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The Transition in Ethylene Copolymers: The β-Transition

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Summary

The well-established data which gives a complex composition dependence for the relaxation of ethylene copolymers has been reexamined. Emphasis is placed on the β-transition. In the reanalysis of the data two new experimentally determined concepts are introduced. These are that this transition is definitely found in the homopolymer linear polyethylene, and that it is a reflection of segmental motions which take place within the interfacial region. With these principles it is possible to separate the β-transition from the glass temperature and thus explain the very unique composition relations.

Introduction

Linear and branched polyethylenes, and ethylene copolymers, display several transitions in addition to melting. In the order of decreasing temperature these have been conventionally designated as the α, β, and γ transitions. Furthermore, the glass temperature is very well defined for the high co-unit completely amorphous copolymers. The β-transitions in the branched polyethylenes, and in copolymers of low co-unit content have often been identified with the glass temperature (KLINE et al., 1956; McCRUM et al., 1967; BOYER, 1973b). When this identification is further related to the glass temperature of the completely amorphous copolymers rather unusual and heretofore inexplicable glass temperature-composition relations result (FLOCKE, 1962; MAURER, 1965; BALDWIN and VER STRATE, 1972). It has been explicitly pointed out that the interpretation of the β-transition in ethylene copolymers will be complicated by crystallinity (FLOCKE, 1962; BALDWIN and VER STRATE, 1972). Its interpretation as a kind of glass temperature is, therefore, not at all apparent or even correct. Recent carbon-13 nuclear magnetic resonance studies of the relaxation parameters of branched polyethylenes have shown that the average correlation time is on the order of 10^{-8} to 10^{-9} sec at the β-transition (DECHTER et al., 1982). These low values for the correlation time, and the fact that resolvable spectra could be obtained at temperatures corresponding, or very close to, the β-transition argue very strongly against this transition being assigned to the glass temperature.

Results and Discussion

In the present work we reanalyze the β-transition temperature-composition data that exists in the literature for a large number of ethylene type copolymers. We bring to bear on this problem the important recent finding that establishes a well-defined β-transition for linear polyethylene (POPLI et al., to be published). This transition has been identified with segmental motion that occurs within the interfacial regions associated with the lamellar crystallites. Its elusiveness, for the linear polymer, is also explained. This reference temperature, for pure polyethylene, together with the well-established glass temperatures of homopolymers of the respective co-units, allows for a consistent analysis and interpretation of the data for the linear and branched polyethylenes as well as the copolymers.

Data for the composition dependence of the β-transition temperature are available for ethylene-norbornene* (WILSON et al., 1974), ethylene-vinyl chloride (REDING et al., 1962), ethylene-vinyl acetate (NIELSEN, 1960; REDING et al., 1962), ethylene-butyl acrylate (REDING et al., 1962), ethylene-ethyl acrylate (REDING et al., 1962), ethylene-propylene (MANARESI and GIANNELLA, 1960; MAURER, 1965; BALDI et al., 1965; CLEGG et al., 1968), ethylene-butene (SHIRAYAMA et al., 1972), ethylene-hexene (SHIRAYAMA et al., 1972) copolymers and high-pressure polymerized branched polyethylene (TANAKA, 1960).

The transitions for these copolymers are plotted in Fig. 1 using the mole percent co-unit as the concentration basis. The β-relaxation temperature for pure linear polyethylene has been obtained from dynamic mechanical measurements at 3.5 Hz (POPLI et al., to be published). It is at -15 ± 5°C and is boldly marked in Fig. 1. The dashed line in the figure represents the equilibrium melting temperature-composition relation for random copolymers as calculated from theory (FLORY, 1949; FLORY, 1955). If co-units are excluded from the lattice on an equilibrium basis, then the melting temperature for random copolymers depends only on the copolymer composition and not on the chemical nature of the co-unit.

Data included in Fig. 1 has been obtained by a number of techniques. Mechanical measurements were used for the ethylene-norbornene, vinyl chloride, vinyl acetate, ethyl acrylate, butyl acrylate, butene and hexene copolymers. Dilatometry was used for ethylene-propylene copolymers and also for high pressure polymerized branched polyethylene (TANAKA, 1960). Heat capacity measurements were used for ethylene-propylene (CLEGG et al., 1968).

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*For norbornene concentrations of 38 and 53% by weight, two relaxations in the temperature range corresponding to that for the β-transition are observed. The higher of these is attributed to the onset of mobility corresponding to pairs of norbornenes separated by no more than a single ethylene unit. It therefore does not correspond to the β-transition of a random copolymer of ethylene-norbornene. Consequently the lower relaxation temperature is taken as the β-transition (WILSON et al., 1974)

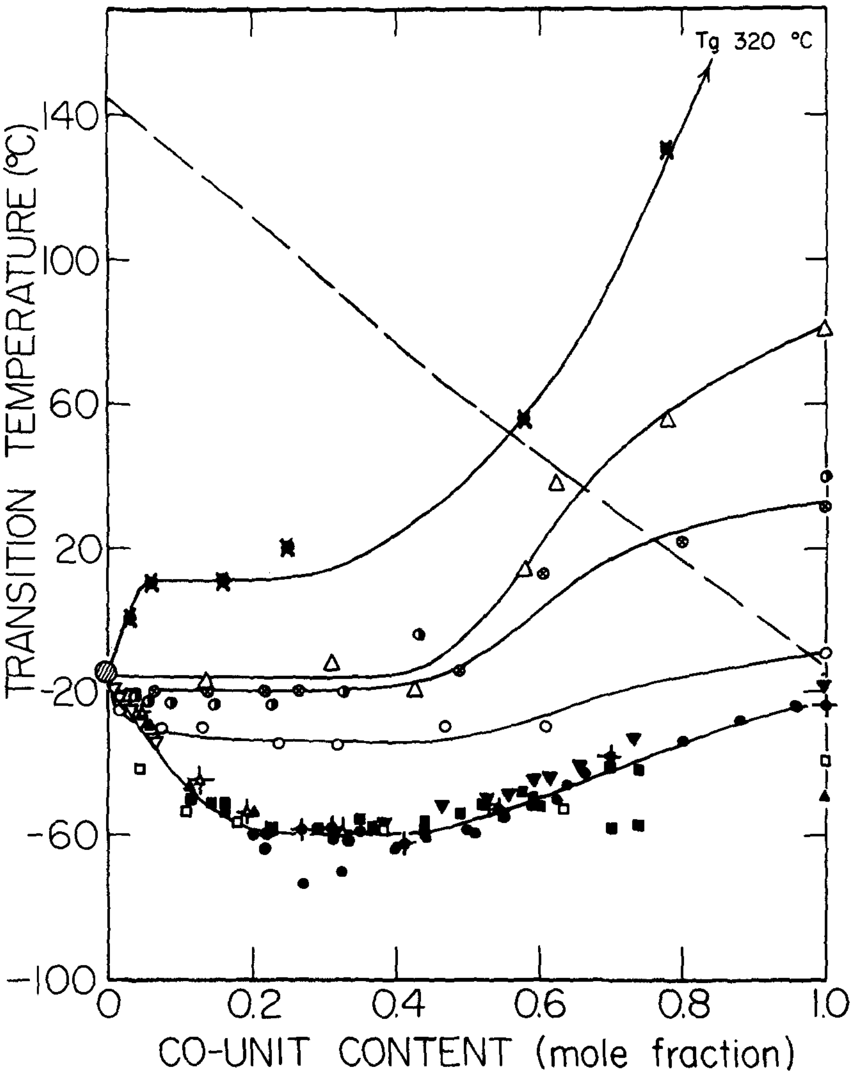

Figure 1: Transition temperature-composition relations for ethylene copolymers. Co-units: norbornene (✱); vinyl chloride (△); vinyl acetate (◐), (⊗); butyl acrylate (□); ethyl acrylate (○); propylene (▼), (■), (●), (✦); hexene (▲); butene (✧); high pressure polymerized branched polyethylene (▽). Linear polyethylene (◍). References cited in text.

Several rather interesting and important features can be found in Fig. 1 with respect to both the β-transition and the glass temperature of the copolymers.* The β-transition is only found in the composition range for which the copolymers are crystalline. Hence, as is seen in Fig. 1 it is always located below the equilibrium melting temperature. For a given type co-unit copolymer this transition temperature is invariant over a large range in copolymer composition. The range of this invariance is very dependent on the nature of the co-unit. It is smaller for the co-units where homopolymers have higher glass temperatures. The co-unit type also determines the temperature of the transition. For example, it is located in the vicinity of +20°C for norbornene copolymers as contrasted with -60°C for ethylene-propylene copolymers. The β-transition temperatures of the semi-crystalline copolymers are in the same order as the glass temperatures of the corresponding homopolymers formed from the co-units. As the co-unit content decreases (higher ethylene), then depending on the chemical type, the β-transition temperature either stays constant, increases or decreases. The straightforward explanation for this apparent divergent behavior, is that the β-transition for the pure linear polyethylene at -15 ± 5°C must be approached.

At higher co-unit concentrations, the transition temperature increases with a further increase in co-unit content. In this composition range, at the temperatures of interest, the copolymers are no longer crystalline. The glass temperature of the completely amorphous polymer formed by the pure co-unit is eventually reached.

The relaxation behavior of ethylene copolymers, that has been described and is illustrated in Fig. 1, can be explained by analysis of the structural features of semi-crystalline polymers and the molecular origin of the β-transition. Associated with the crystallites of semi-crystalline polymers is a diffuse, disordered interfacial region and a liquid-like region wherein the chain units connect crystallites (KITAMARU and HORI, 1978; MANDELKERN, 1979). The extent of the interfacial region is greatly enhanced by random copolymerization (STROBL and HAGEDORN, 1978; GLOTIN and MANDELKERN, 1982). The recent analysis of a large body of low frequency dynamic mechanical data has given strong support to the concept that the β-transition results from segmental motions within the interfacial region (POPLI et al., to be published). With these principles we can examine the apparently complex transition behavior of semi-crystalline ethylene copolymers that are illustrated in Fig. 1.

To aid in the explanation, we focus detailed attention on the transition temperature-composition relation for one copolymer, namely ethylene-vinyl acetate. The data for this copolymer are plotted in Fig. 2, and are taken from the work of Nielsen (NIELSEN, 1960) and typify the results for all random copolymers. There are three distinctly different transitions. The α-transition involves the relaxation of the

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*As has been previously indicated, and as will be further emphasized, a clear distinction must be made in the analysis between these two transitions.

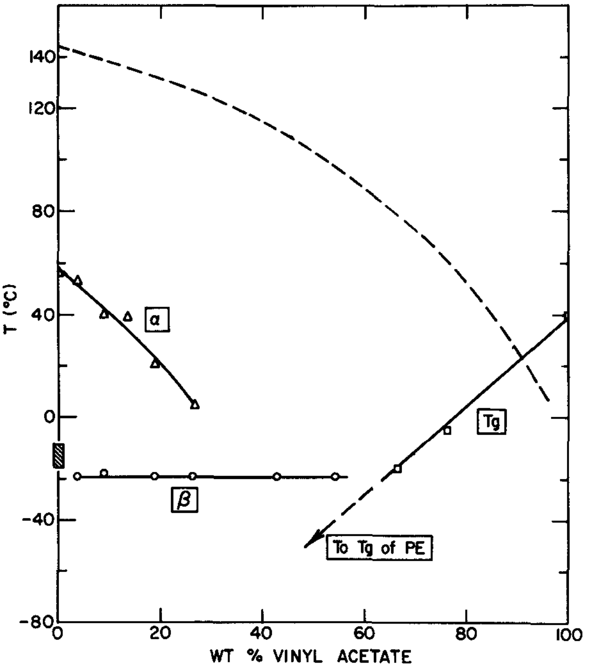

Figure 2: Transition temperature-composition relations for ethylene-vinyl acetate copolymers. Adapted from (NIELSEN, 1960).

crystalline sequences, which will not concern us here; the glass temperature T_g of the amorphous copolymers and homopolymers; and the β-transition which is only found in semicrystalline polymers. As has been pointed out previously crystallinity is a necessary, but not a sufficient condition for this transition to be observed (POPLI et al., to be published). The dashed curve again represents the equilibrium melting temperature-composition relation. The β-transition cannot exist for temperatures and compositions above this curve. However, since non-equilibrium conditions will invariably prevail the actual boundary will be lower. This transition obviously cannot exist over the complete copolymer composition range and must disappear abruptly. For ethylene-vinyl acetate copolymers this transition temperature is coincidentally the same as that for pure linear polyethylene.

In analyzing the data of Fig. 2 in more detail it is convenient to start with pure poly(vinyl acetate). The transition indicated at +40°C corresponds to the dynamic mechanically determined glass temperature T_g for this polymer. As ethylene units are initially introduced into the chain the copolymer remains amorphous. The glass temperature is reduced according to one of the standard relations (GORDON and TAYLOR, 1952; WOOD, 1958), and follows the indicated curve. If crystallization did not intervene, then as much higher concentrations of ethylene units were introduced the glass temperature of pure polyethylene would be approached. The detailed determination of this temperature is not of concern in the present work (STEHLING and MANDELKERN, 1970; DAVIS and EBY, 1973; BOYER, 1975). However, when the equilibrium melting curve is crossed the theoretical possibility begins to exist for crystallization to occur. Crystallinity will eventually take place at some kinetically favorable lower temperature for a given composition. Theoretically, crystallinity can develop in random copolymers at relatively high co-unit content even if found to be amorphous at ambient temperatures (FLORY, 1949; FLORY, 1955). For example, Nielsen found that a 43 weight percent ethylene-vinyl acetate copolymer had 8% cyrstallinity at 30°C. Associated with the crystallites is an interfacial region which is responsible for the β-transition.

The temperature of the β-transition for a given copolymer will thus have as an upper bound the intersection of the equilibrium melting temperature-composition and the glass temperature-composition curves. Since the former is independent of the chemical nature of the co-unit the location of the β-transition will be indirectly dependent on the glass temperature of the corresponding homopolymer. Thus, as is apparent in Fig. 1, copolymers with the highest T_g have the highest β-transition temperatures while conversely the low T_g's of poly(butene) and poly(propylene) yield the lowest transition temperatures.

For a given co-unit the β-transition remains invariant over a large composition range despite the fact that there are large changes in the relative proportion of non-crystalline material. However, the interfacial content does not change very much over this composition range. For example for ethylene-vinyl acetate copolymers over the range of 5% to 28% by weight of co-unit, the enthalpy determined level of crystallinity varies from 12 to 39%, while the interfacial content only changes from 16 to 21% (GLOTIN and MANDELKERN, 1982). Since the structural features of the interface are responsible for the β-relaxation, and these do not change, the observed invariance of the transition is to be expected.

For ethylene-vinyl acetate copolymers the co-unit content from Fig. 1 at which the transition deviates from constancy is slightly above 22 mole %. According to Nielsen (NIELSEN, 1960) crystallinity does not develop above 20 mole % vinyl acetate at room temperature. Thus we see the connection between the β-transition temperature and crystallization and the distinction between this transition and the glass temperature. It has been found that the disappearance of crystallinity in ethylene-propylene copolymers occurs at about 40 mole % propylene (MAURER, 1965; VER STRATE and WILCHINSKY, 1971). From Fig. 1, the β-transition temperature is constant up to about 45 mole % propylene. An increase in the transition temperature towards the glass temperature of polypropylene takes place at higher propylene content. This behavior is similar to that for ethylene-vinyl acetate copolymers and can be presumed to be true for the different copolymers.

The observations clearly distinguish between the β-transitions, which are characteristic of the semi-crystalline copolymers (and homopolymers), and the glass temperatures associated with the completely amorphous copolymers. The constancy of the β-transition temperature rules out it being some type of glass temperature which extrapolates to the value for the completely amorphous polymer (BOYER, 1973a). If this identification could be made, then changes in this transition with the large variation in the level of crystallinity would be expected.

Studies of the carbon-13 nmr relaxation parameters of the branched polyethylenes have made clear that the values for the correlation times do not allow the β-transition to be identified with a glass temperature. The correlation times corresponding to the β-transition are in the range of 10^{-8} to 10^{-9} sec. These values are much too small to be associated with the usual type glass temperature (DECHTER et al., 1982). Recent studies of ethylene-vinyl acetate copolymers (DEKMEZIAN et al., to be published) indicate similar motional characteristics for the methylene backbone carbons. However, the methine carbon of the branch point is a very much slower relaxing carbon in the vicinity of the β-transition. Its characteristic resonance virtually disappears in the vicinity of this transition. A high concentration of branches must be associated with the interfacial structure. Hence these observations are also consistent with the assignment of the β-transition to the interface.

If one is desirous of calling the β-transition some type of pseudo-glass temperature, it must be borne in mind that it is related to the segmental motions of disordered chains located in the interfacial region. It is not associated with an unrestrained completely amorphous polymer.

At higher ethylene contents, the β-transition temperature must approach that for pure linear polyethylene. Hence for vinyl acetate it will coincidentally remain constant; for norbornene copolymers it decreases while for propylene and related copolymers it increases. For the conventional high pressure polymerized branched polyethylenes the β-transitions are usually in the vicinity of -15°C. This reflects the fact that these polymers usually contain only 1-2 mole percent of branch groups. The main point is that the drastically different composition relations at low co-unit content is due to the fact that the transitions for the copolymers must eventually reach the established value for the linear homopolymer.

We have thus seen that the well-known and apparently complex transition temperature-composition relations for ethylene copolymers can be given a straightforward explanation by the adoption of certain principles. It must be recognized that a well-defined β-transition exists for linear polyethylene which is associated with relaxations within the interfacial region. To be observed there must be a sufficient interfacial content associated with the crystallites. Consequently such a transition will be found in the semi-crystalline copolymers and is essentially invariant with composition. It is distinct from the glass transition temperature associated with the liquid-like region which manifests itself in the completely amorphous polymers, and is dependent on copolymer composition. Thus two different relaxation processes are involved which is the reason for the unique composition relations that are observed. Similar phenomena should be observed with other crystalline copolymers when studied over the complete composition range.

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