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New Evidence for Liquid-Liquid Transitions in Polymers

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ABSTRACT

The morphology changes in polyethylene (PE) and polypropylene (PP) melts were studied by rheometrical and x-ray methods. The dependence of viscosity on temperature exhibits reproducible, characteristic inflections within given temperature ranges. Throughout the transition range the variation of viscosity of PE is slower than in adjacent regions. The temperature dependences of the position, height, and half-width of the x-ray amorphous peak also show inflections in the same temperature range as viscosity. However, while the position of the amorphous peak and therefore the distance between chains varies in the transition range slower than in adjacent regions, the half-width and height associated to short range order and molecular chain mobility, respectively, change faster in the transition range than outside it. This means that morphological transformations at the molecular chains level, occurring in the transition range, have to be assigned to an increase of the length of parallel packed chain segments, as well as to the faster decrease of the short range order. The variation of melt viscosity and melt density supports this interpretation. Similar results were obtained for PP melts.

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INTRODUCTION

The structure of melts of all chemical compounds, polymers included, is the focus of major interest in modern research. The crystals of various types melt and yield equally different liquids.

In order to describe melting, one has to know the structure of both phases. While there are fairly efficient x-ray methods of determining crystal structure, the study of the structure of melts is limited to only a few techniques.

The scarcity of data on melts is not limited to macromolecules but extends to substances with small molecules as well. The information available falls short of accounting for the amazingly diverse properties of melts. While the "pseudogas" model has been successfully employed close to the boiling point in most cases, at the melting point it has been impossible to select a "pseudocrystalline" model of wide applicability. The properties of melts close to the melting point are almost as diverse as those of crystals.

It turns out that with rising temperature in various types of melts, various types of structures transform into similar structures that may be described by the same model; the way individual transformations occur depends on the specifics of each initial structure. There is no reason to assume that transformation occurs uniformly throughout all temperature ranges. On the contrary, for strongly anisotropic molecules, such as macromolecules, one can observe some temperature ranges in which transformation is relatively uniform and others in which transformation occurs, to some extent, by jump. This assumption has been confirmed by many works which report nonuniform temperature dependence for most diverse properties of melts (electric, mechanical, acoustical, etc.). The existence of such nonuniformities in the evolution of melt properties has been demonstrated for n-alkanes and many amorphous and semicrystalline polymers [1-36]. This behavior suggests the existence of some "liquid-liquid transition" ($T_{\ell\ell}$). Although the results of investigations carried out by different techniques supports the existence of $T_{\ell\ell}$ transitions, their origin and the nature of the transformations associated with them is not completely clear.

From among the proposed explanations concerning the nature of $T_{\ell\ell}$ transitions, we shall consider briefly only the most important. For example, Boyer [32] analyzed PVT data and proved the transition temperatures ($T_{\ell\ell}$) and their pressure dependence in various amorphous polymers. He concluded that the transition at $1.1 \div 1.2 \times T_g$ is analogous to glass transition and has, to the same extent, a thermodynamic basis. They differ in the fact that $T_{\ell\ell}$ is weaker and more diffuse than but not different in kind from T_g. Other transition points were detected and assigned to some intramolecular nature.

Lobanov and Frenkel [30] studied the temperature dependence of the relaxation time of dipolar polarization (τ) of chain segments in amorphous polymer melts. The transitions occur at $T_{\ell\ell} \simeq T_g + 76°C$. They conclude that the transition is related to the sudden decrease in cooperative character of the thermal motion of chain segments within a narrow interval about $T_{\ell\ell}$, and that the liquid-liquid transition characteristic to polymers with elastic chains is a typically "behavioral"" one which occurs simultaneously at the level of macromolecules and of the melt.

By "cooperativeness" of motion one must understand that several monomeric units undergo a simultaneous, in phase, transition from one equilibrium state to another. After transition the kinetic unit is localized within the limits of the monomeric unit. The authors used the term "segment melting."

Krüger and co-workers [27] showed that the time dependence of sound velocity in polyethylene melts exhibits a change of slope at 60-110°C above the melting point. They assign this change to the transition from a "local nematic" state to an "isotropic" state and point out that it is not clearly established if there is a basic distinction between liquid-liquid transitions in amorphous and semicrystalline polymers.

Ovchinikov and co-workers [6] calculated the radial distribution curves of electron density from x-ray and electron diffraction data, and showed that in polyethylene melts there are regions within which the chains are extended and packed as parallel hexagonal structures. The size of these regions extends throughout at least 2-3 molecular layers, perpendicular to the molecular chains, and throughout ~50 Å along the molecular chains. With increasing temperature, the size of ordered domains decreases (short-range order diminishes).

These conclusions have been confirmed by the radial distribution functions of electron density obtained by Yeh [37] in amorphous polyethylene samples (irradiated with γ-rays) and in molten polyethylene; the size of the ordered regions are 25 and 20 Å, respectively. Because amorphization occurs by the introduction of defects into the crystal lattice, the paracrystalline structure model suits well-amorphized PE. Because the distribution curves for amorphous and molten polyethylene are very similar, the author advances the idea that the paracrystalline structure model may be employed for molten polyethylene. It is worth noting that the experimental data and the theoretical curve obtained for the paracrystalline model agree very well.

In a previous paper [35] we reported some data concerning the temperature dependence of the melt viscosity of different amorphous and crystalline polymers. Slope changes and discontinuities have been observed for most of the polymers studied. This contribution reports some of the results obtained by the x-ray diffraction technique.

EXPERIMENTAL

The flow curves have been determined in a broad temperature range using a capillary rheometer [35].

Use has been made of a DRON-2.0 diffractometer, for the x-ray studies, as has use of CuK_α radiation and graphite monocromator.

The high temperature cell was modified to allow temperature control within ±0.2°C and a temperature gradient on the sample below 0.1-0.3°C. The sample temperature was controlled within ±0.1°C. Rodlike samples (1.2 × 1.5 × 10 mm) were inserted into a special beryllium window cell. The reproducibility was poor for the first heating due to changes in the sample shape and dimensions on melting. For the following three runs the reproducibility of runs was within the statistical deviations determined by the number of pulses recorded at each run. This deviation was maintained within ±0.3%. The runs were restricted to a minimum number of points to allow determination of maximum intensity, half width, and position of the amorphous maximum. The duration of runs was planned to ensure that the intensity drop due to the "dreif" effect could be practically compensated for by the increase of intensity due to absorption in the atmosphere caused by the increase of temperature.

RESULTS AND DISCUSSION

The temperature dependence of viscosity in HDPE, LDPE, and PP exhibits inflections (Figs. 1-4). The inflections and slope changes are reproducible. For PE they lie within a temperature range which coincides with that reported by Krüger from Brillouin spectroscopy [27]. Our conclusion is that a liquid-liquid transition is involved and that the melt flow undergoes changes in this range.

We first studied the behavior of molten HDPE. HDPE-1 ($\overline{M}_w$ = 74,690 and $\overline{M}_w/\overline{M}_n$ = 7.53) was selected because the slope changes are more evident (Fig. 1). It is seen that there is a transition range, not a transition temperature, and the viscosity decreases steeply up to and beyond the transition range and slowly within the transition range.

If the transition were due to a loss in cooperativeness of segment motion, a transition from the "local nematic" structure to an "isotropic" structure or a decrease of short range order, only one slope change would be expected from a moderate to a steeper decrease of viscosity.

The attempt to study the pressure dependence of the transition temperature with capillaries of different lengths and diameters have evidenced a shift toward lower temperatures caused by increasing pressure [35], while the data reported in the literature for amorphous polymers indicate an increase of transition temperature with pressure.

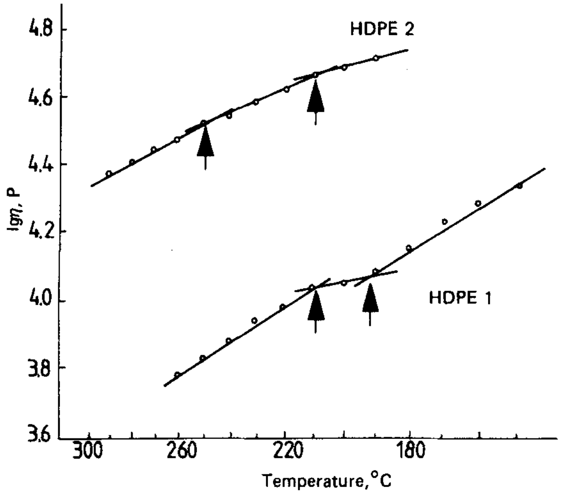

FIG. 1. Temperature dependence of viscosity of two HDPE samples at constant shear rate ($\dot{\gamma}$ = 10 s^{-1}).

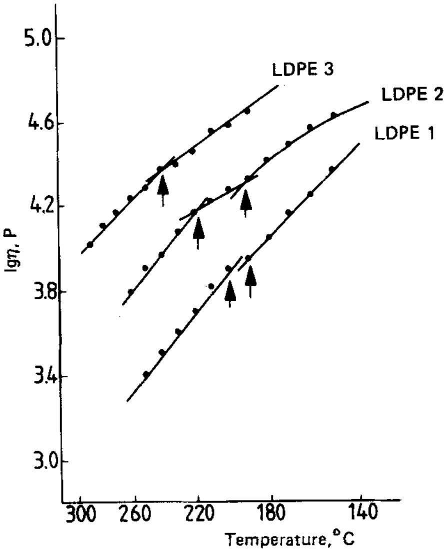

FIG. 2. Temperature dependence of viscosity of three LDPE samples at constant shear rate ($\dot{\gamma}$ = 10 s^{-1}).

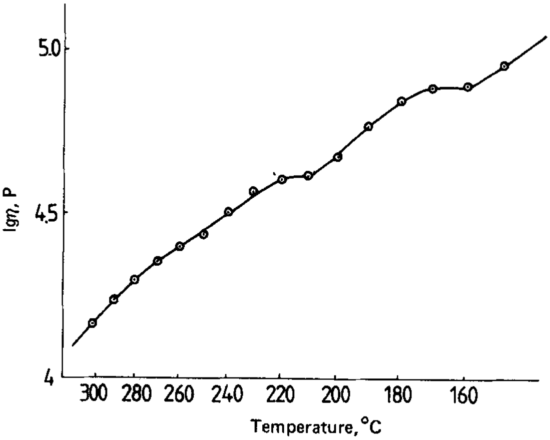

FIG. 3. Temperature dependence of viscosity of a HDPE/LDPE blend at constant shear rate ($\dot{\gamma}$ = 10 s^{-1}).

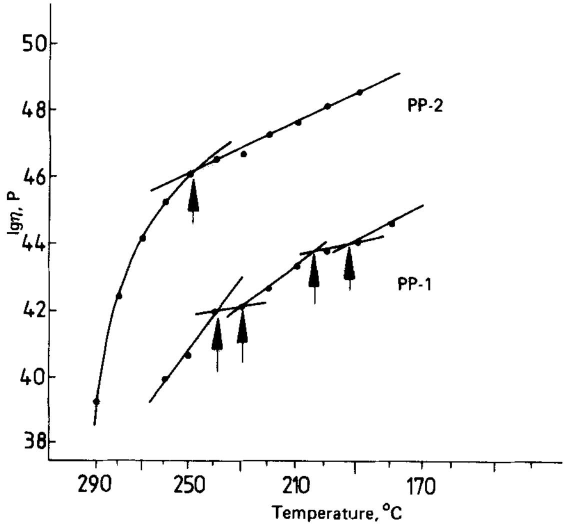

FIG. 4. Temperature dependence of viscosity of two PP samples at constant shear rate ($\dot{\gamma}$ = 10 s^{-1}).

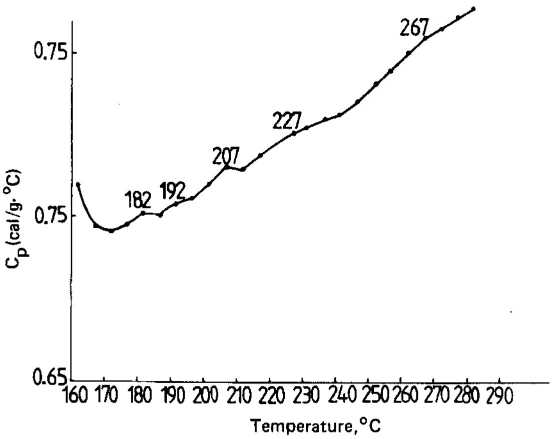

FIG. 5. Specific heat as a function of temperature for HDPE-1 (DSC data).

Since the data we report were obtained under dynamic conditions during the flow of molten polymer through capillaries and the capillary geometry may alter the flow mechanism, we suggest that the transition we evidenced may be regarded as different from that reported elsewhere for amorphous polymers.

The DSC thermograms, recorded at low heating rates (0.5°C/min) (Fig. 5), indicate modification of the heat capacity in the same temperature range as the viscosity modification, but these modifications did not give us additional information.

It is assumed that x-ray diffraction allows the detection and understanding (even partial) of the structure modification taking place in this temperature range.

The results obtained by x-ray diffraction are as follows:

The integrated intensity of the maximum (I) decreases with an increase of temperature (Fig. 6).

The halfwidth (β) increases with temperature, with an inflection within the transition range (180-220°C) (Fig. 7).

The 2θ angle corresponding to the position of the maximum decreases with temperature with an inflection in the quoted temperature range (Fig. 8).

An attempt to draw a straight line through all points resulted in a deviation of points about three times the reproducibility of the runs, so it is affirmed that the inflection observed has a physical significance and is related to a structural change in the melt.

The straight line segments drawn through the experimental points

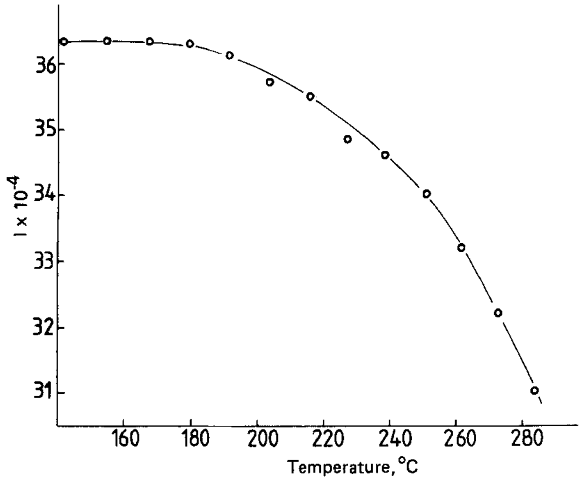

FIG. 6. Integrated intensity of the x-ray diffraction maximum as a function of temperature for HDPE-1.

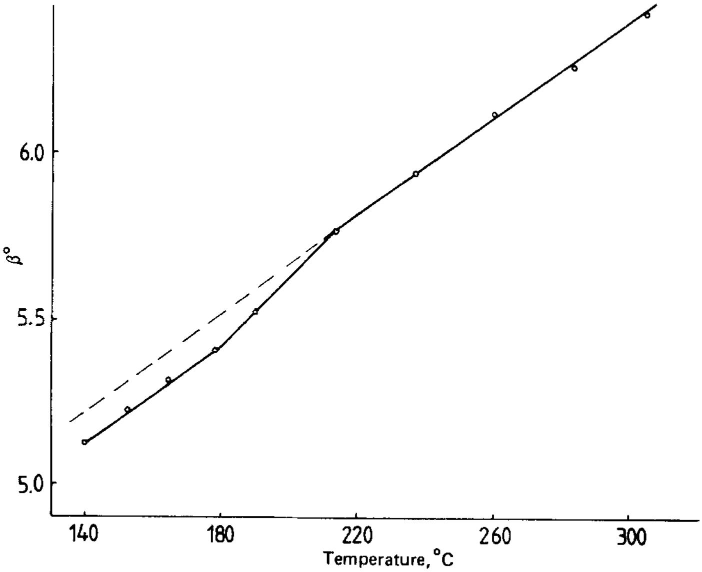

FIG. 7. The dependence of halfwidth of diffraction maximum on temperature for HDPE-1.

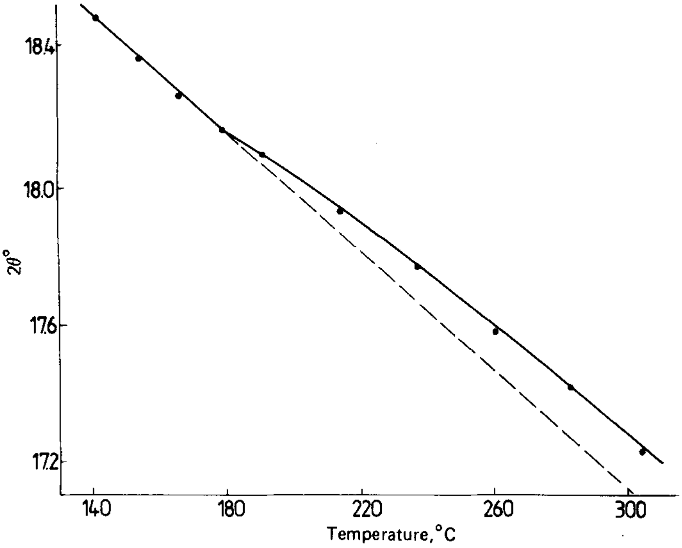

FIG. 8. The dependence of 2θ angle on temperature for HDPE-1.

do not mean that the dependence is linear in these temperature ranges; they are only intended to emphasize the inflection in the transition range. It is now worth focusing on the correlation between the parameters measured and the structure of the melt.

The location of the 2θ maximum may be correlated with the mean distance between macromolecular chains.

The d_{R-am} distance, calculated by the Bragg equation (d_{R-am} = $\lambda/(2 \sin \theta)$) on the basis of 2θ values, is proportional to the mean distance, d_M, between macromolecules. While the values of the proportionality coefficients and the absolute value of d_M, respectively, are still under discussion, the variation of d_M with temperature accurately describes the variation of the distance between macromolecules with temperature. In agreement with expectations, d_{R-am} exhibits an inflection as well (Fig. 9), which is also sensed by d_M (Fig. 10), indicating a slower increase of the distance between macromolecules as a function of temperature in the transition range. This observation correlates perfectly with the behavior of melt viscosity and indicates that the melt density has to have an inflection in this temperature range. Indeed, according to Fig. 11, the temperature dependence of the melt density shows an inflection in the same temperature range [35]. The density ρ_x, calculated on the basis of x-ray data (d_M) by

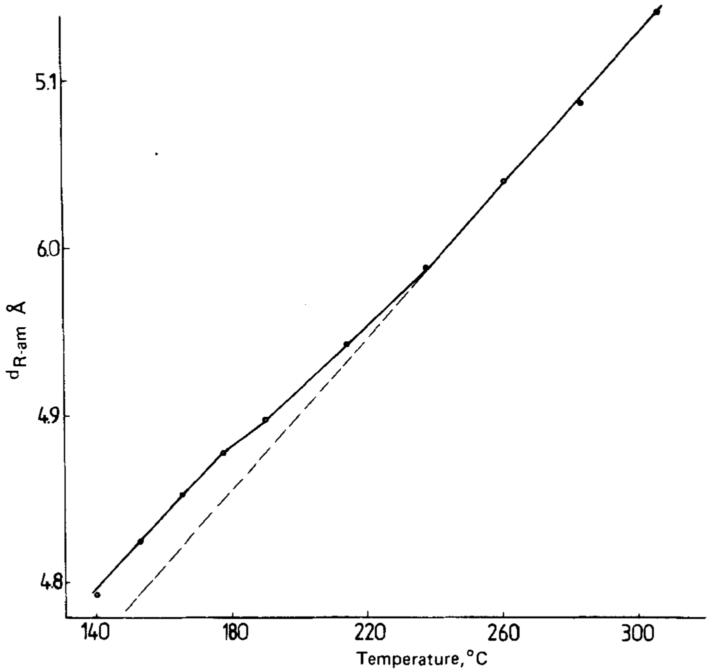

FIG. 9. Variation of $d_{R\text{-am}}$ distance with temperature for HDPE-1.

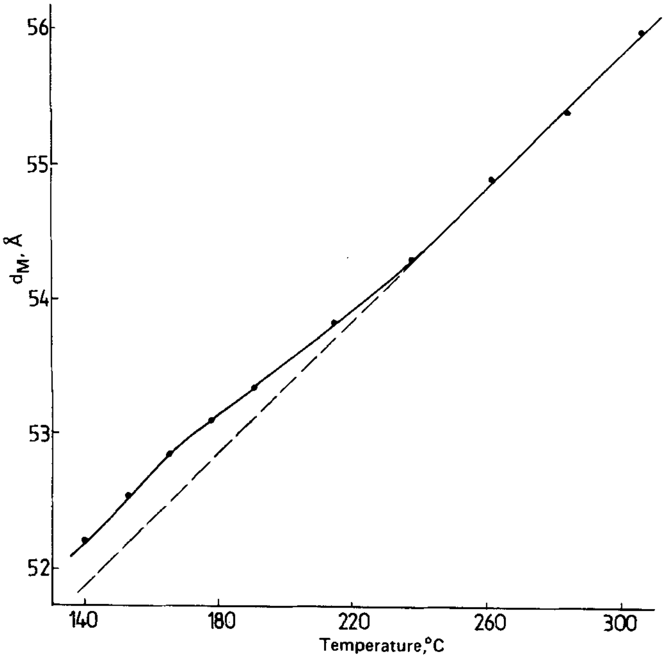

FIG. 10. Variation of d_M with temperature for HDPE-1

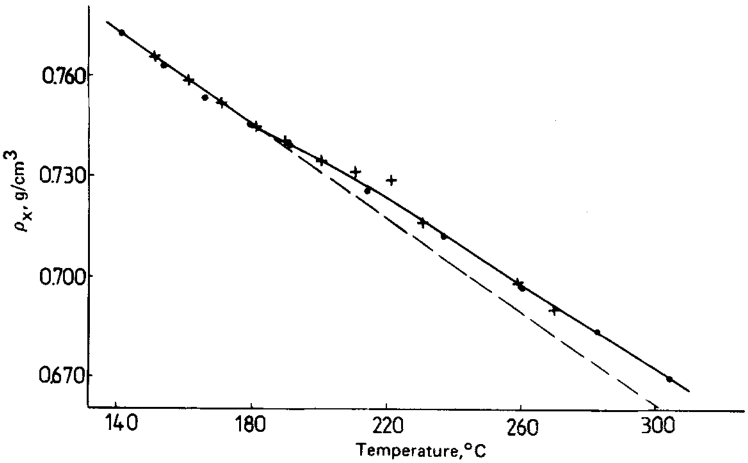

FIG. 11. Melt density as a function of temperature for HDPE-1 (+, experimental; ● , calculated ρ_x).

considering the molecular chains packed in a hexagonal structure and neglecting expansion along the molecular chains, yields a curve whose experimental values are fairly close.

If one now calculates the size of the regions that scatter x-rays coherently in terms of short-range order and paracrystalline network (by the Scherrer equation, $D = k\lambda/(\beta \cos \theta)$, and making use of the halfwidth of the diffraction maximum, β) one obtains dimensions of about 15 Å, which is close to the values obtained for short-range order from the radial distribution curves of electron density (~20 Å). It turns out that the variation of halfwidth, β, is mainly related to the variation of short-range order, and therefore the variation of parameter D directly reflects the variation of short-range order. Figure 12 shows that while the distance between chains increases slowly in the transition range, the short-range order (D) decreases faster. The present representation of the kinetic nature of the liquid-liquid transition cannot explain such a variation of the two parameters. The integrated intensity of the maximum also decreases faster in the transition range and after that (Fig. 6); this has to be understood as a decrease of the size of the coherently scattering domains, a decrease of the "harmonicity" of molecular chain motion. Interesting comments regarding the decrease of the intensity of x-ray amorphous maximum of HDPE with temperature were published by Maeda and co-workers [38]. These authors studied the change of structure with temperature and pressure and found that in the 150-400 MPa range, where crystals with partially extended chains form on cooling, the amorphous peak of the melt is much lower than at pressures below 150 MPa, where crys-

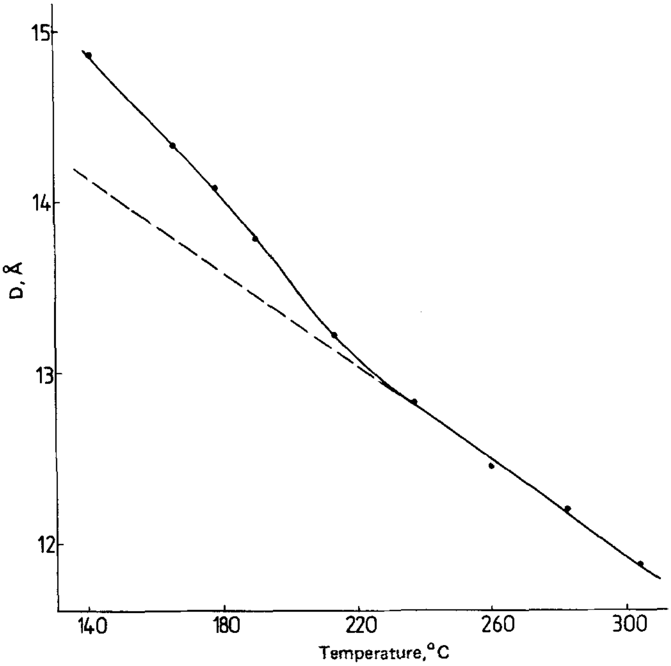

FIG. 12. Variation of the parameter D with temperature for HDPE-1.

TABLE 1

	T_m, °C[a]		
P, MPa	A	B	C
150	172	-	-
320	190	207	-
350	210	216	-
400	-	226	227
450	-	234	236
480	-	237	243
500	-	243	249

[a] A = Folded chain crystals (orthorombic).
B = Extended chain crystals (orthorombic).
C = Extended chain crystals (hexagonal).

tals with folded chains are formed. If pressure exceeds 350-400 MPa, wholly extended chain hexagonal crystals are formed, which on further cooling turn to regular orthorombic crystals and the amorphous peak of the melt disappears (Table 1). Formation of a hexagonal structure is proof of the increased freedom of rotation of macromolecular chains about their axes. This entails a decrease of "cooperativeness" of thermal motion and consequently a decrease of the intensity of the amorphous peak.

Therefore, we think that the essence of the structural transformation of molecular chains in the transition range should be understood as an increase of length of parallel packed chain segments and a decrease of short-range order.

The data suggest that before the transition the response to thermal strain is an increase in amplitude of thermal oscillations with a corresponding increase of the average distance between chains; after transition the response consists mainly of an increase of energy of rotation about chains that entails an increase in the length of parallel packed segments and a decrease of the "harmonicity" of their motion.

Similar results have been obtained for HDPE/LDPE blends (Figs. 13-17).

The x-ray study of PP also revealed the existence of the transition (Figs. 18-20), located in the same temperature range as indicated by viscosity measurements (Fig. 4). The data may be correlated with high pressure DTA data [39]. Thus it was shown that a shift of PP melting temperature to 230-240°C, caused by pressure, yields the γ-crystalline form instead of the regular α-form. This confirms that within this temperature range a modification of chain conformations occurs.

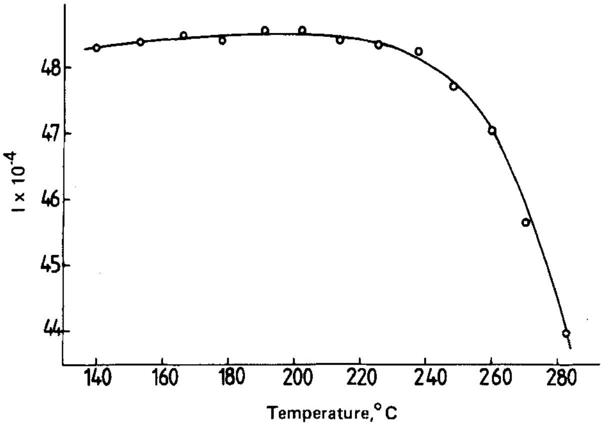

FIG. 13. Integrated intensity of the x-ray diffraction maximum as a function of temperature for HDPE/LDPE blend.

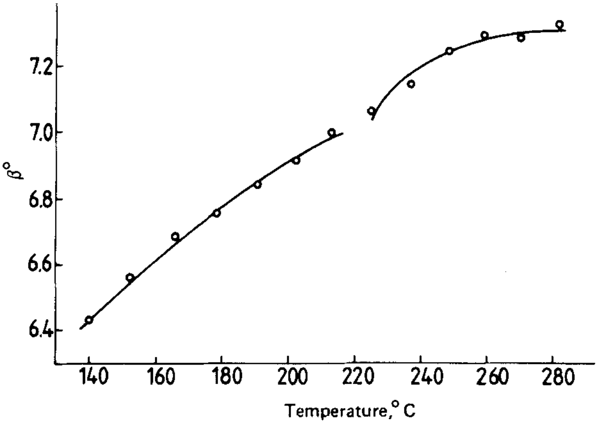

FIG. 14. The dependence of halfwidth of diffraction maximum on temperature for HDPE/LDPE blend.

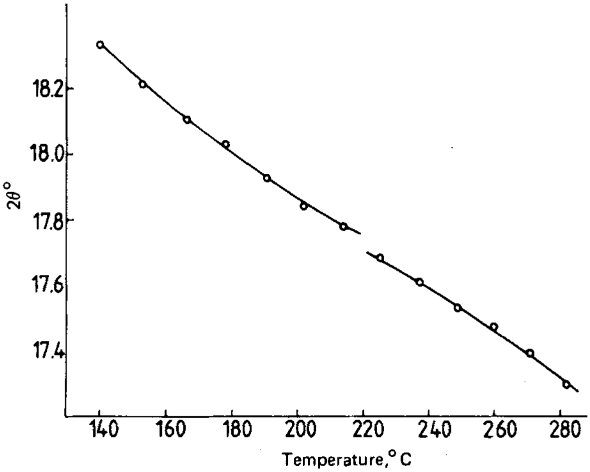

FIG. 15. The dependence of 2θ angle on temperature for HDPE/LDPE blend.

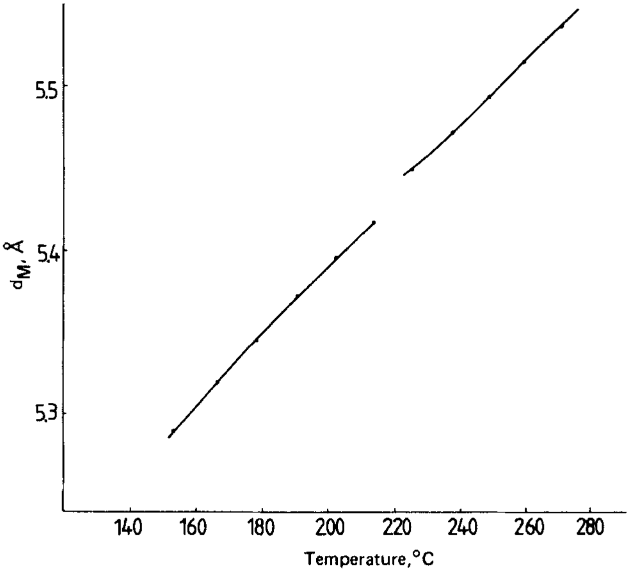

FIG. 16. Variation of d_M with temperature for HDPE/LDPE blend.

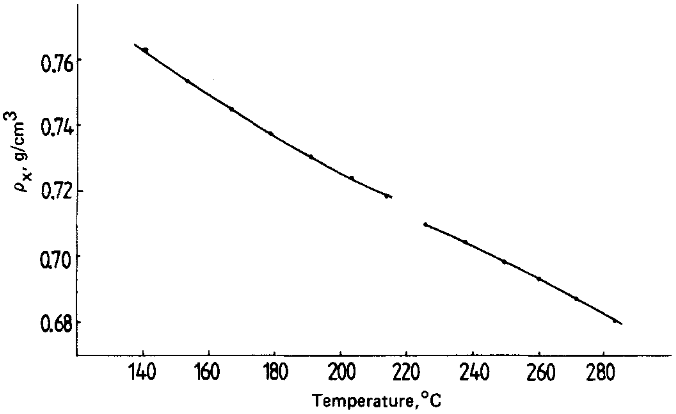

FIG. 17. Calculated melt density as a function of temperature for HDPE/LDPE blend.

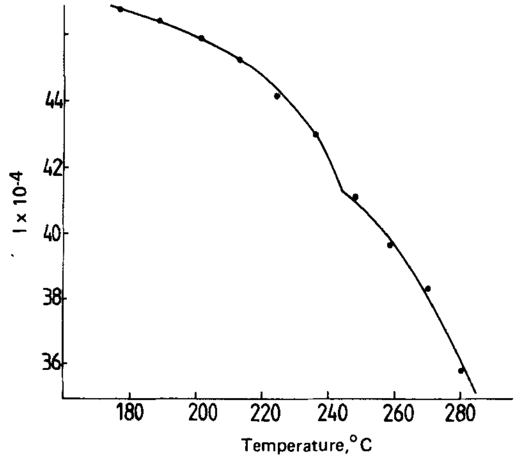

FIG. 18. Integrated intensity of the x-ray diffraction maximum as a function of temperature for PP-2.

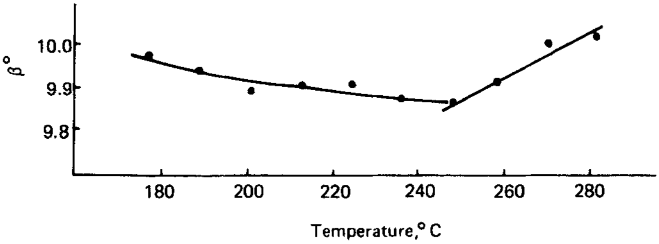

FIG. 19. The dependence of halfwidth of diffraction maximum on temperature for PP-2.

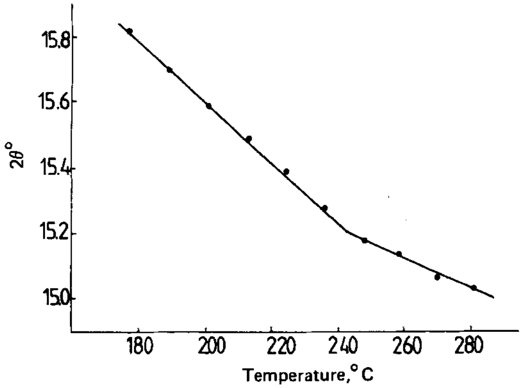

FIG. 20. The dependence of 2θ angle on temperature for PP-2.

It is worth noting that from our x-ray data in PP the halfwidth β is about twice that in PE, while the short-range order parameter, D, is about one-half that in PE. In other words, the interaction between molecular chains is weaker, which correlates with the markedly lower viscosity of PP compared to PE at the same chain lengths.

CONCLUSIONS

The nonuniform dependence of polymer melt properties on temperature was confirmed.

It was shown that in PE and PP the transition studied is related to the morphologic modifications of molecular chains. The increase of temperature causes structural units (atoms, groups of atoms, chain segments of different length, etc.) to participate in various types of motions: vibrations, oscillations, rotations, etc. The onset of each new motion brings about more or less extensive changes of conformations and melt properties.

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