

Characterization of Macroporous 1-Vinyl-2-pyrrolidone Copolymers Obtained by Suspension Polymerization

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ABSTRACT: Radical suspension copolymerization of 1-vinyl-2-pyrrolidone (VP) with three different cross-linkers: divinylbenzene (DVB), trimethylolpropane trimethacrylate (TRIM), and di(methacryloxymethyl) naphthalene (DMN) was used to prepare macroporous microspheres. During the copolymerization, the mixture of toluene and *n*-dodecane as a pore-forming diluent was used. All samples were characterized in terms of particle size and distribution, nitrogen content, specific surface area total pore volume, and pore size distribution. It was found that specific surface area of the obtained beads is strongly dependent on the diluent system and the type of cross-linker and

achieves value from 27 to 845 m²/g. To determine the influence of chemical structure of cross-linkers on the selectivity and polarity of the copolymers, inverse gas chromatography was applied. In addition, VP-DVB and VP-DMN copolymers were modified by sulfonation into cation-exchangers with cation exchange capacity equal 1.98 and 2.31 mmol/g, respectively. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 568–575, 2012

Key words: 1-vinyl-2-pyrrolidone; suspension polymerization; porous structure; polymeric microspheres; inverse gas chromatography

INTRODUCTION

Constant progress in technology and science creates a great demand for new materials. Due to their versatility, polymers are the most pervasive ones. Among them 1-vinyl-2-pyrrolidone (VP) holds the prominent position. It contains a highly polar amide group conferring hydrophilic and polar-attracting properties and also apolar methylene groups in the backbone and the ring, conferring hydrophobic properties. Its amphiphilic character causes that VP is mainly used for preparation of water-soluble forms of poly(vinylpyrrolidone) (PVP). Due to its nontoxicity, biocompatibility and good complexing properties for ionic or p-electron system PVP is widely used in different fields: beauty, textile and chemical industry, pharmacy, medicine. In medicine, PVP is applied as a solution substituting for plasma of blood, in the organism detoxication, for vitreous body substitutes, and as nontoxic polymeric matrices.^{1–6} Hydrogels based on poly(1-vinyl-2-pyrrolidone) have been widely used in controlled drug release materials, cell encapsulation, scaffold materials, contact lenses, burn wounds dressings, artificial cartilages or membranes, and for the encapsulation of living cells.^{7–15}

Most of the mentioned studies are focused on linear or slightly cross-linked PVP form. More cross-linked copolymers of VP and tetrafunctional monomers can be used in chromatographic analysis and fractionation of protein mixtures, as sorbents and supports for binding. However, preparation of VP-based cross-linked copolymers is difficult to carry out. This is caused by the fact that radical copolymerizations involving VP are usually characterized by low value of reactivity ratios r_{VP} . In most cases, they approximately equal zero. For example, for the pair *N*-vinyl-2-pyrrolidone/methyl methacrylate they are equal 0.01 and 4.04, whereas for *N*-vinyl-2-pyrrolidone/styrene 0.057 and 17.2, respectively.¹⁶ Hence, one can assume that VP and most available monomers and cross-linkers do not copolymerize well. In addition, there is a problem associated with preparation of VP copolymers in spherical forms. The most suitable polymerization techniques for this purpose are suspension and suspension-emulsion polymerizations.^{17–19} In these techniques, water is the continuous phase where the organic phase is dispersed. VP shows considerable solubility in water what creates additional restrictions. Consequently, preparation of cross-linked copolymers of VP in the spherical form is difficult to carry out and can be found mostly in the patent literature^{20–23} and only occasionally in scientific articles.^{24–26}

In this article, we present the synthesis of porous copolymers of VP with three different cross-linkers: divinylbenzene (DVB), trimethylolpropane trimethacrylate (TRIM), and di(methacryloxymethyl) naphthalene

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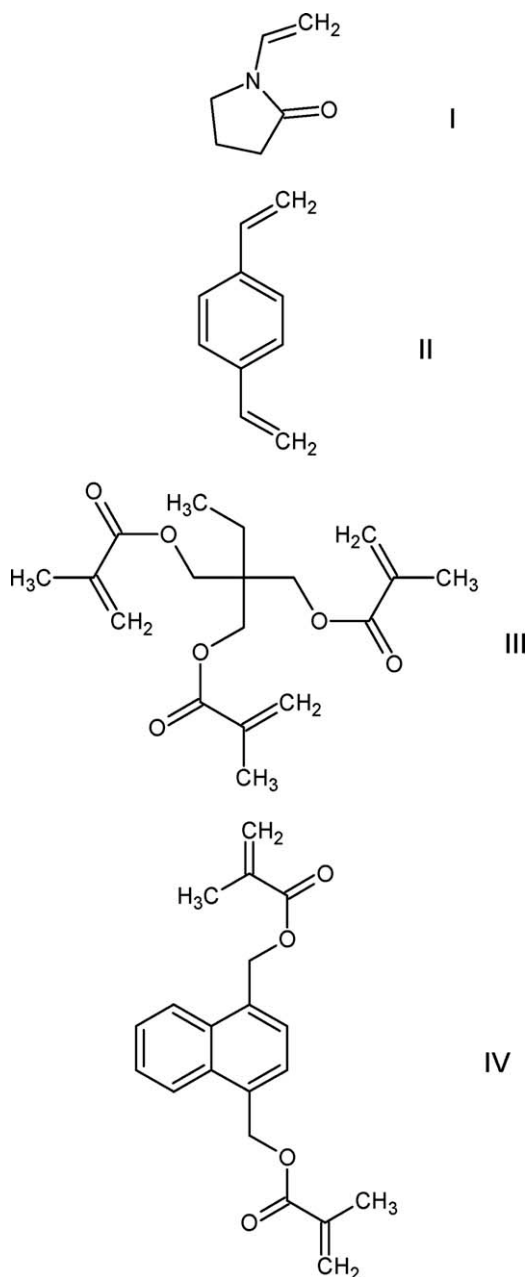


Figure 1 The chemical structures of the used monomers I-1-vinyl-2-pyrrolidone (VP), II-divinylbenzene (DVB), III-trimethylolpropane trimethacrylate (TRIM), IV-di(methacryloxymethyl) naphthalene (DMN).

(DMN). The chemical structures of these monomers are shown in Figure 1.

EXPERIMENTAL

Chemicals

VP (Fluka AG, Buchs, Switzerland), DVB (Merck, Darmstadt, Germany) and TRIM (Sigma Aldrich, Steinheim, Germany) were washed with 5% aqueous sodium hydroxide to remove inhibitors. Polyvinyl alcohol (PVP) and α,α' -azoisobutyronitrile (AIBN)

purchased from Fluka (Buchs, Switzerland) were used without purification. Toluene, *n*-dodecane, acetone, and methanol, sulphuric acid and sodium hydroxide (reagent grade) were from POCh (Gliwice, Poland). Benzene, *n*-butanol, 2-pentanone, pyridine, 1-nitropropane, and 1,4-dioxane used in chromatographical measurements were supplied by Merck (Darmstadt, Germany). DMN 1,4-di(methacryloxymethyl)naphthalene was obtained in our laboratory according to the procedure described elsewhere.²⁷

Preparation of porous copolymers

All porous copolymers were obtained by suspension polymerization using equivalent mole fraction of monomers. For copolymerization with VP, the following monomers DVB, TRIM, and DMN were used. They were copolymerized in the following way: 195 mL of distilled water and 6.5 g of poly(vinyl alcohol) were stirred for 6 h at 80 °C in the three-necked flask fitted with a stirrer, water condenser, and thermometer. To reduce the solubility of VP in water calcium chloride was added. Then the solution containing 15 g of monomers and 0.075 g of α,α' -azoisobutyronitrile in 22.5 mL of diluents (toluene + *n*-dodecane) was prepared and added while stirring to the aqueous medium. Copolymerization was performed for 20 h at 80 °C. Porous beads (the diameter range 50–250 μm) formed in this process were sucked off, washed with hot water, and extracted in a Soxhlet apparatus with acetone, toluene, and methanol. The purified beads were separated into fractions by the sieving.

Sulfonation of VP-DVB and VP-DMN copolymers

The copolymers with presence of aromatic rings were modified into cation-exchangers by the reaction of sulfonation. After drying under vacuum at 80 °C for 24 h, the sample of VP copolymers were placed into a reactor vessel. Fifty microliters of sulfuric acid was poured over each sample and the mixtures were stirred for 5 h at 60 °C. After cooling to room temperature, unreacted acid was sucked off using a glass filter funnel. The sulfonated copolymers were washed with distilled water until neutral and dried under vacuum at 80 °C for 24 h.

The quantitative extent of the sulfonation reaction was evaluated by measurement of the ion exchange capacity of the samples using the standard procedure for polystyrene cation exchange resin.²⁸ 0.5 g of sulfonated particles was placed in 100-mL Erlenmeyer flask. Then 10 mL of 0.1 mol L⁻¹ NaOH solution was added and left overnight. The supernatant solution was back-titrated with 0.2 mol L⁻¹ HCl solution, using phenolphthalein as indicator. The exchange capacity was determined from mass balance.

Characterization of copolymers

Average size and size distribution of the studied copolymers were determined using Mastersized Analyser 2000 (Malvern Instruments, Worcestershire, United Kingdom). The statistic of the distribution was calculated using the derived diameters according to British standard BS2955 : 1993.

To get information on physical and chemical properties of porous beads fraction 0.080–0.125 mm in diameter was isolated and examined. Elemental analysis of the obtained copolymers was made on PerkinElmer CHN analyzer. Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer 1725× spectrophotometer in the 400–4000 cm^{-1} wave number range using KBr pellets.

Textural characterization of the copolymers was carried out by the low-temperature nitrogen adsorption-desorption method. Nitrogen adsorption-desorption measurements were made at 77K using a volumetric adsorption analyzer ASAP 2405 (Micrometrics Inc., USA). The measurements of the surface properties of the copolymers were preceded by outgassing of the samples at 140 C for 2 h. The specific surface areas of the investigated were calculated by the Brunauer-Emmet-Teller (BET) method for the adsorption data in the range of a relative pressure p/p_0 0.05 to 0.25. The total pore volume was estimated from a single-point absorption at a relative pressure of 0.985. The pore size distributions (PSD) were obtained from the desorption branch of the isotherm using the Barrett-Joyner-Halenda (BJH) procedure.

The maximum of PSD was defined as most probable pore diameter in contrast to the average pore diameter calculated as $D_p = 4V_p/S_{\text{BET}}$ (on assumption of a cylindrical shape of pores).

The surface of the obtained beads was also examined using an atomic force microscope (AFM), AFM Nanoscope III (Digital Instruments) operating in contact mode.

Thermal properties of the copolymers were determined out using DSC 204 produced by Netzsch (Günzburg, Germany) with heating run 20–500°C and temperature increase rate 10°C/min. All DSC measurements were carried out in aluminum pans with a pierced lid with sample weight of 10mg in nitrogen atmosphere. In addition, thermogravimetric analyses (TGA) were conducted by means of derivatograph MOM (Budapest, Hungary) within the temperature range 20–1000°C with the sample weight 100 mg and heating rate 10°C/min in air atmosphere.

Chromatographic measurements

Chromatographic measurements were carried out on a Dani GC 1000 gas chromatograph (Dani, Italy) equipped with a thermal conductivity detector,

using stainless-steel columns (100 cm × 1.2 mm I.D.), and helium as carrier gas at a flow-rate of 50 mL/min.

The measurements of retention indices for McReynolds substances (benzene, *n*-butanol, 2-pentanone, 1-nitropropane, and pyridine) were carried out at 140 C²⁹ and those of the selectivity parameters (*n*-butanol, 1-nitropropane, and 1,4-dioxane) at 200 C.³⁰ For all the porous copolymers, the relationships between $I_g V_R$ and carbon number of *n*-alkanes (C₅–C₁₂) were linear at 140 and 200 C, thus the retention indices could be applied for the selectivity measurements. The retention time of the peak of air was considered to be the dead time.

The samples were injected by means of a 1- μL syringe (SGE, North Melbourne, Australia). Each probe was injected separately.

The McReynolds constants (ΔI_i) were calculated by subtracting the average retention indices of the probe solute on graphitized thermally carbon black (GTCB) from those on each of the porous copolymers. The values of the retention indices of *n*-butanol, 1-nitropropane, and 1,4-dioxane on GTCB were taken from the paper by Hepp and Klee.²⁹

The general selectivity ($\Sigma I = x + y + z$) was calculated using the reported retention data on GTCB for benzene (*x*), *n*-butanol (*y*), and 2-pentanone (*z*).³⁰ Retention indices were calculated from the equation done proposed by Kovats³¹:

$$I_x = 100 \lg(t_{R,x}'/t_{R,z}') / \lg(t_{R,z+1}'/t_{R,z}') + 100z$$

where

$t_{R,x}'$ is the reduced retention time of the substance *x*;

$t_{R,z}'$ is the reduced retention time of the homologous alkane with the nearest shortest retention time;

$t_{R,z+1}'$ is the reduced retention time of the next higher homologue eluted after homologue *z*;

z is the number of carbon atoms in the *n*-alkane molecule.

The selectivity parameters (x_i) were calculated using the equation³²:

$$x_i = \frac{\Delta I_i}{\Delta I_b + \Delta I_n + \Delta I_d}$$

where ΔI_b , ΔI_n , and ΔI_d are the McReynolds constants for *n*-butanol, 1-nitropropane, and 1,4-dioxane, respectively.

RESULTS AND DISCUSSION

Preparation of porous beads

Porous copolymers VP–DVB, VP–TRIM, and DMN–DVB were obtained by suspension copolymerization.

TABLE I
Polymerization Recipe

Copolymer	Monomers (g)		Ratio of monomers (mmol)	Ratio of diluents to monomers (mL/g)	Diluents		Stabilizer (g)
					Toluene	<i>n</i> -Dodecane	
VP-DVB	VP 6.9066	DVB 8.0934	62.2:62.2	1.5:1	0	22.5	6.5
					3.4	19.1	
					11.25	11.25	
					19.1	3.4	
					22.5	0	
VP-TRIM	VP 3.7075	TRIM 11.2925	33.7:33.7	1.5:1	0	22.5	6.5
					3.4	19.1	
					11.25	11.25	
					19.1	3.4	
					22.5	0	
VP-DMN	VP 3.7075	DMN 11.2925	33.7:33.7	1.5:1	22.5	0	6.5
					19.1	3.4	

This method of polymerization is particularly suited to the formation of cross-linked porous beads. Synthesis of porous particles requires the presence of inert diluent which leads to the formation of permanent pores in the material after removal of diluents. Stable structure of microspheres is caused by high cross-linking degree. Properties of porous beads depend on the concentration of the cross-linking agent and concentration and nature of the diluent system. During discussed copolymerizations, the mixture of toluene and *n*-dodecane as a pore-forming diluent was used. To study the influence of toluene concentration in the mixture with *n*-dodecane, a series of syntheses was performed using the constant ratio of diluents to monomers equal to 1.5 : 1.0 (mL/g). All copolymers were synthesized using equivalent mole ratio of monomers. A summary of the polymer preparation is presented in Table I. Concentrations of toluene in pore-forming mixture changed from 0 to 100% for the VP-DVB and VP-TRIM copolymers. Unfortunately, the product obtained in presence of pure *n*-dodecane was irregular in shape and coagulated. In addition, DMN monomer has got crystal structure and it had to be dissolved in the diluent mixture before putting it in the polymerization system. Among used diluent system, only pure toluene (Sample 10) and toluene in the mixture with 15 vol % of dodecane (Sample 9) was suitable for this purpose. The main drawback of suspension polymerization is broad size distribution of the obtained microspheres. Figure 2 shows the relative distribution of volume of particles versus particles diameters for the copolymers obtained in presence in the presence of 85% toluene in the mixture with dodecane. In addition, Table II contains the statistic data of particle size distribution. $D(0.1)$ is the size in microns of particle below which 10% of

the sample lies, $D(0.9)$ is the size of particle below which 90% of the sample lies, $D(0.5)$ refers to mass median diameters (MMD) that is the size in microns at which 50% of the sample is smaller and 50% is larger. From this date one can assume that size distribution considerably depends on the type of cross-linker. The highest value of MMD (288 μm) is observed for VP-TRIM copolymer. Significant drop (almost twice) appears for VP-DMN copolymer (155 μm). Cross-linker influenced also the width of size distribution (span). The span is calculated as:

$$\text{span} = \frac{d(0.9) - d(0.1)}{d(0.5)}$$

The smallest value of span (0.614) is observed for the TRIM-VP copolymer which confirms that this copolymer has the narrowest size distribution. The VP-DVB and VP-DMN copolymers possess much higher value of span 1.073 and 1.112, respectively. The same pattern is observed for the uniformity of the copolymers. Uniformity (a measure of the

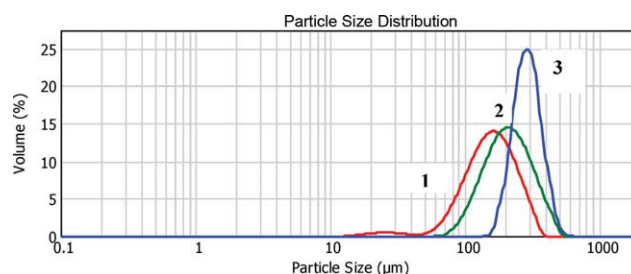


Figure 2 Particle size distribution by volume of the microspheres obtained in the presence of 85% toluene in the mixture with dodecane: 1-VP-DMN, 2-VP-DVB, 3-VP-TRIM. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

TABLE II
The Statistic Data of Particle Size Distribution

Copolymer	$d(0.1)$	$D(0.5)$	$D(0.9)$	Span	Uniformity
VP-DVB	122.8	191.3	222.6	1.073	0.333
VP-TRIM	214.6	288.3	391.7	0.614	0.193
VP-DMN	85.5	155.4	258.3	1.112	0.349

absolute deviation from the media) was calculated using the following equation:

$$\text{uniformity} = \frac{\sum X_i |d(0.5) - d_i|}{d(0.5) \sum X_i}$$

where $d(0.5)$ is the median size of the distribution and d_i and x_i are respectively the mean diameter of, and result in size class i .

Porous structure

The nature of porogenic solvent has significant effect on the polymer microstructure. Vastly different morphologies can be obtained for chemically identical materials, merely by changing the nature of the porogen. In Table III, an influence of toluene concentration in the mixture with *n*-dodecane on the porous structure of the studied copolymers is summarized. In the case of VP-TRIM copolymer, an increase in the proportion of toluene in the mixture with dodecane led to increase in surface area from 27 to 607 m²/g and pore volume from 0.04 to 1.15 mL/g. However, the dependence of surface area on the used solvent followed a different pattern for VP-DVB copolymer, showing the maximum of specific surface area for the product obtained in the presence of 50% (v/v) of toluene. For higher concentrations of

TABLE III
Parameters of the Porous Structure of the Studied Copolymers

Sample	Toluene concentration in the mixture with <i>n</i> -dodecane (%)	Specific surface area (m ² /g)	Pore volume (mL/g)	Most probable pore diameter (Å)
VP-DVB				
1	15	556	0.250	410
2	50	845	1.900	390
3	85	765	1.984	180
4	100	790	1.400	120
VP-TRIM				
5	15	27	0.044	-
6	50	380	0.259	-
7	85	599	1.010	250
8	100	607	1.155	210
VP-DMN				
9	85	224	0.695	480
10	100	323	0.990	330

toluene, specific surface area slightly decreases. Because different applications of macroporous polymers require tailored PSD, it was also of interest to investigate the influence of diluent mixture composition also on the average pore diameter. As the pore formation is directly related to phase separation

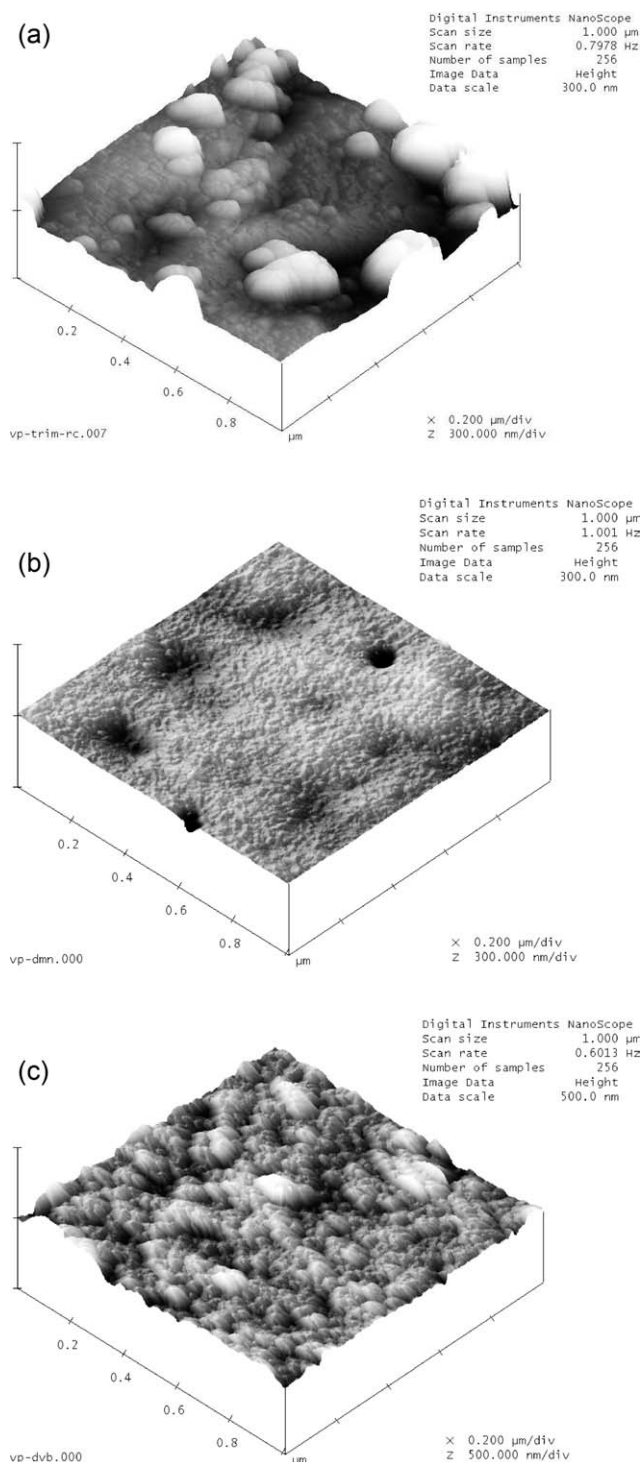


Figure 3 AFM micrographs of the surface of the obtained copolymers (a) VP-TRIM, (b) VP-DMN, (c) VP-DVB.

TABLE IV
Composition of the Obtained Copolymers

Sample	Nitrogen content in the polymer (wt %)	Mole ratio of VP to cross-linker monomers in the copolymer
1	1.56	0.268 :1
2	1.71	0.294:1
3	1.75	0.300:1
4	1.58	0.272:1
5	1.34	0.432:1
6	1.37	0.442:1
7	1.35	0.435:1
8	1.36	0.439:1
9	2.27	0.710:1
10	2.00	0.632:1

phenomena, it is greatly affected by the solvating power of the diluent mixture. It was observed that, for all studied copolymer, the increase in dodecane proportion in the diluent mixture shifted the maximum of PSD toward broader pores sizes. The system with higher concentration of toluene produces structure with smaller average pore diameters. That behavior was the result of the differences in solubility parameters of the used porogenic solvent: 18.2 (MPa)^{0.5} for toluene and 16.2(MPa)^{0.5} for dodecane. It is worth noticing that not only diluent composition but also the type of cross-linker may affect the porous structure of the obtained copolymers. It should be stressed that the highest values of specific surface area and pore volume can be observed for the VP-DVB copolymer.

Differences in the surface texture of the copolymers obtained during copolymerization with different cross-linkers are visualized in Figure 3. This picture shows the contact mode AFM images for microspheres obtained in presence of 85% (v/v) of toluene in the mixture with dodecane. According to Rebollo et al., there is a high degree of correlation between porosity and roughness parameters.³³ The root mean squares (RMSs) roughness for the studied copolymers are as follows: VP-DVB-21.8 nm, VP-TRIM 15.4 nm, VP-DMN 4.9 nm. Hence, one can observe that they are directly proportional to the values of surface area of the samples under study.

Elemental analysis

Table IV contains results of elemental analysis of obtained copolymers. They indicate that comparing

TABLE V
The Cation Exchange Capacity of the Sulfonated Copolymers

Sample	Toluene concentration in the mixture with <i>n</i> -dodecane (%)	Cation exchange capacity (mmol/g)
VP-DVB		
1	15	1.92
2	50	1.98
3	85	1.96
4	100	1.95
VP-DMN		
9	85	2.31
10	100	2.33

with starting polymerization mixture lower amount of VP was incorporated in the copolymer networks. The molar ratio of VP to the cross-linker was calculated on the basis of nitrogen content in the polymer. As the nitrogen occurs only in the functional monomer it was possible to evaluate the molar ratio of VP to cross-linker. In the initial system the ratio was 1 : 1; in the obtained products it fluctuated from 1 : 0.710 to 1 : 0.268 depending on diluent mixture and used monomers. The content of VP in composition of the final copolymer was mainly influenced by the type of cross-linker. The lowest quantity of nitrogen was found in VP-DVB copolymer. Only about 1/4 of initial amount of VP was incorporated into this copolymer network. Better results were obtained for cross-linkers containing methacrylate groups. In case of VP-TRIM copolymers, conversion of VP approached to nearly half of initial amount VP. Copolymerization VP with DMN gives product with relatively high content of VP (Table IV).

The influence of diluent composition on VP content in final products was not so significant.

The presence of pyrrolidone structure units in all copolymers was confirmed by IR absorption at 1650–1660cm⁻¹ parallels to the ester absorption at 1720–1730 cm⁻¹ for the VP-DMN and VP-TRIM copolymers.

Cation exchange capacity of the sulfonated copolymers

The copolymers with presence of aromatic rings (VP-DMN VP-DVB) were successfully modified into cation-exchangers by sulfonation. Table V contains the values of the cation exchange capacity (CEC) of the obtained cation-exchangers. The ion-exchange

TABLE VI
Thermal Properties of Obtained Copolymers

Copolymer	Initial decomposition temperature T_s (°C)	Temperature of 20% weight loss $T_{20\%}$ (°C)	Temperature of 50% weight loss $T_{50\%}$ (°C)	Final decomposition temperature T_f (°C)
VP-DVB	260	390	450	940
VP-TRIM	240	350	400	700
VP-DMN	260	340	420	870

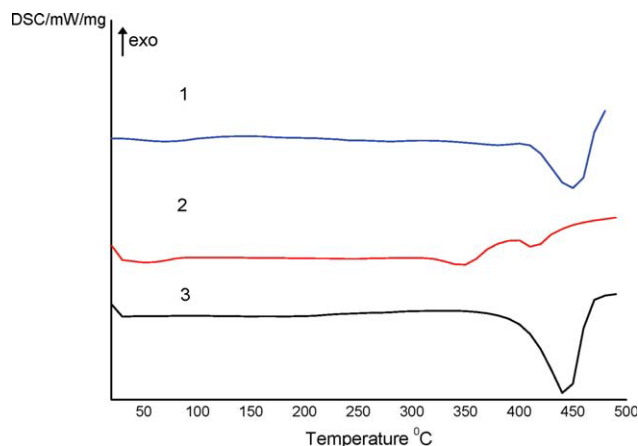


Figure 4 DSC curves of the studied copolymers: 1—TRIM-VP, 2—DMN-VP, and 3—DVB-VP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

capacity of the sulfonated VP-DVB copolymer was found to be about 1.95 mmol/g, whereas for the VP-DMN copolymer about 2.3 mmol/g. On the basis of the data, one can assume that the CEC does not depend on the variation of diluent composition and remains almost constant for the given copolymer. Similar relation was observed by Zaidi et al.³⁴

Thermal properties

Thermal properties of copolymers were studied by means of DSC and TG analyses. The DSC was performed in a nitrogen atmosphere from 20°C to 500°C. The TGA was conducted in air from 20–1000°C.

Thermogravimetric analysis

Table VI summarizes the thermal properties of copolymers. The lowest initial decomposition temperature has copolymer with aliphatic TRIM. Presence of aromatic rings resulted in higher thermal resistance of the product. Initial decomposition temperatures for VP-DVB and VP-DMN are 260°C. Final decomposition temperature for containing two cumulated aromatic rings DMN-DVB copolymer is 870°C. In case of VP-DVB copolymer, this temperature is higher (940°C). Probably this phenomenon is connected with the amount of VP incorporated into

TABLE VII
DSC Data

Copolymer	T_{d1} (°C)	ΔH_{d1} (J g ⁻¹)	T_{d2} (°C)	ΔH_{d2} (J g ⁻¹)
VP-DVB	448.4	295.5	-	-
VP-TRIM	394.1	17.31	461.9	114.9
VP-DMN	346.7	14.8	411.7	13.34

the polymer skeleton. VP-DVB copolymer contains the lowest amount of functional monomer and consequently it has the best thermal properties.

DSC analysis

The DSC curves of the studied copolymers are presented in Figure 4. They had a characteristic, well-shaped calorimetric profile. In addition, the decomposition temperature, T_d and the enthalpy of decomposition (ΔH_d) are given in Table VII. DSC analysis confirmed the high thermal stability of the obtained copolymers. In case of VP-DVB copolymer, no endothermic decomposition peak until 448°C was observed. VP-TRIM and VP-DMN copolymers show similarity in thermal behavior revealing two endothermic peaks. The first one could be associated with the ester bonds breakdown in copolymers.

Inverse gas chromatography

High thermal resistance of all discussed copolymers enabled to carry out investigation of their polarity and selectivity with the use of inverse gas chromatography. For the chromatographic purposes, copolymers obtained in presence 85% toluene in the diluent mixture were chosen.

Table VIII contains the general selectivity ΣI (defined as a measure of polarity of the phase) of the examined copolymers. The polarity changes depending on the used cross-linker and consequently with the amount of VP incorporated into polymer network. The lowest value of general selectivity is observed for the DVB-VP copolymer. It is connected with the structure of DVB (no polar group) and small amount of VP in DVB-VP copolymer (1.75 wt %). Employing TRIM instead of DVB leads to dramatic increase of polarity from 243 to 494. Methacrylate groups presented in TRIM

TABLE VIII
Kovats Retention Indices for the McReynolds' Test Substances and General Selectivities (ΣI) for the Porous Copolymers (140°C)

Copolymer	<i>I</i>					<i>x</i>	<i>y</i>	<i>z</i>	$\Sigma I = x + y + z$
	Benzene	<i>n</i> -Butanol	2-Penta none	1-Nitro-propane	Pyridine				
VP-DVB	615	614	651	671	676	41	116	86	243
VP-TRIM	648	730	753	751	738	74	232	188	494
VP-DMN	631	755	751	823	407	58	266	186	510

TABLE IX
Kovats Retention Indices for *n*-Butanol, 1-Nitropropane, and 1,4-Dioxane, and Copolymers Selectivity Parameters (200°C)

Copolymer	<i>I</i>			ΔI_b	ΔI_n	ΔI_d	$\Sigma \Delta I_i$	x_{acc}	x_{dip}	x_{don}
	<i>n</i> -Butanol	1-Nitro-propane	1,4-Dioksane							
VP-DVB	631	694	668	145	188	184	517	0.281	0.363	0.355
VP-TRIM	718	791	697	232	285	231	748	0.310	0.381	0.309
VP-DMN	746	852	760	260	346	273	879	0.296	0.394	0.310

monomer and higher amount of VP existing in the copolymer structure are responsible for this phenomenon. Substitution of TRIM by DMN which contain both aromatic rings and polar methacrylate groups cause further growth in polarity. It must be stressed that every polar molecule is capable of several polar interactions and that retention on any particular stationary phase depends on the total interaction. It is possible to evaluate relative interactions between any particular stationary phase and polar probes providing that they have identifiable polar characteristics which predominate. In Table IX, $\Sigma \Delta I$ describing the relative polar contributions to retention and selectivity parameters (x_i) for *n*-butanol, 1,4-dioxane, and 1-nitropropane are summarized. In this study, *n*-butanol (hydrogen-bond donor) is used to measure hydrogen-bond acceptor characteristics, 1,4-dioxane (hydrogen-bond acceptor) to measure hydrogen-bond donor characteristics, and 1-nitropropane to measure dipole characteristics of the polymer. Compared with VP-DVB copolymer, the others have stronger hydrogen-bond acceptor properties. This is undoubtedly associated with the presence of lone electron pairs on oxygen in the TRIM and DMN monomers and on nitrogen in VP. Values of selectivity parameters x_{dip} indicate that the higher polarity of stationary phase the stronger interaction with dipole probe.

CONCLUSION

The study gives guidelines for the synthesis of adsorbents on the *N*-vinylpyrrolidone basis of desired porosity, thermal stability, and polarity. Obtained macroporous microspheres can be utilized as functional polymers in various fields of chemistry and as the stationary phases in different kinds of chromatography with the advantage of being an adsorbent for both polar and non-polar eluents. Nontoxicity of *N*-vinylpyrrolidone copolymer allows to use it for sorption of phenol compounds coming from natural sources. Moreover, VP-DVB and VP-DMN copolymers can be easily transformed into cation-exchangers.

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