Journal of Thermal Analysis and Calorimetry, Vol. 69 (2002) 939–946

THE MECHANISM OF α–γ TRANSITION OF POLY-(VINYLIDENE FLUORIDE) IN THE MISCIBLE BLENDS
The simultaneous DSC-FTIR method

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Abstract

The simultaneous DSC-FTIR was used for the observation of crystallization and melting of poly(vinylidene fluoride) (PVDF) and its blends with poly(methyl methacrylate) (PMMA) and poly(ethyl methacrylate) (PEMA). The isothermal crystallization was carried out under the condition of both α–form and γ–form crystallized competitively. The crystal growth rate of α–form and γ–form were evaluated from the absorbance changes at 795 cm^{-1} (α–form, CH_2 rocking) and 810 cm^{-1} (γ–form, CH_2 rocking) obtained by the DSC-FTIR. The crystal growth rate of γ–form decreased at the same crystallization temperature in the order of PVDF/*syn*-PMMA, PVDF/PEMA and PVDF/*at*-PMMA, which was corresponding to the order of interaction parameter. The mechanism of α–γ transition of PVDF in the miscible blends with *at*-PMMA, *syn*-PMMA and PEMA was evaluated from the relationship between the decrease of α–form and the increase of γ–form. The critical crystallization temperature, at which the transformation from α–form to γ–form proceeded only in the solid state, shifted to higher temperature side in the order of interaction parameter.

Keywords: α–form, blend, DSC-FTIR, γ–form, interaction parameter, PVDF, solid state transition

Introduction

DSC is the convenient tool to determine the physical and chemical changes such as phase transitions and reactions. However, it is necessary to use the diffraction or spectroscopic methods to know what is going during these changes. We have reported that the simultaneous DSC-FTIR and DSC-XRD methods give us not only thermal information but also both conformational and structural information on the real time of transitions [1–5]. In this study, the DSC-FTIR method was applied to analyze the multiple transitions of poly(vinylidene fluoride) (PVDF) showing polymorphism from the viewpoint of conformational ordering.

PVDF forms six crystal modifications, I (β), II (α), III (γ), IV, V, and VI corresponding to three conformations (TTTT, T_3GT_3G' and TGTG'), coupling with trans (T)

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1418–2874/2002/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

and gauche (G) conformations, and two packing forms (parallel and anti-parallel). Many researchers have reported that transformations among the crystal forms take place under various conditions such as heat treatment, high pressure and stretching [6–9]. Among these studies, γ–form was obtained by melt-crystallization under high pressure and also by heat treatment of α–form at 285°C [6]. In general, the α–form is predominant in PVDF cooled from the melt, however, the Gibbs energy of the γ–form is slightly lower than that of the α–form. The mechanism of α–γ transformation is considered by two different methods, the one is the conformational rotation from α–form to γ–form occurred in the solid state [10], and the other is the re-crystallization of γ–form occurred immediately after the melting of small α–form crystallites [6].

In previous papers we investigated the miscibility of PVDF and poly(methyl methacrylate) (PMMA) and/or poly(ethyl methacrylate) (PEMA) by analyzing the crystallization dynamics of α–form using the DSC [11] and the simultaneous DSC-FTIR measurement [1, 2]. In the present study, we discuss the α–γ transition mechanism of PVDF, under the isothermal condition of both α–form and γ–form crystallized competitively, in the miscible PVDF/*at*-PMMA, PVDF/*syn*-PMMA and PVDF/PEMA blends using the DSC-FTIR method.

Experimental

PVDF ($M_w=2.6\times10^6$) supplied by Kureha Chemical Co. Ltd, *at*-PMMA ($M_w=1.5\times10^5$, $M_w/M_n=1.51$) supplied by Mitsubishi Resin Co. Ltd, *syn*-PMMA ($M_w=2.0\times10^5$, $M_w/M_n=1.2$) and PEMA ($M_w=2.5\times10^5$, $M_w/M_n=2.6$) were used in this study. PVDF and PMMA (PEMA) were dissolved in N, N-dimethylacetamide at room temperature. The blend samples were prepared by solvent casting. The blend content (ϕ) of PMMA (PEMA) was 0.1 in mass fraction. After casting and drying, the samples were pressed at 200°C and were quenched to ice water. The blend films were further dried under vacuum at room temperature for 24 h.

The simultaneous DSC [12] was set on JASCO FTIR 620 equipped with a MCT (mercury cadmium telluride) detector. DSC scanning rate was 5°C min^{-1}. Wavenumber and time resolutions of FTIR measurement were 2 cm^{-1} and 15 s, respectively. Blend samples were melted at 200°C for 5 min and then cooled to a predetermined crystallization temperature (T_c) at 5°C min^{-1}. During isothermal crystallization, DSC exotherm and FTIR spectra were recorded. Temperature variation during crystallization was controlled within 0.1°C. Isothermal crystallization was carried out at various T_c, at which both a-form and g-form crystallized competitively. The blend sample sandwiched with two thin KBr disks and cramped in an aluminum sample vessel was used for DSC-FTIR measurement. Sample mass used was about 1.5 mg.

Results and discussion

Figure 1 shows the DSC curves during isothermal crystallization at temperatures above 160°C (A) and DSC heating curves (B) after the isothermal crystallization for

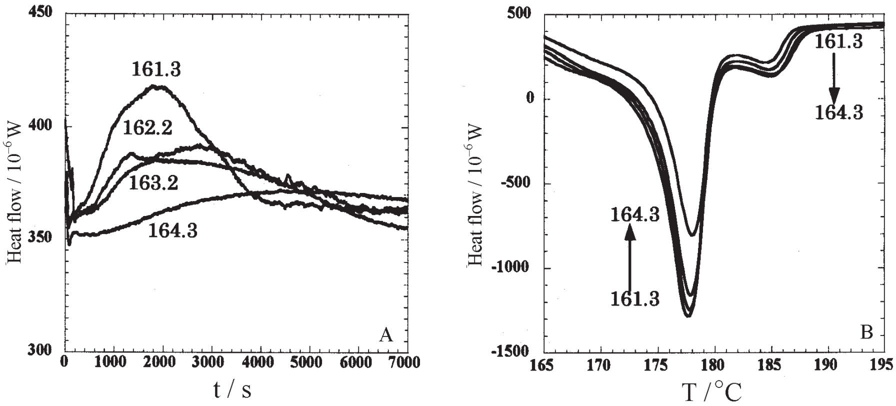

Fig. 1 DSC crystallization curves obtained at isothermal condition (A) and DSC heating curves obtained after isothermal crystallization (B) for PVDF. The numbers in figure indicated the crystallization temperature

PVDF. The heating DSC curves showed two endothermic peaks due to the melting of PVDF at 177 and 185°C, and the melting peak at higher temperature grow with increasing the crystallization temperature. DSC exothermic peaks during crystallization (A) were complex consisted at least two phenomena. PVDF shows polymorphism as mentioned above, however the assignment of each endothermic peak is difficult only by DSC measurement.

Figure 2 (A) shows the stacked FTIR spectra for PVDF/*at*-PMMA blend (ϕ=0.1) during the isothermal crystallization at 165.4°C observed by the simultaneous DSC-FTIR. The assignment of IR spectra of PVDF have reported as follows: α–form (TGTG'); 530 cm^{-1} (CF$_2$ bending), 615 and 763 cm^{-1} (CF$_2$ bending and skeletal bending), 795 cm^{-1} (CH$_2$ rocking), and 975 cm^{-1} (CH$_2$ twisting), γ–form (T$_3$GT$_3$G'); 776 and 810 cm^{-1} (CH$_2$ rocking), 882 cm^{-1} (CF$_2$ symmetric stretching and CC symmetric stretching) [7, 8]. In the present study, the IR bands at 795 cm^{-1} (α–form) and 810 cm^{-1} (γ–form) were used to determine the amounts of each crystalline form during crystallization. Figure 2 (B) shows the absorbance changes at 795 and 810 cm^{-1} and the sample temperature during the isothermal crystallization at 165.4°C. The absorbance was normalized by the value of each band obtained in the molten state in order to compensate the sample thickness. The isothermal condition was established at 2000 s. Before 2000 s, the absorbance at 810 cm^{-1} increased slightly and increased steeply at 5000 s. The absorbance at 795 cm^{-1} increased at 3000 s and leveled off at 6000 s, and then decreased linearly. The slopes of linear increase or decrease of normalized absorbance change were employed as the rate of conformational change. The slope of 810 cm^{-1} evaluated between 5000 and 9000 s and the slope of 795 cm^{-1} between 3000 and 5000 s were used as the γ–form growth rate (G_γ) and the α–form growth rate (G_α), respectively.

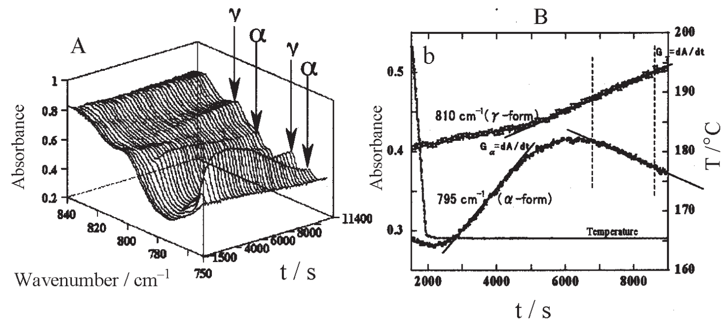

Fig. 2 The stacked FTIR (A) obtained by the simultaneous DSC-FTIR and the absorbance changes at 795 and 810 cm^{-1} (B) during isothermal crystallization at 165.4°C for PVDF/*at*-PMMA blend (ϕ=0.1)

Figure 3 shows the temperature dependence of G_α (A) and G_γ (B) for PVDF and its blends with ϕ=0.1. G_α decreased and G_γ increased with the increase of crystallization temperature (T_c). This result indicates that the crystallization of γ–form occurred selectively for PVDF and its blends at higher crystallization temperature. In the previous work for the miscible PVDF/PMMA blends, the G_α decrease with the increase of miscibility at the temperature range below 160°C at which only α–form crystallize [1]. The G_α difference between PVDF and its miscible blends shown in Fig. 3 (A) is small comparing with the results reported previously [1]. Under the crystallization condition above 160°C, not only α–form but also γ–form crystallized competitively, therefore the crystallization mechanism differed from the condition below 160°C.

Figure 3 (B) indicated that the G_γ for the miscible PVDF blends was slower than that for PVDF at the fixed T_c. Interaction between PVDF and PMMA (or PEMA) may affect crystalline polymer chain conformation, result in the decrease of G_γ of PVDF in blends. The α–γ transition temperature range shifted to the high T_c side in the order *syn*-PMMA, PEMA and *at*-PMMA as the same order in the decrease of G_γ at the fixed T_c. These orders are same with the order in the interaction parameter ($\chi_{1,2}$) between

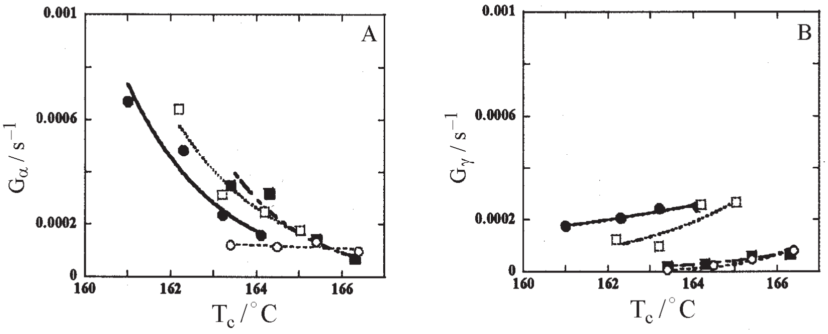

Fig. 3 α-form growth rate G_α (A) and γ-form growth rate G_γ (B) in PVDF (•) and PVDF/*at*-PMMA (▪), PVDF/*syn*-PMMA (□) and PVDF/PEMA (o) blends with ϕ =0.1 at various isothermal crystallization temperatures (T_c)

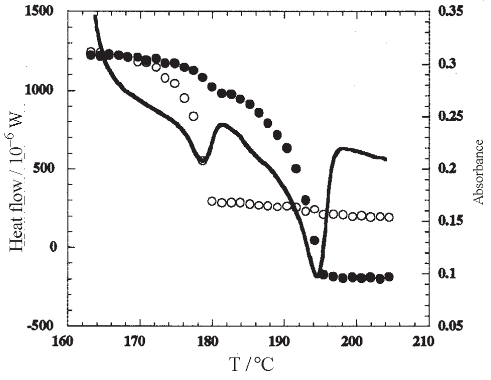

Fig. 4 DSC curve and absorbance changes at 795 cm^{-1} (o: α–form) and 810 cm^{-1} (●: γ–form) for PVDF/ *syn*-PMMA with ϕ=0.1 on heating immediately after the isothermal crystallization at 163.2 C for 200 min

PVDF and PMMA (PEMA), evaluated from the equilibrium melting temperature depression of α–form using Flory-Huggins equation [13]. The $\chi_{1,2}$ value of blends are –0.146, –0.292 and –0.298 mol^{-1} for PVDF/*syn*-PMMA, PVDF/PEMA and PVDF/*at*-PMMA, respectively [14].

Doll and Lando [9] reported that the melting temperature of γ–form prepared crystallization under high pressure was higher than that of α–form. After isothermal crystallization, the melting behavior of samples, in which α–form and γ–form co-existed, was observed by the DSC-FTIR. Figure 4 shows the DSC-FTIR results of PVDF/ *syn*-PMMA during heating immediately after the isothermal crystallization at 163.2°C for 200 min. The DSC curve shows two endothermic peaks at 178 and 194°C as same as the case of PVDF shown in Fig. 1 (B). The absorbance changes at 795 cm^{-1} (α–form) and 810 cm^{-1} (γ–form) are plotted in Fig. 4. The DSC-FTIR results suggested that the lower endothermic peak was due to the melting of α–form and the higher melting peak having a small shoulder at 186°C corresponded to the melting of γ–form.

As shown in Fig. 2 (A), the increase of γ–form accompanying with the decrease of α–form was observed in the late stage of isothermal condition. Figure 5 shows the relationship between the absorbance changes at 810 (α–form) and 795 cm^{-1} (γ–form) for PVDF (A), PVDF/*at*-PMMA (B), PVDF/*syn*-PMMA (C) and PVDF/PEMA blends (D). The negative linear relationships were obtained for all isothermal crystallization. As the IR bands at 810 and 795 cm^{-1} are assigned to the CH_2 rocking mode of PVDF, if the molecular absorption coefficient at 810 and 795 cm^{-1} are same, the slope of –1 in Fig. 5 suggest that α–form changes to γ–form directly in the solid state, that is the α–γ transition. While the slope is larger than –1, it means that the crystallization of γ–form from the molten state addition with the α–γ transition in the solid state.

The evaluated slope values from Fig. 5 are plotted *vs.* the isothermal crystallization temperature (T_c) in Fig. 6. With increasing T_c, the slope value increased and the

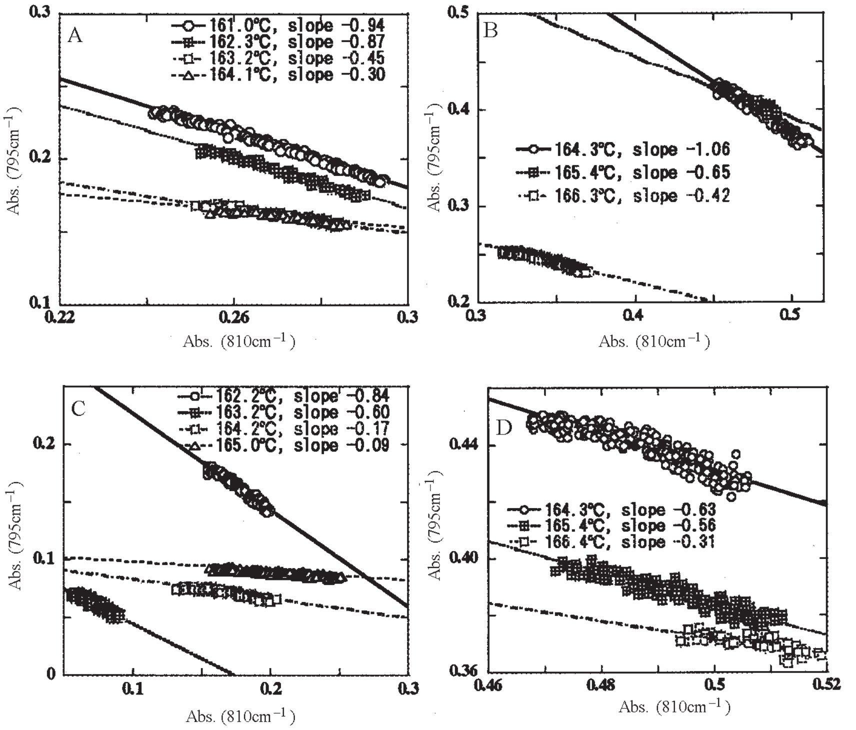

Fig. 5 Relationship between the increase of absorbance at 810 cm^{-1} and the decrease of absorbance at 795 cm^{-1} for PVDF (A) and PVDF/*at*-PMMA (B), PVDF/*syn*-PMMA (C) and PVDF/PEMA (D) blends with ϕ=0.1 at various isothermal crystallization

linear relationship between slope and T_c was observed for PVDF and its miscible blend systems. The critical crystallization temperature ($T_{s\alpha-\gamma}$) was evaluated by extrapolating the linear relationship to –1 of slope. The critical crystallization temperature ($T_{s\alpha-\gamma}$), at which the transformation from α–form to γ–form proceeded only in the solid state, shifted to higher temperature side in the order of PVDF/*syn*-PMMA, PVDF/PEMA and PVDF/*at*-PMMA. This order showed a good agreement with the order of the $\chi_{1,2}$ value of blends. In Fig. 6, another critical crystallization temperature evaluated from the cross point of G_α and G_γ shown in Fig. 3 was plotted at –1 of slope. The G_α was equal to G_γ at this critical crystallization temperature ($T_{\alpha-\gamma}$). $T_{s\alpha-\gamma}$ closed to $T_{\alpha-\gamma}$ for all samples, and the orders of $T_{s\alpha-\gamma}$ and $T_{\alpha-\gamma}$ agreed to that of the $\chi_{1,2}$ value. The estimated $T_{s\alpha-\gamma}$ was lower than $T_{\alpha-\gamma}$ for all systems, because the faster crystallization of α-form was necessary for the solid-state α–γ transition. Both $T_{s\alpha-\gamma}$ and $T_{\alpha-\gamma}$ shifted to higher temperature with increasing the $\chi_{1,2}$ value for the miscible blends.

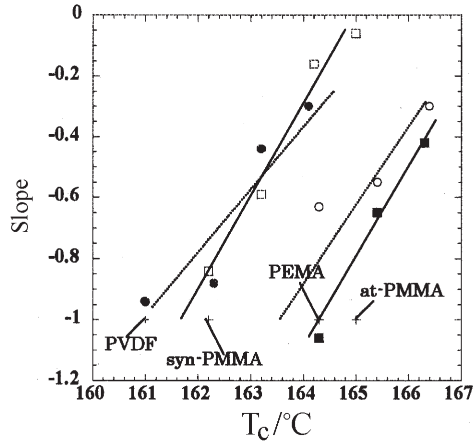

Fig. 6 The crystallization temperature dependence of the slope obtained from the relationship shown in Fig. 5 for PVDF (●) and PVDF/*at*-PMMA (■), PVDF/*syn*-PMMA (□) and PVDF/PEMA (o) blends with ϕ=0.1. The crystallization temperature (+) at which G_α is equal to G_γ is shown in the figure at –1 of slope

Conclusions

The miscibility state and the α–γ transition mechanism of PVDF in the miscible blends were investigated by the simultaneous DSC-FTIR method. In the miscible PVDF blends, the γ–form growth rates at the same crystallization temperature decreased with the order of the $\chi_{1,2}$ value. The linear relationship between the absorption changes at 795 cm^{-1} (α–form, CH_2 rocking) and 810 cm^{-1} (γ–form, CH_2 rocking) was obtained during α–γ transition, and the slope of this relationship suggested α–γ transition mechanism. At the lower T_c used in this experiment, the α–γ transition occurred only in the solid state, however, the γ-form crystallization from the melt occurred addition with the solid state α–γ transition with increasing T_c for PVDF and all miscible blend systems. The critical crystallization temperature ($T_{s\alpha-\gamma}$), at which the transformation from the α–form to γ–form proceeded only in the solid state, shifted to higher temperature side in the order of the $\chi_{1,2}$ value.

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