perature coefficient afford the basis for calculation of a number of other configuration-dependent properties of POE chains that are in good agreement with experiment. Examples are the dipole moments,[8] temperature coefficients of the dipole moments,[9] and optical anisotropies.[10] These conformational energies also give satisfactory results when used to calculate statistical properties of poly(trimethylene oxide)[11] and poly(tetramethylene oxide),[12] two other polymers in the series $[-(CH_2)_mO-]_x$ of which POE is a member. The internal consistency of this broad range of results lends strong support to the overall scheme and to the reliability of the principal quantities employed, including especially the value of d ln $\langle r^2\rangle_0/\mathrm{d}T$ previously given[2] for POE.

Acknowledgment. This work was supported in part by the Directorate of Chemical Sciences, U. S. Air Force Office of Scientific Research Grant No. AFOSR-73 2441.

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Communications to the Editor

On the Selective Interaction of Monovalent Counterions with Polycarboxylates in Water

A variety of evidence indicates that the mode and extent of monovalent counterion binding in aqueous solutions of synthetic polyelectrolytes is a function of the size and/or hydration of the counterions as well as of the nature of the fixed charges along the macroion chains.[1-6]

Data accumulated so far permit a thermodynamic account of the observed "selective" interactions in terms of free-energy differences. However, contrary to the case of the selective uptake of ions by ion exchangers for which direct microcalorimetric experiments have been carried out,[7a-c] no information is presently available concerning enthalpy and entropy changes associated with the "site-binding" of different monovalent counterions by polyions in dilute aqueous solution.

We report here the results of calorimetric and potentiometric experiments from which informations of the type mentioned above may be deduced in the case of two polycarboxylic acids, poly(maleic acid), (MA), and the maleic acid-ethylene (1:1) copolymer, (MAE), for three counterions: Li^+, Na^+, and $(CH_3)_4N^+$. The MAE sample used in this study has been described in earlier reports.[8] The MA homopolymer was prepared by γ ray initiated polymerization of a 50% v/v maleic anhydride-acetic acid mixture.[9] Purification and full characterization of the MA sample are being reported elsewhere.[10] The elemental analysis of the sample was in good agreement with expectations and its intrinsic viscosity in butanone at 25° was 0.1 dl/g.[10] (Lang *et al.*[9] have described a MA sample with $[\eta]$ = 0.127 dl/g in butanone at 25° having a $\bar{M}_w$ = 23,000 measured by light scattering.)

The apparatus and experimental techniques used in the calorimetric and potentiometric experiments have already been illustrated in detail.[8,11]

Our calorimetric data display the dependence of the differential enthalpy of dissociation ΔH_{diss} (kcal/mol of protons) on the degree of neutralization, α, for both MA and MAE partially neutralized with LiOH, NaOH, and $(CH_3)_4NOH$, respectively, in water at 25°.

Data of Figure 1 clearly indicate that the enthalpy of dissociation of the two polycarboxylates depends strongly on the chemical composition of the chain, the charge density, *and* on the nature of counterions. Particularly striking is the case of MA for which we find that ΔH_{diss} is always positive in the range of α values considered (α = 1 corresponds to half neutralization of the polyelectrolytes) and, more interestingly, that the ΔH_{diss} increases as the counterions are changed in the order $(CH_3)_4N^+ \rightarrow Na^+ \rightarrow Li^+$ for α greater than *ca.* 0.2. At α = 0, the three curves for MA merge, yielding an approximate value for the enthalpy of ionization of the discharged polymer of *ca.* 0.6 kcal/mol of H^+.

On the other hand, in the case of MAE, the excess enthalpy of ionization, *i.e.*, the difference between experimental data and the extrapolated ΔH_{diss} value for α = 0 (*ca.* 0.3 kcal/mol of H^+) is always negative, the results exhibiting furthermore only a minor dependence on the type of the ion neutralizing the fixed charges.

In any case, the difference between the calorimetric data for both MA and MAE at any given α with different counterions yield the difference in the enthalpy of the polyelectrolyte-solvent mixture due to the diverse macroions-counterions interactions.

For MA, for example, the replacement of protons by Li^+ ions and with $(CH_3)_4N^+$ ions, respectively at α = 0.5

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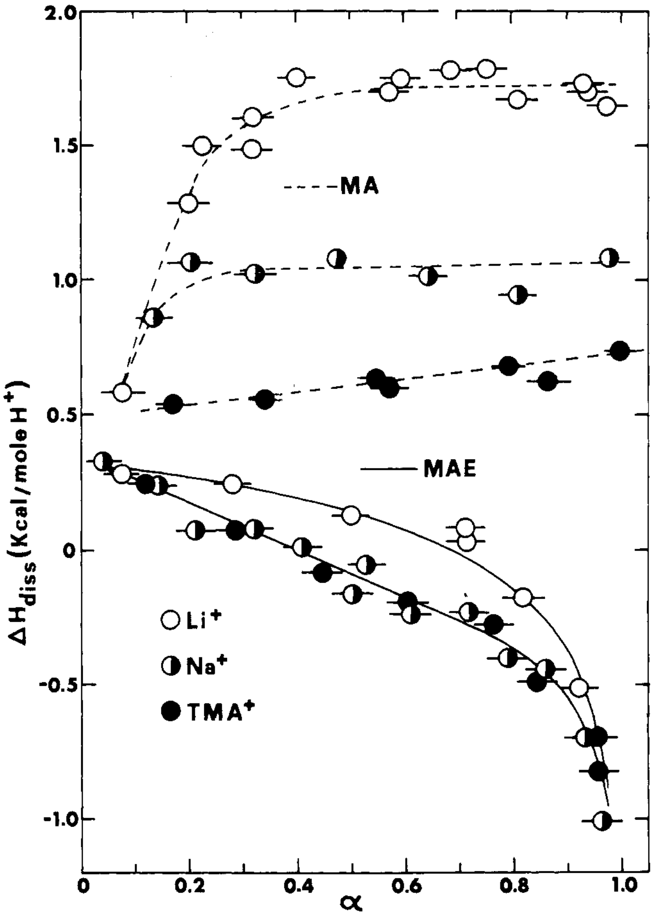

Figure 1. Dependence of the enthalpy of dissociation upon the degree of neutralization, α, for the maleic acid-ethylene copolymer (MAE) and poly(maleic acid) (MA) in water at 25°. Polyelectrolyte concentration 10^{-2} monomol/l. Neutralization with: (○) LiOH, (◑) NaOH, and (●) $(CH_3)_4NOH$. The horizontal bars on the points define the $\Delta\alpha$ actually spanned in the protonation experiments.[8,11]

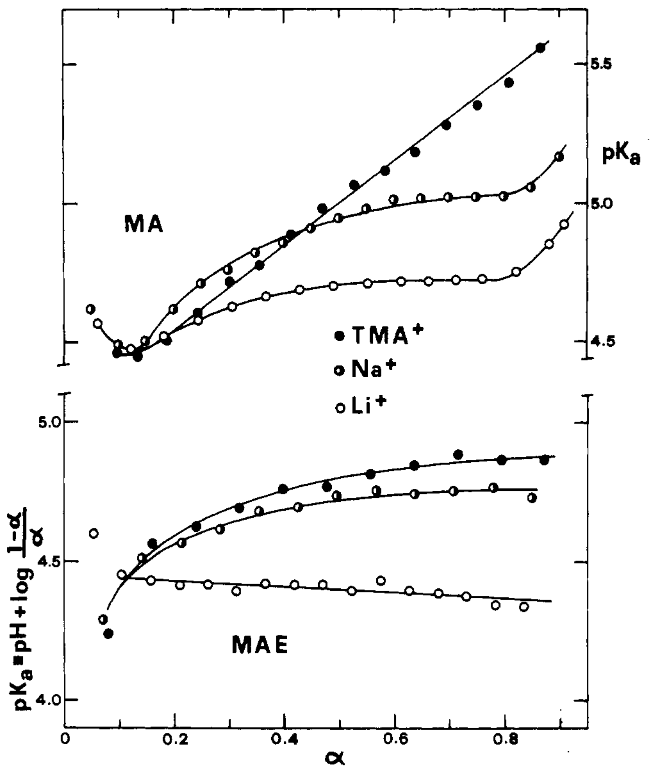

Figure 2. Potentiometric plots for poly(maleic acid) (MA) and the maleic acid-ethylene copolymer (MAE) in water at 25°. Titrant: (○) LiOH, (◑) NaOH, (●) $(CH_3)_4NOH$. Polyelectrolyte concentration: 10^{-2} monomol/l.

differ energetically by *ca.* 1.1 kcal/mol of counterion (see Figure 1). The interaction of MA polyions with Li^+ ions is, therefore, endothermic and, were the interaction with $(CH_3)_4N^+$ ions purely electrostatic (a common assumption in the field of polyelectrolyte solutions), 1.1 kcal/mol would then essentially correspond to the differential enthalpy of "site-binding" Li^+ ions by MA.

By a similar reasoning, Na^+ site binding along MA chains (at $\alpha = 0.5$) would be characterized by an enthalpy gain of *ca.* 0.5 kcal/mol. On the contrary, in the case of MAE no specific interaction occurs with Na^+ ions, the site-binding of Li^+ ions being only slightly endothermic (see Figure 1). Considering now the potentiometric data reported in Figure 2, and recalling that $\Delta G_{diss} = 2.303\ RT(pK_a)$, where ΔG_{diss} is the total free energy for the dissociation of one mole of carboxyl groups, at α, and the neutralization of the fixed charges so created by an equivalent amount of counterions, we see that less work is required in the removal or protons from both MA and MAE chains with Li^+ counterions than with Na^+ or $(CH_3)_4N^+$ counterions. Evidently, one of the factors must be a reduction of the charge density on the polyelectrolytes by Li^+ ion site binding.

For instance, in the case of MA at $\alpha = 0.5$ the pK_a value for the lithium salt is lower than that for the tetramethylammonium salt by 0.3 unit, which corresponds to a difference in free energy of ionization of approximately −0.18 kcal/mol at 25°. This figure may be taken as representative of the free-energy change accompanying the interaction of Li^+ ions with MA polyions through other than coulombic forces.

In any case, the change in entropy associated with the selective interaction of Li^+ ions with both polycarboxylates considered, in particular with MA, is positive on the basis of our data, amounting to about +4 eu at 25° for MA at $\alpha = 0.5$, but increasing with increasing α according to our potentiometric data (Figure 2). This should, in all probability, be due to the release of a number of molecules of water from the hydration shells of both lithium and carboxylate ions.[12]

The rupture of ion-dipole (solvent) bonds, uncompensated by the formation of fewer ionic bonds (between fixed charges and counterions) might help increase the intrinsic endothermicity of formation of the latter type of bonds in water.[13] In this connection it is interesting to recall that complex formation between carboxylated ligands and transition metal ions in aqueous solution commonly occurs with an unfavorable enthalpy and is thus an entropy-driven process.[14] Even a qualitative account of the contribution to the observed effects from changes in enthalpy and entropy of the macroion chains with varying charge density and/or the nature of counterions is beyond the scope of the present discussion. In this connection we wish simply to point out that the striking behavior of MA must be somehow connected to its overcrowded chain structure and that a correlation between structure and properties of polycarboxylates still requires a great deal of additional information.

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Acknowledgments. This work has been sponsored by the Italian Consiglio Nazionale delle Ricerche. The poly(maleic acid) sample used in this work was a kind gift of Dr. G. Barone.

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Received December 26, 1972

Stereospecific Polymerization of *o*-Phthalaldehyde

Recently, Aso *et al.*[1-4] reported the cyclopolymerization of *o*-phthalaldehyde by ionic catalysts to give poly(*o*-phthalaldehyde) the *trans*-oxyphthalan ring content of which varied widely from 15 to 88% depending on the nature of catalyst, including $[R_2AlOCR'NPh]_2$-type catalyst. We found that water or peracetic acid was an indispensable cocatalyst in the stereospecific polymerization of acetaldehyde catalyzed by $[R_2AlOCR'NPh]_2$[5-7] or R_2AlOR'.[8] This paper describes the essential role of water as a cocatalyst for the stereospecific polymerization of *o*-phthalaldehyde and the preparation of the crystalline poly(*o*-phthalaldehyde).

Practically no polymer was obtained when *o*-phthalaldehyde purified by repeated distillation was used as monomer, crystalline $[Me_2AlOCMeNPh]_2$ (**1**) as catalyst and tetrahydrofuran dried throughly over Na-K alloy as solvent. In contrast to this result, the polymerization proceeded smoothly at −78° in a homogeneous state throughout the polymerization in the presence of an appropriate amount of water (Figure 1). The optimum amount of added water for obtaining a maximum yield of the polymer was about $\frac{1}{20}$th mol/mol of **1**. This optimum amount is the same order of magnitude as that observed in the stereospecific polymerization of acetaldehyde catalyzed by $[R_2AlOCR'NPh]_2$[5,6] or by R_2AlOR'.[8]

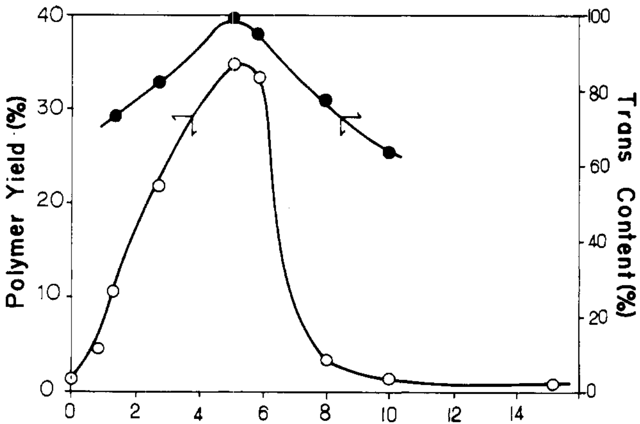
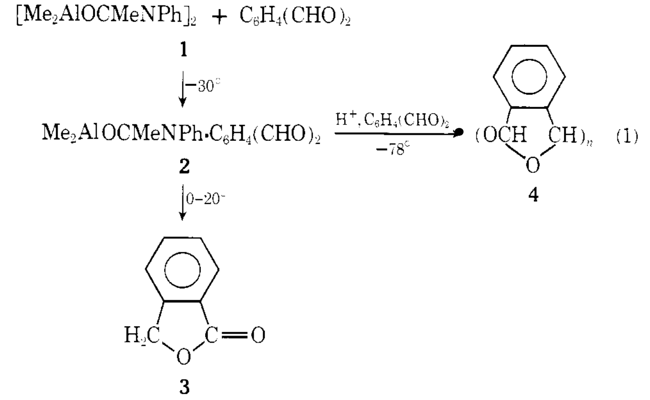


Figure 1. Cocatalytic action of added water in the polymerization of *o*-phthalaldehyde catalyzed by **1**. Catalyst concentration, 1 mol % of monomer. Solvent, toluene (40 ml/g of monomer). Polymerization, −78° for 70 hr.

The polymerization carried out in the presence of an optimum amount of added water gave a fibrous, crystalline polyether whose ir spectrum had no free C═O absorption, while that in the presence of a larger or a smaller amount of added water gave a low-crystalline, powdery polymer. The content of *trans*-oxyphthalan unit was determined by chemical shifts and peak areas of methine proton signals in the nmr spectrum, according to the method developed by Aso *et al.*[3] The nmr spectrum of the polymer (Figure 2) obtained by the catalyst **1** in the presence of an optimum amount of water showed only one sharp methine peak at δ 6.9 ppm in tetrahydrofuran, while that obtained by $BF_3 \cdot OEt_2$ showed a complicated spectrum containing seven peaks and that obtained by Ph_3COK catalyst showed two single peaks in a ratio of 1:1 at δ 6.90 and 6.52 ppm assignable to trans and cis methine protons, respectively. Therefore, the content of *trans*-oxyphthalan unit in the crystalline polymer obtained by **1** is nearly 100%. The trans content decreased and the cis content increased when the amount of added water was larger or smaller (Figure 1).

The 1:1 monomer-catalyst complex **2** was obtained as colorless crystals by mixing **1** with *o*-phthalaldehyde in an equimolar ratio at a temperature slightly higher than the ceiling temperature of polymerization (−40°). The complex **2** is stable only in a narrow temperature range, because it transformed gradually to give phthalide (**3**) quantitatively at 10° and converted to poly(*o*-phthalaldehyde) **4** at below −40° (eq 1). These reactions proceeded also in the presence of excess of *o*-phthalaldehyde.



The composition and structure of **2** were determined by spectroscopic methods. In the nmr spectrum (60 MHz) recorded in toluene-d_8 solution at −10°, the peak area ratio of signals assigned to methyl protons attached to aluminum atom, to those in the OCMeNPh grouping, and the phenyl protons of the *o*-phthalaldehyde moiety corresponded to the formula of **2**. The ir spectrum gave valuable information on the structure of **2**. On forming **2**, the carbonyl absorption of *o*-phthalaldehyde shifted from 1699 to 1679 cm^{-1} and the absorption band assigned to the O-C-N grouping of **1** shifted from 1568 to 1572 cm^{-1}. The latter shift (from 1568 to 1572 cm^{-1}) is equal to that observed in the formation of the benzaldehyde complex $Me_2AlOCMeNPh \cdot PhCHO$.[9] It is reasonable to conclude

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