Melting Behavior of *cis*-Polybutadiene Crystallized under Stress

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Synopsis

Samples of crosslinked *cis*-polybutadiene were crystallized at different temperature and drawing degree. The melting behavior of the crystallized samples was analyzed detecting the retractive stress as a function of temperature. The experimental melting data were extrapolated to the equilibrium conditions to obtain the thermodynamic melting temperature as a function of the drawing degree. The extrapolated data were analyzed with different theoretical approaches. Results agree with a model in which chain-folding and extended-chain crystallization can coexist, depending on crystallization temperature and drawing degree.

INTRODUCTION

Stress-induced crystallization is a complex phenomenon and, depending on crystallization temperature and deformation degree, different crystallization modes occur. Very critical is the effect of the crystallization temperature T_c; at $T_c > T_m^0$, only stress-induced crystallization is possible, T_m^0 being the thermodynamic melting temperature of the unstretched crosslinked system. At a given crystallization temperature, a critical strain value λ_c can be found, λ_c being the minimum deformation necessary to induce crystallization. In this case extended chain crystallization occurs with a typical two stages mechanism.

At $T_c < T_m^0$, thermally induced crystallization is possible, and the growing mechanism can produce chain folding crystallization only, or extended chain crystallization also, depending on the strain value. Different theoretical treatments can be used to explain this complex phenomenology,[1-4] but the number of influent physical and chemical parameters is so large that it is difficult to find a complete overlapping between the experimental behavior and the theoretical description. In previous papers,[5-7] we reported results regarding the crystallization of drawn *cis*-polybutadiene. The polymeric system was characterized by a high steric regularity. The analysis was based on calorimetric, optical, and mechanical measurements. The results obtained, at least qualitatively, can be explained with a phase diagram based on the theoretical approach of Ref. 2.

According to the theoretical model we have found that at $T_c > T_m^0$, there is a minimum strain value necessary to induce crystallization,[5,6] while at $T_c <$

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T_m^0, two different crystallization modes seem to be present, depending on strain.[7] Different crystallization modes give rise to different crystalline morphologies and, in such a case, the melting behavior must be affected by the complex structural organization, and more than a single melting point is expected. In the present paper we describe the melting behavior of drawn samples crystallized below the melting point of the unstretched network. The obtained results are analyzed using some of the available theoretical relationships, and the comparison between experimental and theoretical behavior more clearly confirms the general picture suggested in the previous papers.

MATERIALS AND METHODS

The cis-polybutadiene was an Enichem product obtained with a neodymium based catalyst. The content of 1.4 cis units was about 98%. The molecular weight was $M_w = 652,000$ and $M_n = 57,000$. Dicumylperoxide was used as crosslinking initiator, and the curing was carried out at 140°C for 45 min. The analysis of stress–strain curves gives 1×10^{-4} mol/cm³ as crosslinking density.[8] Samples, drawn at 80°C to the chosen strain, were rapidly quenched to the crystallization temperature T_c in the range -15 to -2°C. The crystallization process was observed detecting the stress-relaxation plots to obtain information about the crystallization rate.[9] The melting behavior was analyzed heating at constant rate (1°C/min), and detecting the stress as a function of the temperature.

RESULTS

The rate of crystallization can be described by the half-time of crystallization $t(1/2)$, calculated from the stress–relaxation plots. The half-time was obtained at different crystallization temperatures T_c, as a function of the deformation degree λ, and the results are reported in Figure 1. The trend in Figure 1 is quite conventional; as a matter of fact, the rate of crystallization increases on increasing λ and on decreasing T_c. Particularly drastic is the influence of λ at the higher temperatures where $t(1/2)$ drops by a factor of 10, in the range λ = 1.5–3.5. However, $t(1/2)$ is an overall parameter that gives a general information on the rate, but that is not useful to give indications on the mechanism. This is evident, analyzing the relaxation plots as shown in Figure 2, where, as an example, results regarding $T_c = -12$°C are reported.

In Figure 2(a) the relaxations refer to values in the range λ ≤ 3.2. It is clear that, after an induction time that can be more or less long, depending on λ, the crystallization occurs in a single stage that is concluded within 30 min. At the lower λ (λ = 1.7) a stress hardening is observable at longer times, indicative of further crystallization. The trend in the range λ ≥ 4 is different. In Figure 2(b) it is shown that the crystallization occurs in a wider time scale, and at 10^3 min it is not yet concluded. However, in terms of half-time (calculated assuming approximately the stress at 10^3 min as equilibrium value), the obtained $t(1/2)$ values are a few minutes. Therefore, the parameter $t(1/2)$ describes the overall kinetic but does not take into account the slow processes following the fast initial stage. The different crystallization mechanism plays a relevant role on the melting behavior.
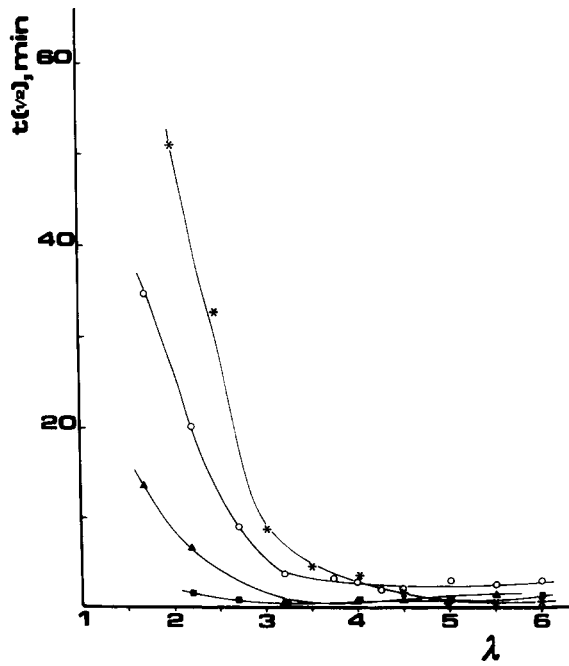
Fig. 1.   Half-time of crystallization reported vs. the drawing degree λ. $T_c(°C)$: (*) -8; ($\bigcirc$) -10; ($\blacktriangle$) -12; ($\blacksquare$) -15.
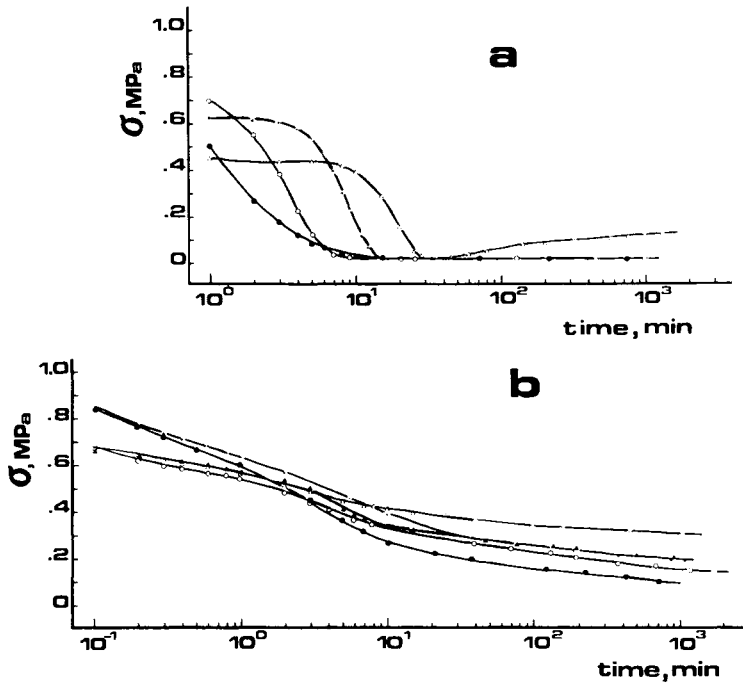

Fig. 2.   Relaxation plots obtained at $T_c = -12°C$, for different values of drawing degree. The stress σ is reported vs. the crystallization time. λ: (a) ($\triangle$) 1.7; (*) 2.2; ($\bigcirc$) 2.7; ($\bullet$) 3.2. (b) ($\bullet$) 4.0; (*) 4.5; ($\bigcirc$) 5.0; ($\blacktriangle$) 5.5; ($\triangle$) 6.0.
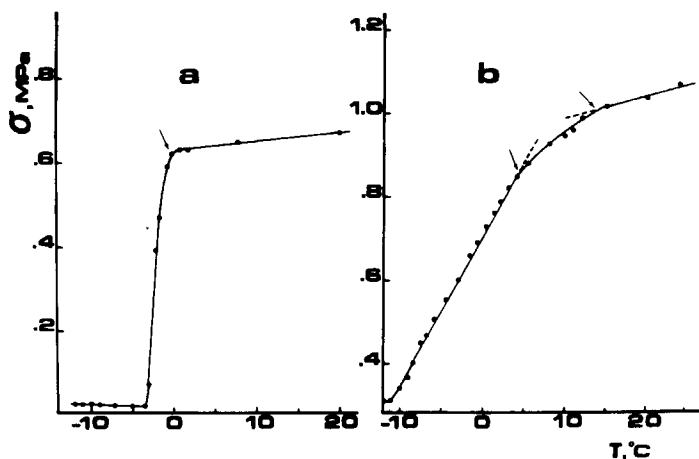
Fig. 3. Melting plots for samples crystallized at $T_c = -12°C$. The retractive stress is reported vs. the temperature. The melting points are indicated by the arrows: (a) $\lambda = 2.2$; (b) $\lambda = 6$.

In Figure 3(a) the melting of a sample, drawn to $\lambda = 2.2$ and crystallized at $-12°C$, is shown. The melting is characterized by a very sharp increase of the retractive force, followed by a trend in which the stress linearly increases with the temperature, according to the well-known thermoelastic behavior.[10] The melting point was taken as the point at which the thermoelastic regime appears, as indicated by the arrow. The trend in Figure 3(b), relative to a sample drawn to $\lambda = 6$, and crystallized at the same temperature, appears different. The melting transition is broad and a lower and upper limit of the transition range can be taken, as indicated by the two arrows. As clear, the arrows indicate the lower and upper deviations from a linear trend. The situation shown in Figure 3 is quite general and can be summarized in the following way. In the deformation range $\lambda \leq 3.5$, the melting trend is similar to Figure 3(a), in the sense that, with a more or less sharp transition, a single melting point can be taken. On the other hand, for $\lambda \geq 4$, the melting trend is similar to Figure 3(b) and, for each crystallization temperature and deformation degree, lower and upper melting temperatures can be taken.

With a similar experimental approach, two melting points were taken detecting the dynamic moduli of highly drawn polybutadiene networks.[11] However, the observed melting points are functions not only of the drawing degree, but also of the crystallization temperature. To obtain a direct and univocal relationship between melting point and drawing degree, it is possible to use the Hoffmann and Weeks equation.[12] Reporting for each λ the observed melting temperature T_m' vs. the crystallization temperature, the thermodynamic melting temperature T_m can be found as a function of λ. T_m corresponds to the condition $T_m' = T_c$ and can be considered the melting temperature of a crystal of infinite dimensions crystallized at infinitely low rate; it represents a point of the equilibrium curve T_m vs. λ.

In Figure 4 the Hoffmann and Weeks plots for the range $\lambda \leq 3.5$ are reported, while in Figure 5 the trend for samples with $\lambda \geq 4$ is shown. In Figure 5 two melting points for each temperature are reported. Figures 4 and 5 allow us to obtain the limit melting temperature as a function of λ,
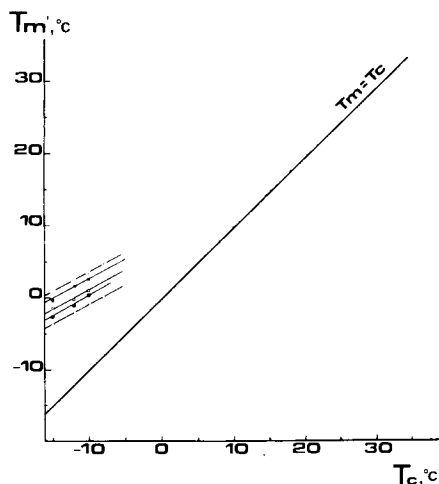
Fig. 4. Hoffmann and Weeks plots. The experimental melting temperature is reported vs. the crystallization temperature. The intercept with the line $T_m = T_c$ gives the thermodynamic melting temperature. λ: (○) 1.25; (●) 1.70; (□) 2.2; (■) 2.7; (∗) 3.2.

extrapolating to the condition $T_m' = T_c$. The obtained values are reported in Table I. Table I indicates that, for $\lambda \geq 4$, a crystalline phase stable at room temperature can be present. This indication was confirmed detecting with a flat camera the X-ray diffractogram at room temperature on a sample stretched to $\lambda = 5.5$ and crystallized at $-10°C$. The obtained diffraction
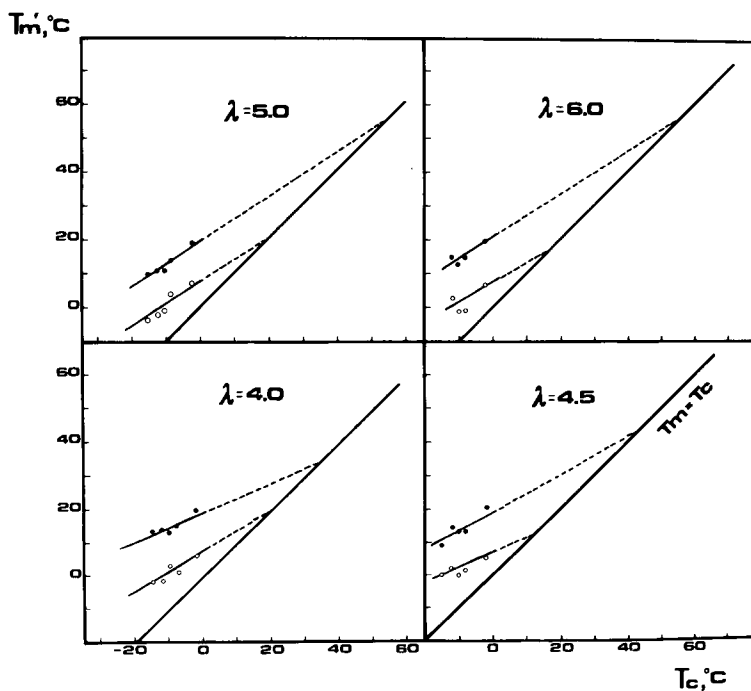

Fig. 5. Hoffmann and Weeks plots. The values of λ are reported in the figure.

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TABLE I
Melting Points (°C) as a Function of λ

λ	T_m	$T_m(L)^a$	$T_m(U)^a$
1.25	11.0		
1.70	14.5		
2.25	15.0		
2.70	18.0		
3.20	20.0		
4.00		20.0	34.0
4.50		12.5	43.0
5.00		20.5	55.0
5.50		18.0	60.0
6.00		17.0	56.0

[a](L) and (U) mean lower and upper.

pattern is characterized by the presence of equatorial and meridional spots and a more diffuse halo, as typical for an oriented semicrystalline system.

The results obtained indicate that when the deformation is higher than a critical value, the crystallization gives rise to a complex structure, in which different crystals coexist. This strain value is here around 3.5–4, and, in the analyzed range, seems to be independent of temperature. The presence of different crystals is supported by the crystallization behavior, as described in a previous paper,[7] and as supported herein by the relaxation plots and, more clearly, by the melting behavior. Of course, different crystals melt at different temperatures and the melting temperatures depend on λ with a different law. In order to verify this last important aspect, we used different relationships that relate the melting to the deformation degree. On the basis of the earlier treatment that was developed by Flory,[13] the following expression can be written:

$$1/T_m = 1/T_m^0 - \frac{R}{2\,\mathrm{Nu}\,\Delta\mathrm{Hu}} F(\lambda) \qquad (1)$$

where T_m and T_m^0 are the thermodynamic melting temperatures for strained and unstrained network, respectively, R is the gas constant, Nu the number of repeating units per network chain, and ΔHu the molar enthalpy of melting. $F(\lambda)$ is a function of the strain λ given by

$$F(\lambda) = (24N/\pi)^{1/2}\lambda - (\lambda^2 + 2/\lambda) \qquad (2)$$

where $N = \mathrm{Nu}/S$, S being the number of repeating units per statistical segment. Twenty years later, Krigbaum and Roe[14] derived a relationship similar to eq. (1) but the expression for the function $F(\lambda)$ was different, and, in particular,

$$F(\lambda) = (\lambda^2 + 2/\lambda - 3) \qquad (3)$$

In Flory's treatment, extended chain crystallization is assumed, with the chain axis parallel to the stretching direction, while in Krigbaum's treatment,
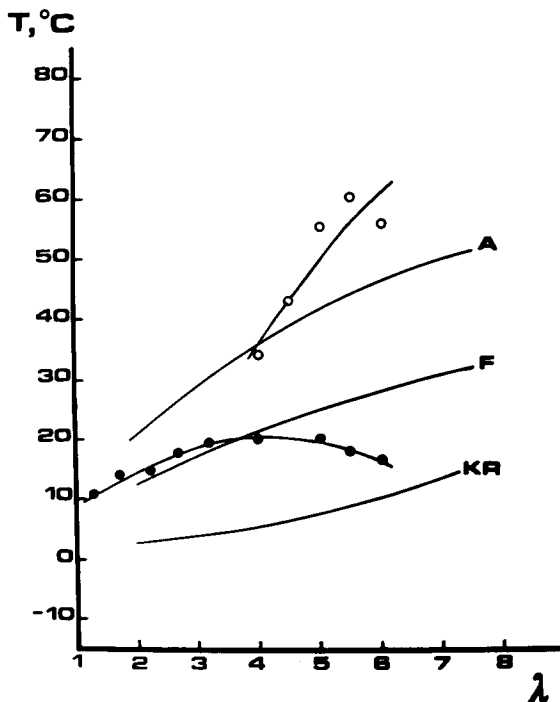
Fig. 6. The thermodynamic melting temperatures are reported vs. the drawing degree λ: (●) lower melting; (○) upper melting; KR = Krigbaum and Roe equation; A = Allegra and Bruzzone equation; F = Flory equation.

there is not a recourse to a specific crystallization mode. However, Krigbaum's treatment is a better representation of the experimental behavior at low extensions, where chain-folding crystallization occurs. More recently, Allegra and Bruzzone[4] reported a model in which extended chain crystallization is assumed, but the chain axis in the crystals is taken parallel to the average end-to-end chain vector. The quantitative relationship is the following:

$$T_m = T_m^0 \Big/ \left\{ 1 - \frac{3R}{2\,\mathrm{Sf}} \left[2\left(\frac{8}{3\pi N} \right)^{1/2} \lambda - \frac{1}{N}(\lambda^2 + 2/f\,) \right] \right\} \qquad (4)$$

where Sf is the molar entropy of melting (that must be referred to a mole of statistical unit and f is the functionability of the junction points. For *cis*-polybutadiene the following parameters can be used: $\Delta Hu = 9.2$ kJ/mol,[15] $\mathrm{Sf} = 66.8$ J/mol K^{-1},[15] $T_m^0 = 275$ K,[16] and $S = 2$[15-17]; on the other hand, the crosslinking density gives $\mathrm{Nu} = 168$, and therefore $N = 84$. Using these parameters, eqs. (1–4) give the theoretical plots shown in Figure 6, where they are compared with the experimental data reported in Table I. It is worth noting that the experimental upper melting points agree in a satisfactory way with Allegra's treatment which assumes extended chain crystallization, while Flory's equation, which also assumes extended chain crystallization, compares well with the lower melting points in the range of lower deformations. However, considering the crystallization temperature, extended chain crystallization can be excluded at low deformations.

On the other hand, the Krigbaum and Roe treatment largely underestimates the effect of drawing, as generally reported in literature. An important aspect that is shown in Figure 6 is the trend of the lower melting, which decreases on increasing λ, in the deformation range in which the upper melting appears. A decrease of T_m on increasing λ is theoretically expected[1-3] for chain-folded crystals, in the range of higher deformations. Moreover, at $\lambda = 4$, the upper melting is about 15 degrees higher than the lower; a similar increase of melting was observed in polyethylene as the folded chains are converted in extended chain crystals.[18]

As reported in a previous paper,[7] again we can adopt the phase diagram suggested by the theoretical approach in Ref. 2. Below the thermodynamic melting point of the unstretched network, folded chain crystallization occurs but, for λ values higher than a minimum critical value, also extended chain crystallization becomes possible. Moreover, a critical λ value can be found, which we indicate as λ^*, which is the minimum strain value necessary at every temperature to induce extended chain crystallization.[2] This value depends on polymer nature and network topology. Therefore, two parameters assume a great relevance, the melting temperature of the unstretched network T_m^0, and the critical deformation λ^*.

The general picture that is observable in Figure 6 confirms the indication given in the previous paper, and well agrees with the adopted phase diagram. As a matter of fact, in Figure 6 the existence of a value ($\lambda \simeq 4$) that can be identified with λ^* is quite evident. For $\lambda \leq \lambda^*$ only chain folding occurs, and a single melting point is observed, while for $\lambda \geq \lambda^*$, both the crystallization modes are possible, and two melting temperatures can be detected.

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