



Confined relaxation dynamics in long range ordered polyesters with comb-like architecture



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ARTICLE INFO

Article history:

Received 29 July 2014

Received in revised form

24 September 2014

Accepted 28 October 2014

Available online 11 November 2014

Keywords:

Comb-like polymers

Glass transition

Dynamic-mechanical measurements

ABSTRACT

The cooperative relaxation dynamics of methylene units in self-assembled amorphous alkyl nanodomains with typical dimensions in the range 5–20 Å is studied in a series of poly(1,4-phenylene-2,5-n-dialkyloxy terephthalate)s (PPAOTs) with $C = 6$ –12 alkyl carbons per side chain. These comb-like polymers are long range ordered on the nanoscale since domains where main chains are stacked in a crystal-like manner alternate with alkyl nanodomains formed by aggregated side chains. Dynamic mechanical data for the investigated PPAOTs show polyethylene-like glass transitions α_{PE} which are similar to those for many other polymer series with comb-like architecture containing long alkyl side groups. Hence, self-assembled PPAOTs are excellent model systems for studies focusing on a detailed understanding of the influence of (i) alkyl nanodomain size, (ii) average volume per CH_2 unit and (iii) number of alkyl groups per interfacial area on the cooperative dynamics of methylene units seen as α_{PE} process. Structural parameters as obtained from X-ray diffraction experiments allow to deduce quantitative information about these influencing factors. The results are compared with those for regio-regular poly(3-alkyl thiophenes) with similar molecular architecture. The comparison shows that important features of the α_{PE} process within amorphous alkyl nanodomains are main chain independent even in case of long-range ordered polymers with quite different main chain packing. It is concluded that the alkyl nanodomain size is the most important factor determining the α_{PE} dynamics of the methylene units. Main chain dependent aspects like average volume per CH_2 unit and interfacial constraints do only weakly influence the relaxation behavior within the alkyl nanodomains.

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1. Introduction

Polymers with comb-like architecture containing long alkyl side chains are of a great interest in various fields of application. They are used as organic semi-conductors in thin-film transistors [1,2], organic photovoltaic cells [3] or light emitting diodes [4] and they are potential candidates for the use as high performance materials with excellent mechanical properties [5]. Alkyl side groups are commonly introduced in order to improve the solubility of functional polymers and act also as covalently bonded plasticizer. Hence, it is important to understand the influence of structural

features of such comb-like polymers on their relaxation dynamics [6]. It has been shown that the long alkyl groups in such polymers tend to aggregate in form of alkyl nanodomains with typical dimensions in the range 5–20 Å. This self-assembling phenomenon is called nanophase separation [7,8] and is found in amorphous and liquid-crystalline polymers with different side chain lengths [9].

Long range ordered comb-like polymers containing disordered alkyl side groups are also excellent model systems to study the confined dynamics in nanodomains with tunable dimensions and well defined interfaces. This touches fundamental questions in the field of glass transition research since there is an ongoing discussion about the influence of domain size [10–14], interactions at interfaces [15–18] and average density effects on the softening behavior of glass forming materials. These topics have been in particular attacked by studies done on glass forming liquids confined in nanoporous host systems like controlled porous glasses

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[10,12,19], self-assembled systems [6,20] and broadly investigated in ultra-thin polymer films [18,21–24]. However, there are still many open questions which are controversially debated although in the recent years there has been some progress with the interpretation of the partly contradicting results [18,22,25]. One of the most fundamental questions of such studies is to what extent simple geometrical confinement on the nanometer scale results in a significant change of the cooperative dynamics. This is related to the question whether or not dynamic heterogeneities [26–29] in glass forming materials exist and which length scale is relevant in this case [30]. A basic limitation of most of the experiments is that interactions at interfaces can influence the situation and small changes in the average density can not be excluded. It is known that both effects are important for the cooperative α dynamics but it is in most of the cases practically impossible to quantify their influence experimentally.

In a recent work regio-random and regio-regular poly(3-alkyl thiophenes) (rran and rreg P3ATs) with comb-like architecture and different side chain lengths have been investigated as model systems allowing to evaluate the influence of main chain packing on the α_{PE} dynamics in amorphous alkyl nanodomains [9]. The thiophene rings in rreg P3ATs are stacked in a crystal-like manner due to a highly regular head-to-tail arrangement of the monomeric units while this is not possible in case of rran P3ATs leading to significant differences in application-relevant properties like conductivity although the backbones in both series contain identical monomers. While rreg P3ATs show a long range ordered lamellar structure where main and side chain layers alternate, this is not the case for rran P3ATs where main and side chains nanophase separate more locally without pronounced long range order. Interestingly, the results of this comparative study incorporating rreg and rran P3ATs indicate that the α_{PE} process is basically unaffected by the packing of the main chains. However, long range ordered polymers like rreg P3ATs with main chains packed in a crystal-like manner have major advantages for studying the influence of the environment on the α_{PE} dynamics since it is possible to quantify structural aspects like (i) alkyl nanodomain size, (ii) average packing density of CH_2 groups in the alkyl nanodomains, and (iii) packing at the interface between main chain domain and alkyl nanodomain. This can be further used to clarify the influence of these factors on the cooperative dynamics in domains with nanoscopic dimensions.

Interesting model systems to extend the knowledge about the influence of the main chain packing on the α_{PE} process in long range

ordered polymers with comb-like architecture might be poly(1,4-phenylene-2,5-dialkoxy terephthalate)s (PPAOTs) consisting of monomers as shown in Fig. 1a. In the 1980s, the structure of these alkoxyated polyesters has been extensively analyzed [5,31–33]. It has been reported that layered structures are commonly formed after attaching long alkoxy side groups. Detailed structural analysis revealed that PPAOTs can exist in three different long-range ordered modifications **A**, **B** and **C** [31]. While modification **C** is only found for samples with $C \leq 4$ alkyl carbons per side chain, modifications **A** and **B** are most relevant for samples with longer alkyl groups. A main difference between both modifications is that the layer spacings d_{100} for modification **B** are much smaller than those for modification **A**. A linear dependence of d_{100} on side chain length is observed in both cases. It was concluded that **A** is a 'layered mesophase' where the side chains show 'positional disorder' while **B** is considered as 'crystalline material' [31,34]. An overall packing of side chains and main chains as shown in Fig. 1 is assumed for mesophase **A**. Although the structural features of PPAOTs have been extensively investigated and dynamic mechanical measurements have been performed for selected samples [35,36], a little is known about the influence of structural properties on the side chain dynamics (α_{PE} process). This is the focus of the study presented here.

In this work poly(1,4-phenylene-2,5-dialkoxy terephthalate)s with $C = 6$ –12 alkyl carbons per side chain are studied as model systems and compared with recent results for corresponding rreg P3ATs to further understand the influence of structural parameters on the confined cooperative dynamics of methylene units in amorphous alkyl nanodomains. The temperature-dependent structure is investigated by X-ray diffraction measurements, model-like specimen containing basically only one PPAOT polymorph are prepared and systematically studied by dynamic shear measurements in a broader frequency range. The results will be used to quantify structural parameters influencing potentially the α_{PE} process related to the frequency-temperature-dependent softening behavior of self-assembled alkyl nanodomains in the amorphous state.

2. Experimental

2.1. Samples

Poly(1,4-phenylene-2,5-*n*-dialkoxy terephthalates) (PPAOTs) with $C = 6$ –12 alkyl carbons per side chain are studied. The average molecular weights of these alkoxyated polyesters as obtained from

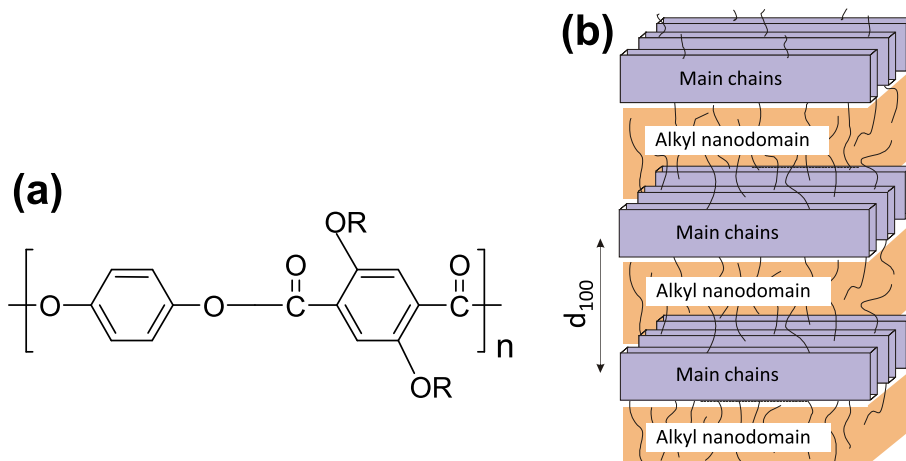


Fig. 1. (a) Repeating unit of poly(1,4-phenylene-2,5-dialkoxy terephthalate)s PPAOTs with R being the alkyl groups. (b) Sketch showing the overall packing of main and side chains in PPAOTs resulting in a long range ordered state with lamellar morphology ($d_{100} = 10$ –20 Å).

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