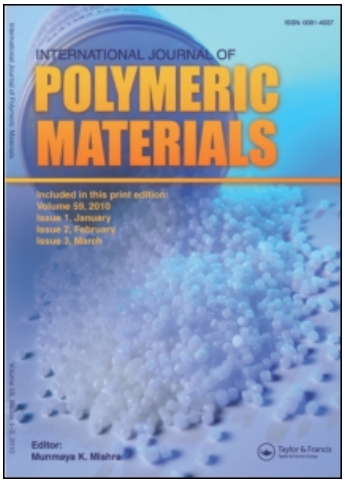

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L. L. Razumova[a]; E. V. Smurova[a]; A. A. Veretennikova[a]; V. A. Krivandin[a]; G. E. Zaikov[a]
[a] Institute of Chemical Physics, Moscow, Russia

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The Stability of Segmented Polyurethanes: Structure Development on Contact with Blood

L. L. RAZUMOVA, E. V. SMUROVA, A. A. VERETENNIKOVA, V. A. KRIVANDIN and G. E. ZAIKOV

Institute of Chemical Physics, Moscow 117334, Kosigin str. 4, Russia

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The segmented polyurethanes (SPU) of Vitur-RM trademark are widely used thrombosis resistant SPUs. The changes in the structure of their colloid level sizes and in stability characteristics were studied after incubation of SPU films in blood serum for a period of 1–2 years at 40°C. The small-angle X-ray scattering using linear coordination detector showed that the domain sizes did not change noticeably on incubations. The strength characteristics decreased by not more than by 10–15% during this of exposure. The characteristics investigated differed markedly from those found with samples with initially low strength, corresponding to the lowest limit of the Russian standard.

KEY WORDS Segmented polyetherurethanes, structure development, blood.

INTRODUCTION

Changes in polymer structures caused by external influences and the connection of these changes with some other properties are an important field of polymer science. In the present paper a series of polymers of interest to heart-vascular surgery was investigated. They are segmented polyurethanes (SPU) trademark "Vitur RM." The best combination of biocompatibility, thrombosis resistance, high and stable strength of the material is important for articles used for long contacts with blood (artificial heart, additional blood circulation pumps, balloon-catheters, etc.). Some SPU satisfy this set of demands, including SPUs based on polyphurite with MM 1000–2000, MDI (4,4′-diphenilmethandiisocianate) and diamines produced by "Ethycon" Company (USA) and the "Vitur RM" SPUs from Russia.

EXPERIMENTAL PART

In the present work, structural (according to the data of small-angle and wide-angle X-ray diffraction scattering) and strength properties for the Vitur RM series were investigated. These SPUs were synthesized using MDI, ethylenediamine and

polyphurite with MM of 1000, 1500, 1800, 2000 (we will denote these materials as RM-1000, RM-1500, etc.). The structure and properties were followed on incubation of SPU films of 150–200 μm thickness in blood serum at 40°C for periods of 6, 12 and more months. Sample preparation, the analysis of structural and mechanical characteristics are the same as in studies.[1–4] Small-angle X-ray diffraction patterns (SAXS) were obtained by the diffractometer with linear coordinate detector. Measurements were performed with a slit band collimation of X-ray, beginning from the scattering angle of $2\theta = 0.1°$, with the step of 0.02°. X-ray tube BSV27-Cu with nickel filter and amplitude discriminator (CuK_α irradiation, $\lambda = 1.54$ Å) was used. Background scattering was excluded from experimental curves. After that they were normalized by sample thickness.

DISCUSSION

Dense side packing of chain molecules and some longitudinal stacking is characteristic for the macromolecular structure of Vitur-RM of the present series. This is indicated by the existence of intense reflexion at about 4.5 Å and a less intense reflexion at about 12 Å[5] of wide-angle X-ray scatterings (WAXS), respectively. The WAXS of RM-1000 sample, the mostly rigid and strong SPU samples of the series, show the presence of some percentage of rigid block crystallites sizes of about hundred of Å.[6]

Colloid level structure of Vitur-RM is also typical for SPU: small-angle X-ray scatterings (SAXS) show a weak and broad background scattering, that decreases with increasing scattering angle (see Figure 1). SAXS reflection is caused by regularly alternating domains of rigid and flexible blocks of SPU. Macroperiods of Vitur-RMs were determined from the position of SAXS reflection. They increased

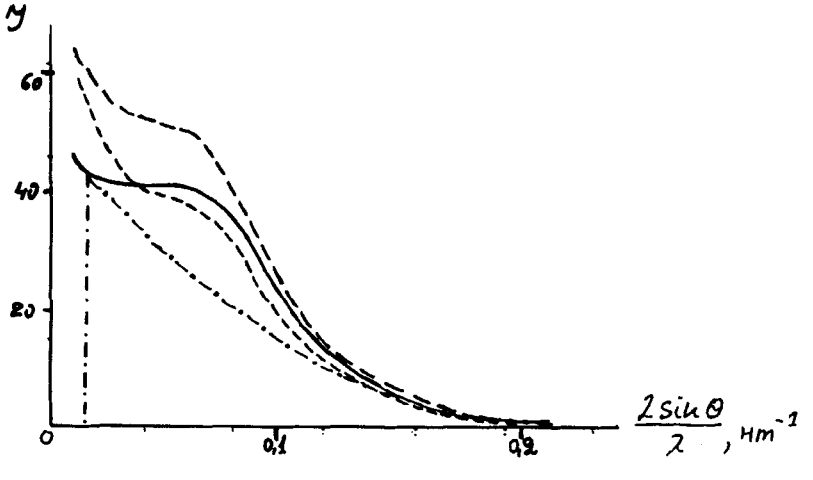

FIGURE 1 Small-angle X-ray diffraction patterns (SAXS) for RM-1800. For initial samples—plane curve; large stipple—for samples incubated in blood serum during 12 months; small stipple—for the ones incubated during 18 months; dot-and-dash line shows the principle of determination of integral intensities J for regular and irregular parts participating in the structure diffraction.

from 110 Å for RM-1000 up to 130 Å for RM-2000. The lengths of rigid blocks, found using the method described in Reference 7, changed from ~55 up to 70 Å. SAXS background is caused by an irregular fraction of SPU structure, that includes both layer-like structures, where alternating regularity of rigid and flexible segments fluctuates by more than 20% (for more detail see Reference 1), and domains of larger and smaller size than those regular fraction, and density fluctuations of the micropores.

It is known from common principles of X-ray scattering that SAXS intensity (J) increases with increasing structure heterogeneity of the material on the colloid size level. SPU structure heterogeneity, connected with the presence of electron density fluctuations, increases with the development of both microphase domains and pore system or other density variations.

The comparison of heterogeneity characteristics of the present Viturs before and after incubation is illustrated by the histogram in Figure 2. The integral intensities of SAXS (J) normalized with respect to exposure time, (sample thickness, and beam intensity), are shown for the regular fraction of the structure (below) and the irregular one (above). The method we used for the separation of SAXS intensity of regular and irregular fractions of structure is illustrated in Figure 1. From the left to the right are shown the data histograms for RM-1000, RM-1500, RM-1800, and RM-2000 samples. The left side column is always for the initial Vitur-RM sample and then to the right follow the samples after an incubation period of 6, 12, 18 and 30 months.

It follows from Figure 2 that:

1) Initial heterogeneity of the structure, which depends on the degree of microphase separation varies with Vitur-RMs investigated.

2) The changes in regular fraction of the structure on incubation in blood serum are practically within the limits of error of the procedure.

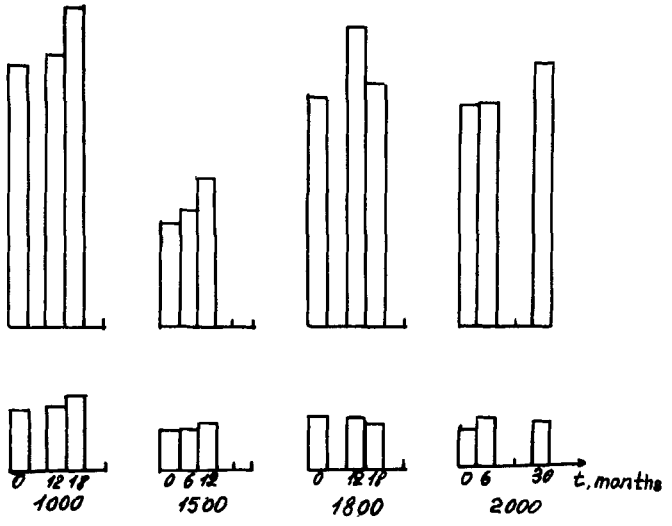

FIGURE 2 Histograms of SAXS integral intensity J changes at SPU incubation in blood serum, in conditional units (see the text).

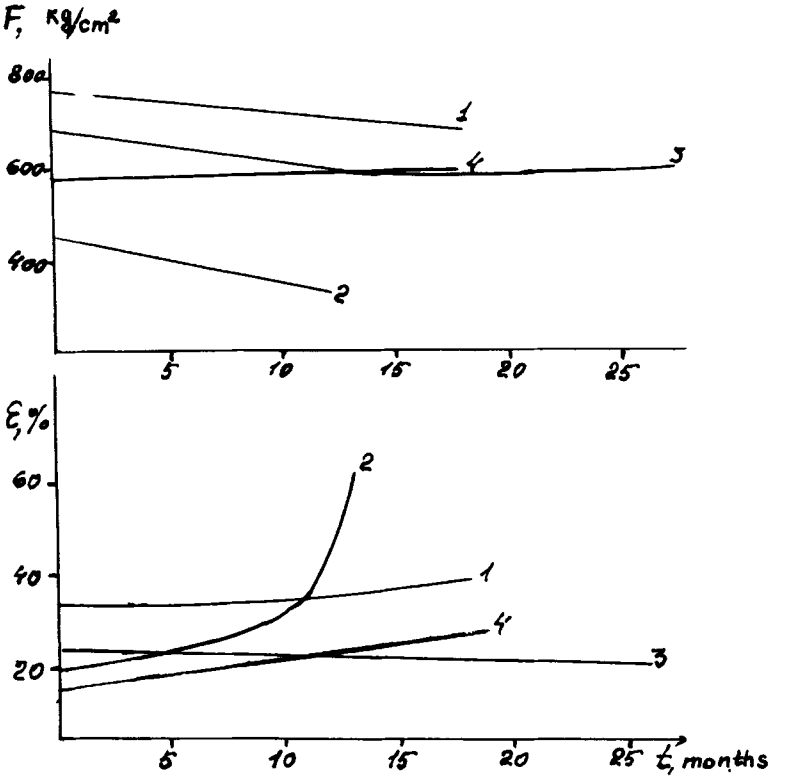

FIGURE 3 Dependence on incubation duration in blood serum at 40°C: a) of tensile strength F, b) of residual lengthening ε, for films of RM-1000 (1), RM-1500 (2), RM-1800 (3), RM-2000 (4).

3) Irregular fractions of the structure intensities differ significantly for various Vitur-RMs, and for various times of their incubation in blood serum.

Figure 3 shows the data on stability characteristics of Vitur-RMs of the present series before and after incubation in blood serum. It is seen from Figure 2 that the most stable Vitur RM-1000 gave the most intense SAXS, and the sample, that has the lowest initial strength, allowed by Russian Standard (RM-1500), showed SAXS of the lowest intensity.

The development of heterogeneity in the polymer structure under the influence of water and water solutions of acids were observed before in polyamides,[8] in polyvinyl alcohol,[9] and on incubation of low-stability Vitur RM-1500 in the blood serum.[2] In the present paper we confirm the structure heterogeneity development in Vitur-RMs during incubation.

Some data on the nature of heterogeneities developed during incubation indicate a SAXS intensity decrease during long incubation in blood serum that was not observed before and was found with RM-1800. A decrease of SAXS under the influence of nitric acid water solutions on polyamides was reported elsewhere,[7] the SAXS intensity of these samples, however, increased previously on long exposure to water. This anomaly was attributed to the decrease of electron density difference of the "polymer-pores" system on filling the pores by nitric acid solution, while

these pores were closed for water. The SAXS decrease in RM-1800 indicates that there were pores in Vitur, and some of them were filled during incubation.

To estimate the distribution of structure heterogeneities by sizes, one can use curves of $J_d\varphi^3$ dependence on φ (where J_d = SAXS intensity, φ = X-ray scattering angle). It was found that for all Vitur-RM samples before and after incubation in blood serum the range of heterogeneity radii is quite wide, no less than from 10 to 50 Å, with the most often observed radius being 20–25 Å. These values do not change noticeably after Vitur incubation in blood serum, but the content of heterogeneities in SPU volume do change (see Figure 2).

Thus, it is sufficient for medical practice that long incubation of Vitur-RM in blood serum does not significantly affect the tensile strength and residual lengthening of the samples having rather high initial strength. Probably, special attention should be paid to the application of materials with the most stable characteristics. It follows from X-ray scattering that, at long incubation, the common character of Vitur-RM structure did not change. This includes the rigid domain sizes, their alternating period of regular SPU fraction, average domain inertia radii and their distribution by sizes.

The present X-ray scattering investigation of Vitur-RMs supplements our preliminary information regarding changes in some polymers at the diffusion of water and water solutions. Evidently, heterogeneity development in polymers in conditions of macromolecule mobility increase is the display of their own properties, typical for chain macromolecules.[10]

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