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Polymorphism and side group location of ethylene copolymers characterized by FTIR and NMR spectroscopy

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Abstract

Fourier transform infrared spectroscopy (FTIR) was used to characterize the polymorphism, crystalline phase transformation, and side group location of ethylene copolymers (poly(ethylene-co-vinyl acetate), ab. EVA and poly(ethylene-co-vinyl alcohol), ab. EVOH). Sample films were prepared through a melt-pressing method, and submitted to cryogenic FTIR spectra measurement. Besides the occurrence of a normally orthorhombic crystalline phase (OCP), a monoclinic crystalline phase (MCP) was also detected for EVA copolymers with a relatively higher comonomer content (>14 wt%). The annealing temperatures greatly influence the transformation from MCP to OCP. As for EVOH copolymers, only thermodynamically stable OCP was found to exist in the crystalline region, and the hydroxyl groups were proved to enter the crystalline region of ethylene segments, while the side groups of EVA exist predominantly in the amorphous region.

Keywords: Poly(ethylene-co-vinyl acetate); Poly(ethylene-co-vinyl alcohol); Fourier transform infrared

1. Introduction

The crystallization behavior of semicrystalline copolymers is an important and intriguing area of study in the field of polymer research [1,2]. Despite extensive investigations in this research area, there are still some unsolved problems concerning the crystallization process and phase structure of the semicrystalline copolymers. Answers for many important questions for unoriented ethylene copolymers, such as the polymorphism, phase transformation among different crystalline phases, and side group location, are needed in order to further understand the crystallization processes and the resulting materials properties.

For polyethylene and ethylene copolymers, the location of side groups has been one of the focuses for the investigation of crystalline structures for several decades [3–9]. Various techniques, including differential scanning calorimetry (DSC), wide angle X-ray diffraction (WAXD), transmission electron microscopy (TEM), nuclear magnetic resonance (NMR) spectroscopy, atomic force microscopy (AFM) etc., have been used for the characterization of the side group location. However, most of these methods (except ^{13}C NMR[9]) could not provide decisive evidence to demonstrate the incorporation of the side groups into the crystalline lattice. Infrared spectroscopy, as a powerful tool for the characterization of crystal lattice vibration, has hardly been used for the investigation of the above question, because of the signal-to-noise (S/N) ratio and the resolution of room temperature.

It is known that polymorphism is a common phenomenon for orientated ethylene copolymers, but seldom occurs in unorientated ethylene copolymers [10,11]. By using high resolution FTIR spectroscopy, however, we have proved that polymorphism can and does exist in such ethylene copolymers with a long side group and a high side group content, such as poly(ethylene-co-dimethylaminoethyl methacrylate) (EDAM) and EVA [12]. However, the mechanism of the polymorphism formation, the transformation among different crystalline phases, and the side group location in the above systems are still not well understood.

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Recently, we developed a new cryogenic FTIR setup [13], which can provide a stable low-temperature condition (close to liquid nitrogen temperature) and enhance the spectra resolution, thus allowing sensitive detection of the crystalline variation of semicrystalline polymers. The purpose of this study is to apply this high-resolution cryogenic FTIR spectroscopy for understanding the crystallization behavior of EVA and EVOH copolymers, including the location of comonomer units in the crystalline lattice, the polymorphism and the phase transformation among different crystalline phases.

2. Experimental section

2.1. Materials and sample preparation

EVA samples were obtained from the Beijing Organic Chemical Factory and their physical parameters are listed in Table 1. Melting temperatures (T_m) and crystallizing temperatures (T_c) of each sample were measured using a Mettler DSC 822e differential scanning calorimeter at a heating rate of 10 K/min. EVOH samples were prepared by homogeneously hydrolyzing reaction of EVA in our laboratory. The hydrolysis degree for all samples was determined to be higher than 98% with ^{1}H NMR spectroscopy.

The crystallization procedure and associated thermal history are prime factors in determining the morphological features and physical–mechanical properties of a given polymer. It is not sufficient in terms of sample preparation to consider only the crystallization condition without also considering sample size and shape. For example, the actual thermal history of samples with different thicknesses varied greatly. In this work, to ensure the consistency of data measured by FTIR and NMR, the sample films were obtained by a method of two-step melt-pressing; i.e. the samples were first melt-pressed to form a film with a thickness of ca. 100 μm and then submitted for the secondary film-pressing to form the final film with a thickness of ca. 40 μm. The sample was sandwiched between two aluminum flakes. To prevent the sample felt, Silicon resin releasing agent was coated on aluminum flakes and was cured at 200 °C. The samples were heated to a temperature 40 °C higher than the melting point of the samples. To investigate the influence of thermal history on the samples, two methods were used to prepare the samples: (1) in the quenching method, the samples were obtained by immersing the molten films in liquid nitrogen so that the temperature of the samples decreased rapidly; (2) in the annealing method, the samples were obtained by keeping quenched samples for 3 h in a constant-temperature oven at 30, 35, 40, 45, 50, 55 and 60 °C, respectively.

Table 1
Basic parameters of EVA and EVOH copolymers

Samples	Comonomer content		D (g/cm^3)	T_m (°C)	T_c (°C)	MI (g/10 min)
	wt%	mol%				
EVA (9)	9	3.3	0.932	98	88	2
EVA (14)	14	5.0	0.935	88	72	2
EVA (18)	18	6.7	0.940	84	69	3
EVA (28)	28	11.2	0.955	65	52	150
EVA (40)	40	17.8	0.980	49	30	50

2.2. Measurements

IR spectra of all samples were recorded on a Nicolet Magna 750 FTIR spectrometer with a 1 cm^{-1} resolution and 64 scans. A MCT detector was used to acquire higher-resolution spectra. To improve the spectra resolution, a cryogenic technique was applied, and the temperature of the samples was controlled at ca. −194 °C during the spectra collection. To prevent the condensation of moisture on the surface of the samples at low temperature, the experiments were carried out in a vacuum.

Solid-state ^{13}C NMR experiments were performed on a Bruker AM-300 spectrometer operated at 75.47 MHz at room temperature. The ^{13}C CP-MAS (cross-polarization and magic-angle spinning) technology was adopted to study the phase structure of the ethylene copolymers. The cross polarization (CP) parameters were as follows: 90° pulse with a 2 μs width, 1 ms contact time, and 3 s recycle time, 4 mm rotors rotating at 4 kHz, and scan number 2400.

3. Results and discussion

In the investigation of EVA and EVOH copolymers with FTIR spectroscopy, four bands between 750 and 700 cm^{-1} are frequently used to describe the methylene rocking bands ($\gamma(CH_2)$) for polyethylene and its co-polymers [14–18]. 733 and 721 cm^{-1} are assigned to OCP, 724 cm^{-1} is assigned to the amorphous fraction, and 718 cm^{-1} is assigned to MCP.

Fig. 1 shows the room temperature and cryogenic FTIR spectra of EVA (18). It was observed that, under cryogenic conditions, the S/N ratios of the IR spectra of EVA were improved significantly and the bandwidths decreased considerably. As a result, the monoclinic band of EVA around 718 cm^{-1}, which can hardly be seen at room temperature, appeared as a shoulder on the right side of the 721 cm^{-1} peak in the cryogenic FTIR spectra with a higher content of side groups.

The second-derivative spectra of $\gamma(CH_2)$ band of EVA copolymers further indicated this trend (Fig. 2). Fig. 2 indicated that the comonomer content significantly influences the crystalline structure of ethylene segments, more specifically, increasing the comonomer content favors the formation of MCP. A similar conclusion about monoclinic crystallite formation in ethylene–butene and ethylene–octene copolymers was also obtained by Hu and Sirota [19].

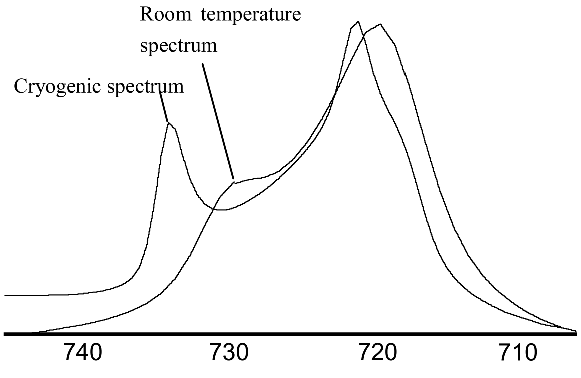

Fig. 1. Room temperature and cryogenic IR spectra of EVA (18).

It should be pointed out that, MCP content dose not increase linearly with the comonomer content. Fig. 2 showed that MCP percentage of EVA (28) is the largest among all the EVA samples. It is well known that MCP is a metastable crystalline structure, which can be transformed to OCP gradually when environmental temperature is close to the T_c. Table 1 showed that the T_m and T_c of EVA copolymers decrease with increasing VA content. The T_c values of EVA (18) and EVA (28) are 70 and 52 °C, respectively, while that of EVA (40) is 30 °C, close to room temperature. In this work, the samples were kept in desiccator at room temperature before testing. At room temperature, monoclinic crystals of EVA (40) will be partly transformed to orthorhombic crystals, leading to a relative decrease of the monoclinic crystal content of EVA (40), compared with that of EVA (28).

Fig. 3 shows the second-derivative FTIR spectra of $\gamma(CH_2)$ of EVOH copolymers with different comonomer content. It was observed that only two bands (733 and 721 cm^{-1}), which represent OCP, exist in EVOH copolymers. Compared with the dimension of acetate group of EVA, hydroxyl group of EVOH is much smaller. Its steric hindrance effect on the movement of ethylene segments can be neglected, therefore, only thermodynamically stable OCP was formed. Meanwhile, interchain interactions also have an important effect on the formation of a condensed-state structure. The intermolecular hydrogen bonds among the hydroxyl groups enhance the interaction between chain segments. All these factors make the phase structure of EVOH differ from that of EVA. To further understand the polymorphism and phase structure of ethylene copolymers, solid ^{13}C NMR measurements were carried out for both EVA and EVOH.

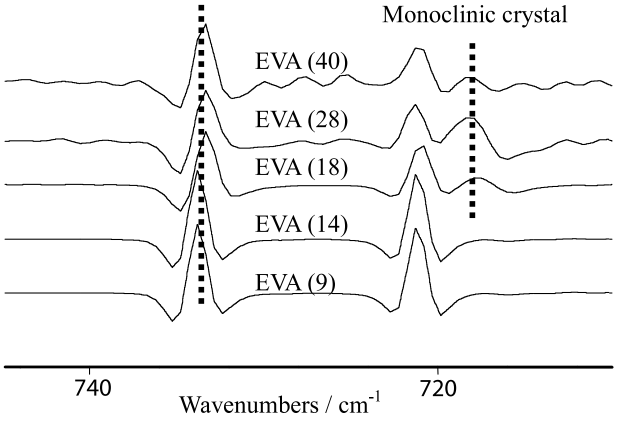

Fig. 2. Second-derivative FTIR spectra of $\gamma(CH_2)$ of EVA copolymers.

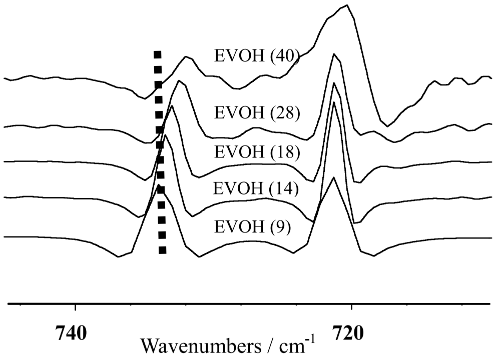

Fig. 3. Second-derivative FTIR spectra of $\gamma(CH_2)$ of EVOH copolymers with different comonomer content.

Figs. 4 and 5 are the curve-fitting results of ^{13}C CP/MAS NMR spectra of EVA (28) and EVOH (28), respectively. The total spectrum has been analyzed in terms of Lorentzian functions centered at 33.4 ppm (monoclinic crystal), 33.0 ppm (orthorhombic crystal) and 31.0 ppm (amorphous component), on the basis of ^{13}C spin–spin relaxation time measurements and line shape analysis. The signals of MCP are quite apparent and can be distinguished easily from the NMR spectra of EVA samples with a higher content of side groups (Fig. 4). In the spectra of EVOH copolymers, however, the signals of the monoclinic phase cannot be observed (Fig. 5). These results are in good agreement with the conclusion obtained from the cryogenic FTIR spectra. The difference in phase structure of EVA and EVOH originates from the difference in their side groups. The hydroxyl groups of EVOH have smaller steric hindrance and interaction between chain segments exists, which result in the formation of the different crystalline behaviors of the two kinds of samples.

At the same time, it was found from the second-derivative spectra of EVOH copolymers that, the peak position of the 733 cm^{-1} band for quenched samples gradually shifted to lower frequencies with increasing comonomer content, while that of the 721 cm^{-1} band remained almost unchanged (Fig. 3). The band shift of the rocking vibration for polyethylene directly reflects the deformation of crystalline structure [20,21]. Hydroxyl groups entering crystalline lattice will disrupt the ordered packing of ethylene segments, and inevitably influence the crystalline state, which is closely related with the crystalline band shift of IR spectra. Crystallization perfection will lead

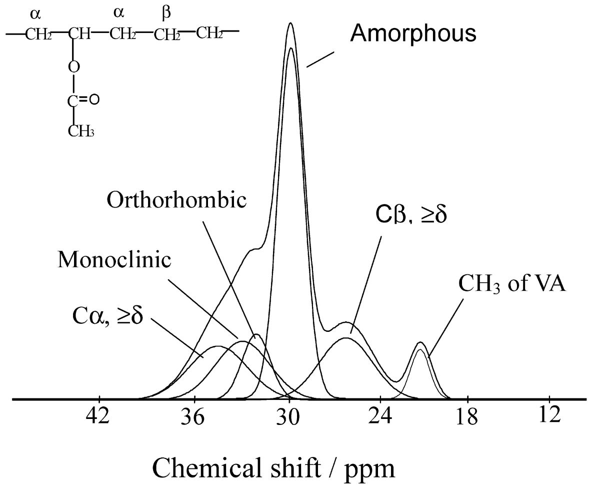

Fig. 4. Component analysis of ^{13}C CP/MAS NMR spectra of EVA (28).

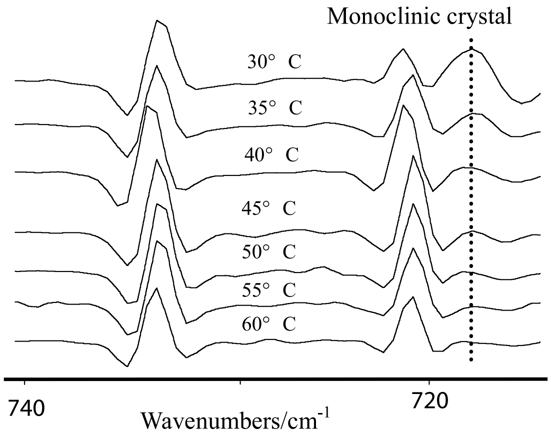

Fig. 6. Second-derivative spectra of γ(CH2) of EVA (28).

to 'blue shift' of the rocking band of the ethylene segments. The higher hydroxyl group content in EVOH copolymers provides more opportunities for hydroxyl groups to be included in the crystalline lattice [7], which in turn causes the crystallization imperfection and the 'red shift' of crystalline bands from 733.8 for EVOH(9) to 730.8 cm^{-1} for EVOH (28).

The 733 cm^{-1} band for EVA copolymers, however, was found not to vary with the comonomer content, indicating that VA groups do not enter the crystalline region of the ethylene segments (Fig. 2).

On the basis of the above observations and discussion, a conclusion can be drawn that polymorphism exists in unorientated EVA films with a higher content of side groups. To better understand the polymorphism of ethylene copolymers, the phase transformation from monoclinic to orthorhombic was investigated under different annealing temperatures for EVA (28). A series of EVA (28) samples were annealed for 3 h at 30, 35, 40, 45, 50, 55 and 60 °C, respectively. The aim is to transform a monoclinic crystal to an orthorhombic crystal as fully as possible, and to study the influence of thermal history on the crystalline transformation.

Fig. 6 shows the second-derivative spectra of the CH_2 rocking vibration of EVA (28) under different annealing temperatures. The variation of different crystalline bands is distinct. With increasing annealing temperature, the peak intensity of 718 cm^{-1} band gradually decreased, and finally disappeared at 60 °C, and only 721 and 733 cm^{-1} bands were left. Curve-fitting results further indicated that the relative content of the MCP gradually decreases with increasing the annealing temperature, while the OCP content increases (Fig. 7).

This result implied that the increased mobility of the polymer chains at high temperature induces the rearrangement of the crystalline ethylene segments, and consequently causes the gradual transformation from MCP to OCP. When the annealing temperature rises up to a certain value (60 °C), MCP disappears completely.

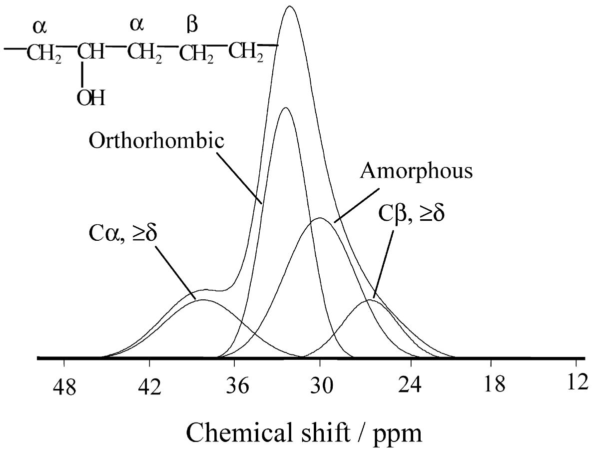

Fig. 5. Component analysis of ^{13}C CP/MAS NMR spectra of EVOH(28).

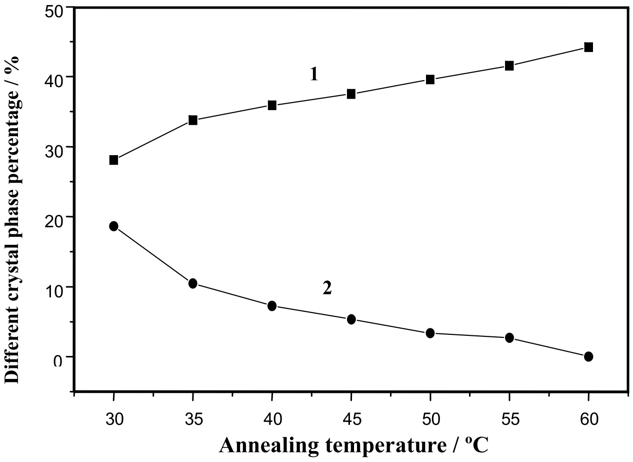

Fig. 7. Relative content of OCP and MCP in EVA copolymers under different annealing temperatures. (1) OCP content: A(733 + 721)/A(733 + 724 + 721 + 717); (2) MCP content: A(717)/A(733 + 724 + 721 + 717).

4. Conclusions

(1) Besides the stable orthorhombic crystal, a monoclinic crystal was also formed in the crystalline region of EVA with a higher comonomer content, and increasing the comonomer content favors the formation of monoclinic crystallites. For EVOH copolymers, however, the monoclinic band cannot be detected in the crystalline regions with high-resolution cryogenic FTIR spectroscopy. The same results were obtained with ^{13}C CP/MAS NMR spectroscopy.

(2) The transformation from MCP to OCP was realized by raising the annealing temperature of EVA films. Metastable MCP was gradually translated into OCP with increasing the annealing temperature.

(3) With direct evidence of the IR band shift of the rocking vibration (733 cm^{-1}) of ethylene segments, it was proved that the hydroxyl groups in EVOH enter the crystalline region while the side groups of EVA copolymers exist predominantly in the amorphous region. So, high-resolution cryogenic FTIR spectroscopy is a powerful technique for characterization whether the side groups of the ethylene copolymers enter the crystal lattice or not.

Acknowledgements

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References

[1] Zhang QJ, Lin WX, Chen Q, Yang G. Macromolecules 2000;33:8904.
[2] Takahashi M, Tashiro K, Amiya S. Macromolecules 1999;32:5860.
[3] Laupret F, Monnerie L, Barthelemy L, Vairon JP, Sanzeau A, Roussel D. Polym Bull 1986;15:159.
[4] Vonk CG, Pijpers AP. J Polym Phys Ed 1985;23:2517.
[5] Vonk CG. J Polym Sci, Polym Phys Ed 1985;23:2539.
[6] Davis GT, Eby RK, Martin GM. J Appl Phys 1968;39:4973.
[7] Salyer IO, Kenyon AS. J Polym Sci, Part A-1 1971;3083.
[8] Bunn CW. In: Hill R, editor. Fibers from synthetic polymers. Amsterdam: Elsevier; 1953.
[9] Alamo RG, VanderHart DL, Nyden MR, Mandelkern L. Macromolecules 2000;33:6094.
[10] Saraf RF, Porter RS. J Polym Sci, Polym Phys Ed 1988;26:1049.
[11] Yan RJ, Jiang BZ. J Polym Sci, Part B: Polym Phys 1993;31:1089.
[12] Kang N, Xu YZ, Wu JG, Feng W, Weng SF, Xu DF. Phys Chem, Chem Phys 2000;2:3627.
[13] Kang N, Xu YZ, Weng SF, Wu JG, Xu DF, Xu GX, The Pittsburgh Conference 51th Anniversary, p. 1768.
[14] Hagemann H, Strauss HL, Snyder RG. Macromolecules 1987;30:2810.
[15] Hagemann H, Snyder RG, Peacock AJ, Mandelkern L. Macromolecules 1989;22:3600.
[16] Snyder RG, Maroncelli M, Strauss HL, Hallmark VM. J Phys Chem 1986;90:5623.
[17] Zhang HP, Xu DF, Xu YZ, Weng SF, Wu JG. Mikrochim Acta (Suppl) 1997;14:425.
[18] Snyder RG. J Chem Phys 1979;71:3229.
[19] Hu W, Sirota EB. Macromolecules 2003;36:5144.
[20] Shen M, Hansen WN, Romo PC. J Chem Phys 1969;51:425.
[21] Vettegren VI, Slutsker AI, Gilyarov VL, Kulik VB, Titenkov LS. Phys Solid State 2003;45:1606.