The first possibility would require the presence of an infinite number of ion pairs with various interionic distances; moreover, the value $a < 3$ Å observed at $\epsilon > 22$ is unrealistically small. We do not believe that stable separated ion pairs are formed in this system. The distance $a \approx 9$ Å (i.e., 6 Å for contact species and $\approx$3 Å for a separating molecule) estimated for such ion pairs is too large to allow formation of the thermodynamically stable species.

It is much more probable that the monomer preferentially solvates onium ions, resulting in smaller than average changes of ϵ. This screening effect of the monomer leads to lower local values of ϵ in more polar solvents and it increases the local dielectric constant in CCl_4 (as shown by the arrow from $\epsilon = 5.4$ to $\epsilon = 6.1$ in Figure 1). This may allow us to estimate the increase of THF proportion from the average 60% ($\epsilon = 5.4$) to 80% ($\epsilon = 6.11$) involved in the surrounding of ion pairs. Of course, this is an oversimplified picture, because we do not know the strength of the interactions and we cannot estimate the influence of the outer solvation shell on the dielectric constant in the immediate neighborhood of active species.

Equation 2 could be corrected by an additional term accounting for the dipole moment of the unsymmetrical onium ions as suggested by one of the reviewers. Unfortunately no data on the dipole moments of onium ions resembling active species in polymerization of heterocyclics are available.

In literature there is some evidence on the preferential solvation of onium ions by nucleophilic solvent. The dissociation constants of the secondary ammonium ions increase 25 times in $C_2H_4Cl_2$ in the presence of 10% of THF. This can be ascribed to the specific interactions (H bonding) since only 20% change was observed under similar conditions for quaternary ammonium ions.[15] Decrease in the mobility of ions and increase of the dissociation constants of triethyloxonium hexafluorophosphate was observed in CH_2Cl_2 solvent with small additions of diethyl ether.[17] On the other hand the behavior in the mixtures of solvents unable to solvate cations specifically (CH_2Cl_2, CH_3NO_2, CCl_4) led to the expected dependences as shown by filled points in Figure 1.

Thus, the observed dependence of dissociation constants of growing ion pairs on the solvent composition in the cationic polymerization of heterocycles indicates preferential solvation of onium ions by nucleophilic monomer molecules.

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Registry No. THF, 109-99-9; oxepane, 592-90-5; conidine, 35848-09-0.

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(6) Quantitative measurement of solvation in similar systems is rare. Arnett[18] has calculated the thermodynamic values of interactions between Na^+ cation and the glyme molecule: $\Delta H° = -3.5$ kcal/mol, $\Delta S° = 12$ eu. The tetrahydrofuranium cation has a much broader charge distribution[19] and should be solvated more weakly than Na^+ cation. Thus, under polymerization conditions ($[THF]_0 \approx 5$ mol/L) no more than 80% of the cations can be complexed at 25 °C ($K < 1$ L/mol). On the other hand the polymodal molecular weight distribution observed in cationic polymerization of *p*-methoxystyrene was explained by the presence of active species complexed by monomer and solvent.[20] The lifetime of these species should be long enough to survive during all propagation. Thus, the exchange of these complexed molecules is slow.
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Dynamic Scattering from Mixtures of Homopolymers and Copolymers in Solution

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Recently, we have developed a theory of dynamic scattering from mixtures of homopolymers[1] and from copolymers in solution[2,3] using the random phase approximation. The main conclusion of this theory was the emergence of two modes of relaxation in the intermediate scattering functions. While these two modes were identified by light scattering in the case of mixtures of homopolymers in solution,[4] the case of copolymers remains to be explored experimentally since, to our knowledge, these two modes were not yet obtained.

In this paper, we would like to see what this theory predicts in the case of a mixture containing two homopolymer species and a diblock copolymer (50/50) made of the same species in solution. To do this, we focus our attention on the relaxation frequency Γ_I of the mode which was characterized as an interdiffusion mode of one species

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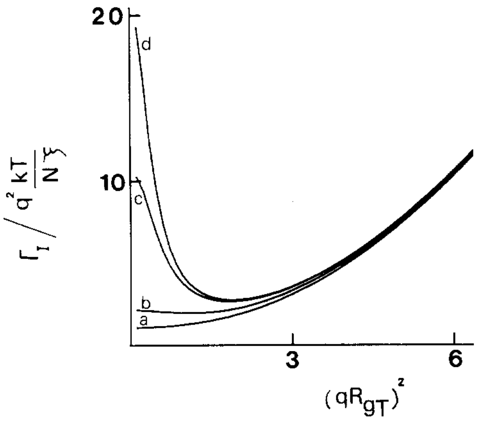

Figure 1. Variation of $\Gamma_I/(q^2(kT/N\xi))$ as a function of $(qR_{gT})^2$; $v\phi_T N = 1$; and $\chi/v = 5 \times 10^{-2}$ for different values of the weight fraction of copolymer y: (a) $y = 0\%$; (b) $y = 50\%$; (c) $y = 90\%$; (d) $y = 95\%$.

with respect to the other. For reasons of simplicity, we assume that our system is made of identical homopolymers except for the contrast factors and the interaction parameter χ between monomer species. The copolymer is merely a junction of two different homopolymers. All quantities used here have their standard meanings and were clearly defined earlier.[1-3] Therefore, these definitions are not reproduced here.

To proceed further, we note the two limits. (i) Mixture of homopolymers in solution with a composition $x = {}^1/_2$ is the first. In this case, Γ_I was found as

$$\Gamma_I = q^2 \frac{kT}{\xi N P(q)}\left[1 - \frac{\chi\phi_T N}{2} P(q)\right] \tag{1}$$

N is the number of monomers per chain, $P(q)$ is the form factor, and ϕ_T is the total polymer concentration. (ii) Diblock copolymers in solution is the second case. Here the following result was obtained:

$$\Gamma_I = q^2 \frac{kT}{2N\xi(P - P_T)(q)}[1 - \chi\phi_T(P - P_T)(q)] \tag{2}$$

where N and P are the number of monomers and the form factor of each block and P_T is the form factor of the chain of $2N$ monomers.

The two relaxation frequencies show an entirely different behavior as a function of q. While Γ_I for a mixture of homopolymers behaves as an ordinary interdiffusion mode and goes to zero as $q \rightarrow 0$, for copolymers it is more subtle and goes to a constant limit when $q \rightarrow 0$. Furthermore, eq 1 shows that Γ_I at $q = 0$ vanishes for $\chi\phi_T N/2 = 1$, whereas in the copolymer case, Γ_I as given by eq 2 cannot be zero at $q = 0$,

$$\Gamma_I = \frac{3kT}{2N\xi R_{gT}}$$

and is independent of χ, where R_{gT} is the radius of gyration of the whole copolymer chain. However, this frequency can vanish at a finite value of the wave vector q_m such that

$$\chi\phi_T N[P(q_m) - P_T(q_m)] = 1 \tag{3}$$

Therefore, since the behavior of Γ_I for two systems was so different in the small q region, it was interesting to see what happens when a fraction y of copolymers is present in the system containing a mixture of homopolymers. The calculation of Γ_I in this case is straightforward and is based on the general formulas given in ref 1 and 2. The result can be verified easily as

$$\Gamma_I = q^2 \frac{kT}{N\xi} \frac{1}{P + y(P - 2P_T)}\left[1 - \frac{\chi\phi_T N}{2}[P + y(P - 2P_T)]\right] \tag{4}$$

One observes that for $y = 0$ (no copolymers) eq 1 is obtained and for $y = 1$ (no homopolymers) eq 2 is recovered correctly. In the figure below, we have plotted the variation of $\Gamma_I/(q^2kT/N\xi)$ as a function of $(qR_{gT})^2$ for various values of the copolymer composition y. It shows that the effect of adding copolymers to the mixture of homopolymers is really significant only for relatively high values of y (i.e., $y > 50\%$). This does not seem to be the case for static properties where a small fraction of copolymers is found to induce a significant compatibilizing effect in mixtures of incompatible homopolymers.[5]

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Polymer Melt Dynamics Model with a Relaxation Time Exponent of 10/3

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Introduction

Reptation provides a clear and useful limiting model of polymer chain motion in dense, entangled fluids[1] and is the basis of current molecular theories of viscoelasticity.[2] In its simplest form, it replaces the three-dimensional Brownian motion of segment beads (c.f., Rouse–Zimm solution theories) by one-dimensional diffusion along a chain contour "tube" created by excluded-volume interactions with neighbor chain molecules. Since chain segments move in directions both parallel and perpendicular to their backbones and since neighbor chains are not stationary, refinements of the simple picture have appeared, improving and extending the fit to experiment, as well as removing unphysical features.[3,4] For the most part though, the important scaling predictions of reptation are not altered, namely, a center-of-mass diffusion constant D

$$D \sim M^{-2} \tag{1}$$

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