

Stress and Thermally Induced Crystallization in Crosslinked *Cis*-Polybutadiene

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Synopsis

Strain and thermally induced crystallization was investigated in crosslinked 1,4-*cis*-polybutadiene. Data obtained at room temperature, where the crystallization can be only strain induced, show that at any given deformation the elastic modulus is a simple function of the crystalline content. On this basis, the modulus data were used to analyze the crystallization phenomena under stress at low temperature. Results show that crystallization occurs with a two-stage mechanism that depends on deformation and temperature.

INTRODUCTION

The phenomenon of stress-induced crystallization in elastomeric systems is of great technological and theoretical importance. From a technological point of view, the crystallization phenomena can play a significant role on the mechanical behavior, particularly if the crystallization is reversible with stress removal and if it occurs with fast kinetics. From the theoretical point of view it is important to elucidate the crystallization mechanism that, as it is known, can be either stress induced or thermally induced, thus giving rise to different morphologies.^{1,2} The appearance of stress- or thermally induced crystallization depends on the physical conditions, and the former can appear without the latter or vice versa, while in other cases, both phenomena can be present even if characterized by completely different kinetic parameters. In previous papers, we reported the results obtained on the stress-induced crystallization in crosslinked polybutadiene. The samples analyzed were characterized by a high 1,4-*cis* content (about 98%) and the crosslinking was introduced by curing with a peroxide initiator. The results, obtained at room temperature, indicate that ordering phenomena can appear at deformations lower than the critical point at which the strain-induced crystallization appears;³ the crystallization occurs with very fast kinetics and is followed, with a typical two-stage mechanism, by a secondary process characterized by a slower and detectable growing rate. The observed two-stage mechanism which confirms data reported by other authors on a very similar elastomeric system,⁴ is predicted by theoretical treatments,^{5,7} and was observed on other polymeric systems.⁸⁻¹⁰ In the present paper we investigated the crystallization phenomena on crosslinked *cis*-polybutadiene previously studied,³ extending the analysis to the low temperature range, where thermally induced crystallization can appear. Our intent was to investigate the reciprocal influence of the two

different crystallization phenomena, and to study the way in which these mechanisms affect the physical behavior of the elastomeric network.

MATERIALS

The polymer used was a polybutadiene (ENICHEM) at high steric regularity obtained by polymerization with a neodymium-based catalyst. The content of 1,4-*cis* units was about 98.5%, and the molecular weight was $M_w = 652,000$ and $M_n = 57,000$. The crosslinked samples were obtained by vulcanizing at 140°C for 45 min with dicumylperoxide as initiator. The crosslinking density was $1 \cdot 10^{-4}$ mol/cm³ and was calculated from stress-strain data.¹¹

EXPERIMENTAL

A quantitative evaluation of the crystallinity content induced by deformation can be obtained by analyzing the photoelastic behavior. In particular, according to the Stein and Norris notation,¹² we can write upon some approximation:

$$\phi_c = \frac{\Delta n - C\sigma}{\Delta n_0 - C\sigma} \quad (1)$$

where ϕ_c is the volume fraction of the crystalline phase, Δn is the birefringence, Δn_0 is the intrinsic birefringence of the perfectly oriented crystals, σ the stress, and C the stress optical coefficient. Eq. (1) is valid if we assume the crystals perfectly oriented along the strain direction and consider the form birefringence negligible. In ideal Gaussian networks C is strain independent,¹ while in real networks it is strain dependent according to the following equation

$$C = \frac{B_1 + B_2/\lambda}{C_1 + C_2/\lambda} \quad (2)$$

where λ is the strain ratio and B_1 , B_2 , and C_1 , C_2 are the optical and the mechanical Mooney-Rivlin coefficients, respectively.¹³ Equation (1) gives ϕ_c as a function of λ and, at a given λ , ϕ_c as a function of time, provided the Mooney coefficients are obtained from the experimental photoelastic data¹³ to calculate C , and provided Δn and σ can be simultaneously measured. The experimental determination of Δn has been previously described,^{3,14} according to a standard method.¹⁵ A second experimental approach was based on the detection of the stress-relaxation at different temperatures and strain values. This method has already been used to obtain data on the crystallization phenomena and on the growth kinetics.^{16,17} Moreover, the elastic modulus was detected at random time intervals, superimposing a very small deformation (less than 2%) to the relaxation curve. It is well known that the modulus increases as crystallinity increases, and this therefore is another physical parameter connected to the crystallization process.

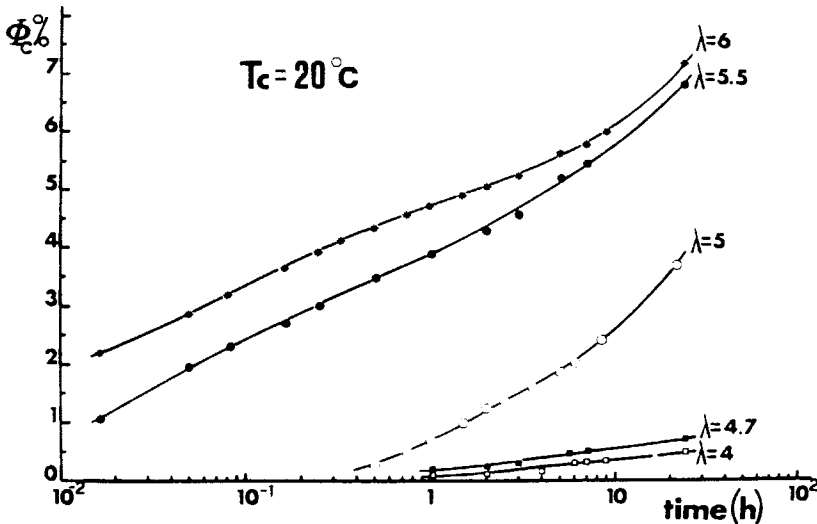


Fig. 1. The crystallinity is reported vs. the time at different strain values. Crystallization temperature 20°C.

RESULTS

Crystallization Under Stress at Room Temperature (20°C)

The optical method was used at room temperature to obtain a quantitative evaluation of ϕ_c . The experimental analysis of the photoelastic behavior gave the following values for the Mooney coefficients: $2C_1 = 2.45 \text{ kg/cm}^2$, $2C_2 = 2.24 \text{ kg/cm}^2$, $2B_1 = 6.8$, and $2B_2 = 11.3$. Therefore, using Eqs. (1) and (2), and adopting a correction to calculate the true stress on the amorphous phase,^{3,18} ϕ_c was obtained as a function of time at different λ values. The results are reported in Figure 1 which shows that for λ lower than 5, the initial crystallinity is zero, while a very slow increase is observable as a function of time, giving rise, after 24 h, to a ϕ_c value lower than 1%. At $\lambda = 5$ the initial crystallinity is still zero, but a more rapid increase is observable and after 24 h the calculated ϕ_c is 3.7%. For λ values greater than 5, an initial crystallinity is observable already in the range of very short times and is 1.1 and 2.2% at $\lambda = 5.5$ and 6.0, respectively, while after 24 h the further growth of ϕ_c bears a crystallinity content close to 7%. These results are in good agreement with previously reported data,¹⁴ and indicate that the critical deformation value necessary to induce a crystallization process is close to 5, and this crystallization, characterized by a very fast growth is followed by a further increase in crystallinity characterized by a detectable growing rate. The elastic modulus was detected at the same temperature and strain values; the results obtained are reported in Figure 2. In agreement with the optical data, a sharp increase in the initial modulus was observed between $\lambda = 5$ and $\lambda = 5.5$, and for $\lambda > 5$ a weak but clearly detectable modulus increase was observed. From the data of Figures 1 and 2, the dependence of E on ϕ_c can be obtained by plotting the isochronous modulus and crystallinity values. The results obtained are shown in Figure 3. In Figure 3 it is clearly evident that $\log E$ is a linear function of ϕ_c at any given λ , as suggested in general for semicrystalline polymers,¹⁹

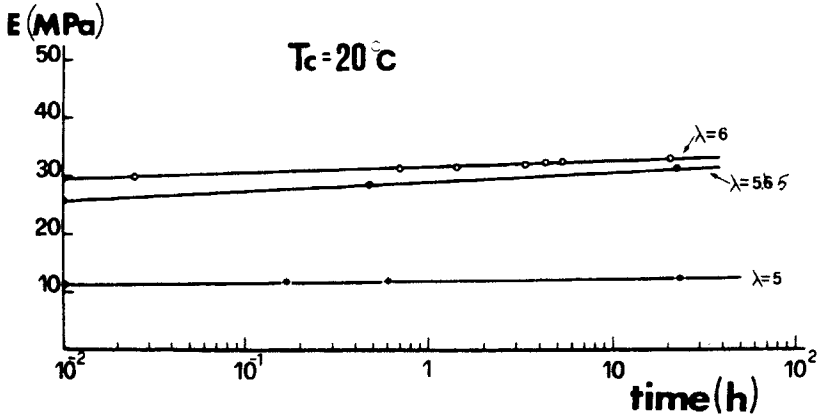


Fig. 2. The elastic modulus is reported vs. the time at different strain values. Crystallization temperature 20°C.

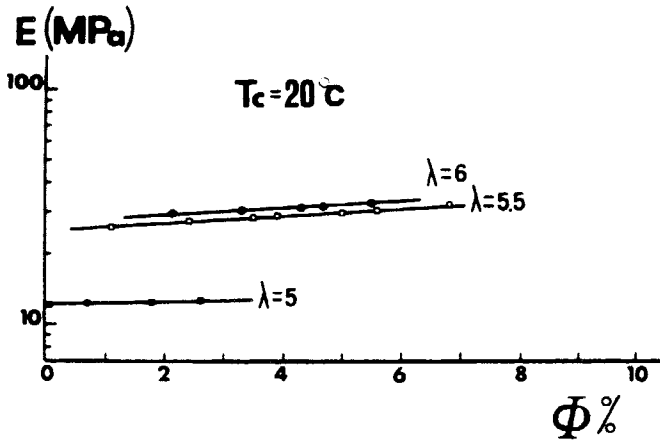
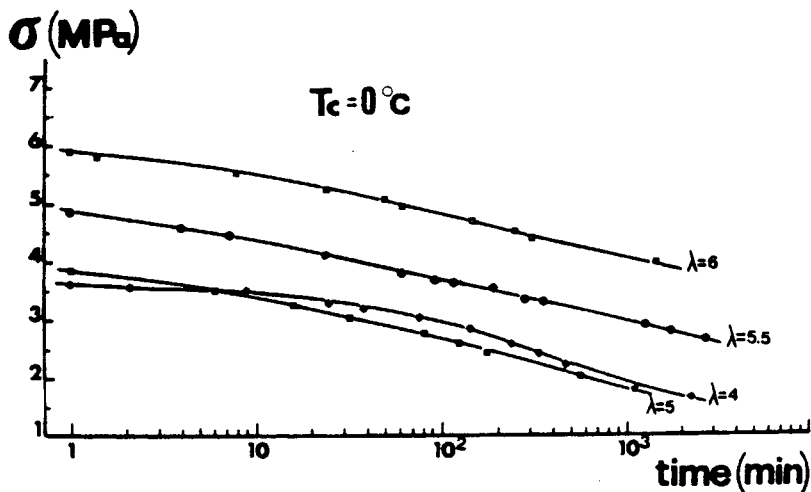
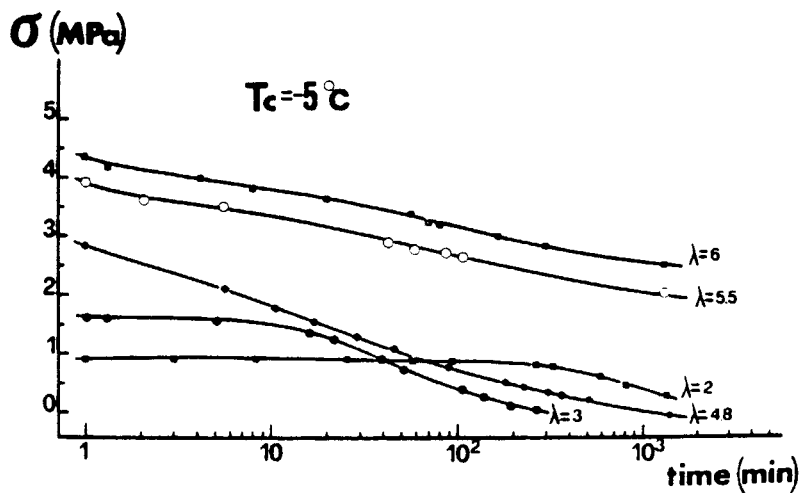


Fig. 3. The elastic modulus is reported vs. the isochronous crystallinity values. Crystallization temperature 20°C.

and as previously observed on a similar crosslinked system.²⁰ On the other hand, Figure 3 shows that the actual quantitative dependence of E on ϕ_c is strongly affected by the value of λ ; as a matter of fact at any given ϕ_c , E increases on increasing λ , and in a more drastic way in the range $\lambda = 5$ to $\lambda = 5.5$. As discussed further on, this means that the modulus depends not only on the crystallinity content, but also, and more significantly so, on the morphological organization. However we can approximately assume, on the basis of Figure 3, that $\log E$ is a linear function of ϕ_c at any given λ , and this assumption will be used later in analyzing the crystallization process at temperatures lower than 20°C.

Crystallization Under Stress at Low Temperatures

The analysis at low temperatures was carried out by detecting the stress relaxation and, at random time intervals, the elastic modulus. The sample was stretched at room temperature up to the chosen λ value, and then was rapidly

Fig. 4. Stress relaxation detected at 0°C at different strain values.Fig. 5. Stress relaxation detected at -5°C at different strain values.

transferred at constant length to the thermostatic bath and connected to a dynamometric cell. In such a way the stress relaxation plots were detected at different strain values, and the results obtained are reported in Figures 4–6. On a relaxing sample, a little deformation was reversibly superimposed at random time intervals to investigate the behavior of the elastic modulus during the relaxation phenomenon. The data so obtained are reported in double logarithmic scale in Figures 7–9. It is important to note that while the stress decreases with time, a modulus hardening is observed during the stress decay, indicating that both are connected to a crystallization process. The observed trend depends on strain and temperature, and in some cases also on the time interval, indicating a change in the relaxation mechanism. It is worth noting that on the basis of the previous assumption and in rough approximation, we can consider $\log E$ as linearly dependent on ϕ_c , and therefore the modulus increase, reported in logarithmic scale, can be considered as directly

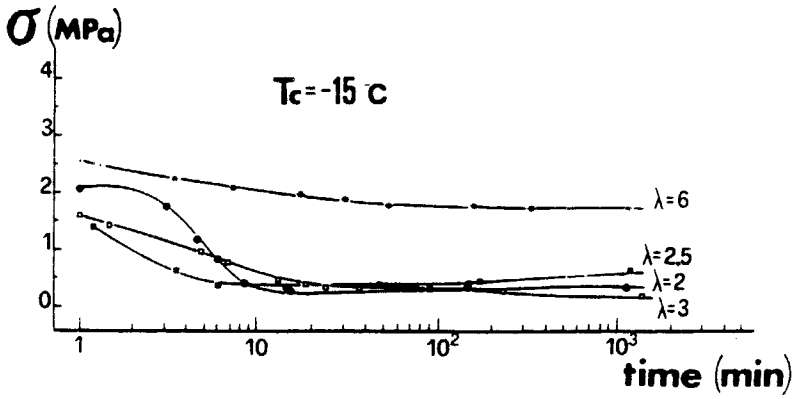


Fig. 6. Stress relaxation detected at -15°C at different strain values.

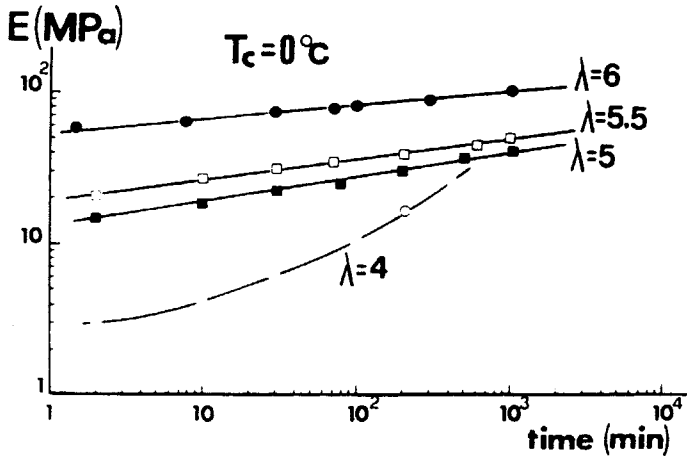


Fig. 7. The elastic modulus is reported vs. the time at 0°C for different strain values.

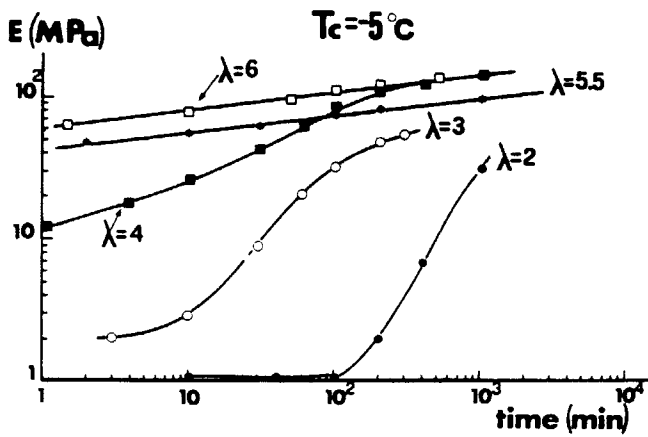


Fig. 8. The elastic modulus is reported vs. the time at -5°C for different strain values.

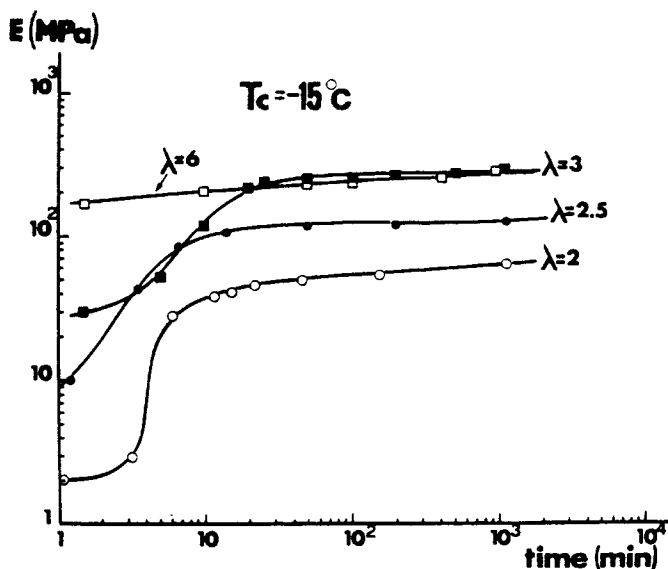


Fig. 9. The elastic modulus is reported vs. the time at -15°C for different strain values.

indicative of a crystallinity increase. However, considering that the actual dependence of $\log E$ on ϕ_c depends of λ , and probably also on the crystallization temperature, the quantitative modulus data reported in Figures 7–9, can allow only a qualitative evaluation of a crystalline phase growth. This is the consequence of a nonunivocal correspondence between crystallinity content and modulus value, at least on the basis of the present results. With this limitation the results reported in Figures 7–9 can be analyzed. At 0°C the growing is a linear function of $\log t$ for $\lambda > 5$, while the function is not linear at $\lambda = 4$ and increases very slowly for $\lambda < 4$ (not reported in Fig. 7). Where the function is linear the initial observable modulus is considerably higher (i.e., higher than 10 MPa, while at $\lambda = 4$ it is only 3 MPa). A similar trend can be seen at $T_c = 5^{\circ}\text{C}$ (Fig. 8), where the function is linear at $\lambda = 5.5$ and $\lambda = 6$ with an initial modulus that is, respectively, 40 MPa and 60 MPa, while the function is not linear and the initial modulus considerably lower for $\lambda < 4$. At this temperature the nonlinear function is characterized by a growing rate that is higher than at 0°C , and therefore also data obtained at $\lambda < 4$ can be reported in a time scale that is within 10^3 min. At $T_c = -15^{\circ}\text{C}$ (Fig. 9), for $\lambda = 6$, the function is linear and the initial modulus is about 200 MPa whereas at $\lambda < 3$ the function is nonlinear and characterized by a detectable growth in a time range that is within 10 min, followed at longer times by a linear growing.

On the basis of the general picture shown in figures 7–9, it is interesting to note that the linearity $\log E$ vs. $\log t$ is extended in all the time scale and starts from a high initial modulus, for λ values higher than or equal to the critical deformation necessary to induce a crystallization process at room temperature. Therefore in these cases, the observed linear growing is a process that we define as secondary, since it follows the strain-induced crystallization, characterized by a fast growing, not detectable with our method, but supported by the initial value of the elastic modulus (value detected at times

shorter than 1 minute). As is typical in a secondary process, the growing function (in this case $\log E$) depends linearly on $\log t$.²¹ At lower λ values, the overall crystallization mechanism is different; as a matter of fact, the linear function, typical of a secondary process, follows a nonlinear increase of $\log E$, detectable in the time scale of our experiments.

DISCUSSION

In unstretched elastomers, crystallization is possible only at temperatures lower than the thermodynamic melting temperature T_m° , and the crystallization kinetics mainly depend on the difference ($T_m^\circ - T_c$), where T_c is the crystallization temperature. T_m° is 275°K for the 1.4 *cis*-polybutadiene.²² However, the stretching induces a free energy change and therefore modifies the equilibrium conditions between the crystalline and the amorphous states. In particular, at $T > T_m^\circ$, strain-induced crystallization is thermodynamically possible^{6,7,23} and an extended-chain crystallization can take place, giving rise to a crystalline phase characterized by a fibrillar morphology. For any polymeric system, at any given $T > T_m^\circ$, the critical λ value, λ_{crit} , depends on T and on the network topology. A theoretical prediction of λ_{crit} can be made according to different theoretical models,⁵⁻⁷ and λ_{crit} increases on increasing T and on decreasing the crosslinking density. On the other hand at temperatures lower than T_m° , strain-induced crystallization can still occur, but chainfolding crystallization is also thermodynamically possible, and becomes competitive with extended-chain crystallization; on increasing the supercooling value $T_m^\circ - T_c$, chainfolding becomes more probable, while the probability of having extended-chain strain-induced crystallizations is drastically reduced. The complex correlation between crystallization mechanism and crystallization condition in terms of temperature, drawing, mechanical, and thermal history, can be shown in a phase diagram in which the melting temperature T_m is reported versus the drawing degree λ . In particular, according to a theoretical treatment⁷ that seems to explain the obtained results, the correlations scheme can be reported as illustrated in Figure 10.

In Figure 10 T_m° is the thermodynamic melting temperature of the unstretched sample, I and II are the equilibrium melting curves for the extended-chain and folded-chain crystals, respectively, and λ^* is the minimum strain value, theoretically predicted, necessary at every temperature to induce extended-chain crystallization. Figure 10 shows at qualitative level the phase diagram of an indefinite polymeric system, and therefore T_m and λ values are in arbitrary scale.

On the basis of this general picture, in the reported results we have to distinguish between room and low temperatures. As a matter of fact, 20°C is a temperature 18 degrees higher than T_m° , and therefore only strain-induced crystallization is possible. The observed λ_{crit} is about 5, that we can consider as the minimum strain value necessary to induce crystallization at 20°C.

At λ values equal to or higher than 5 the crystallization process takes place with a typical two-stage mechanism, as we have already mentioned. It is interesting to note that the crystallization mechanism has a drastic influence on the modulus-crystallinity relationship. As a matter of fact, Figure 3 shows that for a given crystallinity the modulus increases with λ ; the increase is

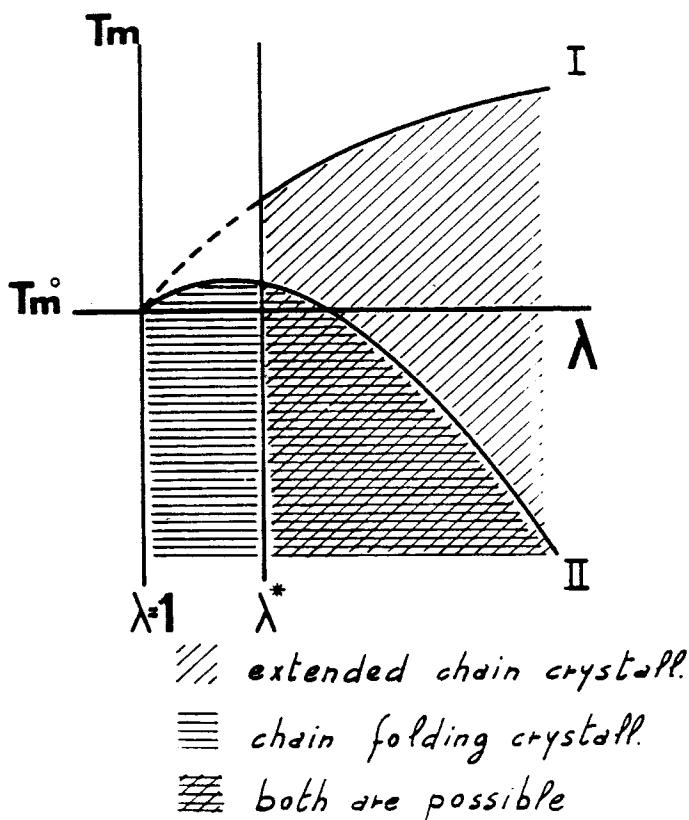


Fig. 10. Phase diagram based on the theoretical approach reported in ref. 7.

more marked in the sharp deformation range, in which λ_{crit} falls. Considering that the strain-induced structure is characterized by a fibrillar morphology, with the chain parallel to the stretching direction, and with a tendency to have a continuity of the crystalline phase,⁸⁻¹⁰ the strong influence of this morphological feature on the modulus value can be easily understood. Therefore, at room temperature the observed linear dependence of $\log E$ on ϕ_c , at a given λ , mainly is related to the second-stage process, characterized by slower growing, detectable with the method we used. This aspect is important in order to discuss the results observed at low temperatures. As previously stated, λ_{crit} decreases on decreasing the temperature, and therefore $\lambda = 5$, which is the minimum value to induce crystallization at 20°C, is the maximum limit at which to observe strain-induced crystallization at lower temperatures. As a matter of fact, the presence of a strain-induced crystallization at $\lambda \geq 5$, is supported by the modulus data in Figures 7-9, where at $\lambda \geq 5$ a drastic hardening of the initial modulus is observable.

Therefore, as in the case of room temperature, the linear increase of $\log E$ observed at $\lambda \geq 5$ is indicative of a linear increase in crystallinity that grows on the strain-induced structure. This second stage, occurring at temperatures lower than T_m^0 , gives rise to a lamellar structure, with the planes of the lamella oriented in the direction normal to the stretching direction,⁸⁻¹⁰ as is typical of a shish-kebab morphology. The lamellar structure is characterized

by a chain-folding crystallization; such a mechanism is expected to produce a stress hardening, in particular the stress is expected to rise as the chains in the extended-chain morphology begin to switch to a folded-chain structure.²⁴ However, in contrast with this picture Figures 4–6 show that at $\lambda \geq 5$ the crystallization occurs with a continuous and quasilinear stress relaxation. This apparent disagreement between crystallization mechanism and relaxation data, was previously underlined;²⁵ to account for this experimental evidence it was suggested that probably prefolded structures were already present in the amorphous phase.²⁵ Moreover we can assume that at high deformations the probability that any crystallizing chain can re-enter in the same lamella by folding, is lower as compared with the probability of its entering into another lamella located along the stretching direction. This mechanism does not require the existence of prefolded structures and is compatible with a stress relaxation during the crystallization process. This mechanism, at high deformations, should be kinetically favored as compared to chain-folding crystallization. Considering the data regarding crystallization at low temperature but at $\lambda < 5$, we observed that the linear trend, when present, follows a detectable nonlinear growth. This is well evident at $T = -15^\circ\text{C}$ (Fig. 9) for λ in the range 2–3. In this strain range the trend observed can be explained on the basis of the scheme in Figure 10; -15°C is lower than T_m° and chain-folding lamellar growth is possible. The chain-folding crystallization characterized by a detectable growing rate, is observable as the nonlinear increase of $\log E$. Moreover, the sharp increase of the initial modulus that is observed (Fig. 9) when the deformation changes from $\lambda = 2$ to $2.5 \div 3$, seems to suggest the presence of a faster initial process that precedes the detectable crystallization stage. This trend could be compatible with a mixed crystallization in which extended-chain and chain-folding structures are present, and this possibility is theoretically foreseen.^{5,7} The linear trend that follows the primary nonlinear stage can be considered, on the basis of the previously reported remarks, the result of a secondary crystallization. Finally, at higher temperatures (-5°C and 0°C) and for the deformation range $\lambda < 4$, the nonlinear stage is not concluded in the time interval analyzed, as a consequence of a slower growing rate. The possibility of a mixed crystallization seems to be present only at $\lambda = 4$ and $T_c = -5$, on the basis of the significant value of the initial modulus (10 MPa).

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