Cocrystallization of poly(vinylidene fluoride) and vinylidene fluoride–tetrafluoroethylene copolymers: 1. Effect of chain structure and crystallization conditions

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Poly(vinylidene fluoride) and vinylidene fluoride–tetrafluoroethylene copolymers cocrystallize depending on the structures present in each. In the α-phase, the maximum difference in the defect concentration of the two polymers (Δ defect) equals 12.3% during isothermal crystallization, and is equal to 10.5% when the system is quenched. In the β-phase, it is 11.8% for isothermal crystallization, and $\sim$5.5% when quenched. Apart from isomorphic cocrystallization between components of the same polymorph, cocrystal formation between the α- and β-polymorphs was also observed. The resulting cocrystal adopts the structure of a particular polymorph, according to the results obtained from potential energy calculations. The interplanar spacings (d_{hkl}) of the α-phase of PVF_2 do not change with the H–H defect concentration, but for the β-phase d_{200} increases with the defect concentration. The reason for this difference in behaviour has been attributed to the more compact nature of the β-polymorph unit cell, when compared to that of the α-polymorph. The limiting value of the Δ defect for cocrystallization in the α-phase has been attributed to the larger difference in the intramolecular potential energy, whereas that of the β-phase has been attributed to the compact nature of the unit cell.

(Keywords: PVF_2; VF_2–VF_4 copolymers; cocrystallization)

INTRODUCTION

Both poly(vinylidene fluoride) (PVF_2) and vinylidene fluoride–tetrafluoroethylene (VF_2–VF_4) copolymers contain some head-to-head ($-CF_2-CF_2-$) units, which are different from the usual head-to-tail ($-CF_2-CH_2-$) units of PVF_2, and these are regarded as being defect structures[1]. Theoretical calculations by Farmer *et al.*[2] on the effects of head-to-head (H–H) defects in both the chain conformation and in the chain packing, and the later experimental verification by Lovinger *et al.*[3], have proved that different amounts of H–H units in the chain produce different polymorphic forms of PVF_2. Recent studies on the equilibrium melting temperature, crystallization kinetics and morphology of PVF_2 fractions[4–6] provide further evidence that defects are entering into the crystalline lattice. However, the limit of the amount of H–H defects that can be accommodated in a particular PVF_2 lattice is still in question. To delineate this aspect of PVF_2 crystallization, the cocrystallization of samples of different commercial grades of PVF_2 having different amounts of H–H defects, and also its copolymers with different VF_4 contents, have been studied under different crystallization conditions, and the results obtained are reported here.

The cocrystallization of polymers is a rare phenomenon and only a few pairs have been reported to cocrystallize[7–11]. This is because in order to produce cocrystals three important requirements for each pair of polymers are needed: (i) structural similarity, (ii) a small intramolecular potential energy difference, and (iii) almost similar crystallization kinetics. These features are generally difficult to achieve among most polymer pairs. The structural similarity helps the mixing of the polymers both in the melt and in the solid state; for cocrystal formation, the component polymers should be miscible in the melt. From the study of amorphous polymer pairs, it has been established that a similarity in chain structure causes the polymer–polymer interaction parameter to become very close to zero, and below the critical χ_{23} value[12,13]. The 'likeness' of the components in each pair should be as good as possible in order to achieve miscibility in the liquid state. A similarity in chain structure also facilitates the packing of the crystalline polymers in a common lattice when forming the cocrystal. Therefore, the crystalline structural requirements are as follows: the same crystal system, almost identical lattice parameters and the same conformation of the chains.

It is pertinent to discuss here the isomorphic cocrystallization of poly(vinyl fluoride) (PVF) and poly(vinylidene fluoride) (PVF_2)[7,14]. Natta *et al.*[7] showed that these two

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polymers cocrystallize isomorphically, whereas Guerra *et al.*[14] have recently reported that they do not, although the two polymers are miscible in the melt, as evidenced by dynamic mechanical measurements. PVF crystallizes in an all-*trans* configuration with a pseudohexagonal unit cell, as reported by the former group from X-ray scattering measurements. In their case, PVF_2 also crystallizes in the β-phase, with the same pseudohexagonal unit cell. Since the van der Waals radii of fluorine (1.35 Å) and hydrogen (~1.25 Å) do not differ by very much, the lattice parameters are therefore not very different and so the two polymers cocrystallize over the whole range of compositions. However, for the latter group of workers the PVF_2 sample was different, crystallizing under their experimental conditions in the γ-phase, with a $T_3GT_3\bar{G}$ conformation, and a monoclinic unit cell. Therefore, mismatching of both the crystal systems and the chain conformations may be the reasons why Guerra *et al.*[14] did not observe any cocrystallization of the two polymers.

Although structural similarity is a necessary requirement, it is not a sufficient condition for cocrystallization. Two crystalline polymers with different intramolecular potential energies cannot remain in the same lattice until and unless the common lattice can tolerate the energies of both of the components. The intramolecular potential energy depends on the branching content, the co-unit content, the H–H defect level and the tacticity, and a small variation in either of these can alter the intramolecular potential energy. Thus, cocrystallization should depend on these parameters as well. Some systems in this category have been studied, e.g. linear and branched polyethylenes[10,11], vinylidene fluoride–trifluoroethylene copolymers[8], etc. The intramolecular potential energy of the monomer units in these copolymers also plays a similar role. If the potential energy difference between the units is small and if the structures of the co-units are similar, then both isomorphic and isodimorphic cocrystallization is possible. The cocrystallization of vinyl fluoride–vinylidene fluoride copolymers, vinyl fluoride–tetrafluoroethylene copolymers[7] and poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate)[9] are good examples of this type of behaviour.

Fulfilment of the above two requirements may not necessarily lead to the formation of cocrystals from the melt unless the crystallization kinetics for each component are comparable, thus allowing them to crystallize simultaneously. The influence of the crystallization kinetics has been manifested by some workers[10,11] for the cocrystallization of linear and branched polyethylenes by crystallizing under isothermal conditions and by quenching, and it was found that cocrystallization is more favoured when using the latter technique. This was explained by the fact that when quenching is carried out the crystallization rates of the two components are comparable, whereas under isothermal conditions some difference in the rates is quite natural.

Although all of the above conditions for cocrystallization are established, they have not all been thoroughly evaluated for the same system. A cocrystallization study of PVF_2 and VF_2–VF_4 copolymers may also help in this respect, because both of these components, when having different amounts of defects, crystallize in different crystal systems with different lattice parameters[3,15,16]. Furthermore, the intramolecular potential energies of the various H–H defect contents in the chains are different[2], and various H–H defect content samples have different crystallization kinetics[5]. Therefore, a suitable variation in the crystallization conditions and choice of sample could reveal a better understanding of the cocrystallization phenomenon. However, we have restricted our choice of samples to those with the lowest levels of H–H defects (i.e. low VF_4 contents), so as to minimize the effects of the small size difference between the fluorine and hydrogen atoms, and also to enable us to study all of those aspects of cocrystallization that have been mentioned above.

EXPERIMENTAL

Samples and their characterization

Two commercially available PVF_2 samples and three commercially available VF_2–VF_4 copolymers, obtained from different chemical companies, were used in the work. Most of the samples were kindly donated by Professor L. Mandelkern of Florida State University, USA. The head-to-head (H–H) defect contents of the PVF_2 samples have been reported earlier[4]; the VF_4 contents and the H–H defect contents of the copolymers were measured by using ^{19}F n.m.r. spectroscopy. The spectra were recorded with a 282 MHz instrument, in *N,N*-dimethyl formamide (DMF)-d_7 solutions (10% (wt/vol)) with a $CFCl_3$ internal standard, and are shown in *Figure 1*. The spectra of these copolymers all show the heptad features that have previously been reported in the literature[17,18], except for copolymer sample Cop-2 which shows an additional doublet, each signal with a relative intensity of 0.009, at −105.9 and −106.3 ppm. These additional peaks may be due to small amounts of branching in the polymer chain[19]. (A report in the literature[20] shows that the additional peaks correspond to a $-CH_2-C(CH_3)_2-$ group in the chain. It therefore appears that Cop-2 is a terpolymer with a small amount of isobutylene units (~1.8 mol%); which may be considered as a tail-to-tail part of the copolymer with methyl branching.) The VF_4 contents in the copolymers were calculated following the method of Cais and Kometani[17], while the H–H defect contents were measured using the method of Wilson III and Santee Jr[1], by extending the process to deal with copolymers.

The molecular weights of the samples were measured by gel permeation chromatography (model no. 510, Waters, USA) in *N,N*-dimethylformamide, using a μ-styragel column at 80°C, with polystyrene standards. The molecular weight of the sample Cop-3, however, was determined by intrinsic viscosity measurements in *N,N*-

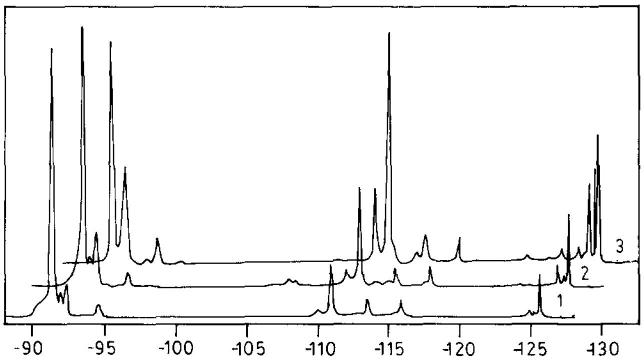

Figure 1 ^{19}F n.m.r. (282 MHz) spectra of the VF_2–VF_4 copolymers used in this work in *N,N*-dimethylformamide-d_7: (1) Cop-1; (2) Cop-2; (3) Cop-3

dimethylacetamide at 25°C, using an Ubbelhode-type viscometer.

The crystalline structures of the samples were determined from wide-angle X-ray scattering (WAXS) measurements, using a Philips PW1710 diffractometer with nickel-filtered CuKα radiation. Investigations were carried out on melt-crystallized films after quenching from the melt (227°C) to 30°C, in air. The diffractograms were recorded over the range from 10 to 45°, at a scan rate of 0.9°, 2θ min^{-1} and are shown in *Figure 2*. It is apparent from this figure that the two PVF_2 samples (KF and KY) crystallize in the α-phase, as evidenced from the strong reflections at $2\theta = 18.4$ and 20°, while all of the copolymers crystallize in the β-phase, as can be seen from the strong reflections at $2\theta = 20.7$ and 41°[14,16]. The characteristics of the samples used in this work are given in *Table 1*.

Preparation of cocrystals

Pairs of these polymers were mixed in 1:1 proportion (by weight) by dissolving in *N,N*-dimethylformamide at 80°C, followed by slow evaporation of the solvent in an air oven at 60°C; they were finally dried *in vacuo* at 70°C for 3 days. The cocrystallizations for the thermal studies were carried out directly in d.s.c. sample pans by taking samples of ~5 mg of the above mixtures. These were then melted in the calorimeter at 227°C and crystallized under three different conditions, i.e. isothermal crystallization for 1 h at 120°C, quenching to 50°C at a cooling rate of 200°C min^{-1} and quenching directly into a methanol–liquid nitrogen mixture, maintained at −70°C. These different procedures were adopted in order to study the effect of the various crystallization conditions on cocrystallization in these systems.

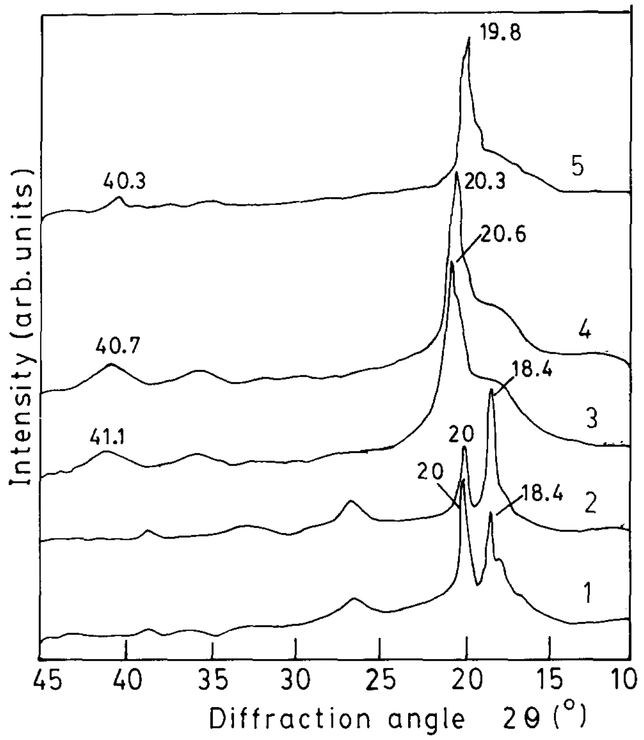

Figure 2 WAXS patterns of PVF_2 and VF_2–VF_4 copolymers crystallized under melt-quenched conditions: (1) KY; (2) KF; (3) Cop-1; (4) Cop-2; (5) Cop-3

Melting and crystallization

The melting of the cocrystals, formed as described above, was studied by using a Perkin–Elmer DSC-7 calorimeter, equipped with a Perkin–Elmer 3700 data station; the instrument was calibrated with an indium standard. The samples produced after quenching were heated from 50 to 227°C at a rate of 20°C min^{-1}, while samples that had been isothermally crystallized at 120°C were heated from this crystallization temperature at the same heating rate. The peak melting temperatures and enthalpies of fusion were obtained from the data station. For the crystallization study carried out under dynamic cooling conditions, the samples were melted at 227°C for 5 min and then cooled at a rate of 2.5°C min^{-1} down to 50°C. The peak temperatures were taken as representing the crystallization temperatures (T_cs), with the enthalpies of crystallization being calculated from the peak areas.

RESULTS

Thermal analysis

Figure 3 shows the melting endotherms of the samples crystallized at 120°C. From this figure it is clear that the KF/KY, Cop-1/Cop-2, KY/Cop-1, and KF/Cop-1 blends melt to give single endothermic peaks, which lie between the endothermic peaks of the two components. This indicates that these four mixtures are miscible in the solid state and produce cocrystals. The other combinations, e.g. KF/Cop-2 and KY/Cop-2, do not cocrystallize, because the individual endotherms of the components are retained during melting, with only a small depression in the peak temperatures of the original components. The use of a higher heating rate than the normal rate of 10°C min^{-1} in these experiments (and also for the quenched samples) is to avoid any confusion that might arise from melt recrystallization, as evidenced from *Figure 4*. The KF/Cop-1 sample, crystallized as above, was heated at the rate of 10°C min^{-1}, and two melting peaks were observed. However, none of these peaks correspond

Table 1 Characteristics of the samples used in the cocrystallization studies

Sample	Source	$\bar{M}_w$ ($\times 10^5$)	$\bar{M}_w/\bar{M}_n$	VF_4 content (mol%)	H–H defect content (mol%)	Polymorph
KF-1000 (KF)	Kureha Chemical Company	4.28	1.47	0.00	3.50	α-phase
KY-201 (KY)	Pennwalt Corporation	7.36	2.04	0.00	5.31	α-phase
Cop-1	Atochem	1.97	2.07	9.10	15.80	β-phase
Cop-2	Atochem	3.23	2.63	14.30	21.30	β-phase
Cop-3	Pennwalt Corporation	3.20[a]	–	17.60	27.60	β-phase

[a] Viscosity-average molecular weight

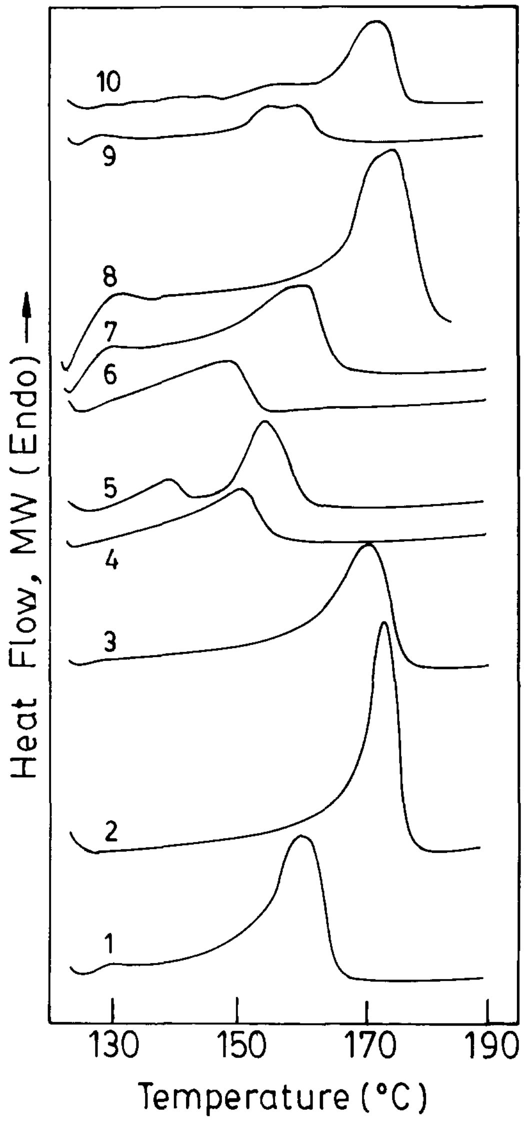

Figure 3 Melting endotherms of PVF$_2$ and VF$_2$–VF$_4$ copolymers and their 1:1 blends, crystallized at 120°C (at a heating rate of 20°C min^{-1}): (1) KY; (2) KF; (3) KY/KF; (4) Cop-1; (5) Cop-2; (6) Cop-1/Cop-2; (7) Cop-1/KY; (8) Cop-1/KF; (9) Cop-2/KY; (10) Cop-2/KF

to the melting point of the Cop-1 sample and this signifies that this polymer component is completely used up in cocrystal formation. The first peak observed for this blend is due to melting of the cocrystal, which after melt recrystallization produces the second peak. However, if the samples were annealed for longer times (e.g. 5 days), this second peak (from melt recrystallization) disappears, as can be seen from the figure. The higher heating rate (20°C min^{-1}), as chosen for the experiments depicted in *Figure 3*, also avoids the process of melt recrystallization, thus giving a single melting peak. Similar statements are also true for other cocrystal systems. The melting point of Cop-3, after quenching to 50°C, is 123.3°C, so the blends of Cop-3 were crystallized at 110°C for 2 h. The resulting melting thermograms are shown in *Figure 5*. From this figure it is clear that the Cop-1/Cop-3 blend exhibits a single melting peak after 2 h of crystallization, while the Cop-2/Cop-3 blend exhibits a peak at 119.5°C and a shoulder at 130.9°C, indicating partial cocrystallization. However, on increasing the crystallization time to 7 h the latter system exhibits a single melting peak, indicating cocrystallization. The longer time that is required for formation of the Cop-3/Cop-2 cocrystals, compared to that of the Cop-3/Cop-1 cocrystal system, may be due to small amounts of branching in the Cop-2 component, with annealing helping in the reorganization of the chains to form the cocrystal. Combinations of Cop-3 with other components do not form cocrystals.

Values for the melting temperature (T_m), enthalpy (ΔH_m), and half-height width of the melting peak ($\Delta T_{0.5}$) for these samples, and also the T_m values for the samples crystallized under two other quenching conditions are presented in *Table 2*. During quenching at −70 and at 50°C, the results remain the same as for isothermal crystallization, except for the KF/Cop-1, Cop-1/Cop-3 and Cop-2/Cop-3 systems which showed immiscibility under these conditions. This indicates that under isothermal conditions the H–H defects acquire sufficient energy to enter into the crystalline lattice forming the cocrystal. The quenched crystals of PVF$_2$ showed melt recrystallization[4] during heating, as indicated by the shoulders or separate peaks in the melting thermograms. For these reasons, the enthalpy of fusion and the half-height widths of the quenched samples are not reported in the table. It is necessary to mention here one interesting observation for the Cop-2 samples, i.e. it exhibits two melting peaks (133 and 155.3°C) during crystallization at 120°C and quenching at 50°C. However, during quenching at −70°C, it exhibits only one melting peak. This behaviour will be discussed further in a separate publication[21]. Another interesting observation is that the melting point of Cop-3 has increased by ~10–13°C during isothermal crystallization at 110°C, when compared to that of the quenched sample. Such a large change is not observed for any of the other polymers, although this change has been found for Cop-3

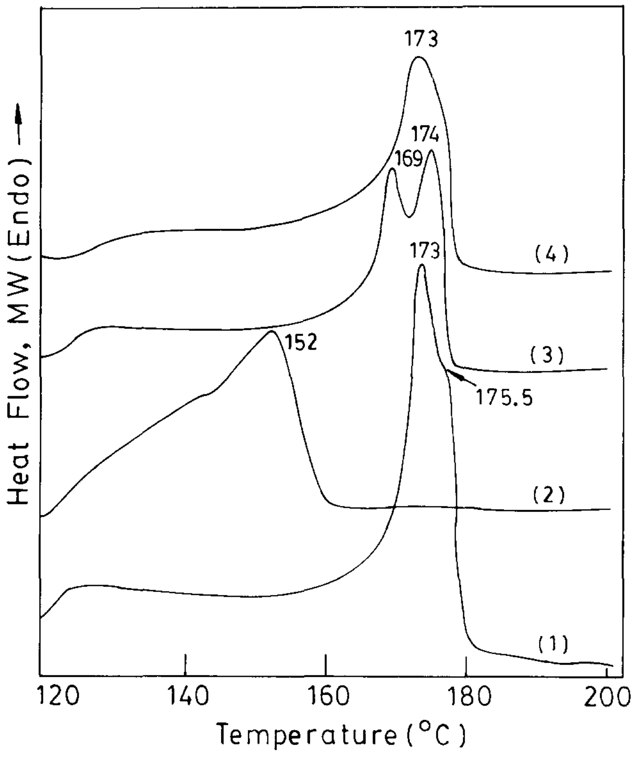

Figure 4 Melting endotherms of PVF$_2$ and VF$_2$–VF$_4$ copolymers and their 1:1 blends crystallized at 120°C for 1 h (at a heating rate of 10°C min^{-1}): (1) KF; (2) Cop-1; (3) KF/Cop-1; (4) KF/Cop-1, crystallized for 5 days at 120°C

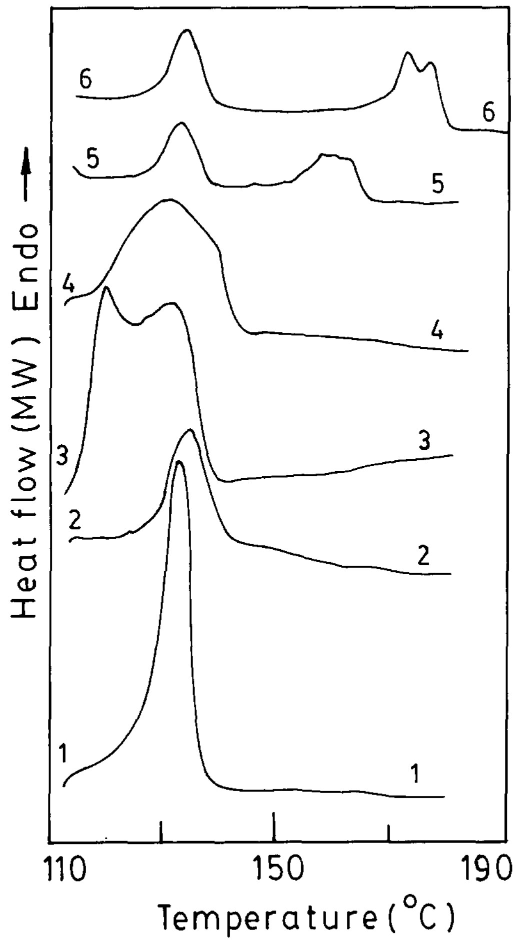

Figure 5 Melting endotherms of Cop-3 and its blends crystallized at 110°C (at a heating rate of 10°C min^{-1}): (1) Cop-3; (2) Cop-3/Cop-1; (3) Cop-3/Cop-2 (2 h); (4) Cop-3/Cop-2 (7 h); (5) KY; (6) KF

blends which do not form cocrystals. For the Cop-1/Cop-3 cocrystal, the melting point is 134.1°C, which is close to the average melting point of the pure components. The reason for such an increase is not yet clear, but a similar increase in the melting point of isothermally crystallized VF_2–TFE (81/19) copolymer has been previously reported[22]. The melting points of the cocrystals are generally some 3 to 4°C higher than the average values calculated on a weight-fraction basis. The reasons for this may be, e.g. attraction between the components, inclusion of H–H defects in the cocrystal, etc. To explain these results, the composition dependence of the melting point needs to be known, and the results of this study will be communicated shortly[23]. For systems that do not form cocrystals, a melting point depression of the component occurs, and this is due to its miscibility in the liquid state.

Cocrystal formation was studied by d.s.c. by cooling the samples from the melt at a rate of 2.5°C min^{-1}, and the resulting exotherms are presented in *Figure 6*. The pure components crystallize to give a single exotherm, except for Cop-2 which shows one peak at 118.8°C and a shoulder at 106.8°C. Among the blends, KF/KY, Cop-1/Cop-2, and KY/Cop-1 crystallize to give single exotherms, while the others do not. These crystallization data may be treated as secondary evidence for cocrystallization, since a single exothermic peak usually indicates that the two components are crystallizing simultaneously. However, if the peak temperature is intermediate between that of the components it may be argued that they are forming a cocrystal[24]. Therefore, the systems KF/KY, Cop-1/Cop-2 and KY/Cop-1 produce cocrystals under these conditions, while the others do not. These results support the earlier observations for quenched systems. The Cop-2/Cop-3 system shows a very close doublet, with the Cop-1/Cop-3 system showing both a peak and a 'hump'. The peak temperatures (T_c) and the enthalpies of crystallization (ΔH_c) are also presented in *Table 2*. From this table, it is apparent that for the systems which produce cocrystals, the exothermic peak temperatures are ~3°C higher than the intermediate values calculated on a weight-fraction basis, indicating that cocrystallization occurs easily. Pure PVF_2 samples crystallize under

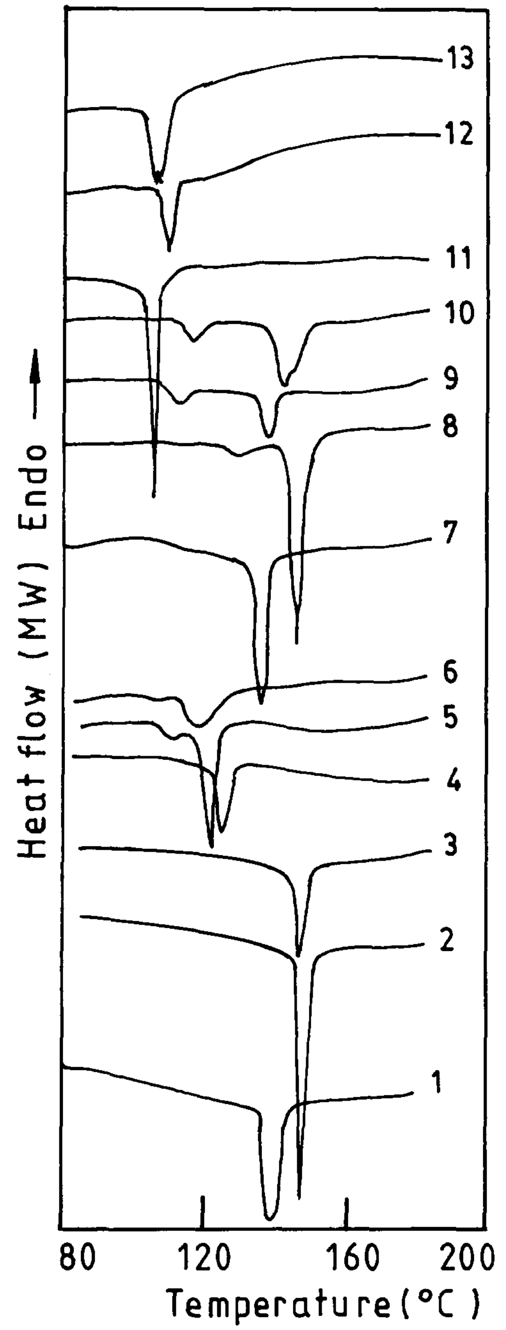

Figure 6 Crystallization exotherms (at a cooling rate of 2.5°C min^{-1}) for PVF_2, VF_2–VF_4 copolymers and their 1:1 blends cooled from the melt at 227°C: (1) KY; (2) KF; (3) KY/KF; (4) Cop-1; (5) Cop-2; (6) Cop-1/Cop-2; (7) Cop-1/KY; (8) Cop-1/KF; (9) Cop-2/KY; (10) Cop-2/KF; (11) Cop-3; (12) Cop-1/Cop-3; (13) Cop-2/Cop-3

Table 2 Melting points, enthalpies and half-height widths ($\Delta T_{0.5}$) of PVF_2, VF_2–VF_4 copolymers and their 1:1 blends[a]

Sample	T_m(°C) for samples quenched at		Isothermal (120°C)			Cooling		
	−70°C	50°C	T_m (°C)	ΔH_m ($J g^{-1}$)	$\Delta T_{0.5}$ (°C)	T_c (°C)	ΔH_c ($J g^{-1}$)	$\Delta T_{0.5}$ (°C)
KF	(169.7), 175.9	173.1	173.5	52	5.7	145.8	62	3.3
KY	161.4	161.5	161	38	10	138.5	48	5
KF/KY	173.1	171.4	171.0	46	10	144.1	49	3.3
	[165.5]	[167.3]	[167.2]	[45]		[142.1]	[55]	
Cop-1	148.3	149.1	150.8	29	12.5	122.0	27	3.3
Cop-2	135.4	135.0	138.5	20	8.8	106.8, 118.8	21	2.5
		155.3	155				4	5
Cop-1/Cop-2	140.5	141.5	146.7	21	14	117.0	24	7.1
	[141.8]			[24]			[26]	
KF/Cop-1	145	142.4, (172.1)	175.8	41	11	130.1, 144.5	60	4.2
	(168.3), 176.9	177.2	[162.1]	[41]			4	12.5
KF/Cop-2	135	174.8	140, (159)			116.5, (108)		
	174.8	(172), 174.7	172.6			141, (144)		
KY/Cop-2	135	131.9, (149.6)	129.5			111.4, 137.2	34	3.3
	160.3	159.8	159.2				16	4.2
KY/Cop-1	159.7	159.8	(159), 161.3	33	16	133.2	33	3.3
	[154.8]	[155.3]	[156.0]	[33]		[130.2]	[37]	
Cop-3	118.4	123.3	132.1	25	5.2	103.6	31	3.3
KF/Cop-3	119, 175	116.6, (170), 175.4	133.1, 171.7, (176)			109.7, 145		
KY/Cop-3	122, 160	118.5, (156.4), 161.5	132.2, 158.8			109.4, 135.7		
Cop-1/Cop-3	119, 145	120.8, 141.2	134.1	18	7.0	109.1	26	3.3
						[112.5]	[29]	
Cop-2/Cop-3	119.4, 131.6	115.8, 130.7	119.5, (130.9)	21		104.4, 105		

[a] Temperatures in round brackets represent shoulders; entries in square brackets are average values

homogeneous nucleation conditions, as evident from kinetic studies of PVF_2 fractions and 'whole' polymers[5]. The higher T_c values, when compared to the intermediate values, may therefore be explained on the basis of nucleation and growth processes. A lower-defect-content PVF_2 sample nucleates and crystallizes faster than an equivalent sample with a higher defect content under the same crystallization conditions, as found from our earlier studies[5]. Once nuclei are formed from the lower-defect-content PVF_2, the higher-defect-content material grows on these nuclei at almost the same rate as the former species, thus producing the cocrystal. This is because crystal growth is a secondary nucleation process with an activation energy which is lower than that of the primary nucleation process[25]. The T_c values for non-cocrystal systems may depend on several factors, such as dilution of the crystallizing components, partial cocrystallization, etc. As for examples in the KF/Cop-1 system, the main peak is depressed by 1.3°C from that of KF and the small peak is increased by 7.9°C from that of Cop-1, which clearly shows partial cocrystallization. The closely spaced doublet of the Cop-2/Cop-3 system is due to partial cocrystallization of the two components. For the KF/Cop-2 and KY/Cop-2 systems, depression in the T_c values from that of the pure components by 2–4°C is due to dilution of each type of crystallizing unit in the melt, where they remain as miscible blends.

Values for the enthalpy of fusion (ΔH_m) for isothermally crystallized cocrystals (*Table 2*) are equal to the average values of the pure components, but the enthalpies of crystallization (during cooling) of the cocrystals are somewhat lower than the average value of the components. On the other hand, the $\Delta T_{0.5}$ value (an index of the distribution of lamellar thicknesses) of the cocrystals retains its component values during cooling, indicating that the lamellar order is not perturbed as a result of cocrystallization[24]. For isothermally crystallized samples, the $\Delta T_{0.5}$ parameter behaves similarly, except in a few cases where it has a somewhat greater value than that of the components[26]. A meaningful analysis of these data will be carried out in the composition-dependence part of these cocrystallization studies[23].

Structure

After elucidation from thermal analysis data of the cocrystallization possibilities of PVF_2 samples with various defect contents, the structural aspects of cocrystallization of such samples will now be discussed. In *Figures 7* and *8* the X-ray diffractograms of the 1:1 blends (quenched from the melt (at 227°C) to 30°C) for each pair of components are presented. From *Figure 7*, it is clear that KF/KY and KY/Cop-1 crystallize purely in the α-phase, whereas KF/Cop-2 and KY/Cop-2 crystallize as a mixture of α- and β-phases. In the case of the KF/Cop-1 system, the Cop-1 component is present as a smaller amount in the blend, due to partial cocrystallization, and this causes the β peak (at $2\theta = 41°$) to appear as a small hump. In *Figure 8*, all of the samples crystallize in the β-phase, but not necessarily all in the same lattice which forms the cocrystal. As an example of this, Cop-1/Cop-2 has a sharp peak at $2\theta = 20.3°$ which is the main reflection of the Cop-2 component, i.e. the mixture takes the shape of the larger unit cell. For the Cop-2/Cop-3 system, the molecular reflection showed a shoulder at 20.2°, in

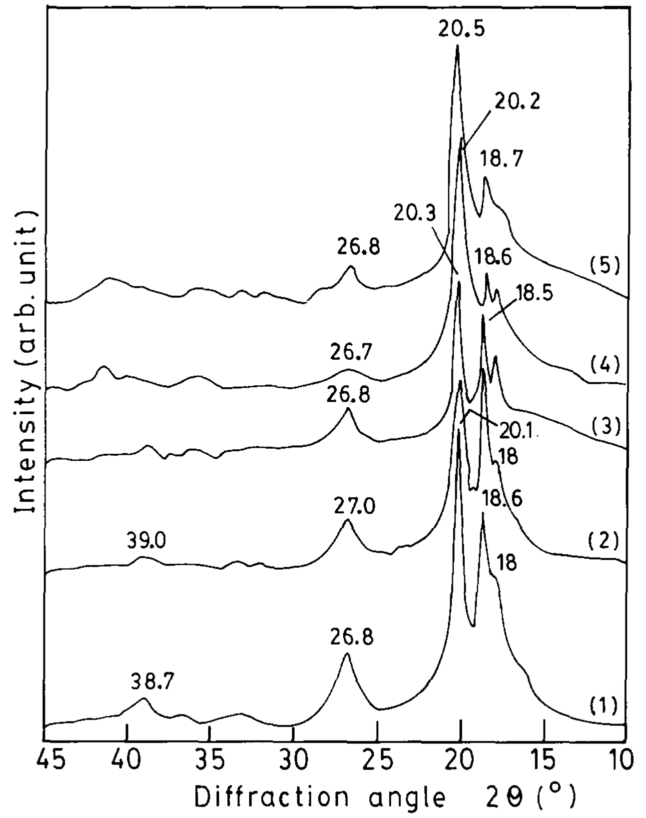

Figure 7 WAXS patterns of blends of PVF_2 and VF_2–VF_4 copolymers crystallized under melt-quenched conditions: (1) KF/KY; (2) KY/Cop-1; (3) KF/Cop-1; (4) KY/Cop-2; (5) KF/Cop-2

addition to the peak at 19.8°. This result clearly relates to mixtures of crystals of the β-phase of the two polymers.

It is now necessary to discuss the KY/Cop-1 system, since the two components crystallize in different phases, i.e. α-and β-phases, respectively. However, the mixture crystallizes in the α-phase. The theoretical calculations of Farmer *et al.*[2] showed that the cross-over point between the α- and β-phases occurs at 15 mol% H–H defect concentration for the copolymer and at 11 mol% defect concentration for PVF_2. Cop-1 has 15.8 mol% defect concentration, just above the cross-over point. The 1:1 mixture of KY and Cop-1 in the melt has an average defect concentration of 10.05 mol%, and therefore during the cocrystallization process it crystallizes purely in the α-phase. A composition dependence of the two polymers with respect to the production of different polymorphs will be reported elsewhere[23]. The spacings of various Miller planes, d_{hkl}, were carefully measured using the Bragg equation by taking average 2θ values from two different diffractograms for each sample. The *d*-values are plotted against the amount of H–H defects present in the samples for both the α- and β-phases, and are shown in *Figures 9* and *10*, respectively. It is clear from these figures that there is no change in the *d*-values with defect concentration for the α-phase for any of the Miller planes. In the β-phase, there is an increase in the *d*-values with increasing defect concentration for the (200) plane only. The results may be clarified by examination of the lattice parameter values of the PVF_2 and VF_2–VF_4 copolymers[16]. From the results given for samples with different defect contents (co-units are considered as being defects), the *b* and *c* values remain almost unchanged for both phases, but the *a* value increases with defect concentration for the β-phase, although it remains constant for the α-phase. Therefore, an increase in the spacing of the (200) plane of the β-phase with defect concentration is as expected. It is possible that the increase in *a* for the β-phase with increasing defect concentration may be due to the more compact nature of the β-phase unit cell (compared to that of the α-phase); this latter point is clearly evident from the density values ($1.97\,g\,cm^{-3}$ for the β-phase, and $1.92\,g\,cm^{-3}$ for the α-phase)[27] of the two polymorphs. Therefore, we can conclude that inclusion of defects does not alter the lattice spacings in the α-phase, but in the β-phase an increase of some of the d_{hkl} values (i.e. for $h \neq 0$) is quite natural.

DISCUSSION

We now wish to outline our results on the general aspects of cocrystallization as mentioned in the Introduction.

Structural similarity

The polymers are very similar in chemical structure, with the only difference being in the amount of H–H defects in the chains. This renders the polymers miscible in the liquid state, because cocrystals were obtained in most cases, and where no cocrystals were produced a large depression in the melting point of each component was observed. From the point of view of crystal structure, the orthorhombic (α-phase) and pseudohexagonal (β-phase)[27] structures are adopted by the polymers, depending on the defect concentration under melt-quenched conditions. Cocrystallization between polymorphs of the α-phase produces α-polymorphs, with a similar situation occurring for the β-polymorphs, indicating isomorphic cocrystallization. However, cocrystallization between α- and β-polymorphs can produce either polymorph, depending upon the resulting H–H defect concentration,

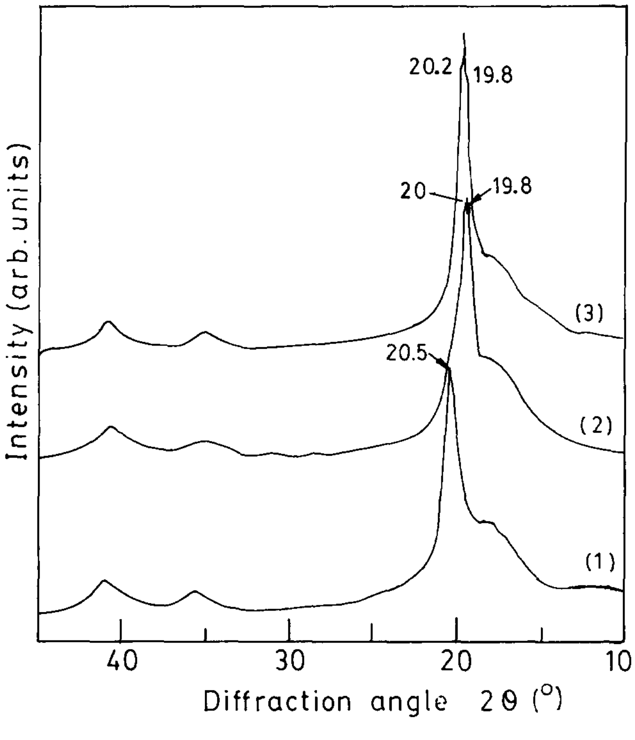

Figure 8 WAXS patterns of blends of VF_2–VF_4 copolymers crystallized under melt-quenched conditions: (1) Cop-1/Cop-2; (2) Cop-1/Cop-3; (3) Cop-2/Cop-3

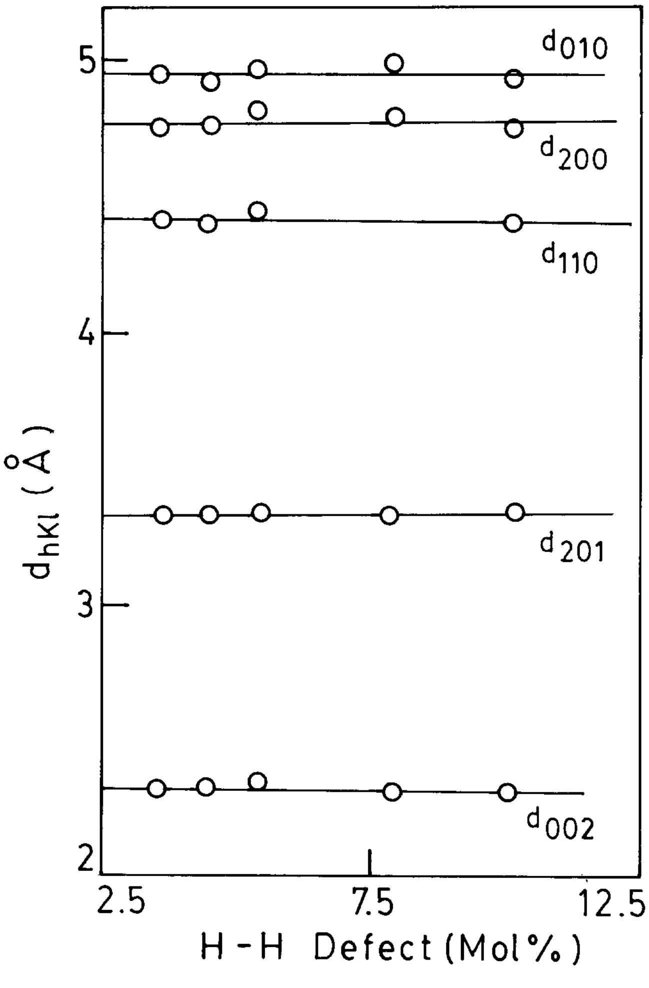

Figure 9 Plots of d_{hkl} as a function of H–H defect content of PVF_2 samples and their cocrystals (α-phase); for each plot, the two points having defect contents >7.5 mol% were taken from measurements on KY/Cop-1 cocrystals with two different compositions

which is either above or below the cross-over point in the potential energy diagrams for the two phases. Therefore, when forming cocrystals, it is not necessary for the components to have the same crystal structure, and the resulting cocrystal can take the structure of either of the components, depending on the resulting potential energy of the melt.

Intramolecular potential energy

The intramolecular potential energies of the PVF_2 and VF_2–VF_4 copolymers used here have been compiled from ref. 2, and are presented in *Table 3* for both the α- and β-phases. From this table, it is clear that the difference in potential energy between the KF and Cop-3 components (for the TGT$\bar{G}$ conformation) has the largest value, while for the β-phase the largest difference is between KY and Cop-3. In both cases, if they form cocrystals they should crystallize in the β-phase, but these pairs do not cocrystallize under any of the conditions described above, probably as a result of these differences being larger than those observed for any of the pairs that do form cocrystals.

Crystallization kinetics

As mentioned in the Introduction, for cocrystallization to take place the kinetic requirement is approximately the same rate of crystallization from the melt for both components. Here, a significantly different behaviour was observed for some systems where cocrystals are produced by isothermal crystallization, but not by quenching[10,11]. A likely reason for this is that the defect size is not much different from that of the head-to-tail (H–T) segments, and under these conditions the defects can acquire enough energy to be incorporated into the crystal lattice. The isothermal thickening of PVF_2[4], and the increase in intermolecular spacing of the β-phase with temperature[15] favour this point of view. The exception, in this case, to others reported in the literature, results from the small size of the defects, when compared to those studied by earlier groups[10,11].

The question concerning the amount of H–H defects that can be accommodated in the PVF_2 lattice will now be considered in the light of the above cocrystallization results. It is apparent from the enthalpies of fusion of the 1:1 cocrystal systems (see *Table 2*), and also from the intermediate d_{200} value of the Cop-1/Cop-2 cocrystal (when compared to that of its components), that the H–H defects of the cocrystals enter into the lattice in a similar way to that of the pure polymers. However, a more meaningful answer in this context is evident from the composition-dependence results[23]. It is evident from this study that the maximum difference in the H–H defect concentration (Δ defect) between the two polymers equals 10.5 mol%, when quenched, and 12.3 mol% under isothermal conditions, for the α-phase. For the β-phase, the corresponding values are 5.5 mol% (quenched) and 11.8 mol% (isothermal). This implies that almost the same amount of defects can be accommodated in both polymorphs. The limiting intramolecular potential energy difference in the cocrystals of the α-phase is ~4.7 (20.1 – 15.4) kcal mol^{-1}, while that of the β-phase is ~1.1

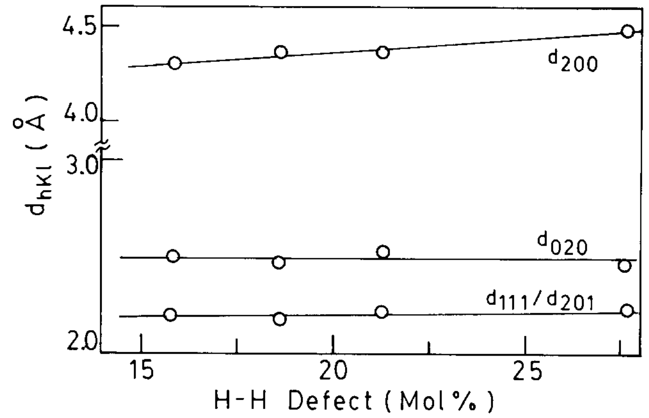

Figure 10 Plots of d_{hkl} as a function of H–H defect content of VF_2–VF_4 copolymers (β-phase) and their cocrystals

Table 3 Intramolecular potential energy values for PVF_2 and VF_2–VF_4 copolymers with different chain conformations (compiled from ref. 2)

Sample	H–H defect content (mol%)	Potential energy (kcal mol^{-1}) TGT$\bar{G}$ (α-phase)	TTTT (β-phase)
KF	3.5	–20.1	–16.6
KY	5.3	–19.2	–16.9
Cop-1	15.8	–15.4	–15.7
Cop-2	21.3	–13.0	–15.2
Cop-3	27.6	–11.4	–14.6

(15.7 − 14.6) kcal mol^{-1}. Since the potential energy difference for the latter is very small, quite a large amount of H–H defect structure in the chain should cocrystallize, but this becomes restricted because of the compact nature of the β-phase unit cell.

CONCLUSIONS

PVF_2 and VF_2–VF_4 copolymers cocrystallize depending on the H–H (or pseudo H–H) defect concentration in the two component polymers. If the defect concentration difference is larger than 12 mol%, cocrystallization in any of α- or β-polymorphs is impossible. For the α-polymorph, the cause is attributed to the larger intramolecular potential energy difference, while for the β-polymorph it is the compact nature of the unit cell. The nature of the polymorph of the cocrystals depends on the resulting H–H defect concentration, i.e. whether it falls above or below the cross-over point in the potential energy diagram. Crystallization under isothermal conditions was found to be more effective than quenching for cocrystallization in these polymer systems. The cocrystallization process does not change the d-spacing of the α-phase, but for the β-phase d_{200} increases with the cocrystallization of higher-defect-content samples.

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