Infrared Spectra of Polyethylene–Poly(ethylene-d_4) Mixed-Crystal Systems

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ABSTRACT: The arguments presented by Stehling, Ergos, and Mandelkern concerning the influence of compositional heterogeneity in polyethylene–poly(ethylene-d_4) mixed crystals on the interpretation of the infrared studies of Bank and Krimm are examined in depth. It is shown that not only are their claims unsubstantiated, but a detailed analysis of their results provides additional support for the conclusion of Bank and Krimm that random reentry is a negligible contribution to chain folding in dilute solution crystals, (110) folding predominating.

On the basis of a normal vibration analysis of crystalline polyethylene,[1] it was shown by Tasumi and Krimm[2] (hereafter referred to as TK) that an infrared study of mixed crystals of polyethylene (PEH) and poly(ethylene-d_4) (PED) could be used to distinguish between chain folding with adjacent reentry in the (110) plane and chain folding with random reentry. Subsequent experimental studies by Bank and Krimm[3] (BK) resulted in the demonstration that the former type of chain folding indeed predominated in PEH single crystals, random reentry folds being negligible. This conclusion was believed to be supported by the spectroscopic analysis in spite of the existence of some small spectral effects which were evidently due to aggregation of individual isotopic species.[3,4]

In a previous paper, Stehling, Ergos, and Mandelkern[5] (SEM) have shown that, because of a difference in melting points between PEH and PED (which parallels a similar difference between n-$C_{36}H_{74}$ and n-$C_{36}D_{74}$), a compositional heterogeneity occurs in the mixed crystals produced by exhaustive crystallization of solutions containing these two polymers. They claim that, as a result of this distribution in PEH/PED ratio among the crystals formed, the results of BK cannot be interpreted unequivocally as indicating adjacent reentry and that in fact the infrared results can be explained just as well as arising from such heterogeneity. Hence, they suggest that adjacent reentry is not the only mechanism for interpreting the infrared results and thus a random reentry model is not excluded.

In the present paper, we wish to show that the analysis by SEM of the infrared spectra of dilute-solution mixed crystals is incomplete and therefore inadequate to substantiate their claims. (The case of melt-crystallized mixed crystals will be considered at a later time.[6]) When the results of SEM are analyzed in somewhat greater depth, it becomes obvious that they, in fact, strongly support the assertion of BK that a predominantly random reentry model of chain folding is untenable.

Since the arguments of both BK and SEM depend in part on the analysis of the mixed-paraffin system, we will consider this system first before discussing the mixed-polymer system.

n-$C_{36}H_{74}$–n-$C_{36}D_{74}$ System

In the work of BK, cocrystals of n-$C_{36}H_{74}$ and n-$C_{36}D_{74}$ were obtained by crystallization from benzene solution. In most cases, the sample used for infrared study consisted of the initial crystals which formed upon cooling, while in some cases the sample consisted of the entire residue left after evaporation of the solvent.[3] In the case of the former type of sample, the band splittings of the H modes for 1H/1D were found to be slightly larger than for the latter type of sample, indicating a small departure from homogeneity in the composition of crystals formed at different stages of the crystallization. Although this effect was not evaluated quantitatively by BK, neither was it considered of great importance, since the results on paraffin mixed crystals that are most relevant are those at the extremes of the compositional range, where greater homogeneity in composition is to be expected.

The work of SEM on mixed-paraffin systems has demonstrated (a) that the melting point of n-$C_{36}D_{74}$ is lower than that of n-$C_{36}H_{74}$, (b) that this is expected to give rise to a compositional heterogeneity when crystallization is carried through to high conversions, and (c) that experimental results on cocrystals prepared from benzene solution are in agreement with predictions of the partitioning which is to be expected. What SEM have not done is to show that their results in fact support the BK interpretation of the infrared data, and since this is relevant to the interpretation of the mixed-polymer system, we wish to examine this point in greater detail.

The distribution of crystal compositions when crystallization is carried to 100% conversion can be calculated if equilibrium crystallization is assumed (which is reasonable for the paraffin system). The results of such calculations are shown in Figure 1, due to Stehling.[7] The experimental results of SEM (Table II of their paper) are in good accord with the predictions of Figure 1.

The predictions of Figure 1 are also in accord with the observations of BK on the infrared spectra of such mixed-crystal systems. Thus, the crystals formed in the early stages of crystallization from a 50:50 mixture should have a relatively higher H content (and therefore a larger splitting in the H-mode doublets) than the crystals obtained from the exhaustive crystallization of this mixture, as is found. Also, as expected, the composition distribution of crystals obtained from

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[1] M. Tasumi and S. Krimm, *J. Chem. Phys.*, **46**, 755 (1967).
[2] M. Tasumi and S. Krimm, *J. Polym. Sci., Part A-2*, **6**, 995 (1968).
[3] M. I. Bank and S. Krimm, *ibid., Part A-1*, 7, 1785 (1969).
[4] M. I. Bank and S. Krimm, *ibid., Part B*, **8**, 143 (1970).
[5] F. C. Stehling, E. Ergos, and L. Mandelkern, *Macromolecules*, **4**, 672 (1971).
[6] J. H. C. Ching and S. Krimm, to be published.
[7] F. C. Stehling, to whom we are indebted for providing the figure and for permission to reproduce it. The calculation is based on I. J. Skeist, *J. Amer. Chem. Soc.*, **68**, 1781 (1946).

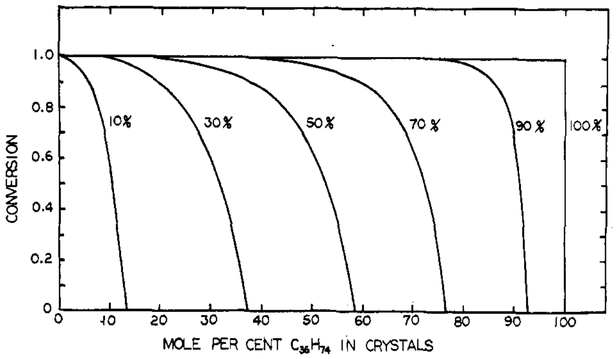

Figure 1. Composition of crystals formed at different conversions from n-$C_{36}H_{74}$–n-$C_{36}D_{74}$ mixtures with various initial compositions.

extreme initial composition ratios is narrower than that obtained in the middle range. For example, from a solution containing n-$C_{36}H_{74}$/n-$C_{36}D_{74}$ initially equal to 90/10, the first 75% of the crystals contain 89–93% n-$C_{36}H_{74}$, while 90% of the crystals are in the 86–93% composition range. For a higher initial H/D ratio, the composition distribution in the major fraction of the crystals will be even narrower. It should be noted that, since the composition of the initial crystals is, however, slightly different from that of the solution, this would necessitate a small change in the curve which relates band splittings of the major species with content of the minor species.[8]

The important conclusion to be drawn from these results—which was stressed by BK—is that the spectra clearly show that for crystals with $H/D > 1$ the minor species is *randomly mixed* in the major species. This is evidenced by the narrow D singlets, which indicate that, despite any slight heterogeneity in *composition*, there is no detectable departure from random *organization* within the crystals. There can be no question, therefore, that in examining the mixed-polymer crystal system we must associate random mixing of isotopic species with singlet bands for the minor component, especially at high dilution.

A quantitative analysis of the results of SEM on n-$C_{36}H_{74}$–n-$C_{36}H_{74}$ mixed-crystal systems thus shows that their findings are consonant with the infrared results and substantiates the major conclusions drawn by BK from their infrared data.

PEH–PED System

In an examination of the PEH–PED system, SEM have shown that these two polymers also have slightly different melting points. They therefore expect a compositional heterogeneity in the crystals formed by exhaustive crystallization, as for example in the cast films studied by BK. Such apparent heterogeneity is demonstrated in the early stages of crystallization at 89° (see their Table IV), from which SEM conclude that since aggregated regions can also give rise to doublets, the interpretations of BK are rendered equivocal and ambiguous and therefore do not constitute a strong argument for folding with adjacent reentry in the (110) plane for dilute-solution crystals.

There are two aspects to assessing the validity of the above arguments. First is the question of whether the above observations and arguments are relevant to the studies carried out by BK. Second is the question of whether a *quantitative* evaluation of the results presented by SEM does indeed leave the situation as ambiguous as they claim.

With respect to the relevance of the SEM results to the BK experiments, the following points should be noted.

(1) While the melting point of an n-paraffin is a well-defined quantity, that of a polymer is less so. The dsc melting point of the PED used by SEM was 4.8° lower than that of their PEH. In the case of the BK polymers, the dsc melting point of the PED was 0.5° lower than that of the PEH. Partitioning in the BK mixed crystals is therefore expected to be much less than that in the SEM mixed crystals.

(2) The experimental data on the basis of which SEM attempt to demonstrate the magnitude of the compositional heterogeneity are obtained at a crystallization temperature of 89° (compare their Table IV). The infrared measurements of BK were done on films cast at 55°. As can be seen from Table III of SEM, the ratio of the crystallization rates of their PEH solutions and PED solutions drops from about 35 at 89.1° to about 5 at 80.1°. (These numerical ratios, incidentally, have little relevance to crystallization rates of PEH and PED from the *same* solution: the early nucleation of PEH undoubtedly influences the rate of crystallization of PED.) This ratio should approach 1 as the crystallization temperature is lowered, since the relative undercoolings of both polymers converge. Thus, crystals obtained by casting at 55° would be expected to show smaller effects of segregation of H and D species than those formed at 89°. This is supported by experimental results,[4] which show that the splittings of the D modes in a 4H/1D mixed crystal are significantly lower in the 55° cast film than in crystals grown at 90°.

(3) In their discussions, SEM continually stress the point that the interpretations of BK depend upon the tacit assumption that the composition distributions in paraffin and in polymer cocrystals of the same average composition are similar. They say that this is unlikely in view of the dependence of distribution on the details of the crystallization kinetics and procedures and therefore that unambiguous conclusions concerning the structural origin of splittings in the PEH–PED system are not possible. First, as we noted earlier, the significant result of the study of paraffin cocrystals is that the minor species is randomly distributed within the host crystal. This is the only tacit assumption involved. Second, it is not true that the composition distributions of paraffin and polymer cocrystals are dissimilar under all conditions. As the H/D ratio increases for the paraffin crystals, a higher proportion of the material becomes relatively more homogeneous in composition (*cf.* the 90 and 100% curves in Figure 1). No matter what the nature of the crystallization in the polymer case, a similar trend must exist in the high H/D region, namely, the precipitation of crystals in which the major portion of the D chains are in crystals in which they constitute a very minor species. (We will shortly show that this is indeed true experimentally.) Third, as a consequence of the above two points, any aggregation of D chains in crystals for which $H/D \gg 1$ (which is the region on which BK based their analysis) must therefore be presumed to arise in some way from the connectedness of the crystalline chain stems by the folds.

We see therefore that the points raised by SEM, on the basis of which they conclude that the interpretations of BK are ambiguous, are themselves of minimal relevance to the original arguments.

We consider next the implications of a more quantitative analysis of their results than was given by SEM. In particular, we wish to inquire into the predicted band shape of the CD_2 bending mode if a 90(PEH)/10(PED) system is crystallized to completion and a random-reentry model is assumed.

From Table IV of SEM we find that for the 90/10 solution

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(8) M. I. Bank and S. Krimm, *J. Appl. Phys.*, 40, 4248 (1969).

the crystals precipitated at time $10\theta_i$ (θ_i being the time at which a precipitate was first observed) comprise 87.4% of the original material (not the 40–50% claimed by SEM!). What is left in solution is close to 50/50 in composition, and if we can assume the results in Table IV for this composition ratio, then we can compute what is precipitated after an appropriate $10\theta_i$. The composition ratio in solution after such a "second stage" of crystallization is about 10/90, and again we may use Table IV to determine the composition of the precipitated material after an additional $10\theta_i$. The results of this calculation are given in Table I, where it is assumed that in the last stage of crystallization all of the remaining material precipitates out together.

While this is admittedly a crude calculation, it nevertheless undoubtedly serves to indicate the general outlines of the kind of heterogeneity which may occur upon crystallization of this mixed-polymer system from solution. The first point which we note is that the results in Table I are strikingly similar in form to those predicted for the 90% paraffin system (*cf.* Figure 1). While exact equivalence is not important, it is also clear that, as stated earlier, the composition distributions in the two systems will further approach each other as the H/D ratio increases beyond 90/10. The second, and more important, point is that the data in Table I permit us to predict a band shape for the CD_2 bending mode on the basis of a random-reentry model. Thus the (at least) 63% of the D chains which occur in crystals with $H/D > 1$ contribute a singlet, while the 37% of the D chains which occur in crystals with $H/D < 1$ give rise to doublets whose splittings can be obtained (even if roughly) from the mixed-paraffin crystals.[8] The intensity ratio of the integrated doublet band to the singlet band (based on our measurements of monoclinic and triclinic paraffins, and consistent with theory) is about 2:1. For this intensity ratio, the predicted CD_2 band for the above case would be dominated by the *singlet* contribution. (This result is essentially independent of the details of the crystallization sequence assumed beyond stage one.) This is in total contradiction to the experimental result,[3,4,6] which shows a well-defined *doublet* for this case. Thus, even if compositional heterogeneity is taken into account quantitatively, the infrared data are inconsistent with an essentially random-reentry model.

Finally, in evaluating the arguments of SEM with respect to the PEH–PED system, it is important to take account of another clear experimental fact. This is that, as observed by BK and presented in greater detail in Figure 2, the limiting band shape of the CD_2 bending mode as the D chains approach infinite dilution is a doublet and not a singlet. We have already noted that at this end of the composition ratio of PEH to PED, as the H/D ratio increases, the fraction of the D chains which would be expected to be isolated from one another also increases. Thus if random reentry prevailed, the D mode should tend toward a singlet at very high H/D. As Figure 2 shows, this is not the case, the limiting situation giving a doublet of about 4.8-cm^{-1} splitting, which is in good agreement with that predicted for (110) folding by TK from a normal vibration analysis (*viz.*, 4.1 cm^{-1}). This result is not consistent with self-aggregation of D chains, since this would give rise to a significantly larger splitting.[2] Of course, it might be argued that this splitting is still consistent with some kind of random reentry. That is, instead of the D chains being essentially completely isolated from one another as they should be in the limit of infinite dilution, they inherently tend to aggregate into regions which incorporate about one-third H chains (which is required by the 4.8-cm^{-1} splitting[8]). Until any rational argument is presented to justify such an unobvious and arbitrary structure, it makes little scientific sense to entertain this possibility. It is much more justifiable to assume that the chain connectedness corresponds to folding with adjacent reentry in the (110) plane.

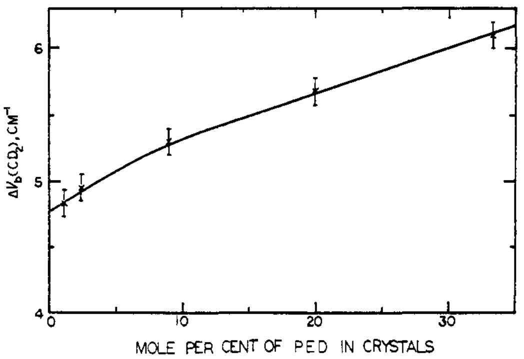

Figure 2. Splitting of CD_2 bending mode in PEH–PED cocrystals formed by film casting at 55° as a function of the initial PED concentration.

TABLE I

COMPOSITION DISTRIBUTION IN EXHAUSTIVE CRYSTALLIZATION OF A 90(PEH)/10(PED) SOLUTION

Stage	PEH in crystal	PED in crystal	(PEH/PED)$_{av}$	Total precipitated
1	83.0	4.4	19/1	87.4
2	6.7	1.9	3.5/1	96.0
3	0.2	1.1	1/5.5	97.3
4	0.1	2.6	1/26	100.0

Conclusions

In summary, the results of SEM are useful in demonstrating the origin of small segregation effects observed by BK in their infrared studies. In addition they help to evaluate this effect more quantitatively than could BK in their work. However, the claim by SEM that their results render ambiguous the conclusion of BK that (110) folding prevails in dilute solution crystals of polyethylene is seen to be unsubstantiated. If anything a detailed analysis of the results of SEM lends additional support to the conclusion of BK by permitting a more exact evaluation of the segregation effects.

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