

Supramolecular Structure of Crosslinked Polyurethane Elastomers Based on Well-Defined Prepolymers

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ABSTRACT: This article provides both quantitative and qualitative evaluations of supermolecular structures present in segmented polyurethane elastomers. This work presents our recent results from investigation of the microdomain morphology of poly-(ether-urethanes) based on polyethylene glycol and poly-(ester-urethanes) based on poly- ϵ -caprolactone diol with different molecular weight as soft segments and hard segments based on the combination of TDI and triethanolamine or 4,4',4''-triphenylmethane triisocyanate (Desmodur RE). Those PU elastomers were obtained not only in a typical one-step method but also in the prepolymer method with the use of urethane oligomers with controlled molecular weight distribution (MWD). Prepolymers with well-defined chain structures and narrow distributions of their molecular

weights (MWD) $\overline{M}_w/\overline{M}_n = 1.1\text{--}1.6$ were produced in a multistage method, i.e., in step-by-step polyaddition of 2,4- and 2,6-TDI with polyoxyethylenediols or polycaprolactonediol of different molecular weights. Isocyanate oligomers obtained at individual stages were then crosslinked with triethanolamine, whereas hydroxyl-terminated oligomers were crosslinked with Desmodur RE. Microdomain morphology of the soft and hard-segments structure was characterized by means of wide-angle X-ray scattering and scanning electron microscope. The phase morphology and microdomain crystallinity were investigated. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3292–3299, 2008

Key words: polyurethane elastomers; WAXS; SEM

INTRODUCTION

Segmented polyurethane elastomers are composed of soft segments and more rigid, polar hard segments. The soft segments are formed generally from polyethers or polyesters and the hard segments based on diisocyanate and a low-molecular-weight chain extender.^{1–23}

Because of thermodynamic incompatibility between the hard and soft segments, they undergo microphase separation, resulting in the heterogeneous phase-separated structure of hard and soft domains. Normally, phase separation is incomplete and the hard and soft segment phases still contain certain amounts of the other segment. The mean domain size increases from 5 to 25 nm as the hard segment content increases and in the case the two-shot process.⁹

Depending on the soft and hard segment concentrations, the polymer has a continuous hard phase with a dispersed soft phase, a continuous soft phase with a dispersed hard phase, or a bicontinuous phase.¹²

The hard-segment and soft-segment units are often crystallizable to form spherulitic structures with a diameter of $\sim 5\text{--}10$ nm, or randomly oriented cylinders with the comparative diameter and the length of ~ 100 nm.^{12,21} Microdomain crystallinity and crystallite sizes are greatly influenced by the chemical structures of raw materials,^{7,18} by the ratio of hard-block and soft-block components,^{2–4} by the average block length employed (including molecular weight distribution),^{5,10,20} by the crosslinking density,¹¹ and by the thermal history of the material.

The normally produced polyurethane elastomers, with a broad distribution of hard segment lengths, crystallized including “para-crystalline” regions (imperfect crystallites). The “ideal” hard segment crystals are reported for some monodisperse model compounds.²⁰

The existence of two or three morphologies for the crystal structure of MDI and BD hard segments was confirmed by many authors^{4,13–16,18,20}. “Type I” crystallites with short-range order, “Type II” crystallites with long-range order, and “Type III” crystallites observed at specimens stretched at about 100°C. “Type I” crystallites are much smaller and badly ordered spherulites. “Type II” ones are well-ordered spherulites with a diameter of ~ 1.7 nm. The poorly ordered state of TDI-derived rigid segments is

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specific for the elastomers which contain less crystallizable TDI in their structures.^{2,22}

Many characterization techniques have been used to understand the relationship between the chemical architecture, morphology, and chemical properties.^{1–23} It is believed that the size, shape, and structure of the hard-segment and soft-segment domains play a decisive role in determination of mechanical properties.^{6,8,19}

The present article reviews the effects of numerous structural and process-related factors on the morphology of supermolecular structures which are present in such polyurethane elastomers. This report refers to our research findings which have been published earlier, within the effects of molecular weights and their distribution in polyurethane prepolymers, and effects of the synthesis method and chemical structure of polyurethane on the phase structure as well as on thermal²⁴ and mechanical²⁵ properties of polyurethane elastomers, which were produced in the multistage polyaddition method of TDI and some selected polyols. This article itself, however, focuses on the effects from a number of structural and process-related factors on morphology of supermolecular structures which can be found in PU elastomers. Attempts were also made to provide some generalization in that field, i.e., the influences from such structural parameters as molecular structures and contents of hard segments and soft segments in polyurethane macromolecules, their crystallizability and susceptibility to microphase separation, as well as the amount and type of crosslinking covalent bonds and hydrogen bonds influence on the structures of phases which can be found in PU elastomers. Moreover, special attention was paid to the effect of molecular weights of urethane prepolymers utilized for the synthesis of crosslinked PUs on the resultant phase structures obtained from the complex polyaddition process; this effect has not been analyzed so far. Based on the findings, the influence of morphology of phase structures on mechanical properties of elastomers was discussed, the properties being directly decisive for the fields of application of said elastomers.

Polyurethane elastomers produced by extending prepolymers with well-defined structures and narrow molecular weight distribution (MWD) were used as applicable in this type of analysis. The MWD of those oligomers was well defined by means of gel permeation chromatography (GPC). Urethaneisocyanate prepolymers which were obtained from the first stage of the polyaddition process were then extended and crosslinked with the use of triethanolamine, while the urethane-hydroxyl prepolymers—with the use of 4,4',4''-triphenylmethane triisocyanate. PU elastomers with known block structures were produced in this way.^{26–28} The wide angle X-ray scattering (WAXS) and scanning electron micros-

copy (SEM) methods were employed to evaluate morphological patterns of supermolecular structures.

EXPERIMENTAL

Raw materials and reagents were described in detail in our earlier paper.²⁵ 2,4- and 2,6-tolylene diisocyanate (TDI) were obtained from Aldrich (Buchs, Switzerland). Polyoxyethylene glycols (POG) with average molecular weight: $\overline{M}_n = 200, 300, 600,$ and 1000 g/mol, from Aldrich. Polycaprolactone diols (PCD) with average molecular weight: $\overline{M}_n = 530$ and 1250 g/mol, from Aldrich. Triethanolamine (TEA) (pure), from POCh-Gliwice, Poland. Desmodur RE (D-RE) (4,4',4''-triphenylmethane triisocyanate), from Bayer A.G., Leverkusen, Germany.

Synthesis of polyurethane elastomers

Prepolymer method

First stage: Synthesis of urethane oligomers with well-defined MWD. The method for the production of urethane oligomers with controlled molecular weights distribution has already been presented in our earlier reports.^{26–28} Those oligomers were obtained in a step-growth polyaddition process which was composed of a few stages and in which excessive amounts of one or the other monomers were used at individual stages. The possible reaction was described in our earlier paper.²⁴

The objective of using a considerable excess of one of the monomers was to restrict the molecular weight and to obtain possibly a monodisperse polymer. Unconverted excess monomers are undesirable because of their disadvantageous effects on the properties of products. Hence, monomers A or B were removed from the reaction mixture after every step by means of extraction. And such purified intermediates were then employed in further polyaddition steps.

Second stage: Synthesis of polyurethane. To produce cast elastomers, the synthesized urethane oligomers with —NCO terminal groups were cured with the use of TEA, while hydroxyurethane oligomers with the use of Desmodur RE. All the crosslinking reactions were carried out at the equimolar ratio of —NCO and —OH groups. After thorough mixing of components and deaeration under reduced pressure (about 270 hPa), the gelating mixture was introduced to closed polytetrafluoroethylene (PTFE) molds provided with silicone liner. The molds were then kept at 25°C over 24 h. The test pieces were pulled out of molds and were subjected to seasoning at ambient temperature over 14 days at minimum. The obtained PUs were marked with symbols, e.g., PU-I-200 (2), where the Roman numeral indicated the stage in which the prepolymer material utilized

TABLE I
Specifications for the Obtained PUs^a

Number of polyurethane sample	Type of polyol (A) and its \bar{M}_n	Symbol of polyurethane sample	Soft segments content (%)	Polydispersity degree (PD) of prepolymer by GPC	Type of chain extender
Polyurethane elastomers obtained in the prepolymer method					
1	POG 200	PU-I-200 (2)	28.56	1.31	TEA
2	POG 300	PU-V-300 (2)	58.07	1.53	TEA
3	POG 600	PU-II-600 (2)	75.59	1.66	D-RE
4	POG 1000	PU-I-1000 (2)	72.40	1.37	TEA
5	PCD 530	PU-IV-530 (2)	73.70	1.26	D-RE
6		PU-V-530 (2)	69.83	1.12	TEA
7	PCD 1250	PU-II-1250 (2)	86.12	1.26	D-RE
8		PU-III-1250 (2)	83.46	1.51	TEA
9		PU-V-1250 (2)	84.58	1.17	D-RE
Polyurethane elastomers obtained in the one-step method					
10	POG 300	PU-V-300 (1)	56.86	1 : 2	TEA
11	PCD 530	PU-III-530 (1)	66.84	3 : 4	TEA

^a The data were taken from Refs. 24, 26–28.

for the production of polyurethane had been synthesized, the Arabic numeral indicated the molecular weight of polyol taken for the synthesis, and the numeral in brackets, i.e. (2), denoted the prepolymer-based method for the synthesis of PU (Table I). The sample codification adopted in that study corresponds to that presented in our earlier paper.^{24–27}

One-step method

PUs were synthesized starting from the same ratio of raw materials as employed for the prepolymer method. The obtained PUs were marked with analogous symbols, e.g., PU-V-300 (1), where the numeral in brackets, i.e. (1), referred the sample to the one-step method (Table I).

For example, the polyurethane PU-V-300 (2) derived from the oligomer A₅B₆, e.g., V-300, and triethanolamine in the prepolymer method, has the corresponding polyurethane PU-V-300 (1) that has been synthesized in the reaction of 5 mol of component A, 6 mol of component B (TDI), and 2/3 mol of triethanolamine.

The measured amounts of raw materials, i.e., TDI, selected polyol and crosslinking agent, were charged to a glass vessel provided with a vacuum connection. After thorough mixing, the composition was deaerated and then test pieces were formed.

WAXS analysis

The WAXS investigations involved the use of Seifert URD-6 diffraction instrument. The radiation of Cu K α and the nickel filter were employed. The operating conditions for the instrument were as follows: accelerating voltage of 40 kV, anode current of 30 mA. The scattering intensities were measured by a scintillation detector scanning in 1.0° steps over the range of angles (2 θ) from 1° to 60°, and at counting intervals of 10 s.

SEM analysis

The fracture surfaces of samples from tensile tests were sputter coated with gold and examined on JEOL JSM-5500 scanning electron microscope (accelerating voltage: 10 kV).

RESULTS AND DISCUSSION

Morphology of polyurethane elastomers

WAXS study

Typical WAXS intensity profiles for all polyurethane elastomers with various contents of soft and hard segments are shown in Figures 1–3. Table II includes

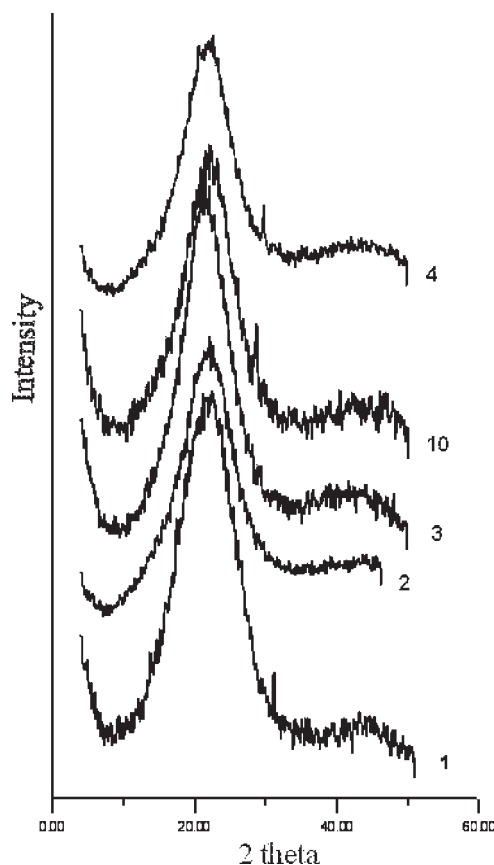


Figure 1 WAXS patterns for the PU elastomers based on polyoxyethylene diols (POG) with $\bar{M}_n = 200, 300, 600,$ and 1000 g/mol. The diffractograms of synthesized elastomers were marked according to Table I.

WAXS angles and d -spacing values for PU elastomers as calculated by the Bragg equation.

The elastomers synthesized from polyethoxylated glycols with various molecular weights (samples 1–4, 10) give one broad peak of diffusion scattering, with the maximum at $2\Theta = 22.56^\circ$ – 21.44° . That peak suggests the presence of a poorly ordered phase with more loose packing. DSC curves for those samples showed a peak which represented melting of rigid segments,²⁴ which additionally confirmed the presence of crystalline structures in those samples (Table II). The wide maximum moves toward lower values of the angle 2Θ (from $2\Theta = 22.56^\circ$ to $2\Theta = 21.44^\circ$) for increased contents of flexible segments. Consequently, the distance between the planes hkl increases, which makes evidence for superior amorphous nature of those samples. No significant differences can be observed in X-ray pictures of the samples which have been synthesized in the prepolymer method and in the one-stage method, if their compositions are similar (samples 2 and 10), despite the different degrees of crystallinity in hard segments (Table II).

Diffraction patterns of the samples synthesized from PCD with $\bar{M}_n = 530$ g/mol (samples 5, 6, and 11) have similar shapes to those for samples 1–4, which shows that their phase order is poor. Low crystallinity of those samples is also confirmed by DSC tests which we have done within our earlier study.²⁴

Samples 7–9, however, reveal much higher degree of ordering. Figure 3 shows two peaks of diffusion scattering. The first of them is wider and more intense. It was recorded for the lower value of $2\Theta = 21.4^\circ$, which indicates the presence of a poorly ordered phase with more loose packing. The second peak, which is narrow and not so intense, was recorded at a higher value of $2\Theta = 23.7^\circ$. That is indicative for the presence of a better ordered phase. Those peaks represent diffraction of X-rays in the planes hkl (110) and (200) of PCD,^{26,27} which forms the soft phase of the polyurethane elastomer.

Crystallizability of the soft phase, which increases for the increasing average molecular weight of PCD and for the increasing content of flexible segments,

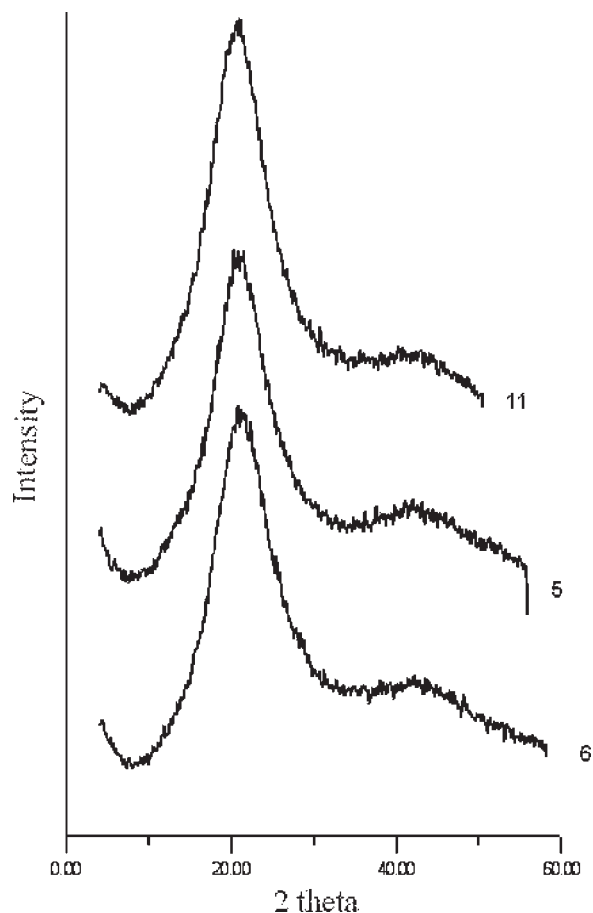


Figure 2 WAXS patterns for the PU elastomers based on polycaprolactone diols (PCD) with $\bar{M}_n = 530$ g/mol. The diffractograms of synthesized elastomers were marked according to Table I.

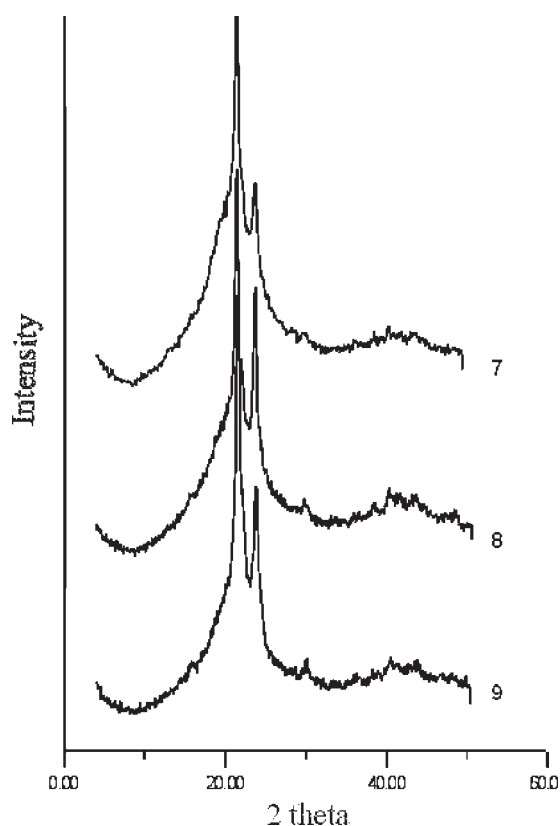


Figure 3 WAXS patterns for the PU elastomers based on polycaprolactone diols (PCD) with $\bar{M}_n = 1250$ g/mol. The diffractograms of synthesized elastomers were marked according to Table I.

was confirmed in our earlier studies by the DSC method.²⁴ The same relation was obtained by Kloss et al. for linear PUs extended with the use of 1,4-butanediol.²³

SEM results

The SEM method was employed to investigate morphology of fractured surfaces in samples of PU elastomers. As can be seen in the presented images (Figs. 4–10), phase microseparation is observed for all PU samples tested. A continuous phase is visible in SEM micrographs which is created by the amorphous part of the soft phase and the intermediate phase, i.e., the so-called matrix. Particles of the dispersed phase are encapsulated in that matrix. They are formed by the hard phase and crystalline part of the soft phase. Three principal thermodynamic factors contribute to the formation of that phase structure: mobility of rigid segments, viscosity of the system, and interactions between rigid segments.²²

The hard phase forms the so-called domains of rigid segments with irregular shapes and with the sizes from a few micrometers up to about 60 μm . The size of a domain is much dependent on its content of rigid segments, which is clearly visible for samples 2 and 4, and on the polyurethane synthesis method (samples 2 and 10). The domains grow bigger with the increasing content of rigid segments, and for PUs synthesized in the prepolymer method. The domains of rigid segments are partly crystalline (e.g., sample 6). Crystallites can be observed in the images which are spherical, and their sizes are of the order of a few micrometers.

The soft phase is amorphous in most cases (Figs. 4–9). The images of fractured sample surfaces reveal scratches, cracks, and corrugation. Crystallization of the soft phase is observed in case of samples 8 (Fig. 10) and 9 only. Those findings are confirmed by the WAXS and DSC tests. The soft phase in elastomer PU 7 is rather amorphous (Fig. 9). A small number of tiny crystallites can be observed in the fractured

TABLE II
Specifications of Degrees of Crystallinity for Soft and Hard Phase ($W_{c,s}$, $W_{c,h}$), WAXD Angles, d -Spacing Values, and Tensile Strength at Break for PU Elastomers

Number of PU sample (as per Table I)	Symbol of PU sample (as per Table I)	$W_{c,s}$ ^a (%)	$W_{c,h}$ ^a (%)	Diffraction angles, 2Θ	d -Spacings (\AA)	TS _b ^b (MPa)
1	PU-I-200 (2)	–	3.72	22.47	3.95	4.62
2	PU-V-300 (2)	–	43.57	22.14	4.01	1.63
3	PU-V-300 (1)	–	32.63	22.20	4.00	1.71
4	PU-II-600 (2)	–	68.07	21.44	4.14	2.20
5	PU-I-1000 (2)	–	37.69	22.56	3.94	2.34
6	PU-III-530 (1)	–	–	21.04	4.22	3.95
7	PU-IV-530 (2)	–	61.88	20.85	4.25	2.86
8	PU-V-530 (2)	–	–	20.75	4.28	2.27
9	PU-II-1250 (2)	–	–	21.43; 3.72	4.14; 3.75	4.42
10	PU-III-1250 (2)	34.67	–	21.40; 23.76	4.15; 3.74	3.55
11	PU-V-1250 (2)	35.09	17.15	21.54; 23.81	4.12; 3.73	3.48

^a $W_{c,s}$, $W_{c,h}$: degree of crystallinity for soft and hard phase detected by DSC. The data were taken from Ref. 24.

^b TS_b: tensile strength at break. The data were taken from Ref. 25.

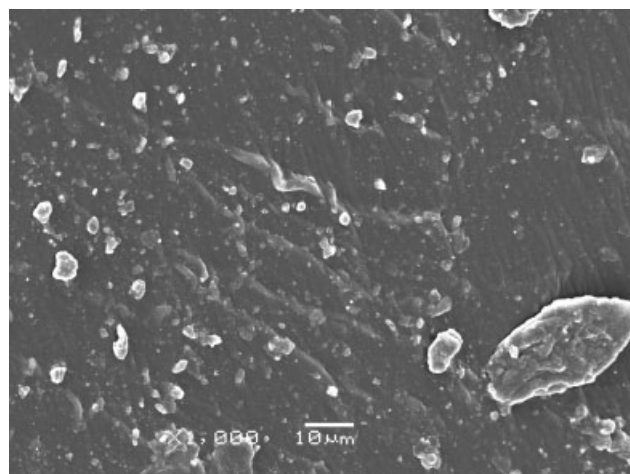


Figure 4 Scanning electron micrograph of PU-V-300 (1). The micrographs were marked according to Table I.

surface only; these yield two X-ray scattering reflections.

Influence of the phase morphology on the mechanical properties of polyurethane elastomers

Mechanical strength of elastomers obtained from POGs with various molecular weights is dependent both on the content of rigid segments and on the degree of crystallinity of hard phase (Tables I and II). Which is remarkable here is the increased strength found for sample 4 in relation to sample 3, despite the comparable content of rigid segments and much inferior crystallinity of the former. That can be accounted for only on the basis of the SEM image in which lower sizes and less regular arrangement of rigid segment domains can be observed

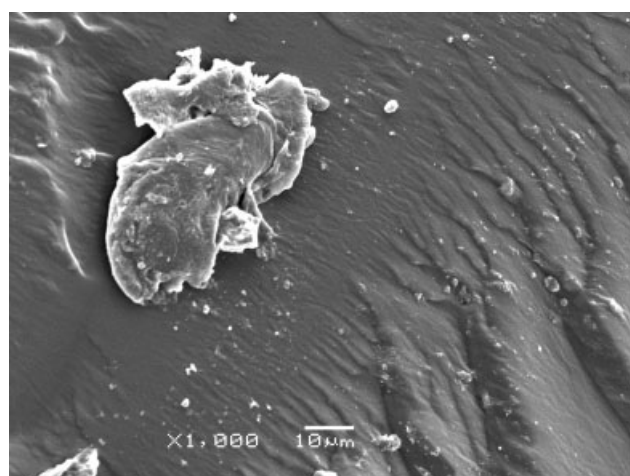


Figure 5 Scanning electron micrograph of PU-V-300 (2). The micrographs were marked according to Table I.

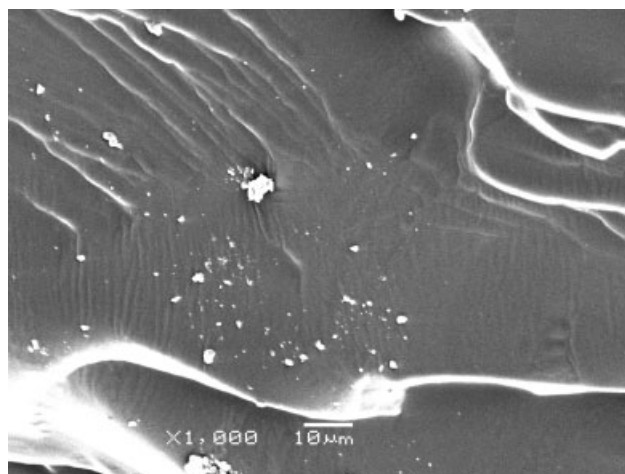


Figure 6 Scanning electron micrograph of PU-II-600 (2). The micrographs were marked according to Table I.

(Figs. 6 and 7). The inferior ordering as discussed above may in this case result from the lower polydispersity degree of prepolymer, from which PU 4 was produced (Table I).

Mechanical strength of sample 2, despite its bigger domains of rigid segments and higher degree of crystallinity, is somewhat lower than that for PU 10; the latter sample has the same chemical composition but it was synthesized in the one-stage method (Table II, Figs. 4 and 5). PU 2, however, has a bit higher content of flexible segments (58.07%) in relation to PU 10 (56.86%), which may be responsible for a small decline in its tensile strength (Table I).

Mechanical strength of PUs synthesized from PCD with $\bar{M}_n = 1250$ g/mol is higher than that of elastomers synthesized from polyester with $\bar{M}_n = 530$ g/mol, despite the higher content of flexible segments

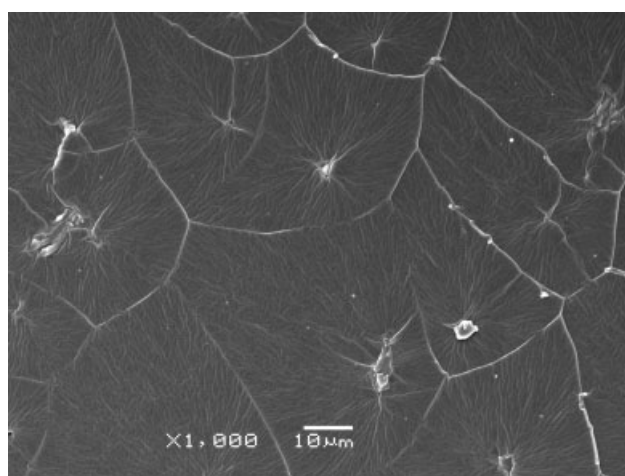


Figure 7 Scanning electron micrograph of PU-I-1000 (2). The micrographs were marked according to Table I.

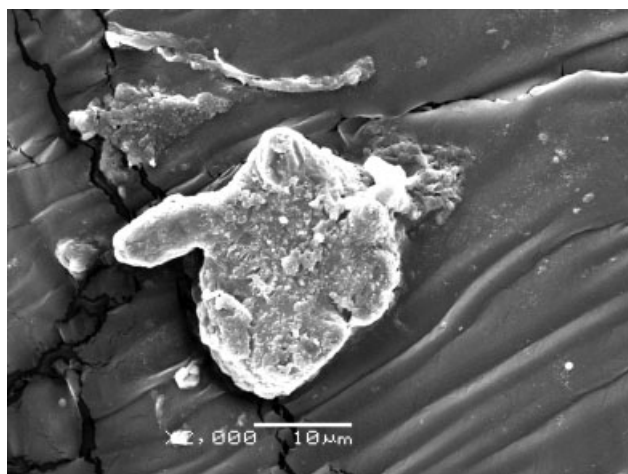


Figure 8 Scanning electron micrograph of PU-V-530 (2). The micrographs were marked according to Table I.

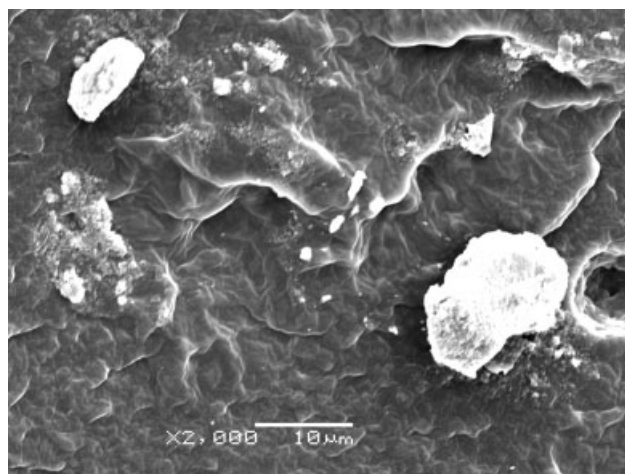


Figure 10 Scanning electron micrograph of PU-III-1250 (2). The micrographs were marked according to Table I.

in the latter. The better strength was derived from the ability of flexible PCD segments with $\overline{M}_n = 1250$ g/mol to crystallize, which was confirmed by the WAXS and SEM investigations.

CONCLUSIONS

WAXS and SEM methods made it possible to investigate morphology of phase structures in polyurethane elastomers, and to show the correlations between the obtained data and the phase structures of those materials (analyzed earlier by the DSC method) as well as the mechanical properties which were described in our earlier reports.^{24,25} It should be highlighted that both presented methods are general enough and they may be also employed to ana-

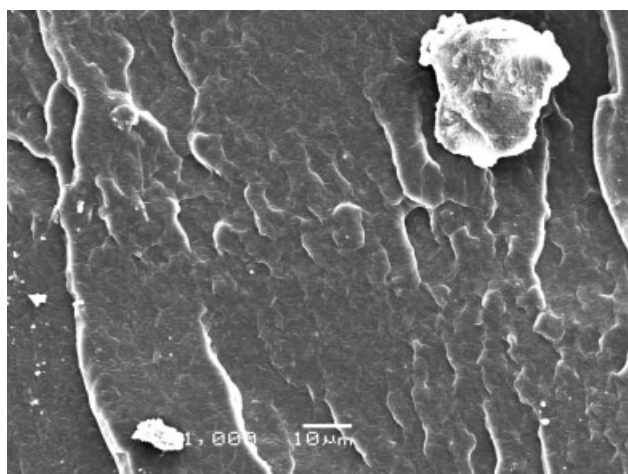


Figure 9 Scanning electron micrograph of PU-II-1250 (2). The micrographs were marked according to Table I.

lyze morphology of phase structures in other polymeric materials.

Careful interpretation of X-ray pictures enabled the qualitative review of phase structures in polyurethane elastomers which were synthesized in various methods but from the same pool of feedstocks. A higher degree of ordering was found for elastomers derived from PCD, which should be accounted for by *inter alia* the structures of crosslinking hydrogen bonds which are well developed in those polymers. On the other hand, no essential differences were observed in X-ray pictures for the samples produced by the prepolymer and one-stage methods.

In turn, the use of SEM technique made it possible to evaluate visually the structures of existing phases. The obtained SEM micrographs unequivocally confirm phase microseparation in all PU samples under investigation. The continuous phase is visible, which is a composition of amorphous part of soft phase and intermediate phase. The matrix is consisted of continuous phase, in which the particles of dispersed phase made of urethane segments of hard phase and crystalline part of soft phase are dispersed.

The obtained findings made it possible to explain the effects of size and regular arrangement of rigid segment domains, as well as the effect of the structure of soft phase, on selected mechanical properties. Tensile strength at break for elastomers derived from POGs with various molecular weights is dependent both on the content of rigid segments and on the degree of crystallinity of hard phase. The highest tensile strength at break, at over 3 MPa, was specific for PCD-derived elastomers, which may be accounted for by their higher contents of crystalline phase. It should be clearly stressed here that the noted values of tensile strength at break were not

sufficient for the obtained elastomers to be employed as structural materials. However, one should have in mind that it was not a general purpose of our research to obtain any new polyurethane materials; the purpose was to analyze the phase structures present in polyurethane elastomers. To this end, elastomers with known chemical compositions and narrow MWDs, synthesized in the prepolymer or single-stage methods, with the use of the same feeds (TDI, POG, and PCD) and intermediates (urethane-isocyanate prepolymers, crosslinked by triethanolamine, and urethane-hydroxyl prepolymers, crosslinked by 4,4',4''-triphenylmethane triisocyanate) turned out very helpful.

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