Pore Size Distribution Induced by Microphase Separation: Effect of the Leaving Group during Polycondensation

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Received June 29, 2000. Revised Manuscript Received November 27, 2000

A mean field theoretical model is developed to investigate the porosity of cross-linked copolymer networks formed by polycondensation. It is found that cross-linking induces microphase separation, and when accompanied by polycondensation, the pore size distribution is affected in an unexpected manner. Pores much larger than the size of the leaving groups are predicted when the leaving group is large. The pore distribution in such cases is found to be multimodal, exhibiting a peak for small pores, a second narrow peak for pores corresponding to the monomer size, and a third peak for very large pores. The model also predicts the extent of microphase separation of the chemically different monomers as a function of the chemical constitution, the degree of cross-linking, and the size of the leaving group.

I. Introduction

In recent years numerous experimental, theoretical, and computational studies have focused on understanding the behavior of polymer networks in different physical and chemical environments. The rigidity[1,2] and elasticity[3] of polymer networks have been examined. Fractal dimensions have been estimated for substructures within the network.[4,5] Interpenetrating copolymer networks have been shown to undergo microphase separation (the separation of the monomers within the polymer network into domains rich in one type of monomer).[6] Investigations of heteropolymer networks have shown to exhibit interesting phase behavior,[7−11] frustrating behavior,[11,12] and various microstructures.[13−16] An important performance parameter of polymer networks is their porosity, which is not only key in determining the permeate flux and other mechanical and separation properties of the polymer network but also important in determining the recognition, removal, or catalysis of species based on size and shape.

The porosity also depends on such factors as the size and chemical characteristics of the cross-linking monomers, reaction kinetics, and the drying process. The cross-linking process itself may result in many topological defects that yield an irregularly cross-linked polymer network.[5] If desired, agents may be added to control the pore size distribution.[13,17] However, in this work we concentrate on yet another factor; we show that the size of the leaving group released during polycondensation greatly affects the pore size distribution. Simple simulations depict heteropolymer networks having different physical and chemical morphologies, dependent on the size of the leaving group.

To this date, surprisingly few theoretical papers have studied the pore size distribution of cross-linked polymer networks. In this paper we present a mathematical model of copolymer networks and pay special attention to the effects of the leaving group and phase separation on the pore size distribution. We attempt to account for polycondensation that occurs upon cross-linking that leads to density fluctuations within the network. We find an unexpected and strong dependence of the pore size distribution on the size of the leaving group. We find that copolymers composed of different fractions of each monomer are characterized by different degrees of phase separation and pore size distributions. We also investigate the effects of the degree of cross-linking on

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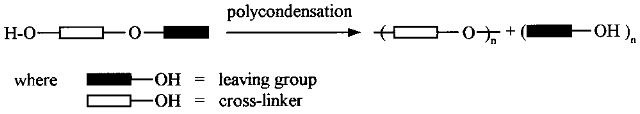
10.1021/cm000537b CCC: $20.00

Scheme 1



the porosity and microstructure of the polymer network. We find that both the degree of cross-linking and the chemical composition play a role in determining the pore size distribution and the microphase separation structure of the copolymer network.

An important application of porous materials is toward molecular templating, where the pore size distribution plays a fundamental role. A controlled porosity is necessary to achieve specific molecular recognition.[17−20] In molecular templates, a specified pore structure can be created in one of three ways: (1) Through synthesis of the matrix with dopants, followed by the removal of the dopants;[21−24] (2) through synthesis of the matrix with covalently bonded “spacers”, followed by their removal;[17,25] (3) leaving-group-induced templates, the subject of this paper. Here, to simulate the cross-linking process, we assume that polycondensation occurs upon cross-linking. That is, the formation of a new bond is accompanied by a release of a molecule. This process corresponds, for example, to the release of water or alcohol when new Si−O−Si bonds are formed in polycondensation of organosilicates used in molecular templates.[25] This approach of the templating procedure is depicted in Scheme 1. In this context, we have predicted that the size of the leaving group in addition to the degree of microphase separation can be used (in addition to other factors)[5,13,17] to control the pore sizes and their distribution within the cross-linked polymer matrix.

II. Model Development

In this section we present a theoretical model of a cross-linked copolymer network, subject to polycondensation. The cross-linked network is modeled from a very long random copolymer chain made up of N monomers. Only one type of monomer is allowed to form cross-links. We specify a fraction, f, out of all N monomers as “cross-linkers”, which are randomly distributed along the backbone of the initial linear polymer chain. We term the remaining $(1 - f)N$ monomers “backbone” monomers. We allow the polymer chain to form on average N_{Cl} cross-links only among the cross-linkers. It has been shown that a long cross-linked polymer chain is a good representation of cross-linked polymer networks because for most purposes only the concentration of the polymer is important and end effects can be neglected.[3,26] To concentrate on the effects of cross-linking on the structure of the polymer matrix, we neglect all long-range interactions between the monomers and with the solvent. Our goal is to obtain expressions for the density fluctuations between the cross-linked and non-cross-linked microdomains.

We begin our mathematical formulation by writing the partition function of a very long polymer chain having N segments, each of persistent length l, subject to the constraint of forming $N_{\mathrm{cl}} \leq fN$ cross-links between the cross-linkers. The partition function, Z, can be written in Feynman’s path integral[27] formulation as

$$Z = \int\int \mathrm{D}\mathbf{r}(s) \exp\left(-\frac{3}{2l}\int_0^L \mathrm{d}s \left(\frac{\partial \mathbf{r}}{\partial s}\right)^2\right) \prod_{e=1}^{N_{\mathrm{cl}}} \int_0^L \mathrm{d}s \int_0^L \mathrm{d}s' \, \delta[\mathbf{r}_e(s) - \mathbf{r}_e(s')]\delta_{\mathrm{CC}} \quad (1)$$

where $L = Nl$ and is the total contour length of the linear chain and $\mathbf{r}(s)$ is the three-dimensional spatial location of the segment at position s along the backbone of the chain. The product enforces N_{cl} cross-links between cross-linkers, where δ_{CC} equals unity when segments encountered at positions $\mathbf{r}(s)$ and $\mathbf{r}(s')$ are cross-linkers. We introduce a variable, $\theta(s)$, which labels the type of segments encountered at position s. We let $\theta(s) = 1$ for cross-linkers and -1 for backbone segments. Using this notation, δ_{CC} in eq 1 is given by

$$\delta_{\mathrm{CC}} = \left(\frac{1 + \theta(s)}{2}\right)\left(\frac{1 + \theta(s')}{2}\right) \quad (2)$$

Taking a Poisson distribution for the cross-links where the average fraction of cross-linked segments is determined by the fugacity of the systmem, μ,[26] and noting the fact that for our system the cross-links are identical, the average over the cross-link distribution results in

$$Z = \left\langle \exp\left(\frac{\mu}{2}\left(1 - \frac{\mu V}{8l^2}\int_0^L \mathrm{d}s \int_0^L \mathrm{d}s' \, \delta[\mathbf{r}(s) - \mathbf{r}(s')]((1 + \bar{\theta})^2 + 2(1 + \bar{\theta}) \, \delta\theta(s) + \delta\theta(s) \, \delta\theta(s'))\right)\right)\right\rangle_{\mathrm{th}} \quad (3)$$

where $\bar{\theta} = 2f - 1$ is the mean value of θ and $\delta\theta(s) = \theta(s) - \bar{\theta}$ measures the fluctuations in the value of θ away from $\bar{\theta}$. The thermal average is with respect to chain conformations.

It is common practice to rewrite the partition function in terms of the density, $\rho(\mathbf{r})$, and the microphase order parameter, $m(\mathbf{r})$, defined as follows:[27−30]

$$\rho(\mathbf{r}) = \frac{1}{L}\int_0^L \mathrm{d}s \, \delta(\mathbf{r}(s) - \mathbf{r}) \quad (4)$$

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$$m(\mathbf{r}) = \frac{1}{L}\int_0^L \mathrm{d}s\ \delta\theta(s)\ \delta(\mathbf{r}(s) - \mathbf{r}) \tag{5}$$

With these definitions, the partition function can be written in terms of the effective energy and entropy,

$$Z = \int\int \mathrm{D}\rho(\mathbf{r}) \int\int m(\mathbf{r})\ \exp(-\beta E[\rho,m] + S[\rho,m]) \tag{6}$$

where

$$\beta E = \frac{\mu}{2} - \frac{\mu V}{8}\int \mathrm{d}\mathbf{r}((1 + \bar{\theta})^2\rho^2(\mathbf{r}) + 2(1 + \bar{\theta})\rho(\mathbf{r})m(\mathbf{r}) + m^2(\mathbf{r})) \tag{7}$$

and

$$S = \ln\int\int \mathrm{D}\mathbf{r}(s)\ \exp\left(-\frac{3}{2l}\int_0^L \mathrm{d}s\left(\frac{\mathrm{d}\mathbf{r}}{\mathrm{d}s}\right)^2\right)\ \delta\left(\rho(\mathbf{r}) - \frac{1}{L}\int_0^L \mathrm{d}s\ \delta(\mathbf{r}(s) - \mathbf{r})\right)\ \delta\left(m(\mathbf{r}) - \frac{1}{L}\int_0^L \mathrm{d}s\ \delta\theta(s)\ \delta(\mathbf{r}(s) - \mathbf{r})\right) \tag{8}$$

where $\beta = 1/k_{\mathrm{B}}T$ and k_{B} is Boltzmann's constant, V is the volume the system occupies, and a is the monomer size.

We calculate the mean-field free energy corresponding to eq 6 by carrying out averages over the configuration space of the polymer chain and the sequence distribution of the two different types of monomers. From the free energy we can obtain thermodynamic properties of the cross-linked polymer for a given set of parameters (chemical composition, degree of cross-linking, chain flexibility, monomer size, etc.). Our solution is in terms of the two variables that arise naturally in the problem, that is, the density at spatial location $\mathbf{r}$, $\rho(\mathbf{r})$, and the order parameter, $m(\mathbf{r})$, which attains nontrivial values when microphase separation occurs between the two different monomer types. The energy and entropy expressions are similar to that of ref 32, apart from the first three terms of eq 7, which are due to the formation of cross-links. We note that the effective contribution from the cross-links appears as short-range interaction terms in the energy expression. The calculation procedure is as in ref 32. Rigorous algebra yields the following equation for the free energy in Fourier space,

$$F = \frac{\mu}{2}\left(1 - \frac{(1 + \bar{\theta})^2\rho^2V^2}{4} - \frac{(1 + \bar{\theta})\rho V}{2}\sum_{k\neq 0} m(-k) - \frac{1}{4}\sum_{k\neq 0} m(k)m(-k)\right) + \frac{1}{\sigma^2}\sum_{k\neq 0}(l^2k^2 + 1/l)m(k)m(-k) + \frac{2\bar{\theta}l}{\sigma^4}\sum_{k_1,k_2\neq 0} m(k_1)m(k_2)m(-k_1 - k_2) + \frac{2V}{l\,\sigma^4}\sum_{k_1,k_2\neq 0}\frac{m(k_1)m(-k_1)m(k_2)m(-k_2)}{k_1^{\ 2} + k_2^{\ 2}} + \frac{l}{\sigma^4}\left(1 + \frac{5\bar{\theta}^2}{\sigma^2}\right)\sum_{k_1,k_2,k_3\neq 0} m(k_1)m(k_2)m(k_3)m(-k_1 - k_2 - k_3) \tag{9}$$

where

$$m(\mathbf{k}) = \int \mathrm{d}\mathbf{r}\ m(\mathbf{r})\mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}} \tag{10}$$

and is the Fourier conjugate of $m(\mathbf{r})$, $\sigma^2 = 4f(1 - f)l$ is the variance of the distribution of the different monomers along the backbone of the polymer chain, and l is the persistence length of the polymer chain.

When eq 9 was obtained, constant density was assumed throughout the polymer network. A mean-field solution of the order parameter is obtained by setting $\delta F/\delta m(k) = 0$ for $k \neq 0$, and the results are

$$m(\mathbf{k}) = \left[\frac{6\bar{\theta}l}{\sigma^4}\sum_{\mathbf{k}_1\neq 0} m(\mathbf{k}_1)m(\mathbf{k} - \mathbf{k}_1) + \frac{4l}{\sigma^4}\left(1 + \frac{5\bar{\theta}^2}{\sigma^2}\right)\sum_{\mathbf{k}_1,\mathbf{k}_1\neq 0} m(\mathbf{k}_1)m(\mathbf{k}_2)m(\mathbf{k} - \mathbf{k}_1 - \mathbf{k}_2) - \frac{\mu(1 + \bar{\theta})\rho V}{4}\right] / \left[\mu/4 - \frac{4}{\sigma^2}(l^2k^2 + 1/l) - \frac{16V}{l\sigma^4}\sum_{\mathbf{k}_1\neq 0}\frac{m(\mathbf{k}_1)m(-\mathbf{k}_1)}{k^2 + k_1^{\ 2}}\right] \tag{11}$$

In the following section we analyze our solutions of heteropolymer networks with various degrees of cross-linking and various compositions. The formation of regions rich in one type of monomer due to cross-linking has already been established.[7-16] We are interested in the local density fluctuations that result from condensation at the cross-linked sites, which in turn lead to a pore size distribution within the polymer matrix. These are practical issues that should be considered in, for example, the design of molecular templates.

We account for three contributions to the density at location $\mathbf{r}$,

$$\rho(\mathbf{r}) = \rho_{\mathrm{C_{cl}}}(\mathbf{r}) + \rho_{\mathrm{C_b}}(\mathbf{r}) + \rho_{\mathrm{F}}(\mathbf{r}) \tag{12}$$

where $\rho_{\mathrm{C_{cl}}}(\mathbf{r})$ is the density of cross-linked segments, $\rho_{\mathrm{C_b}}(\mathbf{r})$ is the density of cross-linkers that are not cross-linked (i.e., $\rho_{\mathrm{C}}(\mathbf{r}) = \rho_{\mathrm{C_{cl}}}(\mathbf{r}) + \rho_{\mathrm{C_b}}(\mathbf{r})$ is the partial density of all cross-linkers at location $\mathbf{r}$), and $\rho_{\mathrm{F}}(\mathbf{r})$ is the partial density of the backbone segments at position $\mathbf{r}$. We initially assume that $\rho(\mathbf{r}) = \mathrm{const}$ in obtaining eq 11. We then assume that the variation in the local density arises only from $\rho_{\mathrm{C_{cl}}}(\mathbf{r})$, as we shall discuss shortly. Although we concentrate on the effects of polycondensation, we note that density fluctuations (and thus a pore size distribution) can also be induced by other factors, such as solvent evaporation and interparticle coalescence. These effects are not discussed in this work.

We calculate the partial density variations of the different types of monomers, $\rho_{\mathrm{C}}(\mathbf{r})$ and $\rho_{\mathrm{F}}(\mathbf{r})$, in terms of the order parameter, $m(\mathbf{r}) = (1 - f)\rho_{\mathrm{C}}(\mathbf{r}) + f\rho_{\mathrm{F}}(\mathbf{r})$. $m(\mathbf{r})$ essentially describes the variation of these partial densities from their mean values given by f and $(1 - f)$, respectively. We term χ the condensation factor, or the relative size of the leaving group during polycondensation to the initial monomer size. χ takes on values between 0 and 1, where for $\chi \to 0$ the size of the leaving group is negligible and for $\chi \to 1$ the monomer *is* the leaving group.

III. Results and Discussion

In our model, as with previous studies of cross-linked heteropolymer networks,[7-16] we observe microphase

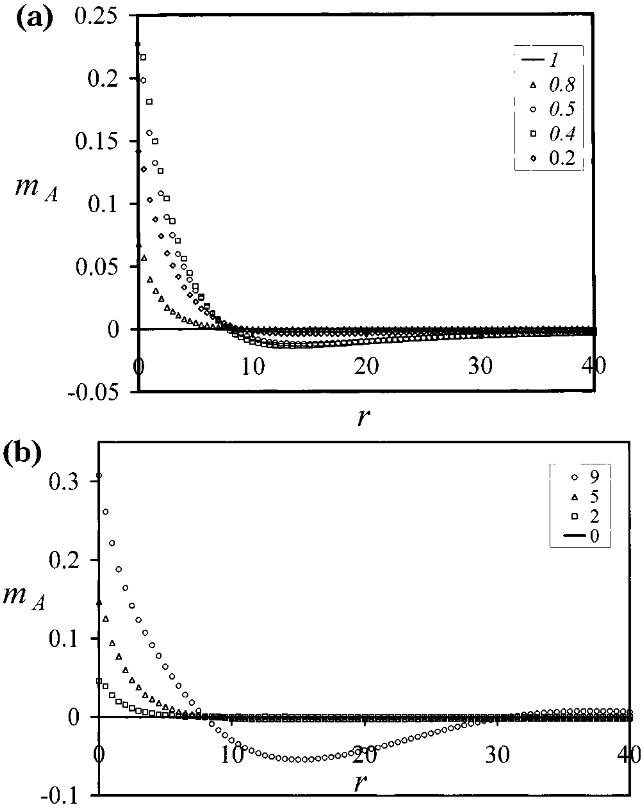
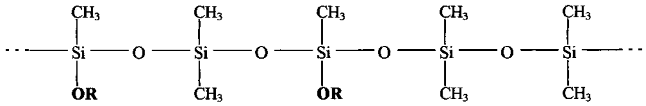


Figure 1. Effects of changing (a) the composition (keeping μ = 9) and (b) the degree of cross-linking (keeping $f = 0.5$) on the microphase separation order parameter. Various values of f and μ are indicated in the legends.

separation of the different monomer units within the network. Interestingly, we find that the degree of microphase separation depends not only on the fraction of cross-linkers, f, but also on the number of these monomers that actually cross-link, determined by μ. It is important to distinguish between the two parameters because experimentally one may have situations where not all monomers cross-link because of physical constraints or because the system is purposely quenched before all monomers are allowed to cross-link.

First, we discuss the effects of changing f and μ on the microphase order parameter, $m(\mathbf{r})$. The results are intuitive and are presented in Figure 1. Figure 1a shows a series of plots of the order parameter for a polymer composed of 50% cross-linkers, where each curve corresponds to a different degree of actual cross-linking. Positive values of $m(\mathbf{r})$ correspond to areas rich in cross-linkers, while negative values correspond to areas rich in monomers that cannot cross-link (backbone monomers). These values are relative to the average partial density of each monomer type. As expected, we see that increasing the degree of cross-linking increases the microphase separation. The cross-linkers seek each other and thus create highly cross-linked microdomains separated by regions rich in "backbone" monomers. In Figure 1b, we show the variation in the microphase order parameter for various polymer compositions, all having 90% degree of cross-linking. We observe a peak in the "ordering" of the polymer network into microdomains when f is increased for a fixed value of μ, with the greatest microphase separation occurring for $f \sim 0.5$ (open circles in Figure 1b). However, solution of eq 11 results in cross-linked polymer networks with overall uniform porosity, although the cross-links in most cases are not uniformly distributed.

Scheme 2



$$\cdots-\underset{\mathrm{OR}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}-\underset{\mathrm{OR}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\cdots$$

We carried out simple simulations that create a cross-section of the network based on the distribution of cross-linkers, shown in Figure 1. In creating the cross-section, we initially place monomers of one type (non-cross-linkers) on a square lattice at evenly spaced intervals. We then replaced monomers with cross-linkers with a probability proportional to $m(\mathbf{r}) + f$, which is the probability of finding a cross-linker at a distance $\mathbf{r}$ from a reference point, chosen as (0,0) on our lattice. Every 100 steps (a step constitutes the placement of one monomer) f was checked, and weights were modified accordingly, until a 1000 × 1000 two-dimenstional cross-section was obtained. Figure 2a is a subsection of the resulting two-dimensional illustration of a network composed of 50% cross-linkers of which 90% form cross-links. It can be seen that cross-linking induces microphase separation, where domains rich in cross-linking monomers (black squares) are separated from those rich in non-cross-linking monomers (gray squares). However, microphase separation itself is not the cause of the fluctuations in the density, $\rho(\mathbf{r})$, in our model. Apart from microphase separation, the cross-linking process may involve the escape of leaving groups, as in the case of organosilicates. For example, given the following starting monomers, $Si(OH)_2(CH_3)OR$ (cross-linker) and $Si(OH)_2(CH_3)_2$ (backbone monomer), a random linear chain composed of these two monomers is shown in Scheme 2.

Our simulations of polycondensation are based on the assumption of an increased local density of cross-linked regions once the leaving group is released. A direct consequence is the formation of larger gaps elsewhere which compensate for the localized densifcation, causing fluctuations in the total density, and thus nonuniform porosity. For simplicity, we assume that there are no steric hindrances associated with an increase or decrease in density. This discussion is made vivid in Figure 2b, where we illustrate the same system as in Figure 2a but with a condensation factor of $\chi = 0.5$ (i.e., the leaving group is one-half the size of the monomer). This schematic is obtained by reducing the distance between adjacent black squares by 50%. We clearly see the formation of pores larger than the average pore size of the corresponding "uniform" network in the domains that are rich in cross-linkers—a direct effect of polycondensation.

In Figures 3a and 3b, we show the density and pore volume modulation profiles of cross-linked networks, respectively, for a wide range of condensation factors. As can be observed, larger leaving groups (increasing χ) create larger density fluctuations and larger variations in the pore sizes within a given network. In Figure 4 we show a semilog plot of collapsed data for the dependence of difference between the maximum and minimum densities on the condensation factor, for various values of f and μ. Regression shows that the dependence obeys an exponential law for most values

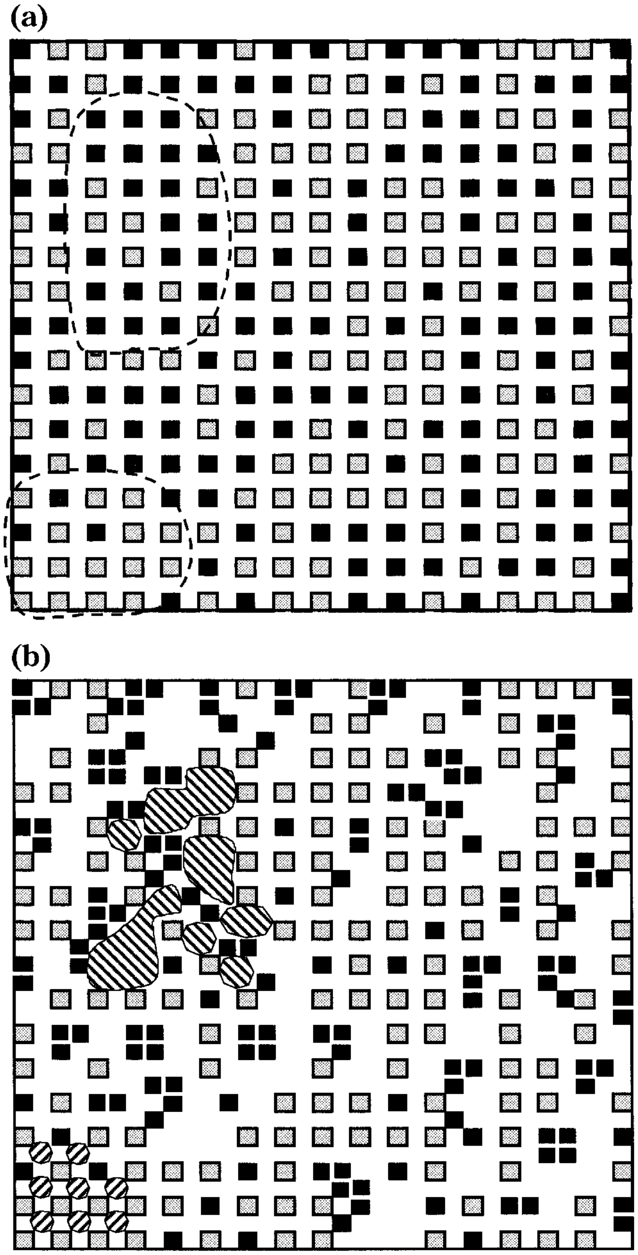


Figure 2. Cross-section of a heteropolymer network made up of 50% cross-linkers and with a high degree of cross-linking ($\mu = 9$). Black squares label cross-linked monomers; gray squares label backbone monomers. (a) The leaving group is negligibly small, $\chi \rightarrow 0$; the pore distribution is nearly uniform, even in the presence of microphase segregation, as is indicated by the encircled areas. (b) The leaving group is 50% the size of the original monomer, $\chi = 0.5$; the pore distribution is multimodal, characterized by a range of small and large pores, as is indicated by the shaded areas corresponding to the encircled areas in Figure 2a.

of χ except the extremities and scales as $\rho_{\text{dif}} \propto e^{5\chi}$. Such a strong dependence on the leaving group is surprising. That is, large leaving groups create pores significantly larger than their size, leading to highly deformed networks.

We calculated the pore size distributions of networks with various condensation factors from the results of Figure 3b. For reference, we also estimated the distribution of a homopolymer having a 50% degree of cross-linking and $\chi = 0.5$, calculated from simple probability statistics of finding M cross-linked monomers near one another on a cubic lattice. The distribution can be generated from the probability of having x nearest neighbors 1 lattice site away, y neighbors $\sqrt{2}$ lattice sites away, and z neighbors $\sqrt{3}$ lattice sites away

$$P = \left(\frac{6!}{l!(6-l)!}P_{\text{cl}}^{l}P_{\text{b}}^{6-l}\right)\left(\frac{12!}{m!(12-m)!}P_{\text{cl}}^{m}P_{\text{b}}^{12-m}\right) \times \left(\frac{8!}{n!(8-n)!}P_{\text{cl}}^{n}P_{\text{b}}^{8-n}\right) \quad (13)$$

with $l \le 6$, $m \le 12$, and $n \le 8$. P_{cl} and P_{b} are the probabilities of finding cross-linked and non-cross-linked monomers as nearest neighbors and equal f and $(1 - f)$, respectively, when the probabilities are not correlated. Because the cross-linked and non-cross-

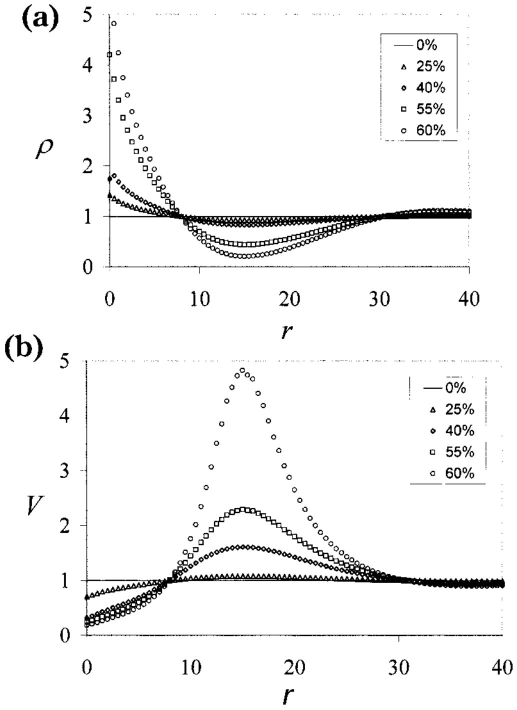


Figure 3. Modulation profile of (a) the density and (b) the pore volume across the polymer network for $f = 0.5$, $\mu = 9$, and various sizes of the leaving group, as indicated in the legends.

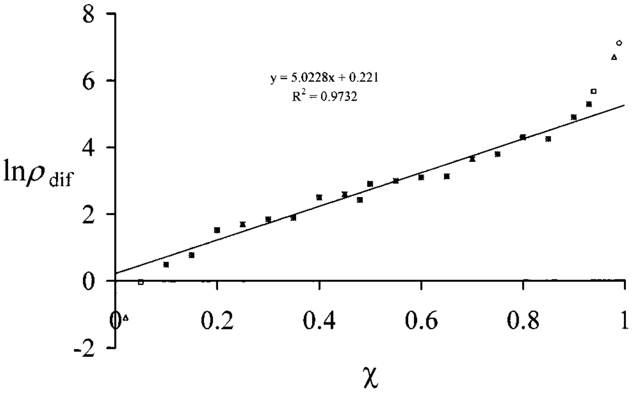


Figure 4. Exponential dependence of the difference between the maximum and minimum densities within the network versus the relative size of the leaving group. Collapsed data has a slope of 5: Diamonds, $f = 0.9$, $\mu = 9$; squares, $f = 0.5$, $\mu = 9$; triangles, $f = 0.4$, $\mu = 7$; circles, $f = 0.3$, $\mu = 3$. Stars correspond to data used to generate the trend line.

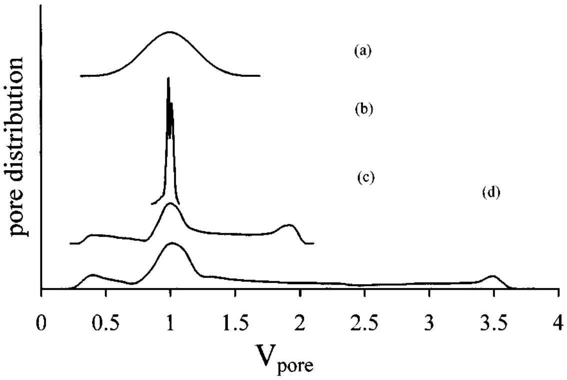


Figure 5. Normalized pore-size distributions of a copolymer network having 50% cross-linkers $\mu = 9$, for various cross-linked bond condensation factors. Unity pore volume corresponds to the average pore distribution in a system with a negligible size leaving group. Pore distribution of a homopolymer having a 50% degree of cross-linking and $\chi = 0.5$ is included as a reference (a). Narrow, homopolymer like networks: (b) $\chi = 0.3$. Widely fluctuating pore distributions: (c) $\chi = 0.85$ and (d) $\chi = 0.93$.

linked monomers are otherwise identical, this situation corresponds to a polymer network without phase separation and corresponds to curve (a) of Figure 5.

Curve (b) of Figure 5 corresponds to a network having relatively small leaving groups and result in narrow unimodal distributions, similar to the homopolymer network. The wider distribution of curve (a) stems from the relatively large leaving group ($\chi = 0.5$). More interestingly, in curves (c) and (d) of Figure 5 we observe very distinguished multimodal pore size distributions when the leaving group is sufficiently large ($\chi > 0.75$), which is the cause of density fluctuations in the polymer network. These distributions exhibit three peaks. The first peak corresponds to the shorter distance between cross-linked monomers. The second and most prominent peak corresponds to the distance between backbone monomers and is typical of the microdomains rich in non-cross-linked monomers. The third peak corresponds to the gaps induced by polycondensation, which appears at (exponentially) increasing pore volumes with increasing χ values. Such networks, characterized by large χ, show an increase in the width of the pore-size distribution, having an especially wide second peak of the large pores. For example, a network characterized by a nominal pore diameter of 20 nm when the leaving group is small (e.g., H_2O) would contain regions having an average pore diameter of 50 nm under conditions characterized by Figure 5d. Therefore, the size of the leaving group is one parameter that can be used to control the nature of the pore size distribution of a given polymer system.

In general, a network characterized by a high degree of cross-linking (high μ) and a fraction of cross-linkers of $0.25 < f < 0.75$ tend to have multimodal distributions and a nonuniform porosity for relatively large leaving groups, $\chi > 0.75$. Other combinations of parameters lead to more uniform networks. Finally, we note that efficient templating requires that the concentration of the template functional groups be small (<25% relative to the total number of monomers). Moreover, this model predicts that templating efficiency by route 3 should be much better for small templates (as is suggested by Figure 5).

IV. Concluding Remarks

We have *shown theoretically* that a nonuniform porosity in copolymer networks can be induced by the leaving groups during polycondensation. In particular, we predict that the leaving groups can create large density fluctuations within the network with substantially larger pores than the size of the leaving group itself. In addition, we find that the cross-links induce microphase separation. The domain size of the different phases depends on the polymer composition as well as the degree of cross-linking. Our results suggest that different combinations of these factors can be used to control and predict the chemical and physical morphology of cross-linked copolymer networks. These results may be important in the design of molecular templates because they *indicate* that successful templating where the pore size distirbution resembles the size of the leaving group is likely to occur under conditions that do not support phase separation ($f > 0.75$, $f < 0.25$, any χ; or $\chi < 0.4$, any f). High-performance multicomponent polymer materials are the subject of considerable current research. Of these composite materials, PMMA–PDMS (poly(methyl methacrylate)–poly(dimethylsiloxane))[36,37] seems to be a reasonable candidate for testing our theoretical predictions, where the leaving group can be water or various alcohols.

Acknowledgment. S.S. thanks the Levi-Eshkol fellowship foundation for funding this project. The project was partially funded by the infrastructure program of the Ministry of Science, Arts, and Sports.

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