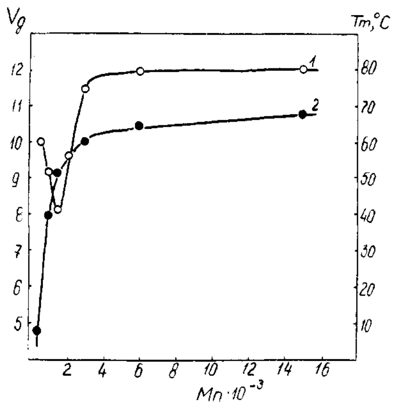

Figure 8. Dependence of V_g (curve 1) and melting point (curve 2) on molecular weight for poly(ethylene glycols). Sorbate, heptane; temperature, 82°C.

film thickness is smaller. This leads to the increase in solubility in good agreement with direct sorption data.[9]

So the data considered above show that the surface nature and the film thickness have an essential influence on the thermodynamic polymer–solvent interaction. There is a need to take these results into account in gas chromatography. From the other side it is evident that this method may become useful for the investigation of these influences on properties of the stationary polymeric phase.

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Mixed-Crystal Infrared Studies of Annealed Poly(ethylene) Single Crystals

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ABSTRACT: The annealing of mixed crystals of poly(ethylene) and poly(ethylene-d_4) results in a transformation, starting at about 100°C, from (110) to (200) folding. This is correlated with the onset of chain motions associated with crystal thickening and is accompanied by spectroscopic evidence for frozen-in chain disorder in the transition region. These results suggest that the fold organization which is stabilized by crystallization from a solvent is not necessarily that which is most stable with respect to the bulk state. In addition, they show conclusively that segregation cannot account for the spectroscopic results on mixed single crystals, as had been proposed; nor can random re-entry be considered a predominant mode of chain organization in single crystals.

Since Keller[1] discovered lamellar single crystals of linear poly(ethylene) grown from dilute solution, and suggested that the long-chain molecules had to fold in order to be accommodated in the crystal, the nature of the chain organization in such crystals has been one of the most controversial problems in the field of polymer science. Flory[2] and Mandelkern[3] have proposed that the re-entry of chains on the surface is predominantly random (the "switchboard" model), while Keller,[4–6] Lindenmeyer,[7] and Kawai et al.[8] have suggested that chain folding occurs with adjacent re-entry in crystallographic planes.

Some years ago a technique was proposed by Tasumi and Krimm[9] to resolve this question, namely mixed-crystal spectroscopy. In this method, poly(ethylene) (PEH) and poly(ethylene-d_4) (PED) are cocrystallized and the pattern of chain organization is deduced from the nature of the band splittings in the infrared spectrum. These splittings arise from interactions between neighboring like chains, and therefore provide a probe of the local environment of the molecules. If, for example, a small amount of PED is cocrystallized with PEH, then chain folding with adjacent re-entry along (110) planes gives rise to PED doublets of about half the splitting as in pure PED, whereas singlets result if the folding is along (200) planes [or (020)] or if random re-entry occurs. The latter two possibilities can be distinguished by analyzing the splittings associated with the PEH molecules, which will be smaller in the case of random re-entry.

These proposals were tested experimentally by Bank and Krimm.[10] By comparing the results on mixed crystals of PEH/PED with those on comparable mixed n-paraffin systems, they could demonstrate conclusively that random re-entry was not a significant component of polymer folding in the crystalline regions. Their results showed that in di-

Table I
Splittings of the CH_2 Rocking Modes of Mixed-Crystal Cast Films

	Annealing temp, °C										
	C.F.	40	50	60	70	80	88	97	106	115	124
PEH/PED	$\Delta\nu_r(CH_2) \pm 0.1$ cm^{-1}										
4[a]	10.23	10.20	10.20	10.24	10.19	10.13		10.06	10.04	9.94	10.00
10[a]	10.40	10.40	10.40	10.43	10.45	10.45		10.37	10.31	10.38	10.38
20[a]	10.50	10.53	10.53	10.50	10.47	10.50		10.39	10.31	10.40	10.52
PEH[a]	10.60	10.61	10.60	10.60	10.58	10.62		10.54	10.50	10.60	10.63
4[b]	10.23	10.20	10.23	10.14	10.20	10.10	10.17	10.03	9.95	10.00	9.94
10[b]	10.40	10.40	10.45	10.40	10.41	10.41	10.47	10.43	10.25	10.42	10.37
20[b]	10.50	10.53	10.50	10.52	10.52	10.40	10.58	10.46	10.41	10.50	10.45
PEH[b]	10.60	10.61	10.60	10.61	10.60	10.58	10.60	10.58	10.50	10.61	10.75

[a] Splittings of one piece of cast film, with specified molar ratio, annealed at successive temperatures. [b] Splittings of individual cast films with specified molar ratio annealed at the specified temperature.

lute solution crystals folding with adjacent re-entry along (110) planes predominated, whereas in melt-crystallized polymer folding along (200) planes was the prevailing mode of chain organization.

Although these conclusions were challenged[11] on the basis that the splittings in single crystals could arise from segregation of species, careful work by Ching and Krimm[12] has shown that when segregation is possible it can be carefully controlled so that it makes no significant contribution to the spectral results. In addition, segregation is totally incompatible with the singlets observed for the melt-crystallized polymer.[13] These conclusions were further substantiated by the finding[14] that the polymer system can exhibit random mixing under special circumstances, namely capillary extrusion.

A detailed analysis of the mixed-crystal technique[15] thus shows that it is a reliable and unique method for studying chain organization in crystalline polyethylene. We report here its application to the study of the annealing process in single crystals. We find that annealing below the melting point produces a transition from (110) to (200) folding. This not only indicates the nature of the reorganization which can take place with the onset of chain motion, but the existence of such a transformation shows conclusively that segregation is not the origin of the splittings observed in single crystals.

Experimental Section

The same polymers were used in this study as in our earlier work: PEH, Marlex 6009, $\bar{M}_w$ = 160000, $\bar{M}_n$ = 11500; PED, Volk Radiochemical Co., $\bar{M}_w$ = 621000, $\bar{M}_n$ = 105600. The difference in DSC melting points of these polymers is 0.5°C.

Single-crystal mats of composition 10 PEH/1 PED were prepared from 0.025% xylene solution at 55°C and at 80°C by filtration. The mats were then annealed in vacuo at 120 and 127°C for 18 hr.

Mixed-crystal samples of varying molar ratios were also cast at 50°C from 0.025% xylene solutions. The cast films were then annealed in vacuo at a specified temperature for 18 hr in two different ways. In the first, a particular film was used throughout the annealing process, being heated successively to higher temperatures. In the second, different films were used and were heated only once to the specified temperature.

Infrared spectra were obtained at room temperature on a Perkin-Elmer Model 180 Spectrophotometer. After annealing, all samples were examined and verified to be free of accidental oxidation.

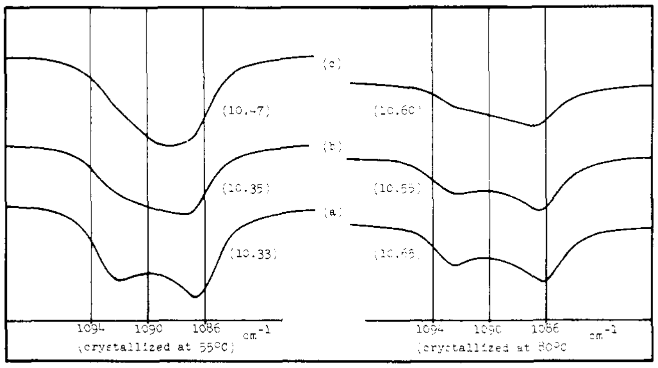

Figure 1. Spectra of the CD_2 bending modes of 10 PEH/1 PED single crystals obtained from 0.025% xylene solutions at 55 and 80°C: (a) single crystal mats; (b) annealed at 120°C for 18 hr; and (c) annealed at 127°C for 18 hr. The corresponding splittings of the CH_2 rocking modes are shown in parentheses.

Results

The spectra of the CD_2 bending modes of 10 PEH/1 PED single-crystal mats obtained from dilute solution at 55 and 80°C are shown in Figure 1. The 80°C crystals are seen to be heterogeneous, as indicated by the fact that the observed splitting of the CD_2 bending mode (6.1 ± 0.15 cm^{-1}) is significantly larger than that (5.2 ± 0.15 cm^{-1}) generally obtained from lower temperature crystallization. The tendency toward segregation under these conditions is confirmed by the larger splitting of the CH_2 rocking mode, and has been noted before.[12,16] After annealing, the spectrum of the CD_2 bending mode of the 55°C mat was dominated by a central singlet, while that of the 80°C mat still exhibited predominantly the original doublet.

A more detailed study was done on the cast films. The splittings of the CH_2 rocking modes of films of different molar ratios which were annealed at increasing temperatures are listed in Table I, and a plot of these splittings is shown in Figure 2 for a pure PEH sample. The spectra of the CD_2 bending modes for some of the films are shown in Figure 3.

The infrared results indicate that, regardless of annealing procedures, the changes in the splittings of the CH_2 rocking modes as well as the spectra of the CD_2 bending modes show a similar trend at various annealing temperatures. Thus, the decrease in splitting of the CH_2 rocking modes near 100°C is common to all samples, as is the progressive transformation of the CD_2 doublet into a singlet as the temperature is raised above 100°C. As the annealing temperature gets close to the melting point, the infrared characteristics of both CH_2 and CD_2 vibrational modes tend to be comparable to those of melt-crystallized samples of the same molar ratio.[10,13,15]

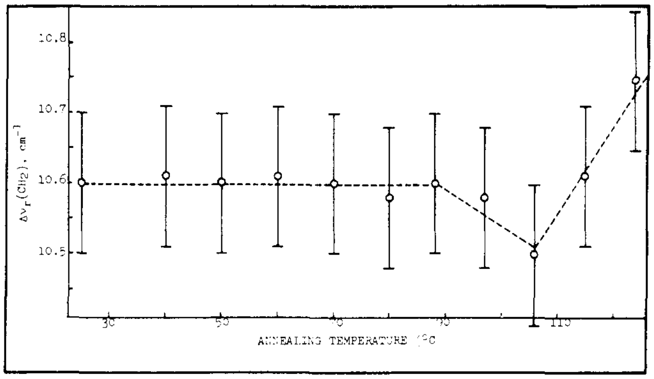

Figure 2. Splitting of the CH_2 rocking mode of pure poly(ethylene) cast films as a function of the annealing temperature. Each point represents a separate film annealed at the specified temperature for 18 hr.

Discussion

As we have shown earlier,[12,13] mixed crystals of PEH/PED can be grown under conditions where segregation of species is minimized. These conditions generally are a small difference in melting points, a high PEH/PED ratio, and a low-crystallization temperature. The influence of these factors is well illustrated by the results shown in Figure 1. Thus, the 80°C crystals show, by their larger splittings, that segregation is present; since this is not expected to be altered (nor is it) by annealing, other changes brought about by annealing are thereby masked. Similarly, we see from Figure 3 that, as the PEH/PED ratio increases, segregation is reduced, and the effects of annealing are more readily visible. This demonstrates our contention[12,13] that the effects of segregation can be controlled and minimized.

It is important to note that annealing of mixed crystals results in the conversion of the CD_2 bending mode doublet into a singlet. This fact alone shows that the doublet could not have been due to segregation, since we would then have to suppose that annealing below the melting point produces a "de-segregation" of species, hardly a likely process. Such an explanation is rendered even less probable, not only by the fact that segregated (80°C) crystals do not behave this way, but by the observation that the splitting of the CH_2 rocking mode remains essentially constant with annealing, finally even increasing slightly. If "de-segregation" occurred, with a dispersal of PED chains among the PEH chains, then the CH_2 splitting should decrease to values comparable to those in equivalent n-paraffin mixtures,[10] as it does in the random organization which prevails in capillary extruded polymer.[14] These results show even more strongly than did our previous analysis[12] that the proposal[11] to explain splittings in mixed single crystals by invoking segregation is invalid. Such splittings are therefore strongly indicated to be due to folding with adjacent re-entry in (110) planes.[9,10]

We consider now the specific nature of the spectral transformation which occurs on annealing. As we have seen, the changes, which begin near 100°C, cannot be explained by a random mixing of chains. On the contrary, the approach toward the melt-crystallized state suggests that, as previously argued[10,15] for the chain organization in this state, the transformation on annealing corresponds to a conversion from (110) to (200) folding. The changes in the CD_2 and the CH_2 splittings are consistent with this interpretation. It should be noted that such a transition in the solid state involves no "molecular acrobatics". It is only necessary that a fold plane in space shall convert from (110) to (200) folding, as is shown in Figure 4. This is dimensionally feasible, since the inter-stem separation along the (110) plane (viz., 4.45 Å) is close to that along the b axis (viz., 4.94 Å), and is dynamically achievable by relatively small rotations of chains about, and translations parallel to, their axes,[17] and small translations of fold planes with respect to one another.

That the above mechanism is a reasonable one is supported by our observation that the transformation begins near 100°C. It is known[18,19] that at about this annealing temperature single crystals begin to undergo thickening, as revealed by an increase in the X-ray long period. This must be accompanied by chain motions, which could easily include the kind noted above. Furthermore, such a process could account for the slight decrease in the splitting of the

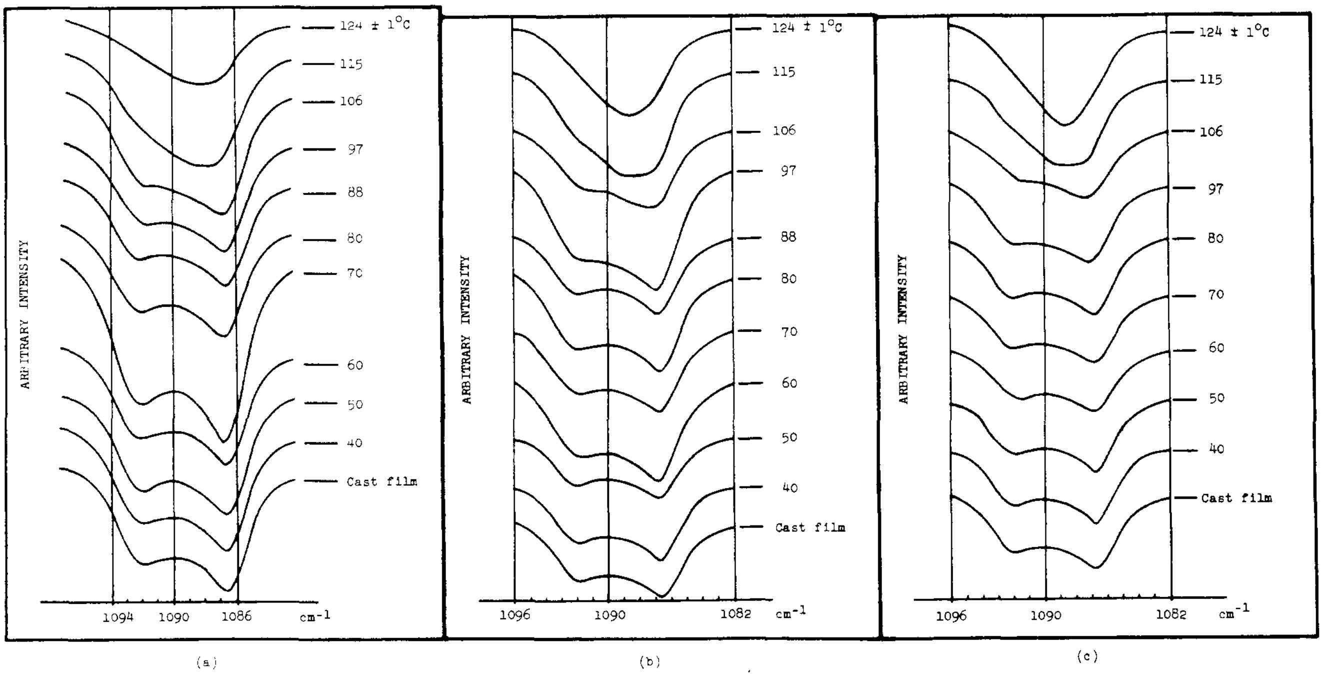

Figure 3. Spectra of the CD_2 bending modes at various annealing temperatures for: (a) 10 PEH/1 PED cast films; (b) 20 PEH/1 PED cast films; and (c) 40 PEH/1 PED cast films.

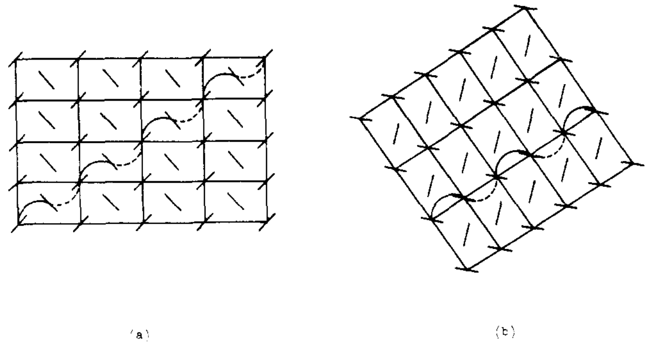

Figure 4. Possible conversion from (a) (110) to (b) (200) folding in which fold plane orientation in space is unchanged.

CH_2 rocking modes which is observed in pure PEH (Figure 2) as well as the mixed crystals (Table I) in the vicinity of 100°C. This decrease must be due to, on the average, weaker inter-chain interactions, which could arise from small increases in the unit cell dimensions. The latter could result from the freezing in of "defective" chain orientations that are not completely eliminated until higher annealing temperatures are reached. It is interesting to note that evidence for such frozen-in disorder has been obtained from X-ray diffraction studies.[19]

The existence of the above dip in CH_2 rocking mode splitting with annealing temperature makes it unlikely that the mechanism of annealing can be explained in terms of a partial melting and recrystallization, as has been suggested.[18,20] If the latter were true, then, since the splitting for melt-crystallized polymer is higher than that for single crystals,[15] we would expect a continuous increase in the splitting as we pass through the transition region and form more (melt) recrystallized polymer. This is not observed, and therefore we must suppose that the reorganization of chains does not proceed through a melt state.

The above results suggest an important conclusion which emerges from these studies, namely that (110) folding in solution-grown single crystals comprises a frozen-in metastable state compared to that which is most stable in the bulk polymer. In other words, crystallization in the presence of this solvent has led to a form of fold organization which, although favored under these circumstances, is not maintained when the chains are given the freedom to move and to adjust to a minimum free-energy state in the bulk. This transformation from (110) to (200) folding upon annealing provides further support for the existence of folding with adjacent re-entry in crystalline poly(ethylene).

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Contribution of Vibrational Free Energy Term to Stability of Polymethylene Crystal Lattices

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ABSTRACT: The vibrational terms of the thermodynamical functions, the internal energy, the entropy, and the Helmholtz's free energy of the orthorhombic, monoclinic, and triclinic modifications of polymethylene have been calculated in a harmonic approximation by means of normal modes treatment of the crystal lattices using Lennard-Jones type and Buckingham type intermolecular hydrogen–hydrogen potential functions. The calculated results for the orthorhombic form reproduce well the thermodynamical functions derived from thermal measurements. The vibrational free energy term of the orthorhombic form is found to be 0.5–0.3 kJ/mol per CH_2 unit less than that of the monoclinic and triclinic forms at 300°K. The value seems large enough to compensate for the static potential energy term which has been estimated as 0.15 kJ/mol per CH_2 unit higher in the orthorhombic form than in the monoclinic form. Thus, the vibrational free energy term contributes to the thermodynamical stability of the orthorhombic lattice of polymethylene under the normal conditions. The free energy of the liquid phase has been derived from the thermal data reported and the results of the present calculation.

As is well-known polyethylene crystallizes into an orthorhombic form under ordinary conditions.[1] Another crystal modification of a monoclinic system has been found to appear when the sample specimen is put under stress.[2,3] Thus, the monoclinic form may be metastable under normal conditions. Yemni and McCullough[4] tried to clarify the transition mechanism between these two crystal forms by calculating the static potential energy of the polymethylene crystal with variations in the cell constants and the orientations of the chains. In contrast to the experimental findings, the monoclinic form was found to be more stable by about 0.15 kJ/mol per CH_2 unit than the orthorhombic