8904 *Macromolecules* **2000,** *33,* 8904−8906

Phase Structure of Ethylene−Vinyl Alcohol Copolymers As Revealed by Variable-Temperature Solid-State High-Resolution ^{13}C NMR Spectroscopy

Qiujin Zhang, Weixin Lin, Qun Chen,* and Guang Yang

Analytical Center and The Key Laboratory of Education Ministry for Optics and Magnetic Resonance Spectroscopy, East China Normal University, Shanghai 200062, P. R. China

Received June 16, 2000

Introduction

The phase structure of semicrystalline ethylene−vinyl alcohol copolymer (EVOH) has been an interesting research subject for many years. Many factors, including the composition and the sequence distribution of the copolymer, the tacticity of the vinyl alcohol segments, the hydrogen-bonding interactions between the hydroxy groups, and also the processing conditions, may have influences on the phase structure.[1,2] There have been some reports on room-temperature solid-state high-resolution ^{13}C NMR study on EVOH.[3−5] However, due to the difficulties in discriminating signals from different phase structures and the difficulties in peak assignment, the technique failed to provide straightforward phase structure information as it did in the studies on many other semicrystalline polymers, such as polyethylene.[6]

To discriminate signals from different phase structures of multiphase polymers by the solid-state NMR techniques, it is usually required that the molecular chains in different phases have marked difference in mobility. Since the glass-transition temperature (T_g) of EVOH is higher than room temperature, the chain mobility of the noncrystalline region does not differ markedly from that of crystalline region at room temperature. Therefore, to study the phase structures of EVOH, it may be appropriate to carry out the NMR experiments at temperatures higher than the T_g of EVOH.

In this work, we present a variable-temperature solid-state high-resolution ^{13}C NMR study on EVOH. The main objective of the work is to study the phase structure of EVOH and its relation with the copolymer composition and to find an optimum condition, under which the phase structures of EVOH can be revealed by solid-state NMR.

Experimental Section

Two EVOH samples with ethylene mole content of 48% (ET48) and 82% (ET82), which are obtained from Kuraray Co. Ltd. and Fudan University, China, were quenched from the melt state under vacuum into liquid nitrogen and then dried under vacuum for 2 days. The glass-transition temperatures are 334 K for ET48 and 324 K for ET82 as determined by DSC measurements. Both of the samples are random copolymers as characterized by quantitative high-resolution ^{13}C NMR spectra. ^{13}C NMR experiments were carried out on a Bruker DSX-300 NMR spectrometer operating at 75.47 MHz. In ^{13}C CP/MAS and ^{13}C DD/MAS experiments, the spin rate of the 4 mm rotor is 4 kHz and the contact time for CP is 2 ms. The ^{13}C $\pi/2$ pulse width is 2.8 μs. The repetition time is 5 s for CP/MAS and 2 s for DD/MAS. The ^{1}H spin−spin relaxation time (T_2) is measured by employing a CP pulse sequence modified by adding a delay window immediately after the ^{1}H $\pi/2$ pulse. To avoid the possible line broadening due to the interference between the molecular motion and ^{1}H decoupling field and to produce marked difference between the chain mobility of the crystalline and the amorphous regions, the variable-temperature experiments are operated at temperature about 20−30 K higher than the T_g of samples.

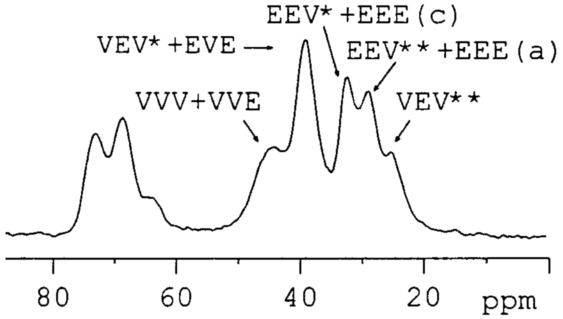

Figure 1. ^{13}C CP/MAS NMR spectra of ET48 at room temperature. * and ** denote the left and right methlyene in the central ethylene in triads; c and a in brackets denote crystalline and amorphous, respectively.

Results and Discussion

The room temperature ^{13}C CP/MAS spectrum of ET48 is shown in Figure 1. Peaks with chemical shifts larger than 65 ppm correspond to methine carbons of the vinyl alcohol unit. These methine carbon peaks can be resorted to central methine carbons in different triad sequences (mmVVV, mrVVV, rrVVV, mVVE, rVVE, and EVE, where E and V represent ethylene unit and vinyl alcohol unit and m and r represent meso and racemic, respectively) and intra/inter-molecular hydrogen-bonding interactions between hydroxyl groups. The detailed assignment of these methine carbon peaks is still a controversial topic.[3−5] Peaks from 20 to 50 ppm correspond to methylene carbons either in V or in E units. The assignments of these methylene peaks are shown in Figure 1. In previous works,[4] efforts have been made to discriminate the crystalline and amorphous signals, based on the assumption that the crystalline and amorphous regions are much different in ^{13}C spin−lattice relaxation times (T_1) and rotating-frame ^{1}H spin−lattice relaxation times ($T_{1\rho}$), which in turn requires that they are quite different in the chain mobility. However, no differences in the chemical shifts of the crystalline and amorphous signals were observed, which is due to that there is no big difference in chain mobility of the crystalline and amorphous regions.

Figure 2a,b shows the ^{13}C CP/MAS NMR spectra of ET82 at room temperature and 353 K. Only two methine peaks instead of three as in Figure 1 are observed in the room temperature spectrum, due to the low content of vinyl alcohol units in the copolymer. It is obvious that the resolution of the spectrum at 353 K is much better than that of the spectrum at room temperature. The methine signal at about 73 ppm and the methylene signal at about 39.5 ppm split into doublets with a distance of about 2 ppm. The relative intensities of the lower-field peaks of these two doublets

---

* To whom correspondence should be addressed.

10.1021/ma001046f CCC: \$19.00

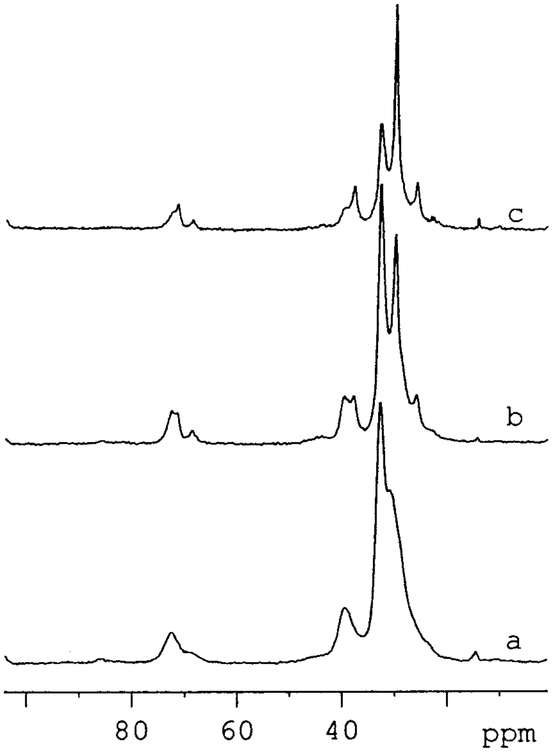

Figure 2. NMR spectra of ET82: (a) ^{13}C CP/MAS at room temperature; (b) ^{13}C CP/MAS at 353 K; (c) ^{13}C DD/MAS at 353 K.

decrease greatly in ^{13}C DD/MAS spectrum (Figure 2c) of ET82 at 353 K. It is known that the ^{13}C CP/MAS NMR spectrum comprises both crystalline and amorphous signals, and the ^{13}C DD/MAS NMR spectrum with short relaxation delay time comprises mainly the signals from the amorphous region. Therefore, the above result may indicate that the lower-field peaks of these two doublets can be assigned to methine and methylene carbons in the crystalline region, while the upfield ones are associated with the methine and methylene carbons in the amorphous region. To further verify this, ^{1}H spin−spin relaxation times were measured by employing the pulse sequence described in the Experimental Section. Figure 3 show the ^{1}H T_2-dependent partially relaxed spectra of ET82 at 353 K. The variations of the peak intensities of the methylene and methine carbons with delay time reflect the spin−spin relaxation behavior of the nearby protons. With the increase of the delay time, the intensity of the lower-field peak of the doublet methylene signal at 39.5 ppm decrease rapidly, similar to the behavior of the peak at 33 ppm corresponding to the crystalline ethylene segment. Although the splitting of the methine peak at 73 ppm is not clearly resolved, the upfield shift of the peak with the increase of delay time indicates clearly that the lower-field peak of the methine signals at 73 ppm is corresponding to the methine carbon in the crystalline region. Thus, it can be concluded safely that the splitting of the methine and methylene signals in Figure 2b is caused by different phase structures. The enhancement of the resolution of Figure 2b is, we believe, due to that the amorphous signals are narrowed by the molecular motion at temperatures several tens of degrees higher than the T_g of the sample.

The resolution of the ^{13}C CP/MAS spectrum of ET48 at 353 K is lower than that of ET82. This is due to the fact that, with higher content of vinyl alcohol unit, the chain mobility of the amorphous region of ET48 is more restricted by intermolecular hydrogen-bonding interactions. However, the methine peak at 73 ppm is found to shift to 71 ppm with the increase of delay time in the ^{1}H T_2-dependent partially relaxed spectra of ET48 (Figure 4). This result reveals clearly that this peak consists of two components: the lower-field component

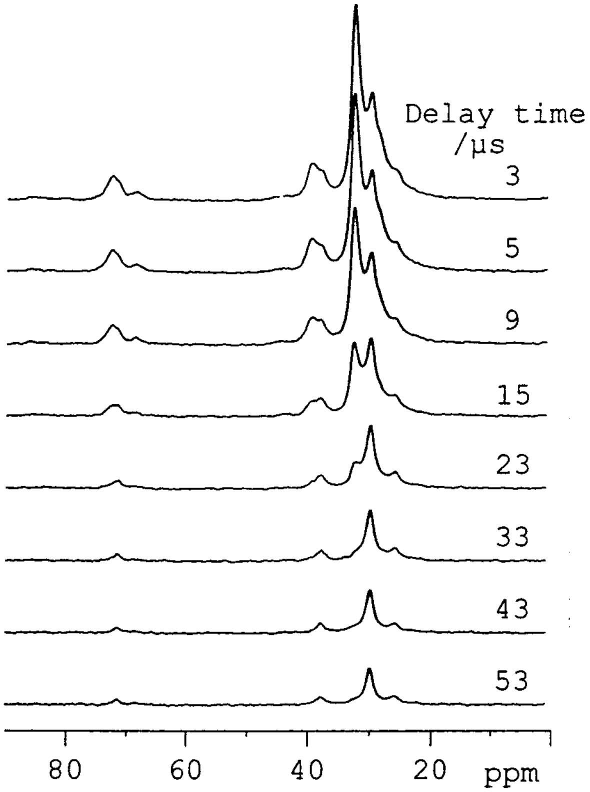

Figure 3. Partially relaxed ^{13}C CP/MAS NMR spectra of ET82 at 353 K with different delay time.

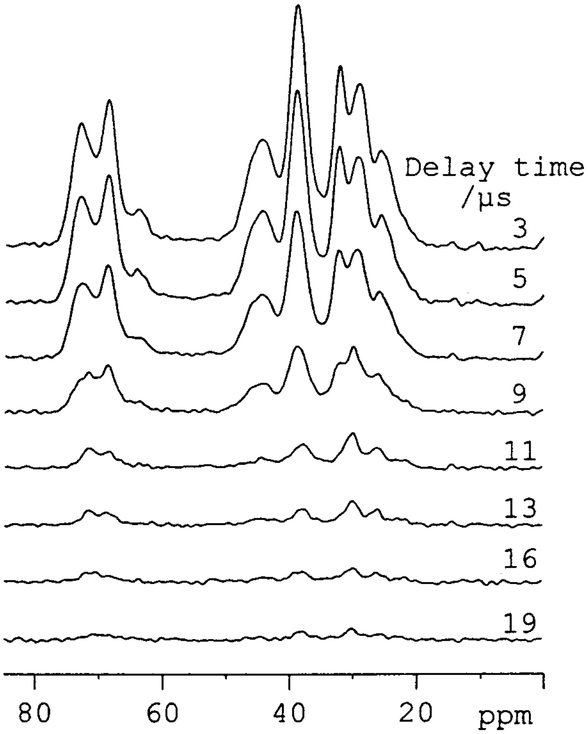

Figure 4. Partially relaxed ^{13}C CP/MAS NMR spectra of ET48 at 353 K with different delay time.

with shorter ^{1}H T_2 corresponds to the methine carbons in the crystalline region and the upfield one with relative longer ^{1}H T_2 to the methine carbons in the amorphous region.

In conclusion, the peak splitting effect due to different phase structures of some methine and methylene carbon peaks is observed in ^{13}C CP/MAS spectra of EVOH copolymers at 353 K, which is about 20−30 K higher than the T_g of the samples. The chemical shift of the methine and methylene carbons in the crystalline region is found to be about 2 ppm higher than those in the amorphous region. Such an experimental approach can be employed to measure the degree of crystallinity and to study the phase partitioning of the vinyl alcohol unit in the crystalline and amorphous regions, which is very important for understanding the crystallization behavior of EVOH copolymers. This result should also be taken into consideration when trying to make complete assignment of the ^{13}C CP/MAS spectrum of EVOH.

Acknowledgment. This work is supported by the KUASHIJI RENCAI foundation of Education Ministry of China and by QIMINGXING project of the Committee of Science and Technology of Shanghai Municipality.

References and Notes

(1) Cerrada, L M.; Pérez, E.; Pereña, M. J.; Benavente, R. *Macromolecules* **1998**, *31*, 2559−2564.
(2) Takahashi, M.; Tashiro, K.; Amiya, S. *Macromolecules* **1999**, *32*, 5860−5871.
(3) Ketels, H.; de Haan, J.; Aerdts, A.; van der Velden, G. *Polymer* **1990**, *31*, 1419−1424.
(4) VanderHart, D. L.; Simmons, S.; Gilman, J. W. *Polymer* **1995**, *36*, 4223−4232.
(5) Kanekiyo, M.; Kobayashi, M.; Ando, I.; Kurosu, H.; Amiya, S. *Polymer* **2000**, *41*, 2391−2404.
(6) Chen, Q.; Yamada, T.; Kurosu, H.; Ando, I.; Shiono, T.; Doi, Y. *J. Polym. Sci., Polym. Phys. Ed.* **1992**, *30*, 591−601.

MA001046F