Determination of lamellae in segmented polyurethanes by electron microscopy

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The morphology of segmented polyurethane was studied with an electron microscope. Polymers were obtained by the prepolymer method from poly(ethylene adipate), 4,4-diphenylmethane diisocyanate and 1,4-butanediol. The unstained sample showed spherulites with fibrillar structure. Attempts were made to enhance the contrast in order to study the fibrillar structure more thoroughly. The staining method used to study the structure of lamellae is described.

(Keywords: segmented polyurethane; electron microscopy; morphology; lamellar structure)

INTRODUCTION

The favourable properties of segmented polyurethanes (PU) can be explained by microphase separation and the presence of domains[1–8]. Domains of hard segments form a kind of physical crosslinking which strengthens the material. A series of studies have supported this thesis. The pattern obtained on transmission electron micrographs is attributed to the presence of domains[9]. The results of d.s.c., X-ray and other measurements have been interpreted similarly[10–14]. Some doubts have been raised by Thomas and Roche[15,16] with regard to the presence of domains in samples observed under the electron microscope (EM). In their studies some micrographs of polymers appear with a pattern resembling domains although the polymers investigated are known not to have that structure. The presence of spherulitic structure in PU has recently been described in a number of publications[17–28]. Owing to the large size of the spherulites, some PU can be studied not only with an EM but also with an optical microscope. A fibrillar structure of the spherulite has been observed in some PU samples. Fibrils of about 10 nm size have no distinct boundaries, and therefore the exact size is difficult to establish. The question remains whether the fibrils are the smallest elements or whether a lamellar structure of the fibril occurs as in other semicrystalline polymers[29–32]. In the work presented here, attempts were made to find such elements in PU that might be considered as lamellae.

EXPERIMENTAL

Materials

The polyurethane was obtained by the prepolymer method from poly(ethylene adipate) (PES) of $M_n = 2000$, *p,p'*-diphenylmethyl diisocyanate (MDI) and 1,4-butanediol (BU) at molar ratio of PES:MDI:BU = 1:3.5:2.5. A 5% molar excess over the stoichiometric amount of MDI was used.

Specimen preparation technique

A reliable technique for determining the fine structure of semicrystalline polymers is the investigation of chemically stained ultra-thin sections by transmission electron microscopy. Various staining agents are used, e.g. chlorosulphonic acid and uranyl acetate[33] for polyethylene (PE), and phosphotungstic acid[34] or a mixture of formaldehyde and OsO_4[35] for polyamides (PA).

None of these agents was found to be successful for PU. Therefore combinations of various treatments were tested. An appropriate technique has to meet two requirements: fixation or hardening of the polymeric material to avoid any plastic deformation and destruction of structural details during the cutting in the ultramicrotome; and enhancement of the contrast between images of the structural elements. Such a technique was found by combined treatment of the samples with chlorosulphonic acid, osmium tetroxide and formaldehyde solution (technique A).

Another technique is a combination of physical treatment by γ-irradiation and a chemical one using chlorosulphonic acid and osmium tetroxide (technique B). Such a combination of physical and chemical treatments was used successfully for investigating several kinds of polymers[36].

Specimens treated with one of these techniques were cut with an ultramicrotome (BS 409 A Tesla, Brno, CSSR) at room temperature and investigated in a TEM (BS 500 Tesla) at 90 kV. To investigate larger structural details of the spherulites, a technique combining chemical treatment and cryo-ultramicrotomy was used, as described in more detail in ref. 28. The thin sections were investigated with a 1000 kV high-voltage EM (HVEM, Jeol, Japan).

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RESULTS

Spherulitic structure

The material investigated shows a clearly pronounced spherulitic structure. *Figure 1* shows spherulites at low and higher magnifications. Some of the spherulites are close to one another or distributed in a matrix. A radial, fibrillar structure inside the spherulite is clearly seen. By using the HVEM, the samples could be investigated at very low electron-beam intensities[37]. In this way it was possible to observe electron-irradiation-induced improvement of the contrast of the spherulite images[28]. This is shown in two micrographs of the same area. *Figure 2a* shows the sample at the very beginning of electron-beam irradiation. The spherulites can only be seen in weak contrast. Intense electron irradiation enhances the contrast and the radial elements inside the spherulites appear much more distinctly (*Figure 2b*). The spherulites are about 2 to 15 μm in size, with an average size of about 7 μm.

Lamellar structure

The combined application of physical (γ-irradiation) and chemical (chlorosulphonic acid and osmium tetroxide) treatments revealed a lamellar structure of the polymer.

Figure 3 shows an area with clearly detectable lamellae but only with weak contrast. Better contrast of the lamellae was reached by using technique A, a combined treatment with several agents (*Figure 4*). The lamellae are clearly visible as long bright bands. The surroundings of the lamellae and mainly their boundary layers, e.g. the surface layers, are darker owing to chemical staining. The arrangement of some of the lamellae is nearly parallel.

Figure 5 shows the central part of a spherulite with predominantly radial arrangement of the lamellae. Lamellae arranged in parallel, which might belong to a fibril, are shown in *Figure 6*.

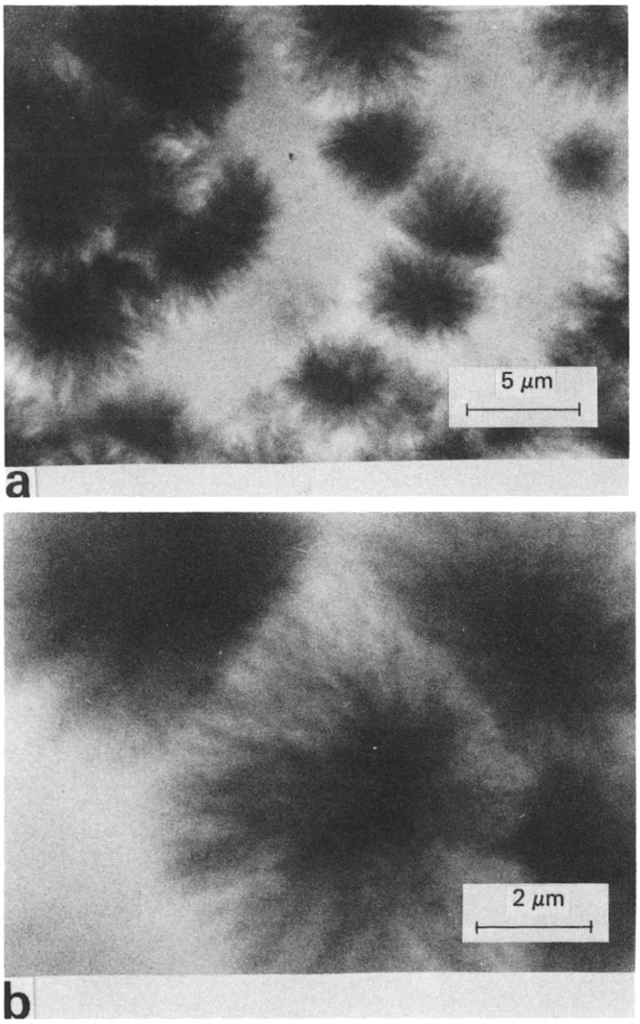

Figure 1 Spherulites in PU at different magnifications

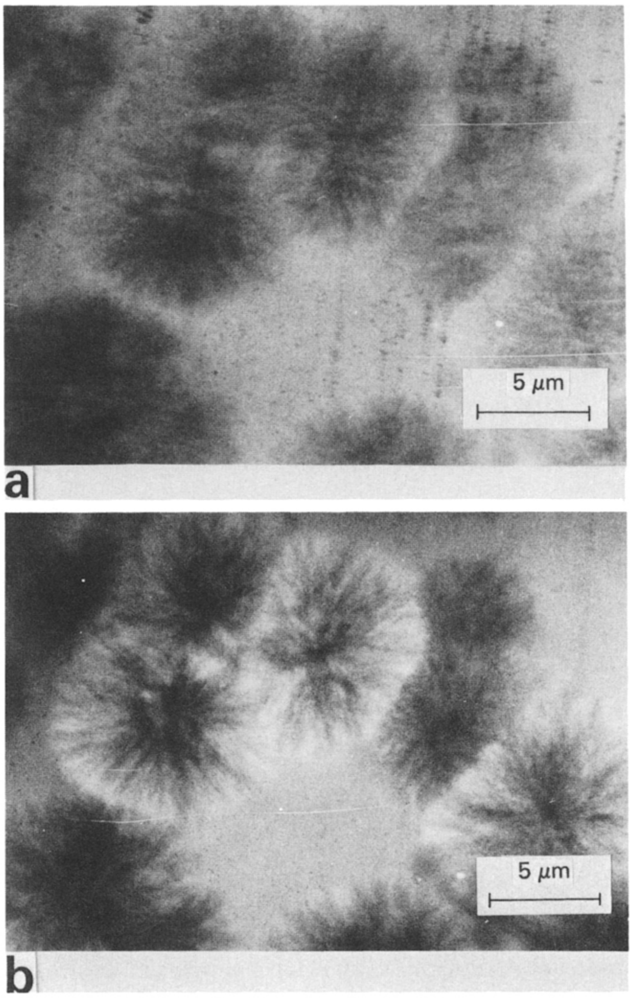

Figure 2 Improvement of the contrast of spherulites by an irradiation-induced contrast enhancement: (a) the beginning of electron irradiation; (b) after intense electron irradiation

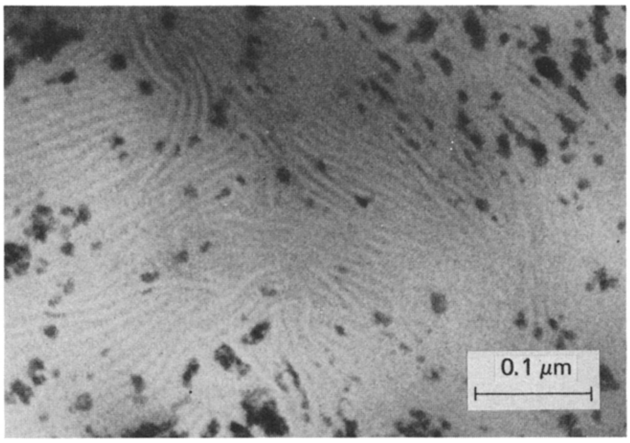

Figure 3 Lamellae in PU revealed by technique B

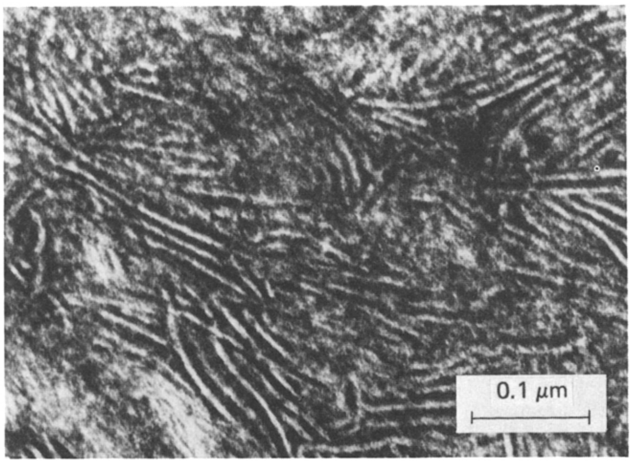

Figure 4 Lamellae in PU revealed by technique A

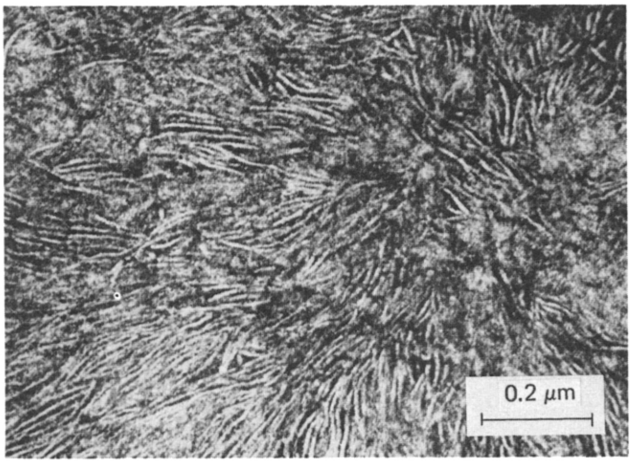

Figure 5 Central part of a spherulite composed of radially arranged lamellae

DISCUSSION

Detailed description of the lamellae

Since the lamellae are particularly well visible with the use of technique A, this method is applied to obtain distributions of lamellar length and thickness (*Figures 7* and *8*). The length of the lamellae varies from 0.1 to 0.3 μm with a mode at the length of 0.19 μm. At places where the arrangement of the lamellae is parallel, bundles of length 0.9 μm to 0.7 μm appear. These bundles are arranged radially near the centre of the spherulites.

The thickness of the bright zones inside the lamellae varies from 5.0 to 12.0 nm with a mode at a thickness of 7.3 nm (*Figure 8*).

The distribution curve has approximately Gaussian form with the exception of a tail of large particles. These thickest lamellae with thicknesses between 10 and 12 nm appear with a frequency of only 2%.

Localization of the lamellae

An important question is how the lamellae are arranged and distributed within the PU spherulite. *Figures 5* and *6* show clearly that the lamellae inside the spherulites are preferentially oriented radially. The bundles of lamellae arranged in parallel appear at lower magnifications as individual structural elements, namely the fibrils seen in *Figures 1* and *2*. The lateral size of a bundle composed of 5 to 15 nm thick lamellae packed in parallel can be estimated from the micrographs as ranging from 50 to 200 nm. The size agrees well with the thicknesses of the fibrils measured at low magnifications (*Figures 1* and *2*).

The length of the stacks reaches several micrometres, although the length of each individual lamella is limited to a maximum of 0.3 μm (compare *Figure 7*). For the lamellae arranged approximately in parallel, the long period (centre-to-centre distance) varies between 12 and 15 nm. The average thickness of a lamella is 7.3 nm, and therefore the thickness of the layers separating the lamellae varies between 5 and 7 nm. Lamellae were also found outside the spherulites, though not closely packed,

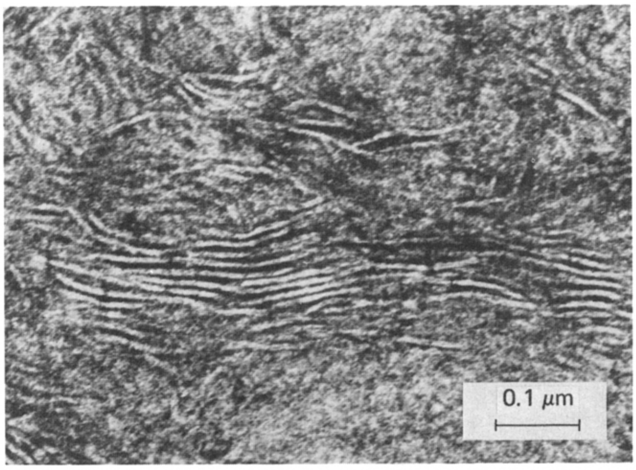

Figure 6 Parallel packed lamellae

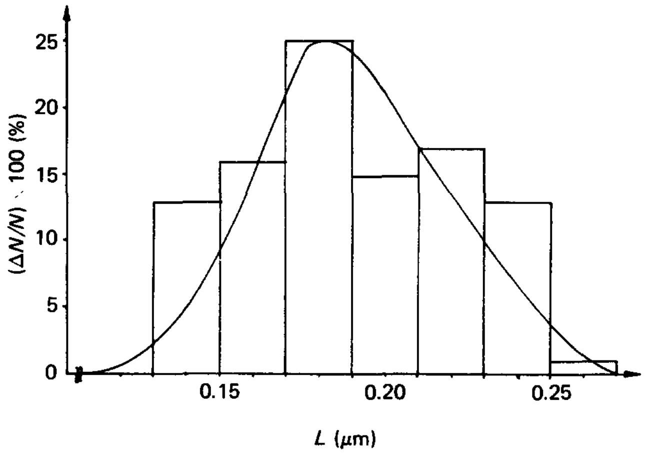

Figure 7 Frequency distribution of the length of the lamellae

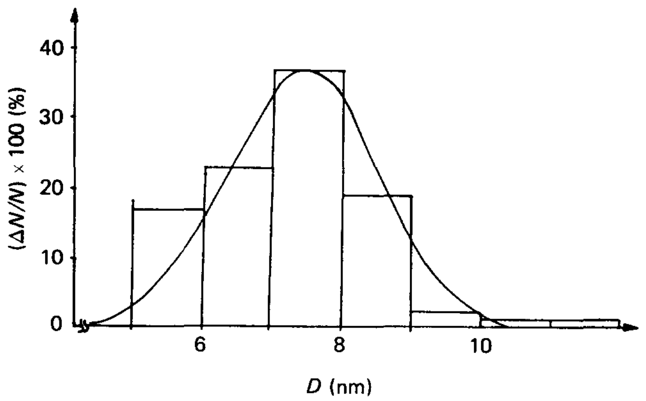

Figure 8 Frequency distribution of the thickness of the lamellae

but distributed randomly. Some areas of the samples seemed free of lamellae.

Comparison with the structure of other crystalline polymers

Typical semicrystalline polymers, e.g. polyethylene of low and high density (LDPE, HDPE), also form spherulites with well ordered arrangement of lamellae inside[29–32]. An example is shown in *Figure 9*[38]. At low magnification, a spherulite shows concentrically arranged rings. Except for the rings, the arrangements of the lamellae inside the spherulites are similar in PE and PU (compare *Figures 9a* and *9b* with *Figures 5* and *6*). A similar arrangement of lamellae inside spherulites was also found in polyamide and other polymers.

Explanation of the electron irradiation effect

After electron irradiation of the thin section in the microscope a marked increase in the contrast of the radial fibrils of the spherulites was observed. Since we have demonstrated the similarity between the spherulite structures of PU and PE, the effect can be explained in the same way as in the case of PE[36,39] (see *Figure 10*). Irradiation of the polymeric material gives rise to chain scission and other so-called primary processes. As a secondary process, crosslinking of macromolecules might occur predominantly in amorphous interlamellar regions[37,39]. The crosslinks reduce the thickness of the amorphous part. In places where the boundary layers of the lamellae are parallel to the normal direction of the ultra-thin section and to the electron-beam direction, the thickness of the sample increases, yielding a darker zone. This effect was described for PE as a special effect of irradiation-induced contrast enhancement[36].

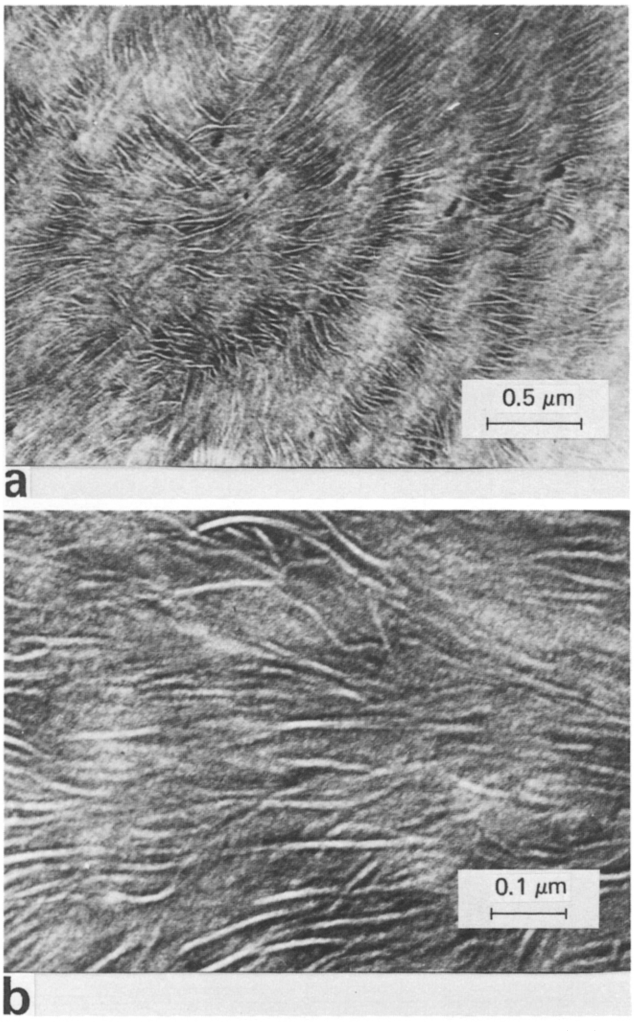

Figure 9 Lamellar structure in PE: (a) spherulite with concentric rings and radially arranged lamellae; (b) radially and nearly parallel ordered lamellae inside the spherulite

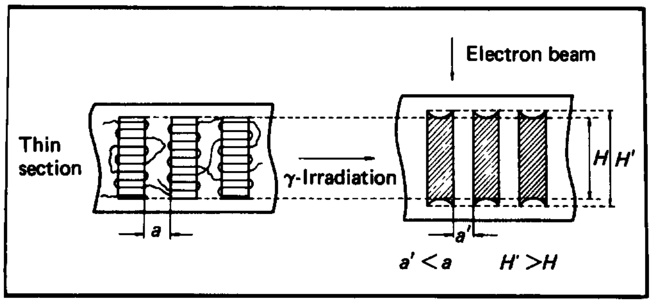

Figure 10 Scheme of the development of contrast between lamellae and amorphous zones as a consequence of irradiation

Structure of the lamellae

The lamellae seen in the PUs, similarly to those found in other polymers (PE, PA), can be assumed to be crystalline and to correspond to the lamellar domains described in the literature. Neither the lamellar domain model suggested by Estes[40] nor that proposed by Bonart[41] can be referred to the PU studied here. In those kinds of model the transverse dimension of a domain is determined by the length of the hard segment (HS). In cases where a distribution of HS lengths exists, diffuse domain boundaries should be expected. According to Bonart this type of diffuse domain boundary is expected in polyurethanes, while the distinct boundary seen between domains containing hard and soft segments in segmented poly(ether–ester) elastomers is due to chain folding of the hard segment in a crystalline lamella. The micrograph shown in *Figure 4* distinctly points to the presence of lamellar structure in PU. The assumption that the hard segment is present within the lamellae showing a relatively sharp boundary and that the soft segment occurs within the intralamellar area brings us to the conclusion that the chains of HS must also be folded in this case (PU), and the size of the lamellae is not related to the length of that segment. This is in agreement with the SAXS results obtained by Schneider *et al.*[19] The authors of that study had obtained comparable sizes of the long period independently of the concentration of HS, i.e. also of its length, a fact difficult to explain on the basis of a model postulating the existence of an extended HS chain in a corresponding domain. The lamellar structure reported in this paper seems also not to correspond to the HS model suggested by Fridman and Thomas[22]. It must be pointed out, however, that the authors of that study[22] had observed spherulites of a different type, which had been obtained in a PU film cast from solution.

Concerning the molecular dimensions of the MDI/BU hard segment analysed by Blackwell[42] it can be concluded that four monomeric HS units would be responsible for 7 nm average size of the lamellae. The lamellae width measured in the micrographs provides a continuous distribution, which means that the lamellar width is not related to a constant multiple of HS monomer length. It must be kept in mind, however, that the observed size of the lamellae varies with the tilt of a lamella with respect to the incident electron beam. Only the lamellae that are parallel to the radiation project their actual size on the electron image. The thickness of the lamellae perpendicular to the beam is impossible to measure, while lamellae at intermediate orientations look smaller in the image than in reality.

Since it seems reasonable to assume that in the investigated PU some distribution of HS lengths exist, a corresponding distribution of lamellar widths could be expected if some kind of segregation occurs.

If the longer hard segments crystallize much better than the shorter ones, it seems much more convincing to presume that only HS longer than four units participate in the formation of lamellae, and consequently that chain folding occurs. Therefore, non-crystallizing shorter HS should be expected to find their places either in interfibrillar regions of the spherulite or outside of the spherulite. As the spherulites in our case are frequently separated by non-spherulitic areas, it seems that the major part of short-HS-containing PU is contained there. This can be considered as a kind of separation of the system into components of different chemical composition (with respect to the length of HS) occurring in macro-regions of a size at least corresponding to the size of the spherulite.

This is in agreement with our former observation[43]. We have found that the PU investigated can be separated into two fractions: a sol with a considerable content of nitrogen, thus also of hard segment; and a gel whose nitrogen content is smaller than in the initial polymer. Similar results were obtained by Xu *et al.*[44], who investigated a different PU system. After extraction with dimethylformamide, they found two fractions differing from each other in HS content, which was smaller in the gel and greater in the sol.

CONCLUSIONS

Electron microscopic investigation gives insight into the structure of segmented PU. Unstained samples show the presence of spherulites with radially distributed fibrillar elements. Suitable staining of the sample permits one to obtain additional contrast enabling observation of lamellae. The results presented here seem to support the model of folded HS chains in the lamellae, rather than that of extended HS chains which would lead to a diffuse boundary between hard and soft domains. It is concluded that HS chain segment lengths vary greatly from one another in the PU investigated and that they differ considerably from the stoichiometry of the raw materials during the synthesis of polymers.

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