Relationship between the Relaxation of Polyethylene Coils in the Melt and the Molecular Weight Distribution. 2. Viscoelasticity Measurements

Bernard Millaud

Rhône-Poulenc, 93308 Aubervilliers, France

Jacques Rault*

Laboratoire de Physique des Solides, Université Paris-Sud, 91405 Orsay, France.

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ABSTRACT: In part 1 it was shown by appropriate melt annealing and quenching experiments that the time τ for polymer coils to reach their equilibrium dimension is given by the law $\tau \sim M^3$ and that this time is of the order of several minutes for a polyethylene fraction of molecular weight $M \sim 60000$. In this paper we show that this time can also be measured by viscoelastic measurements.

Introduction

In polyethylene (PE), the dimension of the coils in the melt state decreases with increasing temperature T of the melt;[1] the variation of the unperturbed end-to-end distance r_0 at the equilibrium temperature is given by the Flory coefficient:

$$\beta = \frac{2}{r_0}\frac{\partial r_0}{\partial T} = -10^{-3}$$

In the semicrystalline state obtained by quenching the melt we have shown that the long period L, which is the sum of the amorphous and crystalline layer thicknesses, is given by the relation

$$L \cong r_0 = M^{1/2} \tag{1}$$

M being the molecular weight of the fraction.

The experimental variation of L with the melt temperature is equal to that of the unperturbed dimension deduced from the Flory coefficient. The correlation between solid and melt expressed by relation 1 permits measurement of the relaxation time of the coils when the temperature of the melt is changed.[2,3] Figure 1 shows the annealing and crystallization procedure for such a determination. The melt at temperature T_1 is annealed for a long time t_1, then quenched to T_2 during a time t_2, and subsequently quenched in liquid nitrogen. The long period expressed as a function of the annealing time t_2 has a sigmoidal shape that increased from L_2 to L_1. The time τ_c which leads to a value $L = (L_2 + L_1)/2$ is called the relaxation time of the coils. The time 2τ is the annealing time required for the melt at temperature T_2 for erasing the thermal history of the sample.

In Part 1,[4] we have shown that this time varies for monodisperse and polydisperse fractions of linear PE as the power law $M_n{}^3$ and increases with the degree of branching of the chains.[3] Similar variations are observed for the viscosity and the reptation time.[5–9]

The aim of this paper is to show that the effect of the melt thermal history can be analyzed by viscoelastic measurements and that the relaxation times determined by this technique are of the same order of magnitude as those determined by the crystallization procedure.

Experimental Part

Two monodisperse polyethylene samples (M_1 and M_2) and one polydisperse polypropylene sample (M_3) were studied.

The PE fractions (polydispersity $I = 1.1$) were supplied by SNEA (Société Nationale des Pétroles d'Acquitaine) and the PP material (polydispersity $I = 5$) was supplied by Naphta-Chimie. The characteristics of these materials are given in Table I.

Table I

sample	M_w	M_n	τ_c, min	τ_g, min	τ_t, s	τ_K, s
PE (M_1)	63 000	59 000	20	5	1.4×10^{-3}	0.4
PE (M_2)	159 000	147 000	100	18	18×10^{-3}	5.5
PP (M_3)	500 000	111 000	4 h			

The fractions (0.5 g) were sandwiched between the cone-and-plate setup of a Rheometrics mechanical spectrometer. In an oven under a nitrogen atmosphere, the PE samples were annealed at temperature $T_1 = 200$ °C during a time $t_1 = 20$ and 40 min, respectively, for M_1 and M_2. Afterward the samples were cooled rapidly to the temperature $T = 150$ °C. The time to reach this temperature is 2 min; the measurements were done 1 min later. The same experiments were done on PP samples but with $T_1 = 240$ °C, $t_1 = 20$ min, and $T_2 = 190$ °C. Figure 2 reports the storage and loss moduli of the M_2 and M_3 samples as a function of the annealing time t at the temperature T_2 (the origin $t = 0$ is 3 min after the beginning of the cooling from 200 °C for PE and from 230 °C for PP, the frequency of the measurement is $\omega = 0.4$ rad s^{-1}, and the strain is 5%).

Discussion

In PP the relaxation time τ_c is about 4 h;[3] therefore during an annealing of 20 min at $T_1 = 230$ °C the polymer coils have not reached their equilibrium dimension r_0. The annealing times at $T_2 = 190$ °C and at $T_1 = 240$ °C are not long enough to change r_0, and therefore the modulus, as explained thereafter, does not vary with t.

The fact that the moduli G' and G'' are constant for small and long times also indicates that the thermal equilibrium is reached 3 min after the beginning of the cooling from T_1 to T_2 and that there is no cross-linking effect. The measured viscosities at T_1 and T_2 are respectively 16 300 and 48 880 P.

For the PE sample, the storage modulus G' increases rapidly up to a time τ_g, which increases with the molecular weight, and for larger time the storage modulus shows a constant moderate increase.

The absence of a plateau for long annealing time indicates that cross-linking appears during the experiments. Degradation by scission of chains would lead to a decrease in viscosity with the time of annealing instead of an increase as observed. Table I compares these relaxation times τ_g to the times τ_c determined by the crystallization procedure. The increase of G' between $t = 0$ and τ_g could be explained in the following manner: According to Graessley and Edwards,[5] the plateau modulus $G_N{}^\circ$ is given by the universal power law

$$G_N{}^\circ \sim l^{2a-3} \tag{2}$$

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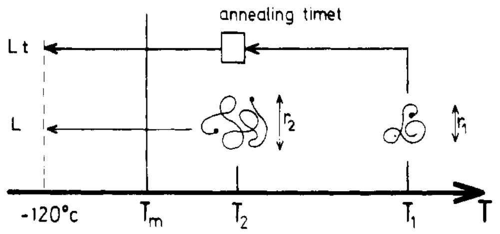

Figure 1. Procedure for determining the relaxation times τ_c and τ_g. The long periods in the semicrystalline state depend on the melt annealing time t at temperature T_2.

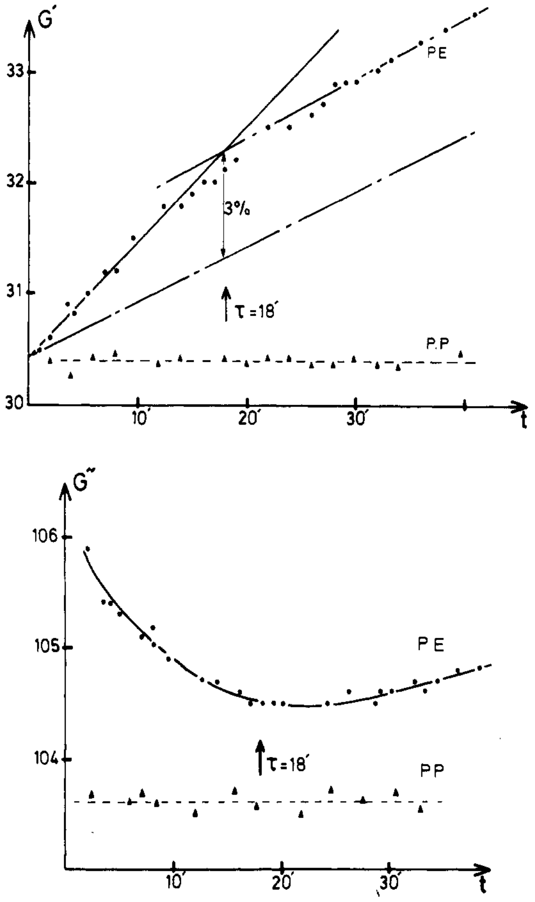

Figure 2. Storage and loss moduli (G' and G'') of PE fraction M_2 in arbitrary units as a function of the time of annealing at $T_2 = 160$ °C. The melt has been previously annealed during 40 min at $T_1 = 200$ °C and the origin of the time is taken 3 min after the beginning of the cooling from T_1 (when the temperature T_2 is stabilized). The dotted line shows the modulus of the PP (M_3) sample as a function of the annealing time at $T_2 = 190$ °C; this time is much smaller than the relaxation time τ_c.

where l is the Kuhn step length of the chain. This relation is to be compared to the relation[6,7]

$$G_N^\circ = \rho RT/M_e \quad (3)$$

where ρ and T are the density and the temperature and M_e is the molecular weight between entanglements.

Prevorsek and de Bona[10] have shown that when the rigidity of the chain decreases, the distance between entanglement increases. This effect can be understood in the following way: For highly coiled chains of very low rigidity, the coils are more compact and the distance between entanglements is large, whereas for very rigid chains each interchain contact must be considered as an entanglement and M_e approaches the molecular weight of a monomer. The procedure shown in Figure 1 permits one to vary continuously the rigidity of the chain and therefore the concentration of entanglements (that is to say the value of M_e) according to relations 2 and 3.

When the coils reach their equilibrium state from the initial state $t = 0$ to the final state $t = \tau_g$, the relative increase of the plateau modulus is

$$\frac{\Delta G_N^\circ}{G_N^\circ} = (2a - 3)\frac{\Delta l}{l} = 2(2a - 3)\frac{\Delta r_0}{r_0} \quad (4)$$

The relative variation $\Delta r_0/r_0$ deduced from the Flory coefficient (with $\Delta T = T_2 - T_1 = -50$ °C) is about 2×10^{-2}. The relative variations $\Delta G'/G'$ of storage modulus between $t = 0$ and τ_g is estimated from Figure 2 for sample M_2.

$$\Delta G'/G' = 3 \times 10^{-2}$$

The effect of cross-linking represented by the dashed line is to increase this value to 5×10^{-2}.

Therefore, if we assume that the variations of the storage modulus at frequency $\omega = 0.4$ rad s^{-1} follow the variations of the plateau modulus, the value of the exponent a in eq 2 is

$$a \cong 2$$

This is the expected value predicted by Graessley and Edwards.[5]

From the loss modulus curve, the same relaxation time τ_g is measured. For annealing times greater than τ_g, G'' is found to be nearly constant; it is well-known that the beginning of cross-linking affects much less G'' than G'.[12]

The rigidity of the chain changes synchronously with temperature. The observed decrease in G'' therefore results from a decrease in M_e, this latter effect being a consequence of increased rigidity. As G' and G'' vary in an opposite way, we can assume that the relationship between G'' and l is of the form

$$G'' \sim 1/l^{2a'-3} \quad (5)$$

In the limit case, $M_e \rightarrow 0$, $l \rightarrow \alpha$, and $G'' \rightarrow 0$ whereas G' increases to the value of the modulus of glassy polymers. The magnitude of the observed variations of G' and G'' implies that the exponents a and a' in relations 2 and 5 are equal.

In conclusion, there is good agreement between the relaxation time of the coils τ_g and τ_c determined by modulus measurements and by the crystallization procedure. The fact that τ_g is somewhat lower than τ_c could be explained probably by the dependence of τ_g on the shear rate, as is the terminal relaxation time.[7] It is worthwhile to note again that these relaxation times τ_g and τ_c, although varying as M^3, are not comparable to the terminal relaxation τ_t[7] and the reptation time τ_K,[8] defined as the time for a chain to reptate out of its initial tube, that is to say to diffuse over a length $r_0 \sim M^{1/2}$. This time has been measured by Klein[9] for low molecular weight materials; in Table I we give values of τ_K extrapolated from his work.

The fact that τ_g (and τ_c) is much greater than the reptation time indicates that the memory of the chain is not lost during the tube renewal.

Finally, we emphasize that our relaxation times, that is to say the times to reach the steady state of the coil dimensions and consequently of the entanglement concentrations, are comparable in magnitude to those deduced from measurement of viscosity of polydisperse melts having different thermal histories.[10,11]

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Registry No. Polyethylene (homopolymer), 9002-88-4; polypropylene (homopolymer), 9003-07-0.

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Viscoelastic Properties of Blends of Styrene–Butadiene Diblock Copolymer and High Molecular Weight Homopolybutadiene

Hiroshi Watanabe and Tadao Kotaka*

Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan. *Received April 15, 1983*

ABSTRACT: Viscoelastic properties of three well-characterized styrene–butadiene (SB) diblock copolymers blended with three high molecular weight homopolybutadienes (hB) were examined. Since hB is a nonsolvent for S blocks, micelles with precipitated S cores and dissolved B cilia are formed in the blends. The blend exhibits a shoulder or plateau often called a second plateau in the low-frequency region of the storage G' and loss G'' moduli. When the SB content c is smaller than a certain critical value c_b^*, the frequency region where the second plateau appears is independent of c. On the other hand, when c is increased beyond c_b^*, the second plateau rapidly extends to the lower frequency region. This critical value c_b^* coincides with the concentration at which the micelles begin to contact and their cilia begin to overlap with each other. These results suggest that the slow relaxation mechanism for the blends with c below c_b^* may be related to the motion of the B cilia entangled with the matrix hB molecules, while that for the blends with c above c_b^* is related to the delayed reptation of the mutually entangled B cilia of the neighboring micelles. From this viewpoint, we are able to explain the dependence of the longest relaxation time τ_p of the blends on the SB content c and on the molecular weights M_{bB} and M_{hB} of the B block and hB molecules, respectively, by employing the "tube renewal" mechanism of Klein and the modified "tube" model of Doi and Edwards and of Kuzuu for star polymers.

I. Introduction

In our previous papers,[1-3] we described rheological properties of blends of styrene–butadiene (SB) diblock copolymers (with S content less than 30 wt %) and a low molecular weight homopolybutadiene (with an M_n of about 2×10^3, coded as chB). The behavior of the blends was basically linear viscoelastic but was quite different from that of ordinary homopolymers in concentrated solutions and melts.[4,5] Namely, as the SB content c is increased beyond a certain critical value c_b^*, the blends begin to exhibit a slow relaxation process in the low-frequency region,[1-3] where an ordinary homopolymer system has no such processes but exhibits a Newtonian flow.[4,5]

We proposed the following mechanism for such a slow relaxation process found in the SB/chB blends.[3] Since chB itself is a Θ solvent for B blocks but a nonsolvent for S blocks, SB molecules tend to aggregate and form micelles with precipitated S cores and dissolved B cilia. With increasing SB content c, the B cilia of neighboring micelles begin to overlap and entangle with one another. The slow relaxation process is a result of retarded reptational motion of the mutually entangled B cilia, because the reptational motion of a polymer chain (in this system, a B cilium) with one end fixed and the other end free would be highly retarded as pointed out by de Gennes.[6]

However, in this earlier study[3] we did not observe the entanglement effect of chB molecules on the relaxation processes, presumably because the M_n of chB was too small to result in effective entanglements. In other words, only the entanglement network resulting from B cilia alone affected the slow relaxation process in the SB/chB blends. To clarify the effect of entanglements between matrix homopolybutadiene and B cilia of the micelles, we examined viscoelastic properties of blends of SB diblock copolymers and high molecular weight homopolybutadiene with M_n at least a few times greater than the average molecular weight M_e^{bulk} between entanglement points in bulk homopolybutadiene.[4,5] The mechanisms of slow relaxation processes in such blends will be discussed in terms of the tube model[7-10] for B cilia entangled with matrix homopolybutadiene and with B cilia of neighboring micelles.

Table I
Characteristics of Polymer Samples

code	$10^{-3}M_n$	M_w/M_n	wt % of PS	$10^{-3}M_n$ of S block	$10^{-3}M_n$ of B block
SB3	134	1.07	24.0	32	102
SB4	192	1.08	17.0	32	160
SB5	294	1.10	11.0	32	262
hB1	27.6	1.05	0	0	27.6
hB2	60.7	1.05	0	0	60.7
hB3	177	1.06	0	0	177

II. Experimental Section

1. **Materials.** Three SB diblock copolymers, SB3, SB4, and SB5, employed in this study were prepared by anionic polymerization using *sec*-butyllithium as the initiator and benzene as the solvent.[11] All of these SB samples were prepared from the same batch of precursor living polystyrene (PS) and, therefore, have S blocks of the same characteristics. Three homopoly-

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