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Influence of Fragility on Polymer Cold Crystallization

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The first-order phase transition by which a supercooled amorphous polymer material transforms into a semicrystalline one continues to be a challenging central problem of polymer physics affecting other fields including material properties and protein crystallization. Although substantial progress has been made in understanding polymer crystallization over the past four decades, several aspects of this process remain open. In particular, the influence of chain cooperativity, dynamic fragility, and correlated motions on polymer crystallization remain unclear. Here we show the existence of a correlation between nucleation kinetics and dynamic fragility when the crystallization process takes place in the proximity of the glass transition temperature.

In general, upon cooling liquids either crystallize or vitrify. Below the equilibrium melting temperature, T_m, but above the glass transition temperature, T_g, a liquid is in a supercooled state. When dealing with crystallizable materials, the supercooled liquid becomes unstable under these conditions due to its higher free energy as compared with that of the crystal. Consequently, there exists a probability that the supercooled liquid tends to reduce its free energy undergoing a first-order phase transition by which molecules self-assemble forming crystals. This transition is known as crystallization.[1−6] Supercooled crystallizable polymers can develop a characteristic folded chain crystalline lamellar morphology at the nanometer level by thermal treatment within the temperature range defined between T_g and T_m. The lamellar morphology consists of stacks of laminar crystals and amorphous regions intercalated between them.[6−8] Although extended chain crystals are thermodynamically more stable, a kinetic factor induces a polymer chain to fold several times building up thin crystal lamellae. During the isothermal crystallization of a polymer the relative amount of crystalline phase, referred to as crystallinity, evolves in a sigmoidal fashion.[6−11] As an example, Figure 1 shows the evolution with time of the crystallinity during isothermal treatment for three characteristic aromatic polyesters.[10−13] In general, the crystallization rate depends strongly on temperature. To emphasize this, Figure 2a shows the induction time of crystallization (t_{ind}), defined as the time at which crystallinity first becomes detectable, for some polymers as a function of the reciprocal temperature normalized by their corresponding glass transition temperatures. In general, upon cooling below T_m crystallization rate first increases, then reaches a maximum, and finally decreases as T_g is approached. This effect has been illustrated in Figure 2a by the dashed line. Customarily, one speaks about melt crystallization for the temperature range below T_m but above the maximum in crystallization rate and about cold crystallization for the temperature range below the maximum and close to T_g. In both regimes, after an initial induction time a primary crystallization process takes place where morphological units, typically spherulites, grow until they completely fill in the material.[6−10] Subsequently, a secondary crystallization regime is achieved where the crystallization rate is strongly reduced. According to the thermodynamics, crystallization would be possible as soon as the energy difference, ΔG_{bulk}, between the free energy of the crystal, G_{cryst}, and that of the melt, G_{melt}, is negative.[9] This process should start as soon as the system is below T_m. Supercooling arises due to the fact that any crystal must start by a much smaller ordered entity with a certain specific surface area. In this case, the free enthalpy of crystallization ΔG (Gibbs free energy) becomes $\Delta G = \Delta G_{bulk} + G_s$, where G_s is the surface energy.[9] The surface term is, in general, always positive, leading to a free enthalpy barrier to crystallization. Therefore, for temperatures below T_m, where ΔG_{bulk} is negative, ΔG exhibits a maximum which corresponds to the critical size nucleus.[9] According to Boltzmann's law, the probability of the presence of a nucleus of given size at constant volume and temperature will be proportional to $\exp(-\Delta G/kT)$. In classical nucleation ΔG corresponds to the difference between a crystal and a quiescent melt.[9] Experiments and theory indicate that in some polymer melts a coupling between density and chain conformation may induce the appearance of a spinodal texture previous to the nucleation step.[14] In this case ΔG would correspond to the difference between a crystal and a preordered melt. In this case one speaks about spinodal-assisted nucleation.[14] In both cases, the free enthalpy barrier to crystallization is overcome by thermal random local fluctuations of order in the melt.[3,9,14,15] In this situation,[9] the rate of nucleation, I^*, can be described by

$$I^* \propto \exp[-(\Delta G^* + \Delta G_\eta)/kT] \quad (1)$$

where ΔG^* corresponds to the free enthalpy for crystallization of a nucleus of critical size and ΔG_η stands for the term which governs the short distance diffusion of the crystallizing element across the phase boundary.[9,15] In general, the ΔG^* term reaches its higher values close to T_m and decreases with temperature upon approaching T_g. On the contrary, the term ΔG_η adopts its higher values close to T_g and decreases rapidly with increasing temperature.[9] Considering the relation of the ΔG_η term with diffusion, it was proposed it to follow a Vogel−Fulcher−Tammann behavior of the type[9]

$$\Delta G_\eta/kT = a + [b/(T - T_0)] \quad (2)$$

where $T_0 < T_g$ is referred to as Vogel temperature and depends on the material. The combination of the two opposite effects in eq 1 makes the rate of nucleation to exhibit a maximum at temperatures in between T_g and T_m. While close to T_m crystallization is thermodynamically driven, in the proximity of T_g is kinetically controlled. Although polymer melt crystallization has been intensively studied in the past 50 years, cold crystallization did not receive similar attention. For polymer crystallization close to T_g, i.e., kinetically driven crystallization (Figure 1a), one can, in a first approach, neglect the ΔG^* term in eq 1 because its value is expected to be much smaller than that of ΔG_η. Polymer crystallization experiments in this regime indicate a close relation between segmental relaxation and crystallization.[16−19] The influence of the term ΔG_η in eq 1 has been investigated applying to eq 2 either the concept of energy barriers or Williams−Landel−Ferry (WLF) expressions.[19] Considering that cold crystallization phenomena in polymers are essentially governed by short distance diffusion, then one may expect fragility to be relevant. Fragility is

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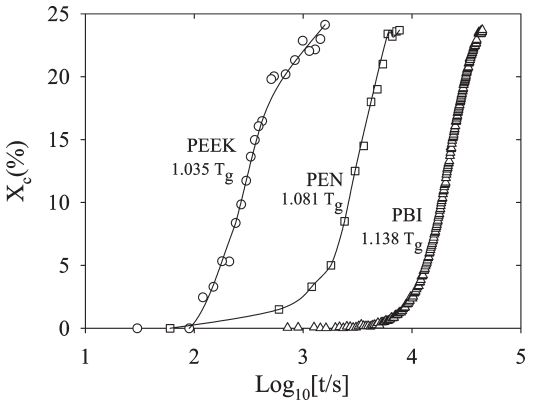

Figure 1. Evolution with time of the crystallinity, X_c, during isothermal treatment at the labeled temperatures (K) for three different characteristic aromatic polyesters:[10−13] PEEK (poly(ether ether ketone)); PEN (poly(ethylene naphthalene-2,6-dicarboxylate)), and PBI (poly(butylene isophthalate)). The continuous lines are guides for the eye.

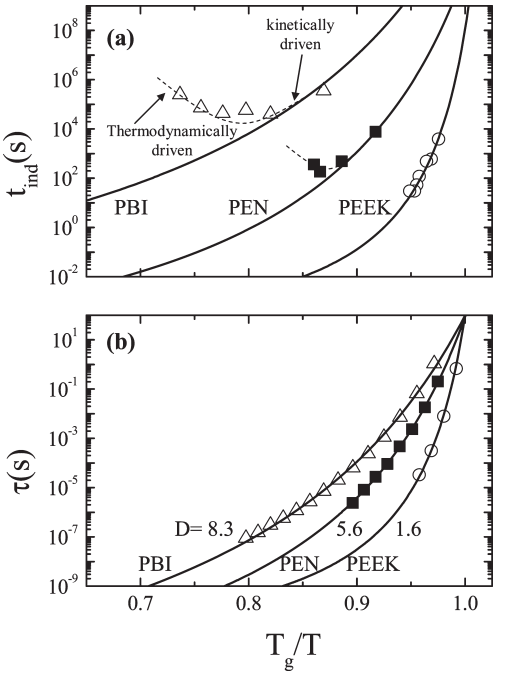

Figure 2. Fragility plot for the induction time, t_i, (a) and dielectric segmental relaxation time (b) for PEEK (○), PEN (■), and PBI (△). Continuous lines are theoretical fits to the Vogel−Fulcher−Tammann equation.[18] Dashed lines in (a) are a guide for the eye. For every polymer, the parameters D are labeled. T_g values quoted from dielectric measurements as the temperature at which the relaxation time of the segmental relaxation is 100 s. In the proximity of T_g crystallization is kinetically driven while at higher temperatures closer to T_m is thermodynamically driven.

a qualitative concept[20] related to the manner in which temperature affects in general the properties of liquids and in particular their viscosity and molecular mobility above T_g. As far as mass transport is concerned, fragility is manifested by different levels of departure from Arrhenius kinetics. Fragility can be quantified,[20−24] for example, by reference to the temperature dependence of the dielectric segmental relaxation time, τ. It has been shown for a wide range of organic and inorganic low molecular weight materials that the kinetic coefficient associated with crystal growth into the supercooled liquid is related to the fragility of the liquid.[25] The deviation from the Arrhenius behavior may be quantified by the strength parameter D in a modified form of the VFT equation:[20−24]

$$\tau = \tau_0 \exp[DT_0/(T - T_0)] \quad (3)$$

In general, polymers are among the most fragile glass-forming materials[21] which are those exhibiting the largest deviations from the Arrhenius law.[21] This corresponds to small D values in eq 3, typically $D < 16$. To quantitatively visualize fragility among different materials, one may plot the relaxation time as a function of the inverse temperature scaled by T_g. Figure 2b shows this normalized plot for different selected crystallizable polymers having different D values.[10,18] It is important to emphasize that Figure 2a shows the induction times for cold crystallization in a similar representation. Comparison of data in Figure 2 suggests that the induction times become faster as the D strength parameter decreases. Intrigued by this observation, we may ask ourselves whether or not fragility may affect cold crystallization in polymers. In this work we attempt to answer this question. On the basis of the analysis of our own results and on literature data, we propose a direct relation between fragility and kinetics of cold crystallization in polymers.

Table 1 collects several magnitudes related to cold crystallization and dielectric relaxation of several crystallizable polymers covering a broad range of D values. In order to seek for a relation among cooperativity and cold crystallization, one should further develop eq 1 in the following way:

- First, we will consider that for pure cold crystallization only the diffusion term, ΔG_η, plays a significant role.
- Second, we will combine eqs 2 and 3 to provide the following expression for the diffusion term:

$$\Delta G_\eta/kT \propto a + [DT_0/(T - T_0)] \quad (4)$$

For simplicity we can assume the proportionality constant to be 1.

- Third, we will consider the nucleation time, t_n, to be inversely proportional to the nucleation rate. This leads to

$$t_n \propto \exp[DT_0/(T_c - T_0)] \quad (5)$$

Experimentally, t_n can be identified with the time needed to achieve a 10% of the final crystallinity as revealed by X-ray measurements.[42] Estimates of t_n can also be obtained from dielectric experiments considering the relation between the relaxation strength of the β-relaxation and the crystallinity.[43]

- Fourth, in order to compare nucleation times measured at different crystallization temperatures, we defined a normalized nucleation time factor, t_n^N, by a factorization of eq 5 according to

$$t_n^N = \ln[t_n](T_c - T_0)/T_0 \quad (6)$$

where T_c is the crystallization temperature. Figure 3 represents values of t_n^N for the different polymers of Table 1 as a function of their corresponding D values. As one sees there is a certain trend in the sense that polymers with higher strength parameters D exhibit higher t_n^N values, which means slower nucleation rates. Fragility, m, in liquids can be defined as the apparent activation energy of either shear viscosity or relaxation time of the α-relaxation:[21,24]

$$m = \left.\frac{\partial \log \tau(T)}{\partial(T_g/T)}\right|_{T=T_g} = \frac{DT_0T_g}{(T_g - T_0)^2 \ln 10} = 16 + 590/D \quad (7)$$

The last term of this equation is obtained[21,24] considering T_g as the temperature at which the relaxation time of the dielectric

Table 1. Cold Crystallization Data for Different Crystallizable Polymers Including Calorimetric Glass Transition (T_g), Nucleation Time (t_n), and Crystallization Temperature (T_c)[a]

polymer[b]	T_g (K)	T_0 (K)	D	t_n (s)	T_c (K)	$M_w \times 10^{-4}$	ref
PEEK	418	410	1.6	150	433	4	12, 28
PET	348	310	4[c]	2600	369	4.5	29, 30
1-4,trans-PI	201.2	179	3.4	420	221	45.5	31
PDMS	145	131	3.7	12000	158.4	13	32
PHB	275	260.7	4.5	10000[e]	288.15	17	33, 34
BPA-PC	420	373	4.6	4×10^{6} [d]	449.5	3−4.6	35, 36
PPT	318.5	272	5.2	1800	320	5.6	37
PLLA	330	286.5	5.3	4500[e]	353	6.4−30	38, 39
PEN	393	340.2	5.6	1200	425	2.50	13, 18
PPA	219	181.5	5.9	6000[e]	227.5	7.55	40
PPS	244	201.6	6.3	3000[e]	298	7.9	40
PBI	292.5	236	8.3	10000	333	2.8	10, 41

[a] Corresponding dielectric data including D and T_0 values of the VFT equation. The last two columns indicate the molecular weight and the reference where the data were extracted from. [b] The acronyms for the polymers read PEEK (poly(ether ether ketone)) and PET (poly(ethylene terephthalate). [c] Average value from refs 29 and 30; 1-4,trans-PI (1,4-*trans*-polyisoprene); PDMS (poly(dimethylphenylsiloxane)); PHB (poly(hydroxyl butyrate)); PBA-PC (bisphenol A polycarbonate). [d] Half-time of crystallization; PPT (poly(propylene terephthalate)); PLLA (poly(L-lactic acid)); PEN (poly(ethylene naphthalene-2,6-dicarboxylate)); PPA (poly(propylene adipate)); PPS (poly(propylene succinate); PBI (poly(butylene isophthalate)). [e] Estimated from dielectric data.

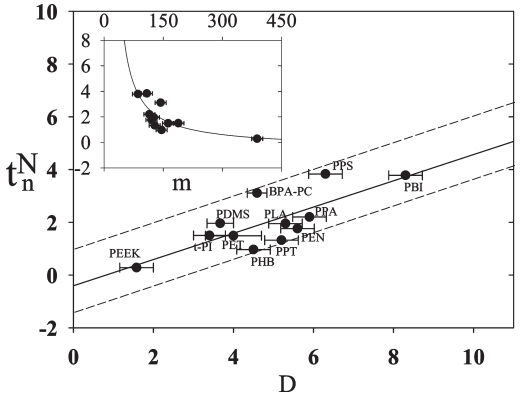

Figure 3. Values of normalized nucleation time factor, t_n^N, for the different polymers of Table 1 as a function of their corresponding D values. Continuous line is the best linear fitting. The inset shows the same data as a function of the fragility index m. In the inset the continuous line and the m values were calculated by eq 7.

α-relaxation is 100 s and $\tau_0 = 10^{-14}$ s. A plot of the normalized nucleation time factors, t_n^N, as a function of m values, calculated by eq 7, has been included in the inset of Figure 3. Accordingly, the experimental correlation observed in Figure 3 seems to indicate that, among a significant amount crystallizable polymers and under cold crystallization conditions, higher fragility implies faster nucleation rates. This correlation can be understood considering that combination of eqs 5 and 6 should render that

$$t_n^N \propto D \tag{8}$$

It is worth to emphasize that fragility in polymers can be molecular weight dependent.[26,27] This effect becomes significant when $M_w < 10^4$. Considering the molecular weights of the polymers reported in Table 1, this effect is not expected to affect the observed correlation. The quantitative estimation of the strength parameter from dielectric measurements may be subjected to some ambiguity depending on the accuracy of the fitting procedure.[24] For some of the polymers reported in Table 1 like PET, t-PI, PDMS, and BPA-PC the experimental uncertainty in D was incorporated into Figure 3 by means of the horizontal error bars, and an average value was taken for the others. Measurements of induction and crystallization times are also subjected to some experimental error particularly when different experiments involving different sample cells and temperature protocols are involved. We believe that the dispersion of the data around the best linear fitting appears mainly as a consequence of this effect. To provide an indication about the uncertainty in the nucleation time factor values, we have drawn in Figure 3 two parallel dashed lines enclosing the date to define the region where data are reported. Fragility in polymers has been related to different mechanisms including the complexity of the segmental relaxation function,[20,23] physical aging,[44] the fast dynamics,[45,46] and segmental cooperativity.[47,48] It is remarkable the specific correlation between fragility and segmental cooperativity understood as the degree to which local structure provokes constraints on the relaxation from neighboring nonbonded segments.[47] More fragile polymers, typically with more rigid backbones, exhibit a strongly intermolecularly cooperative segmental dynamics.[47,48] Accordingly, an increase in fragility should imply that motions of different parts of the polymer chains become increasingly coupled on shorter distances. Similar concepts, extended to intrachain cooperativity, have been used to explain the dependence of fragility and glass transition temperature with the molecular weight[27] and the implication of local dynamics in the segmental relaxation.[30,49] Applying these ideas to our case, we can understand the results of Figure 3 considering that upon increasing the strength parameter D, and consequently decreasing fragility (eq 7), segmental motions in the supercooled melt become increasingly decoupled on a short distance both along the polymer chain and also among neighbor chains. The nucleation step involves the formation in the melt of regions of segmental aggregation with higher local orientational order connected either by the same single chain[50] or by other chains. As the nucleation step appears due to thermal random local fluctuations of order in the melt, one may expect that the formation of a stable nucleus will affect an increasingly broader surrounding volume the higher the fragility. Thus, it is conceivable that an increase in fragility, and therefore in chain cooperativity, may have a positive impact on the probability of occurrence of nuclei in segmental aggregated regions due to an increase in the level of dynamic interconnection of the melt.

In conclusion, here we have shown that there is a correlation between nucleation kinetics and dynamic fragility when the crystallization process takes place in the proximity of the glass transition temperature.

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