and the occurrence of a photoeffect as well as a thermal effect is supportive. There are, however, problems. Half-lives for the contractile process may be obtained from the constant-strain or constant-stress curves. For pyromellitimide the value of $t_{1/2} \sim 38$ min at temperatures near 200°. On returning to room temperature a relaxation $t_{1/2} \sim 40$ min is observed. The values are the same at room temperature and 200° indicating little or no activation energy.

Studies of solution isomerization of simple azo compounds[7,8] show the process to be activated ($\Delta H^{\ddagger} \sim 22$ kcal) with $t_{1/2} \sim 50$ min for comparable compounds slightly above room temperature. π acid and base catalysis was reported.

On comparison with our results, it seems that the rates of isomerization are not controlling the rates of dilation or contraction. Catalysis by adjacent π acids or bases is an attractive possibility but cannot be asserted on present data. It seems probable that the process is controlled by viscoelastic characteristics of the polymer which have small activation energies but these processes cannot be specified as of now.

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Kinetics and Mechanism of the Polymerization of Styrene by Triphenylmethyl Chloride and Mercuric Chloride in 1,2-Dichloroethane, and the Initiation Rate Constant

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ABSTRACT: The polymerization of styrene initiated by triphenylmethyl chloride and mercuric chloride in 1,2-dichloroethane was investigated. The equilibrium involved between triphenylmethyl chloride and mercuric chloride in 1,2-dichloroethane is $Ph_3CCl + HgCl_2 \rightleftharpoons Ph_3C^+HgCl_3^-$. The ion pair $Ph_3C^+HgCl_3^-$ does not dissociate into free ions and mercuric chloride does not help to solvate the ion pair. The visible spectrum of the polymerizing system shows the presence of trityl cations. The rate of polymerization is first order in triphenylmethyl chloride and mercuric chloride, and second order in styrene. The rate of consumption of triphenylmethyl chloride is first order in triphenylmethyl chloride, mercuric chloride, and styrene. A mechanism consistent with the kinetic data has been suggested and the rate of consumption of triphenylmethyl chloride is directly related to the rate of initiation.

The cationic polymerization of styrene has been extensively studied. However, due to the use of complex and highly reactive catalyst–cocatalyst systems only a few generalizations can be made. The use of triphenylmethyl chloride and mercuric chloride to form the well-characterized stable trityl cation *in situ* seemed advantageous. Trityl salts have been used for the polymerization of styrene.[1,2]

The evaluation by kinetics of individual rate constants in cationic polymerization of styrene has only been achieved in a few cases. The propagation, termination, and transfer rate constants have been determined for the nonstationary polymerization of styrene by sulfuric acid.[3,4] In our preliminary communication[5] we reported a spectrophotometric method of measuring the initiation rate constant and this method has been subsequently used by other investigators.[6]

Experimental Section

Purification of Styrene. Styrene (M) was shaken with 10% potassium hydroxide solution to remove *t*-butylcatechol and then washed with distilled water. The styrene was partially dried over anhydrous calcium chloride, allowed to stand over baked barium oxide, and then fractionally distilled under reduced pressure. It was degassed by freezing and pumping several times on a high vacuum line and the middle fractions were used immediately.

Triphenylmethyl chloride (Ph_3CCl) was prepared by refluxing triphenylcarbinol and acetyl chloride in petroleum ether mixture for 1 hr.[7] On cooling, Ph_3CCl crystals were deposited and these were recrystallized from solvent composed of 10% acetyl chloride in petroleum ether. Care was taken to remove all traces of acetyl chloride. The crystals were dried in a vacuum desiccator. Fresh samples of Ph_3CCl were prepared as required.

AR mercuric chloride ($HgCl_2$) was used without further purification. **1,2-Dichloroethane** was partially dried over calcium chloride, refluxed over phosphorus pentoxide, and fractionally distilled through a 35-cm Vigreux column. **Acetyl chloride** was fractionally distilled using a 35-cm Vigreux column.

Procedure. Drybox technique was used for all experiments. The drybox was flushed with dry nitrogen for about 2 hr before use and a brisk flow of nitrogen was maintained during actual manipulations. We feel that this procedure is satisfactory for this system, and it has been shown that water concentration in the range of $1\text{–}3 \times 10^{-3}$ *M* has no effect on the rate of reaction of styrene with Ph_3CSnCl_5.[6]

The progress of polymerization was followed by measuring [styrene] with time. This was achieved by measuring the

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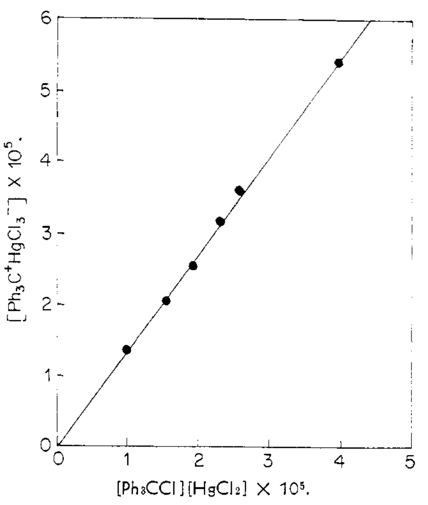

Figure 1. Nature of the equilibrium between Ph_3CCl and $HgCl_2$ in 1,2-dichloroethane.

absorbance of styrene at 291.5 mμ and calculating its concentration c from the relationship

$$A = \epsilon c l$$

where A is the absorbance, $\epsilon = 525$, the molar absorptivity at 291.5 mμ, and l the path length of the optical cell. This technique has been used by Hayes and Pepper.[8] The use of this method is justified under the experimental conditions since the absorbance due to the remaining reactants and products of the system at 291.5 mμ is negligible when compared with the absorption of styrene at this wavelength.

The consumption of Ph_3CCl can be followed by measuring the decay of absorbance of $Ph_3C^+HgCl_3^-$ at 413 mμ.

Isolation of the Polymer. The reaction mixture was poured into methanol. Styrene and 1,2-dichloroethane were removed by steam distillation and the aqueous suspension filtered. The polymer was dissolved in benzene and the solution filtered through a sintered glass funnel. The solvent was removed by freeze drying on a high vacuum line.

Spectra. The infrared spectra were measured on a Hilger H800 double beam instrument. The ultraviolet and visible spectra were measured on a Hilger H700 spectrophotometer fitted with a water-thermostated cell compartment. The temperature was maintained constant within ±0.1°.

Results

Spectra. Solutions of Ph_3CCl in 1,2-dichloroethane were colorless. They immediately developed a greenish color on the addition of $HgCl_2$. The visible spectra of the solutions had two main absorption peaks at 413 and 437 mμ and the spectra were similar to the spectrum of triphenylcarbinol in concentrated sulfuric acid.[9] Since triphenylcarbinol in concentrated sulfuric acid ionizes to give the trityl cation, the absorption maxima at 413 and 437 mμ can be attributed to the presence of trityl cation in the system. The absorption maxima at 413 and 437 mμ are at longer wavelengths than the corresponding maxima in concentrated sulfuric acid. The bathochromic shifts have also been reported for other triarylmethyl cations.[10]

Evans, *et al.*, have determined that the molar absorptivities of certain triarylmethyl cations are the same in formic acid,[11] nitromethane,[12] and *m*-cresol[13] as in sulfuric acid. The molar absorptivity of the trityl cation in sulfuric acid[9] at 410 mμ is 3.6×10^5, while in methylene chloride[14] at 412 mμ it is 3.7×10^5. It is therefore reasonable to assume that the molar absorptivity of trityl cation in 1,2-dichloroethane at 413 mμ is also 3.6×10^5. This value has been used in calculations.

Styrene in 1,2-dichloroethane absorbs strongly below 250 mμ, and has two absorption maxima at 282.5 and 291.5 mμ which have molar absorptivities of 804 and 525, respectively. Mercuric salts can form addition complexes with olefins;[15] however, the addition of $HgCl_2$ to styrene in 1,2-dichloroethane did not modify the styrene spectrum.

Equilibrium between Ph_3CCl and $HgCl_2$ in 1,2-Dichloroethane. If the equilibrium involved between Ph_3Cl and $HgCl_2$ is between un-ionized molecules and ion pairs

$$Ph_3CCl + HgCl_2 \rightleftharpoons Ph_3C^+HgCl_3^-$$

then the equilibrium constant K can be represented by the equation

$$K = \frac{[Ph_3C^+HgCl_3^-]}{[Ph_3CCl][HgCl_2]}$$

A plot of $[Ph_3C^+HgCl_3^-]$ against the product of the equilibrium $[Ph_3CCl][HgCl_2]$ should be linear. The plot is linear as shown in Figure 1 and the slope gives K a value of 1.31 M^{-1} at 30°. The equilibrium is established immediately on mixing and the linearity of the plot indicates that there is no significant dissociation of the ion pair $Ph_3C^+HgCl_3^-$ into free ions and that $HgCl_2$ does not help to solvate the ion pair.[16, 17]

Kinetics of Polymerization. Since there is a quantitative conversion of styrene to polystyrene the rate of disappearance of monomer can be taken to be equal to the rate of polymerization. Typical curves showing the course of polymerization are shown in Figure 2. No induction or inhibition periods were observed in any of the kinetic runs.

The initial rate of polymerization was found to be first order in Ph_3CCl and $HgCl_2$, and second order in styrene. This leads to an initial kinetic expression

$$-d[M]/dt = k_r[Ph_3CCl][HgCl_2][PhCH{=}CH_2]^2$$

A plot of initial rates against $[Ph_3CCl][HgCl_2][PhCH{=}CH_2]^2$ is linear as shown in Figure 3 and the overall rate constant $k_r = 4.1 \times 10^{-1} M^{-3}$ min^{-1} at 30°.

Kinetics of Consumption of Ph_3CCl. The order of this reaction with respect to Ph_3CCl, $HgCl_2$, and styrene was determined in order to obtain information regarding the role of Ph_3CCl in the polymerization mechanism.

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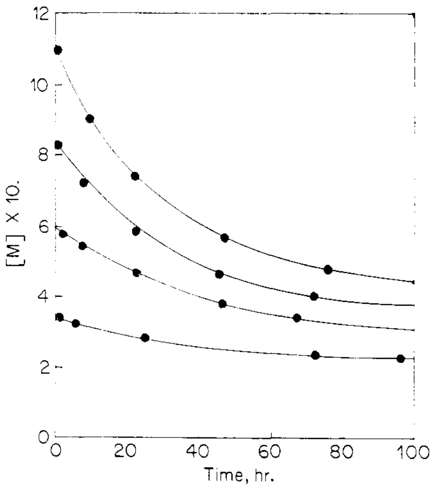

Figure 2. The time course of polymerization.

The main ionic species present in the polymerizing system is the $Ph_3C^+HgCl_3^-$ and its absorbance at 413 mμ decays with time. It is reasonable to assume that the equilibrium

$$Ph_3CCl + HgCl_2 \rightleftharpoons Ph_3C^+HgCl_3^-$$

is immediately established in the system. [Ph_3CCl] can be calculated by knowing [$Ph_3C^+HgCl_3^-$] from its absorbance at 413 mμ and substituting in the expression

$$[Ph_3CCl] = \frac{[Ph_3C^+HgCl_3^-]}{[HgCl_2]K}$$

The initial rate of consumption of Ph_3CCl was found to be first order in Ph_3CCl and $HgCl_2$, and styrene. This leads to a kinetic expression

$$-d[Ph_3CCl]/dt = k_c[Ph_3CCl][HgCl_2][PhCH{=}CH_2]$$

A plot of initial rates against [Ph_3CCl][$HgCl_2$]-[$PhCH{=}CH_2$] is linear as shown in Figure 4 and the rate constant $k_c = 4.8 \times 10^{-3}\ M^{-2}\ \mathrm{min}^{-1}$ at 30°.

Molecular weights of isolated polystyrene were determined by viscometry using a suspended level dilution viscometer. The polymers were isolated at 10% conversion. The intrinsic viscosities were measured in benzene at 25° and the molecular weights calculated from the relationship[4]

$$[\eta] = 4.37 \times 10^{-4}\bar{M}_n^{0.66}$$

The molecular weights were found to be in the region of 3000.

Chemical analysis of four polymer samples showed the presence of C, H, and Cl and their total percentage composition was 100%. The amount of chlorine present was in the range of 0.9–1.5% and this gave $\bar{M}_n$ in the region of 3000.

Infrared Spectra. The end groups of a polymer may be detected if they contribute significantly to the molecular weight of the polymer. Dainton and Sutherland[18] have used infrared analysis in obtaining information about the initiation and termination steps in ionic polymerization.

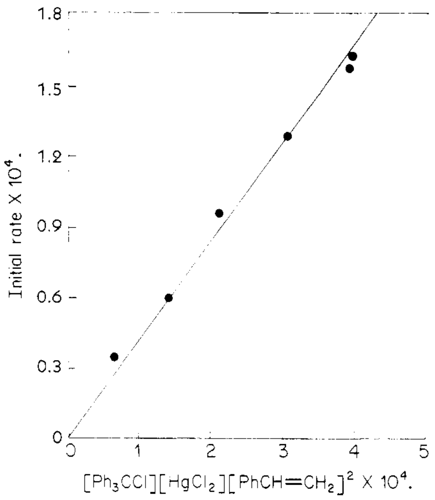

Figure 3. Initial rate of polymerization against [Ph_3CCl][$HgCl_2$][$PhCH{=}CH_2$].^{2}

Triphenylmethane has an infrared spectrum with three strong absorption bands at 700, 734, and 758 cm^{-1}, while C–Cl stretching vibrations absorb in the 700–750-cm^{-1} region in monochlorinated compounds. The infrared spectrum of high molecular weight polystyrene initiated by a free radical mechanism has two strong absorption bands at 700 and 740 cm^{-1}, characteristic of CH out-of-plane in-phase vibrations in a monosubstituted benzene ring, and this spectrum was identical with the spectrum of low molecular weight polystyrene isolated from this system. Hence the triphenylmethyl group and chlorine atom cannot be detected by this method.

Discussion

A mechanism consistent with the kinetic results has been proposed. Initiation may be considered to involve two steps. The first step is the rapid prior equilibrium

$$Ph_3CCl + HgCl_2 \overset{K}{\rightleftharpoons} Ph_3C^+HgCl_3^-$$

and the second step involves the slow addition of $Ph_3C^+HgCl_3^-$ to styrene

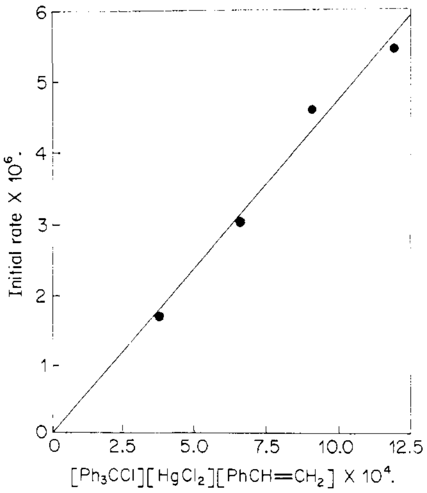

Figure 4. The initial rate of consumption of Ph_3CCl against [Ph_3CCl][$HgCl_2$][$PhCH{=}CH_2$].

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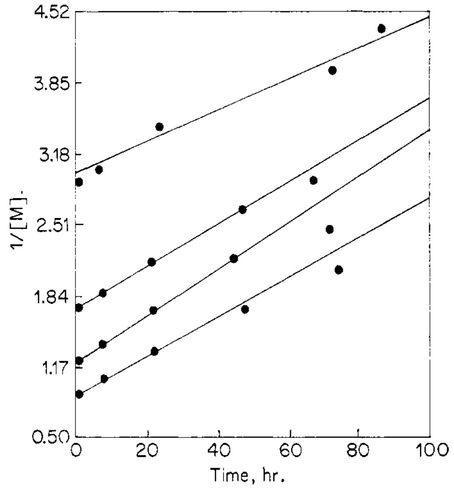

Figure 5. A plot of 1/[M] against time.

$$\mathrm{Ph_3C^+HgCl_3^- + PhCH{=}CH_2 \xrightarrow{k_i} Ph_3CCH_2\overset{+}{C}HPhHgCl_3^-}$$

The rate of initiation R_i will be given by the expression

$$R_i = k_i[\mathrm{Ph_3C^+HgCl_3^-}][\mathrm{PhCH{=}CH_2}]$$

or

$$R_i = Kk_i[\mathrm{Ph_3CCl}][\mathrm{HgCl_2}][\mathrm{PhCH{=}CH_2}]$$

Propagation is simply the successive addition of styrene to the carbonium ion center. Since $\mathrm{Ph_3C^+HgCl_3^-}$ does not dissociate into free ions in 1,2-dichloroethane, it is likely that the gegenion $\mathrm{HgCl_3^-}$ remains in the proximity of the cationic center of a growing chain

$$\mathrm{Ph_3CCH_2CHPh(CH_2CHPh)_{\mathit{n}}CH_2\overset{+}{C}HPhHgCl_3^- + PhCH{=}CH_2 \xrightarrow{k_p} Ph_3CCH_2CHPh(CH_2CHPh)_{\mathit{n}+1}CH_2\overset{+}{C}HPhHgCl_3^-}$$

If $[\mathrm{M_n^+}]$ represents the total number of the growing chains then the rate of propagation $R_p = k_p[\mathrm{M_n^+}][\mathrm{PhCH{=}CH_2}]$.

Chemical analysis of the polymer shows that chlorine is incorporated in the polymer. This is evidence for the termination reaction involving the abstraction of $\mathrm{Cl^-}$ by the growing polymer chain from its gegenion $\mathrm{HgCl_3^-}$. The ion pair acts as a single kinetic unit, and termination reaction is a first-order reaction

$$\mathrm{Ph_3CCH_2CHPh(CH_2CHPh)_{\mathit{n}}CH_2\overset{+}{C}HPhHgCl_3 \xrightarrow{k_t} Ph_3CCH_2CHPh(CH_2CHPh)_{\mathit{n}}CH_2PhCl + HgCl_2}$$

The rate of termination $R_t = k_t[\mathrm{M_n^+}]$.

The initial rate of polymerization can be written as

$$-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_r[\mathrm{Ph_3CCl}][\mathrm{HgCl_2}][\mathrm{PhCH{=}CH_2}]^2$$

or

$$= k_r/K[\mathrm{Ph_3C^+HgCl_3^-}][\mathrm{PhCH{=}CH_2}]^2$$

If stationary state is set up immediately and maintained during the reaction, then

$$-\mathrm{d}[\mathrm{M}]/\mathrm{d}t \propto [\mathrm{PhCH{=}CH_2}]^2$$

and the overall order of reaction should be second order in styrene. For a second-order reaction, a plot of 1/[M] against time should be linear.[19] This is found to be so as shown in Figure 5 for at least up to 30% conversion.

Since a stationary concentration of growing chains is set up from the beginning of the reaction

$$-\mathrm{d}[\mathrm{M_n^+}]/\mathrm{d}t = 0$$

Hence, the rate of initiation must be equal to the rate of termination and this leads to an equation

$$-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = Kk_ik_p/k_t[\mathrm{Ph_3CCl}][\mathrm{HgCl_2}][\mathrm{PhCH{=}CH_2}]^2$$

and the experimentally determined rate constant

$$k_r = Kk_ik_p/k_t$$

and

$$[\mathrm{M_n^+}] = Kk_i/k_t[\mathrm{Ph_3CCl}][\mathrm{HgCl_2}][\mathrm{PhCH{=}CH_2}]$$

Jenkinson and Pepper[20] have shown that triphenylmethyl compounds are chain-stopping agents in the polymerization of styrene by sulfuric acid. $\mathrm{Ph_3CCl}$ can act as a chain-stopping agent by a ring substitution mechanism as proposed by Overberger and Endres[21] for aromatic compounds. The expelled proton can

$$\mathrm{M_n^+ + Ph_3CCl \xrightarrow{k_{tr}} M_nC_6H_4C(Ph)_2Cl + H^+}$$

start another chain by reaction with monomer. If this transfer reaction is occurring in the system to an appreciable degree, then rate of consumption of $\mathrm{Ph_3CCl}$ depends on the initiation and transfer reactions, *i.e.*

$$-\mathrm{d}[\mathrm{Ph_3CCl}]/\mathrm{d}t = Kk_i[\mathrm{Ph_3CCl}][\mathrm{HgCl_2}][\mathrm{PhCH{=}CH_2}] + k_{tr}[\mathrm{M_n^+}][\mathrm{Ph_3CCl}]$$

Substituting for $[\mathrm{M_n^+}]$, we obtain

$$-\mathrm{d}[\mathrm{Ph_3CCl}]/\mathrm{d}t = Kk_i[\mathrm{Ph_3CCl}][\mathrm{HgCl_2}][\mathrm{PhCH{=}CH_2}] + Kk_ik_{tr}/k_t[\mathrm{Ph_3CCl}]^2[\mathrm{HgCl_2}][\mathrm{PhCH{=}CH_2}]$$

Figure 4 shows that the consumption of $\mathrm{Ph_3CCl}$ depends on the first order in $\mathrm{Ph_3CCl}$, and we can either say that $\mathrm{Ph_3CCl}$ does not act as a chain-stopping agent to any measurable extent (or that this kinetic method is insensitive to detect the role of $\mathrm{Ph_3CCl}$ in the transfer reaction). However, molecular weight studies have shown that $\mathrm{Ph_3CCl}$ does not act as a chain-stopping agent.[22]

The experimentally determined rate of consumption of $\mathrm{Ph_3CCl}$ is then the rate of initiation and $k_c = Kk_i$. This gives the initiation rate constant k_i a value of 3.7×10^{-3} M^{-2} min^{-1} at 30°. We feel that this is a reasonable value as k_i derived from molecular weight studies is 7.7×10^{-3} M^{-2} min^{-1} at 30°.[22] Higashi-

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mura, *et al.*,[6] have found that the initiation rate constant of the polymerization of styrene by Ph_3CSnCl_5 in 1,2-dichloroethane is $11.6 \times 10^{-2}\ M^{-1}\ min^{-1}$ at 30°. They have attributed the difference between their value and ours to the ionizing power of the metal halide.[23]

The most probable transfer reaction that can occur is the proton transfer from the active polymer chain to the monomer molecule by a bimolecular process. This leaves a terminal double bond in the dead polymer chain while the activated monomer molecule can start another chain

$$Ph_3CCH_2CHPh(CH_2CHPh)_nCH_2\overset{+}{C}HPhHgCl_5^- + PhCH{=}CH_2 \longrightarrow Ph_3CCH_2CHPh(CH_2CHPh)_nCH{=}CHPh + CH_3\overset{+}{C}HPhHgCl_3^-$$

This reaction was shown to be operative by molecular weight studies.[22]

Conclusion

The use of catalyst systems which produce well-characterized carbonium ions can lead to the possibility of evaluating the initiation rate constant, and thus gain further insight into the reaction mechanism.

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Anionic Polymerization of Styrene in Tetrahydropyran

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ABSTRACT: The propagation reaction in the anionic polymerization of styrene in tetrahydropyran has been studied as a function of alkali metal counterion and concentration of active species. Conductance measurements were made on the systems also, enabling both the ion pair and polystyryl anion rate constants to be measured. The latter was found to be comparable with values found in other ethereal solvents. For the ion-pair constant some differences were found from previously published data.

The presence of three forms of the reactive species in the anionic polymerization of styrene in ethereal solvents is now well established.[1-5] The contributions to the reaction rate of the free anion and the ion pairs can be estimated by a comparison of conductance and kinetic measurements.[6,7] The determination of the relative contributions of contact and solvent separated ion pairs is less easy but some estimates have been made.[5,8] There are large differences in behavior between a solvent of moderate dielectric constant such as tetrahydrofuran (THF) and one of low dielectric constant such as dioxane. In particular the contributions of free anion and solvent separated ion pairs become negligible in the latter solvent, and the order of reactivity of ion pairs as a function of counterion is quite different from that in THF. It is of some interest to investigate solvents of intermediate dielectric constant to describe the transitional behavior. Quite detailed studies have been previously reported[4,8] in tetrahydropyran (THP, dielectric constant ~5.5) with sodium as counterion and the ion-pair rate constant has been reported for K^+, Rb^+, and Cs^+ [9,10] in THP and recently for Li^+.[11] This paper presents data on Li^+ and a reassessment of work with other counterions, together with an estimate of the reactivity of the free polystyryl anion.

Experimental Section

Apparatus. Modifications of the basic apparatus described earlier were used.[12] For lithium as counterion this only involved the replacement of the butyllithium bulb with one containing a low molecular weight polystyryllithium prepared in benzene and freeze dried. For the other alkali metals a small flask was joined to the side of the apparatus. Into this the required alkali metal could be distilled to form a film which was used twice, once to form a "living" polymer solution to wash out the apparatus and later to form the initiator solution. Three styrene bulbs were required for washing, initiator formation, and polymerization, respectively; the styrene was prepared as described previously.[13]

Reaction rates were all measured at 30.0° in a Cary-14 spectrophotometer which was provided with a temperature-controlled cell block of heavier construction than normally supplied for spectrophotometers. A subsidiary temperature-controlled air circulation system was used in addition, to maintain parts of the reaction vessel outside the cell block at

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