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Living Polymers: A Tool in Studies of Ions and Ion-Pairs

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Living Polymers and Their Significance

The linking of small molecules, referred to as monomers, into a giant molecule is known as polymerization, and polyaddition provides an example of such a reaction. Conventional polyaddition consists of three basic steps. Reactive centers are formed first and to these centers molecules of monomer may be added. The subsequent consecutive addition of monomer produces chains of segments, each possessing an active end group which is regenerated by every linking step. Finally, the growth of each polymer stops because of some reaction which destroys the active end groups. Therefore, "dead polymers" are the ultimate products of the overall process in which macromolecules are born in initiation, grow through propagation, and die in termination.

There are conditions under which spontaneous termination may be avoided and the reaction then yields "living polymers" (*1*)—macromolecules able to resume their growth whenever a suitable monomer is added to their solution. The lack of termination does not imply, however, an unlimited growth of the living polymer. In any system the amount of monomer needed for growth is finite; consequently the propagation ceases when the supply of monomer is exhausted, although the polymer still retains its activity. For the same reason living polymers do not become infinitely long.

Novel synthetic, thermodynamic, and kinetic studies become feasible because of the availability of living polymers. The subsequent techniques that have been developed provide methods for the synthesis of polymers of uniform molecular weight and permit the experimenter to distribute different monomers along the polymer chain according to his wishes. Hence, one can prepare block polymers of preconceived patterns (*2*). The high reactivities of living polymers make it possible to attach functional groups to one or both of their ends, and this procedure has led to many new and useful products. Star- and comb-shaped polymers of controlled and predesigned structures have been produced through the application of the living polymer technique. Numerous references to papers describing the methods in which living polymers are used and reporting the results of synthetic studies may be found in a recent monograph (*3*, chapter 2).

The ability of living polymers to grow implies that they also have the capacity to depropagate spontaneously, this being the consequence of the principle of microscopic reversibility. Hence, any solution of living polymers eventually attains a state in which an equilibrium is established between the polymer and its monomer; the ultimate concentration of the monomer determines then the relevant equilibrium constant of propagation. This property of the system allows one to study various problems pertaining to the thermodynamics of propagation (*3*, chapter 3).

Finally, the lack of termination provides a simple method for the determination of the rate constants of homopropagation and copropagation (*4*). Homopropagation does not affect the concentration of living polymers but merely increases their length, and therefore whether their concentration is determined before, during, or after completion of the reaction is immaterial—the same value would be found in each case. Although propagation is a bimolecular reaction, in a living polymer system it obeys pseudo-first-order kinetics—only the concentration of monomer varies with time. This feature simplifies kinetic studies and facilitates investigation of the effects of solvents, additives, living polymer concentration, and other variables upon the bimolecular propagation constant, k_p, which may be defined as the pseudo-first-order constant divided by the total concentration of living polymers.

Kinetic studies of the propagation of living polymers have contributed substantially to our understanding of ionic reactions in organic solvents and shed much light upon the nature of ionic species formed in aprotic media. In the following sections I shall examine these topics and then compare the conclusions with those derived from studies in which alternative approaches to the above problems have been used.

Kinetics of Propagation of Living Polystyrene; Ions and Ion-Pairs

The active end groups of many living polymers are ionic in character. In fact, most of the published studies pertaining to the kinetics of living polymer propagation were performed with carbanions such as living polystyrene,

$$-CH_2CH(C_6H_5)CH_2\bar{C}H(C_6H_5) = \sim\sim\sim S^-$$

In aprotic solvents, say, in ethers, the carbanions may exist in a variety of forms: as free anions, ion-pairs, triple-ions, agglomerates of ion-pairs, or associates of ion-pairs with various com-

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plexing agents. For example, polymerization of living polystyrene may be propagated by free $\sim\sim\sim S^-$ anions, that is,

$$\underset{n\text{-mer}}{\sim\sim\sim S^-} + \text{styrene (S)} \xrightarrow{k_-} \underset{n+1\text{-mer}}{\sim\sim\sim S^-}$$

where k_- characterizes the reactivity of the free ion. Alternatively, the propagation may be carried out by ion-pairs, say, $\sim\sim\sim S^-,Na^+$, and such a reaction proceeds with another rate constant, $k_\pm$,

$$\underset{n\text{-mer}}{\sim\sim\sim S^-,Na^+} + S \xrightarrow{k_\pm} \underset{n+1\text{-mer}}{\sim\sim\sim S^-,Na^+}$$

The propagation constant $k_\pm$ depends on the nature of the cation, because cations are inherent parts of ion-pairs. Therefore, different values of $k_\pm$ are expected for $\sim\sim\sim S^-,Li^+$, $\sim\sim\sim S^-,Na^+$, or $\sim\sim\sim S^-,Cs^+$. Other species may also contribute to the propagation, for example, triple-ions such as $\sim\sim\sim S^-,Cs^+,{}^-S\sim\sim\sim$, quadrupoles, solvated ion-pairs and others, the growth of each species being characterized by its distinct propagation constant.

The various forms of carbanions coexist in equilibrium with each other. The observed propagation constant, k_p, is therefore a weighted average of the individual rate constants of all the species present in the system, the weighting factors being the mole fractions of a respective species. The equilibrium established between them is not perturbed by the propagation because growth does not alter the character of the growing entity. In a special case, when only one kind of living polymer is present in the polymerizing system, the observed k_p has a constant value independent of its concentration and equal to its characteristic rate constant.

The latter case is exemplified by the polymerization of living polystyrene in dioxane. The low dielectric constant (2.2) of this ether hinders the dissociation of ion-pairs into free ions, and, therefore, the concentration of free ions is vanishingly small in this medium. The association of ion-pairs into higher agglomerates is also negligible because, in spite of its low dielectric constant, dioxane is a powerful solvating agent which interacts with the pairs and prevents their association. Consequently, only the ion-pairs of living polystyrene are present in this ether, and the observed propagation constants, k_p, are indeed independent of their concentration *(5–7)*. The values of the respective $k_\pm$'s are collected in Table 1. They increase with increasing atomic number of the alkali cations; that is, the reactivity is the lowest for the Li^+ salt and the highest for $\sim\sim\sim S^-,Cs^+$. The significance of this finding will be considered later.

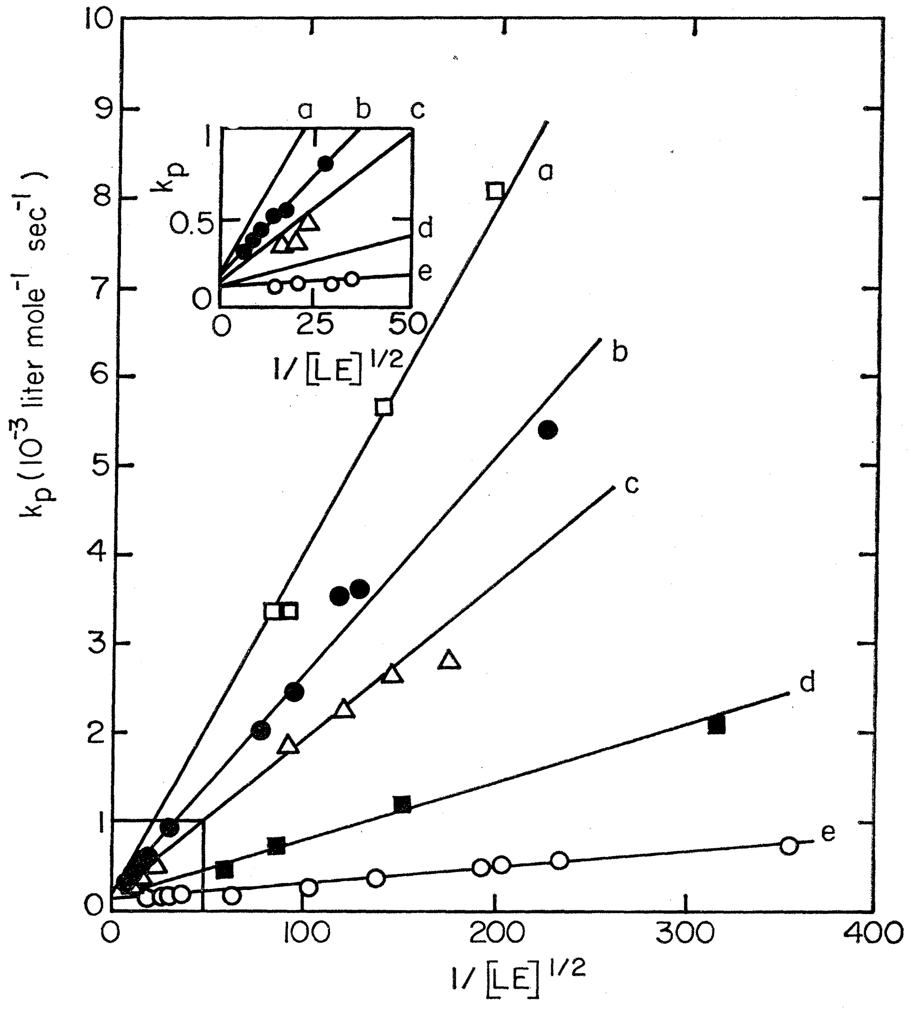


Fig. 1. Plot of the observed propagation constant k_p of living polystyrene versus the reciprocal of the square root of the growing end concentration, $1/[LE]^{\frac{1}{2}}$. Solvent, THF; temperature, 25°C. Curve *a*, Li^+ salt; curve *b*, Na^+ salt; curve *c*, K^+ salt; curve *d*, Rb^+ salt; curve *e*, Cs^+ salt. The intercepts (see insert) give the respective $k_\pm$, and the decreasing slopes manifest the decreasing dissociation of the $\sim\sim\sim S^-$,alkali$^+$ salt ($Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$).

The behavior of polystyrene salts is very different if the reaction is performed in tetrahydrofuran (THF) *(8–10)*. The high solvating power of this ether, coupled with its relatively high dielectric constant (7.4), causes a significant dissociation of ion-pairs into free ions and both contribute then to the polymerization. Let *f* be the fraction of living polymers dissociated into free $\sim\sim\sim S^-$ anions and let k_- and $k_\pm$ be the propagation constants of the free carbanions and of the $\sim\sim\sim S^-$,-alkali+ ion-pairs, respectively. The observed propagation constant is given by

$$k_p = (1 - f)k_\pm + f\,k_-$$

and its value depends on the concentration of living polystyrene, [LE], because its variation affects *f*. In view of the equilibrium,

$$\sim\sim\sim S^-,\text{alkali}^+ \overset{K_D}{\rightleftharpoons} \sim\sim\sim S^- + \text{alkali}^+$$

one finds that

$$f^2/(1-f) = K_D[LE]^{-1}$$

For $f \ll 1$ the approximation

$$f = (K_D/[LE])^{\frac{1}{2}}$$

is justified, and under such conditions k_p is a linear function of $[LE]^{-\frac{1}{2}}$, that is,

$$k_p = k_\pm + (k_- - k_\pm)\,K_D^{\frac{1}{2}}\,[LE]^{-\frac{1}{2}}$$

The above relationship is illustrated by the results presented in Fig. 1. The intercept of each line gives the value of the pertinent $k_\pm$, and the slope is identified with the composite constant $(k_- - k_\pm)\,K_D^{\frac{1}{2}}$.

The nature of the cation affects the properties of ion-pairs and hence it

Table 1. Propagation constants, $k_\pm$, of alkali salts of living polystyrene, $\sim\sim S^-$,alkali$^+$, in dioxane at 25°C. Temperature dependence of the sodium salt, $E_\pm = 9$ kilocalories per mole; $A_\pm = 10^7$ liters per mole per second (*6*).

Cation	$k_\pm$ (M^{-1} sec^{-1}) (*5*)	$k_\pm$ (M^{-1} sec^{-1}) (other published values)
Li^+	0.9	
Na^+	3.4	3–5 (*6*)
K^+	20	28 (*7*)
Rb^+	21.5	34 (*7*)
Cs^+	24.5	15 (*7*)

Table 2. Dissociation constants of the living polystyrene salts in THF at 25°C determined from kinetic and conductometric studies (*8*).

Cation	K_D (kinetic) (× 10^7)	K_D (conductometric) (× 10^7)
Li^+	2.2	1.9
Na^+	1.5*	1.5
K^+	0.8	0.7
Rb^+	0.11	
Cs^+ (one-ended)	0.021	0.028

* A value of 0.8 is reported in reference (*10*).

influences the values of K_D and $k_\pm$. In fact, for the alkali salts of living polystyrene in THF both $k_\pm$ and K_D decrease in the sequence:

$$Li^+ > Na^+ > K^+ > Cs^+$$

Hence, the trend in $k_\pm$ observed in THF is the reverse of that found in dioxane.

The participation of the free $\sim\sim S^-$ ions in the polymerization carried out in THF has been confirmed by studies of the effects exerted upon its rate of propagation by salts sharing a common counter-ion with the living polystyrene. For example, the propagation of $\sim\sim S^-,Na^+$ in this ether is drastically reduced when an excess of sodium tetraphenylboride is added to a dilute solution of the polymer (*8–10*). Alkali tetraphenylborides dissociate in THF to a much greater extent than the corresponding salts of living polystyrene (*11*). Thus, virtually all the free sodium ions present in such polymerizing solution result from the dissociation of the boride; their concentration may therefore be calculated if the dissociation constant of the boride and its concentration are known. Knowledge of the dissociation constant of the salt of living polystyrene is not needed. Under these conditions, the fraction f of the free $\sim\sim S^-$ ions is given by $K_D/[Na^+]$, and hence

$$k_p = k_\pm + (k_- - k_\pm)K_D \times [Na^+]^{-1}$$

that is, the observed propagation constant is linear with the reciprocal of $[Na^+]$. The validity of this relation is demonstrated in Fig. 2. The concentration of Na^+ ions may be varied by changing the concentration of the boride while the concentration of living polystyrene may remain constant.

The results obtained in the presence of boride provide more accurate values of $k_\pm$ than those derived from experiments performed in the absence of the salt. This is clearly seen if one compares Figs. 1 and 2. Because the line shown in Fig. 2 is relatively flat, whereas those of Fig. 1 are steep, the extrapolation to zero is more accurate for the former than for the latter. Moreover, the combined results of experiments performed in the presence and in the absence of the salt permit us to calculate the absolute values of k_- and K_D from kinetic data only. Indeed, if S_1 and S_2 denote, for example, the slopes of the lines pertaining to the sodium salt shown in Figs. 1 and 2, respectively, then

$$K_D = (S_2/S_1)^2$$

and

$$k_- - k_\pm = S_1^2/S_2$$

The K_D values obtained from the kinetic studies are collected in Table 2 where, for the sake of comparison, the dissociation constants derived from conductometric investigations are also included (*11, 12*). Both sets of data are in good agreement.

The behavior of living polystyrene in other ethereal solvents such as dimethoxyethane (DME), tetrahydropyrane (THP), or methyl tetrahydrofuran resembles that observed in THF. Both free ions and ion-pairs participate in polymerization performed in these media and the results have made it possible to determine values of the respective $k_\pm$, k_-, and K_D (*13–16*). Interestingly, the propagation constants, k_-, of the free $\sim\sim S^-$ ions are hardly affected by the nature of the ethereal solvent, as shown by the data in Table 3. Moreover, the temperature dependence of k_- indicates that the activation energy of this reaction is also only slightly influenced by the choice of ether, its value being 5 to 6 kilocalories per mole. These observations indicate that the interaction of carbanions with the ethers is relatively weak. On the other hand, the values of K_D vary enormously for different ethereal solvents, being $14 \times 10^{-7}M$, $1.5 \times 10^{-7}M$, and about $0.002 \times 10^{-7}M$ for DME, THF, and THP, respectively.

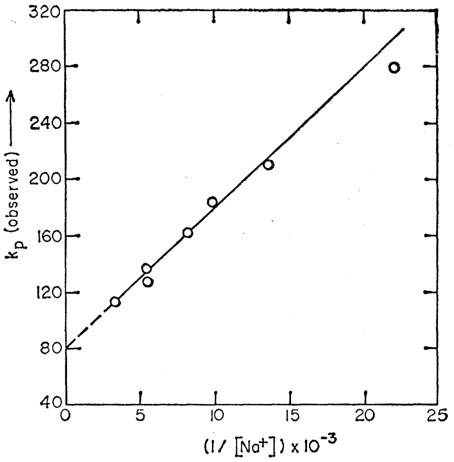
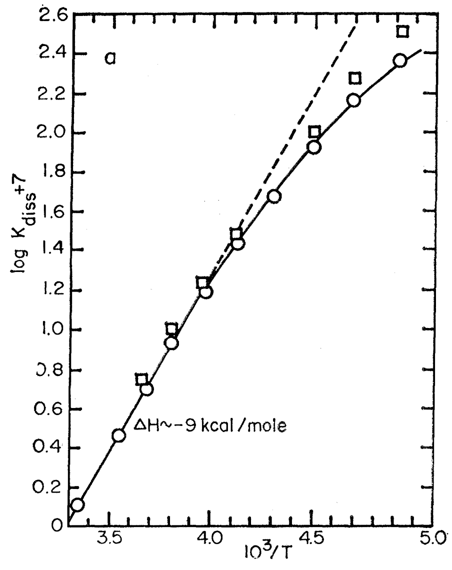


Fig. 2. Plot of the observed propagation constant k_p of sodium polystyryl in THF at 25°C in the presence of variable concentrations of sodium tetraphenylboride versus $1/[Na^+]$. A large scale is possible because the slope of the line is flatter in the presence of the boride than in its absence (see Fig. 1).

The behavior of the ion-pairs contrasts with that of the free $\sim\sim S^-$ anions. For example, at 25°C the propagation constants, $k_\pm$ (in liters per mole per second), of sodium polystyrene is about 3 to 4 in dioxane, 12 to 14 in THP, 80 to 90 in THF, and about 3600 in DME. Furthermore, the gradation of $k_\pm$'s for a series of salts, namely, $\sim\sim S^-,Li^+$,$\sim\sim S^-,Na^+$, . . ., $\sim\sim S^-,Cs^+$, depends on the nature of the solvent. Thus, in dioxane the least reactive is the lithium salt and the most reactive is the cesium salt. The reverse order of reactivities is found in THF, and still more complex gradations are observed in other solvents. These observations led to the belief that the structure of ion-pairs depends on the solvent and that different kinds of ion-pairs may coexist in the same ether. Let us examine, therefore, the nature of ion-pairs in ethereal solvents.

The Nature of Ion-Pairs

The concept of ion-pairs was introduced in 1926 to account for the low conductance of strong electrolytes in nonaqueous solutions (*17*), but 35 years passed before the first direct evidence for their existence was provided. Studies of radical-ions showed that the electron spin resonance (ESR) spectrum of the paramagnetic sodium naphthalenide in THF consists of 25 lines arising from the interaction of



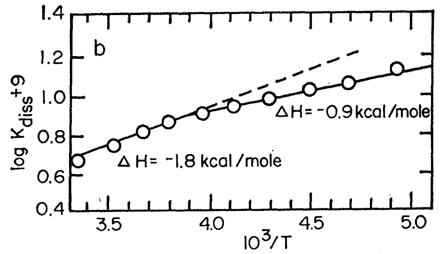


Fig. 3. (a) Van't Hoff plot of the equilibrium constant of dissociation, $K_{\rm diss}$, of the sodium salt of living polystyrene in TFH. □, One living end; ○, two living ends. (b) Van't Hoff plot of the equilibrium constant of dissociation of the cesium salt of living polystyrene in THF.

the odd electron with the four α-protons and four β-protons of the naphthalene moiety (*18*). Subsequently, closer examination revealed that each of the 25 lines is split further into four equally intense lines (*19*), proving that the odd electron interacts not only with the protons but also with the ^{23}Na nucleus endowed with 3/2 spin. Hence, a Na+ cation is associated with the naphthalene $\bar{\cdot}$ radical-anion, and the sharpness of the quadruplets demonstrates that the partners maintain their association for at least 10^{-5} second. The ion-pairs exist therefore as stable, thermodynamically distinct species and not as fleeting, continuously exchanging associates.

In the intervening years our knowledge of ion-pairs has been greatly extended through ESR studies. Splittings arising from the interactions involving other nuclei, for example, ^{7}Li, ^{39}K, or ^{133}Cs have been reported, demonstrating that these cations can also form ion-pairs. The shape of the relevant lines revealed valuable information about the dynamics of processes involving ion-pairs and indicated that these species may exist in more than one form, each being characterized by its own splitting constant (*20*).

The existence of different forms of ion-pairs was, in fact, visualized much earlier since Sadek and Fuoss (*21*) and Winstein *et al.* (*22*) simultaneously reached this conclusion in 1954, although each group of investigators utilized a different experimental and conceptual approach in their work. For the sake of our discussion it seems beneficial to reconstruct the argument developed by Sadek and Fuoss (see also *3*, chapter 5).

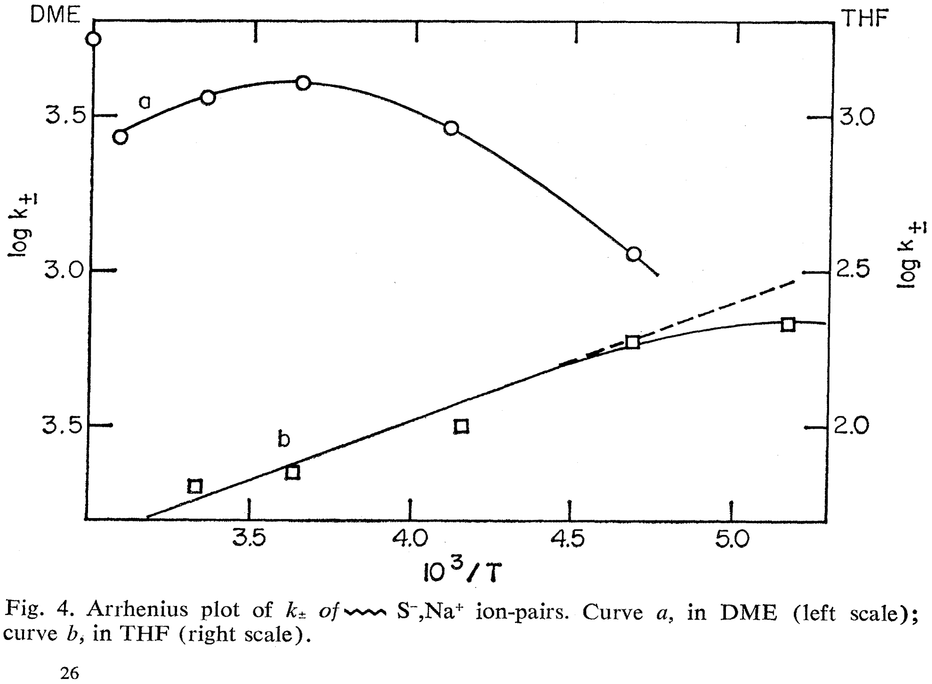


Fig. 4. Arrhenius plot of $k_{\pm}$ *of* ∿∿∿ S⁻,Na⁺ ion-pairs. Curve *a*, in DME (left scale); curve *b*, in THF (right scale).

Free ions in solutions are surrounded by solvent molecules polarized by the electric fields generated by the ionic charges. A sufficiently strong polarization and solvent-ion interaction results in the formation around each ion of a tight solvation shell which participates in its motion. Development of such a shell is reflected in the fact that the Stokes radius of the ion is substantially greater than that anticipated for the bare ion. For example, in THF the Stokes radius of the small Na+ ion is greater than 4 angstroms whereas that of the large Cs+ ion is only 2.4 angstroms (*11*). Apparently, Na+, but not Cs+, is surrounded in THF by a tight solvation shell.

An ion possessing a tight solvation shell may approach a counter-ion without hindrance until its solvation shell contacts the partner. Thereafter, either the associate maintains its structure as a loose, solvent-separated ion-pair, or the solvent molecules separating the partners are squeezed out and then a tight contact ion-pair is formed. Such a result implies that solvent-separated ion-pairs may exist only in those media in which the free ions acquire tight solvation shells; otherwise, only tight contact ion-pairs are produced. Hence, on the basis of Stokes radii we may conclude that the cesium salt of living polystyrene forms only contact ion-pairs in THF whereas the sodium salt in THF may exist, at least partially, in the form of loose, solvent-separated pairs as well as in the form of tight pairs.

If solvent-separated ion-pairs coexist with tight ion-pairs, the interaction of the solvated ion with its counter-ion must be sufficiently powerful to allow for squeezing out the solvation shell. For example, if the solvated ion is paired with a bulky counter-ion the gain in Coulombic energy arising from the coming together of the partners into close contact may not be sufficient to accomplish the destruction of the solvation shell. Therefore, such pairs virtually exist only in the loose form (*23*).

The principles discussed above are important in accounting for the behavior of living polystyrene. Conductance studies of its salts in THF (*10*) indicate that sodium polystyryl exists in this ether mainly in the form of tight ion-pairs. Inspection of Fig. 3 shows that the exothermicity of its dissociation is high, about 8 to 9 kilocalories per mole, whereas the dissociation of ∿∿∿S−,Cs+ produces less than 2 kilocalories of heat per mole. It was pointed out earlier that free Na$^+$ ions, but not Cs$^+$ ions, acquire tight solvation shells in THF. Hence, if ∿∿∿S$^-$,Na$^+$, like ∿∿∿S$^-$,Cs$^+$ forms mainly tight pairs in THF, the dissociation of the former, but not of the latter, should generate much heat as a result of the powerful solvation of the free Na$^+$ ions. Such a gain is not expected for the loose, already solvated pairs.

A word of warning may be desired. Introduction of gaseous ions into ethereal solvents involves Born's solvation energy of 10 to 30 kilocalories per mole while the effects with which we are concerned here amount to few kilocalories per mole only. Changes in Born's solvation energies may distort seriously some of the observed exothermicities, nevertheless the results discussed above seem to demonstrate clearly the phenomena described in this account.

The above observations do not imply that all the ∿∿∿S$^-$,Na$^+$ ion-pairs exist in the tight contact form in THF. A small fraction of them may be present in the form of loose, solvent-separated pairs, and indeed the kinetics of polymerization provides strong evidence for the existence of some loose pairs.

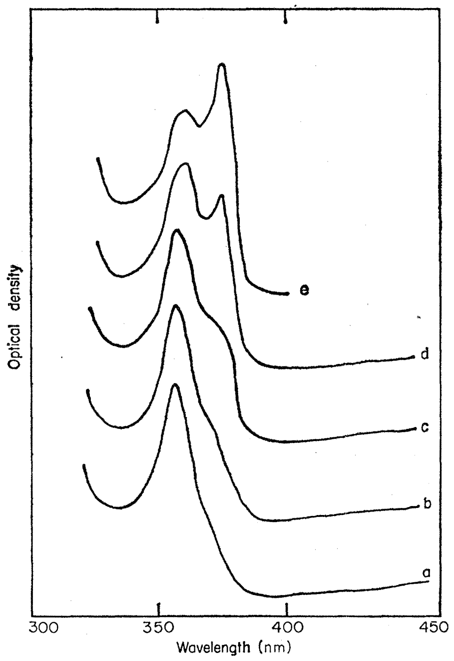


Fig. 5. Spectra of sodium salts of fluorenyl carbanions in THF at the following pressures (in atmospheres): *a*, 1; *b*, 1000; *c*, 2000; *d*, 3000; *e*, 4000. The tight pair corresponds to the 356-nanometer peak, the loose pair to the 373-nanometer peak. For the sake of clarity the zero level is progressively shifted with increasing pressure.

Table 3. Propagation constants, k_-, of the free ∿∿∿S$^-$ anions in various ethereal solvents at 25°C.

Solvent	$k_-(M^{-1}\ \mathrm{sec}^{-1})$	E_- (kcal/mole)	Reference
THF	63,000–65,000	5.9	(*8*)
THP	60,000–70,000	5.1	(*13*)
DME	~40,000	~5.0	(*14*)
THF-dioxane mixtures	~60,000		(*15*)
THF-benzene mixtures	40,000–70,000		(*16*)

The propagation of ∿∿∿S$^-$,Cs$^+$ in THF behaves "normally"; the process requires a positive activation energy of about 5 kilocalories per mole (*10*). The propagation of ∿∿∿S$^-$,Na$^+$ ion-pairs is strikingly different (*10*). As seen from Fig. 4, the observed propagation constant, $k_\pm$, increases with decreasing temperature, a formal implication of a negative activation energy for the overall process. This anomaly suggests that two types of ∿∿∿S$^-$,Na$^+$ ion-pairs participate in the propagation, namely, the slowly growing, tight ion-pairs and the highly reactive, rapidly growing, loose ion-pairs. Denoting the equilibrium constant of the reaction

$$∿∿∿\mathrm{S}^-,\mathrm{Na}^+(\text{tight}) + n\ \mathrm{THF} \rightleftharpoons ∿∿∿\mathrm{S}^-(\mathrm{THF})_n,\mathrm{Na}^+(\text{loose})$$

by K_S and the propagation constants of the tight and loose pairs by k_t and k_l, respectively, we find the observed propagation constant to be

$$k_\pm = (1-\gamma)\,k_t + \gamma k_l$$

Here γ, the fraction of the pairs present in the loose form, is given by

$$\gamma(1-\gamma)^{-1} = K_S$$

that is,

$$\gamma = K_S/(1+K_S)$$

If k_l is $\gg k_t$, the approximation

$$k_\pm = k_l K_S/(1+K_S)$$

is valid and the apparent activation energy is then

$$E_\pm = E_l + \Delta H_S/(1+K_S)$$

E_l denotes the genuine activation energy of propagation of the loose pairs, and ΔH_S is the heat associated with the conversion of the tight pairs into the loose ones. The quantity ΔH_S is negative and therefore $E_\pm$ is < 0 if E_l is $< -\Delta H_S$, provided K_S is small. Apparently, these relations are fulfilled in the polymerization of ∿∿∿S$^-$,Na$^+$ in THF. On the basis of the acceptance of the above mechanism and the collation of all the available data, it was possible to show that k_l is ~ 30,000 liters per mole per second; that is, the loose pairs are much more reactive than the experimentally observed $k_\pm$ would imply.

Since ΔH_S is negative, cooling the solution increases K_S. Therefore, at a sufficiently low temperature, T',

$$E_l = \Delta H_S/(1+K_S')$$

and hence cooling below T' should lead to a decrease of $k_\pm$. Consequently, at $T = T'$ the Arrhenius line, log $k_\pm$ versus $1/T$, has a maximum. Such a maximum cannot be observed when the polymerization is carried out in THF, because T' is lower than the melting temperature of this ether. However, curve *a* of Fig. 4 shows that the maximum was observed (*14, 24*) for the polymerization performed in DME.

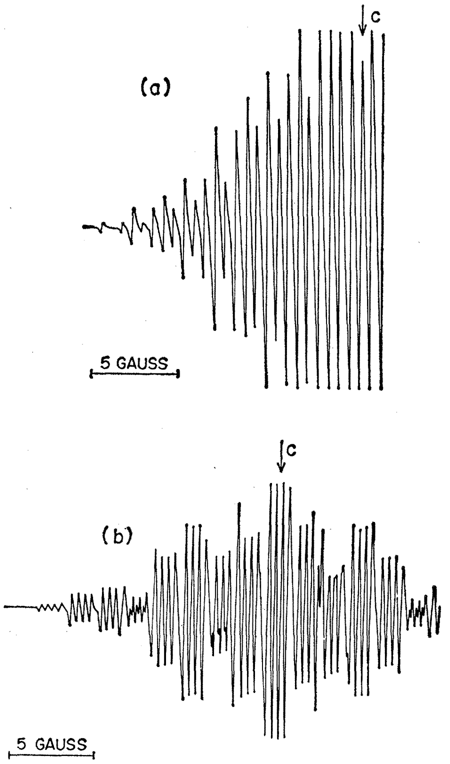


Fig. 6. Electron spin resonance spectra of sodium naphthalenide in THP at 27°C. (a) Spectrum in the absence of glyme, $a_{\mathrm{Na}} = 1.2$ gauss. (b) Spectrum in the presence of $10^{-3}M$ tetraglyme, $a_{\mathrm{Na}} = 0.4$ gauss. Neither the concentration of the radical-ions nor the sensitivity of the spectrograph were changed. The arrows denote the centers of the spectra.

The latter is a more powerful solvating agent than THF, its high solvating power being due to the bidentate nature of its molecule. Therefore, the fraction of the reactive loose ∿∿∿S^-,Na^+ ion-pairs is much greater in DME than in THF, and this is reflected in the $k_\pm$ values. For the polymerization of ∿∿∿S^-,Na^+ in DME at 25°C $k_\pm = 3600$ liters per mole per second because 18 percent of all the ∿∿∿S^-,Na^+ ion-pairs present in this solvent are in the form of reactive loose pairs ($k_1 \sim 20,000$ liters per mole per second). On the other hand, only 0.3 percent of the ion-pairs are in the loose form when ∿∿∿S^-,Na^+ is dissolved in THF. Consequently $k_\pm$ is only 80 to 90 liters per mole per second in the latter solvent, although the k_1 of the loose pairs in THF ($\sim$ 30,000 liters per mole per second) is slightly larger than in DME.

An interesting piece of spectroscopic evidence in support of the coexistence of two types of ion-pairs was found in our laboratory by Hogen-Esch and Smid (*25*). Alkali salts of fluorenyl carbanions have two absorption peaks: one at about 356 nanometers (for the Na^+ salt) and the other at 373 nanometers. Their relative intensities are not affected by dilution, but they depend on the nature of solvent and vary with temperature; if the solution is cooled, the 373-nanometer peak grows at the expense of the 356-nanometer peak. The two peaks were attributed therefore to two distinct types of ion-pairs, and the evidence indicates that the 356-nanometer maximum arises from the presence of a tight pair whereas the loose pairs absorb at 373 nanometers. By means of this simple spectrophotometric technique Chan and Smid were able to quantitatively study the capacity of various ethereal solvents to convert tight ion-pairs into loose ones (*26*).

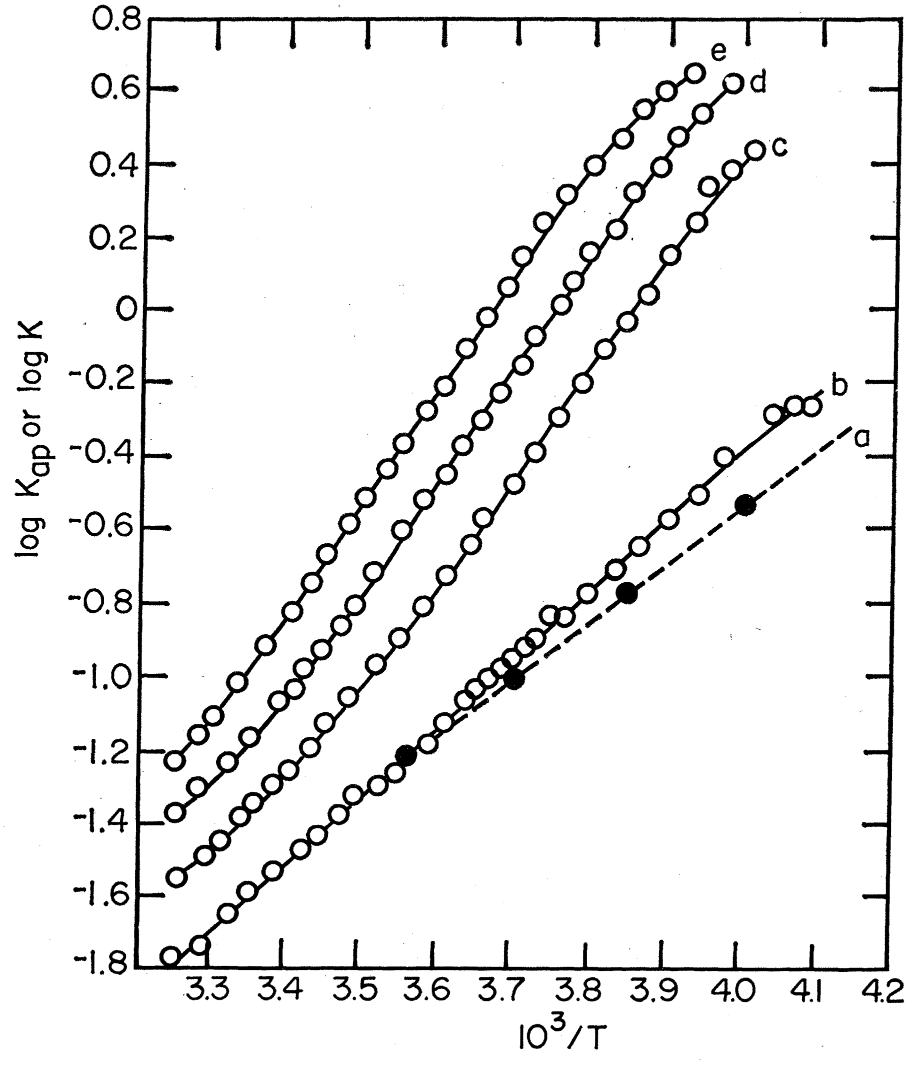


Fig. 7. The equilibrium constant $K = [B^{\cdot-},Na^+]/[B]$ and the apparent equilibrium constant, $K_{ap} = \{[B^{\cdot-},Na^+] + [B^{\cdot-},Na^+,E]\}/[B]$ for the system metallic sodium plus B(solution) $\rightleftharpoons$ ($B^{\cdot-}$,Na^+) (solution), versus $1/T$. Curves *a* and *b*, in the absence of glyme [(open circles), from reference (*29*); (solid circles) from the study by Shatenstein]; curves *c, d,* and *e,* in the presence of progressively increasing concentrations of glyme.

The different types of ion-pairs represent thermodynamically distinct species which can be characterized by their optical spectra, ESR patterns (if one of the ions is paramagnetic), and specific reactivities (for example, k_t and k_1 in the propagation of living polystyrene). We may therefore discuss the equilibria, such as that existing between tight pairs and loose pairs, as well as the rates of transformation of one type of pair into another. The equilibria may be described in terms of the usual thermodynamic parameters such as enthalpy change (ΔH), entropy change (ΔS), volume change (ΔV), and the like. For example, recent spectrophotometric studies (*27*) of the effect of pressure upon the equilibrium between tight pairs and loose pairs has made possible an evaluation of ΔV. The results (Fig. 5) demonstrate that the conversion of tight into loose pairs decreases the volume of the system because the solvent molecules arrange themselves more tightly around the ions when they become separated. This effect is analogous to electrostriction observed in aqueous solutions.

Modification of Ion-Pairs by Added Solvating Agents

In the preceding section I have discussed different types of ion-pairs coexisting in a solvent. Let us now consider systems involving only one type of ion-pair in a pure solvent, but capable of forming new types of ion-pairs on the addition of small amounts of powerful solvating (coordinating) agents. In such systems we deal with equilibria such as

$$A^+,B^- + nX \rightleftharpoons A^+,B^-,X_n$$

where X represents the solvating agent.

The most direct evidence for the formation of such a new type of ion-pair, namely, A^+,B^-,X_n, has been obtained from ESR studies. The addition of minute amounts of tetraglyme (glyme, E, is $CH_3OC_2H_4OC_2H_4OC_2H_4OC_2H_4OCH_3$) to the solution of sodium naphthalenide ($N^{\cdot-}$,Na^+) in THP led to the dramatic change of the ESR spectrum (*28*) shown in Fig.

6. The coupling constant a, arising from the interaction between the ^{23}Na nucleus and the odd electron is $\sim$ 1.2 gauss in pure THP, but, when the glyme is present, even at concentration as low as $10^{-3}M$, its value is 0.4 gauss only. Both sets of lines appear simultaneously in the spectrum if the concentration of the glyme is still lower. Such spectra, for variable concentrations of the glyme, permit one to determine the stoichiometry of the reaction, namely,

$$\mathrm{Na^+,N^{\cdot-} + E \rightleftharpoons Na^+,E,N^{\cdot-}}$$

its equilibrium constant ($\sim$ 240 liters per mole at 25°C), and the rate constants of the forward and backward processes ($\sim 10^7$ liters per mole per second and $\sim 10^5$ per second, respectively).

The formation of new species on the addition of powerful solvating agents may be also demonstrated by other experiments. For example, metallic sodium reacts with biphenyl (B) in THP solution to give sodium biphenylide ($\mathrm{B^{\cdot-},Na^+}$):

$$\mathrm{Na(metal) + B(solution) \overset{K_B}{\rightleftharpoons} B^{\cdot-},Na^+(solution)}$$

The strong absorption band of $\mathrm{B^{\cdot-},Na^+}$ ($\lambda_{max} = 400$ nanometers) permits use of a spectrophotometric technique for the determination of K_B over a wide temperature range; the results are shown graphically in Fig. 7. The addition of triglyme or tetraglyme intensifies the optical density at 400 nanometers (see Fig. 7), an indication that an additional equilibrium is established (*29*), namely,

$$\mathrm{B^{\cdot-},Na^+ + E \overset{K_E}{\rightleftharpoons} B^{\cdot-},Na^+,E,}$$

the new species again absorbing around 400 nanometers. The results have made possible the determination of the stoichiometry of the reaction (1 : 1) and the calculation of K_G, ΔH_G, and ΔS_G.

Separation of tight ion-pairs by powerful solvating agents is indicated also by the spectral changes depicted in Fig. 8. This approach was used extensively in determining the capacity of the added agents to separate tight ion-pairs (*30*).

The replacement of one solvating agent by another in a loose ion-pair was demonstrated by nuclear magnetic resonance spectroscopy (*30*). Another example of such phenomena was provided by the work of Vink *et al.* (*31*), who showed that the addition of THF to Grignard solution in optically active ethers (for example, 1-ethoxy-2-methylbutane) reduces the exalted specific rotation of the ether, an indication that THF replaces the ether in the solvation shell around the magnesium ion.

Studies of the polymerization of living polystyrene provided much information about the association of ion-pairs with some added solvating agents (*32, 33*). The results presented in Fig. 9 show a dramatic increase in the apparent propagation constant caused by the addition of minute amounts of tetraglyme to a THP solution of $\sim\sim S^-,Na^+$. In fact, two effects should be considered:

1) The conversion of the "ordinary" $\sim\sim S^-,Na^+$ ion-pairs into the more reactive "glymated" pairs is reflected by the increasing intercept of the lines as the concentration of the glyme rises.

2) The conversion of the "ordinary" free Na^+ ions into sodium ions solvated by glyme, for example, Na^+,E, shifts the equilibrium between $\sim\sim S^-,Na^+$ and $\sim\sim S^- + Na^+$ to the right because of the equilibrium between $Na^+ + E$ and Na^+,E. Consequently, the fraction of the highly reactive free $\sim\sim S^-$ ion increases, and this makes the lines steeper as the concentration of the glyme increases.

Mathematical treatment of the prob-

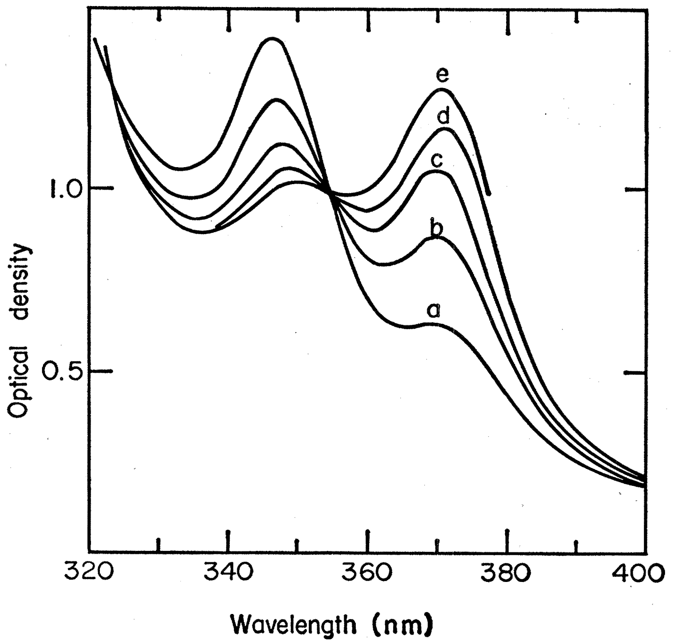


Fig. 8 (above). Conversion of a tight sodium fluorenyl pair into a loose pair by the addition of increasing amounts of dimethylsulfoxide (DMSO); DMSO concentrations (× 10^3M) were as follows: *a*, 2.36; *b*, 5.10; *c*, 8.49; *d*, 11.4; and *e*, 14.7.

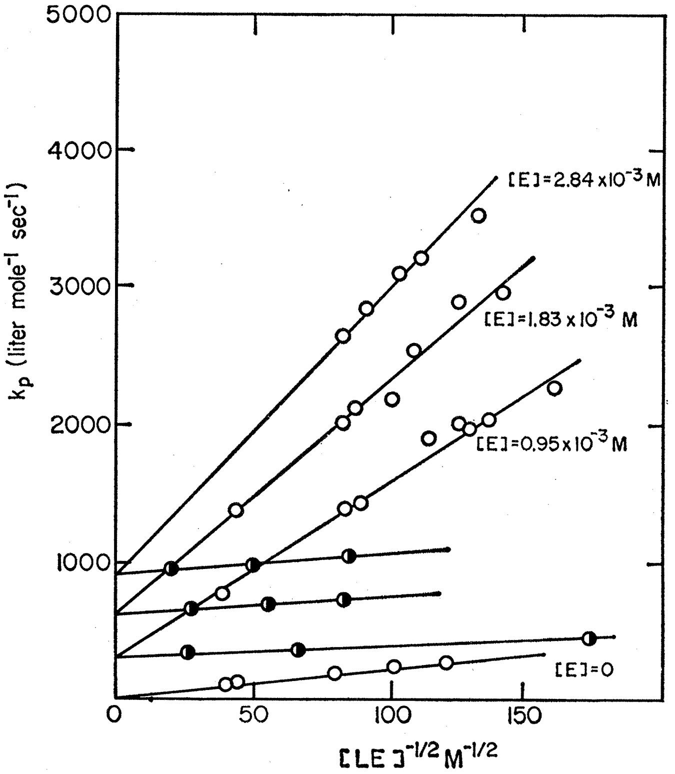


Fig. 9 (right). The effect of increasing concentrations of tetraglyme on the observed propagation constant, k_p, of $\sim\sim S^-,Na^+$ in THP at 25°C. Both the intercept and the slope of the lines increase as the glyme concentration rises. ○, In the absence of added salt (Na^+,BPh_4^-); ◑, in the presence of added salt. The latter points permit accurate determination of the intercepts of the steep lines.

lem, especially in its nonlinear region (*33*), yields from the experimental data the rate constant and activation energy of propagation of "glymated" ion-pairs, their stoichiometry, the equilibrium constant of their formation, and, interestingly enough, the stoichiometry and the equilibrium constant of the reaction

$$\mathrm{Na^+} + n\,\mathrm{E} \rightleftharpoons \mathrm{Na^+(E)}_n$$

Thus, the solvation characteristics of inorganic ions, such as $\mathrm{Na^+}$, may be derived from studies of the propagation of living polymers.

Isomerism of Ion-Pairs

Ions of a pair and the neighboring solvent molecules form a class of variable patterns, the variations being due to Brownian motion. Under some conditions two, or more, nonoverlapping groups of patterns may retain their characteristic configurations for a time greater than 10^{-10} second which is long compared to a Brownian period. Such groups of patterns may be treated as thermodynamically distinct species (*3*, chapter 5; *28*, *34*). The tight and loose ion-pairs fall into this category.

When ion-pairs are associated with a solvating agent in the solution, one may visualize patterns in which such a solvating agent occupies distinctly different positions with respect to the pair, for example, the order cation, solvating agent, anion and the order solvating agent, cation, anion. Whenever the intermediate configurations are improbable, a condition that is fulfilled for "distinct" species, the two forms represent isomeric ion-pairs. The first example of this phenomenon was described by Slates and Szwarc (*29*) and it is discussed below. A few more examples have been discovered subsequently in our laboratory.

In the preceding section the formation of $\mathrm{Na^+,B^{\dot{-}}}$ (sodium biphenylide) ion-pairs associated with triglyme or tetraglyme was discussed. The experimental data give the fractions of $\mathrm{Na^+,B^{\dot{-}}}$ and $\mathrm{Na^+,B^{\dot{-}},E}$ coexisting at various temperatures and at various concentrations of glyme. The optical spectrum of $\mathrm{Na^+,B^{\dot{-}}}$ or $\mathrm{Na^+,B^{\dot{-}}}$ (triglyme) shows only one absorption peak, namely, at $\lambda_{\mathrm{max}} = 400$ nanometers. However, in the presence of tetraglyme two close absorption peaks are discernible, one at 400 nanometers and the other at 407 nanometers, an indication of the presence of two distinct species. For each concentration of the glyme it was possible to find the temperature at which both peaks are equally intense. It was possible to show that the extinction coefficients are approximately identical for these two peaks and therefore that under such conditions the two species (absorbing at 400 and at 407 nanometers) are present in equimolar quantities. From equilibrium studies one can determine the proportion of the non-"glymated" and all the "glymated" species coexisting under these conditions; for example, $\mathrm{Na^+,B^{\dot{-}}}$ and $\mathrm{Na^+,B^{\dot{-}},E}$ are present at 20 percent and 80 percent respectively. Since $\mathrm{Na^+,B^{\dot{-}}}$ absorbs only at 400 nanometers, we must conclude that two distinct $\mathrm{Na^+,B^{\dot{-}},E}$ pairs exist, one containing a glyme molecule on the "outside" of the pair, that is, peripherally "glymated," which absorbs at 400 nanometers (30 percent), and the other pair having the glyme placed between the ions to form a loose pair, which absorbs at 407 nanometers (50 percent). Extension of these studies made possible the determination of the equilibrium constant of this isomerization as well as its ΔH and ΔS.

Studies of some electron-transfer processes (*28*) and changes observed in the spectra of the potassium salt of the fluorenyl carbanion ($\mathrm{K^+,Fl^-}$) on the addition of glyme (*35*) provided further evidence for isomerization of ion-pairs. The equilibrium constant of "glymation" of the potassium fluorenyl is high and the conversion should exceed 90 percent at a reasonably low concentration of the glyme. Nevertheless, the spectrum shows that the proportions of tight (either non-"glymated" or peripherally "glymated") and loose (separated by glyme) ion-pairs approach a constant value as the concentration of the glyme rises. Thus, two species are formed on glymation; that is,

$$\mathrm{K^+,Fl^-} + \mathrm{E} \rightleftharpoons \mathrm{E,K^+,Fl^-}$$

(for peripherally "glymated" ion-pairs) and

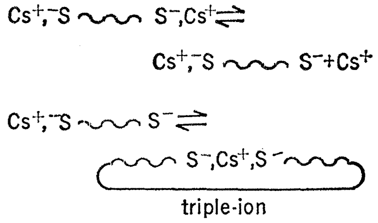
$$\mathrm{K^+,Fl^-} + \mathrm{E} \rightleftharpoons \mathrm{K^+,E,Fl^-}$$

(for ion-pairs separated by glyme). The quantitative treatment of the results fully confirmed this conclusion.

Aggregation of Ion-Pairs

Studies of the kinetics of living polymer propagation have also contributed to our knowledge of the aggregation of ion-pairs. For example, it has been shown that living lithium polystyrene is dimeric in benzene (*36*) and probably tetrameric in cyclohexane (*37*). These aggregates are unreactive and apparently do not participate directly in the polymerization which is propagated by the unassociated polymers coexisting in equilibrium with the aggregates.

Intramolecular formation of triple-ions was observed in the system living cesium polystyrene endowed with two active ends (*38*). Kinetic and conductometric studies provided data which made possible the calculation of the equilibrium constant of the cyclization which produces the triple-ions, and the rate constant of their propagation, that is,



Direct evidence for the existence of triple-ions was provided by ESR studies (*39*). For example, in the presence of sodium tetraphenylboride the hyperfine lines of the protons in the semiquinone anions were split into seven lines, an indication that two equivalent sodium nuclei interact with each anion.

Some interesting observations were made in systems involving aggregated ion-pairs. For the sake of illustration I shall mention two examples. It has been shown recently (*40*) that the sodium salt of $(\mathrm{C_6H_5})\bar{\mathrm{C}}{:}\bar{\mathrm{C}}(\mathrm{C_6H_5})$ in THF is aggregated at low temperatures. The products of its protonation are rapidly reduced by intra-aggregate electron-transfer. The formation of diamagnetic, π-bonded dimers of phenanthrosemiquinone salts requires aggregation of ion-pairs (*41*)—the free ions do not dimerize. It is hoped that further studies of ion-pairs associations will uncover many more interesting phenomena.

Conclusion

Studies of living polymers have greatly enriched our knowledge of the behavior of ions and ion-pairs in organic media. Future investigations will lead to more detailed knowledge of these interesting species. Especially, intramolecular associations or intramolecular solvation by the polymer chains provide promising field for additional studies, and one example of such phenomena was reported recently by Fisher and Szwarc (*42*).

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Millimeter-Wavelength Radio Systems

Use of millimeter wavelengths for radio systems may alleviate crowding at lower frequencies.

L. C. Tillotson

Millimeter waves, that is, that part of the electromagnetic wave spectrum between 30 gigahertz (wavelength = 10 millimeters) and 300 gigahertz (wavelength = 1 millimeter) but sometimes used loosely to include also the region between about 15 and 30 gigahertz, are beginning to attract considerable attention as a possible means for relief of the crowding which is becoming increasingly troublesome at lower frequencies. The basic fact is that, whereas the communication capacity of a band is determined by its width in hertz, the number of hertz available in a given percentage bandwidth increases directly with the carrier frequency. Thus, a 10 percent band centered at 100 gigahertz (wavelength = 3 millimeters) has as much communication potential as the entire radio spectrum up to 10 gigahertz. At present this portion of the spectrum is relatively less used than the longer-wavelength portion, for reasons which will become apparent.

Most of the features which distinguish millimeter waves from the more widely used lower frequencies are a direct consequence of the shorter wavelengths. At these shorter wavelengths it is possible (necessary) to reduce the size of most system components. High-gain, narrow-beam antennas, for example, are of modest size at millimeter wavelengths and hence are more practical at these high frequencies than at lower frequencies. On the other hand, most transmission losses increase with increasing frequency, and this creates problems, especially when millimeter waves are to be propagated through the earth's atmosphere (*1*). The challenge we face is to design around the problems in such a way as to produce a communication system which provides either a new service or performs an old task with reduced cost. The burden of this article is to indicate how this might be done.

Status of Current Technology

Millimeter-wave systems will require terminals which accept from the user in a form convenient to him the information to be carried, process (or modulate) it into a suitable format, and place it at the desired carrier frequency. Also required at intervals are repeaters, including power amplifiers, which strengthen and redirect the signal. Both of these functions require simple and inexpensive millimeter-wave electronics if systems using these frequencies are to compete successfully with alternate means to accomplish the same objectives. Until quite recently, coherent sources of millimeter-wave power have been less than ideal for system use because of high initial cost, short operating lifetime, and burdensome power supply requirements. The advent of solid-state oscillators and amplifiers operating in this portion of the spectrum, and the promise of even more power at still higher frequencies,

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