Sorption of Water Vapor by Hydrophilic Polyurethane-Ureas

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SYNOPSIS

Segmented polyurethane-ureas were prepared from low-molecular weight homopolymers or triblock (PEP) copolymers of ethylene and propylene oxides and 4,4'-diphenylmethane diisocyanate with hydrazine as chain extender. Equilibrium sorption of water vapor at 23°C was measured at eight to nine values of relative vapor pressure, $0.08 \leq p/p_0 \leq 0.97$. The effect of the structure (composition and length) of soft segments was studied. Sorption capacities were found to be lower than the reference values computed under the assumption that the contributions to sorption by the chain constituents are additive. This finding was assigned to the shielding effect of hard segment domains on the interaction of water molecules with hydrophilic (ethoxamer) groups of soft segments. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

If oligomers of ethylene oxide or oligomeric block copolymers of ethylene and propylene oxides are incorporated as "soft" segments into the chain of segmented polyurethanes or polyurethane-ureas, materials with increased sorptive capacity for water vapor (hydrophilicity) are obtained.[1-6] The hydrophilicity depends, among other factors, on the arrangement of ethoxamer and propoxamer groups in the block copolymer. It is particularly high with the PEP copolymers, where the central block consists of a sequence of ethoxamer units and the end blocks are sequences of propoxamer groups.[7]

In previous papers dealing with the properties of hydrophilic segmented polyurethanes and their constituents, the sorption of water vapor by ethylene and propylene oxide oligomers (PEO, PPO, respectively) differing in molecular weights, by PEP block copolymers differing in composition,[8] and by the corresponding polyurethanes (PUR) was investigated.[9] Here, data on the sorption of water vapor by segmented polyurethane-ureas (PURU) built up from PEO, PPO, or PEP units (soft segments), 4,4'-

diphenylmethane diisocyanate (MDI) and hydrazine (H) as chain extender, are presented and the impact of the chemical structure on the hydrophilicity is analyzed. The interaction with water of these polyethers, polyurethanes, and polyurethane-ureas has been discussed elsewhere.[10]

EXPERIMENTAL

Hydroxyl-terminated oligomers of ethylene and propylene oxides and their oligomeric triblock copolymers have been specified.[8] 4,4'Diphenylmethane diisocyanate (MDI) is a product of Bayer A.G., Leverkusen (Desmodur 44M). N,N-Dimethylformamide (DMF), product of Leuna Werke, was distilled before use. It contained less than 0.01 wt % water, 0.001% methanol, and 0.003% formaldehyde. Hydrazine hydrate (HH) was product of Bayer A.G., Leverkusen. It contained 64% wt hydrazine (H) and less than 0.1% wt ammonia.

Polymers

Polyurethane-ureas denoted as PURU (Table I) were prepared in DMF solutions by a two-step process from a diol (PEO, PPO, PEP), MDI, and hy-

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Table I Composition of Polyurethane-Ureas

Sample[a]	M_n[b]	w'_{EO}[c]	n_{EO}[d]	n_{PO}[d]	w_{EO}[e]	ρ[f] (g/cm^3)
PURU-PPO	1040	0	0	17.9	0	1.13
PURU-PEO						
3	290	1	6.6	—	0.353	1.20
4	400	1	9.1	—	0.43	1.19
6	600	1	13.6	—	0.53	1.19
10	1040	1	23.6	—	0.65	1.03
16	1590	1	36.1	—	0.75	0.98
PURP-PEP						
1	990	0.14	3.2	14.0	0.093	1.12
2	860	0.21	4.1	11.0	0.13	1.11
3	1090	0.34	8.5	11.0	0.23	1.10
5	1040	0.50	11.8	7.7	0.33	1.03
7	1280	0.69	2.0	5.6	0.49	1.04

[a] Abbreviations: PPO poly(propylene oxide), PEO poly(ethylene oxide), PEP triblock copolymers of ethylene and propylene oxides.
[b] Number-average molecular weight of polyether diols (PEO, PEP, PPO).
[c] Weight fraction of ethoxamer units in the soft segment.
[d] Number of ethoxamer (n_{EO}) or propoxamer (n_{PO}) units in the soft segment.
[e] Weight fraction of ethoxamer units in PURU.
[f] Density of dry PURU polymers.

drazine in molar proportion 1:2:1. Their hard segment consisted, on the average, of two MDI units connected by a hydrazine unit.

1. Molten MDI was added to a preheated solution of polyetherdiol at 50–60°C under vigorous stirring. The mixture was heated to 90°C and maintained at this temperature for 4 h under dry nitrogen. After cooling, the content of NCO groups was estimated by a standard procedure.

2. The solution of the prepolymer in DMF (26 wt %) was added to a DMF solution of hydrazine hydrate at normal temperature under vigorous stirring. The concentration of hydrazine hydrate was adjusted so that, at the end of reaction, the concentration of the product was about 20 wt % (at molar ratio NCO : H = 0.5). The reaction was stopped when the viscosity was 1.5–4 Pa.s at 30°C. At the end of reaction, the temperature of the reaction mixture increased to about 50°C. After cooling, the polymer solution was degassed at 0.5 kPa, poured on glass plates to form a layer of ca. 1 mm thickness and dried at 110°C and reduced pressure to constant weight. The thickness of films was ca. 0.15 mm.

Before sorption measurement, the foils were extracted with distilled water maintained at room temperature for 48 h, and conditioned at 23–25°C and relative vapor pressure p/p_0 0.5 for about 7 days.

Sample M-PURU, comprising no soft segments, was prepared by mixing DMF solutions of MDI and hydrazine in molar proportion 1 : 1. The final concentration was about 10 wt %. The product precipitated as a powder. It was isolated by filtration, washed with distilled water (14 h), and dried at 110°C to constant weight. In sorption measurements it was used in the powdery form or as a film (0.15 mm thick) which was prepared by molding the powder at 164°C between two aluminum foils.

Sorption Measurements

Sorption was measured at 23°C at eight to nine values of the relative pressure (0.08 $\leq p/p_0 \leq$ 0.97) in an apparatus[7,11] the principle of which has been advanced by Nemitz.[12] It consisted of two parts (Fig. 1): An apparatus for conditioning and weighing of samples (part a) and an apparatus for drying them (part b).

A PURU film (weight ca. 0.2 g, thickness ca. 0.15 mm) was suspended on a polyester fiber, the length of which was adjusted so that the sample was 20 to 30 mm above the bottom of the flask. The flask was
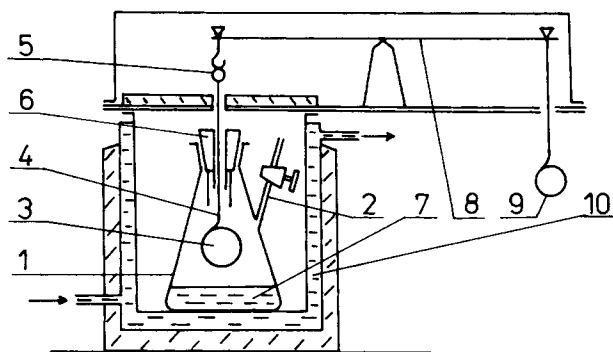
Figure 1(a) Sorption apparatus (for conditioning and weighing of samples): (1) Ehrlenmeyer flask; (2) inlet tube with stopcock; (3) polymer sample; (4) suspending polyester fiber (diameter ca. 4×10^{-3} mm, length ca. 150 mm, weight ca. 5×10^{-4} g); (5) suspending Teflon loop; (6) ground glass stopper (lubricated with silicon vaseline); (7) electrolyte solution; (8) arm of balance; (9) pan with weights; (10) thermostat.

connected to an oil pump and heated for 15 min in the drying oven at 95°C. Then the pressure was decreased below 50 Pa and drying was continued at least for 2 h. Then dry air was introduced and the flask, cooled to room temperature (ca. 30 min), was replaced by another with a layer of P_2O_5 at the bottom, and the sample was allowed to dry for at least 3 days. Thereafter, the flask was suspended on the arm of a balance and the weight of dry sample was determined.

The flask with P_2O_5 was replaced by a flask containing an electrolyte solution of known water activity (Table II) and put into a water thermostat where the temperature (23°C) was maintained at a

constant $\pm$ 0.1°C. The increase in weight was determined at intervals of 4, 8, 24, 48, and 72 h until the difference of two subsequent weights was less than 5×10^{-2} mg. This weight was taken as the equilibrium one. The time necessary to reach equilibrium was longer the higher the content of ethoxamer units in the polymer.

The data were reproducible to ca. 1%. The quality of data obtained with this apparatus was checked against those obtained with the Cahn electrobalance.[13] The correspondence of results was very good in the whole range of vapor pressure (Fig. 2). As expected, the desiccator method, which was used in previous studies with strongly sorbing substances,[8] yielded good results at $p/p_0 \geq 0.5$ only.

The sorption was expressed as the weight W (gram) of water (1), sorbed by 1 g of dry polymer (2) or (as the volume fraction of water in the system, φ_1. The former was converted into the latter by means of the equation

$$\varphi_1 = W/(W + \bar{v}_2/\bar{v}_1) \tag{1}$$

where the ratio of partial specific volumes, $\bar{v}_2/\bar{v}_1$, was replaced by the ratio of specific volumes v_2/v_1 of pure components.

The maximum sorptive capacity $\varphi_{1,m}$ corresponding to $a_1 \equiv p/p_0 \rightarrow 1$ was estimated as

$$\varphi_{1,m} = (A - B)^{-1} \tag{2}$$

where A and B are the parameters of the equation

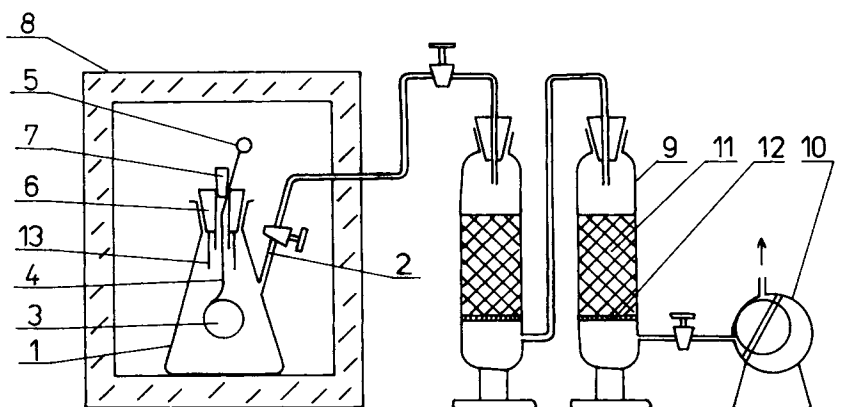$$a_1/\varphi_1, = A - Ba_1 \tag{3}$$

Figure 1(b) Apparatus for drying polymer samples: (1) to (6) as in Figure 1(a); (7) rubber stopper; (8) drying oven with forced air circulation; (9) drying tower; (10) oil pump; (11) P_2O_5; (12) fritted glass; (13) extension tube of the ground glass stopper.

Table II Saturated Aqueous Solutions (ISO 483)

p/p_0 (at 23°C)	Saturated Solution
0.12	LiCl
0.22	Potassium acetate
0.33	$MgCl_2 \cdot 6 \, H_2O$
0.434	$K_2CO_3 \cdot 2 \, H_2O$
0.545	$Na_2Cr_2O_7 \cdot 2 \, H_2O$
0.755	NaCl
0.855	KCl
0.97	K_2SO_4
1.00	Water

which fits the sorption isotherms quite well (cf. refs. 8–10).

RESULTS AND DISCUSSION

Sorption Hysteresis

Polyurethane-ureas display sorption hysteresis. It was investigated in some detail with the samples PURU-PPO, PURU-PEP/5, PURU-PEO/10, and M-PURU. It was particularly distinct with the latter polymer (Fig. 3). With the other polymer samples the difference between sorption and desorption experiments was less than 2%.
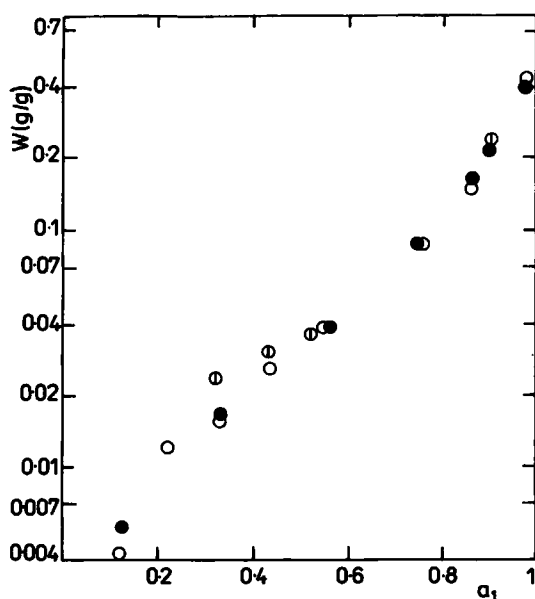
Figure 2 Comparison of sorption isotherms obtained by different methods. Sample PURU-PEO/10 at 23°C. Data points: O hydrostatic apparatus; ● Cahn RG apparatus[13]; ⊕ desiccator method.
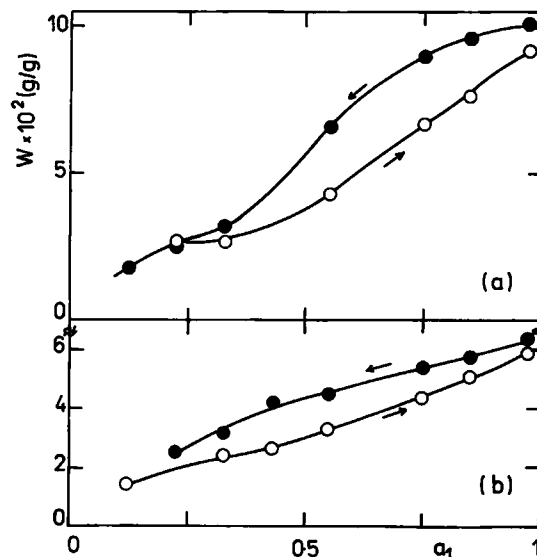
Figure 3 Hysteresis of sorption by M-PURU: (a) Powdery sample; (b) film. Data points: ● desorption, O sorption.

This finding can be explained in terms of the dual model of sorption by glassy polymers.[14] In a previous paper,[10] the sorption isotherms of polyurethane-ureas have been shown to be a combination of a localized (Langmuir) and solution sorption. The former contribution was the strongest with the sample M-PURU (which has no soft segment and is at 23°C in glassy state) and became less significant or even negligible if soft blocks (which are above T_g at 23°C) were incorporated into the chain. It appears that the strong hysteresis observed with M-PURU is due to the glassy state of the polymer. With the PEP samples the rubbery state and hydrophilicity of soft blocks account for an increased "solution" contribution to sorption; however, the "Langmuir" component to sorption, which is due to the hard segment microdomains, though it cannot be detected, may still exist.

The Effect of Polymer Structure on Sorption

Sorption centers in polyurethane-ureas are the groups —CO— and —NH— in hard segments and ether oxygen atoms in soft ones. The structurally simplest sample, M-PURU, binds at $p/p_0 = 1$ approximately one water molecule per repeating unit or, in other words, per two carbonyl groups. In this respect it is similar to more hydrophobic nylons.[15] The NH groups do not participate in the sorption.

The sorption data for PURU samples (Table III) show that the sorptive capacity increases with an

Table III   Sorption of Water Vapor by Polyurethane-Ureas (PURU) at 23°C

p/p_0	0.08	0.12	0.22	0.33	0.43	0.54	0.75	0.85	0.97
					$W \times 10^{-2}$ (g/g)				
PURU-PEO									
3	—	0.07	0.15	0.40	0.75	1.00	1.85	2.95	5.15
4	—	0.40	0.64	1.10	1.75	2.40	4.15	5.75	6.55
6	—	0.40	0.80	1.35	2.25	2.90	5.65	8.60	10.3
10	0.65	0.75	1.25	1.70	2.60	3.60	7.25	12.8	36.0
16	0.65	0.80	1.40	1.95	2.95	3.85	12.2	22.2	33.9
PURU-PEP									
1	—	0.15	0.45	0.85	1.25	1.80	2.50	3.05	3.35
2	—	0.35	0.60	1.00	1.20	1.60	2.55	3.00	9.45
3	—	0.30	0.75	1.30	1.70	2.15	3.70	5.00	10.7
5	0.39	0.45	0.75	1.10	1.90	2.60	4.65	6.55	20.7
7	—	—	1.45	2.10	3.10	3.95	5.15	9.55	34.2
PURU-PPO	—	0.30	0.40	0.50	0.90	1.05	1.65	2.00	2.85
M-PURU[a]	1.45	—	—	2.40	2.65	3.35	4.40	5.15	5.95

[a] Sorption experiments with film.

increase in the content of ethoxamer groups. That can be expected because water is a better solvent for PEO than for PPO. However, by analyzing the values of W at fixed values of water activity in de-
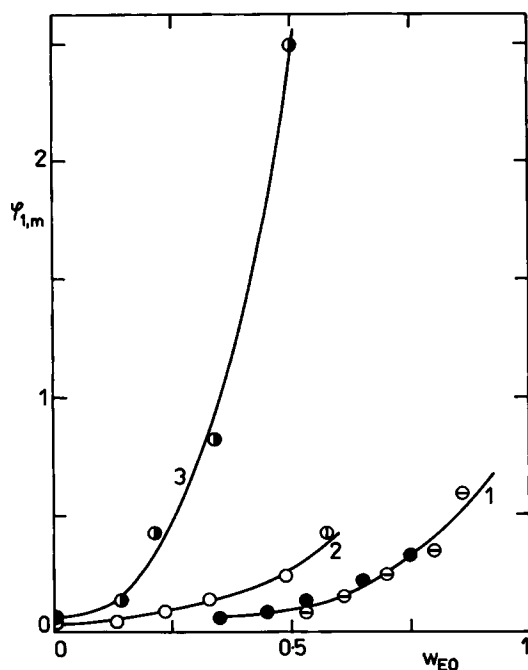

Figure 4   Dependence of the maximum sorptive capacity $\varphi_{1,m}$ on the weight fraction of ethoxamer units w_{EO} in polymers. Data points: PURU-PEO ● and PURU-PEP ○ (this paper); PUR-PEP ⦿ and PUR-PEO ⊖ (from ref. 9); PEP ◑ (from ref. 8).

pendence on the polymer composition, we find that the content of hydrophilic groups is not the only factor governing the sorptive capacity. That is illustrated by Figure 4 where the maximum sorption $\varphi_{1,m}$ calculated with eq. (2) for PURU samples has been plotted against the weight fraction of ethoxamer units w_{EO}.

Figure 4 is completed by data points for oligomeric PEP copolymers and for polyurethane samples (PUR) similar to PURU but containing no hydrazine units.[8,9] It is seen that data for the PUR samples are located at the same curve as those for corresponding PURU samples and that, at a chosen value of w_{EO}, the sorption decreases in the sequence

ether oligomers (PEP, PEO) > PEP-based polyurethanes and polyurethane-ureas > PEO-based polymers of both types.

The latter finding is particularly important and its explanation is based on a comparison of experimental data, W, with the reference values, W_r, computed under the assumption that contributions to sorption by different chain constituents are mutually independent and, consequently, additive. The W_r values have been calculated from sorption data for pure ether oligomers reported previously[8] and for the M-PURU sample (Table III).

In Figure 5 the W values at several activities have been plotted against the weight fraction w'_{EO} of ethoxamer units in the soft segments in PEP-based polyurethane-ureas (PURU-PEP) where the sum
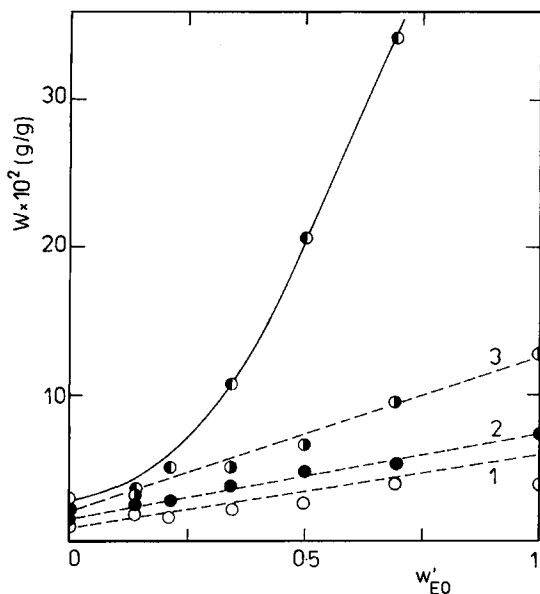
Figure 5 Dependence of sorption W at a fixed water activity on the weight fraction of ethoxamer units w'_{EO} in the soft segment of PURU samples. Data points for a_1: 0.54 ○; 0.75 ●; 0.85 ◐; 0.97 ◑. Dashed straight lines 1 to 3 correspond to $W/W_r = 0.30$.

of weight fractions of ethoxamer and propoxamer units is nearly constant, $s = w_{EO} + w_{PO} = 0.66 \pm 0.04$, but the individual values of w_{EO} and w_{PO} are different. Dashed lines correspond to $W = 0.30W_r$. They indicate that the ratio W/W_r is independent of the vapour pressure and the polyether composition. With the PURU-PEO samples the ratio $W/$
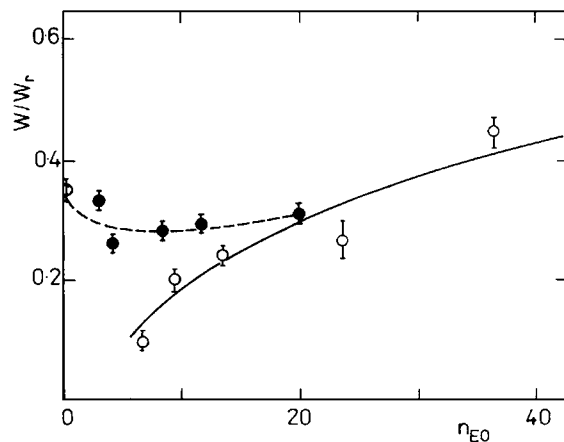

Figure 6 Dependence of the ratio W/W_r on the number n_{EO} of ethoxamer units in the soft segment. Data points for PURU-PPO ◐, PURU-PEO ○, PURU-PEP ●. Vertical bars associated with the data points indicate the range of variation of W with a_1.

W_r is invariant with respect to a_1 but not to the composition.

The invariancy with respect to the vapour pressure facilitates the analysis of data. Figure 6 presents the dependence of W/W_r on the number of ethoxamer units, n_{EO}, in the soft segment. Two dependences can be seen: A monotonically increasing one for PEO-based polyurethane-ureas (PURU-PEO) and an approximately constant value for samples based on the PPO and PEP oligomers. At $n_{EO} < 20$, the ratio is higher with the latter group although the lengths of the ethoxamer sequences are the same.

It is seen that a part of ethoxamer groups in PURU-PEO samples does not participate on sorption. The PEO-based polyurethane-ureas differ from those based on PEP in that the ethoxamer groups in the former are bound directly to the hard segments whereas, in the latter, they are separated from the hard segments by a propoxamer sequence. The position of ethoxamer units with respect to hard segments seems to play a significant role.

The difference observed in Figure 6 disappears if the data are plotted against the length of the soft segment, s (Figure 7). The plot leads us to the conclusion that the ratio W/W_r primarily depends on the length of the soft segment. It is relatively larger the longer the soft segment, irrespective of its chemical structure.

Interpretation of the Effect of Structure

It is well established that the incompatibility of hard and soft segments in polyurethanes leads to microphase separation.[16,17] Hard segments form domains stabilized by hydrogen bonding between CO and NH groups. However, the segregation is not perfect,
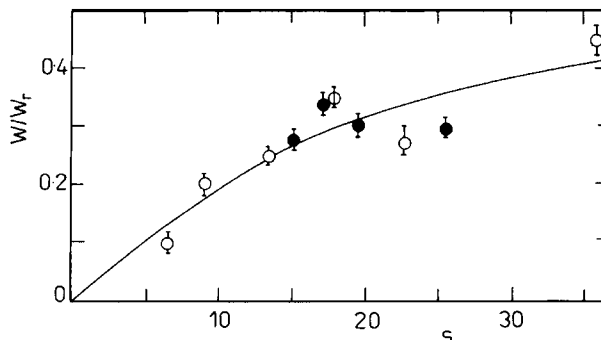

Figure 7 Dependence of the ratio W/W_r on the sum s of numbers of ethoxamer and propoxamer units in the soft segment. Notation of data points as in Figure 6.

particularly with short segments.[18-20] Infrared (IR) spectra indicate[19-23] that hydrogen bonding also forms between the NH groups of hard segments and the oxygen atoms of ether or ester groups of soft segments in the interface between segregated domains or in the region where segregation is not complete. This interaction is stronger with ester carbonyl groups than with ether units.[17,21,23]

Hard domains act as crosslinks and the soft segments represent the deformable part of the physical network. As the polyether sequences in soft segments are rather short, their deformability may depend on their length and distance from the hard segment domain to which they are bound.

The sorption of water molecules depends on the formation of vacancy which, in its turn, is associated with a conformational change of soft segment units. Those which are in the proximity of hard domains are less mobile and less deformable. Hence, their participation on the interaction with water is restricted. The same holds for ether units which are hydrogen bonded to the hard segment in the interface or in the regions where hard and soft segments are mixed. In this case, hydrogen bond formation between water and soft or hard segment units competes with the existing hydrogen bonds between hard and soft segments.

The shorter the soft segment, the less likely are the conditions for a conformational change of ether units and for sorption of water. This hypothesis may explain the dependence of W/W_r on the sum s of the numbers of ethoxamer and propoxamer units in Figure 6 and the increasing trend of curve 1 in Figure 5 (for PEO-based PURU samples).

The contribution to sorption by propoxamer units is substantially weaker than by ethoxamer ones. If the former are prevented from interaction with water by the proximity of hard segment domains or by their hydrogen bonding with NH groups of hard segments, the impact on the sorption is less pronounced than it is if ethoxamer groups are shielded.

The finding (Fig. 4) that the sorption is higher with PURU-PEP than with PURU-PEO at the same weight fraction of ethoxamer units can be understood if we realize the difference in the position of ethoxamer units with respect to the hard segment. In PURU-PEO samples at low s values, the ethoxamer sequences are short and, therefore, more tightly bound to the hard segment domains. Hence, the amount of loci where interaction with water can take place is reduced. The values of W/W_r are low (0.1–0.2) and so is the overall sorption. In PURU-PEP, it is the propoxamer sequence at both ends of the soft segment which is shielded by the hard segment from the interaction with water whereas the ethoxamer sequences in the middle of the soft segment are accessible to water molecules. Because the latter groups are more hydrophilic, the sorption of water is higher than in the previous case.

CONCLUSIONS

The sorption of water by polyurethane-ureas based on triblock copolymers of ethylene and propylene oxides depends not only on the content of ethoxamer units but also on the overall length of the soft blocks and on the position of ethoxamer units with respect to the hard segments. The latter appear to "shield" the neighboring soft segment units from the interaction with water.

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