PROGRESS IN ANIONIC POLYMERIZATION

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INTRODUCTION

During the Wiesbaden meeting of I.U.P.A.C. in 1959, I presented the first review¹ summarizing the progress in anionic polymerization. In those days two features of this reaction attracted considerable attention: (i) the initiation of polymerization through an electron-transfer process, and (ii) the possibility of avoiding termination and chain-transfer, and therefore the feasibility of producing living polymers. Consequently, these two topics formed the core of my talk.

In the following years the concept of electron-transfer initiation was generalized. While anionic polymerization may be induced by transferring an electron from a suitable donor to monomer, the transfer of an electron from an electron-rich monomer to a suitable acceptor may lead to cationic polymerization. Indeed, there is some evidence that this process has been recently accomplished². Also, the lack of termination, originally discovered in anionic polymerization, has been observed lately in other systems. For example, living polymers growing by cationic mechanism have been described³. Polymers possessing some tin complexes as growing group represent another class of living polymers⁴.

My present review of the current progress in anionic polymerization is concerned with the propagation step. Ionic polymerization may be propagated by a variety of active centres: free ions, contact ion-pairs, solvent separated ion-pairs, triple ions, and still higher agglomerates or their complexes. Each of these species has its own characteristics—reactivity in propagation, selectivity in copolymerization, stereochemical preference, *etc.* These have to be determined quantitatively and correlated with the structure of the pertinent centres. We have to understand the role of the counterion and solvent in shaping the character of ion-pairs and of higher agglomerates, the state of solvation of free ions, and so forth. Moreover, the described species may co-exist in the reacting solution and, therefore, it is important to investigate the relevant equilibria and the factors affecting their position, as well as the rates with which they are established.

The programme outlined above is very broad and, although the quest to accomplish its goals has been started only recently, large amounts of interesting data have been gathered and systematized. I intend, therefore, to survey the available material and to discuss its implications. However, before I proceed with this task, I wish to mention briefly an important class of mechanisms which attracted only little attention in the past but may become important in the future—namely, polymerizations involving *activated* monomers.

THE PROPAGATION INVOLVING AN ACTIVATED MONOMER

The propagation process of a conventional addition polymerization involving some monomer M consists of a series of reactions described by the equation,

The reactive moiety X , attached to a chain of n monomeric units linked together by covalent bonds, may be a part of a radical, or of an ion or ion-pair, or of some reactive coordination complex. This group is responsible for the reaction which does not require any *chemical* activation of the monomer beyond the conventional supply of energy resulting from the intermolecular collisions and determined by the Boltzmann distribution. In such a process the initiator participates only in the step creating the growing centres, say $P_1 \cdot X$, but not in the subsequent propagation. A possible exception will be considered later.

A novel type of addition polymerization is encountered in those processes in which the monomer requires a *chemical* activation and only the activated species may participate in the propagation. The initiator affects such a reaction at least in two ways: it participates in the process of formation of the growing centres, the conventional task of an initiator, and it influences directly, or indirectly, the growth of the polymeric molecules. Let us consider some specific examples of such reactions and then try to produce generalized schemes of these interesting processes.

It is well known that Leuch's anhydrides, frequently referred to as NCA's,

may be polymerized to polypeptides by a variety of agents. Blout and his co-workers⁵ discovered that a rapid reaction yielding a high molecular weight polymer ensues when a strong base, *e.g.*, sodium methoxide, is added to the monomer solution. The mechanism of this reaction was elucidated by Bamford and his colleagues⁶ and recently reviewed by the author⁷ it appears that the process involves the following steps:

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* This dimer represents $P_1 \cdot X$, *i.e.* the first member of the series of growing polypeptides, $P_n \cdot X$.

In the first reaction the initiator (CH_3O^- ion) converts the ordinary monomer into its activated form. The latter reacts with an ordinary monomer (reaction 2) and forms an intermediate dimer which regenerates in reaction (3) the activated monomer. The decarboxylation produces the first member, $P_1 \cdot X$, of the series of growing polypeptides, the ring being the active group X .

Only the activated monomer formed in reaction (3), or (1), may react with P_1X , (or P_nX), *viz.*

and then reaction (5) leads to $P_{n+1}X$, simultaneously converting an inactive monomer into an active species. The continuation of the process eventually leads to a high molecular weight polypeptide.

It should be stressed that in such a system the concentration of the initiator (the base) determines the concentration of the growing chains, P_nX , and

the concentration of the activated monomer. Hence, the rate of growth of *each* chain *depends* on the concentration of the initiator—a novel feature of the reaction not encountered in the conventional schemes. Moreover, if the equilibrium,

lies predominantly to the right, the rate of growth of each chain should be independent of the monomer concentration but influenced by the concentration of the initiator.

An obvious question may now occur to the reader. In reaction (2) the activated monomer reacts with the non-activated ordinary monomer giving a dimer from which, eventually, a polymer is evolved. Alternatively, it may react with the growing chain (reaction 4), which represents the proper propagation step. Which of the two is more important and why? The experimental results clearly indicate that the growth (4) is much more probable than reaction (2). Apparently, the carbonyl group adjacent to the ring activates it, and thus such a ring is many times more reactive than the ordinary NCA, *i.e.*,

At the onset of the reaction the activated monomer must react with an ordinary NCA, since the dimers, or polymers, are not yet available. As the reactions proceeds the concentration of the latter increases making the growth more and more probable than the dimer formation. One realizes, therefore, that the number of polymeric molecules formed in such a reaction has no simple relation to the number of base molecules which initiate the process. Therefore, the number average molecular weight of the product formed at the completion of the process is much greater than $[M]_0/[Base]_0$.

The mechanism of NCA polymerization initiated by strong base has been a subject of a long controversy reviewed in reference 7. An experiment which should resolve the ambiguity was proposed by the author⁷ and has been recently performed by Goodman and his students⁸. The result clearly demonstrates the validity of Bamford's suggestion and upholds the concept of activated monomer.

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Anionic polymerization of pyrrolidone and of some related cyclic compounds resembles that of NCA. It is instructive to consider this reaction since it reveals an additional feature of the activated monomer mechanism. The following scheme was first suggested by Nummy, Barnes and Ney⁹ and later

by Sekiguchi and Champetier¹⁰. Thus, steps (1'), (4'), and (5') being analogous to the previously discussed reactions (1), (4), and (5). Reaction (5') produces a new activated pyrrolidone ion which reacts with the growing chain. However, it was shown⁹ that the reaction requires a promoter in addition to the base, namely the presence of compounds such as

is essential for the initiation. These react with the activated monomer and the resulting dimer, as well as the polymer, is capable of continuing the growth. Hence, the concentration of the eventually formed polymeric molecules is given by the concentration of the promoter, whereas the rate of growth of each chain is determined by the concentration of the activator—*i.e.*, the base. Here the concept of a simple initiator needs modification. The polymerization requires a promoter to form a growing centre and an activator to enable its growth. In NCA polymerization the monomer appears to be its own promoter, although not an efficient one. This accounts for the formation of high polymer. The self-initiation of pyrrolidone is extremely slow and therefore an independent promoter is needed for its poly-

merization. The subject of reactivity of a "sensitized" caprolactam or pyrrolidone has been treated recently by Levy *et al.*¹¹

I wish to conclude this discussion by considering a mechanism of polymerization of vinyl carbazole recently proposed by Ellinger¹². Although this mechanism is not yet established, and much work is needed to clarify this process, it deserves consideration since it represents an interesting example of an activated monomer polymerization which may be encountered in future studies.

In Ellinger's mechanism the monomer is activated by complexing with an electron acceptor, *e.g.* tetracyanoethylene. Denoting the acceptor by A, we may write.

In step (7) the hydrogen transfer releases the acceptor which becomes available for activation of another molecule of monomer. The resulting dimer, $P_1 \cdot X$, may continue the growth, *viz.*

This polymerization should be classified as a cationic one, but the proposed scheme may be easily generalized and adopted for some hypothetical anionic propagations. I believe that this type of reaction could be of considerable interest. It provides a bridge between ionic and coordination polymerizations and permits us, in principle, to modify the reactivity of a monomer by complexing it with a suitable agent.

NATURE OF THE GROWING SPECIES IN ANIONIC POLYMERIZATION: IONS AND ION-PAIRS

Anionic polymerization involves negatively charged species; however, since the solution is electrically neutral, positive counterions must be present in an equivalent amount. Most of the investigated polymerizations take place in media having relatively low dielectric constants; therefore, a substantial association of the oppositely charged ions into ion pairs is expected. Hence, one deals with an equilibrium

leading to a relatively small fraction of the free $\sim\sim\sim M^-$ ions mixed with a large excess of $\sim\sim\sim M^-, A^+$ ion pairs.

The ion pair, $\sim\sim\sim M^-, A^+$, as well as the free ion, $\sim\sim\sim M^-$, are capable of propagating the polymerization, albeit the rate constant may be different for each species,

and

Denoting by f the fraction of the free ions present in the polymerized solution, we may express the observed rate constant of propagation, $k_{p,\text{obs}}$

by the equation

$$k_{p,obs} = (1 - f)k_{p\pm} + f \cdot k_{p-}$$

For a low fraction of dissociation, f , say less than 0.05, the approximation $= K_{diss}^{1/2}/[\text{living ends}]^{1/2}$ is valid and

$$k_{p,obs} = k_{p\pm} + (k_{p-} - k_{p\pm}) K_{diss}^{1/2}/[\text{living ends}]^{1/2}$$

The latter equation has been verified for several systems—the propagation of living polystyrene in tetrahydrofuran being the most thoroughly investigated example¹³⁻¹⁷. *Figure 1* shows the results obtained by the Syracuse group;¹⁴ for each counterion the observed k_p was found to increase linearly with the reciprocal of the square root of living ends concentration. Similar results, limited to the sodium salts only, were simultaneously reported by Schulz and co-workers^{15, 16}.

Figure 1. A plot of k_p vs $[\text{living ends}]^{-1/2}$

It is encouraging to see the degree of agreement between the findings of both groups. In spite of different experimental techniques, both teams found the slope of the line $k_{p,obs}$ versus $1/[\text{living ends}]^{1/2}$ to be $25 \text{ l}^{3/2}/\text{mole}^{3/2} \text{ sec}$, and the difference in the reported rate constants amounts to ~ 20 per cent only. This small discrepancy seems to arise from the application of different techniques for determining the concentration of the growing ends.

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Before we proceed further, we should inquire whether the observed relation indeed refers to ionic dissociation,

or does it reflect the dimerization of living ends,

The latter phenomenon was observed in the solution of $\sim\sim\sim\text{S}^-\text{,Li}^+$ in benzene¹⁸. In this system the dimeric living ends are inert and virtually do not grow. Thus, the observed propagation is attributed to the small fraction of the very reactive monomeric ends which are in equilibrium with the associated ones.

Two methods discriminate between these alternatives. The dissociation of living ends increases the molecular weight of the living polymer; however, their dimerization is destroyed on "killing". Hence, the viscosity of a living polymer solution should drastically decrease on the addition of a drop of water or methanol. This is not the case for living polystyrene in THF¹³, although such a phenomenon has been observed¹⁹ in benzene solution of $\sim\sim\sim\text{S}^-\text{,Li}^+$. Therefore, $\sim\sim\sim\text{S}^-\text{,Li}^+$ is dimeric in benzene but in tetrahydrofuran the $\sim\sim\sim\text{S}^-\text{,A}^+$ salts (A^+ is an alkali ion) are monomeric. The increase of the observed k_p on dilution, found in the latter solvent, must therefore be attributed to the ionic dissociation.

Ionic dissociation of a living polymer is depressed by the addition of strongly dissociated salt having a common cation with $\sim\sim\sim\text{M}^-\text{,A}^+$. The addition of such a salt should, therefore, decrease the observed rate constant of propagation. This is precisely the case. The Syracuse group¹⁴ and Schulz¹⁵, observed, a decrease of k_p for $\sim\sim\sim\text{S}^-\text{,Na}^+$ polymerization on the addition of $\text{Na}^+ \text{BPh}_4^-$. Similar retardation was found in the polymerization of other $\sim\sim\sim\text{S}^-\text{,A}^+$ salts^{14b}. Therefore, the existence and the nature of the two growing species in the polymerization of $\sim\sim\sim\text{S}^-\text{,A}^+$ in THF is definitely established.

The increase of the apparent k_p on dilution of the living polystyrene solution (see Figure 1) proves that the growth of the free $\sim\sim\sim\text{S}^-$ ion is faster than that of the ion pairs. This conclusion is by no means trivial. In fact, during the Wiesbaden Meeting in 1959 I pointed out²⁰ that there are valid reasons to expect a faster growth of the free ions, but there are others, based on the assumption of a push-pull mechanism, which predict a higher reactivity of the ion pair.

By how much is the growth of a free $\sim\sim\sim\text{S}^-$ ion faster than that of an ion pair? To answer this question one needs to determine the dissociation constants, K_{diss} of $\sim\sim\sim\text{S}^-\text{,A}^+$ salts. Two methods lead to this goal. A direct approach utilizes the studies of conductance, Λ , of $\sim\sim\sim\text{S}^-\text{,A}^+$ solutions, since for sufficiently low concentrations, c , a plot of $1/\Lambda$ versus c gives a straight line with an intercept of $1/\Lambda_0$ and a slope of $1/K_{\text{diss}} \Lambda_0^0$. The determination of the slope and of the intercept gives therefore the K_{diss} .

The conductance method was refined by Fuoss²¹ who took into account the interactions between the ions, and thus $1/\Lambda$ is replaced by F/Λ and $c\Lambda$ by $f^2c\Lambda/F$. Nevertheless, it is still imperative to perform the measurements at the extremely high dilutions, approaching 10^{-6}M and then considerable

technical difficulties are encountered. These difficulties were eventually overcome by the Syracuse group^{14b}. The salient feature of their technique was to dilute the solutions by removing the solute and not by adding the solvent.

The results of the conductance studies, shown in *Figure 2*, left us with an unresolved problem. Although the slopes of the straight lines are well defined and yield accurate values for $1/K_{\text{diss}} \cdot \Lambda_0^2$, the intercepts giving $1/\Lambda_0$ are too small to be distinguished from zero. This is caused by the steepness of the experimental lines, *i.e.* by the minuteness of K_{diss} .

Figure 2. Fuoss plots, F/Λ vs. $c\Lambda f^2/F$ for $\sim\sim\sim\text{S}^-$, A^+ in THF at 25°C

To overcome this difficulty, we should recall that $\Lambda_0 = \lambda_0^+ + \lambda_0^-$, *i.e.* the limiting conductance is given by the sum of the mobilities of the positive A^+ ion and the negative $\sim\sim\sim\text{S}^-$ ion. λ^+ for A^+ ion in THF may be determined by investigating the conductance of some other salt of this cation which dissociates to a much greater extent than $\sim\sim\sim\text{S}^-, \text{A}^+$, *e.g.* of $\text{A}^+, \text{BPh}_4^-$. This was done by Bhattacharyya, Lee, Smid and Szwarc²², and their results, shown in *Figure 3*, are summarized in *Table 1*. The contribution of the individual ions to the conductance is eventually determined by investigating the conductance of a boride composed of a cation which is equally mobile as the BPh_4^- anion. The transference studies²³ showed that the $\text{Bu}(\text{iso-amy})_3\text{N}^+, \text{BPh}_4^-$ fulfils this condition.

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Figure 3. Fuoss plots, F/A v. cAf^2/F for alkali tetraphenyl borides in THF at 25°C

Table 1. Limiting conductance and equilibrium constants of dissociation of tetraphenylborides in tetrahydrofuran at 25°C

Counterion	Λ_0	λ_0^+	$K_{\text{diss}} \times 10^5 \text{ M}$	$K_{\text{diss M}}/K_{\text{diss Na}^+}$
Bu(iso-amyl) ₃ N ⁺	80.6	40.3 ^a	6.04	0.709
Bu ₄ N ⁺	84.8	44.5	4.32	0.508
Li ⁺	76.9	36.6	7.96	0.935
Na ⁺	88.5	48.2	8.52	1.000
K ⁺	90.1	49.8	3.22	0.377
Cs ⁺	108.7	68.4	0.187	0.0219

^a Assumed $\lambda_0^-(\text{BPh}_4^-) = \lambda_0^+((\text{isoamyl})_3\text{BuN}^+)$.

Inspection of Figure 3 shows that for the series of borides the experimentally determined Λ_0 's are indeed reliable. The value found for Bu(iso-amyl)₃N⁺, BPh₄⁻ gives λ_0^- for BPh₄⁻ anion (equal to λ_0^+ for Bu(iso-amyl)₃N⁺ cation), and subtracting this λ_0^- from the other Λ_0 's leads to the λ_0^+ 's for the respective alkali ions listed in Table 1. The corresponding K_{diss} 's of A⁺,BPh₄⁻ follow directly from the experimental findings.

A discussion of the data listed in Table 1 is not out of place. Although the bare Li⁺ ion is smaller than the Cs⁺ ion, the mobility of Li⁺ in THF (36.6) is lower than that of Cs⁺ (68.4). This result indicates that in tetrahydrofuran the Li⁺ ion is strongly coordinated with THF, binding probably 4 molecules of the ether, whereas the Cs⁺ ion apparently is not associated with the solvent. The degree of the specific co-ordination seems to decrease along the series Li⁺ > Na⁺ > K⁺ > Rb⁺ > Cs⁺.

The values of K_{diss} listed in Table 1 corroborate the conclusions drawn from the magnitude of the respective λ_0^+ 's. It is obvious that the specific

solvation of the cations greatly contributes to the driving force of the ionic dissociation, and therefore $\text{Li}^+, \text{BPh}_4^-$ is much more ionized than $\text{Cs}^+, \text{BPh}_4^-$. As will be shown later, these dissociation processes are exothermic, the gain due to solvation energy being larger than the energy needed to separate the oppositely charged ions (see ref. 33).

Let us now return to our main problem—the determination of Λ_0 's for $\sim\text{S}^-, \text{A}^+$ salts. Since we know now the λ_0^+ for the A^+ cations, we need only to find out the λ_0^- for the $\sim\text{S}^-$ anion to complete our task. There is a phenomenological relation between the mobility, u , of an ion and its diffusion constant D , namely $u = D/kT$. The diffusion constant is expected to be the same for an $\sim\text{S}^-$ ion and for the respective dead polymer of the same DP. In our work we employed living polystyrene of $\text{DP} \sim 25$, and studies of diffusion, carried out by Dr H. Benoit (private communication), showed that the diffusion constant of a dead polystyrene having $\text{DP} \sim 25$ is $3.9 \times 10^{-6} \text{ cm}^2/\text{sec}$ in THF at 25°C . Since $u = 6.47 \times 10^6 \lambda_0^-$ (u and λ_0^- are ion's mobilities expressed, however, in different units), Benoit's findings give a value of 14.4 for λ_0^- of $\sim\text{S}^-$ having a $\text{DP} \sim 25$. We may now calculate the K_{diss} for the $\sim\text{S}^-, \text{A}^+$ from the results of our conductance studies. The relevant data are shown in Table 2.

Table 2. Dissociation Constants of $\sim\text{S}^-, \text{A}^+$ in THF at 25°C

Cation	Λ_0	$K_{\text{diss}} \times 10^7 \text{ M}$ from conductance	Slope of $k_p - C^{-1/2}$ line	$K_{\text{diss}} \times 10^7 \text{ M}$ from reactivity
Li^+	50.0	1.87	30.3	2.18
Na^+	61.6	1.51	25.2 ^a	1.52
K^+	63.2	0.71	18.0	0.77
Rb^+	—	—	6.7	0.11
Cs^+ (one ended)	82.8	0.027	3.0	0.021
Cs^+ (two ended)	82.8	0.16	1.4	0.00465

^a Value of Hostalka, Figini and Schulz is 25.

The dissociation constant for $\sim\text{S}^-, \text{Na}^+$ was previously determined by Worsfold and Bywater²⁴, who estimated the Λ_0 for $\sim\text{S}^-, \text{Na}^+$ by extrapolating the conductance data reported for some salts containing long hydrocarbon chain anions. Their value of $\lambda_0^- = 14$ agrees well with our determination, and since both groups observed the same specific conductance they arrived to identical $K_{\text{diss}} = 1.5 \times 10^{-7} \text{ M}$.

The dissociation constant of $\sim\text{S}^-, \text{A}^+$ may also be determined from the results of kinetic studies of polymerization. This approach was reported simultaneously and independently by our group^{14b} and by Hostalka and Schulz¹⁶. The addition of a strongly ionized salt possessing a common cation with $\sim\text{S}^-, \text{A}^+$ depresses the dissociation of the latter and retards the polymerization. This was observed when $\text{Na}^+, \text{BPh}_4^-$ was added to $\sim\text{S}^-, \text{Na}^+$.

Under the experimental conditions chosen by our group, virtually all the Na^+ ions were formed by the dissociation of $\text{Na}^+, \text{BPh}_4^-$, i.e. $[\text{Na}^+] \gg [\sim\text{S}^-]$. Since $K_{\text{diss}, \text{Na}^+, \text{BPh}_4^-}$ is known (see Table I), the concentration of sodium ions could be calculated for each experiment. The fraction, f , of the free $\sim\text{S}^-$ ions is given under these conditions by $K_{\text{diss}(\sim\text{S}^- \text{Na}^+)}/$

$[\text{Na}^+]$, and the apparent rate constant of propagation, k_p , is therefore

$$k_p = k_{p\pm} + (k_{p-} - k_{p\pm}) K_{\text{diss}, \sim\text{S}^-, \text{Na}^+} / [\text{Na}^+]$$

Hence, a plot of k_p versus $1/[\text{Na}^+]$ is linear, as shown in Figure 4, with an intercept given by $k_{p\pm}$ (the propagation constant of an ion pair) and a slope equal to $k_{p-} - K_{\text{diss}, \sim\text{S}^-, \text{Na}^+}$.

Figure 4. A plot of k_p vs. $1/[\text{Na}^+]$ for $\sim\text{S}^-, \text{Na}^+$ in THF

The slope of the line shown in Figure 1 gives $(k_{p-} - k_{p\pm}) \cdot (K_{\text{diss}, \sim\text{S}^-, \text{Na}^+})^{1/2}$, whereas that seen in Figure 4 gives $(k_{p-} - k_{p\pm}) \cdot K_{\text{diss}, \sim\text{S}^-, \text{Na}^+}$. We may calculate therefore $K_{\text{diss}, \sim\text{S}^-, \text{Na}^+}$ and k_{p-} of the free $\sim\text{S}^-$ ion in THF by combining both values. The result is consistent with that derived from the conductance data, viz. $K_{\text{diss}, \sim\text{S}^-, \text{Na}^+} = 1.5 \times 10^{-7} \text{ M}$, and it leads to $k_{p-} = 65,000 \text{ l./mole-sec}$. The dissociation constant of the other $\sim\text{S}^-, \text{A}^+$ salts may now be calculated from the slopes of the respective lines shown in Figure 1, and these are listed in Table 2. The agreement between the latter and the direct conductometric determinations (the third column of Table 2) is satisfactory—the “two ended” $\text{Cs}^+, -\text{S}\sim\text{S}^-, \text{Cs}^+$ being the only exception. The reason for this apparent discrepancy will be considered in a later section.

Hostalka and Schulz¹⁶ performed similar experiments but under different experimental conditions. The concentration of Na^+ ions in their runs was determined by both: $[\text{Na}, \text{BPh}_4^-]$ and $[\sim\text{S}^-, \text{Na}^+]$. To calculate K_{diss} the value of $k_{p\pm}$ of $\sim\text{S}^-, \text{Na}^+$ was needed and the latter was estimated to be 220 l./mole-sec by a linear extrapolation similar to that shown in Figure 1. Since $k_{p-} \cdot K_{\text{diss}, \sim\text{S}^-, \text{Na}^+}^{1/2} = 25$, the fraction, α , of the dissociated $\sim\text{S}^-, \text{Na}^+$ is $(K_{\text{diss}, \sim\text{S}^-, \text{Na}^+})^{1/2} (k_p - 220) / 25$ where k_p denotes the apparent rate constant of propagation under the conditions of the experiment. It follows that*

* The original equation contains the activity coefficient which is omitted here. This is of little importance since its value is usually close to unity.

$$K_{\text{diss}, \text{S}^-, \text{Na}^+} = \left\{ \frac{\kappa K_{\text{diss}, \text{Na}^+, \text{BPh}_4^-}}{2} \left[-1 + \left(1 + \frac{4[\text{Na}^+, \text{BPh}_4^-]}{(K_{\text{diss}, \text{Na}^+, \text{BPh}_4^-} (1 - \kappa^2 [\text{S}^-, \text{Na}^+]))^{\frac{1}{2}}} \right)^2 \right] \right\}^{\frac{1}{2}}$$

where $(k_p - 220)/25$ is abbreviated by κ . The data of Hostalka and Schulz are given in Table 3 and the last column contains the calculated

Table 3. Determination of $K_{\text{diss}, \text{S}^-, \text{Na}^+}$ from kinetic measurements^a

$[\text{S}^-, \text{Na}^+] \times 10^3 \text{ M}$	$[\text{Na}^+, \text{BPh}_4^-] \times 10^5 \text{ M}$	$k_p \times 10^{-2}$ (l./mole-sec) ^b	$K_{\text{diss}} \times 10^7$ (M)
0.83	0.140	11.0	0.48
0.70	0.319	10.1	0.29
0.76	0.754	8.9	0.58
0.32	0.982	7.6	0.28
0.84	1.11	7.3	0.41
0.64	1.59	6.5	0.41
0.35	3.39	5.2	0.51
		Average	0.41

^a Hostalka and Schulz ref. 11.

^b Due to a different experimental technique used in determining $[\text{S}^-, \text{Na}^+]$ the latter values are by ~ 20 per cent lower than those given by the Syracuse group and consequently k_p are by 20 per cent higher.

$K_{\text{diss}, \text{S}^-, \text{Na}^+}$. This is by about a factor of 4 lower than the value of Worsfold and Bywater and of ours. Since the product $k_p - (K_{\text{diss}, \text{S}^-, \text{Na}^+})^{1/2}$ reported by Schulz *et al.* and by the Syracuse group is identical, the 4-fold decrease in $K_{\text{diss}, \text{S}^-, \text{Na}^+}$ leads to a 2-fold increase in k_p . Thus, Schulz's group concludes that $k_p = 130,000$ l./mole-sec. and $K_{\text{diss}, \text{S}^-, \text{Na}^+} = 0.4 \times 10^{-7}$ M.

It is interesting and instructive to consider the cause for the discrepancy between the values of $K_{\text{diss}, \text{S}^-, \text{Na}^+}$ derived by Hostalka and Schulz on the one hand and by the Syracuse group on the other. This difference may appear surprising since both groups found virtually the same values for k_p , in spite of the greatly different experimental techniques, and reported the same value for the slope of the line giving k_p as a function of $[\text{S}^-, \text{Na}^+]^{-1/2}$. They differ, however, in their estimate of $k_{p\pm}$ —the rate constant of the ion pair.

The Syracuse group noticed^{14b} that the linear extrapolation of k_p versus $[\text{S}^-, \text{Na}^+]^{-1/2}$ gives an unreliable value for the intercept. In fact, their own experiments would give $k_p \pm \sim 150$ l./mole-sec—a not too different estimate from that reported by Schulz *et al.*, *viz.* 220. However, the addition of sodium tetraphenyl boride reduces the rate constant, and the lowest observed k_p is 110 indicating that $k_{p\pm}$ is less than 100. The extrapolation shown in Figure 4 gives a still lower value for $k_{p\pm}$, *viz.* between 80 and 90 l./mole-sec, and the latter was considered by the Syracuse group as the most reliable. At higher concentrations of $\text{Na}^+, \text{BPh}_4^-$ (about 0.3M) the observed k_p seems to increase^{14b} but only slightly.

It was found by Fuoss and Krauss²⁶ that ions may associate with ion pairs into triple ions, *e.g.* $\text{Na}^+ + \text{Na}^+, \text{BPh}_4^- \rightleftharpoons \text{Na}^+, \text{BPh}_4^-, \text{Na}^+$. This associa-

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tion seems to be more extensive than that of BPh_4^- ions with the salt, and therefore the concentration of Na^+ ions eventually *decreases* on increasing the salt concentration. In the above described experiments, this leads to an increase in the concentration of BPh_4^- ions, and also of $\sim\text{S}^-$ ions. Consequently, the reactivity of living polystyrene in the presence of a *high* concentration of the boride becomes higher than expected. The extrapolation might therefore be distorted and give a too high value for $k_{p\pm}$.

A similar problem may arise at the high concentration of the $\sim\text{S}^-$, Na^+ salt. If again the association of Na^+ with the salt is preferred to that with the $\sim\text{S}^-$ ions, the concentration of Na^+ may decrease under these conditions and that of $\sim\text{S}^-$ increase. Consequently, the k_p observed at the highest concentrations of $\sim\text{S}^-$, Na^+ may be too high, and this could vitiate the extrapolation of our and of Schulz's data

Indeed, as pointed out by Tölle, Smid and Szwarc²⁵ the different choice of the value for $k_{p\pm}$ accounts for the discrepancy conclusions of the Syracuse group of Schulz *et al.* The observations of Hostalka and Schulz¹⁶ lead to $K_{\text{diss}} = 0.4 \times 10^{-7} \text{ M}$ and $k_{p-} = 130,000 \text{ l./mole-sec.}$ if $k_{p\pm}$ is 220 l./mole-sec. However, it is shown in Table 4 that the same findings are consistent with $K_{\text{diss}} = 1.5 \times 10^{-7} \text{ M}$ and $k_{p-} = 65,000$ if $k_{p\pm} = 80 \text{ l./mole-sec.}$ Hence, it is impossible to discriminate between the two sets of constants on the basis of the experiments of Hostalka and Schulz.

Table 4.

[Na ⁺ , BPh ₄ ⁻] × 10 ⁵ M	[Living ends] × 10 ³ M		[Na ⁺] ⁻¹ × 10 ⁻³	$k_{p, \text{ obs}}$		$k_{p, \text{ calc.}}$ (l./mole-sec.)
	Schulz	Ours		Schulz (l./mole-sec)	Ours	
132.0	—	0.071	3.38	—	114	111
55.5	—	0.169	5.58	—	127	134
58.6	—	0.151	5.40	—	137	132
29.5	—	0.185	8.22	—	163	160
22.0	—	0.115	8.91	—	184	167
13.5	—	0.167	13.7	—	210	213
7.0	—	0.310	21.9	—	280	294
<hr/>						
Schulz's results (ref. 11)			Schulz's results			
corrected ^a to our scale			corrected ^a to our scale			
3.39	0.35	0.42	37.4	520	433	444
1.59	0.64	0.77	43.5	650	541	635
1.11	0.84	1.01	60.2	730	618	665
0.982	0.32	0.38	78.8	760	634	847
0.754	0.76	0.91	66.6	890	741	730
0.319	0.70	0.84	83.5	1010	840	860
0.140	0.83	1.00	78.8	1100	915	847

^a Because of different standardization [Living ends] (ours) = $1.2 \times$ [Living ends] (Schulz) and k_p (Schulz) = k_p (ours) $\times 1.2$. (Private communication of Schulz). $[\text{Na}^+]$ was calculated on the basis $K_{\text{diss}} \text{Na}^+ \text{B}^- = 8.5 \times 10^{-7} \text{ M}$, and $K_{\text{diss}} \text{S}^-, \text{Na}^+ = 1.5 \times 10^{-7} \text{ M}$. The latter value is not needed for calculating $[\text{Na}^+]$ from the data of the Syracuse group, but it is necessary for calculations of Schulz's data because of the less favourable choice of concentrations.

The distinction is possible²⁵ if the results of Hostalka and Schulz are combined with those reported by the Syracuse group^{14b}. In Figure 5 both sets of

Figure 5. Combined results of Mainz and Syracuse groups plotted as k_p vs. $1/[\text{Na}^+]$. Calculated on the basis:

$$K_{\text{diss}}, \sim\sim\sim\text{S}^-, \text{Na}^+ = 1.5 \times 10^{-7} \text{ M}, K_{\text{diss}}, \text{Na}^+, \text{BPh}_4^- = 8 \times 10^{-5} \text{ M}$$

k_p 's are plotted as functions of $1/[\text{Na}^+]$. The concentration of Na^+ ions is calculated by accepting the values of $K_{\text{diss}}, \sim\sim\sim\text{S}^-, \text{Na}^+ = 1.5 \times 10^{-7} \text{ M}$ and $K_{\text{diss}}, \text{Na}^+, \text{BPh}_4^- = 8.5 \times 10^{-5} \text{ M}$, and one finds then all the points on a common line. This would not be so if the calculations were based on the value of $K_{\text{diss}}, \sim\sim\sim\text{S}^-, \text{Na}^+ = 0.4 \times 10^{-7} \text{ M}$.

The above problem has been fully discussed in order to impress upon the reader the pitfalls and the ambiguities encountered in kinetic studies of anionic polymerization. These, as well as the susceptibility of the reaction to impurities and the frequent ease of isomerization of living ends, call for an utmost care in quantitative studies of such processes.

OTHER SYSTEMS BEHAVING SIMILARLY TO THE SOLUTIONS

A simultaneous growth due to free ions and to ion pairs should be observed in other media having relatively high dielectric constants and a good solvating power. For example, it is probable that the anionic polymerization in liquid ammonia may be propagated mainly by the free ions. Unfortunately, the necessary experimental data are not available yet; the only thorough kinetic study by Higginson and Wooding²⁷ is not sufficiently extensive, although it seems to indicate that the free $\sim\sim\sim\text{S}^-$ ions are responsible for the propagation. There is evidence²⁸ that the polymerization of ethylene oxide initiated by sodium hydroxide in dioxane is propagated by ion pairs. This is not surprising in view of the low dielectric constant of that solvent.

Anionic polymerization of styrene in dimethoxy-ethane involves undoubtedly ions and ion pairs and this system is presently investigated in our laboratory. Similarly, in methyltetrahydrofuran this polymerization shows the characteristic feature of the participation of ions and ion pairs. Preliminary data are available from Dr Van Beylen's (Syracuse) studies of the

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$\sim\sim\sim\text{S}^-$, Li^+ and $\sim\sim\sim\text{S}^-$, Na^+ propagation. Plots of the observed k_p versus [living ends] $^{-1/2}$ are linear. For $\sim\sim\sim\text{S}^-$, Li^+ the intercept is about 50 l./mole-sec and the slope 0.8 l. $^{3/2}$ /mole $^{3/2}$ sec, whereas for $\sim\sim\sim\text{S}^-$, Na^+ the intercept seems to be only 5 l./mole-sec and the slope about 0.4. Unfortunately, the dissociation constants of $\sim\sim\sim\text{S}^-$, Li^+ and $\sim\sim\sim\text{S}^-$, Na^+ in MeTHF are not yet available, and therefore the rate constant of the free $\sim\sim\sim\text{S}^-$ ion in this solvent cannot be yet determined.

Barnikol and Schulz²⁹ investigated the anionic polymerization of $\sim\sim\sim\text{S}^-$, Na^+ in tetrahydropyran (THP). According to their previous work,³⁰ the system behaves normally in this medium. The k_p versus [L.e.] $^{-1/2}$ relation led them to $k_p \pm = 7$ l./mole-sec. and to a slope of 0.4. As expected, the polymerization of $\sim\sim\sim\text{S}$, Na^+ in THP is retarded by the addition of Na^+ , BPh_4^- . Similar results were obtained recently for $\sim\sim\sim\text{S}^-$, Li^+ in THP (M. Fischer, unpublished results from Syracuse).

The anionic polymerization of styrene in tetrahydropyran was independently investigated by Dainton *et al.*¹⁷ The rate constants of propagation for the $\sim\sim\sim\text{S}^-$, Na^+ , $\sim\sim\sim\text{S}^-$, K^+ , and $\sim\sim\sim\text{S}^-$, Rb^+ ion pairs were determined by depressing the concentration of the free $\sim\sim\sim\text{S}^-$ ions through the addition of the respective alkali tetraphenylborides. For $\sim\sim\sim\text{S}^-$, Na^+ , a rate constant was found to be twice that of Barnikol and Schulz, *viz.* 14 l./mole-sec, and the K^+ and Rb^+ salts appeared to be even more reactive, namely 68 l./mole-sec. and 78 l./mole-sec. respectively. These findings are interesting since they show a different pattern of reactivity of ion pairs in THF and THP. I propose, therefore, to discuss fully the solvent effect in the following section.

THE EFFECT OF SOLVENTS AND COUNTER-IONS ON THE REACTIVITY OF ION PAIRS

The reactivities of various alkali ion pairs of living polystyrene in THF increase¹⁴⁶ along the series $\text{Cs}^+ < \text{K}^+ < \text{Na}^+ < \text{Li}^+$. In dioxane, the order of reactivities is reversed³¹ — $\sim\sim\sim\text{S}^-$, Cs^+ is the most reactive ion pair and $\sim\sim\sim\text{S}^-$, Li^+ the least. This remarkable change of the reactivity pattern, see Table 5, calls for some comments. It seems that the transition state of propa-

Table 5. Reactivities of $\sim\sim\sim\text{S}^-$, A^+ ion pairs in propagation

Counterion	Li^+	Na^+	K^+	Rb^+	Cs^+	Remarks
$k_p \pm$ in THF l./mole-sec	160	80	~ 70	~ 60	22	Appreciable dissociation
$k_p \pm$ in MeTHF l./mole-sec	50	5	—	—	—	Medium dissociation
$k_p \pm$ in THP l./mole-sec		14 ^a 7 ^b	$\sim 70^a$ —	$\sim 80^a$ —	— —	Medium dissociation
$k_p \pm$ in dioxane (Syracuse)	0.9	3-4	20	21.5	24.5	No dissociation
(Gee ^c)	—	3-5	—	—	—	
(Dainton ^a)	—	6.5	28	34	15	

^a Dainton *et al.*, ref. 12.

^b Barnikol and Schulz, ref. 24.

^c Gee *et al.*, ref. 27.

gation is different in these two solvents. Tetrahydrofuran has a much greater solvating power, as well as higher dielectric constant, than dioxane. Both factors account for the measurable degree of dissociation of $\sim\sim\sim\text{S}^-$, M^+ in

THF and for virtually a complete absence of free ions in dioxane. The absence of free ions in dioxane accounts for the constancy of k_p in this solvent^{31, 32}; dilution of living ends in dioxane does not enhance the polymerization, while an enhancement is observed in THF.

It seems that the $\sim\text{S}^-\text{M}^+$ (M^+ an alkali ion) forms contact ion pairs in dioxane as well as in THF. However, the solvating power of THF leads to partial separation of the ions in the transition state of propagation. Such a separation is most pronounced for the small cations (Li^+ , Na^+) which become strongly co-ordinated with THF, whereas the bulky Cs^+ ion shows no tendency to co-ordinate with the molecules of the THF (see *e.g.* Table 1 and ref. 33), and therefore it still forms a contact ion pair even in the transition state of propagation.

The separation of the ions by the solvent enhances the reactivity of the pair, since in the propagation process the counterion has eventually to move from the last carbon atom of the growing chain to the β carbon atom of the added monomer. Therefore, the reactivities of ion pairs, as well as their degree of ionization, increase in THF as the radius of the cation decreases.

The poor solvating power of dioxane prevents the formation of solvent-separated pairs even in the transition state, and this lack of solvation—which provides a driving force for propagation—makes the $\sim\text{S}^-\text{M}^+$ pairs in dioxane rather inert. Under these conditions the rate of propagation is determined by the tightness of the pair—hence, the tightest $\sim\text{S}^-\text{Li}^+$ ion pair is the least reactive, and $\sim\text{S}^-\text{Cs}^+$ the most. It is significant that the latter ion pair is equally reactive in THF and in dioxane (see again Table 5), indicating that neither solvent co-ordinates with the bulky Cs^+ ion.

Let us recapitulate our conclusions. Etheric solvents which strongly co-ordinate with cations should enhance the propagation of ion pairs. In the extreme case, the ion pair may be separated by the solvent even in the initial state (and, of course, in the transition state). Its reactivity should be then very high and not much affected by the nature of the cation. In fact, it would be not surprising to find in such a medium a higher reactivity for Cs^+ ion pair than for Li^+ pair.

In THF, and in other solvents of a similar solvating power, the initial state forms a contact ion pair, whereas a solvent-separated pair is produced in the transition state. Two opposing factors affect then the relative reactivity of the different salts. The small ionic radius of Li^+ makes the respective pair unreactive, but by the same token, the great gain in solvation energy more than counteracts this unfavourable size effect. The net result is rather a high reactivity, declining along the series $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Cs}^+$. As the solvating power decreases, one may find in the series of alkali salts a minimum of reactivity, *e.g.* $\text{Li}^+ > \text{Na}^+ < \text{K}^+ < \text{Cs}^+$. Unpublished results of Dr Van Beylen (Syracuse) indicate that this situation may exist in methyltetrahydrofuran. A further decrease of solvating power eliminates the solvation effect and then the reactivity is determined by the tightness of the pair. In such solvents, exemplified by dioxane, the reactivity is low and increases in the order $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+$. The ideas outlined here are somewhat similar to those discussed recently by Shatenstein⁵⁰.

The results reported by Dainton *et al.*¹⁷ (see Table 5), may imply a lack of solvation of the transition state in THF. However, the reported reactivities of

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$\sim\sim\sim\text{S}^-, \text{K}^+$ and $\sim\sim\sim\text{S}^-, \text{Cs}^+$ seem to be too high, and one should check whether the contribution of free $\sim\sim\sim\text{S}^-$ ions was indeed eliminated in the respective experiments.

Additional information about the nature of the transition state of ion pair polymerization may be gained from studies performed in mixed solvents. Two investigations have been reported recently. Worsfold and Bywater³⁴ investigated the polymerization of $\sim\sim\sim\text{S}^-, \text{Li}^+$ in THF-benzene mixtures, whereas the Syracuse group³⁵ studied this reaction in THF-dioxane mixture. It was found that the $\log K_{\text{diss}}, \sim\sim\sim\text{S}^-, \text{Li}^+$ varies linearly with the reciprocal of the dielectric constant of the mixture, see *e.g.* Figure 6. The line found for

Figure 6. A plot of $\log K_{\text{diss}}, \sim\sim\sim\text{S}^-, \text{Li}^+$ vs. $1/\epsilon$ in THF-dioxane mixtures

Table 6. Dissociation constant of $\sim\sim\sim\text{S}^-, \text{Li}^+$ (one-ended) in THF-dioxane mixture at 25°C

Volume % of dioxane	d (g/cm ³)	Dielectric constant, ϵ	$\eta \times 10^3$ (poises)	A_0 (cm ² ohm ⁻¹ eqv. ⁻¹)	K_{diss} (mole/l.)
0	0.880	7.39	4.60	50.1	1.9×10^{-7}
10	0.895	6.76	4.86	47.4	6.25×10^{-8}
23	0.910	6.10	5.24	44.0	1.25×10^{-8}
33	0.923	5.62	5.60	41.2	3.20×10^{-9}
47	0.947	4.81	6.41	35.9	1.80×10^{-10}
68	0.975	3.82	7.78	—	— ^a
100	1.028	2.21	11.96	—	—

All the results are calculated from Fuoss' plots, conductivity being measured down to the concentrations $1-2 \times 10^{-3}$ M.

^a The resistivity of the cell was too high to be measured with the available bridge.

the THF-benzene mixtures is perhaps steeper than that observed for the THF-dioxane system. The latter system shows no anomalies as may be seen from Table 6 and Figure 7 which give the dielectric constants, the densities, and the viscosities of the mixture at various compositions.

Figure 7. Physical properties of THF-dioxane mixtures

The reactivity of $\sim\text{S}^-\text{Li}^+$ ion pair falls rapidly on the addition of small amounts of dioxane to THF, but the addition of small amounts of THF to dioxane affects it only slightly, see Figure 8. In THF-dioxane mixtures, the

Figure 8. A plot of $K_{\pm}$ vs. mole fraction of dioxan in THF-dioxane mixtures

$k_{\pm}$ is not linear with either $1/\epsilon$ or $(\epsilon - 1)/(2\epsilon + 1)$, see *Figure 9* (ϵ = dielectric constant of the solvent) whereas a linear relation of $k_{\pm}$ with $(\epsilon - 1)/(2\epsilon + 1)$ was claimed³⁴ for the $k_{\pm}$ in THF-benzene mixtures. These facts are interesting, but it is premature to discuss their significance at this time.

Figure 9. A plot of $k_{p\pm}$ v. $1/\epsilon$ and $(\epsilon - 1)/(2\epsilon + 1)$ in THF-dioxane mixtures

Extensive study of anionic polymerization in a variety of solvents is highly desirable. The results should shed much light on the role played by the solvent in processes involving ion pairs. A thorough investigation of this field is expected in the near future.

CONTACT ION PAIRS AND SOLVENT-SEPARATED ION PAIRS

The strong interaction of ion pairs with other polar molecules, including those of solvents, is due to their large dipole moments. The interaction energy is quite appreciable, and, in fact, co-ordination of ion pair with solvent molecules may involve energies as large as 10 kcal/mole. Two types of interaction should be distinguished: (i) those in which the interacting solvent molecules remain "outside" the ion pair, and (ii) those having the interacting molecule, or molecules, squeezed in between the two ions of a pair.

The interaction leading to the separation of the ions by a solvent molecule (or molecules) was first visualized by Winstein³⁶ and elaborated by Grunwald³⁷. The potential energy of two ions increases as they are pulled away from their contact position. Initially, their attraction for each other is only slightly attenuated by the solvent since the gap between them is too small to accommodate a solvent molecule. However, at some critical distance a polar solvent molecule may be accommodated and then the energy of the

system decreases as the solvent fills up the vacant space. Further stretching increases again the potential energy which eventually reaches its plateau value at infinite separation. These changes, qualitatively depicted in *Figure 10*, suggest that two distinguishable species may simultaneously exist: a contact ion pair and a solvent-separated ion pair.

Figure 10. Potential energy of an ion-pair at various interionic distances

The concept of contact ion pair and solvent-separated ion pair was shown to be most fruitful in accounting for kinetics of some processes involving ions and ion pairs. For example, many solvolyses involving an asymmetric carbon atom and an intermediate carbonium ion may lead to inversion or retention of the configuration and they may cause racemization of the starting material. Careful studies of kinetics of all these processes, in conjunction with the effects exerted upon them by salts having common counter-ion with the reagents, allowed Winstein³⁸ to show that contact ion pairs, solvent-separated ion pairs, and free ions may participate simultaneously in some reactions. Such a process is described in terms of the following mechanism:

and for some solvolytic reactions all the individual rate constants were determined.

These basic ideas were confirmed by the numerous studies of Winstein's group, as well as of other workers, and their application to reactions of carbanions were pioneered by Cram³⁹.

The first physical evidence revealing the existence of two distinct ion pairs was obtained in Syracuse by Hogen-Esch and Smid⁴⁰. Two absorption peaks were found in the solutions of alkali salts of fluorenyl in tetrahydrofuran; one at 355 m μ , and the other at 373 m μ . Their relative intensities were not

affected by dilution within the range 10^{-2} to 10^{-4} M, nor by the addition of the tetraphenylboride salt having a common counterion with the fluorenyl salt. However, as seen from Figure 11, illustrating a similar behaviour of benzo-fluorenyl sodium, a drastic change occurs in the spectrum as the temperature of the solution is lowered. These observations prove that two species co-exist in equilibrium with each other, but none of them is a free ion. The last conclusion was verified by studies of conductance; the proportion of free ions was found to be too low for a spectrophotometric detection. Hence, it appears that the solution contained contact ion pairs in equilibrium with the solvent-separated pairs.

Figure 11. The spectra of benzo-fluorenyl salts at various temperatures

Only the 373 mμ peak is seen at low temperature, indicating that it belongs to the solvent-separated pair. Further verification of this assignment comes from studies of the toluene solution. In that medium of a poor solvating power, only the 355 mμ peak appears—and obviously this absorption is due to the contact ion pair.

It is known that separation of ions leads to a bathochromic shift in the spectra of radical anions and carbanions^{41, 42}, since the counterion stabilizes the ground state to a greater extent than the excited state⁴³. Therefore, the observed spectral changes are fully justified; the solvent-separated pair should absorb at lower wave length than the contact ion pair.

What are the factors that determine the nature of the ion pair? We mentioned previously two of them: (i) The solvent should strongly interact with the ions, and (ii) in well-solvating solvents, the separated ion pair is more stable when cations are small rather than large, since the former more strongly interact with solvent molecules than the latter. The size of the anion is also important as shown by the following argument.

Consider an ion pair in which the charges are separated by a distance R when the ions are in contact. Formation of a solvent-separated pair may be achieved in two steps: Separate the pair by ΔR , and then solvate the ions. The first step requires energy given by $(e^2/\epsilon_{\text{eff}})[1/R - 1/(R + \Delta R)]$, ϵ_{eff} being the effective dielectric constant. The second provides energy resulting from the co-ordination. Now, for a constant ΔR , the energy of the first step decreases as R increases. Therefore, the bigger the anion, for a constant cation, the greater the stability of the solvent-separated pair. This principle is illustrated by the findings of Roberts and Szwarc⁴⁴, who investigated the mono- and di-anions of tetraphenylethylenes.

In a poorly solvated medium, the contact ion pairs may be transformed into solvated ion pairs by being combined with a suitable solvating agent. If such an agent associates more strongly with the free ion than with the ion pair, its addition increases the equilibrium concentration of free ions. In the reverse case, the concentration of free ions, solvated and non-solvated, decreases. This conclusion is valid whatever the structure of the solvated ion pair and the relations are clarified by the following calculations. Consider a system

In the presence of an agent S two additional equilibria are established

The total concentration of the free cations (or anions) is given by

$$[A^+] + [A^+, S] = [B^-] = xc$$

where c is the total concentration of the salt and x the fraction that ionizes. Application of the mass law leads then to the result

$$\frac{x^2 c}{1-x} = K_1 \times \frac{1 + K_3[S]}{1 + K_2[S]}$$

x increases with $[S]$ for $K_3 > K_2$, whereas x decreases on increasing $[S]$ when $K_3 < K_2$. Note that the equilibrium constant K_4

is given by the equation

$$K_4 = K_1(K_3/K_2)$$

The existence of contact ion pairs and solvent-separated ion pairs may exert a profound influence upon the kinetics of anionic polymerization. It has been suggested by Dr Smid (Syracuse) that the polymerization in

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THF involves a small fraction of highly reactive solvent-separated ion pairs, in addition to the free ions, and the lack of these species in dioxane is responsible for the slow polymerization observed in the latter solvent. This explanation may be preferred to that invoking a partial separation of the ions in the transition state of propagation (see section 4). The formalism of this hypothesis resembles that proposed by Winstein³⁸, *e.g.* for living polystyrene, $\sim\sim\sim\text{S}^-, \text{A}^+$

and in these terms the observed $k_{\text{p} \pm} = (1 - \gamma) \cdot k'_{\text{p} \pm} + \gamma \cdot k''_{\text{p} \pm}$, where γ is the fraction of all the ion pairs present as the solvent-separated species. Since $K_S = \gamma/(1 - \gamma)$, the equation for the overall rate constant of propagation of *all* the ion pairs, solvated as well as non-solvated, is

$$k_{\text{p} \pm} = \{k'_{\text{p} \pm} + K_S k''_{\text{p} \pm}\} / (1 + K_S)$$

The complexity of this expression cannot be revealed by the conventional kinetic study. Any change of concentration of the reagent preserves the relation

$$-d[\text{S}]/dt = k_{\text{p} \pm} [\sim\sim\sim\text{S}^-, \text{A}^+] [\text{S}]$$

and gives no insight into the details of the more sophisticated mechanism. A direct determination of K_S , *e.g.* by spectrophotometric methods, which unfortunately are only applicable when the spectra of the contact ion pairs and solvent-separated pairs sufficiently differ from each other, does not help either. The experiment gives only $k_{\text{p} \pm}$ and K_S and leaves, therefore, two unknowns with only one equation. One may dilute the solution with an inert solvent and change γ by decreasing the concentration of the solvating medium. This is feasible, particularly if γ is given by a mass law with a constant K_S , *i.e.* if dilution does not affect the activity coefficient of the solvent. Nevertheless, this method is still open to a criticism—namely $k'_{\text{p} \pm}$ and $k''_{\text{p} \pm}$ may be affected by the change of the environment.

There are two avenues of approach which might clarify the situation:

(i) The growth of the contact ion pair may produce a product different from that formed by the solvent-separated pair. For example, the contact pair may grow by an isotactic placement only, whereas the growth of the solvent-separated pair may involve only a syndiotactic placement. If this is the case, then $k'_{\text{p} \pm}/k''_{\text{p} \pm}$ is given by the ratio of isotactic to syndiotactic placements in the resulting polymer and thus the additional equation, necessary for solving the problem, is available.

(ii) If one assumes that the rate constants $k'_{\text{p} \pm}$ and $k''_{\text{p} \pm}$ are governed by the simple Arrhenius law, the study of the temperature dependence of the

polymerization may be most helpful. The temperature dependence of anionic polymerization is considered below and, therefore, I propose to discuss this problem in that section.

Finally, it should be stressed that the presence of free ions complicates the study of equilibrium between the contact pair and the solvent-separated pair. Hence, it is advisable to carry such a study in the presence of other salts which depress the ionic dissociation of the investigated living polymer.

CO-ORDINATION OF ION PAIRS WITH THE MONOMER

It has been advocated, particularly by Korotkov⁴⁵ and by Medvedev⁴⁶, that monomers may act in a dual role—as complexing agents as well as the reagents. This idea is plausible since electron-rich monomers, possessing π -electrons, may act as electron donors and co-ordinates with cations. In fact, such π -complexes between *e.g.* Ag^+ ions and olefins or benzene are well known⁴⁷, their quantum-mechanical description being due to Dewar⁴⁸.

We have been speculating⁴⁹ about the feasibility of such intermediates in the anionic polymerization, but unfortunately no clear-cut evidence for their existence is yet available. In principle, their effect upon the kinetics of propagation may be quite complicated. For a fast complexing and a sufficiently high equilibrium constant of association, the rate of polymerization may be determined by the slow, unimolecular rearrangement, *e.g.*

Such a polymerization would be first order in living ends and zero order in monomer.

Korotkov^{45b} considers a case in which rearrangement takes place only on collision with another monomer, and then such a reaction may be second order with monomer.

The problem of monomer complexing is most intriguing, but some solid evidence should be obtained before the subject could be seriously discussed.

THE INFLUENCE OF TEMPERATURE UPON ANIONIC POLYMERIZATION

Changes of temperature have a complicated effect upon the rate of anionic polymerization. It is not infrequent to find an exceptionally low apparent activation energy of propagation if the reaction takes place in polar solvents^{9b, 51}. In fact, in some systems, the apparent activation energy could be even negative; *i.e.* the rate of propagation may increase on lowering the temperature. This phenomenon may be caused by a substantial increase of the dissociation constant, K_{diss} ,

at lower temperatures. The proportion of the highly reactive free ions becomes then larger, and their contribution to the overall process enhances the overall polymerization in spite of lowering the values of k_p^- and $k_p^\pm$.

Most of the ionic dissociations are exothermic. The exothermicity results from two factors: (i) The dielectric constant, ϵ , of polar solvents increases at lower temperatures and usually $\partial \ln \epsilon / \partial \ln T < -1$; (ii) The specific coordination of free ions is more pronounced than that of ion pairs, and thus

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the heat of co-ordination contributes to the exothermicity of the dissociation. The latter factor is particularly important for contact ion pairs involving small alkali ions if they form.

In the absence of co-ordination of the solvent with the ion, the free energy of dissociation is given by the equation^{52, 53}

$$\Delta F_{\text{diss}} = -Ne^2/a \cdot \epsilon + \text{const}$$

where a represents the distance separating the ions in an ion pair. The thermodynamic formalism leads then to

$$\Delta S_{\text{diss}} = (Ne^2/a\epsilon) (\partial \ln \epsilon / \partial T)_p$$

and

$$\Delta H_{\text{diss}} = (Ne^2/a\epsilon)(1 - \partial \ln \epsilon / \partial \ln T)$$

It has been remarked earlier that for many etheric solvents, $\partial \ln \epsilon / \partial \ln T < -1$, e.g. for tetrahydrofuran, methyl-tetrahydrofuran and dimethoxy-ethane, the respective values are³³: -1.16 , -1.12 , and -1.19 . Hence, the simple treatment of Ramsey qualitatively accounts for the exothermicity of the dissociation. The actual value of $-\Delta H$ is usually larger, since the heat of co-ordination adds to the exothermicity of the process.

The temperature dependence of the dissociation constant of living polystyrene (counter-ion Na^+) in THF⁵⁴ is shown in Figure 12. The dissociation

Figure 12. Van't Hoff plot of $k_{\text{diss}}, \sim S^-, \text{Na}^+$

is exothermic, as expected; the exothermicity decreases, however, at lower temperatures. This behaviour is observed for many salts, and for the sake of illustration, the behaviour of sodium, cesium, and tri-isoamyl-butyl ammonium salts of tetraphenylboride in THF and in dimethoxy-ethane is shown in Figures 13 and 14 (The data are taken from ref. 33.). In Figure 15,

Figure 13. Van't Hoff plots of the dissociation constant of tetraphenyl borides in THF

Figure 14. Van't Hoff plots of the dissociation constant of tetraphenyl borides in dimethoxyethane

the temperature dependence of sodium biphenyl in THF is shown (from ref. 55), and again one notes a flattening of the curve at lower temperatures. The lower exothermicity of the dissociation at lower temperatures may be attributed to (a) an increase in the dielectric constant of the solvent since

$$\Delta H_{\text{diss}} = (\text{Ne}^2/a\epsilon) (1 - \partial \ln \epsilon / \partial \ln T)$$

Figure 15. Van't Hoff plots of the dissociation constant of sodium biphenyl in THF

and (b) to a more extensive solvation of ion pairs at lower, than at higher, temperatures. The latter effect may be interpreted as a manifestation of the formation of solvent-separated ion pairs.

In view of the above discussion, it is obvious that, in systems involving simultaneously free ions and ion pairs, not much significance should be attributed to the apparent activation energy of anionic propagation. It is interesting, however, to determine the proper activation energies characteristic of the growth of the individual species participating in the reaction.

Polymerization in dioxan involves ion pairs only. Therefore, the respective activation energy is meaningful and refers to the growth of ion pairs. Studies of Gee *et al.*³² led to $E = 9 \pm 3$ kcal/mole for $\sim\text{S}^-\text{Na}^+$, and the subsequent investigation by Dainton¹⁷ confirmed this result ($E = 9.5$ kcal/mole). On this basis, one finds a reasonable pre-exponential factor of 10^8 l./mole-sec indicating that the initial and the transition states have similar degrees of solvation. Lower activation energies, and correspondingly lower pre-exponential factors, were reported by Dainton *et al.*¹⁷ for $\sim\text{S}^-\text{K}^+$ and $\sim\text{S}^-\text{Rb}^+$ in dioxane. The respective values are ~ 6 kcal/mole and $\sim 10^6$ l./mole-sec for the K^+ salt and about 4.5 kcal/mole and 10^5 l./mole-sec for the Rb^+ salt. It would be desirable to have an independent check for these data.

In tetrahydropyran Dainton *et al.*¹⁷ report for $\sim\text{S}^-\text{Na}^+$, an activation energy of about 7 kcal/mole and a pre-exponential factor of about 10^6 l./mole-sec, whereas Barnikol and Schulz²⁹ claim a value of about 4 kcal/mole only. It is possible that the contribution of the free ions to propagation has not been entirely eliminated.

The activation energy in benzene solution for $\sim\text{S}^-\text{Li}^+$ containing two molecules of THF per living end was reported⁵⁶ to be 10.4 kcal/mole with a frequency factor of 3×10^7 l./mole-sec.

In view of these data, one may assume that the pre-exponential factors for anionic growth of ion pairs are in the range 10^6 – 10^8 l./mole-sec. Some substantially lower values, quoted in the literature, might be in error.

It is possible that ion pairs may form contact ion pairs at higher temperatures and solvent-separated pairs at lower temperatures. It is plausible to expect the latter pairs to be more reactive and to propagate with a lower activation energy than the former. Therefore, the Arrhenius plot for such a system of ion pairs may acquire an S-shaped form. At higher temperature $k_{p\pm}$ would decrease with temperature due to a relatively high activation energy associated with the growth of contact ion pairs. In the intermediate region $k_{p\pm}$ may increase as a result of increasing fraction of the more reactive solvent-separated pairs, and finally at lowest temperature $k_{p\pm}$ would decrease again, since virtually all the pairs are in the form of solvent-separated species and the reaction is then governed by the activation energy of their growth. The appearance of such a curve would provide additional evidence for the participation of two types of ion pairs in the propagation.

The only available data for the activation energy of propagation of the free $\sim\sim\text{S}^-$ ions are those of Toelle, Smid and Szwarc⁵⁴. Their studies in THF led to $E \sim 4$ kcal/mole, and to a pre-exponential factor of about 10^8 l./mole-sec. The results are shown in Figure 16. It is plausible to find similar pre-exponential factors for the free ion and free radical polymerization.

Figure 16. Arrhenius plot of k_{p-} for the $\sim\sim\text{S}^-$ ion in THF

PROBLEM OF MOLECULAR WEIGHT DISTRIBUTION

It was pointed out by Flory⁵⁷ that an addition polymerization deprived of termination should produce a polymer having a Poisson molecular weight distribution. Subsequently, the Syracuse group⁵⁸ emphasized that living polymers provide an excellent opportunity to achieve this goal, and indeed, successful preparations have been reported since by many investigators, *e.g.* refs. 59, 60, and 61.

The success of the method is based on the assumptions that all the polymers grow simultaneously with an *equal* rate, and none is terminated before the completion of the preparation. The presence of living polymers secures the latter conditions, but if free ions and ion pairs participate in the process,

PROGRESS IN ANIONIC POLYMERIZATION

then not *all* the polymers grow with the same rate. For example, in tetrahydrofuran at 25°C, a 10^{-3} M solution of $\sim\text{S}^-\text{Na}^+$ contains about 1 per cent of free ions. Accepting the previously quoted values, *viz.* $k_p \pm = 80$ l./mole-sec and $k_p - = 65,000$ l./mole-sec, we calculate that 1 per cent of the ionized growing chains polymerizes eight times as much monomer as the remaining 99 per cent. In the absence of exchange between the ions and ion pairs, about 1 per cent of the resulting chains should have, therefore, 800 times greater DP than the remaining 99 per cent. However, this is not the case. The ion pairs dissociate, and the ions associate into pairs, and therefore, the molecular weight distribution depends on the rate of exchange *viz.* on the rate constant of ion pairs dissociation:

The molecular weight distribution of the resulting polymer should be indistinguishable from Poisson distribution if the rate of exchange is much faster than the rate of growth. Had this not been the case, there should be some broadening of the molecular weight distribution, and in fact, the extent of the broadening permits one to determine the dissociation rate constant, k_d .

The mathematical treatment of the problem was presented by Figini⁶², and the application of these ideas to the system $\sim\text{S}^-\text{Na}^+$ in THF was reported by Löhr and Schulz⁶³ and further refined by Figini, Löhr and Schulz⁶⁴. In the latter paper, the resulting polymer was fractionated and thus the molecular weight distribution was determined. As seen from Figure 17 taken from their paper, the polymer produced in the presence of

Figure 17. Molecular weight distribution in the presence of Na^+ , BPh_4^-

an excess of Na^+ , BPh_4^- followed the expected Poisson distribution (corrected for the hydrodynamic disturbances caused by the capillary flow). Under these conditions, the fraction of the free ions is negligibly small, and the propagation is due to ion pairs only. In the absence of salt, the molecular weight distribution broadens (see Figure 18) and from the shape of the resulting curve k_d was calculated to be about 75 sec^{-1} . Since $k_d/k_a = K_{\text{diss}}$, the association constant k_a may be calculated. The value is about $2 \cdot 10^9$ l./mole-sec if the low estimate of Schulz *et al*¹⁶, for $K_{\text{diss}} (0.4 \times 10^{-7} \text{ M})$ is accepted.

Figure 18. Molecular weight distribution in the absence of Na^+ , BPh_4^-

For the higher value of $K_{\text{diss}} = 1.5 \times 10^{-7} \text{ M}$, k_a is calculated as $0.5 \times 10^9 \text{ l./mole-sec.}$

One should note that the association is slower (by about a factor of 100) than expected for a diffusion-controlled reaction. I believe that the retarding effect arises from the specific solvation of the Na^+ ions by THF. It is probable that these ions are co-ordinated with four molecules of THF when the ion is free, but at least a part of the solvation shell has to be desolvated when an ion pair (probably a contact pair) is formed. The desolvation may require an activation energy which reduces the rate of the association process. Further studies of the dissociation of ion pairs and the association of ions are highly desirable, and an additional example of such a study has been presented by Dr Figini during this meeting⁶⁵.

The participation of ions and ion-pairs in the propagation of living polystyrene (Na^+) in THF explains some puzzling observations. It was reported⁵⁸ that the viscosity average molecular weight of living polystyrene increases when the reaction is carried out at -76°C ; otherwise, the conditions of the run were the same as those maintained in other experiments performed at room temperature. I believe that the higher viscosity average of the polymer results from a substantial decrease in the rate of exchange between the ions and ion pairs at low temperature.

THE TACTICITY IN ANIONIC POLYMERIZATION

The anionic polymerization may yield stereospecific polymers. For example, the anionic polymerization of methyl methacrylate in toluene at -60°C produces an isotactic polymer^{66, 67}, the lithium initiated polymerization of isoprene in hydrocarbons gives all 1,4-*cis* polymer⁶⁸. The stereospecific polymerization of styrene initiated in benzene by lithium alkyls gives relatively low molecular weight product⁶⁹, whereas the initiation by potassium alkyls^{70, 71} produces a stereospecific high molecular weight polymer. Not every anionic system is stereospecific, but unfortunately, the present state of our knowledge of stereospecific polymerization is not sufficiently advanced to permit us the discussion of factors which are responsible for the stereospecificity and which govern its direction. There is, however, one factor preventing formation of a stereospecific polymer which may be considered now.

It is obvious that each growing species has its own characteristic stereochemical requirement, *e.g.* it may grow entirely through an isotactic placement, while another species may cause a mixed addition, *etc.* Let us consider two growing species—one demanding an isotactic placement, the other propagating through a syndiotactic addition. Although both are stereospecific, the product should be atactic if the growing centres are being rapidly transformed one into another. For example, anionic polymerization of styrene in THF produces an atactic polymer. However, we do not know what is the stereochemical characteristic of the ion pair and of the free ion. Both may be stereospecific but, due to the rapid exchange, the resulting product could be atactic. A similar situation may characterize a solvated and non-solvated ion pair; in fact, it was reported that the addition of small amounts of ether to toluene solution of anionically polymerized methyl methacrylate results in the formation of a stereo-block. Apparently, the non-solvated pair grows by an isotactic process, the solvated adds monomer in a syndiotactic manner, and the exchange of ether between the pairs is sufficiently slow to allow for the formation of relatively long stereo-blocks.

Hence, systems involving two or more simultaneously growing species which differ in their stereochemical requirements cannot yield stereoregular polymers if the exchange between them is rapid.

ASSOCIATION OF IONIC SPECIES

It has been mentioned that ions may associated with ion pairs to form triple ions²⁶. The process is represented by the equations,

The formation of triple ions becomes appreciable at higher salt's concentration, particularly in solvents having low dielectric constant.

Living polymers possessing *two* ionisable ends, *e.g.*

provide an interesting system in which the formation of triple ions may result from an intramolecular reaction, instead of the conventional intermolecular process⁷². Dissociation of an ionisable end of such a polymer produces a polystyryl ion linked by a chain to an $\sim S^-, Cs^+$ ion pair, *viz.*

Even in the most dilute solutions such an ion remains all the time in the close vicinity of the ion pair located on the other end of the polymeric acid. Therefore, it readily associates with its neighbour forming a closed ring polymer, *i.e.*

The cyclization and formation of a triple ion upsets the ionization process,

since the free $\sim\sim\sim\text{S}^-$ ions are removed from the system. Additional living ends have therefore to dissociate to replenish the consumed $\sim\sim\sim\text{S}^-$ ions, and as a result, a new equilibrium is established in which the concentration of Cs^+ ions exceeds that of $\sim\sim\sim\text{S}^-$ ions. Consequently, for the same total concentration of living polymers the solution of two living-ends polymer contains less $\sim\sim\sim\text{S}^-$ ions and more Cs^+ ions than a solution of one-living-end polymer, $\text{X} \sim\sim\sim\text{S}^-, \text{Cs}^+$. This phenomenon manifests itself in two ways: (a) The solution of a two living-ends polymer is less reactive than a similar solution containing a one living-end—because the concentration of the most reactive $\sim\sim\sim\text{S}^-$ ions in the former is lower than in the latter; (b) the conductance of the former is much higher than that of the latter since it contains more of the mobile Cs^+ ions, in addition to the triple ions which also contribute to the electric transport. The corollary of this behaviour is seen in Table 2—the two living-ends polymer of $\text{DP} \sim 25$ having Cs^+ counterions shows an abnormally high apparent K_{diss} , if determined from the conductance measurements, and the apparent K_{diss} determined by its reactivity is abnormally low. In fact, a mathematical treatment of this problem, presented in refs. 14b and 72, permits us to calculate the cyclization constant, K_c , and the propagation constant of the triple

ion. The latter was found to be ~ 2000 l./mole-sec—*i.e.* this type of triple ion is much more reactive than an ion pair, although it is less reactive than a free ion.

The cyclization constant, K_c , was found to be ~ 5.5 for $\text{DP} \sim 25$. Its value depends on the length of the chain and its flexibility. Therefore, the study of K_c dependence on DP may be valuable for characterizing the hydrodynamic behaviour of low molecular weight polymers.

The formation of triple ions shows the complexity encountered in the kinetics of anionic propagation. We learned that free ions and ion pairs contribute to the reaction, and that the latter may exist in various forms characterized by different degrees of solvation. The triple ions represent still another species which should be taken into account when dealing with relatively concentrated solutions or with systems containing a large excess of a dissociable salt, *e.g.* tetraphenylboride. The complications arising under these conditions have been discussed previously. For example, in addition to reactive triple ions, one may anticipate the presence of the unreactive triple ions, such as $\text{Na}^+, \text{BPh}_4^-, \text{Na}^+$. Their formation may lead, however, indirectly to an increase in the reactivity because the concentration of the highly reactive living free ions, *e.g.* $\sim\sim\sim\text{S}^-$, may increase as a result of binding of the Na^+ ions. It may be also necessary to consider the formation of such triple ions as $\sim\sim\sim\text{S}^-, \text{Na}^+, \text{BPh}_4^-$, which probably are more reactive than the $\sim\sim\sim\text{S}^-, \text{Na}^+$ pair. One realizes, therefore, how complex such a system may be.

POLYMERS POSSESSING ONE- OR TWO-LIVING ENDS

Previous discussion should draw our attention to an important difference between the one and two living ends polymers. For a low molecular weight polymer, *e.g.* for a living polystyrene of $DP \sim 25$, the two active ends are on the average in a distance of $\sim 15 \text{ \AA}$ from each other. From the kinetic point of view, such a system is equivalent to about 0.1 M solution (one molecule in a sphere of about $15 \text{ \AA}$ radius). Therefore, in a dilute solution any permissible reaction between these two ends, *i.e.* an *intramolecular* process, should be much faster than an *intermolecular* reaction.

An interesting example of such a reaction has been discovered recently in Syracuse. It was shown by Khanna, Levy and Szwarc⁷³ that anthracene reacts with living polystyrene giving an addition product.

The kinetics of this addition has been recently investigated⁷⁴ and it was found that, in the presence of an excess of anthracene, a quantitative reaction takes place with a one living-end polymer, the process being completed in less than a second. However, only one-half of living ends react rapidly if a two living-ends polymer is used; the remaining ends eventually react, albeit very slowly, and the quantitative conversion is completed in about half an hour. Further studies of this interesting system conclusively proved⁷⁵ that an association may take place between a living end, $\sim S^-, Na^+$, or $\sim S^-, K^+$, and an anthracenated end yielding a physical associate;

The associate reacts only slowly with the excess of anthracene giving two anthracenated polymers,

In a system containing one living-end polystyrene, the reaction with anthracene and the physical association are both intermolecular and, in the presence of an excess of anthracene the addition is faster and, therefore, more probable, than the physical association. The physical association becomes, however, intramolecular in a system containing two living-ends polymers and therefore it competed most efficiently with anthracene addition to the non-anthracenated end.

The fast intramolecular reaction between the two ends of a polymer

should be kept in mind whenever one uses two living-ends polymers as reagents. For example, two living-ends polymers may be carboxylated to form dicarboxylic acids. The intramolecular reaction might cause, however, some complications, *e.g.*

Similarly, one should be careful in interpreting some kinetic results obtained with two living-ends polymers. For example, kinetics of polymerization of $\sim\text{S}^-\text{Li}^+$ in styrene showed that the propagation is proportional to a square root of living-end concentration¹⁸ because the living-ends are associated into dimers and only the non-associated polymers are active. It would be interesting to repeat this study with a low molecular weight two living-ends lithium polystyrene. In this case the propagation is expected to be first order and, for the same concentration of living-ends, much slower than the reaction of a one living-end polymer. It has been reported⁷⁶ that living sodium polystyrene propagates in benzene according to the first order law. However, since the investigated polymer possessed two living-ends per chain, the interpretation of the result may be ambiguous.

It is important, therefore, to investigate in each system the extent of intramolecular association of two-living ends polymers. Neither $\text{Na}^+, \sim\text{S}^-\sim\text{S}^-, \text{Na}^+$, nor $\text{Na}^+, \sim\text{S}^-\sim\text{S}^-$ undergo an intramolecular association in THF. Moreover, the conductivity and the reactivity of the one-ended and two-ended living polystyrenes were shown to be the same.⁵⁴ It has also been established by Mr Shinohara (Syracuse) that the reactivities of both living polymers (one-ended and two-ended) is the same in dioxan. This indicates that no association takes place even in this low-dielectric constant solvent. More work along these lines is desirable.

ASSOCIATION OF ORGANO-METALLIC COMPOUNDS

Association of organolithium compounds is more thoroughly investigated than of any other organometallic compound. The subject has been reviewed recently by Margerison and Newport⁷⁷ and again by Bywater⁷⁸. There is little doubt that in hydrocarbon solvent butyl lithium and ethyl lithium are hexameric, *t*-butyl lithium is tetrameric and at least in benzene, polystyryl lithium is dimeric. The state of agglomeration of other compounds is less certain, *e.g.* it is probable that poly-isoprenyl lithium is mainly trimeric.⁷⁸ Even less is known about the mixed associates, *e.g.* that of butyl or ethyl lithium with polystyryl lithium.

The agglomeration is of a great importance for interpreting kinetic results concerned with the initiation or propagation of polymerization involving Li^+ counterions. The subject is thoroughly discussed in a recent review by Bywater⁷⁸ and therefore will not be treated here. It should be stressed, however, that the interpretation of kinetic results may be ambiguous. For example, it is commonly assumed that the initiation and propagation are

carried out by monomeric species. Therefore, the order of the kinetic reaction is interpreted in terms of simple equilibria, such as

It is inconceivable that the hexamers and monomers are the only forms of BuLi in the solution. Others, such as dimers, trimers, *etc.*, should be also present. The concentration of $(\text{BuLi})_1$, is correctly given by the $1/6$ — root of the hexamer concentration, whatever the concentration of other species, if the system is at equilibrium. However, if the concentrations are determined by the stationary state, then the dependence of $[(\text{BuLi})_1]$ upon total BuLi may acquire different forms depending *e.g.*, on the total concentration of the lithium compounds. The above remarks apply to other systems involving Li, and it is my feeling that much more thorough work is needed before the problem will be finally clarified.

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