

Synthesis and characterization of modified methacrylate  
polymeric packing based on bisphenol-s  
for chromatography

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Synthesis and properties of modified porous polymeric packings for high performance liquid chromatography (HPLC) are presented. As modifiers of the OH groups present in the polymeric matrix,  $\pi$ -donor (2-naphthoic acid chloride),  $\pi$ -acceptor (3,5-dinitrobenzoic acid chloride), and cyclohexyl isocyanate which indicates any polar interactions, are used.

Chemical structure of these packings are confirmed by elemental analysis, FTIR and rentgenography. Additionally, porous structure, thermal resistance, and swelling propensities of polymers are presented.

## 1. INTRODUCTION

In the previous paper synthesis and properties of porous polymeric packings for chromatography based on bisphenol-S and methacrylic acids were described [1].

Monodisperse polymer grains were obtained by means of suspension-emulsion polymerization of the dispersed monomers: di(p-methacrylphenyl)sulfone, (p-hydroxy-phenyl-p-methacrylphenyl)sulfone, and divinylbenzene [AcSP-Polym.-OH] in the presence of pore-forming diluent. In the studies of chromatographic properties of the obtained porous polymers, retention mechanism was taken into account [2].

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It is generally assumed that the retention mechanism on porous polymers is affected by the crosslinking degree and chemical composition of a copolymer [3].

The crosslinking degree is responsible for thermal and mechanical properties and also determines the packing internal structure. High functionality of monomers taking part in polymerization guarantees a high degree of crosslinking. In the case of monomers used by us suspended reactive hydroxyl group in the copolymer matrix provide possibility for chemical modification of its surface.

Chemical structure of chromatographic packing is responsible for selectivity of polymer packing owing to various interactions at the stationary phase – solute interface.

Though there are many reports in literature concerning the interactions: hydrophilic, electrostatic, spherical, hydrogen bonds, dipole-dipole and aromatic  $\pi$ - $\pi$ -, a little information about the last one is found in chromatography [4].

This type of interactions can be defined as the interaction between  $\pi$ -electrons of the chromatographic material and those of the solute species [5,6]. An interaction between  $\pi$ -electron containing compounds is favoured when one of the compounds (e.g. the stationary phase) is electron – rich and the other is electron – poor (e.g. the solute) and vice versa [5,7,8]. In these systems the stationary phase can act as a donor (soft Lewis base), while the solute can act as a recipient (soft Lewis acid) of electrons [9].

To estimate the contribution of aromatic – aromatic ( $\pi$ - $\pi$ ) interactions to the overall retention behaviour, it is important to measure the strength of this type of interactions.

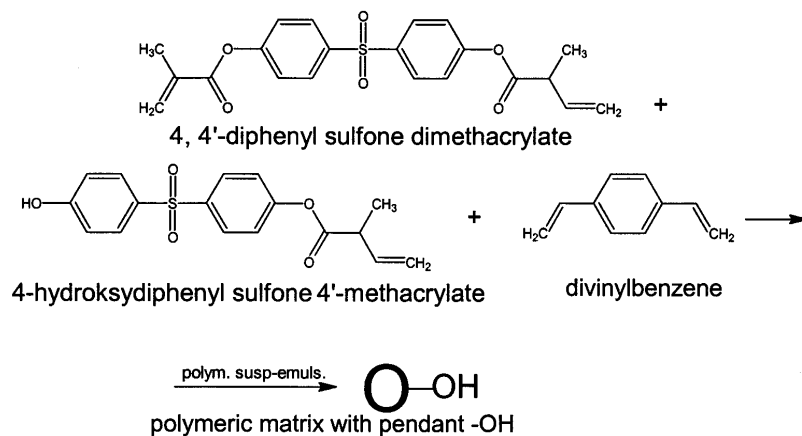
This article presents the synthesis and main properties of these type of chromatographic packings prepared in our laboratory.

Syntheses of the packings modified by cyclohexyl isocyanate, 3,5-dinitrobenzoic acid chloride, and 2-naphthoic acid chloride respectively, are presented in Scheme 1.

## 2. EXPERIMENTAL

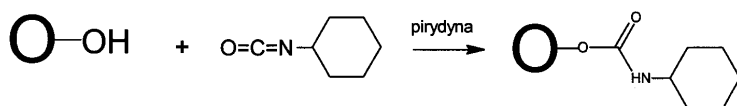
**Materials.** 3,5-Dinitrobenzoic acid chloride was prepared according to the procedure by Rainford [10] whereas 2-naphthoic acid chloride by Browns [11]. Dichloromethane (POCh, Gliwice) was distilled from calcium chloride. Cyclohexyl isocyanate and triethylamine (Fluka, Buchs) were reagent grade purity. Acetone, hexane, methanol and pyridine reagent grade were from POCh, Gliwice.

### A. Synthesis of polymeric matrix AcSP-Polym.M-OH

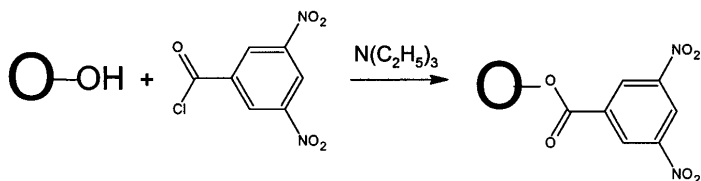


### B. Synthesis of modified matrix AcSP-Polym.M-OH

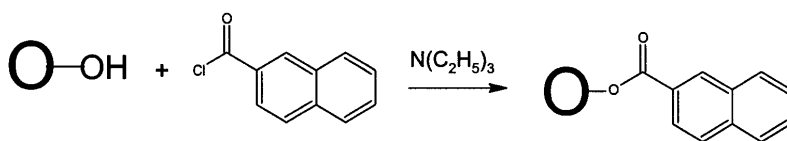
#### a) Synthesis of modified packing AcSP-Polym.M-CH



#### b) Synthesis of modified packing AcSP-Polym.M-DNB



#### c) Synthesis of modified packing AcSP-Polym.M-NAP



Scheme 1.

**Synthesis of Modified Stationary Phases.**

*4,4'-Diphenyl sulfone dimethacrylate, 4-hydroxydiphenyl sulfone 4'-methacrylate – divinylbenzene [AcSP-Polym.M.-OH].* Synthesis of polymeric matrix [AcSP-Polym.M.-OH] with pendant –OH groups was described by us previously [1].

*Modification of AcSP-Polym.M.-OH with Cyclohexyl Isocyanate [AcSP-Polym.M.-CH].* To a suspension containing 5 g AcSP-Polym.M.-OH (7.5 mmol –OH groups), in 80 mL of hexane, 2 drops of pyridine and 1.19 mL (10 mmol) of cyclohexyl isocyanate were added. The mixture was refluxed while stirring for 3 hrs.

The modified beads of copolymer [AcSP-Polym.M.-CH] were collected by filtration and washed with water (200 mL), methanol (200 mL) and acetone (200 mL). Finally, they were dried in vacuum oven at room temperature. The elemental analysis found 0.99% N.

*Modification of AcSP-Polym.M.-OH with 3,5-Dinitrobenzoic Acid Chloride [AcSP-Polym.M.-DNB].* To a suspension containing 5 g AcSP-Polym.M.-OH (7.5 mmol –OH groups) and 1.01 g (10 mmol) triethylamine in 30 mL dichloromethane cooled to 0°C, solution of 2.3 g (10 mmol) 3,5-dinitrobenzoic acid chloride in 15 mL of dichloromethane was added. The mixture was stirred at this temperature for 0.5 h and at room temperature for 1 h. The modified material AcSP-Polym.M.-DNB was collected by filtration, washed with water (500 mL), acetone (200 mL), methanol (200 mL) and finally dried in vacuum at room temperature. The elemental analysis found 1.7 % N.

*Modification of AcSP-Polym.M.-OH with 2-Naphthoic Acid Chloride [AcSP-Polym.M.-NAP].* Modification reaction of AcSP-Polym.M.-OH polymeric matrix with 2-naphthoic acid chloride was performed in the same way as the reaction with dinitrobenzoic acid chloride. In this case dinitrobenzoic acid chloride was replaced by 1.83 g (10 mmol) of 2-naphthoic acid chloride. The modified packing AcSP-Polym.M.-NAP was collected by filtration, washed with water (700 mL), acetone (300 mL), methanol (300 mL) and dried in vacuum at room temperature.

**Measurements.** The Fourier transform infrared spectra (FTIR) of modified packings were run on a Perkin-Elmer model 1725 using KBr pallets.

Characterization of porous structure was made by means of an adsorption analyzer ASAP 2405 N (Micrometrics Inc., USA). Determinations were based on the measurements of adsorption of nitrogen on the surface of the studied sample while cooling it to liquid nitrogen.

Thermograms were run on Paulik, Paulik and Erdey derivatograph (MOM, Budapest, Hungary).

The beads were imaged using LEO 1430 VP numerical scanning electron microscope with the counter shaft and the detector EDX.

### 3. RESULTS AND DISCUSSION

Syntheses of the packings modified by 3,5-dinitrobenzoic acid chloride, 2-naphthoic acid chloride, and cyclohexyl isocyanate are shown in Scheme 1.

The yield of all processes is high. The contents of –OH groups in polymeric matrix is 1.48 mmol/g.

The results from elemental analyses confirm that the modified polymeric beads AcSP-Polym.M.-DNB contain 1.44 mmol/g of dinitrophenyl moiety while AcSP-Polym.M.-CH 1.40 mmol/g of cyclohexylamine moiety.

**Infrared Spectroscopy.** Infrared spectroscopy is the most widely used technique for the chemical reactions performed on the crosslinked polymers and also for identification of the products structure.

In FTIR spectrum of the polymeric matrix AcSP-Polym.M.-OH C-H stretching vibrations of aromatic ring backbone methylene and methyl groups are observed at 3103, 3072, 2984, 2910  $\text{cm}^{-1}$ . The ester carbonyl group gave a sharp band at 1754  $\text{cm}^{-1}$ . The aromatic skeletal absorption is observed at 1590  $\text{cm}^{-1}$ . The bending vibration of methyl groups is visible at 1491  $\text{cm}^{-1}$ . The –SO<sub>2</sub> groups gave intensive absorption bands at 1115 and 1297  $\text{cm}^{-1}$ . FTIR spectrum of AcSP-Polym.M.-DNB shows additionally bands at 1548  $\text{cm}^{-1}$  characteristic for asymmetric vibration and 1345  $\text{cm}^{-1}$  symmetric vibrations of the bond C-NO<sub>2</sub>. In the spectrum of AcSP-Polym.M.-NAP additional absorption bands at 775 and 760  $\text{cm}^{-1}$  characteristic for naphthalene ring are visible.

**Porous Structure Characterization.** The specific surface areas, pore volume, and mean diameters for the polymeric matrix [AcSP-Polym.M.-OH] and the modified packings AcSP-Polym.M.-CH, AcSP-Polym.M.-DNB, and AcSP-Polym.M.-NAP are presented in Table 1. The specific surface area  $S_{\text{BET}}$  was calculated according to the standard method by Brunauer, Emmett and Teller (BET [12]. The pore distribution was calculated from the desorption data using the method by Barrett, Ioyner and Halenda (BIH) [13].

Tab. 1. Characterization of the porous structure of polymeric matrix AcSP-Polym.M.-OH and modified phase AcSP-Polym.M.-CH, AcSP-Polym.M.-DNB and AcSP-Polym.M.-NAP.

Polymeric phase	Specific Surface Area [m <sup>2</sup> /g]	Pore Volume [cm <sup>3</sup> /g]	Mean Pore Diameter [Å]
AcSP-Polym.M.-OH	135	0.37	55
AcSP-Polym.M.-CH	116	0.32	55
AcSP-Polym.M.-DNB	123	0.39	62
AcSP-Polym.M.-NAP	116	0.31	53

Figure 1 for example presents the pore volume distribution versus their radii for the modified AcSP-Polym.M.-NAP. As follows from the curve and the data in Table 1, specific surface and pore volume of modified packings are insignificantly smaller than those of the matrix. Pore diameters are nearly the same. Figure 2 presents exemplary low-temperature isotherm of nitrogen adsorption/desorption for AcSP-Polym.M.-NAP.

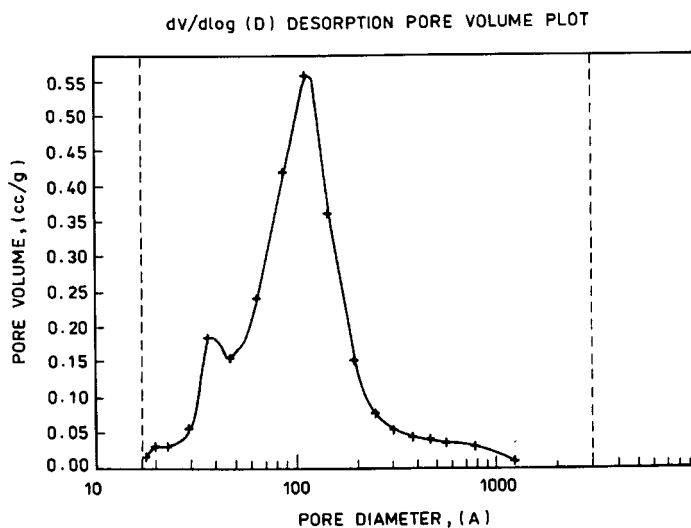


Fig. 1. Pore volume distribution versus their radii for the AcSP-Polym.M.-NAP

Based on the generally accepted classification of adsorbents [14], the isotherms obtained for modified packings can be considered as the isotherms of IV type. The obtained hysteresis loops are typical for mesoporous adsorbents. Such materials are promising packings for chromatographic columns.

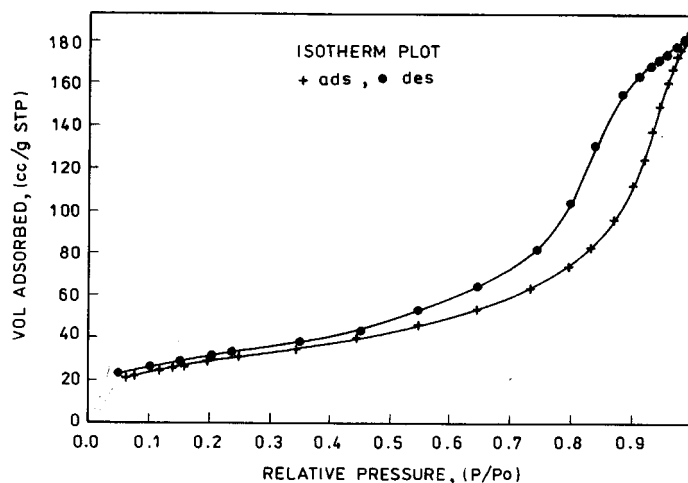


Fig. 2. The low-temperature isotherms of nitrogen adsorption/desorption for AcSP-Polym.M.-NAP

**SEM.** The scanning electron micrograph of AcSP-Polym.M.-CH, AcSP-Polym.M.-DNB, and AcSP-Polym.M.-NAP are shown in Figures 3,4,5. The particles have a perfect spherical shape and porous surface. Figures 6,7,8 present the results of quantitative and qualitative analyses of selected fragments of the packings surface obtained by rentgenographic determination. From these data (presence of O, N atoms) it appears that on the surface of beads there are pendant fragments of compounds which were used for modification.

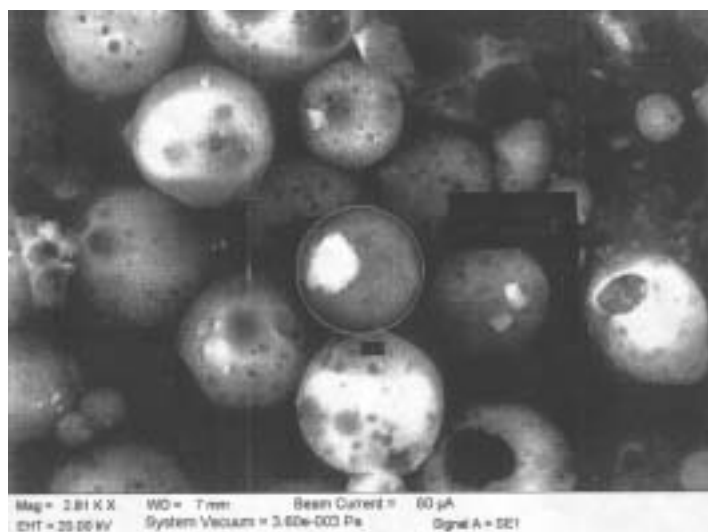
**Thermogravimetric Analysis.** The thermal behaviour of modified beads was evaluated by DTA and TGA analyses. Theromogravimetric curves for the matrix and modifier polymers are shown in Figure 9. The initial decomposition is observed at about 300°C and the final decomposition temperature are about 800°C. The thermal resistance of matrix and modified packings are similar and high.

**Swelling Studies.** Besides porous structure, chemical structure is the main parameter responsible for porous sorbent applications.

The accessibility of functional groups in the skeleton of crosslinked copolymers is associated with swelling. To investigate the swelling behaviour of the samples they wereswollen in a few solvents for 1 h. The excess of solvents was removed by centrifugal methods. The results are expressed as the weight of solvents absorbed per 1 g of dry packing and change of volume after swelling. As follows from the results in Table 2 the volume of matrix after swelling is larger than for the modified packings. The beads absorb a large amount of solvents but the increase of their volume is not higher than 30 % for

the matrix and 10-20 % for the modified materials. In heptane the volume of the polymers is rather constant.

a)



b)

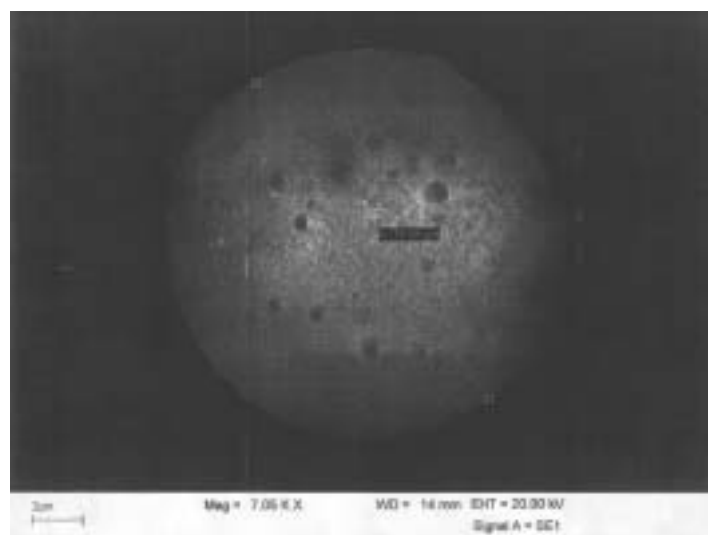
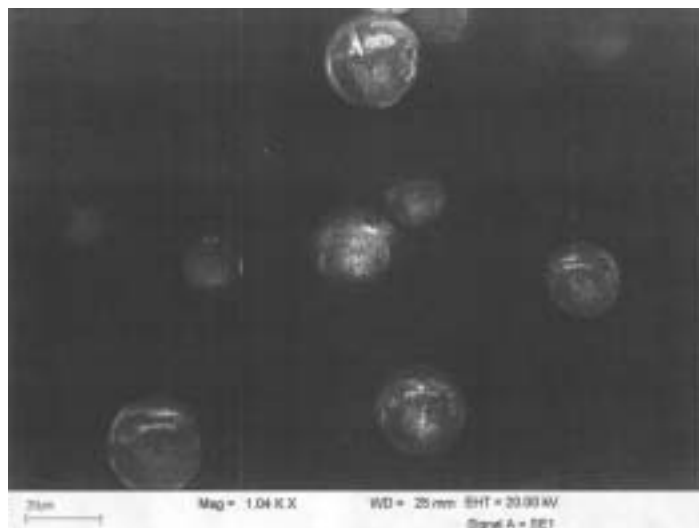


Fig. 3. Scanning electron micrographs of AcSP-Polym.M.-NAP, original magnification x 2810 (A), x 7050 (B)



a)



b)

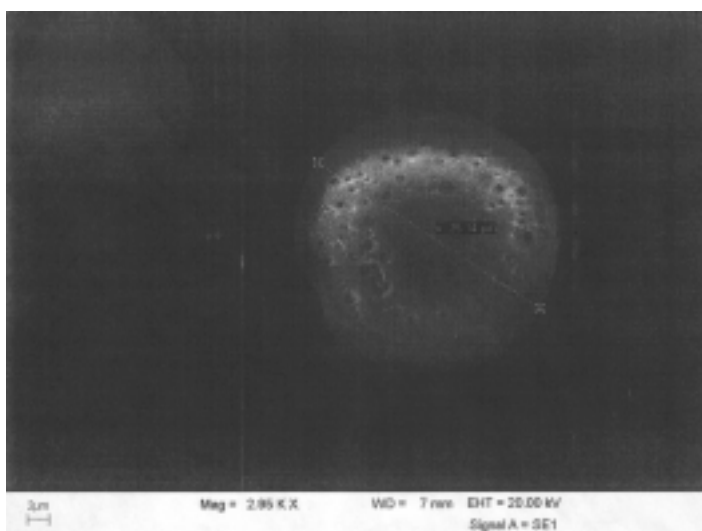
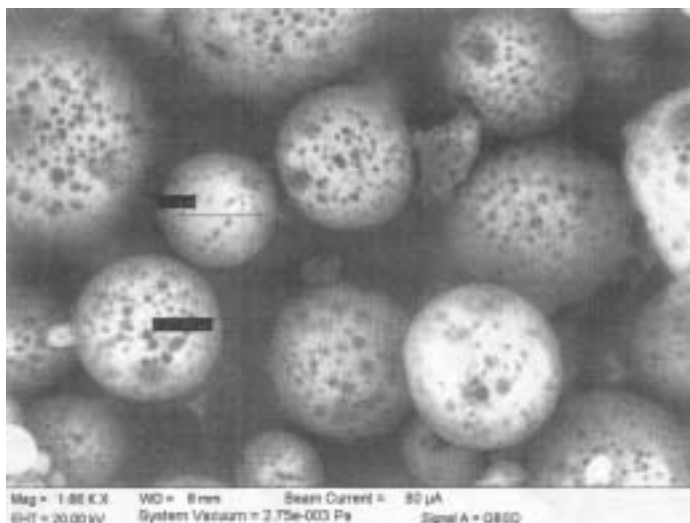


Fig. 4. Scanning electron micrographs of AcSP-Polym.M.-DNB, original magnification x 1040 (A), x 2950 (B)

a)



b)

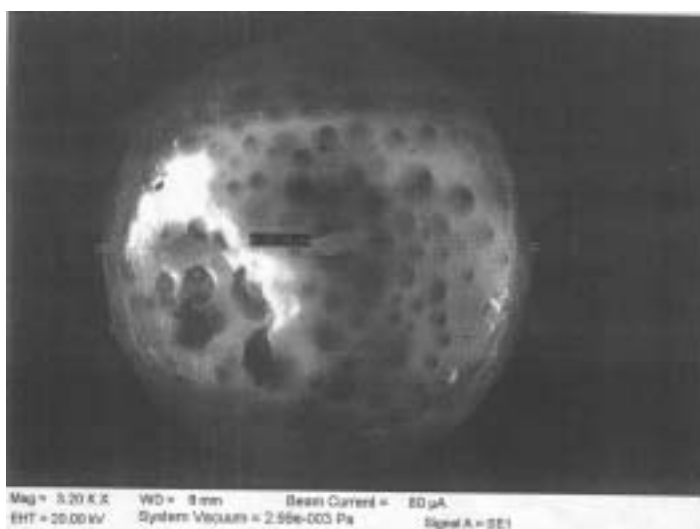


Fig. 5. Scanning electron micrographs of AcSP-Polym.M.-CH, original magnification x 1660 (A), x 3200 (B)

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RONTEC EDWIN WinTools
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*** PUzaf results ***
elem/line  P/B      B      F      c      c(atom)  confid.  h
C  K-ser  @Coat?  1.00000  1.00000  76.48    84.00    +-12.96  d
O  K-ser  @      1.00000  1.00000  15.21    12.54    +- 2.15  d
Si K-ser  @ 10.5  1.00683  1.02017   0.67     0.32     +- 0.02
S  K-ser  @140.6  1.00959  1.00956   7.63     3.14     +- 0.11
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standardless                100.00   100.00   [1s]

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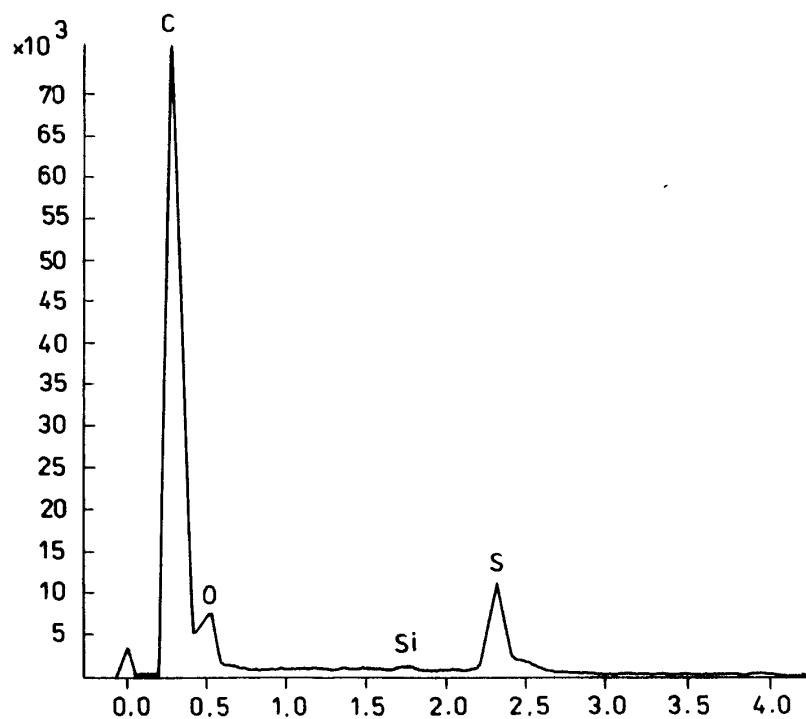


Fig. 6. Roentgenographic analysis of the selected fragment of AcSP-Polym.M.-NAP

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*** PUzaf results ***
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elem/line	P/B	B	F	c	c(atom)	confid.	h
C K-ser	@Coat?	1.00000	1.00000	52.14	60.11	+/- 9.49	d
N K-ser	@	1.00000	1.00000	20.23	20.00	+/- 3.55	d
O K-ser	@	1.00000	1.00000	18.24	15.79	+/- 2.74	d
Si K-ser	@ 10.2	1.00708	1.01982	0.68	0.33	+/- 0.02	
S K-ser	@154.5	1.00993	1.00887	8.72	3.77	+/- 0.15	
standardless				100.00	100.00	[1s]	

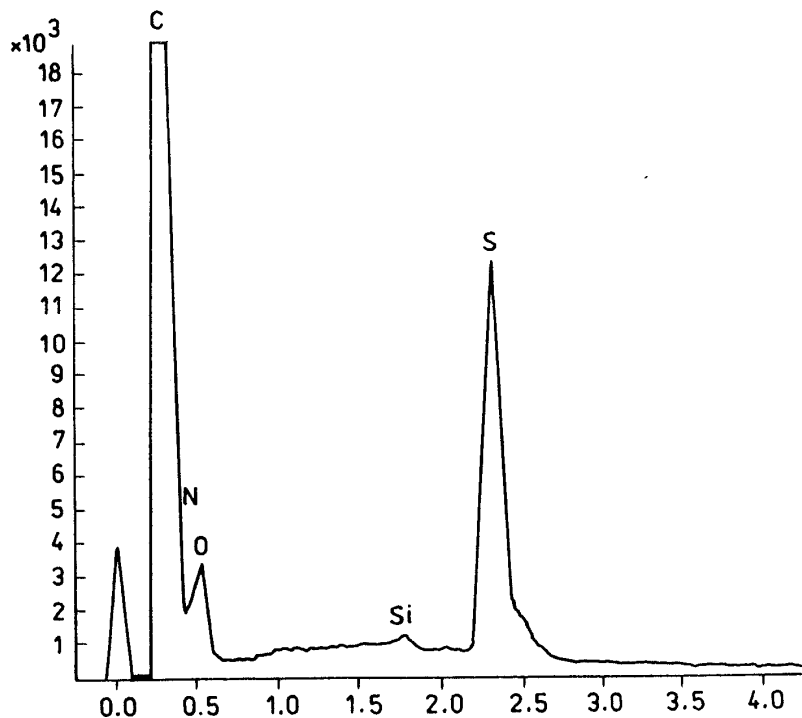


Fig. 7. Roentgenographic analysis of the selected fragment of AcSP-Polym.M.-DNB

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RONTEC EDWIN WinTools
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version: 3.1 eng           Eo:20.0 keV (TO:35.0 TI:28.0)
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*** PUzaf results ***
elem/line  P/B      B      F      c      c(atom)  confid.  h
C  K-ser  @Coat?  1.00000 1.00000  52.97    61.35  +- 9.70  d
N  K-ser  @      1.00000 1.00000  19.34    19.20  +- 3.40  d
O  K-ser  @      1.00000 1.00000  16.98    14.76  +- 2.60  d
Si K-ser  @ 9.9   1.00714 1.02188  0.66     0.33   +- 0.02
S  K-ser  @175.9 1.01002 1.00839  10.05    4.36   +- 0.16
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standardless           ,100.00   100.00   [1s]

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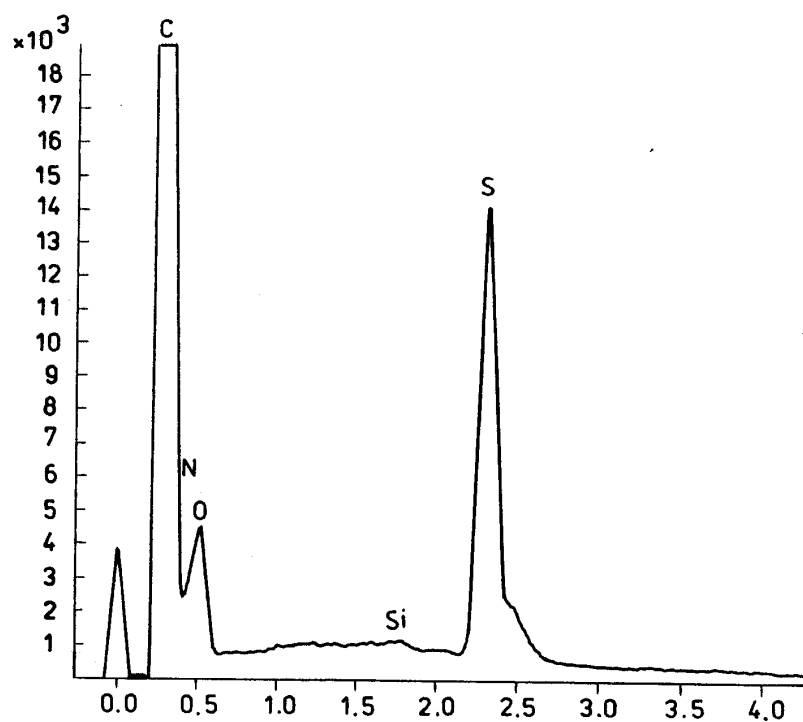


Fig. 8. Roentgenographic analysis of the selected fragment of AcSP-Polym.M.-CH

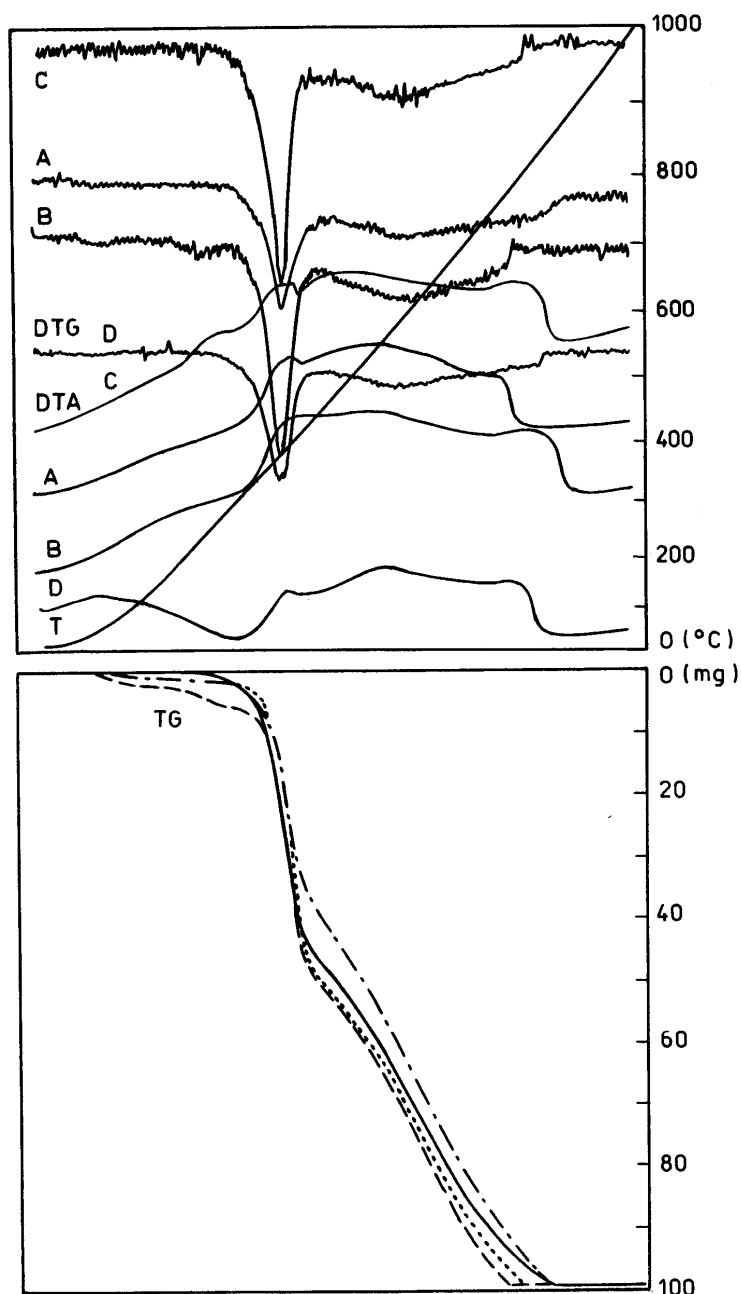


Fig. 9. Thermogravimetric analysis of (A, —) AcSP-Polym.M.-OH, (B, ----) AcSP-Polym.M.-CH, (C, -●-●-●-●) AcSP-Polym.M.-DNB, (D, ●●●●●) AcSP-Polym.M.-NAP

Tab. 2. Swelling studies of polymeric phases

Solvent Poly- meric phase		Acetone	Metha- nol	Hepta- ne	Dichloro- methane	1,4- Dioxa- ne	Isopro- panol	Trichloro - methanol
AcSP- Polym.M.-OH	m <sub>1</sub>	3.44	3.21	1.66	5.44	4.35	3.06	6.30
	V <sub>0</sub>	4.00	4.00	3.90	3.90	4.10	4.00	4.00
	V <sub>1</sub>	5.50	5.00	4.00	5.40	5.40	4.90	5.50
AcSP- Polym.M.-CH	m <sub>1</sub>	3.31	3.16	2.23	5.12	4.17	2.77	5.40
	V <sub>0</sub>	3.80	3.80	3.80	3.70	3.90	3.80	3.80
	V <sub>1</sub>	4.80	4.80	4.20	4.80	5.00	4.50	4.80
AcSP- Polym.M.- DNB	m <sub>1</sub>	2.51	4.48	2.00	4.48	3.55	2.30	4.67
	V <sub>0</sub>	3.90	4.00	3.90	4.00	3.60	3.60	3.90
	V <sub>1</sub>	4.40	4.40	4.10	4.40	4.30	3.90	4.60
AcSP- Polym.M.-NAP	m <sub>1</sub>	2.98	4.55	1.97	4.55	3.67	2.45	4.72
	V <sub>0</sub>	3.60	3.50	3.80	3.60	3.70	3.50	3.60
	V <sub>1</sub>	4.50	4.40	3.90	4.40	4.50	3.90	4.50

m<sub>1</sub> – weight of solvent absorbed per 1 g dry phase

V<sub>0</sub> – volume of 1 g of dry phase

V<sub>1</sub> – volume of 1 g of phase after swelling

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### CURRICULUM VITAE



**Barbara Gawdzik** was born in Lublin (Poland) in 1954. After receiving M. Sc. from Maria Curie-Skłodowska University in 1978 she was employed at the Department of Polymer Chemistry and Technology. She received Ph. D. in 1986 and habilitation in 1993. Since 1998 she has been employed as an associate professor in the Department of Polymer Chemistry and Technology. Research areas: synthesis of new monomers and polymers, preparation of polymeric microspheres for chromatography, porous structure investigations. She is the author and co-author of 70 original papers, over 60 published in conference materials and 10 patents.