

# Study on the Nonisothermal Crystallization Process of mLLDPE/EVA Blends Using FTIR Micro-Spectroscopy

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**ABSTRACT:** The nonisothermal crystallization process has been investigated by Fourier transform infrared (FTIR) micro-spectroscopy for the 40/60 wt % blends of metallocene linear low density polyethylene (*m*-LLDPE) and ethylene/vinyl acetate copolymer (EVA) at the molecular level. In the cooling process, thermal spectra of mLLDPE/EVA blends were collected between 150°C and 67°C at 1°C interval. According to the van't Hoff equation at constant pressure, the changes of absorbance ratio corresponding to high and low vibrational states were calculated; hereby, apparent enthalpy differences of vibration energy states transformation ( $\Delta H_v$ ) of characteristic groups could be obtained. Combining with DSC analysis, two exothermal peaks were ex-

amined in the crystallization process, corresponding to mLLDPE-rich and EVA-rich domains, respectively; while in comparison of the  $\Delta H_v$  values of various characteristic groups corresponding to the two exothermal peaks, the bending vibrational mode of methylene groups has been found to make a prominent contribution to the movement and regular arrangement of mLLDPE and EVA chain segments towards each rich domain in the crystallizing process. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 261–267, 2005

**Key words:** metallocene linear low density polyethylene; ethylene/vinyl acetate copolymer; crystallization process; FTIR micro-spectroscopy

## INTRODUCTION

Nearly all semicrystalline polymers pass the melt and molding process before applications. As to the transition from melting to crystalline state, the crystal structure formed plays an important role in the final properties of the products, resulting from the competition between kinetic and relaxation factors and thermodynamic equilibrium.<sup>1–3</sup> For this reason, the morphology as well as the relationship between the structure and properties of semicrystalline polymers have been widely investigated.

Concerning the study of polymer crystallization, it is well known that nonisothermal crystallizing is very similar to the process of practical production. Meanwhile, the nonisothermal crystallization process is easy to carry out experimentally, together with acquiring more theoretical information. Therefore, the investigation of the nonisothermal crystallization process of polymer materials is of both theoretical and practical importance.<sup>4–6</sup>

As one of the main ways to study nonisothermal crystallization of polymers, differential scanning calorimetry (DSC) analysis could provide intrinsic information of polymers in bulk and the crystallization process, making use of the enthalpy changes during the phase transformation. However, the micro causation and details in the crystallization process could not be obtained by this means. On the other hand, in view of the characteristics of the FTIR spectroscopic method, it has been found that the crystallizing process could have a distinct influence on the infrared spectra of polymers,<sup>7–15</sup> changing absorption intensity, absorption frequency, and the profile of absorbing peaks. This may be ascribed to two factors: (1) the force constant of interior chemical bonds and the intermolecular interactions of polymers were changed by heat shrinkage, accordingly resulting in changed characters of the molecular vibrational dipole moment; and (2) inside the polymer molecular chains, the infrared absorbing concentration of characteristic groups changed as the temperature decreased. Therefore, particular information about the molecular structure accompanying the energy changes of polymers could be obtained with FTIR spectral measurements. Furthermore, the apparent enthalpy related to the

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TABLE I  
Characteristics of Materials Used

Code	Density <sup>a</sup> /(g · cm <sup>-3</sup> )	MI <sup>a</sup> /(g · 10min)	$\bar{M}_n^b$	$\bar{M}_w^b$	$\bar{M}_w/\bar{M}_n^b$
mLLDPE	0.917	1.0	43,529	113,030	2.60
EVA	0.935	0.7	23,068	95,704	4.15

<sup>a</sup> Obtained from supplier.

<sup>b</sup> Measured by PL-210 GPC.

changes of molecular structure could be obtained via calculation; thereby thermal analysis of polymers could be carried out by means of infrared spectra.

For mLLDPE/EVA blends, our previous study<sup>16</sup> focused on the investigation of morphology and performance, that is, the mechanical properties, rheological behavior, dynamic mechanical properties, and crystallization of the samples with varied blend ratios, and a series of significant results have been achieved. In this article, combining the results of DSC measurement, the changes of absorbency ratios along with altered vibrational energy states in the crystallization process, as well as apparent enthalpy differences of vibration energy states transformation  $\Delta H_v$ , were calculated by measuring FTIR micro-spectroscopy of mLLDPE/EVA blends, in the interest of analyzing the molecular structure and the energy changes of corresponding characteristics groups simultaneously, thus providing detailed information for the thermodynamics investigation on the nonisothermal crystallization process of polymers.

## EXPERIMENTAL

### Materials

The metallocene linear low density polyethylene (mLLDPE) used was supplied by ExxonMobil Chemical Company as Exceed350D65 grade. Ethylene/vinyl acetate copolymer (EVA) was provided by Beijing Organic Chemical Plant, China, with vinyl acetate content of 14%. The characterization results of these samples are listed in Table I, in which the molecular weights were evaluated using GPC.

### Preparation of mLLDPE/EVA blends

The blends were prepared by dissolving the two species (40 wt % mLLDPE and 60 wt % EVA, weighed 2g in all) in 200 mL of *p*-xylene, refluxing for 2 h at constant temperature, and rapidly precipitating into 400 mL of methanol at 0°C. The sample was placed for 12 h at room temperature, then filtrated and washed with methanol, and dried in vacuum at 50°C.

### Characterization

Differential scanning calorimetry (DSC)

The DSC thermograms were measured using a Perkin-Elmer DSC-2C calorimeter. The temperature and

heat flow were calibrated before the measurement. All samples were heated from room temperature to 150°C at 80°C/min in nitrogen atmosphere, held at 150°C for 5 min, then cooled down to 50°C at a rate of -2°C/min.

### FTIR micro-spectroscopy

The FTIR measurements were performed in 10kHz rapid-scan at a resolution of 4cm<sup>-1</sup> on a Bio-Rad UMA500 microscope with a Bio-Rad FTS6000 FTIR spectrometer equipped with a MCT detector, and 16 scans were coadded in each scanset. The sample as a clear KBr pellet was laid between KBr windows in ICL Basics<sup>TM</sup> microscope compression stage equipped with the temperature controller in precision better than  $\pm 1^\circ\text{C}$  over the entire temperature range. The sample was heated from ambient temperature to 150°C at 80°C/min, held at 150°C for 5 min, then a cooling rate of -2°C/min was adapted from 150 to 67°C.

## RESULTS AND DISCUSSION

In Figure 1 are reproduced the DSC thermograms measured for mLLDPE/EVA (40/60) blend, pure EVA, and pure mLLDPE samples in the cooling process. It can be seen that there were two separate exothermic peaks on the curve of the mLLDPE/EVA

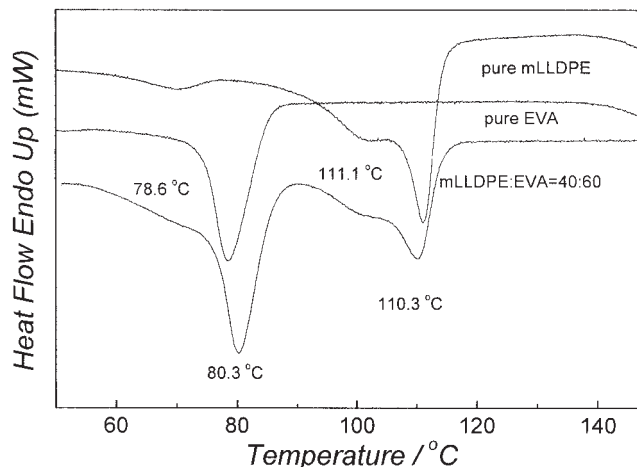
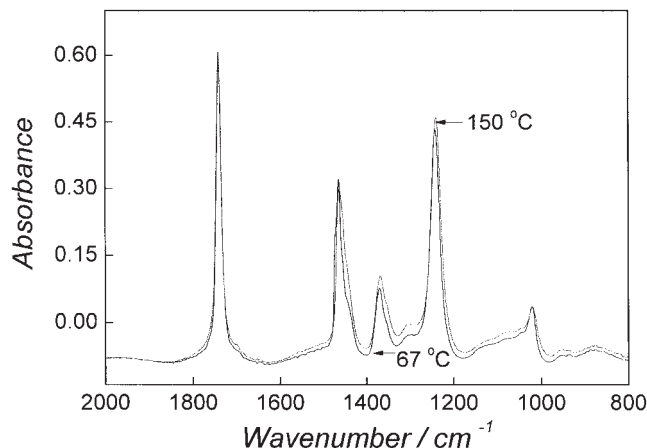


Figure 1 Comparison of DSC thermograms for mLLDPE/EVA blend and the corresponding pure original species in the cooling process.

blend, and they were slightly different in position from those of the original pure species. As previously reported,<sup>16</sup> the changes in peak position on DSC curves indicate that liquid-liquid and solid-liquid phase segregation in the blend system happened under a gradual cooling procedure, which might be a driving force to the movement of polymer chain segments towards each rich domain, accordingly resulting in the formation of crystal structure. Therefore, the crystallization peak at low temperature was considered to relate to the EVA-rich domain, while the other peak corresponded to the mLLDPE-rich domain.

According to Kohji Tashiro and colleagues,<sup>17</sup> the crystallization temperature and peak profile of the polymer blends might be influenced by the lamellar size and the interaction at the boundary between the two lamellae of the different species. In addition, the lamellae of one species might be surrounded not only by the amorphous phase of itself but also by the amorphous chains of the other species. For these reasons the crystallization behavior of each component in the blend system was influenced. As seen in Figure 1, the peak position corresponding to the mLLDPE-rich domain in the blend was lower than that of pure mLLDPE, owing to the insertion of a few EVA chain segments; similarly, owing to the insertion of a few mLLDPE chain segments into the EVA-rich domain, the peak position corresponding to the latter in the blend was higher than that of pure EVA. On account of the changes mentioned above as well as the changes in peak profile, the blend sample of mLLDPE and EVA has been found to show a partial cocrystallization phenomenon. As a result, the chain segment entanglement between the two species led to changes of intermolecular interactions, which might be confirmed in the infrared spectra. To further clarify these circumstances, FTIR spectral measurements were made as described below.

In Figure 2 is reproduced the FTIR spectra of the mLLDPE/EVA blend in the region of 800 ~ 2000cm<sup>-1</sup>, which were taken at 67°C and 150°C, respectively. In comparison of the infrared band at the two temperatures, it can be seen that the characteristic absorption of the groups investigated all showed a shift in peak position to a certain extent, which might be due to the balance achieved between different energy states of the characteristic groups in the same vibration mode. Roughly speaking, the start-point in the measurement (150°C) corresponds to a high energy state, whereas the end-point (67°C) corresponds to a low energy state. Under constant pressure, the equilibrium constant *K* between the two energy states (i.e., from high energy *E<sub>H</sub>* to low energy *E<sub>L</sub>*) was found to correlate with the temperature *T*, and the relationship can be described as follows by using the van't Hoff equation:<sup>18</sup>



**Figure 2** Infrared spectra measured for mLLDPE/EVA blend at 150°C and 67°C.

$$\ln K = \ln[C_H/C_L] = -\Delta G/RT \quad (1)$$

where *C<sub>H</sub>* and *C<sub>L</sub>* are the concentrations corresponding to the two energy states for one single characteristic group. In addition, the relationship among the concentration *C*, the peak absorbance *A*, the mole-absorbance coefficient  $\alpha$ , and the sample thickness *b* are defined by the Lambert-Beer law, namely

$$A_L = \alpha_L C_L b, \quad A_H = \alpha_H C_H b \quad (2)$$

Consequently, the ratio of *C<sub>H</sub>* to *C<sub>L</sub>* can be defined as

$$C_H/C_L = [A_H/\alpha_H]/[A_L/\alpha_L] \quad (3)$$

As to the vibrational modes of the same characteristic group, the Gibbs free energy change  $\Delta G$  in transition of the two energy states can be defined as

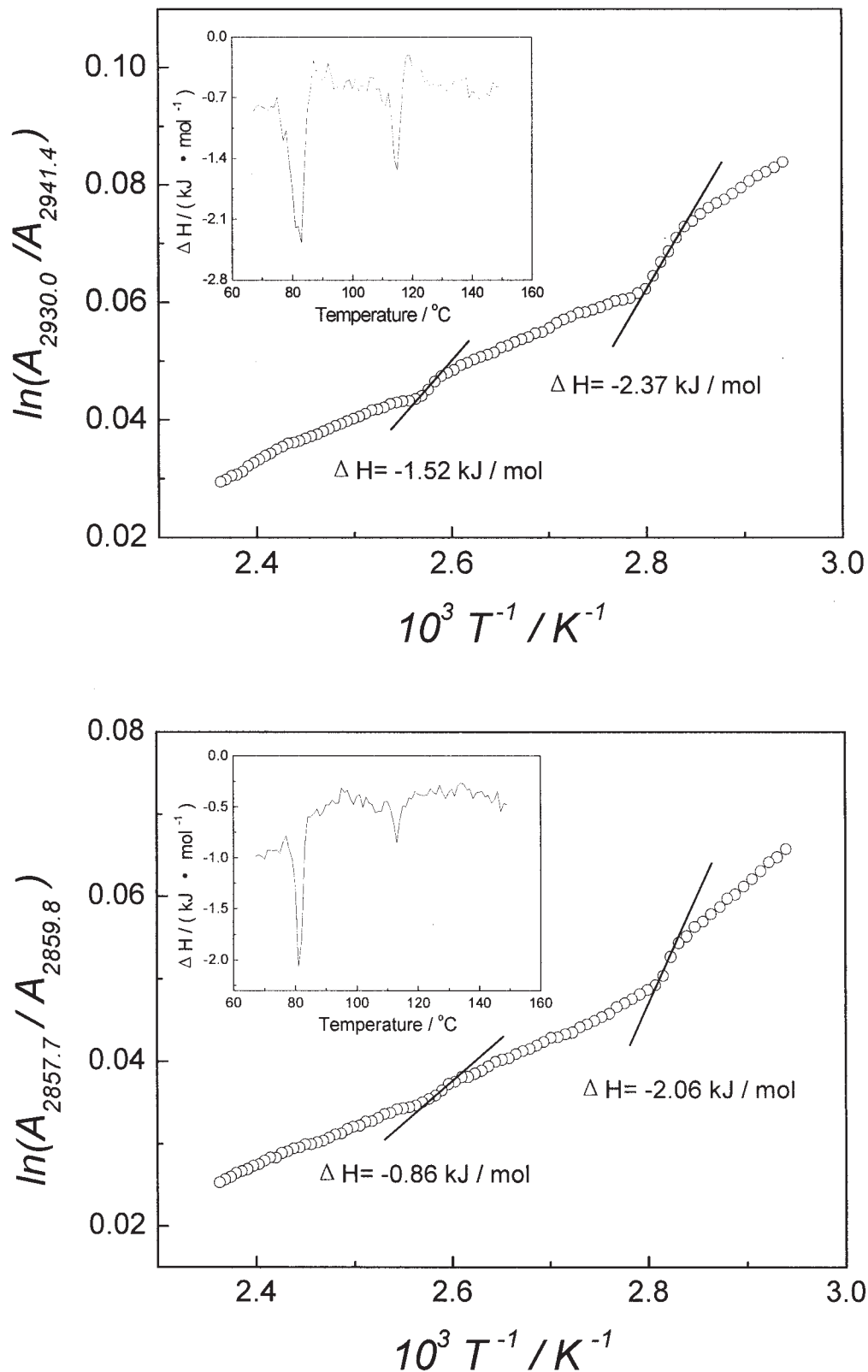
$$\Delta G = \Delta H - T\Delta S \quad (4)$$

where  $\Delta H$  and  $\Delta S$  are van't Hoff energy change and entropy change, respectively.

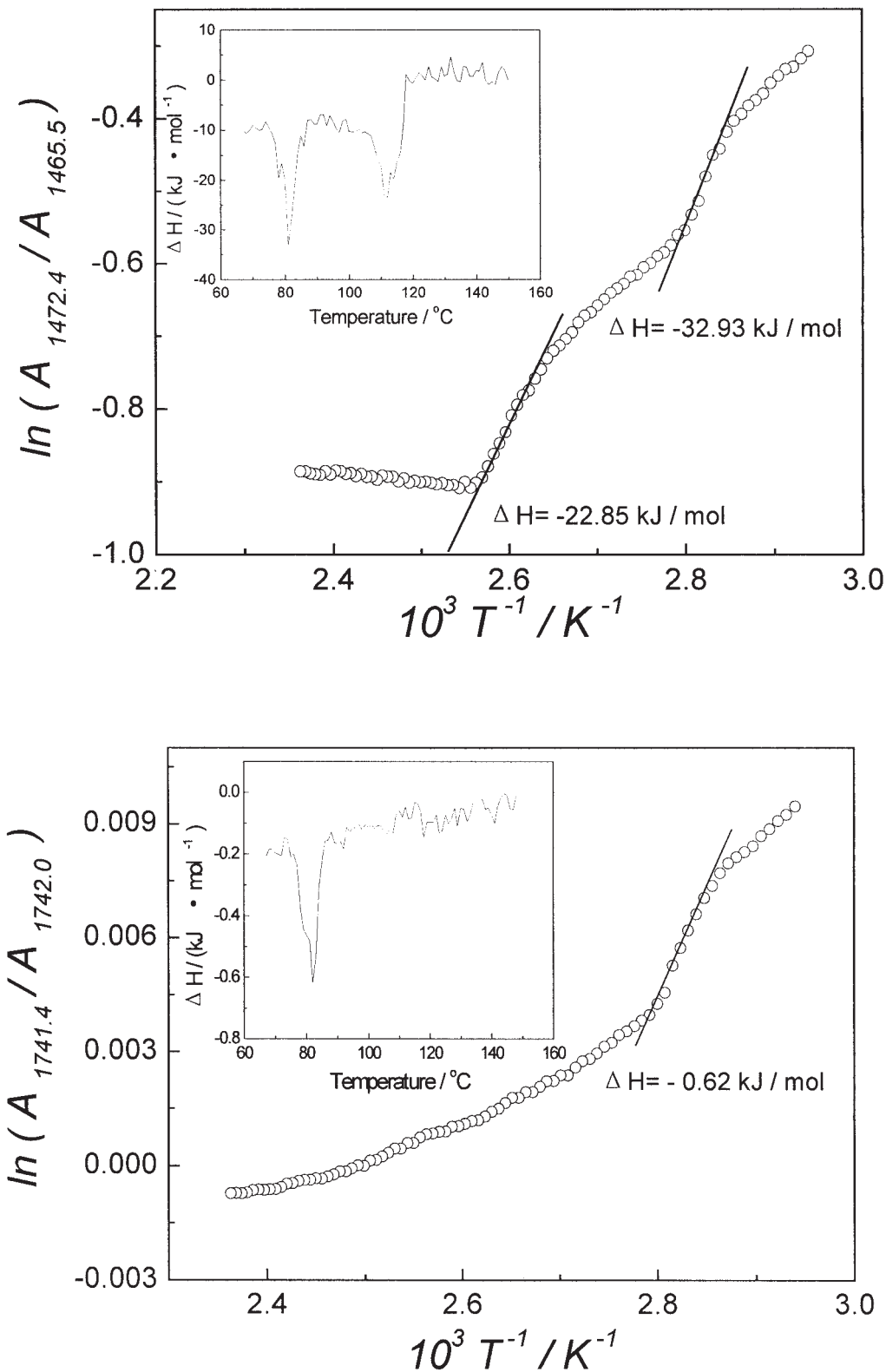
In analyzing data, we combined eqs. (3) and (4) with the van't Hoff equation, and arrived at

$$\ln[A_H/A_L] = -\Delta H/RT + \Delta S/R - \ln(\alpha_L/\alpha_H) \quad (5)$$

Since the sample weight was negligible relative to the heating surface, we may postulate that corresponding to certain vibration modes of the samples, the apparent enthalpy differences of vibration energy states transformation  $\Delta H_v$  and the entropy change  $\Delta S$  of the two energy states in the cooling process were independent of the temperature within minute temperature ranges. Also, related to the high and low energy states, the mole-absorbance coefficients  $\alpha_L$  and  $\alpha_H$  were assumed to have similar correlation with the



**Figure 3** A typical plot of  $\ln(A_L/A_H)$  versus reciprocal temperature represented methylene (stretching vibrations) in mLLDPE/EVA blends.



**Figure 4** A typical plot of  $\ln(A_L/A_H)$  versus reciprocal temperature represented methylene bending mode (above) and carbonyl stretching mode (below) in mLLDPE/EVA blends.

temperature; accordingly, the ratios of  $\alpha_L$  to  $\alpha_H$  approximately remained constant. So we could simplify the apparent enthalpy differences of vibration energy states transformation  $\Delta H_v$  as follows:

$$\Delta H_v = -R\partial[\ln(A_H/A_L)]/\partial(1/T) \quad (6)$$

Thus, it is possible to compare the apparent enthalpy differences of vibration energy states transformation

TABLE II  
Grouped Apparent Enthalpy Differences  $\Delta H$  of Vibration Energy States Transformation  
in mLLDPE/EVA Blends and Band Assignments

Group	$A_L/A_H$	$\Delta H_{80}/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta H_{110}/(\text{kJ} \cdot \text{mol}^{-1})$	IR assignments
—CH <sub>2</sub> —	2930.0/2941.4	-2.37	-1.52	$\nu_{\text{as}}$ (CH <sub>2</sub> )
—CH <sub>2</sub> —	2857.7/2859.8	-2.06	-0.86	$\nu_{\text{s}}$ (CH <sub>2</sub> )
—CH <sub>2</sub> —	2847.6/2849.0	-1.74	-1.47	$\nu_{\text{s}}$ (CH <sub>2</sub> )
—CH <sub>2</sub> —	1472.4/1465.5	-32.93	-22.85	$\delta$ (CH <sub>2</sub> )
—CH <sub>2</sub> —, —CH <sub>3</sub>	1463.9/1465.5	-1.54	-0.93	$\delta$ (CH <sub>2</sub> )
—CH <sub>3</sub>	1454.5/1457.1	-3.41	-3.26	$\delta_{\text{as}}$ (CH <sub>3</sub> )
—CH <sub>3</sub>	1369.4/1367.7	-2.71	-1.67	$\delta_{\text{s}}$ (CH <sub>3</sub> )
—COOR	1741.4/1742.0	-0.62	N	$\nu$ (C=O)
—COOR	1241.1/1239.8	-1.42	N	$\nu$ (—CO—O—)
—COOR	1020.1/1019.6	-0.76	N	$\nu$ (—O—CH—)

$\Delta H_v$  calculated by infrared spectrum with those obtained from DSC measurement, together with some indications of the contributions made by characteristic groups in the blend, in the case of phase transition and the crystallization process as the temperature decreases.

A typical curve recorded in the course of crystallization is shown in Figure 3, relating  $A_L/A_H$  changes to  $\Delta H_v$  of methylene stretching vibrations (symmetrical and asymmetrical) in mLLDPE/EVA blend samples. For the mLLDPE/EVA blend system in Figure 4, a typical plot of  $\ln(A_L/A_H)$  versus reciprocal temperature represented the bending mode of methylene (left) and the stretching mode of carbonyl group (right). The grouped apparent enthalpy differences of vibration energy states transformation and band assignments in the mLLDPE/EVA blend are listed in Table II.

Combining the analysis of Figure 3, Figure 4, and Table II, it can be seen that the vibrational absorption peak of the ethylene and methylene groups all took on sudden changes in the vicinity of 80°C and 110°C and the corresponding  $\Delta H_v$  were negative, indicating the appearance of an exothermal process via gradual regular arrangement of chain segments; whereas the vibrational absorption peak of the ester groups linked with the ethylene main chain only showed sudden changes in the vicinity of 80°C, and  $\Delta H_v$  manifested less values corresponding to 1741.4/1742.0-cm<sup>-1</sup>, 1241.1/1239.8-cm<sup>-1</sup>, and 1020.1/1019.6-cm<sup>-1</sup> bands, indicating that the vibration mode of the ethylene main chain played a dominant role in the formation of the EVA-rich domain. Especially, the bending vibration of methylene, namely, the 1472.4/1465.5-cm<sup>-1</sup> bands represented the most prominent changes, yielding  $\Delta H_v$  value of -32.93kJ/mol at 80°C and -22.85kJ/mol at 110°C. However, related to the temperatures investigated, the  $\Delta H_v$  values of other bands were all under -4kJ/mol. So we might infer that as the main group in the mLLDPE/EVA blend, methylene behaved with significant sensitivity to the changes of supermolecular structure of the macromolecular

chains. Therefore, concerning the formation of both the mLLDPE-rich and the EVA-rich domains in the crystallization process, there were notable changes in the apparent enthalpy differences of vibration energy states transformation for methylene groups.

As to the chain segments structure of pure EVA, there were large amounts of methyl groups corresponding to the 1371.2/1369.4-cm<sup>-1</sup> band, which was considered to relate to the bending vibration modes enhanced by carbonyl groups. However, the band moved to 1369.4/1367.7-cm<sup>-1</sup> in the blend, that is, the shift was near 2 wave-number, accounting for the interactions between methyl groups in the EVA and mLLDPE chain segments. In addition, the enthalpy changes of this band only appeared around 80°C for pure EVA, whereas the corresponding movement could be seen at 80°C and 110°C in the blend, indicating that the interactions mentioned above took place during mLLDPE crystallization. Therefore, we might conclude that in the cooling process, EVA chain segments participated in the crystallization of mLLDPE at 110°C and existed as cocrystallization accordingly. This conclusion is coincident with DSC analysis.

In summary, as verified by the discussion mentioned above, the noncrystallization of polymer blends could be analyzed by means of Fourier transform infrared (FTIR) micro-spectroscopy, presenting significant information on the conformational changes of different groups as well as their contribution to the crystallization process; thus, effective combination could be achieved on the macroscopical properties and the characteristics of micro-molecular structure for polymers. Compared with DSC measurement, the temperature resolution has been found to be lower, and the irregular peak profile of the apparent enthalpy differences of vibration energy states transformation was observed using this method. Nevertheless, as the apparent enthalpy differences arose by varied vibration energy states, the changing tendency was notable, and the band assignments corresponding to the changes of the characteristic groups could be easily

ascertained, thus obtaining more detailed information than by DSC measurement. Therefore, this method might be remarkable in itself and deserves further attention.

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