on the polymers, as well as on a mixed-crystal *n*-paraffin sample of $C_{36}H_{74}$-$C_{36}D_{74}$ (10:1), are given in Table I.

Discussion

It has been shown[5-7] that a study of PEH–PED mixed-crystal systems can provide information on chain organization in the crystalline regions of polyethylene. This derives from the effect which such organization (as determined by the pattern of chain folding, or lack thereof) has on the intermolecular interaction splittings of the internal modes of the guest (in this case PED) and host (PEH) molecules. Thus, for example, whereas the splitting of the CD_2 bending mode, $\nu_b(CD_2)$, is about 7.7 cm^{-1} in pure PED single crystals,[6] in PEH–PED (10:1) single crystals it is 5.4 cm^{-1} (Table I). This shows that the PED chains are indeed mixed with the PEH chains at a molecular level. Also, the good agreement between observed and calculated[5] $\Delta\nu_b(CD_2)$ values, plus the fact that the splitting of the CH_2 rocking mode, $\nu_r(CH_2)$, is significantly higher in the mixed polymer crystal than in the mixed paraffin crystal (where random mixing is expected), supports the conclusion that the chains in single crsytals are folded predominantly along (110) planes.[6] The loss of splitting in $\nu_b(CD_2)$ upon melt crystallization, together with the retention of the same splitting in the $\nu_r(CH_2)$ modes (Table I), argues convincingly for a conversion of (110) to (200) folding as a result of this treatment.[6]

On the basis of the above analyses,[5,6] the interpretation of the spectral results for the capillary extruded samples is straightforward. As is seen from Table I, the PEH–PED (10:1) plug exhibits splittings identical with that of a melt-crystallized sample derived from single crystals. This indicates the predominance of (200) chain folding, as would be expected for this material. In the PEH–PED (10:1) strand, however, while the $\nu(CD_2)$ mode is still a singlet, the $\nu_r(CH_2)$ mode shows a significantly lower splitting, comparable to that of the (randomly mixed) paraffin crystal. If we take into account the fact that, for the hydrogenated compounds, the paraffin crystal splittings are slightly smaller than those for the polymer as a result of the small difference in unit cell dimensions,[6] then we see that the results for the PEH–PED (10:1) strand are indicative of essentially completely random mixing of chains. Such organization does not occur in polymers with folded chain morphologies,[6,7] but it is the expected type of mixing for extended chains. This result thus not only establishes on a firm molecular basis the previous conclusions concerning chain morphology in capillary extruded PEH,[1,2] but it provides confirmation for our prior interpretations of the infrared spectra of mixed PEH–PED crystals.[6,7] As we have noted,[7] there is therefore no basis to the claims[8] that these interpretations are ambiguous.

It should be noted that the magnitude of the splitting of $\nu_r(CH_2)$ in the PEH–PED (10:1) strand suggests that a predominant portion of the material consists of randomly mixed chains. Thus, although the strand was found to be composed of two morphological units[3] (an inner core and an outer sheath), we conclude that random chain organization prevails in both. If, as has been proposed,[2a] the outer sheath contains lamellar structures, then the chain folding in these lamellae must be characterized by nonadjacent reentry, in distinction to the kinds of lamellae formed by dilute solution crystallization or by melt crystallization. It may, however, be the case that extended chain crystallization exists throughout the diameter of the strand, with different organizational features present in the inner core and the outer sheath.

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Dilatometry of Selective Interactions in Synthetic Polycarboxylate Solutions

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In recent reports some peculiar physicochemical properties of poly(maleic acid) in aqueous solution have been discussed on the basis of potentiometric[1] and calorimetric data.[2] One interesting feature is that monovalent counterions, *i.e.*, Li^+, Na^+, and $(CH_3)_4N^+$, diversely influence the thermodynamics of ionization of poly(maleic acid) more than in the case of other weakly ionized polymers in aqueous solution.[3] Extension of the study to the interaction of divalent counterions with poly(maleic acid) has yielded a preliminary indication of a markedly stronger affinity of Ba^{2+} with respect to Mg^{2+} for this polyelectrolyte.[4] We wish to give here additional evidence on the selective interaction of poly(maleic acid) with monovalent (Li^+, Na^+, and $(CH_3)_4N^+$) and divalent (Ba^{2+} and Mg^{2+}) counterions, respectively, in dilute aqueous solution, obtained by means of dilatometric measurements.

For a comparative purpose some dilatometric data for the maleic acid–ethylene copolymer are also reported.

In the experiments with the monovalent counterions, sample solutions of the polycarboxylates half-neutralized ($\alpha = 1$) with a given alkali hydroxide or $(CH_3)_4NOH$ were protonated by successive, separate mixings with aliquots of a HCl standard solution. Volume changes were determined using Linderstrom-Lang dilatometers at 25° after each protonation step.[5]

Such overall volume changes were in each case corrected for the quite small effects essentially due to the dilution of the polyelectrolyte—the resulting values were normalized per monomole of polymer in solution by obtaining the data plotted in Figure 1.

It is seen that distinctly larger volume increases accompany the protonation of half-neutralized poly(maleic acid) when $(CH_3)_4N^+$ ions are the counterions than when these are either Li^+ or Na^+ ions. This is in our opinion consistent with the finding already derived by different experimental means that Li^+ (and Na^+) would be extensively site bound while $(CH_3)_4N^+$ ions would be only "loosely" bound to poly(maleic acid) macroions.

Consider in fact the following scheme for the protonation reaction

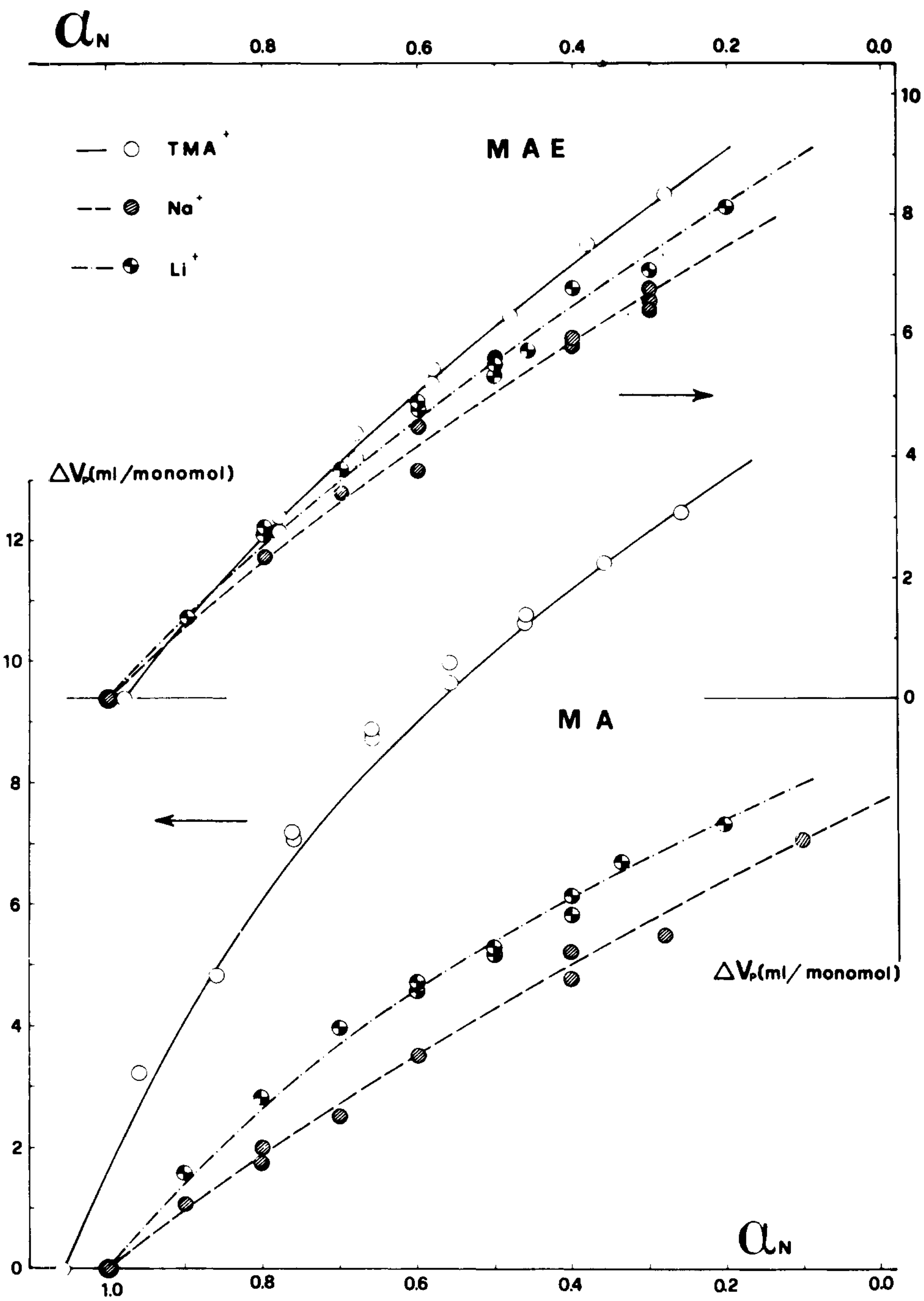

Figure 1. Volume changes upon addition of HCl solutions to half-neutralized poly(maleic acid) (MA) and maleic acid-ethylene copolymer (MAE) solutions in water at 25°. Initial concentration of polyelectrolyte: 2 × 10^{-2} monomol/l.

$$\mathrm{R(-COO^-} \ldots \mathrm{M^+)_{aq}} \xrightarrow{+\mathrm{H^+}} \mathrm{R{-}COOH} + (\mathrm{M^+})_{aq} \qquad (1)$$

In reaction 1 if the counterion M$^+$ is only weakly bound its hydration sheath will not change much while a number of water molecules will be liberated from the initially fully hydrated carboxylate group. If on the contrary site binding prevails, both carboxylate groups and counterions engaged in ion pairs will be less hydrated than in the free state.[7] Protonation (1) then leads to a loosening of fewer water molecules and thus to a relatively small volume increase. As a consequence, the exchange of $(CH_3)_4N^+$ with either Li$^+$ or Na$^+$ counterions along polymaleate chains has to be characterized by a volume *increase, i.e.*, by the liberation of electrostricted water.

If it is assumed that the volume of a solution containing a given number of monomoles of discharged (α = 0) poly(maleic acid) is independent of the simple salt (*i.e.*, LiCl, NaCl, or $(CH_3)_4NCl$) present in equimolar amount, then from our data (Figure 1) we estimate for the exchange process said above a volume increase of approximately 6 ml/mol of counterions (at α = 1.0). This would essentially account for the increase in entropy connected with such process, as evidenced on the basis of calorimetric and potentiometric data.[2]

In practice, according to Figure 1, the effect would be slightly larger with Na$^+$ ions than with Li$^+$ ions. In view of the limited amount of information derivable from our dilatometric data it would be, however, unwarranted to conclude that Na$^+$ is more extensively site bound than Li$^+$ to poly(maleic acid). As a matter of fact the opposite conclusion has been advanced on the basis of previous data from different experimental approaches.[2] To make the line of reasoning schematized above a more quantitative one and to help elucidate this point, more detailed information, in particular from a number of accurate par-

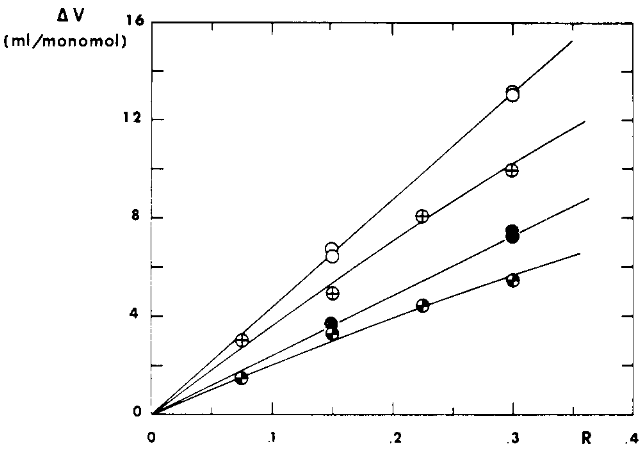

Figure 2. Volume changes upon addition of $MgCl_2$ and $BaCl_2$ solutions to poly(maleic acid) solutions in water at 25°, at different degrees of neutralization of the polymer, α. Counterion (α): Ba^{2+} (1.5), ○; Ba^{2+} (1.0), ⊕; Mg^{2-} (1.5), ●; Mg^{2+} (1.0), ◕.

tial specific volume data for the polyelectrolyte solutions of our concern, would be necessary.

In the case of the ethylene–maleic acid copolymer the dilatometric results also reported in Figure 1 show that the volume of protonation is scarcely sensitive to the nature of the monovalent counterions considered. This is in agreement with earlier evidences[2] leading to the conclusion that with this copolymer site binding of Li^+ (or Na^+) counterions certainly occurs to a lesser extent than with poly(maleic acid).

In comparing the results for the two polyelectrolytes one must however consider that passing from $\alpha = 1$ to $\alpha = 0$ involves a reduction in "linear" charge density for the polymaleate chains double than that for the copolymer chains. Roughly speaking, were the extent of macroions solvation proportional to the density of ionized carboxyl groups and independent of chain backbone chemical structure one might predict a ΔV of protonation with poly(maleic acid) twice that with the maleic acid–ethylene copolymer. Although necessarily in a qualitative fashion, such expectation is verified when both types of polyelectrolytes are half-neutralized with $(CH_3)_4NOH$ (see Figure 1).

On the contrary, and as already discussed above, the increase in volume upon protonation of lithium or sodium polymaleate is comparatively small and happens to be close to that found for the less densely charged copolymer chains. This again indirectly supports the hypothesis that intimate site binding occurs between Li^+ or Na^+ and poly(maleic acid).

In Figure 2 are reported the results of the dilatometric measurements in which partially neutralized $[(CH_3)_4NOH]$ poly(maleic acid) solutions were mixed with dilute $BaCl_2$ or $MgCl_2$ solutions.

In the ordinate ΔV is the volume change (corrected for dilution effects) expressed in milliliters per monomole; in the abscissa, R is the stoichiometric molar concentration ratio of divalent counterions to polyacid monomoles in the final solutions (the initial and final polymer concentration as well as α were constant in each set of experiments). Actually R is very close to the ratio of bound counterions per polymer monomole as we have found, on the basis of a few equilibrium dialysis experiments, that the fraction of either Ba^{2+} or Mg^{2+} associated to the macroions exceeded 99%.

It is then evident from Figure 2 that interaction of poly(maleic acid) with Ba^{2+} ions as compared with Mg^{2+} ions is accompanied by a distinctly larger volume increase.

In terms of volume changes per mole of bound divalent counterions, ΔV_B, we can estimate from the initial slopes of the plots of Figure 2 the following values: for Ba^{2+}, 44 ($\alpha = 1.5$) and 36 ($\alpha = 1.0$); for Mg^{2+}, 24 ($\alpha = 1.5$) and 21 ($\alpha = 1.0$) (always in milliliters per mole of counterion).

The differences in the above ΔV_B figures for Ba^{2+} and Mg^{2+} point out a remarkable desolvation of interacting Ba^{2+} and carboxylate ions of polymaleate chains. As a matter of fact, we have found[8] that ΔV_B for Ba^{2+} binding to the ethylenemaleic acid copolymer is nearly half that reported above for poly(maleic acid), under otherwise similar experimental conditions.

On the other hand, differences in charge density of the macroions cannot explain the differences in ΔV_B for Ba^{2+} binding, as for instance, we have also found that in the case of maleic acid–isobutylene copolymer at $\alpha = 1.5$ ΔV_B happens to be quite close (40 ml/mol) to that for poly(maleic acid) at the same stoichiometric degree of neutralization.[8]

The mode of binding, if not the extent, of alkali earth metal ions by polycarboxylates thus appears to be a rather sensitive function of macroions chains chemical constitution, a factor whose importance is of course magnified, as it is well known, in the case of divalent transition metal ions binding.[6]

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