Polymer Bulletin 37, 497–501 (1996)

Polymer Bulletin

Thermotropic polyester: The influence of the spacer on physical properties. II

Júlia C. A. Martins, Kátia M. Novack, Ailton S. Gomes*

Instituto de Macromoléculas Professora Eloisa Mano (IMA), Universidade Federal
do Rio de Janeiro (UFRJ), P.O. Box 68525, 21945-970 Rio de Janeiro, JR, Brazil

Received: 9 April 1996/Revised version: 10 June 1996/Accepted: 13 June 1996

ABSTRACT

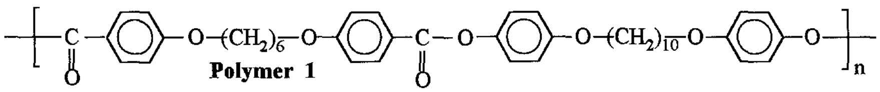
The thermal transitions of liquid crystalline polyesters have been studied by differential scanning calorimetry and thermooptical microscopy. The physical properties of these thermotropic polyesters, particularly the glass transition and the crystallization temperatures have been investigated. The influence of the spacer type on the transitions has been considered. A glass transition at 64 °C was observed of the polyester with oxyethylenic group as flexible spacer while a glass transition could not be observed of the polyester with methylenic groups.

INTRODUCTION

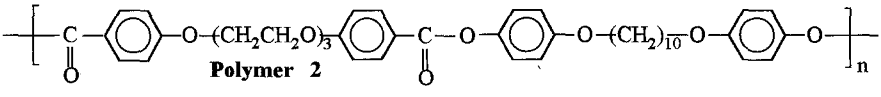
Thermotropic liquid-crystal polyesters which consist of rigid or semi-rigid rod like units have been reported to be second-generation plastics. Thermotropic polyesters are usually rigid along the axes of the backbone and mostly prepared from symmetric monomers, e. g., terephthalic acid and hydroquinone (1-4).

The relation between structure and property in thermotropic polyesters have been gradually clarified. The investigation of the crystallization behavior of semi-flexible polyesters has recently gained significant interest (1).

The polyesters with oxyethylenic and methylenic group as spacers exhibited liquid-crystal behavior and were capable of forming a nematic mesophase on melting. The chemical structure of thermotropic polyesters is as follows:



Polymer 1



Polymer 2

To evaluate the effect of the spacer type on the thermal transitions and anisotropic characteristics of the polyesters, their crystallization behavior was also studied.

---

* Corresponding author

The main objective of this work was to elucidate the structure-property relationship, especially the influence of the spacer type on the stability range of the thermotropic mesophase and the glass transition. The liquid-crystal behavior of the polyesters will be discussed and compared. Indeed thermotropic polymers offer good opportunities for the formulation of blends of commodity polymers to achieve an upgrading of their properties and extending their areas of application.

EXPERIMENTAL

Polymerization reactions were carried out in diphenyl ether as described in a previous report (5). A polarizing microscope equipped with a hot stage was used for visual observations of the thermotropic behavior and the optical textures of the samples. The powered sample was placed between two cover glasses to form a film and then heated to the melt stage. The morphology of the mesophase was surveyed under crossed polarizers.

Thermal analysis was performed by using a Perkin Elmer DSC-7. Polymer samples weighing about 10mg were used for analysis. The thermograms were obtained at heating and cooling rates of 20°C/min under nitrogen atmosphere. The maximum or the minimum of the endotherm or exotherm was taken as the transition temperature. Enthalpy changes were calculated from the endotherm or exotherm peak areas in the thermogram. The glass transition temperature was taken as the inflection point of that transition.

RESULTS AND DISCUSSION

Some properties of two polyesters prepared by polycondensation in diphenyl ether were shown in a previous report (5). Both polyesters exhibited nematic schlieren texture in the melt between melting and isotropization temperatures by polarized optical microscopy. The nature of the stable mesophase was identified as nematic by textural observations and by the isotropizations enthalpy values was 8,3 and 5,1KJ/mol, respectively, for Polymer 1 and 2, consistent with the low degree of order of the nematic phase (6).

The polyesters are crystalline and present anisotropic phases both on heating and on cooling. The formation of liquid crystalline phases by polyesters is reversible, that is, they exhibit melting upon heating and crystallization upon cooling. The experimental data concerning the thermal characterization of the polyesters are summarized in Tables 1 and 2, and the DSC thermograms of the polyesters are shown in Figure 1.

TABLE 1. Thermal Transitions of the Polymers.

Sample	*Tg* (°C)	*Tm*^{a} (°C)	*Ti*^{a} (°C)	*Tc*^{b} (°C)	*Td*^{b} (°C)
Polymer 1	-^{c}	203	241	179	231
Polymer 2	64^{d}	146,5	175	89,5	170

Tg-glass transition temperature, *Tm*-melting, *Ti*-isotropization, *Tc*-crystallization, *Td*-deisotropization.
a-from DSC, 20°C/min heating rate, second heating run; *b*-from DSC, 20°C/min cooling rate, first cooling run; *c*-could not be determined by DSC; *d*-detected after rapid quenching in liquid nitrogen.

TABLE 2. Thermotropic Properties of the Polymers.

Sample	ΔHm^a *(J/g)*	ΔHi^a *(J/g)*	ΔHc^b *(J/g)*	ΔHd^b *(J/g)*
Polymer 1	11,1	24,4	14,0	29,5
Polymer 2	19,7	14,3	9,5	16,9

a-from DSC, 20°C/min heating rate, second heating run; *b*-from DSC, 20°C/min cooling rate, first cooling run.

Polymer 1 exhibited two distinct endotherms in the first and second heating runs. The lower temperature endotherm is assigned to the solid-to-nematic or melting transition temperature and the higher temperature endotherm to the nematic-to-isotropic transition temperature, as confirmed by observations of samples on a hot stage of a polarizing microscope. This polymer showed, respectively, a supercooling of 24°C and 10°C for both the melting and isotropization phase transition temperatures.

Polymer 2 presented a transition from the solid to the nematic phase accompanied by two other first-order transitions. In this case, the solid-nematic transition corresponds to the peak of the highest transition temperature, the multiple melting phenomenon as resulting from a recrystallization of the polymer chains. The oxyethylenic group as flexible spacer in the backbone of Polymer 2 probably does not allow crystal formation with same size, perfection or stability. Although the sum of the areas under the endotherms was taken as the enthalpy of the solid-nematic transition, the higher temperature endotherm was considered to represent the true temperature of the solid-nematic transition and is listed as such. Supercooling of the nematic-isotropic transition occurs to the extent of 5°C and the solid-nematic transition occurs to the extent of 57°C, under the conditions of DSC analysis.

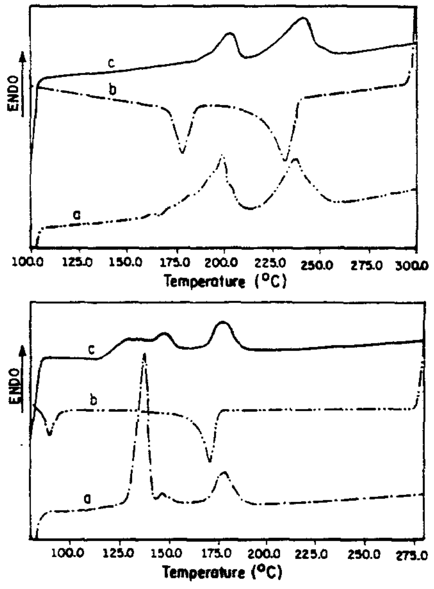


Fig. 1. DSC curves of the polymers.Upper: Polymer 1, lower: Polymer 2. a) first heating run, b) first cooling run, c) second heating run. All runs at 20°C/min.

Transitions of both polymers on cooling from the nematic phase to the solid phase were always at a lower temperature than that for the same transition on heating. Some degree of supercooling or hysteresis on cooling from the isotropic state is inherent in liquid crystalline polymers, possibly due to the great deal of entropy lost in reordering the entanglements of polymers chains (6).

For both polymers the isotropization transitions were relatively sharp and resulted in a biphasic region in which isotropic and anisotropic melts coexisted. On cooling from the isotropic melts, the isotropic-nematic transition always occurred with few degrees of supercooling, whereas the crystallization was rather supercooled because of the complex kinetic control of the nematic-crystal transition.

Polymer 2 showed higher supercooling to crystallization than Polymer 1, which is an indication of the ability to crystallize. Polymer 1 crystallizes faster than Polymer 2. Thus, the polymer with flexible oxyethylenic spacer has more difficulty to recrystallize if it is cooled very fast from the melt to the solid state.

Another DSC thermograms of the polymers are shown in Fig. 2. Polymer 2 presents a glass transition at 64°C, crystalline to nematic transition at 146°C, and a nematic to isotropic transition at 175°C in the second heating cycle after rapid quenching in liquid nitrogen outside the calorimeter. Glassy states were not detected at the maximum cooling rate of the calorimeter. The formation of the glassy-state was only detected by rapid quenching outside the calorimeter. In the third heating cycle a glass transition temperature was not found but endotherms arose in the same positions of the thermogram and with the same enthalpy changes. The absence of the glass transition temperature in the third cooling cycle indicates that this polymer also easily crystallizes from the isotropic state. Only Polymer 2 had a clearly distinguishable glass transition temperature by DSC after quenching in liquid nitrogen and subsequent heating. However, it was not possible to observe the glass transition temperature in this way for Polymer 1, indicating probably a high fraction of three dimensional order for this polymer.

A glass transition is the temperature at which segmental motion starts, i. e., where the chains become able to change their conformations. The glass transition temperature in the isotropic phase depends on the rate of cooling and above this temperature rubber elasticity can be observed and crystallization can take place (7,8). In the case of Polymer 2 the mobility of the chains is frozen in at 64°C where a step in the DSC thermogram is observed.

Polymer 2 presented a glass transition temperature after very rapid quenching, as a consequence of the higher mobility of the oxyethylenic groups in comparision with the methylenic groups. The substitution of a methylenic group by an oxyethylenic one resulted in a decrease in the rigidity of the polymer chain and, therefore, a decrease in crystallinity. Polymer 1 has higher crystallinity than Polymer 2 and, hence, higher melting temperature. Experiments are in progress to study the kinetics of crystallization of polyesters under non-isothermic conditions.

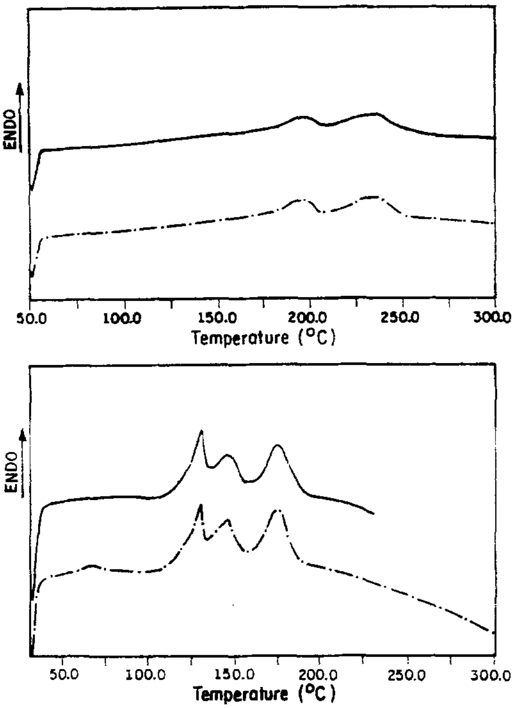


Fig. 2. DSC curves of the polymers.Upper: Polymer 1, lower: Polymer 2. *Traced line*-second heating run after quenching in liquid nitrogen outside of calorimeter; *full line*-third heating run after fast cooling in calorimeter. All runs at 20°C/min.

ACKNOWLEDGEMENT

The authors wish to thanks the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ) and Conselho de Ensino para Graduados e Pesquisa (CEPG/UFRJ) for finantial support.

REFERENCES

1. Liu, S. F. & Lu, Y. -D., *Macromol. Chem. Phys.*, **196**, 629 (1995).
2. Lenz, R. W., *Polym. J.*, **17**, 105 (1985).
3. Ober, C., Jin, J. -I. & Lenz, R. W., *Polym. J.*, **14**, 9 (1982).
4. Braun, D., Lienert, M. & Wilhelm, V., *Die Angew. Makromol. Chem.*, **224**, 191 (1995).
5. Martins, J. C. A., Novack, K. M. & Gomes, A. S., *Polym. Bull.*, to be published.
6. Griffin, A. C. & Havens, S. J., *J. Polym. Sci. Polym. Phys.*, **19**, 951 (1981).
7. Edwards, S. F., *Polym.*, **35**, 3827 (1994).
8. Spies, C. & Zachmann, H. G., *Polym.*, **35**, 3816 (1994).