The results of this work, along with those of other Monte Carlo studies, show that simulation techniques provide an accessible, realistic approach in describing the dimensional properties of uniform star-branched polymers. In this paper, we have compared our results in three dimensions both with experimental measurements on real systems and with the predictions of the detailed theoretical description developed by Miyake and Freed. With respect to the latter, we find that, typically, our estimates (of a quantity such as $g(f)$) match theirs quite closely for stars having a small number of branches, the differences increasing with f. This indicates that a more extensive theoretical treatment is indeed necessary for systems having a large ($f \geq 6$) number of branches. In two dimensions, the discrepancies are more severe.

Acknowledgment. We acknowledge helpful conversations with K. F. Freed and J. L. Martin. This research was financially supported, in part, by NSERC of Canada and by NATO (Grant RG85/0067). M.K.W. is grateful to SERC for the award of a research studentship, and J.E.G.L. has benefited from being awarded a NATO Science Fellowship.

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(21) In two dimensions, the analogous scaling prediction[6] is $g(f) \sim f^{-1}$. We find that all our data ($f \leq 6$) are consistent with $fg(f) \simeq 2.03$, though the agreement is less good than in three dimensions.
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Conjectures on the Transport of a Melt through a Gel

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ABSTRACT: Certain networks (with X monomers between branch points) may possibly be swollen by a melt of linear, chemically identical, chains (M monomers per chain). We discuss two basic transport properties of these systems: (1) permeability of the swollen gel with respect to the M chains; (2) diffusion of a labeled M chain. We find *six* different regimes for the permeability, depending on the values of X and M and the distance between entanglements (N_e) in the melt. In one of the six regimes, the permeability K is controlled by the friction of an M chain on surrounding M chains, which are themselves entangled with the network: K then becomes independent of the gel parameters (of X). For diffusion of a labeled M chain, we are led to distinguish only *three* different regimes: free draining, reptation, and "strangulation". In the first two regimes, the diffusion constant $D^*(M)$ is expected to be independent of X. In the strangulation regime, the chain reptates in a tube defined by the network.

I. Introduction

Can a network (X) be swollen by mobile chains (M) of the same chamical composition? Clearly, the invasion of X by M is at best very slow. But, more fundamentally, the final swelling equilibrium is controversial.[1,2] The existence, or absence, of swelling depends on certain weak terms in the free energy; an essential role may be played by the compatibility (or incompatibility) or the cross-linking units with the M chains.[2]

In the present text, we shall assume that the gel is indeed swollen by the M chains. Furthermore, we consider that the network has been synthesized under good solvent conditions so that there is no delicate distinction between chemical neighborhood and spatial neighborhood in the system of cross-links.[3] Finally the distribution of length of the network chains (of X) is assumed to be relatively narrow. Then we can think of the X chains as following a "c^* theorem":[4] each chain occupies a volume with linear dimension D, and each volume D^3 is occupied by one chain. The gel fraction is $\phi = Xa^3/D^3$ where a^3 is a monomer volume. We focus our attention on cases where $\phi \ll 1$, i.e., to gels that are strongly swollen (the M fraction $1 - \phi$ is then close to unity).

The equilibrium swelling laws (the formulas for $D(X,M)$) are then easily deduced from the behavior of a single X chain dissolved in a matrix of (chemically identical) M

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chains: with the simplest scaling scheme[5] one finds two regimes: (a) ideal X coils when $X < M^2$; (b) swollen coils when $X > M^2$.

Mose of our discussion will make use of the first case (a), where the mesh size of the network is

$$D = aX^{1/2} \qquad (X < M^2) \tag{I.1}$$

The opposite case (b) leads to an increase of D, induced by excluded volume effects

$$D = aX^{3/5}M^{-1/5} \qquad (X > M^2) \tag{I.2}$$

Having now specified the static conditions, we shall proceed to define two dynamical problems of interest.

(1) Permeability K. The swollen network is placed between two reservoirs of M chains, and a (low) pressure gradient ∇p is imposed between them. We expect a current of M through the gel, J ((volume/cm^2)/s), of the form

$$J = K(-\nabla p) \tag{I.3}$$

We call K the *permeability* of the network. This permeability is of course very low when M is large but could still be measured by using a thin film of gel supported by a macroporous solid. The definition (I.3) of the permeability K differs from the traditional one ($\tilde{K}$) used in the fluid mechanics of porous media,[6] where the viscosity η of the fluid phase is separated, $K = \tilde{K}/\eta$. For these porous media, with a large porosity ($1 - \phi \sim 1$), K has the scaling form

$$K \cong D^2/\eta \tag{I.4}$$

D being the average pore size. This equation can retain a meaning for our gels (D being the mesh size) only in a macroscopic regime: when D is very large. One of our aims will be to locate the exact limit of validity of (I.4). But most realistic values of D lie below this limit: the structure of K must then be obtained by a more delicate analysis.

(2) Diffusion Coefficients. As usual, for a binary system ($X + M$) we must distinguish carefully two diffusion coefficients.

(a) *Self-Diffusion* $D^*(M)$. This is obtained by following the displacement $X(t)$ of a *single* labeled M chain during a macroscopic time t

$$D^* = X^2/2t$$

Various techniques (forced Rayleigh scattering, photobleaching) are adequate for a measurement of D^*, but an essential condition is that the labels must be dilute.

(b) *Cooperative Diffusion* $D_{\text{coop}}(M)$. This is obtained by monitoring the overall concentration of M chains as a function of space and time: the coefficient D^{coop} is related to the osmotic pressure $\Pi(\phi)$ of the M chains in the gel and to the permeability, K, by the standard relation[11]

$$D_{\text{coop}} = K|\mathrm{d}\Pi/\mathrm{d}\phi|$$

The two coefficients D^* and D_{coop} coincide only in one special limit: namely, when the volume fraction ($1 - \phi$) of the M chains is small. Since D_{coop} is directly related to K we need not discuss it separately. But measurements of D_{coop} (by optical techniques) may be more convenient than the direct measurement of K described above.

Recently certain diffusion coefficients have been measured by Antonietti and Sillescu in PS networks cross-linked by a Friedel–Crafts reaction.[7] The values of X are in the interval 10–50. They impregnate the dry gel with linear chains of PS (labeled with a suitable optical dye) and measure a diffusion coefficient D_1 of these labeled chains as a function of M and X: D_1 is very sensitive to M but nearly independent of X for the domain investigated.

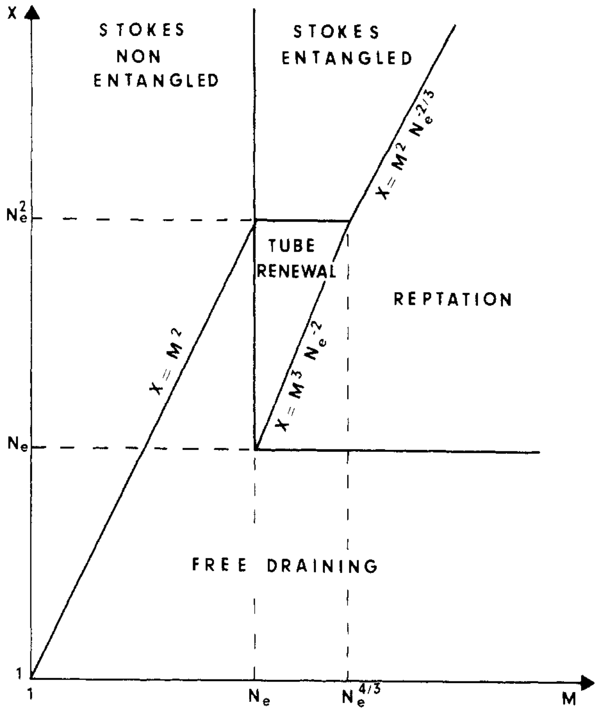

Figure 1. Different regimes for the mobility of one linear chain (X monomers) in a melt of chemically identical chains (M monomers per chain). N_e is an average number of monomers between entanglement points. The scales in X and M are logarithmic.

This situation is probably somewhat different from what we have in mind here: (a) all mobile chains are labeled, thus we are in principle dealing with a D_{coop}; (b) the concentrations ($1 - \phi$) of mobile chains is imposed and maintained small ($\lesssim 5\%$). In this limit D^* and D_{coop} coincide. But we are then not dealing with the strongly swollen gels that we have assumed in the present discussion: we cannot compare our conjectures with the Antonietti–Sillescu data.

(3) A Related Problem. There is a certain analogy between the permeability problem for a network of adjacent X chains and another problem, which has already been explored:[8–10] the mobility μ_X of *one* X chain moving in a melt of M chains (defined as the ratio of velocity/total force on the chain).

The two situations are not identical: for instance a single X chain can reptate, while an X chain in a network cannot. But the variety of regimes found in the μ_X problem provides some helpful hints for the K problem.

The major regimes expected for the μ_X problem are displayed in Figure 1, which is mainly taken from ref 8 (plus some minor adjustments).

(a) For $M < N_e$ (the entanglement limit) and $X > N^2$, the M chains behave like a low molecular weight solvent with a Rouse viscosity

$$\eta_R(M) = \eta_0 M \qquad (M < M_e) \tag{I.5}$$

The mobility of the X chain follows Stokes' law

$$\mu_X = 1/6\pi\eta_R R(X) \sim 1/\eta_R D \tag{I.6}$$

since $R(X)$ is proportional to the radius of gyration D (eq I.2). We call this regime "nonentangled Stokes".

(b) For $M > N_e$ and in a certain region showed in Figure 1, we still have a Stokes behavior, but now the viscosity of the melt η_{ent} is increased by entanglements: within the simplest reptation model[11]

$$\eta_{\text{ent}} = \eta_0 M^3 N_e^{-2} \tag{I.7}$$

and

$$\mu_X \sim 1/\eta_{\text{ent}} D \qquad \text{(I.8)}$$

(c) When both M and X are large, the matrix M may be considered as immobile and the X chain reptates through a fixed network, with a mobility[11]

$$\mu_X \sim N_e/\eta_0 a X^2 \qquad \text{(I.9)}$$

(d) When X is relatively small, the X chain moves by free draining (*Rouse chain*), with a mobility

$$\mu_X \sim 1/\eta_0 a X \qquad \text{(I.10)}$$

This crosses over to (I.6) when $X = M^2$.

(e) In a certain intermediate region (shown in Figure 1) the X chain is long ($X > N_e$) but the M chains are only weakly entangled: then they do not behave as a fixed matrix for X. This is the process of *tube renewal* discussed repeatedly by Klein[9] and others.[8] In the simplest version each matrix cahin relaxes *one* constraint after a time τ equal to its own reptation time

$$\tau(M) \sim \tau_0 M^3 N_e^{-1} \qquad \text{(I.11)}$$

This leads to a Rouse motion of the tube with a characteristic time

$$T_R(X) = (X/N_e)^2 \tau(M) = X^2 M^3 N_e^{-3} \tau_0 \qquad \text{(I.12)}$$

and to a mobility

$$\mu_X \sim \frac{D^2}{T_R(X)} \sim \frac{1}{X}\left(\frac{N_e}{M}\right)^3 \frac{1}{\eta^0 a} \qquad \text{(I.13)}$$

In eq (I.13) we have used the ideal coil value (I.1) for D; we can check later that tube renewal is important only in the domain $X < M^2$, where the X coil is indeed ideal.

Recently a new possiblity has been suggested by the Pau group[10] and worked out more precisely by Klein.[9] The idea is that one matrix chain M (with $M < X$ for our purposes) may impose *more than a single constraint* to the X chain. The number of contacts between M and X (in the ideal chain regime) is of order $M^{1/2}$, and the resulting number of constraints may be of order $M^{1/2}/N_e$. Thus whenever $M > N_e^2$ the formulas for tube renewal have to be reconstructed. However, as may be seen from Figure 1, the domain of applicability of tube renewal for our purposes is entirely to the left of the line $M = N_e^2$: thus we tend to believe that the naive formula (I.13) is valid here.

On the whole we have listed *five* typical regimes for the mobility μ_X of one X chain in an M matrix. Comparing the resulting forms of μ_X, we can then construct the crossover lines shown in Figure 1: we must of course insist on the fact that there are not sharp transition lines but that they correspond to very smooth crossovers. Because of these restrictions, the regime of tube renewal, which is confined to a relatively small region, may never be observable in total purity.[15] However, the list of regimes and the approximate regions shown in Figure 1 may be helpful. In section II we transpose these ideas to the gel permeation problem: but we also find that some new ingredients are required!

Finally, in section III, we turn to the self-diffusion problem, which turns out to be noticeably simpler than the permeation problem. There are two reasons for this: (a) the labeled chain is in a matrix of other chains M with the *same* length, but for such a case, the "Stokes regimes" of eq I.6 and I.7 are never relevant (they would become relevant only when the labeled chain is much longer than the matrix chains); (b) in a self-diffusion process, one may (roughly) think of the matrix as immobile, while in the K problem, the macroscopic regimes involve many chains flowing together.

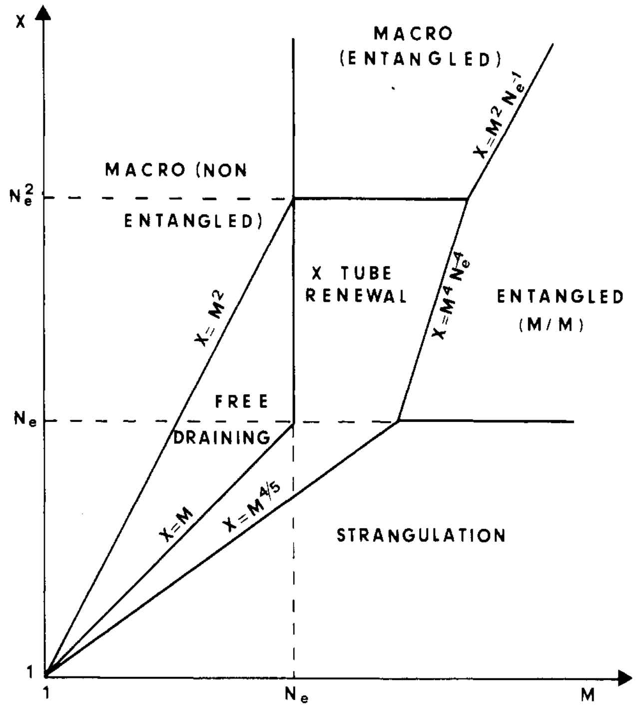

Figure 2. Different regimes for the permeability of a network (X monomers between cross-links) swollen with chemically identical chains (M monomers per chain). N_e is an average number of monomers between entanglement points in the M melt. The scales in X and M are logarithmic.

In section IV we discuss some possible future experiments.

II. Permeation

The best starting point for our reader is Figure 2, where the six main regimes are displayed in an (M, X) diagram. Many of these regimes are the direct counterpart of those found in Figure 1, and we shall begin our discussion with them.

(1) Macroscopic Regimes. When the mesh size D of the network is sufficiently large, we can omit the inner structure of the moving fluid M and describe the permeation of M through its macroscopic viscosity η. The scaling law for the permeability is then described in eq (I.4). We have two possibilities: (a) for nonentangled M chains, we use the Rouse viscosity (I.5) and obtain

$$K = D^2/\eta_0 M \qquad (M < N_e) \qquad \text{(II.1)}$$

(b) for entangled chains, we use the reptation value (I.7), giving

$$K = D^2 N_e^2/\eta_0 M^3 \qquad (M > N_e) \qquad \text{(II.2)}$$

(2) Free Draining ($M < M_e$). In the macroscopic regimes described above, the flow field of the M fluid is very inhomogeneous, with relatively rapid flow in the regions of low density of the X network and negligible flow in the regions of high density. But, in some other circumstances, the flow may be more uniform. To understand this, it is convenient to go back to the early ideas of Debye and Bueche[12,13] and to extract from there a certain *hydrodynamic screening length* κ^{-1}. When κ^{-1} is smaller than D, a macroscopic picture holds. But when $\kappa D < 1$ the flow becomes uniform. The Debye–Bueche theory assumes a constant filling fraction $\phi(\mathbf{r}) = \phi$ for the network and a local friction proportional to ϕ: the resulting hydrodynamic equation for the velocity field $V(\mathbf{r})$ of the M chains is

$$\eta \text{ curl curl } \mathbf{V} + \zeta\phi\mathbf{V} = -\nabla p \qquad \text{(II.3)}$$

from which one obtains a screening parameter

$$\kappa^2 = \zeta\phi/\eta \cong \phi(\eta_0/\eta)a^{-2} \qquad (\text{II.4})$$

where we have written $\zeta \sim \eta_0 a^{-2}$ for the local friction coefficient. If D is smaller than κ^{-1}, the terms curl curl $\mathbf{V}$ ($\sim V/D^2$) are negligible in eq II.3 and $\mathbf{V}$ is uniform. The permeability is then

$$K = \frac{V}{-\nabla p} = \frac{1}{\zeta\phi} \cong \frac{a^2}{\eta_0\phi} \qquad (\kappa D < 1) \qquad (\text{II.5})$$

The crossover $\kappa D = 1$ is interesting. Using eq II.4 for κ^2 and eq I.1 and I.2 for D, we can check that it corresponds to $X = M^2$: static screening and dynamic screening occur at the same moment. This feature was already discussed in early work on dynamic screening of semidilute solutions.[14]

(3) Tube Renewal. This corresponds to a "knitting" motion of the mobile chains M around one X chain, allowing for a renewal of the tube surrounding X.[8,9] We can derive the resulting permeability K rather simply from the form of μ_X in this regime (eq I.12). The correspondence between μ_X and K comes directly from a balance of forces. The force on the M matrix (per cm^3) is $-\nabla p = J/K$. The force on the network f_X (per cm^3) is equal and opposite; the force per chain is

$$X(a^3/\phi)f_X = V/f_X$$

where V is the relative velocity of the X chains with respect to the M matrix. Here (since $\phi \ll 1$) $V \cong -J$. Thus we must have

$$K = \mu_X X a^3/\phi \qquad (\text{II.6})$$

Inserting the appropriate form of μ_S (eq I.13) for $M > M_e$, we arrive at

$$K = (a^2/\eta_0\phi)(N_e/M)^3 \qquad (X > N_e) \qquad (\text{II.7})$$

There is one complication, however: eq II.7 holds only if the relaxation time of the M chains is controlled by M/M entanglements (as is true for the one X chain problem of section I). But, for the network problem, if $X < N_e$ (as is often the case), the dominant entanglements of one M chain are established with the network: we must then replace N_e by X in eq II.7, and we obtain

$$K = (a^2/\eta_0\phi)(X/M)^3 \qquad (X < N_e) \qquad (\text{II.8})$$

(4) Entangled (*M*/*M*) Regime. Let us again assume $M > N_e$ and consider the case where the mobile chains are rather strongly trapped by the network. Then one particular M chain must reptate through an ambient medium (mainly other M chains) that is practically immobile. We can then derive K from a simple reptation formula.[11] The drift velocity of one chain (J) is of the form

$$J = \mu(M/M)f_{\text{tot}} \qquad (\text{II.9})$$

where f_{tot} is the force per chain $f_{\text{tot}} = Ma^3(-\nabla p)$, while $\mu(M/M)$ has the scaling structure[11]

$$\mu(M/M) = \mu_1 Ne/M^2 \qquad (\text{II.10})$$

This leads to

$$K = (a^2/\eta_0)(N_e/M) \qquad (\text{II.11})$$

(5) Strangulation (*M*/*X*). This word has been coined by the Mainz group[7] to cover special situations where entanglements in the X chains reduce the mobility. We give it here a more broad meaning, describing all situations where the network has a spacing smaller than the entanglement length ($X < N_e$). Then the mobile chains are "strangled" in a narrower tube (of diameter X^2a), and we should replace N_e by X in eq II.11, obtaining

$$K = (a^2/\eta_0)(X/M) \qquad (\text{II.12})$$

We have now listed (tentatively) all the six types of permeation that can occur in our swollen gel. To find the domains of existence of all these types, we construct the crossover lines between them: some of these lines are obvious (i.e., entanglement processes between the M chains occur only at $M > N_e$). Many crossover lines are obtained by equating two different forms of K. Some of the crossovers can be further understood by a physical argument; e.g., the line separating "free draining" from "macroscopic flow" corresponds to a hydrodynamic screening length κ^{-1} that becomes equal to the mesh size D of the network, as explained after eq II.4.

The final product is the diagram of Figure 2, which is rather complex; there is a certain similarity with Figure 1 (dealing with *one* X chain), but some features are specific to a network (e.g., the strangulation process).

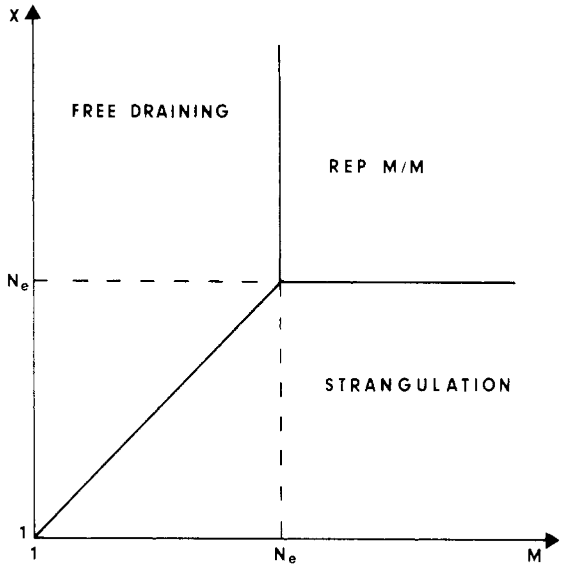

Figure 3. Different regimes for the self-diffusion of one labeled M chain in a gel (X monomers between cross-links) swollen by other M chains.

III. Self-Diffusion D^*

We are now concerned with the diffusion of *one* labeled M chain inside a swollen network. This leads to a rather simple classification with only three dominant regimes: (1) *free draining* at $M < M_e$ and $X > M$, with a diffusion coefficient of the form

$$D^*_M = D_0 M^{-1} \qquad (\text{III.1})$$

where D_0 is a microscopic diffusion constant; (2) *simple reptation* at $M > M_e$ and $X > M_e$, with

$$D^*_M = D_0 N_e M^{-2} \qquad (\text{III.2})$$

(3) *strangulation* at $X < M_e$ and $X < M$, with

$$D^*_M = D_0 X M^{-2} \qquad (\text{III.3})$$

The crossover lines are obtained by equating the three forms of D^*_M in pairs: the resulting domains in the (M, X) plane are shown in Figure 3.

IV. Discussion

(1) All our analysis assumes that certain networks may be strongly swollen by linear chains based on the same monomer. As pointed out in ref 2, this requires a delicate

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balance of forces: even the presence of a few cross-linking points, with different solubility parameters, or of a few labeling units on the mobile chain may upset the compatibility.

(2) If we do have enough compatibility, we should be able to swell the dry gel in a reasonable time if the gel particles are small enough (below our micron). One of the interesting tricks used by the Mainz group[7] is based on the self-cross-linking of dilute PS chains: this generates very small gel particles—in fact a little too small, because the size of the particle may now become comparable to other lengths of interest.

(3) If the resulting gel is of acceptable optical quality, we can measure the diffusion coefficient D^* by the current optical techniques (with a small fraction of M chains labeled). D_{coop} is more difficult to reach, since in our swollen gels labeling all the mobile chains would probably lead to exceedingly high concentrations of labels. Also all measurements of D_{coop} (or of K) may be sensitive to defects in the gel texture (cracks or gel-free regions allowing for fast permeation).

(4) But, if all these difficulties can be ultimately removed, the transport properties will be extremely interesting. Figure 2 displays the amazing variety of regions that are expected. Some of these are very tentative. Some may be constantly unobservable (e.g., the thin region of tube renewal at $X < N_e$). But the broad features should remain relevant: for instance, the strangulation regime or the entangled regime M/M—where permeation becomes independent of the level of cross-linking!

Acknowledgment. The stimulus to write this paper was provided by Dr. H. Sillescu—in spite of the fact that our theoretical thoughts do not cover exactly his experimental conditions. Discussions with him, and with J. Klein, on related subjects, are gratefully acknowledged.

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Studies of Fiber Formation in Tubular Flow: Polypropylene and Poly(ethylene oxide)

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ABSTRACT: The flow-induced crystallization of isotactic polypropylene (PP) and poly(ethylene oxide) (PEO) solutions has been studied by using the technique of seeded growth in tubular flow. Similar to earlier studies with polyethylene, fiber formation from 0.01 wt % solutions in tetralin of an ultrahigh molecular weight polypropylene was found to occur by a sequence involving rapid formation of an unoriented, amorphous precursor followed by nucleation and axial growth of oriented crystallites in the precursor phase. Time constants for the development of birefringence in the precursor followed a pattern with temperature and solution flow rate similar to that of the earlier study and could be explained on the basis of stress-induced crystallization. Studies with 1 wt % solutions of a lower molecular weight polymer showed that the same precursor-to-crystalline fiber transformation occurs. Reduced initiation rates also enabled direct observations to be made of the precursor axial growth process. Fiber formation from solutions of an ultrahigh molecular weight PEO was found to be much reduced compared to that of either of the polypropylenes and was confined to a small temperature range slightly above the quiescent crystallization temperature. Observations were also made regarding entanglement formation during solution preparation. The discussion emphasizes the role of entanglement formation and chain stiffness on the precursor formation and fiber crystallization processes.

Introduction

The phenomenon of oriented fibrous crystallization during flow of high molecular weight polymer solutions has been extensively studied over the past two decades. Most investigations have employed Couette geometries, with a number of the more recent studies utilizing the surface growth technique. The latter experiments have contributed important information regarding the existence and probable nature of the entangled, gel-like liquid layer which forms on the rotor surface and from which fiber growth proceeds. Unfortunately, the existence of the self-regulating mechanism during surface growth and the possibility of postcrystallization drawing during fiber takeup severely limit the usefulness of the rate data one so obtains.[1]

A great deal of attention has also been directed to a number of methods for producing ultrahigh-modulus and -strength polyethylene fibers using techniques that are

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