Dynamic Mechanical Behavior and Structure of Polyurethaneimides

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Synopsis

Dynamic mechanical behavior and X-ray diffraction of two series of segmented poly-urethaneimides (PUI) prepared either from poly(ethylene adipate) glycol (PEA), pyromellitic dianhydride (PMDA) and 4,4'-diphenylmethane diisocyanate (MDI), or from PEA, PMDA, and a mixture of 2,4- and 2,6-tolylene diisocyanate (TDI) were studied. All samples have a two-phase structure of the soft polyester (PE) phase and hard polyimide (PI) phase. PI microdomains containing MDI units are semicrystalline, whereas those with TDI are crystalline only at highest contents of TDI. The storage modulus E' increases with increasing fraction of the hard phase. The MDI-containing hard phase has a stronger effect on E' and also makes the plateau on the dependence of E' on temperature more pronounced.

INTRODUCTION

In a previous study[1,2] the synthesis, thermal, mechanical, and electric properties of polyurethaneimides (PUI) prepared from polyester-based macro-diisocyanate, free aromatic diisocyanate, and pyromellitic dianhydride were described. It was found that these copolymers were of good thermal stability and showed high tensile properties. Dielectric losses measurement revealed that the T_g of soft segment in PUI was lower than that of typical linear polyurethanes,[3] which may be ascribed to a more extensive phase separation of the hard aromatic polyimide segments in the soft polyether– or polyester–urethane matrix.[2]

In this work the X-ray scattering and temperature dependence of dynamic mechanical properties of two PUI series were studied over a wide temperature range. The results were correlated with the chemical and physical structure of the investigated polymers.

EXPERIMENTAL

Materials

The series of polyurethaneimide (PUI) samples were prepared from polyes-ter-based macrodiisocyanate, free diisocyanate, and dianhydride of pyromel-litic acid (PMDA) as described previously.[4]

The macrodiisocyanates (PU-1 and PU-2), which form the soft segments of the PUI, were synthesized by the reaction between: (a) poly(ethylene

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adipate)glycol (PEA), of the number average molecular weight $M_n = 2000$, hydroxyl number 56 (Organika-Zachem, Poland), and (b) tolylene diisocyanate (TDI) (mixture of 80% 2,4- and 20 % 2,6-isomer (Organika-Zachem), or 4,4'-diphenylmethane diisocyanate (MDI) (Bayer).

The diisocyanates were in molar excess and the reaction was carried out at 70–85°C for 30 min. The PU obtained was dissolved in dimethylformamide (DMF) to form a 60 wt % solution and reacted with 0.5 mol PMDA per NCO group.
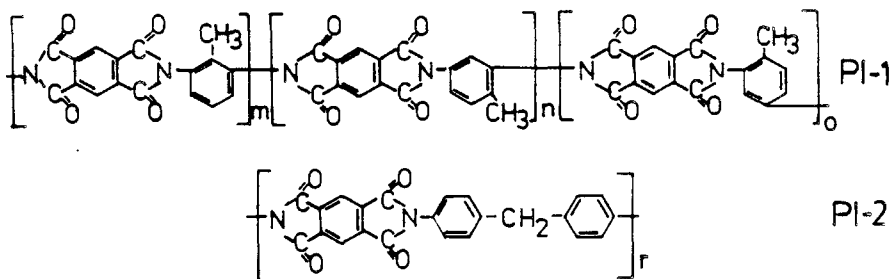
The PUI films were prepared by pouring the obtained solution into a centrifugal barrel and by gradual heating from 50 to 100°C. Next, the 0.18–0.25 mm thick films were annealed for 0.5 h at 140°C and for 2 h at 200°C, which caused the thermal imidization:
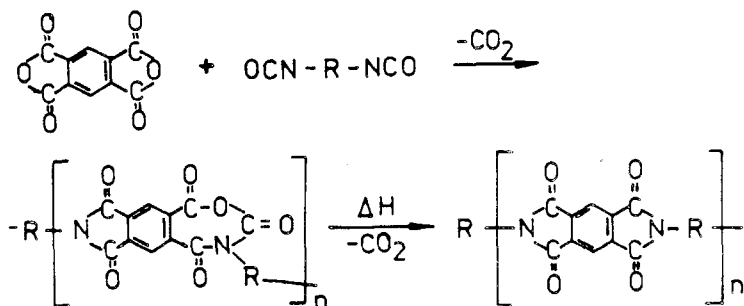
The structure of the soft segments of the polymers is given by the following formula:

PU-1 : R = (methyl-substituted phenyl isomers) and   PU-2 : R = phenyl-CH₂-phenyl
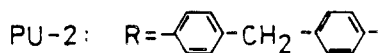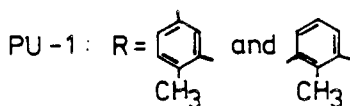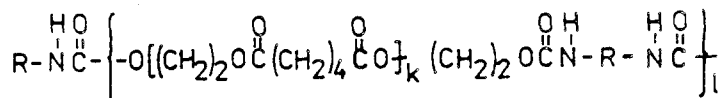
The structure of the polyimide (PI) hard segments:

PI-1

PI-2

PEA was dehydrated before the synthesis by heating at 90–100°C for 3 h under reduced pressure. MDI used was of commercial grade. TDI was distilled under reduced pressure at 110°C. PMDA (Fluka, mp = 272–275°C, containing

2.9% pyromellitic acid) was used as received or after sublimation at 230–240°C under reduced pressure. The solvent DMF was dried for 24 h over P_2O_5 and distilled under reduced pressure.

Three series of PUI were obtained (Table I): (A) Samples PUI-1–3 were obtained from PU-1; the weight fractions w_H of the PI-1 segments were 28.0, 40.8, and 49.3%, respectively. (B) PUI-4–8 were obtained from PU-2 with the weight fraction w_H of PI-2 segments: 27.2, 35.9, 39.8, 43.3, and 46.4%, respectively. In this series, as opposed to the two others [(A) and (C)], PMDA was purified by sublimation prior to the reaction. (C) PUI-9–13 were obtained from PU-2 with the weight fraction w_H of PI-2 as in PUI-4–8, and PUI-14–16 with the weight fraction of PI-2 51.4, 56.3, and 60.3%.

The weight fractions w_H were calculated similarly to the calculations of the hard segment content in typical polyurethanes, i.e., as the ratio of the weight of PMDA + TDI or PMDA + MDI to the total weight of the reagents. The evolution of CO_2 in PUI synthesis was taken into account in these calculations.

The model polymers PU-1, PU-2, and PI-1, PI-2 were prepared under the same reaction conditions as for preparation of PUI, using the molar ratio NCO : OH and NCO : anhydride group 1 : 1 for PU and PI models, respectively.

Methods of Measurements

The dynamic mechanical measurements were made using a Rheovibron Dynamic Viscoelastometer, Model DDV II (Toyo Measuring Instruments Company, Tokyo, Japan). The temperature range covered was from −60 to 250°C. [However, for PUI of very low polyimide content (28%) the tan δ values were beyond the measurement range above 119°C for PUI-1 and above 220°C for PUI-4 and PUI-9.] The samples were heated at a rate of 1.3–1.5°C/min and the frequency used was 110 Hz.

The wide-angle X-ray scattering (WAXS) was recorded using the flat film camera Kiessig. CuKα radiation filtered by the Ni foil was used.

Small-angle X-ray measurements (SAXS) were made by means of a Kratky camera equipped with a proportional counter. The X-ray source was operated at 40 kV and 30 mA using a tube with a Cu target. For elimination of CuKβ radiation, X-rays were filtered through an Ni foil. Pulse height analysis of the output of the proportional counter was used. For the scattered intensity measurements, a step scan method was used.

TABLE I
Composition of Samples

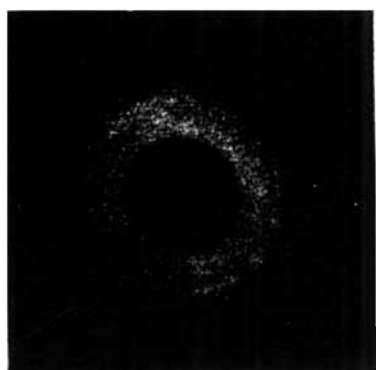| Sample	1	2	3	4	5	6	7	8
w_H^a	0.280	0.408	0.493	0.272	0.359	0.398	0.433	0.464
Sample	9	10	11	12	13	14	15	16
w_H^a	0.272	0.359	0.398	0.433	0.464	0.514	0.563	0.603

$^a w_H$ is the weight fraction of hard segments, samples 1–3 were obtained from PU-1, samples 4–16 were obtained from PU-2, and in samples 4–8 the PMDA was purified by sublimation.
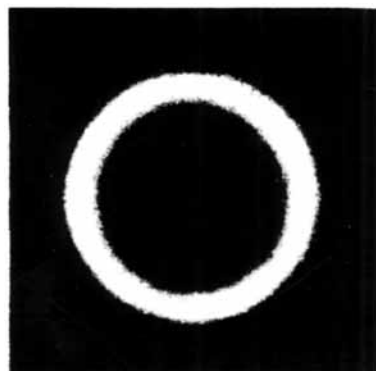
Fig. 1.   WAXS photographs of models of soft segments (PU-1, PU-2) of hai.. segments with TDI (PI-1) and MDI (PI-2) and polyurethaneimides (PUI-1, PUI-16).
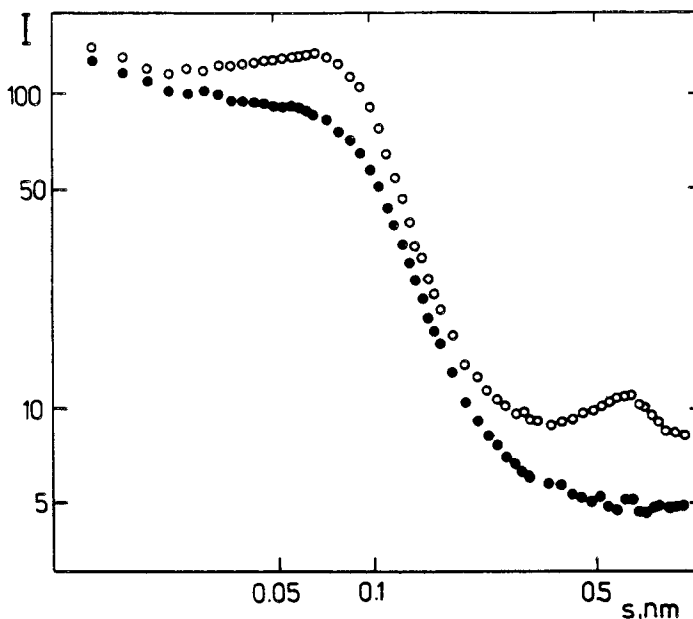
Fig. 2. Smeared SAXS curves of polyurethaneimides (●) PUI-3, and (○) PUI-4, I-relative intensity, $s = 2 \sin \theta / \lambda$

RESULTS AND DISCUSSION

X-Ray Study

PUI and models of their hard and soft segments were investigated by WAXS (Fig. 1) and SAXS (Fig. 2). WAXS photographs of soft segments of PU-1 and PU-2 contain several sharp reflections, indicating a well-ordered crystalline phase (about 50 vol. % in each component). A WAXS photograph of the model PI-2 (hard segment with MDI) has one sharp reflection at 1.6 nm, which corresponds to periodicity along the chain, and a broader reflection at 0.49, characterizing the interchain order.[5] Hence, the sample is partly crystalline, with a more perfect order along the chains. A WAXS photograph of the model PI-1 with TDI shows two very diffuse reflections at 0.32 and 0.48, which indicates that the model is noncrystalline. WAXS photographs of polyurethaneimides 4, 8, 9, 13 (with MDI) have a sharp reflection at 1.6 nm and two overlapping reflections at 0.49 nm: The samples are partly crystalline. The reflection at 1.6 nm becomes sharper with increasing MDI fraction, which means that the size of the crystallites increases in the direction of chains L_c (Table II). These values were obtained using Scherrer's equation

$$L_c = \lambda / \beta \cos \theta$$

where β is the integral breadth of reflection profile, λ is the wavelength of used radiation, and 2θ is the scattering angle. According to the WAXS photograph (Fig. 1), the sample PUI-1 (with TDI) is amorphous, while PUI-3 with a double TDI fraction is partly crystalline. While the models PU-1 and PU-2 are crystalline in the pure state, soft segments of both types of PUI are

TABLE II
Structure Parameters of PUI Samples[a]

Sample	ρ (g cm^{-3})	v_H	L_c	L	l_h	l_p (nm)	l_H (nm)	l_S (nm)
PUI-1	1.262	0.280	—	10.6	3.0	2.9	3.9	11.6
PUI-3	1.323	0.450	—	10.3	4.6	2.7	4.9	5.0
PUI-4	1.263	0.248	6.8	10.5	2.6	2.7	2.0	10.9
PUI-8	1.299	0.435	7.4	11.0	4.8	2.9	5.1	6.7
PUI-9	1.260	0.248	6.3	10.5	2.6	2.7	2.0	10.9
PUI-16	1.326	0.574	8.1	9.3	5.3	2.4	4.2	5.6

[a] ρ is the density, v_H is the volume fraction of hard segments, L_c is the mean size of crystallites, L is the long spacing, l_h is the mean thickness of hard lamellar microdomains, l_p is the range of inhomogeneities, and l_H and l_S are the transversal lengths of hard and soft microdomains

amorphous. The measured density and composition values of PUI gave 1.22 g cm^{-3} for the density of the soft phase, which corresponds to the density of amorphous PEA. The density of hard microdomains of PUI is about 1.42 g cm^{-3}. If we start from the reported density values[6] of crystalline and amorphous polyimide, the crystallinity of hard microdomains does not exceed 15 vol. %.

The SAXS curves of both models of soft segments correspond to the two-phase structure with supermolecular periodicity 16 nm. The SAXS curve of model PI-1 (with TDI) corresponds to a one-phase structure; that of model PI-2 corresponds to a two-phase structure with supermolecular periodicity 7.5 nm. The SAXS curves of PUI correspond to a two-phase structure in all cases (Fig. 2). The small-angle maximum on the curves is due to alternating soft and hard lamellar domains in stacks[6,7] with an average period L of about 10 nm (Table II). From the long spacing L and the volume fraction of hard segments v_H, the average thickness of hard lamellar microdomains l_h was estimated by means of the relation

$$l_h = v_H L$$

The l_h value increases with increasing content of hard segments (Table II). Furthermore, the SAXS curves were interpreted using Porod's theory of scattering from two-phase systems.[8] In this theory the range of inhomogeneity l_p and transversal lengths of hard l_H and soft l_S microdomains are defined by

$$l_p = \int_0^\infty sI(s)\,ds/2\pi \lim_{S \to \infty} s^3 I(s) = v_H l_S = v_S l_H$$

where $I(s)$ is scattered intensity, $s = 2\sin\theta/\lambda$, and v_H and v_S are volume fractions of hard and soft segments. Both the inhomogeneity range l_p and the transversal length of hard (l_H) and soft (l_S) microdomains were determined for the copolymers (Table II). With increasing fraction of hard segments, the transversal length of hard microdomains should increase, while that of soft microdomains should decrease.
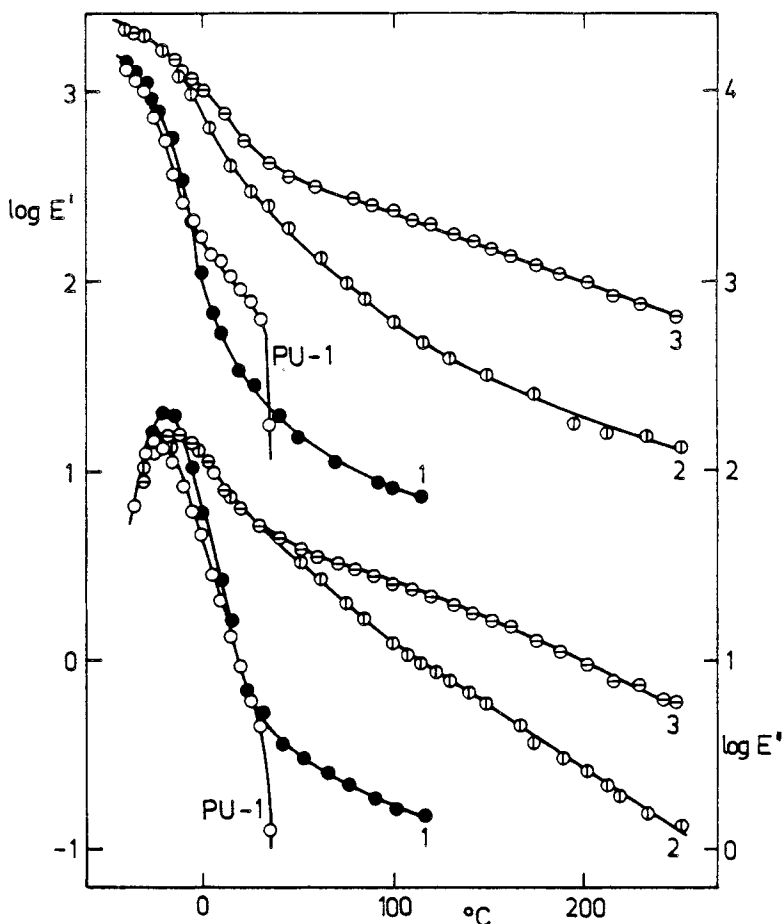
Fig. 3. Temperature dependences of the real E' (MPa) and imaginary E'' (MPa) component of the Young modulus of PUI copolymers with TDI. Samples are denoted as in Table I.

Dynamic Mechanical Behavior

Figures 3, 4, 5 show the temperature dependences of components of the dynamic Young elasticity modulus E' and E'' of segmented polyurethane-imides (PUI), along with their models PU-1, PU-2, and PI-2 (no sample for mechanical measurements could be prepared from model PI-1 based on TDI). As expected, the temperature dependences of E' and E'' of PUI samples lie in the range between the E' and E'' dependences of the corresponding models. PUI samples with the lowest content of the hard segments are an exception: in the range between 10 and 20°C, their E' values lie below those of the corresponding models (Figs. 3–5). The finding is in agreement with conclusions drawn from X-ray measurements and indicates decomposition of the crystalline structure of soft segments in PUI. Due to the large content of the crystalline phase, an unpronounced plateau of the modulus E' can be seen with models PU-1 and PU-2 in the temperature range 0–30°C (Figs. 3 and 4). A fast decrease in E' at higher temperatures is connected with melting of crystalline domains (for PEA, the melting point is 56°C). As expected, the
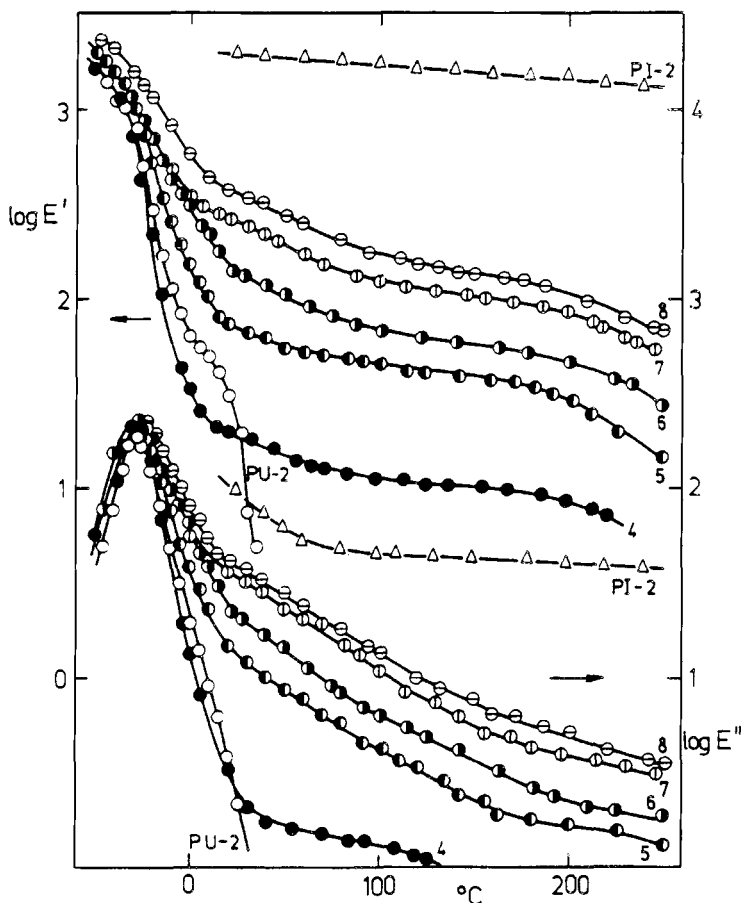
Fig. 4. Temperature dependence of the real E' (MPa) and imaginary E'' (MPa) component of the Young modulus of PUI copolymers with MDI and sublimed PMDA. Samples are denoted as in Table I.

replacement of TDI for MDI does not virtually affect the temperature position of the maximum E'' of both PU-1 and PU-2 ($T_m = -25°$C, Figs. 3 and 4); this fact is in agreement with the X-ray measurement. On the other hand, the E' vs. T dependence of the model PI-2 clearly shows that up to 250°C the sample is in the glassy state (Fig. 4). The temperature stability of PI-2 is probably favorably affected by the presence of the crystalline phase (cf. X-ray measurement).

It can be seem in Figure 3 that the PUI samples with TDI show temperature dependences of E' and E'' typical of nonhomogeneous systems, in agreement with the X-ray scattering measurement. The two-phase behavior is also suggested by the fact that the temperature of the maximum T_m in the E'' vs. T dependence is only little affected by the amount of the hard phase PI (T_m varies in the range from -26 to $-8°$C). With increasing content of the hard phase, both components of the dynamic modulus of PUI samples increase. The comparatively fast decrease of E' and E'' with temperature in the range $T > 0°$C (together with increasing T_m with the content of the PI
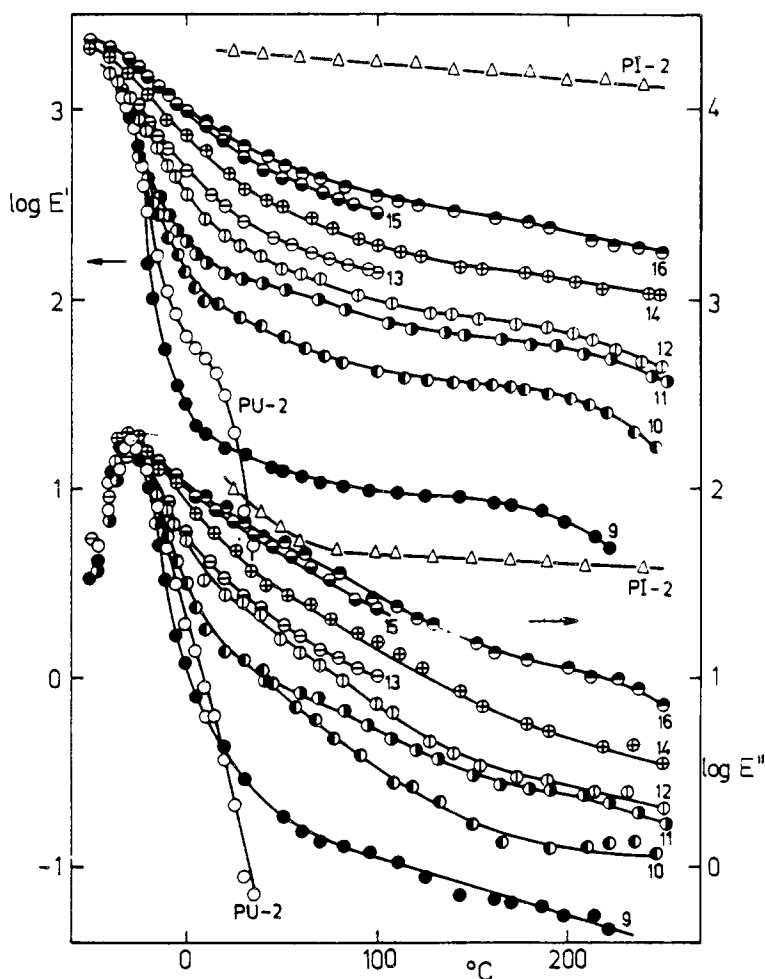
Fig. 5. Temperature dependence of the real E' (MPa) and imaginary E'' (MPa) component of the Young modulus of PUI copolymers with MDI and commercial PMDA. Samples are denoted as in Table I.

component) indicate a considerable mutual influence of the two components and an extensive interaction between the phases.

The PUI samples based on MDI show a more pronounced two-phase behavior than those with TDI (Figs. 4 and 5). This finding is in accord with the X-ray measurement, where all PUI with MDI were found to contain the crystalline phase in the hard PI segment. In this case, the temperature of the maximum remains virtually unaffected by the content of the hard phase, and all the temperature dependence of E' of PUI has an extensive plateau up to 220°C. The unpronounced temperature dependence of E' for $T > 20$°C suggests a weak interaction between the hard and soft phase and is determined by the temperature dependence of the PI component. These conclusions are the same for all samples prepared with MDI, irrespective of the PMDA used (commercial or purified). Generally, the temperature dependences of the mechanical behavior of polyurethaneimides are more favorable than those of
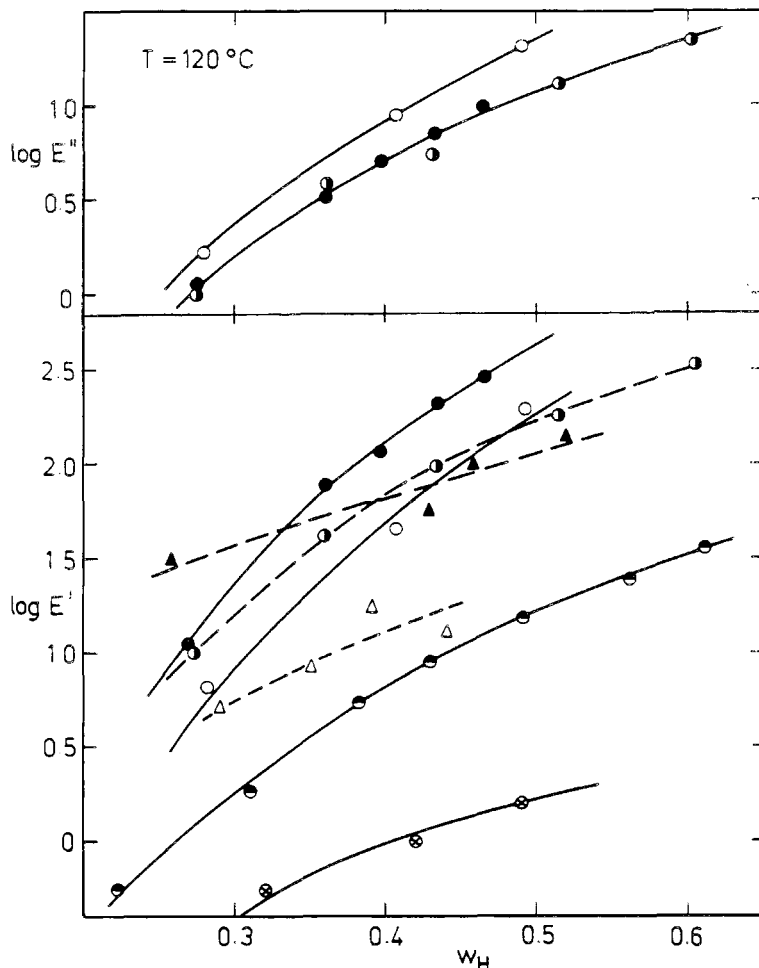
Fig. 6. Dependence of the real E' (MPa) and imaginary E'' (MPa) component of the Young modulus measured for $T = 120°C$ on the weight fraction of the PI block w_H: (○) samples of series A; (●) samples of series B; (◑) samples of series C; (⊗) polycaprolactone diol–TDI/1,4-bitanediol (Ref. 11); (◓) polycaprolactone diol–MDI/1,4-butanediol (Ref. 11); △ poly(ethylene adipate)diol–MDI/1,4-butanediol (Ref. 10); (▲) poly(ethylene adipate)diol–MDI/3,3-dichloro-4,4'-diaminodiphenylmethane/1,4-butanediol (Ref. 10).

typical polyurethanes based on low-molecular weight glycols or diamines, for which a drop in the modulus was observed[3,9,10] already in the temperature range from 160 to 190°C.

The effect of the content of hard PI segments on values of the components of the complex moduli E' and E'' at 120°C can be seen in Figure 6. As expected, with increasing weight fraction of the hard PI phase, w_H, both components of the modulus increase. The loss modulus E'' of samples with TDI is higher than E'' of samples with MDI; the dependence of E'' on w_H of samples with MDI is independent of the purity of the starting PMDA. The higher values of E'' samples with TDI indicate a higher mobility in these polyurethaneimides. On the other hand, PUI with MDI have higher values of

the E' modulus than samples with TDI. Similar results have been obtained earlier[3] for copolymers poly(caprolactone)diol–MDI/1,4-butanediol, or poly(caprolactone)diol–TDI/1,4-butanediol, but their E' moduli are more than 10 times lower compared with those of our PUI.

Values of the E' modulus of samples prepared from commercial PMDA and MDI lie between those of samples of sublimed PMDA and of samples with TDI. The acid content in commercial PMDA leads to shorter PI chains,[12] and thus destroys the structure of the PI blocks. It is interesting[10] that generally at the same content of the hard component polyurethanes based on poly(ethyleneadipate)glycol–MDI/1,4-butanediol have the storage modulus lower than PUI samples with TDI. Only after the replacement of MDI with 3,3'-dichloro-4,4'-diaminodiphenylmethane in the hard block[10] E' values obtained at higher w_H become comparable with those of PUI samples with TDI. Thus, PI blocks with TDI have the same influence on the increase in the modulus as aromatically substituted urea groups in typically segmented polyurethanes[13] from MDI. The greatest improvement of mechanical and temperature properties was reached with polyurethaneimides containing MDI.

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