An Unusual Crystallization Peak of Poly(vinyl chloride)

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ABSTRACT: Owing to an efficient quenching process that ensure r-poly(vinyl chloride) to be amorphous enough, crystallization of rPVC at lower temperatures has been found in samples with various processing histories. Through a modified Avrami analysis, kinetics of the isothermal crystallization at these low temperatures was studied, proving that the crystal growth in the studied temperature range was controlled by segment mobility, which should follow a WLF-type relationship. Such a mechanism is unusual compared to ordinary growth controlled by chain reptation. Also discussed were implications of the results to further crystallization study of PVC and to that of polymers in general. The treatment distinguished itself in that it can give out both spacial growth exponent and dependency of the dimension on time. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63**: 1747–1754, 1997

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INTRODUCTION

The crystallinity in poly(vinyl chloride) (PVC) plays an important role in the gelation of PVC rigid compounds.[1–3] Though crystallinity in commercial suspension-polymerized PVC is generally as low as about 10% by weight,[4,5] the endotherms on DSC curves have been experientially used to characterize the level of its fusion or gelation.[1–3] Poor knowledge about the nature of melting and recrystallization prohibits further development of the method. Although lattice parameters had been obtained from PVC/DOP gel,[6] lamellar thickness calculated from WAXD data,[5,7] and isothermal crystallization kinetics studied to find an Avrami exponent near to unity,[8,9] the tacticity necessary to ensure the crystallization[10,11] can sel-

dom be found in commercial PVC.[4,12] Therefore, rather than being a proper description of microcrystals as for many other polymers,[13] the lamillae model was able to be formulated[7] only on a tutorial background. Lack of thermodynamic data has seriously hindered the understanding of crystallization. in r-PVC.

To avoid difficulties in morphology observation that originate from imperfection and poor crystallization ability of the PVC, kinetic studies are necessary through sensitive methods, such as differential scanning calorimetory. In this work, a novel crystallization peak was found in a temperature range of about 10°C higher than the glass temperature. Isothermal experiments were carried out to analyze its kinetics, following the original methodology of Avrami.[14–16]

EXPERIMENTAL

A mass suspension-polymerized PVC (TK800, Nippon Shinetsup, Japan) was dry-blended with
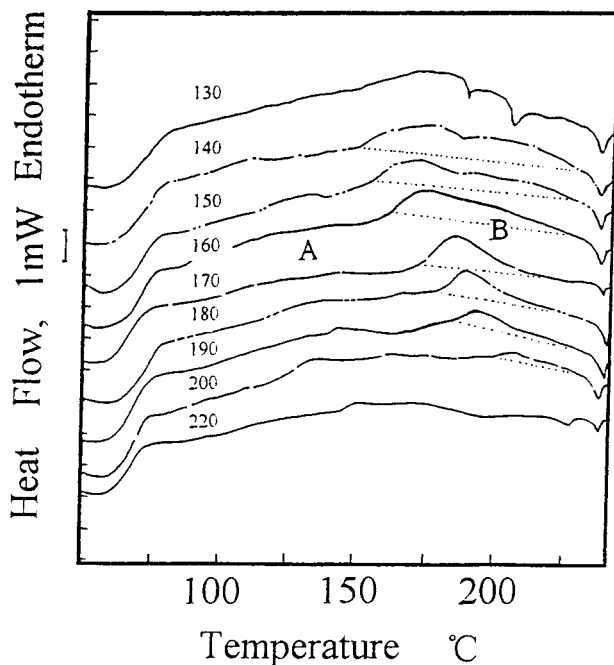
Figure 1 DSC analysis of as-compressed PVC. Numbers above each curve denote processing temperature T_p.

4 phr organic tin stabilizer (Termolite 892, M&T, U.S.A.) and 0.5 phr stearic acid (chemical pure) in a 10 L high speed mixer. Mixing time was controlled to ensure end temperature of the compound no higher than 130°C. The compound was then mounted between two glossy steel sheets at predetermined processing temperature T_p heated for 5 min, gradually compressed to reach an apparent final normal stress of about 7 MPa in 5 min, kept for 5 min, and then cooled with a rate of 20°C/min to room temperature under the pressure. Sample each weighing about 1 g were then cut from the compressed films and enveloped in aluminium foils. The samples were thus heated at predetermined temperatures in an air-ventilated stove for 5 min and quenched with isoprane, which had been kept at its liquid-solid transition point in a liquid nitrogen bath. The method had been proved to be the most efficient quenching medium by far.[3] For isothermal crystallization, samples were kept at 220°C for only 3 min in order to avoid degradation while providing sufficient melting.

A Perkin-Elmer differential scanning calorimeter, DSC-7, was used to study the samples, each weighed 10 ± 0.5 mg, with a scanning rate of 20°C/min. For isothermal crystallization, several

seconds was estimated to be required for a sample in the DSC chamber to reach equilibrium in the temperature range studied, allowing the recorded heat flow data after its maximum usable to investigate the effects of crystallization. Apparent isothermal crystallization enthalpy was routinely calculated by integrating heat flow over the time range between onset value, and the end one taken as 3 min. Glass temperature T_g was measured also with differential scanning calorimetry (DSC) on separated double runs.

RESULTS AND DISCUSSION

Low-temperature Crystallization Exothermic Peaks

Thermal behavior of r-PVC changes with both processing history and post-treatment conditions. Changes in the shape of the DSC traces of as-compressed samples are in good agreement with what had been found by Gilbert and collegues (Fig. 1), revealing an increased gelation level at higher processing temperature.[1] It can be seen from Figure 2 that DSC traces of samples quenched from 220°C are completely different. A narrow, well-defined exotherm arises at around
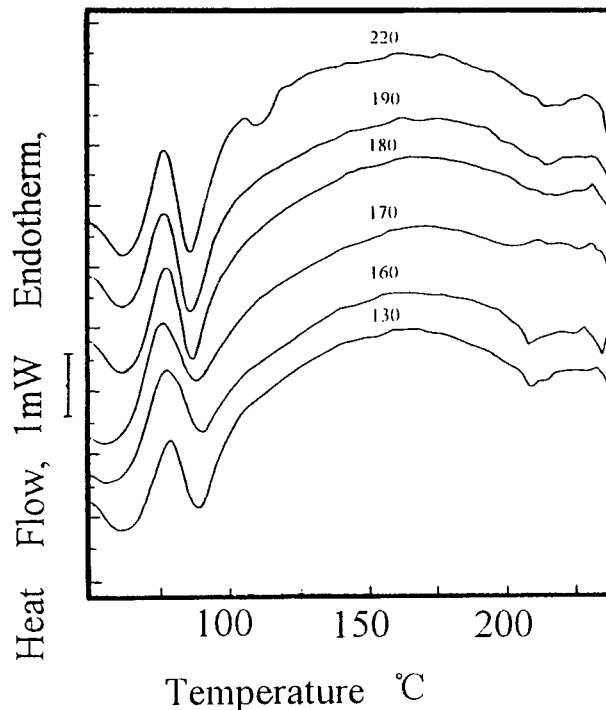

Figure 2 DSC scans of PVC samples quenched from 220°C.

Table I Enthalpy of the Low-temperature Exothermic Peaks

T_{proc}, (°C)	Onset Temp. T_{on} (°C)	Peak Temp. [T_{max} (°)]	Enthalpy ΔH_c^1 (KJ/mono mol)	Enthalpy ΔH_c^2 (KJ/mono mol)
130	79	89	0.250	
170	79	89	0.321	0.133
180	80	87	0.336	0.219
190	79	87	0.338	0.306
200	79	86	—	0.326
220	81	86	0.350	

1) quenched from 220°C melts
2) quenched from temperatures identical to T_{proc}

85°C, whatever the processing temperature had been.

The result is different from what had been observed by Hay et al.[9] Using samples quenched with liquid nitrogen, they found an exothermic peak at around 200°C and another broader, weaker one at about 140°C. The authors presented no explanation for origin of the latter but attributed the former to PVC crystallization, which would form 3–5% crystallinity corresponding to a melting enthalpy about 0.35–0.55 KJ/monomer mol. It can be seen from Figure 2 and Table I, however, that enthalpy of the low temperature exotherm, rather than that of the high-temperature one, reached such values at an elevated processing temperature. This means this low-temperature exotherm bears much common character with the crystallization peaks found by Hay et al.[9] Moreover, compared with the upper bound of melting endotherms in Figure 1 (Table II), these values are about one third to a half of the maximum melting enthalpy of the primary crystallites or that of the secondary ones in as-compressed sheets. Such lower values of enthalpy suggest that the correspondent physical transition

cannot reach thermodynamic limit within the DSC scanning time scale. Because no chemical or other physical changes have ever been found in these temperature ranges in these compressed samples, the low temperature exothermic peak in Figure 2 is thus believed to originate from crystallization of PVC from amorphous state. The lower value of the enthalpy bears exactly characteristics of the low-temperature crystallization.

Similar effects of quenching can also be found in samples quenched from temperatures that are identical to that of compression (Fig. 3). While endothermic peaks are in good agreement with the effects on annealing,[3,4,17] exothermic ones at lower temperatures can be found again, provided that melt temperature are high enough in quenching. Because quenching efficiency depended on the melt temperature from which a sample was taken out and put into the cold bath; i.e., the higher the melt temperature the more effective the quenching would be; results in Table II and Figure 3 reveal that the more amorphous a sample is, the more profound this low-temperature crystallization would be. It should be pointed out that the major difference between the above ex-

Table II Fusion Enthalpy of Primary and Secondary Crystallites (from Fig. 1)

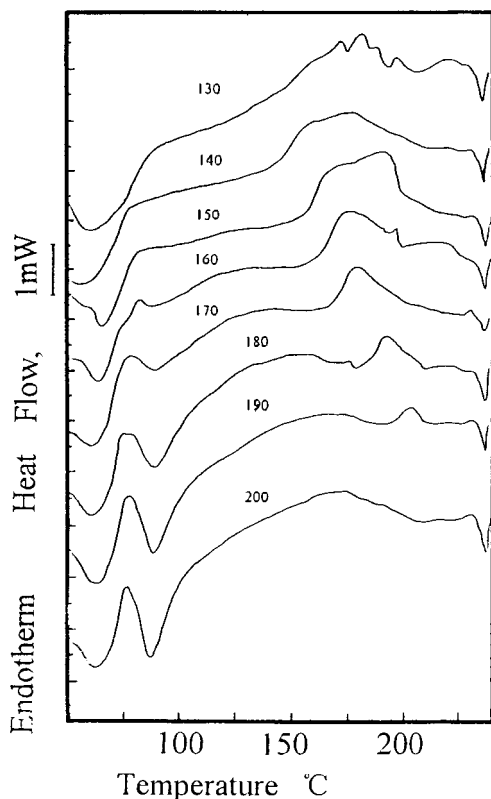| Processing Temp. [T_{proc} (°C)]	Primary Crystallites ΔH_B (KJ/monomer mol)	Secondary Crystallites ΔH_a (KJ/monomer mol)
150	0.780	0.072
160	0.558	—
170	0.403	0.102
180	0.327	0.175
190	0.184	0.265
200	0.094	0.531

Figure 3 DSC traces of PVC quenched from temperatures identical to T_p.

periments and those of Hay et al.[9] is a much more efficient quenching procedure. The crystallization peak temperature shifted from the conventionally seen value (140°C)[3,4] to 85°C; therefore, means crystallization can begin at a temperature slightly higher than glass temperature if the samples are amorphous enough; changes in ΔH_c with processing and quenching condition (Table I), compared to melting enthalpy listed in Table II, can only suggest that this low-temperature crystallization tends to be delayed by the poor mobility of the polymer at such temperature.

Nature of the Low-temperature Crystallization

Crystallization thermodynamics of commercial rPVC are generally difficult to study through melting point analyses.[18] Because tacticity of the polymer is usually on the order of 55%,[4,10,11] crystalline entities are generally imperfect[5] and small in size.[7] For crystallization process that occurs between T_g and 140°C, the low and varying enthalpy values as depicted in previous section suggest that crystalline entities formed at such tempera-

ture tend to anneal further at higher temperature during the measurement of melting point. Kinetic study would be an alternative to probe into the nature of this process.

It can be found from isothermal DSC traces of the quenched samples (Fig. 4 and Table III) that this crystallization process is dominated by temperature. With elevated crystallization temperature, the time required for thermal flow (dH/dt) to reach its maximum (t_{max}) decreases, while apparent crystallization enthalpy ΔH_c increases. Although uncertainty about t_{max} exists because it is not large enough compared to the time required for samples to reach the predetermined temperature, change in ΔH_c quantitatively shows the effect of temperature on crystallization in this temperature range. This can be confirmed by the annealing effects on melting enthalpy.[3,4] Such monotonic increase with temperature suggests that acceleration in growth caused by increasing temperature had surpassed its negative effects through delaying nucleation. Because further knowledge about the growth and nucleation cannot be obtained through traditional treatments,[14–16,19] due to experimental difficulties in direct observation of any crystalline entities and
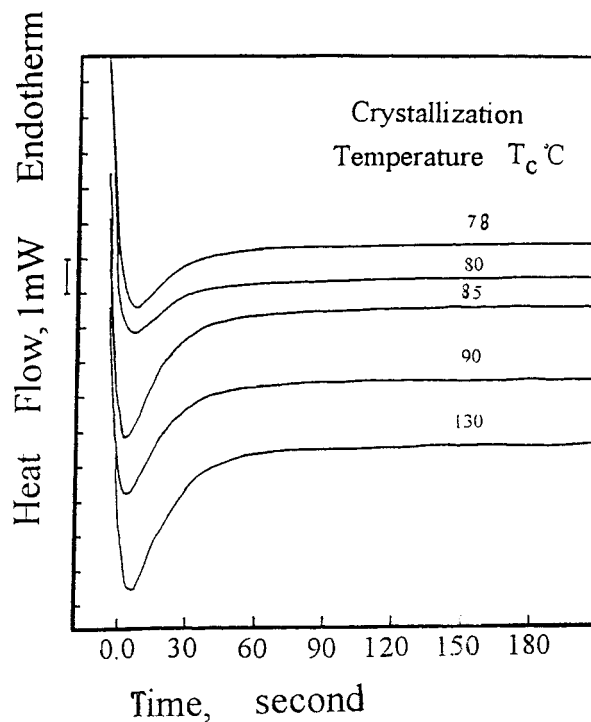

Figure 4 Isothermal DSC traces of PVC processed at 190°C and then quenched from 220°C.

Table III Enthalpy and Growth Exponents of the Isothermal Crystallization of rPVC Compressed at 190°C and Quenched from 220°C

Crystallization Temp. (°C)	t_{max} (s)	Crystallization Enthalpy H_c (KJ/monomer mol)	$n\alpha$-1	α
78	37.7	0.090	0.376	1.376
80	36.4	0.112	0.316	1.316
85	34.1	0.117	0.680	1.680
90	34.8	0.126	0.443	1.443
130	30.1	0.866	0.866	1.866

measurement of small changes in bulk properties with crystallinity, kinetics of this low-temperature crystallization have to be studied following modified Avrami analysis. Most of the classical treatments of Avrami analyses[14–16] will be obeyed, except the linearity of normal growth of crystallizing surface with respect to time.

Spontaneous Nucleation

Suppose nucleation is spontaneous in isothermal crystallization, the enthalpy change rate of which can be one of the DSC traces in Figure 4. When time t changes from its onset value t_0, to the peak one t_{max}, the dramatic change of heat flow results mainly from the fast nucleation. When $t > t_{max}$, it is reasonable that further nucleation can be omitted. Thus, the number of nuclei in this region can be taken as a constant N:

$$N(T_c) = N(t_{max}) \qquad (1)$$

at a certain temperature T_c. Following the linear propagation supposition of Avrami,[14–16] at the instance $t > t_{max}$, the mass of polymer that has crystallized M_n is

$$M_n \sim N[r(t)]^n \qquad (2)$$

where n is the dimension of the growing crystals, and the term $r(t)$ is growing crystal size along the direction normal to its surface. The dependence of r on t can be written as the following scaling law without losing any generality:

$$r(t) \sim t^\alpha \qquad (3)$$

in which α is a scaling exponent determined by (1) the mobility of chains under crystallization temperature, T_c and (2) volume constraints that

result from the decrease in the amount of crystallizable polymers. By combining eq. (1) to (3), it is easy to find

$$dM_n/dt \sim n\alpha t^{n\alpha-1} \qquad (4)$$

For isothermal crystallization in a DSC chamber, the theorem of proportion law of mass transfer to heat flow must be followed; i.e., the heat flow is proportional to the mass that is crystallizing if viscous terms can be omitted, as follows:

$$dH/dt \sim dM_n(t)/dt \qquad (5)$$

From eqs. (4) and (5), kinetics of the isothermal crystallization can thus be written in terms of heat flow as

$$dH(t)/dt \sim \alpha n N t^{n\alpha-1} \qquad (6)$$

Considering that n is the dimension of the crystal and α is the growth exponent of its surface along the normal direction, regression of the $dH(t)/dt$ data can thus yield both the spacial dimension of crystals in growth through the exponent n and its dependency on time through α.

It is worthy to note that the exponent α has, in fact, been taken for granted as unity in previous works[19–21] so that apparent growth dimension of isothermal crystallization in classical Avrami treatments[19–22] can be correlated with morphological crystallite dimensions. Such apparent growth exponent, usually obtained through the dependency of some changing macroscopic crystallinity on time, is identical to $n\alpha$ in eq. (6) and, thus, an apparent dimension averaged on all the growing crystallites and over the whole time scale. Besides dimension of crystallites and volume constraints imposed by their impingement, the apparent

growth exponent relies also on the way polymer chains are being packed into crystalline phase; i.e., it also depends on thermodynamics of polymer chains and volume constrains produced by the already formed crystalline entities. In another words, it reflects information about spacial dimension and time dependencies of both packaging of chains in crystalline phase and stacking of morphologically observed crystallites.

In the case of rigid PVC, however, size of crystalline domains is very low.[5] For low-temperature crystallization studied here, the upper limit of crystallinity formed should be on the order of 3–5%. Crystallites impingement can seldom be an issue at this range. On the other hand, it had been estimated that the long period should be on the order of three to five times the length of monomeric segments; i.e., crystallites in this polymer of low tacticity must be very imperfect.[4,12] Crystallization kinetics, therefore, should be decided by the way in which tactic sequences enter the crystalline phase. The exponent n and α should thus be a measure of this process of chain packaging. From $dH(t)$ data as depicted in Figure 4, complex exponent $(n\alpha - 1)$ was obtained with good confidence through a double-logarithm linear regression and listed in Table III. Accuracy of the calorimetory had not allowed any confident extrapolation for n, so only $(n\alpha - 1)$ and α will be discussed. Because no information about exact crystal dimension were available until now, exponent α was calculated by taking $n = 1$, which will not affect the discussion because of the linear relationship between $(n\alpha - 1)$ and α. It can be found in Table III that the components change with crystallization temperature. There is no reason to think that spacial dimension of PVC crystal at this temperature range cannot be taken as constant; the variation in $(n\alpha - 1)$ must result from the dependency of α on temperature, especially on the difference between T_c and T_g, the latter having been measured to be 72°C. On a plot of $\ln(n\alpha - 1)$ and $\ln \alpha$ vas $\ln(T_c - T_g)$ (Fig. 5), linear regressions following least-squares-root principle yield straight lines, though data is somewhat scattered. Considering that the time scale in the isothermocrystallization experiments is not long enough, this scattering should be originated from data recording rather than the double-linear logarithm regression. Results in Figure 5, therefore, reveals an important fact that the dependency of the growth exponent α on temperature is a WLF-type mechanism. In another words, the exponent is
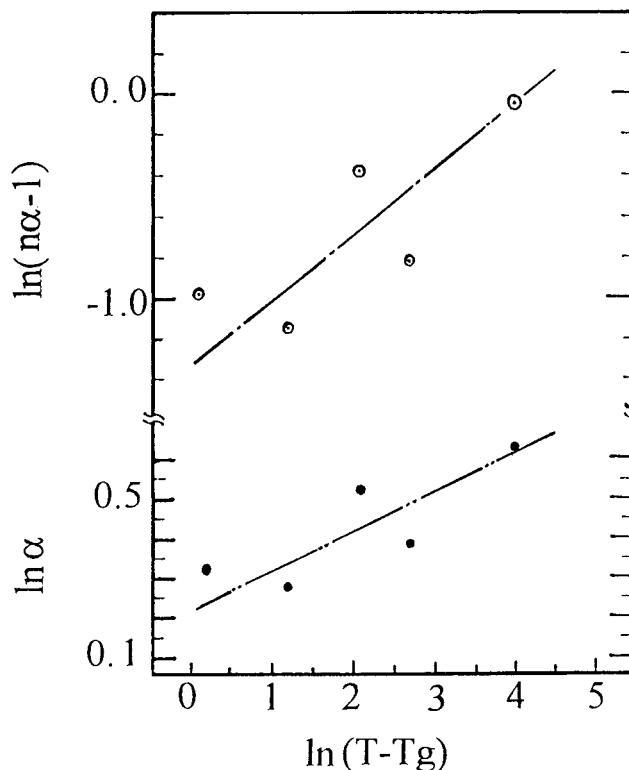

Figure 5 Growth exponents vas$(T-T_g)$.

comparable to shift factor in the well-known WLF equation, and crystallization kinetics here has been controlled by polymer segment mobility in the way a typical relaxation process takes place. The result sounds astonishing at first sight, for successful application of Hoffman's nucleation theory[23] has proved that chain reptation dominates crystallization at least in polymers such as polyehtylene[23] and poly(ether ether ketone).[24] However, low tacticity and low mobility in present experiments on rPVC make the result natural. At the temperature studied, the whole-chain movement could barely occur on the experimental time scale. Consequently, segment mobility becomes the dominant factor in any kinetic processes, including this unusual crystallization at lower temperatures. In fact, Avrami kinetics for polymers in its classical forms,[14–16,19–22] is no more than a theory for low molecules. Although suitable to describe many observation of time-dependent growth rate in polymer crystallization, it does not consider the complex nature of polymer chain movements and has revealed mainly dimension of microcrystal assemblies, e.g., dimensions of spherullites. Hoffman's kinetics, on the other

hand, had been funded on the sound assumption of surface nucleation, which, in turn, based on extensive morphology results about lamellae structure. It dealt well with dependency of growth rate on temperature by formulating different re-entry mechanisms of chains in reptation for crystallization at different temperatures. The question then naturally arises whether the growth mechanism dominated by viscous WLF process of segments found in this article means it is indeed the nature of homogenous nucleation in polymer system. It would be convenient to start from the present treatment to reach more general kinetics theories, which can encompass all kinetic characteristics of macromolecules and be suitable for various microcrystals.

Nonspontaneous Nucleation

Above discussion has taken the liberty that nucleation is spontaneous. Although this is most reasonable because the super cooling is as low as 100 K or more, another consideration should be given briefly for inspontaneous nucleation. Suppose eqs. (1) to (3) hold except that a time-dependent N must be introduced, i.e.,

$$N(t) = N_0(1 - e^{\beta t}) \tag{7}$$

where N_0 is the number of nuclei at onset time, the exponent that decides the decaying in the rate of nucleation. It would then not be difficult to reach

$$dH/dt \sim N_0 t^{n\alpha-1}(n\alpha - n\alpha e^{-\beta t} + \beta t e^{-\beta t}) \tag{8}$$

which predicts nonlinear dependency of $\ln(dH/dt)$ on $\ln t$. For present data, least-squares-root regression yields linear fit much better than any higher order ones that would be reasonable. This confirms the presumption about spontaneous nucleation. It must be pointed out that to reach eq. (8), the only presumption about the growth process is the constancy of crystal dimension. It is reasonable to say that dimension must be constant for a defined lattice and a defined way of chains entry. Therefore, eq. (8) would help to test the validity of the assumption about spontaneous nucleation. Besides, it is easy to see that the claim that Avrami kinetics cannot treat time-dependent nucleation process[25] is not true. Details about growth can be analyzed through the exponents α,

β, and n. While n can be correlated with spacial dimension of crystalline entities, it reveals information on volume constraints. If nucleation follows molecular mechanism different to growth, further examination of β would also be fruitful. Avrami theory, like Hoffman's lamellae growth treatment, with its insight into the characteristic of phase transition, can always show us a proper methodology to explore crystallization kinetics, i.e., to apply correct molecular kinetics on the basis of the right knowledge about the crystalline phase.

Crystalline or Ordered Amorphous State

The above discussion has been carried out by taking this formation of order as crystallization. It must pointed out, however, that crystalline entities, if they ever exist, must be smaller and/or more imperfect than PVC crystallites found in samples annealed at higher temperature. Considering now the poor perfectness and small size of PVC lamellae[4,7] in the latter, the question naturally arises as to how ordered it is in the crystalline entities formed at such low temperature. Investigation into this may help to answer the question whether there is certain order in the amorphous state to participate in crystallization.

CONCLUSION

1) Well-defined crystallization peaks of rPVC were found at low temperatures. Their peak temperatures can be as slow as 14 to 17°C higher than T_g during a +20°C/min run, provided that the polymer is effectively quenched.

2) Isothermal crystallization temperatures correspond to these exothermal peaks was studied with DSC and through a modified Avrami analysis. The results reveals that for PVC crystallization at this temperature range, nucleation is spontaneous, while growth is decided by segment mobility, following a WLF-type law.

3) The modified Avrami analysis developed in this work distinguished itself from classical treatments in that it has taken the nonlinear growth of crystal surface. The method can yield both spacial growth dimension and its time dependency.

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