

## Addition polymerization in a nematic medium: Effects of an anisotropic solvent in a kinetic gelation model

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A kinetic gelation model with rodlike anisotropic solvent is used to study the addition polymerization in a nematic medium. The structure of the polymer network is extended in the direction of the director of anisotropic solvent, since the order parameter of the anisotropic solvent is not zero. Finite-size scalings show that there is no change in the universal behavior of the sol-gel transition in the presence of the anisotropic solvent.

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Polymerization in nematic liquid crystals has received considerable attention. For fundamental scientific reasons, polymerization in an anisotropic solvent is an interesting subject [1]. For great practical applications, the materials of polymer dispersed liquid crystals have been used in many types of displays, switchable windows, and other light shutters [2]. The materials can be formed by addition polymerization in liquid crystals with free radical initiators. For studying the radical addition polymerization, a kinetic gelation model taking into account kinetic aspects of the polymerization process has been used [3]. The model first proposed by Manneville and de Sèze [4] has been studied and modified by various researchers over the course of the past decade. The modifications to the kinetic gelation model include the addition of a solvent [5], the movement of monomers [6], directed growth [7], various initiation mechanisms [8], and the crank-shaft-type motion of monomers and polymers [9]. However, the kinetic gelation model with anisotropic solvent has never been studied. Here we introduce a rodlike anisotropic solvent to the kinetic gelation model to simulate the addition polymerization in a nematic medium. The purpose of this study is to investigate the effects of the anisotropic solvent on the universal behavior of the sol-gel transition and the conformation of polymers in the kinetic gelation model.

The model is essentially the same as that studied by others, except for the addition of the quenched anisotropic solvent. We assume that each anisotropic solvent is represented by a rod and the rod direction is only allowed to be parallel to one of the three principal axes of coordinate. Rod length and order parameter of the rods are used to characterize the rodlike anisotropic solvent. The rod length  $l$  is defined as the number of connected sites which belong to a single solvent molecule, and the order parameter  $Q$  is defined as

$$Q = \frac{3 N_{\parallel}}{2 N} - \frac{1}{2}, \quad (1)$$

where  $N_{\parallel}$  is the number of rods which are parallel to the director  $\vec{n}$  of the anisotropic medium, and  $N$  is the total number of rods. To place each rod for a specific order parameter, we determine the rod direction by choosing a

random number  $r$  uniformly distributed over the range  $0 < r < 1$ . If  $r < \frac{2}{3}(Q + \frac{1}{2})$ , the rod direction is parallel to  $\vec{n}$ ; otherwise, the rod direction is perpendicular to  $\vec{n}$ .

Initially, the zero functional rodlike anisotropic solvent and bifunctional and tetrafunctional monomers are randomly placed on a three-dimensional cubic lattice of size  $L$  with periodic boundary conditions, and a fraction  $C_i$  of initiators are placed on randomly selected monomers. The functionality of the monomer gives the maximum number of bonds that can be formed. The monomer connected to an initiator reduces one bond and acts as the active center for growth. The concentration  $C_s$  of the rodlike anisotropic solvent and the concentration  $C_b$  of bifunctional and  $C_t$  of tetrafunctional monomers are related through  $C_s + C_b + C_t = 1$ . The total number  $N$  of the anisotropic solvent obeys the relation  $N = L^3 C_s / l$ . Polymerization growth begins with a randomly chosen available active center and a nearest neighbor. If the nearest neighbor is a monomer and not fully bonded, a bond is formed between the two sites and the active center is transferred to the nearest neighbor. If the nearest neighbor is an active center, the two active centers bond together and annihilate. As all of the nearest neighbors of an active center are fully bonded, the active center is trapped. Growth stops when all of the active centers are annihilated or trapped. In this study, the number of samples used are 2000, 1000, 500, and 250 for lattice size  $L = 32, 48, 64, \text{ and } 128$ , respectively.

To examine the universal behavior of the sol-gel transition in this model, we calculate the chemical conversion factor  $p$  which specifies the degree of polymerization, the average molecular weight or susceptibility  $\chi$ , and the gel fraction  $G$ . The chemical conversion factor  $p$  is defined as the number of bonds grown divided by the maximum possible number of bonds  $3L^3$ , and the gel fraction  $G$  and susceptibility  $\chi$  are, respectively, defined as

$$G = 1 - \sum_s s n_s, \quad (2)$$

$$\chi = \sum_s s^2 n_s, \quad (3)$$

where  $n_s$  is the number of clusters of size  $s$  and the sum excludes the largest cluster. As  $p$  approaches the gel

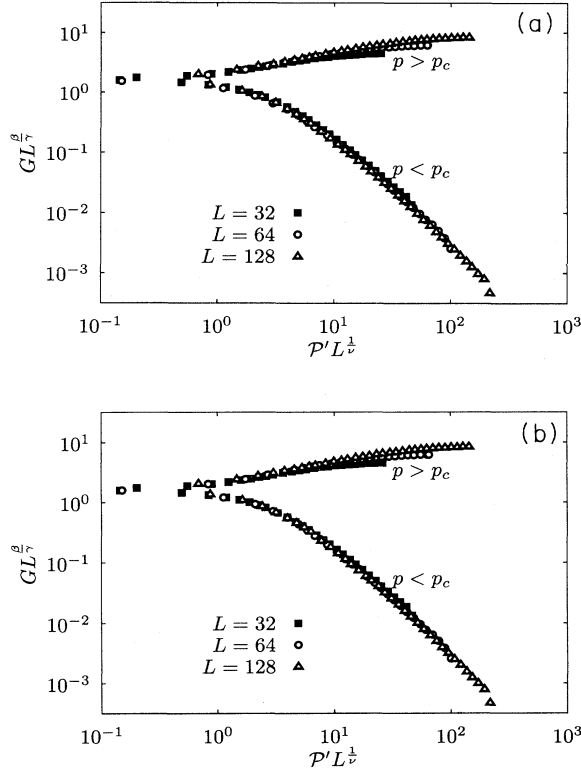


FIG. 1. Finite-size scaling of  $G$  for  $l = 3$  and (a)  $Q = 0.5$  with  $p_c = 0.1350$ ,  $\beta = 0.40$ , and  $\nu = 0.90$ . (b)  $Q = 1.0$  with  $p_c = 0.1350$ ,  $\beta = 0.40$ , and  $\nu = 0.90$ .

point  $p_c$ , the gel fraction  $G$  and the susceptibility  $\chi$  behave as

$$G \sim \mathcal{P}^\beta \quad p > p_c, \quad (4)$$

$$\chi \sim \begin{cases} \mathcal{P}^{-\gamma} & p < p_c \\ \mathcal{P}'^{-\gamma} & p > p_c, \end{cases} \quad (5)$$

respectively, where  $\mathcal{P} = (p_c - p)/p$  and  $\mathcal{P}' = (p - p_c)/p_c$ . Because of strong finite-size effects, finite-size scaling is used to extract the infinite lattice critical behavior [3,5,10]. For the gel fraction  $G$ , the scaling form is given by

$$G = L^{-\beta/\nu} \mathcal{G}(x), \quad (6)$$

where  $\mathcal{G}(x)$  is a scaling function and the scaling variable  $x = \mathcal{P}L^{1/\nu}$ . For the susceptibility  $\chi$ , the scaling form is given by

$$\chi = L^{\gamma/\nu} \mathcal{X}(x), \quad (7)$$

where  $\mathcal{X}(x)$  is a scaling function, and the scaling variable  $x = \mathcal{P}L^{1/\nu}$  for  $p < p_c$  and  $x = \mathcal{P}'L^{1/\nu}$  for  $p > p_c$ .

In Figs. 1 and 2, we show the finite-size-scaling plots for the gel fraction  $G$  and susceptibility  $\chi$ , respectively. The critical exponents determined from these data are identical for  $C_i = 3 \times 10^{-2}$ ,  $C_s = 0.2$ ,  $C_t = 0.4$ ,  $l =$

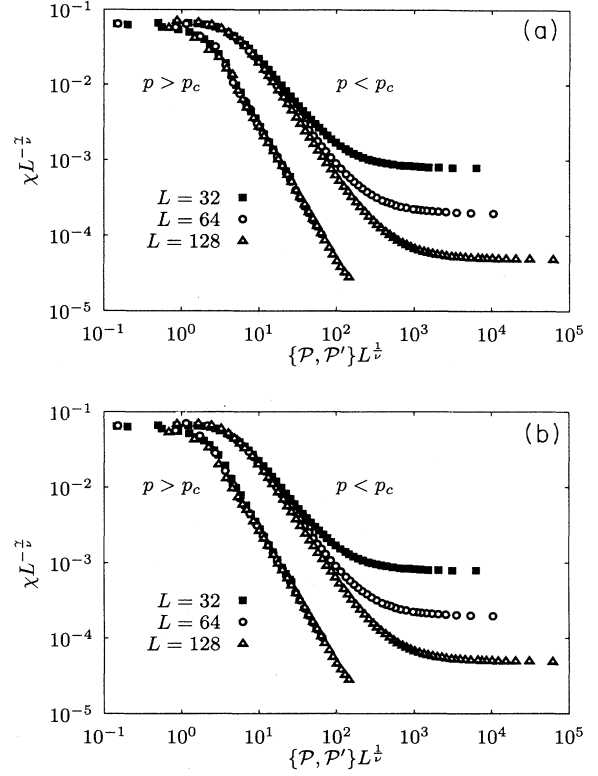


FIG. 2. Finite-size scaling of  $\chi$  for  $l = 3$  and (a)  $Q = 0.5$  with  $p_c = 0.1350$ ,  $\gamma = 1.80$ , and  $\nu = 0.90$ . (b)  $Q = 1.0$  with  $p_c = 0.1350$ ,  $\gamma = 1.80$ , and  $\nu = 0.90$ .

3, and  $Q = 0.5$  and  $1.0$ , individually:  $\gamma = 1.80 \pm 0.1$ ,  $\nu = 0.90 \pm 0.05$ ,  $\beta = 0.40 \pm 0.05$ . The finite-size-scaling analyses are also performed for  $l = 2, 4$  and  $Q = 0.5, 1.0$ , and the critical exponents determined from the analysis are well in agreement with the above values. These values for  $\gamma$ ,  $\nu$ , and  $\beta$  obtained in our analysis are consistent with those found in the kinetic gelation model with or without the isotropic solvent [5] as well as percolation values [11]. The results show that the rodlike anisotropic solvent do not affect the universal behavior of the sol-gel transition in the kinetic gelation model.

To study the anisotropic effects on the kinetic gelation model with the rodlike anisotropic solvent, we calculate the average radii of gyration  $R_{\parallel}, R_{\perp}$  of polymers in the parallel and perpendicular directions of the director  $\vec{n}$  during the course of polymerization. The average radii of gyration  $R_{\parallel}$  and  $R_{\perp}$  are, respectively, defined as

$$R_{\parallel, \perp}^2 = \sum_s n_s s R_{s, \parallel, \perp}^2, \quad (8)$$

where  $R_{s, \parallel, \perp}$  are the radii of gyration for a polymer with size  $s$  in the two different directions and the sum excludes the largest cluster. The definitions of  $R_{s, \parallel, \perp}$  are given by [12]

$$R_{s, \parallel, \perp}^2 = \sum_{i, j} \frac{|\vec{r}_{i, \parallel, \perp} - \vec{r}_{j, \parallel, \perp}|^2}{2s}, \quad (9)$$

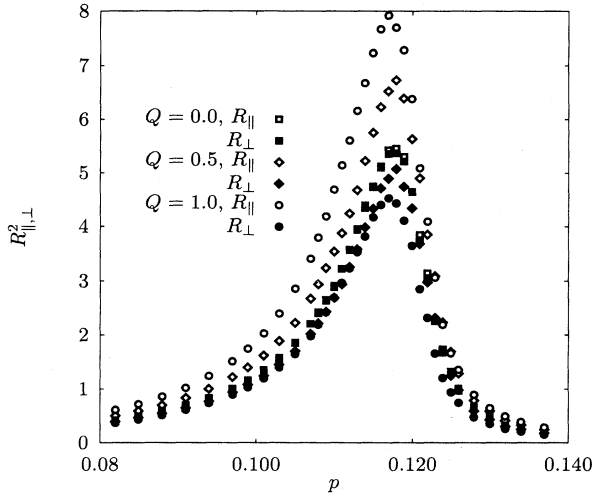


FIG. 3.  $R_{||}^2$  and  $R_{\perp}^2$  plotted as a function of the chemical conversion factor  $p$  for  $C_i = 3 \times 10^{-2}$ ,  $C_s = 0.4$ ,  $C_t = 0.6$ ,  $l = 3$ ,  $L = 64$ , and  $Q = 0.0, 0.5$ , and  $1.0$ .

where  $\vec{r}_{i||,\perp}$  are the position of the  $i$ th molecular in the polymer in the parallel and perpendicular direction of the director  $\vec{n}$ , respectively.

In Fig. 3, we show  $R_{||}^2$  and  $R_{\perp}^2$  versus chemical conversion factor  $p$  for  $l = 3$  and  $Q = 0.0, 0.5$ , and  $1.0$  individually. We find that  $R_{||} > R_{\perp}$  for  $Q \neq 0.0$ . Since  $Q \neq 0.0$ , i.e., the rodlike anisotropic solvents are preferred to align in the parallel direction of the director  $\vec{n}$ , the growth of a polymer is more easily confined in the direction. Thus, it is reasonable that  $R_{||} > R_{\perp}$  for  $Q \neq 0.0$ . The results show that the rodlike anisotropic solvent molecules with nonzero value of order parameter imply anisotropic polymer networks whose extended directions are parallel to the director  $\vec{n}$ .

In addition, we are interested to investigate whether the radii of gyration  $R_{||}, R_{\perp}$  have the same universal behavior of the sol-gel transition. As  $p$  approaches the gel point  $p_c$ , we assume that  $R_{||}$  and  $R_{\perp}$  are expected to diverge as [12]

$$R_{||,\perp}^2 \sim \begin{cases} \mathcal{P}^{-(2\nu_{||,\perp}-\beta)}, & p < p_c \\ \mathcal{P}'^{-(2\nu_{||,\perp}-\beta)}, & p > p_c. \end{cases} \quad (10)$$

Thus, the finite-size-scaling form for  $R_{||,\perp}$  should be given by

$$R_{||,\perp}^2 = L^{2-\beta/\nu_{||,\perp}} \mathcal{R}_{||,\perp}(x_{||,\perp}), \quad (11)$$

where  $\mathcal{R}_{||,\perp}(x_{||,\perp})$  are scaling functions and the scaling variables  $x_{||,\perp} = \mathcal{P}L^{1/\nu_{||,\perp}}$  for  $p < p_c$  and  $x_{||,\perp} = \mathcal{P}'L^{1/\nu_{||,\perp}}$  for  $p > p_c$ .

In Fig. 4, we show the finite-size-scaling plots for the radii of gyration  $R_{||}$  and  $R_{\perp}$  for  $Q = 1.0$ . The best estimates for the critical exponents are  $\nu_{||} = 0.90 \pm 0.05$ ,  $\nu_{\perp} = 0.90 \pm 0.05$ , and  $\beta = 0.40 \pm 0.05$ . We find that the scaling functions  $\mathcal{R}_{||,\perp}(x_{||,\perp})$  are different but the critical exponents  $\nu_{||,\perp}$  are essentially identical and well in

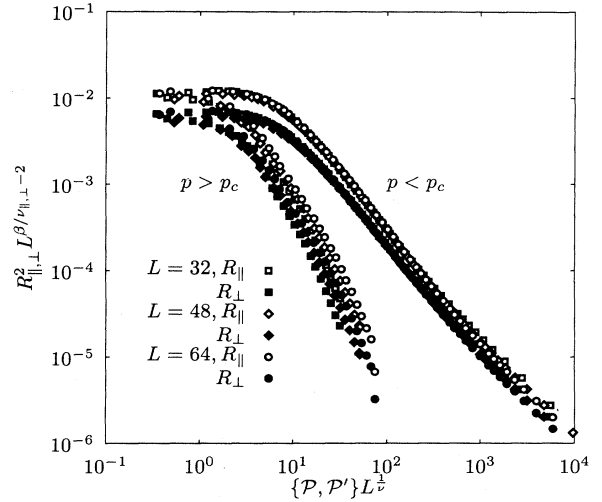


FIG. 4. Finite-size scaling of  $R_{||}$  and  $R_{\perp}$  for  $C_i = 3 \times 10^{-2}$ ,  $C_s = 0.4$ ,  $C_t = 0.6$ ,  $l = 3$ , and  $Q = 1.0$  with  $p_c = 0.1185$ ,  $\beta = 0.40$ ,  $\nu_{||} = 0.90$ , and  $\nu_{\perp} = 0.90$ .

agreement with the above value  $\nu$ , i.e.,  $\nu_{||} = \nu_{\perp} = \nu$ . The results show that the radii of gyration  $R_{||}, R_{\perp}$  have the same universal behavior of the sol-gel transition and further show that the universal behavior of the sol-gel transition is not changed.

Recently, it has been studied that electro-optical properties of polymer dispersed liquid crystals strongly depend on the anisotropic structure of polymer networks [13–15]. To achieve the anisotropic polymer network, polymerization reaction is in the nematic liquid crystals which are aligned by rubbing treatment of substrates [13,14] or applying an external electric field [14]. The formed polymer network in experimental observation of scanning electron micrograph is anisotropic and its orientation is parallel to the alignment direction of nematic liquid crystals. The experimental observation is consistent with our simulation results.

In conclusion, we have used the kinetic gelation model with a quenched rodlike anisotropic solvent to study the addition polymerization in a nematic medium. The rodlike anisotropic solvent led to anisotropic growth of a polymer and implied the polymer has an anisotropic structure in which the extended direction is parallel to the director of the anisotropic solvent. Finite-size scalings for the gel fraction, susceptibility, and radii of gyration show that the rodlike anisotropic solvent does not affect the universal behavior of the sol-gel transition in the kinetic gelation model. Although considering the mobility and elastic deformation of the anisotropic solvent is more general for real systems, this model should be appropriate for the system in which the time scale for polymerization growth is short compared to that for the mobility and elastic deformation of the anisotropic solvent.

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