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SAXS and XPCS study of irradiation effects on polyurethane microstructure

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Two studied polyurethanes were composed with different ratio of NCO/OH - 0.84 and 0.92 for PU1 and PU2, respectively The aim of the study was to investigate the subsequent changes in each polyurethane mesostructure by exposure to UV iradiation. Each polyurethane was irradiated with increasing time of irradiation to get a set of samples. The exposition time (s) became the second part of each sample name.
The experiment was performed at the ID10A beamline of the ESRF. The SAXS geometry and CCD detector were applied. The SAXS intensity functions were recorded together with XPCS time-dependent intensities which were registered in 15 different q - points, for each sample. The correlation time occurred extremely long, of about 10^4 s, which is typical for polyurethanes [1]. The intensity correlation functions, $g^{(2)}(q,t)$, were calculated on-line at ESRF correlation package.
The PU1 analysis. For PU1-00, PU1-30, and PU1-60 the correlation functions are of two-bends shape and, to get correlation rate, $\Gamma(q,t)$, the two-exponent fitting was applied - Γ_s for slow exponent and Γ_f for fast one. For the PU1-120 because of one-bend correlation function shape only Γ_s was obtained. To each Γ_s vs.q plot, as it is showed in Fig.1, a horizontal straight line was fitted. It means that the Γ_s is related to the elastic fraction only. Height of cross the y-axis by Γ_s allows to evaluate the elatic fraction level [1-3] (Table I).

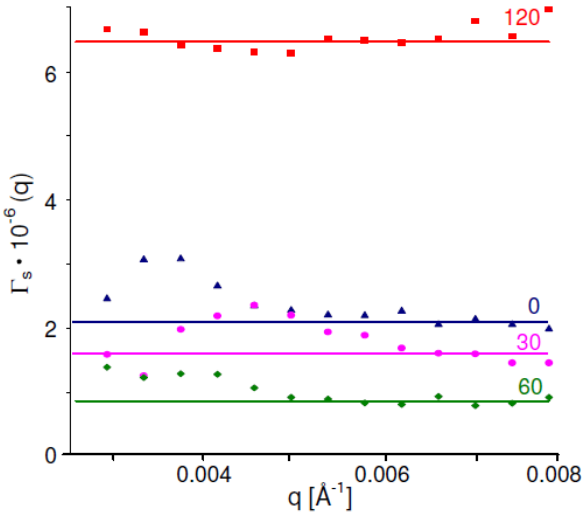

Fig.1 PU1 elastic fraction correlation rate, Γ_s (q)

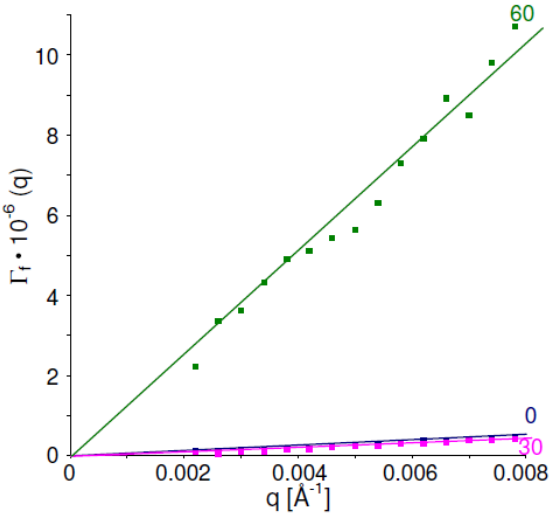

Fig.2 PU1 viscous fraction correlation rate, Γ_f (q)

For the fast exponent, Γ_f, all fitted lines are sloped and crossed y-axis nearly zero (Fig.2), so they were generated only by viscous fraction and increase in the slope means an increase of this fraction.
Course of changes $\Gamma(q,t)$ dependent on the irradiation doses, for subsequent PU1 samples showed two phases of changes. First, a **degradation phase** starts with a moderate decrease in elastic fraction, (PU1-00, PU1-30, PU1-60 samples) (Fig.1). These changes suggest a decrease in number of inter-chain hydrogen bonds. Then, as it is showed in Fig.2, for the fast-

viscous fraction, Γ_f (q), a rapid growth of this fraction is recorded for PU1-60, as huge increase in the fitted line slope. It is probably generated by in-chains bonds breaking that create a large number of free and loose moieties Then the second **phase of structural reconstruction** starts by self-assembly. The large viscous fraction completely disappears in this phase (Fig.2 - lack of the PU1-120 data) suggesting that the loose elements are attached to the main network of the single elastic fraction (Fig.1, PU1-120). The SAXS study results are (i) the R_g values indicated almost the same values for first 3 samples, and smaller one for PU1-120 (Table I) and (ii) the pair distribution functions, p(r), showed (Fig.3), for PU1-120, more regular Gauss-like shape than for PU1-60. It is an evidence that only elastic fraction formed by self-assembly in PU1-120 contains better ordered, smaller aggregates.

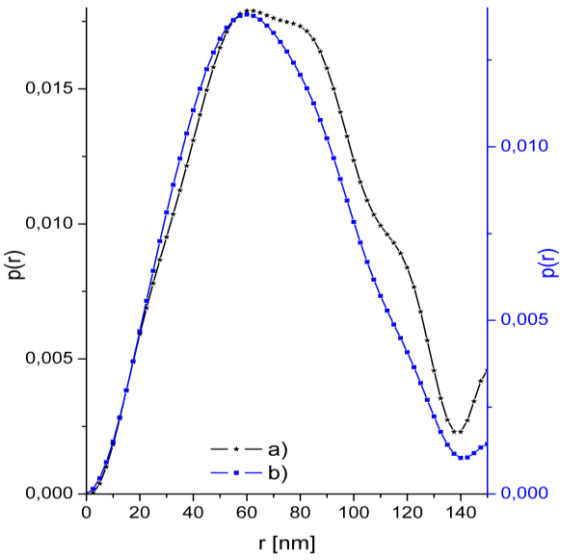

Fig.3 Pair function, p(r), for: a/ PU1-60 and b/ PU1-120

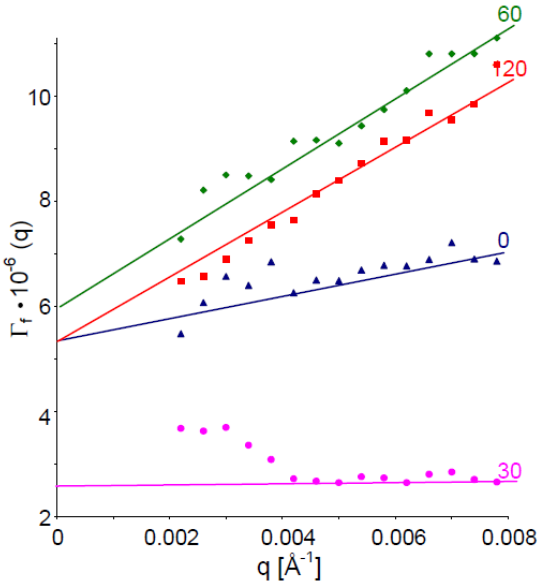

Fig.4 PU2 correlation rates, Γ(q)

Table I Structural and dynamic parameters

sample	PU1-00	PU1-30	PU1-60	PU1-120	PU2-00	PU2-30	PU2-60	PU2-120
R_g [Å]	574	573	570	526	567	557	544	591
Γ_s [s^{-1}]	2.2	1.6	1.0	6.5	5.4	2.7	6.0	5.4
Γ_f slope $=\Delta\Gamma_f/\Delta q$	0.07	0.068	1.2	0	2.1e-4	0	6.1e-4	6.1e-4

The PU2 analysis. For PU2 polyurethane, the viscous fraction is about hundred times less compared to this of PU1. Through the irradiation course this fraction first increases (Fig.4), as for PU1, but together with simultaneous growth of the elastic fraction. After the next doses of irradiation the dynamic parameters remain almost unchanged, without any sign of self-assembly (Table I). It could be an evidence of a jamming state with "arrested" dynamics [4]. Finally, the most irregular polymer aggregate structure is observed.
Two polyurethanes differing only slightly in composition showed completely different course of structural changes that is difficult to understand and needs further studies.

References

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