

## Formation of poly(vinylidene fluoride) crystalline phases from tetrahydrofuran/N, N-dimethylformamide mixed solvent

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Received: 22 July 2007 / Accepted: 8 October 2007 / Published online: 23 October 2007  
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Poly(vinylidene fluoride) (PVDF) is one of the semicrystalline polymers with at least four crystalline forms referred to as  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  phase, among which the  $\beta$  phase has gained substantial importance due to its advantageous pyro- and piezo-electric properties [1, 2]. It requires a better method to induce the formation of  $\beta$  phase crystal in order to improve the electrical properties of PVDF.  $\beta$  phase is not usually obtained by crystallization from the melt, but it is normally obtained by various methods including tensile deformation and uniaxial compressional deformation of  $\alpha$  phase [3, 4], blending with small contents of poly(methyl methacrylate) (PMMA) [5, 6] or poly(*o*-methoxyaniline) (POMA) [7], quenching and then annealing process [8], applying a strong electric field [9] and crystallizing from solution at appropriate conditions [10–12]. In all these methods which used to prepare  $\beta$  phase of PVDF, the one grown from a single solvent is widely used because of its facility and controllability. However, few literatures are concentrated on the solvent-induced  $\beta$  phase formation in the mixed solvent. In this letter a novel method to achieve the  $\beta$  phase of PVDF is carried out by crystallizing from swelling agent/solvent mixture.

Dissolution of a semicrystalline polymer, such as PVDF, requires disruption of strong interchain forces in order regions. So the rate of polymer dissolution is dependent on the type of liquid [13]. It has been reported that

tetrahydrofuran (THF) is a good swelling agent at 60 °C for PVDF; N, N-dimethylformamide (DMF) is a solvent for it at 20 °C [13]. The aim of this study is to include the effects of the THF/ DMF mixture with various mass ratios of each component on the crystalline phase formation and crystallization behavior in the PVDF film by solution casting. It was characterized by Fourier transform infrared (FTIR), wide angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC), and scanning electron microscope (SEM) techniques.

The PVDF (Kynar K-761,  $\overline{M}_w = 441000$ ) utilized in this work was supplied by Elf Atochem of North America Inc. (USA). PVDF resin was dissolved in the THF/ DMF mixture with different mass ratio (m/m composition of THF/DMF = 9:1, 8:2, and 5:5) at 50 °C. The solubility of the PVDF was improved by an increase of DMF content in the mixture of solvents because of the reinforced disruption of the intermolecular polymer bonds (via interaction of the C = O dipole with the CH<sub>2</sub>CF<sub>2</sub> dipole or by limited hydrogen bonding) [14, 15].

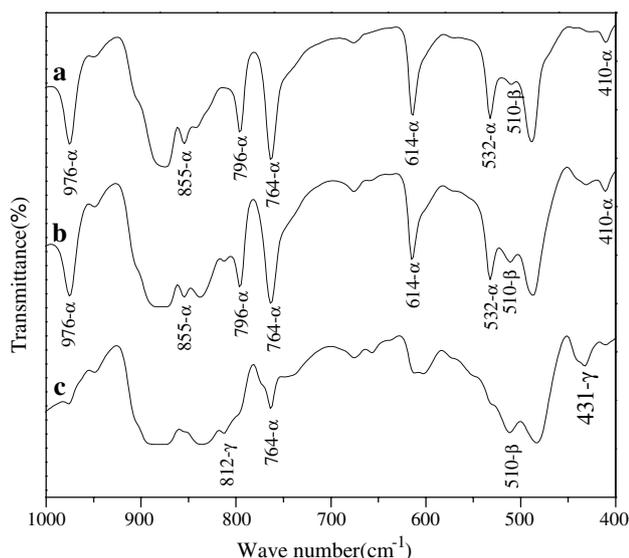
Films (thickness: ~50  $\mu\text{m}$ ) of PVDF were quiescently cast from each solution with 10 wt% PVDF (initial polymer concentration) at 50 °C, and the glass substrate was used for solution casting. After the solvents evaporated the films were peeled off from the glass substrate at room temperature. The residue of DMF and THF was allowed to evaporate in an air oven for about 1 week at room temperature. FTIR spectra of films were obtained on a FTIR spectrometer (Bruker Vector-22). WAXD was done in a Shimadzu XRD-6000 diffractometer (Cu K $\alpha$  radiation, 40 kV and 30 mA) at a scanning velocity of 4°/min. The melting behavior of the films was measured with a Perkin–Elmer DSC-7C differential scanning calorimeter using a heating rate of 10 °C/min. SEM micrographs were taken on a Jeol JSM-5900 microscope.

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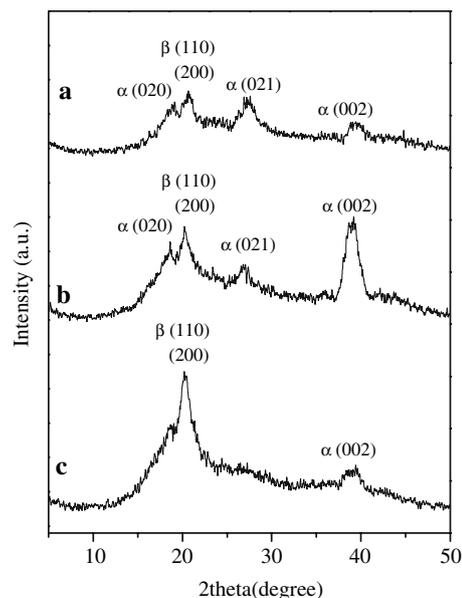
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Figure 1 shows the FTIR spectra in the range from 1,000 to 400  $\text{cm}^{-1}$  for the solution-cast films derived from mixed solvents with m/m composition of THF/DMF at 9:1, 8:2, and 5:5. The vibrational spectra of the three principal phases ( $\alpha$ ,  $\beta$ , and  $\gamma$  phases) of PVDF have been investigated extensively [10, 11]. The absorption bands at 410, 532, 614, 764, 796, 855, and 976  $\text{cm}^{-1}$  correspond to the  $\alpha$  phase, while the bands at 510  $\text{cm}^{-1}$  exclusively refers to the  $\beta$  phase and the bands at 431 and 812  $\text{cm}^{-1}$  represent the  $\gamma$  phase. It is clear from the figure that both  $\alpha$  phase and  $\beta$  phase exist in the films when the mass ratio of THF/DMF is 9/1 and 8/2. As the DMF concentration increased further more (THF/DMF = 5/5), most absorption bands for  $\alpha$  phase disappear or decrease in the intensity; and much more increase in the characteristic of the  $\beta$  phase. This implies the fact that as the THF/DMF = 5/5 the presence of DMF in the solution favors the  $\beta$  crystal formation. In addition, it seems that  $\gamma$  phase formed (bands at 431 and 812  $\text{cm}^{-1}$ ) as THF/DMF = 5/5 in the solution.

Wide angle X-ray diffractograms of the film samples are shown in Fig. 2. It reveals that films grown in the solution with THF/DMF = 9/1 and 8/2 present peaks at  $2\theta = 18.5$ , 26.8, and 39.0°, referent to the diffractions in planes (020), (021), and (002) respectively, all characteristic of the  $\alpha$  phase of PVDF [9, 10]. In addition, both of them have a weak peak at  $2\theta = 20.3^\circ$ , referent to the sum of the diffractions in plane (110) and (200), characteristic of the  $\beta$  phase [9, 10]. However, as for the intensity of the peaks at  $2\theta = 20.3$  and  $39.0^\circ$  which characteristic of the  $\beta$  phase and  $\alpha$  phase respectively are enhanced as THF/DMF = 8/2, in comparison with the result obtained as THF/DMF = 9/1. This may be due to the fact that the solubility of PVDF is



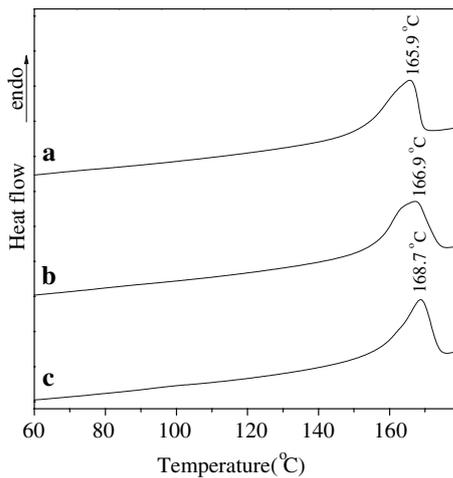
**Fig. 1** FTIR spectra of PVDF films by casting from the solution with various mass ratio of THF/DMF: a) 9:1; b) 8:2; c) 5:5



**Fig. 2** WAXD diffractograms for PVDF films by casting from the solution with various mass ratio of THF/DMF: a) 9:1; b) 8:2; c) 5:5

much more improved at THF/DMF = 8/2 than that at THF/DMF = 9/1. In this case (THF/DMF = 8/2), once the chains are disentangled, the increased mobility promotes crystallization of PVDF. With respect to the case for THF/DMF = 5/5 main peak at  $2\theta = 20.3^\circ$  which represents the  $\beta$  phase is predominate, while the peaks assigned to  $\alpha$  phase, i.e., the reflections of (020) and (021) crystal planes, completely disappear. The consequences of WAXD diffractograms fit well to the results of FTIR experiments except one for the film prepared from THF/DMF (5/5) mixture in which absorption bands of  $\gamma$  crystal appear. It can be attributed to the small extent of  $\gamma$  crystal in the bulk film.

It is observed that the films obtained from solution with THF/DMF = 9/1 and 8/2 show two endothermic peaks, as it can be seen in the DSC scans in Fig. 3a, b. The melt temperatures of  $\alpha$  phase and  $\beta$  phase are seen to coincide at the same temperature, as reported in the articles [4, 10, 11], which the lower temperature endotherm (at circa 162  $^\circ\text{C}$ ) corresponding to the melting of  $\alpha$  phase and the higher one referring to the  $\beta$  phase. As DMF content increased to the level (THF/DMF = 5/5), only one peak emerges in DSC trace (Fig. 3c) and the  $\alpha$  phase endotherm disappears. It can be concluded that remarkable formation of  $\beta$  phase performed at this condition; in contrast, the strong reflections of  $\alpha$  phase have essentially disappeared, which also confirmed by FTIR and WAXD analysis mentioned above. As shown in Fig. 3, the peak melt temperature of  $\beta$  phase shifts to higher-temperature. It maybe due to the perfect crystalline structure formed at good solubility of PVDF (high DMF content in the mixed solvent). Additionally, the



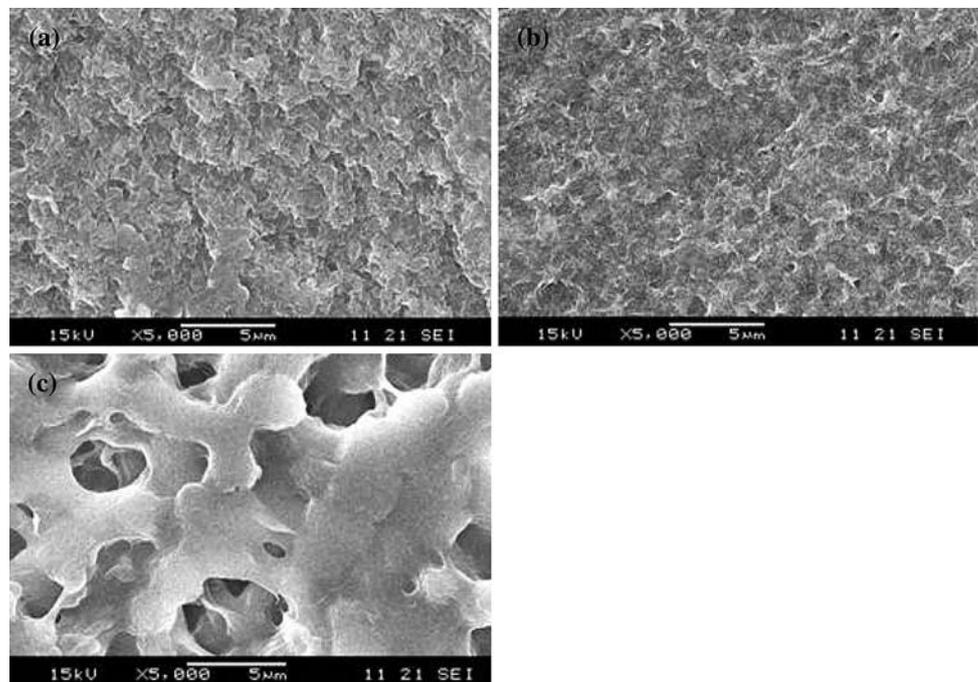
**Fig. 3** melting curves of DSC trace for PVDF films by casting from the solution with various mass ratio of THF/DMF: a) 9:1; b) 8:2; c) 5:5

melting peak is shrunk as DMF content increased in the mixed solvent. It is suggested that as DMF is low in the mixed solvent (THF/DMA = 9/1 and 8/2) both  $\alpha$  and  $\beta$  phase of PVDF formed in the films. To the contrary, predominantly  $\beta$  phase of PVDF induced by more DMF in the mixed solvent (THF/DMA = 5/5), resulting in a narrow peak melt temperature (Fig. 3c).

The surface topography of the cast films can be clearly seen in the SEM photographs, as shown in Fig. 4. Films cast from THF/DMF = 9/1 and 8/2 have the similar surface structure with indiscernible spherulite, which assigned to  $\alpha$

phase of PVDF in corresponding to FTIR and WAXD results. The crystalline structure is more accurately described as polygonal crystals. Similar morphology of PVDF sample which crystallizing from the melt was reported in Lovinger's work [16], and it is characteristic of the  $\alpha$  phase crystals. When THF, which is considered as a good swelling agent for PVDF, predominates in the solvent mixture (9/1 and 8/2), the spherulites present in Kynar resin are not observed by SEM, because the interlamellar regions are dissolved and the lamellae loose their characteristic radial spherulitic configuration, however their  $\alpha$  crystalline structure may remain and can be detected by FTIR and WAXD. In this way the lamellae becomes randomly dispersed in the amorphous phase, resulting in the morphology shown in Fig. 4a, b. Hence, at THF/DMF mass ratios of 9/1 and 8/2, the resulting film is predominantly  $\alpha$  phase with minor amounts of  $\beta$  phase. Whereas film cast from THF/DMF = 5/5 shows a very different feature illustrating distinct spherulites which correspond to the  $\beta$  crystals of PVDF [6, 11, 17]. When at THF/DMF = 5/5, the crystalline and amorphous phases of PVDF are dissolved and at 50 °C the film crystallizes predominantly in the  $\beta$  phase. As reported by Gregorio and Cestari [10], the dissolved PVDF can crystallize into the  $\beta$  phase below 70 °C in the solution; and the  $\alpha$  phase was the original PVDF resin that did not undergo dissolution. In this work, all of the solutions were transparent, which like that dissolved in DMF. The existence of the  $\alpha$  phase in the resulted films are not clarified and the further investigation is continuing. He and Yao reported that during the solution

**Fig. 4** SEM micrographs of PVDF films by casting from the solution with various mass ratio of THF/DMF: a) 9:1; b) 8:2; c) 5:5



crystallization the dipolar interaction and hydrogen bonding at the interface between PVDF nucleus and DMF molecules can preferably lead to *trans* conformation packing of CH<sub>2</sub>–CF<sub>2</sub> dipoles, which is the  $\beta$  phase [15, 18]. This suggests that the more DMF in the mixed solvents, the more  $\beta$  phase forms in the film; to the contrary, the  $\alpha$  phase formation will be hindered. It is implied that the  $\beta$  phase formation occurs as DMF induced in the mixed solvent. It is fit well to the results obtained by FTIR, WAXD, and DSC.

From the aforementioned results and discussion, it is apparent that DMF content in the mixed solvent has a definite effect on the crystalline phase of PVDF and the resulting morphology of the films. As PVDF crystallized from a THF/DMF solution at 50 °C, the resulting crystalline phase depended on the THF/DMF mass ratio. In particular, the content of the  $\beta$  phase in the cast film can notably be influenced by the incorporation of DMF in the mixed solvents. The best solubility and the stronger interaction between the PVDF chains and DMF molecules can dramatically favor the  $\beta$  crystal formation. The mixed solvent at a 5/5 ratio resulted in the clear spherulitic structure with a diameter of about 3  $\mu$ m on the surface of the film (Fig. 4c).

**Acknowledgement** This research is supported by the Key Project of BMSTC (D0406003040191).

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