

SMALL ANGLE X-RAY SCATTERING STUDY OF POROSITY VARIATION IN A STYRENE-DIVINYLBENZENE COPOLYMER

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Porosity variations induced by swelling agent exchange were studied in a styrene-divinylbenzene copolymer. Standard methods were used in the characterization of copolymer porosity in the dry state and the results were compared with related structural parameters derived from small angle X-ray scattering (SAXS) measurements as developed for the characterization of two-phase systems. The SAXS method was also used for porosity determination in swollen samples. The differences in the porosity of dry samples were found to be an effect of the drying process, while in the swollen state the sample swells and deswells isotropically.

Styrene-divinylbenzene copolymers prepared in the presence of inert diluents may have two ranges of inhomogeneity¹. The inhomogeneity of the copolymer network always arises in the vinyl-divinyl copolymerization resulting in more or less crosslinked regions². If phase separation occurs during the copolymerization, an inhomogeneity, *i.e.* porosity, of the product is also observed³.

The porosity of dry copolymers (understood below as the volume fraction of pores having radii smaller than about 7500 nm) is readily measurable as the pore walls are well defined. In a swollen copolymer, the situation is somewhat more complicated. The porosity may be defined either as the total volume fraction of swelling agent in the copolymer bead or, preferably, as the fraction of the agent filling the pores. According to the latter concept, the copolymer bead is considered as a two-phase system consisting of the swollen gel and the swelling agent in which the volume fraction of polymer is zero.

It was found in many cases⁴⁻⁶ that the porosity of dry styrene-divinylbenzene copolymers (and related products⁷) depends on the preswelling of samples before characterization. Therefore, one may accept the effect of copolymer inhomogeneity (a broad distribution of segment densities) in the morphology of swollen copolymer, the effect being induced by swelling agent exchange.

Small angle X-ray scattering (SAXS) measurements may serve as a tool providing insight into the structure of copolymers⁸. Using a two-phase model (for dry copolymer: pores/polymer matrix, and for the swollen one: the pores filled with solvent/swollen gel), the porosity, p , may be derived from the SAXS curves. According to Porod's theory of scattering in a two-phase sys-

tem^{9,10} it holds

$$p(1 - p) = 219 \cdot 2 \frac{aQ}{dP_0\lambda(q_1 - q_2)^2}, \quad (1)$$

where a is the distance between the sample of thickness d and the plane of registration, P_0 is the intensity of the incident beam having the wavelength λ , q_1 and q_2 are the electron densities of phase 1 and 2, respectively, and

$$Q = \int_0^\infty sI(s) ds, \quad (2)$$

where $I(s)$ is the intensity of the scattered radiation and s is the scattering vector ($|s| = 2 \sin \theta / \lambda$).

The average lengths of intersects through the pores, $\langle l_p \rangle$, and through the matrix, $\langle l_m \rangle$, are

$$\langle l_p \rangle = \frac{l_p}{1 - p}, \quad \text{and} \quad \langle l_m \rangle = \frac{l_p}{p}, \quad (3)$$

where

$$l_p = \frac{Q}{2\pi \lim_{s \rightarrow \infty} s^3 I(s)} = \frac{Q}{2\pi k}. \quad (4)$$

The interfacial specific surface area, S/V , may be estimated from the equation

$$S/V = (1/Q) 8\pi k p(1 - p). \quad (5)$$

EXPERIMENTAL

Samples

Styrene-divinylbenzene copolymer in the form of very uniform (0.1–0.3 mm in diameter) beads was prepared from monomers using the standard suspension technique. Styrene and divinylbenzene were purified by removing the inhibitor with subsequent distillation *in vacuo*. Divinylbenzene used contained 43.0 wt.-% of *m*-divinylbenzene and 16.8 wt.-% *p*-divinylbenzene (by GLC), the rest being essentially ethylstyrenes. The monomer mixture which contained 10wt.-% of *m*- and *p*-divinylbenzene was diluted with octane. The volume fraction of monomers in the resulting mixture was 0.5; 1 wt.-% of benzoyl peroxide (based on the weight of the reaction mixture) was used as initiator. Methocel K-100 (Dow Chemical Co.) was used as suspension stabilizer. Polymerization was performed at 80°C for 12 hours and the resulting polymer beads were washed with hot water and finally extracted with hot benzene in a Soxhlet extractor.

The copolymer sample preswollen in toluene is referred to as T. The samples C, A, and M were obtained by equilibration of the copolymer with cyclohexane, acetone and methanol, respectively. Thus, the samples C and A were obtained either by prolonged heating of the dry sample T in cyclohexane and acetone, respectively, or by passing the respective solvent through a column packed with the swollen sample T. Both procedures gave the same results for individual samples. Sample M was obtained by passing methanol through the column filled with swollen sample A.

Prior to measurements carried out in the dry state the samples were kept at $25 \pm 0.2^\circ\text{C}$ for a time sufficient to remove the swelling agent (at least 2 weeks, to constant weight). The sample T was additionally dried at 60°C .

All the properties measured after repeated solvent exchange and drying steps were found to be reversible and reproducible.

Characterization of Samples

The porosity of the samples was calculated from the relation

$$p = 1 - d_0/d_{0p}, \quad (6)$$

where d_0 is the apparent density measured in a mercury pycnometer¹¹, and d_{0p} is the density of a copolymer of the same crosslinking prepared without any diluent; $d_{0p} = 1.029 \text{ g cm}^{-3}$ was assumed to be true copolymer density.

In the swollen state, the porosity may be calculated from the equation

$$1 - p = \varphi_g = (d_s - d_d)/(d_g - d_d), \quad (7)$$

where d_d is the density of the swelling agent and d_s is the mean density of combined copolymer-solvent system, *i.e.*

$$d_s = (B + 1) d_p d_d / (B d_p + d_d), \quad (8)$$

where B is the weight of the swelling agent per gram of copolymer (at swelling equilibrium) as determined by centrifugation¹².

The total pore volume, V_t , was calculated from pycnometry

$$V_t = 1/d_0 - 1/d_{0p}; \quad (9)$$

the volume of pores penetrable by mercury, V_m , was measured directly using a Carlo-Erba Model AG-67 porosimeter.

From the same measurements, the radii, \bar{R} , of the "representative" pores were evaluated, corresponding to the maximum on the curve $R \, dV_m/dR$ vs $\log R$.

The surface area was measured using the method of nitrogen thermal desorption¹³.

SAXS Measurements

The scattering curves were measured with a Kratky camera. The scattered $\text{CuK}\alpha$ radiation was recorded with a proportional counter. A β -filter and an amplitude analyser were used for monochromatization of the radiation. The value of P_0 from Eq. (1) was estimated by using a calibration sample (Lupolen) kindly supplied by Prof. Kratky's laboratory.

As the samples were measured in capillaries, the interparticle voids had to be taken into account. The thickness of the dry samples, d , was estimated by a measurement of the absorption, A , of an X-ray beam⁸. Accordingly, Eq. (1) takes the form

$$p = -219.2 \frac{aQ(\mu/\varrho_0) \varrho_0}{\varrho_1^2 P_0 \ln A}, \quad (10)$$

where (μ/ϱ_0) is the mass adsorption coefficient and ϱ_0 is the density of the polymer.

Measurements on the swollen samples were made after sedimentation of copolymer beads in a capillary filled with the swelling agent. The thickness of the sample was calculated from the average density of the copolymer-solvent system (Eq. (8)); the weight of the swelling agent, m_d , the weight of the sample, m_c , and the diameter of the capillary, t_c , were determined according to

$$d = w_s t_c = d_d(m_c - m_d)/m_d(d_s - d_d), \quad (11)$$

where w_s is the volume fraction of swollen copolymer in the capillary including pores filled with solvent. Since the volume of the capillary was very small ($<0.2 \text{ cm}^3$), the inaccuracy of the difference in the numerator of Eq. (11) was the main source of error in the evaluation of the copolymer structural parameters.

RESULTS AND DISCUSSION

The porous structure of the copolymer studied in the dry state varies to a quite high extent depending on sample pretreatment. Both the porosity and pore dimensions increase with decreasing swelling degree for a given order of solvents (Table I). The pore radii are small, but considerably large differences in the values of pore volumes

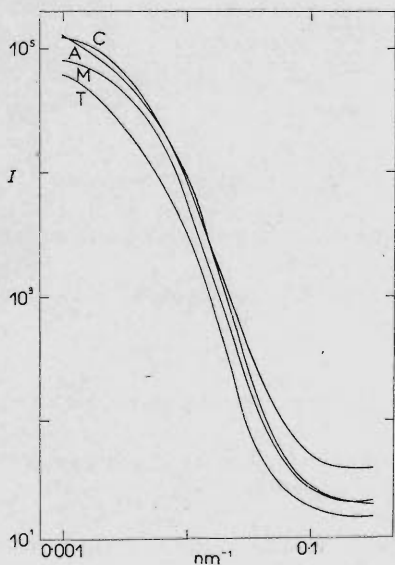


FIG. 1

SAXS curves of dry styrene-divinylbenzene copolymer pretreated with toluene (T), cyclohexane (C), methanol (M) and acetone (A); $s = 2 \sin \theta / \lambda$

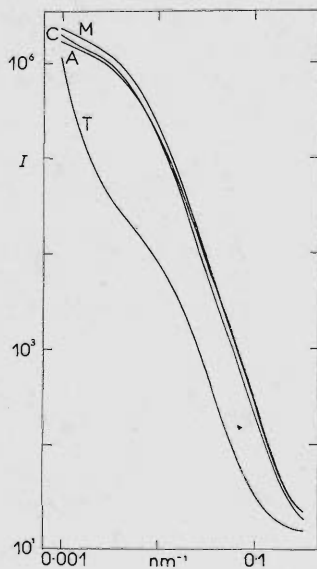


FIG. 2

SAXS curves of swollen styrene-divinylbenzene copolymer; designation as in Fig. 1

as determined by pycnometry, V_p , and porosimetry, V_m , indicate an amount of micropores or closed pores, which are not detectable by the mercury porosimeter used by us. Therefore, the true pore radii may be slightly different.

Curves of scattered radiation intensity for dry samples are shown in Fig. 1. The shape of the curves is typical of scattering from a two-phase system. The intensity falls off rapidly with increasing scattering angle. The tail of curves plotted as $\log I(s)$ vs $\log s$ linearizes with a slope close to -3 according to Porod's theory^{9,10}.

The structural parameters of the dry samples are listed in Table II. The porosity values are lower than those determined pycnometrically. This is probably due to the insensitivity of the SAXS method to large pores which do not contribute to the intensity of scattered radiation⁸. On the other hand, the radii of pores which determine the pore volume (representative radii) are lower by a factor larger than 2 than the linear parameter describing the average diameter of pores evaluated from SAXS curves.

TABLE I

Porosity parameters of the copolymer samples. S surface area, V_0 apparent volume = $1/d_0$; for remaining symbols and abbreviations see text

Sample	d_0 g/cm ³	p	V_t cm ³ /g	V_m cm ³ /g	S m ² /g	S/V_0 m ² /cm ³	\bar{R} nm
T	1.005	0.025	0.023	0	0	0	0
A	0.612	0.405	0.662	0.52	73.1	44.7	18.1
C	0.562	0.454	0.808	0.52	87.3	54.1	17.3
M	0.547	0.468	0.856	0.53	122.4	66.9	14.0

TABLE II

Parameters of dry copolymers derived from SAXS

Sample	T	A	A ^a	A ^b	C	C ^a	C ^b	M	M ^b	M ^c
l_p , nm	2.1	53.3	58.0	88.9	52.4	58.0	50.0	40.4	90.5	74.3
l_m , nm	1 780	80.6	97.8	218.0	98.9	109.6	313.9	85.7	373	298
S/V , m ² /cm ³	2.2	29.8	25.7	13.0	26.4	23.9	11.0	31.7	8.6	10.8
p	0.012	.399	.372	.292	.347	.346	.137	.320	.19	.20

The samples heated additionally at: ^a 110°C for 6 h, ^b 150°C for 150 h, ^c 150°C for c. 2 months.

This apparent contradiction may arise from the different geometrical models of pores used in the two methods. The occurrence of closed pores may also affect the results, provided that their dimensions are high.

The porosity variation in styrene-divinylbenzene copolymers has been interpreted in terms of the disappearance of small pores resulting from the superimposed effects of solvent surface tension and the mobility of polymer segments⁴⁻⁷. The copolymer swollen in a "good" solvent (*i.e.* in toluene) is in the rubber-like state — its glass transition temperature, T_g , lies below room temperature. Relaxation of deswelling tension occurs easily until the content of the swelling agent is lowered enough by drying to increase T_g to the vicinity of room temperature. Most of the good solvent has to be removed in order to increase T_g in this way. However, if a poor solvent is used, it suffices to remove only a small amount to reach T_g and segmental motion is restricted. The morphology of the swollen copolymer is thus fixed. The surface tension of the solvent may, obviously, favour the collapse of pores, especially those of small radius provided the polymer segments are movable enough.

TABLE III

Parameters of the swollen samples derived from SAXS measurements

Sample	l_p nm	l_m nm	S/V m^2/cm^3	p
T	78.5	84.9	24.5	0.48
A	71.8	87.8	25.0	0.45
C	81.6	72.0	26.0	0.53
M	67.8	68.6	29.3	0.50

TABLE IV

Apparent densities of the samples after thermal treatment performed in the dry state

Sample	None	Conditions of treatment				
		110°C 6 h	150°C 6 h	150°C 30 h	150°C 150 h	150°C 30 h ^a
A	0.612	0.598	0.785	0.799	0.871	1.025
C	0.562	0.565	0.750	0.761	0.780	1.029
M	0.547		0.703	0.710	0.796	1.026

^a After swelling in toluene.

A question arises as to whether the morphology of a swollen porous polymer is a function of the degree of swelling (*i.e.* of the thermodynamic quality of the solvent). Inhomogeneity of the polymeric gel may disturb the isotropy of swelling. Regions of different crosslinking may differently change their dimensions upon replacement of the swelling agent.

An answer to this question may lie in the results of SAXS measurements done with swollen samples (Table III). Porosity values are almost the same for each swollen samples, thus indicating isotropy of swelling. The structural parameters, although affected by inaccuracy in the determination of interparticle porosity, show an increase of pore dimensions while the matrix dimensions decrease compared with the parameters obtained for dry samples.

The effect of swelling on porosity variation in the styrene-divinylbenzene copolymer becomes clear if one tries to reduce the porosity by heating the samples to a temperature higher than T_g for polystyrene segments (Tables II and IV). Even much prolonged heating without any solvent does not reduce the porosity to the level observed after drying from toluene.

CONCLUSIONS

- (1) The porosity of styrene-divinylbenzene copolymer may vary to a high extent depending on the kind of solvent in which the copolymer is swollen before drying.
- (2) This porosity variation is a result of the drying process only.
- (3) Upon replacement of the swelling agent, the porosity seems to remain unchanged, *i.e.* changes in swelling from solvent to solvent do not affect the morphology of the porous copolymer.

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