Mixed-crystal infrared studies on melt-crystallized polyethylene

J. H. C. Ching and S. Krimm

Harrison M. Randall Laboratory of Physics, University of Michigan, Ann Arbor, Michigan 48104

In order to minimize the occurrence of heterogeneities, or segregation, of polyethylene and poly(ethylene-d_4) in mixed-crystal systems during melt crystallization, it has been found that conditions of high molar ratio of PEH/PED and a small difference in melting points between the two species are necessary. Under these optimum conditions the infrared spectral results observed in melt-crystallized polyethylene have to be attributed predominantly to chains which fold essentially with adjacent reentry along (200) planes.

INTRODUCTION

Mixed-crystal infrared studies, which are based on an analysis of the splittings of vibrational frequencies due to the intermolecular interactions within crystalline regions, have been shown to provide a distinctive means of characterizing chain folding in crystalline polyethylene directly at a molecular level.[1-5] However, it has been reported that, due to a difference in melting points between polyethylene (PEH) and poly(ethylene-d_4) (PED), a compositional heterogeneity of the two species could occur during cocrystallization.[6] As a result, it was claimed[6] that segregation of species could occur, and therefore that ambiguity existed in the interpretation of the spectroscopic results in terms of folding with adjacent reentry.

It had been shown by Bank and Krimm[7] that segregation of species was minimal under their normal experimental conditions. In a more detailed study, Krimm and Ching[8] demonstrated that the degree of heterogeneity in mixed-crystal systems obtained from dilute-solution crystallization can be minimized under optimum conditions, namely, a high molar ratio of PEH/PED, low crystallization temperatures, and a small difference in melting points between the two species. Under these conditions the splitting of the CD_2 bending mode of mixed crystals, for example 10 PEH/1 PED, can not arise accidentally from segregation, but derives from chains which fold predominantly with adjacent reentry along (110) planes.[2]

In this paper we report an investigation of the conditions which lead to a minimization of heterogeneity in melt-crystallized mixed-crystal systems. In such systems Bank and Krimm[2] have concluded that chains fold predominantly with adjacent reentry along (200) planes.

EXPERIMENTAL

PEH M and PED V (the physical properties of PEH's and PED are listed in Table I) were used. Samples of different molar ratios were first dissolved at 0.025% in a boiling xylene solution and then cast at 55 °C. Then they were melted under vacuum at 140, 150, and 170 °C for a specified period. At the end of the period they were cooled down to room temperature at a rate of about 0.5 °C/min.

The melt-crystallization process was repeated as mentioned above with PEH's of different molecular weights. Cast films were melted under vacuum at 150 °C for 40 h and then cooled down to a specified temperature and held there for another 50 h. Finally, the films were brought down to room temperature at a rate of about 0.5 °C/min.

The infrared spectra were obtained with a Perkin-Elmer Model 180 Spectrophotometer. It should be noted that all samples were examined for the possibility of accidental oxidation which might occur during the preparations. Only those which were free of oxidation were used for this study.

RESULTS AND DISCUSSION

As mentioned above, all samples were prepared from cast films of different molar ratios which were kept at temperatures above the melting point for a considerable period. Thus, the spectral results on the final crystallized materials were completely independent of their previous history, but depended only on the crystallization conditions and on their physical properties. In other words, any previous distributions of PEH and PED in the cast films were no longer retained after melting, and a new distribution was formed which depended on the crystallization conditions and physical properties of the two polymers.

The splittings of the CH_2 rocking modes of melt-crystallized mixed crystals with different molar ratios, $(PEH)_M/PED$, kept in the melt for different periods are shown in Table II. The spectra of the CD_2 bending modes of the 10 $(PEH)_M/1$ PED mixed-crystal sample are shown in Fig. 1. In general, the splittings of the CH_2

TABLE I. Physical properties of polyethylenes used in this study.

Polyethylene	Melting point T_m (°C)	Weight–average molecular weight
F [a]	132	983 000
P [b]	131	633 000
M [c]	129	160 200
A [d]	127.5	
Poly (ethylene—d_4)		
V [e]	128.5	621 000

[a] Special sample provided by Dow Chemical Co.
[b] Special sample provided by Monsanto Co.
[c] Marlex 6009.
[d] Ameripol.
[e] Produced by Volk Radiochemical Co.

TABLE II. Splittings of the CH_2 rocking modes for melt-crystallized $(PEH)_M$/PED samples at different melting temperatures.

PEH/PED	Day				
	1	2	3	4	5
140 ± 2 °C					
4 [a]	10.20	10.11	10.08	10.14	9.95 ± 0.1 cm⁻¹
6	10.27	10.20	10.15	10.25	10.14
10	10.48	10.43	10.50	10.51	10.48
20	10.75	10.52	10.75	10.71	10.68
40	10.76	10.63	10.82	10.79	10.75
PEH	10.84	10.79	10.84	10.81	10.83
4 [b]			10.06		10.15
6			10.22		10.16
10			10.37		10.43
20			10.60		10.67
40			10.77		10.76
PEH			10.86		10.78
150 ± 2 °C					
4 [a]	10.07	10.00	10.04	10.00	9.95 ± 0.1 cm⁻¹
6	10.16	10.14	10.08	10.08	10.09
10	10.53	10.45	10.45	10.41	10.30
20	10.67	10.74	10.56	10.57	10.57
40	10.74	10.75	10.76	10.60	10.66
PEH	10.85	10.83	10.83	10.70	10.72
4 [b]			10.04		10.10
6			10.08		10.15
10			10.43		10.47
20			10.60		10.70
40			10.74		10.72
PEH			10.80		10.77
170 ± 2 °C					
4 [a]	10.10	10.18	9.87	9.98	9.95 ± 0.1 cm⁻¹
6	10.00	10.07	9.90	9.95	10.00
10	10.21	10.54	10.42	10.31	10.39
20	10.55	10.50	10.50	10.52	10.55
40	10.70	10.56	10.65	10.65	10.70
PEH	10.68	10.79	10.74	10.68	10.72
4 [b]			9.85		9.86
6			9.89		10.00
10			10.20		10.20
20			10.39		10.41
40			10.56		10.60
PEH			10.70		10.65

[a] The same sample was used for the successive melting and cooling steps.
[b] Different samples were used for the specified melting period.

(a)

(b)

(c)

FIG. 1. Spectra of the CD_2 bending modes of 10 $(PEH)_M$/ 1 PED melt-crystallized samples kept for different time periods at (a) 140 ± 2 °C, (b) 150 ± 2 °C, and (c) 170 ± 2 °C.

rocking modes for molar ratios of 10 or higher increased slightly on initial melting (compared to those of the cast films) and then decreased slightly with prolonged melting time. The CD_2 bending modes appeared as a singlet, instead of the doublet observed in cast films, and remained a singlet as a function of time in the melt. Since splittings of the vibrational frequencies arise from intermolecular interactions between adjacent chains on 110 planes in the crystal or from small local aggregates of like chains,[1] these results indicate that either PED chains are isolated from one another (such as would occur in random mixing) or they are folded along (200) planes.[1] (The results are also consistent with folding along 020 planes, but other considerations[3,5] make this unlikely.) However, the observed
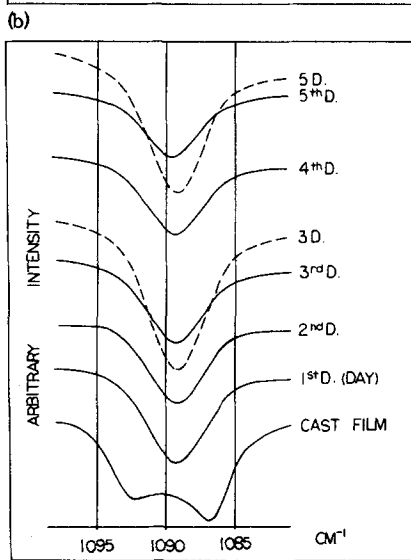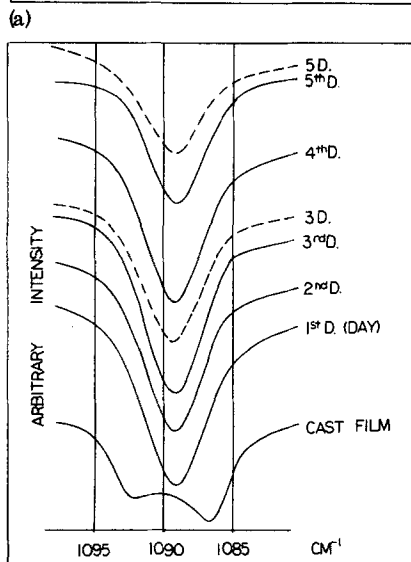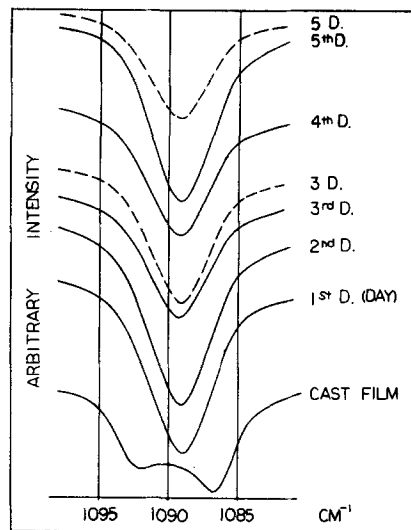
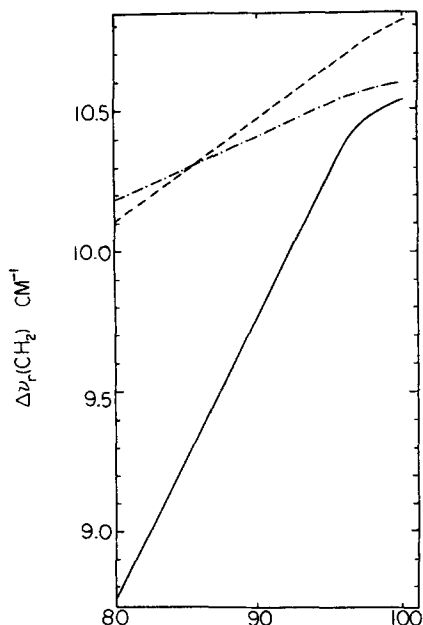splittings of the CH_2 rocking modes of melt-crystallized samples are comparable to those of single crystals and

FIG. 2. Splittings of the CH_2 rocking modes of mixed-crystal cast films (-.-.-), melt-crystallized samples (-----), and paraffin cocrystals (———) with different compositions.

FIG. 4. Spectra of the CD_2 bending modes of mixed crystals with specified molar ratio melted at 170 °C for 24 h and recrystallized at 124 °C for 72 h.

are always greater than those of paraffin cocrystals with the same molar ratio, as shown in Fig. 2. Therefore, random mixing (as in paraffin cocrystals) cannot be predominant, and these combined results can only be attributed to the continued presence of adjacent reentry folding but with a change in the fold plane. In short, chains in melt-crystallized samples fold essentially with adjacent reentry along (200) planes. It should be noted that, for the same melting temperature, the splittings of the CH_2 rocking modes of samples with the same molar ratio tend to decrease slightly with increasing time in the melt. This can be explained by a slight randomization of species in the crystal, perhaps due to enhanced ciliary penetration between lamellae.[9]

Since the band shape of the CD_2 bending modes for melt-crystallized 10 $(PEH)_M/1$ PED is essentially a pure singlet, this means that the two species are well mixed. If there were a high degree of heterogeneity, or segregation, then any aggregated portions of the minor
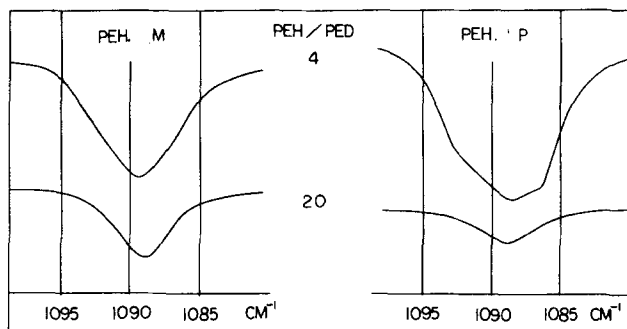
component would give rise to intermolecular interactions within the unit cell that would lead to a contribution having split CD_2 bending modes. Thus, any significant amount of aggregation (within infrared detectability) would cause the appearance of shoulders on both sides of the singlet. This situation is exhibited by high-molecular-weight materials, especially at high crystallization temperatures, as shown in Fig. 3. There are traces of shoulders on both sides of the singlet of 10 PEH/1 PED mixed crystals of PEH F and PEH P melt crystallized at high temperatures. The effect of segregation can be further emphasized by using mixed crystals with low molar mixing ratios, as shown in Fig. 4. Cast films of molar ratios of 4 and 20 with PEH P and PEH M were melted at 170 °C for 24 h and then recrystallized at 124 °C for 72 h. It is clearly seen that the degree of heterogeneity becomes more pronounced for high-molecular-weight polymers at low molar ratios, while there is no obvious evidence of this effect for PEH M whose melting point is comparable to that of PED V.

In conclusion, in melt-crystallized mixed-crystal systems the effect of segregation of PEH and PED can be minimized by utilizing high molar ratios of PEH/PED and polymers with small differences in melting points. Under such optimum conditions the observed CD_2 bending mode is a singlet, and the splitting of the CH_2 rocking modes is significantly larger than that for mixed paraffin cocrystals. Thus, a random mixing of
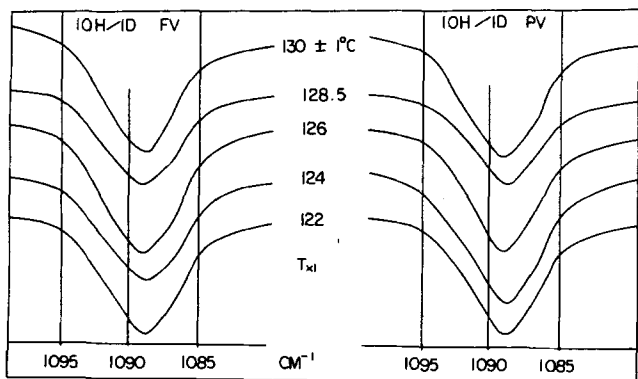
FIG. 3. Spectra of the CD_2 bending modes of 10 PEH/1 PED melt-crystallized samples.
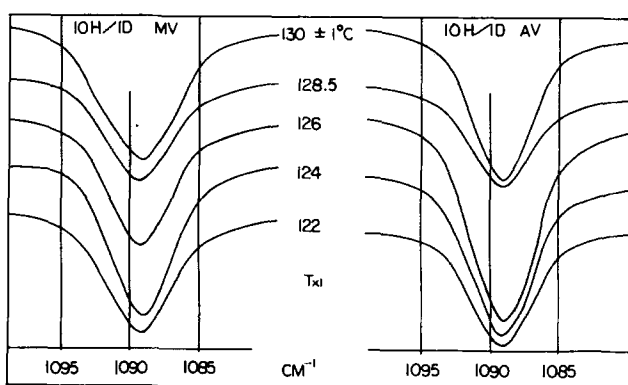
the polymer chains is excluded as the predominant mode of chain organization, making a "switchboard" model[10] extremely unlikely. Our present results substantiate earlier conclusions[2] that folding with adjacent reentry in (200) planes predominates in melt-crystallized polyethylene.

ACKNOWLEDGMENT

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