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Multiscale organization of thermoplastic elastomers with varying content of hard segments

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ABSTRACT

Thermoplastic elastomers (TPEs) based on segmented block-copolymers containing poly(-tetrahydrofuran) (pTHF) and terephthalate-based diamide groups (T4T) were synthesized via poly-condensation. While pTHF is known to be flexible and amorphous at rest, the more rigid T4T crystallized in different ways depending on both chain composition and sample preparation conditions. Increasing the content of hard-segments (HS) from 5 to 20% in weight leads to a substantial increase of the melting point T_m by more than 60 °C. We have systematically investigated the multiscale (1 Å - 50 nm) organization of the HSs (of fractions from 5% to 20%) by means of DSC, WAXS and (ultra) small angle X-ray scattering (U)SAXS. By increasing HS content, hence the rigidity of the chain, scattering experiments unambiguously show the formation of bigger and better defined ribbon-like crystallites, as well as the densification of the network they form. We propose a scenario for rationalizing the local T4T-HSs packing and the crystallites anisotropy at the mesoscale (1–10 nm) for HS fraction above 5%. Moreover, following in-situ the crystallization of TPEs with large HS fraction (20%), we highlight the presence of "persistent aggregates" present at $T > T_m$ and study the ribbon-like crystallites growth mechanism during cooling from the melt state.

1. Introduction

The name "thermoplastic elastomer" (TPE) refers to polymeric materials exhibiting a dual rubber/melt rheological behavior as opposed to classic vulcanized rubbers [1,2]. Their high elasticity and flexibility at operating temperature (−50 to 50 °C) reflects thermo-reversible phase separation [1], which gives rise to rubber-like properties without involving chemical crosslinks. This reversibility makes the TPEs good candidates for a more sustainable rubber production (recycling of vulcanized rubber is difficult and marginal [2]), in particular in terms of reshaping and recycling many daily consumer goods. Since the 1960's, a wide variety of industrial relevant TPEs have been synthesized [3]. One of the most popular examples is the PS-PB-PS tri-block copolymer [4] where the segregation of the PS blocks forming rigid subdomains confers rubber-like mechanical properties to the material. While the general phase separation mechanism of these systems is understood, it stays crucial for the industry to be able to control and tailor their properties in order to use them in many different applications. This requires being able to control the transition from their melt to their gel state (and vice versa) in terms of both temperature and mechanical properties. In this direction, rather than letting the (in) compatibility of the two blocks controlling phase separation kinetics and final morphology [5], researchers have developed new generations of TPEs based on supramolecular interactions, which involve new parameters to tailor the properties of such materials. One of the most popular approaches is the synthesis of segmented

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(or multi-block) copolymers with flexible units made of poly(-tetrahydrofuran) (pTHF) (also called poly-tetramethylene oxide, pTMO) linear motifs (soft-segments "SS") and rigid units (hard-segments "HS") based on urea [6], urethanes [7] or amide groups, as thoroughly studied by Gaymans [8]. The latter segmented copolymers are of particular interest due to their ability to generate multiple hydrogen bonds through the amide (i.e. N–H vs. C=O) groups, enhancing the aggregation and/or crystallization of the rigid segments in a similar way as in the well-known polyamides PA6 and PA66 *Nylons* [9]. In this context, several studies have shown the importance of monodisperse HSs which crystallize [8,10] by forming a regular ribbon-like structure (elongated soft objects), providing to the material tunable rheological properties as well as enhanced thermal and chemical stability. Monodisperse HSs also ensure a very fast crystallization upon cooling and a high melting temperature. Furthermore, using short and monodisperse hard segments allows reducing liquid-liquid demixing of the hard and soft segments when reducing temperature, while keeping a high rate of crystallization [11].

So far, a lot of effort has been put on the description of the thermomechanical properties [12], the identification of the crystalline phases [13] as well as the synthesis of new SS/HS motifs [14] with the key result being the systematic raise of both melting point and plateau modulus with increasing the HS content. However, many questions remain about the structure at the mesoscale level (5–100 nm) of the crystalline hard phase, which is a difficult task for semi-crystalline polymers. Nevertheless, this is of central importance for understanding their mechanical and viscoelastic behavior. The most frequently used techniques for determining the structure of such TPEs at the mesoscale level are atomic force microscopy (AFM) [15] and transmission electronic microscopy (TEM) [16] applied on solvent casted films. However, while they reveal interesting structures [6b,16-17], one needs to account for the fact that the observed organization strongly depends on the protocol used to prepare the sample. Indeed, structure in solvent casted films significantly differs from the one of the samples processed by extrusion from the melt state (without solvent), i.e. the ones of interest for studying viscoelastic and mechanical properties as well as for developing possible applications (3D printing, fibers production …). The latter, in fact, seem to be characterized by a more complex organization, in which the crystallites are likely more polydisperse and less aligned, hardly accessible with those techniques [6a].

Small Angle X-ray (or Neutron) Scattering (SAX(N)S) is widely employed [18] but often limited to the observation of the inter-crystallite distance [17] except for the extensive and inspiring work by Sijbrandi et al. [13] which provides a quantitative analysis of the crystal lattice as well as the mesoscale (hexagonal) structure of polyamide based ribbon crystallites. Moreover, the scattering cross section per unit sample volume, or "scattering intensity" $I(q)$, is almost exclusively expressed in arbitrary units (rather than absolute units) limiting *de facto* the structural analysis to the extraction of typical distances in the materials (along the q axis), i.e. ignoring the mass of the scattering objects required to establish a coherent model. Then, because of the very short (yet monodisperse) length of HSs, one cannot use the available molecular theory for similar block-copolymers [19] where phase segregation appears at high values of the Flory-Huggins parameter $(N\chi) \approx (N\chi)_c$ (where $(N\chi)_c$ is the critical value for spinodal decomposition with N the degree of polymerization). Indeed, it does not seem suitable for quick crystallization processes generating phase separation on a micrometer scale.

Going further in the employment of SAXS, one could model ribbon-like objects by using the form factor of semi-flexible chains with self-avoidance calculated by Pedersen et al. [20] This method, which has been successfully used by Hamley et al. [21] for worm-like micelles having a fractal dimension of $D_f \approx 1.7$, allowed the authors to determine directly the contour length, the persistence length and the cross-sectional radius of such elongated structure. However, this model lies on the fact that such objects do not interact with each other, i.e. that their volume fraction must be kept smaller than 1 vol%, far from the type of samples investigated in this work (ca. 5 to 20%v).

Thus, despite the above developments, many questions still need to be addressed in order to understand and control the structure of these TPEs, processed in the melt state. They concern, in particular, (i) the local packing of the T4T units leading to polymorphic crystals, (ii) the crystallites shape and their orientation at the mesoscale being of great interest for the rheology comprehension and (iii) the growth mechanism from the initial state (melt or in solvent). In this context, the key goal is to develop criteria for designing TPE materials with desired performances easily processable at the industrial scale.

The objective of the present work is to combine DSC, WAXS and (U)SAXS techniques in order to investigate the multiscale structure of segmented copolymers with a monodisperse hard-segment made of T4T diamide consisting mainly in two terephthalate "T" groups separated by four "4" carbon atoms [22]. (Other "T-amides" groups are reported in the literature) [23]. In particular, we would like to study the influence of the HS density on the crystallization and melting of such TPEs. The HS is characterized by a high melting (or crystallization) temperature, e.g., close to $T_m = 158$ °C (or $T_c = 136$ °C) [24] for 20%HS in the chains. On the other side, the SS is made of a sequence of 3 and 8.6 pTHF motifs (respectively called $pTHF_{250}$ and $pTHF_{650}$) between which a terephthalate group is intercalated to limit their crystallization (see Fig. 1). Based on these two elementary building blocks, we prepared four different copolymers (following a Flory-type statistic) by adjusting the HS nominal mass fraction to 5, 10, 15 and 20%. The average molar mass of the SSs is varied from 6840 g/mol (5%HS) to 3299 g/mol, (10%HS), 2078 g/mol (15%HS) and 1470 g/mol (20%HS) so that the total molecular weight of the four TPEs remain comparable (see Table 1).

The outline of this article is as follows. After the materials and methods description in section 2, the results are presented and discussed in section 3. DSC thermograms of the four TPEs and the neat pTHF are provided in section 3.1. The analysis of the crystal lattice using WAXS is presented in section 3.2, where new arguments to rationalize the T4T diffractograms are provided. Finally, section 3.3 is devoted to the (U)SAXS experiments in which we propose a method to determine the "micro-" (<10 nm) and "meso-" (10–50 nm) scale structure of the ribbons-like crystallites. In this last part, we also propose a growth mechanism based on time resolved SAXS measurements performed between T_m and T_c.

2. Material and methods

2.1. Materials

1,4-Diaminobutane (DAB), acetone and acetonitrile were obtained from Sigma Aldrich, USA, Dioctyl terephthalate (DOT) from Eastman chemicals, pTHF (650 g/mol and 250 g/mol) from BASF chemicals, Irganox 1330 from Ciba, Switzerland. Sodium ethoxide (21 wt% in ethanol) with Acroseal© from Acros, Belgium. All chemicals were used as received. Sodium ethoxide 21 wt% in ethanol was used to prepare sodium ethyl hexoxide 1 molar solution by replacing ethanol by ethyl hexanol using a distillation setup.

2.2. Synthesis T4T-dioctyl

DAB (30 g, 0.34 mol) and DOT (574 g, 1.46 mol) were introduced