

Surface Properties of Poly(ethylene oxide)-Based Segmented Block Copolymers with Monodisperse Hard Segments

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ABSTRACT: The surface properties of segmented block copolymers based on poly(ethylene oxide) (PEO) segments and monodisperse crystallizable tetra-amide segments were studied. The monodisperse crystallizable segments (T6T6T) were based on terephthalate (T) and hexamethylenediamine (6). Due to the crystallinity of T6T6T being high (~ 85%), the amount of amorphous T6T6T dissolved in the polyether phase was limited. The length of the PEO segments was varied (between 600 and 4600 g/mol) and effect of extending the PEO segments with terephthalic groups was investigated. Studied was the hydrophilicity of the surface by contact angle measurements and of the

bulk copolymers by water absorption measurements. The results were compared with data of PEO-poly(butylene terephthalate) (PEO-PBT) copolymers. For a given hydrophilicity of the bulk copolymer, the surface hydrophilicity decreased in the order PEO-PBT, PEO-T6T6T, and (PEO-T)-T6T6T. The use of short monodisperse hard segments resulted in low contact angles, with a lowest observed value of ~ 29°. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1264–1269, 2009

Key words: poly(ethylene oxide); contact angle; water absorption

INTRODUCTION

Segmented block copolymers, consisting of alternating soft and hard segments, can find use in a variety of fields such as coatings, as packagings, or in the textile industry, and applications include membranes for separation processes, contact lenses, catheters, wound dressings, and coatings for blood and protein storage devices.^{1–6} The materials are processable into complex shapes and exhibit tunable properties and their surface composition can be modified. Several block copolymers, such as polyurethanes^{7–12} and polyesters,^{13–16} are applied as biomaterials. However, problems like surface-induced thrombosis, infections, and calcification remain issues after short- or long-term contact with blood.^{1,3}

Poly(ethylene oxide) (PEO) is a synthetic, water-soluble, and nontoxic polymer, and PEO-based block copolymers can be employed to diminish protein adsorption at the polymer surface. Polymers that contain PEO have a high degree of hydration and a

low interfacial free energy with water.^{2,5,14,17–19} Polyurethane (urea) copolymers based on PEO have been evaluated as biomaterials due to their good biocompatibility and excellent mechanical properties.^{11,20–23} Nevertheless, non-phase-separated hard segments can be present at the polymer surface. This must be avoided as these hard segments may induce protein adsorption at the surface, ultimately denaturing the proteins.² An enhanced phase separation between soft and hard segments improves the blood compatibility.^{21,22,24,25}

By increasing the crystallinity of hard segments, the amount of non-crystallized hard segments dissolved in the soft phase can be reduced. Furthermore, the crystallinity of the hard segments can be improved by using segments of monodisperse length, giving rise to a near complete crystallization.^{26–29}

It is possible to obtain an interesting combination of properties by employing segmented block copolymers with PEO segments and monodisperse tetra-amide segments (T6T6T) (Fig. 1).

The T6T6T segments consist of terephthalic acid (T) and hexamethylenediamine (6) units,^{28–31} and because the T6T6T crystallinity in the copolymers is high (~ 85%), the amount of noncrystallized rigid segments dissolved in the PEO phase is minimal. The T6T6T segments have a low molecular weight (624 g/mol) and, as a result, the PEO concentrations

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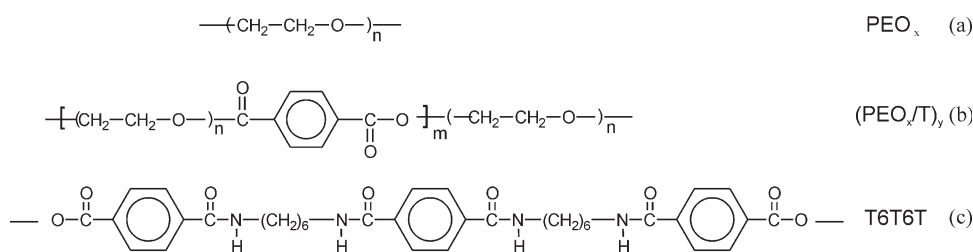


Figure 1 Chemical structures of PEO_x , $(\text{PEO}_x/\text{T})_y$, and T6T6T.

in the copolymers can be high with still good mechanical properties.^{30,31} The soft phase was based on PEO_x segments with a molecular weight ranging from 600 to 4600 g/mol.³⁰ Moreover, copolymers with PEO segments extended with terephthalic groups $(\text{PEO}_x\text{-T})_y$ were also investigated (Fig. 1). In this way, the maximum molecular weight of the soft segment could be increased.³¹ PEO segments have a hydrophilic nature and, by modifying the PEO concentration and molecular weight, the hydrophilicity of the copolymers can be varied over a wide range.³²

It is interesting to explore whether, by using non-dissolving monodisperse hard segments, the surface hydrophilicity can be lowered at a given bulk hydrophilicity. The surface properties were studied on wetted samples by using the static captive (air) bubble method, and the results were compared with PEO-PBT copolymers, a system that has been thoroughly investigated.^{13–16}

MATERIALS AND METHODS

$\text{PEO}_x\text{-T6T6T}$ block copolymers

The $\text{PEO}_x\text{-T6T6T}$ copolymers were synthesized by a polycondensation reaction by using PEO segments with a molecular weight (x) of 600–4600 g/mol and T6T6T.³⁰

$(\text{PEO}_x/\text{T})_y\text{-T6T6T}$ block copolymers

The $(\text{PEO}_x/\text{T})_y\text{-T6T6T}$ copolymers were synthesized by a polycondensation reaction by using PEO segments, extended with terephthalic units, and T6T6T.³¹ The molecular weight of the PEO (x) and the total molecular weight of the flexible segment (y) were varied.

Water absorption

The water absorption (WA) at equilibrium was measured on specimens of injection-molded polymer bars ($70 \times 9 \times 2 \text{ mm}^3$). The samples were placed in a desiccator filled with demineralized water for 4 weeks at room temperature. The WA was defined as the weight gain of the polymer according to eq. (1):

$$\text{Water absorption} = \frac{m - m_0}{m_0} \times 100\% \quad [\text{wt}\%] \quad (1)$$

where m_0 is the dry sample weight and m is the weight of the sample after conditioning to equilibrium. The measurements were performed in duplicate. After 4 weeks the samples were dried and m_0 was remeasured to exclude weight loss during the experiment. The volume fraction of water (ϕ_{water}) can be determined by using PEO, DMT, and T6T6T densities of 1.13, 0.98, and 1.32 g/cm³, respectively.^{32,33} On this basis, it was assumed that the densities of the copolymers were similar to that of the homopolymer. The water concentration, ϕ_{water} (vol %), was calculated according to eq. (2):

$$\phi_{\text{water}} = \frac{m - m_0}{(m - m_0) + (m/\rho_{\text{polymer}})} \quad (2)$$

Preparation of polymer films

The polymer films were made by compression molding and displayed thicknesses of $\sim 300 \mu\text{m}$. Prior to the contact angle (CA) measurements, the films were ultrasonically cleaned in *n*-hexane for 5 min and subsequently wiped with cotton and rinsed with *n*-hexane. The films were then dried in a vacuum oven for 24 h to remove all *n*-hexane. Approximately 5 h before the measurements, the films were placed in demineralized water to allow the materials to absorb water until an equilibrium was reached ($\sim 4 \text{ h}$).

Contact angles

Static captive (air) bubble CA measurements were performed by introducing a 10- μL air bubble from a microsyringe below the surface of a polymer film, which, in turn, was placed in an optical cuvette filled with demineralized water. The experiments were carried out at 22°C and a video-based Optical Contact Angle Meter OCA15 plus (DataPhysics Instruments Fielderstadt, Germany) was used. Immediately after the air bubble was placed on the surface, CA were calculated with a SCA20 software, applying ellipse fitting. The results were averages of at least 20 measurements and the standard deviation in the CA was $\sim 2^\circ$.

RESULTS AND DISCUSSION

The present article describes the relation between the PEO soft segment length and the CA of the copolymer with water. With increasing PEO segment length, the PEO concentration in the copolymer as well as the WA by the copolymer was increased. The following discussion concerns two series: PEO_x-T6T6T and (PEO_x/T)_y-T6T6T.

Under dry conditions, the copolymers could contain a semi-crystalline PEO phase at room temperature provided that the PEO molecular weight was 2000 g/mol or higher. The presence of polyether crystals in the copolymer could have an unfavorable effect on the CA. Moreover, for a copolymer having absorbed water, the PEO melting temperature becomes strongly reduced.³² As a result, the polyether phase was amorphous under the conditions of the CA measurements.

PEO is a hydrophilic segment and the concentration of water of PEO_x-T6T6T copolymers at 100% relative humidity (RH) was found to increase with the concentration of PEO in the (dry) copolymer (Fig. 2). As can be seen, the volume concentration of water in the (PEO_x/T)_y-T6T6T copolymers as a function of the PEO concentration was only slightly lower than that of the PEO_x-T6T6T copolymers. The presence of apolar terephthalic units thus gave rise to a slight reduction in the WA of the PEO phase.

PEO_x-T6T6T copolymers

In the PEO_x-T6T6T copolymer series, the PEO molecular weight (*x*) was varied from 600 to 4600 g/mol (Table I). As the PEO_x segment length increased, the PEO concentration was raised, whereas the T6T6T concentration decreased. The copolymers had a high

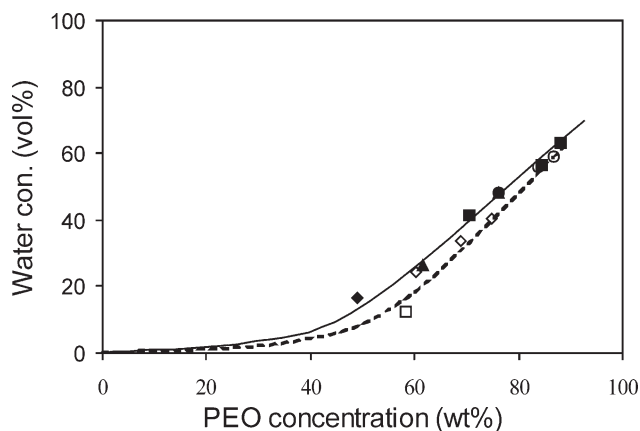


Figure 2 Effect of PEO concentration in the dry copolymer on the water concentration in the copolymer at 100% RH. The solid symbols are for PEO_x and the open symbols for (PEO_x/T) segments: □, (PEO₃₀₀/T); ◆, PEO₆₀₀; ◇, (PEO₆₀₀/T); ▲, PEO₁₀₀₀; △, (PEO₁₀₀₀/T); ●, PEO₂₀₀₀; ○, (PEO₂₀₀₀/T); ■, PEO₁₅₀₀; PEO₃₄₀₀; PEO₄₆₀₀.

TABLE I
Water Absorption and Contact Angles of PEO_x-T6T6T Copolymers

PEO _x (g/mol)	Conc. T6T6T (wt %)	Conc. PEO (wt %)	WA ^a (wt %)	φ _{water} (vol %)	CA ± SD (°)
600	51.0	49.0	18	18	46 ± 2
1000	38.4	61.6	35	30	33 ± 3
1500	29.4	70.6	69	45	33 ± 2
2000	23.8	76.2	91	51	36 ± 2
3400	15.5	84.5	127	59	35 ± 2
4600	11.9	88.1	170	66	31 ± 2

^a Water absorption as defined by eq. (1)

molecular weight (around 20,000 g/mol) with a T6T6T crystallinity in the copolymers of ~ 85%. Moreover, the materials were transparent,³⁰ suggesting that neither a spherulitic structure nor a liquid-liquid demixed phase was present.

The surface properties of the melt-pressed films were studied on wetted samples using the static captive (air) bubble method (Table I). For these hydrophilic copolymers, the captive bubble method provided reproducible results, and the CA of PEO_x-T6T6T copolymers are given as functions of the PEO segmental molecular weight in Figure 3(a) and as

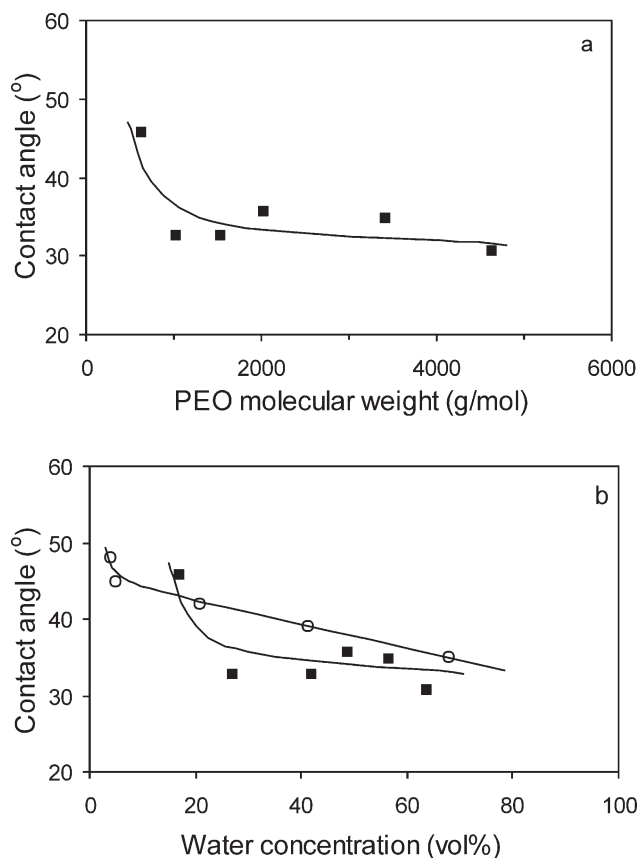


Figure 3 Contact angle as a function of the PEO molecular weight (a) and the water concentration (b): ■, PEO_x-T6T6T; ○, PEO_x-PBT.¹⁴

TABLE II
Water Absorption and Contact Angles of $(\text{PEO}_x/\text{T})_y$ -T6T6T Copolymers

x (g/mol)	y (g/mol)	Conc. T6T6T (wt %)	Conc. PEO (wt %)	Conc. T (wt %)	WA ^a (wt %)	ϕ_{water} (vol %)	CA \pm SD ($^\circ$)
300	2500	19.9	58.4	21.7	14	14	41 \pm 3
600	600	51.0	49.0	0.0	18	18	46 \pm 2
600	1250	33.3	60.4	6.3	30	26	43 \pm 2
600	2500	20.0	69.0	11.0	49	37	33 \pm 2
600	5000	11.1	74.8	14.1	66	43	31 \pm 1
1000	1000	38.4	61.6	0.0	35	30	33 \pm 3
1000	3000	17.2	76.3	6.5	78	48	30 \pm 1
1000	5000	11.1	80.6	8.3	92	52	29 \pm 1
2000	2000	23.8	76.2	0.0	91	51	36 \pm 2
2000	4000	13.5	83.8	2.7	130	60	32 \pm 2
2000	6000	9.5	86.8	3.7	145	63	29 \pm 2

^a Water absorption as defined by eq. (1)

functions of the water volume concentration in Figure 3(b).

As can be seen, the CA decreased with increasing molecular weight of the PEO_x segments, particularly at the low segmental molecular weights. With an increasing PEO length, the amount of T6T6T decreased and the amount of T6T6T at the surface was consequently expected to be lowered. Another relevant relationship was that of the CA as functions of the volume concentration of water (vol %) [Fig. 3(b)]. The CA values decreased with increasing water concentration, and the most significant drop occurred, again, at low water concentrations.

Deschamps et al. studied segmented block copolymers based on PEO and poly(butylene terephthalate) (PBT) hard segments, in which the PEO segment lengths were varied from 300 to 4000 g/mol and the PBT content ranged from 30 to 70 wt %.¹⁴ From their data the water concentrations were calculated and CA as a function of water concentration was plotted [Fig. 3(b)]. The PEO-PBT copolymers also demonstrated a decrease in CAs with an increasing water volume concentration. As compared to the PEO-PBT copolymers, the PEO-T6T6T materials mainly displayed lower CA values. Only at low water concentrations the PEO-T6T6T values were higher. The PBT crystallinity was rather low (\sim 35%), indicating that \sim 65% noncrystallized PBT was present in the amorphous PEO phase. It was plausible that this noncrystallized PBT was present at the polymer surface, resulting in a higher CA. This suggests that the use of monodisperse crystallizable segments led to less hard segment being present at the surface.

There are several possible explanations for the decrease in CA with the molecular weight of the PEO (e.g., the increase in chain flexibility of the soft segment, the increased PEO concentration, the increased water volume concentration, and/or the decreasing hard segment concentration at the sur-

face). At this point, it remains unclear which explanations are relevant.

Terephthalic-extended PEO segments

The PEO molecular weight in the segmented block copolymers was limited to 4600 g/mol due to phase separation by liquid-liquid demixing taking place for higher PEO molecular weights. A way to create longer flexible segments without the occurrence of such liquid-liquid demixing consists of extending the PEO segments with terephthalic units (T).³¹ Such copolymers were prepared and denoted $(\text{PEO}_x/\text{T})_y$ -T6T6T (Fig. 1). Here, both the PEO molecular weight (x) and the molecular weight of the total soft segment (y) were varied (Table II).

Extending the PEO with terephthalic groups resulted in an increase in the soft-segment molecular weight (y), an increase in the PEO concentration, and a decrease in T6T6T concentration. The terephthalic segments were dissolved in the PEO phase and exhibited a hydrophobic nature, consequently affecting the hydrophilicity of the polymer as demonstrated in Figure 2. The WA and ϕ_{water} of the $(\text{PEO}_x/\text{T})_y$ -T6T6T copolymers increased significantly with increasing PEO concentration in the same way as for the PEO_x -T6T6T copolymers (Table II). The presence of the terephthalic group lowered the WA of the PEO phase, and their influence on the hydrophilicity of the polymer surface was studied.

By extending the soft segment with terephthalic units the water concentration increased and the CAs were lowered (Fig. 4).

For the $(\text{PEO}_x/\text{T})_y$ -T6T6T copolymers, the trend in CA as a function of the water volume concentration was similar to that of the PEO_x -T6T6T copolymers, however, with somewhat lower values [Fig. 4(a)]. This suggests that the presence of the terephthalic groups increased the surface hydrophilicity to a larger extent

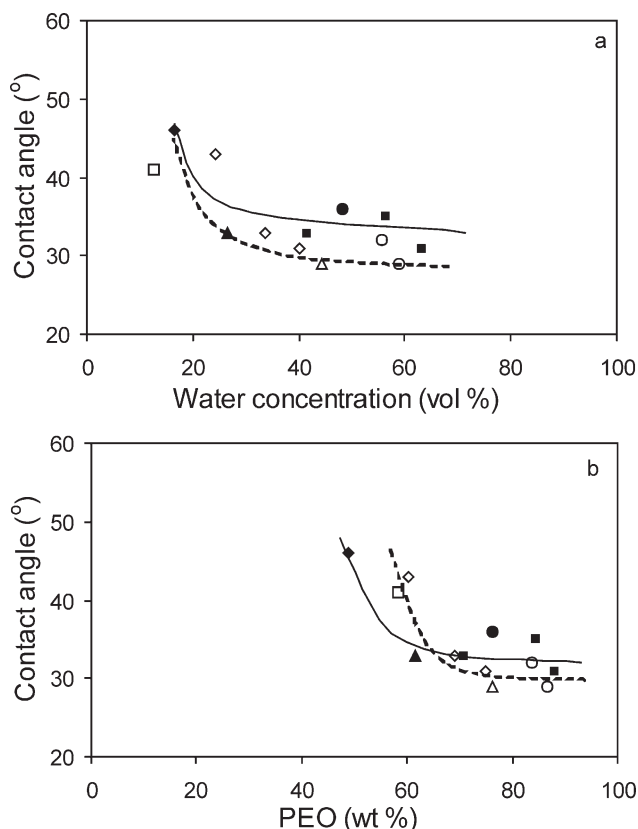


Figure 4 Contact angle as a function of the water concentration (a) and PEO concentration (b). The solid symbols are for PEO_x and the open symbols for (PEO_x/T) segments: □, (PEO₃₀₀/T); ◆, PEO₆₀₀; ◇, (PEO₆₀₀/T); ▲, PEO₁₀₀₀; △, (PEO₁₀₀₀/T); ●, PEO₂₀₀₀; ○, (PEO₂₀₀₀/T); ■, PEO₁₅₀₀, PEO₃₄₀₀, PEO₄₆₀₀.

than expected based on the bulk hydrophilicity. The reason the copolymers with terephthalic groups displayed lower CA values is not completely clear.

The plot of the CA as functions of the PEO concentration showed that there was a decrease in CA, but that this effect leveled off at higher PEO concentrations [Fig. 4(b)]. This trend was apparent for both the (PEO_x/T)_y-T6T6T and the (PEO_x-T6T6T) series. At higher PEO concentrations, the (PEO_x/T)_y-T6T6T copolymers seemed to present lower CA values, which was surprising considering their lower WA (Fig. 2). With an increasing PEO concentration in the copolymer, the amount of T6T6T in the surface must have decreased too. The lowest measured CA was about 29°, which is low as compared to other segmented block copolymers. With the monodisperse hard segment distribution, the amount of hard segments dissolved in the polyether phase is low and this seems to be the reason for the low CA.

CONCLUSIONS

On a series of PEO-based segmented block copolymers with a very low concentration of dissolved

hard segments in the PEO phase, the hydrophilicity of the copolymers was changed and the surface hydrophilicity was studied. The CA of the copolymers decreased with increasing PEO concentration (concentration of water) and decreasing hard segment (T6T6T) concentration. At a given hydrophilicity, the (PEO/T)-T6T6T copolymers displayed even lower CA values as compared to their PEO-T6T6T counterparts. The introduction of terephthalic units in the PEO, in the form of PEO/T, thus lowered the bulk hydrophilicity to a larger extent than the surface hydrophilicity. Apparently, only few terephthalic units seemed to be present at the surface. The lowest observed CA value was 29°.

Moreover, the CAs of PEO-T6T6T were compared to those of PEO-PBT copolymers and found to be lower. This indicates the PEO-T6T6T copolymers that had less dissolved hard segments in the PEO phase had a more hydrophilic surface. The use of short monodisperse hard segments thus clearly had a positive effect on the surface hydrophilicity.

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