Polymer Bulletin 2, 373-381 (1980)

Polymer Bulletin

© by Springer-Verlag 1980

Memory Effect in Liquid Polyolefine

Jacques Rault[1] and Elisabeth Robelin[2]

[1] Physique des Solides, Université Paris-Sud, 91405 Orsay, France

[2] Institut Textile de France, 92100 Boulogne, France

Summary

The long periods of semi-crystalline polymers depend on the rigidity of the chain in the liquid state just before crystallization. We show that by changing the temperature of annealing of the liquid, the long period of quenched materials is changed. The variations of the long periods, correlated to the variations of the unperturbated dimensions of the coils in the liquid state, are found to depend on the annealing time of the melt. This memory effect of the liquid whose experimental study is reported in this paper is dependent on the molecular weight, its distribution, and the nature of the chain.

Introduction

We have shown (RAULT 1978) that the long period observed in semicrystalline polymers is proportional to the rigidity $C = \frac{r_o^2}{na^2}$ of the chain ; r_o and n being respectively the unperturbated dimension and the number of chains units of length a. The limiting value of the long period L measured in material crystallized from the melt is a characteristic of the nature of the chains. Extended chains in the liquid state (rigid chains) give extended chain crystals, and coiled chains (flexible chains) gives folded chain crystals. By quenching the polymer melt, the folded chains in the crystalline state can be considered as the image of the coiled chains in the liquid state. The interest of melt crystallization studies is that the coils in the initial liquid state have in general the unperturbated dimension r_o. It is well known that in the ideal liquid state the dimension r_o is temperature dependent (FLORY 1968). A temperature coefficient β of the liquid is defined :

$$\beta = \frac{\partial \mathrm{Log} C}{\partial T_i} = \frac{2}{r_o}\frac{\partial r_o}{\partial T_i} \tag{1}$$

in a similar way we have defined the temperature coefficient α of the solid phase

$$\alpha = \frac{1}{L}\frac{\partial L}{\partial T_i} \tag{2}$$

0170-0839/80/0002/0373/$01.80

The long period L of quenched melt polymers is dependent on the temperature T_i of the melt. We have experimentally established (RAULT and al. 1979, ROBELIN et al. 1979) the relationship between these two characteristics of the solid and liquid phases for polydispersed and monodispersed polymers. It is evidentthat this memory effect depends on the previous thermal treatment of the liquid. When rapidly changing the temperature of the melt, the coils reach their unperturbated dimensions in a finite time, which defines a relaxation time τ , that is dependent on the nature of the chain and its length. By quenching the liquid in the non-equilibrium state, the measure of the long period gives a measure of the non-equilibrium dimensions of the coils in the liquid state, if the exact relationship between the long period and the coils dimensions is known.

The purpose of this paper is to show the importance of the thermal cycles in the melt on the properties of the solid obtained by quenching. We discuss the influence of the nature of the polyolefine chains on the relaxation time, and the time of annealing the liquid for erasing the memory of the liquid.

Experimental

The commercial polymers studied are low density polyethylene (LDPE), polypropylene (PP) and polybutene (PB). The number molecular weight M_N and the weight molecular weight M_W are given in Table 1. The polymers melt (2mm x 10mm x 10 mm) sandwiched between copper plates were annealed in a Mettler oven. The quenching was obtained by throwing the sample in liquid nitrogen or water. The cooling rate is about 10° to 20°C/S. The results obtained indicate that the long period is independent of the cooling rate. It is well known that for a slow cooling rate, this is no longer true : thickening appearing during crystallization is time and crystallization temperature dependent. In some cases, the melt was annealed without copper plates for analysing the effects of the degradation, oxydation and chains scissions.

The small angle X-ray scattering recording was made on the experimental set-up of the synchrotron of LURE-Orsay, using a proportional counter, a distance between sample and counter of $\simeq$ 1 m, and synchrotron radiation having $\lambda = 1{,}9$ Å. The maximum of the intensity curve was determined according to the procedure given by RAULT et al.(1979). The straightforward application of Bragg's equation gives the long period L. The accuracy on L is about $\Delta L/L = 10^{-2}$. It is well known that the values of L do not agree exactly with those inferred from other techniques and that a more complicated analysis of the SAXS pattern is necessary. The simple analysis using Bragg's law is however adequate for determining the variation of the long periods and the relaxation time.

a) Measure of the temperature coefficient α of the solid phase

The melt is annealed at a temperature T_i for a time, that is much greater than the relaxation time defined hereafter, and then quenched. The long period L (independent of the annealing time in this

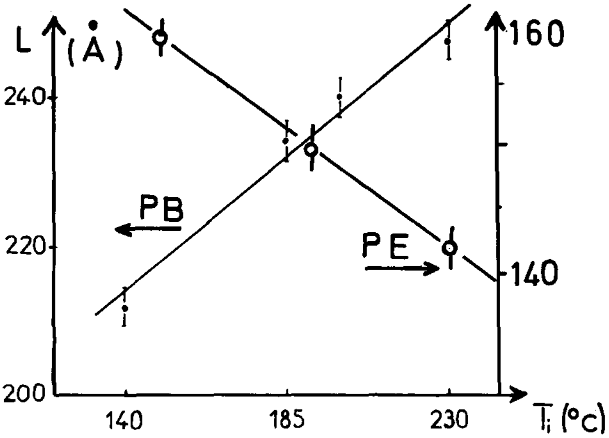

Fig.1 :Long period of quenched polyethylene and polybutene as a function of the melt temperature. P.E and P.B have respectively a negative and positive temperature coefficient β of the liquid phase

case) is reported in figures 1 and 2 as a function of the temperature of the melt. In these samples no variation of the crystallinity x is measured, accuracy on the measurements $\Delta x \simeq 0{,}02$.

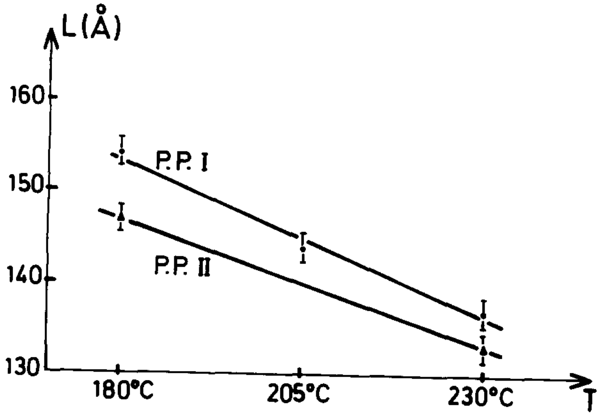

Fig.2 : Long period of two polypropylene samples of different molecular weight as a function of the melt temperature.

P.P. 1 M_W = 500 000 M_N = 111 000
P.P. 2 M_W = 320 000 M_N = 71 000

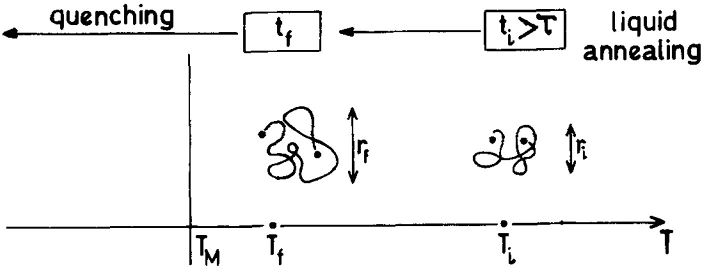

Fig.3 : Thermal cycles of the polymer melts. The long period in quenched semi-crystalline material depend on the melt temperature and on the annealing time t of the melt. In the liquid the unperturbated dimensions depend on the temperature and on the annealing time.

b) Measure of the relaxation time

Figure 3 gives the experimental procedure. The melt is annealed at a temperature T_i for a long time (2 hours) for LDPE and PB and 10 hours for PP) quenched to T_f and annealed at that temperature for a time t_f, and then quenched at a low temperature, LDPE and PP crystallize during quenching, PB crystallizes from the glassy state or can crystallize during quenching if the cooling rate is very low.

Figures 4 and 5 give the long period as a function of the annealing time. For PB we have given the two cases $T_i > T_f$ and $T_i < T_f$, for PP $T_i < T_f$ and for LDPE $T_i > T_f$ (corresponding to fig.3).
A relaxation time τ can be defined, it is the time of annealing of the melt at temperature T_f, for which the long period of the quenched material has the value $\frac{L(T_i)+L(T_f)}{2}$.
It is the time where the curve $L = f(t_i)$presents an inflection point.

The time 2τ is about the annealing time of the liquid for erasing the memory of the melt. It is obvious that this time depends on both temperatures T_i and T_f. For experimental conveniences we have chosen $\Delta T = |T_i - T_f| \simeq 100°C$. In industrial polyolefines transformation the difference between the temperature of processing and the temperature of melting is somewhat less than 100°.

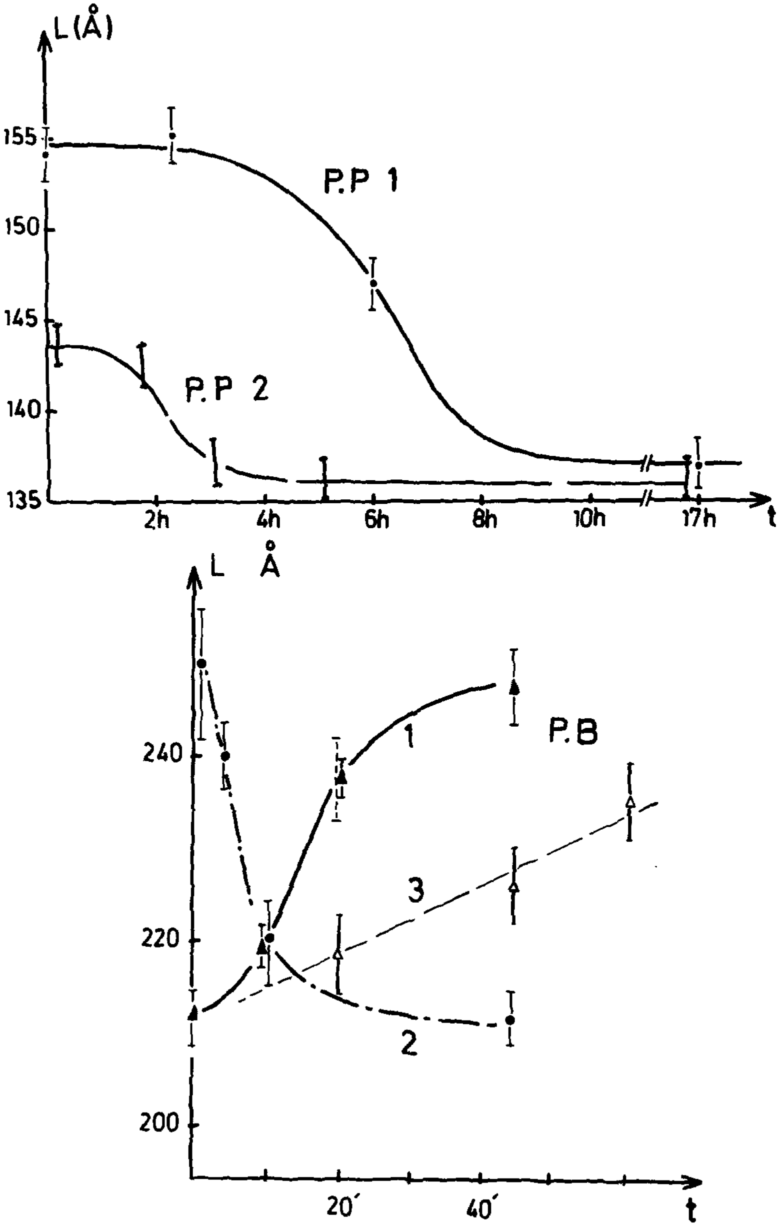

Fig. 4 : Long period in quenched polymers as a function of the annealing time of the melt at temperature T_f,
The thermal treatment of the liquid is described in fig.3.

P.P T_i = 280°, T_f = 180°C
P.B curve 1, T_i = 150°, T_f = 230°, curve 2, T_i = 230°,T_f = 150°

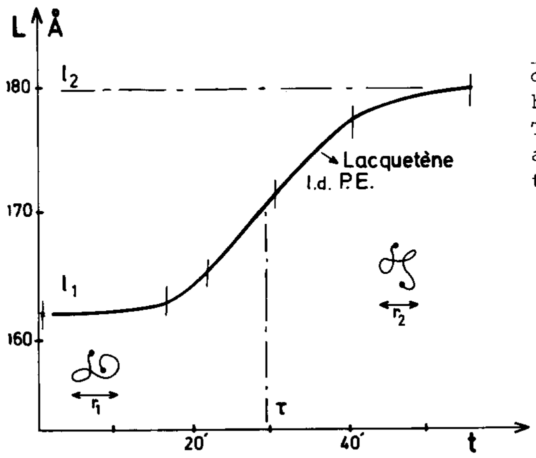

Fig.5 : Long period of quenched LDPE. The melt has been annealed at T_i = 230°C for 2 hours and at T_f = 180°C for a time t.

TABLE 1

	$10^3.M_W$	$10^3.M_N$	$\alpha L(\text{Å}K^{-1})$	$\beta L(\text{Å}K^{-1})$	$L(T_m)$ (Å)	τ
LDPE (Lacquetene, MNPE)	65.	11	-0.24	-0.20	162	30'
Polypropylene (Napryl, Naphtachimie)						
PP1	500	111	-0.23	-0.38	158	6 h
PP2	320	71	-0.20	-0.26	150	2h30
Polybutene 1- PB (CDF-Chimie)	394	80	+0.03 +0.11	+0.25	210	18'

Discussion

The linear relationship found to describe the dependence of the long period on the temperature of annealing of the melt is :

$$L(T_i) = L(T_o)\ 1 + \alpha(T_i - T_o) \qquad (3)$$

where T_o is a temperature of reference, for example 5° or 10°C above the melting temperature of the polymer.

Because of the weak variation of L, α given by (3) or (2) is considered as a constant which is a characteristic of the nature of the chain. Figure 2 shows that α does not vary conspicuously with the molecular weight. This is a result that we have found for monodispersed polyethylene (ROBELIN et al. 1979). That is the reason why the two independent molecular parameters α and β, characteristic of the solid and liquid phase must be compared. In table 1, the comparison between $\alpha L(T_m)$ and $\beta L(T_m)$ is given. These two parameters give the linear variation of the long period and the unperturbated dimensions of the coils with the temperature of the melt. The value of $L(T_m)$ is the long period extrapolated to the melting temperature T_m in figures 1 and 2. For LDPE the temperature coefficients α and β are of the same order of magnitude $\sim -10^{-3}\ K^{-1}$. The same value is found for linear polyethylene (RAULT et al. 1979). It should be pointed out that the crystalline lamella thickness ℓ_c measured by Raman spectroscopy shows the same variations with the temperature of the melt (HENDRA and MARSDEN 1977). The temperature coefficient $\frac{1}{\ell_c}\frac{\partial \ell_c}{\partial T_i}$ is equal to α.

An important result is the difference in behavior of polybutene compared to the other polyolefine, polypropylene or low density and high density polyethylene. For PP and PE the coils expand when the temperature of the melt is decreased that correspond to the schema of figure 3 $\beta < 0$. For polybutene, the opposite behavior is observed (MARK and FLORY 1963). The values of β are $0.1\ 10^{-3}$ and $0.5\ 10^{-3}$ respectively for isotactic and atactic chains. The presence of tacticity defects in isotactic chain would increase the value of β and would explain the difference between the two temperature coefficients α and β reported in Table 1.
Concerning the relaxation time, we emphasize the great difference between linear and branched PE chains which amounts to one order of magnitude for the same molecular weight distribution. Long branches are expected (DE GENNES 1978) to hinder the reptation process of the chains, one branch longer than the distance between two entanglements is able to produce a drastic effect, including an important increase of the viscosity and of the relaxation time.

Molecular weight dependence

The two samples PP 1 and PP 2 have same polydispersity M_W/M_N. The molecular weight ratio r_m is $r_m = M(PP\ 1)/M(PP\ 2) = 1.56$. In the case where the relaxation time is proportional to the reptation time, the de Gennes law applies $\tau \simeq M^3$, and the relaxation ratio would be : $\tau(PP\ 1)/\tau(PP\ 2) = r^3 \simeq 4$. The experimental ratio is about 3. This small discrepancy probably arises because of the polydispersity of the materials. In monodispersed polyethylene, the law $\tau \sim M^{\alpha}$ with $\alpha \simeq 3 \mp 0.5$, similar to the viscosity law, has been found (ROBELIN and RAULT 1979).

Nature of the chain

The measured relaxation time depends on the chain length and on the nature of the chain, therefore it is difficult to compare two different commercial polymers. However in our case, polybutene and polypropylene 2 can be compared, for they have nearly the same chain length distribution. The difference in τ values arises only from the nature of the chains. It should be interesting to compare these 2 values with the melt viscosities.

Processing temperature

Before extrusion, blow moulding, injection moulding ... the polymer is molten in a reservoir at a certain temperature T_i for a rather long time. If the deformation and the temperature gradients are not too important, the long period of the final product after crystallization will be a function of the temperature T_i of the reservoir, and on the time t of melt annealing. Curve 2 of figure 4 shows this memory effect. The commercial product polybutene, for which the processing temperature was unknown, was heated at 150°C during a time t and then quenched to liquid nitrogen. The variation of the long period defines a relaxation time somewhat different from that given by curve 1. For short times, the long period is equal to the long period measured on material annealed at 230°C for a long time. Therefore, it is concluded that the commercial product before crystallization has been heated to a temperature of about 230°C for a time greater than 2τ. It is obvious that the existence of high temperature gradients, and high shear rates during processing would modify this conclusion. Nevertheless the knowledge of the variation laws $L = f(t)$ and $L = g(T_i)$ allow to have some idea of the temperature of processing of semi-crystalline polymers.

Effect of oxydation

The described effects are reversible, and therefore cannot be attributed to the degradation of the polymers during annealing. If the polymer melt is annealed in the presence of oxygene without metal covers, oxydation occurs and the long period of quenched materials is not equal to that of the unoxyded materials and submitted to the same thermal treatments. Curve 3 of figure 4 shows the oxydation of polybutene. For long annealing time the maximum of intensity in the S.A.X.S. pattern tends to disappear. In this sample, the crystallinity x decreases with the annealing time, whereas x was constant in materials not oxyded. This points out the non-reversibility of the phenomenon. It is well-known that oxydation has two consequences, oxydation of the α carbon in the branches, and chain scissions. Chain scissions would imply a decrease of the long period, and oxydation of the branches could change the visocisty of the melt and then the relaxation time. These two effects can explain the form of curve 3 compared to curve 1 in figure 4. However more work is needed (G.P.C. and I.R. spectroscopy) for analysing the importance of these two effects.

Conclusion

It is well known that the kinetics of crystallization depends on the annealing time of the polymer melt, and on the temperature of annealing. In the liquid, seeds are still present and act as nucleation centers when the sample is cooled below the crystallization temperature. The enhanced nucleation could be shown to persist through several meltings. This effect is called crystalline memory of liquid (C.M.L.) (WUNDERLICH 1976, TURSKA and GOGOLEWSKI 1975) and is based upon the fact that the annealing of the melt is not long enough for the coils to attain the equilibrium state.

Although in this paper we have not treated the crystallization kinetics in relation to the thermal treatment of the liquid, we have analysed the correlation between the long period in quenched materials and the unperturbated dimension of the coils in the liquid state just before crystallization. This effect is called the liquid memory of the solid, L.M.S., and is fundamentally different from the opposite effect C.M.L.

We emphasize that S.A.X.S. is a valuable method for polymer characterization. The variations of the long period in quenched materials with the melt temperature and with the time of melt annealing are characteristic of the chains, and of the molecular weight. These experiments point out the correlations existing between the solid and liquid state (RAULT 1978), and show that the study of quenched semi-crystalline polymer gives important information on the chain dynamics in the liquid state.

References

FLORY, P.J., Statistical mechanics of chain molecules. Interscience publishers, New-York 1968

DE GENNES, P.G., J. de Physique, 36, 1179 (1975)

HENDRA, P.J., MARSDEN, E.P., 1977, Polymer Letters, 15, 258 (1977)

MARK, J.E. and FLORY, P.J., J. Am. Chem. Soc. 67, 1396 (1963)

RAULT, J., J. Macrom. Sci. B 13, 4 (1978)

RAULT, J., SOTTON, M., RABOURDIN, C., ROBELIN, E., submitted to J. Physique (1979)

ROBELIN, E., ROUSSEAU, F., LEMONNIER, M., RAULT, J., submitted to J. Physique (1979)

TURSKA, E. and GOGOLEWSKI, S., J. Appl. Polym. Sci. 19 (3), 637 (1975)

WUNDERLICH, Macromolecular Physics, Academic Press, New-York 1974

Received February 29, 198o
Accepted March 4, 198o