

DENSITY, EQUILIBRIUM HEAT OF FUSION AND EQUILIBRIUM MELTING TEMPERATURE OF NYLON 1010

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ABSTRACT

The density, equilibrium heat of fusion and equilibrium melting temperature of Nylon 1010 were determined by means of infrared spectrum, differential scanning calorimetry, wide angle X-ray diffraction and density measurement techniques. According to Starkweather's method crystalline density ρ_c and amorphous density ρ_a were estimated to be 1.098 and 1.003 g/cm³ respectively by extrapolating the straight lines of the IR absorbance against density to zero intensity. Owing to the less intense in absorbance and less sensitive to the change in crystallinity of the amorphous band the thus obtained ρ_c was too low in value. Thereby the value of the ratio ρ_c / ρ_a is far less than generally accepted mean value for most crystalline polymers. Accordingly, traditional X-ray diffraction method was used through determining the crystalline dimension ($a=4.9 \text{ \AA}$, $b=5.4 \text{ \AA}$, $c=27.8 \text{ \AA}$, $\alpha=49^\circ$, $\beta=77.0^\circ$, $\gamma=63.5^\circ$), and a rather correct value of ρ_c or the crystal density 1.13 g/cm³ was obtained. The equilibrium heat of fusion ΔH_m^0 was estimated to be 244.0 J/g plotting ΔH_m 's of specimens with different crystallinity against their corresponding specific volumes $\bar{V}_{sp}$ and extrapolating to completely crystalline condition ($\bar{V}_{sp}^c = 1/\rho_c$). As to the equilibrium melting temperature T_m^0 , because of the easiness of recrystallization of melt crystallized Nylon 1010 specimen, the well-known Hoffman's $T_m - T_c$ method failed in determining this value and an usually rarely used Kamide double extrapolation method was adopted. The so obtained value of T_m^0 487 seems to be fairly reasonable.

INTRODUCTION

Nylon 1010 is one of the important polyamide engineering plastics specifically produced commercially in China. In addition to a combination of high strength, elasticity, toughness and abrasion resistance in common with other polyamides, it features lower moisture absorption and thus higher dimensional stability. Irrespective of Nylon 1010 has been widely used in industry, its important physical parameters, such as crystalline density ρ_c , amorphous density ρ_a , equilibrium heat of fusion ΔH_m^0 and equilibrium melting temperature T_m^0 have so far not been correctly determined. Since these parameters are indispensable to the technical or fundamental research of the polymer, in the present paper, an effort has been made to evaluate these parameters by using IR, DSC, EAXD and density measurement techniques.

EXPERIMENTAL

Sample

Nylon 1010 used in this study was a granular commercial product of Jilin Union

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Chemical Works, Ji Lin City. The granules were dissolved in hot ethanol under pressure and transformed into powdered sample after precipitation on cooling. The $\overline{M}_n$ determined by dissolving it in *m*-cresol was 1.34×10^4 ^[1]. After drying, films of 0.1 mm and sheets of 0.5 mm thick (d) were compression moulded at ca. 220 °C. Thereafter, they were annealed in different conditions in order that specimens of various crystallinity were prepared.

Apparatus and techniques

FTIR: Infrared spectra were examined on a Digilab FTS-20E infrared spectrometer at a resolution of 8 cm⁻¹. A series of film specimens with different density were scanned in the range from 800–1200 cm⁻¹.

WAXD: The crystallographic parameters were evaluated by oscillation photographic technique with a cylindrical camera (*R*=28.65mm). Specimens had been drawn with a draw ratio about 6-fold in length. The repeat distance along the *c*-axis was calculated from the layer lines of the fiber pattern.

DSC: (a) Isothermal crystallization from the melt: The melt isothermal crystallization experiments were carried out on a computerized Perkin-Elmer differential scanning calorimeter, Model DSC-7. The specimens were melted by raising the temperature at a rate of 320K/min to 220 °C for a period of 5 mins. Then they were undercooled rapidly to the predetermined crystallization temperature *T_c* at a rate of -80K/min and held the temperature constant until the crystallization was completed. Thereafter the specimens were heated again without prior cooling to obtain the DSC endotherms at a rate of 2.5K/min.

(b) Isothermal annealing (partial melting and recrystallization) of the specimen: At first the processing history of specimens was erased by heating in a Perkin-Elmer differential scanning calorimeter (DSC-2C) interfaced with a 3600 TADS microprocessor at a rate of 320K/min to 230 °C for 5 mins, and then cooled at the same rate to the room temperature. The specimens were heated again up to a prescribed temperature near the melting point at a rate of 320K/min and annealed isothermally for a prescribed time. Then specimens were heated again without cooling at a rate of 5 °C/min to record DSC thermograms.

The temperature reading and calorific measurement of both calorimeters were calibrated by using standard indium and the experiments were performed under flowing nitrogen atmosphere.

Density: The density of the samples was measured in a density gradient column of 20±0.1 °C. Carbon tetrachloride was used as the heavy liquid and *n*-heptane, the light liquid.

RESULTS AND DISCUSSION

1. ρ_c and ρ_a of Nylon 1010

ρ_c and ρ_a are important physical parameters of a crystalline polymer. Theoretically, they reflect the packing condition of a bulk polymer and are indispensable parameters for most fundamental research of macromolecules. Specifically they are the basis for the estimation of percentage crystallinity of nonporous crystalline polymers. Although ρ_c and ρ_a values of most nylons have been correctly determined, those values for Nylon 1010 have not been published in the literature.

Starkweather et al.^[2] have determined the ρ_c and ρ_a by plotting the intensities of crystalline and amorphous infrared band of Nylon 66 and 610 against density and extrapolating to zero intensity. Since it is unnecessary to have completely crystalline or completely amorphous samples, this approach is an absolute method and is particularly attractive for the evaluation of ρ_c and ρ_a of Nylon 1010. Accordingly, based on the results of preliminary tests, we observed that 1133 cm^{-1} is the amorphous band, 1007 and 940 cm^{-1} are the crystalline bands in Nylon 1010. The 1007 cm^{-1} was chosen in the later experiments because it was reported that^[3] the correlativity between the absorbance and density is inferior in the case of 940 cm^{-1} band. In Fig. 1 absorbances (A) per unit thickness for the crystalline and amorphous bands in Nylon 1010 are plotted against density. Both lines show better linearity. Through linear regression and putting A_c/d and A_a/d into zero, we got $\rho_c = 1.098\text{ g/cm}^3$ (correlation factor $r=0.9966$) and $\rho_a = 1.003\text{ g/cm}^3$ ($r=0.9989$) respectively.

The ρ_a value 1.003 g/cm^3 might be reasonable as it is close to the value 1.0014 g/cm^3 which was estimated by us through extrapolating the data recently published in the reference^[3]. As to ρ_c , however, its value seems too low. According to van Krevelen^[4], the mean value of the ratio ρ_c/ρ_a equals 1.13 for most crystalline polymers, whereas ρ_c/ρ_a for Nylon 1010 obtained here by infrared method is 1.095 only. Probably the systematic error resulted from the less intense in absorbance and less sensitive to the change in crystallinity of the amorphous band is responsible for the reduction in ρ_c value. Consequently, although the linearity of the data points is fairly well, the extrapolated value is unacceptable.

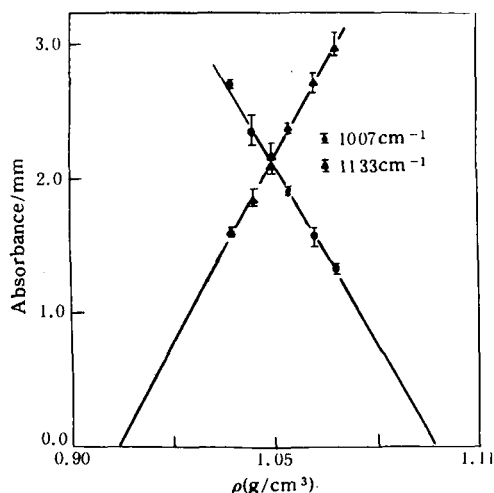


Fig. 1 Infrared absorbance per unit thickness A_a/d and A_c/d vs. density for Nylon 1010.

In order to evaluate a reasonable value of ρ_c , the traditional, most classic method, i. e. to calculate the ρ_c directly from the unit cell dimension was adopted. Early in 1940s, Baker^[5] reported $c=25.6\text{ Å}$ for Nylon 1010, but the remaining 5 parameters have not been published until now. From the fiber pattern of the drawn Nylon 1010 specimen, we found that the c value should be 27.8 Å , which is nearly the same with the calculated value 27.7 based on the chain length of the repeating unit with planar zigzag conformation. By referring to the data of other structural analogues such as Nylon 66 or 610, we determined by trial and error method that the unit cell parameters of Nylon 1010 are $a=4.9\text{ Å}$, $b=5.4\text{ Å}$, $c=27.8\text{ Å}$, $\alpha=49^\circ$, $\beta=77^\circ$, $\gamma=63.5^\circ$. Having established the size and shape of the unit cell, the crystalline density ρ_c of Nylon 1010 was calculated to be 1.135 g/cm^3 . As

judged by "conditions limiting possible reflections", it appears that only triclinic space group PI is possible. Besides, one unit cell contains one polymer chain^[6]. A detailed description of its crystalline structure will be reported elsewhere.

Not only is the value $\rho_c = 1.135 \text{ g/cm}^3$ obtained by WAXD method higher than that obtained by IR absorbance extrapolation, but in comparing with those values for Nylon 66 (1.24) and 610 (1.157) calculated by Bunn and Garner^[7] based also on unit cell dimension, this value also seems to be fairly reasonable. Therefore, we suggest that for ρ_a the value 1.003 g/cm^3 estimated by infrared method should be adopted, whereas for ρ_c , the value 1.135 g/cm^3 derived from X-ray diffraction method is preferred.

2. Equilibrium thermodynamic parameters of Nylon 1010

Equilibrium heat of fusion ΔH_m^0 and equilibrium melting temperature T_m^0 are important thermodynamic parameters characterizing the inter- and intramolecular actions, and are of significance in the fabrication and application of polymers. Since crystals of flexible linear macromolecules of large dimension are difficult to grow, equilibrium values are often not available by direct measurement, thus indirect or extrapolation method must be used.

(a) ΔH_m^0 : In the early days, as the direct calorimetric determination of ΔH_m^0 was rather difficult, Flory et al. through the more easily determinable melting temperature depression, estimated ΔH_m^0 of Nylon 1010 by copolymerization and dilution method to be $24.5^{[8]}$ and $23.1 \text{ cal/g}^{[9]}$. Since in the derivation of the equation of the latter method, equilibrium condition was assumed, which was not normally achieved experimentally at that time, whereas in the former method, the crystal size reduction due to copolymerizing was ignored, these values are thus much underestimated. This has long been evidenced by the fact that both values are even lower than the DSC measured heat of fusion of Nylon 1010 specimen in the metastable state. Therefore resort has to be made to evaluate the correct value.

A number of methods are now available to determine ΔH_m^0 of a crystalline polymer^[10]. Among them the approach to extrapolate the linear relationship between ΔH_m and the specific volume, $\bar{V}_{sp}$, of samples with different degree of crystallinity to 100% crystalline condition has been proved to be successful in the determination of ΔH_m^0 for many linear semicrystalline polymers^[11]. Therefore, specimens with different percentage of crystallinity were prepared by annealing in different conditions. Heat of fusions of the samples were determined by using DSC and their respective specific volumes were measured with a density gradient column. Shown in Fig. 2 is the plot of ΔH_m against corresponding $\bar{V}_{sp}$ of the differently annealed Nylon 1010 samples, wherein a pair of data, i. e. $\bar{V}_{sp}^a (= 1/\rho_a = 0.997 \text{ cm}^3/\text{g})$ obtained above and $\Delta H_m = 0$ is also included. Through linear regression, an expression in the form

$$\Delta H_m = 2099.5 - 2106.1 \bar{V}_{sp} \quad \text{J/g} \quad (1)$$

was given with a correlation factor $r = -0.9991$. If $\bar{V}_{sp}^c$ (specific volume of hypothetical 100% crystalline Nylon 1010 i. e., $0.881 \text{ cm}^3/\text{g}$ (or 1.135) as calculated based on the unit cell dimension is substituted for $\bar{V}_{sp}$, $\Delta H_m^0 = 244.0 \text{ J/g}$ (or

58.3 cal/g) is derived. From Fig. 2, it is further ascertained that the value of ρ_c and ρ_a suggested in the above section are reasonable. Firstly, ρ_a determined by IR absorbance extrapolation method can be fairly connected in the straight line with other seven pairs of experimental data points with a high correlation factor ($r > 0.999$). Secondly, in comparison with ΔH_m^0 of Nylon 66 (45 cal/g) determined by PVT method^[12] and 610 (50.6 cal/g)^[13] also by $\Delta H_m - V_{sp}$ method, $\Delta H_m^0 = 58.3$ cal/g for Nylon 1010 should be acceptable, since for polyamides, there is a trend that the longer the hydrocarbon segment in the repeating unit, the higher the value of ΔH_m^0

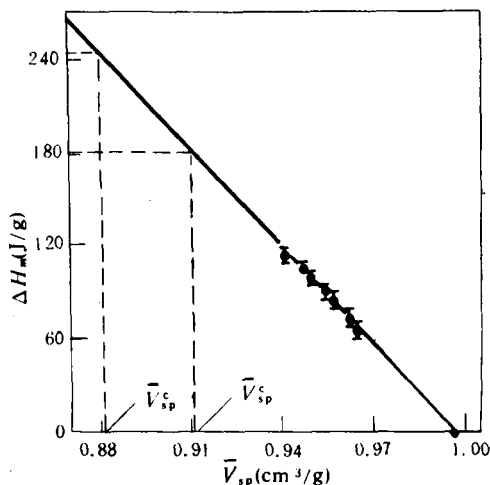


Fig. 2 ΔH_m vs. V_{sp} plot of Nylon 1010 samples with different crystallinities.

and the lower the T_m^0 ^[4,16]. If $\rho_c = 1.098$ is substituted in Eq. 1, ΔH_m^0 is 180.8 J/g (43.2 cal/g) only, which is even lower than that of the value of Nylon 66.

(b) T_m^0 : The equilibrium melting temperature T_m^0 is perhaps the most important macroscopic quantity to characterize a given crystal of a flexible linear macromolecule. The prevailing approach to evaluate T_m^0 is the so-called Hoffman's $T_m - T_c$ extrapolation method^[14]. The method rests on the observation that when melting temperatures T_m of metastable crystals are plotted as a function of their crystallization temperature T_c from the melt, one finds a linear relationship between T_m and T_c . If the line is extrapolated and intersect with the equilibrium line $T_m = T_c$ (i. e. a state wherein melt and crystal are in equilibrium is attained.) the point of intersection is T_m^0 . In the previous work^[13], we have successfully determined the T_m^0 of Nylon 610 to be 517.6K by this method. The merit of the method is that only calorimetric technique is required. However, data points available only in a narrow temperature range and a rather long extrapolation are its shortcomings. Besides, in the present case, an unexpected situation, which has never been reported in the literature, renders the application of this method impossible.

DSC melting traces of Nylon 1010 specimens melt-crystallized at different T_c and then heated at a rate of 2.5 K/min right after the completion of crystallization are shown in Fig. 3. It reveals that when crystallization takes place below 186°, recrystallization occurs during heating and the recrystallization exothermic peak is not separable from the melting peak II. When $T_c > 186^\circ\text{C}$, recrystallization exotherm could hardly be observed. Fig. 4 illustrates the plot of melting temperature vs. corresponding crystallization temperature of isothermally melt crystallized Nylon 1010 samples. The temperatures of peak III are almost constant and independent of T_c . It suggests that they are the ultimate metastable melting temperature of Nylon 1010 in the given condition. Although T_m (I) varies linearly with T_c , it is parallel with the $T_m = T_c$ line. Therefore both peak I and III are useless in the determination of T_m^0 .

$T_m(\text{II})$ does vary linearly with T_c but depending upon whether recrystallization occurs or not, the line $T_m - T_c$ interrupts abruptly between $186 - 187^\circ\text{C}$. Above 186°C , it is also in parallel with the line $T_m = T_c$, whereas below 186°C , it intercepts the equilibrium line at a temperature as low as 199.9°C . This is an absurd value because it is even lower than the melting temperature of the metastable crystal, 203°C . The failure of the use of Hoffman's method is presumed to be due to the fact that for samples crystallized $< 186^\circ\text{C}$, peaks II are partly merged with the recrystallization exotherms and $T_m(\text{II})$ are shifted to lower temperatures, whereas for samples crystallized $> 186^\circ\text{C}$, reorganization and perfection of the

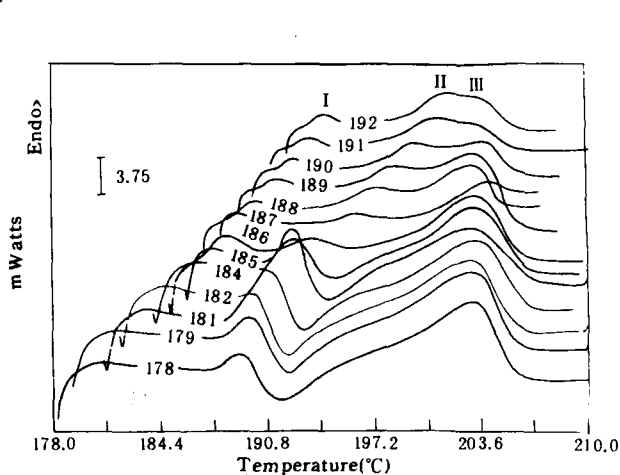


Fig. 3 DSC heating curves of isothermally melt crystallized Nylon 1010 samples.

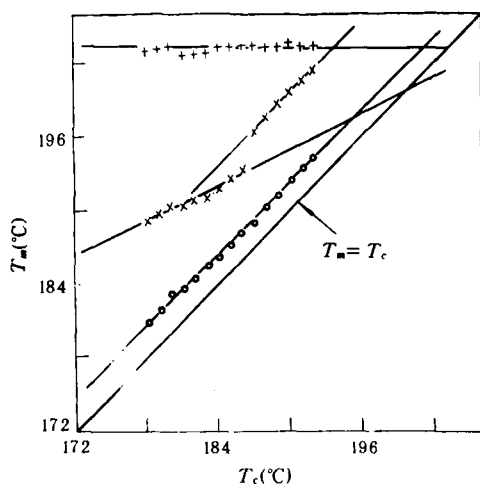


Fig. 4 Relationship between T_m and T_c of isothermally melt crystallized Nylon 1010.
• $T_m(\text{I})$; × $T_m(\text{II})$; + $T_m(\text{III})$

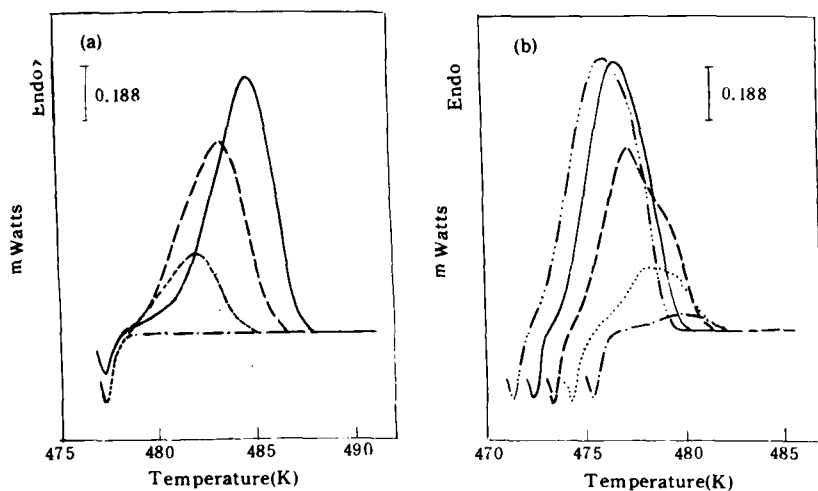


Fig. 5 DSC thermograms for Nylon 1010 specimens (a) annealed at 447K for the indicated times and (b) annealed for 30 min at indicated temperatures

(a) — 900 min; --- 300 min; 90 min; - · - · - 30 min

(b) — 471K; --- 472K; 473K; - · - · - 474K; - - - - - 475K

crystals formed T_c during programmed heating in the calorimeter result in an increased apparent melting point. Thereby the measured T_m (Π) in both cases bears no relation to the original isothermal crystallization temperature.

Although the determination of T_m^0 by Hoffman's method has been proved to be a failure owing to the easiness of recrystallization of Nylon 1010 sample, this property can readily be used as a basis of the adoption of an often unnoticed Kamide double extrapolation method^[15]. The principle of the method lies in the observation that after the initial partial melting at a sufficiently high annealing temperature is over, the samples increase slowly in crystallinity, however, at the highest annealing temperature, the time needed for completion of annealing tends to infinity, and the final crystallinity reached remains practically zero. This highest temperature is assumed by Kamide to be practically equal to the thermodynamic equilibrium melting temperature, at which the driving force for crystallization $\Delta T (= T_m^0 - T_c)$ and thus the crystallization rate are equal to zero. Rapid partial isothermal melting and recrystallization are the prerequisite of this method, so that the effect of recrystallization only would be observed in the successive DSC scanning. Being moderate in molecular weight, Nylon 1010 fulfils this requirement. Shown in Fig. 5 are the thermodiagrams for Nylon 1010 specimens annealed at 447K for different times (a) and annealed at different temperatures for 30 mins (b).

The observed melting temperature T_m was plotted against the annealing time t and ΔH_m (Fig. 6). When compared at a constant t , ΔH_m is smaller at the higher annealing temperature. On the other hand, as the annealing temperature approaches the equilibrium temperature T_m^0 , the rate of recrystallization should become infinitely small, implying $\Delta H_m = 0$ at T_m^0 and the thermodynamical equilibrium between the remaining crystal and the surrounding polymer melt should be attained after annealing of infinitely long time. Therefore, the double extrapolation of T_m to annealing time $= \infty$ and $\Delta H_m = 0$ should give T_m^0 .

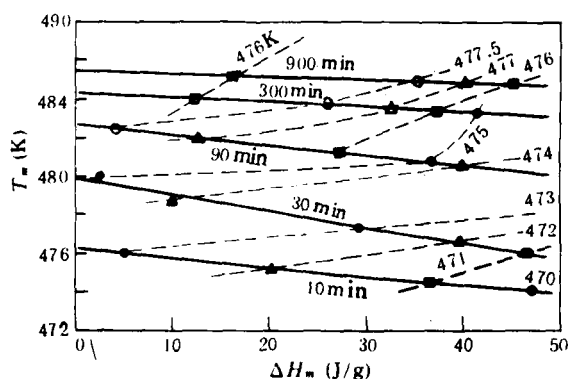


Fig. 6 Relationship between the observed T_m and ΔH_m for Nylon 1010 samples annealed at different temperatures. Solid lines are given for the indicated annealing times.

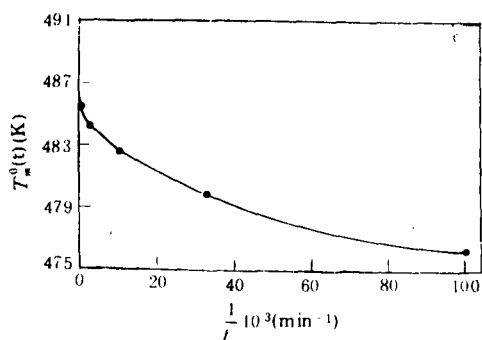


Fig. 7 $T_m^0(t)$ of Nylon 1010 plotted against reciprocal of the annealing time.

By extrapolating the contour (solid) lines for the constant annealing time to

$\Delta H_m = 0$, $T_m^0(t)$ are given and defined as (Fig. 6)

$$T_m^0(t) = \lim_{\Delta H_m = 0} T_m(\Delta H_m, t) \quad (2)$$

As the annealing temperature reaches T_m^0 , the degree of recrystallization is infinitesimal (or $\Delta H_m = 0$) even though the annealing time is infinitely long (or $t = \infty$). This temperature can be derived if $T_m^0(t)$ is further extrapolated to $t = \infty$. i. e.,

$$T_m^0 = \lim_{t = \infty} T_m^0(t) = \lim_{t = \infty} T_m(\Delta H_m, t) \quad (3)$$

Therefore, $T_m^0(t)$ extrapolated from Fig. 6 are plotted vs. $1/t$ in Fig. 7 from which T_m^0 of Nylon 1010 was found to be 487K by extrapolating to $1/t = 0$. The non-linear extrapolation in Fig. 7 might give inevitably some uncertainty to the value of T_m^0 . However, because of the short extrapolation distance ($< 3K$), possible errors should be small.

As stated above, for polyamides, longer $-\text{CH}_2-$ segment results in lower melting point. In comparison with Nylon 66 (553.2K)^[17] and 610(517.6)^[13], the value $T_m^0 = 487K$ for Nylon 1010 can be granted to be reasonable, and indeed this value was used successfully in the study of the isothermal crystallization kinetics of γ -irradiation crosslinked Nylon 1010 sample^[18].

Keywords:

Nylon 1010; Crystalline and amorphous densities; Equilibrium heat of fusion; Equilibrium melting temperature.

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