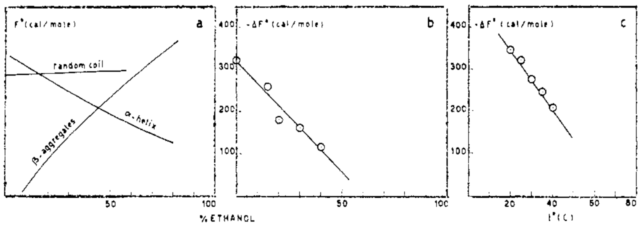

Figure 8. (a) Schematic diagram representing the dependence of the free energy, F°, for uncharged conformers on solvent composition; (b) free energy, ΔF°, of formation on the uncharged β aggregates from the uncharged random coil at 25° as a function of ethanol per cent; (c) free energy of formation of the uncharged β aggregates from the uncharged random coil in 0.1 *M* KCl as a function of the temperature.

mole of residue of uncharged conformers, F^0, as a function of ethanol content in Figure 8a. In water the β conformation is more stable than either the random coil or the α helix. If, by a rapid lowering of pH, the slowly occurring coil to β transition is by-passed, the random coil is observed at every value of the charge. At a certain alcohol concentration, between 0 and 20% we have $F^0_{\text{coil}} > F^0_{\text{helix}}$, so that the uncharged α helix becomes more stable than the random coil, and the coil → α-helix transition is encountered in the rapid titration experiments.

Above the composition corresponding to the crossing of the F^0_{helix} and F^0_β curves, the α helix is the stable conformer, and for higher values of ethanol concentration the coil → α-helix transition occurs independently from kinetic factors.

We may now attempt to give a more quantitative interpretation of our results, considering that the $\mathrm{p}K_{\text{app}}/\alpha$ curve which we have reported here and in the preceding paper allows us to evaluate the free energy of transition between uncharged random coil and β form as a function of alcohol content and of the temperature.

The area between the extrapolated titration curve of the random coil and the β aggregates, titration curve is, of course, a measure of such a free energy change, according to the relationship[16,17] $\Delta F^0 = -RT\int \alpha \mathrm{d} \ln a_{\mathrm{H}}$. It represents, in other words, the free energy of formation of uncharged equilibrium β aggregates from uncharged random coil, and is, therefore, in the hypothesis of an intermolecular mechanism, the really meaningful quantity. It must be remarked that the experimental values may be affected by a rather large error, owing to the very narrow range of α in which the titration of the random coil occurs in several cases, and to the fact that the point of incipient transition is often not easily detectable. The values of the free energy of formation of the uncharged β form from the uncharged random coil, ΔF^0, at 25° and at 0, 15, 20, 30, 40% ethanol are reported as a function of the solvent composition in Figure 8b. This plot yields a value of about 60% for the ethanol composition at which $\Delta F^0 = 0$. Such points cannot of course be experimentally observed, because above 45% ethanol the α helix becomes the uncharged stable conformer. Finally, values of ΔF^0 in 0.1 *M* KCl are reported as a function of the temperature in Figure 8c. From this plot the values of ΔH^0 and ΔS^0 are obtained, which are equal to −2400 cal/mol and to *ca.* −7 eu, respectively. They probably include the contribution of side chain–side chain interactions, as seems to be indicated by their strong negative values as compared with the experimental values of the enthalpy and entropy of hydrophobic bond formation for tyrosyl residues reported by Brandts.[18]

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A Study of the Effect of Impurities in Living Anionic Polymerization

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ABSTRACT: Kinetics of homopolymerizations of polystyrylcesium were investigated in tetrahydrofuran at 25° by using solvents of various degrees of purity, and those of polystyryllithium were also briefly studied in 2-methyltetrahydrofuran. The apparent propagation constant k_{p} was greatly decreased by using seed polymer solutions, the purity of which was not sufficiently high. From conductivity measurements, it was demonstrated that the decrease in k_{p} was due to that in the free-ion rate constant k_{p}''. The value of k_{p}'' was $1.3 \times 10^5\ M^{-1}\ \mathrm{sec}^{-1}$ when the system was most elaborately purified, and decreased to $4 \times 10^4\ M^{-1}\ \mathrm{sec}^{-1}$ in the presence of impurities.

The anionic polymerizations of styrene in ethereal solvents have been studied by several authors.[1-5] However, the agreement among kinetic data reported is not always satisfactory. The cause of the disagreement has been discussed by the Syracuse and Mainz groups.[6-10]

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Whenever we aim at an accurate determination of kinetic constants, the purity of reagents is one of the most crucial factors. We wanted to study the influence of impurities (*e. g.*, water, oxygen, and carbon dioxide) present in the sytem on the kinetic data by intentionally varying the degree of solvent purity. For this purpose, it is important that the growing ends are stable even in the impure solvent. As one such system, we chose the anionic propagation of polystyrylcesium, having one living end per chain, in tetrahydrofuran (THF). This particular combination of monomer–gegenion–solvent has been studied twice by the Syracuse group.[1a,b] They reported discrepancies in the slopes of the apparent rate constant k_p *vs.* [living end]$^{-1/2}$ plot and in the dissociation constants of ion pairs. This fact clearly shows how difficult it is to determine accurately the kinetic constants of living anionic polymerizations even by an expert technique. In addition, we report preliminary findings concerning the influence of impurities in anionic polymerization of polystyryllithium in 2-methyltetrahydrofuran (MTHF).

Experimental Section

The detailed technique of solvent purification has been described earlier.[5,11,12] In order to control the quantity of impurities, we changed both the time of the drying–deaeration cycle in the solvent purification process and the number of cycles performed. THF, which can be believed to be of the highest purity in the present work, was obtained by repeating the drying–deaeration cycle for 1 week with violent stirring and in contact with Na–K alloy dispersion. The solvent thus obtained is designated THF (A). THF, which is believed to be of the lowest purity, was obtained by performing only one cycle of drying–deaeration mentioned above. After having confirmed the presence of the characteristic blue color, the THF was distilled into ampoules, which were sealed off under vacuum. The THF thus obtained is designated THF (C). THF (B) was obtained by mixing THF (C) with a small amount of pure living polymer solution (seed (a) which will be described below). The order of the purity of solvents seems to be (A) > (B) > (C).

The purification of MTHF was similar to that of THF (C). Thus the designation is MTHF (C). Styrene was purified as described previously.[5a]

The polymerization was started by low molecular weight living polymers. Preparations of both cesium and lithium salts of living polystyrene as seed polymers have been described previously.[11] The apparatus and the experimental procedure for polymerization have also been described earlier.[5a,11] The solvent in the seed polymer solution was thoroughly removed under high vacuum immediately prior to polymerization, and the polymerization was started by dissolving the solid seed polymer in monomer solution. The propagation rate constants were determined spectrophotometrically at 25° as described before. The absorption peak (λ_{max}) was at 342 mμ for the cesium salt in THF. It occasionally shifted to 346 mμ in the systems containing impurities. λ_{max} of the lithium salt was 340 mμ in the elaborately purified MTHF,[11] but always shifted to 330 mμ when MTHF (C) was used.

The electric conductivity was measured as described in previous studies.[5,11,12] The solvent correction was effected. The conductivities of solutions of the two salts were practically time independent.

Results

Solutions of the monomer dissolved in THF (A), (B), and (C) are designated monomer (A), (B), and (C), respectively. The seed polymer solution prepared with THF (A) is designated seed (a). Both seeds (b) and (c) were obtained by replacing the solvent of seed (a) by THF (C). Seed (b) was used immediately after the replacement, and seed (c) was used after 24-hr storage in the freezer (−30°). Seed (a), with which the inside walls of the several sets of apparatus were rinsed, was used as seed (d) after keeping it for 24 hr in the freezer. The orders of the purity of monomers and seeds are believed to be (A) > (B) > (C) and (a) > (b) ≈ (c) > (d), respectively.

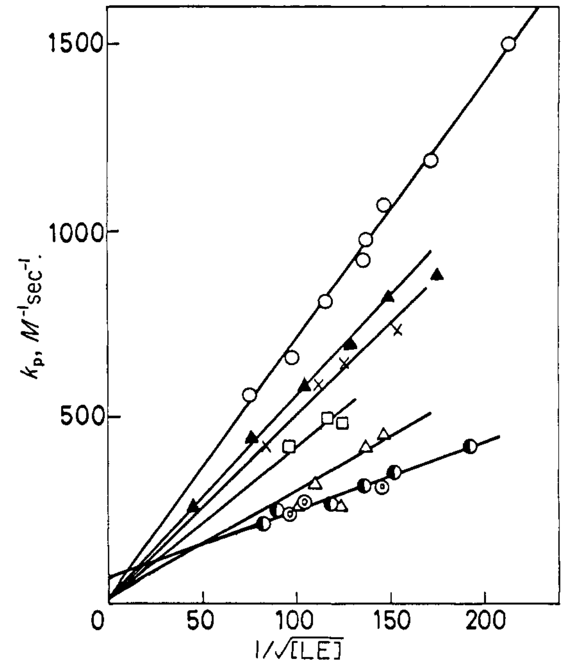

Figure 1. Dependence of the apparent propagation rate constant on polystyrylcesium (with one end per chain) concentration in THF at 25°: ○, monomer (A) + seed (a); ▲, (B) + (a); ×, (C) + (a); □, (C) + (b); △, (C) + (c); ◐; (B) + (d); ⊙, (C) + (d).

The concentrations of these seed polymer solutions were 3–4 × 10^{-2} *M*. The plots of the apparent propagation rate constant k_p against [LE]$^{-1/2}$ ([LE] = living end concentration) for polystyrylcesium in THF are shown in Figure 1. The intercept gives the ion-pair rate constant k_p' and the slope $k_p''K^{1/2}$ (where k_p'' is the free-ion rate constant and K the ion-pair dissociation constant). Straight lines show the results for, from the top, the following combinations of the monomer and seed: (A) + (a), (B) + (a), (C) + (a), (C) + (b), (C) + (c), and (B) and (C) + (d). The slope of the plot ($k_p''K^{1/2}$) decreases as the impurity level increases, whereas the intercept k_p' seems to be unaffected except for seed (d). The values of k_p' and $k_p''K^{1/2}$ estimated from Figure 1 are given in Table I. The k_p' value is in satisfactory agreement

TABLE I

KINETIC CONSTANTS OF POLYSTYRYLCESIUM IN THF AT 25° IN THE PRESENCE AND ABSENCE OF IMPURITIES

Expt	Monomer[a]	Seed polymer[a]	k_p', M^{-1} sec^{-1}	$k_p''K^{1/2}$,[b] $M^{-1/2}$ sec^{-1}	$k_p'' \times 10^{-4}$ M^{-1} sec^{-1}
1	A	a	20 ± 5	6.8	13
2	B	a	20 ± 5	5.3	10
3	C	a	20 ± 5	4.8	9.0
4	C	b	20 ± 5	4.0	7.7
5	C	c	20 ± 5	2.8	5.4
6	B	d	[70][c]	2.0	4.0
7	C	d	[70][c]	2.0	4.0

[a] See text for details. [b] K was determined to be 2.7 × 10^{-9} *M* for all cases studied here. [c] Large uncertainty is associated with these values.

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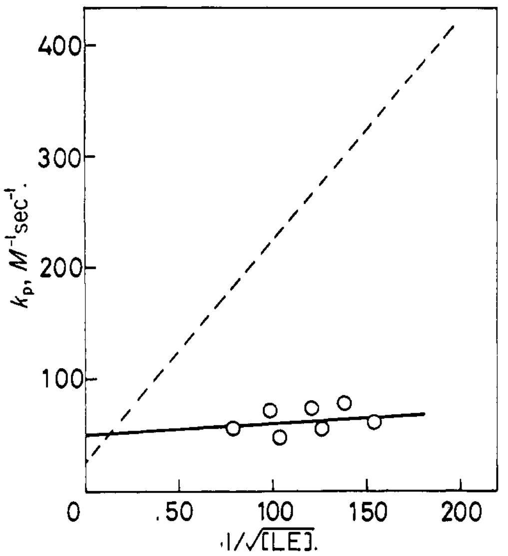

Figure 2. Dependence of the apparent propagation rate constant on polystyryllithium in MTHF at 25°: ○, monomer (C) + seed (c); — — —, results in the absence of impurities, see ref 11.

with the result published previously.[1a,b] It seems that impurities present in the seed-polymer solutions have a greater effect on $k_p''K^{1/2}$ than those in the monomer solution (compare expt 1, 2, and 3 with 4 and 5). When seed (d) is used, $k_p''K^{1/2}$ is about one-third of that when seed (a) is used.

The spectrum of polystyrylcesium remained unchanged whatever the impurity level. On storage of seed (d) at room temperature, the 342-mμ peak gradually decreased in intensity over a period of few days and a new peak at 540 mμ with a shoulder at 430–440 mμ appeared, as was found previously.[13] For seed (a), the appearance of the new peak was even slower. The results for polystyryllithium in MTHF containing impurities are shown in Figure 2. For comparison, the result previously obtained in the absence of impurities[12] is shown by a broken line. The influence of impurities in MTHF is striking; the slope ($k_p''K^{1/2}$) is nearly zero. k_p' appears to be $50 \pm 15\ M^{-1}\ \text{sec}^{-1}$.

The concentration dependence of the equivalent conductance of the cesium salt is shown in Figure 3. In all combinations of the monomer and seed, the points lie close to a line of slope $-1/2$, in spite of the vitiating effects of the impurities on the kinetic data. The ion-pair dissociation constant K was evaluated by the method of Fuoss,[14] using the equivalent conductance at infinite dilution reported previously.[1b] The K value was $2.7 \times 10^{-9}\ M$ for all cases studied here and the corresponding value of k_p'' is listed in Table I.

Discussion

The k_p'' value of $1.3 \times 10^5\ M^{-1}\ \text{sec}^{-1}$ in the absence of impurities (expt 1) is in good agreement with the value found by Schulz, *et al.*,[2a] and also the K value of $2.7 \times 10^{-9}\ M$ agrees with the value previously reported by Bhattacharyya, *et al.*[1a] It is remarkable that k_p'' was reduced to $4 \times 10^4\ M^{-1}\ \text{sec}^{-1}$ by using seed (d) (expt 6 and 7). These results show that impurities react with free anions exclusively. Judging from the living end concentration and the K value under our experimental conditions, it seems that the concentration of impurities present in the system is $10^{-6} \sim 10^{-7}\ M$ or below. Gas chromatographic analyses, of course, showed negative results for the presence of impurities. Though the specification of the impurities is impossible, it is not plausible that some strongly polar impurities (*e.g.*, hexamethylphosphoramide) are present. In our experiments, the solvents were purified by using Na-K alloy. The $k_p''K^{1/2}$ terms were found to increase with time of the contact of the solvent with the Na-K alloy. Thus, impurities present in the system would be materials that can be removed gradually with the drying-deaeration procedures described in the Experimental Section.

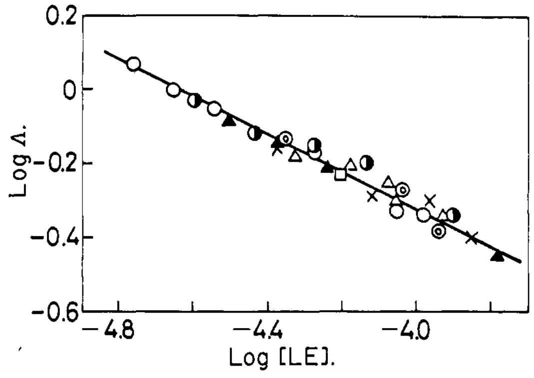

Figure 3. Dependence of the equivalent conductance on the polystyrylcesium concentration in THF at 25°; symbols as in Figure 1.

Therefore, we believe that oxygen, water, and carbon dioxide are impurities. Obviously, the effects of impurities are larger after prolonged contact with the living ends than in bringing the reagents into contact just before polymerization. This indicates that reactions between the living ends and impurities are slow; 100% conversion requires more than 20 min, the time required for replacing the solvent (compare expt 3 and 4).

For reactions of the living ends with impurities, at least two possibilities should be considered. (1) Reactions of free $\sim S^-$ ions with impurities might lead to formation of new anions (*e.g.*, $\sim C{-}O^-$) which may or may not associate with the living ends. If reactivity of the newly formed anions or these complexes is low, the polymerization will be retarded. Recently, Yamashita, *et al.*, have found that in the presence of oxygen, styrene polymerizes steadily by particular active species, although with very low rates.[15] (2) Impurities like oxygen, water, and carbon dioxide might play a role as Lewis acids when their quantities are very small. These compounds might form complexes with free anions. This prevents monomer molecules from reaching the free ions. A clear mechanism for these reactions, however, is not known at present.

Whatever the mechanism of the reactions of the living end with impurities is, it is clear that the purity of the reagents is one of the most critical factors in kinetic studies of anionic polymerizations. An initiator freshly prepared should be used immediately after preparation, especially when solvent is not extremely pure.

The present paper illustrates that the kinetic data of living anionic polymerizations are very sensitive to the degree of purity of materials. It is extremely difficult to attain the same degree of purity in different research groups, and at different times even in one group. Therefore the discrepancies in the kinetic data reported by various researchers should be tolerantly admitted. In future papers, it is hoped that much more detailed accounts of the purification procedure will be given.

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