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Mesoporous polymer network produced from *N*-vinylpyrrolidone and triethylene glycol dimethacrylate as potential macromolecularly imprinted material and oligopeptide carrier

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Experimental

Table of Contents

Materials and methods

N-vinylpyrrolidone monomer (VP, Alfa Aesar) was distilled in vacuum to remove the NaOH inhibitor. Triethylene glycol dimethacrylate (TEGDM, Aldrich) as comonomer and 1-decanethiol (DT, Alfa Aesar) as a chain-transfer agent were used without additional purification.

Synthesis of the nonporous and porous network copolymers

The nonporous network copolymer was obtained by the 3D radical bulk polymerization initiated by AIBN (0.2 wt%) at 60 °C. The VP–TEGDM monomer mixture (40 : 60, w/w) was placed in 3 mm diameter glass ampoules, evacuated, and sealed. This network was shaped as a monolithic (block) sample with a diameter of 2.5 mm.

The branched copolymer (20 wt%) was dissolved in the VP–TEGDM monomer mixture (40 : 60, w/w). The obtained monomer–polymer mixture was placed in 3 mm diameter glass ampoules, evacuated and sealed. The 3D radical bulk polymerization initiated by AIBN (0.2 wt%) was performed in the presence of the branched copolymer at 60 °C. A copolymer composite was obtained.

The sol–gel analysis of the copolymer composite with the ultimate conversion of C=C bonds was performed on a Soxhlet apparatus for 5 h at the boiling temperature of solvent (isopropanol). After extraction of soluble products, a densely cross-linked copolymer with a diameter of 2.5 mm was obtained. It was dried to a constant weight under vacuum.

Synthesis of the branched copolymer

The branched copolymer of VP and TEGDM was obtained by 3D radical copolymerization at a molar ratio of [VP] : [TEGDM] : [DT] = 100 : 12 : 12 in toluene (75 vol%). After copolymerization, the high-molecular-weight fraction was isolated from the mixture by precipitation in a tenfold excess of hexane. The copolymer was dried to a constant weight under vacuum to remove toluene and hexane.

The MTII sorption–desorption by polymer matrices I and II from aqueous solutions

Sorption of MTII was carried out by the mesoporous network copolymer and a control sample – the network copolymer obtained without branched copolymer. The samples were kept in water at room temperature (22 °C) for 10 days to wash out the branched copolymer completely, and were dried to a constant weight in air. Then, mesoporous and nonporous copolymers with a mass of ~0.1 g were placed in the aqueous solution of MTII with the concentration of 7.8×10^{-4} м. The change in optical density of the absorption band of MTII at the wavelength of ~280 nm was observed using a ‘SPEKS SPP-705-1’ spectrometer and the dependences of MTII sorption–desorption on time were plotted. The values of sorption and desorption were calculated by the following formulae:

$$S_{\mathrm{sorb}} = (\Delta D_{\mathrm{sorb}}/D_0)\times100\%,$$

where ΔD_{sorb} is the optical density of the solution when the polymer matrix is saturated with the MTII at a given time, D_0 is the optical density of the initial MTII solution, and

$$S_{\mathrm{des}} = D_{\mathrm{des}} / \Delta D_{\mathrm{sorb}} \times 100\%,$$

where ΔD_{sorb} is the difference in optical density of MTII aqueous solution before and after sorption, D_{des} is the optical density of the solution appropriating desorption at a given time.

2 and 10 mm thick cuvettes were used for the sorption-desorption study.

Transmission electron microscopy

TEM image of the VP–TEGDM branched copolymer was obtained from the aqueous solution (0.1 mg ml^{-1}) using a Leo 912 AB equipment. Phosphotungstic acid was used to contrast the sample.

Dynamic light scattering

The dynamic light scattering method was used to determine the size of scattering centers in aqueous solution of the branched copolymer at the detection angle of 90°. We used a Photocor Compact particle size analyzer (Photocor Instruments Inc., USA) equipped with the diode laser, operating at the wavelength of 654 nm. The solutions of the copolymer were previously passed through the filter with the pores of 0.45 μm in diameter. Before measuring, the vial with the solution was thermostated for *ca.* 20 min. The hydrodynamic radii R_{h} of the copolymer were calculated using the Einstein–Stokes equation

$$D = {k \times T}\Big/{6 \times \pi \times \eta \times R},$$

where D is the diffusion coefficient, k is the Boltzmann constant, T is the absolute temperature, and η is the viscosity of the medium, in which the dispersed particles are suspended.

Quantum chemical calculations

The calculations were carried out within the framework of the density functional theory (DFT) with full optimization of the geometry of the molecule (tpssh / 6-31G*) using the Gaussian 09 program.[S1]

According to the calculation results, there are no imaginary oscillation frequencies, all the optimized structure corresponds to the minimal potential energy.

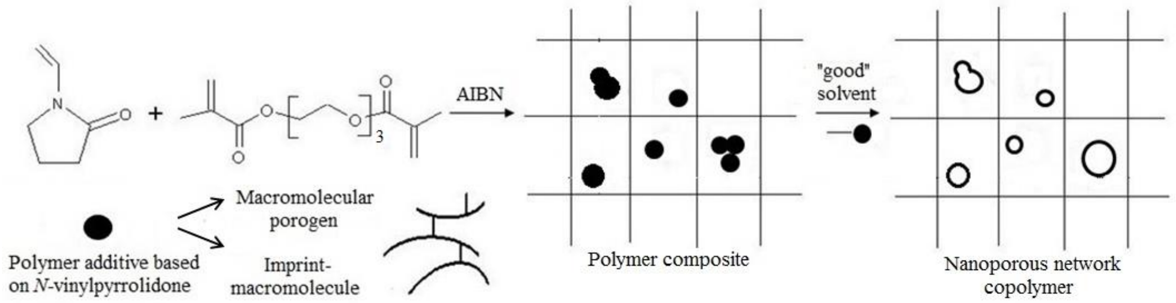
The BET analysis

Previously, the porous structure was evacuated at ca. 100 °C and investigated by low temperature nitrogen adsorption on an ‘Autosorb-1’ analyzer (Quantachome Instruments corp., USA). The specific surface area (S_{sp}) of the networks is determined using the Brunauer–Emmett–Teller (BET) equation:

$$\frac{1}{W\times\left[\left(P_0/P\right)-1\right]}=\frac{1}{W_{\max}\times C}+\frac{C-1}{W_{\max}\times C}\times\left(P/P_0\right),$$

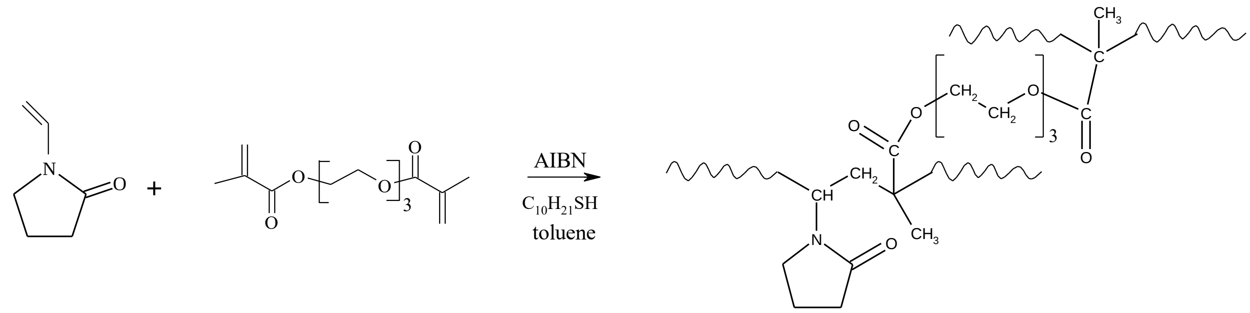
where P is the nitrogen pressure in the sample cell, P_0 is the saturated nitrogen vapor pressure at 77 K, W is the weight of nitrogen absorbed at a given value of P/P_0, W_m is the weight of the adsorbate in the surface monolayer, C is the parameter of the BET equation characterizing the adsorbent–adsorbate interaction. The value of the total pore volume V_p was determined by measuring the amount of nitrogen adsorbed at the value of P/P_0 close to 1. The pore size distribution curves were plotted using the Barrett, Joyner, and Halenda (BJH) method.[S2] The error in V_p and S_{sp} values determination did not exceed 7%.

Preparation of the polymer matrix I



Scheme S1 Preparation of polymer matrix I by non-covalent macromolecular imprinting. The branched copolymer as a macromolecular porogen and a protein imprint model.

Synthesis of the branched copolymer



Scheme S2 Synthesis of the branched VP–TEGDM copolymer by radical copolymerization in toluene in the presence of a chain transfer agent.

Table S1 The molar composition, average molecular weight, polydispersity, glass transition temperature and hydrodynamic radius of the branched copolymer.

Composition (mol%)	$M_w \times 10^{-3}$	P	T_g/°C	$R_h{}^a$/nm
80.5 : 12.4 : 7.1	20.0	1.8	53.8	4

[a] 1% copolymer solution in isopropyl alcohol at 25 °C.

TEM image of the branched VP–TEGDM copolymer

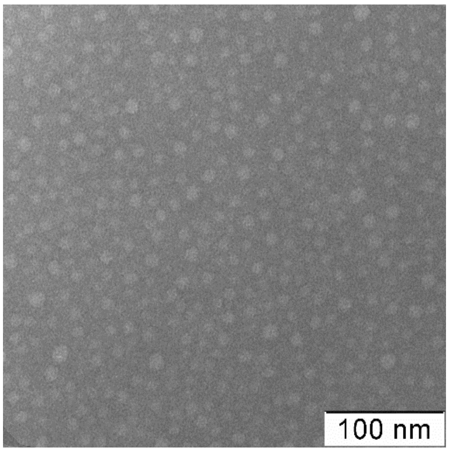


Figure S1 TEM image of the branched VP–TEGDM copolymer.

DLS curve of the branched VP–TEGDM copolymer

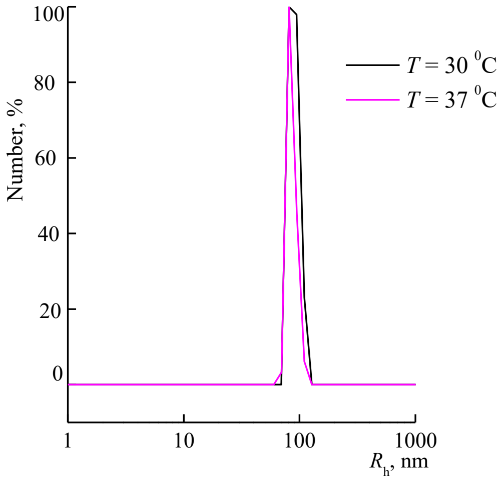


Figure S2 DLS curve of the branched VP–TEGDM copolymer in the aqueous solution at various temperatures.

Absorption spectrum of the aqueous MTII solution

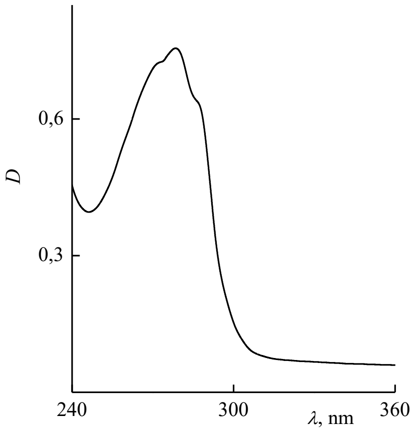


Figure S3 Absorption spectrum of the aqueous MTII solution with the concentration of 7.8×10^{-4} M at 25 °C.

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S2 S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area and Porosity*, Academic Press, New York, 1982.