Chemical Reaction Rates Reflecting Physical Properties of Polymer Solutions

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The physical properties of high polymeric materials reflect both the properties of individual chain molecules and their mutual interaction in concentrated systems. In dilute solution, we approach separation of the chain molecules from each other, and the properties of the individual macromolecules may be investigated. Such studies are concerned, for instance, with the average molecular weight and the molecular weight distribution of polymer samples, the size and shape of the molecular chains, and the thermodynamic interaction of the polymer molecules with the solvent medium or the interaction of chain molecules carrying a high density of ionic charges along the chain backbone with mobile small counterions. The methods employed, such as osmometry, light scattering, spectroscopy, or the study of the frictional properties of the polymer solutions, are unconcerned with the chemical reactivity of the material.

This discussion is concerned with the question of whether the study of polymer solutions by the classical physical and physicochemical methods can be usefully supplemented by employing as part of the evidence the rates of chemical reactions in such systems. The results suggest that this approach may throw new light on a variety of problems such as (1) the rate with which flexible chain molecules change their shape, (2) the flexibility of randomly coiled polymer chains, (3) the distribution of mobile ions in polyelectrolyte solutions and the rate of exchange of "free" and "bound" counterions.

The Change of Shape of Randomly Coiled Chain Molecules

Long-chain molecules exist in a very large number of possible conformations which are rapidly interconverted by rotation around bonds in the chain backbone. This is the basis of the long-range elasticity characteristic of rubbers which has been the subject of extensive studies. On the other hand, studies of randomly coiled chain polymers in dilute solution have generally been concerned with the average shape of the molecules, and only very little attention has been paid to the question of how fast a given molecule can undergo conformational transitions.

Kuhn and Kuhn[1a] were the first to recognize that the height of the potential energy barriers impeding changes in molecular shape may affect the behavior of dilute polymer solutions in strong shear gradients. They introduced the concept of an "internal viscosity" of the chain molecule equal to the force, in excess of the equilibrium force of rubber elasticity, which is required to separate the chain ends at a unit rate in a medium of zero viscosity.[1b] If the internal viscosity is low, the chain will periodically change its shape as it rotates in a shear gradient, while chains in which conformational transitions are difficult will rotate as rigid bodies. Only recently has the extent of this periodic chain deformation in a shear gradient been measured by a light scattering technique and the results have demonstrated the importance of internal viscosity effects.[2] Rates of conformational transitions are also reflected in the dielectric dispersion of dilute polymer solutions.[3]

In our work we tried to determine the extent to which rotation around a given type of chemical bond is slowed down when this bond is part of the backbone of a long chain molecule. In Figure 1 we represent schematically two processes. (a) If the only change in the chain molecule is the rotation around a single bond, then a large part of the chain has to swing through the solvent, and such a process is obviously inconceivable in a viscous medium. (b) If two rotations are correlated in time, then the transition will involve only the motion of a short segment of the chain, and such a "crankshaft-like motion,"[4] originally proposed for conformational transitions in the backbone of chain molecules in bulk, has also been considered for polymers in dilute solution.[3] The requirement to correlate two conformational transitions should lead to a significant increase in the activation parameters characterizing the process, and the quantitative evaluation of such an effect was the motivation for our study.

We first used the nmr method, originally proposed by Gutowsky and Holm,[5] to compare the rates of rotation around the amide bonds in dilute solutions of piperazine polyamides (I) and in their low molecular weight analog, diacetylpiperazine (II).[6] The solvent

(1) (a) W. Kuhn and H. Kuhn, *Helv. Chim. Acta*, **29**, 71 (1946). (b) In principle, the potential energy differences between different conformers may be altered by solvation of the chain molecule and the internal viscosity may, therefore, be dependent on the solvent medium.

(2) F. R. Cottrell, E. W. Merrill, and K. A. Smith, *J. Polym. Sci., Part A-2*, **7**, 1415 (1969), **8**, 289 (1970).

(3) W. H. Stockmayer, *Pure Appl. Chem.*, **15**, 539 (1967).

(4) T. Schatzki, *J. Polym. Sci.*, **5T**, 496 (1962); *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **6**, 646 (1965), *J. Polym. Sci., Part C*, **14**, 139 (1966); B. Wunderlich, *J. Chem. Phys.*, **37**, 2429 (1962); R. F. Boyer, *Rubber Chem. Technol.*, **36**, 1303 (1963).

(5) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

(6) Y. Miron, B. R. McGarvey, and H. Morawetz, *Macromolecules*, **2**, 154 (1969).

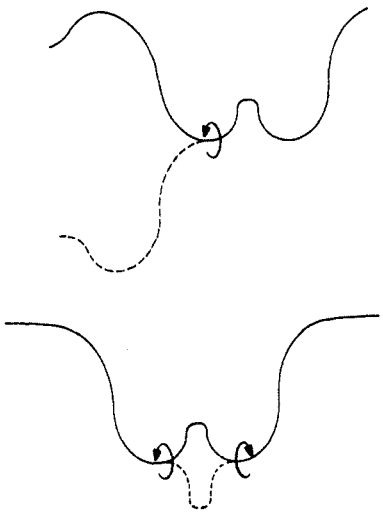
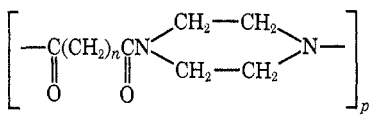


Figure 1. Schematic representation of conformational transition in a flexible chain molecule: (a) rotation around a single bond; (b) correlated rotation around two bonds.

Table I

Compound	$\delta\nu_c$, cps	T_c, °C	$\Delta G_c^{\ddagger}$, kcal/mol
Diacetylpiperazine	27.0	91 ± 2	18.5 ± 0.2
Poly(succinylpiperazine)	12.5	72 ± 2	18.0 ± 0.2
Poly(adipylpiperazine)	20.0	79 ± 2	18.1 ± 0.2
Poly(sebacylpiperazine)	19.4	79 ± 2	18.1 ± 0.2
Dibenzoylpiperazine	25	43	16
Poly(terephthalylpiperazine)	45	29	15



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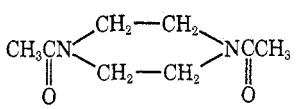
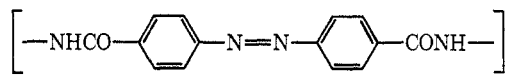


II

medium contained 92.5 wt % phenol and 7.5 wt % water. In Table I we list $\delta\nu_c$, the chemical shift at coalescence of the methylene protons cis and trans to the carbonyl, the coalescence temperature, T_c, and the free energy of activation, $\Delta G_c^{\ddagger}$, for the rotation around the amide bond at the coalescence temperature. It may be seen that the $\Delta G_c^{\ddagger}$ values are almost identical for the polymers and their low molecular weight analogs, *i.e.*, that rotation around the amide bond is not significantly slower when the bond forms part of a polymer chain backbone than when it occurs in a small molecule. This is particularly striking in the comparison of dibenzoylpiperazine with poly(terephthaloylpiperazine), a polymer containing only stiff bonds in the chain backbone.

The nmr method is limited to kinetic studies in systems of low viscosity in which spectra of good resolution can be obtained. To broaden the scope of the study and to check the conclusion arrived at using the nmr method, we investigated a system of another type which does not restrict us to polymer solutions of low concentration.

It is well known that azobenzene may be photoisomerized from the stable trans form to the cis form and that the reverse reaction, which occurs in the dark, can be followed conveniently by ultraviolet spectroscopy.[7] We have, therefore, synthesized polyamides containing in the chain backbone units of type III or IV and compared their cis–trans isomerization rates



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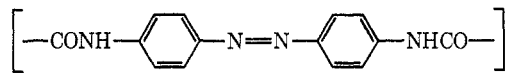

IV

with those of suitably chosen small molecules.[8] Again it was found that the isomerization rate of the azobenzene moiety is not significantly impeded by incorporation into the polymer backbone. Moreover, this rate remained unaltered at polymer concentrations corresponding to very extensive interpenetration of the chain molecules.

During the cis–trans isomerization of an azobenzene group the distance between the two carbons in the para position increases from 5.5 to 9 Å and the angle between the bonds linking this group to the rest of the chain is altered from 62 to 0°. It is obvious that such a drastic change cannot take place without an extensive conformational transition of the polymer chain backbone into which the azobenzene moiety is incorporated. We must then explain how it is possible that this restraint is without any effect on the kinetics of the process. The necessity for an extensive rearrangement of the chain as the transition state in the cis–trans isomerization is being approached will, indeed, slow down the approach to the transition state, but it will reduce equally the rate at which the strained azobenzene group returns to its ground state. We should, therefore, not expect the isomerization rate to be reduced unless the time required for the change in chain conformation to a form consistent with the transition state of the azo group is comparable with the relaxation time of the cis–trans isomerization in the absence of this added restraint.

When cis–trans isomerizations occur in short side chains attached to a polymer, then it is not surprising to observe rates similar to those in analogous small molecules. Even so, it may be somewhat unexpected that these processes occur with considerable ease in bulk polymers, even in a glassy state.[9] We have initiated a detailed study of such systems and find that the isomerization rate of azobenzene residues attached to a polymethacrylate backbone is identical with that in

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(8) D. Tabak and H. Morawetz, *Macromolecules*, **3**, 403 (1970).
(9) H. Kamogawa, M. Kato, and A. Sugiyama, *J. Polym. Sci., Part A-1*, **6**, 2967 (1968).

dilute solution when the bulk polymer is studied above the glass transition temperature, T_g. Below T_g and with short irradiation times, the dark cis–trans isomerization does not follow first-order kinetics, but has a component much faster than the rate observed in solution.[10] We are currently exploring the significance of this observation; it may suggest that irradiation of azobenzene moieties in a glass leads to the trapping of a high-energy distorted cis form, which can return faster to the trans form than a normal cis azobenzene residue.

Intramolecular Catalysis in Solutions of Chain Molecules Carrying Reactive and Catalytic Chain Substituents

In his classical study of the flexibility of long-chain molecules, Kuhn showed that, in "freely jointed chains" containing Z links of length b,[11] the end-to-end displacement h is characterized by a probability distribution function $F(h)$ given by eq 1, and the mean square

$$F(h)\mathrm{d}h = (b/\sqrt{2\pi Z/3})^{-3} \times \exp(-3h^2/2Zb^2)4\pi h^2\mathrm{d}h \quad (1)$$

end-to-end displacement becomes

$$\langle h^2\rangle = Zb^2 \quad (2)$$

Kuhn also pointed out that $F(h)\mathrm{d}h/4\pi h^2\mathrm{d}h$ has the dimensions of concentration and that it approaches a limit for $h^2/\langle h^2\rangle \ll 1$. Specifying this "effective concentration" of the second chain end in the neighborhood of the first chain end in units of moles/liter, one obtains eq 3, where $\bar{N}$ is Avogadro's number. In principle,

$$c_{eff} = (1000/\bar{N})[3/(2\pi\langle h^2\rangle)]^{3/2} \quad (3)$$

c_{eff} could be measured by following an intramolecular reaction involving two reactive groups attached to the chain ends. If intermolecular reactions between these groups are characterized by a second-order rate constant, k_2, then the intramolecular process between the two chain ends will have a first-order rate constant, $k_1 = k_2 c_{eff}$. We see then that Kuhn's model predicts a one-to-one correspondence between k_1 and $k_2/\langle h^2\rangle^{3/2}$.

The backbone of real molecular chains consists, of course, of atoms joined by chemical bonds with a fairly closely defined bond angle θ. In addition, the flexibility of the chain reflects a characteristic distribution of the internal angles of rotation ϕ and correlations between the values of ϕ characterizing the rotation around two adjoining bonds.[12] With all these restraints, real molecular chains are much stiffer than freely jointed chains with the same number and length of bonds. In addition, one has to consider effects due to the long-range interaction of chain segments, resulting both from their finite volume and from forces acting between them in a given solvent medium. Flory has shown[13] that solvent media can be found in which the "excluded volume effect" due to such long-range interactions vanishes and has designated them as "Θ solvents." In such solvents $\langle h^2\rangle$ is still proportional to the chain length, although the value of the proportionality constant reflects the chain stiffness resulting from the various short-range restraints alluded to above.

The question now arises whether it is legitimate to expect c_{eff} to be given by eq 3 for real chains. The most extensive data on the probability of ring formation as a function of the spacing of interacting groups were obtained by Stoll and Rouvé on α,ω-hydroxyalkanecarboxylic acids.[14] These reagents can either react intramolecularly, to form lactones, or intermolecularly, to form polymers. The lactone yield is a function of the ratio of c_{eff} to the initial reagent concentration.[15] The data show that rings containing 8–13 atoms form with extreme difficulty because of the crowding of hydrogens in the interior of the ring. For rings containing about 18 atoms this factor ceases to control the ring-closure probability, and c_{eff} passes through a shallow maximum. However, even a 24-membered ring (the largest investigated by Stoll and Rouvé[14]) is too small to justify the use of the statistical treatment leading to eq 1–3. For instance, $\langle h^2\rangle/Z$ attains only about 70% of its limiting value in alkanes of such a length,[16] and direct enumeration of the conformations of dimethylsiloxane oligomers leads to a higher estimate of the probability of cyclization than calculations based on Kuhn statistics and the known flexibility of polydimethylsiloxane chains.[17,18] In addition, the derivation of eq 3 disregards changes in conformational energy accompanying ring formation. The increased frequency of gauche conformations in the ring, as compared to the open chain from which it is formed, makes a significant contribution to the free energy of activation for ring formation, and this must slow down the cyclization.

The probability of ring closure in flexible chain molecules may also be investigated by studying the ring–chain equilibria in polycondensation reactions.[19] Predicted distributions of ring sizes have been compared with experimental results for polydimethylsiloxane,[17,18,20] but the use of this technique is limited by the rapid decrease in the concentration of cyclic molecules with increasing size of the ring. A remarkable test of theory was obtained with a special type of deoxyribonucleic acid (DNA) in which mutually

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(11) W. Kuhn, *Kolloid-Z.*, **68**, 2 (1934).
(12) (a) M. V. Volkenstein, "Configurational Statistics of Polymer Chains," Interscience, New York, N. Y., 1963, Chapter 6; (b) P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience, New York, N. Y., 1969.
(13) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter XLV.
(14) M. Stoll and A. Rouvé, *Helv. Chim. Acta*, **18**, 1087 (1935).
(15) Although the quantitative estimate of c_{eff} by Stoll and Rouvé[14] is in error (H. Morawetz and N. Goodman, *Macromolecules*, **3**, 699 (1970), their qualitative conclusions of the dependence of c_{eff} on ring size are valid.
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(17) J. Carmichael and J. Kinsinger, *Can. J. Chem.*, **42**, 1966 (1964).
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(19) H. Jacobson and W. H. Stockmayer, *J. Chem. Phys.*, **18**, 1600 (1950).
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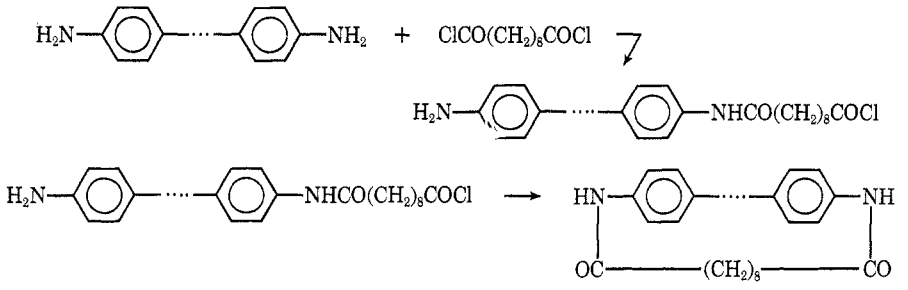
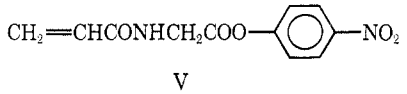


complementary single strands extend beyond the end of the double-helical polynucleotide structure.[21,22] Such DNA molecules may undergo cyclization, and both the rate and the equilibrium of this process appear to agree with predictions based on hydrodynamic estimates of chain stiffness. Much less convincing is the result of Koenig and Banderet,[23] who studied the reaction of polymer chains terminated by two arylamine groups with sebacyl chloride. The reaction proceeds in two steps (eq 4a, b), and the authors claim that they could identify the second stage of the reaction by precise conformity to first-order kinetics. This is hard to accept, since the polymer used contained chains of widely different length and these should cyclize at correspondingly varying rates.

In our work[24] we utilized copolymers of acrylamide with small proportions of reactive monomers V and catalytic monomers VI, since pyridines catalyze the



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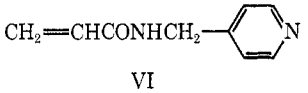

VI

hydrolysis of *p*-nitrophenyl esters.[25] We worked in highly dilute solutions, so that interaction of reactive and catalytic groups attached to different chain molecules could be neglected. Thus, the reaction rate reflected the frequency of *intramolecular* contacts between these two types of chain substituents. However, each reactive chain substituent is at a different spacing from the catalytic groups attached to the same chain and we must, therefore, interpret the kinetic pattern in terms of a probability distribution of the rate constant k. The fraction x of ester groups remaining at time t is, therefore

$$x(t) = \int W(k) \exp(-kt)\, dk \qquad (5)$$

To estimate $W(k)$ we generated on a computer a sample of 100 chains containing 1000 monomer units with a probability $\omega = 0.012$ that any jth unit picked at random carried a catalytic group. The reactive group was placed in the 500th chain segment, and interaction with catalytic groups was considered possible only if $|j - 500| > 10$. The rate constant characterizing the reactive group on the ith chain was then computed as

$$k_i = C\left(\sum_{x=-500}^{x=-10} p_{ij}|x|^{-a} + \sum_{x=10}^{x=500} p_{ij}|x|^{-a}\right) \qquad (6)$$

where $x = j - 500$ and $p_{ij} = 1$ or $p_{ij} = 0$ depending on whether the jth segment of the ith chain does, or does not, carry a catalytic substituent. For the "ring closure exponent" we used either $a = 3/2$ as predicted by eq 2 and 3 or $a = 2$, as estimated for chains subject to an excluded volume effect.[26]

Figure 2 illustrates the dependence of $W(k)$ on the ring-closure exponent. In Figure 3 the experimental result is compared with the kinetic curves computed for the two distributions $W(k)$, after adjusting C in eq 6 to match the initial slope of the curves. It may be seen that the ring-closure exponent $a = 2$ gives an excellent fit to the experimental data. The initial apparent first-order rate constant (which must be equal to the average value of k_3) corresponds to $c_{eff} = 0.031\ M$. Assuming c_{eff} to be proportional to the density of catalytic residues along the chain, we arrive at $c_{eff} = 2.7\ M$ for a chain in which each monomer is catalytically active. This is about twice as high as previously estimated on the basis of eq 3 and the flexibility of vinyl polymer chains,[27] in spite of the fact that the excluded volume effect would tend to reduce the value of c_{eff}.

Curves describing the intramolecularly catalyzed hydrolysis in solutions of different pH are strictly superimposable if the experimental time is multiplied by the fraction of the pyridine residue which exists in the basic, catalytically active, form. This proves, in agreement with the interpretation of the DNA ring-closure experiment,[22] that for reactions with a reasonably high activation energy the intramolecular reaction rate is not limited by the rate of conformational transitions required for a mutual approach of the interacting groups.

Rates of Ionic Reactions in Polyelectrolyte Solutions

Polyelectrolyte solutions contain long flexible poly-

(21) J. C. Wang and N. Davidson, *J. Mol. Biol.*, **19**, 469 (1966).
(22) J. C. Wang, *ibid.*, **28**, 403 (1967).
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(26) F. T. Wall, L. A. Hiller, Jr., and W. E. Atchison, *J. Chem. Phys.*, **29**, 2314 (1955); C. Domb, J. Gillis, and G. Wilner, *Proc. Phys. Soc., London*, **85**, 625 (1965); M. E. Fisher, *J. Chem. Phys.*, **45**, 1469 (1966).
(27) H. Morawetz, "Macromolecules in Solution," Wiley, New York, N. Y., 1965, p 433.

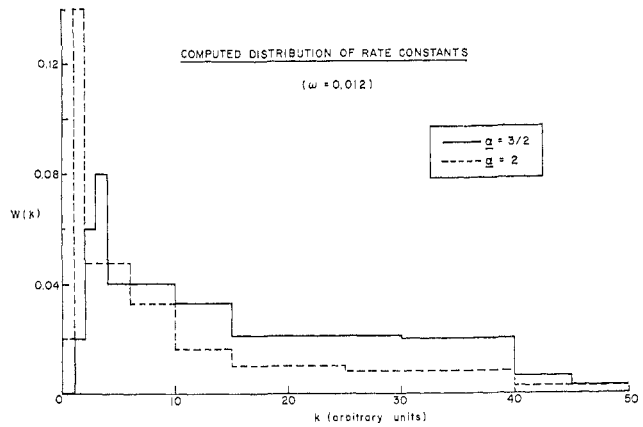

Figure 2. Computer-generated distribution functions of rate constants $W(k)$.

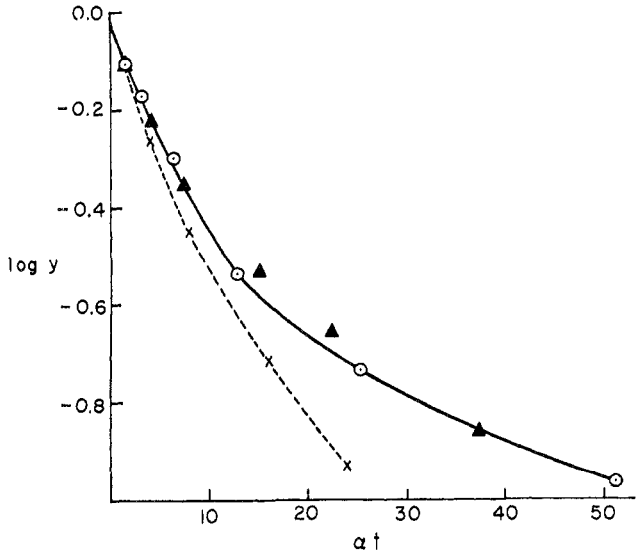

Figure 3. Hydrolysis of acrylamide copolymer with 1.0 mole % of monomer V and 1.2 mole % of monomer VI; temperature 25° (viscosity-average molecular weight of copolymer 340,000). Since the experiment was carried out at pH 5, where part of the pyridine residues were in the catalytically inactive protonated form, the experimental time t was multiplied by α, the fraction of pyridine residues in the basic form. Comparison of experimental result (—○—) with kinetic points computed for a ring-closure exponent $a = {}^3/_2$ (×) and $a = 2$ (▲).

mer chains with a high density of ionized groups attached to the backbone of the macromolecule. When such solutions are sufficiently dilute, so that these polyions are far from one another, the domains occupied by the polymer may be at a very high electrostatic potential relative to the intervening spaces. Ions carrying charges of a sign opposite to that of the polyions (the so-called counterions) will be concentrated in the polymer domain, while the by-ions, carrying charges of the same sign as the polyion, will tend to be largely excluded. The detailed characterization of the fluctuation of the electrostatic potential in polyelectrolyte solutions is a major unsolved problem in this area of physical chemistry.

A study of effects produced by polyions on the rates of chemical reactions involving two charged species should yield useful data in this context.[28] Qualitatively, it would be expected that the introduction of a polyion will inhibit reactions of ions of opposite charge, since one of the reagents will be concentrated and the other excluded from the vicinity of the polyion, so that encounters of the two reagents become much less frequent. Such an inhibition was observed in the hydroxyl ion catalyzed hydrolysis of a cationic ester in the presence of polyanions.[29] Conversely, polyions should act as catalysts for reactions involving two counterions, since they are both concentrated in the polymer domain. This was observed when polymeric acid solutions were employed as solvent media for the benzidine rearrangement (which involves interaction of two cationic species in its rate-determining step)[30] and for the hydrogen ion catalyzed hydrolysis of peptides[31] and cationic esters.[32,33] However, the spatial distribution of the organic reagents in the system is undoubtedly strongly influenced by hydrophobic interactions with the polymer. In particular, if the polyanion carries bulky hydrophobic residues, as in poly(styrenesulfonate), the esterolytic efficiency in aqueous solutions of the polyelectrolyte is higher than in solutions of mineral acid of the same pH even if the ester is uncharged, and it increases on ascending the homologous series of alkyl esters.[32,33] This effect is similar to kinetic effects in micellar solutions.[34]

With reactions of compact inorganic ionic species, complications due to hydrophobic interactions are avoided. If it can be assumed that the distribution of the ionic reagents in a polyelectrolyte solution is governed by Coulombic forces only and that the rate of the reaction in a small volume element depends only on the local reagent concentration, the acceleration or inhibition of a given reaction on addition of a polyelectrolyte will yield a parameter characterizing the distribution of the electrostatic potential in the system. By employing reagents with charges of different signs and magnitudes, a series of such parameters could be obtained, and it was hoped that this procedure would lead to a detailed description of the distribution of electrostatic potentials in polyelectrolyte solutions. Unfortunately, application of a theory based on this simple model[29a] is not justified since the concentration of the reagent ions in the polyion domain also leads to a change in the effective solvent medium which affects different reactions to a different extent.[35]

(28) H. Morawetz, *J. Polym. Sci.*, **42**, 125 (1960).
(29) (a) H. Morawetz and J. A. Shafer, *J. Phys. Chem.*, **67**, 1293 (1963); (b) *Biopolymers*, **1**, 71 (1963).
(30) C. L. Arcus, T. L. Howard, and D. S. South, *Chem. Ind. (London)*, 1756 (1964).
(31) W. Kern, W. Herold, and B. Scherlag, *Makromol. Chem.*, **17**, 231 (1956).
(32) I. Sakurada, Y. Sakaguchi, T. Ono, and T. Ueda, *ibid.*, **91**, 243 (1966).
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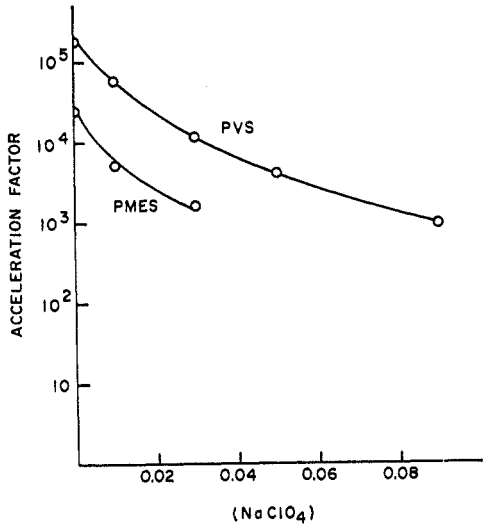
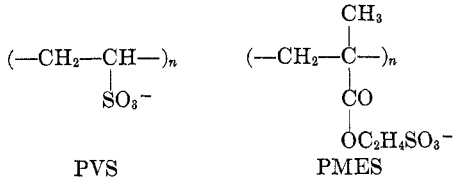


Figure 4. Acceleration of Hg^{2+}-catalyzed aquation of $Co(NH_3)_5Cl^{2+}$ in 5×10^{-5} N polysulfonic acid solutions (10^{-3} M $HClO_4$, 5×10^{-6} M $Co(NH_3)_5Cl^{2+}$, 5×10^{-5} M Hg^{2+}, 5°).

When studying the effect of polyanions PVS and PMES on the rate of reaction 7, a catalytic efficiency



PVS PMES

of astonishing magnitude was observed.[36] As shown

$$Co(NH_3)_5Cl^{2+} + Hg^{2+} + H_2O \longrightarrow Co(NH_3)_5H_2O^{3+} + HgCl^{+} \quad (7)$$

in Figure 4, as little as 5×10^{-5} N PVS accelerates the reaction by a factor of 176,000. The catalytic efficiency of PMES is somewhat lower, as expected, since the ionized groups are further from the chain backbone and represent, therefore, a smaller charge concentration. The catalytic effect is sharply reduced on adding simple electrolyte because of the reduction of the electrostatic potential in the polymer domain.

Figure 5 illustrates the effect of a variation in the polyion concentration, at different concentrations of simple electrolytes, on the rate of reaction 7.

For very low polymer concentrations, the rate is about proportional to the amount of polymer added, but eventually the rate passes through a maximum and decreases sharply on further polymer addition. This effect is easily explained. As long as only a small fraction of the reagent ions are bound in the polymer domains, increasing polyion concentrations increase the fraction of the reagent concentrated in these regions and the reaction rate will increase. However, if we increase the polyion concentration beyond the point at which virtually all the reagent ions are in the vicinity

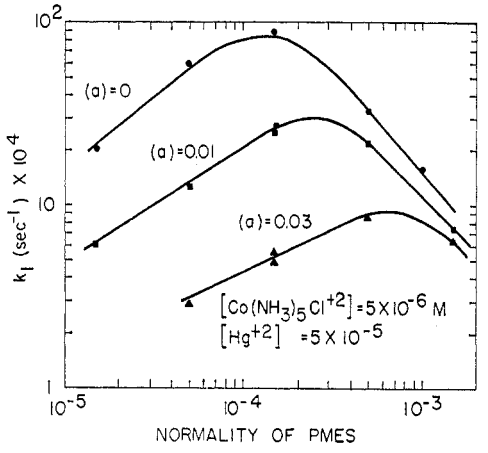


Figure 5. Effect of added $NaClO_4$ (a) on the PMES-catalyzed reaction of $Co(NH_3)_5Cl^{2+}$ with Hg^{2+} (10^{-3} M $HClO_4$, 5°).

of the polymer, they will have to be shared by a larger number of polymer domains, their local concentration in these domains will decrease, and so will the reaction rate. We see from Figure 5 that at high polyion concentrations the catalytic effect is almost independent of the concentration of simple electrolyte. Under these conditions almost all reagent ions are bound to the polyions and the acceleration of the reaction is a measure of the local concentration of the reagent ions in the polymer domains. At low polyion concentration, the catalytic efficiency is controlled also by the affinity of the reagent ions for the polymer, which decreases sharply on addition of uni-univalent electrolytes. Analysis of the kinetic pattern led to estimates of polyion–reagent ion association constants which were in remarkable agreement with dialysis equilibrium data.

The above study has been extended to electron-transfer reactions involving $Co(NH_3)_5Cl^{2+}$, *cis*-$Co(NH_3)_4(N_3)_2^{+}$, and *trans*-$Co(NH_3)_4(N_3)_2^{+}$ as the oxidants and Fe(II) as the reducing agent.[35] The results plotted in Figure 6 show that at low PVS concentration the catalytic efficiency drops sharply as the charge of the cobalt complex decreases from 2+ to 1+. This would be expected because of the lower affinity of the singly charged counterion for the polyion. However, at high polyion concentrations, the catalytic efficiency for the reaction of *trans*-$Co(NH_3)_5(N_3)_2^{+}$ is much higher than for the cis isomer or even the doubly charged $Co(NH_3)_5Cl^{2+}$. This is so because *trans*-$Co(NH_3)_5(N_3)_2^{+}$ (unlike the other two species) exists in strongly acid solution in a protonated form which is much more rapidly reduced.[37] Thus, the polyanion serves with this reagent not only the function of concentrating the participants of the redox reaction in its vicinity but enhances also the transformation of *trans*-$Co(NH_3)_4(N_3)_2^{+}$ to its more reactive conjugate acid because of the high local hydrogen ion concentration.

Our latest study[38] dealt with the effect of PVS on the efficiency of the quenching of the UO_2^{2+} fluorescence by Fe^{2+}. This reaction differs from the cases discussed above in that one of the reagents, the ex-

(36) H. Morawetz and B. Vogel, *J. Amer. Chem. Soc.*, 91, 563 (1969). The much smaller catalytic effects found by N. Ise and F. Matsui (*ibid.*, 90, 4242 (1968)) are due to the fact that inhibition of polyelectrolyte catalysis by the triply charged reaction product was important under their experimental conditions.

(37) A. Haim, *J. Amer. Chem. Soc.*, 85, 1016 (1963).

(38) I. A. Taha and H. Morawetz, *ibid.*, in press.

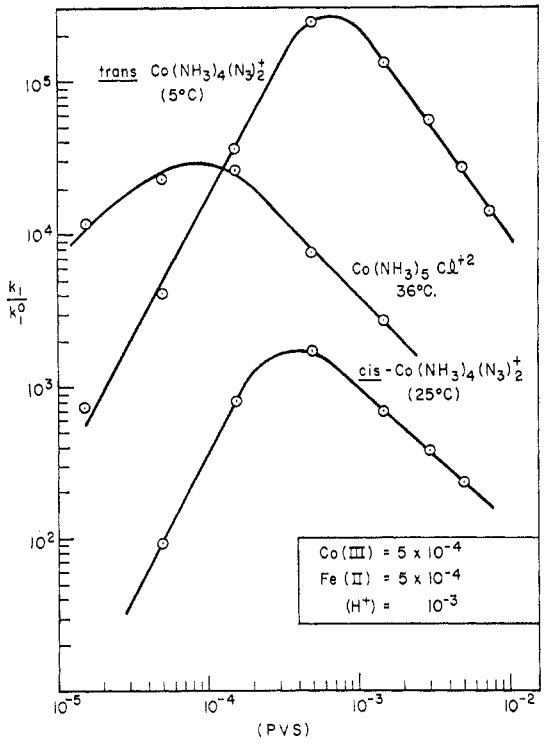


Figure 6. Effect of PVS on the rate of reduction of Co(III) complexes by Fe^{2+}.

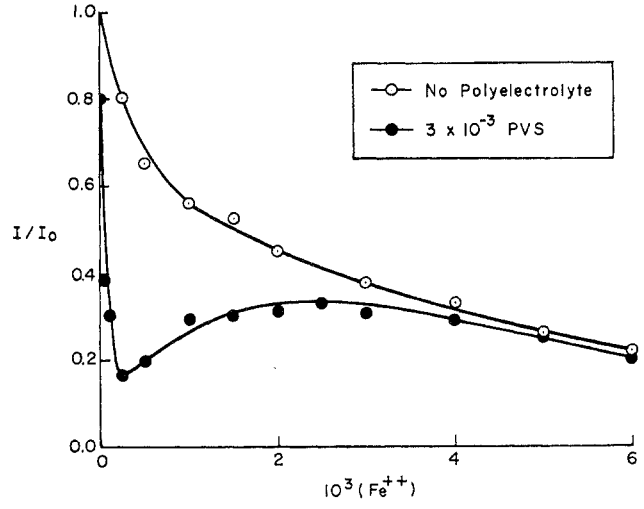


Figure 7. Effect of PVS on the quenching of the UO_2^{2+} fluorescence by Fe^{2+} (10^{-3} M $HClO_4$, 5×10^{-4} M UO_2^{2+}, 25°).

cited UO_2^{2+}, has a lifetime of only 1.5×10^{-6} sec.[39] The quenching of UO_2^{2+} fluorescence in the absence and presence of PVS is plotted in Figure 7 as a function of the concentration of added Fe^{2+}. In the absence of polyions, the quenching follows the Stern–Volmer relation[40] $I_0/I = 1 + K(Fe^{2+})$, where I_0 and I are the fluorescence intensities in the presence and absence of the quenching agent and $K \approx 1400$ l. mole^{-1}. In the presence of PVS the behavior is much more complex. At very low Fe^{2+} concentrations, the polyion increases by a large factor the quenching efficiency by concentrating the excited uranyl ion and the quenching agent in the polymer domain. At higher Fe^{2+} concentrations, the fluorescence intensity increases, since the UO_2^{2+} is now being displaced from the polyanion sites by the Fe^{2+} and fluorescence of the free uranyl ions is quenched much less efficiently. At much higher Fe^{2+} concentrations the fluorescence decreases again, this time because of the quenching of the fluorescence of free UO_2^{2+}.

This pattern can only be understood if there is no effective exchange of polyion-bound and free reagent ions during the lifetime of the excited UO_2^{2+}. Under these conditions, even a small fraction of UO_2^{2+} outside the polymer domain will make a large contribution to the fluorescence if the free Fe^{2+} concentration is small compared to $1/K$. On the other hand, if exchange were rapid, a sizable fraction of the lifetime of excited UO_2^{2+} spent in the vicinity of the polyions with their high local Fe^{2+} concentration would lead to effective fluorescence quenching. In principle, it should be possible to use experiments with excited species characterized by different lifetimes to bracket the exchange rates of bound and free counterions in polyelectrolyte solutions.

Concluding Remarks

This survey was designed to convey an impression of the variety of problems concerning the physical properties of polymer solutions which may be elucidated by a study of chemical reaction kinetics. Another problem which seems to invite this approach concerns the extent of interpenetration of randomly coiled chain molecules in dilute solution. We have studied this question[41] by following the reaction kinetics in solutions containing mixtures of two similar copolymers, one with a small number of catalytic groups, the other with a small number of reactive substituents. However, the results of that investigation are not understood theoretically, and further work along that line is indicated.

The small amount of work reported on studies of this type is undoubtedly a consequence of scientific specialization. Physical chemists interested in the problems we have raised shy away from the synthesis of unusual polymers, while organic chemists have little interest in the preparation of substances which present no challenge from their point of view. Nevertheless, this no-man's land would seem to be worth exploring.

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(39) J. L. Krapp, *J. Chem. Phys.*, **46**, 843 (1967).
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