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Phase transitions of a main-chain thermotropic copolyester: crystallization, melting behaviour and glass-transition studied by DSC

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Summary

The thermal behaviour of a main-chain thermotropic co-polyester has been investigated by Differential Scanning Calorimetry. Crystallization and melting have been studied through the effect of the annealing time and temperature on the transition temperatures and enthalpies. Two melting peaks are observed, the first one clearly developping on annealing. Hypotheses are suggested about the crystallization mechanism. The glass-transition (rate-dependent) appears broadened and does not show hysteresis on heating and cooling through the transition temperature.

Introduction

Para-linked aromatic polyesters tend to exhibit a liquid crystalline melt, usually a nematic one, intermediate between a partially ordered solid and an isotropic fluid state (1-4). In main-chain liquid-crystalline polymers the formation of a mesophase is due to the high anisotropy of the polarizability of rigid components, such as aromatic rings, in the main chain. The most diffuse are aromatic co-polyesters, as the homopolyesters derived from acid terephtalic and hydroquinone or from hydroxybenzoic acid alone cannot be processed due to their high melting point (about 600° C) (5). Instead the introduction of comonomers depresses the melting point, so that liquid-crystalline co-polyesters are favourable. They can be oriented in the molten state and keep their orientation in the solid state, which results in materials having high mechanical and thermal properties. It is, therefore, very important to control their transitions, which play a key role in their processing and use conditions.

Differential Scanning Calorimetry (DSC) is a tool increasingly used to determine phase transitions in thermotropic liquid-crystalline systems, as well as for polymers, in general.

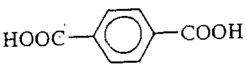
In this paper we report a complete thermal characterization, by DSC, of the thermotropic co-polyester GRANLAR®. The crystallization kinetics and the melting behaviour have been investigated by performing crystallization experiments at variable cooling rates and submitting the samples to thermal annealing in the melting range.

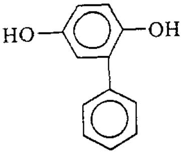
The mechanism of vitrification has also been investigated, through the effect of the dependence of the glass transition on the scanning rate and on thermal histories.

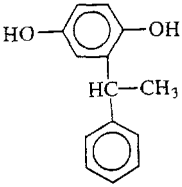
Experimental

Materials

The copolymer used in this study is composed of







with mole ratio 50/25/25, and was supplied by Montedison S.p.A. in form of pellets.

Thermal analysis

Thermal properties were investigated by using a Differential Scanning Calorimeter (DSC 7, Perkin Elmer) equipped with a 1020 Personal Integrator. All runs were performed on 10±0.5 mg samples with nitrogen atmosphere. Before the measurements the samples were taken at 370° C and kept at this temperature for 1 minute. The annealing was performed in the DSC apparatus, in nitrogen atmosphere for times ranging from 1 to 360 minutes. The transition temperatures correspond to the maxima (or the minima) of the peaks and their uncertainty is ±0.3° C. The heats of transition have been evaluated using a standard software of computing the partial areas and their uncertainty is ±0.5 J/g.

In order to investigate the glass-transition the sample was examined in the range from 50 to 200°C, using the following heating rates: 10, 20, 50 and 80°C/min. Thermal histories were carried out cooling the samples from 370° C at the following scanning rates: 5, 10, 20 and 50°C/min and then heating them at rates of 20 and 50°C/min. Glass-transition temperatures, Tg, were taken as the temperatures of half-devitrification of the sample at the given heating rate.

Results and discussion

The DSC curve of the as-supplied sample (Fig. 1) reveals the presence of the glass-transition at about 140°C and an endothermic broad and complex peak at about 328° C corresponding to the melting (solid state - nematic state). The transition to the isotropic phase could not be analyzed because of prior decomposition. The melting curves recorded at different heating rates show the presence of two melting peaks, the lower temperature one strongly developping on increasing the heating rate; correspondingly the higher temperature one is reduced (Fig.2).

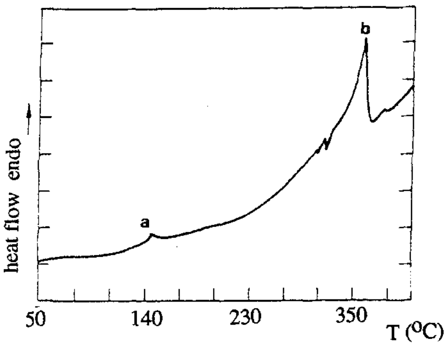


Fig.1. DSC heating curve at 20°C/min for the as-supplied sample. The glass-transition (a) and the solid state-nematic state transition (b) are shown. The heat flow scale is 15 mW.

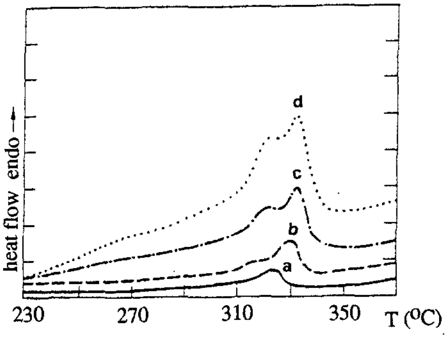


Fig. 2. DSC curves from 230 to 370°C recorded at 10 (a), 20 (b), 50 (c) and 80°C/min (d). The heat flow scale is 30 mW.

On cooling from the nematic state an exothermic peak (crystallization) is observed, whose shape and location strongly depend on the cooling rate; in fact only one peak is present at a cooling rate of 20°C /min while two peaks are present at a cooling rate of 10°C/min and lower. The position of the lower temperature peak is not influenced by the cooling rate, while the higher temperature one slightly decreases on increasing the cooling rate. On reheating at 10°C/min the samples it can be observed that the decrease of the cooling rate causes an increase of the lower-temperature peak (and also its temperature moves towards higher values) at expence of the higher temperature one (Fig.3).

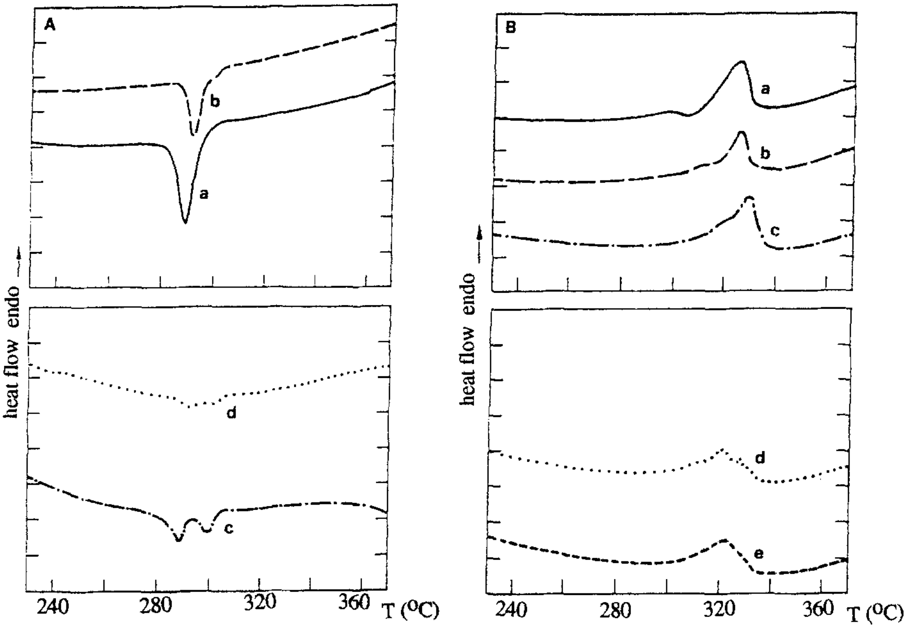


Fig.3. (A) DSC curves recorded on cooling the nematic phase at the following scanning rates: 20 (a), 10 (b), 3(c) and 1.5°C/min (d). The heat flow scale is 20 mW for (a) and (b) and 5 mW for (c) and (d). (B) DSC curves recorded on reheating at 10°C/min the samples cooled at 200 ("quenched") (a) , 20 (b), 10 (c), 3 (d) and 1.5 °C/min (e). The heat flow scale is 10 mW for (a), (b) and (c) and 5 mW for (d) and (e).

In order to better investigate the crystallization process, the samples were submitted to isothermal annealing in the range from 200 to 300° C, for times ranging from 1 to 360 minutes. In Fig.4 the DSC curves recorded on reheating at 10° C/min the annealed samples are reported in the case of T_a=270 and 280°C. Two endothermic peaks are always present, nevertheless the lower temperature one strongly develops on annealing, in fact prolonged and/or higher temperature annealings cause this peak to become more intense and shifted to higher temperatures. In Fig.5 the heat of transition associated to the whole process ΔH_t and the heats of transition associated to the lower and higher temperature peaks, ΔH_1 and ΔH_2 respectively, are reported as a function of the logarithm of the annealing time t_a, for samples annealed at different temperatures. ΔHt and ΔH_1 increase in a non-linear manner, in contrast ΔH_2 tends to decrease. As far as the peak temperatures are concerned it can be noted that T_1 strongly increases as t_a increases, while T_2 is about constant.

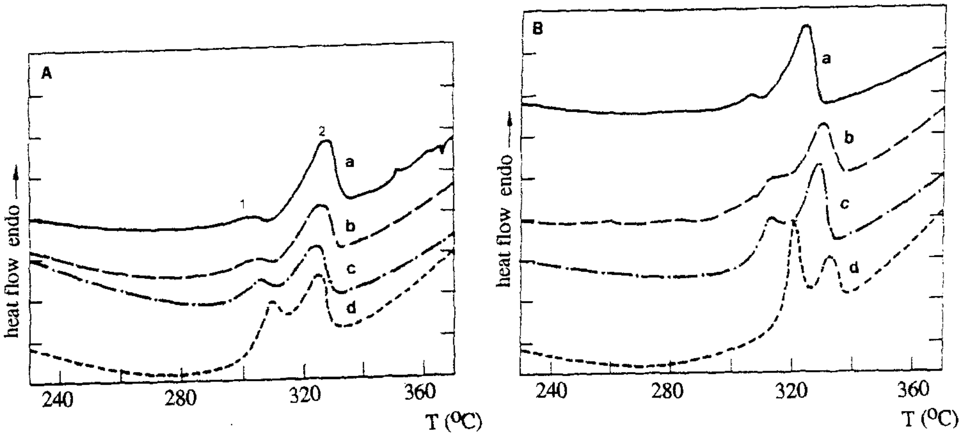
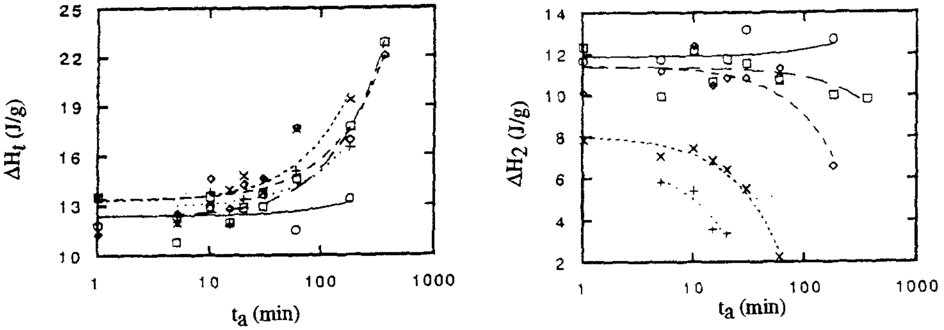


Fig.4. DSC curves recorded on heating at 10°C/min the samples annealed at 270 (A) and 280°C (B) for t_a=1 (a), 30 (b), 60 (c) and 180 (d) minutes.



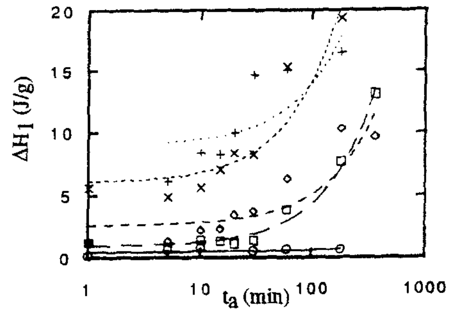


Fig. 5. Total heat of transition ΔH_t, heats of transition associated to peak 1 ΔH_1 and to peak 2 ΔH_2 as a function of the annealing time for annealing temperatures in the range from 200 to 300°C.
(T_a=200°C (○), 270°C (□), 280°C (◇), 290°C (×) and 300°C (+)).

The most important features stemming from the described calorimetric study are the reduction of higher temperature melting peak and the corresponding increase of the lower temperature one occurring : a) on reheating samples cooled at decreasing cooling rates, b) on reheating samples submitted to prolonged annealings and/or to higher temperature annealings, c) on heating samples at increasing scanning rates. All these results may be interpreted on the basis of what occurs for the melting of polyethylene- and polytetramethyleneterephtalate (6), i.e. only the lower temperature melting peak corresponds to the melting of crystals actually present in the sample before the analysis, while the higher temperature melting peak is relative to the melting of more perfect crystals formed during the heating. The observed increase of the lower temperature melting peak and the reduction of the higher one in the previously described conditions may be tentatively explained by admitting that more defectous crystals (i.e. crystals obtained on annealing at lower T_a and/or t_a) during the subsequent heating are able to experience a recrystallization. Instead more perfect crystals (i.e. those obtained at higher T_a and/or t_a) are not able to further perfect during the subsequent heating. In the same way the behaviour observed on reheating samples cooled at decreasing scanning rates and on heating samples at increasing scanning rates can be explained.

As previously observed, the as-supplied sample reveals an increase in the heat capacity at about 140°C, which is likely to correspond to the glass-transition. The glass-transition has been analyzed either as a function of the heating rate or as a function of thermal histories, as described in the experimental section. However, it can be noted that the indications of the glass-transition are vague, due its occurrence in a wide temperature range, in fact ΔT_g (the width of the glass-transition region) is about 20°C, larger than the value normally observed for fully amorphous homopolymers and random copolymers (ΔT_g in the range from 5 to 10°C) (7). As for other thermotropic co-polyesters hysteresis is not observed when the cooling rate is slower than the heating one : this behaviour has been attributed to the partial order present in the nematic glassy state (7-9). In Fig.6 T_g is reported versus the heating rate; as expected a strong dependence on the scanning rate is observed. In Fig. 7 T_g is reported as a function of the cooling rate at fixed heating rates. T_g decreases as the cooling rate decreases as expected for a normal glass-transition.

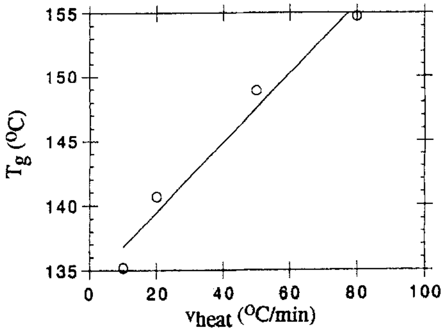


Fig. 6. Location of the glass-transition temperature as a function of the heating rate.

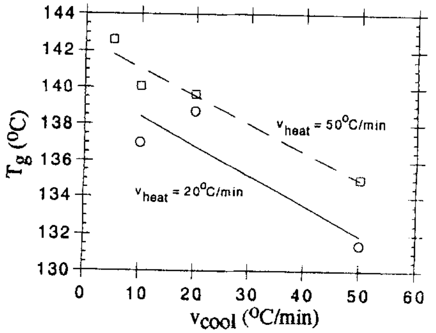


Fig.7. Glass-transition temperature as a function of the cooling rate at the indicated heating rates.

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