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STRUCTURE AND SORPTION PROPERTIES OF POROUS COPOLYMERS OF ACRYLONITRILE AND DIVINYLBENZENE

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SUMMARY

The effect of the chemical structure of porous copolymers formed from acrylonitrile (AN) and divinylbenzene (DVB) containing various weight fractions of polar units (12, 19, 26, 40 and 58% AN) on their physicochemical and sorption properties has been examined. With increasing content of the polar units in the copolymers, their Kováts indices increase, suggesting the presence of stronger interactions of the polar sorbates with the copolymer surface. The sorption degrees of phenols and anilines have been found to depend more on the surface polarity than on its total area. The Hammett equation describes the sorption process well, thus suggesting that physical interactions are dominant. The selectivity of sorption, expressed in terms of the process constant in the Hammett equation, decreases as the content of AN units increses.

INTRODUCTION

Relatively little is known about specific electronegative adsorbents. They can be obtained either from other adsorbents by modification of their surfaces, chemically or by adsorption, or by synthesis of polymeric sorbents using appropriate monomers, *e.g.* acrylonitrile (AN).

It has been found that the addition of AN to a mixture of styrene and divinylbenzene considerably improves the mechanical stability of the resulting suspension copolymer particles[1–3] and, due to the polarity of their surfaces, also the sorption properties with respect to phenols and anilines[4].

In this paper, the structure and the sorption properties of porous copolymers of acrylonitrile and divinylbenzene (AN–DVB) with respect to phenols and anilines are discussed.

EXPERIMENTAL

The copolymers were obtained using the suspension polymerization technique. A 4% solution of sodium chloride was used as the aqueous phase. The compositions of the monomer phases are listed in Table I. The copolymers were extracted with hot

TABLE I

THE COMPOSITION OF THE POLYMERIZATION MIXTURE AND THE CONTENT OF AN IN
THE RESULTING COPOLYMERS

Sample	m- and p-DVB in commercial product (%)	DVB (cm³)	AN (cm³)	Nominal cross-link (%)	AN content found (%)
12AN–DVB	59	84.0	16.0	50	12
19AN–DVB	63	79.4	20.6	50	19
26AN–DVB	63	63.5	36.5	40	26
40AN–DVB	63	47.6	52.4	30	40
58AN–DVB	58	34.6	65.4	20	58

toluene, dried and classified on a screen in order to collect a fraction with bead diameter 0.1–0.3 mm. The content of acrylonitrile in the copolymers was calculated from the overall nitrogen content.

The apparent density, d_0, was measured pycnometrically, and the porosity, P, and macroporosity, Q, were calculated therefrom using the standard relationships[5].

The specific surface area, S, was measured using the dynamic nitrogen desorption method on a Sorptomat 1800 apparatus (Carlo Erba). The mean radius of the pores, $\bar{r}$, and that of gel agglomerates, $\bar{R}$, was calculated assuming a cylindrical pore shape using the relationships[6]

$$\bar{r} \text{ (nm)} = c \cdot 10^3 R/S \tag{1}$$

and

$$\bar{R} \text{ (nm)} = 3 \cdot 10^3/d_2 S \tag{2}$$

where d_2 is the true density of the copolymers and c is a constant[6].

The weight swelling ratio, W, was determined by removing the excess of swelling solvent by centrifugation. The volume swelling ratio, B, was calculated from the relationship[7]

$$B = d_0[1/d_2 - (W - 1)/d_1] \tag{3}$$

where d_1 is the density of the solvent. The volume fraction of a copolymer in the swollen gel, v_2, was taken to be $1/B$.

The sorption experiments were carried out in columns under the conditions described elsewhere[4]. Each column was packed with the same amount of sorbent. Aqueous solutions of sorbates having initial concentration, $c_0 = 0.12$ g/dm³ were introduced to the columns at a constant rate. From the break-through curves, the distribution coefficient, K_x, was calculated as

$$K_x \text{ (cm}^3\text{/g)} = V/m \tag{4}$$

where V is the volume of solution up to the break-through point and m is the weight of dry sorbent.

Using the substituent constants[8], π, the applicability was verified of the Hammett equation in the form

$$\log K_x - \log K_0 = \rho\pi \tag{5}$$

where K_x and K_0 are the distribution coefficients of the substituted and unsubstituted compounds, respectively, and ρ is considered to be the sorption process constant.

RESULTS AND DISCUSSION

The mechanism of the porous structure formation during copolymerization of styrene (S) and divinylbenzene is quite well understood[9-16]. The effects of the kind and amount of inert diluent of the monomers as well as that of the cross-linking degree are known. It has been found that the replacement of styrene units by acrylonitrile ones does not influence significantly the porous structure of copolymers having a nominal cross-linking degree of 50% (w/w) of divinylbenzene[4]. Nevertheless, the surface properties of such polymers are different; the latter copolymer has a higher sorption capacity with respect to phenols than S-DVB copolymer[4].

The parameters characterizing the porous structure of AN–DVB copolymers prepared using various ratios of the monomers are presented in Table II. As is seen, with increasing fraction of AN in the monomer mixture, the porosity of the resulting copolymers also increases. This is exactly opposite to the known relationship between the porosity and cross-linking degree (DVB content) for S–DVB copolymers. One of the reasons is that the presence of acrylonitrile in the monomer mixture considerably changes the conditions of polymerization.

The reactivity ratios for some of the monomers present in the system AN–commercial DVB were reported by Schwachula[1]. Thus, for p-DVB (monomer 1), m-DVB (2) and AN (3) the reactivity ratios are $r_{13} = 4.52$, $v_{31} = 0.2$, $r_{23} = 1.55$, $r_{32} = 0.26$, $r_{12} = 1.55$ and $v_{21} = 0.42$. These values suggest that, as for the system S–DVB, the AN–DVB copolymer formed at the initial stages of polymerization contains more DVB units than the monomer mixture and therefore there is a tendency to form microgels. However, whereas the microgels are well solvated by aromatic monomers, the acrylonitrile monomer is a poor solvent. The larger is the fraction of AN in the system, the earlier the phase separation or precipitation of microgels occurs. In the resulting two-phase system, the polymer will be connected to the surface portions of microgels and less interpenetration will take place than in the case of the S–DVB system. The polymerization accompanied by precipitation in which the monomer itself is a non-solvent with respect to the polymer formed leads to a linear polyacrylonitrile (PAN) having a porosity of 0.71 and a specific surface area of 30 m^2/g. An additional factor facilitating the formation of porous structure, particularly at high concentrations of AN, is the tendency to form an ordered structure and strong dipole–dipole interactions[17].

The presence of nitrile groups in copolymers makes the surface polar and hence modifies the interactions between the surface and sorbate molecules. The Kováts retention indices are often used as a measure of these interactions. The method proposed by Rohrschneider[18-20] is most frequently used for characterizing the polarity of stationary phases in gas–liquid chromatography. In this method, the polarity is

TABLE II

THE POROUS STRUCTURE OF AN-DVB COPOLYMERS

Sample	Porosity, p	Macroporosity, Q (cm³/g)	Surface area, S (m²/g)	Mean radius (nm)		Volume fraction of		
				Of pores, $\bar{r}$	Of agglomerates	Micropores	Mesopores	Macropores
12AN-DVB	0.48	0.79	570	1.88	4.70	0.30	0.59	0.11
19AN-DVB	0.57	1.19	600	3.29	4.46	0.20	0.38	0.42
26AN-DVB	0.68	1.88	430	8.51	6.23	0.09	0.46	0.45
40AN-DVB	0.75	2.65	210	24.76	12.76	0.03	0.10	0.87
58AN-DVB	0.72	2.24	40	110.00	66.96	0.00	0.12	0.87

TABLE III

POROSITY, P, VOLUME SWELLING RATIO, B, AND THE VOLUME FRACTIONS OF THE POLYMER IN SWOLLEN GEL, v_2, FOR AN-DVB COPOLYMERS

Sample	DMF (a)			DMF (b)			Isobutanol			Water		
	P	B	v_2	P	B	v_2	P	B	v_2	P	B	v_2
12AN-DVB	0.25	3.80	0.30	0.27	3.44	0.29	0.39	2.68	0.37	0.48	1.77	0.57
19AN-DVB	0.50	2.22	0.45	0.53	2.12	0.47	0.64	1.70	0.59	0.57	1.63	0.61
26AN-DVB	0.68	1.50	0.67	0.70	1.33	0.75	0.73	1.22	0.82	0.68	1.34	0.74
40AN-DVB	0.74	1.43	0.70	0.75	1.32	0.76	0.78	1.21	0.82	0.75	1.34	0.74
48AN-DVB	0.70	1.41	0.71	0.71	1.35	0.74	0.73	1.095	0.91	0.72	1.10	0.90

expressed in terms of constants calculated from differences in Kováts retention indices measured for five standard sorbates (benzene, ethanol, methyl ethyl ketone, nitromethane, pyridine) on the test and a standard non-polar (squalane) stationary phase. Thus, the effect of non-specific interactions is eliminated. Lukáš[21] replaced squalane with Carpopack B, thus extending the method to polymer sorbents.

For the copolymers (Table II), the relationship between the retention time and the number of carbon atoms in n-alkanes is linear, and therefore the retention indices are easy to determine. For the copolymer (58AN–DVB) cross-linked with 20% DVB, at the temperature of the measurements (above the glass transition temperature, T_g), changes in supermolecular structure occur resulting in sorption in the bulk. The indices could not be determined for this copolymer. The values collected in Table IV indicate the increase in the constants as the content of AN in the copolymer increased. The strongest specific interactions during separation of aromatic compounds, alcohols and other types of sorbates were observed on the copolymer with the highest content of AN.

The ability to swell when in contact with a liquid or vapour is the specific property of polymers. In the case of porous copolymers, the swelling ratio is not easy to measure directly because a part of the swelling solvent is present in the pores. For porous S–DVB copolymers it is often assumed that the swelling is isotropic, i.e., that the porosity of a swollen copolymer is the same as the volume fraction of pores in its dry form[13]. The validity of this assumption have been confirmed by small angle X-ray scattering studies[22]. Here, the same assumption is made and the volume fraction of polymer in the swollen gel, v_2, is taken to be the inverse of the volume swelling ratio, B (Table III). The swelling measurements were carried out in water, isobutanol which according to its solubility parameter should be a good solvent for AN–DVB copolymer and in the polar solvent dimethylformamide (DMF), known to dissolve linear polyacrylonitrile. The porosities calculated from apparent density measurements are also shown in Table III. The samples were also pretreated with the solvent specified in this Table. As is seen, the porosity changes on passing from a "good" (DMF) to a "bad" (water) solvent are observed only for the copolymers with the nominal cross-linking degree of 50% (12AN–DVB). For porous S–DVB copolymers such changes were observed also at much higher cross-linking degrees[16,23]. The changes were attributed to structural variations due to the inhomogeneity of the gel. The lack of porosity changes in AN copolymers may indicate that the gel is more homogeneous.

The solvent regains (g/g), e.g., solvent contents in swollen copolymer beads,

TABLE IV

ROHRSCHNEIDER CONSTANTS FOR THE NON-POLAR (S–DVB) AND POLAR (AN–DVB) SORBENTS

Sample	x'	y'	z'	u'	s'
S–DVB	0.6	0.9	0.7	1.2	1.2
12AN–DVB	0.6	1.6	1.3	2.0	1.8
19AN–DVB	0.9	1.6	1.5	2.4	1.9
26AN–DVB	1.3	2.4	2.0	3.2	2.5
40AN–DVB	2.1	3.5	3.0	4.7	4.4

measured for AN–DVB copolymers slightly increase with increasing cross-linking degree, which might also suggest an uniformity of the gel. The fraction of polymer in the swollen gel, however, calculated aftger subtracting the amount of solvent present in the pores (isotropic swelling), has been found to decrease in all solvents including water and DMF, although for the latter the volume fractions of the solvent in the gel, $(1 - v_2)$, were the highest. The swelling measurements in DMF were made twice: (a) after equilibrating with the solvent in room temperature and (b) after preheating the copolymers in boiling solvent for 1 h followed by cooling to room temperture. The results indicate that the network was fully relaxed. It seems that the high v_2 values obtained can be explained by assuming the existence of ordered fragments of the copolymer gel in which additional physical cross-linking occurs[17]. Detailed studies of the structure, including X-ray analysis, will be reported elsewhere.

The differences in the chemical composition (surface polarity) and structure (fractions of meso- and macropores, surface area) of the sorbents were expected to affect considerably their sorption properties. Previously, it had been found that the sorption of phenols on non-specific adsorbents (porous S–DVB copolymers) can be described by the Hammett equation and that the process constant in this equation, which could be considered as a measure of the sorption selectivity, does not depend on the surface area. Porous AN–DVB copolymers, however, can be treated as specific adsorbents, linking either the hydrophilic or hydrophobic part of a sorbate molecule. Molecules having a high dipole moment can also be sorbed on the surface of AN–DVB copolymers.

A higher degree of sorption of phenols on a porous AN–DVB copolymer than on a S–DVB was observed[24] for sorbents having similar porosity characteristics. For the present group of sorbents, the situation is slightly more complicated since the changes in surface polarity are accompanied by changes in surface areas. The results of sorption experiments become difficult to interpret, particularly for highly polar compounds (Table V). It seems that the distribution coefficients for phenols are more sensitive to polarity variations than to changes in surface area.

It seemed of interesting to verify whether or not the specific interactions would affect the sorption process to the extent that the Hammett equation would no longer be valid. A linear relationship between $\log (K_x/K_0)$ and the substituent constants has

TABLE V

SUBSTITUENT CONSTANTS, π, AND DISTRIBUTION COEFFICIENTS, K_x, FOR PHENOLS

Sorbate	π	12AN–DVB	19AN–DVB	26AN–DVB	40AN–DVB	58AN–DVB
Phenol	0	230.2	380.7	222.2	252.9	150.3
p-Aminophenol	−1.63	7.7	47.6	61.3	68.3	26.8
m-Aminophenol	−1.29	61.4	76.1	61.3	32.7	35.8
p-Hydroxyphenol	−0.87	61.4	114.2	99.6	116.7	43.0
m-Hydroxyphenol	−0.66	76.7	161.8	114.9	136.2	57.3
p-Cresol	0.48	506.4	590.0	321.8	389.0	229.1
m-Cresol	0.56	506.4	723.3	344.8	359.8	214.8
p-Nitrophenol	0.50	613.9	628.1	306.5	369.6	200.6
m-Nitrophenol	0.54	782.7	751.8	360.2	398.7	214.8
p-Chlorophenol	0.93	828.7	1037.4	513.4	573.8	286.4
m-Chlorophenol	1.04	844.1	989.8	406.1	496.0	314.0

TABLE VI

RESULTS OF CORRELATION OF LOG K_x/K_0 AND SUBSTITUENT CONSTANTS, π (PHENOL DERIVA·TIVES)

Number of compounds is eleven in each case.

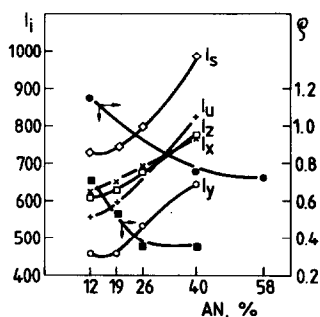|	12AN–DVB	19AN–DVB	26AN–DVB	40AN–DVB	58AN–DVB
Correlation coefficient	0.960	0.998	0.994	0.998	0.980
Process constant, ρ	0.69	0.52	0.36	0.36	0.44
Intercept when $\pi = 0$	−0.004	−0.046	−0.027	−0.015	−0.070

Fig. 1. The Kováts indices and process constants, ρ, for phenol (■) and aniline (●) derivatives on AN–DVB copolymers; I_x, benzene; I_y, ethanol; I_z, methyl ethyl ketone; I_u, nitromethane; I_s, pyridine.

TABLE VII

SUBSTITUENT CONSTANTS, π, AND DISTRIBUTION COEFFICIENTS, K_x, FOR ANILINE DE·RIVATIVES

Sorbate	π	12AN–DVB	40AN–DVB	58AN–DVB
Aniline	0	230.0	194.5	86.0
p-Aminophenol	−1.29	7.7	68.1	26.8
m-Aminophenol	−0.73	61.4	82.7	35.8
p-Nitroaniline	0.49	767.0	680.8	329.3
m-Nitroaniline	0.47	890.0	661.3	315.0

TABLE VIII

RESULTS OF CORRELATION OF LOG K_x/K_0 AND SUBSTITUENT CONSTANTS, π (ANILINE DERIVATIVES)

Number of compounds is five in each case.

	12AN–DVB	40AN–DVB	58AN–DVB
Correlation coefficient	0.980	0.004	0.966
Process constant, ρ	1.189	0.676	0.704
Intercept when $\pi = 0$	0.015	0.204	0.213

been found to exist despite the interactions. The correlation coefficients for these relationships werehigh (Table VI). However, as is seen from Fig. 1, a large proportion of AN units in the copolymers reduces their sorption selectivity (smaller slopes of the lines, ρ). This finding contradicts the conclusion that can be drawn by examining the Kováts indices determined by the gas chromatograhy method. Probably, the presence of water which interacts with both the sorbates and the polar surface, brings about a hydration competition such as is described by the Snyder–Soczewiński model[25,26].

The preliminary sorption experiments involving aniline derivatives (Table VII) seem to confirm this hypothesis. For this series of compounds, the straight line obtained misses the origin, despite high correlation coefficients (Table VIII, Fig. 1). However, the number of sorbates studied is too small for us to determine whether or not this is due to additional specific interactions affecting the overall mechanism of sorption.

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