Dielectric relaxation of poly (trimethylene terephthalate) in a broad range of crystallinity

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ABSTRACT

Here we present dielectric relaxation experiments carried out in semicrystalline poly (trimethylene terephthalate) (PTT) samples covering a broad range of crystallinity values. Special attention has been devoted to characterize the two extremes of low and high crystallinity. In particular a high temperature relaxation in the dielectric spectra of highly crystalline PTT, attributed to a Maxwell–Wagner–Sillars process, has been revealed. Moreover, the existence of ordering phenomena during the induction period prior to crystallization has been characterized by dielectric spectroscopy.

1. Introduction

Poly (trimethylene terephthalate) (PTT) is a linear aromatic polymer [1] which belongs to the family of the terephthalic acid containing polyesters like poly(ethylene terephthalate) (PET), poly (butylene terephthalate) (PBT) and their related copolymers [1–3]. Recently PTT has attracted industrial interest mainly for two reasons. On one hand, PTT combines the properties of PET and the processing characteristics of PBT. On the other hand, a new and economically attractive synthesis route has been developed [4]. The outstanding mechanical and optical properties of PTT make it a suitable material for the fiber industry as well as for optoelectronic and nanophotonic applications [5–7]. The longer aliphatic moiety of the PTT monomer makes it less rigid as compared to PET and lowers its glass transition temperature to a value of $T_g \approx 44\,^\circ$C. The relaxation behavior of PTT is characterized by the appearance of a process, α, associated with the segmental motions arising at temperatures higher than T_g and a subglass relaxation, β, associated to local processes [8,9]. For aromatic polyesters the β relaxation was proposed to be a contribution of the three conformationally flexible bonds of the monomer [3], namely the aromatic ring carbon to ester carbon bond (CA–C), the ester ether oxygen to aliphatic carbon bond (O–C), and the aliphatic carbon–carbon bond (C–C). For PTT, the subglass process consists of a bimodal relaxation, where the high frequency component β_1 is associated with the (O–C) bond and the low frequency component, β_2, with the (CA–C) bond [10]. PTT can crystallize quite homogeneously by thermal treatment in the temperature window defined by its T_g and its melting temperature [9,11]. Most of the physical properties of semicrystalline polymers are mainly determined by its degree of crystallinity, thus influenced by the proportion of crystalline and amorphous phases present in the material [12–15]. This arrangement of different phases has a strong impact on the polymer dynamics since polymer chain segments in the amorphous phase are constrained between the crystalline lamellae and their motions might be hindered [16,17]. Due to these restricted conditions cooperative relaxation processes such as the dielectric α relaxation can be strongly affected [18–21]. As far as semicrystalline PTT is concerned, dielectric relaxation experiments have been restricted to a limited range of crystallinities [8,9] being the limits defined by the early stages of crystallization and by the high crystallinity still unexplored.

In this work a further step toward the understanding of the structure-dynamics relationship in PTT is intended by presenting a dielectric study accomplished in well characterized semicrystalline samples. Special attention has been devoted to characterize the two extremes of low and high crystallinity. In particular a third relaxation in the dielectric spectra of highly crystalline PTT, attributed to the Maxwell–Wagner–Sillars process, has been revealed. In addition, the existence of ordering phenomena during the induction period prior to crystallization has been characterized by dielectric spectroscopy.

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Table 1
Description of the studied PTT samples: crystallization temperature (T_c), crystallinity calculated by WAXS (X_c^{WAXS}), long spacing determined by SAXS (L_B) and thicknesses of the crystalline and amorphous layers, l_c and l_a respectively. Linear degree of crystallinity (X_{cL}). Long spacing corresponding to the position of the first maximum of the correlation function (L_c^M). Long spacing corresponding to twice the position of the first minimum of the correlation function (L_c^m).

Sample	T_c (°C)	X_c^{WAXS}	L_B (nm)	l_c (nm)	l_a (nm)	X_{cL}	L_c^M	L_c^m
0	–	0.00	–	–	–			
1	45	0.15	–	–	–			
2	50	0.18	5.74	2.80	2.80	0.5	5.6	5.2
3	55	0.20	5.59	3.39	2.11	0.61	5.5	5.0
4	150	0.38	6.90	4.00	2.40	0.62	6.4	5.6
5	175	0.40	7.49	4.93	2.37	0.67	7.3	6.2
6	200	0.45	8.33	5.13	2.77	0.65	7.9	7.0

2. Experimental part

PTT samples, synthesized using the polycondensation procedure previously described [22], were melted at 255 °C and pressed for 2 min under 5 bar pressure and 2 min under 15 bar pressure. The samples were subsequently quenched in ice cold water. Films with different degrees of crystallinity were obtained by thermal treatment in vacuum at a given crystallization temperature T_c (Table 1), and quenched in air. After the thermal treatment the films were stored in a refrigeration chamber at 4 °C.

Wide angle X-Ray Scattering (WAXS) experiments were performed by using a Seifert XRD 3000 θ/θ diffractometer with Ni-filtered Cu K_α radiation ($\lambda = 0.154$ nm) at a scanning speed of 0.03 °/s. WAXS diagrams were used to calculate the degree of crystallinity of the different samples. The diagram was considered as a linear combination of the amorphous and crystalline contributions [23], thus the degree of crystallinity, X_c, can be estimated by calculating the ratio between the area under Bragg peaks A_C and the total area under the WAXS curve, $A_c + A_a$, being A_a the area under the amorphous halo:

$$X_c^{WAXS} = \frac{A_c}{A_c + A_a} \tag{1}$$

The SAXS data were analyzed by using the formalism of the correlation function [24,25] in order to estimate the long spacings (L) and the amorphous phase (l_a) and crystal phase (l_c) thicknesses as a function of crystallinity by using the SASDAP software [26,27]. With the latter, all SAXS profiles were analyzed by a calculating the correlation function $\gamma_{1,r}$ defined by:

$$\frac{\gamma_{1,r}}{Q} = \frac{\int_0^\infty (I - I_b)q^2 \cos(qr)\exp\left(\sigma^2 q^2\right)\mathrm{d}q}{\int_0^\infty (I - I_b)q^2 \mathrm{d}q} \tag{2}$$

where $q = (4\pi/\lambda)\sin\theta$ is the scattering vector and 2θ is the scattering angle. I_b represents the contribution to the total scattering intensity due to density fluctuations, also called liquid scattering, and σ is a term related to the thickness of the interface between amorphous and crystalline phases. Q is the scattering power (or scattering invariant) that can be determined by integration of the SAXS profile over all scattering angles:
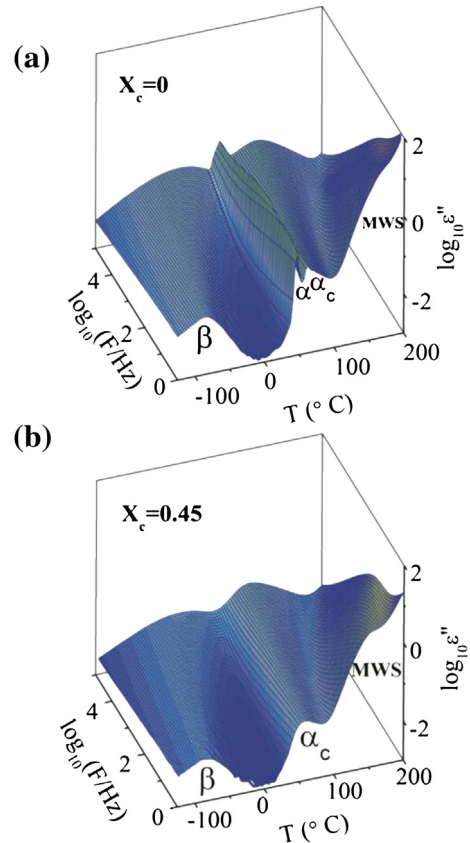
$$Q = \int_0^\infty \left(I - I_b\right)q^2 \mathrm{d}q \tag{3}$$

Fig. 1. Logarithm of the dielectric loss, ε'', as a function of temperature and frequency for (a) initially amorphous PTT and (b) a highly semicrystalline ($X_c = 0.45$) PTT.

By appropriate evaluation of the correlation function it is possible to obtain two correlation distances that can be tentatively assigned to the amorphous and the crystalline phases [21,26,27].

Measurements of the complex dielectric constant ε^* were carried out in a broad frequency range of $10^{-1} < F\,(\mathrm{Hz}) < 10^7$ covering a temperature range of $-150 < T\,(°\mathrm{C}) < 150$ by means of a Novo-control spectrometer integrating an ALPHA dielectric interface and a temperature controlled nitrogen gas jet (QUATRO from Novocontrol) with a temperature error of ± 0.1 °C during every single sweep in frequency. PTT films were sandwiched between the two metallic electrodes of the spectrometer. Due to the low glass temperature of PTT no gold evaporated/sputtered electrodes were used in order to avoid crystallization induced by the deposition. Dielectric data were treated using the Havriliak–Negami formalism for the complex dielectric permittivity [28]:

$$\varepsilon'' = \left(\frac{\sigma}{\varepsilon_0 \omega}\right)^s + \mathrm{Im}\left[\frac{\Delta\varepsilon}{\left[1 + (i\omega\tau_{HN})^b\right]^c}\right] \tag{4}$$

Being $\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty$ the relaxation dielectric strength, ε_0 and ε_∞ the static ($\omega = 0$) and optic ($\omega = \infty$) dielectric constants, τ_{HN} the characteristic relaxation time of the Havriliak–Negami relaxation function, and b and c ($1 \geq b, c > 0$) are shape parameters that describe, respectively, the symmetric and asymmetric broadening of the relaxation time distribution function. The average relaxation time value of the distribution can be calculated as follows [28]:

$$\langle\tau\rangle = \frac{1}{2\pi F_{max}} = \tau_{HN}\left[\sin\frac{b\pi}{2+2c}\right]^{-1/b}\left[\sin\frac{bc\pi}{2+2c}\right]^{1/b} \tag{5}$$