# Size effect of metastable states on semicrystalline polymer structures and morphologies

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## Abstract

A classical concept of a metastable state is a local free energy minimum that may ultimately relax to the stable equilibrium state of a global free energy minimum via an activation process. This process is different from the barrier-free relaxation that spontaneously takes place when an unstable state relaxes. In order to be classified as metastable, the lifetime of a metastable state must be longer than the timescale of observation, which in turn is practically limited by experimental equipment and the patience of the observer. In the classical concept of metastable states there is an assumption that the systems are large enough so that there is no need for consideration of size or other kinetic effects on the system. In general, polymers are much more prone to access the metastable region than small molecules. Polymeric materials, with their various hierarchies of microstructure, may have metastable states present due to small phase size, composition, external fields and other causes. In this review, our focus will be on concepts and experimental observations of metastable states in polymer phase transformations where two ordered structures exist. The phase stability relationships of these structures will be discussed with respect to the phase size, namely, the lamellar thickness. The concepts involved in metastable states and metastability are not only important in the scientific understanding of condensed polymer physics, but are also useful for practical materials development and applications. © 1999 Elsevier Science B.V. All rights reserved.

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## 1. Introduction (concepts of classical metastable states)

When one deals with phase and phase transitions, there are two important but different concepts: *equilibrium* and *stability*. Fig. 1 shows analogs of classical mechanics to illustrate the difference between these two concepts. An equilibrium state is reached when the summation of the forces on a system is equal to zero. However, the stability of a system reflects how

that system responds to an outside perturbation. If the system diminishes this perturbation, it is stable. On the contrary, if the system enlarges this perturbation, it is unstable. In Fig. 1, case (a) is thus an unstable equilibrium, while case (b) shows a stable equilibrium and a random equilibrium is shown as case (c).

To transfer these two concepts to thermodynamics, we consider a plot between the free energy of the system ($F$) and order parameter ($\Phi$) to replace the relationship between height and position shown in Fig. 1. For a phase to be in thermodynamic equilibrium, it is required that $dF/d\Phi=0$. For a stable equilibrium phase, it is also necessary that $d^2F/$

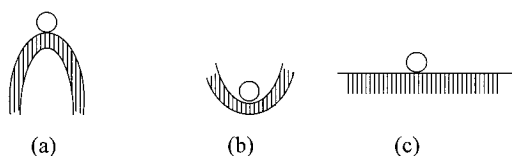*Corresponding author. Tel.: +1-330-972-6931; fax: +1-330-972-8626; e-mail: cheng@polymer.uakron.edu

Fig. 1. Schematic drawing of the concepts of equilibrium and stability based on classical mechanics: (a) unstable equilibrium, (b) stable equilibrium, and (c) random equilibrium [8].

$d\Phi^2>0$. At $d^2F/d\Phi^2=0$, which is the limit of (thermodynamic) stability, the first violation of these criteria occurs. In order for a system to have a stability equal to the limit of stability, it is required that $d^3F/d\Phi^3=0$ and $d^4F/d\Phi^4>0$. In general, therefore, the phase stability criterion can be stated as a system where the lowest-order non-vanishing even derivative is positive and all lower-order derivatives are zero [1,2].

The metastable state is an important concept in both scientific understanding and practical material applications. For a single component, the definition of the metastable state is that a state may exist even though it is thermodynamically less stable than its ultimate equilibrium state. This state is stable with respect to infinitesimal fluctuations but is not at the global $F$ minimum, which is where the equilibrium state of the system is located [2,3]. It is interesting to note that Ostwald clearly reflected this understanding in the end of the last century with the formulation of his "stage rule" [4]. According to this rule a transformation from one stable state to another will proceed via metastable states, whenever such exist, towards stages of increasing stability. However, this rule did not explain why this trend occurs.

Theoretically, as can be seen in a plot of $F$ and $\Phi$, $dF/d\Phi=0$ and $d^2F/d\Phi^2>0$ in the metastable state. In this way, metastable states are analogs to the ultimate equilibrium state. It is not difficult to surmise that $F(\Phi)$ is the most critical function needed in order to use thermodynamic criteria to judge the stability and metastability of a system and to describe its phase and phase transition behaviors. In order to obtain an analytical expression for $F(\Phi)$ one has to rely on theories such as the mean-field theory, the field theory and renormalization groups. Note that these theories are useful only under certain assumptions and when using specific simplifications.

Although the metastable state will ultimately relax into the stable equilibrium state, how long this relaxa-

tion process will take is a kinetic issue. In order to experimentally observe a metastable state, the lifetime ($\tau$) of this metastable state must be longer than the observation timescale ($\tau_{obs}$). However, the molecular relaxation time ($\tau_{rel}$) of a specific measurable property must at the same time be shorter than the lifetime ($\tau>\tau_{obs}\gg\tau_{rel}$). Relaxation of a metastable state can occur via two types of processes: nucleation and spinodal decomposition. Based on their definitions, the relaxation of a metastable state towards the equilibrium state requires the metastable state to overcome a $F$ barrier. According to classical nucleation theory, this barrier never vanishes, and therefore, no unstable state exists. The height of this activated barrier depends on the system's depth of penetration into the metastable state (undercooling, $\Delta T$), and overcoming this barrier is classified as a nucleation process. The kinetic rate at which a nucleus of critical size is reached depends entirely upon the height of the $F$ barrier and the magnitude of thermal fluctuations of atoms or molecules. In this process, fluctuations are localized but exhibit large amplitudes. Contrary to classical nucleation theory, unstable states do exist and relaxation from an unstable state towards equilibrium (spinodal decomposition) is spontaneous, energy barrier free, and growth of the equilibrium phase is characterized by long wavelength fluctuations with small amplitude [2,3].

One example of the metastable state is in the condensation of a gaseous phase or the evaporation of a liquid phase between the binodal and spinodal lines of a phase diagram. In this area, one may have a superheated metastable liquid phase or an undercooled metastable vapor phase. Fig. 2 is a schematic illustration of the relationship between pressure ($P$) and volume ($V$) in the vicinity of the critical point. It is noted that below the critical temperature and pressure, the binodal line represents a first-order transition at which coexistence of both phases can be found ($dF/d\Phi=0$), the limit of thermodynamic stability ($d^2F/d\Phi^2=0$) is reached at the spinodal line. We thus have to look at the inequality ($d^4F/d\Phi^4>0$), which is only held at the critical point and not at other points on the spinodal line. Therefore, the critical point is the stable limit of stability, whereas all other points are the unstable limits of stability. Both of the metastable states (superheated liquid or undercooled vapor) are terminated at the spinodal
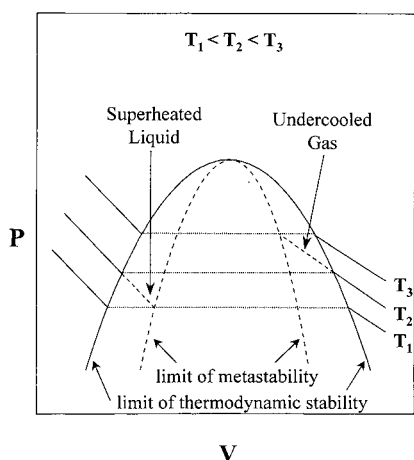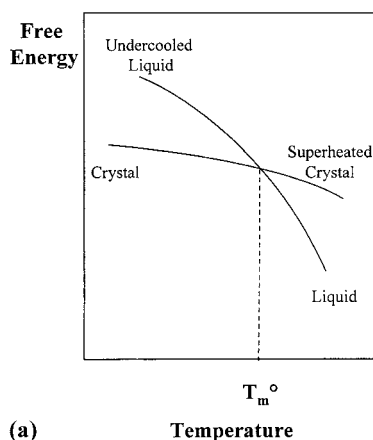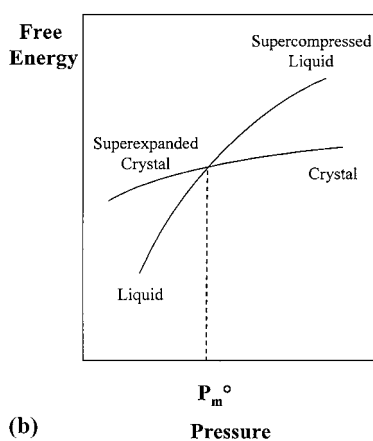
Fig. 2. Schematic of the relationship between pressure and volume near the critical point [7,8].



Fig. 3. Schematic plots of (a) free energy versus temperature at a constant pressure and (b) free energy versus pressure at a constant temperature, both plots are in the vicinity of a first order transition [7,8].

line, defining the spinodal line of the limit of meta-stability.

Another example of the metastable state occurs in the vicinity of the first-order transition temperature for a crystal–liquid transition. In this case, there may be a superheated metastable crystal phase at a temperature higher than the transition temperature or an under-cooled metastable liquid phase at a temperature lower than the transition temperature. This can schematically be represented in a plot of $F$ versus temperature ($T$) in the vicinity of a first-order transition temperature. This plot is actually a cross-sectioned surface at constant $P$ (in Fig. 3(a)) of a three-dimensional $F–T–P$ phase diagram (the same cross-section can be made at constant $T$ for a $F–P$ plot as shown in Fig. 3(b)). The equilibrium transition temperature is thus a projection of the phase boundary line. In the phase diagram of a crystal–liquid transition, no critical point exists since there is a symmetry breaking at the transition. The phase boundary lines extend towards infinity or meet with other phases. This behavior is different than that of the liquid-vapor transition described previously where both of the phases possess the same symmetry. The main uncertainty in Fig. 3(a) and (b) is where the $F$ lines for the metastable states should end as they reach their limit of metastability. Note that unlike the liquid-vapor transition, no spinodal line can be obtained for this transition. This is equivalent to stating that no unstable state exists for this system and the crystallization nucleation barrier never goes to

zero. Due to the lack of spontaneous relaxation, we know little about the singular properties of the limit of metastability in crystal–liquid transitions. A similar delineation may also exist between different crystal solid phases (polymorphs). In this case, it is essential to realize that, unless we are at the cross-over of the $F$ lines, all but one of the possible polymorphs correspond to metastable states.

The absolute limit of metastability is determined by thermodynamics. Nevertheless, in many phase transitions, kinetics is the practical determining factor of the limit of metastability. The Ostwald stage rule is puzzling as to the microscopic origin of the existence of metastable states. One may ask why the atoms (or

molecules) can be trapped into a local $F$ minimum. A generalized explanation is that there is a larger probability that atoms (or molecules), due to a limited fluctuation amplitude, will chose a pathway which possesses a lower $F$ barrier, regardless of the resultant stability of the atoms (or molecules) after the barrier is overcome. In other words, the atoms (or molecules) are ''blind'' and they cannot predict the thermodynamic outcome behind the $F$ barrier. In this way, a macroscopic, metastable state forms which can be detected when enough atoms (or molecules) are in the $F$ local minimum on a time and size scale compatible with those of experimental observations. One may thus phenomenologically propose that, during a transformation process, a metastable state may exist due to its fast kinetic pathway (lower $F$ barrier) even though this state is thermodynamically less stable than the ultimate equilibrium state.

## 2. Size effect of metastable states in polymers

When viewed via classical concepts, thermodynamic states are considered to be of infinite size. However, there is a broad class of metastable states in polymers and other materials where their metastability is dictated by their microscopic phase size. It is certainly necessary to define the size scale of a metastable phase in three-dimensional space. Therefore, it is important to distinguish between phases which are three-dimensionally small, two-dimensionally small, and phases which are one-dimensionally small. Limited phase size can be caused by many different reasons including exhaustion of available materials, geometric restrictions, molecular mobility, and phase formation kinetics, etc. The thermodynamic features of these metastable states are identical to those in classical ones; they also are in a local $F$ minimum, and have the tendency to change with time, either by transformation and/or relaxation, slowly or quickly, depending on the circumstances of the available thermodynamic and kinetic pathways.

In experimental observations of polymer phase transitions, complicated phase behavior can frequently be found. This is because in many cases two kinds of metastable states may be inter-linked. An important yet not well-recognized example is when liquid–liquid phase separation occurs in solu-

tions or blends of polymers. These systems do not usually proceed to a state of ultimate equilibrium stability as in a case of a phase separated mixture of water and oil, but rather they provide a variety of phase morphologies which are obtained by either nucleation or spinodal decomposition. If phase separated polymer blends always quickly reached their stable equilibrium states, metastable phase morphologies would not appear and this research field might not be as interesting and rewarding as it is today. If one of the components is crystallizable after phase separation, an additional crystal morphology may form within another phase morphology formed by the initial liquid phase separation. However, in order to preserve this phase separated morphology, a vitrification process is necessary to freeze the phase morphology formed via the liquid–liquid phase separation. For this reason, any crystallization which takes place after vitrification occurs in a geometrically confined space. This results in a hierarchy of crystal and phase morphologies, each with a corresponding hierarchy of metastabilities.

For the crystalline state in homopolymers, a fully crystalline system with extended chain crystals is the stable equilibrium state. However, this state has never been reached. In reality, crystalline polymers are semicrystalline in nature and they universally possess a crystalline-amorphous ratio which is always less than 100% (crystallinity). This can be caused by a range of factors which are associated with the long chain nature of macromolecules and multiple relaxation processes. It is also important to note that the amorphous content in these semicrystalline polymers comprises a range of cases from localized fully amorphous domains to crystal surface regions, with intermediate stages which may be characterized as strained amorphous and rigid amorphous.

## 3. Size effects in semicrystalline polymers on structures and morphologies

It is difficult to propose a quantitative formula to describe metastable states in polymers due to the different hierarchies in and sizes of these states. However, one distinct and definitive structural feature, the chain folded lamellar crystal, may provide an opportunity to precisely illustrate the concept of the

size dependence of the metastable state. This is not only uniquely important for the case of crystalline polymers, but it is also essential for reaching wide generalizations about the phase behavior of matter in order to define communal relationships of size-effects on metastability. The concept of a morphological metastable state is based on the fact that the basic crystal habit in a flexible polymer is a chain folded lamella. The thickness of lamellar crystals ($l$) is generally in the range of 10–50 nm. The thermodynamic stability of these lamellar crystals is represented by the melting temperature of the crystals. This can be approximately expressed through the Gibbs–Thomson relation [5] which, as applied to polymer crystals in the Hoffman–Weeks formulation [6], is

$$T_m = T_m^0 \left( 1 - \frac{2\sigma_e}{l\Delta H} \right), \qquad (1)$$

where $T_m$ is the melting point of the crystal having a thickness $l$, $T_m^0$ is the ultimate equilibrium crystal melting point (i.e., with $l \rightarrow \infty$), $\Delta H$ is the heat of fusion of crystal melting, and $\sigma_e$ is the fold surface free energy of the lamella under the assumption that the effect of the lateral side surface on the crystal stability is considered negligible. In almost every semicrystalline polymer with a lamellar crystal habit, Eq. (1) is closely obeyed. This is shown in a schematic illustration in Fig. 4. Similar equations can be easily derived which take the lateral side surface energy into account.
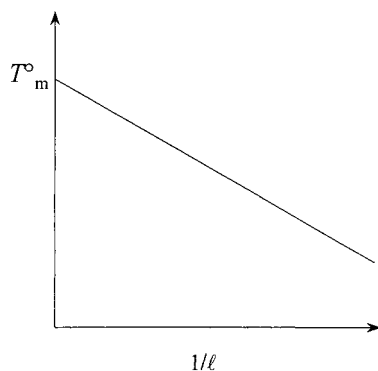


Fig. 4. A schematic illustration of Eq. (1) describing the relationship between $T_m$ and the reciprocal of lamellar thickness. The $T_m^0$ can be obtained by extrapolating the reciprocal lamellar thickness to zero.

The reason for the one-to-one correspondence between the lamellar thickness and $\Delta T$ indicated in Eq. (1) is due to kinetic considerations. Classical nucleation theory states that at a particular $\Delta T$ only one nucleation barrier is set with respect to the nucleus size. This is schematically represented by placing the system at the bottom of a hyperbolic paraboloid $F$ surface, which represents the lowest $F$ barrier needed for crystal growth. This lowest $F$ barrier corresponds to the crystal thickness. For this reason, growth along the thickness direction in polymer lamellar crystals is generally found to be negligible after primary nucleation. The crystal thickness may therefore be recognized as a distinct metastable structure: a morphological "polymorph". Therefore, the morphological metastability caused by lamellar thickness can be considered as the second level in the hierarchies of metastability while the classical crystal polymorph serves as the first level.

## 4. Relationships between classical and morphological metastabilities

In practical studies of polymeric materials, linear, flexible polymers with relatively high structure symmetry (such as polyethylene (PE), polyoxymethylene, isotactic and syndiotactic polystyrene and others) may generally grow lamellar crystals from the melt and solution. Many polymers possess more than one crystalline form and thus exhibit several polymorphs. Intrinsically, these polymorphs belong to the classical metastable states, or the first level in the hierarchy of metastability, and they can be described by crystal lattices with different symmetries. However, as described previously, all but one polymorph corresponds to a metastable state at each specific $T$ and $P$. Each crystal polymorph also exhibits different lamellar thicknesses at each $\Delta T$, depending upon their own formation kinetics. Therefore, we now have one class of metastability which is related to the lattice (the classical metastable state) and another which is related to the limited thickness (the morphological metastable state), both of which are inter-linked [7,8].

Establishing the relationship between these two categories of metastable states may lead to significant consequences. Based on Eq. (1), if the size dependence for each polymorph is different due to different
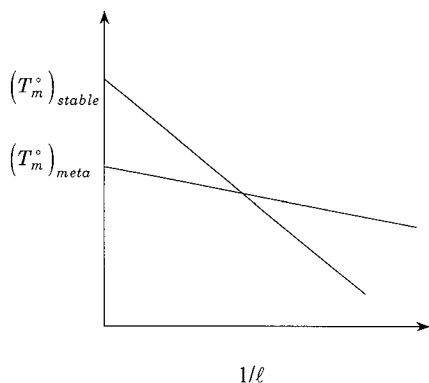
Fig. 5. A schematic illustration of two real phases, each of which obeys Eq. (1). Since $(T_m^0)_{st} > (T_m^0)_{meta}$, and $(\sigma_e/\Delta H)_{meta} < (\sigma_e/\Delta H)_{st}$ holds throughout the parameters given, these two lines can cross-over, i.e., when the crystal size becomes small, there is a critical size beyond which $(T_m)_{meta} > (T_m)_{st}$. As a consequence, we may achieve a stability inversion with size [7–11].

values of the parameters $\sigma_e$ and $\Delta H$, each polymorph has its own linear relationship between $T_m$ and $1/l$ with an intercept of $T_m^0$ and a slope of $T_m^0$ ($\sigma_e/\Delta H$). Assuming that we have two different polymorphs: one stable and the other metastable in their infinite sizes, $(T_m^0)_{st} > (T_m^0)_{meta}$, and $(\sigma_e/\Delta H)_{meta} < (\sigma_e/\Delta H)_{st}$ holds throughout the conditions used, these two lines can cross-over. For example, when the crystal size becomes small, there is a critical size beyond which $(T_m)_{meta} > (T_m)_{st}$. As a consequence, we may achieve a stability inversion with size as shown in Fig. 5. This is conceptually important, since it indicates that when a metastable state possesses a dimension that is small enough, it may become the stable state, and conversely, a conventionally stable phase may become metastable when its size is sufficiently small. This possibility of stability inversion with size, as recently recognized, may also have important potential consequences for polymer crystallization [9–11].

When we further consider the formation kinetics of these polymorphs, it is apparent that the critical nucleus is the smallest size needed for achieving crystal (or phase) growth, and furthermore, the lower $F$ barrier of this smallest nucleus size leads to a faster growth rate. If phase stability inversion occurs with size, the metastable phase (referring to the phase when at infinite size), which is the more stable phase in the case of a small enough critical nucleus size, may grow faster. Accordingly, a metastable phase can evolve

preferentially to a form due to the fact that the metastable phase (at its small size) is the stable phase, therefore (again, by virtue of its small size), becoming the rate determining factor at that time. Further discussion leads to whether or not such a phase will keep the same crystal structure throughout its continuing growth in size. This depends entirely on the molecular mobility in the metastable phase. If the molecular mobility is very limited, this phase may permanently keep its metastable structure. However, if the molecular mobility is high enough, this phase may transform into its ultimate stable state which exhibits another crystal structure, destroying any indication of the transient initial phase.

One of the many well-known examples of polymorphic activity is in PE, which shows orthorhombic (orth) and hexagonal (hex) crystal structures (we will be ignoring the mechanically induced triclinic polymorph in this discussion). The orth phase is found at low $T$ and $P$ while the hex phase is recognized in experiments at high hydrostatic $P$ [13,14]. The resulting $T$–$P$ phase diagram is shown as Fig. 6 [12]. Structural analyses reveal that these two crystal forms differ not only in terms of symmetry and atomic positions but that they also exhibit different molecular mobility. In the orth structure the chains are in a crystal register (a stable state) while the hex structure is a mesophase with large mobility along the chain direc-
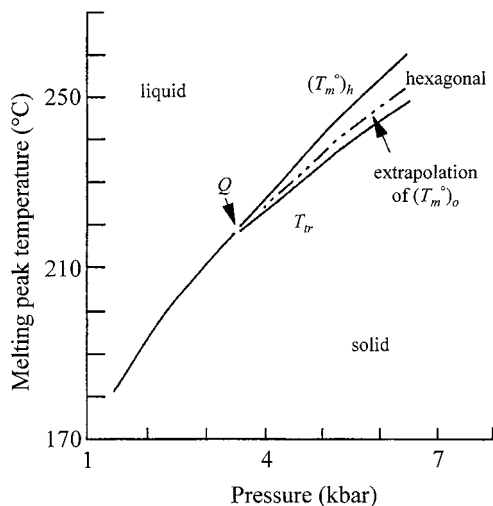


Fig. 6. A diagram of PEs phase relationship with pressure and temperature. A high-pressure hex phase can be found [12].

tion (a metastable state). In the former case, the crystals grow only laterally with a fixed $\Delta T$ determined thickness ($l$), while in the latter, the mesophase also contains growing in the thickness direction. This "thickening growth" is terminated only by structural impingement or material exhaustion [15]. This makes the hex phase very interesting, due to the fact that it exhibits the characteristic extended chain crystal morphology [13] when crystallized at elevated pressures [14]. Subsequently, it was observed that hex phase can also start growth below the "triple point" ($T_Q$) as shown in Fig. 6 [15,16]. This is in the orth phase region where the resulting hex phase will thus be metastable.

Studies of wide angle X-ray diffraction (WAXD) experiments at elevated pressure [17] revealed that crystallization occurring not too far below the triple point always initiated the metastable hex phase and it proceeded both laterally and in the thickness direction until an hex→orth transformation took place, i.e., a solid state transformation into the phase which possessed the ultimate stability (Fig. 6). At the same time as this transformation, the remarkable simultaneous observations under polarized light microscopy at elevated pressures discovered that the crystal growth along the thickness direction stopped while the lateral growth slowed down substantially [15]. These results

imply that, compared with the orth phase which is ultimately stable at an infinite size, the ultimately metastable phase (hex, also in infinite size) possesses higher stability in the initially small phase size. This phase also grows at a faster rate, which results in the larger kinetic counterpart of its higher stability at small sizes. This certainly accounts for the Ostwald stage rule, and above all, comprises the important phase stability inversion effect. In particular, thickening growth becomes a stability controlling factor which governs the stability inversion and results in the hex→orth transformation [18,19]. This process is schematically illustrated in Fig. 7. Note that this phenomenon is fully consistent with the expected high chain mobility of the hex phase, which in turn induces (or promotes) lamellar thickening through chain refolding as envisaged via sliding diffusion [18,19].

Another possible phase relationship encountered when applying Eq. (1) to two polymorphs is that the metastable and the stable phases do not invert their stability throughout their entire size range. This can be expressed by using Fig. 8 as a schematic illustration. However, the size effect on phase metastability in this case can also be clearly seen in several experimental examples. When we use Eq. (1) to represent the phase relationships shown in Fig. 8, [9], the results are that $(T_m^0)_{st} > (T_m^0)_{meta}$ and
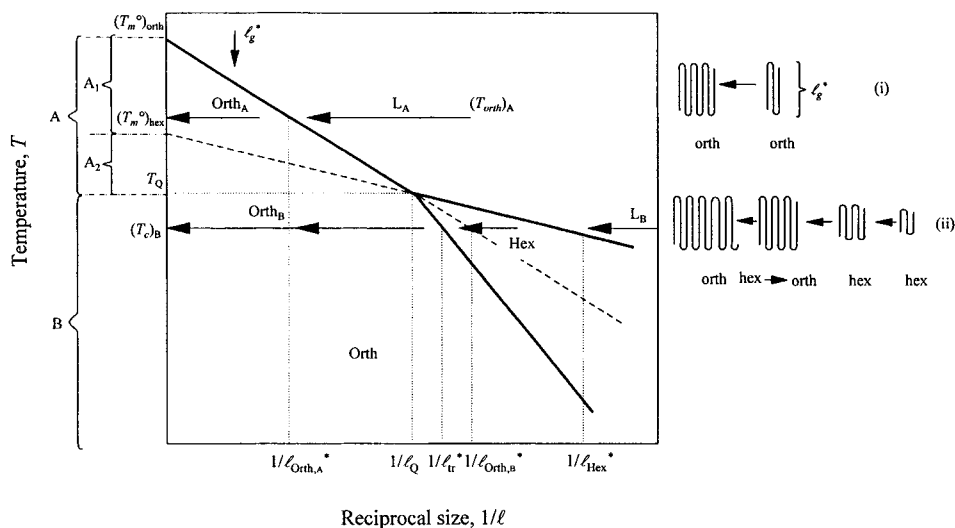


Fig. 7. An illustration of the lamellar thickening process for the phase stability inversion of PE. When lamellal are thin, the hex phase is more stable than the orth phase. The orth phase becomes stable as soon as the lamellar thickness exceeds the stability boundary during annealing.
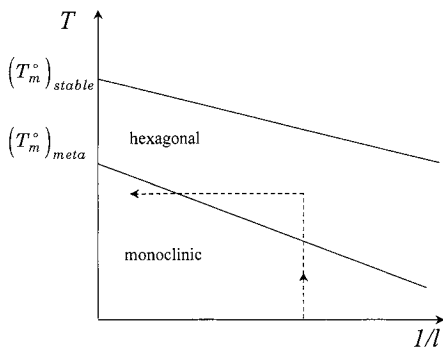
Fig. 8. A schematic illustration of two real phases, each of which obeys Eq. (1). Since $(T_m^0)_{st} > (T_m^0)_{meta}$, and $(\sigma_e/\Delta H)_{meta} \approx (\sigma_e/\Delta H)_{st}$ holds throughout the parameters given, these two lines cannot cross-over, i.e., in a whole size region $(T_m)_{meta} < (T_m)_{st}$ no matter the crystal size. The dashed line indicates the route of the text [9].

$(\sigma_e/\Delta H)_{meta} \approx (\sigma_e/\Delta H)_{st}$ for all phase sizes. For this reason, the phase lines are more or less parallel and no cross-over exists, i.e., no matter what the crystal size, small or large, $(T_m)_{meta}$ is always lower than $(T_m)_{st}$.

An example of this kind of phase relationship can be found in poly-*trans*-1,4-butadience (PTB) as shown in Fig. 9 [20]. A monoclinic (mono) phase has been identified that at low temperatures. This phase melts at around 70°C, depending upon on the crystal size (lamellar thickness), and enters a hex phase which possesses considerable conformational disorder. Similar to the case of PE, this polymer also exhibits a substantial thickening process in the hex phase. A
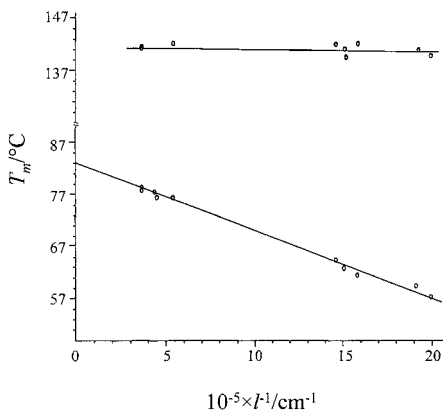
careful experiment can be designed using PTB to get results analogous to the dashed line shown in Fig. 8 in the following way. Lamellar crystals of PTB with a fixed thickness can be formed via isothermal solution crystallization. The crystals can then be precipitated and collected in their solid state form. These samples are then heated up to a temperature that is slightly higher than the mono→hex transition and annealed at that temperature. During this annealing, the lamellae start to thicken, a phenomena which is equivalent to a horizontal shift towards the left in Fig. 8 (increase of the crystal size). As soon as the lamellar thickness crosses the stability line of the mono→hex transition, there must be a transformation of the hex phase back to the mono phase. This is indeed the case as detected using synchrotron WAXD experiments and shown in Fig. 10 [21]. In this figure, the WAXD patterns follow exactly the heating and annealing processes described. The (200) reflection in the mono phase exhibits a reflection at $2\theta = 22.4°$. This reflection disappears when the samples are heated to 68.5°C and a new reflection which represents the (100) reflection appears at $2\theta = 20.7°$. This indicates the formation of the hex phase. However, after 20 min annealing, the reflection at $2\theta = 22.4°$ reappears, indicating a transformation of the hex phase back to the mono phase due to lamellar thickening. This clearly illustrates that with increasing the lamellar thickness (the
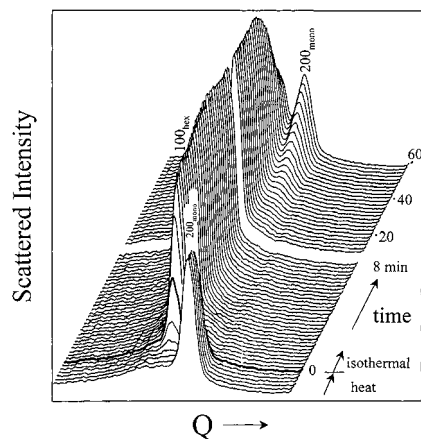


Fig. 9. A phase stability diagram for the mono and hex phases for poly-*trans*-1,4-butadiene [20].



Fig. 10. Real-time synchrotron WAXD results for poly-*trans*-1,4-butydiene obtained during heating and annealing. It is evident that a mono→hex phase transition occurs during heating and a hex→mono phase transition takes place during annealing [21].

crystal size), the metastable mono phase at 68.5°C inverts to become stable phase.

## 5. Conclusion

Although we may discuss the existence of phases which are truly metastable, are not subject to external constraints, and are of infinite (i.e., macroscopic) size (such are, e.g., all conventional polymorphs), as we have shown, it is possible to consider metastable phases that can arise through a size induced shift of stability in the initial stages of their evolution, as opposed to a system having some intrinsic preference for metastability. Without the recognition of such possibilities the role and importance of a metastable phase due to whatever cause and at whatever stage of the phase evolution even those unrelated to any shift instability criteria cannot be assessed or even adequately discussed. It is hoped that by at least raising these issues a step towards the understanding of size-induced metastability has been made.

## Acknowledgements

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