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Changes in the phase structure of the polyethylenes after long-time storage at room temperature

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Summary

The long-time crystallization of a set of polyethylenes, that have a variety of different molecular structures, has been studied under storage conditions well removed from those where partial melting or relatively rapid crystallization takes place. For high molecular weight linear polyethylenes, branched polyethylenes and ethylene copolymers a density increase of about 5% is observed. However, analysis of the Raman internal modes indicates that the core crystallinity remains constant. It is found that the density change reflects an increase in the partially ordered interfacial region at the expense of the disordered liquid-like region.

Introduction

The isothermal crystallization of polymers from the pure melt has been established as a well defined kinetic process. Usually, after crystallization has been initiated, most of the transformation takes place at an accelerated rate in a narrow time interval when based on a logarithmic scale. Certain situations are known, however, where further crystallinity develops, or changes in the crystallinity level and structure can be induced. After the major portion of the crystallinity has developed a tail portion persists where very small but perceptible amounts of crystallization continue to occur over very long times (1) - (3). This part of the process has been very often termed secondary crystallization. It has been shown that for linear polyethylene a significant crystallite thickening process also takes place isothermally in this flat region of the kinetic isotherm (4). In another example, when a well developed crystalline system, formed from either the bulk or dilute solution, is brought to a temperature not far removed from the melting temperature, i.e. annealed, an increase in the crystallinity level and long-period is observed (5)(6). This type of annealing involves a partial melting-recrystallization process. (7)

The two situations that have been described involve changes in the crystallinity level and phase structure at temperatures in the vicinity of the melting temperature. Studies of any changes that might take place in crystallinity level, or phase structure, for samples rapidly crystallized from the melt (quenched) and then maintained at temperatures far removed from the melting temperature, have not as yet been reported or discussed.

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Recently a more comprehensive understanding of the phase structure of semi-crystalline polymers has evolved (8)(9). Concurrently, several new experimental techniques have been developed that quantify the different structural elements that are involved (8)(10)-(12). Hence, it appeared opportune to examine quantitatively the long-time crystallization of polymers under storage conditions well removed from those of partial melting or relatively rapid crystallization rates. For this purpose we have directed our attention to a set of polyethylenes that have a variety of different molecular structures. The changes that occurred in the phase structure were monitored by density and Raman internal mode measurements.

Experimental

Materials. The molecular characteristics of the different polyethylenes used in this work are listed in Table I. Samples A, B and C are commercial, unfractionated linear polyethylenes having widely different molecular weights and molecular weight distributions. Samples D and E are commercial polyethylenes that were free-radically polymerized under high pressure. Therefore, these polymers contain both short and long chain branches whose concentrations are also indicated in the Table. Sample P108 is a hydrogenated polybutadiene of narrow molecular weight and composition distribution that was obtained from the Phillips Petroleum Co. It can be considered to be a copolymer with randomly distributed ethyl branches. (13)

Procedures. Sheets, 5 x 5 cm square, and approximately 250 µm thick were molded in a Carver press at 160°C and quenched rapidly into a 2-propanol bath at -78°C. The samples were then stored at ambient temperature and periodically tested. The densities were measured at 23°C in a 2-propanol-triethylene glycol density gradient column calibrated with standard glass floats (14). The sensitivity of the column was about 0.0001 g/cm^3 per mm. The density was measured in at least two portions of the same specimen. The measured density was converted to the degree of crystallinity by means of the relation given by Chiang and Flory (15). The Raman spectra in the internal mode region were obtained using a SPEX 1430 spectrometer with two planar holographic gratings. The incident radiation was the 514.5 source of a Spectra - Physics model 165 Ar$^+$ Laser. The laser power varied between 100 and 200 mW. The detailed analysis of the data has been described previously (8)(16).

Results and Discussion

The structural changes were analyzed by periodically measuring the density and the Raman internal modes of these samples for about 392 days as is indicated in Table I. The Raman spectra yield the fraction of core crystallinity, α_c, the fraction of liquid-like region, α_a, and the fraction of the interfacial region, α_b (8)(16). It has been found that for a very large number of polyethylene systems that have been studied the core crystallinity, α_c, is very close to the level of crystallinity $(1-\lambda)_{\Delta H}$ that is determined from enthalpy of fusion measurements (9), i.e.

$$\alpha_c \equiv (1\text{-}\lambda)_{\Delta H} \qquad (1)$$

It has also been established that the level of crystallinity determined from the density, $(1\text{-}\lambda)_d$ is always greater than α_c (or $(1\text{-}\lambda)_{\Delta H}$). Based on a large amount of experimental data (8)(9), $(1\text{-}\lambda)_d$ can be quantitatively expressed as

$$(1\text{-}\lambda)_d \equiv \alpha_c + \alpha_b \qquad (2)$$

Thus the density determined level of crystallinity measures the core crystallinity as well as the contribution from the interfacial region. It is thus a significantly different quantity than $(1\text{-}\lambda)_{\Delta H}$.

The ranges in the density, as well as the liquid-like, interfacial and crystalline contents of the samples studied are given in the last four columns of Table I for the time period studied. Small but significant changes are observed in all but one sample. As can be seen in what follows, these data can be analyzed in a systematic manner. We consider first the three linear polyethylene samples. The lowest molecular weight, sample A, shows essentially no change over this time period. However, the two high molecular weight samples, B and C, do indicate significant changes in the density and the quantities derived from the internal modes. Taking polymer C, which has a very high molecular weight and broad distribution as an example we find a very steep increase in the density with storage time as is illustrated in Figure 1a. The accompanying changes in phase structure, as were deduced from analysis of the Raman internal modes, are given in Figure 1b. The samples were analyzed over a one year time period. We find that the fraction of core crystallinity, α_c, remains very constant over this time period. On the other hand, the fraction of the liquid-like region, α_a, systematically decreases from 0.48 to 0.41. This decrease in α_a, is compensated by a corresponding increase in the fraction of the interfacial region from 0.11 to 0.20. Most of the changes that were observed take place in the first 10 days. However, an increase in the density was observed over a longer period of time. Similar structural changes were found for sample B over the same period of time. For this polymer, α_a, decreases from 0.48 to 0.42 and the crystalline content remains basically constant, α_c = 0.40. Therefore the interfacial content increases to compensate for the decrease of the amorphous part. An increase in density was also observed in sample B although the experimental data are more scattered than in sample C.

Table I. Molecular Weights and Total Structural Changes

						[c]		
Sample	M_W	M_W/M_N	Mol % Branch Pts.	Time [a] (days)	Density [b] (g/cm^3)	α_a	α_b	α_c
A	150000	12.5	-	392	0.9521/ 0.9531	34/33	16/16	50/51
B	2 x 10^6 (M_V)	-	-	392	0.9274/ 0.9285	48/42	12/19	40/39
C	8 x 10^6 (M_v)	-	-	392	0.9260/ 0.9310	48/41	11/20	41/40
D	150000	6.6	0.7	30	0.9201/ 0.9220	48/43	13/18	39/38
E	950000	57	1.6	30	0.9118/ 0.9133	57/55	14/17	29/28
F	108000	1.3	2.2	392	0.8997/ 0.9052	68/55	10/22	22/23

(a) total time at which the samples were periodically tested

(b) total density change during above time period

(c) total structural change during above time period expressed in percent

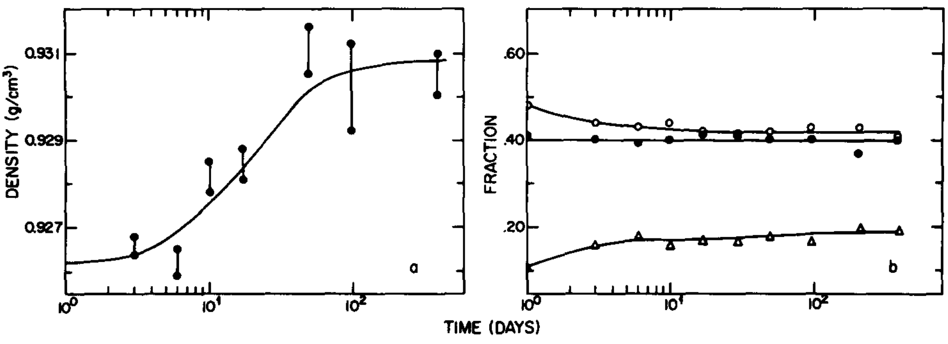

Figure 1 (a) Plot of variation of density with time after storage of sample C at room temperature. (b) Plot of variation in the liquid-like (o), crystalline (●) and interfacial content (Δ) with time for the same sample.

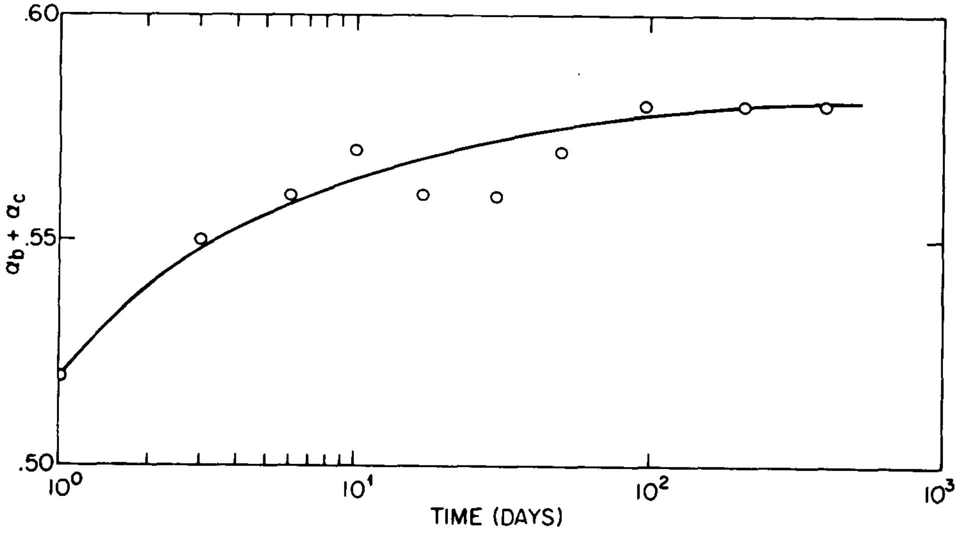

Figure 2 Plot of the variation of α_b + α_c, equivalent to the level of crystallinity derived from density, with time for sample B.

The change in $\alpha_b + \alpha_c$, equivalent to the level of crystallinity derived from density, is given in Figure 2 for sample B. Interestingly, we find the rather surprising result that the density increase does not in fact reflect a corresponding increase in the level of crystallinity since the core crystallinity remains constant. Rather, the changes in the phase structure reflect the further development of the partially ordered interfacial region with time at the expense of the liquid-like region. Thus, the density increase only reflects the increased proportion of interfacial region that develops over time.

A similar analysis was made of the branched polymers. The results for sample D, a high pressure free-radical polyethylene, are given in Figures 3a and 3b. The trends in Figure 3 are very similar to those described in Figure 1 for the linear polymers. Changes were followed in a shorter period of time in these samples. However, it is clear that most of the transformation occurs in the first few days after quenching.

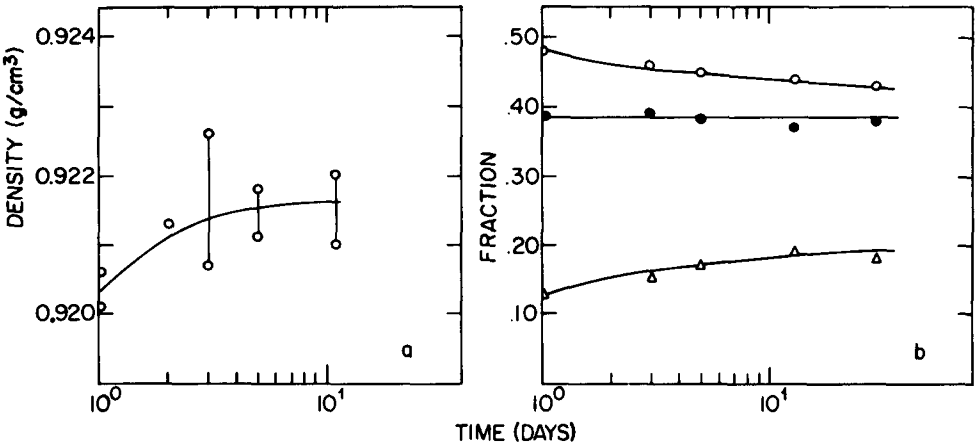

Figure 3 (a) Plot of the variation of density with time after storage of sample D at room temperature. (b) Plot of the changes of the liquid-like (o), crystalline (●) and interfacial content (Δ) with time for the same sample.

The results for sample F, the random copolymer with only ethyl branches and a higher branch content than samples D and E, are indicated in Figures 4a and 4b. The changes that are observed follow a pattern that is similar to those reported for the other polymers. On a density basis the level of crystallinity appears to increase from 0.35 to 0.39 over the 390 days of observation. Again, this apparent change in the level of crystallinity is not reflected in the core crystallinity which remains constant at $\alpha_c = 0.23$. We note once again the significant difference between $(1-\lambda)_d$ and α_c which is typical of random copolymers (13) (17). However, in contrast, the fraction liquid-like region substantially decreases from 0.68 to 0.56. There is a concomitant increase in the fraction of the interfacial region. Thus, the changes in the phase structure with time in the random copolymer, the high pressure branched polyethylenes and the high molecular weight homopolymers are very similar to one another.

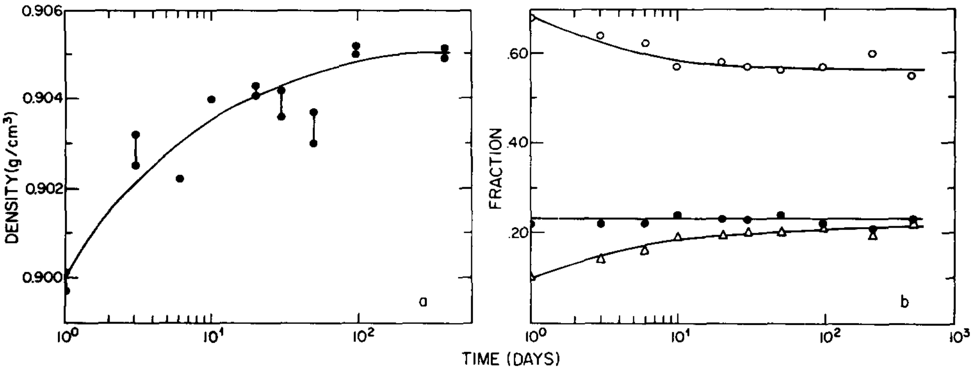

Figure 4 (a) Plot of the variation of density with time after storage of sample F at room temperature. (b) Plot of the changes in the liquid-like (o), crystalline (●) and interfacial content (Δ) with time for the same sample.

The major conclusion that is reached from this work is that during the storage of the polyethylenes at room temperature, a temperature that is well removed from the melting point and crystallization region, the core crystallinity does not change with time. In contrast, the changes in density would appear to indicate an increase in the crystallinity level over the same time period. However, in fact what actually happens is that the fraction of the partially ordered interfacial region increases at the expense of the completely disordered liquid-like region. This process, which occurs at relatively low temperatures, is quite different from annealing at elevated temperatures where partial melting and recrystallization take place. These changes in phase structure, over long periods at ambient temperature, would be expected to influence many macroscopic properties. The reality of this expectation is currently being investigated.

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