



# Copolymers of acrylate derivatives of diphenyl sulfone and divinylbenzene as materials of $\pi$ -electron donor–acceptor properties

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## Abstract

Optimization of the synthesis of porous polymers of di(*p*-acrylphenyl)sulfone, (*p*-hydroxyphenyl-*p*-acrylphenyl)sulfone, and divinylbenzene is presented. Porous structure of the obtained copolymers were studied. Polymer of the most regular porous structure was chemically modified in order to obtain materials of  $\pi$ -electron donor–acceptor properties which can be applied as specific sorbents. The influence of modification process on their porous structures was also studied.

**Keywords** Diphenyl sulfone · Acrylate derivatives · Porous structure · Copolymerization

## 1 Introduction

Studies on new polymeric packing and methods of their modification make it possible to obtain materials of specific chromatographic properties. For many years the most popular were macroporous spherical beads of polystyrene crosslinked with divinylbenzene (ST-DVB) (Arshady 1990; Downing et al. 2000). As these materials are highly hydrophobic they possess limited applications. Recently searching for more hydrophilic materials have been made. These new materials are obtained from monomers containing polar functional groups or by chemical modification of the non-polar ST-DVB polymeric matrix (Gawdzik et al. 2006; Podkościelna et al. 2009; Huang and Turner 2018).

Although a large number of papers are available on the determination of polar interactions, there is little information about characterization of  $\pi$ – $\pi$  interactions. This type of interaction can be defined as the interaction between  $\pi$ -electrons of the chromatographic packing and those of the solute species (Hyun and Pirkle 1987; Hradil et al. 2000). According to Léon, Reubsæet and Vieskar (1999) an interaction between  $\pi$ -electron containing compounds is favoured when one of the compounds, for example the stationary

phase, is electron-rich and the other one is electron-poor (i.e. the solute) or vice versa. In these systems the stationary phase can act as the  $\pi$ -electron donor (soft Lewis base) or the  $\pi$ -electron acceptor. Depending on its chemical nature it can interact with solutes being Lewis acid or with  $\pi$ -electron donors (Zhu et al. 2004).

In this work we present new chromatographic stationary phases capable of  $\pi$ – $\pi$  interactions. Among the synthesized polymeric stationary phases one has 3,5-dinitrophenyl pendant groups ( $\pi$ -acceptor), and the other 2-naphthyl functional groups ( $\pi$ -donor). Besides, inert polymeric material with cyclohexyl groups on the surface was also synthesized. Porous structures of these materials are studied and compared with that of unmodified polymer.

## 2 Experimental

### 2.1 Materials

Di(*p*-hydroxyphenyl)sulfone (bisphenol-S), benzoil chloride, acrylic acid,  $\alpha,\alpha'$ -azoisobutyronitrile, and bis(2-ethylhexyl)sulfosuccinate sodium salt (DAC, BP) were from Fluka AG (Buchs, Switzerland). Acetone, hexane, isopropanol, dichloromethane, chlorobenzene, hexan-1-ol, acryloyl chloride, and sodium hydroxide were from POCh (Gliwice, Poland). Divinylbenzene, 1,4-dioxane and methanol were bought from Merck (Darmstadt, Germany). Di(*p*-hydroxyphenyl)sulfone, 3,5-dinitrobenzoyl

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chloride, 2-naphthoyl chloride, cyclohexyl isocyanate, phenothiazine, and terabutylammonium chloride (TEBACl) were from Sigma–Aldrich.

## 2.2 Synthesis of monomers

### 2.2.1 Preparation of di(*p*-acrylphenyl)sulfone (DAS)

To obtain di(*p*-acrylphenyl)sulfone, 25 g (0.1 mol) of bisphenol-S was diluted in 300 mL of 3% water solution of NaOH. 0.02 g of phenothiazine as an inhibitor, and 1 g of TEBACl was dissolved in 300 mL of dichloromethane while stirring. The obtained solutions were cooled to 10 °C and mixed. At this temperature 20.8 g (0.23 mol) of acryloyl chloride was added dropwise. Next, the temperature was increased to room temperature and under these conditions the mixture was stirred for 1 h. Organic phase was separated from water phase and washed with 3% of aqueous sodium hydroxide (2 × 100 mL) and distilled water (2 × 100 mL), and dried using magnesium sulfate. Dichloromethane was distilled off under the reduced pressure. The obtained raw compound (DAS) was purified by recrystallization from the mixture of dichloromethane and hexane (1:2; v/v). M.p. of di(*p*-acrylphenyl)sulfone was 103–105 °C (Kämmerer and Mück 1969).

### 2.2.2 Preparation of (*p*-hydroxyphenyl)(*p*-acrylphenyl)sulfone (HAS)

To 350 mL of 3% water solution of NaOH, 25 g (0.1 mol) of bisphenol-S was dissolved while stirring. The solution was cooled to 6 °C, and then 9.96 g (0.11 mol) of acryloyl chloride was added dropwise. The mixture was then stirred at a temperature 6–8 °C for 1 h. The obtained compound was sucked off and washed with 200 mL of 3% HCl, 3 × 100 mL of water, and dried in air. This raw product was purified by recrystallization from chlorobenzene. M.p. of this compound was 169 °C.

The chemical structures of the monomers are presented in Fig. 1.

### 2.3 Preparation of porous copolymer beads

Copolymerization was performed in the aqueous medium. In the typical experiment, 190 mL of distilled water and 2.3 g of bis(2-ethylhexyl)sulfosuccinate sodium salt were stirred for 1 h at 80 °C. Then the solution containing monomers (HAS + DAS), divinylbenzene (DVB), and  $\alpha, \alpha'$ -azoisobisbutyronitrile (AIBN) diluted in chlorobenzene (or chlorobenzene + decan-1-ol) was prepared and added while stirring to the aqueous medium. Copolymerization was performed for 18 h at 80 °C (Gawdzik et al. 2006a, b; Podkościelna and Gawdzik 2010).

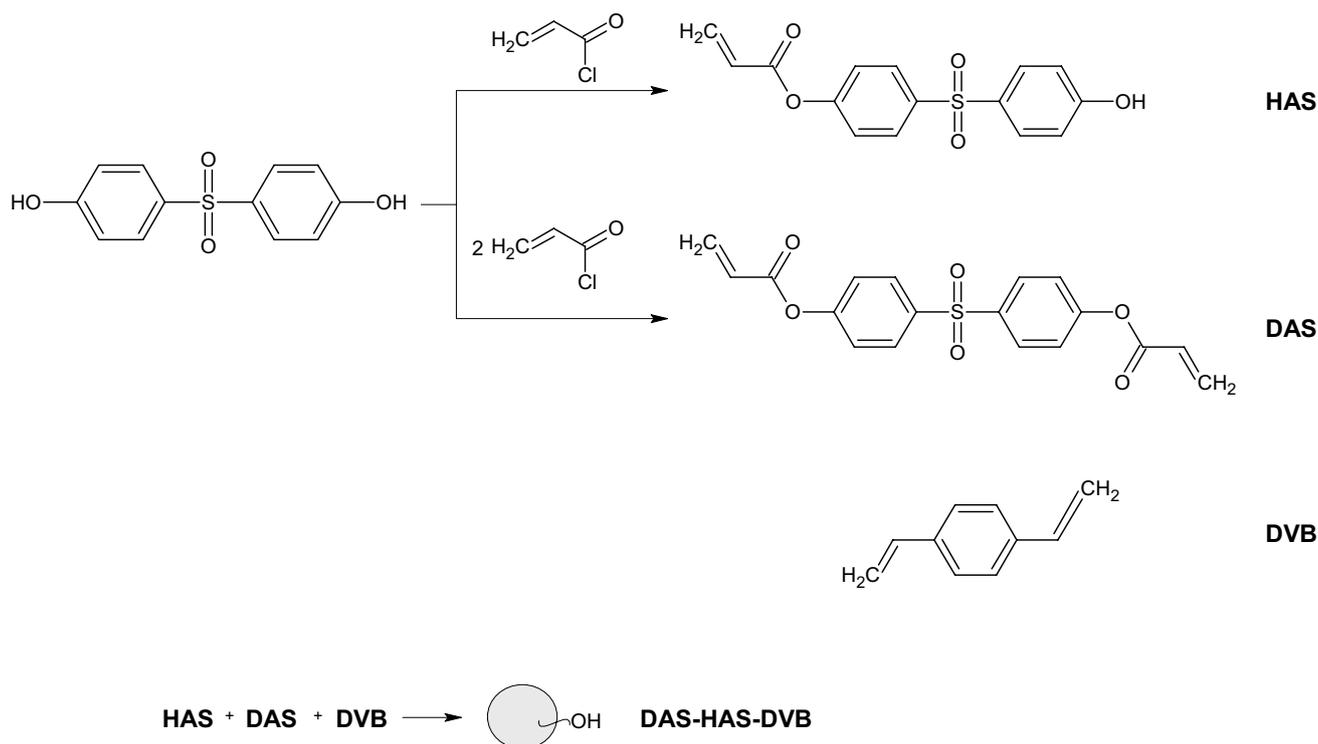


Fig. 1 Chemical structures of monomers used for DAS-HAS-DVB copolymer synthesis

**Table 1** Syntheses of the HAS-DAS-DVB polymers

Polymer	Monomers (g)			AIBN (g)	Chlorobenzene (mL)
	DAS	HAS	DVB		
DAS-HAS-DVB-I	0.64	6.08	1.3	0.154	12.0
DAS-HAS-DVB-II	3.68	3.04	1.3	0.169	14.0
DAS-HAS-DVB-III	5.20	1.52	1.3	0.184	16.0
DAS-HAS-DVB-IV	5.92	0.76	1.3	0.195	18.0

**Table 2** Influence of diluent composition on the porous structure of the DAS-HAS-DVB-I polymers

Diluent composition (relative volume ratio of chlorobenzene to decan-1-ol)	Specific surface area S, (m <sup>2</sup> /g)	Pore volume V, (cm <sup>3</sup> /g)
10:0	120	0.41
9:1	196	0.56
8:2	194	0.58
7:3	163	0.47
6:4	103	0.33
5:5	71	0.22

The obtained copolymers (DAS-co-HAS-co-DVB) in the shape of beads were washed with hot water and then acetone and methanol in a Soxhlet apparatus. Detailed recipes are given in Table 1.

For the chosen molar ratio of monomers (DAS-HAS-DVB-I) a series of copolymers with increasing amounts of decan-1-ol in a mixture with chlorobenzene was obtained.

Details of the composition of the reaction mixtures are presented in Table 2.

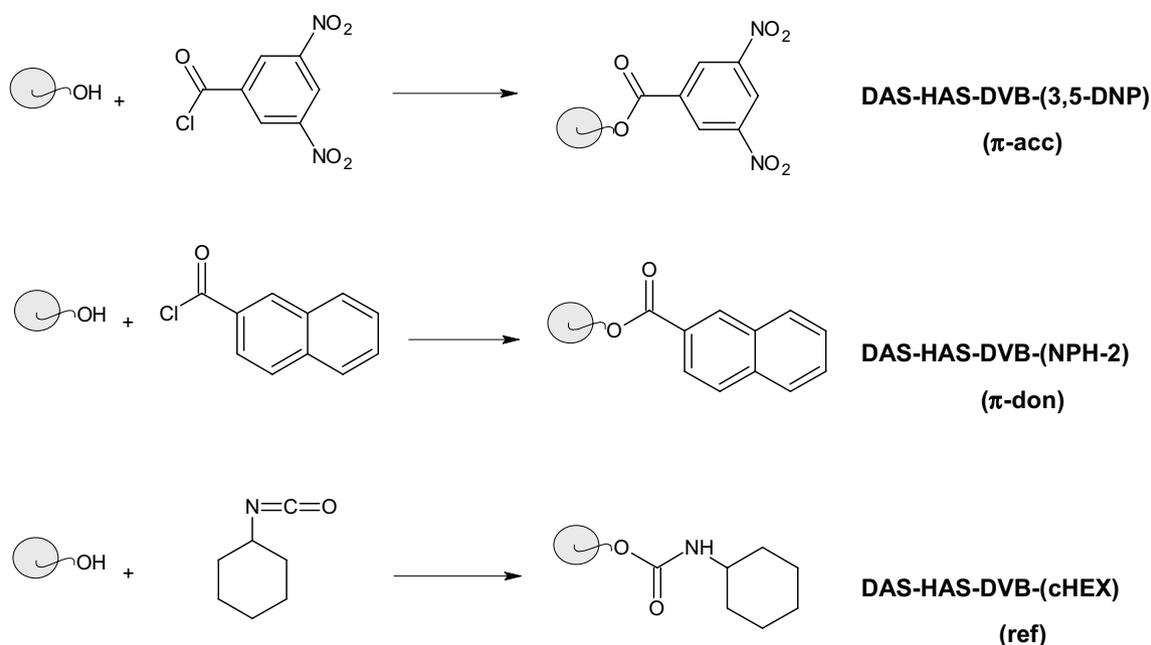
## 2.4 Chemical modification of the DAS-HAS-DVB-I polymers

For chemical modification the polymer DAS-HAS-DVB-I was chosen. In the chemical modification 3,5-dinitrobenzoyl chloride (induction of  $\pi$ -acceptor group), 2-naphthoyl chloride (induction of  $\pi$ -donor group), and cyclohexyl isocyanate (induction of nonpolar, reference group) were used. The reactions were controlled by FTIR and elemental analyses. The chemical structures of the modified copolymers are presented in Fig. 2.

## 2.5 Characterization of porous structure

Characterization of porous structure was performed using inverse size-exclusion chromatography (ISEC) and nitrogen adsorption–desorption measurements. In a dry state such parameters as specific surface areas, pore volumes, pore size distributions were determined by the method of nitrogen adsorption. These determinations were made using an adsorption analyzer ASAP 2405 (Micrometrics Inc., USA). The specific surface area in this method was calculated by the BET method, assuming that the area of a single nitrogen molecule is 16.2 Å<sup>2</sup>.

In a swollen state the beads were characterized by the inverse size-exclusion chromatography technique introduced by Halász and Martin (1975). The main assumption in this

**Fig. 2** Chemical structures of modified DAS-HAS-DVB copolymers

method is that in the good solvent chains of macromolecules form coils of a diameter corresponding to the polymer molecular weights. The diameter of the probe molecules ( $\Phi$ , in Å) was calculated from equation (Halász and Martin 1978):

$$\Phi = 0.63M_w^{0.59}$$

where  $M_w$  is the gram-molecular weight of the probe.

The diameter of the probe molecule is associated with a pore diameter ( $\Phi$ ) which corresponds to the smallest pore allowing unhindered access for the probe of a given molecular weight.

As the pore-size probes, toluene, alkylphenones, phthalates, and polystyrenes were used (Nevejans and Verzele 1985; Gawdzik 1991; Grochowicz et al. 2008).

The cumulative pore size distribution was determined from the plot  $1 - K_0(EC)$  versus  $\log\Phi$ , where  $K_0(EC)$  is the distribution constant in exclusion chromatography calculated from equation (Halász and Martin 1978):

$$K_0(EC) = \frac{V_R - V_0}{V_P} = \frac{V_R - V_0}{V_i - V_0}$$

where  $V_R$ —the retention volume of the probe,  $V_0$ —the interstitial volume equal to the retention volume of a totally excluded molecule,  $V_i$ —the retention volume of a totally included molecule;  $V_P$ —the pore volume (calculated as  $V_i - V_0$ ).

Retention volumes of the ISEC probes were determined with a Hewlett–Packard HP-1050 liquid chromatograph equipped with a diode array UV detector, a Rheodyne 7125 injection valve with 20  $\mu$ L sample loop and columns packed with the copolymers described above. Each substance was injected separately as a 0.1% solution in tetrahydrofuran (THF). The columns were thermostated at 30 °C. In the ISEC measurements THF was the mobile phase. The eluent flow-rate was 0.5 mL min<sup>-1</sup>.

## 2.6 Swellability coefficients

Swellability coefficients,  $B$ , were determined by equilibrium swelling in acetone, methanol, hexane, methyl benzoate, and trichloroethylene, using the centrifugation method.  $B$  is calculated as (Tuncel and Pişkin 1996; Podkościelna et al. 2009):

$$B = \frac{V_s - V_d}{V_d} \times 100\%$$

where  $V_s$  is the volume of the copolymer after swelling while  $V_d$  is the volume of the dry copolymer.

## 2.7 Selectivity studies

In selectivity studies, mixture containing acetylsalicylic acid ( $\pi$ -acceptor), diazepam ( $\pi$ -donor) and toluene (no specific interaction) proposed by Jost et al. (1990) and Németh et al.

(2007) to characterize HPLC solid phases particularly for toxicological screening was used.

4 empty, glass columns used in the SPE technique were filled with one of the tested copolymers (200 mg). The obtained polymer beds were conditioned with 10 mL of methanol using a vacuum manifold and water aspirator, then 5 mL of water (Milli-Q) were added to prepare surface of the sorbents for adsorption.

Stock standard solutions were prepared by weighing suitable amount acetylsalicylic acid (ASA), diazepam (DZP) and toluene (TOL) and dissolving them in methanol. A standard methanolic solution contained 100  $\mu$ g/mL of ASA and TOL and 50  $\mu$ g/mL of DIA (Gawdzik 1992). Water samples of test compounds were prepared from methanolic stock standard solution by dilution to 2  $\mu$ g/mL (for DIA 1  $\mu$ g/mL) with Milli-Q water.

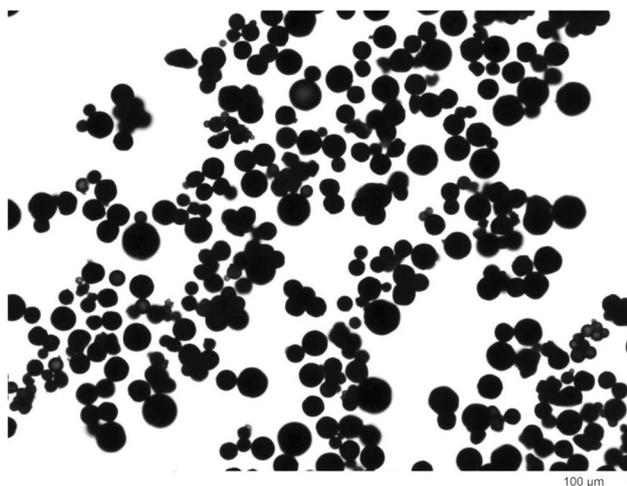
Different volumes of water samples were sucked through the column containing copolymer bed connected by PTFE tubing (Chrompack, Middelburg, Netherlands) to the water aspirator. After the sample had passed through the column, the vacuum was maintained for 5 min in order to dry the copolymer bed. The analyte compounds were then eluted with three 500  $\mu$ L aliquots of methanol. After all the compounds had eluted from the column, each sample was diluted with methanol to 2 mL or to a multiple of this volume. Sorbent regeneration was carried out using 10 mL of methanol and 5 mL of doubly distilled water.

In order to determine the recoveries of the test compounds, 20  $\mu$ L of preconcentrated solutions were injected into Hewlett–Packard HP-1050 liquid chromatograph. The same volume of standard solution (20  $\mu$ g/mL) was also injected under the same conditions.

The percentage recovery of the studied compounds was calculated from a comparison of peak areas. Recoveries were calculated as mean values of three analyses.

## 3 Results and discussion

For preparation of polymers in the form of microspheres acrylate derivatives of diphenyl sulfone (DAS and HAS) and divinylbenzene (DVB) were used. The list of synthesized polymers DAS-HAS-DVB is presented in Table 1. In all cases porous polymers with regular spherical shapes were obtained (Photo 1). In Table 3 the results of their porous structure characterization obtained from nitrogen adsorption method are shown. These polymeric microspheres have an additional good feature. They contain hydroxyl groups in their chemical structure which can be applied for different modifications. As the polymer DAS-HAS-DVB-I has the largest concentrations of hydroxyl groups it was chosen for further modifications. In additional experiments the effect of decan-1-ol content in the diluent composition



**Photo 1** Microscopic image of starting DAS-HAS-DVB-I polymer

**Table 3** Characterization of the porous structure of the studied polymers

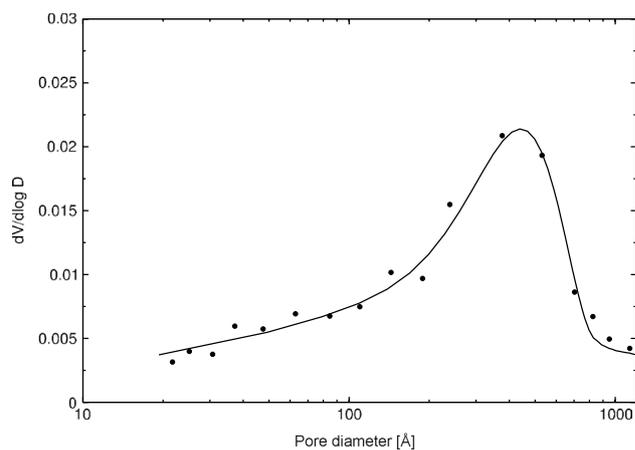
Polymer	Specific surface area $S$ , ( $\text{m}^2/\text{g}$ )	Pore volume $V$ , ( $\text{cm}^3/\text{g}$ )
DAS-HAS-DVB-I	120	0.41
DAS-HAS-DVB-II	140	0.55
DAS-HAS-DVB-III	160	0.58
DAS-HAS-DVB-IV	180	0.66

was investigated. The results show that the introduction of decan-1-ol increases the specific surface area of the copolymer, while increasing its content in the diluent composition reduces the specific surface area of the products obtained (Table 2). For further research, DAS-HAS-DVB-I was chosen which differs from the others only by the relative molar ratio of the comonomers (while maintaining the diluent composition).

Pore size distribution (PSD) obtained from the results of nitrogen adsorption/desorption method for DAS-HAS-DVB-I as typical PSD for all DAS-HAS-DVB copolymers was presented in Fig. 3.

The aim of chemical modifications was to obtain packing materials for HPLC which are capable of  $\pi$ - $\pi$  interactions. Before their use as packing materials their porous structures were studied in detail. As the packing in the HPLC column has a contact with organic solvents, its porous structure under such conditions (swollen state) should be known. For this reason besides nitrogen adsorption method also inverse exclusion chromatography (ISEC) measurements were made.

Obtained results for modified and unmodified (initial) polymers are collected in Table 4.



**Fig. 3** Pore size distribution of the DAS-HAS-DVB-I polymer obtained by low-temperature nitrogen adsorption/desorption method

Table 5 presents the results of selected parameters characterizing the porous structure of the copolymers studied, obtained by two methods, i.e. low-temperature nitrogen adsorption (copolymer in the dry state) and ISEC (copolymer in the swollen state).

Analyzing the results obtained for the dry sample, it can be concluded that the modification of the chemical structure of the copolymers does not significantly affect the porous structure—the values of the parameters characterizing the surface, pore volume and the most probable diameter remain almost unchanged. The use of ISEC (swollen sample) made it possible to determine the volume of micropores, while the technique of low temperature adsorption and nitrogen desorption did not confirm their existence.

All polymers, in swollen state, contain micropores in their internal structure. The determined volume of micropores varies within a wide range, depending on the type of modification of the structure of the initial copolymer and is the largest for DAS-HAS-DVB-(3,5-DNP), whereas the smallest for DAS-HAS-DVB-(cHEX). The probable differences result from the ability of the functionalized surface of copolymers to interact with THF molecules.

For all copolymers studied pore size distributions obtained from the data of nitrogen adsorption/desorption and ISEC methods are similar. As an example, Fig. 4 shows the results obtained for DAS-HAS-DVB-(3,5-DNP). The pore size distributions obtained with both mentioned methods indicate the presence of macropores with similar diameter in the structure of the analyzed copolymers, while the micropores are visible only when using ISEC.

Values of swellability coefficients (Table 6) deliver information about changes of chemical nature of the studied copolymer samples. Depending on the type of organic solvent used, these values varies from 6% for the copolymer with 3,5-dinitrophenyl groups (in hexane) to 30% for

**Table 4** Diameters ( $\Phi$ ) and retention volumes of the probes on the studied copolymers measured by ISEC technique

No. probe	Molecular weight M (g/mol)	$\phi$ (Å)	Retention volumes $V_R$ (mL)			
			DAS-HAS-DVB-I	DAS-HAS-DVB-(3,5-DNP)	DAS-HAS-DVB-(NPH-2)	DAS-HAS-DVB-(cHEX)
1. Toluene	92	9.1	1.044	1.097	1.113	1.009
2. Acetophenone	120	10.6	1.005	1.110	1.058	1.100
3. Butyrophenone	148	12.0	1.006	1.106	1.061	1.093
4. Dimethyl phthalate	194	14.1	1.006	1.107	1.053	1.090
5. Diethyl phthalate	222	15.3	1.005	1.089	1.019	1.082
6. Dipropyl phthalate	250	16.3	1.005	1.070	1.005	1.064
7. Dibutyl phthalate	278	17.4	1.005	1.069	0.996	1.057
8. Dipentyl phthalate	306	18.5	1.004	1.035	0.983	1.055
9. Dioctyl phthalate	390	21.3	1.004	1.030	0.974	1.040
10. Dinonyl phthalate	418	22.2	1.039	1.027	0.970	1.037
11. Dilauryl phthalate	502	24.7	1.038	1.021	0.960	1.028
12. Polystyrene	580	26.9	1.016	1.013	0.958	1.031
13. Polystyrene	2450	62.9	0.978	0.998	0.933	1.017
14. Polystyrene	5100	97.0	0.920	0.976	0.938	0.992
15. Polystyrene	11,600	157.5	0.888	0.967	0.936	0.965
16. Polystyrene	30,300	277.6	0.835	0.911	0.912	0.911
17. Polystyrene	68,000	447.2	0.795	0.846	0.846	0.853
18. Polystyrene	120,000	625.3	0.746	0.781	0.786	0.799
19. Polystyrene	390,000	1253.3	0.695	0.715	0.726	0.734
20. Polystyrene	750,000	1843.4	0.640	0.680	0.690	0.687
21. Polystyrene	1,260,000	2503.6	0.640	0.650	0.644	0.687
22. Polystyrene	2,750,000	3967.8	0.640	0.650	0.624	0.687
23. Polystyrene	3,840,000	4831.7	0.640	0.650	0.624	0.687

**Table 5** Porous structure of chemically modified copolymers

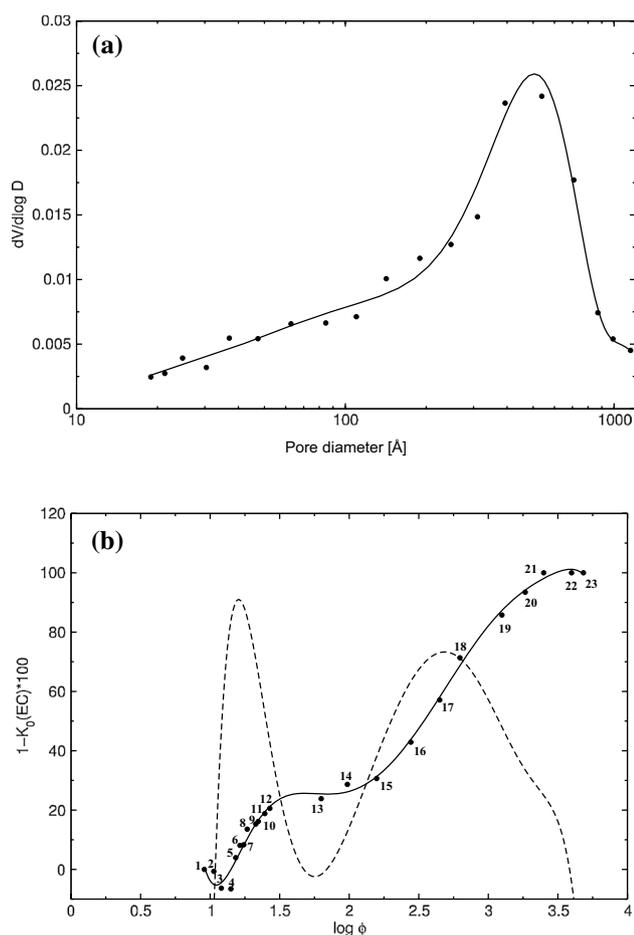
Porous structure	DAS-HAS-DVB-I		DAS-HAS-DVB-(3,5-DNP)		DAS-HAS-DVB-(NPH-2)		DAS-HAS-DVB-(cHEX)	
	BET	ISEC	BET	ISEC	BET	ISEC	BET	ISEC
Specific surface area ( $\text{m}^2\text{g}^{-1}$ )	120	NA	116	NA	122	NA	121	NA
Pore volume (mL/g)	0.40	0.47	0.49	0.54	0.45	0.53	0.41	0.47
Volume of micropores (mL/g)	–	0.049	–	0.205	–	0.114	–	0.042

NA not applicable

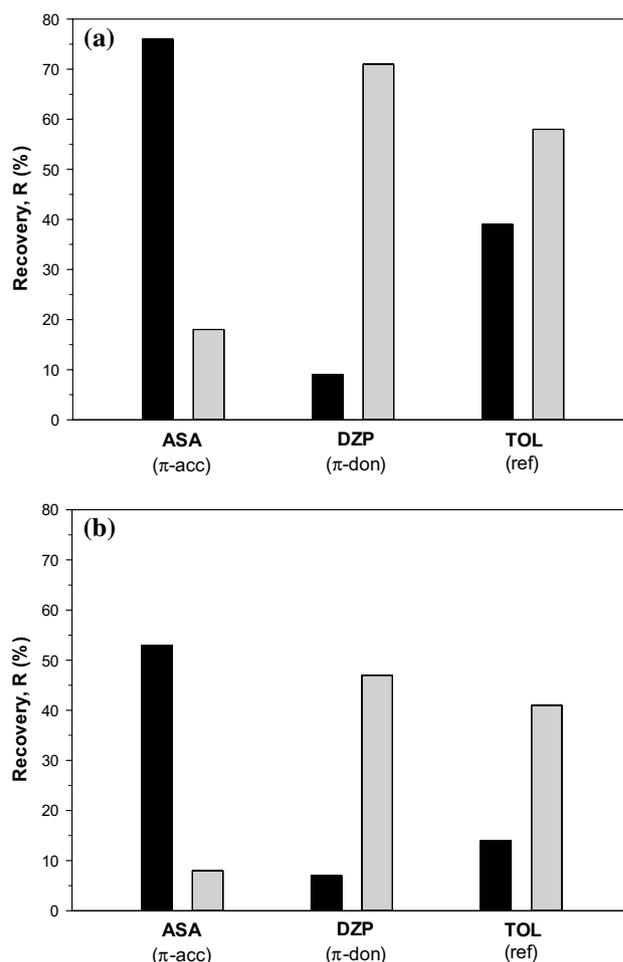
that with 2-naphthyl groups (in acetone). DAS-HAS-DVB-(3,5-DNP) as a material with  $\pi$ -acceptor character indicates the most swelling in trichloroethylene, representing  $\pi$ -donor compounds while that DAS-HAS-DVB-(NPH-2) with  $\pi$ -donor nature swells the most in methyl benzoate and acetone, i.e. compounds belong to the group of  $\pi$ -acceptor properties (Zhu et al. 2004). DAS-HAS-DVB-(cHEX) swells most in non-polar hexane. It should be taken into account that tendency to swell is a result of solvents interactions with complicated net of the copolymers. For solvents not only pendant groups are available but also acrylate and sulfone functional groups existing in their structure, for this reason also the unmodified copolymer DAS-HAS-DVB-I swells to

varying degrees depending on the  $\pi$ -(donor/acceptor) properties of the organic solvent used.

Swelling confirms the existence of  $\pi$ - $\pi$  interactions between the studied polymeric materials and solvents. These results suggest that the synthesized microspheres can be used as specific sorbents. The sorption properties of these materials were examined using the SPE method. Recoveries of test compounds determined for 100 and 400 mL samples are presented in Fig. 5. For copolymer with  $\pi$ -donor nature i.e. DAS-HAS-DVB-(NPH-2), the highest recovery (76%) was determined for ASA representing  $\pi$ -acceptor compounds. In the case of DAS-HAS-DVB-(3,5-DNP) the highest recovery achieved



**Fig. 4** Pore size distribution of the DAS-HAS-DVB-(3,5-DNP) polymer obtained by low-temperature nitrogen adsorption/desorption (a) and ISEC (b) methods. Numbers on cumulative curve refers to probenances included in Table 6



**Fig. 5** Recoveries of test mixture containing acetylsalicylic acid (ASA,  $\pi$ -acceptor), diazepam (DZP,  $\pi$ -donor) and toluene (TOL, non-specific interaction) for 100 ml (a) and 400 ml (b) of sample volume on copolymer modified with 2-naphthyl groups (black,  $\pi$ -donor) or 3,5-dinitrophenyl groups (gray,  $\pi$ -acceptor)

**Table 6** Swellability coefficients of the studied copolymers

Solvent	Swellability coefficients, B (%)			
	DAS-HAS-DVB-I	DAS-HAS-DVB-(3,5-DNP)	DAS-HAS-DVB-(NPH-2)	DAS-HAS-DVB-(cHEX)
Acetone	24	20	30	24
Methanol	22	13	19	22
Trichloroethylene	12	24	9	12
Methyl benzoate	15	10	30	15
Hexane	15	6	10	30

DZP (71%) (compound with  $\pi$ -donor properties). As far as toluene recovery is concerned, one can see that they are larger on an  $\pi$ -acceptor copolymer, reaching 57 and 40% respectively for 100 and 400 mL samples. For the

DAS-HAS-DVB-(NPH-2)  $\pi$ -donor polymer, toluene recovery changes in the range of 36% for 100 mL and 15% for 400 mL sample volume. Its recoveries indicate that the choice of toluene as a compound without specific interaction was not entirely successful.

Recoveries of ASA and DZP on copolymer beds exhibiting the same  $\pi$ - (donor / acceptor) properties as the molecules of a given analyte are clearly lower. It means that acetylsalicylic acid shows a greater affinity towards the polymeric sorbent with 2-naphthyl groups, whereas diazepam towards polymer with 3,5-dinitrophenyl groups. Differences in  $\pi$ - $\pi$  interactions between analyte molecules and sorbent surface are responsible for observed copolymer selectivity.

Selectivity for DAS-HAS-DVB-(3,5-DNP) and DAS-HAS-DVB-(NPH-2) visible for 100 mL the test substance standard solution (Fig. 5a) is also maintained for larger volumes of this solution (Fig. 5b).

## 4 Conclusions

Acrylate derivatives of diphenyl sulfone and divinylbenzene are used for preparation of parent copolymers in the form of microspheres. Porous structures of the obtained copolymers were studied. Copolymer which contains hydroxyl functional groups in its structures and simultaneously has the most regular porous structure was used for chemical modifications. During this process polymeric packings with 3,5-dinitrophenyl ( $\pi$ -acceptor), 2-naphthyl ( $\pi$ -donor), and cyclohexyl (which has no-specific polar interactions) pendant groups were obtained. Studies of their porous structures suggest that chemical modification has influence not only on their chemical character but also on their internal structures.

These results suggest that the synthesized microspheres can be used as specific sorbents. Materials with 3,5-dinitrophenyl and 2-naphthyl groups exploiting  $\pi$ - $\pi$  interactions in sorption process are promising sorbents for the sorption of organic contamination of different chemical nature from water. The phenomenon will be much more pronounced in HPLC, when the studied copolymers are used as stationary phases for the separation of analytes with different  $\pi$ - (donor / acceptor) properties.

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