motion of flexible side groups are not taken into account in eq 5.

The results reported here suggest a relation between the number of external degrees of freedom as found from volumetric data with that calculated from the steric factor. Since $\sigma$ values obtained with different experimental methods and in different theta solvents show significant variations, only semiquantitative significance can be assigned to eq 5.

**Acknowledgment.** For financial support, the authors are grateful to the donors of the Petroleum Research Fund administered by the American Chemical Society and to the Paint Research Institute.

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## Mixed-Crystal Infrared Study of Chain Organization in Polyethylene Crystallized under Orientation and Pressure

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*Received January 21, 1974*

When high-density polyethylene (PEH) is crystallized under certain conditions of orientation and high pressure, for example, by extrusion from an Instron capillary rheometer, samples (which we will refer to as capillary extruded PEH) are obtained which have unusual physical properties.[2a] It has been suggested,[2a] primarily on the basis of melting point data[2a] and X-ray[2b] and electron diffraction patterns,[3] that extended chain structures exist in such specimens, and that they account for the different physical properties. The above, as well as other, techniques of characterization provide, however, only an indirect inference of the kind of chain organization in such polymer samples. The object of the present study was to determine the nature of the chain organization by the more direct method of mixed-crystal infrared spectroscopy.

Theoretical[4,5] and experimental[6,7] studies have shown that the infrared spectra of mixed crystals of PEH and poly(ethylene-$d_4$) (PED) can be used to identify the relative location of portions of the same chain within a polyethylene crystal. This means that the pattern of chain folding in the crystal can be identified.[6] If folding does not occur, but the chains crystallize in their fully extended state, then the infrared spectra of such mixed crystals exhibit predictably different features. We have studied the infrared spectra of extruded samples of PEH containing, for optimization of the technique,[7] small amounts of PED. The spectra of such mixed-crystal systems indicate that extended chain morphology can predominate in capillary extruded polyethylene.

**Table I**
**Infrared Splittings (in $cm^{-1}$) for Capillary Extruded Polyethylenes**

| Sample | $\Delta\nu_b(CD_2)$ | $\Delta\nu_r(CH_2)$ |
|---|---|---|
| Marlex 6009 plug | | $10.9_5 \pm 0.1$ |
| Marlex 6009 strand | | $10.9_5$ |
| PEH–PED (10:1) S.C.[a] | $5.4 \pm 0.15$ | 10.4 |
| PEH–PED (10:1) M.C.[b] | 0[c] | $10.4_5$ |
| PEH–PED (10:1) plug | 0[d] | 10.4 |
| PEH–PED (10:1) strand | 0[e] | $9.9_8$ |
| $C_{36}H_{74}$–$C_{36}D_{74}$ (10:1)[f] | 0[g] | $9.9_3$ |

[a] S.C. = single crystals; $T_{x1} = 55°$. [b] M.C. = melt crystallized; single crystals heated to 150° for 24 hr and cooled to room temperature. [c] $\nu_b = 1089.0 \pm 0.2$ $cm^{-1}$. [d] $\nu_b = 1088.8 \pm 0.2$ $cm^{-1}$. [e] $\nu_b = 1089.0 \pm 0.2$ $cm^{-1}$. [f] Cast at room temperature and then melted at 80° for 3 hr. [g] $\nu_b = 1088.7 \pm 0.2$ $cm^{-1}$.

### Experimental Section

The polymers used in this study were a Marlex 6009 PEH ($M_w \cong 155{,}000$) and a Volk Radiochemical Co. PED ($M_w \cong 245{,}000$), the same materials used in earlier work.[6,7] The mixed-crystal samples were PEH–PED (10:1) on a molar basis. The material used in the Instron was either Marlex 6009 or single crystals of 10:1 PEH–PED prepared by cocrystallization of the two polymers from dilute xylene solution, the crystallization temperature being 55°. (The latter procedure was used in order to ensure an initially mixed sample.[6])

Specimens were prepared as follows. The barrel of the Instron rheometer was charged with polymer and maintained at 160° for 1 hr under a force of about 6 lb on the ram. The temperature was then allowed to drop slowly to 136° with about 2 lb of ram force. The melt was then extruded at a shear rate of 0.3 $sec^{-1}$ until a steady force was obtained. The force was then removed, and when the stress reached zero the extrusion procedure was repeated. The attainment of the same steady-state values of the force suggests that complete melting of the polymer sample was attained. At this point the rate of shear was increased abruptly to 15 $sec^{-1}$. The pressure increased rapidly, and was maintained at about 2400 atm for 20 min. The temperature was then allowed to drop to 110° at about 0.5°/min while maintaining the pressure at 2400 atm. At this point the pressure was released and the extrudate was removed from the capillary. The capillary had a length of 2.000 in. and a diameter of 0.050 in.

The final sample consisted of a thin relatively transparent strand (which derived from the capillary region of the die) attached to a thick opaque plug (which came from the rheometer barrel). X-Ray diffraction patterns showed the strand to have very high axial chain orientation, as previously reported,[2a] whereas the plug exhibited no orientation. All experiments involving the strand were performed on the very highly oriented portion immediately adjacent to the plug.

Melting points were determined using a differential scanning calorimeter cell in a DuPont 900 thermal analyzer operating at 10°/min. The melting points for the plug and strand were 134 and 140°, respectively, for the Marlex 6009, and 133 and 140°, respectively, for the mixed-crystal specimen. X-Ray diffraction patterns, taken with a mirror-monochromator Guinier focusing camera employing Cu $K\alpha_1$ radiation and a 127-mm specimen-to-film distance, showed that the (110) and (200) spacings were respectively identical in the plug and strand of both Marlex 6009 and the mixed-crystal sample. Thus, the orthorhombic unit cell dimensions are unaffected by the different physical treatment or the cocrystallization with PED. Infrared spectra were obtained on a Perkin-Elmer Model 180 spectrophotometer, using ~3-mil thick sections from the plug and the strand. The spectral observations

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.

**Acknowledgment.** We are indebted to Mr. James B. Stamatoff for obtaining the X-ray diffraction patterns. This research was supported in part by National Science Foundation Grant GP-38093.

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## Dilatometry of Selective Interactions in Synthetic Polycarboxylate Solutions

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*Received April 1, 1974*

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