Infra-red spectroscopy study of equilibrium association of urethane groups in poly(ether urethane)s

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The equilibrium association of urethane groups in a series of 4,4′-diphenylmethane diisocyanate/poly(propylene oxide)-based poly(ether urethane) elastomers was studied on the basis of infra-red spectroscopy data. Thermodynamic parameters of the urethane-group association were estimated. The hard-segment equilibrium state was shown to fit a model of monomer solution association.

(Keywords: polyurethanes; infra-red Fourier spectroscopy; amide I band; urethane-group association; thermodynamic parameters)

INTRODUCTION

The majority of the rather numerous publications on the morphology of poly(ether urethane) elastomers (PUE) have been devoted to the structural study of a diisocyanate-based hard domain[1–3]. However, not enough attention has been paid to thermodynamic factors defining microheterogeneity of these polymer systems. Apparently, this accounts to a great extent for the lack of reliable quantitative data characterizing the equilibrium state of microheterogeneity in PUE, which makes difficult the experimental testing of rare attempts to describe the PUE morphology in terms of Flory–Huggins theory relative to polymer blends and block copolymers[4,5]. We think that, experimentally, thermodynamic parameters of hard segment–soft segment incompatibility may be determined by considering the structure of hydrogen bonds as distinctive markers that characterize the equilibrium state of a urethane group in aggregates (associates) of different types.

It appears that the best evidence on hard–soft segment incompatibility in PUE may be obtained using i.r. spectroscopy to study the structure of the amide I absorption band, the latter being very capable of differentiating between the hydrogen bonds of the urethane group. This approach was implemented in ref. 6, which made it possible to calculate in the first approximation the values of ΔH and ΔS for hydrogen bonds in polyurethane systems. However, in this paper, as in most other publications[4,7], the amide I band was considered only as a two-component one. Further studies[8,9] showed that the amide I band included more components and, therefore, the values of the thermodynamic parameters obtained in ref. 6 may be considered only as indicative ones.

In the present study an attempt is made to define by means of i.r. spectroscopy the basic thermodynamic parameters of intermolecular interactions in typical hydrogen-bonded PUE structures relying upon the recent data of amide I absorption band analysis[10].

EXPERIMENTAL

PUE samples were synthesized in bulk from 4,4′-diphenylmethane diisocyanate (MDI) and poly(propylene oxide) (PPO) of various molecular weights. The components were mixed at 80°C in the presence of stannous octoate as a catalyst. The spectra in the main i.r. region were obtained from 5–15 μm thick films cast from 5 wt% dimethylformamide (DMF) solution on CaF_2 windows. The main portion of the solvent was evaporated in the oven at 70°C for 2 days and the samples were then dried under vacuum at 40 to 50°C for 24 h. To obtain the spectra at elevated temperatures, a thermostated cell was used, namely an air oven with forced air circulation. The cell temperature was controlled within ± 0.5°C accuracy. I.r. spectra were recorded on a Bruker IFS-85 spectrophotometer at a resolution of 2 cm^{-1}.

RESULTS AND DISCUSSION

The iteration procedure of damping least squares[11] was used to describe a separate band contour by means of an equation that is a Lorentzian and Gaussian combination. The number of separate bands comprising the complex amide I band contour was determined previously for some PUE samples and model systems using both deconvolution and subtraction methods[10]. The fit of the estimated and experimental complex band

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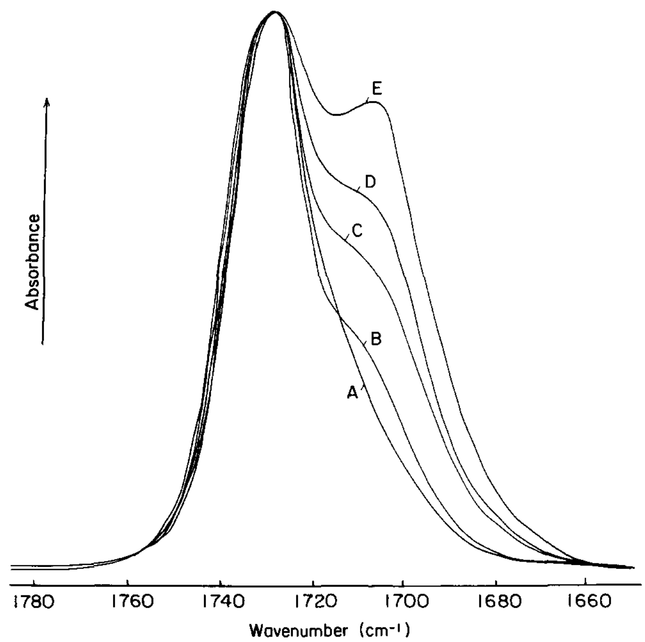


Figure 1 I.r. spectra of PUE samples in the amide I band region at 20°C: 0.876 mol kg^{-1} MDI (A); 1.576 mol kg^{-1} MDI (B); 2.181 mol kg^{-1} MDI (C); 2.712 mol kg^{-1} MDI (D); 3.464 mol kg^{-1} MDI (E)

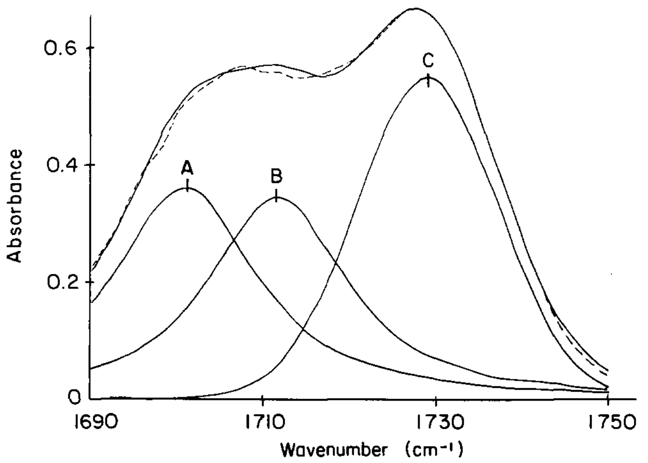


Figure 2 Experimental (- - -) and estimated (——) contours of complex and separated (A–C) bands of PUE (20°C, hard-segment concentration 3.464 mol kg^{-1})

contours was fair, but we took as a criterion of adequacy the invariability (for all the samples tested) of separate band parameters derived from the iteration procedure, such as frequency and half-width, which are crucial for the quantitative assessment of urethane groups corresponding to separate components of the complex amide I band. The iteration software was written in FORTRAN-77 for an IBM PC. Two versions of the program were used: calculation of all the parameters for every band, and iteration with stabilization of frequencies and half-widths. The first version resulted in slightly scattered values of the parameters owing to inevitable experimental errors caused essentially by some uncertainty in noise elimination. The data obtained were used to calculate the average values (except for the absorption intensities), which then served as the basis for the second-stage calculation with parameter stabilization.

For the room-temperature-based computation, the system was optimized as a three-component one for all the PUE samples tested. Excellent consistency of the calculated parameters and hence of the ratios of separate component absorption intensities were observed within a wide range of urethane group levels. As an example the amide I band contours for a series of PUE samples at 20°C are given in *Figure 1*. The deviation of a calculated contour from the experimental one for a PUE sample, as well as the results of the complex band splitting into components, are reported in *Figure 2*. At temperatures above 40°C two additional components appeared at 1738 and 1720 cm^{-1} (see *Figure 3*). Averaged values of frequencies and half-widths (in parentheses) for all the isolated absorption bands were as follows: 1737.8 (15.1), 1729.1 (18.1), 1719.9 (18.0), 1711.3 (19.2), 1700.8 (20.3). To calculate the content of urethane groups corresponding to certain absorption bands, one has to know their absorptivity coefficients. It was shown[12] that for amide groups of similar composition the amide I band absorptivity coefficient values may not be sensitive to hydrogen-bonding build-up. In this case the integral amide I band absorptivity coefficient is not dependent on the degree of association at increasing urethane-group content in the system. The determination of the absolute values of absorptivity coefficients directly in polymer films is difficult, since, at high urethane-group content, film thickness measurements in the range of 2–5 μm are not sufficiently accurate and, moreover, the film thickness may vary over the sample length. The use of a reference band does not afford the necessary reliability, as it is not certain that the band chosen as an inherent reference is not affected by urethane-group association. For example, the aryl absorption band at 1600 cm^{-1} in *N*-arylurethanes is quite sensitive to hydrogen bonding. In this respect we used model systems, i.e. solutions of *N*-phenylbutylurethane in carbon tetrachoride, in which spectrum virtually the same amide I band structure occurs as in PUE at temperatures higher than 40°C. High accuracy of the interferometric cuvette thickness measurements allowed us to estimate the absolute integral absorptivity coefficient values of the amide I band (*Figure 4*). The negligible (within 5%) dependence of this coefficient on the degree of urethane-group association makes it possible to determine the fraction of urethane

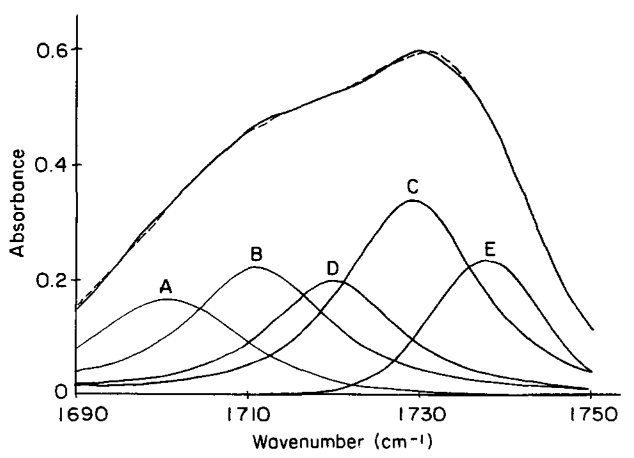


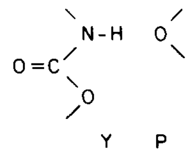
Figure 3 Experimental (- - -) and estimated (——) contours of complex and separated (A–E) bands of PUE samples (100°C, hard-segment concentration 3.464 mol kg^{-1})

groups associated with the corresponding absorption band as the ratio between the integral absorption intensity of the band characteristic of the urethane groups occupying a certain position in the associate, and the total integral absorption intensity of the complex amide I band. The fractions, *F*, of the bands isolated for the case of calculation with parameter stabilization are given in *Table 1*.

Calculation of constants and thermodynamic parameters of urethane-group association

A model of urethane-group association has been proposed in the form of a chain associate[7,10]. This model is in good agreement with the results of structural analysis, including X-ray diffraction[2,13,14]:

I



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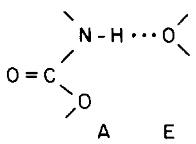

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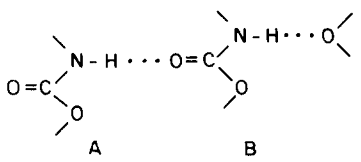

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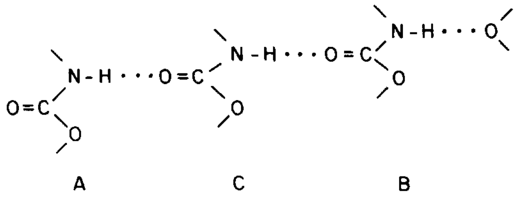

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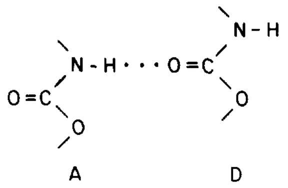

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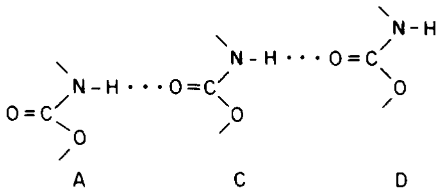


Here P and E are polyether fragments, free and hydrogen-bonded with the urethane group, respectively. According to the above model the urethane group Y free from any hydrogen bonds absorbs at 1738 cm^{-1} and appears distinctly only at a temperature as high as 40°C; therefore it could not be recorded in ref. 15. The urethane group A, which is the end-group in any associate, absorbs at 1729 cm^{-1}. The urethane group B, which is the 'head' group in all associates except **II**, absorbs at 1711 cm^{-1}, and the internal urethane group C absorbs at 1701 cm^{-1}. It might be assumed that the band at 1720 cm^{-1}, which

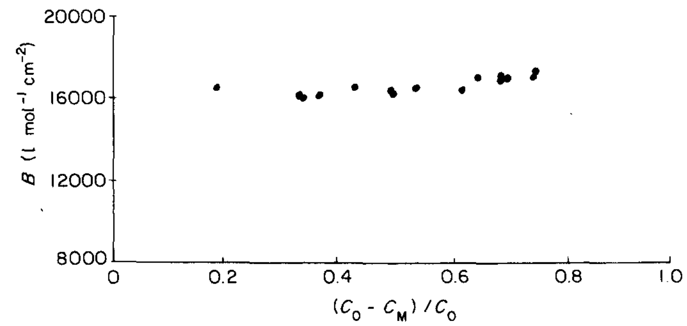


Figure 4 The variation of amide I band integral absorptivity coefficient values (B) as a function of the degree of urethane-group association for a series of *N*-phenylbutylurethane solutions in carbon tetrachloride (0.027–1.160 mol l^{-1})

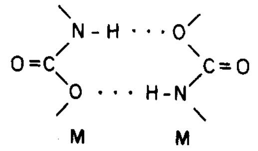
Table 1 Urethane-group contents[a] in PUE samples that correspond to separate components of the amide I band

MDI level (mol kg^{-1})	1738 cm^{-1} *F*	1738 cm^{-1} *C* (mol kg^{-1})	1729 cm^{-1} *F*	1729 cm^{-1} *C* (mol kg^{-1})	1720 cm^{-1} *F*	1720 cm^{-1} *C* (mol kg^{-1})	1711 cm^{-1} *F*	1711 cm^{-1} *C* (mol kg^{-1})	1701 cm^{-1} *F*	1701 cm^{-1} *C* (mol kg^{-1})
60°C										
0.88	0.210	0.18	0.529	0.46	0.080	0.07	0.135	0.12	0.046	0.04
1.58	0.151	0.24	0.475	0.75	0.097	0.15	0.178	0.28	0.098	0.15
2.18	0.137	0.30	0.410	0.89	0.100	0.22	0.186	0.41	0.166	0.36
2.71	0.101	0.27	0.430	1.17	0.073	0.20	0.219	0.58	0.178	0.48
3.46	0.098	0.34	0.385	1.33	0.091	0.32	0.235	0.81	0.231	0.80
80°C										
0.88	0.301	0.26	0.447	0.39	0.105	0.09	0.105	0.09	0.042	0.04
1.58	0.222	0.35	0.418	0.66	0.110	0.17	0.140	0.22	0.110	0.17
2.18	0.181	0.40	0.381	0.83	0.121	0.26	0.175	0.38	0.142	0.31
2.71	0.144	0.39	0.373	1.01	0.117	0.32	0.214	0.58	0.151	0.41
3.46	0.124	0.43	0.344	1.19	0.130	0.45	0.228	0.79	0.220	0.76
100°C										
0.88	0.342	0.30	0.401	0.35	0.113	0.10	0.100	0.09	0.044	0.04
1.58	0.279	0.44	0.383	0.60	0.127	0.20	0.140	0.22	0.070	0.11
2.18	0.235	0.51	0.368	0.80	0.140	0.31	0.147	0.32	0.110	0.24
2.71	0.183	0.50	0.326	0.88	0.158	0.43	0.195	0.53	0.139	0.38
3.46	0.161	0.56	0.292	1.01	0.153	0.53	0.211	0.73	0.183	0.63

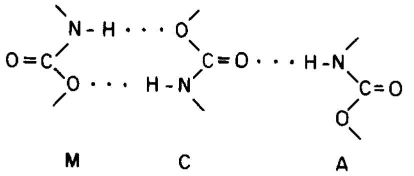
[a] *F* values have been estimated with root mean square error ± 5% at 95% confidence level

appears at higher temperatures simultaneously with the band at 1738 cm^{-1}, was attributable to the urethane groups D forming polyether free linear associates. However, it appeared that the proposed model was far from the real association since in that case some of the calculated constants had negative values. It is shown[16] that the dimer formed as a result of monomer urethane association in carbon tetrachloride solution, in the absence of competing proton acceptors, exists most probably in the cyclic form. In this case the associates **V** and **VI** will be rearranged into their cyclic form:

VII



VIII



Here M, C and A are the urethane groups absorbing at 1720, 1701 and 1729 cm^{-1} respectively. To simplify calculations, we decided to confine ourselves to the formation of the cyclic dimer **VII**. Thus, the mechanism of association may be generalized as follows:

$$\mathrm{C_{PE}+C_M \overset{k_1}{\rightleftharpoons} C_A}$$

$$\mathrm{C_A+C_M \overset{k_0}{\rightleftharpoons} C_D}$$

$$\mathrm{C_D+C_M \overset{k_0}{\rightleftharpoons} C_T}$$

$$\vdots$$

$$\mathrm{C}_{n-1}+\mathrm{C_M} \overset{k_0}{\rightleftharpoons} \mathrm{C}_n$$

$$\mathrm{C_M+C_M \overset{k_2}{\rightleftharpoons} C_{CD}}$$

where we use the following notation: $\mathrm{C_{PE}}$, free polyether; $\mathrm{C_M}$, free urethane; $\mathrm{C_A}$, urethane groups linked only with polyether oxygen; $\mathrm{C_D}$, urethane dimers **III**; $\mathrm{C_T}$, urethane trimers **IV**; and so on; C_n, urethane *n*-mers; $\mathrm{C_{CD}}$, cyclic urethane dimers. It may be easily shown that the concentrations of urethane groups attributable to the components resulting from amide I band splitting will be expressed (using *italics* to represent concentrations of corresponding species) as:

$$C_{1729}=k_1C_{\mathrm{PE}}C_{\mathrm{M}}+(k_1k_0C_{\mathrm{PE}}C_{\mathrm{M}}^2+k_1k_0^2C_{\mathrm{PE}}C_{\mathrm{M}}^3+\cdots$$
$$+k_1k_0^nC_{\mathrm{PE}}C_{\mathrm{M}}^{n+1}+\cdots)$$

$$C_{1720}=2k_2C_{\mathrm{M}}^2$$

$$C_{1711}=k_1k_0C_{\mathrm{PE}}C_{\mathrm{M}}^2+k_1k_0^2C_{\mathrm{PE}}C_{\mathrm{M}}^3+k_1k_0^3C_{\mathrm{PE}}C_{\mathrm{M}}^4+\cdots$$
$$+k_1k_0^nC_{\mathrm{PE}}C_{\mathrm{M}}^{n+1}+\cdots$$

$$C_{1701}=k_1k_0^2C_{\mathrm{PE}}C_{\mathrm{M}}^3+2k_1k_0^3C_{\mathrm{PE}}C_{\mathrm{M}}^4+3k_1k_0^4C_{\mathrm{PE}}C_{\mathrm{M}}^5+\cdots$$
$$+nk_1k_0^{n+1}C_{\mathrm{PE}}C_{\mathrm{M}}^{n+2}+\cdots$$

$$C_0-C_{\mathrm{M}}=k_1C_{\mathrm{PE}}C_{\mathrm{M}}+[2k_1k_0C_{\mathrm{PE}}C_{\mathrm{M}}^2+3k_1k_0^2C_{\mathrm{PE}}C_{\mathrm{M}}^3+\cdots$$
$$+(n+1)k_1k_0^nC_{\mathrm{PE}}C_{\mathrm{M}}^{n+1}+\cdots]$$

for $n=1, 2, 3, \ldots$ and where C_0 is total concentration of the urethane groups. With

$$C_{\mathrm{M}}=\frac{C_{1729}-C_{1711}}{k_0C_{\mathrm{PE}}}$$

and the concentration of the hydrogen-bond-free polyether being

$$C_{\mathrm{PE}}=C_{\mathrm{PE}}^{\circ}-C_{1729}$$

the solution of the set of equations for k_1, k_0, k_2 yields:

$$k_1=\frac{C_{1729}-C_{1711}}{(C_{\mathrm{PE}}^{\circ}-C_{1729})C_{\mathrm{M}}}$$

$$k_0=\frac{C_{1701}}{(C_{1711}+C_{1701})C_{\mathrm{M}}}$$

$$k_2=\frac{C_{1720}}{2C_{\mathrm{M}}^2}$$

where C_{PE}° is total concentration of the polyether. The content of monomer units in the polyether was taken as its concentration, since, according to the calculations, this is the only assumption permitting one to obtain values of the association constants.

Table 2 The ratio of association constants for DU solution in THF at 20°C

DU level (mol l^{-1})	$k_2^{1/2}/k_1$ (mol$^{1/2}$ l$^{-1/2}$)	$k_2^{1/2}/k_0$ (mol$^{1/2}$ l$^{-1/2}$)
0.326	5.1	1.1
0.488	4.8	0.9
0.562	4.6	0.9
0.671	5.6	0.8
0.922	5.0	0.9
1.08	4.3	1.0

To validate the proposed association model, we estimated the ratio of association constants for a model MDI/*N*-butanol-based diurethane (DU) solution in tetrahydrofuran (THF); see *Table 2*. In this case absolute values of the constants could not have been determined because of the extremely low concentrations of urethane groups totally free from hydrogen bonds. A polyether concentration term in the expressions for calculating equilibrium constants was substituted for a THF concentration one.

The association constants obtained for PUE samples at different temperatures are reported in *Table 3*. By isolating a dimerization constant from the chain association one, which is the routine procedure in chain association computations[17], we realized that for this complicated association scheme the values of the constants for dimerization and subsequent association are essentially the same.

Thermodynamic parameters calculated from the log *K* *versus* 1/*T* relationship are given in *Table 4*. They are close to those defined for model urethane solutions in carbon tetrachloride[16]. It is seen from the data shown in *Table 4* that the association enthalpy of a hydrogen-bonded system is relatively low.

CONCLUSION

Thus, for some types of PUE, containing no low-molecular-weight chain extenders (which provides for

Table 3 Urethane-group association constants

MDI level							
(wt%)	(mol kg^{-1})	k_1 (kg mol^{-1})	$\bar{k}_1$ (kg mol^{-1})	k_2 (kg mol^{-1})	$\bar{k}_2$ (kg mol^{-1})	k_0 (kg mol^{-1})	$\bar{k}_0$ (kg mol^{-1})
60°C							
10.9	0.88	0.126	(0.16±0.03)[a]	1.04	(1.3±0.2)	1.38	(1.5±0.1)
19.7	1.58	0.150		1.35		1.49	
27.3	2.18	0.140		1.22		1.58	
33.9	2.71	0.204		1.32		1.64	
43.3	3.46	0.181		1.37		1.46	
80°C							
10.9	0.88	0.076	(0.10±0.01)	0.662	(0.9±0.2)	1.09	(1.14±0.08)
19.7	1.58	0.095		0.708		1.26	
27.3	2.18	0.097		0.847		1.14	
33.9	2.71	0.106		1.04		1.06	
43.3	3.46	0.109		1.22		1.14	
100°C							
10.9	0.88	0.059	(0.066±0.009)	0.552	(0.68±0.15)	1.02	(0.86±0.09)
19.7	1.58	0.066		0.518		0.758	
27.3	2.18	0.080		0.581		0.835	
33.9	2.71	0.068		0.870		0.839	
43.3	3.46	0.057		0.852		0.833	

[a] In parentheses average values with root mean square error at 95% confidence level

Table 4 Thermodynamic parameters of the urethane-group association

Equilibrium	$-\Delta H$ (kJ mol^{-1})	$-\Delta S$ (e.u.)
$C_{PE}+C_M \overset{k_1}{\rightleftharpoons} C_A$	22.9 (±0.2)[a]	20.1 (±0.2)
$C_M+C_M \overset{k_2}{\rightleftharpoons} C_{CD}$	16.1 (±0.3)	11.0 (±0.3)
$C_{n-1}+C_M \overset{k_0}{\rightleftharpoons} C_n$ ($n \geqslant 2$)	14.6 (±0.2)	9.7 (±0.2)

[a] In parentheses root mean square error at 95% confidence level

hard-segment monodispersity), the hard-segment equilibrium state may be easily described in the framework of a model of monomer association in solutions. Evidently, for the majority of real PUE systems having hard-segment molecular weights as low as 1000, the theories developed for conventional block copolymers or polymer mixtures are not sufficiently valid to estimate correctly hard (isocyanate) and soft (polyether) segment interaction.

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