

Influence of Crosslinker and Monomer Ratio on Bead Size Distribution, Swelling and Polymer Network Flexibility of 4-Nitrophenylacrylate Polymer Supports[†]

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Abstract

Sphere shaped polymer supports with styrene and 4-nitrophenylacrylate as monomers and divinylbenzene (DVB) or ethyleneglycoldimethacrylate (EGDMA) as crosslinkers were prepared by free radical polymerization in suspension medium. Ratio of monomers as well as the crosslinking degree varied in order to test the influences on bead size distribution, swelling and polymer network flexibility. The amount of crosslinker had an effect on bead size, average bead diameters being between 10 μm and 35 μm when 5% of crosslinker was applied and between 35 μm and 55 μm when 20% was used. The crosslinking degree also affected swelling in dichloromethane, water, methanol, toluene and acetonitrile, being more intense with lower concentrations of DVB or EGDMA. The flexibility of polymer network was investigated using reactions with 1,8-diaminooctane. High degrees of additional crosslinking was observed, namely between 58 and 95% indicating high flexibility of polymer network.

Key words: polymer supports, 4-nitrophenylacrylate, suspension polymerisation, bead size distribution

Introduction

Polymer supports for anchoring a reactive species, be it a substrate, a reagent, a catalyst, a scavenger or a part of a sensor system, have through the last decades proven to be an invaluable tool facilitating synthesis and separation techniques. Since the first reported tetrapeptide synthesis on solid support,¹ the field of polymer supported chemistry is rapidly expanding.² The most commonly used form of polymer support for batch operations are spherulated particles prepared by free radical polymerisation in a suspension medium. The reasons for that are in the relative ease of preparation and in the suitability of the method for producing bead shaped particles between 10 and 500 μm . Such particles can be easily manipulated by the use of standard laboratory equipment for separation. New forms of polymer supports, such as monolithic columns and disks,³ are appearing, especially for separation techniques. On the other hand, beads still remain the most commonly used form of support, especially for batch type setups. With regards to the chemistry of supports, the majority is prepared from 4-vinylbenzyl chloride (VBC) and crosslinked with DVB. Chloromethyl groups enable further chemical modifications of supports and many derivatives of crosslinked chloromethylated polystyrene

are now commercially available.⁴ The drawback of VBC/DVB supports are their mainly non-polar structure, which limits the spectrum of solvents they can be used in. Namely, since the majority of reactive sites are positioned inside the particle, the polymer particle must swell in the reaction medium to enable contacts with the substrate in the solution. Higher degrees of crosslinking partly solve this problem, however for most times the reacting medium is still the swollen gel. Reactive acrylates have been introduced into the field of polymer supports in order to address this problem.⁵ Crosslinked copolymers of 4-nitrophenylacrylate and styrene in the form of beads have been prepared by suspension polymerisation⁶ and in the form of monoliths by emulsion polymerisation.⁷ Studies on the functionalisations of these supports have also been published.^{8,9} The work on 4-nitrophenylacrylate supports so far has proven the suitability of the monomer for inclusion into polymer supports. It has been demonstrated that it can easily be prepared from 4-nitrophenol and acryloyl chloride and polymerizes well with styrene and divinylbenzene. We therefore wished to study more in detail how the ratio of styrene to 4-nitrophenylacrylate, crosslinker type and degree influence bead size distribution, swelling of beads and polymer network flexibility. The results are presented in the present paper.

Experimental section

Materials

Commercially available 4-nitrophenol (Aldrich), acryloylchloride (Merck), triethylamine (Fluka), dichloromethane (DCM, Merck), sodium hydrogen carbonate (Kemika), magnesium sulphate (Kemika), chlorobenzene (Aldrich), *N,N*-dimethylformamide (Carlo Erba Reagenti), methanol (Fluka), 1,8-diaminooctane (Aldrich), acetonitrile (Riedel-de Haën), α,α' -azoisobutyronitrile (AIBN; Fluka) and poly(vinylpyrrolidone) (Aldrich, $M = 40000$) were used as received. Divinylbenzene (DVB; Aldrich, a mixture of 80% ethylstyrene and 20% of a mixture of isometric divinylbenzene), styrene (S; Aldrich) and ethylene glycol dimethacrylate (EGDMA; Aldrich) were washed with NaOH (5%) and water before use. 4-nitrophenylacrylate (A) was prepared by literature methods.¹⁰ FTIR spectra were taken on a Perkin-Elmer FT-IR 1720X spectrometer (KBr pellets). Combustion elemental analyses were done on a Perkin-Elmer 2400 CHN analyzer. Optical micrographs were recorded on a Nikon EPIPHOT 300U microscope with a digital camera.

Preparation of crosslinked copoly(styrene-4-nitrophenylacrylates) (1a, 1b, 2a, 2b, 3a, 3b, 1a', 1b', 2a', 2b', 3a', 3b')

Water phase, consisting of 1.67 g of poly(vinylpyrrolidone) dissolved in 250 mL of de-ionized water, which was previously degassed under reduced pressure for 15 min, was put in a 350 mL polymerisation reactor. To this, under stirring with an overhead stirrer at 750 rpm, the oil phase, consisting of a chlorobenzene solution of monomers, crosslinker and radical initiator, was added (5 mL of chlorobenzene, 150 mg of AIBN, 4-nitrophenylacrylate, styrene, divinylbenzene or ethylene glycol dimethacrylate – their amounts are given in Table 1).

Table 1. Preparation data for polymer supports.

Polymer	Acrylate to styrene ratio	Crosslinker	m_A (g)	m_S (g)	m_{DVB} (g)	m_{EGDMA} (g)
1a	1/1	5% DVB	1.737	0.936	0.157	–
1b	1/1	20% DVB	1.737	0.936	0.783	–
2a	2/1	5% DVB	2.316	0.624	0.157	–
2b	2/1	20% DVB	2.316	0.624	0.783	–
3a	1/0	5% DVB	3.474	–	0.157	–
3b	1/0	20% DVB	3.474	–	0.783	–
1a'	1/1	5% EGDMA	1.737	0.936	–	0.188
1b'	1/1	20% EGDMA	1.737	0.936	–	0.891
2a'	2/1	5% EGDMA	2.316	0.624	–	0.188
2b'	2/1	20% EGDMA	2.316	0.624	–	0.891
3a'	1/0	5% EGDMA	3.474	–	–	0.188
3b'	1/0	20% EGDMA	3.474	–	–	0.891

The reaction mixture was stirred for 4 hours at 80 °C and for 4 hours at 90 °C. The resulting polymer beads were filtered, purified by Soxhlet extraction with methanol for 24 hours and dried at room temperature for 48 hours. The following amounts of air-dry products were isolated: 2.205 g of 1a, 2.620 g of 1b, 2.297 g of 2a, 2.946 g of 2b, 2.741 g of 3a, 4.028 g of 3b, 1.925 g of 1a', 3.061 g of 1b', 2.398 g of 2a', 3.443 g of 2b', 2.886 g of 3a', 3.754 g of 3b'.

Polymer beads were analyzed by FTIR spectroscopy. For combustion analyses air-dry products were further dried for 3 hours at 110 °C in vacuo and dry samples were obtained with the following compositions:

1a (crosslinking DVB 5%, A:S = 1:1); Calcd.: C 70.10%, H 5.21%, N 4.43%, found: C 70.25%, H 5.42%, N 5.20%; 3.7 mmol of 4-nitrophenyl groups per gram. FTIR (KBr): 3493, 2926, 1756 (CO), 1614, 1592, 1519, 1490, 1452 (NO₂), 1347, 1206, 1113, 1012, 863, 747, 700, 495 (cm⁻¹).

1b (crosslinking DVB 20%, A:S = 1:1); Calcd.: C 74.04%, H 5.65%, N 3.64%, found: C 72.52%, H 5.70%, N 4.27%; 3.1 mmol of 4-nitrophenyl groups per gram. FTIR (KBr): 3113, 2925, 1760 (CO), 1615, 1592, 1520, 1490, 1452 (NO₂), 1348, 1206, 1112, 1012, 862, 747, 701 (s), 495 (cm⁻¹).

2a (crosslinking DVB 5%, A:S = 2:1); Calcd.: C 65.43%, H 4.69%, N 5.36%, found: C 66.98%, H 5.05%, N 5.43%; 3.9 mmol of 4-nitrophenyl groups per gram. FTIR (KBr): 3494, 2929, 1757 (CO), 1615, 1593, 1520, 1490, 1452 (NO₂), 1348, 1206, 1115, 1012, 863, 747, 701, 495 (cm⁻¹).

2b (crosslinking DVB 20%, A:S = 2:1); Calcd.: C 69.76%, H 5.17%, N 4.50%, found: C 69.85%, H 5.35%, N 4.78%; 3.4 mmol of 4-nitrophenyl groups per gram. FTIR (KBr): 3492, 2927, 1757 (CO), 1615, 1592, 1524, 1490, 1452 (NO₂), 1347, 1206, 1113, 1011, 862, 747, 702, 494 (cm⁻¹).

3a (crosslinking DVB 5%, A:S = 1:0); Calcd.: C 57.64%, H 3.81%, N 6.92%, found: C 57.40%, H 4.09%, N 6.78%; 4.8 mmol of 4-nitrophenyl groups per gram. FTIR (KBr): 3491, 2935, 1759 (CO), 1615, 1593, 1522, 1490, 1449 (NO₂), 1348, 1206, 1128, 1012, 862, 747, 690, 495 (cm⁻¹).

3b (crosslinking DVB 20%, A:S = 1:0); Calcd.: C 62.68%, H 4.38%, N 5.91%, found: C 63.09%, H 4.09%, N 6.00%; 4.3 mmol of 4-nitrophenyl groups per gram. FTIR (KBr): 3486, 2933, 1759 (CO), 1615, 1592, 1520, 1490, 1448 (NO₂), 1348, 1291, 1206, 1161, 1124, 1012, 863, 747, 710, 495 (cm⁻¹).

1a' (crosslinking EGDMA 5%, A:S = 1:1); Calcd.: C 68.20%, H 5.19%, N 4.40%, found: C 69.01%, H 5.51%, N 4.72%; 3.4 mmol of 4-nitrophenyl groups per gram. FTIR (KBr): 3646, 2931, 2858, 1760 (CO), 1683, 1634, 1615, 1593, 1520, 1490, 1453 (NO₂), 1348, 1206, 1113, 863, 748, 701, 495 (cm⁻¹).

1b' (crosslinking EGDMA 20%, A:S = 1:1); Calcd.: C 66.68%, H 5.56%, N 3.53%, found: C 66.51%, H 5.68%, N 3.64%; 2.6 mmol of 4-nitrophenyl groups per gram. FTIR (KBr): 3646, 3083, 2942, 1760 (CO), 1732 (CO), 1615, 1593, 1525, 1491, 1453 (NO₂), 1347, 1206, 1110, 862, 747, 700, 493 (cm⁻¹).

2a' (crosslinking EGDMA 5%, A:S = 2:1); Calcd.: C 63.50%, H 4.65%, N 5.37%, found: C 64.67%, H 5.01%, N 5.44%; 3.9 mmol of 4-nitrophenyl groups per gram. FTIR (KBr): 3649, 2936, 2859, 1759 (CO), 1684, 1616, 1593, 1524, 1490, 1453 (NO₂), 1348, 1205, 1111, 862, 747, 701, 494 (cm⁻¹).

2b' (crosslinking EGDMA 20%, A:S = 2:1); Calcd.: C 62.99%, H 5.09%, N 4.38%, found: C 62.90%, H 5.29%, N 4.58%; 3.3 mmol of 4-nitrophenyl groups per gram. FTIR (KBr): 2940, 1760 (CO), 1731 (CO), 1616, 1593, 1525, 1490, 1453 (NO₂), 1348, 1206, 1112, 862, 747, 700, 494 (cm⁻¹).

3a' (crosslinking EGDMA 5%, A:S = 1:0); Calcd.: C 56.20%, H 3.81%, N 6.87%, found: C 56.19%, H 4.04%, N 6.89%; 4.9 mmol of 4-nitrophenyl groups per gram. FTIR (KBr): 3647, 2938, 2860, 1760 (CO), 1616, 1593, 1520, 1489, 1449 (NO₂), 1348, 1202, 1124, 862, 746, 689, 494 (cm⁻¹).

3b' (crosslinking EGDMA 20%, A:S = 1:0); Calcd.: C 56.91%, H 4.34%, N 5.76%, found: C 56.81%, H 4.53%, N 5.88%; 4.2 mmol of 4-nitrophenyl groups per gram. FTIR (KBr): 3646, 2945, 1760 (CO), 1731 (CO), 1616, 1593, 1519, 1490, 1450 (NO₂), 1348, 1206, 1117, 1012, 885, 862, 746, 690, 494 (cm⁻¹).

Reactions of crosslinked copoly(styrene-4-nitrophenylacrylates) (**1a**, **1b**, **2a**, **2b**, **3a**, **3b**, **1a'**, **1b'**, **2a'**, **2b'**, **3a'**, **3b'**) with 1,8-diaminooctane.

Copoly(styrene-4-nitrophenylacrylate) **1a** (0.1504 g) or **1b** (0.1510 g) or **2a** (0.1524 g) or **2b** (0.1508 g) or **3a** (0.1517 g) or **3b** (0.1518 g) or **1a'** (0.1515 g) or **1b'** (0.1509 g) or **2a'** (0.1509 g) or **2b'** (0.1505 g) or **3a'** (0.1509 g) or **3b'** (0.1530 g) was suspended in 5 mL of *N,N*-dimethylformamide and the appropriate amount of 1,8-diaminooctane was added (0.3430 g for **1a**, 0.2818 g for **1b**, 0.4160 g for **2a**, 0.3483 g for **2b**, 0.5354 g for **3a**, 0.4601 g for **3b**, 0.3396 g for **1a'**, 0.2729 g for **1b'**, 0.4181 g for **2a'**, 0.3386 g for **2b'**, 0.5323 g for **3a'**, 0.4453 g for **3b'**, at a molar ratio of 4-nitrophenylacrylate to 1,8-diaminooctane 1 to 5). The reaction mixture was heated

at 50 °C under stirring for 24 hours. The solid product was filtered, washed with *N,N*-dimethylformamide (3x5 mL), a mixture of *N,N*-dimethylformamide and triethylamine (1:1; 3x5 mL) and methanol (3x5 mL) and dried at room temperature for 20 hours and in vacuo at 90 °C for 3 hours. FTIR and elemental analyses data are as follows:

4a (derived from **1a**); found 5 mmol of amido and amino groups/g. FTIR (KBr): 3299, 2927, 2854, 1652 (CO), 1602, 1540, 1494, 1452, 1385, 1248, 1095, 1029, 761, 701, 668, 544 (cm⁻¹).

4b (derived from **1b**); found 4.1 mmol of amido and amino groups/g. FTIR (KBr): 3626, 3314, 2926, 2853, 1652 (CO), 1520, 1452, 701 (cm⁻¹).

5a (derived from **2a**); found 5.5 mmol of amido and amino groups/g. FTIR (KBr): 3306, 2927, 2854, 1652 (CO), 1543, 1452, 702 (cm⁻¹).

5b (derived from **2b**); found 4.6 mmol of amido and amino groups/g. FTIR (KBr): 3317, 2926, 2852, 1651 (CO), 1521, 1451, 702 (cm⁻¹).

6a (derived from **3a**); found 7 mmol of amido and amino groups/g. FTIR (KBr): 3305, 2929, 2855, 1652 (CO), 1549, 1445, 720 (cm⁻¹).

6b (derived from **3b**); found 5.8 mmol of amido and amino groups/g. FTIR (KBr): 3439, 2929, 2855, 1652 (CO), 1540, 711 (cm⁻¹).

4a' (derived from **1a'**); found 4 mmol of amido and amino groups/g. FTIR (KBr): 3304, 2928, 1729 (CO), 1654 (CO), 1541, 1453, 1386, 1180, 1106, 762, 701 (cm⁻¹).

4b' (derived from **1b'**); found 3.7 mmol of amido and amino groups/g. FTIR (KBr): 3417, 2928, 1732 (CO), 1661 (CO), 1539, 1453, 761, 701 (cm⁻¹).

5a' (derived from **2a'**); found 5.6 mmol of amido and amino groups/g. FTIR (KBr): 3303, 2928, 1729, 1652, 1453, 1385, 1250, 1192, 1097, 762, 702 (cm⁻¹).

5b' (derived from **2b'**); found 4.1 mmol of amido and amino groups/g. FTIR (KBr): 3413, 3062, 3027, 2929, 2855, 1732 (CO), 1661 (CO), 1540, 1495, 1454, 1386, 1109, 762, 702, 668, 467 (cm⁻¹).

6a' (derived from **3a'**); found 7.2 mmol of amido and amino groups/g. FTIR (KBr): 3308, 2929, 1730 (CO), 1654 (CO), 1547, 1457, 1385, 722 (cm⁻¹).

6b' (derived from **3b'**); found 5.8 mmol of amido and amino groups/g. FTIR (KBr): 2930, 1732 (CO), 1661 (CO), 1548, 1456, 1166, 668 (cm⁻¹).

Table 2. Swelling capacities of polymer supports (mL/g).

Solvent/Polymer	1a	1b	2a	2b	3a	3b	1a'	1b'	2a'	2b'	3a'	3b'
Methanol	2.6	2.0	2.0	1.8	2.4	2.5	4.0	1.7	2.7	1.9	2.5	1.5
Water	2.8	1.7	2.0	1.7	2.7	2.6	3.9	2.0	3.2	1.7	2.3	1.4
Acetonitrile	4.2	3.6	3.4	3.3	5.6	3.2	3.9	3.2	2.7	3.8	4.4	2.8
Dichloromethane	17.4	3.9	7.3	3.5	8.6	4.7	5.8	4.2	11.6	4.5	5.8	3.4
Toluene	4.1	3.3	3.0	3.0	3.3	3.1	3.1	3.6	3.8	3.3	2.6	2.2

Table 3. Elemental analysis data of polymer supports.

Polymer support	Acrylate to styrene ratio	Crosslinker	Elemental analysis-calculated (%)			Elemental analysis- found (%)		
			C	H	N	C	H	N
1a	1/1	5% DVB	70.10	5.21	4.43	70.25	5.42	5.20
1b	1/1	20% DVB	74.04	5.65	3.64	72.52	5.70	4.27
2a	2/1	5% DVB	65.43	4.69	5.36	66.98	5.05	5.43
2b	2/1	20% DVB	69.76	5.17	4.50	69.85	5.35	4.78
3a	1/0	5% DVB	57.64	3.81	6.92	57.40	4.09	6.78
3b	1/0	20% DVB	62.68	4.38	5.91	63.09	4.09	6.00
1a'	1/1	5% EGDMA	68.20	5.19	4.40	69.01	5.51	4.72
1b'	1/1	20% EGDMA	66.68	5.56	3.53	66.51	5.68	3.64
2a'	2/1	5% EGDMA	63.50	4.65	5.37	64.67	5.01	5.44
2b'	2/1	20% EGDMA	62.99	5.09	4.38	62.90	5.29	4.58
3a'	1/0	5% EGDMA	56.20	3.81	6.87	56.19	4.04	6.89
3b'	1/0	20% EGDMA	56.91	4.34	5.76	56.81	4.53	5.88

Determination of the swelling capacities of polymer resins.

10 mL of solvent (methanol or water or acetonitrile or dichloromethane or toluene) was poured over 1 mL of air-dry polymer resin, which was weighed and placed in a graduated cylinder. After 24 hours the volume of swollen beads was measured. The swelling capacities per gram of polymer are presented in the Table 2.

Results and discussion

Preparation of beads

4-Nitrophenylacrylate was chosen as a monomer due to its proven reactivity both in terms of polymerisation (together with DVB) and in terms of possible further functionalisations (reactive ester due to its good leaving group).^{8,9} Furthermore, 4-nitrophenylacrylate can be easily prepared from 4-nitrophenol and acryloyl chloride. The method of suspension in conjunction with free radical polymerisation (by using azobisisobutyronitrile as the initiator) has already been successfully applied for 4-nitrophenylacrylate.⁶ However, the effects of the reactor size and shape, stirrer shape and stirrer speed have not been studied in detail. Previously, we have set the overhead stirrer speed to 285 rpm to obtain the beads of approximately 200 μm to 500 μm in diameter. This time we wished to make them smaller; around 100 μm . By using a 350 mL three neck reactor with a blade type PTFE overhead stirrer at 750 rpm (stirrer type IKA Euro – ST PCV) we were able to obtain beads with the size distribution around the desired value. Thus for all our investigations and bead preparations the overhead stirrer with the PTFE blade set at a speed of 750 rpm was used. Further modification of the beads preparation procedure in comparison with our previously reported procedures⁸ was in the purification

of polymer beads. There were some indications that traces of the stabilising agent (polyvinylpyrrolidone) and unreacted monomers were still present inside the polymer beads after washing. We therefore used Soxhlet extraction (24 hours with methanol) to remove all the remaining stabiliser and monomers. The combustion elemental analysis (see Table 3) proved that all samples were purified satisfactorily as the values of elemental percentage were very close to the calculated ones. At the same time, this presented one of the evidence for the successful polymerisation of both the monomer and the crosslinker. Additionally, FTIR spectroscopy was used to determine the polymer structure. Peaks at 1760 cm^{-1} (4-nitrophenylacrylate carbonyl groups), 1730 cm^{-1} (EGDMA carbonyl groups), 1345 cm^{-1} (nitro groups) were all strong, proving the presence of the groups in the polymer structure.

The yields of bead shaped particles from suspension polymerisations were very high, ranging from 80% upwards. In order to study the effects of the crosslinker type and degree and monomer ratio on the bead parameters, we prepared polymer supports crosslinked with DVB or EGDMA (both types with either 5% or 20% of crosslinker) and with the ratios of acrylate (A) to styrene (S; styrene was added to the monomer mixture to alter the overall polarity of the polymer matrix and to »dilute« the reactive sites on the backbone) varying from 1:1 to the supports with no styrene present (Table 1). In all cases except in the case of the polymer supports **3a** (S/A = 0/1, 5% DVB), **1a'** (S/A = 1/1, 5% EGDMA) and **3a'** (S/A = 0/1, 5% EGDMA) sphered polymer supports were obtained. In the case of **1a'**, **3a** and **3a'** particles were mostly of elliptic shape (see Figure 1). We can thus conclude that this modified procedure of suspension polymerisation is very suitable for the preparation of 4-nitrophenylacrylate based polymer supports with a narrower bead size distribution.

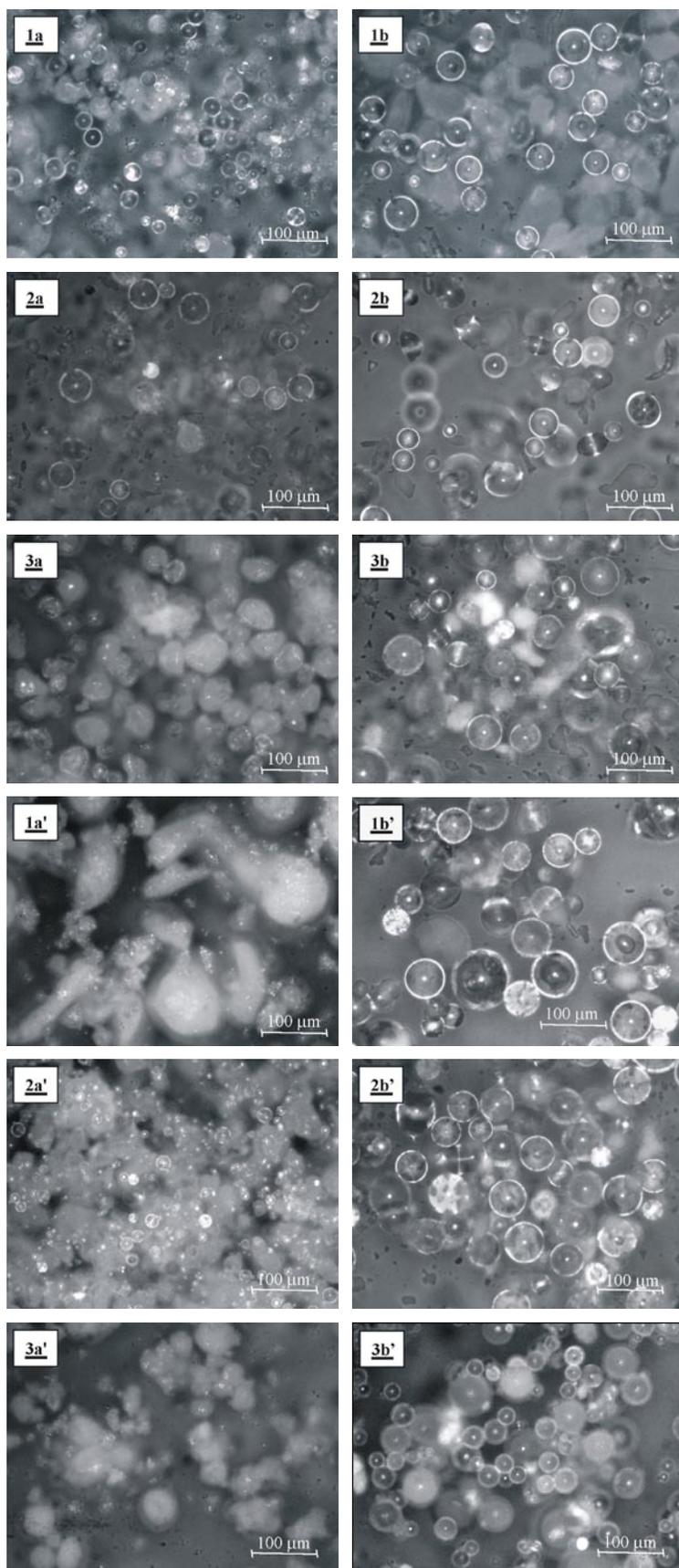


Figure 1. Optical micrograph of polymer beads 1a, 1b, 2a, 2b, 3a, 3b, 1a', 1b', 2a', 2b', 3a', 3b'.

Bead size distribution

Bead size distribution of spherical polymer supports can be determined by the use of a sieve and weighing the fractions obtained. While this is still the most common method, it requires a lot of equipment and is time consuming. Another method is to use laser diffraction. Recently, in parallel with the advent of digital photography, optical microscopy in conjunction with appropriate software has been used to measure the bead size and evaluate the data.¹¹ We used a Nikon EPIPHOT 300U microscope with a digital camera to measure the bead diameters. The data of diameters were processed by Microsoft Excel and expressed as bead size distribution columns (see Figure 2). Bead size distribution is very important since the size of the beads influence the reaction kinetics while when beads are used as a separation medium in a chromatography column, the characteristics of the column much depend on the bead size.

With an intent of testing the effect of crosslinking degree on the average bead diameter we prepared polymer supports with 5% and 20% of crosslinker (molar percentage), both DVB and EGDMA crosslinked. The measurements of bead diameters showed that regardless of the type of crosslinker, beads with 5% of crosslinker were smaller compared to beads with 20% of crosslinker (5% crosslinked **1a** 20.6 μm , 20% crosslinked **1b** 35.4 μm ; see Table 4). While the type of the crosslinker didn't have a profound effect, the styrene to acrylate ratio influenced the bead size distribution, being broader for samples with more styrene incorporated into the polymer matrix (see Figure 2). Generally, the bead size distributions columns reveal the most of the beads to be between 25 and 40 μm (Figure 2), which is a relatively narrow bead size distribution considering that the particles were prepared by suspension polymerisation technique, which usually gives broader size distribution.

Table 4. Average bead diameters.

Polymer	\bar{r} (μm)
1a	20.6
1b	35.4
2a	35.0
2b	42.2
3a	–
3b	41.5
1a'	–
1b'	52.5
2a'	11.7
2b'	55.2
3a'	–
3b'	28.9

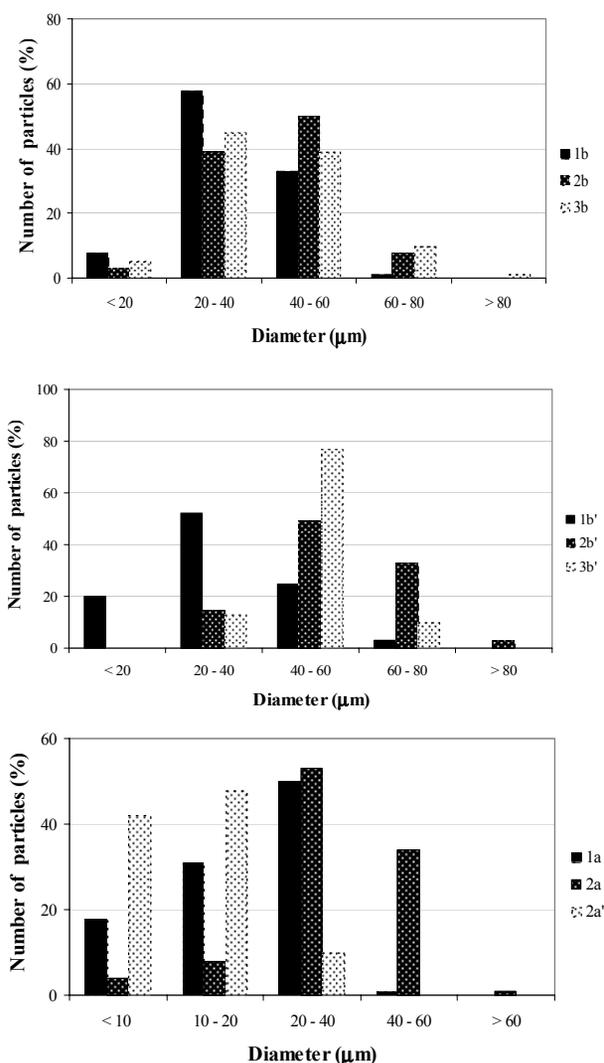


Figure 2. Bead size distribution of polymer supports.

Polymer network flexibility

Polymer network flexibility can be of great importance when a polymer support is used in a synthesis setup. Site-site interactions can have substantial influence on the reaction pathway.¹² By varying the loading of the reactive group on the polymer (the amount of reactive groups in the polymer, usually given in mmol per gram of polymer) these interactions can be changed. With the introduction of multifunctional reagents, polymers can be additionally crosslinked. The amount of additional crosslinking taking place gives us the information about polymer network flexibility. The phenomenon of subsequent crosslinking the already formed polymer supports has been described before. Booth and Hodges prepared an electrophilic scavenger resin by reacting chloromethylated polystyrene with tris(2-aminoethyl)amine and approximately 25% of free amine groups reacted with another chloromethyl group

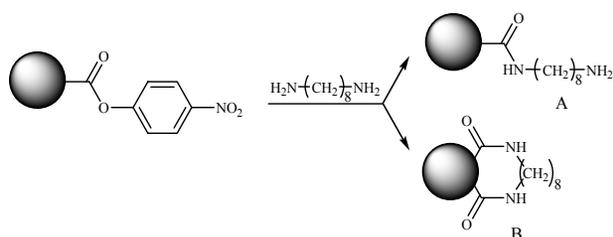
Table 5. Structure of products after the reactions with 1,8-diaminooctane.

Polymer support	Acrylate to styrene ratio	Crosslinker	Calculated %N for structure A	Calculated %N for structure B	Found % N	% additional crosslinking*
1a	1/1	5% DVB	8.73	5.62	7.02	61
1b	1/1	20% DVB	7.2	4.41	5.74	58
2a	2/1	5% DVB	10.53	7.22	7.78	87
2b	2/1	20% DVB	8.86	5.73	6.48	81
3a	1/0	5% DVB	13.5	10.34	9.91	over 95
3b	1/0	20% DVB	11.58	8.25	8.18	over 95
1a'	1/1	5% EGDMA	8.66	5.57	5.53	over 95
1b'	1/1	20% EGDMA	6.98	4.25	5.42	68
2a'	2/1	5% EGDMA	10.53	7.22	7.82	86
2b'	2/1	20% EGDMA	8.62	5.54	5.69	over 95
3a'	1/0	5% EGDMA	13.42	10.25	10.11	over 95
3b'	1/0	20% EGDMA	11.29	7.96	8.06	over 95

* calculated from mathematically constructed curves for each polymer.

on the polymer thus crosslinking it.¹³ Similar behaviour was observed when preparing a monolithic polymer scavenger.¹⁴ The method of using 1,8-diaminooctane to test polymer network flexibility has already been used on copoly(styrene-4-nitrophenylacrylate; 1:1 monomer ratio), crosslinked with 2% or 4% DVB.⁸ By determining the amount of nitrogen in the polymer, a good estimate of reaction product is possible providing the ester groups are completely removed.

To evaluate the polymer network flexibility of polymer supports (various amounts of crosslinker and various monomer ratio; see Table 1), we reacted them with 1,8-diaminooctane (see Scheme 1) at 50 °C in *N,N*-dimethylformamide for 24 hours. Proceedings of the reactions were monitored by FTIR spectroscopy in order to check the presence of the signal for nitro group at 1345 cm⁻¹.

**Scheme 1**

For all the samples spectroscopic data suggested the complete removal of the phenoxy groups and all polymers were subjected to combustion elemental analysis. The results are summarized in Table 5.

Since one amine molecule replaces two phenoxy groups in the case of additionally crosslinked product B (Scheme 1), the percentage of nitrogen in the product is lower than in the case of replacing one phenoxy group (product type A). We calculated the theoretical values of nitrogen for both types of product and for products

having partially structure A and partially structure B. For every sample of starting beads (**1a**, **1b**, **2a**, **2b**, **3a**, **3b**, **1a'**, **1b'**, **2a'**, **2b'**, **3a'**, **3b'**), a curve of nitrogen content dependency on the structure was constructed and a mathematical relation calculated (see Table 6). From these relations, we could estimate the ratio of A to B type product for all the samples (**4a**, **4b**, **5a**, **5b**, **6a**, **6b**, **4a'**, **4b'**, **5a'**, **5b'**, **6a'**, **6b'**).

Table 6. Coefficients for the relation: $AC = ax^2 + bx + c$ (AC = additional crosslinking in %; x = percentage of nitrogen found by elemental analysis).

Polymer	a	b	c
1a	-2.64	5.79	150.59
1b	-2.70	-4.45	172.11
2a	-2.82	19.99	102.24
2b	-2.67	7.04	147.01
3a	-4.25	69.97	-170.14
3b	-3.14	32.57	44.72
1a'	-2.54	3.92	156.82
1b'	-2.72	-5.95	174.4
2a'	-2.84	20.46	100.12
2b'	-2.66	5.39	151.68
3a'	-4.14	66.72	-149.77
3b'	-3.04	28.80	63.07

The first finding was surprising, namely we found no severe effect of the crosslinking degree on the structure of the product (61% of additionally crosslinked product derived from **1a**, 58% additionally crosslinked product derived from **1b**; 87% of additionally crosslinked product derived from **2a**, 81% additionally crosslinked product derived from **2b**; over 95% of additionally crosslinked product derived from **3a**, over 95% additionally crosslinked product derived from **3b**). As expected, samples with higher content of acrylate gave products with more additional crosslinking (samples

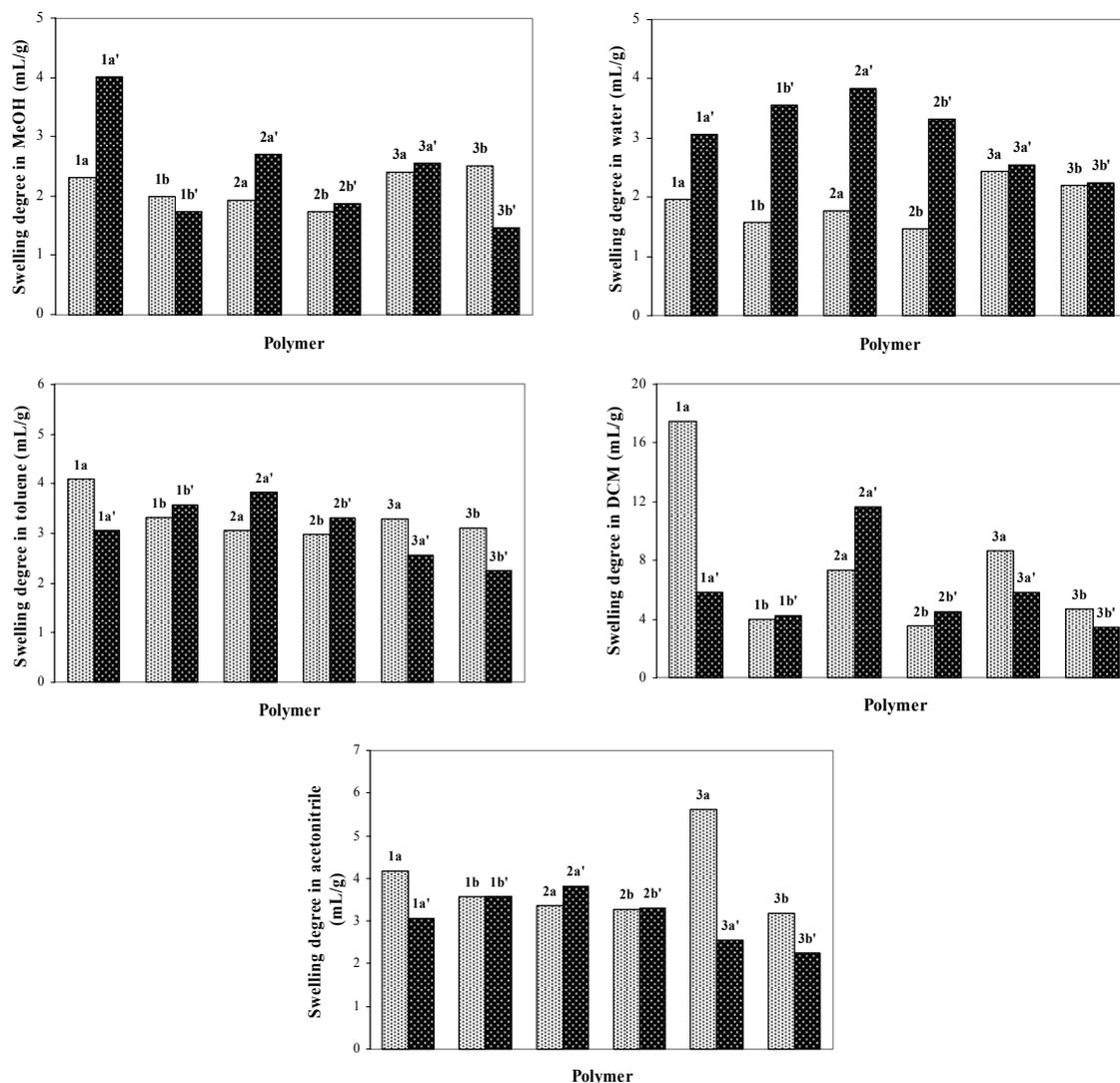


Figure 3. Swelling degrees of polymer supports.

3a, 3b, 1a', 2b', 3a', 3b' yielded only product type B indicating that all amine groups reacted, while samples **2a, 2b, 2a'** yielded products with mostly B type structure, as approx. 85% of additional crosslinking took place). All polymer supports proved to have a highly flexible polymer matrix as with none of them the ratio of A to B type product was lower than 1 to 1 (at least 58% additional crosslinking) and with half of the polymer supports almost all amine groups reacted.

Swelling capabilities

All prepared polymer supports were subjected to swelling tests, namely in solvents: water, methanol, dichloromethane, acetonitrile and toluene. Tests were done by measuring the volume of solvent uptake by the beads; volume of swollen beads taken after suspending 1 mL of beads in 10 mL of solvent for 24 hours. We noticed that all swellings took place rapidly as there was

no change in the volume of the swollen beads after 15 minutes and 24 hours. As expected, crosslinking degree affected swelling in all solvents, being more intense for the beads with 5% of crosslinker. The difference in swelling of 5% crosslinked beads in comparison with 20% crosslinked is between 2 and 4 fold (17,4 mL/g in dichloromethane for 5% crosslinked resin **1a**, 3.9 mL/g in dichloromethane for 20% crosslinked resin **1b**; 7.3 mL/g in dichloromethane for 5% crosslinked resin **2a**, 3.5 mL/g in dichloromethane for 20% crosslinked resin **2b**; see Table 2 and Figure 3). The type of crosslinker (DVB vs. EGDMA) had a smaller effect than the degree of crosslinking. Generally, polymers crosslinked with DVB swell to a larger extent than polymers crosslinked with EGDMA (**3a** (5%, DVB crosslinked) 5.6 mL/g in acetonitrile, polymer **3a'** (5%, EGDMA crosslinked) 4.4 mL/g in acetonitrile). Swollen volumes of beads are between 1.4 mL/g (polymer **3b'**

20% EGDMA, in water) and 17 mL/g (polymer **1a** 5% DVB, in dichloromethane). For most polymers swelling capabilities dependence on solvent was as follows: DCM, acetonitrile, toluene, methanol and water, being highest in DCM and lowest in water.

Conclusions

With an appropriate choice of reaction vessel, stirrer type and speed we were able to produce 4-nitrophenylacrylate based polymer supports crosslinked with either DVB or EGDMA. High yield of spherical particles and relatively narrow bead size distribution were achieved for the polymers with different amount of crosslinker and ratios of styrene to acrylate. All crosslinked polymers proved to have a very flexible backbone as high levels of additional crosslinking occurred after the reactions with a bifunctional amine although excess amine concentrations were used and further studies will be needed to confirm this nature of the polymers.

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Povzetek

Stirenske in 4-nitrofenilakrilatne nosilce zamrežene z divinilbenzenom ali etilen glikol dimetakrilatom smo pripravili s suspenzijsko polimerizacijo. Pri različnem razmerju monomerov in stopnji zamreženja smo analizirali porazdelitev velikosti delcev, nabrekanje v različnih topilih in fleksibilnost polimerne matrike. Ugotovili smo, da stopnja zamreženja vpliva tako na velikost delcev kot tudi na njihovo nabrekanje v različnih topilih. Povprečni premer 5% zamreženih nosilcev je v intervalu med 10 in 35 μm , premer 20% zamreženih nosilcev pa v intervalu med 35 in 55 μm . 5% zamreženi nosilci nabrekajo bolj kot 20% zamreženi, kar velja za obe zamreževali. Fleksibilnost polimerne matrike smo določili z modelno reakcijo z 1,8-diaminooktanom. Visoka stopnja dodatnega zamreženja (48 do več kot 95%) kaže na fleksibilnost polimerne matrike.

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