Notes

Solvation of Onium Ions in Cationic Ring-Opening Polymerization

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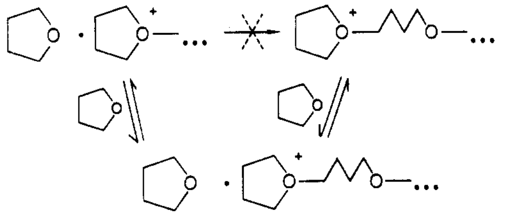
It is well established that the active centers in the cationic polymerization of a large majority of heterocyclic monomers have the structure of onium ions (i.e., oxonium, sulfonium, or ammonium), but a more detailed picture of the solvation shell of these ions is still obscure.[1] It was proposed some time ago[2] that the active species in these systems are surrounded by clusters of monomer molecules, which are the most nucleophilic and best solvating agents in the system. This idealistic picture was later criticized,[3] showing that solvent molecules must also be present in the vicinity of the active centers, because rate constants of propagation vary with the average dielectric constant of the mixture in the usual way (lower k_p's were found in more polar solvents[4]). Recently, a kinetic isotope effect was observed in the homopolymerization of tetrahydrofuran (THF) and acetals, indicating the complexation of a monomer with an active center prior to propagation.[5] On the other hand, the kinetics of the polymerization of THF is internally perfectly first order (in respect to monomer), suggesting that the unimolecular rearrangement of the complex of onium ion with THF cannot be the slowest step in propagation.[4] The energy of the complexed monomer molecule might be too low to induce ring opening of the tetrahydrofuranium ion within the complex, and propagation requires a collision with an external monomer molecule having sufficient energy.



(1)

Although interactions between onium ions and monomers (e.g., THF) cannot be very strong and only a fraction of the active centers can be complexed,[6] there is indeed an indication of the preferential solvation of ions by monomer.

We have previously measured dissociation constants (K_D) of living chains in the polymerization of THF, oxepane, and conidine in different solvents.[7] Values of K_D decrease in less polar solvents. The dependence of dissociation constants of ion pairs with interionic distance a on the dielectric constant ϵ was quantitatively treated by Bjerrum[8] and later by Fuoss.[9]

$$K_D = \frac{3000}{4\pi N a^3} \exp\left[\frac{-zz_1e^2}{a\epsilon k_B T}\right] \qquad (2)$$

The preexponential factor shows the probability of contact of two neutral spheres. The exponent is a Boltzmann's weighting factor for spheres with charges z and z_1. Analysis of the diffusion-controlled formation and dissociation of encounter ion pairs produces a similar equation.[10] Equation 2 loses its usefulness for concentrated solutions and at high dielectric constants ($\epsilon > 40$). This equation gave less than 10% variation in a value of a for tetraisoamylammonium nitrate in dioxane–water mixtures in spite of a 10^{15}-fold increase in the values of the dissociation constant.[11] Equation 2 describes satisfactorily a dissociation of triphenylmethylium hexafluoroantimonate[12] and tetrabutylammonium tetraphenylborate[13] in mixtures of aprotic solvents CH_3NO_2/CH_2Cl_2 and $C_6H_5NO_2/CCl_4$ as shown by solid points in Figure 1.

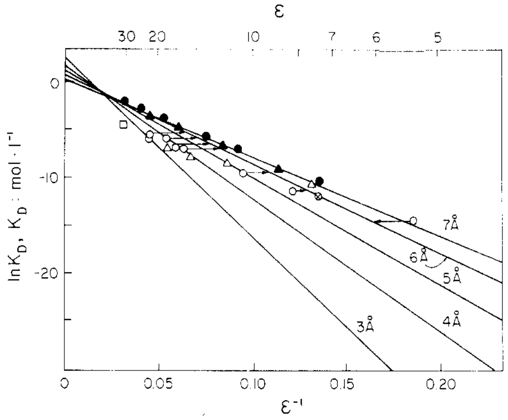


Figure 1. Dependence of dissociation constants (K_D) of living chains in polymerization of THF (○), oxepane (△), and conidine (□) on dielectric constant at 25 °C. Solid lines were calculated from eq 2 (⊗) measured in neat THF. Filled points: (●) tetrabutylammonium tetraphenylborate;[13] (▲) triphenylmethylium hexafluoroantimonate.[12]

In Figure 1 the theoretically calculated dependences of dissociation constants (ln K_D) on the macroscopic, i.e., average, dielectric constant (ϵ^{-1}) are shown for ion pairs with the interionic distances a = 3–7 Å. The values of the dissociation constants of the above salts indicate a = 7 Å. On the other hand the experimental values of ln K_D measured in the polymerization of THF (○), oxepane (△), and conidine (□) do not fit any of the theoretical plots. Before discussing the reasons for this deviation, let us estimate the interionic distance in the contact oxonium and ammonium ion pairs. We used bulky anions such as SbF_6^-, AsF_6^-, $CF_3SO_3^-$, and I^- with radii ranging from r_- = 2.0 to 2.5 Å.[14] The radii of growing onium ions are not known but the size of the macromolecular substituent has no effect on the values of dissociation constants and ion mobilities.[15] We use tetramethyl- (r_4 = 3.5 Å) or tetraethylammonium (r_+ = 4 Å)[16] as models of conidinium and tetrahydrofuranium or oxepanium ion pairs. The size of the acyclic part of any growing onium ion should be intermediate between that of methyl and ethyl groups. The size of the free electron pair in an oxonium ion is less important since it is placed on the side opposite to the counterion. Thus, the value of the interionic distance in the contact ion pair should be equal to $a = r_- + r_+ \approx 6$ Å.

This value (a = 6 Å) is found in Figure 1 at the dielectric constant ϵ = 7.5, i.e., in bulk – in pure THF (⊗). In less polar media (mixtures with CCl_4) a higher apparent value of a was calculated, whereas in more polar mixtures (CH_3NO_2, $C_6H_5NO_2$) lower values of a were calculated.

This may originate either from the real variation of the interionic distance or in the smaller than average changes of the dielectric constant in the proximity of active centers.

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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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(4) Penczek, S.; Matyjaszewski, K. *J. Polym. Sci., Polym. Symp.* **1976**, *56*, 255. Rate constants of propagation decrease with dielectric constant because the transition state is more polar than the ground state. Therefore, the passage to the transition state is accompanied by desolvation which is favored in less polar solvents.

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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: $\Delta H^\circ = -3.5$ kcal/mol, $\Delta S^\circ = 12$ 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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