

SMALL-ANGLE X-RAY SCATTERING FROM MACROPOROUS POLYMERS: STYRENE DIVINYLBENZENE COPOLYMERS, CELLULOSE IN THE BEAD FORM

J. BALDRIAN, J. PLEŠTIL and J. ŠTAMBERG

*Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, 162 06 Prague 6*

Received November 26th, 1975

Possibilities of the determination of the structure parameters of porous polymer systems by means of the small-angle X-ray scattering have been demonstrated. The method presented in the paper is used for the description of the macroporous structure of styrene divinylbenzene copolymers or of bead cellulose.

Widespread uses of macroporous polymers and copolymers call for an insight into their structure. Since these polymers possess a two-phase structure and structural formations (polymer matrices, pores) ranging from tenths to tens of nanometers, the method of the small-angle X-ray scattering can be employed in this case.

Basic relationships between the X-ray intensity scattered at small angles and the structure of an ideal two-phase system (constant electron densities in both phases, sharp transition of electron density at the phase boundary) have been derived by Porod^{1,2}. The intensity of small-angle scattering for a macroscopic isotropic sample is given by

$$I(s) = Vp(1 - p)(\rho_1 - \rho_2)^2 \int_V \gamma(r) \exp [2\pi i \mathbf{r} \cdot \mathbf{s}] dV, \quad (1)$$

where $s = (2 \sin \theta / \lambda)$ is the magnitude of the diffraction vector \mathbf{s} , V is the irradiated volume of the sample, p is the volume concentration of one phase, and ρ_1, ρ_2 respectively are electron densities of phase 1 and 2. The function $\gamma(r)$ is Porod's "characteristic function" indicating the probability that two points of the given system at a distance r from each other are in the same phase. From Eq. (1) it follows that the intensity of scattering is proportional to the square difference of electron densities in the phases. In the case of a porous system the electron density in pores ρ_2 can be neglected with respect to the electron density of the polymer matrix ρ_1 .

For experimental reasons, the intensity $J(s)$ measured with an infinitely high primary beam is very frequently used instead of the intensity $I(s)$ corresponding to the point cross-section of the primary beam. All the following relationships in this paper will be given for the intensity $J(s)$.

It follows from the scattering theory from ideal two-phase systems^{1,2} that the intensity $J(s)$ has an asymptotic course for $s \rightarrow \infty$ proportional to s^{-3} . This relationship (Porod's law) can be expressed in the form

$$\lim_{s \rightarrow \infty} s^3 J(s) = \frac{Q}{2\pi \cdot l_p}, \quad (2)$$

where the parameter l_p — “range of inhomogeneity” — gives the mean length of the segments restricted by the phase boundaries on the straight lines passing through the system in all directions, and the invariant Q is defined as $Q = \int_0^\infty sJ(s) ds$. A further parameter of magnitude suggested by Porod is the “length of coherence” l_c

$$l_c = \int_0^\infty J(s) ds / \pi Q \quad (3)$$

the value of which gives the integral width of the characteristic function $\gamma(r)$.

Méring and Tchoubar-Vallat^{3,4} have found that transformations of the scattering curve enable the function $g(r)$ to be calculated:

$$g(r) = 2 \int_0^\infty \left[\lim_{s \rightarrow \infty} 4\pi^2 s^2 J'(s) - 4\pi^2 s^2 J'(s) \right] \cos(2\pi r s) ds,$$

$$J'(s) = 2 \int_0^\infty J(\sqrt{s^2 + y^2}) dy, \quad (4)$$

where y is an auxiliary integration variable. The function $g(r)$ has for a diluted system of particles the meaning of the distribution of lengths of the segments averaged over all directions and all particles.

As has been shown by Perret and Ruland⁵, the parameters l_p and l_c can be expressed as

$$l_p = \int_0^\infty r g(r) dr / \int_0^\infty g(r) dr, \quad (5)$$

$$l_c = \int_0^\infty r^2 g(r) dr / \int_0^\infty r g(r) dr. \quad (6)$$

The values of all the quantities given so far can be obtained without measuring intensities on an absolute scale, *i.e.* without knowing the intensity of the primary beam.

If the intensity $J(s)$ on the absolute scale is known, it is possible to determine the volume fraction of pores p (porosity) by using the relationship⁶

$$p(1 - p) = 2\pi 10^{24} a Q / i_c N^2 d \varrho_1^2 P_0 \lambda, \quad (7)$$

where a (cm) is the distance of the sample from the registration plane, i_c is Thompson's constant, N is the Avogadro number, d (cm) is thickness of the sample, ϱ_1 (mol/cm³)

is electron density of the polymer matrix, and P_0 is intensity of the primary beam per one cm of length in the plane of registration.

By using porosities, some further parameters can be determined from relationship (7):^{1,2}

1) Phase boundary area per volume unit of the sample

$$S/V = 8\pi p(1 - p) \lim_{s \rightarrow \infty} s^3 J(s)/Q, \quad (8)$$

2) Mean length of intersects passing through the pores $\langle l \rangle_p$ and through the polymer matrix $\langle l \rangle_m$

$$\langle l \rangle_p = l_p/(1 - p), \quad \langle l \rangle_m = l_p/p. \quad (9)$$

EXPERIMENTAL

Samples

Macroporous styrene divinylbenzene copolymers were prepared as described earlier⁷. They differ in the content of the crosslinking agent and heptane (as an inert component in the copolymerization mixture); the respective contents in samples PD 1, 3, 4 were 30% and 45%_n and in sample PD 2 20% and 50%. Sample PD 3 was thoroughly extracted with ethanol after copolymerization; the other samples were extracted only with hot distilled water.

Cellulose in the bead form was prepared by using the original procedure as a new chromatographic material. Its properties have been described elsewhere⁸.

The samples of both types were of a regular spherical shape. The distribution of diameters was very broad, the average value being 0.1 mm. The polymer matrix densities were measured in a pycnometer by a method described in paper⁹.

Apparatus

The small-angle X-ray scattering was measured with a Kratky camera. The $\text{CuK}\alpha$ radiation was used. The radiation was monochromatized with Ross's filters and recorded with a proportional counter provided with an amplitude analyzer. Owing to the large intensity of the small-angle scattering at the lowest angles the radiation was weakened by means of a series of Al films with known absorptions.

RESULTS AND DISCUSSION

Fig. 1a shows small-angle scattering curves of the copolymers styrene/divinylbenzene and Fig. 1b shows scattering curves of cellulose in the coordinates $\log J(s)$ vs $\log s$. A steep increase in intensity in the region of the lowest angles has been observed for the sample of the copolymer PD3 and for the cellulose sample C1. The increase is probably due to the fact that along with micropores which yield the scattering curves in the region of larger angles the samples also contain a considerable number of markedly larger pores. In the region in which scattering from large pores was

observed the measured values were replaced with the Gaussian curve in the further evaluation; the curve started in a region not affected by scattering from these pores. The structure parameters thus determined are therefore only those of the micropores.

For a perfect two-phase system the tail of the intensity curves in the $\log J(s)$ - $\log s$ plot (Fig. 1) should have a slope-3 (Porod's law). However, for the styrene/divinylbenzene samples the slope deviates from this ideal value, which suggests that their two-phase structure is disturbed. The most frequent deviations from an ideal two-phase structure are electron density fluctuations inside the phases and an unsharp phase boundary. The electron density fluctuation inside the phases is reflected in a positive deviation from Porod's law. The intensity course in the tail can here be described by¹⁰

$$J(s) = K_1 s^{-3} + K_2 \quad (10)$$

On the other hand, the finite width of the phase boundary is reflected in a negative deviation from Porod's law, and the intensity course for sufficiently large scattering angles can be approximated by^{11,12}

$$J(s) = K_1 s^{-3} - K'_2 s^{-1} \quad (11)$$

The constant K_1 in relationships (10) and (11) has the meaning $\lim_{s \rightarrow \infty} s^3 J(s)$ and serves for the determination of the phase boundary area S/V (Eq. (8)). The constants K_2 and K'_2 are related to the degree of deviations from a perfect two-phase structure.

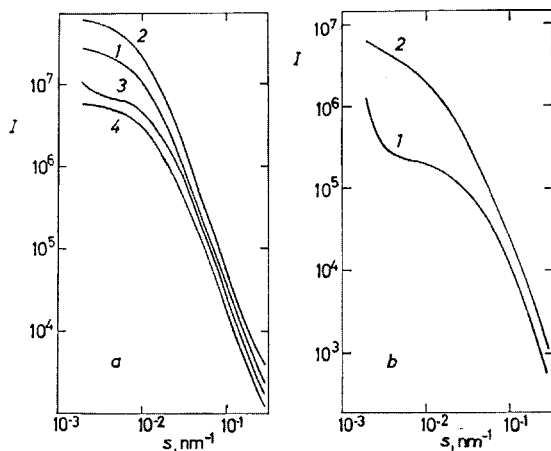


FIG. 1

Course of Intensity of Small-Angle X-Ray Scattering for Porous Copolymers Styrene/Divinylbenzene (PD) and Cellulose (C)

a : 1 PD1, 2 PD2, 3 PD3, 4 PD4; b : 1 C1, 2 C2.

It can be seen from Fig. 2a that the scattering curves of copolymer samples show positive deviations from an ideal behaviour. Consequently, the polymer matrix in these samples cannot be regarded as homogeneous. The behaviour of tails of the scattering curves of cellulose (Fig. 2b) suggests that the system is a perfect two-phase one. The wide-angle X-ray diffraction suggests, however, that both cellulose samples are partly crystalline (about 30 wt.-%). Consequently, the polymer matrix of these samples must exhibit density fluctuations (of the crystalline and amorphous regions). The apparently ideal behaviour of tails of their scattering curves can be explained by the fact that also the phase boundary (polymer-pore) has a finite width and that the scattering effects on both types of deviations of the structure from an ideal two-phase one compensate each other.

Eqs (10) and (11) allow us to separate scattering due to the imperfectness of the two-phase system. After such treatment of the scattering curve it is possible to determine the structure parameters given in the preceding chapter and derived for a perfect two-phase system. Since in samples of the copolymer styrene/divinylbenzene

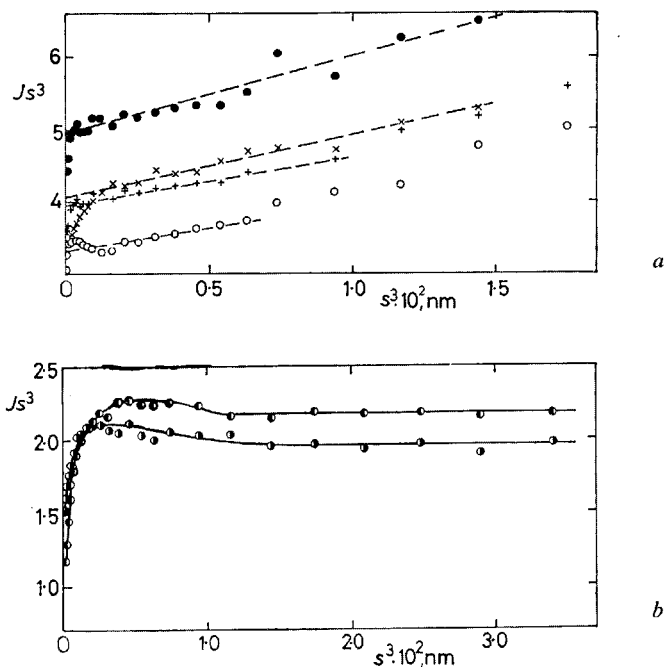


FIG. 2

Course of the Function $s^3 J(s)$ vs s^3 for Porous Copolymers Styrene/Divinylbenzene (PD) and Cellulose (C)

a: x PD1, PD2, PD3, + PD4; b: C1, C2.

the scattered intensity deviations in the tail were positive, the intensity was corrected by using Eq. (10). In the $s^3 J(s)$ vs s^3 plot the tail of the scattering curve is linearized (Fig. 2). It was used to determine the constants K_1 and K_2 .

The samples were measured in capillaries. Because of the spherical shape of the polymer particles, the sample possessed — along with its own porosity — also pores between the individual particles. This untrue porosity does not contribute to the small-angle scattering in the region investigated by us, but prevents direct determination of the sample thickness needed for porosity calculations. The sample thickness was therefore determined by measuring the X-ray absorption. For porous systems it holds

$$A = J/J_0 = \exp [-(\mu/\rho_0) \rho_0(1 - p) d], \quad (12)$$

where (μ/ρ_0) is the mass absorption coefficient of the polymer, ρ_0 is its density (g cm^{-3}). Eqs (7) and (12) yield a rearranged relationship for porosity

$$p = -219.2 \frac{a Q(\mu/\rho_0) \rho_0}{\lambda \rho_1^2 P_0(\ln A)}. \quad (13)$$

A disadvantage of such procedure consists in the not too exactly tabulated values¹³ of the coefficient (μ/ρ_0) . More exact results could probably be obtained by measuring

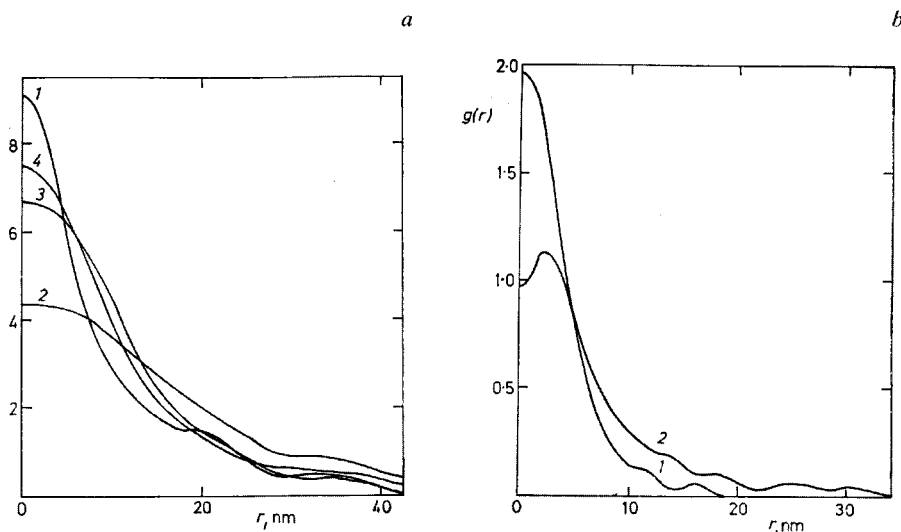


FIG. 3

Course of the Function $g(r)$ for Porous Copolymers Styrene Divinylbenzene (PD) and for Porous Cellulose (C)

a: 1 PD1, 2 PD2, 3 PD3, 4 PD4; b: 1 C1, 2 C2.

the mean density of samples (pores + matrix). If the samples under investigation do not contain closed pores, the polymer matrix density r is comparatively easy to measure, but measurements of the mean density of incompact porous samples meet with considerable experimental difficulties. We therefore regard the determination of porosities by the procedure described above as more advantageous.

In order to determine the porosities, the intensity of small-angle scattering must be measured on an absolute scale, that is, it is necessary to determine P_0 in Eq. (13). In this measurement we used a calibration sample (Lupolen) from Professor Kratky's laboratory¹⁴ with a known conversion factor K_L between the intensity of scattering $J_{E,15}$ at an angle corresponding to Bragg's distance 15 nm and the intensity of the primary beam

$$P_0 = K_L J_{E,15} a A. \quad (14)$$

Fig. 3 shows a plot of the curves $g(r)$ for porous copolymers and cellulose. For all samples except cellulose C2 these functions have a maximum at the beginning ($r = 0$) and then decrease to zero. The function $g(r)$ of the sample C2 has a maximum at 24 nm. At high r values ($r > 20$ nm for sample C1, $r > 60$ nm for the other samples) the calculated curves oscillate around zero. The negative $g(r)$ values have of course no physical meaning; they are related with the inaccurate determination of the scattering curve at the lowest angles where extrapolation is required. We therefore did not consider points in the above regions when calculating integral parameters of this function. The nonzero $g(0)$ values observed for all samples indicate a certain

TABLE I
Structure Parameters of Porous Polymers
Meaning of symbols is indicated in the text.

Sample	Density g cm^{-3}	p	S/V m^2/cm^3	l_c , nm		l_p , nm		$\langle l \rangle_p$, nm		$\langle l \rangle_m$, nm	
				$J(s)$	$g(r)$	$J(s)$	$g(r)$	$J(s)$	$g(r)$	$J(s)$	$g(r)$
Polystyrene/divinylbenzene											
PD1	1.062	0.29	68.4	29.1	25.8	12.1	11.7	17.0	16.5	41.7	40.3
PD2	1.057	0.29	48.4	33.0	30.9	17.1	16.8	24.1	23.7	59.0	57.9
PD3	1.062	0.20	59.5	21.4	19.6	10.9	10.7	13.6	13.4	54.5	53.5
PD4	1.062	0.25	69.7	24.1	20.7	10.8	10.5	14.4	14.0	43.2	42.0
Cellulose											
C1	1.52	0.20	166	8.0	6.4	3.8	3.6	4.8	4.5	19.0	18.0
C2	1.52	0.55	128	21.8	15.6	7.7	7.2	17.1	16.0	14.0	13.1

angularity of the pores^{3,4}. Owing to the high porosity values (Table I), the $g(r)$ curves do not offer such straight information about the structure of the samples as they would give for dilute systems.

The values of the structure parameters of the gels under investigation are given in Table I. The calculated porosities of all samples except C2 do not exceed 30 per cent by volume; the porosity of the cellulose sample C2 is higher than 50%. Owing to the increase in intensity at low scattering angles, it can be expected that the porosities of the sample C1 and PD3 determined in this work are somewhat lower than the actual values.

The values of the range of heterogeneities l_p and of the coherent length l_c were calculated both directly from the scattering curve (Eqs (2) and (3)), and from the function $g(r)$ (Eqs (5) and (6)). The values of both parameters calculated from the scattering curve were in all cases higher than those calculated from the function $g(r)$. The deviations are obviously due to the fact that in integrating in Eqs (5) and (6) we had to omit the region of high r where the function $g(r)$ determined by means of experimental data was not well defined any more. This limitation was particularly apparent in the values of the parameter l_c because it is given by the higher moments of the function $g(r)$.

A number of useful parameters characterizing porous polymeric systems and obtained by the small-angle X-ray scattering with the only assumption of the existence of a two-phase structure shows that the method used is very suitable for this type of determination.

REFERENCES

1. Porod G.: *Kolloid-Z. Z. Polym.* 124, 83 (1951).
2. Porod G.: *Kolloid-Z. Z. Polym.* 125, 51 (1952); 125, 109 (1952).
3. Méring J., Tchoubar-Vallat D.: *C. R. Acad. Sci.* 261, 3096 (1965).
4. Méring J., Tchoubar-Vallat D.: *C. R. Acad. Sci.* 262, 1703 (1966).
5. Perret R., Rulland W.: *J. Appl. Crystallogr.* 1, 308 (1968).
6. Kratky O., Miholic G.: *J. Polym. Sci., Part C*, 2, 449 (1963).
7. Seidl J., Malinský J., Dušek K., Heitz W.: *Advan. Polym. Sci.* 5, 113, (1967).
8. Peška J., Štamberg J., Hradil J., Ilavský M.: *J. Chromatogr.*, in press.
9. Rožan J., Vaniček O.: *Pigmenty*. Published by SNTL, Prague 1959.
10. Luzzati V., Witz J., Nicolaieff A.: *J. Mol. Biol.* 3, 367 (1961).
11. Ruland W.: *J. Appl. Crystallogr.* 4, 70 (1971).
12. Vonk C. G.: *J. Appl. Crystallogr.* 6, 81 (1973).
13. *International Tables for X Ray Crystallography*, Vol. III. Kynoch Press, Birmingham 1962.
14. Kratky O.: *Z. Anal. Chem.* 201, 161 (1964).

Translated by L. Kopecká.