EFFECT OF MOLECULAR WEIGHT ON MECHANICAL BEHAVIOUR OF SEGMENTED POLYURETHANES

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Dedicated to Dr Blahoslav Sedlacek on the occasion of his 70th birthday.

The effect of molecular weight of polyurethanes on their dynamic mechanical and ultimate behaviour was investigated in wide frequency and temperature ranges. The polyurethanes were prepared from α,ω-dihydroxy-poly(oxypropylene), 1,4-butanediol, 1-butanol and 4,4′-dicyclohexylmethane diisocyanate at constant stoichiometric molar ratio of OH and NCO groups. Molecular weight (MW) of the copolymers was varied by replacing partly the butanediol by equivalent amounts of butanol; the calculated values of MW ranged from 6 000 to infinity. In all samples the constant soft-segment concentrations (≈50 wt.%) were obtained. Two transition regions located around –30 °C and 70 °C, corresponding to the soft polyether and hard polyurethane domains, respectively, were observed with all samples in the temperature dependences of both components of the dynamic modulus measured at 1 Hz. Due to high miscibility of the phases, both transitions overlap; the two-phase character of the structure increases with decreasing MW. At $T > 120$ °C the samples are homogeneous and the frequency–temperature superposition could be applied. Quenching of the samples from 150 °C down to –80 °C preserves quasi-homogeneous structure; the rate of re-establishment of the two-phase structure increases with decreasing MW. The ultimate properties, strain-at-break and tensile strength measured at room temperature decrease with decreasing MW.

The variation of segmental morphology and chemical composition of polyurethanes make them suitable for a number of applications[1,2]. The phase separation of hard and soft segments is a characteristic of segmented block polyurethane copolymers[3]. The driving force for microdomain segregation is the difference in solubility parameters of hard and soft segments. The mixing of phases is governed not only by thermodynamic but also by viscoelastic parameters[3]. The size of microdomains depends on the length of soft segments and their concentration; longer soft segments generally lead to more segregation than shorter ones[2]. The hard segments, usually polyurethane blocks composed of a diisocyanate and a short diol, have glass transition temperature above room temperature and are responsible for good mechanical properties. Usually, hard domains act as fillers or physical crosslinks for soft matrix[1–5]. The two-phase structure of polyurethanes is temperature-dependent and reverses to a single-phase one on heating. Therefore, these systems show different morphology and physical properties depending on thermal history.

The chemical composition, molecular weights and concentrations of soft and hard segments affect the dynamic mechanical and ultimate properties of segmented polyurethanes. An increase in soft segment molecular weight at fixed hard-segment length results in a decrease in modulus and tensile strength but increases strain-at-break due to a decrease in physical crosslinking. A reverse trend is observed with increasing concentration of hard segments. In all cases, the physical properties of the polyurethanes depend on the degree of segregation and domain interfaces[6–9]. One can expect that the rate and degree of segregation and the final two-phase structure will be affected not only by the lengths and concentrations of soft and hard segments but also by the average length of segmented copolymer molecules.

In this work we have studied the effect of molecular weight of segmented polyurethane copolymers prepared from α,ω-dihydroxy-poly(oxypropylene)diol (PD, MW = 1 000), 1,4-butanediol (BD) and 4,4′-dicyclohexylmethane diisocyanate (HMDI) on the dynamic mechanical and ultimate behaviour. Molecular weight of the copolymers was controlled by replacing BD in the reaction mixture by 1-butanol (BuOH) in the mole ratio 1 : 2. Samples were prepared at mole ratio HMDI : (BD + BuOH) : PD = 3 : 2 : 1 (OH : NCO = 1) which gives a constant (ca 50 wt.%) soft-segment concentration in all copolymers.

EXPERIMENTAL

Sample Preparation

Commercial α,ω-dihydroxy-poly(oxypropylene) (PD, M_n = 1 000, hydroxy group content, C_{OH} = 3.4 wt.%) was dried by azeotropic distillation with benzene. The concentration of hydroxy groups was determined by the reaction with an excess of phenyl isocyanate, treating the unreacted isocyanate with dibutylamine and determining its excess by potentiometric titration with HCl. The water content determined by coulometry was less than 0.002 wt.%. 4,4′-Dicyclohexylmethane diisocyanate (HMDI), 1,4-butanediol (BD) and 1-butanol were dried by distillation. Dibutyltin dilaurate (DBTL, ≈0.001 wt.%) was used as catalyst.

The synthesis of copolymers was carried out by prepolymer technique. The polymeric diol and diisocyanate were mixed and heated at 60–70 °C for 1 h under dry nitrogen. Then, the butanediol chain extender and 1-butanol (BuOH) together with DBTL catalyst were added. After mixing for about 30 s, the mixture was poured into a heated mold, kept at 100 °C for about 20 min, and subsequently taken out of the mold for post-curing at 80 °C for 24 h.

The copolymers were prepared at constant stoichiometric ratio of reactive OH and NCO groups $[NCO]_{DI}/[OH]_{PD}/[OH]_{BD}+[OH]_{BuOH} = 3 : 1 : 2$. This ratio leads to the constant soft segment concentration ≈50 wt.% as the number-average molecular weight of the repeating unit $M_0 \approx 1\,966$. Molecular weight of the samples was controlled by addition of BuOH. For our case of structure build-up, the following equation for the number-average molecular weight M_n is valid[10,11]

$$M_n = \frac{n_{\mathrm{PD}}M_{\mathrm{PD}} + n_{\mathrm{BD}}M_{\mathrm{BD}} + n_{\mathrm{BuOH}}M_{\mathrm{BuOH}} + n_{\mathrm{HHDI}}M_{\mathrm{HMDI}}}{1 - [p_{\mathrm{OH}}(2n_{\mathrm{PD}} + 2n_{\mathrm{BD}} + n_{\mathrm{BuOH}}) + p_{\mathrm{NCO}}\, 2n_{\mathrm{HMDI}}]\,/\,2}\ , \qquad (1)$$

where n and M are molar fractions ($\Sigma n_i = 1$) and number-average molecular weights of the components, respectively, and p are conversions of OH and NCO groups. As spectroscopic measurements revealed that no NCO groups were present at the end of the reaction we believe that full conversions of the reactive groups were achieved ($p_{\mathrm{OH}} = p_{\mathrm{NCO}} = 1$). Six samples with theoretical values of M_n 6 000, 12 000, 21 200, 31 800, 66 200 and were prepared.

Methods of Measurement

Dynamic mechanical measurements were performed on a Rheometrics RDA II analyzer. Both components of the complex shear modulus ($G^*(\omega) = G' + iG''$, where G' and G'' are the storage and loss modulus, respectively) were determined. Two types of measurements were carried out:

– The temperature dependence of the modulus G^* at a constant frequency $f = 1$ Hz in temperature region –100 to 150 °C in the torsion rectangular mode. The rate of the increase of temperature was 2 K/min.

- The measurement of the modulus G^* in a broad angular rate range $\omega = 10^{-2}$ to 10^2 rad/s and temperature interval from 0 to 160 °C in the parallel-plate mode. By applying the frequency–temperature superposition to the data, superimposed curves of the moduli $G'_{\mathrm{p}} = G'b_T$ and $G''_{\mathrm{p}} = G''b_T$ against reduced angular frequency ω_{a_T} shifted to $T_0 = 100$ °C for some samples were obtained. The horizontal a_T and vertical b_T shift factors were also determined.

Stress-strain measurements were carried out with dumbell-shaped specimens ($l_0 = 2.5$ cm) on an Instron tensile tester. Tensile strength, σ_{b}, and strain at break, ε_{b}, were determined at three different rates of strain $\dot{\varepsilon} = (l(t) - l_0)/l_0 = 0.1$, 1 and 20 min^{-1} at room temperature ($l(t)$ and l_0 are deformed and initial sample lengths, respectively). The values σ_{b} and ε_{b} are averages of five measurements. Together with ultimate characteristics also values of the initial Young modulus, $E_{\varepsilon\to 0}$, and of the Young modulus at 100% of the strain, $E_{\varepsilon=1}$, were determined from stress-strain dependences.

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependences of the real modulus, G', and the loss tangent, tg $\delta = G''/G'$, for samples with $M_n = 6\,000$ and $M_n \to \infty$ annealed at room temperature for at least two months. Two transition regions located at temperatures ≈ –30 °C (soft PD phase) and ≈70 °C (hard HMDI–BD–BuOH phase) can be observed. Both transitions are better developed for sample with $M_n = 6\,000$ than for sample with $M_n \to \infty$; this means that the segregation of the segments into microdomains increases with decreasing molecular weight of copolymer. Overlapping of two broad maxima observed in temperature dependences of tg δ suggests the high miscibility of the hard and soft phases, especially for sample with $M_n \to \infty$. The shift of the soft segment transition to higher temperatures observed for sample with $M_n \to \infty$ suggests that in this case some urethane blocks are dispersed in the soft phase. Higher values of storage modulus G' in temperature region from 30 to 100 °C found for the sample with lower

M_n in comparison with sample with higher M_n also show that two-phase structure is better developed for sample with M_n = 6 000 than for sample with $M_n \to \infty$.

An example of the effect of quenching from 150 °C down to –80 °C is shown in Fig. 2 for a sample with M_n = 66 200. While the original sample shows two-phase behaviour (two overlapping transitions), the quenched sample preserves a quasihomogeneous mixed structure with one broad transition (one broad maximum in tg δ). As expected, in temperature region from 30 to 100 °C, where the hard phase dominates, the values of

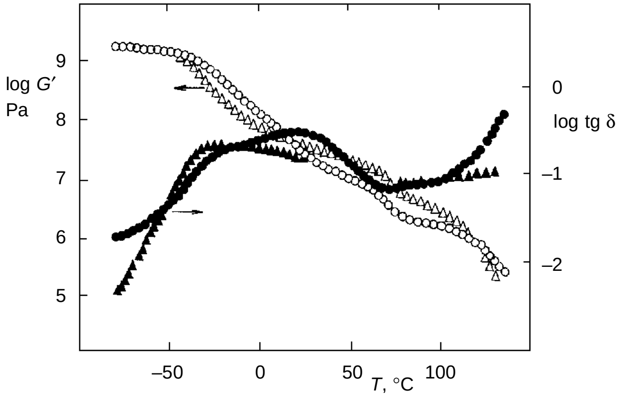

FIG. 1
Temperature dependence of the storage modulus, G', and loss tangent, tg δ, measured at f = 1 Hz for samples with M_n = 6 000 (Δ, ▲) and →∞ (❍, ●)

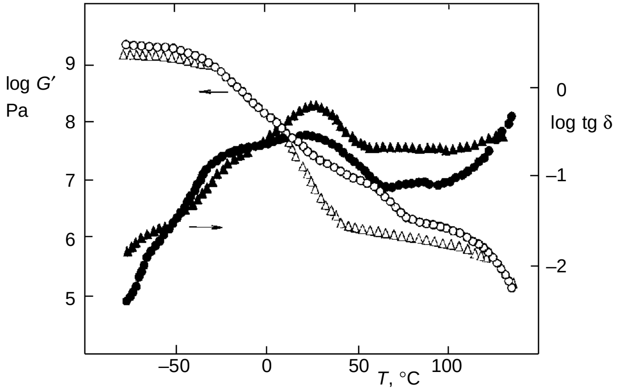

FIG. 2
Temperature dependence of the storage modulus, G', and loss tangent, tg δ, measured at f = 1 Hz for original (❍, ●) and quenched (Δ, ▲) sample with M_n = 66 200

G' of quenched sample are much lower than those of original sample. Similar behaviour was found also in other segmented polyurethane systems[9,12].

In the region of $T > 120$ °C all samples are homogeneous; the frequency–temperature superposition could be easily applied and smooth superimposed mechanical functions were obtained (Figs 3 and 4). On the other hand, for temperatures $T < 100$ °C systematic deviations in superimposed mechanical functions appeared (especially in the loss tangent, Fig. 4). In the same temperature region, at $T < 100$ °C, abrupt changes in the dependences of the horizontal, a_T, and the vertical, b_T, shift factors on temperature can

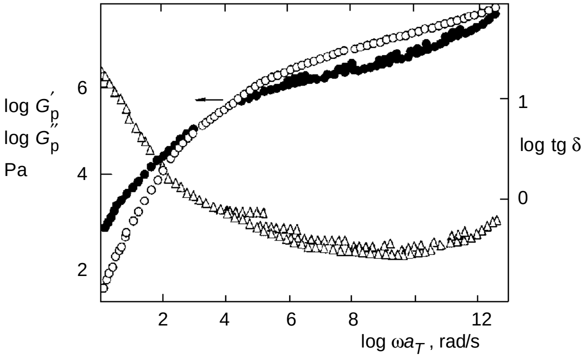

FIG. 3
Frequency dependence of the reduced storage, G_p' (○), loss G_p'' (●) moduli and of the loss tangent, tg δ (Δ) for sample with M_n = 6 000

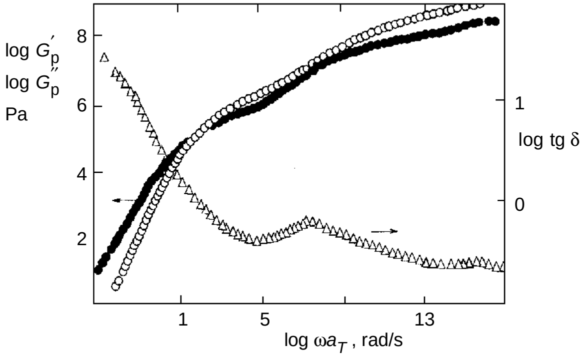

FIG. 4
Frequency dependence of the reduced storage, G_p' (○), loss G_p'' (●) moduli and of the loss tangent, tg δ (Δ) for sample with M_n = 66 200

be observed (Fig. 5). The lower is the molecular weight of the sample the larger changes in the shift factors are found. All these observations suggest that below 100 °C samples show thermorheologically complex behaviour as degree of segregation of phases strongly depends on temperature and time. Similar complex mechanical beha-

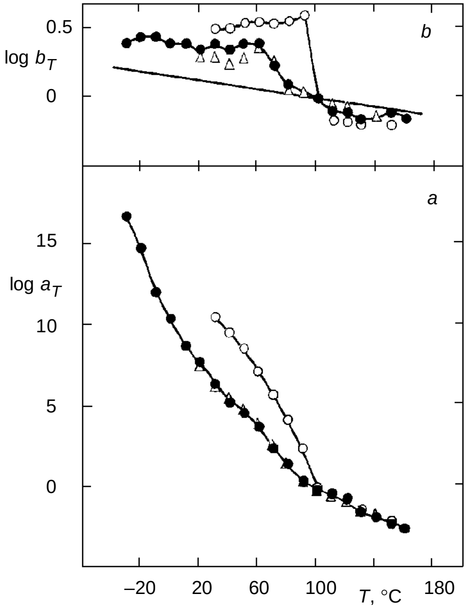

FIG. 5
Temperature dependence of the horizontal shift factor, log a_T (*a*) and of the vertical shift factor, log b_T (*b*) for samples with M_n = 6 000 (❍), 66 200 (●), →∞ (Δ); full line: T_0/T

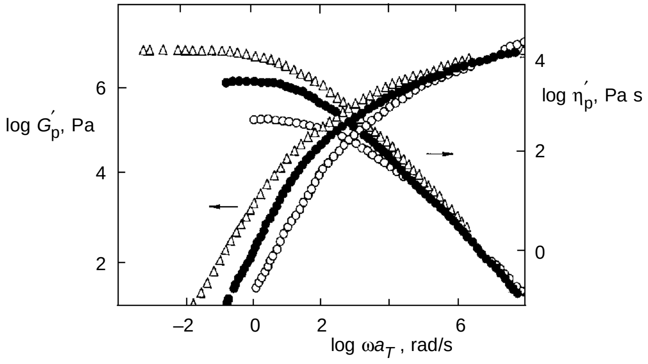

FIG. 6
Frequency dependence of the reduced storage modulus, G_p', and of the reduced storage viscosity $\eta_p' = G_p''/\omega$ for samples with M_n = 6 000 (❍), 66 200 (●), →∞ (Δ)

viour for multiple-phase systems was found earlier[13–15] for segmented copolymers and blends of random copolymers.

As expected, the extent of the rubbery plateau of the superimposed storage modulus G'_p on the reduced frequency ωa_T in the homogeneous state (for $T > 120$ °C) increases with increasing molecular weight of sample (Fig. 6). A similar behaviour is shown also by the real part of viscosity, $\eta'_p = G''_p/\omega$ (Fig. 6), where the constant values, independent of frequency in the low-frequency region η'_0 and increasing with increasing M_n of samples were observed. The constant η'_0 values correspond to the Newtonian behaviour of the systems[16].

An example of the time dependence of the re-establishment of two-phase structure after temperature jumps from 160 °C (isotropic state) down to 70 or 100 °C is shown in Fig. 7 for two samples with M_n = 6 000 and $M_n \to \infty$. As expected, the rate of reformation of the domain structure increases with decreasing molecular weight of copolymer and increasing difference in temperatures at temperature jumps. While for the jump from 160 to 70 °C the crossover of G' and G'' (gel point for physical network formed by the hard-phase interactions) appears at time t_g = 11 min (sample with M_n = 6 000)

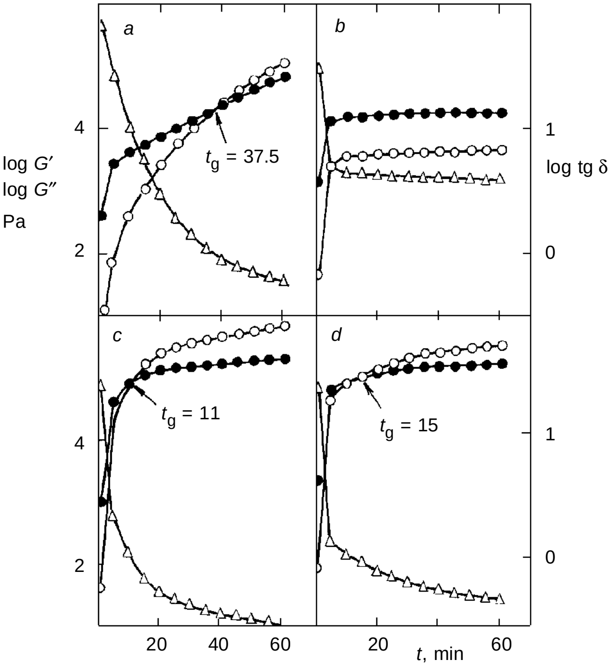

FIG. 7

Time dependence of the storage, G' (❍) loss, G'' (●) moduli and of the loss tangent, tg δ (Δ), measured at f = 1 Hz after indicated temperature jumps: 160 → 100 °C (*a* and *b*), 160 → 70 °C (*c* and *d*). M_n = 6 000 (*a* and *c*), →∞ (*b* and *d*) and t_g = 15 min (sample with $M_n \to \infty$), for the jump from 160 to 100 °C t_g = 37.5 min (sample with M_n = 6 000), and for sample with $M_n \to \infty$ the crossover of G' and G'' does not exist.

Although the soft-segment concentrations and molecular weights of soft and hard segments are roughly constant in all samples, the initial $E_{\varepsilon \to 0}$ and 100% strain $E_{\varepsilon = 1}$ Young moduli measured at room temperature increase with decreasing M_n of co-

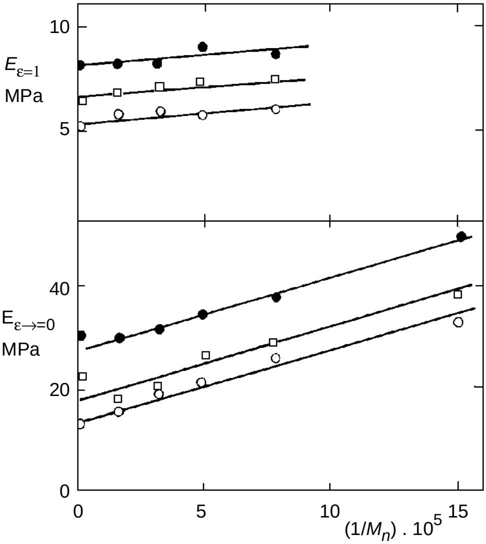

FIG. 8
Dependences of the initial, $E_{\varepsilon \to 0}$, and 100% strain, $E_{\varepsilon=1}$, Young moduli on the inverse molecular weight $1/M_n$ for various strain rate $\dot{\varepsilon}$ = 20 (●), 1.0 (❐), 0.1 (❍) min^{-1}

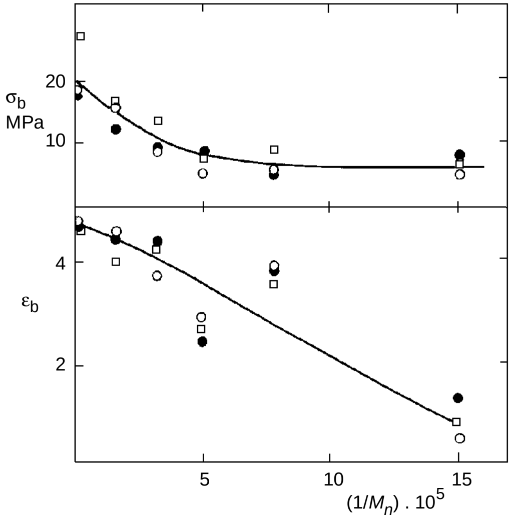

FIG. 9
Dependences of the tensile strength, σ_b, and strain at break, ε_b, on the inverse molecular weight $1/M_n$ for various strain rates $\dot{\varepsilon}$ = 20 (●), 1.0 (❐), 0.1 (❍) min^{-1}

polymers (Fig. 8). This fact is in accord with previously discussed results from which it followed that decreasing M_n enhances segregation which leads to the better developed two-phase structure. Increasing elongation suppresses the effect of structural irregularities due to the orientation of the hard segments and the increase in the $E_{\varepsilon=1}$ values with M_n is lower than the increase in $E_{\varepsilon\to0}$ values with M_n. Due to the viscoelastic nature of the deformational behaviour both moduli, $E_{\varepsilon\to0}$ and $E_{\varepsilon=1}$, increase with increasing strain rate.

Despite of the large scatter, a pronounced decrease in the value of the strain-at-break, ε_b, with decreasing M_n of copolymers was observed (Fig. 9). Such decrease is usually found[17,18] for systems with increasing crosslinking density. As the hard segment concentration is constant in our samples, the observed decrease in ε_b suggests that the increasing phase segregation, due to the stabilization of the soft and hard blocks, increases effective physical crosslinking. Although both moduli, $E_{\varepsilon\to0}$ and $E_{\varepsilon=1}$, increase with decreasing M_n, the tensile strength σ_b decreases. This means that in tensile strength the decrease in ε_b overcompensated the increase in the modulus with increasing M_n. The change in the strain rate $\dot{\varepsilon}$ has only a minor effect on the molecular weight dependences of σ_b and ε_b.

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