Structural and dynamical study of PDMS and PS based block copolymers

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ABSTRACT

Block copolymers represent an interesting class of materials, combining properties of individual components and capable of developing nanoscopic domain morphologies. Copolymers which comprise polystyrene and poly (dimethylsiloxane) attract special attention due to their effective segregation and the highly contrasting thermal properties of individual blocks. This work covers structural studies of copolymeric domain architecture and investigates the molecular dynamics observed in bulk PDMS, diblock PS-PDMS and triblock PS-PDMS-PS. Utilization of atomic force microscopy and NMR spin diffusion provide a thorough picture of phase separated systems. Dielectric spectroscopy reveals the dynamic heterogeneity of PDMS amorphous phase. Two distinct structural relaxations, namely α and α_c, were observed and attributed correspondingly to PDMS mobile amorphous fraction and PDMS rigid amorphous fraction. Unexpectedly, the segmental reorientations observed in the case of copolymers were faster that that observed for bulk PDMS.

1. Introduction

Block copolymers (BCs) belong to the group of self-assembled systems which undergo spontaneous phase separation below a certain critical order-disorder temperature T_{ODT}. This thermodynamically driven, molecular rearrangement leads to the development of specific domain morphologies, which can be characterized by distinctive and repetitive structural motifs. Depending on BC molecular weight and the relative volume fraction of its constituent blocks, a number of different domain topologies have been observed both experimentally [1] and via computational studies [2,3]. Furthermore, BC domain sizes are tuneable by the degree of polymerization control, accordingly giving access to sub-10-nanometric feature sizes [4–6]. The above mentioned properties, together with the relatively low costs of BC production, make them attractive and promising potential candidates for nanolithographic purposes. Partly because of this, BC patterning has become a dynamically developing field in nanotechnology and there are numerous fruitful examples of BC application in nanolithography [5,7] and advanced materials fabrication [8–10]. Technology based on BC may potentially compete with standard lithographic methods provided: (i) there is a negligible population of defects present on these organic matrices and (ii) there is a sharp enough interface between dissimilar phases. Fulfilment of the latter condition enables production of structural elements surpassing the size limitations met in classic photolithography. Correspondingly, in order to design a substantially dense and compact BC template it is necessary to work with materials characterized by relatively large Flory-Huggins interaction parameter χ, meaning strong segregation even for relatively low molecular weights [11]. One of the most commonly used copolymers which does belong to this group, and which can be successfully utilized in nanolithography [12–14] is poly(styrene-b-dimethylsiloxane) (PS-PDMS). It combines two components which are distinctively different in terms of their thermal properties. There is a significant glass transition temperature T_g contrast (exceeding 200 °C) between these two polymers. Consequently, at room temperature, one block (PS) is a rigid solid while the second one (PDMS) is already in the melted state. This feature makes the system very attractive for the study of molecular dynamics under spatial confinement with specified nanoscopic geometry [15,16]. It partially resembles restricted dynamics problems found in classical porous systems, except for the fact that in this case the soft polymeric chains are covalently anchored at their terminal site to the rigid organic matrix. Moreover, it is worth adding that by experimenting with co-polymerization stoichiometry it is possible to eventually obtain various domain morphologies (for example rigid PS cylindrical domains embedded in a soft PDMS matrix) and monitor how both, dimensionality and topology affect polymer chain dynamics [17]. It has been well documented [18–20] that copolymeric blocks reveal slightly different mobility than their corresponding homopolymers measured individually as a reference sample. It means that, despite establishing an effective phase segregation, both components still influence one another in terms of dynamics. Intuitively, in most cases a rigid component hinders the mobility of its soft neighbour and, accordingly, chains
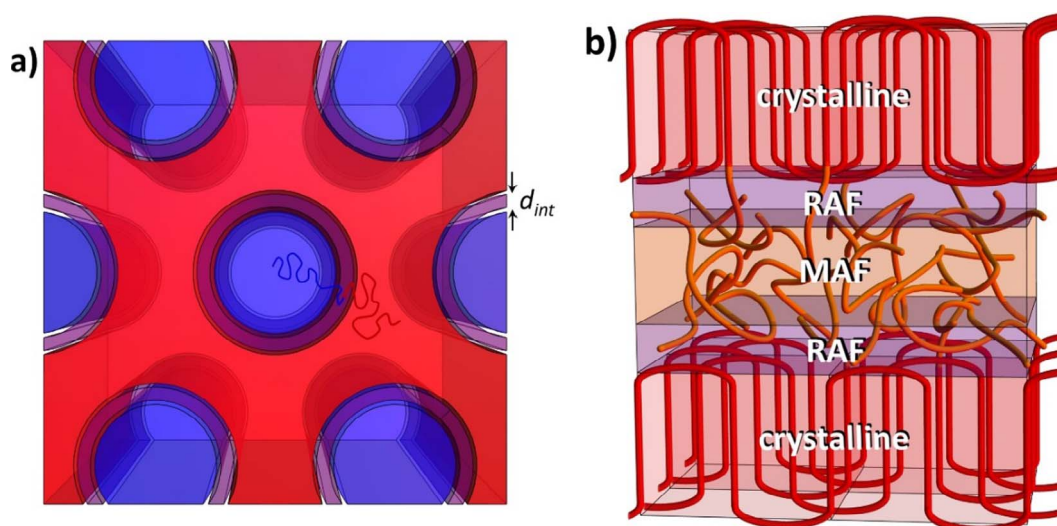
Fig. 1. Schematically presented (a) BC cylindrical domain structure with interfacial regions, (b) complex structure of semicrystalline polymer comprising crystalline, mobile amorphous (MAF) and rigid amorphous (RAF) fractions.

exhibiting lower T_g, may accelerate the dynamics of an adjacent stiff phase. Therefore, at least in the so called interfacial region (Fig. 1a) there might be either a low or high mobility gradient present. Although, such a description seems to be reasonable, Valle-Carrandi et al. [17] reported quite opposite behaviour namely, unexpectedly faster segmental dynamics of PDMS block in PS-PDMS copolymer in comparison to the bulk PDMS. Strikingly, according to the authors this effect is topology-dependent and stems from inequivalent chain packing for different domain architectures. It appears that in lamellar morphology PS-PDMS does follow the general trend [21], while cylindrical and spheroidal architecture leads to the unexpected reduction of activation energy barrier for PDMS segmental motions. It is also worth pointing out that semicrystalline PDMS alone inherently reveals dynamical heterogeneity due to its complex phase structure involving mobile amorphous (MAF), rigid amorphous (RAF) and crystalline fraction [22,23]. As schematically depicted in Fig. 1b the RAF represents chain segments residing within interface region dividing the MAF and crystalline phases (i. e. chain units forming loops between the points where the chain enters crystal phase). Employing dielectric spectroscopy Kirst et al. [24] proved that PDMS reveals a certain fraction of chains exhibiting constrained α_c-relaxation, which they attributed to RAF. Lund et al. [25] provide a comprehensive study of PDMS crystallization kinetics and clearly indicates two dynamically distinct amorphous regions. Comparable results have been reported by Jancelewicz et al. [26] where the authors discussed the influence of the sample thermal history on both MAF and RAF. Using molecular simulations, Lee et al. [27] have recently shown that RAF exhibits similar features to the near-interface regions observed in the case of thin films, nanocomposites, or layered structures. Taking into consideration all the above mentioned results, it is clear that PS-PDMS copolymers exemplify a quite complex and heterogeneous system consisting of at least three distinct PDMS amorphous fractions namely, bulk-like amorphous, rigid amorphous, and domain interfacial amorphous. In order to scrutinize these systems we have combined two powerful spectroscopic methods: Nuclear

Magnetic Resonance (NMR) and Broadband Dielectric Spectroscopy (BDS), along with Differential Scanning Callorimetry (DSC) analysis and Atomic Force Microscopy (AFM). Diblock and triblock copolymers have been examined and confronted. Although constituent chemical units remain the same in both cases, fixing the middle block covalently at both its terminal sites to the rigid-like polymer may change the physical properties of studied material. It is due to loop/bridge chain conformations and the presence of their entanglements and knots [28–31]. Gehlsen et al. [32] have shown that triblock copolymers may exhibit higher order-disorder transition temperature than diblocks. Moreover, the middle blocks appear to attain more expanded conformations [33] and reveal a broader distribution of correlation times observed for global chain motions (described in dielectric spectroscopy as normal mode relaxation). Although PDMS does not possess a parallel to the chain contour dipole moment component (the fluctuations of the end-to-end vector do not affect dielectric spectra) the structural α-relaxation can be well exposed and analysed by BDS. The data presented in this work demonstrates that despite their local nature, segmental chain reorientations can be sensitive to topological constraints imposed by BC domain morphology due to different chain packing.

2. Experimental

2.1. Materials

Poly(styrene-b-dimethyl siloxane) diblock and poly(styrene-b-dimethyl siloxane-b-styrene) PS(22 k)-PDMS(1104 k)-PS(22 k) triblock copolymers were provided by Polymer Source TM. Neat PDMS was received from Poznan Science and Technology Park. Number average molar mass, polydispersity index, and PS volume fractions as well as characteristic temperatures for studied materials are collected in Table 1.

Table 1
Studied samples characteristics.

id	(PS) M_n ($\cdot10^3$)	(PDMS) M_n (10^3)	M_w/M_n	f_{PS}	T_g^{PDMS} (K)	T_m^{PDMS} (K)	T_g^{PS} (K)
PDMS	–	80	–	–	148	234	–
PS-PDMS	21	46	1.45	0.23	157	232	350[a]
PS-PDMS-PS	44	104	1.3	0.22	154	228	377[a]

[a] temperatures provided by producent.