the transition, this fraction increases rapidly to a maximum of $\sim 18\%$ at $\tilde{T} = 0.6375$. Also to be noted is the fact that the average sequence length involved in these deviations also increases as the system approaches the transition.

This conformational perturbation is accompanied by increased local correlations, as shown by the local orientational order parameter between segments of different chains plotted against the intersegmental distance in

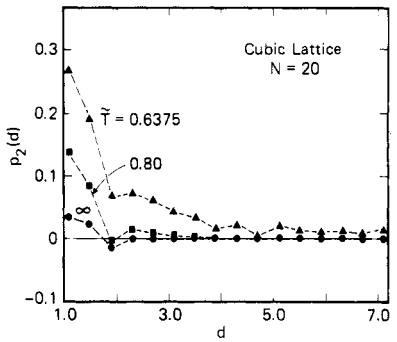


**Figure 5.** Local orientational correlations between segments of different chains as a function of the intersegmental distance in lattice units evaluated by the Monte Carlo method for the disordered states at the indicated values of $\tilde{T}$.

Figure 5. At the limit of complete flexibility, $\tilde{T} = \infty$, the local orientational correlation is virtually absent; only the near neighbors separated by less than two lattice units exhibbit a statistically meaningful correlation of $p_2 \sim 0.03$. As $\tilde{T}$ is decreased, the near-neighbor correlations begin to increase, but the correlations between segments separated by more than two lattice units remain less than 0.1 even in the region just prior to the transition. The near-neighbor correlations increase significantly to the extent of $p_2(1) \sim 0.27$ at $\tilde{T} = 0.6375$ just before the transition. Furthermore, the value of the nearest-neighbor correlation $p_2(1)$ is found to correlate closely with the fractions of bonds involved in the conformational perturbations, as shown by the results listed in Table I.

The conformational perturbation to favor more extended conformers accompanied by the closely matched local orientational correlations limited primarily to near neighbors is indicative of the presence of embryonic ordered regions, or nuclei, that comprise mainly two straight-chain sequences lying next to each other. The size of such regions, the fraction of segments involved, and their dependence on $\tilde{T}$ are likely to follow the features of the conformational perturbations plotted in Figure 4.

Also listed in Table I is the transition entropy calculated from the transition temperature and the transition enthalpy

$$\Delta H = \epsilon(g_d - g_0) \tag{7}$$

where $g_d$ and $g_0$ refer to the fractions of gauche bonds in the disordered and the ordered states at the transition, respectively, taken from the results in Figure 1. The transition entropy of $\Delta S/k_B \simeq 0.54$ per segment is considerably smaller than the corresponding value of 0.72 predicted by the mean-field theory, reflecting the effect of the embryonic ordered regions present in the disordered state at the transition.

## Discussion

Inasmuch as the basic cell size of periodic boundary conditions is nearly identical with the length of individual chains, the calculations here do not include the contributions due to correlated locations of chain ends in ordered states. This effect due to chain ends, however, becomes negligible for long chains. The calculations are therefore designed to simulate a large system of long chains.

Our Monte Carlo results on a cubic-lattice polymer system further confirm the prediction of Flory's mean-field lattice theory that as the chain flexibility is decreased from the completely flexible limit, the disordered state of chains formed initially in the bulk undergoes a first-order phase transition to an ordered state at a critical degree of flexibility. Furthermore, mean-field theory is found to predict very closely the quantitative details of the Monte Carlo results; hence, in this regard its deficiencies, which are rather significant in two dimensions, are much reduced in three dimensions.

The fact that the average chain conformation of bulk amorphous polymers shows a considerable deviation from that of the unperturbed chains in stable disordered states near the transition raises a serious question concerning the predictions of thermodynamic theory of glass transition,[16,17] which relies on mean-field lattice theory at temperatures significantly below the disorder–order transition. In this regard, previous estimates[18] of conformational contribution to the specific heat difference between liquid and glass, carried out by employing unperturbed chain conformations, will also need to be reevaluated.

As Flory pointed out repeatedly,[1,19] mean-field theory accounts for only the completely disordered chain configurations devoid of any correlations among neighboring chains or chain segments. For the chains with sufficient flexibility, the number (or the partition function) of such completely disordered configurations is so large that the effect of any deviations or local correlations neglected by the mean-field approximation becomes negligible. However, as the chain flexibility decreases to approach the transition and thus the number of completely disordered configurations is decreased significantly, contributions of these deviations become appreciable even before the transition. In the metastable disordered states below the transition, the contributions of completely disordered configurations to the total partition function is reduced further and may become even smaller than those of the deviations.

The nature of the deviations or local correlations in disordered states at temperatures just above the transition deserves further study. Monte Carlo results, demonstrating conformational perturbations favoring more extended conformers and local orientational correlations limited primarily to the nearest neighbors, indicate the presence of embryonic ordered regions, however.

In this regard, it is of interest to note some experimental results relevant to this aspect of Monte Carlo calculations. In the case of poly(methylenes), the presence of local orientational correlations in the melt has been well demonstrated by depolarized Rayleigh scattering studies.[20-23] The magnitude of depolarized Rayleigh scattering intensities is indicative primarily of near-neighbor correlations. Also, although the experimental method is subject to a large error, the IR spectrum of the $CD_2$ group[24] inserted in the poly(methylene) chain shows a somewhat larger ratio of the trans–trans bond pairs to the trans–gauche pairs in the melt than predicted for the unperturbed chain, indicating conformational perturbation. In most small-angle neutron scattering measurements,[25] chain dimensions in bulk amorphous polymers are nearly identical within experimental error with those of the unperturbed chains in Θ solvents. However, in some cases (e.g., polycarbonate) the ratio of the mean-square radius of gyration to the number of skeletal bonds is reported to be somewhat larger (by ~20% for polycarbonate)[26-28] than that of the unperturbed chain. Hence, the conformational perturbations and local orientational correlations found in the Monte Carlo results seem to have bearing for some real polymers. However, more careful and systematic investigations are definitely needed in order to ascertain and further characterize these deviations in the marginally stable disordered states of bulk polymers.

The critical degree of flexibility below which an ordered state is predicted to be more stable for chain molecules in

the bulk is denoted here as the average fraction of gauche bonds of the unperturbed chain. This value determined here for the cubic-lattice system is not directly relatable to real chains. However, one may relate the ratio $\langle r^2 \rangle / L$ of the mean-square end-to-end distance to the fully extended chain length following the derivation of Flory[4]

$$\langle r^2 \rangle / L = l(2/g - 1) \tag{8}$$

$l$ being the bond length, or the width of the cubic lattice. This value corresponds to the Kuhn length of the equivalent freely jointed chain model,[29] and its axial ratio is then simply

$$x_K = 2/g - 1 \tag{9}$$

From the results in Figure 1, the value $g$ of the unperturbed chain at the transition is ~0.45 for the system of chains comprising 20 segments and containing voids of ~4.8%. The corresponding value of $x_K$ is ~3.4. This value will decrease for the completely filled system of infinite chains for which the critical value of $x_K$ is 2.63 in the mean-field approximation. In this regard, it is interesting to note the predictions of $x_K$ ca. 6.4 and ca. 4.5 by the mean-field theories relying on the freely jointed chain[30] and a wormlike chain model,[31] respectively. Hence, the exact value of $x_K$ critical to forming an ordered phase depends strongly on the chain model. Nevertheless, it should be noted that the degree of chain stiffness necessary to bring about an ordered state of bulk polymers is not very large.

For the cubic-lattice chain considered here, the ordered states below the transition exhibit nearly perfect order both in conformation and in orientation. On the other hand, the degree of order predicted by a recent mean-field theory using a wormlike chain model is much smaller.[31] The degree of order assumed by real chains, therefore, is likely to depend strongly on the details of their conformational characteristics. Furthermore, the disorder–order transition observed here occurs without any assitance from the intermolecular dispersion forces, whereas in real polymers ordered states usually involve more favorable intermolecular interactions. These considerations show clearly that it will be necessary to investigate the effect of chain models as well as the contribution of the intermolecular dispersion energy in order to fully understand the details of disordered and ordered states and their phase transitions in real polymers.

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# Phase Transition in Swollen Gels. 6. Effect of Aging on the Extent of Hydrolysis of Aqueous Polyacrylamide Solutions and on the Collapse of Gels

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ABSTRACT: The aging of aqueous polyacrylamide solutions and gels prepared under similar conditions was investigated in parallel. The colorimetric determination of the concentration of ammonium ions produced by the hydrolysis of amide groups of polyacrylamide in solution proved that with increasing time of aging, $\tau$, from 0 to 103 days the mole fraction of $COO^-$ groups increased from 0 to 0.052. Light scattering revealed the existence of a polyelectrolyte effect in solutions of aged PAAm. The light scattering data also showed that the hydrolysis of PAAm was not accompanied by degradation processes. For networks with the time of aging, $\tau$, >12 days, a phase transition was observed in acetone–water mixtures. By introducing the effective degree of ionization, an agreement can be reached between the swelling data and those predicted by the molecular theory describing swelling equilibria in polyelectrolyte networks. The discontinuity in volume in the phase transition is accompanied by a jumpwise change in the equilibrium shear modulus of the gel.

Under certain conditions, in polyacrylamide (PAAm) networks swollen in acetone–water mixtures, a transition can be observed between two polymer phases differing in the conformation and concentration of segments. The time of aging (or curing) of the gels had a decisive influence on the phase transition (collapse). Aging took place either

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