CALORIMETRIC STUDY ON KINETICS OF MESOPHASE TRANSITION IN THERMOTROPIC COPOLYESTERS

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ABSTRACT

Macromolecular crystallization behaviour, especially those of liquid crystalline polymers, has been a subject of great interest. The crystallization process for the polyester samples under discussion are analyzed assuming a nucleation controlled process and by using the Avrami equation. The study mainly deals with the crystallization process from the mesophase of two thermotropic liquid crystalline polyesters exhibiting smectic order in their mesophasic state. In order to analyze crystallization behavior of the polyesters, crystallization rate constant and the Avrami exponent have been estimated. Total heat of crystallization and entropy change during the transition has been calculated for both the polyesters.

Keywords: *Crystallization; Mesophase; Nucleation; Orthorhombic; Smectic.*

1. INTRODUCTION

The transition kinetics of liquid crystal polymers appears to be of great interest in order to control the effect of processing conditions on the morphology as well as on the final properties of the materials. These LC polymers show at least three main transitions: a glass transition, a thermotropic transition from the crystal to the mesophase and the transition from the mesophase to the isotropic melt. The kinetics of phase transition in liquid crystals may be analyzed for three different processes, the three dimensional ordering from both the isotropic melt state and the mesophase and the formation of the mesophase from the isotropic melt. In many cases transformation from the isotropic state can not be analyzed because the samples degrade at or very close to their isotropization temperatures.

The flexible polymers generally follow a chain folded mechanism, where as, rigid or semi   rigid polymers which frequently display mesophases, crystallize from their melt via aggregation of chain molecules[1].The macroscopic overall crystallization process is based on the theory developed by Avrami[2]. Considering the nucleation rate and growth geometry, the Avrami equation is expressed as,

$$X(t) = 1 - \exp(-Kt^n) \qquad (1)$$

Where X(t) is percent crystalinity at time t, K is the crystallization rate constant that contains information regarding diffusion and nucleation rates and n, the Avrami exponent, is a constant and is dependent on the nature of nucleation and geometry of crystal growth process.

Different Avrami exponents have been reported for different LCPs ranging from 1−4. This indicates that the crystallization kinetics of LCPs is influenced by the liquid crystalline phase itself. When n is equal to 1, it often described as a process of instantaneous nucleation and rod like growth. However, when n is within 2 to 4, it is described as a process of disc like or sphere like growth. This concept has been used to characterize the liquid crystallization behavior of some liquid crystal polymers. Since the smectic phase possesses two dimensional orders, the liquid crystallization process of a smectic mesophase is often characterized by the n values ranging from 2 to 4[3].The kinetics of phase transitions from isotropic states to the nematic mesophase of a thermotropic main-chain liquid crystalline polymer has been studied by Bhattacharya et al [4] using DSC and optical microscopy. Avrami analysis of the data gives an exponent close to 1 which suggests a rod like nucleation controlled growth. The values of the exponent n have been determined from the experiments performed by Lin et al[5] with an aromatic thermotropic polyester to be 4 and 1 for crystallization and liquid crystallization processes respectively. Kinetics of liquid crystallization of polyesters with trimethylene and decamethylene spacers has been studied by Pracella et al[6]. When the spacer is a trimethylene glycol, n was found to be 2 and for the decamethylene glycol, it was found to be between 3 and 4. Hence, it has been established that the crystallization kinetics of LCPs is related to the length of the spacers and the efficiency of packing. Two series of copolyesters with very low n values have been reported by S.Z.D.Cheng[7]. They have suggested a diffusion controlled growth rate of the crystals. The crystallization

process does not follow a constant radial crystal growth when it is diffusion controlled and in this case the apparent coefficient is considered as 0.5n. Hence for one dimensional crystal growth, n becomes 0.5 and for two and three dimensional growth, it becomes 1.0 and 1.5 respectively. J.Grebowicz et al[8] found similar values for n while working with PTFE. Jonsson et al[9] reported that the process of crystallization follows the Arrhenius equation with an activation energy value of about 400-800 KJ mole^{-1}. The transition entropies and enthalpies of the copolymers were found to be surprisingly low as reported by S.Z.D.Cheng[7]. If the crystallization rate is high enough one may expect only nucleation (aggregation) as the rate determining step and the value of n must be close to 2 as previously reported by Warner and coworkers [10]. The lower values of n, less than or close to 1 in other systems have been observed by several workers [7, 8, 11, 12].

2. EXPERIMENT

Kinetics of crystallization of liquid crystal polymers have been studied in isothermal condition using Differential Scanning Calorimetry (DSC). A Mettler FP 84 HT hot stage was used for this purpose. 15-20 mg of sample was taken in an aluminium crucible and heated on a hot stage above its melting temperature. The sample was kept there for 5 minutes to avoid prior thermal history. It was then cooled to the predetermined crystallization temperature T_C, obtained in DSC study, and kept there for different time period t_c, ranging from 5−120 minutes. The sample was again heated without further cooling above its melting temperature and corresponding heating traces were recorded. Enthalpy of crystallization was considered to be equal to that of the melting of the crystals formed at that particular crystallization temperature for the particular time period. The experiment was repeated for several times at different crystallization temperatures Tc, few degrees above and below the predetermined crystallization temperature. The instrument was run at 20^0C/min in N_2 atmosphere.

2. RESULT AND DISCUSSION

The crystallization processes are analyzed assuming a nucleation controlled process and by using Avrami equation. The process of nucleation is favored by a large under cooling effect; hence it is not possible in the present discussion to study the kinetics of liquid crystallization process by calorimetric measurement owing to the small under cooling effect. The study mainly deals with the crystallization processes of two thermotropic liquid crystalline polyesters exhibiting smectic order in their mesomorphic state. During crystallization there are at least three hindering effects: translational and rotational movements and nucleation (aggregation) of the molecules. Overall kinetics of the transition most likely results from a combination of the three effects which are largely dependent on crystallization conditions and chemical structure of the counits. Molecular structures of the polyesters under study are presented below,
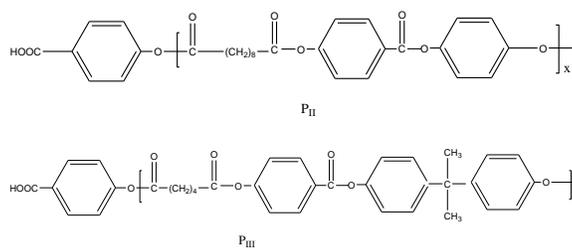
Transition temperatures of polyesters P_{II} and P_{III} were studied by DSC and are presented in Table 1. For the isothermal crystallization study, two temperature regions have been chosen in the mesophase transition region of the polymers. The low temperature region lies below the onset temperature of the mesophase and the other above it. The DSC thermograms for isothermal study did not provide any distinct endotherm due to very low heat of crystallization involved in the structural rearrangement during crystallization because the structure of the solid crystals closely resembles that of the liquid crystals. After isothermal treatment at a fixed crystallization temperature, the polymer is heated above its melting temperature and the corresponding endotherms were considered and the heat of crystallization value(ΔH) were expressed in terms of enthalpy for melting of the same.

The total heat of crystallization values (ΔH) for the polyesters were found to decrease with increasing crystallization temperature over the whole temperature region, although there is a narrow temperature region, for polyester P_{II} between 128^0C−132^0C and for polyester P_{III} between 140^0C−142^0C in which ΔH was found to increase with increasing temperature, as shown in Figure 1 and Figure 2.
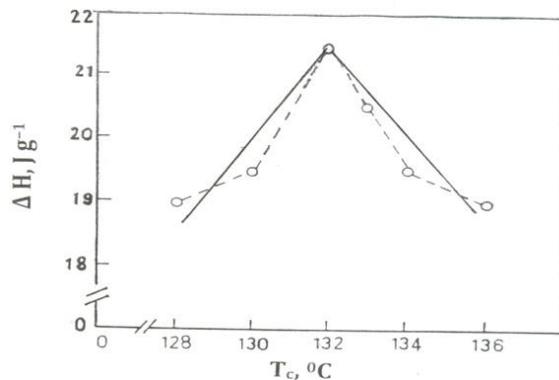
Figure 1

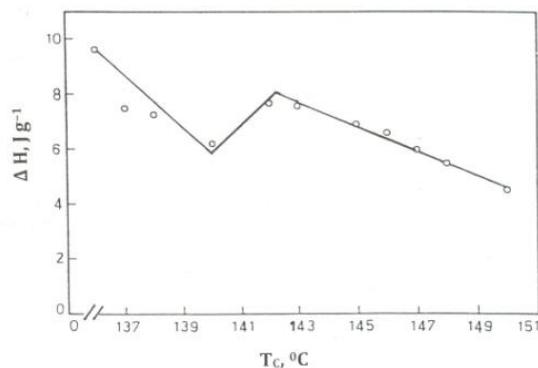Figure1. *Dependence of ΔH on crystallization temperature T_C for polyester P_{II}.*

Figure 2

Figure2. *Dependence of ΔH on crystallization temperature T_C for polyester P_{III}.*

At higher temperature, only a small fraction or the longer chains of the polymers were transformed into crystals and with decreasing temperature, a progressively larger fraction have the thermodynamic potential for transformation into solid crystals. The reason for the increase in ΔH is related to the slower process. At temperature higher than 132^0C for P_{II} and 142^0C for P_{III} the slower process has not been recorded and ΔH value measured was only associated with the rapid process, where as at lower temperature the ΔH values partially or fully include the contribution from the slower process. The rapid process displayed the features of a nucleation process, the rate decreasing with increasing temperature. The slower process displayed temperature dependence opposite to that of the rapid process. The rate was found to increase with increasing temperature. The process thus, can not be controlled by nucleation, but was possibly a rearrangement of the crystals against a higher degree of perfection.

The activation energy values involved in the phase transition processes were evaluated by using the Arrhenius equation,

$$\ln (1/t^*) = \ln A - E_a/RT \qquad (2)$$

The negative slope of the ln (1/t*) Vs 1/T line represents the activation energy value where 1/t* is the time at which the rate of crystallization is at maximum and T is the crystallization temperature. Figure 3 and Figure 4 indicate that the processes follow the Arrhenius equation, with an activation energy of about 750-900 KJ mol^{-1}.
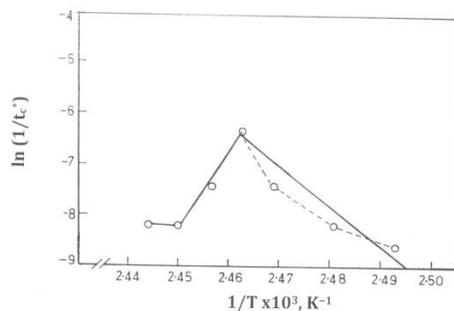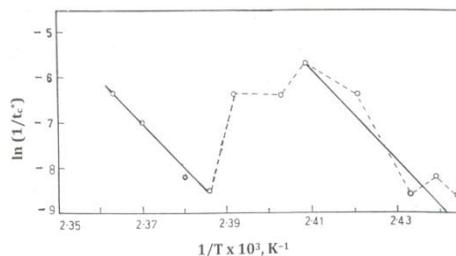
Figure 3. *Determination of activation energy from Arrhenius plot for polyester P_{II}.*

Figure 4. *Determination of activation energy from Arrhenius plot for polyester P_{III}.*

The negative slope of the Arrhenius expression revealed the fact that a major phase change was taking place in this temperature region. It was obtained from the DSC thermogram that the onset of mesophase for P_{II} took place at 134^0C which is well supported by the negative slope the Arrhenius expression and the phase change involved 756 KJ mol^{-1} of activation energy. The Arrhenius expression was satisfied for P_{III} at 136^0C-142^0C and 146^0C-150^0C region. The results obtained from the DSC thermogram are well in accordance with the fact that onset of mesophase occurred at 140^0C and involved 831.43 KJ mol^{-1} activation energy and an inter mesophase transition occurred at 151^0C and involved 886 KJ mol^{-1} of activation energy.

As time progresses the growth of the crystals was affected by the hindering effects due to the previously formed crystals and the Avrami plots do not show linearity after certain time period. For polyester P_{II}, the plots were linear up to around 20 minutes of crystallization for the whole temperature region except at 130^0C. At this particular temperature, linearity of Avrami expression was maintained only for the early period of crystallization for 10 minutes. At this temperature ,the hindrance exerted by the previously formed crystals were effective enough for making the crystal growth rate nonlinear, i.e. independent of time after 10 minutes. It indicated that crystals of polyester P_{II} formed most rapidly at 130^0C, the temperature well below its flow temperature. Above this temperature, (130^0C$<$T$<134^0$C) the molecules were activated to take part in the melting process, which would occur at 134^0C and only few chains would have the potential energy to be transformed into crystals. But at 130^oC, a larger fraction had been transformed into solid crystals and provided the hindering effect towards the crystal growth.
A parallel study was carried out with polyester P_{III}. The Avrami plots were found to obey linearity for the early stage of crystallization .For a period of 30 minutes, the crystallization process followed linear relationship with time over the temperature range under study. The exception was found to occur at 140^0C, at which the linearity was maintained for 10 minutes. In order to analyze the crystallization behavior of a polymer one has to estimate the Avrami parameters K and n. K is a rate constant that includes the temperature dependent terms and contains information regarding diffusion and nucleation rates. n, the Avrami exponent is a constant dependent on the nature of nucleation and geometry of crystal growth process.
Consequently, a plot of double logarithm of the amorphous content as a function of logarithm of time permits the determination of K from the intercept and n from the slope of the straight line. It has been asserted that the Avrami treatment holds good only for an early stage of diffusion controlled growth transformation process for which the growth rate of a new phase is dependent both on temperature and time of crystallization and follows a non-linear crystal growth rate. However, due to lack of sensitivity of double logarithmic plot, the method of estimating K and n

from Avrami plots directly was found not to be highly accurate. A potentially more precise method to determine K and n involves the use of crystallization half life method. The method consists of the determination of the crystallization half time $t_{(1/2)}$, from a graph of amorphous content as a function of time and calculation of the slope s, of the curve at $t = t_{1/2}$. The crystallization half- time method using equation (1) at $t = t_{(1/2)}$ consists of the determination of n and K.

$$n = \ln (\ln 2)/ \ln t_{(1/2)} \qquad (3)$$

$$K = \ln 2 / t^n_{(1/2)} \qquad (4)$$

n is the slope of the curve of amorphous content as a function of logarithm of time at $t = t_{(1/2)}$.
For oriented macromolecules growing longitudinally, the Avrami equation can be satisfied as two dimensional growths if molecules are all parallel. But two sets of low values of n, in the range of 0.2–0.8, for both the polyesters have been observed. A very simplified and possible explanation for the low values of n is that each individual crystal does not grow with constant growth rate. Equation 1 can be rewritten as

$$1 – X_t = \exp (- g N v^n t^n) \qquad (5)$$

v is the radial growth rate, g is a geometrical factor (which is $4\prod/3$ for sphere) and N represents the number of nuclei per unit area. If v is characterized to be a linear rate of crystal growth, equation (5) is equivalent to equation (1) with $K = gNv^n$. However, if v is not a constant radial growth rate, it can be expressed in a form of $v = v_0 t^m$, equation (1) must be cast into

$$\log [- \ln (1 – X_t)] = \log g + \log N + n \log v_0 + n (m +1) \log t = \log K^* + n (m+1) \log t \qquad (6)$$

Where $K^* = gNv_0$ and n (m+1) is called the apparent coefficient. One possible mechanism that alters the linear crystal growth rate is a diffusion controlled transition in which case growth rate would be denoted as $t^{0.5n}$. According to equation (6), the apparent coefficient becomes 0.5n and it would be 0.5, 1.0 and 1.5 for one, two and three dimensional growth respectively. The exponential number in equation (5) is smaller than zero if the radial growth rate slows down with respect to time (m = 0, when v is the linear crystal growth rate). The apparent coefficient in this case, therefore, is always smaller than the dimensionality n expressed in equation (1) for a linear crystal growth rate, lower apparent coefficient may be due to previously formed crystals, therefore reducing molecular mobility. However, it is insufficient to predict the nucleation type and growth mechanism of a crystallization process exclusively from the exponent n, the lower values of n (n < 1) may be attributed to a one dimensional (rod shaped parallel molecules) diffusion controlled crystal growth for both the polyesters.
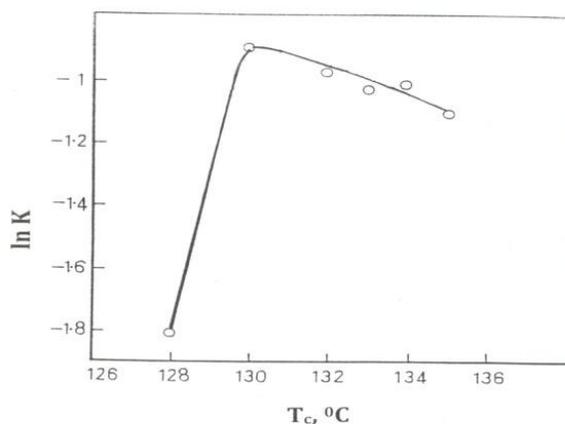In Figures 5 and Figure 6, the logarithm of K is represented as a function of crystallization temperature.

Figure 5

Figure 5. *Determination of the temperature for highest rate of crystallization for polyester P_{II}.*
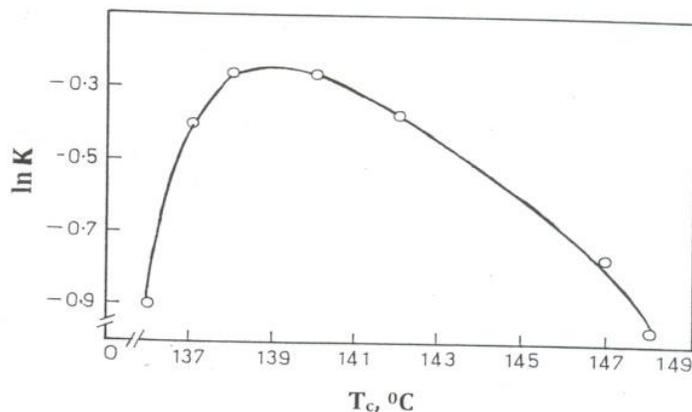
Figure 6

Figure 6. *Determination of the temperature for highest rate of crystallization for polyester P_{III}.*

More or less symmetric shapes with maxima of log K were found. The rate constant maxima for both the polyesters lie below their mesophase transition temperature, i.e. for polyester P_{II} it was found at 130^0C and for polyester P_{III} at 140^0C. It indicated that at those particular temperatures a particular percent crystallinity (in this study it is 50%) was attained in the shortest time. As the crystallization temperature was lowered, the under cooling effect was more pronounced and increased number of nucleating sites was expected to generate, and an increased growth rate of the crystals was favored. But the mobility of the polymer chains decreased as the viscosity of the system increased with reducing temperature. The reduced mobility of the chains resulted in a reduced crystal growth rate. In order to achieve maximum growth rate, an optimization of under cooling effect and chain mobility were required. The rate constant maxima for polyester P_{II} at 130^0C denotes that the particular temperature was favorable for nucleation as it was well below the clearing temperature of the polyester and also provided the necessary chain mobility as well as thermodynamic potential for crystal growth. The fact is true for polyester P_{III} as its rate constant maxima was found at 140^0C which was also suitable for the optimization of under cooling effect and chain mobility. Two sets of curves consisting of the logarithm of $t_{(1/2)}$ as a function of crystallization temperature for polyester P_{II} and P_{III} are shown in Figure7 and Figure 8 respectively.
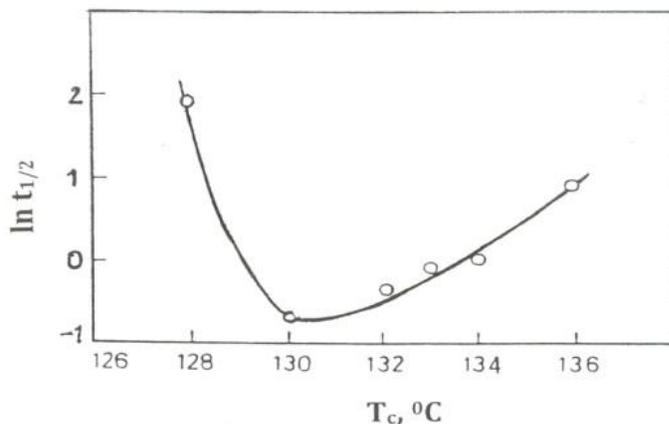

Figure 7

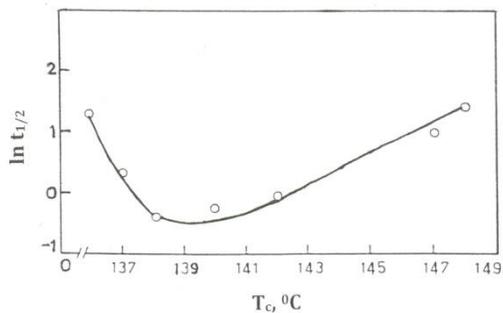Figure 7. *Determination of the temperature for shortest crystallization half time for polyesterP_{II}.*

Figure 8

Figure 8. *Determination of the temperature for shortest crystallization half time for polyester*P_{III}.

Minima of log $t_{(1/2)}$ at T = 130^0C for P_{II} and T = 138^0C for P_{III} were found, indicating that the fastest transition occurred at those particular temperatures and transition slowed down with both decreasing and increasing temperature. Below these temperatures growth rate was hindered by decreased chain mobility and above this by reducing the undercooling effect.

For both the polymers, entropy changes during the transitions can be calculated on the basis of $\Delta S = \Delta H/T$. For polyester P_{II}, $\Delta S = 0.048 \pm 0.005$ J K^{-1} g^{-1} and for polyester P_{III}, $\Delta S = 0.018 \pm 0.005$ J K^{-1} g^{-1}. The mesophase transitions in the present study are thus characterized by very low enthalpy and entropy values compared to $\Delta H = 20 - 50$ KJ Kg^{-1} and $\Delta S = 40 - 100$ J K^1 Kg^{-1} in usual cases[13] .

Calorimetric data regarding the kinetics involving smectic to solid crystal transition of the polyesters are presented in Table 2.

Table 1. Thermal analysis data for polyesters

Sample	Transition temperature,^{0}C (crystal→ mesophase)	Transition temperature,^{0}C (mesophase→ mesophase)	Transition temperature,^{0}C (mesophase→ isotropic)	Glass transition temperature, ^{0}C
P_{II}	134.8	181.7	216.5	115
P_{III}	140.4	150.3	161.6	110

Table 2. Crystallization kinetics data for polyesters

Sample	Crystallization temperature,^{0}C	ΔH, KJ Kg^{-1}	ΔS, J K^{-1} g^{-1}	n	K	$t_{1/2}$, minute
P_{II}	128	−19.0	−0.047	0.37	0.16	7.38
	130	−19.5	−0.048	0.24	0.41	0.47
	132	−21.6	−0.053	0.23	0.37	0.70
	134	−19.5	−0.048	0.14	0.35	1.00
	136	−19.0	−0.046	0.28	0.39	6.00
P_{III}	136	−9.70	−0.024	0.46	0.37	3.66
	138	−7.50	−0.018	0.30	0.77	0.66
	140	−6.13	−0.014	0.57	0.77	0.81
	142	−7.65	−0.018	0.46	0.69	1.00
	148	−5.40	−0.013	0.43	0.38	4.00

4. CONCLUSION

The crystallization kinetics of two liquid crystal copolyesters has been investigated in isothermal condition by a calorimetric study. Avrami exponent, a parameter related to the mechanism of nucleation and crystal growth rate, is found to have a range of values between 0.2 to 0.8.These low values of Avrami exponent suggest a diffusion controlled rod like crystal growth process. The phase transition processes involve activation energy in the range of 700−800 KJ mol^{-1}.The thermodynamic parameters for the phase transition processes have also been calculated which are found to be very low compared to the values in other cases.

5. ACKNOWLEDGEMENT

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