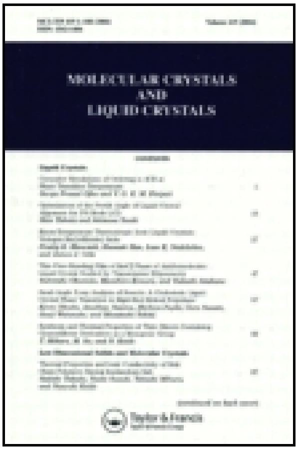

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THERMAL CHARACTERIZATION OF LIQUID CRYSTAL POLYESTERS BASED ON MESOGENIC AROMATIC TRIAD UNITS[†]

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Abstract The isothermal crystallization and melting processes have been investigated in liquid crystal polyesters based on mesogenic bis(4-carboxyphenyl) terephthalate units and flexible alkylene spacers. The kinetic and thermodynamic parameters for the nucleation and growth of crystals from the smectic phase are presented and discussed with reference to the polymer chain structure.

INTRODUCTION

It has been shown that the nature and the stability of liquid crystalline mesophases in polymers specifically depend on the chemical and chain structure of the anisotropic groups as well as of the flexible segments present in the repeating unit.[1-3] The study of the crystallization kinetics from the mesophase and from the isotropic melt can provide information on the process of formation and growth of crystals with reference to the type and degree of order existing in the

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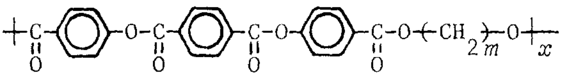
fluid phase. However, only a few studies on these topics have been published.[4,5]

In the present work, attention was focused on the morphological and thermal properties of liquid crystalline thermotropic polyesters containing bis(4-carboxyphenyl) terephthalate (HTH) units (rigid segment) and glycol residues (soft segment) of different length ($m = 3$, 10).



The isothermal crystallization and melting processes have been investigated in order to study nucleation and growth of crystals from the mesomorphic state, and then to correlate the variation of corresponding kinetic and thermodynamic parameters with polymer chain structure.

EXPERIMENTAL PART

Polymer samples HTH-3 ($m = 3$) and HTH-10 ($m = 10$) were prepared as described elsewhere[2] and have intrinsic viscosity values in the range 0.1-0.2 dl/g. Original samples were obtained as powders by precipitation from solution.

Polymer structure and morphology were analyzed under various thermal conditions by means of a X-ray diffractometer (Phillips 1010/25) and by an optical polarizing microscope (Reichert) equipped with a hot stage (Mettler).

The isothermal crystallization kinetics from the mesophase were studied using a differential scanning calorimeter (Perkin-Elmer DSC2).[6] After heating to the smectic phase (525 K for HTH-3 and 505 K for HTH-10), the samples were rapidly cooled down to the crystallization temperature, T_c. The heat developed during the process was recorded as a function of time and the fraction of polymer crystallized after time t, X_t, was evaluated by the ratio of the corresponding area of the crystallization exotherm to the total area at the end of the heat emission revealed by the calorimeter. Melting temperatures, mesophase transition temperatures, and corresponding heats of crystallization were determined from the maxima and the areas of the DSC curves obtained at heating rates of 10 and 20 °/min, respectively. The crystallinity of the polymers after different thermal treatments was evaluated on the basis of the X-ray diffraction spectra.

RESULTS

Liquid crystalline properties. The various mesophases observed for the two polyesters, with relevant transition temperatures, are reported in Table I. Characteristic fan-shaped and schlieren textures were observed by optical microscopy for polyester HTH-10 and in the mesophase of HTH-3 below 535 K (smectic C type). The relative amounts of the two textures depended on the thermal history of the sample.

TABLE I. Liquid crystalline properties of the investigated polyesters.

Polyester	Spacer *m*	Phase transition temperatures (in K) for original samples
HTH-3	3	$k \xrightarrow{510} s \xrightarrow{538} n \xrightarrow{568} i$
HTH-10	10	$k \xrightarrow{490} s \xrightarrow{533} i$

The X-ray diffraction pattern of the liquid crystal phase of polyester HTH-3 at temperatures higher than 535 K shows two broad halos centered around $2\Theta \simeq 21°$ and $2\Theta \simeq 4.6°$, which are consistent with a nematic structure. The diffraction profile of the liquid crystal phase of polyester HTH-10 shows a strong reflection at $2\Theta = 2.94°$ with a spacing $d = 30.12$ Å which corresponds to the length of the polymer repeating unit in the almost extended conformation[7] This finding confirms the existence of a smectic phase for HTH-10.

<u>Isothermal crystallization kinetics.</u> The crystallization processes from the smectic phase of polyesters HTH-3 and HTH-10 were studied in the temperature ranges 487-492 K and 465-476 K, respectively. Examples of crystallization isotherms at various T_c for sample HTH-10 are reported in Fig.1.

In all cases the value of half-time of crystallization, $t_{0.5}$, increases exponentially with T_c. The kinetics of the phase transition were analyzed on the basis of the Avrami equation:

$$1 - X_t = \exp(-K_n t^n) \qquad |1|$$

where K_n is the kinetic constant of the process, and n is a parameter dependent on type of nucleation and crystal growth geometry[8] In Figs.2 and 3 plots of $\log|-\ln(1 - X_t)|$ versus $\log t$ at various T_c are reported for both polyesters examined. The linear trends fit eq. |1| quite well up to high degrees of conversion with $n \simeq 3$-4 for polyester HTH-10 and $n \simeq 2$ for polyester HTH-3. Such values are consistent with a primary crystallization process initiated by athermal nucleation with a three-dimensional growth of the crystal in the

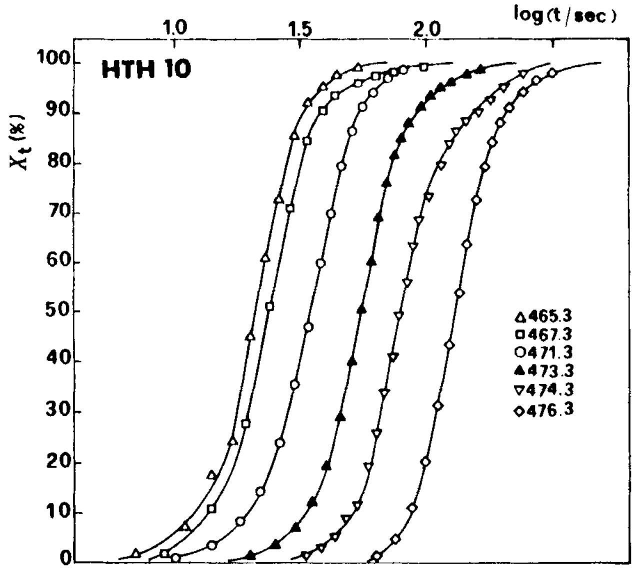


FIGURE 1. Crystallization isotherms from the smectic phase for polyester HTH-10 at various T_c.

case of sample HTH-10, and with a two-dimensional growth in the case of sample HTH-3. For higher values of X_t, n approaches 1, thus indicating the occurrence of secondary crystallization phenomena^8.

Thermodynamics of phase transition. The solid-smectic transition of isothermally crystallized samples exhibits a different behavior for the two polyesters examined. The DSC thermograms of sample HTH-10 crystallized from the mesophase display a double melting endotherm (Fig.4). The melting temperature of the first peak, $T_m(I)$, increases linearly with increasing T_c according to the Hoffmann equation^9:

$$T_m(I) = T_m^o\left(\frac{\gamma - 1}{\gamma}\right) + \frac{T_c}{\gamma} \qquad |2|$$

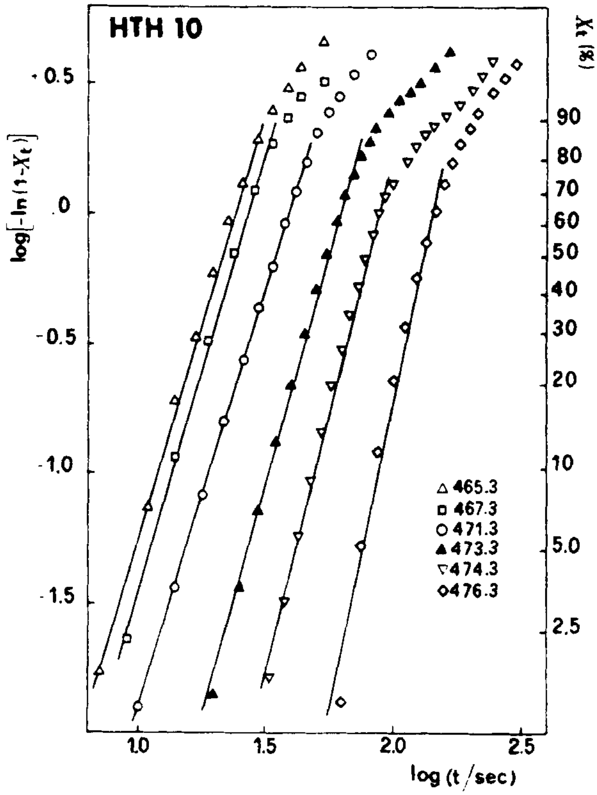


FIGURE 2. Avrami plots for polyester HTH-10 at various T_c.

where γ is the ratio of the average thickness of the crystals (at the end of the crystallization) to the thickness of the initial nuclei, and T_m^o is the equilibrium melting temperature for $T_c = T_m$ (Fig.5).

The melting temperature of the second peak, T_m(II) is independent of T_c and coincides with the value of $T_m^o = 490 \pm 1$ K. The melting area of the first peak increases with T_c, while

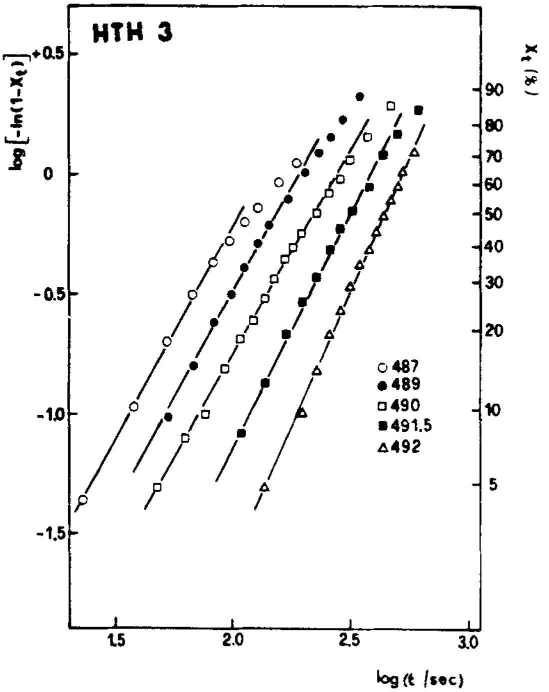


FIGURE 3. Avrami plots for polyester HTH-3 at various T_c.

the area of the second peak decreases, thus suggesting the occurrence of a recrystallization of the molecules during the melting. The total melting enthalpy of the crystalline polymer is $\Delta H_m^o = 14$ cal/g and the isotropization enthalpy is $\Delta H_i = 3.7$ cal/g. In the case of polyester HTH-3 only one broad melting peak is observed. The T_m value does not increase with increasing T_c and extrapolates to $T_m^o = 511.5 \pm 1$ K for $T_c = T_m$.

Analysis of the overall crystallization rates. According to polymer nucleation theories, the variation of the crystalli-

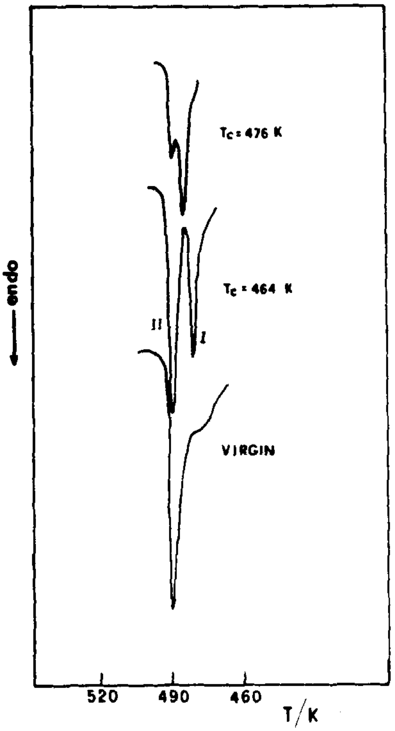


FIGURE 4. DSC melting endotherms of virgin and isothermally crystallized HTH-10 polyester samples.

zation rate (here expressed as the reciprocal of the half-time of crystallization, $t_{0.5}$) with temperature can be correlated with the formation energy of the secondary critical nuclei, $\Delta\Phi^*$, by applying the derived form of the Turnbull-Fischer equation[9]:

$$\log(1/t_{0.5}) = A_o - \frac{\Delta\Phi^*}{2.3kT_c} \qquad |3|$$

where A_o is a term (taken constant to a first approximation)

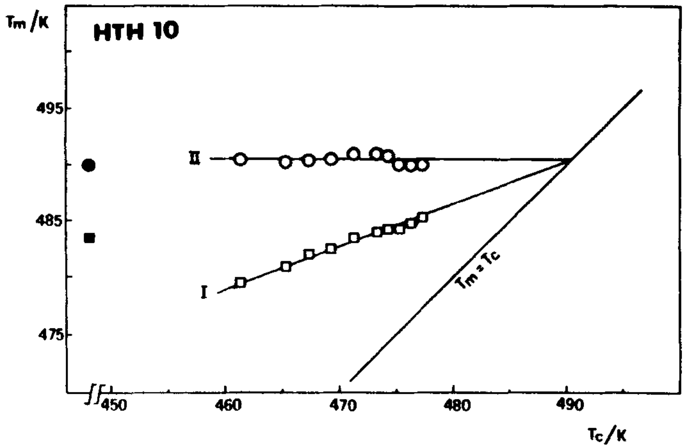


FIGURE 5. Temperatures of DSC melting peaks for polyester HTH-10 versus T_c: ●,■ virgin sample; ○,□ isothermally crystallized samples.

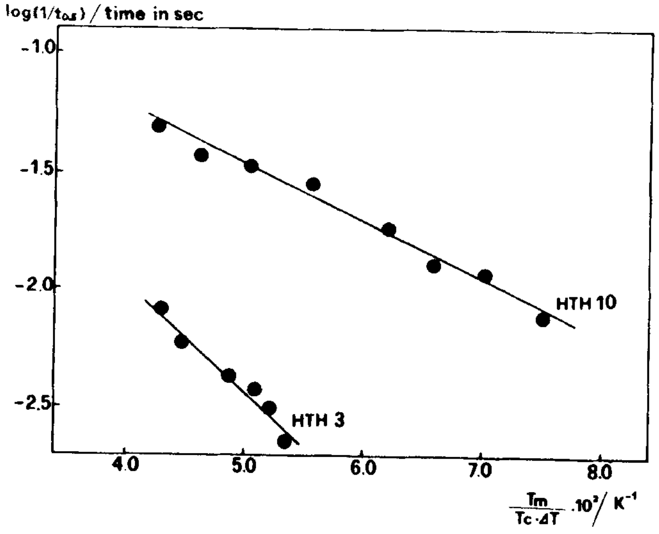


FIGURE 6. Temperature dependence of the reciprocal of half-time of crystallization according to eq.|3|.

including the nucleation density and the diffusion of the macromolecules in the anisotropic melt, and $\Delta\Phi^{*} = (0.4b_o^2\sigma_e T_m^o)/\Delta T$, b_o being the distance between crystallographic planes of growth (4.49 Å from X-ray data), σ_e being the surface free energy of crystals in the direction perpendicular to the chains, and $\Delta T = (T_m^o - T_c)$ being the degree of supercooling. According to eq.|3|, plots of $\log(1/t_{0.5})$ versus $T_m^o/(T_c\Delta T)$ give straight lines (Fig.6) from whose slopes $(0.4b_o^2\sigma_e/2.3k)$ the values of σ_e and $\Delta\Phi^{*}$ were calculated. The surface free energy σ_e was found to be 18 erg/cm^2 for HTH-3 and 10 erg/cm^2 for HTH-10. In Fig.7 the values of $\Delta\Phi^{*}$ for HTH-3 and HTH-10 samples are plotted as functions of temperature in the crystallization range up to the equilibrium melting temperature T_m^o.

CONCLUSIONS

From the reported results it is possible to draw the following conclusions:

i) The kinetics of the smectic-crystal phase transition in the temperature ranges investigated are controlled mainly by athermal nucleation, and the crystal growth geometry changes with varying the length of the flexible segment in the repeating units. Moreover, secondary crystallization phenomena are more pronounced in the case of polyester HTH-10, probably owing to the increased molecular flexibility of this polymer.

ii) The melting behavior is influenced by the chemical structure of the two polymers. The linear increase of T_m $(\gamma \simeq 2)$ observed for polyester HTH-10 with increasing T_c in-

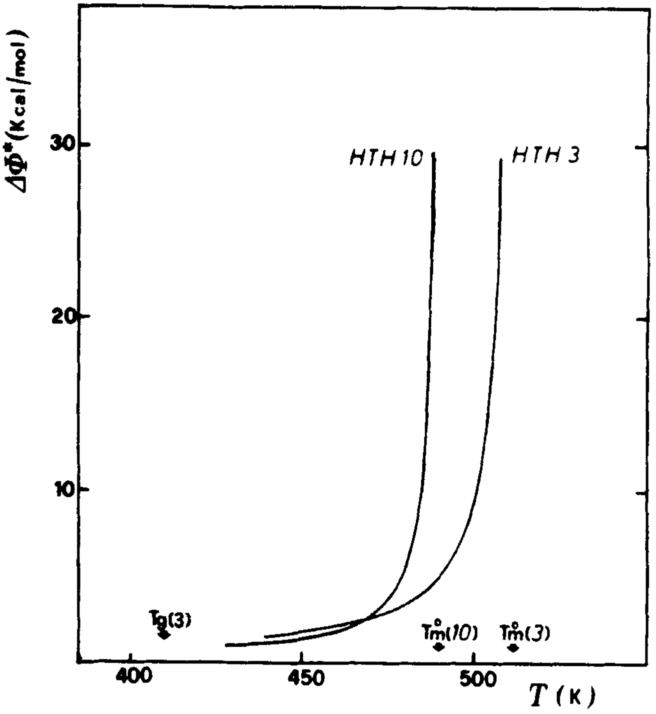


FIGURE 7. Temperature dependence of the crystalline critical nuclei, $\Delta\Phi^*$, with temperature.

dicates that the crystals can thicken during the isothermal crystallization.

iii) The temperature dependence of the crystallization rate can be described on the basis of the nucleation rate theories. The energy of formation of the critical nuclei of crystallization depends on the 'flexibility' of the molecular chains. Accordingly, the higher rate of crystallization observed for polyester HTH-10 can be accounted for mainly by a lower energy of formation of growth nuclei with respect to polyester

HTH-3 at the same degree of supercooling.

REFERENCES

1. V.Petraccone, A.Roviello, A.Sirigu, E.Martuscelli, and M.Pracella, Eur.Polym.J., 16, 261 (1980).
2. C.Ober, J.I.Jin, and R.W.Lenz, Polymer J., 14, 9 (1982).
3. G.Galli, E.Chiellini, C.Ober, and R.W.Lenz, Makromol. Chem., 183, 2693 (1982).
4. J.Grebowicz and B.Wunderlich, J.Polym.Sci., Polym.Phys. Ed., 21, 141 (1983).
5. M.Pracella, S.dePetris, G.Galli, and E.Chiellini, 5th National Meeting of Calorimetry and Thermal Analysis, Trieste (Italy), 1983, Preprints p.217.
6. L.Crispino, E.Martuscelli, and M.Pracella, Makromol.Chem., 181, 1747 (1980).
7. V.Frosini, S.dePetris, G.Galli, E.Chiellini, and R.W. Lenz, Mol.Cryst.Liq.Cryst., 98, 223 (1983).
8. A.Sharples, Introduction to Polymer Crystallization, (Arnold Publisher, London, 1966).
9. J.D.Hoffmann, G.Thomas Davis, and J.I.Lauritzen, in Treatise on Solid State Chemistry, vol.3, edited by N.B. Hannay (Plenum Press, New York, 1976).