Structure–property relationships for a series of crown ether-containing polyurethane-ureas

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Polyurethane-ureas with dibenzo-18-crown-6 in the rigid chain fragments were characterized by small-angle X-ray scattering (SAXS), differential scanning calorimetry (d.s.c.), deformation calorimetry and gas transport measurements. As-cast samples are structurally microheterogeneous systems in which the composition and the relative content of different microphases varies with the chain length and the chemical nature of the soft component. As a general trend, the thermodynamic affinity between rigid and soft fragments becomes worse (i.e. the degree of microphase separation α^* increases) when the chain length of the latter increases and/or when an oligoether component is replaced with an oligoester of similar length. Thermoelastic and gas transport properties of the samples depend not only on their nominal chemical composition and α^* but also on the pattern of molecular packing within the rigid fragment-containing microphases.

(Keywords: segmented polyurethane-ureas; phase morphology; thermoelasticity)

INTRODUCTION

Segmented polyurethanes belong to a large family of thermoplastic elastomers whose properties depend on the relative proportions of the rigid and flexible chain fragments as well as on the degree of phase separation, α^*, between the components. The latter effect arises due to the contribution from a special 'boundary interphase' (BI) of intermediate composition which owes its existence to the limited mutual solubility of two pure components[1]. Theoretically, the contribution from the BI would vary from highest at $\alpha^* = 0$ (i.e. in the case of a perfect mixing of components with no pure phase of either component available) to vanishingly small at $\alpha^* = 1$ (in the other extreme case of an infinitely thin boundary between two incompatible components). However, in practice, the case of α^* close to unity should be regarded as very unlikely for block copolymers (segmented polyurethanes included) even at complete incompatibility of different blocks due to covalent bonds between the latter.

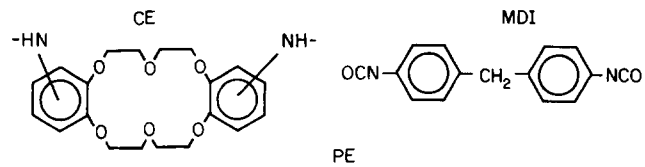
According to general thermodynamic arguments[1,2], the value of α^* (and, consequently, the contribution from the BI) may be varied in a fairly broad interval by changing either the length of an uninterrupted sequence of components or the chemical composition of the latter, or both. A simple and attractive way to reach this goal is to choose fragments with different molecular architecture for construction of the rigid chain blocks. This approach seems promising for improvement of not only mechanical properties but also of transport characteristics of polyurethanes since it satisfies the general criterion for selection of a membrane material with good gas separation properties from polymers with 'chemically heterogeneous' chain repeating units[3–5].

It is the purpose of the present paper to characterize the effect of the incorporation of a crown ether into the rigid chain blocks of a series of polyurethane ureas (CPUUs) on the phase morphology, and thermophysical and transport properties.

EXPERIMENTAL

Materials

CPUUs of the general structure, [–CE–MDI–PE–MDI–], where CE is dibenzo-18-crown-6, MDI is 4,4'-diphenylmethane diisocyanate and PE is oligopropylene glycol with molecular mass of 430, 1050 and 2100 (samples CPUU-1/430, CPUU-1/1050 and CPUU-1/2100, respectively), oligoethylene glycol with molecular mass of 400 (sample CPUU-2) or oligoethylene glycol adipate with molecular mass of 430 (sample CPUU-3),



$[CH_2CH(CH_3)]_n$ --► (CPUU-1) $[(CH_2)_4O]_n$ --► (CPUU-2)

$[(CH_2)_2OCO(CH_2)_4COO]_{2.5}$ --► (CPUU-3)

were synthesized in two stages[6]. In the first stage, a prepolymer was obtained by reaction between MDI and PE; in the second stage, a stoichiometric quantity of CE dissolved in DMF was added to the prepolymer solution. After careful degassing of CPUU solutions under low pressure at room temperature for several hours, thin (0.1–0.3 mm), visually defectless films were prepared by solution casting onto a Teflon substrate and subsequent evacuation to a constant weight. As judged by intrinsic

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viscosity measurements in DMF at room temperature (0.88–0.99 ml g^{-1}), all of the CPUUs obtained had comparable molecular masses.

Methods

The heat capacity C_p of initial (as-cast) and homogenized (quenched into liquid nitrogen after heating to 450–470 K) samples was measured (maximum error below 4%) in the temperature interval 140–450 K with the aid of a home-made differential calorimeter with diathermal cells[7] at a constant heating rate $q = 2$ deg min^{-1}. Complementary measurements at higher temperatures (400–520 K) were carried out with a commercial differential scanning calorimetry (d.s.c.) instrument, model DSM-2M (Biophysical Instrumentation C Pushchino, Russia) at $q = 16$ deg min^{-1}. In the region of overlap, the experimental data agreed to within 6%.

An RRM-type diffractometer (Ni-filtered copper radiation, $K\alpha = 0.154$ nm) was used for small-angle X-ray scattering (SAXS) measurements in the range of scattering angles from 0.1 to 3° at a sample-to-detector distance of 25 cm[8]. The scattering curves were normalized by scattering volume and corrected for absorption of X-rays by the studied samples.

Mechanical work, W, and concomittant heat effects, Q, were measured (mean errors 2 and 3%, respectively) at room temperature with the aid of a home-made deformation calorimeter[9]. Two regimes of uniaxial deformation were employed, the first (loading–unloading regime) involving stretching the sample to a predetermined elongation, λ, waiting for a complete relaxation of both stretching force and heat flow, and subsequent contraction after unloading at the same cross-head speed. In the second regime, (step-like loading regime), the sample was stretched to a predetermined elongation, allowed to relax keeping λ constant, and stretched once again to higher λ. In both regimes, measurements were carried out at a constant deformation rate of 1.7×10^{-3} s^{-1}.

Coefficients of permeability, K, and of diffusion, D, of helium, argon, oxygen, nitrogen and carbon dioxide through films were measured (relative error of the order of 20%) at room temperature with the aid of a chromatographic device with a heat conductivity detector[10,11].

Room-temperature densities ρ were determined by a simple hydrostatic weighing technique (medium: isooctane; mean error below 0.1%); bulk thermal expansivities, $\alpha = -d\ln\rho/dT$, in the temperature interval 230–470 K were estimated from the temperature dependence of the thickness, $h = (0.5\text{–}1.0) \times 10^{-3}$ m, of disc-shaped specimens assuming isotropicity (i.e. $\alpha = 3\, d\ln h/dT$), with the aid of the thermo-mechanical analysis (t.m.a.) block of a DuPont 1090 thermoanalyser.

RESULTS AND DISCUSSION

Phase morphology

A distinct shoulder and a well-resolved peak on the SAXS curves at $2\theta < 1°$ for samples CPUU-1/2100 and CPUU-3 respectively (*Figure 1*) are typical for phase-separated systems. The experimental value of the long period for the latter sample, $L = 8$ nm, is very close to the total contour length (i.e. that corresponding to a completely extended conformation) of the chain repeating unit, $L^* = L_R^* + L_L^* = 7.8$ nm, where $L_R^* = 4.0$ nm

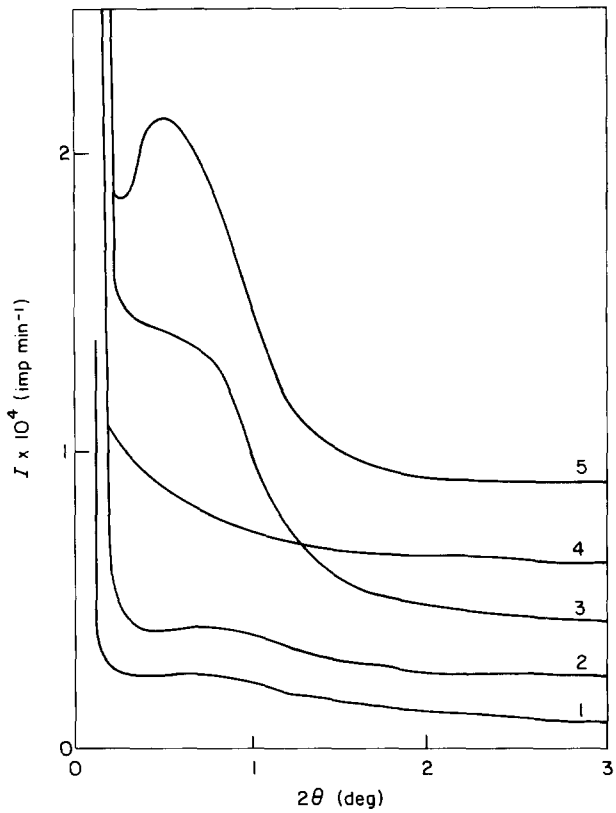

Figure 1 SAXS patterns for: (1) CPUU-1/430; (2) CPUU-1/1050; (3) CPUU-1/2100; (4) CPUU-2; (5) CPUU-3. For clarity, all curves beginning from 2, were shifted upwards

and $L_L^* = 3.8$ nm are contributions from rigid MDI–CE–MDI fragments and soft PE fragments respectively. On the other hand, for sample CPUU-1/2100 the observed long period, $L = 10.5$ nm, turned out to be about half the sum of the contour lengths of the same rigid fragment, $L_R^* = 4.0$ nm, and of the longer soft fragment, $L_S^* = 18.0$ nm; however, it exceeded by only 30% the sum of L_R^* and the root-mean-square, end-to-end distance for a PE fragment in a randomly coiled, unperturbed conformation, $(\langle h^2\rangle^{1/2}) = 4.0$ nm (estimated from $(\langle h^2\rangle/M)^{1/2} = 0.88$ nm[12]). These data are, therefore, qualitatively consistent with the general notion of gradual transition of flexible-chain polymers from an extended into a coiled conformation in the course of a continuous increase in the chain length[13–15].

As can be inferred from the considerably smaller SAXS intensity in the same range of scattering angles (*Figure 1*), the degree of phase separation in the other samples is much lower (i.e. their structure is more homogeneous), although the presence of weak plateaux and shoulders above the SAXS background may be regarded as evidence of a finite microheterogeneity. More quantitative data about the degree of phase separation may be obtained from the standard equation[16,17]

$$\alpha^* = \langle(\Delta\rho^*)^2\rangle / \langle(\Delta\rho^*)^2\rangle_0 \qquad (1)$$

where $\langle(\Delta\rho^*)^2\rangle$ is the experimental value of the mean square electron density fluctuations defined as the product $K'Q'$; $\langle(\Delta\rho^*)^2\rangle_0 = \varphi(1-\varphi)(\rho_1^* - \rho_2^*)^2$ is the corresponding theoretical quantity; Q' is the SAXS invariant; K' is the calibration constant; φ is the volume fraction of a rigid phase; ρ_1^* and ρ_2^* are electron densities of the soft and rigid phases respectively (in the calculations, $\rho_1^* = 330$, 340 and 350 el nm^{-3} were assumed

for the soft phases of CPUU-1, CPUU/2 and CPUU/3 respectively, and $\rho_2^* = 410$ el nm^{-3} for the rigid phase in all the samples). The values of α^* obtained in this way are listed in *Table 1*. As might have been expected, the highest values of α^* (close to unity) were observed for samples CPUU-1/2100 and CPUU-3 which exhibited strongest SAXS maxima (*Figure 1*).

A further insight into the phase state of the components in the CPUUs studied may be gained from the composition dependence of the density (or the specific volume $v = 1/\rho$). As can be seen from *Figure 2*, values of v for the first two members of the CPUU-1 series plotted *versus* the weight fraction of the rigid phase, w, fall on the straight line running from $v_1 = 1.00$ cm^3 g^{-1} for a pure oligoether (i.e. at $w = 0$) to $v_2 = 0.655$ cm^3 g^{-1} for a hypothetical pure rigid phase at $w = 1.0$, while the experimental point for the sample CPUU-1/2100 lies considerably (by some 9%) above. On the other hand, similar linear plots for both samples CPUU-2 and CPUU-3 extrapolated to $w = 1.0$ (*Figure 2*) yielded $v_2 = 0.730$ cm^3 g^{-1} (i.e. about 11% higher). Moreover, the apparently deviating point for sample CPUU-1/2100 rather nicely fell on the straight line connecting $v_1 = 1.000$ cm^3 g^{-1} at $w = 0$ and $v_2 = 0.730$ cm^3 g^{-1} at $w = 1.0$ (*Figure 2*). It thus appears that in the composition interval $w < 0.5$, (as is the case with samples CPUU-1/430 and CPUU-1/1050), the chain segments of the rigid phase possess sufficient mobility and space in the course of the film casting process for a dense (crystal-like) packing within the rigid domains ($v_2 = 0.655$ cm^3 g^{-1}), whereas steric hindrances in the 'overcrowded' ($w > 0.5$) samples CPUU-1/2100, CPUU-2 and CPUU-3 inhibit the efficient packing of the rigid fragments, so that the resulting inner structure of the domains corresponds to a looser, glass-like packing pattern ($v_2 = 0.730$ cm^3 g^{-1}).

Table 1 Properties of initial samples

Sample	w	$[\eta]$ (dl g^{-1})	α^*
CPUU-1/430	0.68	0.99	≈1
CPUU-1/1050	0.48	0.95	0.5
CPUU-1/2100	0.31	0.96	0.7
CPUU-2	0.70	0.92	0.8
CPU-3	0.68	0.88	≈1

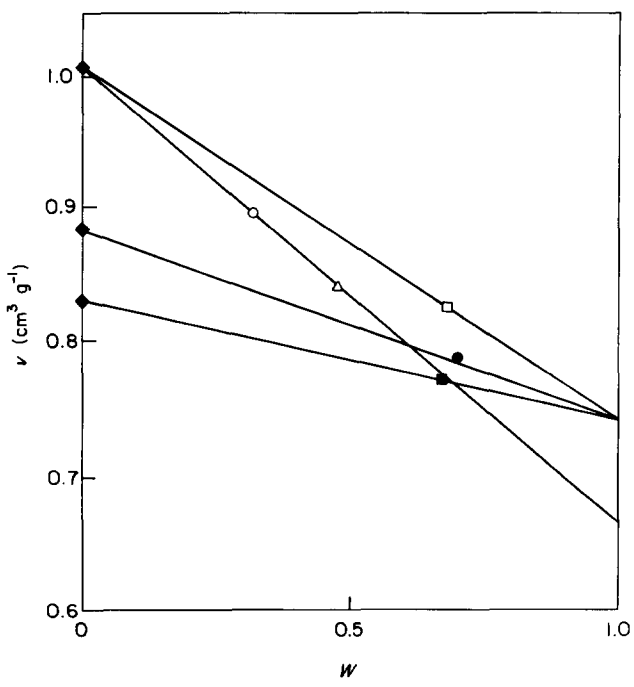

Figure 2 Dependence of specific volume on the weight content of rigid fragments for: (□) CPUU-1/430, (△) CPUU-1/1050, (○) CPUU-1/2100, (●) CPUU-2 and (■) CPUU-3. Straight lines are the additivity dependences drawn as described in the text

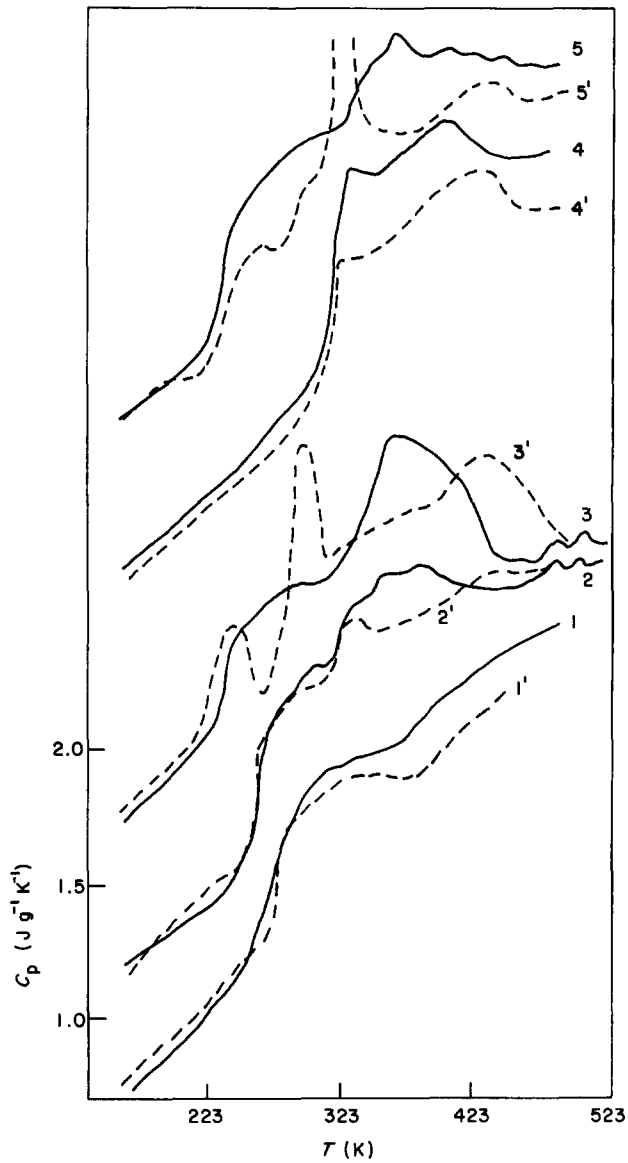

Figure 3 Heat capacity of (——) initial and (– – –) homogenized by quenching samples of CPUU-1/430 (1,1'), CPUU-1/1050 (2,2'), CPUU-1/2100 (3,3'), CPUU-2 (4,4') and CPUU-3 (5,5'). For clarity, all curves beginning from 2,2' were shifted upwards

Thermal transitions

The complete absence of characteristic melting endotherms of either the PE phase in CPUU-2 and/or the CE phase in all of the studied CPUUs (*Figure 3*) shows that these species lost crystallizability when incorporated into CPUU chains[6]. A strong endothermic effect with maxima located at 485 and 495 K was recorded, however, for the phase-separated sample CPUU-1/2100; traces of this endotherm were also observed for sample CPUU-1/1050, whereas no evidence

of this effect could be found on the thermograms of all the other samples. In view of the data obtained in the preceding section, it may be suggested that the endotherms referred to above reflect the melting of the ordered microphases of [CE+MDI] in CPUU-1/1050 and CPUU-1/2100; the absence of such endotherms in all the other systems with a much higher content of rigid fragments means that the latter may exist only in a disordered state both in homogeneous, mixed microphases and in a single-component microphase.

On the other hand, in the temperature intervals below 450 K, one observes several processes of enthalpy relaxation, the most prominent of which may be attributed to the glass transitions of different mixed phases of soft and rigid fragments, that is, those enriched with either PE (low-temperature relaxation at T'_g) or with [CE+MDI] (higher-temperature relaxation at T''_g). Qualitatively similar data were obtained from t.m.a. measurements: volume relaxations manifested themselves as sudden jumps of an expansion coefficient, α, approximately in the same temperature intervals in which enthalpy relaxations were observed.

We will start our analysis of the above data by noting that among the samples of series CPUU-1, it is the one with the lowest degree of phase separation (i.e. CPUU-1/430) for which the higher-temperature relaxation is the weakest. One may assume, therefore, as a crude approximation, that the only temperature interval of a jump-like increase of the heat capacity, ΔC_p, and of the expansion coefficient, $\Delta\alpha$, for this sample corresponds to the glass transition, T_g, of a homogeneous (i.e. single-phase) mixture of soft and rigid fragments at nominal composition ($w=0.68$). Assuming, further, the additivity of the heat capacity jump at T_g for a two component, single-phase mixture[18], one derives (*Figure 4*) from the relevant experimental values, $\Delta C_{p,1}=0.70+0.05\ J\ g^{-1}\ K^{-1}$ for a pure PE phase ($w=0$)[6] and $\Delta C_p=0.45+0.05\ J\ g^{-1}\ K^{-1}$ for an initial sample of CPUU-1/430 (*Table 2*), the value of $\Delta C_{p,2}=0.35+0.05\ J\ g^{-1}\ K^{-1}$ for a hypothetical homopolymer of rigid fragments ($w=1.0$). The glass transition temperature of the latter, $T_{g,2}$, may be estimated now with the aid of Couchman's equation for compatible, single-phase mixtures, as[18]

$$\ln T_g=[(1-w)\ln T_{g,1}+w\ln T_{g,2}K_g]/[(1-w)+wK_g] \quad (2)$$

where $K_g=\Delta C_{p,2}/\Delta C_{p,1}$. The value $T_{g,2}=390+7$ K, calculated in this fashion, agrees well with the corresponding experimental value (387 K[19]).

As can be seen from *Figure 4*, the experimental values of T'_g for all the initial samples of series CPUU-1, are reasonably well accounted for by equation (2). However, the values of corresponding ΔC_ps for CPUU-1/1050 and CPUU-1/2100 are well below the additivity line (*Figure 4*); moreoever, for these samples, higher-temperature relaxations at T''_g become pronounced. These data are indicative of the appearance of structural microheterogeneity in those samples which consist of not only microregions of nominal composition with T'_g obeying equation (2), but also of coexisting microregions of different composition with glass transition at T''_g (*Table 2*). The relative content of those latter microregions may be estimated as

$$v=\Delta C_p/\Delta C_p^0 \quad (3)$$

(where ΔC_p and ΔC_p^0 are the experimental and 'theoretical' (additive) heat capacity jumps at T''_g), while substitution

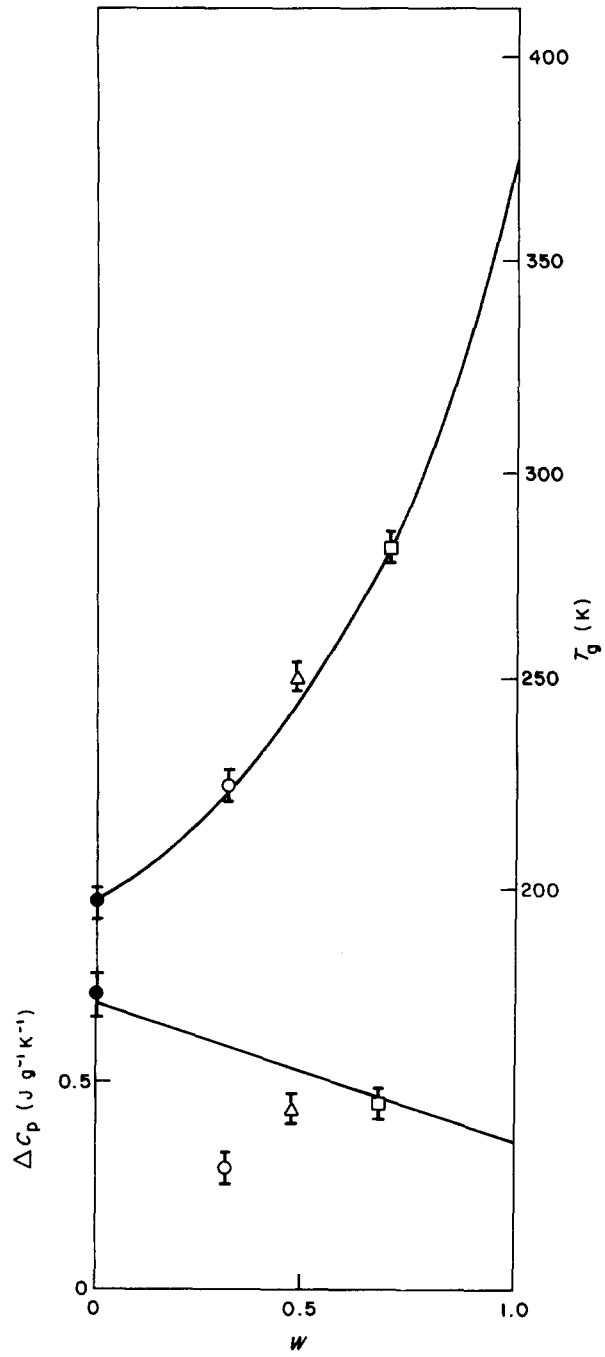

Figure 4 Composition dependence of the glass transition temperatures and corresponding changes in heat capacity for initial samples of series CPUU-1. The upper curve was constructed according to Couchman's equation (9), the lower straight line corresponds to additivity

of experimental values of T''_g into equation (2) would yield their composition.

For example, $v=0.8$ obtained after substitution of $\Delta C_p=0.43\pm0.05\ J\ g^{-1}\ K^{-1}$ at $T'_g=252$ K and $\Delta C_p^0=0.53\ J\ g^{-1}\ K^{-1}$ for CPUU-1/1050 into equation (3), means that about 80% (by mass) of that sample has the nominal composition ($w=0.48$), whereas the major portion of the remaining 20% with $T''_g=350$ K refers to microregions enriched with rigid fragments ($w=0.85$) (the contribution of the minor portion consisting, presumably, of soft segments was probably too weak to be detected). Similar estimates for the initial sample of CPUU-1/2100 have shown to consist, in equal proportions, of a microphase of nominal composition

Table 2 Glass transition quantities of initial and homogenized (by quenching) samples

Sample	T'_g (K)		ΔC_p ($J\,g^{-1}\,K^{-1}$)		T''_g (K)	
	Initial	Homogenized	Initial	Homogenized	Initial	Homogenized
CPUU-1/430	285	293	0.45	0.42	–	–
CPUU-1/1050	252	253	0.43	0.44	350	320
CPUU-1/2100	222	213	0.29	0.28	350	400
CPUU-2	297	295	0.62	0.58	390	410
CPUU-3	226	226	0.52	0.39	340	410

($w=0.31$) and of a microphase enriched with [CE + MDI] ($w=0.85$). The above data are qualitatively consistent with the concept that thermodynamic 'affinity' between components of the block copolymer becomes worse, the higher the component chain length is[1,2].

Quenching did not appreciably affect the patterns of the heat capacity of samples CPUU-1/430 and CPUU-1/1050 in the interval of T'_g, except the shift of T''_g for the latter to lower temperatures (see *Table 2*). On the other hand, drastic changes occurred after quenching of CPUU-1/2100 (*Figure 3*): T'_g decreased by 9 K, while T''_g became weaker and increased: in the intermediate temperature interval, exothermic and endothermic relaxations appeared with maxima located at 253 and 285 K respectively. Analysis of these data along the lines depicted above led to the conclusion that about 45% (mass) of the sample with composition $w=0.75$ was involved in the low-temperature relaxation at T'_g; 10–15% was a pure phase of rigid fragments ($w=1.0$) participating in the higher-temperature relaxation at T''_g, and the remaining part was responsible for the occurrence of intermediate relaxations. The molecular mechanism of the latter is still obscure; however, it might well involve a sort of cooperative conformational rearrangement like ordering (exothermic effect) and subsequent disordering (endothermic effect) phenomena within CE and adjacent PE segments.

As was the case with sample CPUU-1/430, on the heat capacity curve of an initial sample of CPUU-2, one observes a weak relaxation at T''_g and a large ΔC_p jump at T'_g (see *Figure 3* and *Table 2*); however, the latter is narrower and located some 15 K above the corresponding relaxation in CPUU-1/430. It may be concluded from these data that this sample consists essentially of a homogeneous phase of nominal composition. Changes in the heat capacity pattern after quenching were not significant.

Finally, two processes of enthalpy relaxation located at $T'_g=226$ K and $T''_g=340$ K were observed for an initial sample of CPUU-3 (*Figure 3*). Substituting $T_{g,1}=214$ K and $C_p=0.85+0.05\,J\,g^{-1}\,K^{-1}$ for a pure PE component[6] into equation (2), it can be shown that the former and the latter relaxations referred to above correspond to glass transitions of microphases with compositions $w'=0.23$ and $w''=0.83$ respectively, which should be compared to a nominal composition, $w=0.68$. These findings may be explained by a lower (compared to the case of oligoethers for series CPUU-1 and CPUU-2) affinity of an oligoester (PE component in CPUU-3) to the rigid-chain fragments, which is the most probable cause of a microphase separation into PE-rich and [CE + MDI]-rich regions in an initial CPUU-3.

Given the relative content of the high-temperature microphase $v=0.45$ (estimated by substitution of pertinent values, $\Delta C_p=0.20\,J\,g^{-1}\,K^{-1}$ and $\Delta C_p^0=0.44\,J\,g^{-1}\,K^{-1}$, into equation (3)), one may conclude that this microphase consists of $vw''/w=54\%$ of the total mass of rigid fragments available and of $v(1-w')/(1-w)=25\%$ of soft fragments. If all remaining 75% of the latter were involved in the low-temperature microphase ($w'=0.23$), that would have required only 10% of rigid fragments, and the expected value of $\Delta C_p^0=0.25\,J\,g^{-1}\,K^{-1}$ would be much lower compared to the one observed experimentally, $\Delta C_p=0.52\,J\,g^{-1}\,K^{-1}$. The only plausible way to rationalize this apparent discrepancy would be to suggest, as was done in a similar situation with other phase-separated block copolymers[20], that the rigid fragments located in the BI between two coexisting microphases are in the expanded state with excessive free-volume content (and, consequently, with higher-than-additive ΔC_p).

Quenching results in a reduction in the height of the ΔC_p jump for T'_g down to the additive value and in an upward shift of T''_g; moreover, in the intermediate temperature interval one observes a weak exotherm followed by a strong endothermic relaxation with a maximum at 310 K (*Figure 3*). As far as these effects resemble those observed for a quenched specimen of another phase-separated sample, CPUU-1/2100 (see above), it is safe to conclude that for both samples the anomalous enthalpy relaxations in the temperature intervals between T'_g and T''_g reflect cooperative conformational rearrangements involving CE fragments.

Thermoelasticity

According to the data collected in *Table 2*, all our samples may be classified as either solids or rubbers. The former would be defined as those in which the rigid microphase with T''_g above the temperature of measurements ($T=293$ K) is continuous. The experimental data on the thermoelastic behaviour of such samples (i.e. CPUU-1/2100, CPUU-2 and CPUU-3) will be treated with the aid of the following classical equations for elastic solids[21]:

$$W/m=(E/2\rho)\varepsilon^2 \tag{4a}$$

$$Q/m=\mathrm{ET}\alpha\varepsilon/3\varepsilon^2 \tag{4b}$$

where m is the sample mass, E is Young's modulus and $\varepsilon=\lambda-1$ is the strain.

On the other hand, in samples CPUU-1/1050 and CPUU-1/2100 it is presumably the soft microphase with $T'_g<T=293$ K which forms a continuous matrix

reinforced with discontinuous, rigid domains. In this case, one would expect the following equations for rubbers[21] to apply

$$W/m = A(E/6\rho)f_1(\lambda) \quad (5a)$$

$$Q/m = -(W/m)[1 - T\beta - 2\alpha T/f_2(\lambda)] \quad (5b)$$

where $A = \langle h^2\rangle_0/\langle h^2\rangle_x$ is the front factor (usually, $A = 1$ is assumed), $\langle h^2\rangle_0$ and $\langle h^2\rangle_x$ are the mean-square, end-to-end distances of an isolated, unperturbed chain and of the same chain in the network respectively, and $\beta = d\ln\langle h^2\rangle_0/dT$ is the temperature coefficient of unperturbed chain of dimensions; $f_1(\lambda) = \lambda^2 + 2/\lambda - 3$; $f_2(\lambda) = \lambda^2 + \lambda - 2$.

Before attempting a quantitative analysis of the experimental data with the aid of equations (4) and (5), one qualitative remark is in order. In a range of elongations studied (up to the limiting elongation at break which varied from ca. $\lambda = 1.2$–1.3 for solid samples to $\lambda = 1.5$–1.8 for rubbery ones), there was a reasonable agreement between the data obtained in both deformation regimes for all samples except CPUU-1/1050. For this sample both the stretching force and the concomitant heat effects recorded in regime 2 (i.e. step-like loading), were consistently higher than those in regime 1 (loading–unloading cycles). Apparently, this phenomenon should be attributed to the inherent structural instability of an initial CPUU-1/1050 sample which yields easily and thus can be transformed into a structurally different ('stress-hardened') state on stretching; this new structure may be either fixed (at = constant, as in regime 2), or destroyed (after unloading, as in regime 1). Since the primary aim of the present study was structural characterization of as-cast (i.e. 'unperturbed') samples, in the subsequent discussion our main attention was focused on the data obtained in deformation regime 1 which is better suited to check the onset of structural changes at the yield point which separates the regions of elastic and inelastic deformation behaviour.

As can be seen from *Figure 5*, the experimental data for our 'solids' and 'rubbers' are in fair agreement with equations (4) and (5) respectively, albeit in a rather narrow range of elongations. The 'material constants' E and α derived from the data fitting procedure are listed in *Table 3* (for 'rubbers' $\beta = 4.4 \times 10^{-4}\ K^{-1}$ was assumed, as for a pure oligoether[22]. In the 'solids' series, the modulus tends to increase (and, simultaneously, thermal expansivity decreases) as the degree of microphase separation α^* becomes lower. This is somewhat unexpected from the point of view of composite mechanics theory[23] which predicts that (at roughly the same volume content of a high-modulus component) the modulus must be higher in the case of 'discrete soft inclusions

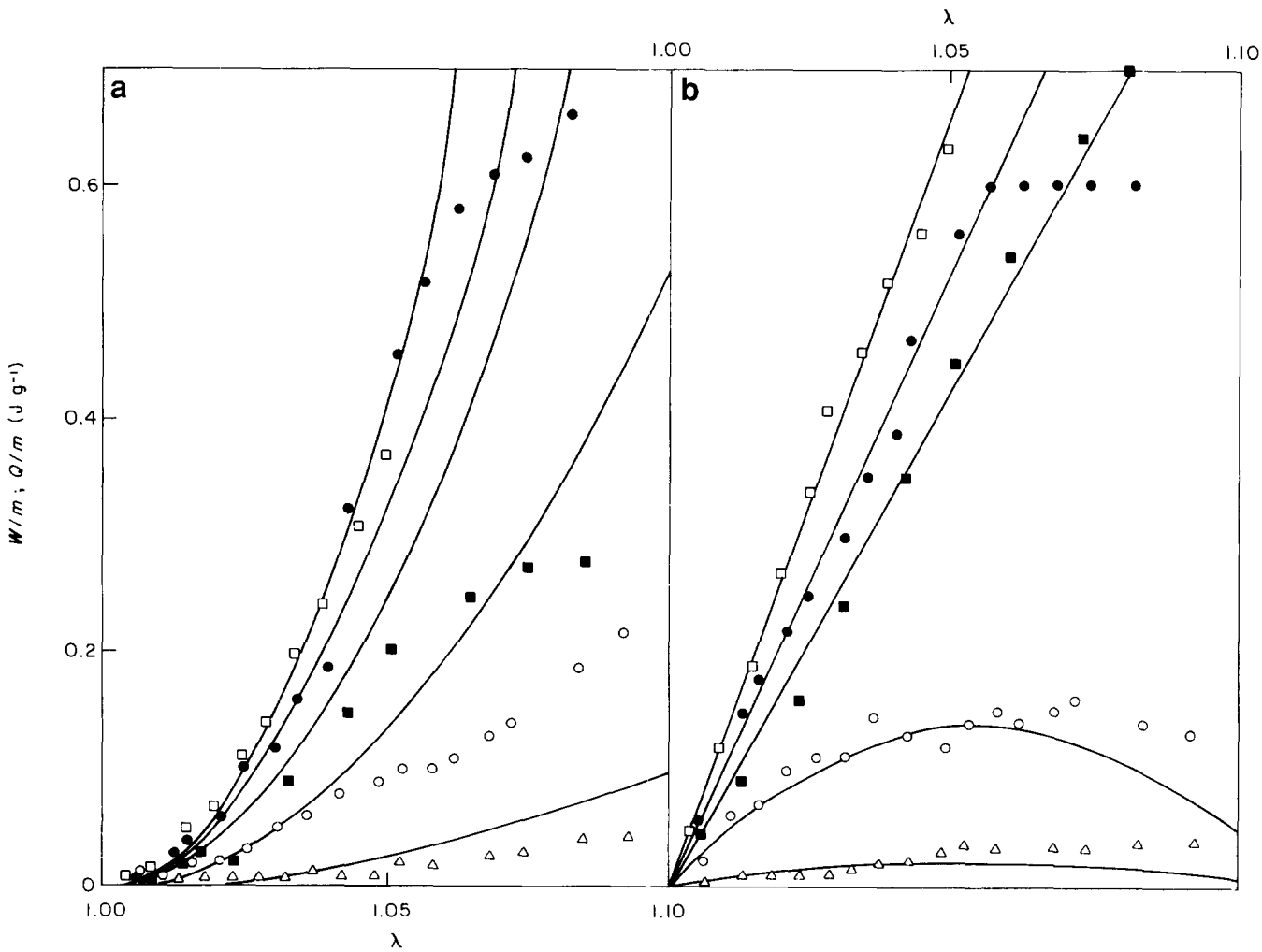

Figure 5 Dependence on the stretching ratio of (a) mechanical work and (b) heat effects for samples indicated as in *Figure 2*. The three upper and two lower lines were constructed according to equations (4) and (5) respectively

in a continuous rigid matrix'-type morphology (in our terminology, at high α^*), than in the case of 'two continuous, interpenetrating phases'-type structure (presumably, this would correspond to lower α^*). It is likely, however, that the deficit of E (as well as the 'excess' of) for sample CPUU-3 is caused by a contribution from the BI with rigid fragments in a loosely packed, expanded state, as discussed in the previous section.

With regard to the situation with the 'rubbers' series, the modulus for a phase-separated sample of CPUU-1/2100 is almost five-fold higher than that for sample CPUU-1/1050 with lower α^* (*Table 3*) which should be considered a natural consequence of a smaller contribution from the BI in the former sample. It is pertinent to remark here that the contributions from rigid fragment-rich microphases, which were roughly estimated by subtracting the experimental values of W/m and Q/m from theoretical curves (*Figure 5*), behave essentially in agreement with equation (4) for elastic solids (*Figure 6*). It can thus be concluded that the deviations of experimental points for these samples from the behaviour predicted by equation (5) for rubbers occur at the onset of elastic deformation of rigid microphases.

Table 3 Thermoelastic properties of initial samples

Sample	ρ ($cm^3\,g^{-1}$)	E (MPa)	$\alpha \times 10^4$ (K^{-1})
CPUU-1/430	1.213	420	3.1
CPUU-1/1050	1.197	25	5.0
CPUU-1/2100	1.125	121	5.5
CPUU-2	1.265	352	4.6
CPUU-3	1.317	268	5.4

Gas transport properties

The coefficients of permeability, K, and diffusion, D, of five gases through the studied CPUUs (*Table 4*) are of the same order of magnitude as those for other segmented polyurethanes[10,24]. As can be seen from semilog plots of K *versus* molecular diameter, d, of one-atom and two-atom penetrants (*Figure 7*), for all samples K is about the same for He ($d = 0.22$ nm) and for O_2 ($d = 0.36$ nm), whereas one observes an abrupt fall

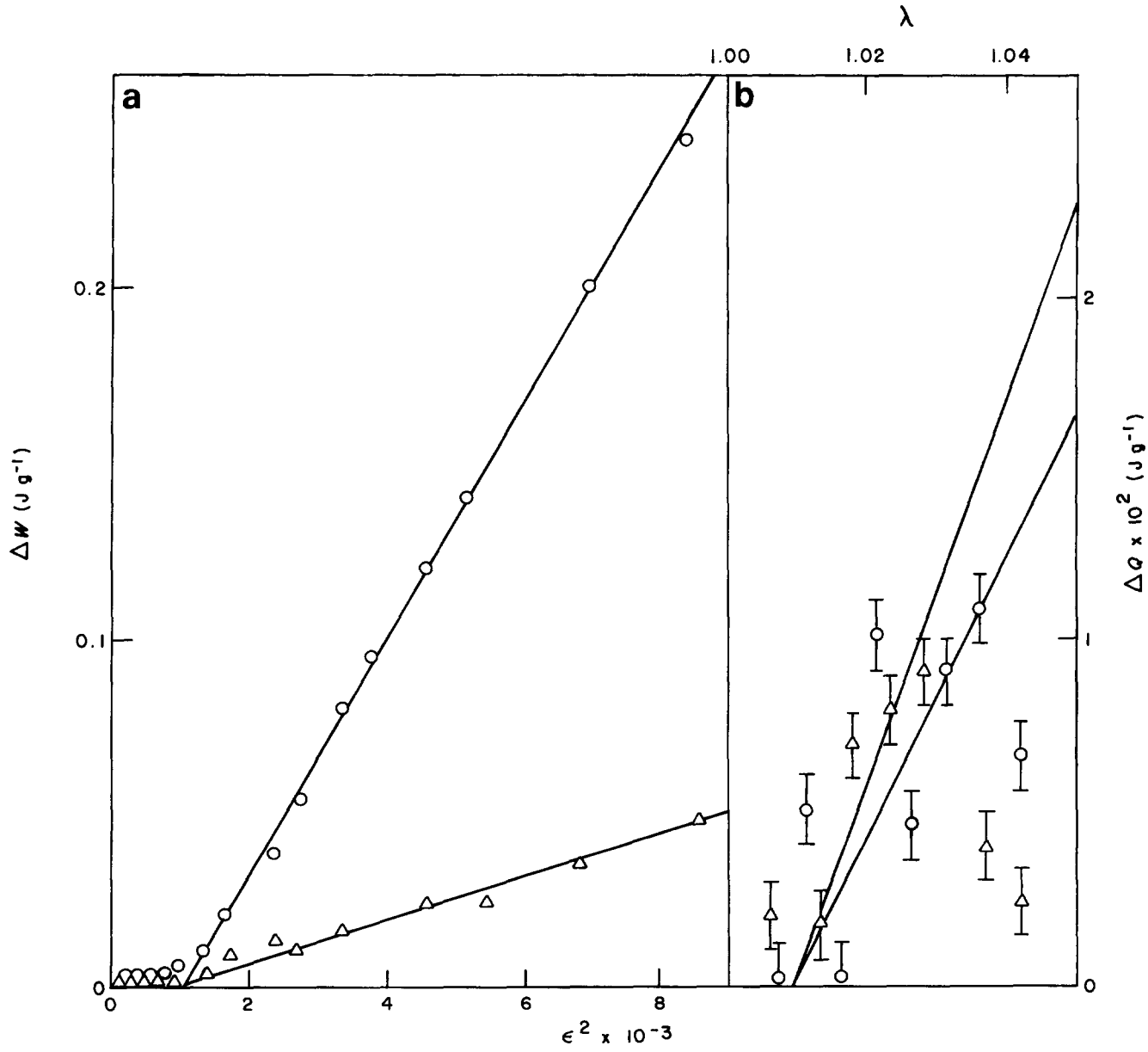

Figure 6 Dependence of (a) 'residual' mechanical work and (b) heat effects for two 'rubbery' samples of series CPUU-1 on the square of strain and stretching ratio respectively

Table 4 Permeability (K) and diffusivity (D) of initial samples[a]

Sample	N_2		O_2		CO_2		He		Ar	
	K	D	K	D	K	D	K	D	K	D
CPUU-1/43	0.076	3.4	1.4	3.0	0.3	3.8	1.3	–	0.12	4.0
CPUU-1/1050	0.029	2.8	0.09	4.4	0.12	4.3	0.18	–	–	–
CPUU-1/2100	0.11	4.6	0.48	5.0	6.3	5.7	0.87	–	0.35	–
CPUU-2	0.01	–	0.01	–	0.02	0.14	0.06	–	–	–
CPUU-3	0.01	0.25	0.04	0.11	0.03	0.31	0.09	–	0.02	0.81

[a] K in 10^2 Barrer; D in $10^8\,cm^2\,s^{-1}$

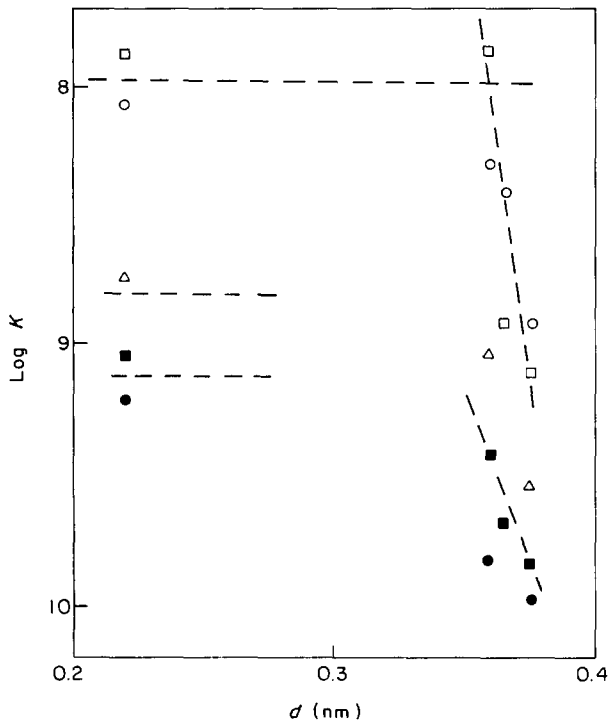

Figure 7 Dependence of permeability on molecular diameter of a penetrant

in K at larger values of d. The origin of this behaviour is uncertain, although it is tempting to associate it with the distribution of free-volume entities ('holes') in membranes (e.g. that the maximum of this distribution is located somewhere below 0.36 nm). This simple 'geometrical' argument, however, fails to account for the observed values of D (*Table 4*); evidently, composition dependence of the thermodynamic parameter, solubility, $S = K/D$, should also be invoked for this purpose (this would be especially needed to rationalize the difference in gas transport properties for samples of different compositions in the case of a three-atom gas, CO_2).

In the 'rubbers' series, significantly higher values of both K and D for sample CPUU-1/2100 compared to CPUU-1/1050 (*Table 4*) would have been expected in view of the higher content in the former of a PE-rich, rubbery microphase through which, presumably, the largest portion of the total gas flux is transported.

Extending this argument further, one would also expect even lower values of K and D for sample CPUU-1/430 because not only is the PE content smallest in this particular sample, but its major part is in the solid (glassy) state (see above) with intrinsically poorer gas transport performance[25]. In our opinion, the only reasonable explanation for an exactly opposite situation (see *Figure 7* and *Table 4*) would be the following. As suggested above, the rigid fragments of the two rubbery samples CPUU-1/1050 and CPUU-1/2100 form the densely-packed, crystal-like microphases which are nearly impenetrable to gas molecules (in fact, this was implicitly assumed when analysing the difference in gas transport properties of these two samples). However, for other samples (CPUU-1/430 included), the packing density within the rigid fragment-rich microphases is so low that the gas molecules have the choice of travelling through not only PE-rich, but also [CE+MDI]-rich microregions with the net result of substantial increases in K and D.

Finally, we will analyse the difference in transport properties between the samples of the 'solids' series which have essentially similar contents of rigid fragments but differ in the degree of phase separation α^* and in the chemical nature of the PE fragments. The major point of concern here is the significantly smaller values of both K and D for sample CPUU-2 compared to CPUU-1/430 (*Table 4*), in spite of comparable values of α^* and very similar properties (e.g. chain stiffness, polarity, etc.) of PE fragments (oligoethylene glycol (OEG) in the former, and oligopropylene glycol (OPG) in the latter). It is pertinent to recall in this connection the unusually high cohesion energy of molten OEG[26], which implies that the barrier for transport of gas molecules in OEG-containing microphases would be higher than for OPG-containing microphases.

CONCLUSIONS

As-cast samples of studied CPUUs are structurally microheterogeneous systems, in which the composition and the relative content of the different microphases varies with the chain length and chemical nature of the soft component. As a general trend, the thermodynamic affinity between rigid and soft fragments becomes worse (that is, the degree of microphase separation α^* increases) when the chain length of the latter increases (as in the case of the series CPUU-1) and/or when an oligoether component is replaced by an oligoester of a similar chain length (as in sample CPUU-3).

The crown ether is completely immobilized within the rigid fragment-rich microphases of all the initial (as-cast) samples; however, heating the phase-separated samples CPUU-1/2100 and CPUU-3 well above the apparent glass transition temperature of the rigid domains seems to restore the individual thermal mobility of the CE fragments, which manifests itself in the heat capacity curves of the quenched specimens as a

succession of exothermic and endothermic relaxations in the temperature intervals between the glass transition temperatures of the microphases enriched with soft and rigid fragments respectively.

The thermoelastic and gas transport properties of the studied samples, apparently, depend not only on their nominal chemical composition and α^*, but also on the pattern of molecular packing within the rigid fragment-containing microphases.

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