



# SILOXANE–ETHYLENE OXIDE–URETHANE BLOCK COPOLYMERS: SYNTHESIS AND PROPERTIES<sup>§</sup>

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## Abstract

Siloxane–ethylene oxide–urethane block copolymers were synthesized by the interaction of oligosiloxane organodiols of the general formula  $\text{HO}(\text{CH}_2)_2\text{OCH}_2\text{Me}_2\text{SiO}[\text{SiR}_2\text{O}]_n\text{SiMe}_2\text{CH}_2\text{O}(\text{CH}_2)_2\text{OH}$  ( $\text{R} = \text{Me}, \text{Et}$ ) and oligo(ethylene oxide) (OEO)  $(-\text{CH}_2\text{CH}_2\text{O}-)_m$  with 4,4'-diphenylmethane diisocyanate. The copolymers obtained were studied by differential scanning calorimetry (DSC), scanning electron microscopy (SEM), atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS). The effect of the bulk composition on the composition and structure of the surface was established.

**Key words:** polysiloxanes, polyurethanes, block copolymers, surface.

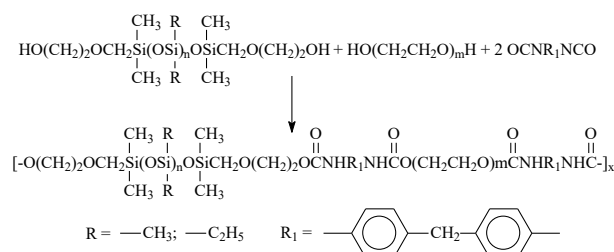
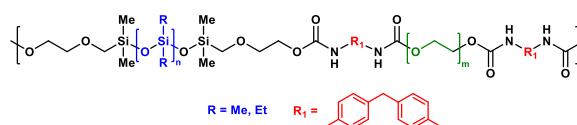
## Introduction

Siloxane–ethylene oxide–urethane block copolymers (BCs) are of particular interest owing to a combination of the useful properties of OEO (hydrophilicity, thermal sensitivity, bio- and hemocompatibility) with the unique properties of polysiloxanes (hydrophobicity, gas permeability, low glass transition temperature, low surface energy). The absence of Si–O–C bonds in their structures ensures the hydrolytic stability, while the presence of diurethane (DU) fragments able to form hydrogen bonds can have an additional impact on the formation of various structures.

Using XPS, earlier we have studied the surface of dimethylsiloxane–ethylene oxide–urethane copolymers of a triblock structure and their blends with PVC [1]. In this work, DSC, SEM, AFM, and XPS were used to study diethylsiloxane–ethylene oxide–urethanes of a polyblock structure and compare them with polydimethylsiloxane–ethylene oxide–urethanes obtained previously [2]. Interest in diethylsiloxane–ethylene oxide BCs is dictated by a number of specific properties of polysiloxanes containing diethylsiloxane (DES) units, in particular, the lowest glass transition temperature among linear polysiloxanes ( $-137^\circ\text{C}$ ) [3].

## Results and discussion

The target BCs were obtained by the reactions of oligosiloxane organodiols (OSD) of the general formula  $\text{HO}(\text{CH}_2)_2\text{OCH}_2\text{Me}_2\text{SiO}[\text{SiR}_2\text{O}]_n\text{SiMe}_2\text{CH}_2\text{O}(\text{CH}_2)_2\text{OH}$  ( $\text{R} = \text{Me}, \text{Et}$ ) and OEO  $(-\text{CH}_2\text{CH}_2\text{O}-)_m$  with 4,4'-diphenylmethane diisocyanate according to Scheme 1. Diethylsiloxane organodiols were synthesized according to the previously described method [4].



**Scheme 1.** Synthesis of polysiloxane–ethylene oxide–urethanes.

Some characteristics of the resulting BCs and model polysiloxane–urethanes are given in Tables 1 and 2.

The results of DSC analysis are presented in Tables 1 and 2, and the typical DSC curves are depicted in Fig. S1 in the Electronic supplementary information (ESI).

**Table 1.** Compositions and properties of the polydimethylsiloxane–ethylene oxide–urethanes and model polydimethylsiloxane–urethanes [2]

Polymer	OSD MM/n	OEO MM/m	$T_g$ , $^\circ\text{C}$	$M_p$ , $^\circ\text{C}$	$[\eta]^a$	$M_w$ , kDa	$M_w/M_n$
BC-1Me	282/1	1240/28	-7	-	0.29	38	2.1
BC-2Me	282/1	2740/62	-51	50	0.68	68	2.1
BC-3Me	282/1	3870/88	-52	53	0.68	65	2.0
BC-4Me	740/7	1450/33	-44	40	0.22	22	2.7
BC-5Me	740/7	3870/88	-56	60	0.37	31	2.9 (2.1) <sup>b</sup>
BC-6Me	1850/22	1240/28	-41	40	0.26	22	3.1
BC-7Me	1850/22	2740/62	-54	56	0.24	32	2.1
BC-8Me	1790/20	3870/88	-64	62	0.22	18	2.6
BC-9Me	282/1	-	30	-	-	-	-
BC-10Me	1000/11	-	-22	-	-	-	-

<sup>a</sup> at  $20^\circ\text{C}$  in dioxane;

<sup>b</sup> a bimodal distribution; the bracketed value refers to the high-molecular peak.

**Table 2.** Compositions and properties of the polydiethylsiloxane–ethylene oxide–urethanes and model polydiethylsiloxane–urethanes

Polymer	OSD MM/n	OEO MM/m	$T_g$ , °C	Mp, °C	$[\eta]^a$	$M_w$ , kDa	$M_w/M_n$
BC-1Et	760/5	550/12	-15	-	0.07	-	-
BC-2Et	790/6	550/12	-22	-	0.17	10	1.9
BC-3Et	1263/10	550/12	-23	-	0.13	-	-
BC-4Et	2845/25	550/12	-17	-	-	-	-
BC-5Et	790/6	1450/33	-47	-	0.37	25.5	2.6
BC-6Et	2845/25	2200/50	-64	49	0.38	20	2.4
BC-7Et	1130/8	2740/62	-55	56	0.14	-	-
BC-8Et	2180/19	2740/62	-56	52	0.26	-	-
BC-9Et	1380/11	3040/69	-57	51	0.32	20	2.1
BC-10Et	670/4	3040/69	-56	58	0.32	20	2.0
BC-11Et	790/6	3870/88	-	58	0.46	27	2.4
BC-12Et	670/4	-	-23	-	-	-	-
BC-13Et	1380/11	-	-52	-	-	-	-
BC-14Et	2845/25	-	-137	-	-	-	-

<sup>a</sup> at 20 °C in dioxane.

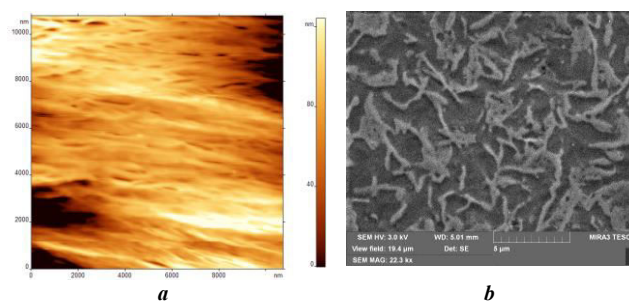
As can be seen from Tables 1 and 2, the glass transition temperatures of the block copolymers under consideration lie in the temperature range of 15–60 °C. The value of  $T_g$  is mainly determined by the length of the OEO blocks: an increase in the length of the OEO block leads to a noticeable decrease in the glass transition temperature, which approaches the glass transition temperature of the PEO homopolymer (67 °C) [5]. This is typical for both the BC-Me and BC-Et polymers.

Note that the DSC curves of the BC-Et polymers do not show a jump in heat capacity in the region of the glass transition temperature of high-molecular polydiethylsiloxane (-137 °C). Probably, DES forms a common amorphous phase with DU and OEO, and the thermal behavior of BC is determined mainly by the OEO content in it. In the BCs with  $m \geq 30$ , the OEO phase acquires the ability to crystallize [6]. Typical diffraction patterns of crystallizing BCs are shown in Fig. S2 in the ESI. The degree of crystallinity probably depends on both the bulk composition and the history of the sample and, in general, increases with the increasing OEO content.

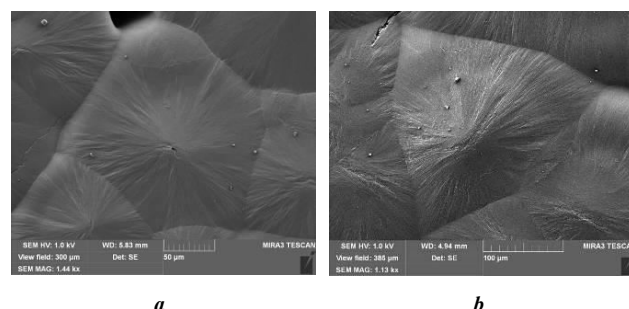
A comparison of the thermal characteristics of BC-4Me and BC-5Et, which feature similar compositions, revealed that, despite their close glass transition temperatures, the OEO blocks in BC-4Me are capable of forming a crystalline phase, while the BC-5Et copolymer is completely amorphous (Tables 1 and 2). This indicates that an increase in the length of the side substituents in the siloxane blocks complicates the crystallization of the OEO phase.

The AFM studies revealed the formation of fibrils on the surface of the partially crystallizing BC (Fig. 1a); the height of fibrils varies from 1 to 5 nm and their diameter ranges from 40 to 100 nm. Using SEM, it was shown that, depending on the value of  $m$ , the degree of crystallinity, and the substituent at the silicon atom, the fibrils can form sheaves, agglomerates of sheaves, and spherulites (Figs. 1b, 2). Spherulites are large, with the diameters ranging from 100 to 900 nm, depending on the sample.

Figure 2 depicts the SEM images of spherulites for BC-5Me and BC-11Et featuring similar compositions. A comparison of the micrographs shows that the spherulites of similar sizes are formed in these copolymers, and the observed difference is



**Figure 1.** AFM image of fibrils in BC-10Et (a) and SEM image of agglomerates of sheaves in BC-7Et (b).



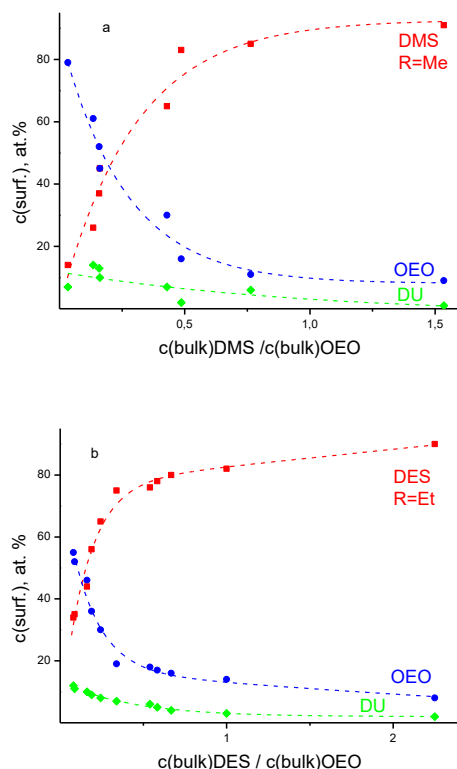
**Figure 2.** SEM images of spherulites in BC-5Me (a) and BC-11Et [6] (b).

probably determined by the crystallization conditions of the OEO phase and does not depend on the substituent at the silicon atom.

The surface composition was determined by XPS (Figs. S3, S4 in the ESI). The quantitative analysis was performed based on the integrated intensities of photoelectron lines taking into account the atomic sensitivity factors. The surface concentration of OEO was determined by the component of the carbon 1s line with a binding energy of 286.6 eV, which is responsible for the presence of OEO on the surface.

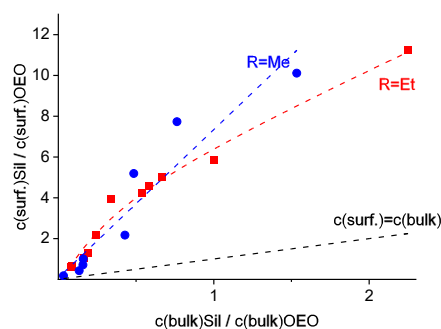
Figure 3 shows the dependences of the surface compositions on the ratio of the bulk concentrations of the siloxane and OEO blocks. The concentrations are expressed in atomic percents, which shows how many atoms out of every 100 non-hydrogen atoms belong to the given component. As can be seen from this figure, an increase in the volume content of the siloxane block also leads to an increase in its surface concentration. At the same time, there is a decrease in the surface content of OEO and DU, which is due to the low surface energy of the siloxane component.

The enrichment of the surface with the siloxane component is confirmed by Fig. 4, which demonstrates the dependences of the ratios of the surface concentrations of the siloxane and OEO blocks on their contents in the volume. The black dotted line corresponds to the equality of the surface and bulk compositions. As follows from Fig. 4, in all the samples explored, the ratio of the concentrations of the siloxane and OEO components on the surface exceeds their ratio in the volume. It is also evident from Fig. 4 that in the BC with a low content of siloxane blocks, the substituent at the silicon atom does not have a significant effect on the surface composition, and the observed difference can be explained by the conditions of the sample preparation. The effect of the substituent at the silicon atom is observed only in the samples with high contents



**Figure 3.** Dependence of the surface concentration  $c(\text{surf.})$  on the ratio of the volume concentrations of the siloxane and OEO blocks for OEO, DU, DMS (R = Me) (a) and DES (R = Et) (b).

of the siloxane component. In these polymers, the enrichment of the surface with the siloxane block in BC-Me is higher than in BC-Et, which can also be explained by the difference in the surface energy [7]. It should also be noted that in the BCs explored, no effect of the absolute length of the blocks and the degree of crystallinity on the surface composition was detected.



**Figure 4.** Dependence of the ratio of the siloxane and OEO surface concentrations  $c(\text{surf.})\text{DES} / c(\text{surf.})\text{OEO}$  on the ratio of the bulk concentrations  $c(\text{bulk})\text{DES} / c(\text{bulk})\text{OEO}$ .

## Conclusions

Thus, the siloxane–urethane–ethylene oxide block copolymers were synthesized and the effect of the substituent at the silicon atom on the properties of the resulting samples was studied. It was found that the substituent at the silicon atom does not have a noticeable effect on the thermal properties, and the glass transition temperature decreases with an increase in the

length of the OEO blocks and approaches the glass transition temperature of neat OEO.

No significant effect of the substituent at the silicon atom on the surface composition was found either. Only in the samples featuring a high content of the siloxane component, the more enriched surface was observed for BC-Me than for BC-Et.

The substituent at the silicon atom affects the ability to crystallize. Although the formation of the crystalline phase is determined mainly by the conditions for OEO crystallization, an increase in the length of the substituent at the silicon atom can hamper crystallization.

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## Electronic supplementary information

Electronic supplementary information (ESI) available online: the DSC, XRD, and XPS curves. For ESI, see DOI: 10.32931/ieo2437a.

## References and notes

- § This work is dedicated to the memory of Prof. A. J. Pertsin, our teacher and mentor.
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