Ion and Ion-Pair Contributions to the Polymerization of Tetrahydrofuran

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ABSTRACT: The cationic polymerization of tetrahydrofuran is generally considered to be effected by an oxonium chain end in the form of an ion pair. Consideration of expected ionic dissociation constants of salts in typical solvents for these reactions suggests that appreciable concentration of free oxonium ions would be present under polymerization conditions. The dissociation constants of such salts have been measured in methylene chloride solution and shown to be in near 4×10^{-6}, sufficiently high that a contribution to the polymerization by free ions could be expected. Rate constants for the propagation reaction of the polymerization initiated by triethyloxonium tetrafluoroborate have been measured, in both the presence and absence of the common-ion salt tetrabutylammonium tetrafluoroborate. From the dependence of the rate constant on the initiator concentration and from its reduction by varying concentration of the free common ions, it is possible to calculate the ion-pair rate constant to be 1.4×10^{-3} M sec^{-1} and the free oxonium ion rate constant to be 1.0×10^{-2} M sec^{-1}.

It has been well established in living anionic polymerizations of hydrocarbon monomers in solvents of only moderate dielectric constant that the chain-propagation step is carried by both the free anion and the ion pair of the growing polymer chain–alkali metal salt.[1] In comparable cationic polymerizations, such as those of cyclic ethers by oxonium salts, where the lifetime of the growing chain is long compared with the time of polymerization, the propagation reaction is consistently said to proceed *via* an ion-pair reaction, even in solvents such as the chlorinated hydrocarbons with ϵ in the region of 10.

Consideration of the expected dissociation constants[2] of the polymerizing oxonium salts in these solvents would suggest that several per cent free ions could well be present. Unless these free ions have a rate constant the same or lower than that of the ion pair, their presence should be detectable by kinetic measurements.

The polymerization of tetrahydrofuran initiated by oxonium tetrafluoroborate salts is a reaction which has been well studied[3,4] and characterized as a typical living cationic polymerization with few complications in dry systems at not too high temperatures, apart from the rather high equilibrium monomer concentration due to its low heat of polymerization. Each initiator molecule has been shown to give one polymer chain after a rapid initiation reaction. To determine if a free-ion contribution is likely in this polymerization, conductance studies have been made on the system triethyloxonium tetrafluoroborate, methylene chloride, tetrahydrofuran at −0.5°. Measurements were also made of the rate of polymerization in the presence and absence of the common-ion salt tetrabutylammonium tetrafluoroborate, methods used with success in anionic systems.[1,5]

Experimental Section

Tetrahydrofuran was refluxed over and fractionated from potassium metal. It was stored on calcium hydride on a vacuum line and immediately before use stirred over sodium–potassium alloy to give the blue solution of potassium.

Methylene chloride was stirred with sulfuric acid for 2 days and washed with water, then with dilute potassium hydroxide solution, and again with water. It was dried over Drierite, fractionally distilled, and then stored on calcium hydride on the vacuum line.

Boron trifluoride etherate was distilled under reduced pressure of dry nitrogen and stored on the vacuum line. Epichlorohydrin, reagent grade, was dried and used directly. Triethyloxonium tetrafluoroborate was prepared in 0.025-mol batches in a vacuum apparatus, by the method of Meerwein.[6] The product was washed six times with diethyl ether. It was dissolved in methylene chloride filtered under vacuum and stored as a 0.1 M solution under nitrogen at −25°.

Tetrabutylammonium tetrafluoroborate was prepared from silver tetrafluoroborate and tetrabutylammonium iodide in methanol solution. The product was crystallized from carbon tetrachloride and stored either under vacuum or in solution under nitrogen.

The conductances were measured under vacuum or dry nitrogen, over a concentration range of 5×10^{-6}–3×10^{-4} M, in a cell described before.[5]

The rate measurements were made in a dilatometer. A reservoir was filled with monomer and solvent under vacuum, pressurized with dry nitrogen, and brought to temperature. An aliquot of the catalyst solution was added, and an attached evacuated dilatometer filled with the reaction solution *via* a greaseless stopcock, which was then closed to seal the dilatometer.

The reaction rates and conductances were measured at −0.5°. At this temperature the rate of destruction of the living chain ends was sufficiently slow not to interfere with measurements on the early stages of the reaction. The rate of initiation was sufficiently rapid that it was essentially complete by the time the dilatometer was filled and temperature equilibrium reestablished. The reaction was followed for less than 5% conversion to give the rate of the early part of the reaction only.

The concentrations of oxonium ions in the stock solutions of triethylfluoroborate and the reaction mixtures were measured, initially, in two ways, first by analysis for fluorine by Amadac-F after ignition with sodium hydroxide and second by the spectrophotometric method of Saegusa, *et al.*[7] The two methods gave good agreement, but because of the greater reproducibility of the latter method, this was the preferred method.

The low molecular weight living polymer used for conductance measurements was prepared by adding tetrahydrofuran (5 M) to 0.1 M triethyloxonium tetrafluoroborate in methylene chloride and allowing it to react for 2 hr at 0°. The solvent and excess tetrahydrofuran were then distilled off at low temperature and the residual colorless oil was pumped at 0° for several hours under high

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† NRCC No. 12560.

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TABLE I
SALT CONDUCTIVITIES

Salt	Solvent	Temp, °C	Λ_0[a]	10^6K_D[a]
$Et_3O^+BF_4^-$	CH_2Cl_2	−0.5	121	5.4
$Et_3O^+BF_4^-$	CH_2Cl_2	−10.9	114	5.3
$Et_3O^+BF_4^-$	CH_2Cl_2	−22.1	99	6.0
$\sim OC_4H_8^+BF_4^-$[b]	CH_2Cl_2	−0.5	95	4.4
$Bu_4N^+BF_4^-$	CH_2Cl_2	−0.5	100	42
$Bu_4N^+BF_4^-$	CH_2Cl_2, 65%–THF, 35%	−0.5	91	39

[a] Λ_0 and K_D were obtained by the method of successive approximations from the equation $1/\Lambda F = (1/\Lambda_0) + (f^2F\Lambda C/K\Lambda_0^2)$. The method and the terms are described by T. Shedlovsky, *Tech. Org. Chem.*, **1**, 1651 (1949). [b] Poly(THF) salt; OC_4H_8, tetrahydrofuranyl.

TABLE II
DIELECTRIC CONSTANTS OF THF–CH_2Cl_2 MIXTURES[a]

Vol % THF	ϵ	Vol % THF	ϵ
0	9.9045	60.0	9.879
15.0	10.114	70.0	9.594
30.0	10.188	77.5	9.344
34.7	10.201	85.0	9.024
40.0	10.163	92.5	8.733
50.0	10.045	100	8.2434

[a] Temperature −0.5°.

vacuum. The residue was dissolved in methylene chloride and the conductance measured over the usual range of concentrations. The product could not, however, be considered satisfactory, as there was a small residue insoluble in methylene chloride, and the concentration of oxonium ion in the solution was only half that expected from the initial triethyloxonium salt added.

Measurements of dielectric constant were made on equipment described before.[8]

Results and Discussion

The conductance of triethyloxonium trifluoroborate in methylene chloride was measured at three temperatures. The solutions were found to be stable for reasonable periods of time at 0° and below, as the conductances did not change significantly in 2 hr. The limiting equivalent conductances and dissociation constants derived are in Table I, together with data for tetrabutylammonium tetrafluoroborate. Also in this table are the results of the conductance study on the low molecular weight polytetrahydrofuranoxonium tetrafluoroborate in methylene chloride, but as the preparation of this salt was questionable, these results should be treated with more reserve than others.

From these data it is evident that appreciable concentrations of free ions are present in these solutions at typical polymerization concentrations. For 10^{-3} *M* solutions, the degree of ionization would be near 7% for the oxonium salts and 20% for the tetrabutylammonium salt. If the free ion has a rate constant appreciably greater than that of the ion pair, some effect should be seen on the kinetic order of the reaction.

The concentration of tetrahydrofuran in the reaction mixture for the kinetic studies was sufficiently high, 4.4 *M*, that it could be expected to change the dielectric constant of the reaction medium. This in turn might have significant effects on the dissociation constants of the reactants. The dielectric constants of a series of methylene chloride–tetrahydrofuran mixtures were measured at the reaction temperature, Table II. Significant deviation from normal behavior was observed, the dielectric constant going through a maximum at a 2:1 mole ratio of methylene chloride to tetrahydrofuran. This could be interpreted in terms of some complex formation, but if so it is not reflected in density measurements of these mixtures, which exhibit almost ideal behavior. The reaction mixture is near the maximum of the dielectric constant curve, and this might be reflected in ionic dissociation constants higher than in the pure methylene chloride. The measured dissociation constant of the tetrabutylammonium salt in this mixture is in fact slightly lower than that found in the pure solvent. Unfortunately, it was not possible to measure the dissociation constants of oxonium salts in the mixture, but they also could be expected not to be lowered the severalfold expected if the solvents had exhibited ideal dielectric behavior.

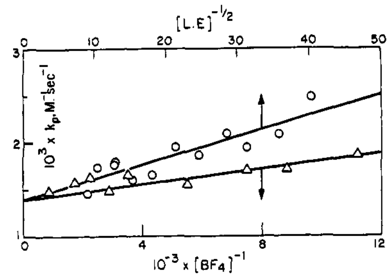

Figure 1. Propagation rate constants in the oxonium ion polymerization of THF: (Δ) in the presence of added BF_4^- ion, (O) in the absence of added salt.

The rate constants for the propagation are obtainable from the equation

$$-\frac{d[THF]}{dt} = k_p[L.E.]([THF]_0 - [THF]_e)$$

where k_p is the overall rate constant of propagation; [L.E.] is the growing chain concentration, taken as the initial concentration of triethyloxonium tetrafluoroborate, a close approximation as shown by previous work; and $[THF]_e$ is the equilibrium tetrahydrofuran concentration, taken as 2.62 *M*, after Vofsi and Tobolsky.

The equations derived by Szwarc, *et al.*,[1] which govern the rate constants of propagation of mixed free-ion, ion-pair polymerizations are

$$k_p = k_\pm + (k_+ - k_\pm)K_d^{1/2}/[L.E.]^{1/2}$$

where $k_\pm$ is the ion-pair rate constant, k_+ is the oxonium ion rate constant, K_d is the ionic dissociation constant of the polymerizing oxonium salt, and in the presence of the common-ion salt

$$k_p = k_\pm + (k_+ - k_\pm)K_d/[BF_4^-]$$

where $[BF_4^-]$ is calculated from the dissociation constant of the tetrabutylammonium tetrafluoroborate.

The rate constants of the propagation reaction are shown in Figure 1, plotted against the inverse half-power of the living end concentration, a plot designed to show the deviation from first-order kinetic dependence of the ion-pair reaction produced by the concurrent free-ion reaction. Also shown in Figure 1 are similar rates in the presence of the common-ion salt, plotted against the inverse of the common-ion concentration, showing how it depresses the free-ion reaction.

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It is evident from these results that although the bulk of the reaction is carried by the ion pair, a significant portion of the reaction is carried by the free ion. From these plots it is possible to derive from the intercept that the ion-pair rate is 1.40 $\times$ 10^{-3} M^{-1} $\sec^{-1}$. From the different dependence on k_p of the two slopes, the dissociation constant of the living end ion pair is 3.7 $\times$ 10^{-6}, and the free-ion rate constant is calculated as 1.0 $\times$ 10^{-2} M^{-1} $\sec^{-1}$.

This dissociation constant compares with the 5.4 $\times$ 10^{-6} found for triethyloxonium tetrafluoroborate and 4.4 $\times$ 10^{-6} for the low molecular weight polymer oxonium salt, both found from conductance data in pure methylene chloride. Although the kinetic figure is probably not too reliable, it is evidently close to the expected value and lends credence to the suggestion that the free ions are participating in the reaction.

The calculated free-ion rate is only a factor of 7 greater than that of the ion pair, compared with the factor of 10^3 in the anionic polymerization of hydrocarbon monomers. This factor was found recently to be low also for the polymerization of episulfides[9] and was ascribed to the attack being on the carbon α to the charged atom instead of on the charged atom as in the anionic case. Here also the attack is at the carbon α to the charge. This ratio was also found to be low for the polymerization of ethylene oxide by potassium alkoxides in hexamethylphosphoramide,[10] but in general the kinetic behavior was complex in this system.

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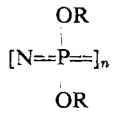
Communications to the Editor

Synthesis of Poly(organophosphazene) Copolymers and Cross-Linked Polymers by Ligand Exchange

High molecular weight poly(alkoxy- and aryloxyphosphazenes) of structure I can be synthesized by the interaction of sodium alkoxides and aryloxides with poly(dichlorophosphazene), $(NPCl_2)_n$.[1,2]



$$\left[N{=}\underset{OR}{\overset{OR}{P}}{=}\right]_n$$

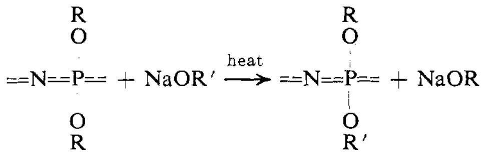
I

Polymers have been prepared which contain ligands such as OCH_3, OC_2H_5, OCH_2CF_3, $OCH_2C_2F_5$, $OCH_2C_3F_7$, and OC_6H_5, with 15,000 or more repeating units in the chain. With one exception,[3] where two different nucleophiles were allowed to react simultaneously with poly(dichlorophosphazene), the organo-substituted polymers reported to date have been homopolymers. The rubbery or thermoplastic polymers prepared by this route are not cross-linked, a fact which limits their applicability.

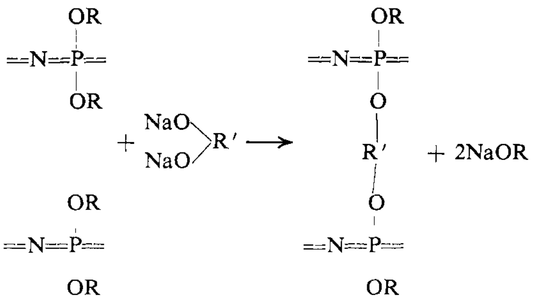
We now report a method for the preparation of alkoxyphosphazene copolymers or cross-linked poly(organophosphazenes) by ligand-exchange reactions. The two processes are exemplified by the reactions shown in Schemes I and II.

For example, poly[(heptafluorobutoxy)(trifluoroethoxy)-phosphazene], $[NP(OCH_2C_3F_7)(OCH_2CF_3)]_n$, can be prepared by allowing sodium 2,2,3,3,4,4,4-heptafluorobutoxide to react with a solution of poly[bis(trifluoroethoxy)phosphazene], $[NP(OCH_2CF_3)]_n$ (II), in dry tetrahydrofuran. The copolymers formed by this method vary from elastomers to gums, depending on the ratio of alkoxide to polymer in the reaction mixture. In a similar manner, poly[(pentafluoropropoxy)(trifluoroethoxy)phosphazene], $[NP(OCH_2C_2F_5)(OCH_2CF_3)]_n$, can be prepared from II and sodium 2,2,3,3,3-pentafluoropropoxide.

SCHEME I



SCHEME II



II can be cross-linked by reaction with the disodium salt of 2,2,3,3,4,4-hexafluoro-1,5-pentanediol in tetrahydrofuran. The cross-linked polymers formed by this process swell in solvents such as tetrahydrofuran, but, unlike the precursor polymer, they do not dissolve. The degree of cross-linking is enhanced by increases in the ratio of diol salt to poly(organophosphazene), with the degree of swelling being correspondingly reduced. Extensive cross-linking is also accompanied by a change in the polymer properties from those of a flexible thermoplastic to those of a stiff, leathery material. Poly[bis(heptafluorobutoxy)phosphazene], $[NP(OCH_2C_3F_7)_2]_n$, reacts similarly with the hexafluoro-1,5-pentanediol salt in a Freon TA–tetrahydrofuran solvent system.

Copolymer Formation. A solution prepared from 2,2,3,3,-4,4,4-heptafluorobutanol (3.00 g, 0.015 mol) and sodium (0.35 g, 0.015 g-atom) in dry tetrahydrofuran (100 ml) was added to a stirred solution of poly[bis(trifluoroethoxy)phosphazene] (2.43 g, 0.010 mol/monomer unit) in dry tetrahydrofuran (200 ml) at 25°. The mixture was heated to reflux and allowed to react for 4 hr. After cooling, the polymer was precipitated into cold water (2000 ml), washed with water, and reprecipitated from Freon TA into heptane by pressure filtration through a Millipore filter. The resultant polymer was a

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