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Wide-Angle X-ray Diffraction Study of the Phase Behavior of Vinyl Alcohol−Ethylene Copolymers

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ABSTRACT: The influence of the composition and thermal history on the type of lattice developed has been studied by wide-angle X-ray diffraction measurements in three vinyl alcohol−ethylene, VAE, copolymers with different compositions, which were crystallized from the melt at various cooling rates. The results are compared with those of the corresponding homopolymers, poly(vinyl alcohol) and low-density polyethylene. Both the composition and the cooling rate have been found to determine the crystalline structure of these VAE copolymers. Thus, for the samples slowly crystallized from the melt, a monoclinic lattice is obtained for copolymers VAE71 and VAE68 (with compositions of 71 and 68 mol % VA, respectively) while an orthorhombic lattice has been found for copolymer VAE56 (56 mol % VA). The effect of the cooling rate is very important, since copolymers VAE71 and VAE68 lead to the orthorhombic form when the samples are quenched from the melt. Copolymer VAE56 has been found to crystallize in an orthorhombic lattice under all the crystallization conditions here studied. The polymorphism exhibited by these copolymers is not the usual case for two different unit cells with well-defined lattice parameters: VAE71 and VAE68 show, by the influence of the cooling rate, a continuous change of some of the lattice constants. For instance, the angle β of the monoclinic lattice decreases smoothly from an "equilibrium" value of about 92.2° in the slowly crystallized samples to a final value in the quenched samples of 90° (orthorhombic unit cell). The degree of crystallinity determined from the X-ray diffraction patterns has been found to be in the quenched specimens considerably smaller than that in the slowly crystallized samples, standing in contrast to the constancy of the enthalpy of melting. Moreover, it seems that there are no differences in the melting temperatures between the two crystalline modifications.

Introduction

Vinyl alcohol−ethylene (VAE) copolymers, which find useful applications[1] as barrier resins, adhesives, compatibilizers, etc., are essentially random copolymers and typical amphoteric materials composed of hydrophobic and hydrophillic segments, where the properties are expected to vary widely with the copolymer composition. The relationships between the chemical composition and both crystalline structure and some physical properties have been previously investigated for a series of VAE copolymers.[2−8] These copolymers are crystalline irrespectively of composition, this fact being quite unusual. It was pointed out[2] long time ago that crystalline properties of poly(vinyl alcohol) (PVA) were unchanged when a small amount of ethylene was introduced by copolymerization. It was reported later[3] that both ethylene and vinyl alcohol residues were incorporated into the crystalline regions, thus forming "mixed crystals". Other investigators,[4−9] employing thermal analysis, X-ray diffraction, and ^{13}C NMR, have argued for similar conclusions. The existence of three types of crystalline systems depending on the composition of VAE copolymers have been proposed:[5,6] orthorhombic for 0−20 mol % vinyl alcohol, pseudohexagonal in the composition range from 20 to 60 mol % vinyl alcohol, and monoclinic for compositions above 60 mol % vinyl alcohol (evidently, the pseudohexagonal form is also an orthorhombic lattice).

X-ray diffraction of polymers is used not only for the determination of the crystalline structure but also for estimation of the degree of crystallinity. The separation of amorphous and crystalline contributions is a necessary step in the study of the structure of the less-ordered regions and in the calculation of crystallinity of a semicrystalline polymer. The diffraction pattern of a polymer with a high degree of crystalline order can be fitted with easily resolvable crystalline peaks, and the intensity not attributable to the crystalline peaks can be regarded as amorphous scattering.[10]

Table 1. Molar Fraction in Vinyl Alcohol, f_{VA}, of VAE Copolymers

	f_{VA}		
copolymer	nominal	^{1}H NMR	^{13}C NMR
VAE71	0.71	0.76	0.77
VAE68	0.68	0.73	0.72
VAE56	0.56	0.61	0.62

In the present work, X-ray diffraction studies will be presented concerning the phase behavior of three VAE copolymers, and the results will be compared with those for the parent homopolymers (PVA and low-density polyethylene, LDPE). The type of crystalline structure developed for these VAE copolymers is analyzed as a function of composition and thermal history.

Experimental Section

Three commercially available VAE copolymers, VAE71, VAE68, and VAE56 (from Solvay, Kuraray and DuPont, respectively), were used. Table 1 shows the composition in vinyl alcohol, VA, determined by using ^{1}H and ^{13}C NMR spectroscopies. Sheet specimens were obtained as films by compression moulding in a Collin press between hot plates (210 °C), and at a pressure of 2.5 MPa for 5 min.

The parent homopolymers were commercial grades, and for LDPE, the grade was that used for the production of the VAE

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Table 2. X-ray Crystallinity, f_c, of the Different Sample Preparations

specimen	cooling rate (°C/min)	f_c (%)
VAE71-S	~2.5	48
VAE71−10	10	50
VAE71−20	20	51
VAE71−40	40	49
VAE71−60	60	45
VAE71-Q	~100	35
VAE68-S	~2.5	49
VAE68−10	10	50
VAE68−20	20	45
VAE68−40	40	44
VAE68−60	60	44
VAE68-Q	~100	35
VAE56−1	1	50
VAE56-S	~2.5	51
VAE56−20	20	43
VAE56-Q	~100	30
PVA-S	~2.5	60
PVA-Q	~100	38
LDPE-S	~2.5	48
LDPE-Q	~100	46

copolymers studied. The two PVA homopolymer specimens were obtained by melt compression under the same conditions as those for the VAE copolymers. On the other hand, LDPE films were obtained by melt compression at 140 °C.

Each one of the VAE samples was crystallized under two different conditions: Q and S. The first treatment, Q, consisted of fast cooling between plates cooled with water after melting in press. The S specimens were slowly cooled from the melt, allowing the press to cool after switching off the power. The corresponding cooling rates are, approximately, 100 °C/min for the Q samples and 2.5 °C/min for the S ones.

Further thermal treatments were applied to the VAE copolymers. For that purpose, film samples were placed in a Mettler FP82HT hot stage and crystallized from the melt at different cooling rates. The various preparations can be observed in Table 2.

Wide-angle X-ray diffraction patterns were recorded in the reflection mode at room temperature by using a Philips diffractometer with a Geiger counter, connected to a computer. Ni-filtered Cu Kα radiation was used. The diffraction scans were collected over a period of 20 min between 2θ values from 3 to 43°, using a sampling rate of 1 Hz. The goniometer was calibrated with a standard of silicon.

The crystalline diffractions and the amorphous component have been separated with a fitting program which allows to estimate the crystallinity of the samples and to determine the spacings corresponding to the diffraction peaks. Considering the relatively high noise level of the diffractograms, the baseline has been taken just as a straight line in the 2θ range from 8 to 36°, and no further correction has been applied. The amorphous peak of the different samples was found to be centered at $2\theta = 20.1 \pm 0.3°$, the lower limit for LDPE and the upper one for PVA. The error in the crystallinity determinations, when these are expressed as percentage, is estimated to be ±5 units.

Calorimetric analyses were carried out in a Perkin-Elmer DSC7 calorimeter, connected to a cooling system, and calibrated with different standards. The sample weights ranged from 5 to 7.5 mg, and the heating rate was 10 °C/min.

Results and Discussion

Figure 1 shows the X-ray diffraction patterns of the two homopolymer samples crystallized under the two crystallization conditions. It can be observed that there are no significant differences with thermal history for LDPE, and it crystallizes under the typical orthorhombic lattice. The degrees of crystallinity are also very similar (see Table 2). In the case of PVA, however, the diffractions are appreciably sharper and better resolved for the S specimen, suggesting better ordering (longer crystallites). Moreover, the crystallinity is much smaller for the Q specimen (Table 2). The two diffractograms correspond to the monoclinic lattice of PVA.[5] Therefore, there is no change of crystalline lattice for the two homopolymers in the studied crystallization conditions.

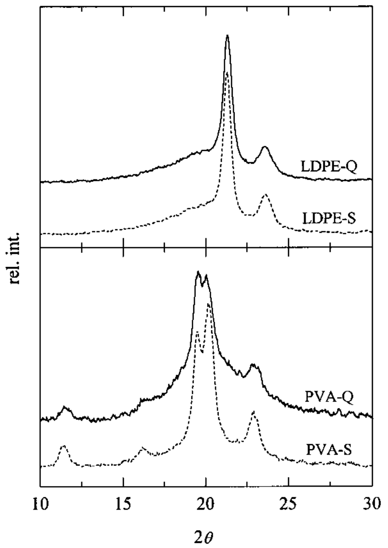

Figure 1. X-ray diffraction patterns, normalized to the same total intensity, for the two homopolymers: PVA (lower) and LDPE (upper), both quenched (continuous lines) and slowly crystallized (dashed lines) from the melt.

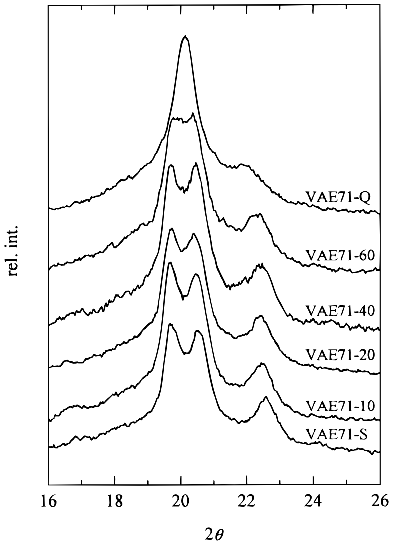

Figure 2. X-ray diffraction patterns, normalized to the same total intensity, of the different sample preparations corresponding to copolymer VAE71. The cooling rates are, from top to bottom, 100, 60, 40, 20, 10, and 2.5 °C/min.

The situation is different for the copolymers. Thus, Figure 2 shows the diffractograms corresponding to sample VAE71 for different thermal histories. It can be seen that the diffraction pattern for the S specimen (crystallized at about 2.5 °C/min) is similar to those of PVA, i.e., corresponding to a monoclinic lattice. On the contrary, the quenched sample leads to a pattern characteristic of an orthorhombic lattice, while the diffractogram of the sample cooled at 60 °C/min represents an intermediate state between the two modifications, where the two main diffractions are beginning to collapse.

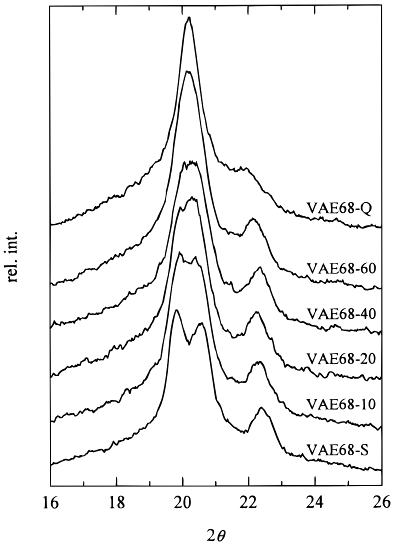

Figure 3. X-ray diffraction patterns, normalized to the same total intensity, of the different sample preparations corresponding to copolymer VAE68. The cooling rates are, from top to bottom, 100, 60, 40, 20, 10, and 2.5 °C/min.

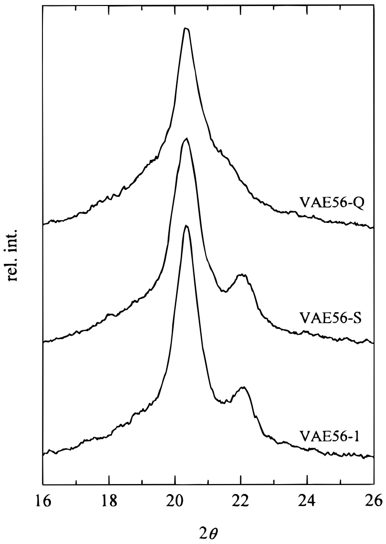

Figure 4. X-ray diffraction patterns, normalized to the same total intensity, of the different sample preparations corresponding to copolymer VAE56. The cooling rates are, from top to bottom, 100, 2.5, and 1 °C/min.

In the case of copolymer VAE68, Figure 3 shows that the monoclinic lattice is also produced in the S specimen and the Q sample leads to an orthorhombic unit cell. However, the “intermediate” state is obtained at slower cooling rates than in the case of VAE71, since approximately similar diffractograms are obtained for VAE71 at 60 °C/min and VAE68 at only 10 °C/min.

Finally, Figure 4 shows the diffraction patterns corresponding to VAE56. Now, the orthorhombic form is obtained under all the crystallization conditions used.

The conclusion from all these experiments is that both the composition and the thermal history are determining the crystalline structure in these VAE copolymers. Thus, previously reported maps of crystalline lattice vs composition,[5,6] showing that the pseudohexagonal (orthorhombic) lattice is obtained for compositions between 20 and 60 mol % VA and that the crystalline regions are isomorphous to PVA (monoclinic lattice) above 60 mol % VA, are only valid for slowly crystallized samples, and those limits will change for other crystallization conditions. Another important factor for the phase behavior may be the influence of pressure, taking into account that polyethylene, under high pressure, crystallizes from the melt first to a hexagonal phase and later to the normal orthorhombic phase.[11−13]

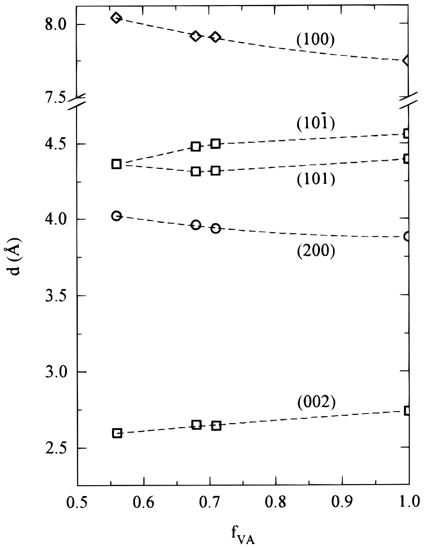

Figure 5. Variation with the composition in VA of the different diffraction spacings, for the S-coded samples (slowly crystallized from the melt).

The deconvolution of the diffractograms in the amorphous component and the crystalline diffractions allowed us to estimate the degree of crystallinity and to determine the diffraction spacings. The degrees of crystallinity, listed in Table 2, are very similar for the three copolymers when the thermal history is the same. In general, it can be observed that the degree of crystallinity decreases considerably when the cooling rate increases, although the results are very similar, and is inside the experimental error, for the lower cooling rates. Since the variation of the crystallinity with the cooling rate for copolymer VAE56 is very similar to that for VAE71 and VAE68 and if we consider that VAE56 leads to the orthorhombic lattice under all the studied conditions, the conclusion is that the cooling rate seems to affect very much to the degree of crystallinity determined from the diffractograms, but the crystalline modification is not an important factor.

The changes in crystalline lattice are, of course, reflected on the variation of the different spacings as a function of both comonomer composition and thermal history. Figure 5 shows the variation of the different resolvable spacings as a function of the composition in VA for the S samples. The results are very similar to those previously reported,[5,6] showing the collapse of the two more intense reflections for samples with composition below about 60 mol % VA, representing the change from the monoclinic to the orthorhombic lattice. It is interesting to note that some spacings decrease with the comonomer content while others increase.

A similar change can be monitored in samples VAE71 and VAE68, produced by the change of the cooling rate. Thus, Figure 6 shows the variation of the three more intense diffractions as a function of the cooling rate (the cooling rate has been represented with increasing values from right to left in order to get the same perspective than that in Figure 5). The collapsing of the two main diffractions is clearly faster for VAE68, in such a way

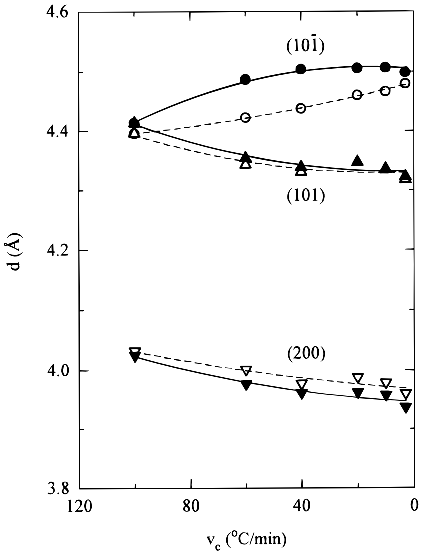

Figure 6. Variation of the spacings corresponding to the three main diffractions as a function of the cooling rate for copolymers VAE71 (filled symbols) and VAE68 (open symbols). The cooling rate increases from right to left in order to get the same perspective than that for Figure 5.

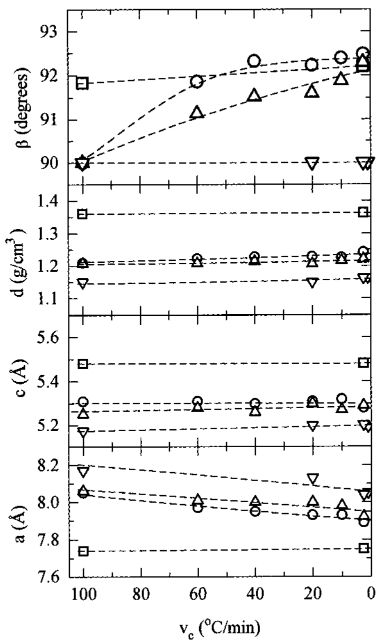

Figure 7. Variation of the lattice constants (*a* and *c* axes, density of the crystal, *d*, and angle, *β*) as a function of the cooling rate: (□) PVA; (○) VAE71; (△) VAE68; (▽) VAE56. The *b* axis (fiber axis) has been taken as 2.53 Å in all cases.[5] The cooling rate increases from right to left in order to get the same perspective as that for Figures 5 and 6.

that a continuous decrease is observed for the $(10\bar{1})$ peak of this copolymer while the decrease for VAE71 is observed only for cooling rates above 40 °C/min.

The behavior of the (101) diffraction is similar for the two copolymers, and the two curves showing the variation of the spacing for that diffraction lie rather parallel (with a small shift due to the different comonomer content, as happens with the (200) diffraction, and with the remaining ones not shown in Figure 6).

It may be deduced from the previous results that the two modifications (monoclinic and orthorhombic) can be produced in VAE copolymers (at least in those with high VA content) just by changing the cooling rate (or, alternatively, by isothermally crystallizing at different undercoolings). However, judging from Figures 5 and 6, a small variation in the comonomer content is reflected very much in the conditions necessary to obtain a certain crystalline lattice. In principle, therefore, the monoclinic modification might be obtained also in sample VAE56 at very slow cooling rates, while the orthorhombic one would be produced in PVA homopolymer under very fast quenching conditions. We have not been able to prove this point under the present experimental conditions, since PVA leads to a monoclinic lattice even for the quenched sample (see Figure 1) and VAE56 is orthorhombic even at a cooling rate of only 1 °C/min (Figure 4). Nevertheless, the differences between the diffractograms of samples PVA-S and PVA-Q seem to go in the expected direction. Moreover, an orthorhombic lattice has been reported for a quenched sample of PVA and a hexagonal one for a single crystal of this polymer.[14]

The lattice constants, determined from the previous spacings, show a clear dependence with both the vinyl alcohol content and the cooling rate. The variation of the lattice constants with the cooling rate is shown in Figure 7. It can be observed that, in the case of the copolymers, the *a* axis increases with the cooling rate while the *c* axis does not change significantly. The density of the corresponding crystal can be determined, provided that the dimension of the *b* axis and the value of the angle *β* (in the case of the monoclinic lattice) are known. Considering a value[5] of 2.53 Å for the *b* axis (fiber axis) and the results obtained for the angle *β* (upper part of Figure 7), a very small decrease of the density of the crystal with the cooling rate is observed for the copolymers, since the increase in the *a* axis is partially compensated with the decrease in the angle *β*.

For a given cooling rate, it can be observed that when the vinyl alcohol content increases, the *a* axis decreases while the *c* axis increases. The density of the crystal shows also a significant decrease as the vinyl alcohol content diminishes.

The variation of the lattice angle *β* is rather interesting. The upper part of Figure 7 shows that this angle takes the value of 90° for all the preparations of copolymer VAE56 (as corresponds to an orthorhombic unit cell). On the contrary, the other two copolymers (and PVA) show an “equilibrium” value of *β* around 92.2° for the specimens slowly crystallized from the melt. For VAE71 and VAE68, this angle is decreasing rather smoothly as the cooling rate is increased, and a value of 90° is obtained for the quenched specimens. However, the values corresponding to VAE68 decrease more rapidly than those for copolymer VAE71.

In the case of PVA homopolymer, the difference in the lattice constants between the specimens slowly crystallized and quenched is inside the experimental error, and only the value of the angle *β* seems to be slightly smaller in the case of the quenched sample.

It can be deduced from these results that a small variation in the composition affects very much the ability of producing the orthorhombic or the monoclinic unit cell in VAE copolymers in such a way that when the VA content is around 70 mol % it is rather easy to change from one modification to the other. However, if the content deviates significantly from that value, it would be rather difficult to obtain the monoclinic modification in the case of lower contents or the ortho-

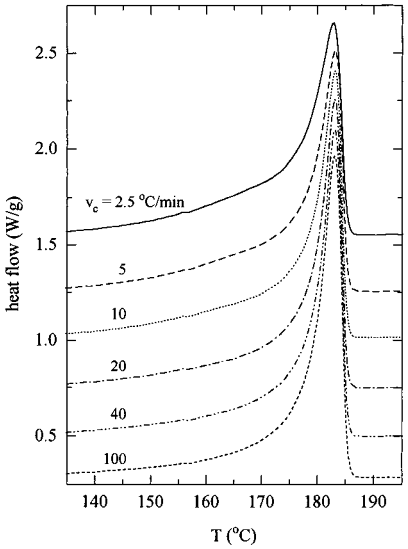

Figure 8. DSC melting curves corresponding to copolymer VAE68 crystallized from the melt at the indicated cooling rates.

rhombic lattice for high contents (and for PVA itself), although, in principle, this seems to be a matter of just increasing or decreasing the cooling rate (or changing the crystallization conditions in general). If this is true in the case of PVA, precise determinations of its unit cell parameters need to report the actual crystallization conditions, as happens with copolymers VAE71 and VAE68.

Another aspect can be derived from Figure 7. One orthorhombic unit cell becomes pseudohexagonal when the a axis equals to $b\sqrt{3}$ ($c\sqrt{3}$ in our case, since the b axis is the fiber axis). In other words, for an orthorhombic unit cell the value $r = \sqrt{3}\,c/a$, which will be unity for a real pseudohexagonal lattice, gives an idea of how far away we are from this kind of lattice. For the three copolymers here studied, the quantity r takes the values of 1.15, 1.13, and 1.10 for VAE71, VAE68, and VAE56, respectively, in the case of the quenched specimens where an orthorhombic cell is obtained. Thus, the value of r is decreasing with the VA content, but it is relatively far from unity even in the case of VAE56. In fact, if the values of r are determined from the results given in ref 5, a minimum value of 1.03 is obtained for a copolymer which is 28 mol % in VA. Therefore, a pseudohexagonal lattice is really approached for VA contents around 20−30 mol %, specially if we consider that a further decrease of r is expected if the samples are quenched (in our case of copolymer VAE56 the value of r changes from 1.12 for the sample slowly crystallized to 1.10 for the quenched specimen).

A pseudohexagonal lattice has been also reported in the case of ethylene−propylene copolymers with a content of 25 mol % in propylene.[15]

We have studied possible differences in the melting temperatures of the two crystalline lattices. For that purpose, we have analyzed copolymers VAE71 and VAE68 by DSC. Figure 8 shows the melting patterns for copolymer VAE68 crystallized from the melt at different cooling rates. All these endotherms display peak melting temperatures in the range 183.0 ± 0.2 °C. Moreover, the same value of the enthalpy of melting, inside the experimental error, is obtained in all the cases. Similar conclusions apply for copolymer VAE71. Thus, there are no appreciable differences in the melting points (and in the enthalpies of melting) between the monoclinic and orthorhombic modifications, provided that the two crystal lattices are obtained in the calorimeter at approximately the same rates as in the specimens prepared for the X-ray analysis. This seems to be true, since the DSC melting curves corresponding to two pieces of the X-ray films of samples VAE-Q and VAE-S are practically the same as those displayed in Figure 8 for the specimens prepared at 100 and 2.5 °C/min, respectively.

The constancy of the melting temperatures might be just a consequence of a transformation, on melting, from the orthorhombic to the monoclinic lattice. This transformation will imply the corresponding changes on the lattice parameters, which are rather subtle in all the cases, as we have seen above. Therefore, it is expected that the thermodynamic parameters of the two modifications will be very similar. Moreover, from the results in Figure 7 it is reasonable to expect that if this transformation would occur, there will be a smooth change of the lattice parameters. We plan to perform real-time variable-temperature diffraction experiments using synchrotron radiation to see if the orthorhombic modification is converted into the monoclinic form on melting.

The only appreciable difference in the melting endotherms of Figure 8 is the presence of a shoulder in the low-temperature side, with increasing intensity as the cooling rate decreases. Since the monoclinic form is produced under crystallization conditions closer to equilibrium and its packing is somewhat more efficient (slightly higher density), it is expected that if there were appreciable differences in the melting temperature, the melting of the monoclinic modification would occur at slightly higher temperatures. Therefore, the obtention of a more prominent shoulder in the low-temperature part of the endotherm in the case of slowly crystallized samples is contrary to expectations based on differences in melting temperatures between the two modifications.

The appearance of that shoulder is, however, a general feature in olefin copolymers, and it has been attributed to the fact that polymeric chains with higher comonomer content than the average are able to crystallize at these slower rates.[16,17] Therefore that shoulder presents higher relative intensities in the case of copolymers with more heterogeneous chemical composition. In fact, the relative intensity of this shoulder is very different for the three copolymers here studied, as it was reported previously.[18]

The constancy of the enthalpy of melting with the cooling rate for VAE68 stands in contrast to the relatively big differences in the degree of crystallinity determined from the X-ray diffractograms. One of the reasons for this behavior is the progressive decrease of the crystal thickness as the cooling rate increases, leading to wider diffraction peaks and making more difficult the deconvolution between crystalline and amorphous components.[19] An additional reason is the relative importance of the interfacial regions,[20,21] which may change in the different sample preparations and may be accounted for in a different manner when determining the X-ray crystallinity.

Conclusions

Both the composition and the cooling rate have been found to determine the crystalline structure of these VAE copolymers. Thus, for the samples slowly crystallized from the melt, a monoclinic lattice is obtained for copolymers VAE71 and VAE68 (with compositions of 71 and 68 mol % VA, respectively) while an orthorhombic lattice has been found for copolymer VAE56 (56 mol % VA). The effect of the cooling rate is very important, since copolymers VAE71 and VAE68 lead to the orthorhombic form when the samples are quenched from the melt. Copolymer VAE56 has been found to crystallize in an orthorhombic lattice under all the crystallization conditions here studied.

The polymorphism exhibited by these copolymers is not the usual case of two different unit cells with well-defined lattice parameters: VAE71 and VAE68 show, by the influence of the cooling rate, a continuous change of some of the lattice constants. For instance, the angle β of the monoclinic lattice decreases smoothly from an "equilibrium" value of about 92.2° in the slowly crystallized samples to a final value in the quenched samples of 90° (orthorhombic unit cell).

The degree of crystallinity determined from the X-ray diffraction patterns has been found to be considerably smaller in the quenched specimens than in the slowly crystallized samples, standing in contrast to the constancy of the enthalpy of melting. Moreover, it seems that there are no differences in the melting temperatures between the two crystalline modifications.

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References and Notes

(1) Okaya, T.; Ikari, K. In *Polyvinyl Alcohol—Developments*; Finch, C. A., Ed.; John Wiley and Sons: London, 1992; Chapter 8.
(2) Bunn, C. W.; Peiser, H. S. *Nature* **1947**, *159*, 161.
(3) Illers, K. H. *Eur. Polym. J.* **1969**, *Supplement*, 133.
(4) Bodily, D.; Wunderlich, B. *J. Polym. Sci., Part A-2* **1966**, *4*, 25.
(5) Matsumoto, T.; Nakamae, K.; Ogoshi, N.; Kawasoe, M.; Oka, H. *Kobunshi Kagaku* **1971**, *28*, 610.
(6) Nakamae, K.; Kameyama, M.; Matsumoto, T. *Polym. Eng. Sci.* **1979**, *19*, 572.
(7) Ramakrishnan, S. *Macromolecules* **1991**, *24*, 3753.
(8) Ketels, H.; de Haan, J.; Aerdts, A.; van der Velden, G. *Polymer* **1990**, *31*, 1420.
(9) VanderHart, D. L.; Simmons, S.; Gilman, J. W. *Polymer* **1995**, *36*, 4223.
(10) Murthy, N. S.; Minor, H. *Polymer* **1990**, *31*, 996.
(11) Basset, D. C.; Khalifa, B. A.; Turner, B. *Nature* **1972**, *239*, 106.
(12) Rsatogi, S.; Hikosaka, M.; Kawabata, H.; Keller, A. *Macromolecules* **1991**, *24*, 6384.
(13) Tashiro, K.; Sasaki, S.; Kobayashi, M. *Macromolecules* **1996**, *29*, 7460.
(14) *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; John Wiley: New York, 1989.
(15) Ruiz de Ballesteros, O.; Auriemma, F.; Guerra, G.; Corradini, P. *Macromolecules* **1996**, *29*, 7141.
(16) Lucas, J. C.; Alamo, R. G.; Mandelkern, L. *Polym. Prepr.* **1994**, *35*, 408.
(17) Pérez, E.; Benavente, R.; Bello, A.; Pereña, J. M.; Aguilar, C.; Martínez, M. C. *Polym. Eng. Sci.* **1991**, *31*, 1189.
(18) Fonseca, C.; Pereña, J. M.; Benavente, R.; Cerrada, M. L.; Bello, A.; Pérez, E. *Polymer* **1995**, *36*, 1887.
(19) Benavente, R.; Pereña, J. M.; Bello, A.; Pérez, E.; Locatelli, P.; Fan, Z.-Q.; Zucchi, D. *Polym. Bull.* **1996**, *36*, 249.
(20) Glotin, M.; Mandelkern, L. *Colloid Polym. Sci.* **1982**, *260*, 182.
(21) Alamo, R.; Domszy, R.; Mandelkern, L. *J. Phys. Chem.* **1984**, *88*, 6587.

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