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Formation of β-phase microcrystals from the melt of PVF_2–PMMA blends induced by quenching

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High-rate quenching at lower temperatures will result in the formation of β-phase microcrystals in PVF_2–PMMA blends with low PMMA contents directly from their melts. Annealing at higher temperature (120° C) promotes the growth of β phase. Almost pure β-phase crystallization in thin films of the blends could be obtained by this procedure. The morphology of the blends quenched and then annealed is similar to that of pure PVF_2.

1. Introduction

Poly(vinylidene fluoride) (PVF_2) is a semicrystalline polymer which has at least four forms of crystalline structure, i.e. α, β, γ and δ phases. Among these four polymorphs, however, most attention has been paid to the β phase, because of its extensive applications in piezoelectric and pyroelectric properties. β phase is normally obtained by mechanical deformation [1–4] or by applying an extremely high electric field [5–7] to the α-phase PVF_2. In general, α phase is predominant in samples of PVF_2 cooled from its melt, and transition to β phase must be induced by stretching. Only very recently, however, an unoriented β-phase PVF_2 has been obtained directly from its melt by high-rate quenching [8–10].

In previous papers we reported the formation of β phase directly from PVF_2 melt induced by ultra-high rate quenching [10] and the effect of poly(methyl methacrylate) (PMMA) on the crystalline structure in highly oriented PVF_2–PMMA blends [11]. In the present paper, we discuss the formation of β-phase microcrystals from melts of PVF_2–PMMA blends induced by high-rate quenching and subsequent annealing, as determined by Fourier transform infrared spectroscopy (FTIR), electron microscopy and wide-angle X-ray scattering (WAXS) techniques.

2. Experimental Procedure

The PVF_2 sample ($M_w = 5 \times 10^5$) used in this work was supplied by Polysciences Inc. and the PMMA sample ($M_n = 2.2 \times 10^5$, $M_w/M_n = 2.15$) was Elvacite 2041 provided by DuPont Co. Films of PVF_2–PMMA blends were cast from a hot 0.2% dimethylformamide solution on to a thin mica sheet. The thickness of the films was about 5 μm for FTIR and WAXS analysis and about 50 to 100 nm for electron microscopy. The two types of film supported on the mica were melted at 210° C for 10 min and then plunged very quickly into the quenchant, e.g. ice water or water at temperatures of 0 to 80° C. Annealing of the films was carried out in an oven at 120° C for 24 h.

Infrared spectra of both the as-quenched and annealed PVF_2–PMMA films were recorded with an FTS-20E FTIR spectrophotometer. X-ray profiles of the films were taken using a Rigaku 2028 wide-angle diffractometer in the reflection mode with nickel-filtered CuKα radiation. A Hitachi 600 transmission electron microscope (operated at 100 kV) was used to study the morphology of thin films of PVF_2–PMMA blends.

3. Results and discussion

3.1. Effect of blending with PMMA

The FTIR spectra of the two principal phases (α and β phases) of PVF_2 have been investigated extensively [12–15]. It is known that the vibrational bands at 410, 530, 615, 765, 795, 855, 975, 1214 and 1383 cm^{-1} refer to the α phase, while the bands at 455, 470, 510, 840 and 1280 cm^{-1} correspond to the β phase. Fig. 1 shows typical vibrational spectra of the α and β phases of PVF_2, obtained by quenching at different temperatures [10], in which the solid arrows represent the characteristic bands of the α phase, while the broken arrows indicate the vibrational bands of the β phase.

Fig. 2 shows the FTIR spectra recorded at room temperature in the frequency range 1500 to 400 cm^{-1} for film specimens (quenched at 0° C) of PVF_2–PMMA blends of various compositions. The spectra in Fig. 2 show that the quenched samples of PVF_2–PMMA blends with PMMA content below 30 wt % exhibit the characteristics of the β phase, as the bands at 530, 615, 765, 795, 855, 975, 1214 and 1383 cm^{-1}, which correspond to the α phase, disappear completely. For the blends with higher PMMA content, e.g. over 40 wt %, there are no strong characteristic bands of either α or β phase, because of the very imperfect and low crystallinity of PVF_2.

Fig. 3 shows the effect of annealing (at 120° C for

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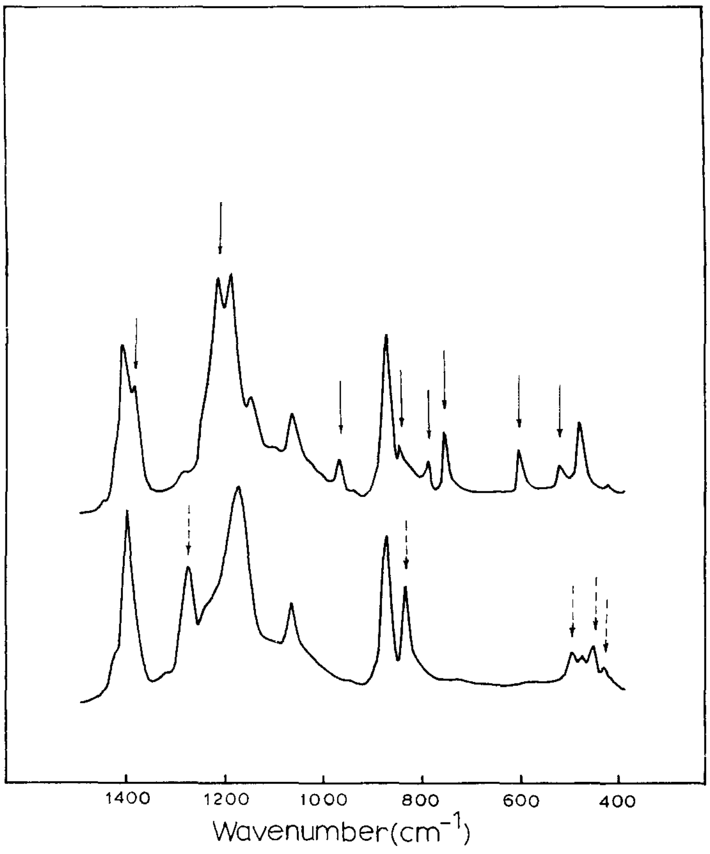

Figure 1 FTIR spectra of the α and β phases of PVF$_2$, obtained by quenching at 70° C and 0° C, respectively.

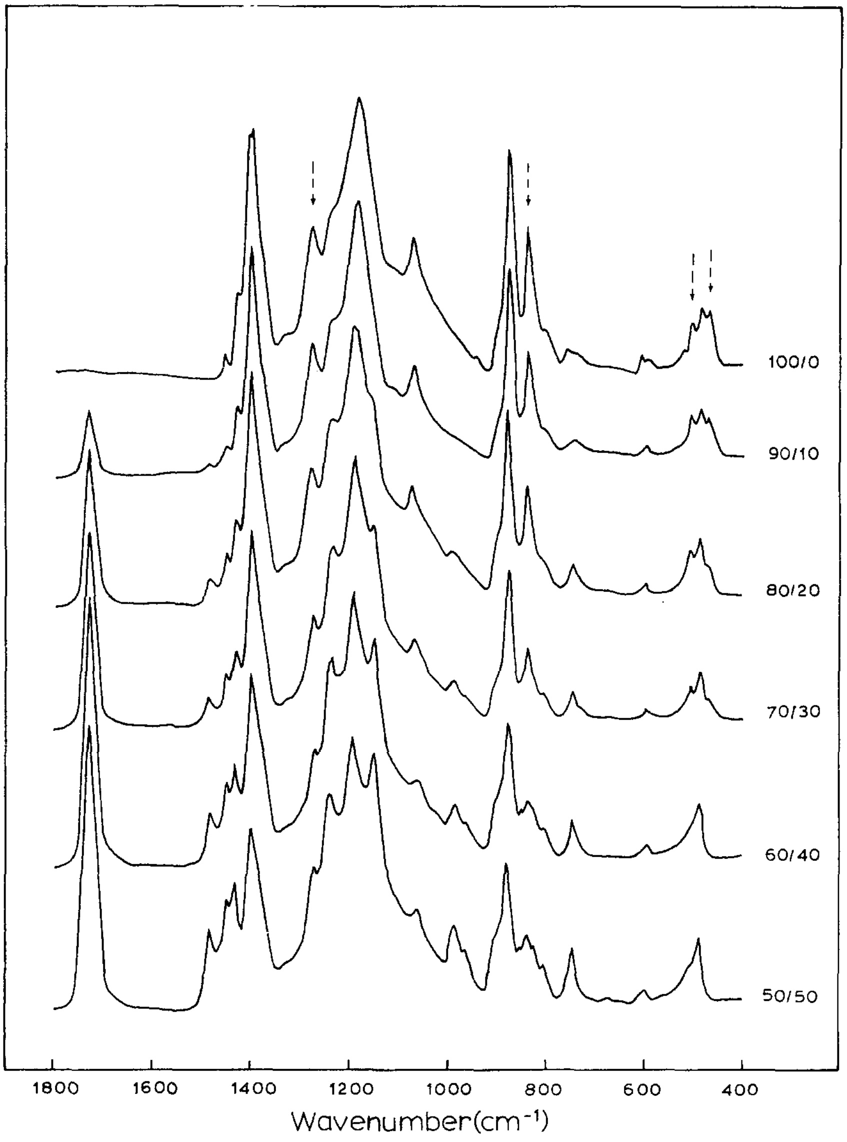

Figure 2 FTIR spectra of various PVF$_2$–PMMA blends quenched at 0° C.

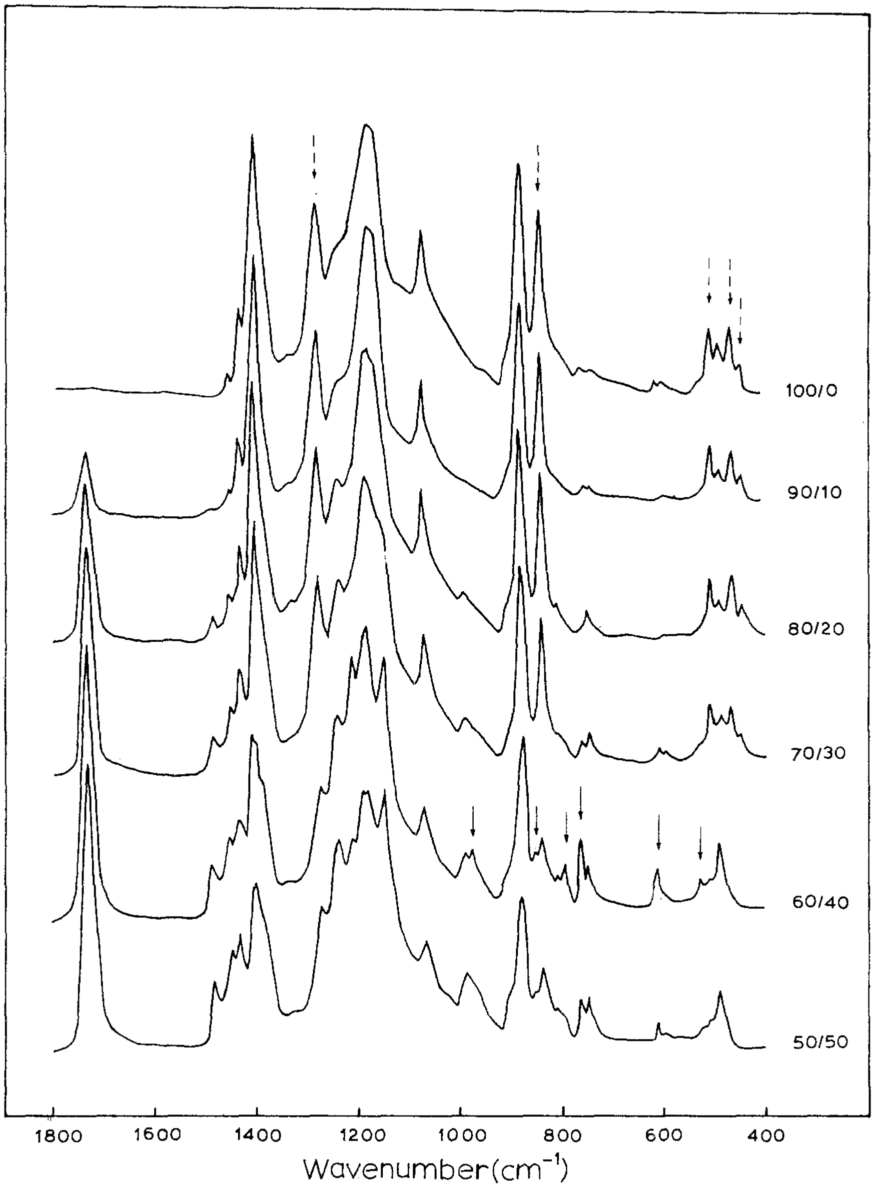

Figure 3 FTIR spectra of quenched (at 0° C) and then annealed (at 120° C for 24 h) PVF$_2$–PMMA blends.

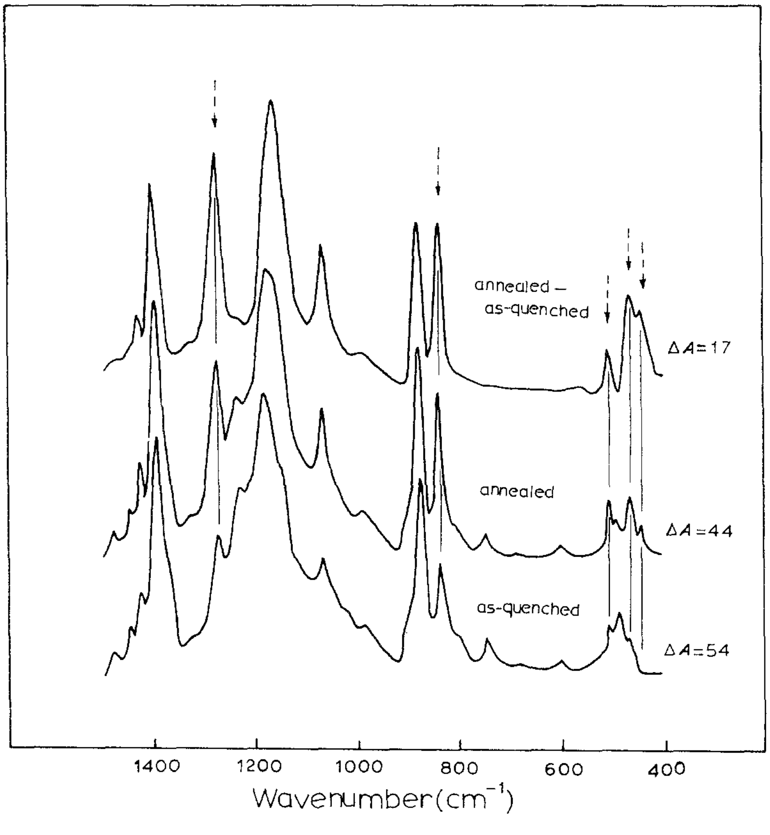

Figure 4 Difference spectra of PVF$_2$/PMMA = 80/20 blend before and after annealing.

24 h) on the quenched films of PVF_2–PMMA blends. It is apparent that annealing results in an increase in crystallinity of PVF_2 in the blends. However, it seems that the changes of β and α phase induced by annealing are different with an increase of PMMA content in the blends. In order to observe the effect of annealing on crystal growth more clearly, the difference spectrum technique was used for convenience, in which the spectrum of the as-quenched sample is subtracted from that of the annealed one (Fig. 4). The criterion for the subtraction amount is removing the contribution from the amorphous regions of the film. Particular attention was paid to amorphous bands around 500, 600 and 1200 cm^{-1}. In Fig. 5 are the difference spectra of PVF_2–PMMA blends with various compositions before and after annealing. These spectra indicate that annealing mainly results in an increase in β phase for samples with PMMA contents $\leqslant$ 30 wt %. On the other hand, when the PMMA content was over 40 wt %, the development of α phase predominated during annealing. A possible explanation is that high-rate quenching results in nucleation of the β phase [8], in which case annealing will certainly cause an increase in β phase. For the blends with PMMA content $\geqslant$ 40 wt %, however, because of the imperfectness of crystallinity in the as-quenched sample, annealing will induce further crystallization of PVF_2 at 120° C, including both nucleation and growth. Hence in this case the blends exhibit an increase in the α phase.

TABLE I Change in relative amount of β phase, $F(\beta)$, with composition of PVF_2–PMMA blend

PVF_2/PMMA	100/0	90/10	80/20	70/30	60/40	50/50
As-quenched	0.88	0.89	0.85	0.80	0.55	0.64
Annealed	0.90	0.97	0.98	0.91	0.56	0.66

As discussed above, both the as-quenched and the annealed samples consist of two crystalline phases, β phase and α phase. The relative percentage of β phase, $F(\beta)$, i.e. the ratio of the amount of β phase to the total amount of β phase and α phase, can be calculated by using the absorbance intensity D of the bands at 510 cm^{-1} (β phase) and 530 cm^{-1} (α phase), through the equation $F(\beta) = D_{510}/(D_{510} + 0.81D_{530})$ [8, 16]. The contents of β phase in as-quenched and annealed samples are listed in Table I. $F(\beta)$ remains unchanged

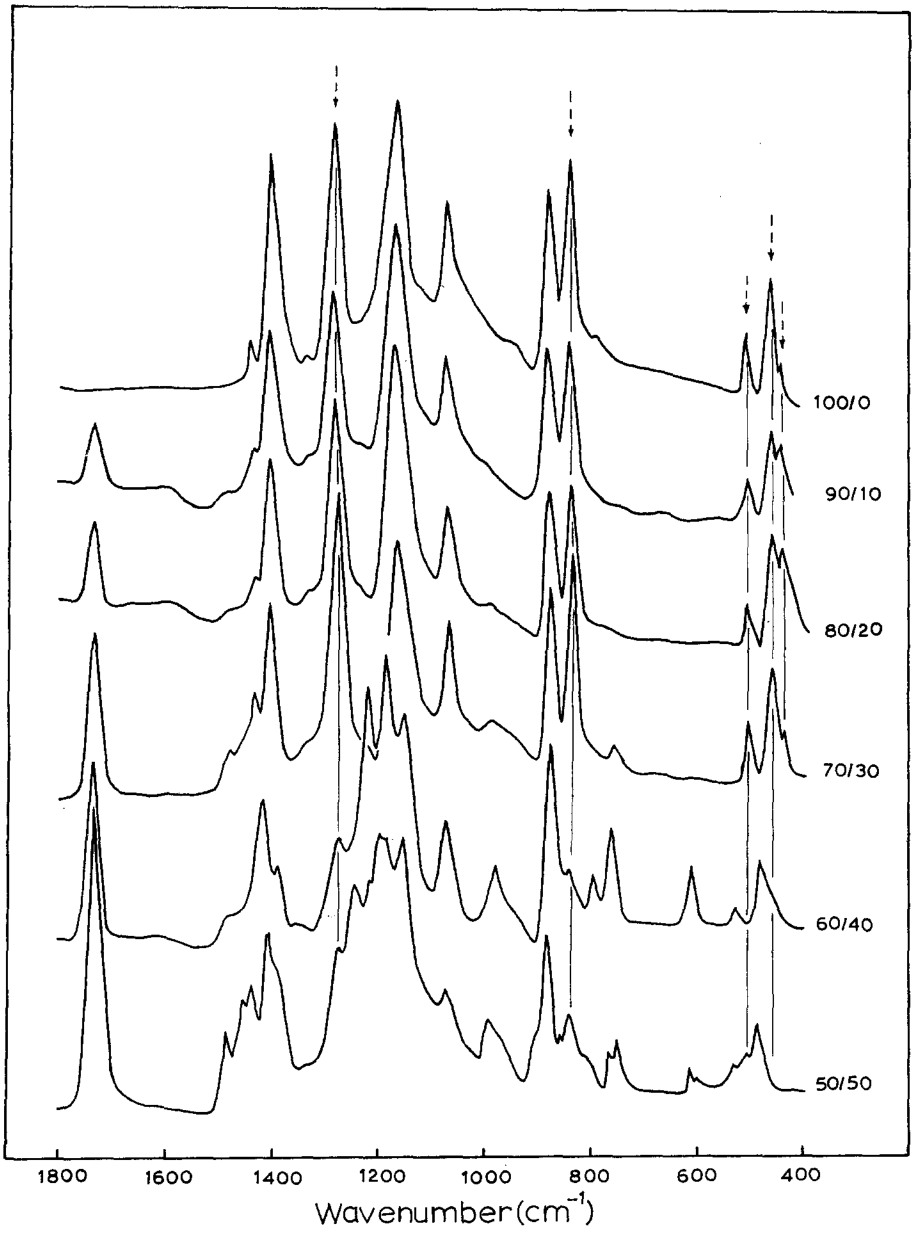

Figure 5 Difference spectra of various PVF_2–PMMA blends before and after annealing.

with the growth of crystals during annealing within experimental error for pure PVF_2 and the blends with higher PMMA content ($\geqslant$ 40 wt %), indicating that the two crystalline phases developed during annealing at nearly the same rate. On the other hand, the presence of a small amount of PMMA in the blends promotes the growth of β phase during annealing. Actually, almost pure β-phase PVF_2 will be obtained by this method when the content of PMMA in the blends is $\leqslant$ 20 wt % (Table I).

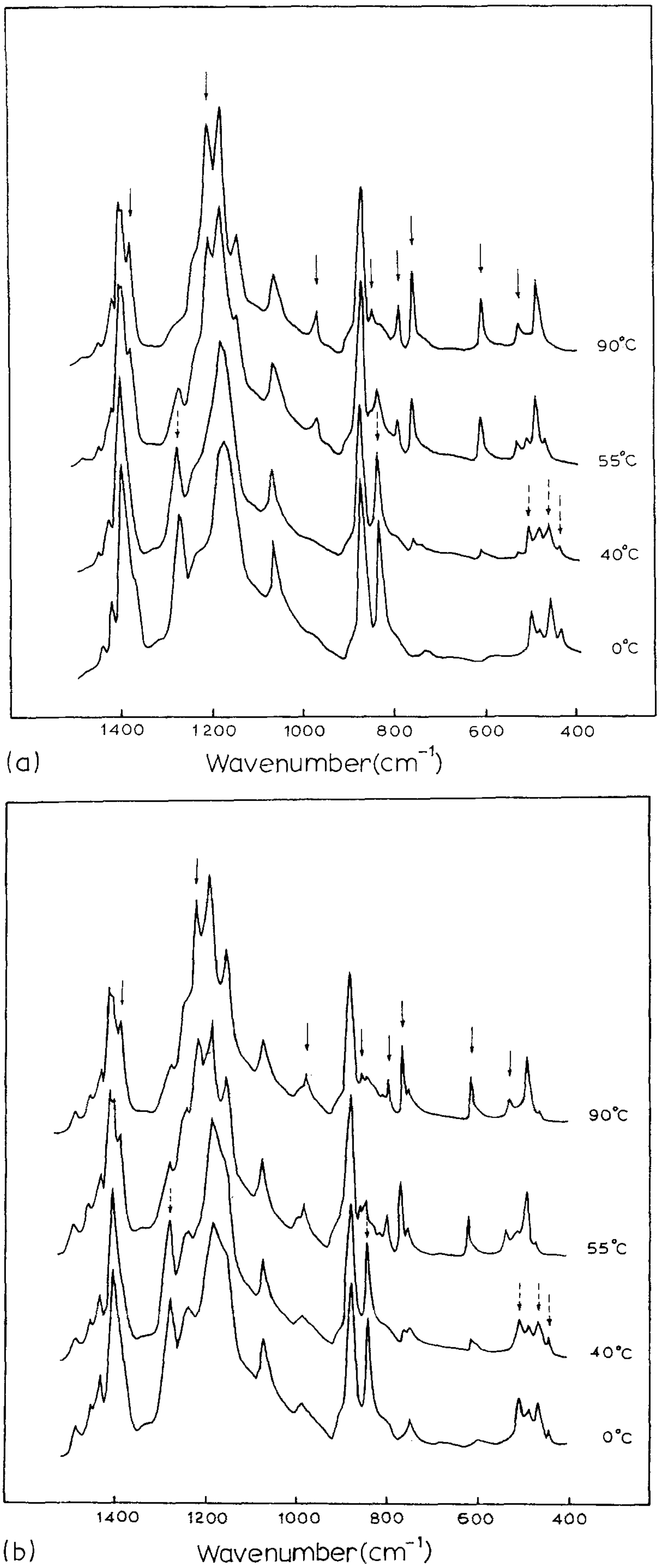

Figure 6 FTIR spectra of PVF_2/PMMA = (a) 90/10 and (b) 70/30 blends quenched at various temperatures and then annealed at 120° C for 24 h.

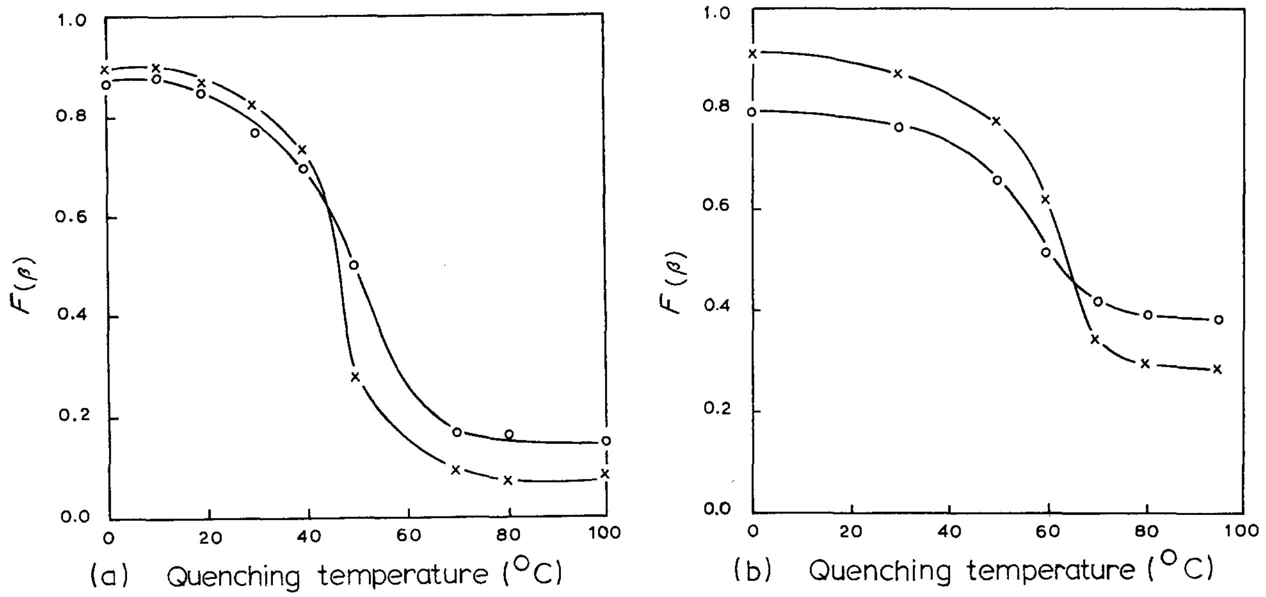

Figure 7 Dependence of relative amount of β phase, $F(\beta)$, on quenching temperature for (a) pure PVF_2 and (b) PVF_2/PMMA = 70/30 blend. (o) As-quenched, (x) annealed.

3.2. Effect of quenching temperature

As described in our previous paper [10], the critical quenching temperature for β-phase formation for pure PVF_2 is about 30° C. In Fig. 6, as an example, is shown the effect of quenching temperature on the formation of β phase in two blends of PVF_2–PMMA (90/10 and 70/30). It is noticed that the critical quenching temperature is about 40° C. When the content of PMMA in the blends is over 40 wt %, no marked critical quenching temperature has been observed, probably due to the fact that the samples were not well crystallized.

Fig. 7 shows the dependence of the relative amount of β phase, $F(\beta)$, calculated by the equation given above [8, 16], on the quenching temperature for pure PVF_2 and the PVF_2–PMMA (70/30) blend before and after annealing, respectively. It indicates that the critical quenching temperature of PVF_2–PMMA blends (PMMA content $\leqslant$ 30 wt %) is about 10° C higher than that of pure PVF_2 (compare Figs 7a and b). The

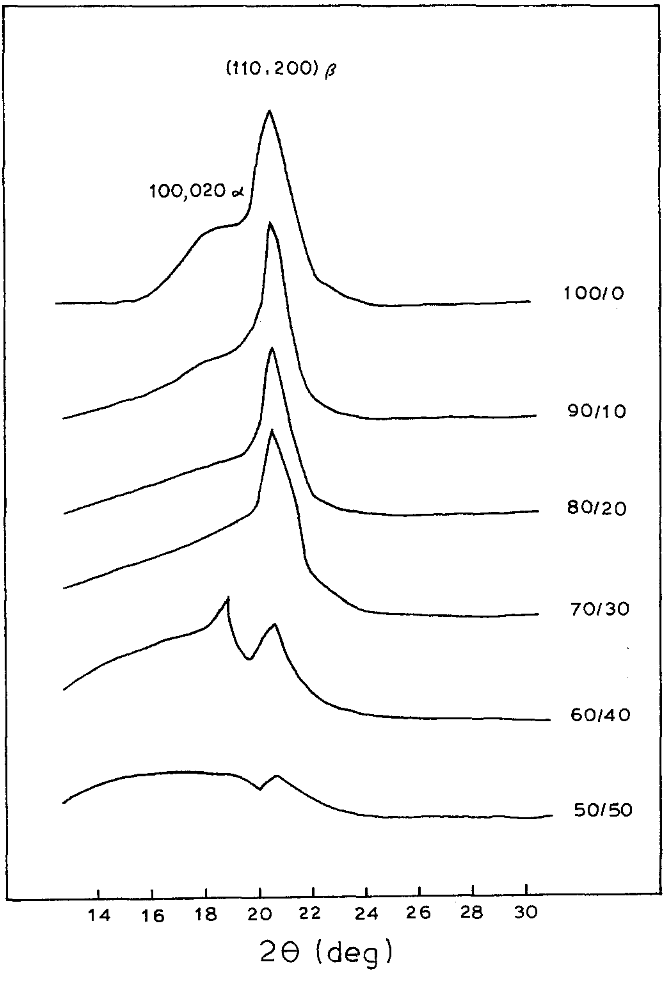

Figure 8 X-ray diffraction scans of various PVF_2–PMMA blends quenched at 0° C and then annealed at 120° C for 24 h.

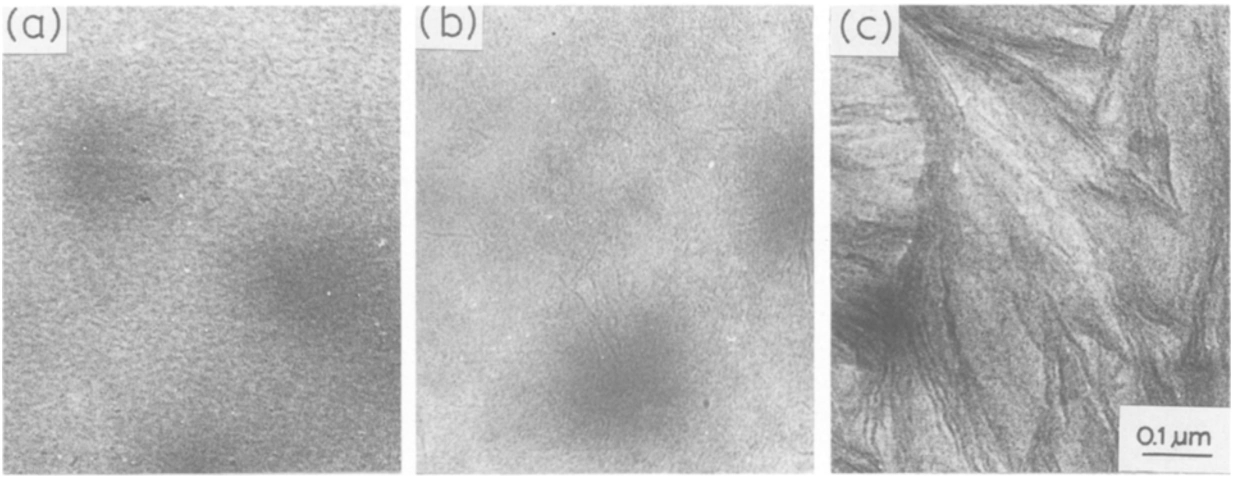

Figure 9 Electron micrographs of PVF_2/PMMA = 70/30 blend quenched at (a) 0° C, (b) 50° C, (c) 100° C, and then annealed at 120° C for 24 h.

growth rates of α and β phases are quite different below and above the critical quenching temperature. When the quenching temperature is below the critical value the growth rate of the β phase induced by annealing, especially in the blends, is higher than that of the α phase. On the other hand, the growth rate of α phase is higher than that of β-phase when above the critical quenching temperature.

In order to confirm the influence of PMMA on the β-phase formation in the blends induced by quenching and subsequent annealing, X-ray analyses have been carried out. Fig. 8 shows X-ray diffraction scans of the samples quenched at 0° C and then annealed at 120° C for 24 h. When the content of PMMA in the blends is below 30 wt %, only the peak at $2\theta = 20.8°$ is observed, which represents the strong unresolved (1 1 0) and (2 0 0) reflections of the β phase [5], while the peaks assigned to α phase, i.e. the reflections of (1 1 0), (0 2 0), (1 0 0), (1 2 0) and (0 2 1) crystal planes, completely disappear. For pure PVF_2 and the blends with higher PMMA content ($\geqslant$ 40 wt %), however, weak reflections of (0 2 0) and (1 0 0) corresponding to the α phase can still be observed. These results are consistent with those of FTIR.

It should be pointed out that the results discussed above are different from those reported by Leonard *et al.* [17] and Servet *et al.* [18], which showed that only blends with about 30 wt % of PMMA quenched at lower temperature would result in β-phase formation. A possible reason lies in the quenching rate used in their experiments not being high enough. Oka and Koizumi [8] indicated that the effective rate to obtain β phase was more than 800° C sec^{-1}. Thus it is necessary to use some special experimental technique so as to achieve a quenching rate high enough to induce the formation of β phase.

3.3. Morphology of quenched blends

Electron microscopy was used for study of the morphology of the quenched and subsequently annealed PVF_2–PMMA blends. In a previous paper [10] we discussed the microstructure of pure PVF_2 quenched and then annealed. Fig. 9, as an example, shows electron micrographs taken under defocus of PVF_2–PMMA (70/30) blend quenched at various temperatures and annealed at 120° C for 24 h. The morphologies of the blends with PMMA content below 30 wt % are similar to that of pure PVF_2. The blends quenched below the critical quenching temperature, 40° C, consist of β-phase microcrystals (Fig. 9a), while coexistence of β-phase crystallites with α-phase lamellae or incomplete spherulites was observed in the sample quenched at 50° C (Fig. 9b). When the quenching temperature is much higher, e.g. 100° C, a normal α-phase spherulite was observed in the film (Fig. 9c). No marked crystalline morphology has been identified for the blends with higher PMMA contents (above 40 wt %) because of their poorly developed crystallinity.

4. Conclusion

Quenching at lower temperature with subsequent annealing of thin films of PVF_2–PMMA blends with low PMMA contents will result in the formation of β-phase microcrystals directly from the melt. The critical quenching temperature is about 40° C. Blending PVF_2 with small amounts of PMMA ($\leqslant$ 30 wt %) promotes the growth of β phase during annealing of the quenched samples.

Acknowledgement

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References

1. J. B. LANDO, H. G. OLF and A. PETERLIN, *J. Polym. Sci. A1* **4** (1966) 941.
2. R. J. SHUFORD, A. F. WILDE, J. J. RICCA and G. R. THOMAS, *Polym. Engng Sci.* **16** (1976) 25.
3. J. C. McGRATH and I. M. WARD, *Polymer* **21** (1980) 855.
4. K. MATSUSHIGE, K. NAGATA, S. IMADA and T. TAKEMURA, *ibid.* **21** (1980) 1391.
5. G. T. DAVIS, J. E. McKINNEY, M. G. BROADHURST and S. C. ROTH, *J. Appl. Phys.* **49** (1978) 4998.
6. D. K. DAS-GUPTA and K. DOUGHTY, *ibid.* **49** (1978) 4601.
7. B. A. NEWMAN, C. H. YOON, K. D. PAE and J. I. SCHEINBEIM, *ibid.* **50** (1979) 6095.
8. Y. OKA and N. KOIZUMI, *Bull. Inst. Chem. Res. Kyoto Univ.* **63** (1985) 192.

9. C. C. HSU and P. H. GEIL, *Polym. Commun.* **27** (1986) 105.
10. D. C. YANG and Y. CHEN, *J. Mater. Sci. Lett.* **6** (1987) 599.
11. D. C. YANG and E. L. THOMAS, *ibid.* **6** (1987) 593.
12. G. CORTIL and G. ZERBI, *Spectrochim. Acta* **32A** (1967) 2216.
13. G. KOBAYASHI, K. TASHIRO and H. TADOKORO, *Marcomolecules* **8** (1975) 158.
14. M. A. BACHMANN, W. L. GORDON, J. L. KOENIG and J. B. LANDO, *J. Appl. Phys.* **50** (1979) 6106.
15. K. TASHIRO, M. KOBAYASHI and H. TADOKORO, *Macromolecules* **14** (1981) 1757.
16. S. OSAKI and Y. ISHIDA, *J. Polym. Sci., Polym. Phys. Edn.* **13** (1975) 1071.
17. C. LEONARD, J. L. HALARY, L. MONNERIE, D. BROUSSOUX, B. SERVET and F. MICHERON, *Polym. Commun.* **24** (1983) 110.
18. B. SERVET, D. BROUSSOUX, S. RIES and F. MICHERON "Interrelations between Processing Structure and Properties of Polymer Materials" (Elsevier, Amsterdam, 1984) No. 81.

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