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ORIGINAL CONTRIBUTION

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Dynamic mechanical properties of poly-ether-urethane elastomers with chain-extended or chain-folded molecularly uniform poly (*N*-alkylurethane) hard segment domains

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Abstract Segmented polyether-urethanes with distinctively different morphologies, i.e., with chain-extended or chain-folded crystallized hard segments, could be created by small constitutional changes in the hard segment architecture. The different superstructure was achieved by building-in specially designed constitutional units in the middle of the otherwise regularly built hard segment which for flexibility or sterical reasons allowed an adjacent reentry chain-folded and/or chain-extended crystallization of the hard phase forming polyurethane segments. The material properties of the thermoplastic elastomers correlated systematically with the hard domain superstructure which was determined by the primary structure of the macromolecule and could be reversibly altered by the thermal history in the case of the flexible center unit. The softening temperature was determined by the hard domain height of the chain-folded lamellar or the chain-extended cylindrical domains; variation of the modulus in the elastomeric region could be related to imperfections in the hard segment packing which affected the effective hard domain filler.

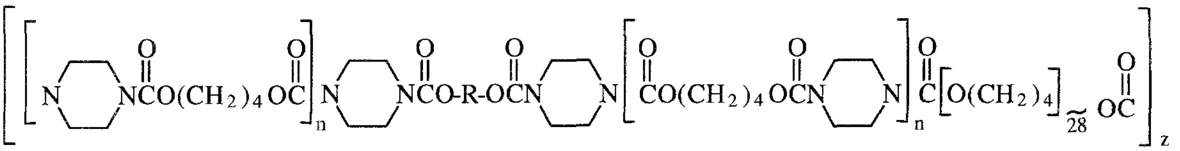
Key words Polyurethane elastomers – segmented block copolymers – poly(N-alkylurethane) – hard segment – chain folding – dynamic mechanical properties

Introduction

Segmented multiblock copolymers, in which the miscibility of the alternating (e.g., polyether) soft segments and the polyurethane (PU) hard segments is rather limited, form a microphase separated system upon cooling from the melt or solvent evaporation [1, 2]. The elastomeric properties of the material result from the segregation of the hard segments under formation of domains in a more or less continuous soft segment phase. At the service temperature, the soft segment phase is liquid and is therefore responsible for the elasticity of these materials, whereas the hard domains act as multifunctional, physical crosslinks and as fillers.

With the example of specially designed, segmented polyether-urethanes (PEU-N) with molecularly uniform poly(N-alkylurethane) hard segments it has been shown that the hard domain structure could be controlled and adjusted by the hard segment architecture and the sample history, respectively [3–9].

The different morphology was caused by a crystallization of the PU hard segments with or without chain-folding due to the specific conformation or the given stereogeometry of a chosen constitutive unit R, which has been built into the middle of the molecularly uniform hard segment; this center constitutional unit R replaced a tetramethylene unit of the piperazinediylcarbonyloxy-tetramethyleneoxycarbonyl repeating unit of the hard segment. The packing model of the hard segments in these



PEU-N (N = 2n+1)

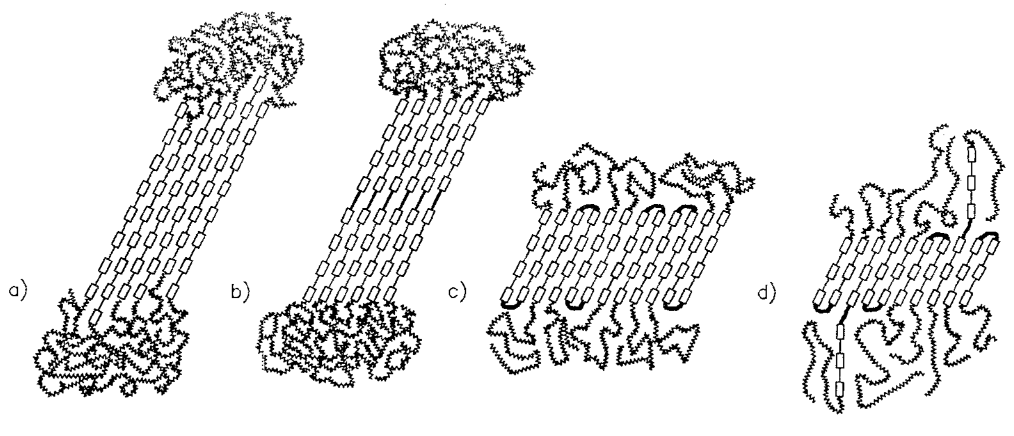
N = total number of piperazinediylcarbonyloxyalkyleneoxycarbonyl constitutional repeating units;
n = number of piperazinediylcarbonyloxytetramethyleneoxycarbonyl repeating units;
R = center constitutional unit; for R = tetramethylene, the then regularly built hard segments consist of piperazinediylcarbonyloxytetramethyleneoxycarbonyl repeating units only (cf. [3, 10].

polyether-urethanes-N (PEU-N) in the chain-extended and the chain-folded form, respectively, which has been derived from single crystal x-ray analysis of molecularly uniform oligourethane model compounds [11], powder diffraction pattern in the wide-angle region [8] and small-angle x-ray scattering (SAXS) data [8] as well as differential scanning calorimetry (DSC) measurements [3, 8, 11] of microcrystalline oligourethane model compounds, and also from SAXS and DSC data of PEU-N [3, 4, 9] is schematically shown in Fig. 1 (cf. [9]).

The chain-extended (Fig. 1a, b) and chain-folded (Fig. 1c) packing models have also been confirmed by transmission electron microscopy using the element spectroscopic imaging (ESI) technique [5–7, 9]: The imaging of the net element distribution of nitrogen, an element only present in the hard segments, has revealed a cylindrical shape for chain-extended crystallized hard segments (cf. [12]), whereas domains consisting of chain-folded hard segments exhibited a lamellar structure. The differences in the organization of the hard segments (chain-extended (Fig. 1a, b), and chain-folded without (Fig. 1c) or with packing irregularities (Fig. 1d)) could also be detected by differential scanning calorimetry [4–7, 9] (cf. [3]). Chain-extended hard domains melted at a significantly higher temperature than the corresponding chain-folded crystallized segments, and the melting temperature of the hard domains and the heat of fusion could be directly related to the domain height and the hard segment packing order; a critical fold length consisting of four piperazinediyl constitutional units (PEU-7, $n = 3$, R = $(CH_2)_8$) was required to obtain the almost pure chain-folded modification (Fig. 1c), whereas for polyether-urethanes with shorter hard segments (PEU-5, $n = 2$, R = $(CH_2)_8$) a fraction of the hard segments participated with one-half only in the hard domain formation (Fig. 1d) [9].

In this paper, the dynamic mechanical properties of these model PEU-N with molecularly uniform hard segments and different hard segment center units R will be discussed. Since the material properties of thermoplastic PU elastomers are closely related to the molecular architecture, i.e., to the hard an soft segment length and segment

Fig. 1 Model of the packing of the hard segments in the hard domains of polyether-urethanes PEU-N: a) PEU-7a ($n = 3$; R = tetramethylene) where the chain-extended hard segments are randomly displaced against each other by one repeating unit in the cylindrical domain; b) Chain-extended modification of PEU-7c ($n = 3$; R = octamethylene) in cylindrical domains with sharp phase boundary; c) Chain-folded modification of PEU-7c ($n = 3$; R = octamethylene) with randomly distributed chain folds on the lamellar surface; d) Packing model of PEU-5c ($n = 2$; R = octamethylene) for chain-folded PU hard segment domains with incomplete incorporation of hard segments into the lamella. □- : 1,4-piperazinediylcarbonyloxytetramethyleneoxycarbonyl unit; ▮: center unit R in extended conformation; **C** : center unit R in folded conformation; ~ : poly(oxytetramethylene) soft segment



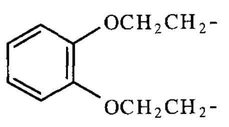
length distribution [3, 10, 13–16] it will be demonstrated that the occurrence of chain-folded or chain-extended crystallized hard segments has a significant impact on the dynamic mechanical properties which can be controlled by the hard segment architecture and the sample treatment, respectively.

Experimental

Synthesis

The synthesis of the polyether-urethanes PEU-5 ($n = 2$) and PEU-7 ($n = 3$) with R = tetramethylene, hexamethylene, octamethylene and 1,2-bis(oxyethylene)phenylene by polycondensation of polymolecular α,ω-piperazinyl-terminated poly(oxytetramethylene) (POTM; $M_n = 2000$ g/mol) and bischloroformates of corresponding molecularly uniform poly(N-alkylurethane) telechelic hard segment precursors has been described in detail in previous publications [8, 9] (cd. [3]).

The abbreviations of the PEU-N (see formula in the introduction) with different center constitutional units R and varying number of repeating units are complied below.

	R			
N(n)	$-(CH_2)_4-$	$-(CH_2)_6-$	$-(CH_2)_8-$	
5(2)	PEU-5a	PEU-5b	PEU-5c	
7(3)	PEU-7a	PEU-7b	PEU-7c	PEU-7d

The number average molar mass M_n of the resulting segmented block copolymers was $40000 < M_n < 50000$ as determined by gel permeation chromatography (polystyrene calibration) [9].

Characterization

Dynamic mechanical measurements were carried out with a Brabender torsion automat by using polymer films of $3.5 \times 5 \times 0.5$ mm in size. The temperature range of the dynamic mechanical measurements was $-130\,^{\circ}$C to $+180\,^{\circ}$C; heating rate 1 K/min; frequency 1 Hz. Samples with chain-extended hard segment domains of PEU-5b/c and PEU-7b/c were obtained by 10 min annealing of $CHCl_3$-solution cast films or compression-molded films in the temperature range of the melting of the chain-folded hard domains as determined by DSC (cf. [9]) (PEU-5: annealing temperature 405 K; PEU-7: annealing temperature 415 K). The PEU-5a and PEU-7a samples which occurred only in the chain-extended hard domain morphology were prepared by film casting from $CHCl_3$-solution. PEU-5b/c and PEU-7b/d samples with the chain-folded modification of the hard domains were obtained by compression molding and in the case of PEU-7d by casting from $CHCl_3$-solution, too.

Table 1. Melting temperature T_m and heat of fustion ΔH_m of the hard domains in polyether-urethanes PEU-N with chain-extended and chain-folded crystallized hard segments (cf. [9]).

Sample	Type of hard segment crystallization	T_m[a]) in K	ΔH_m[b]) in KJ/mole
PEU-5a	extended	446	97
PEU-5b	folded[c])	357	17
	extended	412	85
PEU-5c	folded	376	52
	extended	407	96
PEU-7a	extended	465	150
PEU-7b	folded[c])	403	84
	extended	438	100
PEU-7c	folded[c])	419	99
	extended	436	144
PEU-7d	folded	408	88

[a]) peak maximum of DSC trace, heating rate 20 K/min.
[b]) calculated from DSC trace.
[c]) chain-folded and chain-extended hard domains occurred side-by-side (cf. [8, 9]).

The hard domain melting temperature and heat of fusion as obtained from DSC analysis of the various PEU-N samples differing in the center constitutional unit and the number of repeating units in the hard segment as well as the hard domain morphology are compiled in Table 1 (cf. [9]).

Results and discussion

As has already been mentioned in the introduction, the morphology of segmented polyether-urethanes PEU-N, i.e., the occurrence of chain-folded or chain-extended hard domains could be controlled by building-in appropriate constitutional units R in the middle of the hard segment [4–9]. Polyether-urethanes with regularly built hard segments (e.g, PEU-5a and PEU-7a; R = $-(CH_2)_4-$) occurred in the chain-extended modification only [3]. The replacement of the central tetramethylene unit by a more flexible hexamethylene (PEU-5b and PEU-7b) or octamethylene (PEU-5c and PEU-7c) unit allowed the formation of chain-folded or chain-extended hard domain structures, and both modifications could be reversibly transformed by the sample treatment [9].

Depending on the morphology, the specimen exhibited distinctly different dynamic mechanical properties. The temperature dependence of the storage modulus G' and the loss factor $\tan\delta$ of the homologous polyether-urethanes PEU-5c and PEU-7c consisting of 5 and 7 piperazinediylcarbonyloxyalkyleneoxycarbonyl hard segment units, respectively, and either chain-folded or chain-extended hard domains are depicted in Figs. 2 and 3. As already mentioned above, the occurrence of the chain-folded modification was enabled by the central octamethylene constitutional unit in the hard segment which allowed a sharp chain-fold and adjacent reentry [4–9]. Both modifications revealed a similar change in the storage modulus G' and the loss factor $\tan\delta$ when going through the glass-rubber transition of the soft segment (drop in G' starting at 190/210 K, loss peak maximum at about 210 K) and during the melting of the soft segment crystallites (shoulder in the decrease of G' around 250 K and second maximum in the loss peak at 260/270 K); this is similar to that observed for polyether-urethanes with regularly structured molecularly uniform and extended-chain crystallized hard segments [3, 16]. However, the chain-extended and chain folded modification of PEU-5c exhibited differences: The height of the storage modulus and above all, the temperature range of the elastomeric behaviour, which is reflected in the relatively constant modulus in the plateau region until the final drop associated with hard domain melting occurs, was much smaller for the sample with chain-folded hard domains (compression molded sample) than for the specimen with chain-extended crystallized hard segments (sample annealed for 10 min in the temperature range of the chain-folded modification). The temperature difference between the hard segment microcrystallite melting of chain-folded and chain-extended modifications reflected from dynamic mechanical analysis is similar to that observed by DSC (cf. [9]). The modulus of the chain-folded modification was lower than the modulus observed for the sample with extended domains, although the hard segment volume fraction is identical in both modifications.

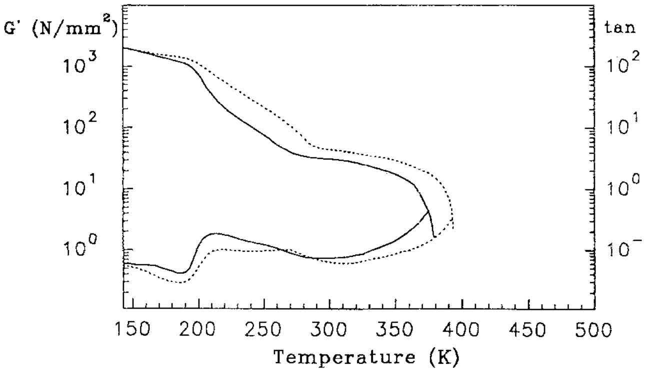
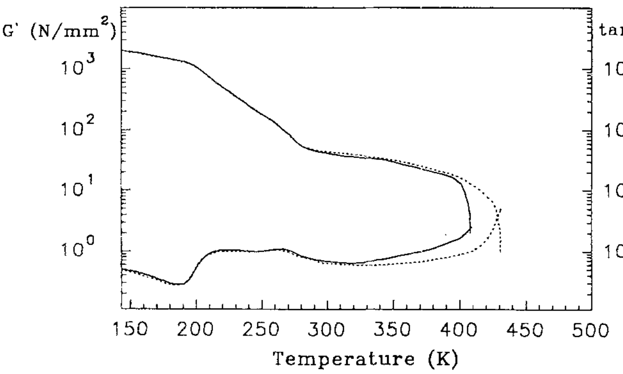


Fig. 2 Dynamic mechanical properties of segmented PU elastomer PEU-5c with chain-extended hard segments in cylindrical domains (....) and chain-folded hard segments in lamellar domains (———); G' = storage modulus; tan δ = loss factor

Fig. 3 Dynamic mechanical properties of segmented PU elastomer PEU-7c with chain-extended hard segments in cylindrical domains (....) and chain-folded hard segments in lamellar domains (———); G' = storage modulus; tan δ = loss factor



The differences in the dynamic mechanical behaviour can be explained by the change in the hard domain superstructure from the chain-folded lamellar to the chain-extended cylindrical form.

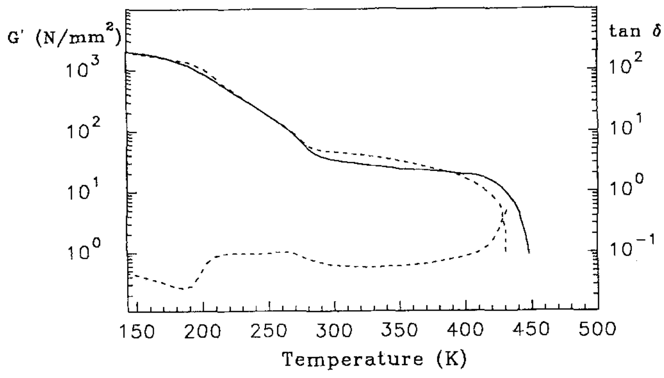
The fact that the hard domain softening temperature, as reflected by the sharp drop of the storage modulus at elevated temperatures and which was consistent with the onset temperature of the hard segment melting in the DSC [9], was much smaller for the samples with chain-folded hard domains then for the samples with chain-extended crystallized hard segments is related to the decrease of the domain height due to chain-folding (cf. Fig. 1) which determines the melting temperature.

Beyond the function as thermoreversible crosslinks, crystallized hard segments also act as reinforcing filler [1, 2]. The higher modulus of the chain-extended modification, which was most prominent for PEU-5, could be attributed to the greater effective filler content induced by cylindrical hard domains, since the glass transition temperature of the POTM soft phase was determined to be 188 K in both cases indicating a similar degree of microphase separation.

An obvious reason for the lower hard phase content in the chain-folded PEU-5c could be due to the fact that chain-folding could not be achieved completely since the critical chain length found for chain-folding in oligourethanes (about 70 Å [17]) is not sufficiently exceeded [9]. As a consequence, an appreciable amount of the hard segments participated with one-half only in the hard domain formation as schematically depicted in Fig. 1d. This was also reflected from the significantly lower heat of fustion $\Delta H_m = 52$ kJ/mole of PEU-5c as compared to $\Delta H_m = 99$ kJ/mole of PEU-7c, both with chain-folded hard domains [9]; considering that the length of the chain folds of PEU-7c and PEU-5c differed by one repeating unit only, the difference was expected to be much smaller based on the heat of fusion per repeating unit which has been determined to be 23 kJ [3, 8]. Compared to PEU-5c, in the case of PEU-7c, which is longer by one piperazinediylcarbonyloxytetramethyleneoxycarbonyl repeating unit at both sides of the chain-folding unit R, perfect and quantitative chain-folding is possible [9]. Therefore, the reinforcing filler content, and consequently the height of the storage modulus G' in the plateau region, is almost identical with that of the sample with the chain-extended PU hard segment domains (Fig. 3).

The impact of the replacement of the central tetramethylene constitutional unit R in the molecularly uniform hard segment by a octamethylene (PEU-7c) unit on the stability of chain-extended crystallized hard segment domains and thus on the dynamic mechanical behaviour of PEU-7 is illustrated in Fig. 4. In the case of PEU-7c, the chain-extended domain structure has been obtained by annealing solution casted films at 415 K in the temperature range of the melting of chain-folded hard segment crystallites (suitable temperature determined by DSC), whereas the hard segments of PEU-7a did crystallize in the chain-extended modification only, because of the insufficient conformational isomerism of the tetramethylene center unit with regard to adjacent reentry chain-folding [3–5, 9]. The central octamethylene constitutional unit in the hard segment caused a shift in the softening (melting) of the hard domains to a lower temperature which consequently lead to a smaller temperature range of the elastomeric behaviour; similar properties were observed for PEU-7b. This can be explained with the perturbation of the regularly built hard domain – whose crystal lattice is defined by periodic piperazinediylcarbonyloxytetramethyleneoxycarbonyl units – by the longer alkylene (e.g. octamethylene) constitutional unit. This finding is in agreement with the DSC measurements (Table 1; cf [9]); PEU-7a has shown a higher hard domain melting temperature than the corresponding PU elastomer PEU-7c, where as the heat of fusion was almost the same. Although the regularly structured PEU-7a exhibited elastomeric properties over a wider temperature range, the storage modulus in the plateau region was smaller than observed for PEU-7c (or PEU-7b) with chain-extended hard domain morphology. The different height of the storage moduli can be attributed to the differences in the hard segment packing as related to the given center unit R. The regularly built urethane chains in PEU-7a form hard domains with a fringed top surface due to the displacement of hard segments by one repeating unit against each other (Fig. 1a), which is possible without disturbing the periodic arrangement within the hard segment microcrystallite. A fraction of the ultimate repeating units of these hard segments does not contribute to the reinforcing filler but to the soft phase [3, 18]. This was directly reflected from a limiting value of the heat of fusion of the hard domains with increasing hard segment length which was much lower than calculated on the basis of the heat of fusion per repeating unit (21 kJ), and has been discussed in detail elsewhere [3].

Fig. 4 Dynamic mechanical properties of segmented PU elastomer PEU-7a (———) and PEU-7c (– – –) with chain-extended hard segments in cylindrical domains; G' = storage modulus; tan δ = loss factor



A central hard segment unit R which is different from the periodic order of the tetramethylene unit causes a formation of hard domains with a smooth top surface since the central constitutional hard segment units R are aligned within the middle of the domain in order to minimize the microscopic defect (Fig. 1b). This picture is backed by the structure analysis and melting behaviour of corresponding model oligourethanes, where it was found that the regularly structured oligourethane consisting of seven repeating units had a distinctively lower heat of fusion ($\Delta H_m = 145$ kJ/mole; $T_m = 468$ K) than corresponding model compound with an octamethylene center unit ($\Delta H_m = 187$ kJ/mole; $T_m = 460$ K), which amounted almost to the figure calculated from the number of repeating units [8].

A random displacement of the urethane chains against each other as observed for PEU-7a (see Fig. 1a) would lead to locally small but far-reaching amorphous defects, which are not tolerated and could be avoided by regularly placing the wrong motif (octamethylene constitutional unit) in the middle of the lamellae and thus to take account for the continuing of the chain [9]. Thus, polyetherurethanes with a regular hard segment architecture (R = tetramethylene) and with hard domains containing defect units (R = octamethylene) exhibit a drastically different interphase between the top and bottom surface of the chain-extended hard domains and the soft segments. Since hard segment repeating units protruding from the hard segment microcrystallite did not act as filler, a smaller plateau modulus resulted for PEU-7a than for the PU-elastomers PEU-7b and PEU-7c. The fact that the heat of fusion of PEU-7c is not higher than that of PEU-7a (as was expected from the findings of the hard segment model compounds, see above) is attributed to limitations in achieving complete rearrangement of the first existing chain-folded into the chain-extended hard domain morphology in the annealing.

In connection with the discussion of the nature of the top and bottom surface of hard domains consisting of chain-extended crystallized PU chains in the context of hard domain filler volume fraction, the adjacent soft segment repeating units should not be neglected. A smooth top/bottom surface (see Fig. 1b) reduces the mobility of the adjacent soft segment repeating units which was also detected by solid-state ^{2}H-NMR measurements of polyether-urethanes with molecularly uniform poly(*N*-alkylurethane) hard segments and partly deuterated POTM soft segments [19] and by DSC measurements of poly(oxytetramethylene-block-*N*-alkylurethane-block-oxytetramethylene) triblock copolymers with a molecularly uniform PU middle block [20]. This phenomenon, i.e., the occurrence of relatively immobile or even crystallized soft segment repeating units adjacent to chain-extended hard domains, could lead to a contribution of the soft phase to the filler content; thus, a higher modulus is expected to be observed. This is in contrast to chain-folded, lamellar domains where soft segment coiling can directly occur at the hard/soft-segment interface because a greater volume is at the soft segment's disposal (cf. Fig. 1c and [9]).

Qualitatively similar variations in the dynamic mechanical properties have been found for the chain-extended modifications of the corresponding PEU-5 samples PEU-5a, PEU-5b and PEU-5c; the hard domain softening (melting) of PEU-5a occurred at a higher temperature than observed for PEU-5b or PEU-5c, but exhibited a smaller modulus in the plateau region.

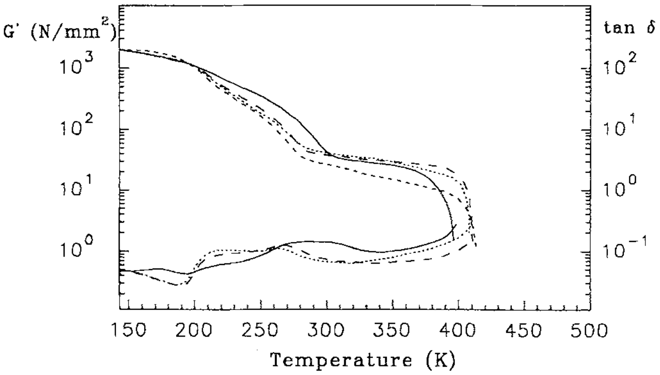


Fig. 5 Dynamic mechanical properties of segmented PU elastomer PEU-7b (———) PEU-7c (. . . .) and PEU-7d (— —) with chain-folded hard segments in lamellar domains as well as dynamic-mechancial properties of the regularly structured segmented PU elastomer PEU-4 (- - -) with chain-extended hard segments in cylindrical domains; G′ = storage modulus; tan δ = loss factor

PU elastomers with chain-folded hard domains showed a different dynamic mechanical behaviour depending on the chain-folding constitutional unit, as demonstrated in Fig. 5. As has already been outlined above, hard segment chain-folding could be achieved by building-in central structure elements R in PEU-N which allowed an adjacent reentry of the poly(*N*-alkylurethane) chain for flexibility (hexamethylene or octamethylene unit) or sterical reasons (1,2-bis(oxyethylene)-phenylene unit) [4, 9]. The Polyether-urethanes PEU-7c and PEU-7d with chain-folded hard domain morphologies (both compression molded samples) exhibited an almost identical dynamic mechanical behaviour, because the conformational isomerism of the central octamethylene and the stereogeometry of the 1,2-bis(oxyethylene)-phenylene unit, respectively, in the middle of the hard segment allowed the perfect formation of sharp folds and adjacent reentry. The fact that the temperature range of the elastomeric behaviour of PEU-7b (compression molded specimen as well) was much smaller than for PEU-7c and PEU-7d is due to the influence of the chain-folding constitutional hard segment unit, located at the lamellar surface (cf. Fig. 1b), on the packing behavior of the adjacent piperazinediylcarbonyloxytetramethyleneoxycarbonyl units next to the chain-fold. Since the hexamethylene center unit is not as suitable for chain-folding as the octamethylene or 1,2-bis(oxyethylene)-phenylene unit because of conformational restrictions, a certain strain resulted on the crystallographic packing of the piperazinediylcarbonyloxytetramethyleneoxycarbonyl units near the fold surface and these effects lowered the melting point of the chain-folded domains. This result has also been confirmed by the data obtained from DSC measurements (Table 1; cf [9]).

A common feature of polyether-urethanes with perfectly chain-folded hard segments (e.g., PEU-7c and PEU-7d) and PU elastomers with regularly built hard segments consisting only of piperazinediylcarbonyloxytetramethyleneoxycarbonyl repeating units is that the softening temperature of the elastomers with chain-folded hard domain morphology is almost the same as in the regularly structured polymers with one piperazinediylcarbonyloxytetramethyleneoxycarbonyl unit more in the chain-extended crystallized hard segment (PEU-4 with R = tetramethylene) than in the fold lamellae, but the modulus in the plateau region is distinctly higher (Fig. 5). The differences in the storage modulus G' are given by the different hard segment content in both elastomers and its impact on the reinforcing filler volume fraction. This coincidence in the hard domain softening (melting) temperature is not that conclusively explained and could be associated with two facts which are coupled with each other: first, similar heights of the chain-folded hard segment lamellae crystallites (given by three repeating units) and of the "crystalline core" of the chain-extended hard segment cylinders (given by three repeating units since one repeating unit randomly protrudes from the top and bottom surface, see packing model Fig. 1a); second, similar contribution of surface effects (fold surface of PEU-7 c/d and fringed surface in the case of PEU-4) on this different type of hard segment crystallites. Both explanations are compatible with the DSC data which exhibit a sharp melting endotherm between 410 K and 430 K for the case of the chain-folded PEU-7c [9] and a relatively broad endotherm between 410 K and 450 K in the case of PEU-4 [3], since the hard domain softening as observed in the torsion pendulum experiment always occurs at the temperature range of the onset of the DSC melting endotherm.

Conclusion

The above data have illustrated that the mechanical properties of segmented polyether-urethanes can be controlled by the proper design of the hard segment. The variation in the dynamic mechanical behaviour is due to the different superstructure of the hard domains which is related to the chemical structure of the central hard segment constitutive unit and which can be also reversibly altered by the sample history. This exemplary example for segmented multiblock copolymers could be transferred to other macromolecular systems and demonstrated new possibilities to modify the material properties of polymer materials by means of small changes in the architecture of the macromolecule. The impact of the chain-extended or chain-folded domain type on the stress-strain properties will be elucidated in a forthcoming publication [21].

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