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Relationship between the Relaxation of Polyethylene Coils in the Melt and the Molecular Weight Distribution. 1. Crystallization Measurements

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ABSTRACT: We have shown recently that the correlation between the semicrystalline state and the melt of polymers permits, by appropriate annealing and quenching experiments, measurement of the relaxation time of the polymer coils in the molten state. In this article we show that in polyethylene this time is given by the law $\tau = M_n^3$, where M_n is the number-average molecular weight. This time is found to be of the order of magnitude of the stress relaxation time measured by de Vries and Tochon on similar samples and 3 orders of magnitude greater than the reptation time measured by Klein.

Introduction

It has been shown recently[1,2] that in polyethylene quenched from the melt the long period of the lamellar structure is given by the weight average of the end-to-end distance according to the relationship

$$L = r_w^* = \sum w_i M_i^{1/2} + \sum w_j M^{*1/2} \qquad (1)$$

where w_i and w_j are the weight fractions of species having molecular weight M_i and M_j.

In high molecular weight materials the long chains of mass $M_i > M^* = 10^5$ can be visualized as a series of individual chains of mass M^* which crystallize independently.

In low molecular weight $M_i < 10^5$ the long period is given by the first term of eq 1, that is to say, by the moment $(+{}^1/_2)$ of the distribution function of the molecular weight.

In general, this average in polydisperse materials is not known; only well-known are the weight- and number-average molecular weights M_n and M_w, which are, respectively, the moments −1 and +1 of the distribution function. In ref 1, the long periods of polydisperse polyethylene (PE) of various molecular weight distributions were measured. It has been shown that there is no general law between L and M_w but that for low molecular weight material, L can be expressed as a function of M_n according to the relation

$$L \cong M_n^{1/2} \qquad \text{for } M_n < 10^5 \qquad (2)$$

regardless of the value of M_w. In that case it can be concluded that the long period is given principally by the end-to-end distance r of the coils having the molecular weight M_n. The relationship $L \sim r$ explains the dependence of the long period with the melt temperature and the time of annealing. When the time of annealing in the melt state is long enough, the coils reach their equilibrium size, which is a function of the temperature. In that case the variation of dL/dT is equal to dr/dT and permits the calculation of the Flory coefficient β of the polymer chain in the melt.[3]

It is obvious that if the time of annealing is not long enough, the dimension of the coils is dependent not only on the temperature but also on the previous temperature and time of annealing; therefore the long periods in quenched material are also dependent on the melt history.[4]

The procedure depicted in Figure 1 allows the measurement of the time 2τ for erasing the thermal history of a melt.

For the two melt states 1 and 2 at temperatures T_1 and T_2 during the times t_1 and t_2, the equilibrium end-to-end distances are r_1 and r_2 and the long periods of the materials subsequently quenched to liquid nitrogen are L_1 and L_2. The melt at T_1 is then quenched to the temperature T_2 and held at that temperature during a time t and then quenched to liquid nitrogen temperature. The long period measured, L, presents a sigmoidal shape varying from L_1 to L_2 with increasing time t of annealing. The relaxation time τ_c is defined as the time of annealing of the melt for which the long period of the semicrystalline state is equal to $(L_1 + L_2)/2$. It is to be remarked that this is a self-consistent procedure: the time of annealing t_1 of the state 1 must be greater than the measured relaxation time; otherwise the long period is also a function of t_1 and the thermal history before t_1.

In Figure 1, T_1 is greater than T_2. It is obvious that the opposite thermal path ($T_1 < T_2$) can be adopted for measuring the relaxation time. For these two opposite thermal treatments, the sigmoidal curves $L(t)$ are opposite and give relaxation times of the same order of magnitude.

Another procedure, somewhat more complicated, can be investigated for showing the reversibility of the configurational equilibrium of the coils in the melt.

Experimental Part

In this article we restrict ourselves to the procedure given in Figure 1 where T_1 = 220 °C and T_2 = 150 °C. For each set of experiments the annealing time t_1 of the initial melt state is greater than the measured time τ_c.

The characteristics of the PE fractions are given in Table I. The monodisperse fractions (M) were supplied by SNEA and the fractions P were prepared as described in ref 1. P_3 is a commercial product (manolène, MNP), P_2 is a mixture of fractions M_2 and M_3, and P_1 is a mixture of M_5 and a polydisperse PE (M_n = 9700, M_w = 26 000).

Figure 2, which gives the long period of these materials as a function of M_n, shows that relation 2 applies; all these materials have been annealed at 220 °C during a long time and then quenched in liquid nitrogen.

The long periods L have been measured at the synchrotron source of Lure by small-angle X-ray scattering under the same conditions as those given in ref 1–3. In Table I, we have reported the estimated errors $\Delta\epsilon$ in the determination of L, which determine the precision $\Delta\tau$ in the relaxation time.

Figure 3 gives typical relaxation curves of monodisperse and polydisperse PE as a function of the time t of annealing at T_2 = 150 °C, and Figure 4 gives the relaxation times deduced from Figure 3 expressed as a function of the number-average molecular weight.

Discussion

Figures 3 and 4 show that polydisperse materials having different M_w values but the same M_n values have the same

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Table I
Characteristics of the Monodisperse and Polydisperse Fractions

sample	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	$I = M_w/M_n$	L	ΔL	$\Delta\epsilon$	Δr	τ, min
M_1	9.950	10.48	1.1	200	3.3	2	4.1	0.17
M_2	30.7	32.2	1.1	220	8	2.5	7	1.13
M_3	59	61.6	1.19	265	11	3	10	20
M_4	112	118	1.10	300				
M_5	246	264	1.15	300	33	6	21	510
P_1	14.8	87	5.9	197	24	3	12	0.5
P_3	27	197	7.3	248	13	3	18	1
P_4	40.8	47.8	1.17	240	16	3	9	2

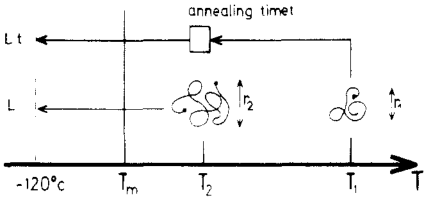

Figure 1. Procedure for measuring the relaxation time of the coils in the melt (T_1 = 220 °C and T_2 = 150 °C).

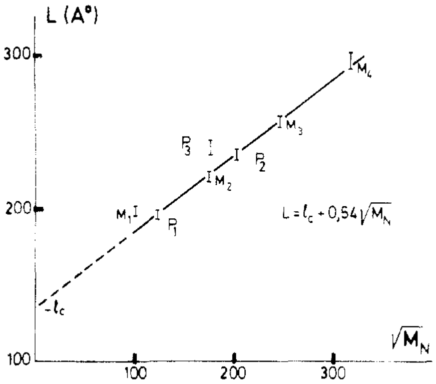

Figure 2. Correlation between the long periods of quenched monodisperse (M) and polydisperse (P) polyethylene and the number-average molecular weight M_n. The samples have been annealed at 220 °C for a long time before quenching.

relaxation times. The paramount conclusion of this work is that the relaxation time τ is given by the number-average molecular weight according to the scaling law

$$\tau = \tau_0 M^3 \qquad \tau_0 = 3 \times 10^{-12} \text{ s} \qquad (3a)$$

or

$$\tau_c = \tau_1 N^3 \qquad \tau_1 = 8 \times 10^{-9} \text{ s} \qquad (3b)$$

N being the number of CH_2 groups in the PE chain.

The characteristic time τ_1 is of the same order of magnitude as the correlation time measured in melt polymers[13] by various techniques such as dielectric relaxation and electron spin resonance.

Relation 3 is relevant with the fact that the long periods are given mostly by M_n and not by M_w. For high molecular weight materials $M > 10^5$ the long periods do not vary with M, but the relaxation time is still increasing according to relation 3. Regarding the process of crystallization, the long chains during nucleation and/or crystal growth can be separated into smaller portions of chains of mass M^* which crystallize independently, but it is evident that in the melt when the coils reach their equilibrium this notion of blob does not apply. The dashed line in Figure 4 reports the law $\tau = \tau_0 M^{3.4}$, having the same scaling form as the experimental viscosity law.[5,7]

It must be noticed that the accuracy of the exponent in relation 3 comes mostly from the accuracy of the relaxation

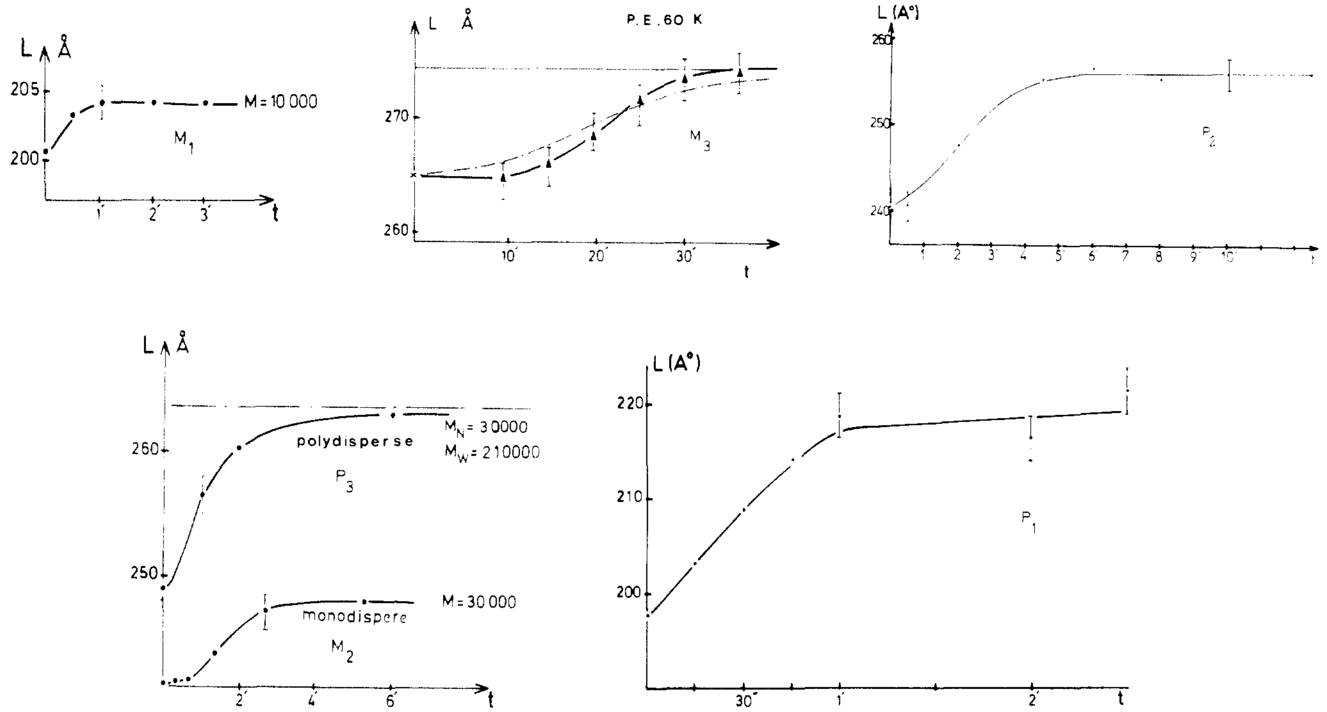

Figure 3. Relaxation curves of various PE materials treated according to the annealing procedure given in Figure 1; long periods L as a function of the annealing time t at T_2 = 150 °C. The molecular weights M_n and M_w of the monodisperse (M) and polydisperse (P) samples are given in Table I.

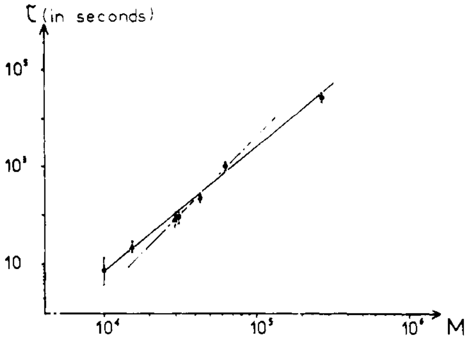

Figure 4. Relaxation times of PE coils in the melt state as a function of the number-average molecular weight. The dashed line has a slope of 3.4.

Table II

τ_c, s	τ_t, s	τ_r, s	τ_s, s	τ_K, s
3.000	6.8×10^{-3}	3.6×10^{-2}	8.500	0.03

time of the high molecular weight materials. In that case, it should be remembered that annealing at high temperature can degrade and cross-link the polymer chains and change the molecular weight distribution; samples studied in this work and in previous works[1-4] did not present the yellow color observed in oxidized polymers. Therefore we think that the effect of degradation must be discarded. The effect of cross-link and formation of branches would be to increase the exponent in relation 3.

We compare in Table II the relaxation time τ measured by our crystallization technique with other various theoretical and experimental relaxation times for a PE sample of molecular weight 10^5.

(a) τ_t is the terminal relaxation time deduced from the zero-shear viscosity η_0 and the plateau modulus $G_N°$. According to Graessley,[5,7] for PE

$$\tau_t = 4\frac{\eta_0}{G_N°} \sim N^{3.6} \qquad (4)$$

At $T = 190$ °C values of η_0 and $G_N°$ are $\eta_0 = 3.4 \times 10^{-14}M^{3.6}$ P and $G_N° = 2 \times 10^7$ dyn/cm^2. In other polymers the exponent in the above relation is 3.4 instead of 3.6.[5-7]

(b) τ_r is the theoretical reptation time of de Gennes.[8] The time for a chain of length Na to get out of its tube is

$$\tau_r = \tau_m N^3 \qquad (5)$$

where τ_m is a microscopic time $\sim 10^{-11}$ s divided by the number N_e of CH$_2$ groups between entanglements ($N_e \sim 100$).

(c) τ_s is the greatest stress relaxation time measured by de Vries and Tochon[9] on PE melts of molecular weight $M_w = 80\,000$ according to the procedure of Tobolsky and Murakami[10] at $T = 160$ °C.

(d) τ_K is the extrapolated relaxation time deduced from the work of Klein;[11] a polymer chain of end-to-end distance $R = (Na)^{1/2}$ diffuses over a distance R in a time

$$\tau_K = R_0^2/(6D) \sim N^3$$

For $M = 10^5$ the extrapolated value of the diffusion coefficient at 176 °C is $D = 5 \times 10^{-11}$ cm^2 s^{-1}, and $R_0 = 0.95M^{1/2} = 300$ Å.

From Table II, one concludes that our relaxation time is very similar to the time measured by stress relaxation experiments. It is worth noting that these long relaxation times have been measured also in other polymers: polybutene, low-density polyethylene, and polypropylene.[4]

In highly polydispersed PE, using the same technique Hsiue et al.[16] also found relaxation times of the same order of magnitude as those reported in this paper.[16] Ishizuka and Koyama[12] have shown that the rheological properties of polypropylene melts depend on the thermal history and that under certain conditions, the time for the melt to reach the equilibrium is greater than 1 h.

In part 2,[15] we show that the relaxation time of the coils when the temperature of the melt is changed can be also determined by viscoelasticity measurements. The comparison between our relaxation time and those obtained by other authors utilizing different techniques shows that our approach of crystallization based mainly on the correlations between the solid and melt states could bring some new understanding on the chain dynamics in the liquid state. The discrepancy between our relaxation time and the reptation time is however very puzzling, because one would expect that the time for the chain to get out of its tube is the time for the chain to lose its memory. In a subsequent paper, we show that this relaxation time τ_c can be measured by viscoelastic measurements.

Finally, we point out that the form of the relaxation curves of Figure 3 is very similar to the expected time dependence of the entanglement density between two chains that have been brought into close contact (see Figure 4 of ref 14). This suggests that the process of deformation of the coil when the temperature of the melt is changed involves a change in the density of entanglements.

Registry No. Polyethylene (homopolymer), 9002-88-4.

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