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Relationship between microstructure and phase and relaxation transitions in ethylene–(vinyl acetate) copolymers prepared by emulsion copolymerization

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The relaxation and phase transitions in ethylene–(vinyl acetate) (EVA) copolymers prepared by emulsion copolymerization were studied. Substantial deviations of the basic characteristics of the transitions (glass transition temperature, T_g, melting temperature, T_m, and degree of crystallinity, W_c) from those known for commercial products and, to a greater extent, for low-conversion copolymers synthesized in solution were found. These deviations were explained by the effect of the microstructure and particularly by the configurational heterogeneity of the copolymer chains. Thus, different fractions of EVA copolymer fractionated according to the chemical composition revealed values of T_g, T_m and W_c suggesting the existence of two parts in the copolymer chains. The comonomer units in one part show a tendency to alternate while the ethylene units in the other part show an enhanced tendency to form blocks. A similar model of the microstructure of the copolymers studied was presented in our previous communication where the distribution of the comonomer units along the polymer chains was studied by means of ^{13}C n.m.r. spectroscopy. It is now established that the overall chemical composition of the copolymer and its fractions studied, calculated based on the experimental values of T_g, T_m and W_c, fitted fairly well with the composition found experimentally, thus confirming the correctness of the model of the microstructure proposed. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: ethylene–(vinyl acetate) copolymers; relaxation; phase transitions)

INTRODUCTION

The study of the phase and relaxation transitions in copolymers of ethylene (E) and vinyl acetate (VA) is both of applied and fundamental interest. The performance of commercially available copolymers of E and VA (EVA) depends strongly on the characteristics of these transitions. On the other hand, EVA copolymers can be regarded as a suitable model for investigation of phase and relaxation transitions in polyethylene, which in its turn is the most suitable object for a general study of those transitions in polymers[1].

The main efforts in the study of EVA copolymers have been directed towards the determination of the dependence of T_g and the basic thermodynamic melting parameters (T_m and W_c) on the chemical composition (CC) of the copolymers[2–7]. Dynamic mechanical testing[2,5], differential thermal analysis (DTA) and X-ray analysis[6], refractive index measurements[3] and differential scanning calorimetry (DSC)[4,7] have been used as experimental methods.

Low-conversion laboratory samples[2–4], prepared by bulk[2], solution[4] and emulsion[3] copolymerization and commercial high-conversion products obtained in bulk have been used in these studies.

According to the general concepts, the characteristics of phase and relaxation transitions in copolymers have to depend, first of all, on the primary parameters of copolymer chains, i.e. CC, compositional and configurational heterogeneity, type of branching, molecular weight (MW) and molecular weight distribution. In their turn, the primary parameters of copolymer chains depend on the synthesis conditions like pressure, temperature, reaction medium, type and concentration of the initiator.

The chemical composition as a basic parameter determining the microstructure of EVA copolymer chains can be considered as decisive when the following conditions have been met:

1. Compositional homogeneity, i.e. all the copolymer chains have the same CC. It is worth noting that as a result of the compositional homogeneity, MW has to be independent of CC. In the opposite case, when the change of CC is accompanied by changes in the chain lengths in the limits suggesting a MW dependence of the relaxation and phase transition parameters, it is difficult to correlate these parameters solely with the change of CC.
2. Homogeneity with respect to the type and distribution of alkyl branches (ABs).
3. Configurational homogeneity, i.e. persistence of the type of distribution of comonomer units along the polymer chains.

In fact, the analysis of results on the microstructure of high-conversion bulk-polymerized EVA copolymers reveals deviations from the above-mentioned 'homogeneities'.

Thus, the results from fractionation followed by determination of MW and CC of the fractions[8,9] have shown that for a copolymer having a high E content (12 mol% VA

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units), the high-molecular-weight fractions were 10–12% richer in E content than the low-molecular-weight fractions. Therefore, a substantial deviation from the compositional homogeneity occurred in this case. Maybe these disturbances in compositional homogeneity have been the reason for the deviation from completely random distribution of the comonomer units observed experimentally in EVA copolymers prepared in bulk[10,11]. Thus, for example, analysis of the sequence distribution in EVA copolymers containing 14–67 mol% VA units by means of ^{13}C n.m.r. spectroscopy showed that the population of E-E-E and VA-VA-VA triads was higher than expected for random distribution of comonomer units[10].

Another reason for the observed deviation from a random distribution of comonomer units may be the presence of disturbances in the configurational homogeneity manifested by an alteration of the distribution type of comonomer units along the individual chain during its growth under changed conditions. In this case a compositional heterogeneity occurs as well, but within an individual chain.

Information about the type and distribution of alkyl branches is confined only to the results from study of EVA copolymers of various compositions without any characterization of different fractions. Thus, ^{1}H and ^{13}C n.m.r. spectroscopic studies of the length and frequency of ABs in commercial EVA products (2.3–12.4 mol% VA units)[12] revealed the presence of both short-chain and long-chain ABs analogous to low-density polyethylene (LDPE). This analogy applied not only to the average number of ABs (about two ABs per 100 C atoms) but also to their length distribution (butyl and amyl ABs represented 80% of the total number of ABs).

The effect of VA branches on the melting parameters of the copolymers is similar to the influence of short-chain ABs (SABs) in LDPE[1].

In all the papers where the phase and relaxation transitions have been studied, the EVA copolymers have been *a priori* regarded as homogeneously related to both the chemical composition and the type of distribution of comonomer units and alkyl branches. The deviations from those 'homogeneities' must affect the characteristics of the phase and relaxation transitions in EVA copolymers.

From this point of view, the results from crystallization of EVA copolymers containing 6.2–20 mol% VA are of interest[7]. Two melting peaks have been observed in their thermograms. The low-temperature peak has been related to the melting of extended chain crystals, its relative intensity being enhanced on increasing the VA content. The second peak has been assigned to the melting of folded-chain crystals. The formation of crystals of the two types can be related to the different content of chain defects in the copolymer chains. At higher contents of such defects, crystallization by the folded-chain mechanism cannot proceed, as was suggested by Okui and Kawai[7]. In this case the bicomponent crystallization can be regarded as a consequence of the presence of fractions of different CC in the samples studied. It can be assumed that, besides the compositional heterogeneity, the presence of fractions of different MW can also be a reason for bicomponent crystallization, as the presence of a low-molecular-weight fraction is a prerequisite for extended-chain crystal formation.

It is worth noting that different type of T_g and T_m dependencies on CC have been obtained for EVA copolymers of different degrees of conversion. Thus, copolymers prepared by solution copolymerization at a low degree of conversion[4] revealed an essentially linear dependence of T_g on the CC in a wide range of VA content (14.7–81.8 mol%). This dependence is essentially the same as that reported by Illers[3] for EVA copolymers containing 31.0–74.5 mol% VA units prepared by emulsion copolymerization at a low degree of conversion.

However, two areas are discernable in the curves of CC *versus* T_g for EVA copolymers prepared at high degrees of conversion, particularly under large-scale conditions[2,5,7].

This dependence is similar to that observed for copolymers prepared at low degrees of conversion when the VA content is higher than 33–35 mol%. At lower content of VA units, however, T_g does not depend on the CC of copolymers and levelled down at about −25°C.

Nielsen[2] suggested that the persistency of T_g on the variation of the CC is a result of the constant CC of the amorphous phase. However, Nielsen did not comment upon the fact that for copolymers containing less than about 33–35 mol% VA units, i.e. under conditions when the CC of the amorphous phase does not correspond to the overall CC, the composition of the crystalline phase cannot correspond to the overall composition as well. Therefore, the experimental melting point T_m also cannot conform to the overall composition.

Thus, the choice of CC as a basic parameter of the microstructure of EVA copolymers determining the characteristics of phase and relaxation transitions in these copolymers is insufficient. When the conditions of copolymerization suggest deviation from randomness it is very important that other parameters of the microstructure to be found for a more precise and fair explanation of these transitions. Such deviations can arise as a result of changes in the composition of comonomer mixture assuming that the comonomer reactivity ratio was constant. When the copolymerization proceeds in two or more phases the composition of the feed has to be different in these phases. Changes in composition can also occur when the concentration of one of the comonomers is kept constant during the copolymerization.

From this point of view, high-conversion EVA copolymers prepared by emulsion copolymerization are very suitable for illustrating the deviations from 'homogeneities' on the microstructural level and the corresponding macroscopic levels. In our previous communication[13], results from the investigation of the microstructure of these copolymers have been presented and discussed. By using ^{1}H and ^{13}C n.m.r. spectroscopy it was shown that EVA copolymers are characterized both by compositional and configurational heterogeneity and by the presence of ABs (both long-chain and short-chain), irrespective of their composition and MW. Both the content and the length distribution of ABs were calculated. In the present paper we have tried to find out the relationship between microstructure and phase and relaxation transitions in EVA copolymers. We suggested a model of the microstructure of the copolymer chain based on the analysis of our results on the phase and relaxation transitions (using DSC) from the standpoint elaborated in the study of phase transitions in PE[1]. Subsequently, we compared the model thus obtained with our previously proposed model based on the study of the microstructure of EVA copolymers using n.m.r. spectroscopy.

EXPERIMENTAL

Samples were prepared by emulsion copolymerization of

Table 1

No.	Copolymer	VA (mol%)	W_i (wt%)	AB^{100C}	$AB_E^{100C\,a}$	$MW_{ap}10^{-3}$
1	EVA-1	91	100	–	2	237
2	EVA-3	88	100	–	2	195
3	EVA-4	77	100	–	2.5	145
4	EVA-5	55	100	–	2.5	105
5	EVA-6	24	100	1.8	2.8	–
6	6SA	43	14.50	2.0	3.5	11
7	6SH	14	12.80	2.7	3.5	23
8	$6SX_1$	19	1.30	2.3	–	25
9	$6SX_2$	20	3.65	2.3	–	38
10	$6SX_3$	22.3	4.38	1.3	–	105
11	$6SX_4$	21.4	4.41	–	–	178
12	$6SX_5$	21	3.65	–	–	235
13	$6SX_6$	20	30.95	1.7	2.7	305
14	$6SX'$	23	24.40	1.7	2.7	–

[a] For 100 C atoms of E units

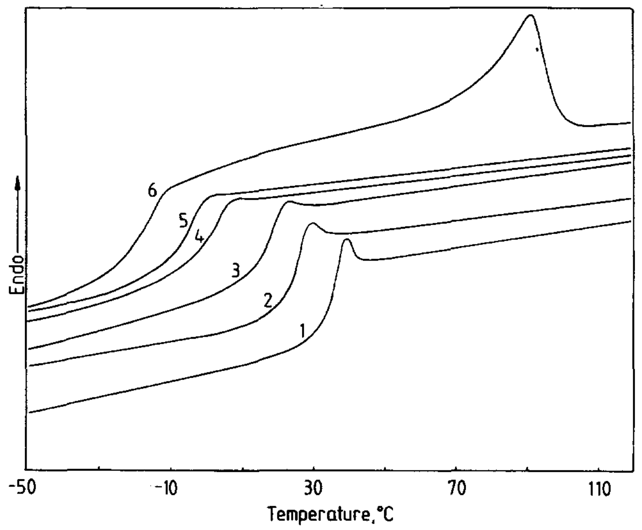

Figure 1 DSC traces of poly(vinyl acetate) and of EVA copolymers: 1, poly(vinyl acetate); 2, EVA-1; 3, EVA-3; 4, EVA-4; 5, EVA-5; 6, EVA-6

E and VA in the presence of a redox initiating system (ammonium peroxidisulphate–sodium sulphite) at 40°C, pressure 1, 3, 4, 5 and 6 MPa (EVA-1, EVA-3, EVA-4, EVA-5 and EVA-6 respectively) with high VA conversion (95–96%). EVA-6 copolymer was fractionated according to the scheme described in detail in our previous paper[13]. Fractions were separated by consecutive extraction by selective solvents (acetone and heptane) followed by fractionation of the residue by extraction in xylene with gradual temperature increase. Fractions referred to as 6SA and 6SH were extracted by acetone (at 50°C) and heptane (at 45°C) respectively; $6SX_1$ to $6SX'$ were extracted by xylene at 20, 30, 35, 40, 45, 50 and 150°C respectively.

Procedures for the determination of CC, content and length distribution of comonomer units along the polymer chains are described elsewhere[13].

Gel permeation chromatography (g.p.c.) data for EVA copolymers were obtained on a Waters 244 instrument. Measurements were made in tetrahydrofuran (THF) at 45°C (flow rate, 1 ml min^{-1}) with μ-styragel columns system. Calibration was effected with polystyrene standards. As is well known, the apparent MW (MW_{ap}) thus obtained did not represent the actual values of the MW. They are only informative of the order of magnitude, mainly for different fractions of EVA-6.

DSC measurements were taken on a Perkin-Elmer DSC 7 instrument in the temperature range −60–130°C, in argon, with heating rate of 10°C min^{-1}. Samples were melted first at 130°C for 5 min and cooled down to −60°C at a cooling rate of 10°C min^{-1} in order for a similar thermal prehistory to be reached. The instrument was calibrated by using a standard procedure[14] with indium and lead. Degree of crystallinity was calculated from the melting enthalpy of partially crystalline samples by using the value of 293 J g^{-1} for the enthalpy of melting of a perfect polyethylene crystal[1].

RESULTS AND DISCUSSION

Data on CC, content of AB and MW_{ap} of EVA-1–EVA-6 and different fractions of EVA-6 are presented in *Table 1*.

As seen, the copolymer EVA-6 is non-homogeneous in terms of CC. It is noteworthy that the MW of EVA copolymers obtained by emulsion polymerization is generally high, which in principle is characteristic of this method of polymer preparation. In the case of EVA-6 a substantial inhomogeneity of the MW, which is also characteristic of emulsion polymerization, was observed as well.

It should be noted that the difference in MW_{ap} of low-molecular-weight (6SA, 6SH, $6SX_1$ and $6SX_2$) and high-molecular-weight ($6SX_3$–$6SX_6$) fractions is almost one order of magnitude. In addition (with the reservation about the imperfection of the method of MW determination), MW_{ap} values of the low-molecular-weight fractions suggest the two possibilities of crystal formation, i.e. both of extended-chain and folded-chain crystals.

All the copolymers irrespective of CC have nearly the same AB content, approximately 80% of ABs being butyl SABs as shown previously[13]. A tendency to enhance the AB content on decreasing the MW can be noted.

Thermograms of the copolymers on heating are presented in *Figure 1*–*Figure 3*.

The temperature range where a relaxation transition occurred is shifted down to lower temperatures on decreasing the VA content from 100% (pure poly(vinyl acetate)) to 55 mol% (EVA-5). On further drop of VA content from 43 mol% (6SA) to 14 mol% (6SH), however, the relaxation transition always occurred in the range −36°−−10°C.

Starting from the VA content of 43 mol% (6SA), an endothermal effect related to the melting of the crystalline phase was observed.

The basic characteristics of the relaxation and phase transitions (T_g, T_m and W_c) of all the copolymers and the main fractions of EVA-6 are presented in *Table 2*. Results of other authors are also summarized in the table. The dependence of T_g *versus* CC for the EVA copolymers studied is depicted in *Figure 4*.

Analysis of the results obtained revealed that the copolymers studied differed considerably from those described by other authors with respect to both relaxation and phase transitions.

As is evident from *Figure 4*, the dependence of T_g *versus* CC is linear up to 75 mol% VA units, then in the range around 50 mol% it is less expressed, and finally on decreasing the VA content from 43 to 14 mol% T_g is practically constant, levelling down at about −20°C.

A similar deviation from linearity of the dependence of T_g *versus* CC (or otherwise independence of T_g with respect to CC in a defined range of VA content) is characteristic of high-conversion EVA copolymers, as was shown above. The lower limit of VA content varies at around 33–35 mol%. According to the Reding *et al.*[5], the CC of the amorphous phase does not change on further

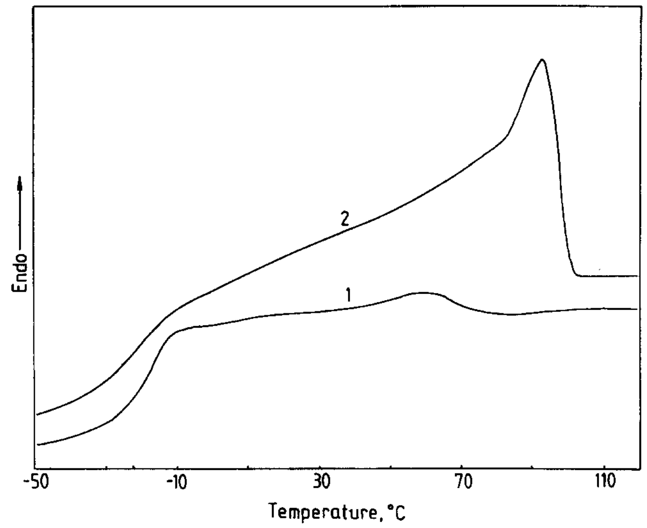

Figure 2 DSC traces of EVA-6 fractions: 1, fraction 6SA; 2, fraction 6SH

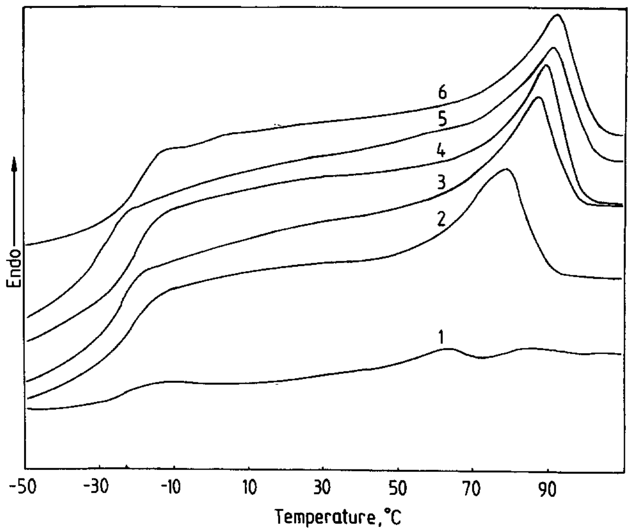

Figure 3 DSC traces of EVA-6 fractions: curves 1–6 correspond to fractions $6SH_1$–$6SH_6$ respectively

Table 2

No.	Copolymer	VA (mol%)	T_g (°C)	T_m (°C)	W_c (wt%)
1	EVA-1	91	23.6	–	–
2	EVA-2	88	15.6	–	–
3	EVA-4	77	− 0.5	–	–
4	EVA-5	55	− 6.7	–	–
1	EVA-6	24	− 17.9	91	7.4
2	6SA	43	− 18.2	58.8	3.5
3	6SH	14	− 21.2	92.7	16.75
4	$6SX_6$	20	− 19.9	91.5	7.2
5	$6SX^{l}$	23	− 19.4	90.7	6.7
6[a]	EVA-14.7[4]	14.7	− 63	36	–
7[b]	EVA-31[3]	31	− 30	–	–
8[c]	EVA-10.6[2]	10.6	− 25	0	–
	EVA-1.1[2]	1.1	− 25	53	–
9[d]	EVA-20[5]	20	− 25	–	–
10[e]	EVA-6.2[6]	6.2	− 25	78	–
	EVA-20[6]	20	− 25	0	–
11[f]	EVA-4.9[7]	4.9	− 25	87	–

[a] Low-conversion copolymers of 14.4–81.8 mol% VA units obtained by copolymerization in solution; T_g varies from −63° to +22°C

[b] Low-conversion copolymers of 31.0–74.5 mol% VA units obtained by emulsion copolymerization; T_g varies from − 30° to + 17°C

[c] Laboratory samples of 1.1–50.5 mol%: T_g varies from −5° to −25°C at VA content 50.5–33.0 mol%; at VA content lower than 33.0 mol% T_g is equal to about −25°C

[d] Commercial products of VA content 7.4–63.0 mol%. At VA content lower than about 35.0 mol% T_g does not change and is equal to about −25°C. The crystalline phase disappears at about 20 mol% VA units

[e] Commercial products of VA content 6.2–20 mol%

[f] Commercial product

decrease of VA content, remaining at the above-mentioned level. The authors emphasized that the samples studied were compositionally homogeneous. In this case, if a fraction having CC corresponding to the amorphous phase did not coexist with other(s) fraction(s) enriched in E units, most probably this is an indication of configurational heterogeneity of copolymer chains.

A similar independence of T_g with respect to CC was observed by us for fractions of EVA-6 obtained by fractionation according to CC. Hence, in this case, all the fractions (homogeneous in terms of CC) were configurationally inhomogeneous irrespective of CC.

Therefore, the limiting CC of EVA copolymers corresponds to CC of chain segments forming the amorphous phase, having the indicated temperature range of the relaxation transition.

As is evident from *Figure 4*, the CC of those chain segments (parts) is close to equimolar. Moreover, T_g values of different EVA fractions are situated between the T_g of the random copolymer of equimolar CC (−10°C) and that of the alternative copolymer (−40°C)[4]. Hence, it could be suggested that the chain segments (parts) which constitute the amorphous phase possess a tendency to alternation.

As far as the total content of VA units in EVA-6 and its fractions is less than the presumable CC of the copolymer chains forming the amorphous phase, chains or their segments of VA content lower than the overall CC have to exist. According to the above discussion, they should be chain segments (parts). Thus, the suggestion for the presence of chain parts of considerably lower VA content as compared to the overall CC allows us to explain the presence of the crystalline phase in EVA-6 and its fractions.

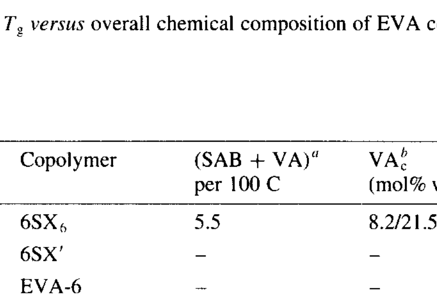

Figure 4 T_g *versus* overall chemical composition of EVA copolymers

As is evident from *Table 2*, in low-conversion and commercial high-conversion samples the crystalline phase disappeared in the range of about 15–20 mol% VA units. This practically corresponds to the range of chain defects content (including SABs present) leading to a total amorphization of LDPE.

In our samples, a crystalline phase was observed even in 6SA, where the VA content is 43 mol%. Moreover, T_m of EVA-6 and its high-molecular-weight fractions ($6SX_3$-6SX′) is approximately equal to that of commercial EVA copolymers, containing about 5 mol% VA units, the properties of which can be regarded as very close to LDPE. Hence, the well-known dependencies of T_m and W_c on the SAB content of LDPE[1] can be used in this case. It is known[1] that these dependencies correlate the thermodynamical parameters of melting with the number of chain defects in the case of the formation of folded-chain crystals.

It can be assumed that a low MW and/or a great number of chain defects (both SAB and VA branches) may result in the possibility of formation of extended chain crystals. This could be the case for the low-molecular-weight fractions of EVA-6. Then, the known dependencies of the thermodynamical parameters of melting of LDPE on the content of chain defects cannot be used.

Thus, the analysis of the studied characteristics of the relaxation and phase transitions in EVA-6 and its fractions allows the following model of the microstructure of the chain to be suggested. Three main fractions of different CC are present in EVA-6 (*Table 1*). Each copolymer chain of these fractions has two main parts whose CC is different from the overall CC of the whole chain. The CC in the first part is close to equimolar and the monomer units E and VA have a tendency to alternate. These parts of the different chains form the amorphous phase characterized by relaxation transition in the temperature range −36°– − 10°C and T_g of about −20°C. The second part of each chain has a CC allowing it to attend the formation of the crystalline phase. In fact, these are PE blocks of different lengths and various defect contents determining the phase transition characteristics (T_m and W_c) of EVA-6 and its fractions.

This model of the microstructure based on ^{13}C n.m.r. analysis has already suggested in our previous communication[13].

Now, we tried to estimate the model quantitatively in order to get additional confirmation. Using (a) the well-known dependence of T_m and W_c of LDPE on the defect

Table 3

No.	Copolymer	(SAB + VA)[a] per 100 C	VA_c^b (mol% wt%)	VA_a^c (mol% wt%)	W_c^d (wt%)	W_{cc}^e (wt%)	c/a[f] (wt%/wt%)	VA[g] (mol%)	VA_{exp} (mol%)
1	$6SX_6$	5.5	8.2/21.5	48–52/74–77	7.2	13	55/54	21–22	20
2	6SX′	–	–	–	6.7	13	52/48	22–23	23
3	EVA-6	–	–	–	7.4	15	57/43	20–21	24

[a] According to Wunderlich[1], the T_m value determined experimentally corresponds to the presence of 5.5 SAB (predominantly butyl branches) in LDPE which in our case corresponds to the sum of SAB and VA branches

[b] The chemical composition (VA content) of the parts of copolymer chains taking part in the crystalline phase formation (VA_c) was calculated as the difference between 5.5 and the actual SAB (butyl) content (determined by means of ^{1}H and ^{13}C n.m.r. spectroscopy) which amounted to 1.8 per 100 C atoms in the main chain. Thus, the estimated value of 3.7 VA branches per 100 C atoms in the main chain corresponds to 8.2 mol% (21.5 wt%) VA units

[c] The chemical composition of the parts of the copolymer chains, located in the amorphous phase of T_g about −20°C (VA_a) is close to equimolar. In the calculations the values of 48 and 52 mol% VA units were used

[d] W_c is the degree of crystallinity calculated, based on the experimentally determined enthalpy of melting and the weight of the sample

[e] According to Wunderlich[1], the presence of 5.5 SAB (1.8 SAB plus 3.7 VA branches) corresponds to W_c of about 13 wt%, which, in our case, corresponds to the degree of crystallinity of the parts of copolymer chains taking part in the crystalline phase formation (W_{cc})

[f] Percentages by weight of the parts of copolymer chains of chemical composition VA_c and VA_a; '*c*' and '*a*', respectively, were calculated considering that: $c(\mathrm{wt\%}) = W_c/W_{cc}$; $a(\mathrm{wt\%}) = 100 - c$

[g] The overall chemical composition was estimated as: $\mathrm{VA(wt\%)} = (VA_c \cdot c + VA_a \cdot a)/100$

content, (b) the number of SABs found in our previous work[13] and (c) the values of T_m and W_c of the high-molecular-weight EVA-6 fractions ($6SX_6$ and 6SX′) found experimentally in this work, we calculated the CC and weight percentage of the part of the polymer chains, 'c', taking part in the formation of the crystalline phase. Assuming that the other part of the polymer chains of a weight percentage 'a', taking part in the formation of the amorphous phase, has a CC close to the equimolar, we calculated the overall CC of the copolymer chains of the fractions $6SX_6$ and 6SX′, and of EVA-6 as well. Details of the calculations and the results obtained are presented in *Table 3*.

It is evident that the overall CC of the copolymer EVA-6 and its main fractions thus calculated correlates fairly well with the corresponding compositions determined experimentally by using several independent methods (i.r. and ^{1}H n.m.r. spectroscopy, elemental analysis)[13]. This is evidence for the correctness of the proposed model for the microstructure of EVA copolymer chains.

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