

NOTES

Comments to the Paper "The Determination of the Pore Structural Parameters of Isoporous Resins by Inverse GPC," by Anyou Wang, Juntan Yan, and Rognan Xu

Recently, Anyou Wang et al.¹ published a paper describing application of inverse GPC for determination of the pore structural parameters of so-called isoporous resins obtained by postpolymerization cross-linking of swollen polymers. Their designation as "isoporous" by their inventors Davankov and Tsyurupa² was based on the not too safe supposition of statistical distribution of the newly formed cross-links and was not supported by reliable experimental evidence. Recently, a more apt term, "hypercross-linked polymers," was adapted by Davankov and Tsyurupa themselves.³

We have investigated a polymer prepared by a method identical to that used by Wang et al. and by a similar inverse chromatographic method supplemented by evaluation of the accessibility of polymer mass by partial sulfonation.⁴ Our results, obtained by both methods, suggested rather heterogeneous morphology of this polymer, characterized by the presence of both apparently low-cross-linked, well-accessible domains and high-cross-linked, functionally poorly accessible regions. This morphology differs from the idea of isoporous structure, but it is in our opinion more compatible both with the conditions at which this morphology was built and the spectacular properties of this type of material. Cross-linking of the swollen polymers cannot be a completely random process producing a uniform distribution of the cross-links. The successful creation of a cross-link requires the proximity of the partner polymer chain, which means that it should be more favored in the regions of a higher local density of polymer mass. Hence, in the vicinity of an already existing cross-link, the formation of a new bond is more probable than in the other regions. The rigid, highly cross-linked backbone with voids filled by less cross-linked domains then results. The easy swelling of these materials even in "bad" solvents² is responsible for considerable stress created in the rigid backbone by the collapse of the swollen structure during drying.

The idea of a heterogeneous morphology of hypercross-linked polymers is in the data obtained by Wang et al.

corroborated by the results of the investigation of their polymers in the dry state by nitrogen adsorption (Table III).¹ Found were substantial pore volumes (v_p), but relatively low BET surface areas (S). According to the model of cylindrical pores, the corresponding medium pore diameter \bar{d}_p (nm) = $4 \times 10^4 v_p$ (cm³/g)/ S (m²/g) for both polymers investigated by this method is around 55 nm. However, in the swollen state, no pores with diameters greater than ca. 2 nm were detected. It can be easily imagined that pores observed in the dry samples are the result of the collapse of the low-cross-linked regions in the otherwise rigid backbone. In this particular case, this collapse had to be especially easy and uncommonly complete. For the hypercross-linked polymers, extremely high surface area (> 500 m²/g) is much more typical.

The reason why the bidisperse porous structure was not demonstrated by A. Wang et al. in their chromatographic results could be the low-resolution method of the chromatographic data treatment used. The very simplified approach to the description of the relation between pore size and its accessibility for solute molecules proposed by Halász,⁵ recognizing only either totally accessible or totally inaccessible pores, was an appropriate starting point at the very beginning of the development of the inverse GPC (or may be, more correctly, inverse steric exclusion chromatography [ISEC]) when it was published. But this extreme simplification of the much more complex situation⁶ should not be used any more. The authors of the discussed paper recognized that Halász's approach was criticized in recent years and newer methods for ISEC data treatment were developed, but they gave no reason why they selected the oldest known approach.

In Table II of the discussed paper is shown a sample of the original experimental data. In trial treatment of the data using a more rigorous method,⁷ we obtained from these data results quite similar to those from our own investigation of the hypercross-linked polymers,⁴ compatible with the idea of the bidisperse swollen pore morphology of these materials. This is, of course, not a proof. Available was a limited set of data only and we had to use in our treatment some improvisations as we are normally using a different type of standard solutes. That is why we are not showing our results here in detail. But it is certainly

an indication that a more careful study of these interesting polymers would be desirable.

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