Rheological Mechanism and Overview of Nucleated Crystallization Kinetics

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ABSTRACT: Although the function of a nucleating agent in shortening the initiation time and thus enhancing the crystallization rate is well understood, an increased rate at higher melt → crystalline conversions (e.g., ≥10%), where the active nuclei are in abundance, is less straightforward to explain. Such a behavior is typical of nucleated crystallization of polymer melts. However, its existence and, especially, the underlying mechanism have not been discussed in the literature. In this paper, we have presented (1) a rheological technique for studying the crystallization kinetics and shown it to be more sensitive than conventional techniques like differential scanning calorimetry (DSC) and (2) two possible mechanisms to account for enhanced rate at higher conversions for nucleated crystallization of polymer melts.

Introduction

Nucleated crystallization of polymers has been the subject of several studies over the last 30 years or so.[1-3] In a relatively simple case of isothermal crystallization, a nucleating agent (NA) shortens the induction time as well as enhances the overall rate of transformation from the molten state to the crystalline solid state. A shortening of the induction time due to a NA is obviously understandable since the polymer melt does not have to form its own seeds to initiate crystallization; self-nucleation being a time-dependent phenomenon as it results from the statistical fluctuations in the local order. However, what is *not* readily understandable is the enhanced rate of overall crystallization by a NA at higher conversions (e.g., >10%) where (1) there are abundant seeds within a nonnucleated or nucleated polymer melt and where (2) due to isothermal conditions[4] nucleation and growth rates of the remaining melt (e.g., <90%) should be the same.

The purpose of this paper is to present two hypotheses which explain an increased rate of crystallization in the presence of a nucleating agent at such conversions where the active nuclei are in abundance. An increased crystallization rate and a shortened induction time are the characteristic features of a NA which are apparent in isothermal and nonisothermal processes; the latter being typical of polymer processing operations.

Experimental Section

The data on crystallization kinetics of nylon 6 with and without talc nucleator, based on differential scanning calorimetry (DSC), have been taken from our previous publications.[6-9] The activation energy of nonnucleated (E_{NN}) and nucleated (E_N) crystallization of nylon 6 was obtained from isothermal DSC data. The effect of a sorbitol nucleator (Millad 3905) on polypropylene and that of a proprietary nucleator on poly(chlorotrifluoroethylene) or poly(CTFE) were measured in terms of the E_{NN} and E_N parameters evaluated by the nonisothermal DSC method of Ozawa.[10]

The activation energy of viscous flow (E_η) was obtained by determining the temperature dependence of the zero-shear melt viscosity (η_0) using a Rheometrics stress rheometer (RSR 8600) for polypropylene and poly(CTFE) and by using a capillary rheometer (Kayeness, Galaxy V) for nylon 6.

Some of the isothermal kinetics work presented in this paper was obtained using a Rheometrics dynamic spectrometer (RDS 7700 II). Typically a disk of about 1.3-mm thickness and 25-mm diameter was placed between parallel plates and melted to erase the crystalline memory (e.g., 270 °C/5 min for nylon 6). Subsequently, the parallel plates were cooled to the desired isothermal temperature (190–210 °C for nylon 6) and the data collected as a function of time through the completion of the crystallization; strain and frequency were 2% and 10 rad/s, respectively.

Background

We provide an overview of the nucleated crystallization of polymers as it is considered necessary to address the issues to be discussed.

Bulk Crystallization. Under otherwise similar conditions, the bulk crystallization, i.e., from the molten state, depends mainly on the temperature and is described by nucleation and growth mechanisms. In homogeneous nucleation, the nuclei are formed within the supercooled melt through thermal fluctuations at the local order level as opposed to heterogeneous nucleation where nuclei formation is catalyzed by foreign particles. For a homogeneous process, the steady-state nucleation rate per unit volume and time (N) can be expressed as[5]

$$N = N_0 \exp\left(\frac{-E_D}{RT} - \frac{\Delta G^*}{RT}\right) \tag{1}$$

where N_0 is a constant, E_D is the transport energy at the solid–liquid interface, and ΔG^* is the free energy of formation of a stable nucleus in the supercooled melt.

Due to the dependence of ΔG^* on $1/\Delta T^2$, as the crystallization temperature is lowered below T_m, ΔT increases, which lowers the ΔG^* term, and as a consequence N increases as per eq 1. However, when the isothermal crystallization temperature is too low, E_D, the transport energy, increases sharply, thus causing N to be lower in accordance with eq 1. As a consequence of competing ΔG^* and E_D terms, the nucleation rate, N, goes through a maxima between T_g and T_m (Figure 1).

Studies on the temperature coefficient of the overall crystallization rate have established that the polymer crystallization is a nucleation-controlled process.[4] Therefore, the growth rate (G) or even the overall crystallization rate (K) can be expressed by an equation similar to eq 1. Figure 1 reiterates that the nucleation, growth, and, thus, the overall crystallization rates are affected by temperature in a similar way. Polymers with fast crystallization rates, e.g., polyethylene, can only be studied at temperatures between the maximum and T_m whereas only very slow crystallizing polymers, e.g., poly(trimethylene oxide) and isotactic polystyrene, can be studied over the entire temperature region (Figure 1). For a thorough understanding of this subject matter, ref 5 is highly recommended.

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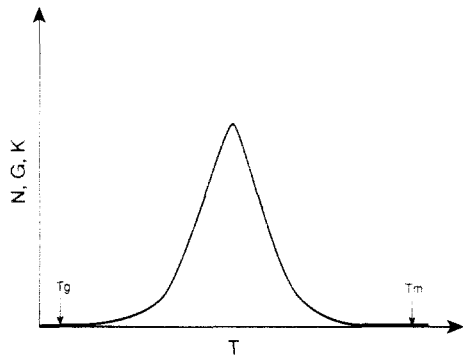

Figure 1. Idealized curves showing the dependence of nucleation (N), growth (G), or overall (K) rates of crystallization on the crystallization temperature (T). T_g and T_m are the polymer glass transition and melting temperatures, respectively.

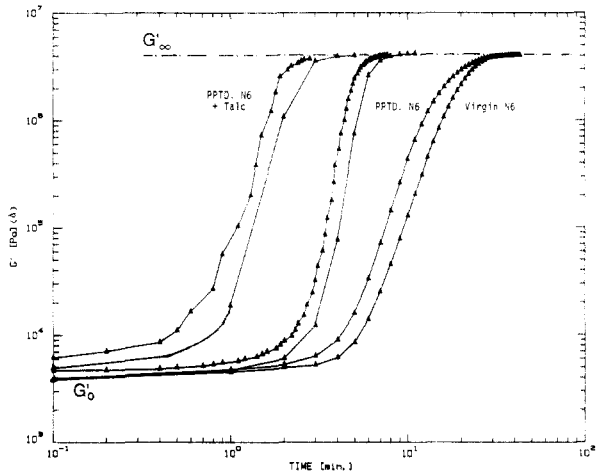

Figure 2. Melt stiffness (G') vs time curves at 200 °C for various types of nylon 6 melts.

Spherulitic Growth. Spherulites are a morphological feature of melt-crystallized polymers and consist of a large number of chain-folded lamellar crystallites, radiating in all directions from a central nucleus with molecular chains oriented tangentially. Just like the nucleation rate, the spherical growth rate of the spherulites is usually measured by polarizing microscopy. It is important to note that the spherulite size of a polymeric article is dictated by the nucleation conditions and does not relate to the growth rate, i.e., radial growth per unit time.

A larger spherulitic size is typically associated with reduced transparency and poor impact properties. For a nonnucleated polymer, spherulite size can be decreased by using a faster cooling rate which pushes the melt crystallization temperature (T_{CC}) to lower temperatures, which, in turn, promotes the nucleation density (Figure 1) as well as reduces the time scale over which the crystallization is completed (Figure 3), both being detrimental to the development of large, orderly arrangements of lamellar crystallites, i.e., large spherulites. However, fast cooling or quenching is effective only for thinner articles and, therefore, there is always a need for nucleating agents for molding applications.

The function of the nucleating agent is to provide abundant active sites to initiate the crystallization process; e.g., 1 ppm of a NA of 100-Å diameter and 1 g cm^{-1} density can induce 10^{12} nucleating sties/g of the polymer.[3] When the spherulites begin growing at abundant sites, these impinge on each other, thereby arresting the growth. In addition to reducing the spherulite size, NA's shorten the induction time and, thus, enhance the overall crystallization rate.

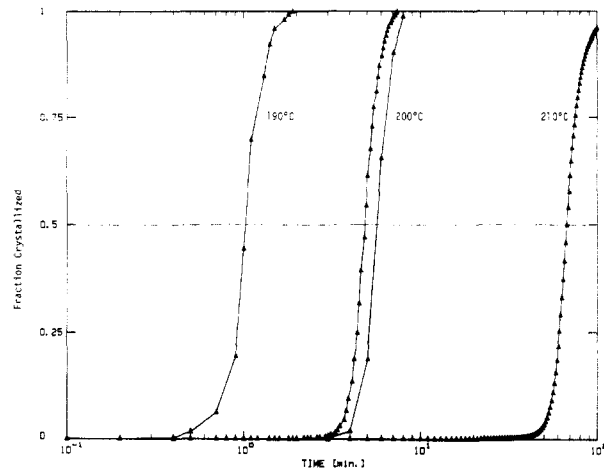

Figure 3. Rheological determination of crystallization isotherms over an unusually wide temperature range for a precipitated nylon 6.

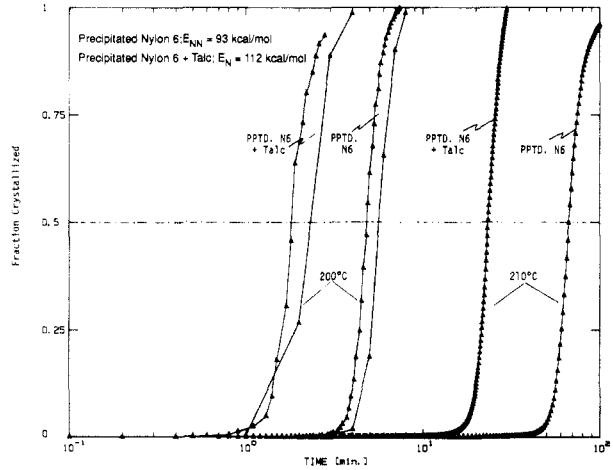

Figure 4. Rheological measurement of crystallization isotherms for activation energy of a nonnucleated (E_{NN}) and talc-nucleated (E_N) precipitated nylon 6.

Nucleating Agents. Although there is no clear-cut way of predicting the effectiveness of a nucleating agent for a particular polymer, there are general features common to the effective NA's.[2,3] For example, (1) they are crystalline and insoluble in the polymer melt, especially prior to its crystallization, (2) they consist of parallel layers or rows of molecules and expose a nonpolar surface while the polar groups are confined in the center (an example being nonpolar surfaces of benzene rings in nucleating benzoic salts[11]), and (3) most of the NA's allow epitaxial crystallization of polymers. In this manner, the universal activity of benzoic acid salts can be explained. For example, polypropylene with helical conformation aligns its $-CH_3$ groups in rows at the nonpolar benzene rings, whereas polyethylene with extended-chain conformation crystallizes through the interaction of its $-CH_2-$backbone with the benzene ring surfaces.[3-11] Even polar polymers like aliphatic polyesters and polyamides characterized by the presence of a $-CH_2-$sequence are believed to crystallize through an epitaxial mechanism. The existence of an epitaxial relationship between a polymer and benzoic acid salt surface can be interpreted in terms of a *two-dimensional lattice matching* of the polymer and the NA crystals.[3] A similar epitaxial relationship has been suggested for the nylon 6 and its most effective NA, talc.[12] In contrast to a physical mechanism, NA's may also act by a chemical mechanism; e.g., (4) a chemical reaction between poly(ethylene terephthalate) and a NA, e.g., sodium 2-chlorobenzoate, has been claimed as the reason for

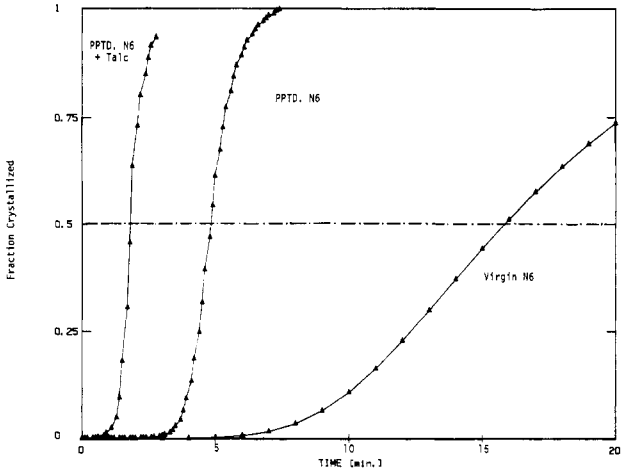

Figure 5. Rheological demonstration of increasing crystallization rate at higher conversions due to a nucleating agent for nylon 6 at 200 °C.

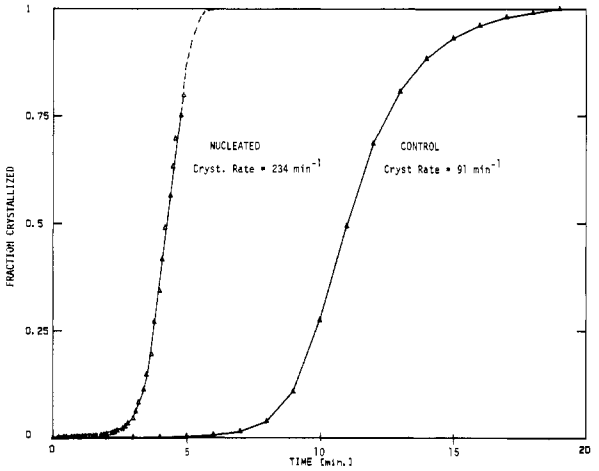

Figure 6. Rheological demonstration of increasing crystallization rate at higher conversions due to a nucleating agent for polypropylene at 130 °C.

nucleating activity.[3] In this system, chain scission is followed by the formation of ionic end groups which associate in clusters, thus forming very active nuclei.

Results

Figure 2 shows the time dependence of melt stiffness (G') of various types of nylon 6 melts at 200 °C. The ranking of nucleated polymer > solution precipitated > virgin resin in terms of crystallization rates is in accordance with our previous conclusions.[8] The data in Figure 2 were converted into the fraction crystallized (ϕ = 0–1) at time t as follows:

$$\phi \equiv \frac{G_t' - G_0'}{G_\infty' - G_0'} \tag{2}$$

where G_0', G_t', and G_∞' are the melt stiffness values at time 0, t, and infinity, respectively. A preferred way to evaluate G_∞' would be to measure the shear modulus of the polymer in the solid state, e.g., by a torsion/rectangular test on a well-crystallized bar sample.

Figure 3 demonstrates clearly an advantage of the rheological measurements whereby the isothermal data could be obtained over a range of at least 20 °C as opposed to only about 5 °C in a technique like DSC.[6-8] Moreover, DSC normally does not allow the evaluation of induction times. Figure 4 represents the E_{NN} from the crystallization rate ($t_{0.5}^{-1}$, min^{-1}) measurements. [Note: In this paper, we have frequently referred to activation energy which should not be confused with the classical Arrhenius activation energy. First, because of multiple/complex stages in polymer crystallization, the concept of activated complex well-known for simple molecules

$$[H_2 + I_2 \rightarrow \begin{matrix}[H...I] \\ \vdots \\ [H...I]\end{matrix} \rightarrow 2HI]$$

is not valid. Second, for crystallization of materials exhibiting undercooling, the rate varies inversely with temperature, i.e., a case of negative activation energy, whereas for simple molecules Arrhenius activation energy is always positive. The only reason we use the term "activation energy" is because we view it as a "Temperature Coefficient of Rate", which will be "negative for the crystallization of materials from the molten state. Therefore, our Temperature Coefficient of Crystallization Rate" TCCR (or activation energy) has no molecular significance as the Arrhenius activation energy but serves as a *valuable characterization parameter* for comparing materials.] A value of 93 kcal/mol is in excellent agreement with 97 kcal/mol obtained from DSC[7] using $t_{0.5}^{-1}$ measurements, thereby supporting the reliability of the rheological technique.

Discussion

Figure 5 indicates a characteristic feature of a nucleating agent; i.e., it reduces the induction time. This is no surprise since the melt contains a suitable substrate on which the crystallization can be initiated. Due to shortening of the induction time, the overall crystallization rate, e.g., reciprocal of the time required for 50% crystallization, is known to be higher.

However, past the induction stage or even after the initial stages of crystallization ($\phi \approx 0.10$), the conversion rate is higher for the talc-nucleated resin (Figure 5). This behavior is even more clearly demonstrated for the polypropylene melt (Figure 6). Such an aspect of the nucleated crystallization has not been addressed so far and is difficult to understand since, at an isothermal temperature, nonnucleated as well as nucleated melts should have the same nucleation and growth rates (Figure 1), both being in a state where nucleating sites are in abundance, i.e., >10% crystalline fraction. The faster crystallization rate due to NA at *higher conversions* is apparent in a steeper slope, higher T_{CC} in DSC, and a higher temperature coefficient of the crystallization rate, i.e., activation energy. We are presenting two mechanisms, one or both of which might account for the above-noted observation.

(A) As discussed earlier, one of the characteristics of a nucleated crystallization is to yield smaller spherulites. Consider that the volume of a large sphere (radius r_2, nonnucleated melt) is the same as that of several (N) smaller spheres (radius, r_1, nucleated melt). It has been known that the linear growth rate of the spherulites is only temperature dependent for a particular polymer melt.[4] Therefore, under isothermal conditions when the spheres r_1 and r_2 grow by a radius Δr in a given time, the volume of crystallized material in that given time can be described as follows:

$$\Delta V_1 = N\frac{4}{3}\pi[(r_1 + \Delta r)^3 - r_1^3] \qquad \text{nucleated melt} \tag{3}$$

$$\Delta V_2 = \frac{4}{3}\pi[(r_2 + \Delta r)^3 - r_2^3] \qquad \text{non-nucleated melt} \tag{4}$$

Table I. Activation Energies for Crystallization and Viscous Flow

polymer	difference in activation energies of crystallizn, kcal/mol	activation energy of viscous flow, kcal/mol
nylon 6	$E_N(112) - E_{NN}(93) = 19$ obtained rheologically from $t_{0.5}^{-1}$ at 200 and 210 °C	$E_V = 18$ obtained from ln η_0 vs $1/T$ using capillary rheometer (corr coeff = 0.97)
polypropylene	$E_N(41) - E_{NN}(32) = 9$ obtained by DSC using Ozawa method[9] (corr coeff = 0.96–0.98)	$E_V = 11$ obtained from ln η_0 vs $1/T$ using a stress rheometer (corr coeff = 0.99)
poly(chlorotrifluoroethylene)	$E_N(40) - E_{NN}(27) = 13$ obtained by DSC using Ozawa method[9] (corr coeff = 0.98–0.99)	$E_V = 15$ obtained from η_0 at 240 and 250 °C using stress rheometer; higher temperatures were avoided due to degradation

Since $Nr_1^3 = r_2^3$ or $r_2 = N^{1/3}r_1$, eq 4 becomes

$$\Delta V_2 = \frac{4}{3}\pi[(N^{1/3}r_1 + \Delta r)^3 - Nr_1^3] \quad (5)$$

Equations 3 and 5 upon simplification become

$$\Delta V_1 = N\frac{4}{3}\pi[r_1^3 + 3r_1^2\Delta r + 3r_1\Delta r^2 + \Delta r^3 - r_1^3] \quad (6)$$

$$\Delta V_2 = \frac{4}{3}\pi[Nr_1^3 + 3N^{2/3}r_1^2\Delta r + 3N^{1/3}r_1\Delta r^2 + \Delta r^3 - Nr_1^3] \quad (7)$$

$$\frac{\Delta V_1}{\Delta V_2} = \frac{N[3r_1^2 + 3r_1\Delta r + \Delta r^2]}{[3N^{2/3}r_1^2 + 3N^{1/3}r_1\Delta r + \Delta r^2]} \quad (8)$$

Based on the above expression, Figure 7 exhibits how the $\Delta V_1/\Delta V_2$ ratio changes with the number N. It is clear that $\Delta V_1/\Delta V_2$, i.e., volume (or mass) crystallized per unit time, is greater for the smaller spherulites resulting from the nucleated melt.

(B) The phenomenon of yield stress is well-known and well documented in the literature on the melt rheology of filled polymers.[13-15] Yield stress is characterized by an enormous increase in melt viscosity at low shear rates, and its magnitude increases with increasing filler content and decreasing particle size;[13,14] the phenomenon is attributed to an interparticle association leading to network formation.[13] These conditions can very well be applicable to the case of a nucleated crystallization. For example, (1) crystallization occurs under stationary conditions equivalent to infinitely low shear rates; (2) at higher melt → crystalline conversions (e.g., ≥10%), crystallites in the melt can be considered as fillers, and (3) for a nucleating agent to be most effective, its degree of dispersion has to be high[2] and its particle size as small as possible.[3] At a fixed conversion, a nucleated melt as opposed to a nonnucleated melt will have a fine dispersion of smaller crystalline particles, a condition leading to yield stress (Figure 8).

Therefore, at higher melt → crystalline conversions, a nucleated melt can be expected to have an enhanced yield stress and enhanced melt viscosity. [Note: This cannot be shown experimentally since a melt containing crystallites is unstable as opposed to a melt containing an inert filler. As a result, melt viscosity vs shear rate data cannot be obtained for a melt containing crystallites. However, Figure 5 indirectly reveals that a nucleated melt builds up melt stiffness or viscosity (i.e., our experimental parameter) at a faster rate.] Since the addition of a NA (typically ≤0.1%) does not affect the molecular weight/distribution, an enhanced melt viscosity arising from the proposed yield stress phenomenon is equivalent to a lowering of the crystallization temperature, which, in turn, should result in increased rates of nucleation, growth, and overall crystallization (Figure 1). The support to the yield stress (i.e., melt viscosity buildup) hypothesis comes from

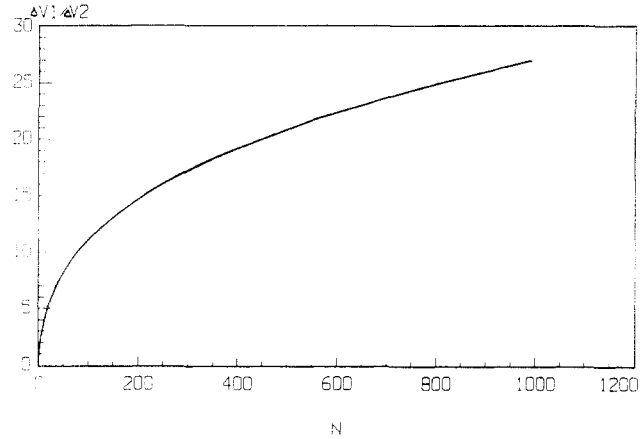

Figure 7. Variation of $\Delta V_1/\Delta V_2$ with N, the latter reflecting the effectiveness of the nucleator.

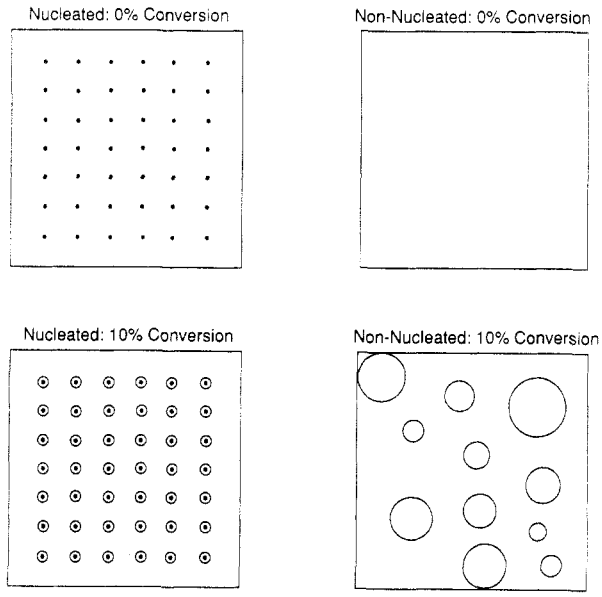

Figure 8. Schematic showing how and why an enhanced yield stress would occur in a nucleated melt.

the activation energy measurements. If a nucleated melt builds up excess melt viscosity, its temperature coefficient of the crystallization rate (i.e., activation energy E_N) should include the temperature coefficient of the viscous flow (i.e., activation energy, E_v). Thus, $E_N - E_{NN} \simeq E_V$, E_{NN} being the temperature coefficient of the crystallization rate for the nonnucleated melt. Table I demonstrates that E_N-$E_{NN} \sim E_v$ for the three polymers studied, namely, nylon 6, polypropylene, and poly(chlorotrifluoroethylene).

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