

Thermal and Dynamic Mechanical Properties of a Polypropylene Random Copolymer

Mohammad Razavi-Nouri

Department of Plastics, Faculty of Processing, Iran Polymer and Petrochemical Institute,
P.O. Box: 14965/115, Tehran, I.R. Iran

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ABSTRACT

Isothermal crystallization kinetics, melting, structure and dynamic mechanical properties of a polypropylene (PP) random copolymer with low ethylene content were studied. In order to study the effect of cooling rate on melting, two different cooling rates were applied to the samples. While water-cooled samples revealed a broad single melting endotherm with α -crystalline structure, slow-cooled samples showed a shoulder at lower temperature followed by a sharp melting endotherm and a mixture of α and γ -crystalline phases. The effect of annealing on $\log E''$ of the β -relaxation for the PP copolymer showed that the β -transition increased in intensity with increasing annealing temperature. No considerable difference was found in the activation enthalpy of relaxation, ΔH , values for the annealed compared to that of the water-cooled samples using the Arrhenius equation. The isothermal crystallization kinetics was also studied for PP and the values of nucleation constant, K_g , and end-surface free energy of the crystal growth, σ_e , were calculated using Lauritzen-Hoffman theory.

Key Words:

polypropylene random copolymer;
crystallization kinetics;
DMTA;
melting;
DSC.

INTRODUCTION

The production and synthesis of polypropylene (PP) copolymers resulted from a natural development of polyolefin technology from the manufacturing of PP homopolymer. Two main types of propylene-ethylene copolymers are available in the

market today, which are usually prepared using heterogeneous catalysts [1]. These are block and random copolymers. The introduction of random copolymers expanded the range of properties available depending on ethylene content. Low ethylene con-

(*)To whom correspondence should be addressed.
E-mail: m.razavi@ippi.ac.ir

tent copolymers are interesting lower crystalline materials because the insertion of a second monomer into the propylene backbone would inhibit the crystallization and produce a copolymer with lower melting point and higher impact strength than the homopolymer. For these PP copolymers, the structure and crystallization behaviour depend on molecular weight and molecular weight distribution as well as tacticity, comonomer content and comonomer sequence distribution. It is worth mentioning that the actual copolymerization technique used has not been disclosed and there is also little information about dynamic mechanical properties, structure and morphology of these copolymers [2].

Isotactic polypropylene (i-PP) is readily crystallized and the polymer chain exists in the crystal as a 3/1 helix with 3 monomer units per turn of the helix. Four different chain conformations exist which have identical intramolecular interaction energies. However, their intermolecular interactions with each other in the crystal depend on packing geometry. When the nearest neighbours of left-handed helices are enantiometric right-handed helices and vice versa the best packing is achieved [3]. From different packing geometries four well-known crystallographic forms have been observed for PP. These are monoclinic (α), hexagonal (β), triclinic (γ) as well as a quenched form. A less common δ -form structure has also been proposed. Among these crystalline structures the α -form is the most common [3-7].

This paper investigates the isothermal crystallization kinetics and dynamic mechanical properties of a PP random copolymer to understand the effect of annealing on the dynamic mechanical relaxation spectrum and also cooling rate on the structure and melting behaviour of the PP studied.

EXPERIMENTAL

Polypropylene random copolymer was supplied by Himont (Italy) with the trade name of Moplen EP (TP-

176 AM). The melt flow index of the PP copolymer as measured by Davenport MFI apparatus at 230°C is 0.18 g.min⁻¹. Table 1 shows the other specifications of the material.

By pressing the granules between two PTFE sheets, square sheets of PP (1.6 mm thick) were prepared in a hydraulic press at 220°C for 5 min. The sheets then were quenched in two different ways. A slow cooling rate was achieved by cooling the sample in the press, i.e. the hot press heaters were switched off and allowed to cool the sample to room temperature over about 5 h (slow-cooled sample). In the other method the sheets were quenched in water. Annealing of the quenched sample was carried out in an oven for 24 h at 70 and 100°C and subsequently requenched in water.

Melting and crystallization kinetics studies were carried out using a Perkin-Elmer differential scanning calorimeter (model DSC-2) interfaced to a PC. The temperature scale of the calorimeter was calibrated using the melting points of indium, tin and stearic acid and the thermal response from the enthalpy of indium. For melt isothermal crystallization, the samples were cooled from above the observed melting point at a rate of 160 K.min⁻¹ to the crystallization temperature and kept at that temperature until the DSC trace returned to the calorimeter baseline. Each result is an average of three experiments.

The radial growth rate of PP spherulite was measured with a polarized light microscope (Leitz Dialux) fitted with a Linkam hot stage (TH600). The temperature of the hot stage was controlled with a temperature controller (PR600). The temperature scale was also calibrated using zone refined stearic and benzoic acid.

The dynamic mechanical relaxation spectrum of the sample was obtained using a Polymer Laboratories dynamic mechanical thermal analyzer (DMTA) controlled by an IBM PS-2 computer. The dimensions of the samples were 40×12.7×1.6 mm³ and sub-ambient temperatures were achieved by liquid nitrogen purging through the DMTA jacket. The experiments were carried out in the temperature range -100 to 150°C and fre-

Table 1. Polymer characteristics.

Material	\bar{M}_w (kg mol ⁻¹)	\bar{M}_n (kg mol ⁻¹)	PDI	Density (g cm ⁻³)	Type of comonomer	Comonomer content mol (%)
PP (random copolymer)	365	101	3.6	0.902	Ethylene	5

quencies 0.1, 1 and 10 Hz.

The X-ray studies of the samples were carried out using a Philips X'pert wide angle X-ray diffractometer (WAXD) which was interfaced to a PC computer, and operated with $\text{CuK}\alpha$ radiation ($\lambda=1.54 \text{ \AA}$) at 40 keV and 30 mA. The scans were recorded in the range of 2θ values from 5 to 65° in steps of 0.02° . The count time was 1 s per step.

RESULTS AND DISCUSSION

Melting Behaviour and Structure

The melting behaviour of water and slow-cooled PP copolymer samples are shown in Figure 1. It can be seen that while the water-cooled sample shows a broad single melting endotherm, there is a shoulder on it at lower temperature in the slow-cooled sample. The lower temperature endotherm is probably produced by the chains crystallizing at lower temperatures than bulk sample on slow cooling. Therefore, two distinct melting endotherms appear as a result of molecular segregation during slow cooling. The degrees of crystallinity of water and slow-cooled samples as measured by DSC were found to be $36\pm 2\%$ and $43\pm 2\%$, respectively.

In order to study the effect of cooling rate on molecular segregation, samples were cooled at different cooling rates from the melt and then heated to melt at $10 \text{ K}\cdot\text{min}^{-1}$. Figure 2 shows the effect of different cooling rates on the subsequent melting endotherms of the PP copolymer. At high cooling rate only one broad melting endotherm was observed but as the cooling rate decreased to $10 \text{ K}\cdot\text{min}^{-1}$ the low temperature shoulder

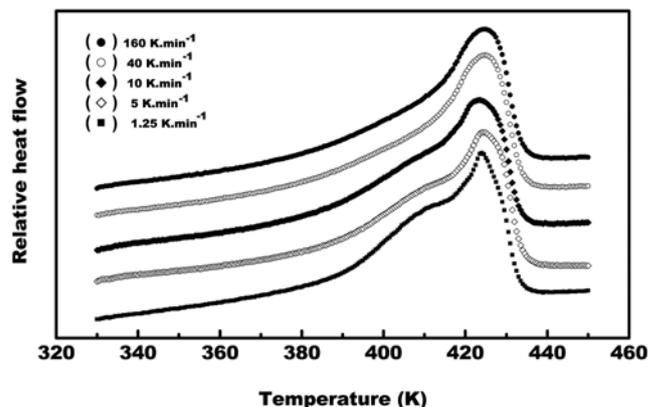


Figure 2. PP Melting endotherms after cooling at different cooling rates (rate of heating $10 \text{ K}\cdot\text{min}^{-1}$).

became more apparent. Obviously with slow cooling more time becomes available at the lower temperature for crystallization to occur.

The WAXD patterns of water and slow-cooled PP are shown in Figure 3. The patterns have a broad amorphous background superimposed upon sharper diffraction lines due to the crystalline regions. In the water-cooled sample, the α -form was present with diffraction lines at 2θ values equal to 14.02 , 16.78 , 18.4 , 21.12 and 21.52° . These represent diffraction from the 110, 040, 130, 111, 131 and 041 lattice planes. The diffraction line at 21.52° is due both to the 131 and 041 planes. The WAXD pattern of slow-cooled PP shows diffraction lines belonging to the α -form as well as an additional line at 2θ equal to 19.6° , which is characteristic of the 140 and 130 planes of the γ -form crystals [5]. This is in agreement with results reported previously [8-10] for slow-cooled sample in which a mixture of α and γ crys-

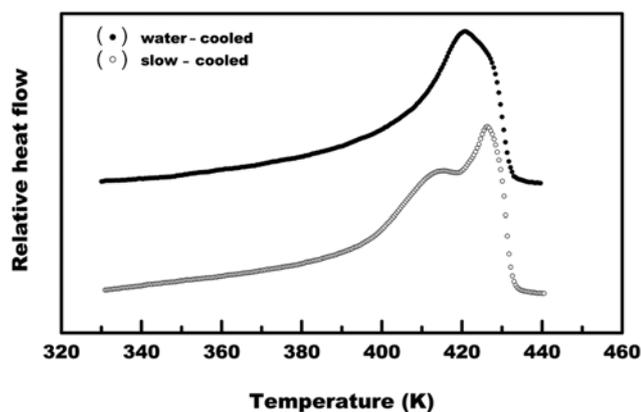


Figure 1. The effect of slow and rapid cooling on the melting endotherm of PP copolymer (rate of heating $5 \text{ K}\cdot\text{min}^{-1}$).

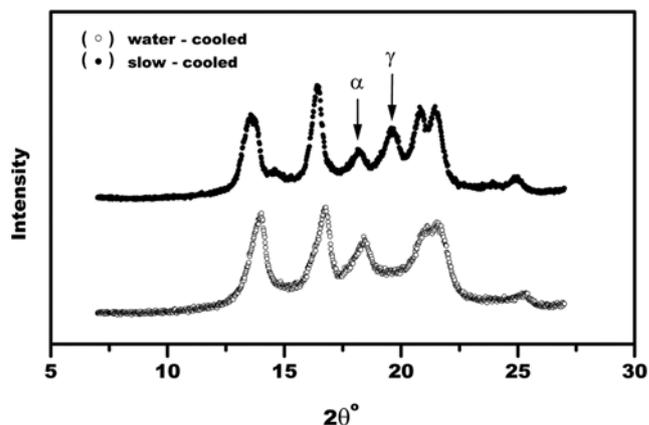


Figure 3. WAXD Spectra for water and slow-cooled PP copolymer.

tals are formed during the crystallization of PP random copolymers. It has been suggested [11] that the incorporation of ethylene units into regular i-PP sequences in the chain is responsible for an increase of the number of defects within the crystal and due to the incorporation of the comonomer unit into the crystal, the crystallographic structure can be changed to the γ -form. The characteristic peak of the β -form, which appears at $2\theta = 15-16^\circ$ was not observed and so no β -form is present in the samples. There was also no peak at $2\theta = 23.9^\circ$, which is due to polyethylene (PE) crystals and to diffraction from the 200 plane. There were insufficiently long ethylene sequences in the sample for PE crystals to be detected by WAXD.

Crystallization Rate Studies

Isothermal crystallization from the melt was studied using the Avrami equation such that [12]:

$$-\ln\left(1 - \frac{X_t}{X_{p,\infty}}\right) = Zt^n \quad (1)$$

where n is Avrami exponent which adopts different values for different crystallization mechanisms [13], Z is composite rate constant, X_t is the degree of crystallinity formed only during the primary process at time t and $X_{p,\infty}$ is that formed at the end of the primary process. Accordingly,

$$\log\left[-\ln\left(1 - \frac{X_t}{X_{p,\infty}}\right)\right] = \log Z + n \log t \quad (2)$$

An average rate constant Z can also be calculated from the half-life, $t_{1/2}$, and the value of n at $t_{1/2}$, as:

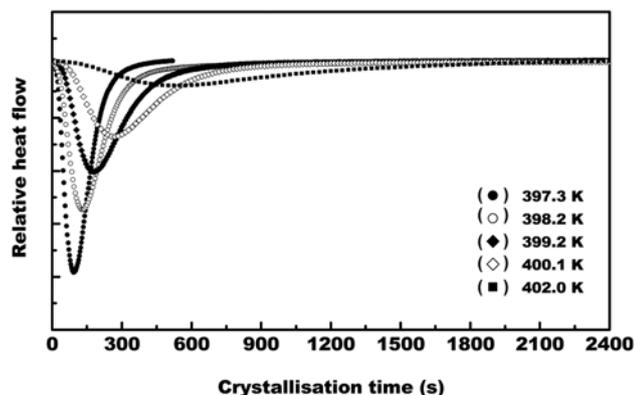


Figure 4. DSC Exotherms of isothermal crystallization of the PP copolymer.

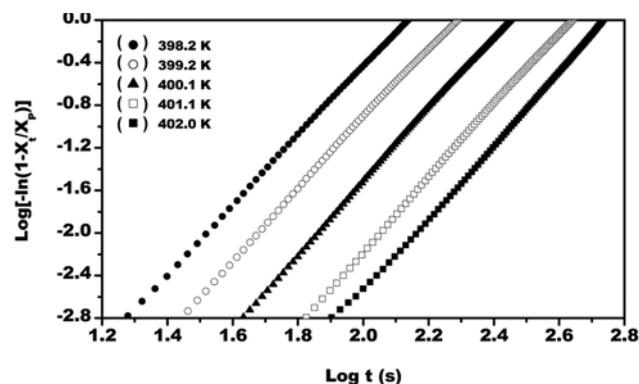


Figure 5. Avrami analysis of primary crystallization of the PP copolymer.

$$Z = \frac{\ln 2}{(t_{1/2})^n} \quad (3)$$

The corrected isothermal crystallization exotherms for PP were obtained at different temperatures and are shown in Figure 4.

The weight fraction crystallinity, X_t , at time t was calculated from the DSC crystallization isotherm as the area under the peak at time t divided by the total area under the peak such that [14-15]:

$$X_t = \frac{\int_0^t \frac{dH}{dt} \cdot dt}{\int_0^\infty \frac{dH}{dt} \cdot dt} \quad (4)$$

By separating the primary and secondary crystallization processes and using eqn (2), the Avrami parameters for the primary crystallization were calculated. The

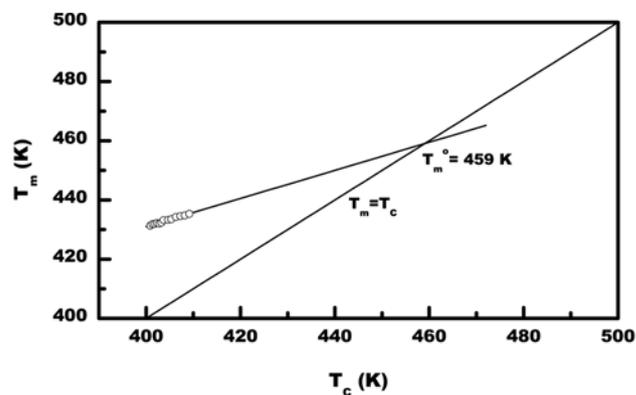


Figure 6. The plot of T_m against T_c according to Hoffman-Weeks method.

Table 2. Crystallization rate parameters.

Crystallization temperature (K)	Half-life, $t_{1/2}$ (s)	n Value \pm 0.2	Rate constant, $Z \times (10^4 \text{ min}^{-n})$
397.3	93	3.1	1781.5
398.2	132	3.2	556.0
399.2	178	3.3	191.6
400.1	269	3.4	42.2
401.1	386	3.3	14.9
402.0	572	3.3	4.1
403.0	896	3.1	1.6

results are shown in Figure 5 for PP random copolymer. The slopes of straight lines were equal to the Avrami exponent and intercept at $\log t = 0$ of $\log Z$ for the primary crystallization. Table 2 lists the Avrami parameters determined for melt crystallization of PP. At all temperatures, the n value was 3.2 ± 0.2 which is close to the integer 3.0 and consistent with three-dimensional spherical growth from athermal nuclei. It can also be seen that the half-life increased with increasing crystallization temperatures. Increasing $t_{1/2}$ and decreasing Z were consistent with nucleation control of growth and dependence on the degree of supercooling.

The radial growth rate, g , of the PP spherulites was measured at various temperatures using a micrometer eyepiece. The results are given in Table 3. The decrease of the radial growth rate with temperature was consistent with nucleation controlled growth and it followed the same dependence as the half-lives.

The equilibrium melting point, T_m^0 , was measured using Hoffman-Weeks [16-17] method in which the

Table 3. Radial growth rates of PP spherulites at different temperatures.

Crystallization temperature (K)	Radial growth rate (μmmin^{-1})
388.4	13.69
390.5	9.04
392.5	6.73
394.6	4.29
396.5	3.43
398.5	2.11
400.6	1.36

polymer was crystallized at different temperatures, T_c , and then the melting points, T_m , relative to each corresponding temperature was obtained.

According to Hoffman-Weeks equation a plot of T_m against T_c gives a linear relationship as:

$$T_m = T_m^0 \left(1 - \frac{1}{2\beta}\right) + \left(\frac{1}{2\beta}\right) T_c \quad (5)$$

where β is the thickening factor. Figure 6 shows the relationship between T_m and T_c for PP copolymer. The intersection of the straight line with the diagonal $T_m = T_c$ gave a value for T_m^0 of 459 ± 2 K. The β value from the slope of the line was also found to be 1.05. This confirms that the amount of crystal perfection and recrystallization are negligible.

Turnbull and Fisher [18] developed an equation for the temperature dependence of the rate of growth in condensed systems. The steady-state growth rate is given by:

$$g = g_0 \exp\left(\frac{-\Delta E}{RT}\right) \exp\left(\frac{-\Delta G^*}{RT}\right) \quad (6)$$

where g_0 is a temperature independent quantity and depends upon molecular parameters. For the case of nucleation control of growth, g_0 is also a function of crystal geometry. ΔE is the energy barrier for transport of material across the crystal-liquid interface and its influence on the temperature dependence of the nucleation process can be neglected at small supercoolings. ΔG^* is the work required to build a nucleus with critical size, T is temperature and R is the universal gas constant.

Hoffman and coworkers reformulated the Turnbull and Fisher equation in molecular terms which is usually referred to as Lauritzen-Hoffman theory [19-24]:

Table 4. Crystallographic unit cell dimensions for PP [27].

110 growth plane	
a_0 (m)	5.49×10^{-10}
b_0 (m)	6.26×10^{-10}
a_0b_0 (m ²)	3.43×10^{-19}

$$g = g_0 \exp\left(\frac{-\Delta E}{R(T_c - T_\infty)}\right) \exp\left(\frac{-K_g}{fT_c\Delta T}\right) \quad (7)$$

where K_g is the nucleation constant, T_c is crystallization temperature, T_∞ is the temperature below which motions cease and is taken to be $T_\infty = T_g - 30K$, $\Delta T = T_m^0 - T_c$ and is the degree of supercooling, f is a factor which accounts for the variation in the enthalpy of fusion, ΔH_f , with temperature and is given by:

$$f = 2T_c / (T_m^0 + T_c)$$

The kinetic data obtained from PP crystallization were analyzed using eqn (7). Eqn (8) is obtained by rearranging eqn (7) as:

$$\ln g + \frac{\Delta E}{R(T_c - T_\infty)} = \ln g_0 - \frac{K_g}{fT_c\Delta T} \quad (8)$$

K_g can also be expressed as:

$$K_g = \frac{nb_0\sigma\sigma_e T_m^0}{k\Delta H_f} \quad (9)$$

where σ and σ_e are the lateral and end-surface free energies of the growing crystal, respectively, b_0 is the molecular thickness and k is the Boltzmann constant. The n value depends on the crystallization regime. At low supercooling, an extended chain is laid down on the growth face of a crystallite, followed by alignment of the segments onto adjacent positions until the surface is completely covered. This is referred as regime I and $n=4$. In regime II, the rate of secondary nucleation is larger than regime I and several chain segments are laid down independently on a growth face, followed by subsequent addition of chains adjacent to the initial segments. Chain addition takes place until the growth face is totally covered. In regime II, $n=2$. Regime III takes place when the degree of supercooling is even larger than regime II. The rate of nucleation is high and the separation between the nuclei reaches a minimum.

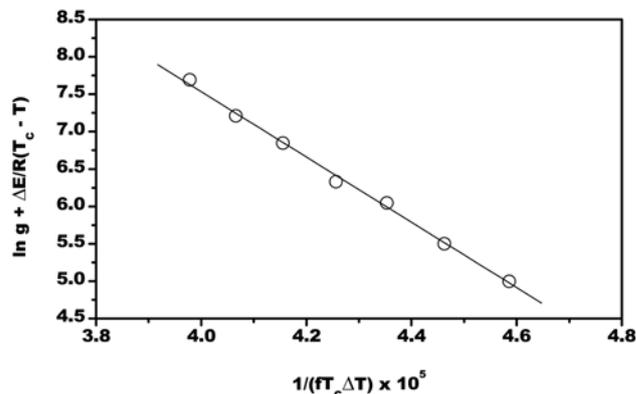


Figure 7. The plot of $[\ln g + \Delta E/R(T_c - T_\infty)]$ against $(1/fT_c\Delta T)$ according to Lauritzen-Hoffman theory.

Here $n=4$ as in regime I [25-26].

Compared with the references [27-28], it is assumed that all crystallizations were carried out in Regime III. In determining σ_e , the σ is estimated as:

$$\sigma = \alpha(a_0b_0)^{\frac{1}{2}} \Delta H_f \quad (10)$$

where a_0b_0 represents the cross-sectional area of the polymer chain and α was obtained empirically to be 0.1 [29]. The constants were used for PP in the analysis are listed in Table 4.

Figure 7 shows the plot of $[\ln g + \Delta E/R(T_c - T_\infty)]$ as a function of $1/fT_c\Delta T$, obtained from the experimental values of g , T_c , T_m^0 and a standard quantities of $\Delta E = 6280 \text{ J.mol}^{-1}$ and $T_\infty = 239.6 \text{ K}$ [27]. The values of K_g can be calculated directly from the graph where the slope gives $-K_g$. The values of K_g and σ_e were found to be $4.37 \times 10^5 \text{ K}^2$ and 0.0895 J.m^{-2} , respectively which are similar to the results reported by Feng and Hay for PP copolymers [29].

Dynamic Mechanical Behaviour

i-PP Homopolymer in the temperature range between -100 to 100°C shows three transitions. The relaxation, which occurs at the lowest temperature, is attributed to the γ -relaxation and is usually assigned to the local mode relaxation in the amorphous phase. The main relaxation around 0°C is attributed to a β -relaxation. This has generally been attributed to the glass transition of the polymer. Another peak, which can usually be observed as a shoulder on the melting of PP, in the range 35-90°C, is attributed to the α -relaxation and has

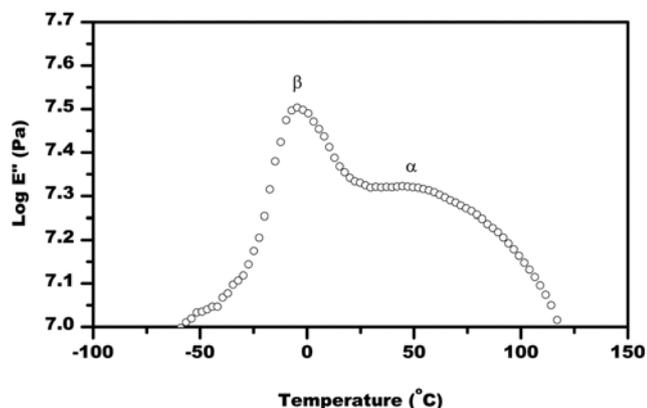


Figure 8. Variation in $\log E''$ with temperature for PP copolymer at 1 Hz.

generally been related to the crystalline phase [30].

The $\log E''$ spectrum of water-cooled PP copolymer at 1 Hz is shown in Figure 8. It has been reported [31] that the DMTA spectrum of random copolymer is similar to that of the *i*-PP homopolymer. As it can be observed from the peak in $\log E''$, the α and β -relaxations for the PP copolymer appear to be about 45 and -5°C , respectively. Due to the inclusion of some ethylene comonomer units within the propylene chain, the β -relaxation of the copolymer decreased by a few degrees from that of *i*-PP homopolymer.

The dynamic mechanical response of semicrystalline polymers is dependent on the thermal history of the polymer. Figure 9 shows the effect of annealing on the $\log E''$ in the temperature region of the β -relaxation for the PP copolymer. The β -peak increases in intensity with increasing annealing temperature. This behaviour has also been reported by others [31-33]. It is not

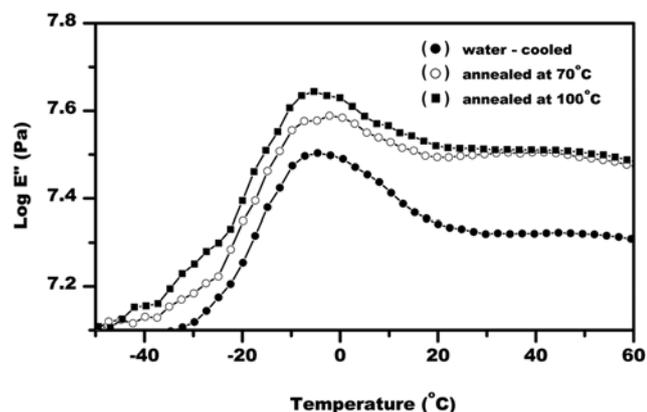


Figure 9. The effect of annealing temperature on the β -relaxation of PP copolymer.

clear why this should happen, but, it may be due to relaxation of constrained amorphous regions on annealing. Water-cooled samples are considered to contain constrained amorphous regions, in which segmental motions are strongly inhibited. In the amorphous sample, the constraints on the segmental motions result from several sources: tie molecules, loose loops, spatial prohibition by surrounding crystalline phases and internal strains in the amorphous chains. However, spatial restriction applied by the crystalline phases is considered as the major reason for the constraints. On annealing, the constraints would relax and if lamellae thickening occurred during annealing only to a limited extent, the relaxation of constraints between lamellae can play a major role in increasing the β -peak.

The activation enthalpy for relaxation was calculated using the Arrhenius equation [31, 34-35], i.e.

$$\ln f = \ln A + \frac{\Delta H}{RT_r} \quad (11)$$

where f is the frequency, ΔH is the activation enthalpy of relaxation, A is a constant, R is the gas constant and T_r is the relaxation temperature. Using eqn (11), the ΔH for β -relaxation was determined and it was in the range $250 \pm 50 \text{ kJ.mol}^{-1}$. This did not change with annealing temperature.

CONCLUSION

The effect of cooling rate on the crystalline structure of PP random copolymer has been studied. While water-cooled samples showed only a broad single melting endotherm and the α -crystalline phase, the slow-cooled samples revealed a shoulder at lower temperature followed by a sharp melting endotherm and a mixture of α and γ -crystalline phases.

The effect of annealing on $\log E''$ of the β -relaxation for the PP copolymer showed that the β -transition increased in intensity with increasing annealing temperature which could be attributed to the relaxation of constrained amorphous region on annealing.

The activation enthalpy for the β -relaxation of PP copolymer was calculated using the Arrhenius equation. No considerable difference was found in the ΔH values for the annealed compared to that of the water-cooled samples. These results show that microstructure

has a primary effect in determining the properties of the copolymer.

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