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# Influence of ester group size in PMAs on β phase crystallization of $PVF_2$ in highly oriented films of $PVF_2$/PMAs blends

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## Summary

Influence of ester group size in polymethacrylates ( PMAs ) , including PMMA, PEMA and PBMA, on β phase crystallization of poly(vinylidene fluoride) ($PVF_2$) in highly oriented films of $PVF_2$ /PMAs=80/20 blends has been investigated by FTIR and TEM. The melt-drawn films of pure $PVF_2$ consist of highly oriented lamellae, in which the α phase is predominant. Adding a given amount of PMAs (20 wt%) into $PVF_2$ results in formation of fibrillar crystals and increase of relative amount of the β phase. The influence extent is in order of PMMA > PEMA > PBMA, regarding the ester group size in the PMAs.

## Introduction

The blending systems of $PVF_2$ with PMAs are thermodynamically compatible in the amorphous state. Most of the previous investigations focus on the compatibility between them ( 1-6 ), while only a few publications are related to the influence of PMAs(mainly, PMMA) on the crystalline modifications of $PVF_2$(7-9). In a previous paper(8) we reported the crystalline structure of highly oriented films of $PVF_2$ in the blends of $PVF_2$ with PMMA. In the present paper we discuss the effects of ester group size in PMAs on morphology and β phase formation of $PVF_2$ in highly oriented films of $PVF_2$/PMAs blends.

## Experimental

The samples of $PVF_2$ and PMAs used in this work were supplied by Polysciences Inc. The molecular weights are $1.4\times10^5$ ($PVF_2$), $3.5\times10^5$ (PMMA), $3.4\times10^5$ (PEMA) and $3.2\times10^5$ (PBMA) , respectively. Highly oriented films of $PVF_2$/PMAs=80/20 blends were prepared by a melt-drawn technique (10) with a high longitudinal rate gradient (about $10^4$ $sec^{-1}$) and large supercooling rate. The common solvent utilized for $PVF_2$ and PMAs was cyclohexanone. The concentration of the blends in the solvent was 0.5 wt% . The preparation temperature was about 140℃. The thickness of the films prepared was about 50 to 100 nm, which could be directly used for TEM observations. By continuously winding the film on a roller, thicker multilayered films could be obtained, which were used for FTIR measurement. Annealing the films(140℃, 2h) was carried out on the surface of glycerol for single layer film or in an oven for multilayered films.

A Hitachi H-600 electron microscope operated at 100 kV was used to characterize the single layer film of the blends. Infrared spectra were taken with a Digilab FTS- 20E Fourier transform infrared spectrophotometer.

## Results and discussion

Fig.1 shows FTIR spectra of highly oriented films of pure $PVF_2$ and the $PVF_2$/PMAs=80/20 blends, in which the solid arrows represent the characteristic bands of the α phase of $PVF_2$, while the broken arrows indicate the vibrational bands of the β phase. For pure $PVF_2$ , the spectrum exhibits mainly the characteristics of the α phase, as the bands at 530, 615, 765, 795, 855, 975, 1214 and 1383 $cm^{-1}$, which corresponds to the α phase(11-13), are very strong. As for $PVF_2$/PMAs blends, in addition to the characteristic bands of the α phase, the vibrational bands at 510, 840 and 1280 cm$^{-1}$ occur in the spectra, which represent the characteristics of the β phase of PVF$_2$ (11 -13). The relative percentage of β phase, F(β), i. e. the ratio of the amount of β phase to the total amount of β 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 $F(\beta) = D_{510} / (D_{510} + 0.81 D_{530})$(14). The relative amounts of β phase in the highly oriented films of pure PVF$_2$ and PVF$_2$ /PMAs blends are listed in Table 1. Clearly, adding PMAs into PVF$_2$ promotes the β phase formation of the latter during the melt - drawing process. Meanwhile, the relative amount of the β phase is related to the size of the ester groups in PMAs. The F(β) increases with the decrease of the ester group volume(number of carbon atom), i. e. the influence extent of PMAs on the β phase crystallization of PVF$_2$ in the blends is in order of PMMA>PEMA> PBMA .

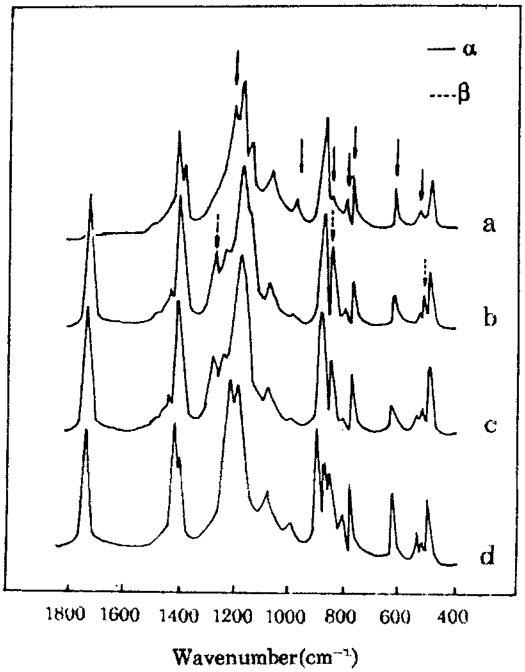

Fig.1 FTIR spectra of highly oriented films of PVF$_2$/PMAs - 80/20 blends, (a) PVF$_2$, (b) PVF$_2$/PMMA,(c) PVF$_2$/ PEMA,(d) PVF$_2$/PBMA.

Table.1 Relative amount of β phase, F(β), in the films of $PVF_2$ and $PVF_2$/PMAs - 80/20 blends

| samples | $PVF_2$ | $PVF_2$/PMMA | $PVF_2$/PEMA | $PVF_2$/PBMA |
|---|---|---|---|---|
| F(β) | 14.0 | 70.0 | 46.5 | 28.0 |

Fig.2 shows bright field defocus phase contrast electron micrographs of the highly oriented films of pure $PVF_2$ and the $PVF_2$/PMAs = 80/20 blends. The arrow represents the drawing direction, i.e. the chain direction. In the underfocus electron micrographs, the bright areas represent the amorphous regions, while the dark areas are the crystalline regions . The pure $PVF_2$ films contain highly oriented lamellae with their growing direction perpendicular to the drawing direction(Fig.2a). Adding PMAs into $PVF_2$ results in formation of fibrillar crystals parallel to the drawing direction( Fig.2b-d ). The length of the fibrillar crystals varies from a few ten to several hundred nanometres. The content of the fibrillar crystals in the $PVF_2$ /PMAs films is related to the species of PMAs. In the case of $PVF_2$/PMMA, the fibrillar crystals are predominant in the highly oriented films. Comparing the results with that obtained from FTIR, it is ready to understand that the increase of F( β ) in the films of $PVF_2$ /PMAs blends has direct regard to the formation of the fibrillar crystals.

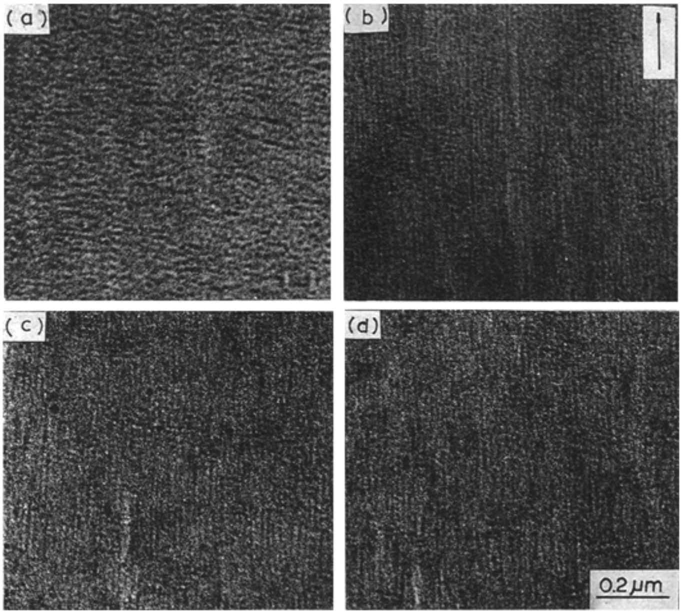

**Fig.2** Electron micrographs of highly oriented films of pure $PVF_2$ and $PVF_2$/PMAs = 80/20 blends. (a) $PVF_2$, (b)$PVF_2$/PMMA, (c)$PVF_2$/PEMA, (d)$PVF_2$/PBMA.

The above results indicate that during melt-drawn process of $PVF_2$ the presence of a certain amount of PMAs not only affects the morphology of crystalline $PVF_2$ but also the formation of the crystalline phases. This may be due to the effect of the hydrogen bonding interaction between $PVF_2$ and PMAs molecules (15, 16). The hydrogen bonding interaction is confirmed with the change of the stretching mode $\nu$ =1730cm$^{-1}$ of the carbonyl group of PMAs in $PVF_2$/PMAs blends. The difference FTIR spectra between the C=O stretching frequency of PMAs in the blends and that of pure PMAs display positive absorptions at low frequency and negative absoptions at high frequency (Fig.3). It indicates that the C=O stretching mode of PMAs in the blends is shifted to lower frequency, resulting from the hydrogen bonding interaction(16).

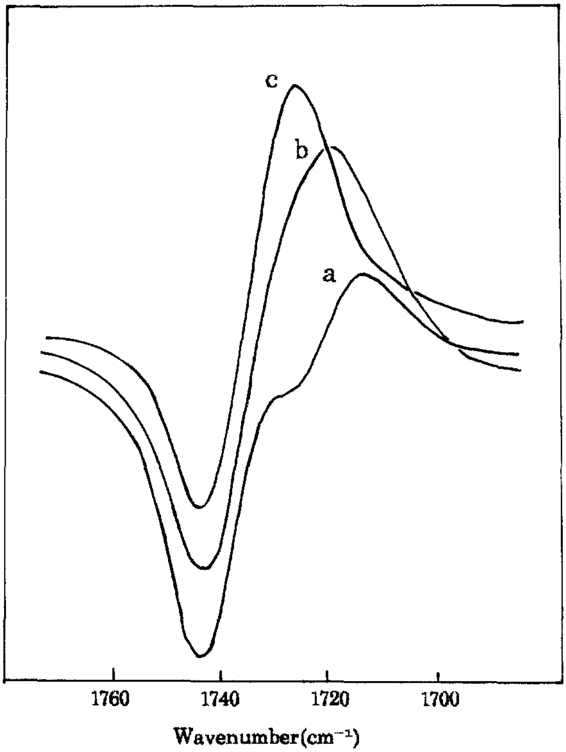

Fig. 3 Defference FTIR spectra between the C-O stretching frequency of PMAs in the blends and that of pure PMAs. (a)$PVF_2$ /PMMA, (b) $PVF_2$/PEMA, (c) $PVF_2$/PBMA.

During melt-drawn process, chain extension and chain relaxation are competitive processes each other. For pure $PVF_2$, the relaxation time is very short because the molecular weight is not high enough . Accordingly, no large amount of fibrillar crystals with extended chain could form during the melt-drawn process. In the $PVF_2$ /PMAs blends, however, the relaxation process of the $PVF_2$ molecules is slowed down due to the hydrogen bonding interaction, resulting in formation of fibrillar crystals. In addition, the hydrogen bonding interaction also affects chain conformation of $PVF_2$(15). The specific interaction may induce all-trans conformation sequences of $PVF_2$, which act as nucleating sites for the β phase, forming β phase crystals in both the lamellae and the fibrils. Meanwhile, the specific interaction is very sensitive to the distance between the interacting groups. The hydrogen bonding strength falls off rapidly when the atomic distance increases. The size of the ester groups in PMAs is in order of $—COOCH_3 < —COOC_2H_5 < —COOC_4H_9$. Owing to the steric hindrance effect the hydrogen bonding strength between the molecules of $PVF_2$ and PMAs must be in the reverse order, i. e. PMMA >PEMA >PBMA. It is evidenced by the results of the difference spectra(Fig.3) in which the shifting of the C=O stretching frequency of PMAs in the blends is in the same order ( see the positive absorptions). Therefore, it is ready to understand why the contents of both the β phase and the fibrillar crystals of $PVF_2$ in the blends with PMMA are much higher than that with PEMA and PBMA.

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