Polymer Bulletin 16, 465–472 (1986)

Polymer Bulletin

Kinetics of phase transition of a liquid crystalline polymer

S.K. Bhattacharya[1], A. Misra[1*], R.S. Stein[2], R.W. Lenz[2], and P.E. Hahn[2]

[1]Centre for Material Science and Technology, Indian Institute of Technology, New Delhi 110061, India
[2]Polymer Research Institute, University of Massachusetts, Amherst, MA 01003, USA

Summary

The kinetics of phase transition from the isotropic state to the nematic mesophase of a main-chain, thermotropic liquid crystalline polymer has been studied by DSC and optical microscopy. Avrami-type analysis of the data gives an exponent close to 1.0 which suggests nucleation followed by rod-like growth.

Introduction

The kinetics of phase transitions of liquid crystalline materials has been a matter of interest in recent times. In the case of low molecular weight liquid crystalline materials the transitions from isotropic phase to mesophases (cholesteric, smectic or nematic) and from different mesophases to the solid state have been studied by various workers.[1-8] Price and coworkers have studied the phase transitions of several cholesteryl esters viz. myristate,[1,5] acetate[4] and nonanoate[3] by dilatometry and optical microscopy. They have found the transitions to be nucleation controlled which can be described by an Avrami type equation

$$X_t = 1 - \exp(-Kt^n)$$

where 'X_t' is the fraction of crystalline component, 'K' is a constant and 'n' is the Avrami exponent which depends upon the geometry of growth process. For cholesteryl myristate the values of Avrami exponent corresponding to the transition from smectic to solid, cholesteric to smectic and isotropic to cholesteric were reported to be 4, 2 and 2 respectively, as determined by dilatometry. For cholesteric nonanoate, smectic to solid and isotropic to cholesteric transitions were found to be associated with Avrami exponent $n = 4$ and $n = 1.8$ respectively. Jabarin and Stein[2] have studied the transition of cholesteryl myristate from an isotropic to cholesteric phase by microscopy. They have found that this transition occurs in two steps. The first is a rapid transition to a homeotropic state and the second is a slower one to a more ordered structure. The kinetics of transformation of the later step fit the Avrami equation giving the value of 'n' to be 3. Adamski and Klomczyk studied the transition for cholesteryl pelargonate[6] and caproate[7] from the liquid crystal state to the fully ordered crystalline state. The Avrami exponent was found to be close to 4, as determined by microscopy. The kinetics of transition from liquid crystal to the fully ordered crystal of polymeric liquid crystals have also been studied. Warner and Jaffe[8], with the help of optical microscopy, calorimetry and wide angle x-ray diffraction, have found that this transition in the case of the copolyesters of hydroxybenzoic acid, naphthalene

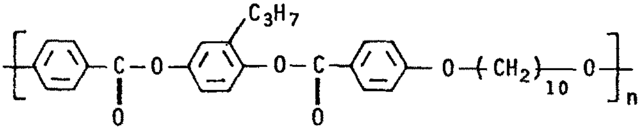
---

[*] To whom all correspondence should be sent

dicarboxylic acid, isophthalic acid and hydroquinone, corresponds to an n value of 2.

In this paper an attempt has been made to determine the kinetics of transition from isotropic to nematic mesophase of a liquid crystalline polymer using differential scanning calorimetry (DSC) as our investigative technique. The nematic mesophase is characterized by lack of long range order of the centers of gravity of the macromolecules, but order exists in the orientation of the mesogenic groups. The average orientation of an unoriented sample, however, is arbitrary in space. In practice this is imposed by minor forces such as the driving effect of the wall of the container, etc. Positive and negative directions are not distinguished.

Material. The polymer under study was the condensation polymer of 1,10-bis(p-chloroformyl benzolyloxy) decane and 2-propyl hydroquinone. The inherent viscosity of the polymer was 0.54 dl/g in tetrachloroethane and M_w was approximately 9000.[9]



Results and Discussion

The thermograms for the polymer in the first and second heating cycles are given in Figures 1 and 2 respectively. Both the heating and cooling rates were 10°C/min. The endotherm between 92° and 100°C (365.15° and 373.15°K) has been identified as the melting transition, and the one at 106.5°C (379.65°K) as the isotropization temperature. It is very interesting to note that, in both the cycles, during cooling there is only one exotherm instead of two, as is expected for a liquid crystalline material showing only the nematic mesophase. Moreover, no supercooling was observed. Even while cooling at 2°C/min from isotropic melt only one exotherm and no supercooling was observed. It is likely that a nematic glass is formed and that the exotherm observed at approximately 60°C (333.15°K) is due to crystallization of the nematic glass above T_g.

Polarizing microscopy studies were carried out with films of the polymer cast from a 5% solution in chloroform. The film was heated in a hot stage up to 120°C under a polarizing microscope (with crossed polars), kept at that temperature for 10 minutes for temperature equilibration and then cooled at a rate of 1°C/min.

Anisotropy was first observed at 109°C in the form of specks of light in the dark field of vision. At 105°C the texture formation was complete and the same texture remained when the film was finally cooled to room temperature. Isothermal phase transition of the polymer was also studied under the polarizing microscope by quenching a film of the polymer from 120° to 108°C and following the transition optically under the microscope. The results of this are presented in Figures 3 and 4.

The process of the development of an anisotropic texture from an isotropic melt is clearly time dependent in a manner similar to crystallization behavior of crystalline polymers. At temperatures below 108°C it develops almost instantaneously. But once the anisotropic texture develops, it does not change significantly either with temperature or time. It is interesting to note that the same texture which develops in the so-called mesophase on cooling is also retained in the solid state. This observation coupled with DSC thermograms suggest that, in fact, there was

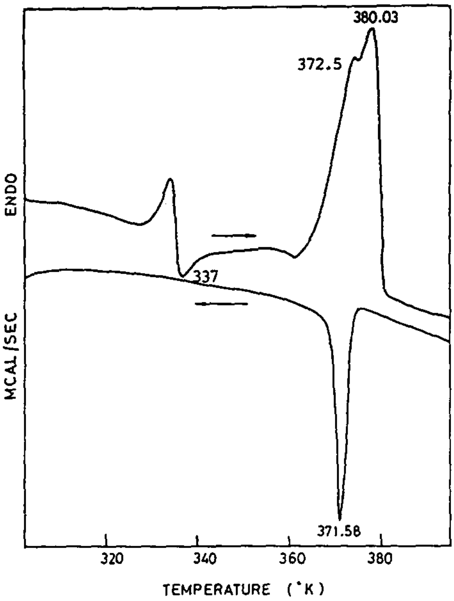


Figure 1. Thermograms of the polymer under study during the first heating cycle.

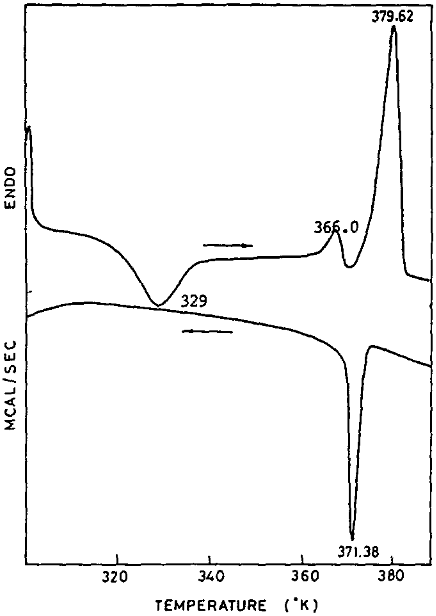
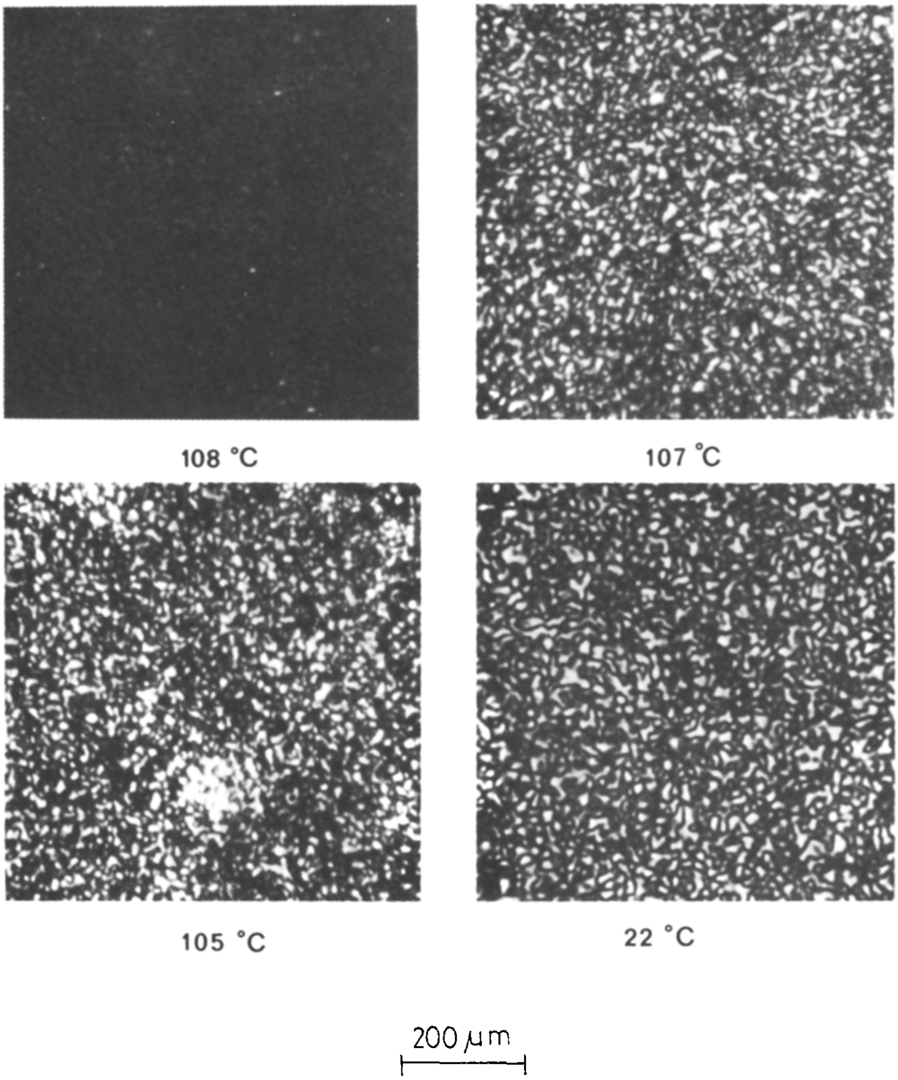


Figure 2. Thermograms of the polymer under study during the second heating cycle.



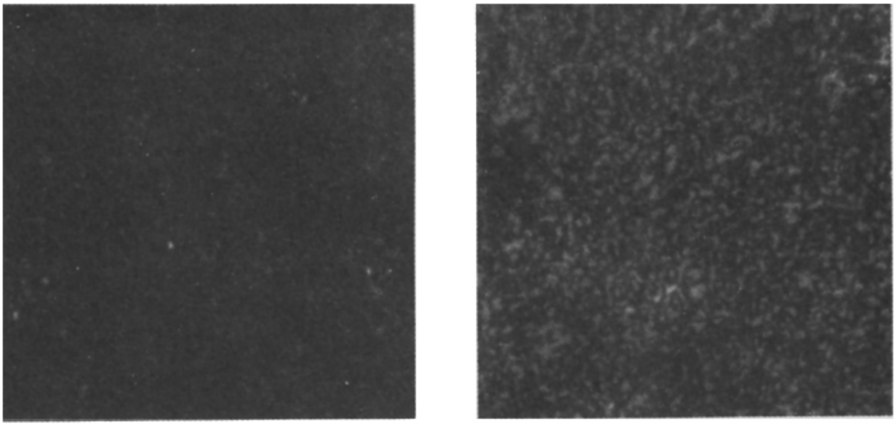
108 °C

107 °C

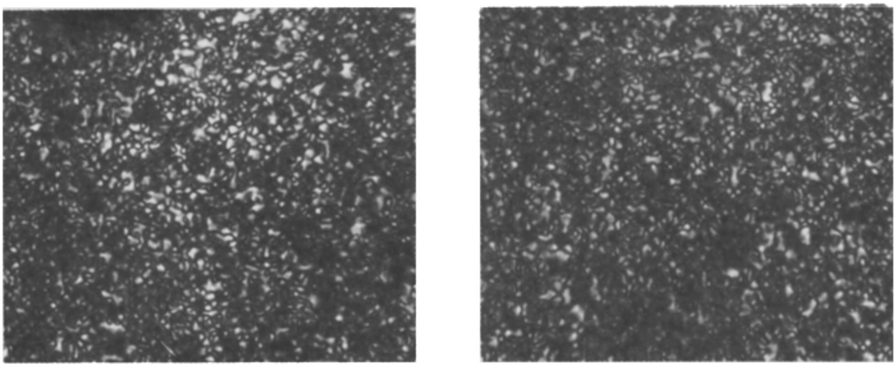
105 °C

22 °C

Figure 3. Photomicrographs of the textures of the polymer sample under crossed polars, when cooled from melt at 120°C with a cooling rate of 10°C/min.



0 minute 15 minutes



30 minutes 60 minutes

200 μm

Figure 4. Photomicrographs of the textures of the polymer sample at various times, when cooled from melt at 120°C to 108°C.

only one phase transition when the isotropic polymer was cooled from melt. Moreover, the heavily-threaded texture that was observed under polarizing microscope is a typical nematic texture. These observations suggest that the material formed a frozen nematic phase on cooling from isotropic melt.

The phase kinetics experiments were carried out with the polymer using DSC (Perkin-Elmer). In these experiments the polymer was heated to 142°C (415°K) in DSC, kept at that temperature for 10 minutes and then quenched to various temperatures, namely, 105°C, 107°C, 109°C and 110°C to follow the thermal changes at these temperatures. The change in the heat involved during isothermal phase transitions at each temperature was plotted as a function of time (Figure 5). It may be noted that these heat changes were very small in magnitude. It was observed that the amount of heat change involved and time required to achieve a 100% phase transition decreases as the temperature approaches nematic-isotropic transition temperature. This is interesting but not obvious. In addition to the amount of material convertible to the mesophase at a given temperature and time, the amount of material ultimately convertible and the order parameter are strongly dependent upon temperature in this two phase region of the isotropization transition. At temperatures below 105°C, the initial heat change occurs very rapidly so it is difficult to measure it completely by DSC. For each chosen temperature the fraction conversion (X_t) was calculated as a function of time using the following equations:

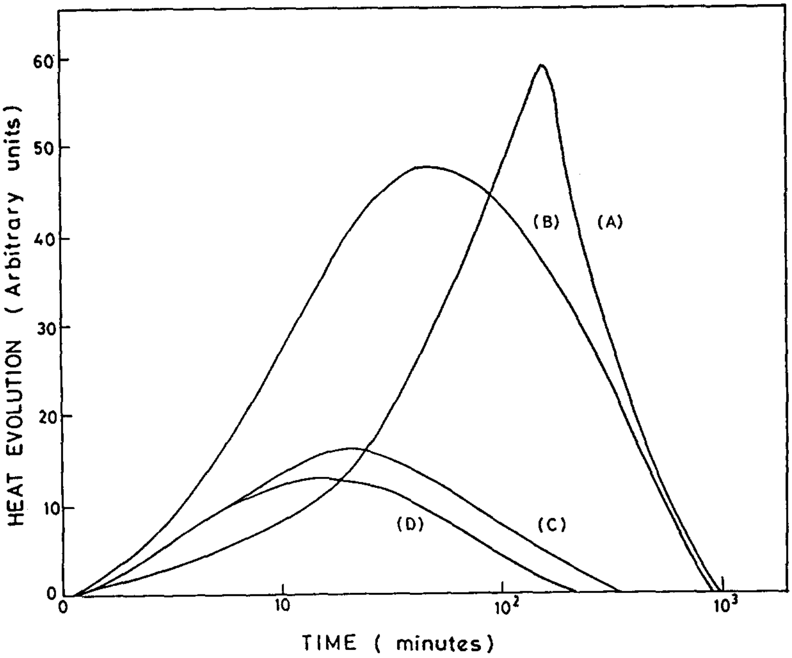


Figure 5. Isothermal phase transition of the polymer sample at:
A) 105°C, B) 107°C, C) 109°C and D) 110°C.

$$X_t = \frac{\text{amount converted at time t and temp T}}{\text{amount converted at infinite time and temp T}} = \int_0^t \left(\frac{dH_t}{dt}\right) dt \bigg/ \int_0^\infty \left(\frac{dH_t}{dt}\right) dt$$

The X_t values were plotted against log time for various temperatures (Figure 6). The Avrami plots were constructed in which log $[-\ln(1-X_t)]$ was plotted against log t (Figure 7). The values of the Avrami exponent 'n' calculated as the slope of the straight lines were 0.68, 0.75 and 0.85 at 105°C, 107°C and 109°C respectively.

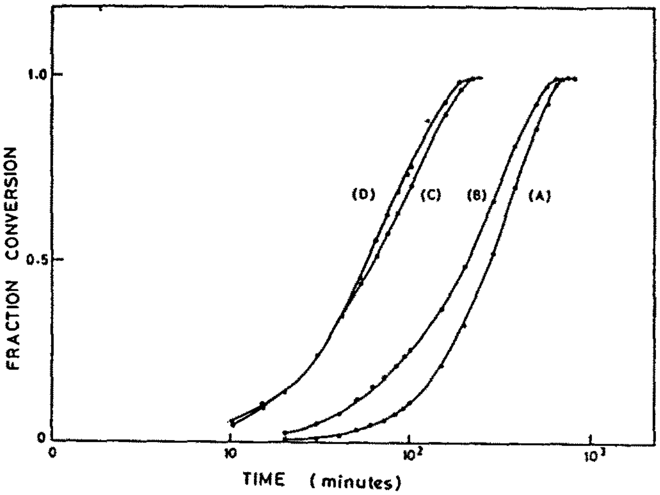


Figure 7. Avrami plot for isothermal phase transition of the polymer polymer sample at: A) 105°C, B) 107°C, C) 109°C and D) 110°C.

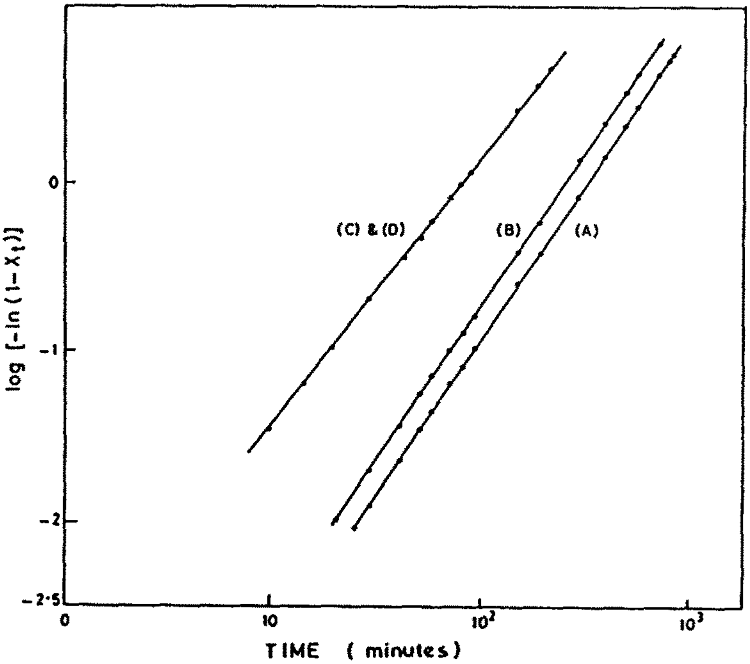


Figure 6. Fraction conversion versus time plot for isothermal phase transition of the polymer sample at: A) 105°C, B) 107°C, C) 109°C and D) 110°C.

Conclusion

On cooling from isotropic melt the polymer transforms to a frozen nematic state which has only one dimensional order; therefore, the value of the Avrami exponent $n \approx 1$ seems to be justified because it signifies instantaneous nucleation with rod-like growth.[10] Similar values of 'n' have been reported by other authors for non-mesophase systems.[11]

We have demonstrated that the process of ordering in the liquid crystalline state is time dependent for the case of a polymer which forms a frozen nematic phase while cooled from isotropic melt. This phenomena is somewhat similar to crystallization process in semicrystalline polymers. So, by analogy, it may be termed as "liquid crystallization". The degree of order in the time period will be different and, hence, we may call it as the "degree of liquid crystallinity" in this case. It is quite probable that many liquid crystalline polymers behave in a similar manner when cooled from the isotropic melt to a temperature above the melting temperature but below isotropization temperature which are yet to be explored. The intermolecular forces of attraction, molecular packing characteristics and molecular weight are expected to affect this type of behavior. This behavior may, in turn, have a very significant effect on the crystallization behavior of liquid crystalline polymers below their melting temperatures.

Acknowledgment

The authors gratefully acknowledge the financial support for this project by the National Science Foundation (USA) as part of an India-U.S. cooperative research program.

References

1. F.P. Price and J.H. Wendorff, J. Phys. Chem., 75, 2839 (1981).
2. S.A. Jabarin and R.S. Stein, J. Phys. Chem., 77, 409 (1973).
3. F.P. Price and J.H. Wendorff, J. Phys. Chem., 76, 276 (1972).
4. F.P. Price and J.H. Wendorff, J. Phys. Chem., 75, 2849 (1971).
5. F.P. Price and A.K. Fritzsche, J. Phys. Chem., 77, 396 (1973).
6. P. Adamski and S. Klomczyk, Sov. Phys. Crystallogr., 23, 82 (1978).
7. P. Adamski and R. Czyzewski, Sov. Phys. Crystallogr., 23, 725 (1978).
8. S.B. Warner and M. Jaffe, J. Crystal Growth, 48, 184 (1980).
9. Q.F. Zhou and R.W. Lenz, J. Poly. Sci., Polym. Chem. Ed., 21, 3313 (1983).
10. J. Schultz, Polymer Materials Science, p. 385, Prentice Hall, Inc., New Jersey, 1974.
11. Y. Mitsubishi and M. Ikada, J. Poly. Sci, Part A-2, 4, 283 (1966).

Accepted September 29, 1986 *K*