Journal of Chromatography, 196 (1980) 75–83
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 12,853

STRUCTURE AND SORPTION PROPERTIES OF POROUS COPOLYMERS OF STYRENE, ACRYLONITRILE AND DIVINYLBENZENE

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(First received January 11th, 1980; revised manuscript received March 25th, 1980)

SUMMARY

The sorption properties of a series of styrene–acrylonitrile–divinylbenzene terpolymers, containing from 0 to 100% of acrylonitrile relative to the styrene, with respect to phenol, *p*-nitrophenol and *p*-nitroaniline were studied by batch and dynamic methods. The copolymers were obtained by the suspension method in the presence of inert diluents under constant synthesis parameters. The porosity of styrene–divinylbenzene copolymers containing added acrylonitrile was found to be similar to that for two-component copolymers, but they were found to differ in their morphology. The chemical structure of these copolymers has no influence on the sorption, which was found to depend on the structure of the sorbate molecule.

INTRODUCTION

There have been numerous publications on the purification of water from phenol derivatives (*e.g.*, refs. 1–4). Classical sorbents, *e.g.*, activated charcoals, exhibit good sorption properties, but cannot be regenerated, so that there is increasing interest in various non-ionic polymeric adsorbents. These products are mostly styrene–divinylbenzene copolymers with modified structures.

The literature data indicate that both the chemical and physical properties of such copolymers and ion exchangers[5,6] derived from them can be improved by the introduction of a third monomer. Such a modification also improves the homogeneity and mechanical strength of the polymer[7–10]. Poinescu *et al.*[11] reported that by introducing acrylonitrile into a mixture of styrene and divinylbenzene the porosity of the terpolymer obtained is higher than that for the corresponding styrene–divinylbenzene copolymer. Hence it was of interest to study the effect of the presence of acrylonitrile in terpolymers with styrene and divinylbenzene on their sorption properties.

EXPERIMENTAL

Copolymers of styrene with divinylbenzene (S/DVB) and acrylonitrile with divinylbenzene (AN/DVB) and terpolymers with various acrylonitrile contents

0021-9673/80/0000–0000/$02.25

(S/xAN/DVB) were obtained by suspension copolymerization in the presence of inert solvents under constant synthesis conditions[12]. The acrylonitrile content in the copolymers was determined by nitrogen elemental analysis.

For the macroporous copolymers obtained the skeletal and apparent densities[13], the total porosity and the volume fraction of pores[14] were determined by known methods. The water and acetone regains were determined by the centrifugation technique[15]. The compositions of the copolymer and their properties are given in Table I.

The pore size distribution was determined with a Carlo Erba AG-67 high-pressure mercury porosimeter and the specific surface areas, S_{N_2}, were determined by the comparative nitrogen desorption method with an S-272 sorptiograph (ICSO, Blachownia, Poland).

The sorption properties of the copolymers with respect to phenol, *p*-nitrophenol and *p*-nitroaniline were examined by the static (batch) method using aqueous solutions of these compounds of various concentration (from 0.075 to 1.500 g/dm^3 for the first two and 0.030 to 0.600 g/dm^3 for *p*-nitroaniline). Their concentrations in the solutions were determined by colorimetry[16].

The dynamic (column) sorption experiments were carried out in glass columns (20 × 0.5 cm I.D.) with a sorbent bed volume of 3.5 cm^3. The concentration of the solutions of the compounds was 0.6 g/dm^3, being limited by the low solubility of *p*-nitroaniline in water. The volume flow-rate of the solutions was 40 cm^3/h.

RESULTS AND DISCUSSION

On the basis of our earlier results[17] on the synthesis of sorbents for the removal of phenol and *p*-nitrophenol, we chose a copolymer exhibiting the best sorption properties, namely a copolymer of styrene and divinylbenzene obtained in the presence of a mixture of inert organic diluents. A portion of styrene in subsequent samples was replaced with acrylonitrile until the monomer mixture contained only this monomer and divinylbenzene. The properties of these copolymers are given in Tables I and II.

TABLE I

CHEMICAL COMPOSITION OF COPOLYMERS AND THEIR SOLVENT REGAINS

Sample	*Content of acrylonitrile in mixtures with styrene (%)*	*Nitrogen content (%)*		*Water regain (g/g)*	*Acetone regain (g/g)*
		Calculated	*Found*		
S/DVB	0	—	—	1.77	2.06
S/3AN/DVB	18.75	1.00	1.00	1.78	—
S/5AN/DVB	31.25	1.70	1.36	1.30	—
S/10AN/DVB	62.5	2.64	1.93	1.59	—
AN/DVB	100	4.00	3.20	2.07	2.15

It can be seen from Table II that the copolymers obtained exhibit porosity changes induced by the different treatments of the samples before the determination. The samples treated with water and dried from water generally have higher porosities than those dried from benzene. These differences are in agreement with the data reported by Häupke and Pientka[18]. The treatment procedure and the interpretation of

TABLE II

POROSITY CHANGES IN COPOLYMERS BROUGHT ABOUT BY DIFFERENT TREATMENT OF SAMPLES BEFORE THE DETERMINATION

	Porosity (%)				
	S/DVB	*S/3AN/DVB*	*S/5AN/DVB*	*S/10AN/DVB*	*AN/DVB*
Before treatment	23.9	28.1	30.3	32.0	36.4
After treatment	47.6	37.4	45.3	45.3	47.6

the observed changes have been reported elsewhere[19]. As all experiments reported in this work were carried out with aqueous solutions, the morphological characteristics of the samples treated with water are listed in Table III.

TABLE III

MORPHOLOGICAL CHARACTERISTICS OF THE COPOLYMERS STUDIED

Sample	*Skeletal density (g/cm^3)*	*Apparent density (g/cm^3)*	*Specific volume (cm^3/g)*	*Specific surface area (m^2/g)*	*Pore radius distribution (%)*		
					Pore radii 10–100 nm	*Pore radii 100–1000 nm*	*Pore radii 1000–7500 nm*
S/DVB	1.07	0.574	0.81	492	87.6	9.3	3.1
S/3AN/DVB	1.14	0.715	0.52	292	90.7	8.3	1.0
S/5AN/DVB	1.14	0.625	0.72	310	88.2	8.1	3.7
S/10AN/DVB	1.14	0.625	0.72	281	90.5	8.5	1.0
AN/DVB	1.14	0.599	0.79	465	88.0	10.4	1.6

Our results (Table III) indicate that the differences in the copolymer porosities are small, but the specific surface areas and pore volumes of the terpolymers are lower than those for S/DVB and AN/DVB copolymers. The two-component copolymers have almost identical porosity characteristics.

Assuming that the macroporous cross-linked copolymers are composed of submicroscopic spherical particles with pore between them, Hradil[20] proposed a method for the calculation of the average particle radius, $\bar{R}$, the average pore radius, $\bar{r}$, and the quantity $\bar{a}$, defined as the average distance between edges of neighbouring particles from the pore volume and specific surface area data. The magnitude of $\bar{a}$ is a measure of both the particle distribution uniformity and their size distribution. For strictly monodisperse copolymers with the densest possible packing of submicroscopic spherical particles, the value of this correction factor is zero. The usefulness of these parameters for terpolymer structure characterization has been confirmed by Žůrková *et al*[21].

The results in Table IV indicate that the terpolymers were composed of polydisperse particles further apart and more loosely packed than those in the S/DVB and AN/DVB copolymers.

Whether a change in the copolymer morphology or the presence of acrylonitrile units in the copolymers affects their sorption properties was studied by experiments in which the sorption of phenol, *p*-nitrophenol and *p*-nitroaniline on these copolymers was measured. The sorption isotherms shown in Figs. 1–3 indicate that both the course

TABLE IV

CHARACTERISTICS OF MACROPOROUS STRUCTURES OF COPOLYMERS

Sample	*Average particle radius, $\bar{R}$ (nm)*	*Average pore radius, $\bar{r}$ (nm)*	*Average distance between particles, $\bar{a}$ (nm)*	*Corrected average pore radius, $\bar{r}_c$ (nm)*
S/DVB	5.70	2.23	0.43	1.80
S/3AN/DVB	9.01	2.35	0.68	1.67
S/5AN/DVB	8.49	3.16	0.64	2.52
S/10AN/DVB	9.37	3.48	0.71	2.77
AN/DVB	5.66	2.31	0.43	1.88

of this process and the sorption capacities of the terpolymers are the same as those found for S/DVB and AN/DVB copolymers. Such a relationship seems to suggest that perhaps an increase in the inter-particle distance enables these compounds to be more easily adsorbed. Such an conclusion is further corroborated by a comparison of specific surface areas calculated from phenol sorption data (Table V, S_F).

Good agreement between these properties obtained for the terpolymers may indicate that the entire surface of the sorbent is accessible to the sorbate molecules. The specific surface areas for two-component S/DVB and AN/DVB copolymers calculated from phenol sorption isotherms were found to be lower than those deter-

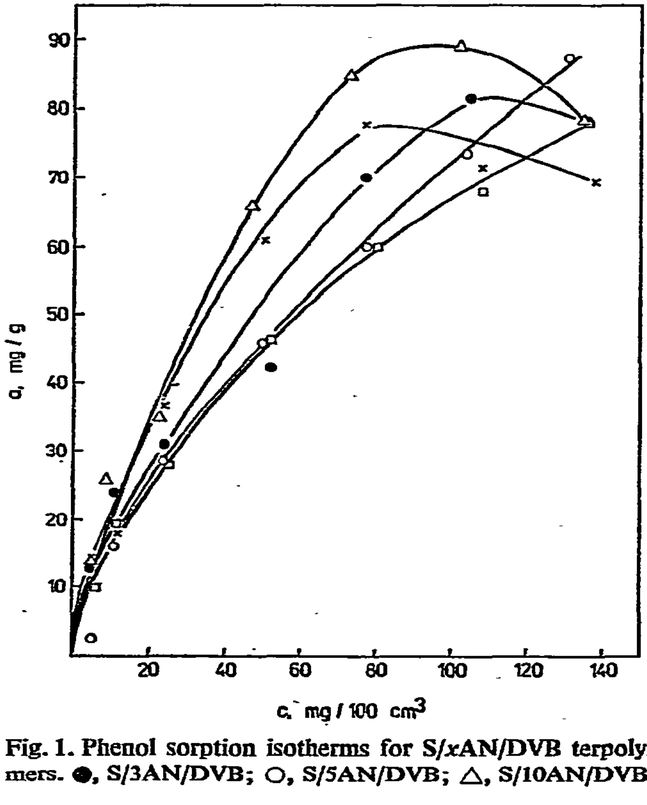

Fig. 1. Phenol sorption isotherms for S/xAN/DVB terpolymers and S/DVB and AN/DVB copolymers. ●, S/3AN/DVB; ○, S/5AN/DVB; △, S/10AN/DVB; □, S/DVB; ×, AN/DVB.

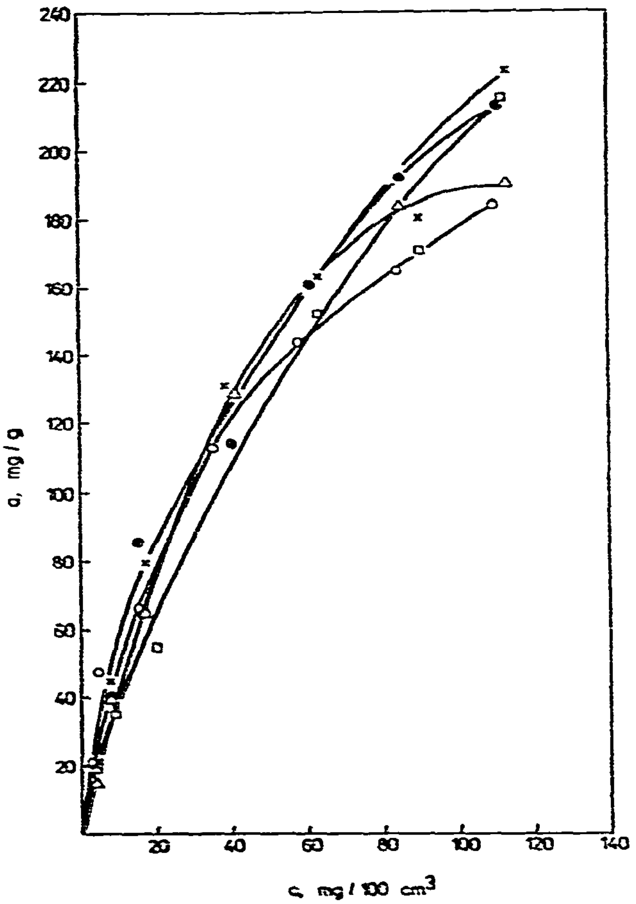

Fig. 2. p-Nitrophenol sorption isotherms for S/xAN/DVB terpolymers and S/DVB and AN/DVB copolymers. Symbols as in Fig. 1.

mined by the nitrogen desorption method. It seems possible that some diffusion constraints play a role here. If so, then a greater distance between particles in the terpolymers makes possible the better use of the sorbent surface during the sorption of phenol compared with two-component copolymers. When interpreting sorption isotherms, a simplifying assumption is usually made that the sorbate layer is monomolecular. The p-nitrophenol molecule can assume an orientation parallel or perpendicular to the sorbent surface. The data in Table V (S_{n-F}) indicate that in the systems studied the p-nitrophenol molecule usually assumes a perpendicular orientation toward the sorbent surface; this result is in disagreement with the data reported by Seidl and Krška[3] on the sorption of phenol on Amberlite XAD sorbents.

The lack of differences in the sorption properties of the copolymers studied seems to indicate that independent of the sorbent composition, *i.e.*, the replacement of styrene with acrylonitrile units sorption probably proceeds according to the same mechanism. It was found that the degree of sorption is mainly influenced by the structure of the sorbate molecule, and perhaps its dipole moment (Table VI).

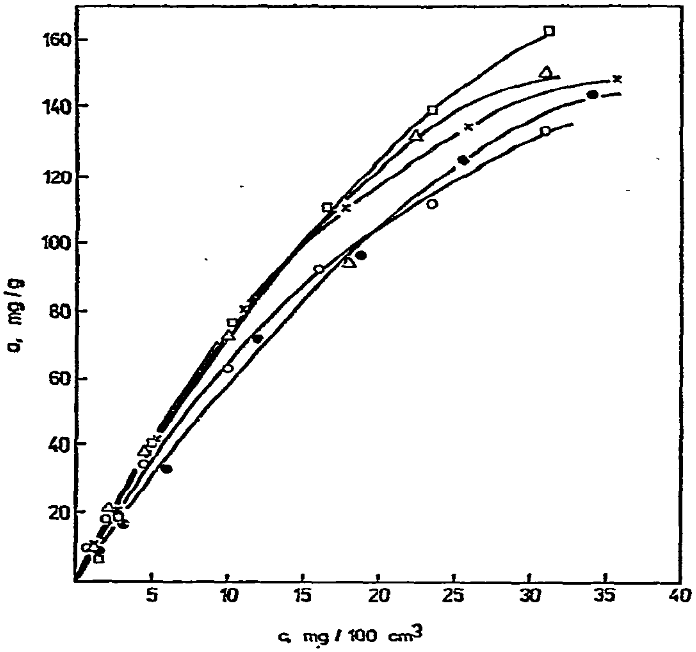

Fig. 3. *p*-Nitroaniline sorption isotherms for S/*x*AN/DVB terpolymers and S/DVB and AN/DVB copolymers. Symbols as in Fig. 1.

Sorption studies carried out by the static (batch) method did not reveal any significant differences between S/DVB and AN/DVB copolymers. Only when the dynamic (column) method was applied did the advantage of AN/DVB copolymers over S/DVB copolymers become evident. Using the same bead size fraction, bed height and solution flow-rate, it was found that a column packed with AN/DVB sorbent had the greatest breakthrough volume for phenol and *p*-nitrophenol solutions (Figs. 4 and 5; Table VI). The desorption was carried out with acetone; it was found to be in the range 85–100% (Table VI), and in all instances investigated the entire amount of sorbate adsorbed was desorbed with only 10 cm^3 of acetone. The performance of these sorbents in the second cycle was not worse than in the first cycle. Because of small differences in the water and acetone regains exhibited by the AN/DVB copolymer (bed volume change 4%, Table I), no difficulties in the column operation

TABLE V

COMPARISON OF SPECIFIC SURFACE AREAS OBTAINED BY DIFFERENT METHODS

Sample	S_{N_2} (m^2/g)	S_F (m^2/g)	$S_{\kappa\text{-}F}$ (m^2/g)	
			Parallel	*Perpendicular*
S/DVB	492	316	591	281
S/3AN/DVB	292	264	568	271
S/5AN/DVB	310	316	568	271
S/10AN/DVB	281	316	568	271
AN/DVB	465	400	568	271

TABLE VI

SORPTION RESULTS BY THE DYNAMIC METHOD

Sorbate	*Property*	*S/DVB*	*AN/DVB*
Phenol (μ = 1.4 D)	1st cycle:		
	Breakthrough capacity (mg/g)	42.6	46.0
	Total capacity (until equalization of concentration) (mg/g)	95.9	90.5
	Desorption yield (%)	84.0	91.0
	2nd cycle:		
	Breakthrough capacity (mg/g)	63.9	46.0
	Total capacity (mg/g)	86.5	88.1
	Desorption yield (%)	100.0	99.3
p-Nitrophenol (μ = 5.05 D)	1st cycle:		
	Breakthrough capacity (mg/g)	106.5	153.5
	Total capacity (mg/g)	141.6	198.7
	Desorption yield (%)	92.3	89.2
	2nd cycle:		
	Breakthrough capacity (mg/g)	127.8	161.1
	Total capacity (mg/g)	159.4	207.6
	Desorption yield (%)	87.3	85.0
p-Nitroaniline (μ = 6.17 D)	1st cycle:		
	Breakthrough capacity (mg/g)	213.0	184.1
	Total capacity (mg/g)	306.5	306.6
	Desorption yield (%)	84.0	90.7
	2nd cycle:		
	Breakthrough capacity (mg/g)	234.4	184.1
	Total capacity (mg/g)	282.5	339.8
	Desorption yield (%)	100.0	90.3

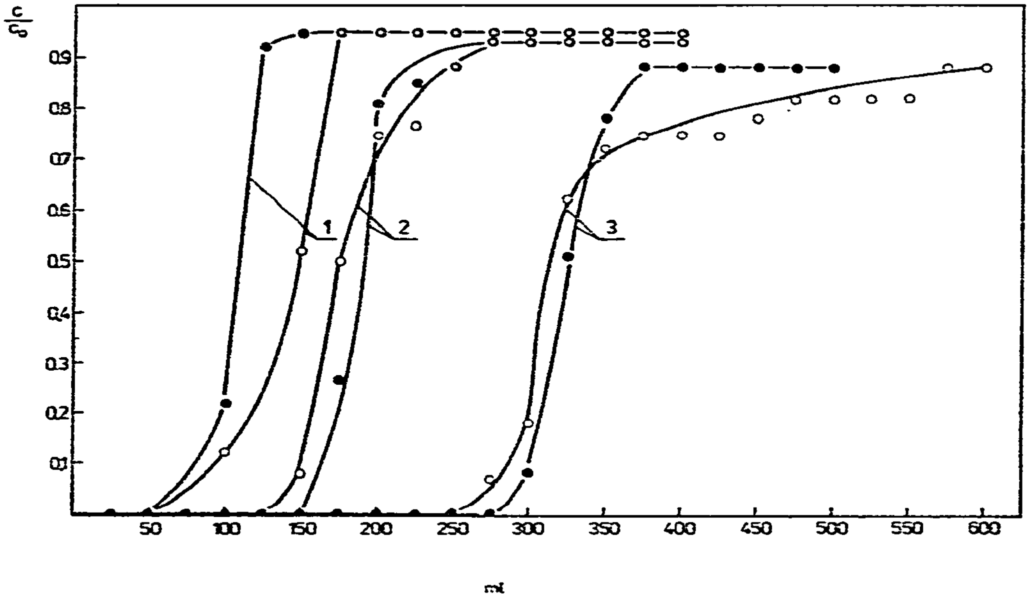

Fig. 4. Sorption of phenol (1), *p*-nitrophenol (2) and *p*-nitroaniline (3) on S/DVB sorbent. ○, 1st cycle; ●, 2nd cycle.

were encountered during its working cycle. The S/DVB copolymer shows a greater swelling in acetone than in water (bed volume change 16 %), so that before the desorption the sorbent bed should be loosened, but some destruction of the sorbent beads cannot be avoided.

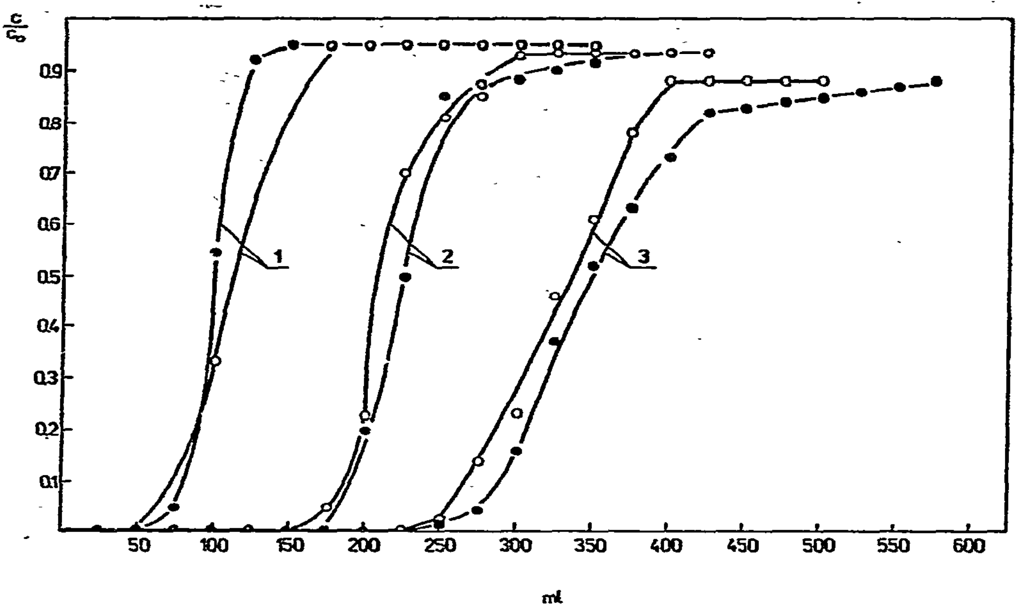

Fig. 5. Sorption of phenol (1), *p*-nitrophenol (2) and *p*-nitroaniline (3) on AN/DVB sorbent. ○, 1st cycle; ●, 2nd cycle.

CONCLUSIONS

The introduction of acrylonitrile into a styrene–divinylbenzene monomer mixture leads to terpolymers with a structure similar to that of the two-component copolymers. The S/*x*AN/DVB terpolymers are built of loosely packed particles with a polydispersity greater than that found in S/DVB and AN/DVB copolymers. Such a structure gives rise to an improvement in the sorption properties of these copolymers toward phenol, *p*-nitrophenol and *p*-nitroaniline.

Independent of the chemical structure of the sorbents, the magnitude of sorption increases in the order phenol < *p*-nitrophenol < *p*-nitroaniline. The dipole moments of these three sorbate molecules increase in the same order.

The small changes in swelling of the AN/DVB copolymer upon transferring it from water to acetone and *vice versa* make this sorbent suitable for dynamic (column) operation.

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