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Poly(dithiotriethylene adipate): Melting behavior, crystallization kinetics and morphology

L. Finelli [a], V. Siracusa [b], N. Lotti [a,*], P. Marchese [a], A. Munari [a]

[a] *Dipartimento di Chimica Applicata e Scienza dei Materiali, Università di Bologna, Viale Risorgimento 2, 40136 Bologna, Italy*
[b] *Dipartimento di Metodologie Fisiche e Chimiche per l'Ingegneria, Università di Catania, Viale A. Doria 6, 95125 Catania, Italy*

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Abstract

The melting behavior and the crystallization kinetics of poly(dithiotriethylene adipate) (PSSTEA) were investigated by differential scanning calorimetry and hot-stage optical microscopy. The observed multiple endotherms, commonly displayed by polyesters, were influenced by the crystallization temperature (T_c) and ascribed to melting and recrystallization processes. Linear and nonlinear theoretical treatments were applied to estimate the equilibrium melting temperature for PSSTEA, using the corrected values of the melting temperature; the nonlinear estimation yielded a higher value by about 15 °C. Isothermal crystallization kinetics were analyzed according to the Avrami's theory. Values of the Avrami's exponent n close to 3 were obtained, independently of T_c, in agreement with a crystallization process originating from predeterminated nuclei and characterized by three-dimensional spherulitic growth. As a matter of fact, space-filling spherulites were observed by optical microscopy at all T_c's. The rate of crystallization became lower as T_c increased, as usual at low undercooling, the crystallization process being controlled by nucleation.

Keywords: Polyesters; Poly(dithiotriethylene adipate); Melting behavior; Crystallization kinetics; Spherulites

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1. Introduction

Engineering plastics containing sulfur atoms, such as poly(phenylenesulfide), poly(ethersulfone) and poly(sulfone), have been put into practical use, due to their good mechanical properties and excellent resistance to heat and chemicals. In particular, the excellent properties mentioned above were also achieved by introducing sulfur atoms into polyesters, as in the case of copolycondensation of bis(4,4′-hydroxyphenyl)sulfide (TDP)/bisphenol-A and adipoyl dichloride (APC), by means of which the brittleness of the homopolymer between TDP and APC was greatly reduced [1]. In this view, the incorporation of sulfur atoms into polymers is expected to result in improved properties, including those cited above. Consequently, recently, the number of studies on linear polymers containing sulfur atoms has been increasing.

Owing to the renewed attention devoted to sulfur-containing polyesters, we recently synthesized a series of new polythioesters by direct melt polymerization, starting from aliphatic or aromatic dimethyl ester of dicarboxylic acids and aliphatic thioglycols [2,3]. All

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[*] Corresponding author. Tel.: +39 051 2093215; fax: +39 051 2093220.

E-mail address: nadia.lotti@mail.ing.unibo.it (N. Lotti).

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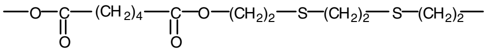
the polyesters synthesized were carefully characterized in terms of molecular structure and thermal and mechanical properties with the purpose of evaluating structure–properties relationships [2,3]. In addition, the melting behavior, the crystallization kinetics and the crystal structure of some of these thiopolyesters were investigated to clarify the origin of the observed multiple melting peaks and obtain information on the specific mechanism of the crystallization process, crucial parameter to optimize their process conditions [4,5]. As, up to now no work has been published in the literature on these relevant arguments with respect to poly(dithiotriethylene adipate) (PSSTEA), in the present paper, we focused our attention on this thiopolyester.

2. Experimental

2.1. Materials

Poly(dithiotriethylene adipate) (PSSTEA) was synthesized according to the well-known two-stage polycondensation procedure, as previously reported [3], starting from dimethyl adipate and dithiotriethylene glycol, with titanium tetrabutoxide ($Ti(OBu)_4$) as catalyst. The monomeric unit can be represented as follows:



$-\mathrm{O}-\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}-(\mathrm{CH_2})_4-\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}-\mathrm{O}-(\mathrm{CH_2})_2-\mathrm{S}-(\mathrm{CH_2})_2-\mathrm{S}-(\mathrm{CH_2})_2-$

SSTEA

The polymer was previously characterized by some of us from the molecular and thermal point of view [3]. The chemical structure was confirmed by means of ^{1}H NMR, and the number molecular weight, determined by GPC, turned out to be about 13,900 ($M_w/M_n = 2.0$). At room temperature the polymer appeared as a semicrystalline solid: the calorimetric trace, obtained after rapid cooling from the melt, showed an intense glass transition ($T_g = -52$ °C and $\Delta c_p = 0.559$ J/g °C), followed by an exothermal "cold crystallization" peak ($T_c = -24$ °C, $\Delta H_c = 47$ J/g) and a melting endotherm at higher temperature ($T_m = 83$ °C, $\Delta H_m = 56$ J/g). The enthalpy associated with the crystallization phenomenon is lower than that of the fusion endotherm, indicating that this polyester cannot be frozen into a completely amorphous state by quenching. Nevertheless, a portion of the amorphous material, once T_g is exceeded, acquires enough mobility to rearrange and crystallize.

2.2. Calorimetric measurements

The isothermal crystallization behavior of PSSTEA was investigated with a Perkin–Elmer DSC7 calorimeter. The external block temperature control was set at −60 °C. All the measurements were carried out under a nitrogen atmosphere to minimize the oxidative degradation. The instrument was calibrated with high-purity standards (indium and cyclohexane) for melting temperature and heat of fusion. Heating rates of 5, 10, 20 and 40 °C/min were used whenever needed. Relatively small size samples (ca. 5 mg) were used to minimize the effect of the thermal conductivity of the polymer; a fresh specimen was used for each run.

To erase the previous thermal history, the samples were heated up to 135 °C, held there for 3 min, and then rapidly cooled by liquid nitrogen to the predeterminated crystallization temperature T_c. The T_c range was chosen in order to avoid crystallization on the cooling step and to obtain crystallization times no longer than 60 min. The heat flow evolving during the isothermal crystallization was recorded as a function of time and the completion of the crystallization process was detected by the leveling of the DSC trace. For a better definition of the starting time (t_{start}), for each isothermal scan a blank run was also performed with the same sample at a temperature above the maximum of melting endotherm at which no phase change occurred [6]. The blank run was subtracted from the isothermal crystallization scan and the start of the process was taken as the intersection of the extrapolated baseline and the resulting exothermal curve. The isothermally crystallized samples were then heated directly from T_c up to melting at 10 °C/min. The melting temperature (T_m) was taken as the peak value of the endothermic phenomenon of the DSC curve.

The melting enthalpy of samples with different crystallinity degree was measured with the aim of obtaining information about the possible presence of a crystal-amorphous interphase. To obtain samples characterized by a different crystal/amorphous ratio, the polymer was heated above the corresponding melting temperature, quenched outside the calorimeter by immersion in liquid nitrogen with different speed of transfer, below the glass transition temperature and reheated at 20 °C/min. The specific heat increment Δc_p, associated with the glass transition of the amorphous phase, was calculated from the vertical distance between the two extrapolated baselines at the glass transition temperature. The heat of fusion of the crystal phase developed in spite of the melt quenching was approximately calculated from the difference between the enthalpy associated with the melting endotherm and the cold-crystallization exotherm.

2.3. Optical crystallization measurements

The isothermal rate of crystallization was measured through the observation of the spherulitic radial growth with a Zeiss Axioscop 2 optical polarizing microscope, equipped with a Linkam TMS94 hot stage and a Linkam LNP cooling system. Isothermal crystallization measurements were performed on a small fragment of