

Cocrystallization of poly(vinylidene fluoride) and vinylidene fluoride-tetrafluoro-ethylene copolymer blends:

3. Structural study

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The structure of poly(vinylidene fluoride) (PVF₂) and vinylidene fluoride-tetrafluoroethylene (VF₂-VF₄) copolymer blends has been investigated by wide angle X-ray scattering (WAXS) study. Blends of two PVF₂ samples (KF, H-H defect = 3.5 mol% and KY, H-H defect = 5.3 mol%) and two copolymers (Cop-1, Cop-2, H-H defect = 15.8 and 21.3 mol%, respectively) were crystallized at 30°C, 120°C and 156°C (130°C for copolymers). From the WAXS results it has been observed that both the KF/KY PVF₂ and Cop-1/Cop-2 blends cocrystallize at all the temperatures in the α and β phases, respectively. However, in the KF/Cop-1 or in the KY/Cop-1 blends cocrystallization is not found for all the compositions of the blends. In PVF₂ rich compositions α phase cocrystals were found and in Cop-1 rich compositions both α and β polymorphs were found. The latter results indicate the absence of cocrystallization at the Cop-1 rich compositions for both the systems. The results support the theoretical prediction of crossover point composition from α to β phases, particularly for systems where cocrystallization is occurring. The spacing d_{hkl} increases with H-H defect for both the phases at all temperatures, but the rate of its increase with H-H defect is maximum for crystallization at 120°C. Further the rate of increase of d_{hkl} with H-H defect is more for β phase than that for α phase and has been attributed to the more compact nature of β unit cell. The lattice parameters for zero% H-H defect PVF₂ measured from the least square intercept of d_{hkl} vs H-H plots are somewhat higher than the values predicted from the theoretical calculations by Farmer *et al.* © 1997 Elsevier Science Ltd.

(Keywords: poly(vinylidene fluoride); vinylidene fluoride-tetrafluoroethylene (VF₂-VF₄) copolymer; polymorph)

INTRODUCTION

Depending upon the crystallization conditions PVF₂ can crystallize in five different polymorphs. The most common polymorph is α , with a monoclinic unit cell and a TGT \bar{G} chain conformation^{1,2}. The piezoelectric β polymorph has an orthorhombic unit cell with all *trans* chain conformation^{3,4}. The γ phase also has an orthorhombic unit cell with a T₃GT₃ \bar{G} chain conformation⁵. There is a polymorph called γ' whose unit cell is analogous to that of γ but has a morphology analogous to that of α -phase⁶. It is produced by the solid state transformation of α phase in the presence of γ phase⁷. The δ and ϵ polymorphs are the polar and nonpolar analogues of the α and γ ones, respectively⁸⁻¹⁰. PVF₂ produces cocrystals and it depends on the amount of H-H defect present in the chain and also on the cocrystallization conditions¹¹. In this paper, the structure of the cocrystals studied from wide angle X-ray scatterings have been discussed.

It has been reported earlier that the PVF₂ samples (KF and KY; H-H defect 3.5 and 5.3 mol%, respectively) crystallize from the melt in the α phase whereas the VF₂-VF₄ copolymers (Cop-1, Cop-2, H-H defect 15.8 and

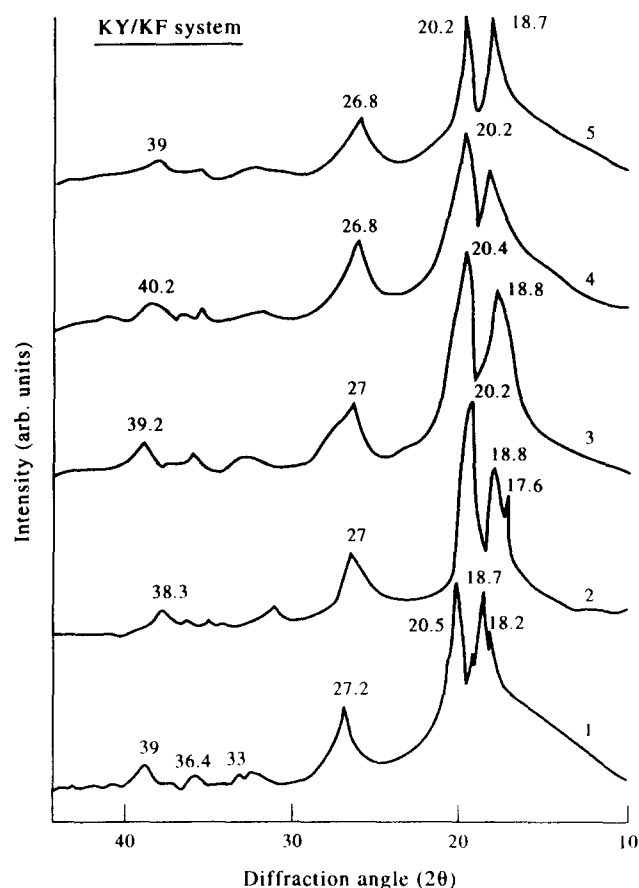
21.3 mol%, respectively) crystallize in the β phase¹¹. This different behaviour is due to the different amount of H-H defect present in the chains of the PVF₂ sample. Farmer *et al.*¹² predicted from the potential energy calculation that PVF₂ with less than 11 mol% H-H defect concentration will crystallize in the α -phase whereas PVF₂ greater than 11 mol% defect concentration crystallize in the β -phase. However, for the pseudo H-H defects (-CF₂-CF₂- units without CH₂-CH₂ part) the crossover point composition between the α and β phases is 15 mol% defect concentration (~8 mol% VF₄ units). The theoretical prediction has been experimentally proved by Lovinger *et al.*^{13,14}. However, for the copolymers it has been shown by Lando and Doll¹⁵ that for VF₂-VF₄ copolymers the crossover point from α to β phase occurs at 7 mol% VF₄ concentration.

During cocrystallization the PVF₂/VF₂-VF₄ copolymers should be miscible in the melt and the nature of the polymorph produced will therefore be guided by the resultant H-H defect concentration. By the WAXS study the nature of polymorph can be detected. So from the study of WAXS patterns we shall be able to judge the formation of the cocrystals and we can verify also the theoretical prediction of Farmer *et al.*¹² during the cocrystallization process.

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Table 1 Characteristics of the samples used for cocrystallization study

Sample	Source	$M_n \times 10^{-5}$	PDI	VF ₄ content mol%	H-H defect mol%	Polymorph at melt quenched state
KF-1000 (KF)	Kureha Chem. Company	4.28	1.47	0.00	3.5	α
KY-201 (KY)	Pennwalt Corp.	7.36	2.04	0.00	5.31	α
Cop-1	Atochem	1.97	2.07	9.1	15.8	β
Cop-2	Atochem	3.23	2.63	14.3	21.3	β

**Figure 1** WAXS patterns of KF/KY PVF₂ blend system crystallized at 120°C: 1. $W_{KY} = 0.00$; 2. $W_{KY} = 0.27$; 3. $W_{KY} = 0.49$; 4. $W_{KY} = 0.74$; 5. $W_{KY} = 1.00$

As evidenced from our earlier report¹⁶⁻¹⁸, H-H defects are entering into the lattice and the accommodation of H-H defect in the lattice is larger, for the larger amount of H-H defect content in the chain. So during crystallization with higher H-H defect there will be increase in d spacing and hence the lattice parameters. This is because the H-H units have larger dimension than the H-T unit. The Vanderwaal radius of fluorine is 1.35 Å and that of hydrogen is 1.25 Å. Therefore, larger incorporation of H-H defect will increase the size of the unit cell and hence d spacings.

By WAXS study, presented in the paper, it will be possible to comprehend the cocrystallization of the components, the structure of the cocrystals (hence it will help the verification of theoretical calculation of Farmer *et al.* for a blended system) and it will also be possible to monitor the relative accommodation of H-H defect in the lamella from the compositional and temperature variation of d spacing.

EXPERIMENTAL

The characteristics of the samples used in the work are presented in *Table 1*. The blends of different compositions are prepared by dissolving the two polymers in *N,N*-dimethyl formamide in definite proportion by weight. These homogeneous solutions (concentration 1% w/v) of the blends were dried in an air oven at 60°C and the films were finally dried at 70°C in vacuum for three days. The films were crystallized under three different conditions: (i) quenching to 30°C, (ii) crystallizing at 120°C and (iii) crystallizing at 156°C (130°C for copolymers). Films of required size were wrapped in aluminium foil and sealed in a glass tube evacuated to 10^{-3} mm of Hg. They were then melted in a closed heater set at 227°C for 5 min to destroy all the nuclei and quickly transferred to the thermostatic oil bath set at predetermined crystallization temperature. Sufficient time to complete the crystallization process has been given in each case. The time of crystallization for high T_c s has been determined from the flat portion of the crystallization isotherms of the samples¹⁹.

The crystalline structure of the samples crystallized at different conditions were determined from WAXS measurements using a Philips PW 1710 diffractometer with nickel-filtered CuK_{α} radiation. The diffractograms were recorded over the range 10–45° at the scan rate of 0.9° 2θ min⁻¹. The spacings of the various Miller planes of the PVF₂ crystals were measured using Bragg's equation for the 1st order reflection

$$\lambda = 2d_{hkl} \sin \theta \quad (1)$$

where λ has been taken to equal 1.54 Å.

RESULTS AND DISCUSSION

The X-ray diffractograms of the samples were recorded for the whole composition of the blends crystallized at three different temperatures, e.g. 30°, 120°, and 156°/130°. In *Figures 1-4* the X-ray diffractograms of the samples crystallized at 120°C are shown. It is clear from *Figure 1* that all KF/KY PVF₂ blends cocrystallize in the α phase as evidenced from strong reflection at $2\theta = 18.4^\circ$ and $2\theta = 20^\circ$ and it is also apparent from *Figure 2* that the Cop-1/Cop-2 blends cocrystallize all in the β phase as indicated from the reflections at $2\theta = 20.7^\circ$ and 41° ^{15,20}. It is interesting to observe the X-ray diffractograms of the KY/Cop-1 and of the KF/Cop-1 blends (*Figures 3* and *4*). In these systems both KF and KY PVF₂ crystallize in the α phase whereas the Cop-1 crystallizes in the β phase. It is apparent from *Figure 3* that in blends at the compositions $W_{Cop-1} = 0.31$ and $W_{Cop-1} = 0.48$ only α phase is produced, but at $W_{Cop-1} = 0.68$ the β phase peak at 41° is also seen. This indicates that the composition $W_{Cop-1} = 0.68$ do not produce cocrystals

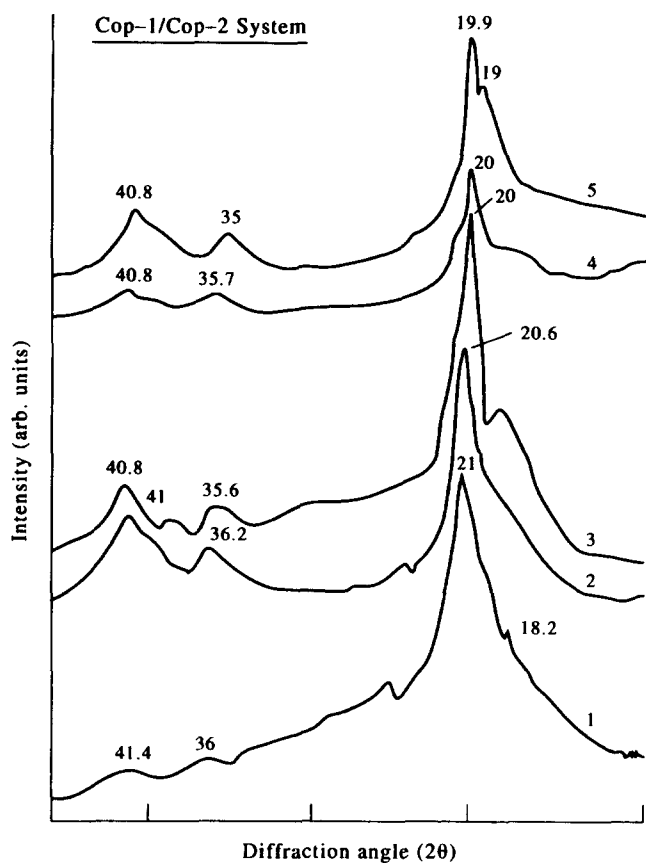


Figure 2 WAXS patterns of Cop-1/Cop-2 copolymer blend systems crystallized at 120°C: 1, $W_{\text{Cop-2}} = 0.00$; 2, $W_{\text{Cop-2}} = 0.27$; 3, $W_{\text{Cop-2}} = 0.49$; 4, $W_{\text{Cop-2}} = 0.74$; 5, $W_{\text{KY}} = 1.00$

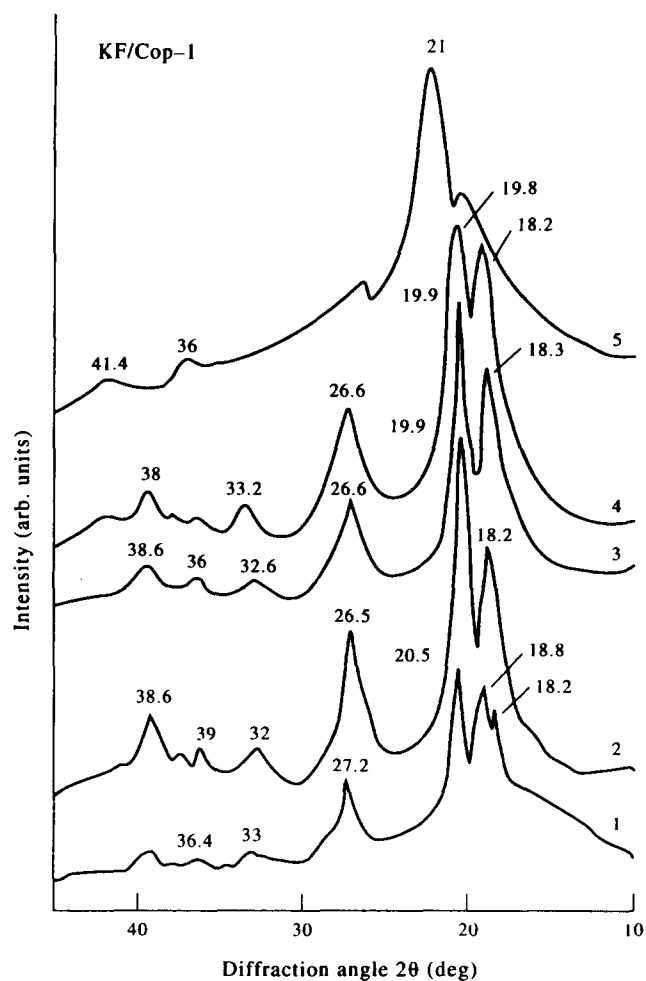


Figure 4 WAXS patterns of KF/Cop-1 blend system crystallized at 120°C: 1, $W_{\text{Cop-1}} = 0.00$; 2, $W_{\text{Cop-1}} = 0.28$; 3, $W_{\text{Cop-1}} = 0.50$; 4, $W_{\text{Cop-1}} = 0.68$; 5, $W_{\text{Cop-1}} = 1.00$

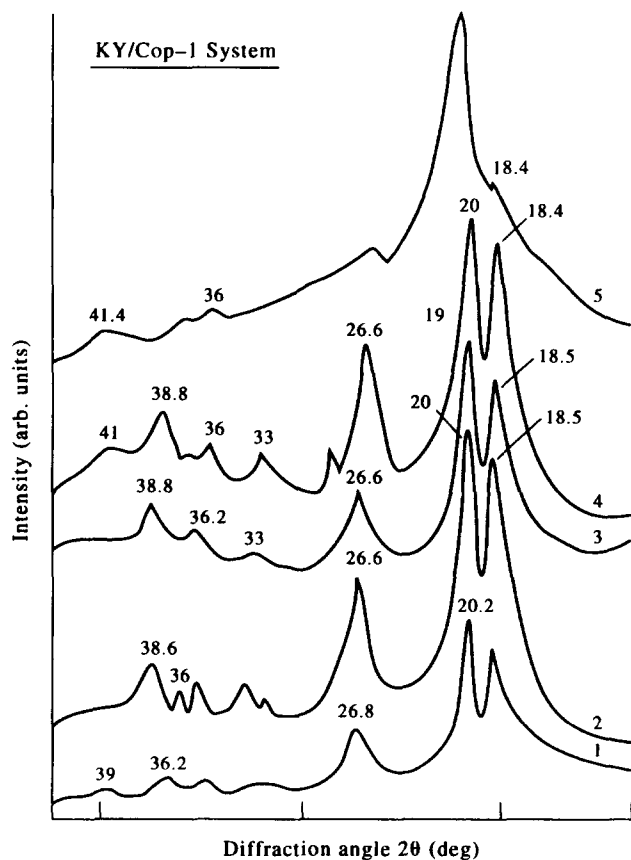


Figure 3 WAXS patterns of KY/Cop-1 blend system crystallized at 120°C: 1, $W_{\text{Cop-1}} = 0.00$; 2, $W_{\text{Cop-1}} = 0.31$; 3, $W_{\text{Cop-1}} = 0.48$; 4, $W_{\text{Cop-1}} = 0.68$; 5, $W_{\text{Cop-1}} = 1.00$

because both α and β phase are produced. In *Figure 4* also KF/Cop-1 blend with composition $W_{\text{Cop-1}} = 0.28$ and 0.50 crystallize purely in the α phase but the blend with $W_{\text{Cop-1}} = 0.74$ crystallizes in the mixture of α and β phases indicating crystallization is not occurring at this composition. These X-ray results tally excellently with the phase diagrams reported earlier²¹.

Now the H-H defect concentrations of the melt at the compositions $W_{\text{Cop-1}} = 0.48/0.50$ for KY/Cop-1 and KF/Cop-1 systems (H-H defect = 10.5 mol% and 9.6 mol%, respectively) are less than the cross-over point composition (11 mol%) of the pure PVF₂ from α phase to β phase. So at these compositions α phases should be produced as predicted from the work of Farmer *et al.*¹². At all the temperatures studied we observe α phases and this is very much apparent from *Figures 3* and *4*. Thus, the theoretical prediction of Farmer *et al.* is well verified. Now for the compositions $W_{\text{Cop-1}} = 0.68$ for KY/Cop-1 system the H-H defect concentration is 12.4% and for KF/Cop-1 system for $W_{\text{Cop-1}} = 0.68$ the H-H defect concentration is 11.8 mol%, respectively. At these compositions, according to the prediction of Farmer *et al.*, α phase should be produced. [The crossover point composition from α to β phase of the melt ($W_{\text{Cop-1}} = 0.68$) is 13.7 mol% H-H defect. It has been calculated assuming its linear variation with the addition of VF₂-VF₄ copolymer.] However, at these compositions we observe both α and β

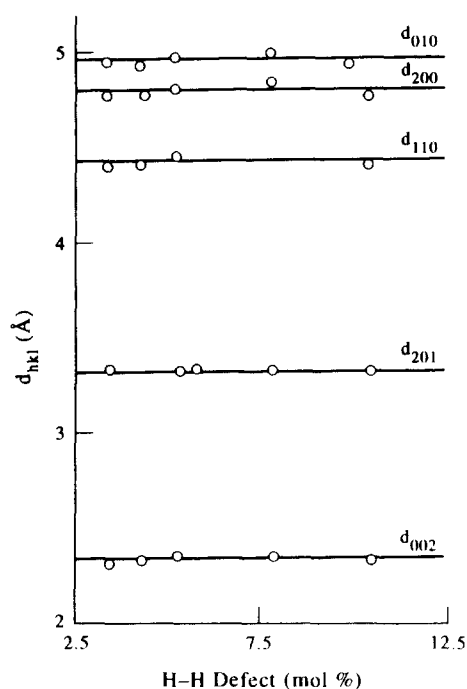


Figure 5 Plots of d_{hkl} as a function of H-H defect for KF:KY PVF₂ blends (α -phase) at 50°C

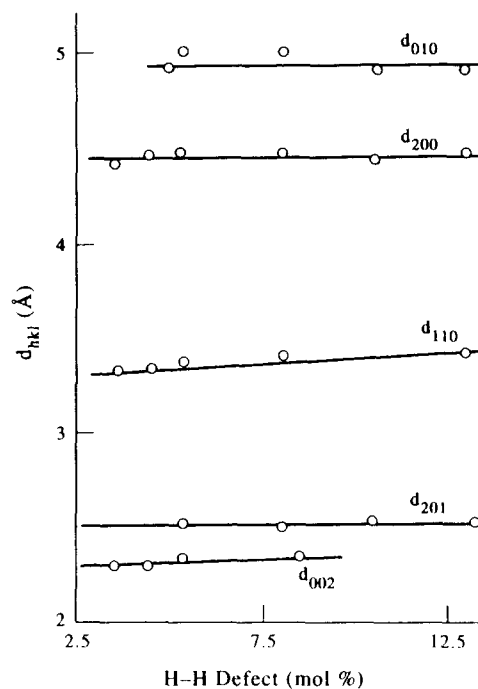


Figure 7 Plots of d_{hkl} as a function of H-H defect for KF:KY PVF₂ blends (α -phase) at 156°C

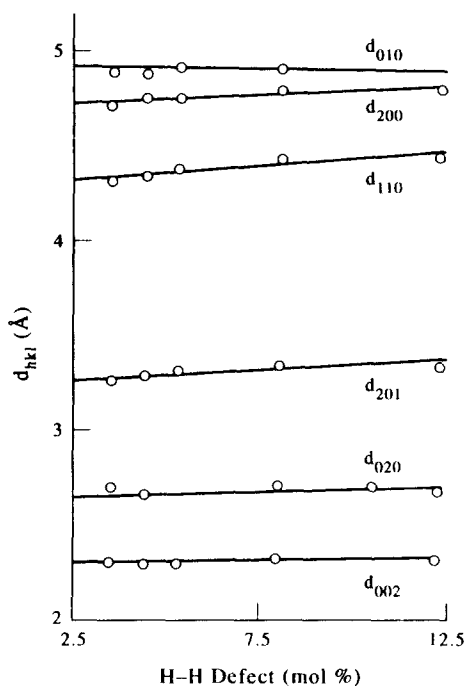


Figure 6 Plots of d_{hkl} as a function of H-H defect for KF:KY PVF₂ blends (α -phase) at 120°C

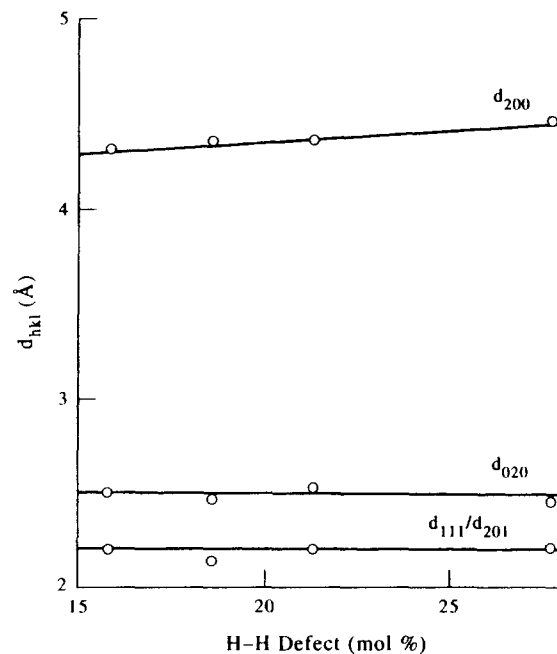


Figure 8 Plots of d_{hkl} as a function of H-H defect of Cop-1/Cop-2 copolymer blends (β -phase) crystallized at 50°C

phases. The possible cause of not forming cocrySTALS at this composition for both the systems is probably due to the liquid-liquid phase separation in the melt as discussed in the previous publication²¹. Thus we can conclude from these results the theoretical predictions of Farmer *et al.*¹² is applicable for the compositions up to which cocrySTALLIZATION is occurring.

In Figures 5-7 the d_{hkl} for various Miller planes of the α -phase of PVF₂ are presented for measurements at different temperatures. At 50°C the variation of d_{hkl} with H-H defect is almost negligible, while at 120°C the variation is quite significant. However, at 156°C the

variation is moderate with H-H defect. In Figures 8-10 the variation of various d_{hkl} planes with H-H defect for β -phase has been presented. Here the same pattern of variation of d_{hkl} with H-H defect are also observed. To make a quantitative analysis on the variation of d_{hkl} with H-H defect the least square slopes and intercepts of the plots are calculated and are presented in Tables 2 and 3. The slope values indicate an increase of spacing of the Miller plane (hkl) with H-H defect and the intercept values indicate the d_{hkl} for zero% H-H defect into the lattice. A comparison of the data with temperature on both the tables indicate that at 120°C the slope value is highest showing a maximum and this is true for all the

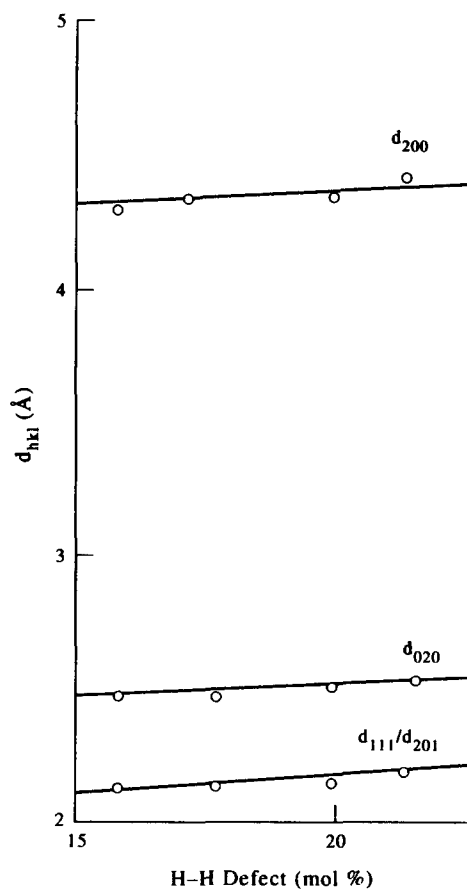


Figure 9 Plots of d_{hkl} as a function of H-H defect for Cop-1/Cop-2 copolymer blends (β -phase) crystallized at 120°C

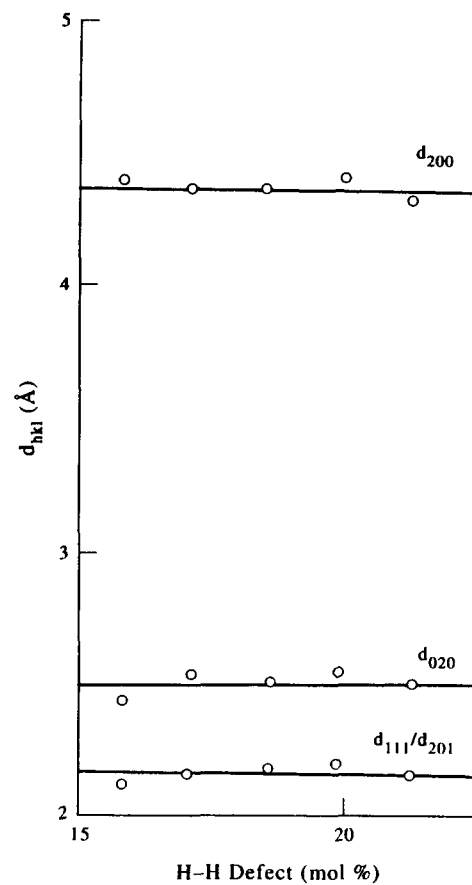


Figure 10 Plots of d_{hkl} as a function of H-H defect for Cop-1/Cop-2 copolymer blends (β -phase) crystallized at 130°C

Table 2 Least square slopes and intercepts of d_{hkl} vs H-H defect plots for α polymorph of PVF₂ produced at different temperatures

d_{hkl}	At 50°C		At 120°C		At 130°C	
	Slope	Intercept (Å)	Slope	Intercept (Å)	Slope	Intercept (Å)
d_{010}	0.0002	4.95	0.012	4.83	0.0010	4.87
d_{220}	0.0017	4.77	0.007	4.71	0.003	4.79
d_{110}	0.005	4.40	0.01	4.3	0.003	4.79
d_{201}	0.0046	3.35	0.0074	3.26	0.0071	3.30
d_{310}	-	-	0.004	2.69	-	-
d_{020}	-	-	0.0037	2.44	0.008	2.50

Table 3 Least square slopes and intercepts of d_{hkl} vs H-H defect plots for β polymorph of PVF₂ produced at different temperatures

d_{hkl}	At 50°C		At 120°C		At 130°C	
	Slope	Intercept (Å)	Slope	Intercept (Å)	Slope	Intercept (Å)
d_{200}	0.013	4.08	0.022	3.97	0.001	4.38
d_{020}	0.002	2.46	0.010	2.31	0.010	2.34
$d_{111/201}$	0.003	2.13	0.005	2.08	0.004	2.11

hkl planes for both the phases. The reason is yet uncertain and a probable cause is that it is a temperature where fractionation of H-H defect from entering into the lattice is minimum due to quenching. Further, the activation energy at this T_c gained by the defects to be introduced into the lattice is significantly higher. These two effects make this crystallization temperature an

optimum temperature where a maximum amount of defects is entering into the lattice. These results, therefore, indicate that the rate of accommodation of H-H defect into the PVF₂ lamella with H-H defect concentration in the chain is larger at 120°C and this may be a reason why at 120°C better cocrystallization was observed for KF/Cop-1 and KY/Cop-1 systems than

Table 4 Lattice parameters (Å) for zero mol% H-H defect of PVF₂ in the α and β polymorph

Polymorph	Theoretical ^a			Experimental		
	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>
α	8.75	4.65		9.42	4.83	4.56
β	8.05	4.25		7.94	4.62	2.63

^a From ref. 12

by crystallization at 50°C^{11,21}. Now a comparison of the data of Tables 2 and 3 reveal that the rate of increase of d_{hkl} with H-H defect is larger for the β phase than that for the α phase. An explanation for this behaviour may be due to the fact that β phase is more compact than the α phase as evidenced from density data (ρ of α phase PVF₂ = 1.92 g cm⁻² and ρ of β phase PVF₂ = 1.97 g cm⁻²)²².

Now from the intercept values of d_{hkl} in Tables 2 and 3, we calculated the unit cell dimensions of zero mol% H-H defect concentration. From the intercept value, the values of *a* and *b* were calculated from the unit cell pattern of Lando and Doll¹⁵. These experimental values of *a*, *b* and *c* together with the theoretical values of *a* and *b* for the zero% H-H defect¹² of PVF₂ are presented in Table 4. In the measurement of *a*, *b* and *c* the intercept (d_{hkl}) values at 120°C were taken because the minimum intercept values are observed at this temperature. A comparison of the data of Table 4 reveals that the experimental lattice parameter values for zero mol% H-H defect are still higher than the theoretical ones. But the experimental values of *a*, *b* and *c* for zero% H-H defect are much lower than the *a*, *b*, *c* values of lowest H-H defect content PVF₂¹².

CONCLUSION

These results on the structure of cocrystals support the theoretical prediction of Farmer *et al.* for the cross-over point composition of α and β phases with H-H defect content of PVF₂. Also the results on the cocrystallization of PVF₂ with VF₂-VF₄ copolymers indicate a case similar to isodimorphism, because PVF₂ and VF₂-VF₄ copolymers crystallize in the α and β phases, respectively and their cocrystals crystallize in the α phases. However, in the Cop-1 rich compositions cocrystallization was not observed, probably because of liquid-liquid phase separation in the melt. The d_{hkl} increases for both the α and β phases with increases in H-H defect concentration. The rate of increase of d_{hkl} with H-H defect is larger for the samples crystallized at 120°C than those at

50°C and 156°C (130°C for the copolymer). The experimental *a* and *b* for the zero% H-H defect content PVF₂ samples are higher than that predicted from the theoretical calculation of Farmer *et al.* Also the increase in the d_{hkl} with H-H defect is larger for β phase than that for α phase at all temperatures due to the more compact nature of the β unit cell than that for α unit cell.

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