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Infrared Spectroscopic Examination of the Surfaces of Hydrated Copoly(ether–urethane–ureas)

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ABSTRACT: The surface morphologies of a series of copoly(ether–urethane–urea) elastomers differing in polyether block molecular weight and structure were studied in the desiccated, water-hydrated, and deuterium oxide (D_2O) hydrated states. Infrared spectra obtained by attenuated total reflection showed an increased extent of urethane carbonyl hydrogen bonding and the appearance of free (not hydrogen bonded) NH groups upon equilibrium hydration of desiccated polymer films. Hydration-associated vibrational band alterations were noted for the urethane and urea carbonyl groups as well as the polyether C–O–C group. Results of infrared dichroic ratio measurements suggest that, upon hydration, portions of the polymer chain in the surface region become sufficiently mobile to reorient. Spectroscopic evidence does not support changes in phase separation in the surface region upon hydration. These results are consistent with a model where water or D_2O, in the surface region, becomes a hydrogen bond donor for some urethane carbonyls while free NH is generated by breakage of NH–polyether oxygen bonds.

Introduction

Results of contact angle experiments on a variety of methacrylate-based hydrogel polymers have suggested that surface molecules may reorient to maximize polar group interaction with water.[1-3,42,43] Even more rigid polymers such as polystyrene may reorient upon contact with water.[4] Yasuda et al.[5] have suggested that molecular mobility, as well as the number of hydrophilic groups, determines if a molecule will reorient at the surface upon hydration. Employing X-ray photoelectron spectroscopy (XPS), Ratner et al.[6] have observed hydration-associated changes in the structure of methacrylate hydrogels grafted to silastic rubber.

Copoly(ether–urethanes) are composed of short, alternating blocks of polyether and polyurethane segments. The two blocks are mutually insoluble, resulting in a two-phase microstructure of urethane segment domains dispersed in a matrix of polyether.[7] Bulk morphology changes of the copoly(ether–urethanes) have been studied with respect to hydrogen bonding, phase separation, and molecular orientation upon mechanical stress.[7-17] Spectroscopic studies of desiccated copoly(ether–urethane) films indiate that the surface region is enriched in polyether segments.[7,16] Recent reports suggest that hydration of selected copoly(ether–urethanes) may influence the morphology in the surface region. Grasel et al.[8] observed that the surface of some alkylated copoly(ether–urethanes) became more hydrophilic upon immersion in water, suggesting a change in the surface morphology of the polymer. Contact angle hysteresis in a series of commercially available copoly(ether–urethanes) and copoly(ethersiloxane–urethane–ureas) varying in polyether block molecular structure and weight suggested to Tingey et al.[18] that hydration resulted in changes in surface molecular orientations. Tingey et al.[18] have also presented preliminary infrared spectra of desiccated and hydrated copoly(ether–urethane) surfaces indicating hydration-dependent alterations in both urethane and polyether spectral regions.

The present study examines the morphology of a series of copoly(ether–urethane–urea) (PEUU) surfaces in the desiccated and equilibrium hydrated states. Of particular interest is the effect of hydration on hydrogen bonding and molecular orientation in the surface region. Since XPS studies have indicated that copoly(ether–urethane–urea) surfaces are enriched in polyether segments,[16,19,20] hydration effects on the PEUU films will be studied as a function of polyether block molecular structure and weight. Studies of the surface morphology are carried out by Fourier transform infrared spectroscopy with attenuated total reflectance (FTIR-ATR) under dichroic conditions to provide surface structural information of fully hydrated polymer films.

Experimental Section

Dimethyl sulfoxide (DMSO, EM Science, Inc.) was distilled at reduced pressure after drying over $CaSO_4$ for 24 h. The fraction boiling at 69.5–71 °C/7 mmHg pressure was taken and stored in an amber bottle at 5 °C. Methyl isobutyl ketone (MIBK, Mallinckrodt, Inc.) was dried for 24 h over $CaSO_4$ and distilled at atmospheric pressure. The fraction boiling at 107–108 °C was taken and stored at 5 °C. Methylenebis(4-phenyl isocyanate) (MDI, Eastman Kodak Co.) was purified by dissolving in an equal volume of boiling hexane and used immediately. The hot solution was treated with charcoal and filtered into an equal volume of ice-cold hexane. Poly(tetramethylene oxide) (PTMO, Polyscience, Inc., molecular weight 1000 and 2000) was degassed for 3 h at 100 °C under vacuum and stored in a desiccator. Poly(propylene glycol) (PPG, Baker Chemical, molecular weight approximately 1000 and 2000) was degassed overnight at 100 °C and stored over molecular sieves. Ethylenediamine (Fisher Scientific Co.) was freshly distilled at atmospheric pressure, and the fraction at 109–110 °C was collected.

The synthetic procedure has been previously reported by Knutson and Lyman.[19] Two series of PEUU polymers were prepared, each series consisting of a high and a low molecular weight polyether block. The first series was based on poly(tetramethylene oxide) (PTMO), and the second series was based on poly(propylene glycol) (PPG). The urethane–urea segments were identical for all four polymers.

In 100 mL of solvent (equal parts DSMO/MIBK), 0.03 mol of PTMO, molecular weight 1000 or 2000, was combined with 0.06 mol of MDI and heated to 80 °C for 2 h. After the mixture cooled to room temperature, 0.03 mol of ethylenediamine was added. The reaction mixture was stirred for an additional 20 min and then precipitated in deionized water. The copoly(ether–urethane–ureas) based on PTMO 1000 and 2000 molecular weight segments are denoted as PEUU-P1 and PEUU-P2, respectively.

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For the PPG-based polymers, 0.1 mol of PPG, molecular weight approximately 1000 or 2000, was combined with 0.2 mol of MDI and heated to 85 °C for 2 h. After the mixture cooled to room temperature, 0.1 mol of ethylenediamine was added. The reaction mixture was stirred for an additional 20 min and then precipitated. The copoly(ether–urethane–ureas) based on PPG 1000 and 2000 molecular weight segments are denoted as PEUU-G1 and PEUU-G2, respectively. Sixty milliliters of filtered polymer solution (3% w/v in distilled DMAC) was rapidly added to 500 mL of deionized water, and the precipitant was collected and washed several times with deionized water. Finely cut solid polymer was dispersed in equal parts of methanol (HPLC grade) and deionized water and stirred continuously for 1 week at room temperature. The swelling solvent was changed twice. The polymer was dispersed in deionized water for another week and then vacuum-dried for 24 h before storing at room temperature.

Films of polymer were solution cast by spreading 2 mL of a 10% solution (w/v) in DMAC on a precleaned (hot Micro solution followed by a 2-day soak in chromic acid) standard glass microscope slide (18.75 cm^2). Solvent was removed by heating for 1 h at 70 °C followed by vacuum drying (approximately 3-μm pressure) at room temperature for 24 h. Water-extractable components were removed by soaking the films for 2 weeks in deionized water. The films were then vacuum dried for 24 h. To ensure that phase separation had reached equilibrium, desiccated polymer films were stored at room temperature for 1 month prior to use.[21]

All FTIR-ATR spectra were collected on a Digilab FTS 20/80 spectrometer (Digilab Division, BioRad, Inc., nitrogen gas purged and a liquid nitrogen cooled MCT detector). A 4× beam condensing ATR accessory (Harrick Scientific, Inc.) was used with germanium crystals (25 mm × 5 mm × 2 mm) aligned at an incident angle of 60°. A quadrupole diamond high-efficiency beam polarizer (Harrick Scientific) was employed. All spectra (1024 scans at 1-cm^{-1} resolution, triangular apodization) were collected at 27 °C. Band absorbances were determined after baseline flattening at 3750, 2450, 1790, and 885 cm^{-1}. Band positions were determined by a center of gravity algorithm.[22] Band position reproducibility for ATR measurements is ±1 cm^{-1}.

Since the effective sampling depth probed by internal reflection is dependent on the infrared radiation polarization, the simple ratio of absorbances is not an accurate estimate of the dichroic ratio.[23] The x, y, and z components of the infrared radiation absorption coefficient ($k(x)$, $k(y)$, and $k(z)$, respectively) can be determined where the x–y plane is considered to be the polymer film surface in contact with the crystal and the z-axis extends perpendicularly into the film. If the film is isotropic in the x–y plane, the dichroic ratio $k(z)/k(x)$ can provide structural information about molecular groups near the surface.[24-27] The absorption coefficients $k(x)$, $k(y)$, and $k(z)$ were determined from polarized FTIR-ATR reflectivity measurements by the method of Fluornoy and Schaffers[28]

$$\ln R_e = -4{n_2}^2 k(x)/({n_1}^2 \tan\phi[1 - ({n_{21}}^2/\sin^2\phi)(1 - {n_{21}}^2)]) \quad (1)$$

$$\ln R_m = \frac{-4{n_2}^2(k(z) + k(y)[1 - ({n_{21}}^2 \sin^2\phi)])}{({n_1}^2 \tan\phi[1 - ({n_{21}}^2/\sin^2\phi)(1 - ({n_{21}}^2/\sin^2\phi) + {n_{21}}^4 \cot^2\phi)])} \quad (2)$$

where $n_{21} = n_2/n_1$ and R_e and R_m are the reflectivities under perpendicular and parallel polarization, respectively. The refractive index of the polymers (n_2) was estimated to be 1.5, and the refractive index of the germanium internal reflection crystal (n_1) was 4.0. The angle of incidence (ϕ) was 60°. Substitution of these values simplies eqs 1 and 2 to

$$\ln R_e = -0.4192k(x) \quad (3)$$

$$\ln R_m = -0.3574k(y) - 0.4399k(z) \quad (4)$$

If the polymer sample is rotated 90° in the x–y plane, eqs 3 and 4 become

$$\ln R_e = -0.4192k(y) \quad (5)$$

$$\ln R_m = -0.3574k(x) - 0.4399k(z) \quad (6)$$

From the spectra of the sample in the two orthogonal positions and at the two orthogonal polarizations, the three absorption coefficients can be calculated.

Table I
Ratio of XPS Carbon 1s Band Areas

	ratio	observed	theoretical
PEUU-P1	C–O/C–C[a]	0.73	0.38
	N–C–O/C–C[b]	0.035	0.054
PEUU-P2	C–O/C–C	0.81	0.49
	N–C–O/C–C	0.028	0.035
PEUU-G1	C–O/C–C	1.09	0.52
	N–C–O/C–C	0.047	0.06
PEUU-G2	C–O/C–C	1.3	0.69
	N–C–O/C–C	0.03	0.04

[a] C–O/C–C: band area ratio of carbon bonded to oxygen/carbon bonded to carbon. [b] N–C–O/C–C: band area ratio of carbamate carbon/carbon bonded to carbon.

Polymer films were hydrated for at least 3 weeks at room temperature in deionized water or deuterium oxide (D_2O 99.9%, Cambridge Isotope Laboratory). For FTIR-ATR experiments, two pieces of polymer were removed from the hydrating solution and blotted with clean lens paper to remove excess liquid, and the glass-cast side was applied against the germanium crystal. The crystal and polymer were wrapped with a piece of precleaned aluminum foil to maintain hydration. Infrared spectra were collected in both the parallel and perpendicular polarization modes as described.

The fraction of urethane carbonyl groups participating in hydrogen bonding (X_B) was calculated by

$$X_B = (A_B/1.2)/[A_F + (A_B/1.2)] \quad (7)$$

where A_B and A_F are the absorbance intensities of the hydrogen-bonded and free urethane carbonyls, respectively.[31] The reported values are the average of results obtained under parallel and perpendicular polarizations.

Thermal analysis (DSC) of desiccated and water-hydrated polymers was carried out by using a Perkin-Elmer DSC-4 linked to a Perkin-Elmer thermal analysis data station. The heating rate was 20 °C/min, and the sample masses were 15 ± 3 mg.

Fixed-angle X-ray photoelectron spectroscopy (XPS or ESCA) of the glass-cast surface of desiccated PEUU films was performed with a Hewlett-Packard Model 595B spectrometer.[19] Monochromatic Al K_α radiation and a 6-eV flood gun were employed. Operational pressure was 10^{-9} Torr. Scans were collected at an angle of 37° and a pass energy of either 100 or 25 eV. All data manipulations employed standard Hewlett-Packard software. The curve-fitting routine utilized a Gaussian function. Band areas were determined from the curve-fitted peaks.

Results and Discussion

Copoly(ether–urethane–urea) morphology has been extensively studied and is thought to consist of urea segment domains interfacing through the urethane linkage to the polyether matrix.[19,29-33] In general, the XPS carbon 1s spectra of copoly(ether–urethane–ureas) are composed of three overlapping bands centered near 289.5 eV (carbamate carbon), 286.5 eV (carbon σ-bonded to oxygen), and 285 eV (carbon bonded to carbon or nitrogen), representing urea domains and urethane interface, polyether matrix, and remaining carbons, respectively.[16,19,34] Listed in Table I are the band area ratios of carbamate carbon/carbon bonded to carbon and carbon bonded to oxygen/carbon bonded to carbon, along with the theoretical ratios of the carbon atoms participating in bonds representative of a bulk sample, as determined from the repeat unit, for the four PEUUs employed in the present study. Compared to the theoretical band area ratios, an increase in carbon bonded to oxygen and a decrease in carbamate carbon is observed. These results indicate that, within the first 100 Å or so, the glass-cast PEUU surfaces are dominated by excess polyether blocks.[19]

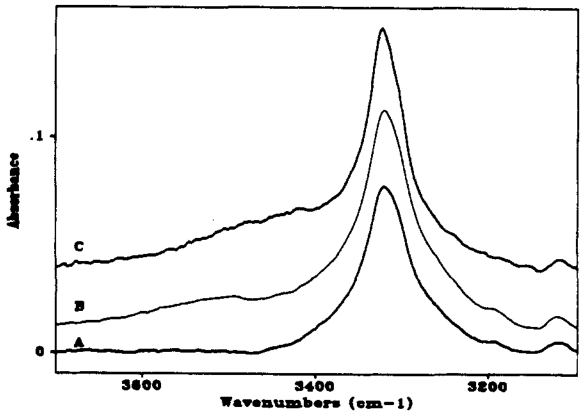

Figure 1. Infrared spectra of the N–H stretching vibrations of desiccated (A), water-hydrated (B), and D_2O-hydrated (C) PEUU-P1.

Figure 1 shows the 3700–3000-cm^{-1} region of PEUU-P1 in the desiccated and hydrated states. Center of gravity band positions and tentative assignments for all polymers examined are listed in Table II. For the desiccated film of PEUU-P1, a single symmetrical band is observed near 3320 cm^{-1} corresponding to the hydrogen-bonded NH stretching vibration. Free (not hydrogen bonded) NH stretching bands absorbing near 3500 cm^{-1} are not present in the desiccated spectrum.[7,32] For the water-hydrated film, the dominant band is still observed near 3320 cm^{-1}, and a shoulder has appeared near 3500 cm^{-1} suggesting that hydration results in the freeing of some NH groups from hydrogen bonding. Since the OH stretching band vibrations of water overlap in this spectral region,[35] the polymer NH stretching region was examined after hydration in D_2O. Following hydration in D_2O, a shoulder is again observed near 3500 cm^{-1}, as well as the band at 3320 cm^{-1}, confirming that hydration of the film does lead to the freeing of some NH groups from hydrogen bonding. Similarly, while only hydrogen-bonded NH stretch bands are observed in the desiccated PEUU-P2, PEUU-G1, and PEUU-G2 films, the infrared spectra of water and D_2O-hydrated films show both hydrogen-bonded (3320 cm^{-1}) and free (a shoulder near 3500 cm^{-1}) NH stretch bands (spectra not shown). Hydration has no effect on the asymmetric and symmetric CH stretching vibration band positions of all polymers examined.

Figure 2 shows the 1800–1600-cm^{-1} region of PEUU-P1 in the desiccated and hydrated states. For the desiccated PEUU-P1 film, the free and hydrogen-bonded urethane carbonyl stretching frequencies absorb near 1730 and 1707 cm^{-1}, respectively. The hydrogen-bonded urea carbonyl stretching vibrations are centered at 1636 cm^{-1}. The urea and urethane carbonyl stretching bands exhibit slight shifts to lower frequencies upon water or D_2O hydration. Similar frequency shifts of the urethane and urea carbonyl band positions are observed for hydrated PEUU-P2, PEUU-G1, and PEUU-G2 films (spectra not shown). Free (not hydrogen bonded) urea carbonyl stretching bands absorbing near 1695 cm^{-1} are not present in any desiccated or hydrated polymer spectra.[32] In the desiccated state, the bands appearing at 1535 and 1224 cm^{-1} represent mixed vibrational modes of NH bending and CN stretch and upon hydration in water shift to higher frequencies. In the 1600–1400-cm^{-1} region, significant spectral differences are observed between D_2O-hydrated and H_2O-hydrated films and may be attributed to NH-to-ND group exchange.[32] For all polymers examined, the aromatic C–C stretching bands near 1412 cm^{-1} are unaffected by hydration. For PEUU-P1 and PEUU-P2, the ether stretching vibration position near 1110 cm^{-1} is not influenced by hydration while a slight shift to lower frequencies is observed upon hydration of PEUU-G1 and PEUU-G2.

Table II
Vibrational Frequencies and Tentative Assignments of Desiccated, Water-Hydrated, and D_2O-Hydrated PEUU

vibrational frequency, cm^{-1}			
desiccated	water hydrated	D_2O hydrated	tentative assignment
		PEUU-P1	
	3494(sh)	3485(sh)	NH stretch (free)
3320.9	3320.9	3322.9	NH stretch (H-bonded)
2941.4	2941.4	2941.4	CH_2 stretch (asymmetric)
2857	2857	2857	CH_2 stretch (symmetric)
1731.5	1730.6	1725.8	C=O stretch urethane (free)
1708.4	1707.9	1702.1	C=O stretch urethane (H-bonded)
1636.1	1635.1	1634.7	C=O stretch urea (H-bonded)
1535.8	1537.2	[a]	NH bend, CN stretch
1413.3	1413.4	[a]	C–C stretch (benzene)
1221.9	1224.3	[a]	NH bend, CN stretch
1110.0	1109	[a]	CH_2–O–CH_2 stretch
		PEUU-P2	
	3541(sh)	3500.3(sh)	NH stretch (free)
3322.8	3321.8	3325.2	NH stretch (H-bonded)
2940.9	2940.9	2940.9	CH_2 stretch (asymmetric)
2855.6	2855.6	2856	CH_2 stretch (symmetric)
1732.0	1731.5	1726.7	C=O stretch urethane (free)
1709.4	1708.9	1704.1	C=O stretch urethane (H-bonded)
1637	1636.5	1635.6	C=O stretch urea (H-bonded)
1535.8	1536.7	[a]	NH bend, CN stretch
1413.1	1413.1	[a]	C–C stretch (benzene)
1221.4	1224.9	[a]	NH bend, CN stretch
1110.0	1110	[a]	CH_2–O–CH_2 stretch
		PEUU-G1	
	3494(sh)	3496(sh)	NH stretch (free)
3319.9	3322.8	3322.3	NH stretch (H-bonded)
2972.3	2972.7	2972.7	CH_2 stretch (asymmetric)
2869.1	2871	2871.5	CH_2 stretch (symmetric)
1727.7	1726.7	1722.4	C=O stretch urethane (free)
1710.3	1708.9	1705	C=O stretch urethane (H-bonded)
1635.6	1634.6	1633.2	C=O stretch urea (H-bonded)
1534.8	1536.7	[a]	NH bend, CN stretch
1413.3	1413.4	[a]	C–C stretch (benzene)
1224.7	1226.7	[a]	NH bend, CN stretch
1104.2	1102.4	[a]	CH–O–CH_2 stretch
		PEUU-G2	
	3494(sh)	3507(sh)	NH stretch (free)
3323.3	3323.3	3323.3	NH stretch (H-bonded)
2971.3	2971.8	2917.8	CH_2 stretch (asymmetric)
2869.1	2870.5	2870	CH_2 stretch (symmetric)
1729.1	1727.7	1724.3	C=O stretch urethane (free)
1711.3	1709.4	1707.9	C=O stretch urethane (H-bonded)
1636.5	1634.1	1633.2	C=O stretch urea (H-bonded)
1535.3	1536.7	[a]	NH bend, CN stretch
1413.3	1413.4	[a]	C–C stretch (benzene)
1224.1	1225.7	[a]	NH bend, CN stretch
1104.2	1102.0	[a]	CH–O–CH_2 stretch

[a] Band vibrational assignment unclear due to overlap by OD or ND bending.[35] sh = shoulder

Listed in Table III are the full bandwidths at half-height for the urea carbonyl stretching bands and the ether group stretching bands in the desiccated and hydrated states. For all polymers examined, the widths of the urea carbonyl stretching bands and ether group stretching bands increase upon hydration.

Hydrogen bonding in desiccated copoly(ether–urethane–urea) films has been extensively studied.[3,19,29,30,32,33] In the urea segment domains, the urea NH groups are the proton donors and the urea carbonyl groups serve as proton

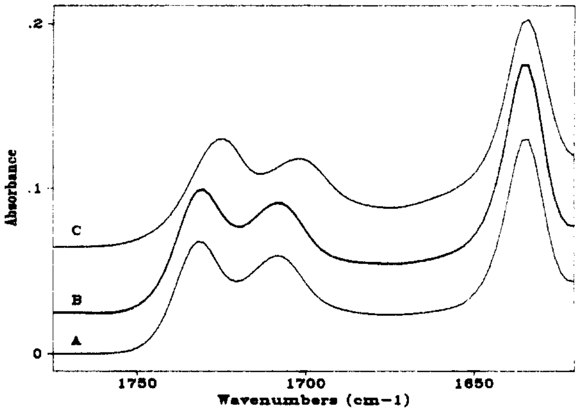

Figure 2. Infrared spectra of the urethane and urea carbonyl stretching vibrations of desiccated (A), water-hydrated (B), and D_2O-hydrated (C) PEUU-P1.

Table III
Full Bandwidths at Half-Height of Urea Carbonyl Stretch and Ether Stretch Vibrations for Desiccated and Hydrated PEUU

PEUU	desiccated[a]	water hydrated[a]	D_2O hydrated[a]
	Urea Carbonyl Stretch Band		
PEUU-P1	17.4 ± 0.1	23.8 ± 1.1	21.5 ± 0.8
PEUU-P2	19.0 ± 0.2	23.2 ± 0.1	21.0 ± 0.8
PEUU-G1	19.8 ± 0.1	25.3 ± 0.7	22.0 ± 0.1
PEUU-G2	20.5 ± 0.8	25.7 ± 0.4	21.4 ± 0.1
	Ether Stretch Band		
PEUU-P1	46.1 ± 1.2	50.6 ± 0.9	*b*
PEUU-P2	41.9 ± 0.1	46.6 ± 0.8	*b*
PEUU-G1	71.2 ± 0.1	75.6 ± 0.5	*b*
PEUU-G2	65.0 ± 0.7	68.5 ± 0.8	*b*

[a] Average value ± 95% confidence limits. [b] Bandwidth unclear due to overlap by ND bending.[35]

Table IV
Fraction of Urethane Carbonyl Groups Hydrogen Bonded for Desiccated, Water-Hydrated, and D_2O-Hydrated Polymers

	fraction bonded[a]		
PEUU	desiccated	water hydrated	D_2O hydrated
PEUU-P1	0.430 ± 0.004	0.440 ± 0.005	0.441 ± 0.004
PEUU-P2	0.359 ± 0.003	0.370 ± 0.005	0.405 ± 0.002
PEUU-G1	0.362 ± 0.001	0.387 ± 0.002	0.376 ± 0.005
PEUU-G2	0.321 ± 0.005	0.337 ± 0.005	0.332 ± 0.001

[a] Average value ± 95% confidence limits.

acceptors.[19,30,36] It has been postulated that, in a well phase separated PEUU, a single proton-accepting urea carbonyl forms a three-dimensional dihydrogen bond between two neighboring proton-donating NH groups.[19,30,36] Since such a network of interurea hydrogen bonds would be largely disrupted upon phase mixing, the extent of urea carbonyl hydrogen bonding indicates the degree of hard domain phase separation.[19] In the interfacial region, urethane NH groups are the proton donors, while possible proton acceptors include both urethane carbonyl groups and polyether oxygens.[3,10,19] In those instances where the interfacial region is narrow, most of the urethane carbonyl groups are hydrogen bonded, leaving only a small fraction of urethane NH groups hydrogen bonded to the polyether oxygens.[19] When the interfacial region is broad, additional urethane NH groups interact with polyether oxygens, resulting in a higher fraction of free (nonbonded) urethane carbonyls.[19]

Reported in Table IV are the fractions of urethane carbonyl groups that are hydrogen bonded for the desiccated and hydrated states. The results for desiccated films indicate a majority of the urethane carbonyl groups are not hydrogen bonded. Since in the desiccated state the infrared spectra show no evidence of free (nonbonded) NH stretching vibrations, the majority of the urethane NH groups of the desiccated polymers must be hydrogen bonded to polyether oxygens. In the desiccated state, the higher molecular weight polyether block PEUU shows a lower fraction of hydrogen-bonded urethane carbonyls than the corresponding lower polyether molecular weight PEUU, suggesting the urethane interfacial regions for PEUU-P2 and PEUU-G2 contain more urethane–polyether oxygen–hydrogen bonds than those of PEUU-P1 and PEUU-G1.

Table V
Glass Transition Temperatures (°C) of Desiccated and Water-Hydrated Polymers

	dry[a]	H_2O hydrated[a]
PTMO-1000	-80.1 ± 0.3 (-83.5 to -72.5)	
PTMO-2000	-80.6 ± 0.2 (-83.4 to -68.5)	
PEUU-P1	-54.5 ± 0.7 (-56.7 to -40.6)	-55.4 ± 0.5 (-61.0 to -41)
PEUU-P2	-71.7 ± 0.4 (-74.6 to -59.5)	-71.6 ± 0.3 (-74.4 to -60.1)
PEUU-G1	-26.5 ± 0.5 (-30.1 to -20.1)	-27.2 ± 0.9 (-32.4 to -22.7)
PEUU-G2	-50.8 ± 0.3 (-54.5 to -40.3)	-51.2 ± 0.6 (-55.5 to -38.2)

[a] Average value ± 95% confidence limits. Numbers in parentheses are the temperature range over which the T_g was observed.

Upon hydration, urethane carbonyl hydrogen bonding increases for all polymers studied (Table IV). For copoly(ether–urethane) elastomers in the desiccated state, increases in the extent of urethane carbonyl hydrogen bonding have been interpreted to be as a result of an increase in phase separation.[10,20,31,32] In the present study, the DSC data (Table V) do not support an increased phase segregation upon hydration. T_g values of hydrated polymer films are identical with those of the desiccated films, indicating that no change in bulk-phase segregation has occurred upon hydration. Spectroscopic evidence does not indicate an increase in phase separation in the surface region upon hydration since increased phase separation should not result in the appearance of free NH stretching vibrations (the shoulder observed at 3500 cm^{-1}). Spectroscopic evidence also indicates no decrease in phase separation in the surface region since such a decrease should break the extensive interurea hydrogen-bonding network, resulting in the appearance of free (nonbonded) urea carbonyl stretching vibrations. In all cases, hydrated films did not show any evidence of free urea carbonyl vibrations. In a study of a series of desiccated PEUU films, Wang and Cooper[31] attributed increased urethane carbonyl hydrogen bonding to an increase in urethane–urea domain ordering. In the present study, the observation of free NH stretching bands suggests hydration-induced increases in domain ordering are probably not occurring.

In order to be confident that a real increase in urethane carbonyl hydrogen bonding was being observed, possible sources of error were evaluated. It could be argued that the strong water OH bending band absorbing near 1640 cm^{-1} (ref 35) could interfere with a quantitative determination of hydrogen bonding of the carbonyls. Compared to desiccated films, an increase in hydrogen bonding of D_2O-hydrated films is observed, indicating the increase in hydrogen bonding with hydration is not an artifact of overlapping OH bending vibrations. Another possible mechanism to explain hydration-sensitive carbonyl hydrogen bonding would be as a result of polymer degradation similar to that observed for polyester-based urethane elastomers.[37,38] In the present study, the urethane hydrogen bonding returned to original values upon redesiccation (data not shown). Therefore, polymer degradation is probably not occurring.

The shifts of band position of the urethane and urea carbonyl stretching bands as well as bandwidth broadening of the urea carbonyl and ether stretching bands suggest that water interacts with the urea domains, the interfacial urethane regions, and the polyether matrix. The simultaneous increase in hydrogen bonding of the urethane carbonyls and decrease in hydrogen bonding of NH groups suggest that water, and not urethane NH, is acting as the proton donor for these carbonyls. The hydration-associated vibrational frequency shifts of the urethane carbonyl bands are consistent with this hypothesis. Since no free urea carbonyl bands are observed, interurea hydrogen bonding is probably not disrupted upon hydration. This suggests the free NH groups observed upon hydration are generated in the interfacial regions by breaking either interurethane or urethane-to-polyether oxygen–hydrogen bonds. Since Isihara et al.,[32] Sung and Schneider,[13] as well as Srichatrapinuk and Cooper[10] have shown that interurethane hydrogen bonds are much stronger than those between urethane and polyether oxygens, the free NH groups in hydrated PEUU films may be the result of breaking of the lower energy urethane-to-polyether oxygen–hydrogen bonds.

In order to gain more insight into the interaction with water, infrared dichroism studies of the surface region of the PEUUs were also undertaken. The orientation behavior of molecular groups expected to interact with water was studied by measuring the dichroic ratio changes of the urea carbonyl stretching bands, the urethane hydrogen-bonded carbonyl stretching bands, and the ether stretching bands. These bands were chosen for their unambiguous vibrational assignments in the desiccated and hydrated states. The x, y, and z components of the absorption coefficient ($k(x)$, $k(y)$, and $k(z)$, respectively) were calculated from eqs 1–6. Since the method of Flournoy and Schaffers[28] requires the collection of four spectra to determine the three unknown variables, two values of $k(z)$ can be estimated. Garton et al.[26] and Castillo et al.[39] have indicated that when the ratio of the redundant values is one, reproducible optical contact between the samples and the internal reflection element has been achieved. For each vibrational band examined, the ratio of (redundant) $k(z)$ values was 1.0 ± 0.2 (average value ± 95% confidence limits), indicating that equivalent optical contact was attained for the two orientations of the film.

In order to confirm that the optical contact was equivalent for desiccated and hydrated films, the integrated intensities of the aromatic C–C stretching bands (1412 cm^{-1}) were examined. This vibrational band did not exhibit hydration-associated alterations in band position, bandwidth, or dichroic ratio and therefore could be employed as a measure of optical contact. For each polymer, no difference was observed between the integrated intensities of the aromatic stretching bands of desiccated and hydrated films when spectra obtained under identical polarization were compared (data not shown). This observation confirms that the optical contact between the sample and the internal reflection element was equivalent for the desiccatted and hydrated polymers. Thus, any hydration-associated changes in the dichroic ratios are real and not an artifact of varying optical contact.

Table VI
Dichroic Ratios of Desiccated, Water-Hydrated, and D_2O-Hydrated PEUU

frequency, cm^{-1} [a]	desiccated[b]	water hydrated[b]	D_2O hydrated[b]
	PEUU-P1		
1731	0.852 ± 0.026	0.874 ± 0.043	0.869 ± 0.059
1708	0.920 ± 0.033	0.988 ± 0.032	0.983 ± 0.039
1635	0.465 ± 0.031	0.586 ± 0.046	0.544 ± 0.043
1413	0.803 ± 0.011	0.798 ± 0.077	c
1111	0.890 ± 0.025	0.994 ± 0.046	0.943 ± 0.024
	PEUU-P2		
1731	0.805 ± 0.031	0.851 ± 0.040	0.854 ± 0.027
1709	0.798 ± 0.033	0.876 ± 0.042	0.891 ± 0.028
1636	0.592 ± 0.023	0.666 ± 0.044	0.695 ± 0.024
1412	0.742 ± 0.035	0.775 ± 0.063	c
1110	0.879 ± 0.046	0.998 ± 0.057	0.960 ± 0.026
	PEUU-G1		
1728	0.814 ± 0.013	0.798 ± 0.013	0.848 ± 0.046
1709	0.792 ± 0.016	0.867 ± 0.011	0.879 ± 0.032
1636	0.534 ± 0.039	0.739 ± 0.012	0.643 ± 0.022
1412	0.725 ± 0.073	0.713 ± 0.013	c
1105	0.808 ± 0.014	0.849 ± 0.012	0.850 ± 0.036
	PEUU-G2		
1728	0.818 ± 0.013	0.799 ± 0.081	0.841 ± 0.066
1709	0.869 ± 0.013	0.839 ± 0.075	0.843 ± 0.041
1637	0.587 ± 0.016	0.649 ± 0.081	0.634 ± 0.029
1412	0.744 ± 0.020	0.703 ± 0.082	c
1105	0.869 ± 0.015	0.965 ± 0.098	0.964 ± 0.025

[a] Frequency listed is that of the desiccated polymer. [b] Average value ± 95% confidence limits. [c] Uncertain as to assignment due to overlap with ND and OD bending.

For all polymers and all frequencies examined, $k(x)/k(y) = 1$ (data not shown), indicating as expected that no preferential orientation of any molecular group occurred in the x–y plane. Changes in orientation of molecular segments in the surface region with respect to the z-axis should be reflected in changes in the dichroic ratio $k(z)/k(x)$.[24,39] Table VI lists the dichroic ratios for all polymers examined in the desiccated and hydrated states. For all polymers, the dichroic ratios of the hydrogen-bonded carbonyl stretching bands, the urea carbonyl stretching bands, and the ether stretching bands are significantly greater in the hydrated state than in the desiccated state. This suggests that hydration results in the orientation of the urethane carbonyls, the urea carbonyls, and the polyether oxygens within the surface regions such that the resulting moments of transition of the molecular group vibrations are, on average, preferentially pointing along the z-axis.[24] While the urea carbonyl groups do seem to undergo preferential orientation upon hydration, the lack of an effect observed on the aromatic C–C stretching band (1412 cm^{-1}) suggests that packing within the urea segment domains is not significantly influenced. Dichroic ratio changes of the hydrogen-bonded urethane carbonyl stretching bands are consistant with the conclusion that water is the proton donor in the hydration-associated increase in urethane carbonyl hydrogen bonding. Dichroic ratio changes of the ether oxygen stretching bands are consistent with the previous conclusion that PEUU hydration results in the disruption of urethane NH-to-polyether oxygen–hydrogen bonds. Taken together, these results suggest that, within the surface regions sampled, portions of the polymer chains seem to have sufficient mobility to reorient. The reorientation is probably to maximize polar interactions with water.

Since the surface regions of PEUUs are enriched in polyether segments,[16,19] it was expected that polyether molecular structure and weight would influence the properties of the hydrated polymer surface. The hydration-associated urethane carbonyl hydrogen-bonding changes listed in Table IV and the dichroic ratio changes observed in Table VI indicate that the infrared spectra of both the PTMO- and PPG-based PEUU are similarly influenced by hydration. These results are consistent with those of Schneider et al.,[40] who found water vapor transport rates to be nearly identical for PTMO- and PPG-based copoly(ether-urethane) films. The results may also be related to the observations of Takahara et al.,[33,41] who found the water contents of hydrated PPG- and PTMO-based copoly(ether-urethane) films to be equal for polyether segment molecular weights 1000 and 2000. While clearly deserving more study, the apparent equal influence of hydration on PPG- and PTMO-based PEUU may be related to the fact that, at room temperature, the polyether blocks are approximately 50-70 °C above their glass transition temperature (Table V).

Conclusions

Hydration of PEUU surfaces results in an increase in the hydrogen bonding of the urethane carbonyl groups and a decrease in the hydrogen bonding of the amide nitrogens. Water is probably the proton donor for the increased urethane carbonyl hydrogen bonding and seems to be involved in the breaking of urethane NH-to-polyether oxygen-hydrogen bonds. These changes may be the result of orientational rearrangements of the functional groups in the urea domain, the interfacial urethane region, and the polyether matrix upon hydration. In the range studied, polyether segment structure and molecular weight have no effect on hydration-associated orientation and hydrogen-bonding changes. The results of the present study clearly indicate that the desiccated surface is not an adequate model for the chemical morphology of the PEUU-aqueous interface.

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References and Notes

(1) Holly, F. J.; Refojo, M. F. *J. Biomed. Mater. Res.* **1975**, *9*, 315.
(2) Ratner, B. D. In *Hydrogels in Medicine and Pharmacy*; Peppas, N., Ed.; CRC Press: Boca Raton, FL; 1986; Vol. 1, p 85.
(3) Ko, Y. C.; Ratner, B. D.; Hoffman, A. S. *J. Colloid Interfac. Sci.* **1981**, *82*, 25.
(4) Good, R. J.; Kotsidas, E. D. *J. Colloid Interfac. Sci.* **1978**, *66*, 360.
(5) Yasuda, H.; Sharma, A. K.; Yasuda, T. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1285.
(6) Ratner, B. D.; Weathersby, P. K.; Hoffman, A. S.; Kelly, M. A.; Shcarper, L. H. *J. Appl. Polym. Sci.* **1978**, *22*, 643.
(7) Lelah, M. D.; Cooper, S. L. *Polyurethanes in Medicine*; CRC Press: Boca Raton, FL, 1986.
(8) Grasel, T. G.; Pierce, J. A.; Cooper, S. L. *J. Biomed. Mater. Res.* 1987, *21*, 815.
(9) Brunette, C. M.; Hsu, S. L.; MacKnight, W. J. *Macromolecules* **1982**, *15*, 71.
(10) Srichatrapinuk, V.; Cooper, S. L. *J. Macromol. Sci., Phys.* **1978**, *B15*, 267.
(11) Huh, D. S.; Cooper, S. L. *Polym. Eng. Sci.* **1971**, *11*, 369.
(12) Sung, C. S. P.; Schneider, N. S. *J. Mater. Sci.* **1978**, *13*, 1689.
(13) Sung, C. S. P.; Schneider, N. S. *Macromolecules* **1977**, *10*, 452.
(14) Seymour, R. W.; Cooper, S. L. *Macromolecules* **1973**, *6*, 48.
(15) Wilkes, G. L.; Dziemianowicz, T. S.; Ophir, Z. H.; Artz, E.; Wildnauer, R. *J. Biomed. Mater. Res.* **1979**, *13*, 189.
(16) Ratner, B. D.; McElroy, B. J. In *Spectroscopy in the Biomedical Sciences*; Gendreau, R. M., Ed.; CRC Press: Boca Raton, FL, 1988.
(17) Seymour, R. W.; Estes, G. M.; Cooper, S. L. *Macromolecules* **1970**, *3*, 579.
(18) Tingey, K. G.; Andrade, J. D.; Zdrahala, R. L.; Chittur, K. K.; Gendreau, R. M. In *Surface Characterization of Biomaterials*; Ratner, B. D., Ed.; Elsevier: Amsterdam, 1988; p 255.
(19) Knutson, K.; Lyman, D. J. In *Biomaterials: Interfacial Phenomena and Applications*; Cooper, S. L., Peppas, N. A., Eds.; ACS Advances in Chemistry Series; American Chemical Society: Washington, DC, 1982; p 109.
(20) Globe, G. L.; Gardella, J. A.; Chin, R. L.; Salvanti, L. *Appl. Spectrosc.* **1988**, *42*, 989.
(21) Wilkes, G. L.; Bagnodian, S.; Humphries, W.; Widnauer, R. *Polym. Lett.* **1975**, *13*, 321.
(22) Cameron, D. G.; Kauppinen, J. K.; Moffatt, D. J.; Mantsch, H. H. *Appl. Spectrosc.* **1982**, *36*, 245.
(23) Harrick, N. J. *Internal Reflection Spectroscopy*; Harrick Scientific Corp.: Ossining, NY, 1987.
(24) Tshmel, A. E.; Vettegren, V. I.; Zolotarev, V. M. *J. Macromol. Sci., Phys.* **1982**, *B21*, 243.
(25) Sung, C. S. P. *Macromolecules* **1981**, *14*, 591.
(26) Garton, A.; Carlsson, D. J.; Wiles, D. M. *Appl. Spectrosc.* **1981**, *35*, 432.
(27) Jasse, B.; Koenig, J. L. *Rev. Macromol.* Chem. **1979**, *C17*, 61.
(28) Flournoy, P. A.; Schaffers, W. J. *Spectrochim. Acta* **1966**, *22*, 5.
(29) Wilkes, G. L.; Abouzahr, S. *Macromolecules* **1981**, *14*, 458.
(30) Sung, C. S. P. *Macromolecules* **1981**, *14*, 212.
(31) Wang, C. B.; Cooper, S. L. *Macromolecules* **1983**, *16*, 775.
(32) Isihara, H.; Kimura, I.; Saito, K.; Ono, H. *J. Macromol. Sci., Phys.* **1974**, *B10*, 591.
(33) Takahara, A.; Tashita, J.; Kijiyama, T.; Takayanagai, M.; McKnight, W. J. *Polymer* **1985**, *26*, 987.
(34) Andrade, J. D. In *Surface and Interfacial Aspects of Biomedical Polymers*; Vol. 1; Andrade, J. D., Ed.; Plenum Press: New York, 1985; p 105.
(35) Pinchas, S.; Laulicht, I. *Infrared Spectra of Labelled Compounds*; Academic Press: New York, 1971.
(36) Bonart, R.; Marbitzer, L.; Muller, E. H. *J. Macromol. Sci., Phys.* **1974**, *B9*, 447.
(37) Brown, D. W.; Lowry, R. E.; Smith, L. E. *Macromolecules* **1980**, *13*, 248.
(38) Brown, D. W.; Lowry, R. E.; Smith, L. E. *Macromolecules* **1982**, *15*, 453.
(39) Castillo, E.; Koenig, J.; Anderson, J.; Kiment, C. K.; Lo, J. *Biomaterials* **1984**, *5*, 186.
(40) Schneider, N. S.; Dusablon, L. V.; Snell, E. W.; Prosser, R. A. *J. Macromol. Sci. Phys.* **1969**, *B3*, 623.
(41) Takahara, A.; Tashita, J. I.; Kajuyama, T.; Takayanagi, M. T. *Int. Prog. Urethanes* **1985**, *4*, 16.
(42) Andrade, J. D.; Gregonis, D. E.; Smith, L. M. In *Surface and Interfacial Aspects of Biomedical Polymers*; Andrade, J. D., Ed.; Plenum Press: New York, 1985; Vol. 1, p 15.
(43) Andrade, J. D.; Smith, L. M.; Gregonis, D. E. In *Surface and Interfacial Aspects of Biomedical Polymers*; Andrade, J. D., Ed.; Plenum Press: New York, 1985, Vol. 1, p 249.