Computerized infra-red study of the interaction of poly(vinylidene fluoride) with stereoregular poly(methyl methacrylate)

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A computerized infra-red study was carried out on blends of poly(vinylidene fluoride) (PVF_2) with isotactic or syndiotactic poly(methyl methacrylate) (it- and st-PMMA) to investigate the effect of tacticity of PMMA on the interaction with PVF_2. A calibration method for the infra-red spectra had to be developed to insure that sum and difference spectra were performed correctly. Any influence of stereoregular PMMA on the infra-red spectrum of PVF_2 could be ascribed merely to the loss of crystallinity of PVF_2. In PMMA poor blends, PVF_2 crystallized in the α(II) modification. In some of these blends, recrystallization was observed, but this did not lead to another crystalline form. The infra-red spectra of it- and st-PMMA were influenced strongly by PVF_2, especially vibrations of the carbonyl group. A considerably larger spectral change in the homogeneous blends of amorphous PVF_2 with it-PMMA compared with blends with st-PMMA indicated that the interaction of the PVF_2 segments is stronger with the isotactic than with the syndiotactic segments. This is in agreement with our previous study on melting point depressions of PVF_2 and points to a better fit of it-PMMA with the dipoles of PVF_2 segments.

INTRODUCTION

Since the compatibility of poly(vinylidene fluoride) (PVF_2) with commercial poly(methyl methacrylate) (PMMA) was reported by several authors[1–3], considerable research effort has been dedicated to the interaction of PVF_2 with PMMA and other oxygen containing polymers. In these studies, melting point depression of PVF_2 crystals[3,4] and the height of the lower critical solution temperature[5] (LCST) were taken indicative for the interaction of PVF_2 with the blended polymer. The first method was developed by Nishi and Wang[3] for the PVF_2/PMMA system and also applied by Kwei *et al.*[4] in the PVF_2/poly(ethyl methacrylate) (PEMA) system. The larger melting point depressions observed in the PVF_2/PMMA blends, compared with the PVF_2/PEMA blends led to the conclusion that the binary polymer–polymer interaction is stronger in the first system than in the latter one. These results were supported by a study of the LCSTs of blends of PVF_2 with some oxygen-containing polymers, showing a higher LCST if the binary interaction parameter of the two polymers, as determined by melting point depression, is more negative[6]. In previous work we used the method of melting point depression to study the interaction of PVF_2 with stereoregular PMMAs and from the results we concluded a stronger interaction of PVF_2 with isotactic PMMA (it-PMMA) than with syndiotactic PMMA (st-PMMA)[7].

Melting point depression and position of LCST only predict the strength of the binary interaction and do not reveal anything about the nature of this interaction. To disclose the latter, spectroscopic techniques like n.m.r. and i.r. should be applied. However, with ^{13}C and ^{19}F n.m.r. Bovey[8] did not observe any special interaction or complex formation in mixed concentrated DMF solutions of PVF_2 and atactic PMMA (at-PMMA). Coleman *et al.*[9] demonstrated in a Fourier transform infra-red study that the carbonyl group is involved in the interaction between at-PMMA and PVF_2. They suggested that the PVF_2 conformation might be affected in blends with tactic PMMA, so we performed a computerized infra-red study on blends of PVF_2 with stereoregular PMMAs.

From previous work, it was known that these blends are completely compatible in the molten state[7]. However, PVF_2 crystallizes upon cooling from blends containing up to about 60 wt% PMMA. Coleman *et al.* demonstrated that the i.r. spectra of such heterogeneous blends are nearly identical to the sum spectrum composed from the separate polymers[9]. At higher PMMA contents the rate of crystallization of PVF_2 is diminished drastically so PVF_2 does not crystallize any more from the blend upon cooling, leading to homogeneous blends. Of course, these homogeneous blends are more suitable to study the interaction of PVF_2 with the PMMAs.

EXPERIMENTAL

Preparation and characterization of the PMMAs used were performed as previously described[7]. The intrinsic viscosity of it- and st-PMMA amounted to 1.25 and 1.39 dl/g, corresponding with $\bar{M}_v$ of 3.5×10^5 and 3.8×10^5, respectively. The tacticities of the PMMAs were measured by n.m.r., yielding 93% isotactic triads in it-PMMA and 89% syndiotactic triads in st-PMMA. PVF_2 was the KF resin from Kureha Chemical Industry Co. Ltd. and was the same as used previously.

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Blends of PVF_2 with it- and st-PMMA for infra-red experiments were prepared by dissolving definite weights of PVF_2 and it- or st-PMMA in boiling acetone. After cooling to room temperature, the clear solutions were diluted to a total polymer concentration of 1 g/dl and 0.075 ml of the solution was homogeneously spread with a micropipette on a KBr pellet. The solvent was allowed to evaporate steadily in a flat dish and complete removal of the last traces of solvent was achieved by heating at 50°C *in vacuo* overnight. This procedure led to an average film thickness of about 5 μm. From each solution, three samples were prepared and scanned between 330 and 1980 cm^{-1} and between 2600 and 3200 cm^{-1} on a Perkin-Elmer 580B infra-red spectrometer with a maximum resolution of 2 cm^{-1}. The spectra were transformed into absorbance units, averaged over the three samples and stored on magnetic tape. From the results, however, it appeared that the film thickness showed large deviations, so we had to look for a calibration method. From Coleman's[9] study we knew that the PVF_2 absorption band at 875 cm^{-1} was not affected by blending with at-PMMA. Moreover, in infra-red spectra shown by Cortili[10], this absorption band was even present in molten PVF_2. So we chose this absorption band as an internal standard.

PMMA is denoted as component 1, with a weight fraction w_1 in the blends and PVF_2 as component 2, with a weight fraction $(1-w_1)$ in the blends. Spectra are represented as absorbance (*A*) *versus* wavenumber (σ): $A_1(\sigma)$, $A_2(\sigma)$ and $A_{12}(\sigma)$ for PMMA, PVF_2 and the blends, respectively. Spectra of PVF_2-containing samples were normalized (indicated by an index *n*) by dividing $A_{12}(\sigma)$ by the correction factor $A_{12}(875).(1-w_1)^{-1}$ leading to:

$$A_{2,n}(\sigma) = A_2(\sigma)/A_2(875)$$

for the normalized spectrum of pure PVF_2 and

$$A_{12,n}(\sigma) = A_{12}(\sigma)/A_{12}(875).(1-w_1)^{-1}$$

for the normalized spectra of the blends.

For pure it- and st-PMMA the above correction factor goes to the limit for $(1-w_1) \to 0$ and $A_{12}(875) \to 0$. According to the Lambert–Beer law:

$$A_{12}(875) = \epsilon_2(875).(1-w_1).c_{tot}.t$$

where $\epsilon_2(875)$ is the extinction coefficient of PVF_2 at 875 cm^{-1}, c_{tot} is the total polymer concentration in the film and *t* is the thickness of the film. The limit can now be found as follows:

$$A_{1,n}(\sigma) = \lim_{\substack{w_1 \to 1 \\ A_{12}(875) \to 0}} A_{12}(\sigma)/A_{12}(875).(1-w_1)^{-1}$$

$$= \lim_{\substack{w_1 \to 0 \\ A_{12}(875) \to 0}} A_{12}(\sigma).(1-w_1)/\epsilon_2(875).(1-w_1).c_{tot}.t$$

$$= \{A_1(\sigma)/\epsilon_2(875).c_{tot}.t\}.\epsilon_1(1730)/\epsilon_1(1730)$$

$$= \{A_1(\sigma)/A_1(1730)\}.\epsilon_1(1730)/\epsilon_2(875)$$

In this expression, $\epsilon_1(1730)$ is the extinction coefficient of PMMA at 1730 cm^{-1}. The factor $\epsilon_1(1730)/\epsilon_2(875)$ was calculated from the absorbances at 1730 and 875 cm^{-1} in the spectra of the 80:20 PVF_2/it-PMMA and the PVF_2/st-PMMA blends and amounted to 0.41 and 0.46, respectively. Sum and difference spectra were then calculated as follows:

Sum spectrum: $\Sigma = w_1 A_{1,n}(\sigma) + (1-w_1)A_{2,n}(\sigma)$

Difference spectrum:

$$\Delta_1 = \{A_{12,n}(\sigma) - (1-w_1)A_{2,n}(\sigma)\}/w_1$$

and

$$\Delta_2 = \{A_{12,n}(\sigma) - w_1 A_{1,n}(\sigma)\}/(1-w_1)$$

The sum spectra were compared with the normalized spectra of the blends with corresponding composition. Difference spectra Δ_1 were compared with the normalized spectrum of it- or st-PMMA and the difference spectra Δ_2 were compared with the normalized spectrum of PVF_2. In *Figure 1* the spectrum of an amorphous 40:60 PVF_2/st-PMMA blend is compared with the sum spectrum. Large parts of the spectra reasonably match each other, except the disappearance in the blend of vibrational bands of PVF_2 at 530, 610, 760, 795 and 855 cm^{-1}, which can be related to the loss of crystallinity of PVF_2 in this blend[10]. This good agreement can be considered as a test for the calculation method. For a control of the crystalline structure of PVF_2 in heterogeneous blends, a sample was pressed for 2 min at 200°C in a circular mould of 19 mm diameter and 1 mm thickness. An X-ray pattern of this sample was re-

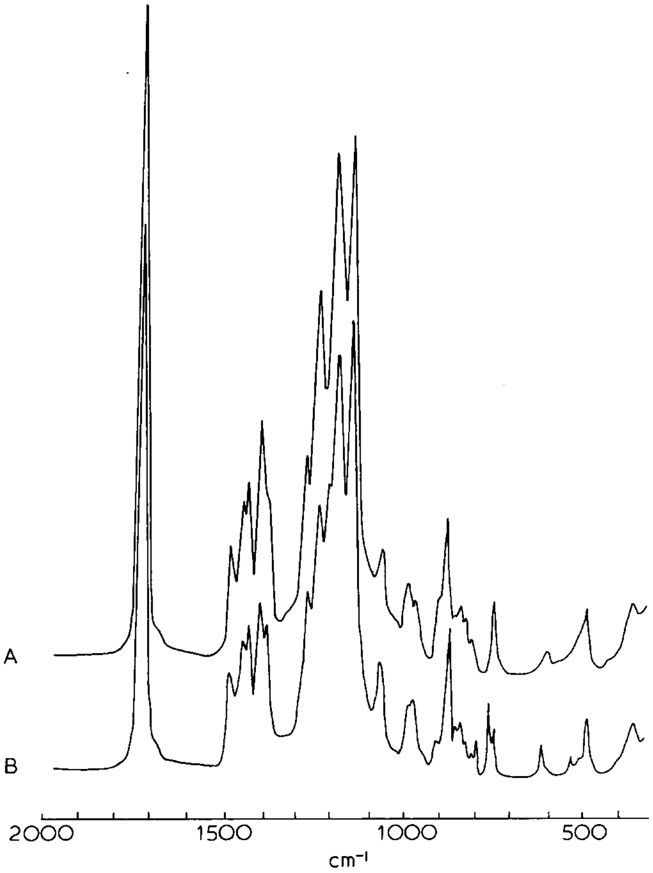

Figure 1 (A) Infra-red spectrum of an amorphous 40:60 PVF_2/st-PMMA blend; (B) infra-red sum spectrum (Σ) of partly crystalline PVF_2 and st-PMMA in a 40:60 composition

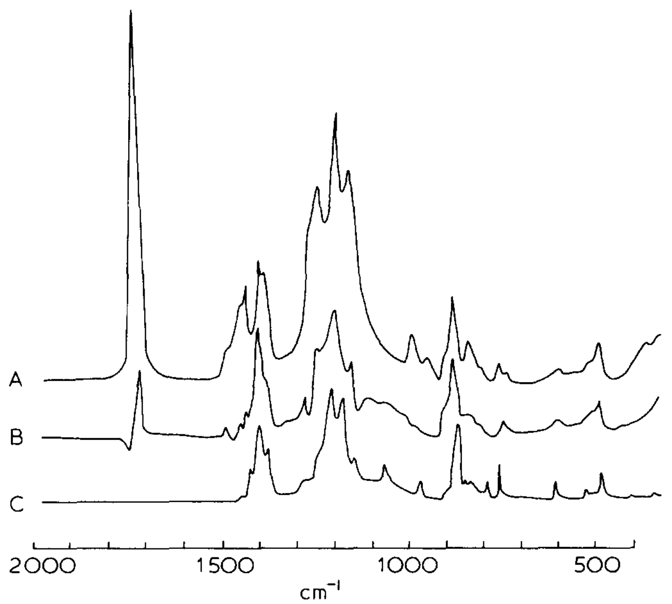

Figure 2 (A) Infra-red difference spectrum (Δ_2) of a 20:80 PVF$_2$/it-PMMA blend after subtraction of the it-PMMA part; (B) infra-red difference spectrum (Δ_2) of a 20:80 PVF$_2$/st-PMMA blend after subtraction of the st-PMMA part; (C) infra-red spectrum of PVF$_2$

corded on a powder diffractometer (Philips) with a scan speed of 0.5°/min and a slit width of 1°.

RESULTS

From d.s.c. experiments, we could derive the relative amounts of crystallized PVF$_2$ in the 80:20, 60:40 and 40:60 PVF$_2$/it-PMMA blends as well as in the 80:20 and 60:40 PVF$_2$/st-PMMA blends. However, a useful study of the influence of the tacticity of PMMA on the infra-red spectra of the blends can only be made in homogeneous, amorphous blends with the same content of it- or st-PMMA as was the case for our 20:80 PVF$_2$/PMMA blends. Difference spectra of the 20:80 PVF$_2$/PMMA blends and the PMMA parts show large deviations from pure PVF$_2$. The most salient effect is seen for the $\nu_{C=O}$ band at 1730 cm^{-1} in the difference spectrum for it-PMMA, indicating that the extinction of this band is strongly increased in the blend compared with pure PMMA (*Figure 2*). The oscillation band at about 1720 cm^{-1} in the difference spectrum of the 20:80 PVF$_2$/st-PMMA blend with a positive absorption at 1715 cm^{-1} and a small negative absorption at 1730 cm^{-1} indicates a shift of the $\nu_{C=O}$ to lower frequency in the blend compared with pure PMMA. From *Figure 2* it can also be seen that PVF$_2$ has lost its vibrational bands at 530, 610, 760, 795, 855, 970 and 1065 cm^{-1}.

If partly crystalline PVF$_2$ is subtracted from the spectra of amorphous blends, the above mentioned vibrational bands appear evidently as negative absorptions (*Figure 3*). The resulting difference spectrum also shows a positive absorption at 880 cm^{-1} and a negative absorption at 870 cm^{-1}, indicating that the PVF$_2$ band at 875 cm^{-1} is shifted to a somewhat higher frequency. This was also observed in a spectrum of molten PVF$_2$ by Cortili[10]. Besides, from a good agreement of the spectrum of it- or st-PMMA with these difference spectra in the region between 1100 and 1500 cm^{-1}, it was clear that this subtraction technique has completely cancelled out the strong CF$_2$ stretch vibrations at 1182, 1213 and to a lesser extent the vibrations at 1292 and 1382 cm^{-1}. Therefore, no shift of these CF$_2$ stretch vibrational bands could be observed. Although the CH stretch vibration of PVF$_2$ at 3020 cm^{-1} lies sufficiently apart from the CH stretch vibrations of the PMMAs, an influence of it- or st-PMMA on this PVF$_2$ band could not be detected.

If the PMMA content is lower than 60%, PVF$_2$ crystallizes from the blends, thus making them heterogeneous. The infra-red spectra of these blends are almost identical to the sum spectra composed from the separate polymers. Their difference spectra show again the same oscillation band at about 1720 cm^{-1} as found for homogeneous blends (*Figure 2*B), but now to a smaller extent indicating that $\nu_{C=O}$ of PMMA in heterogeneous blends is shifted to a lower frequency, too. In *Figure 4* this is shown for the difference spectrum of a heterogeneous 80:20 PVF$_2$/it-PMMA blend after subtraction of the it-PMMA part (curve B). Besides, these difference spectra as well as that of pure PVF$_2$ (curve A) point to the presence of PVF$_2$ in the crystalline α(II) phase with absorptions at about 485, 530, 610, 760, 795, 855 and 975 cm^{-1} [10–12] (*Figure 4* A and B). Moreover, X-ray powder diffractograms of such heterogeneous blends show reflections at 2θ = 18.0, 18.7, 20.4, 26.1, 27.0, 32.6, 36.2, 37.5, 38.9 and 46.5°. These values differ less than 0.3° from those belonging to the α(II) crystalline modification reported by Hasegewa[11] (*Figure 5* A and B).

As some heterogeneous samples exhibited double melting in d.s.c. experiments, the possibility of the occurrence of different crystalline modifications of PVF$_2$ had still to be investigated. For this reason, a double melting 40:60 PVF$_2$/it-PMMA blend, obtained by isothermal crystallization at 88°C, was annealed during 12 h at 157°C, which was just between the two melting temperatures. Although this long annealing procedure caused a complete 'shift' of

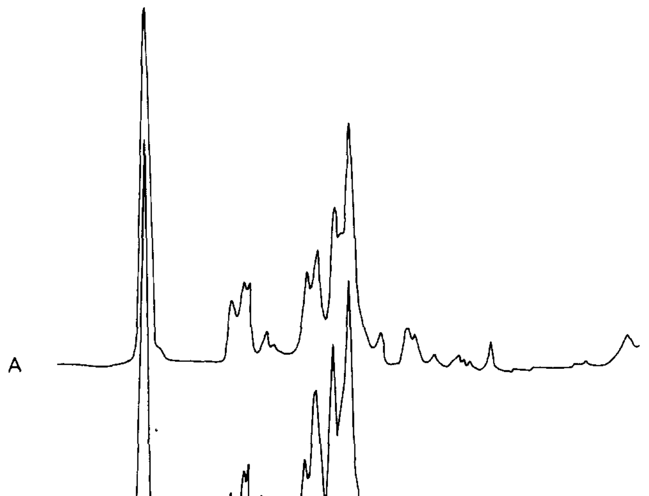

Figure 3 (A) Infra-red spectrum of a 40:60 PVF$_2$/st-PMMA blend; (B) infra-red difference spectrum (Δ_1) of an amorphous 40:60 PVF$_2$/st-PMMA blend after subtraction of the PVF$_2$ part

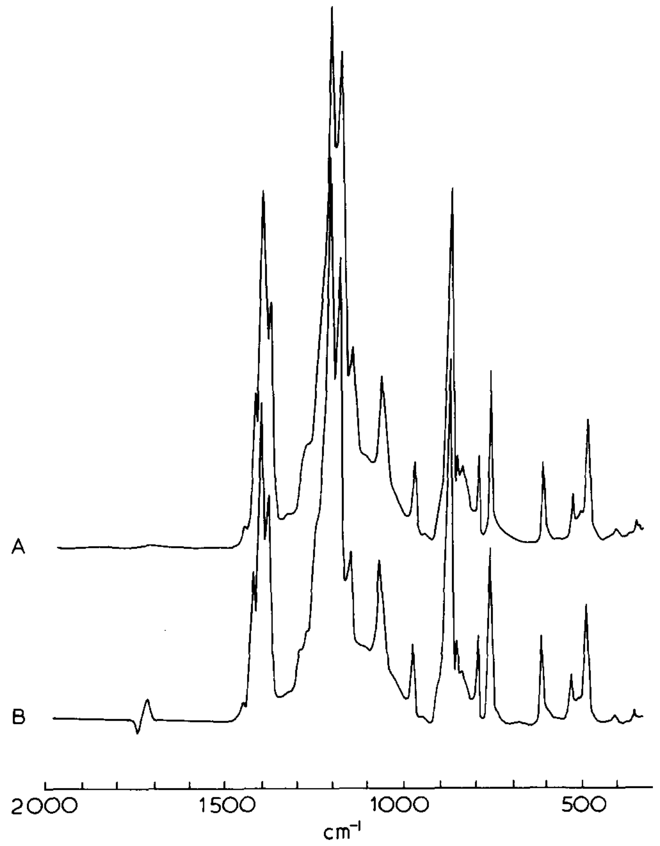

Figure 4 (A) Infra-red spectrum of partly crystalline PVF_2 in the α(II) modification; (B) infra-red difference spectrum (Δ_2) of a 80:20 PVF_2/it-PMMA blend after subtraction of the it-PMMA part

the first melting endotherm to the second one, we did not observe any change in the infra-red spectrum and only a negligible change in the X-ray pattern (*Figure 5*C). If the heating rate in the d.s.c. experiments was increased, a decrease in melting temperature of the second endotherm was observed, whereas the first melting temperature remained fairly constant, which was also the case for the total heat of melting. So, this double melting does not originate from melting of different crystalline forms but can be ascribed to recrystallization of the primary crystalline α(II) structure into higher melting more perfect α(II) crystals[13]. A more detailed description of double melting in blends of PVF_2 with PMMA in general will be given in ref 14.

DISCUSSION

As reported by Coleman[9], spectra of blends of PVF_2 with at-PMMA can be considered as the sum of the spectra of the separate polymers as long as PVF_2 is partly crystalline. The spectra are supposed to be synthesized by weighted absorbance additions of the partly crystalline PVF_2 phase and the amorphous PMMA phase. However, based upon the glass transition behaviour in blends of PVF_2 with it-, at- and st-PMMA, we suggested in our previous work that the amorphous PMMA phase contains a part of the PVF_2 molecules rejected from the crystals[7]. The small shift of $\nu_{C=O}$ of PMMA to a lower frequency in the difference spectra of the heterogeneous blends with crystalline PVF_2 supports this suggestion (*Figure 4*B).

The large deviations of the difference spectrum of the homogeneous amorphous 20:80 PVF_2/it-PMMA blend and the it-PMMA part, compared with the spectrum of PVF_2, is in our opinion indicative of the rather strong interaction between PVF_2 and it-PMMA (*Figures 2*A, C). In the difference spectrum of the amorphous 20:80 PVF_2/st-PMMA blend and the st-PMMA part, deviations also arise from PVF_2, but now to a smaller extent (*Figures 2*B, C). The strongly increased absorbance of the $\nu_{C=O}$ in the amorphous 20:80 PVF_2/it-PMMA blends dominates the small shift of this band and hence no oscillation band is observed in the difference spectrum with it-PMMA. In PMMA poor blends the stronger interaction of PVF_2 with the isotactic PMMA segments was already derived from a larger melting point depression[7]. So, the infra-red method confirms this point of view.

The difference spectrum of the amorphous 20:80 PVF_2/st-PMMA blend and the st-PMMA part (*Figure 2*B) is almost identical to the difference spectrum of a 25:75 PVF_2/at-PMMA blend and the at-PMMA part shown by Coleman[9]. As at-PMMA has a predominantly syndiotactic structure, an agreement with our difference spectrum for the 20:80 PVF_2/st-PMMA blend could be expected rather than with our difference spectrum for the 20:80 PVF_2/it-PMMA blend. The most important result of the i.r. investigation is the shift of $\nu_{C=O}$ towards lower frequency coupled with an increase in extinction of this band, especially in it-PMMA rich blends. The same type of effects are also observed when a hydrogen bond is formed with the carbonyl group[15,16]. In the case of hydrogen bonding, for instance between two carboxylic groups in dimeric carboxylic acids, both the C=O and the OH stretch vibrations are influenced markedly. In the homogeneous 20:80 PVF_2/it-PMMA blend the increase in extinction (about 60%) of the C=O stretch is comparable with the difference in extinction between monomeric and dimeric propionic acid[16]. However, as we could not detect any change of the CH stretch vibration of PVF_2 caused by interaction with C=O of PMMA, we suppose that the interaction between PVF_2 and it-PMMA does not involve hydrogen bonding. We think that C=O bonds of the PMMAs in homogeneous blends are polarized and weakened by the dipole moment of PVF_2 segments, resulting in an increase in extinction and a shift to lower frequency. The special role of the carbonyl groups in the interaction of PVF_2 with oxygen-containing polymers was already emphasized by Bernstein *et al.*[17]. Based upon the compatibility of PVF_2 with poly(vinyl methyl ketone), poly(methyl acrylate) and poly(vinyl acetate) and its incompatibility with the carbonyl missing polymer

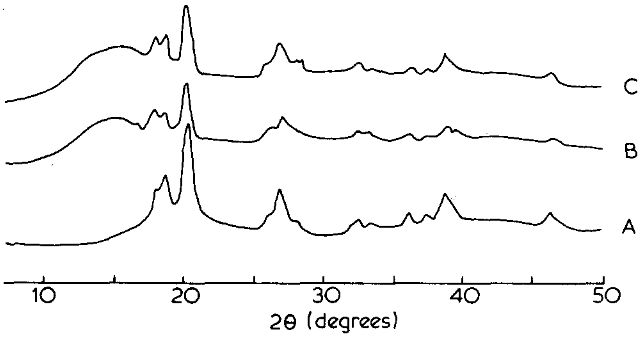

Figure 5 (A) X-ray pattern of PVF_2 in the α(II) modification; (B) X-ray pattern of a 40:60 PVF_2/it-PMMA blend isothermally crystallized at 88°C; (C) X-ray pattern of a 40:60 PVF_2/it-PMMA blend, 12 h annealed at 157°C after crystallization at 88°C

poly(vinyl methyl ether), they suggested that the ether linkage plays a far less important role than the carbonyl group.

The differences in interaction of PVF_2 with it- and st-PMMA should be ascribed to the different configurations of these PMMAs. In the planar zigzag conformation proposed for st-PMMA in the amorphous state[18], every other carbonyl group is unable to interact with the dipole moment of the same PVF_2 chain. However, it is also unlikely that the interaction of PVF_2 with it-PMMA occurs over a large number of sequential segments, since real complex formation of PVF_2 with it-PMMA has never been noticed. Nevertheless, it may be concluded that the interaction of PVF_2 with PMMA is rather stereoselective (see *Figure 2*) and that computerized dispersive i.r. spectroscopy is a powerful tool to investigate the nature of the interactions in compatible polymer blends.

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