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ScienceDirect
Mendeleev Commun., 2014, **24**, 125–127
Mendeleev Communications

Promising macromolecular nanoobjects for the template synthesis of network copolymers with mesoporous structures

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DOI: 10.1016/j.mencom.2014.03.021

The copolymer of *N*-vinylpyrrolidinone with a branched topology was proposed as a promising blowing agent to produce mesoporous network copolymers.

Polymeric materials with controlled pore structures have numerous practical applications including the separation, storage and transport of guest molecules. According to the IUPAC classification, porous materials are divided into the following groups:[1] macroporous materials with pore widths greater than 50 nm; mesoporous ones – between 2 and 50 nm; and microporous materials with diameter $d < 2$ nm. The term 'nanoporous' refers to micro- and mesoporous materials.[2] The specific surface area (S_{sp}) accessible to interactions with gases and liquids can be very high, *e.g.*, $S_{sp} > 1000$ m^2 g^{-1} in microporous polymers.[2] These polymer networks usually contain meso- and macropores. Different classes of nanoporous polymer networks and methods for their preparation have been reviewed.[2]

Polymeric materials with stable meso- and macroporous structures can be prepared by the three-dimensional radical (co)polymerization of mono- and divinyl monomers in the presence of 'poor' solvents as blowing agents.[3] Another approach is based on the use of templates as blowing agents such as organic gels,[4] polystyrenes modified by vinylpyrrolidinone and carboxyl groups[5] and silica particles.[6] After curing monomer-template compositions, the additives are removed to form stable pores in network polymers. A combination of inorganic particles and organic solvents such as propan-1-ol or butane-1,4-diol[7] results in a uniform pore sizes distribution owing to micro-, meso- and macropores.

Dendritic polymers as templates are promising to produce nanoporous polymeric materials.[8–10] However, their synthesis and isolation are difficult to perform, and these polymers should be often functionalized by special groups for compatibility with different monomers.

The copolymers based on vinyl monomers with a branched topology can also be candidates for producing a network polymer with a controlled porous structure. The size and topology of macromolecules and their surface chemistry can be easily varied by changing vinyl monomer, chain transfer agent ratio, branch unit structure and polymerization conditions.[11] Monomers bearing OH, COOH and COOR groups can be chemically modified after polymerization.

The goal of this work was to study the copolymer of *N*-vinylpyrrolidinone (VP) and triethylene glycol dimethacrylate (TEGDM) with a branched topology as a template with blowing agent function for the synthesis of a network copolymer. As a template, we used an amphiphilic copolymer of VP (**1**) obtained by the radical copolymerization of a mixture with the molar ratio [VP] : [TEGDM] : [DT] = 100 : 12 : 12 in toluene, where TEGDM (Aldrich) and DT – decane-1-thiol (Alfa Aesar) were branching and chain transfer agents, respectively.[12] The latter restricted the growth of polymer chains to prevent their cross-linking and to produce a branched copolymer. Copolymer **1** with the physicochemical parameters† M_w = 21 100, $[\eta]$ = 0.09 dl g^{-1} and T_g = = 63.3 °C contains branches as a result of the participation of the pendant double bonds of bifunctional comonomer TEGDM in the reactions of the growth and branching. The branched character of copolymer **1** was established previously.[12] Copolymer **1** can serve as a multifunctional macromonomer[13,14] to participate in VP and TEGDM free radical copolymerization due to the presence of unreacted double bonds (0.56×10^{-3} mol g^{-1}).

According to IR-spectroscopic data,[12] the polymer chains consist of 0.67 and 0.33 mole fractions of hydrophilic VP and hydrophobic methacrylate units, respectively. Copolymer **1** is entirely soluble in chloroform, isopropanol and *N*-methylpyrrolidone. High content of VP units in the polymer chains provides its solubility in the vinyl monomer. In spite of the presence of methacrylic units in polymer chains, copolymer **1** is not soluble in dimethacrylate. When the [VP] : [TEGDM] ratio is 20 : 80 wt%, only 20 wt% copolymer **1** dissolved in this mixture. At such mono- and multifunctional monomer ratio, we obtained the final network copolymer with high degrees of cross-linking and conversion of the C=C bonds.

The VP–TEGDM (20 : 80 wt%) reaction mixtures with 10 and 20 wt% copolymer **1** were viscous liquids without an interphase boundary. However, despite visual optical transparency and the absence of the interphase boundary, the monomer–polymer mixture is still a heterogeneous system, namely, a colloidal solution of copolymer **1** particles. Light scattering from the monomer–polymer reaction mixture was observed (the Tyndall effect).

Upon the bulk polymerization‡ of monomer–polymer mixtures, monolithic glassy network copolymers **2**–**4** with known conversions§ were obtained. Copolymers **3** and **4**, unlike **2**, have opalescence characteristics, indicating the presence of scattering

† MWD was measured by gel permeation chromatography; the intrinsic viscosity was measured using a VPZh viscometer; T_g was measured in two or three cycles of heating–cooling from 0 to 150 °C on a Mettler Toledo differential scanning calorimeter at a heating rate of 5 K min^{-1}. The C=C bond concentration was determined by ozonolysis.

‡ Initiator AIBN (0.2 wt%) was added into the VP–TEGDM mixture containing 0, 10 or 20 wt% copolymer **1**. The reaction mixtures were placed in glass ampoules, which were evacuated and sealed. The cross-linking bulk radical polymerization was carried out at 60 °C.

§ The conversion of C=C bonds in network copolymers **2**–**4** was determined by IR spectroscopy. The oil suspension of samples was prepared and the spectra were recorded between KBr plates using a Specord 75IR spectrophotometer. The conversion of C=C bonds in final network copolymers is ~98%.

centres. The optical heterogeneity of final network copolymers increased with the content of copolymer **1**. Changes in the optical properties of network copolymers **3** and **4** are apparently associated with phase separation induced by cross-linking radical copolymerization. As a result, the aggregated macromolecules of **1** separate in certain areas, evenly distributed over the network copolymer volume.

Network copolymers **2**–**4** were treated with isopropanol.¶ The solvent was chosen due to its high thermodynamic compatibility to copolymer **1**. The structure of the soluble part (sol fraction) was analyzed by IR spectroscopy. Sol fraction isolated from copolymer **2** represents VP homopolymer; C=O groups of its lactam ring are associated with the solvent OH groups by hydrogen bonding. Its appearance in the product of cross-linking radical copolymerization of VP and TEGDM is caused by different reactivity of the comonomers.[11] Sol fractions isolated from copolymers **3** and **4** consist of copolymer **1**. The main absorption bands in the IR spectra of copolymer **1** and the sol fraction coincide; the IR spectrum of the sol fraction has a characteristic absorption band due to the C=O group of methacrylic units. It cannot be excluded that the sol fraction also contains VP homopolymer formed during the cross-linking radical copolymerization of VP and TEGDM. According to gravimetric data, the total weight of sol and gel fractions, namely, the insoluble part of copolymers in all experiments was higher than the weight of the original sample by 10–20%. Apparently, the solvent bonded to the polymer chains due to intermolecular interactions remains in the copolymer. This assumption is supported by an analysis of the IR spectra of the sol fraction: intense absorption bands corresponding to the stretching vibrations of the OH groups at 3000–3400 cm^{-1} are present, while the absorption bands at 1040 and 1110 cm^{-1} are related to the C–O bond vibrations. The absorption band of the C=O group of a lactam ring is shifted from 1680 to 1670 cm^{-1} owing to hydrogen bonding with the solvent OH groups.

After the extraction of copolymer **1** from network copolymers **3** and **4**, the appearance of pores can be expected. It is indirectly indicated by the density of copolymers **3** and **4** measured according to a published procedure[15] before and after the extraction of copolymer **1**. The density of copolymer **3** was practically unchanged (1.22 g cm^{-3}) while the density of copolymer **4** after the extraction of template **1** decreased from 1.21 to 1.12 g cm^{-3}.

Direct proof was determined by nitrogen adsorption measured by a static volumetric method using an Autosorb-1 instrument (Quantachrome, USA).†† The adsorption–desorption curves of network copolymers **2** and **4** [Figure 1(*a*)] are different. A pronounced hysteresis in the adsorption–desorption curve [Figure 1(*a*), curve *2*] of network copolymer **4** after extraction of the template indicates its porous structure. Figure 1(*b*) shows a pore size distribution in the test network copolymer. The maximum in the distribution curve up by pores with a size of ~8 nm. Attention is

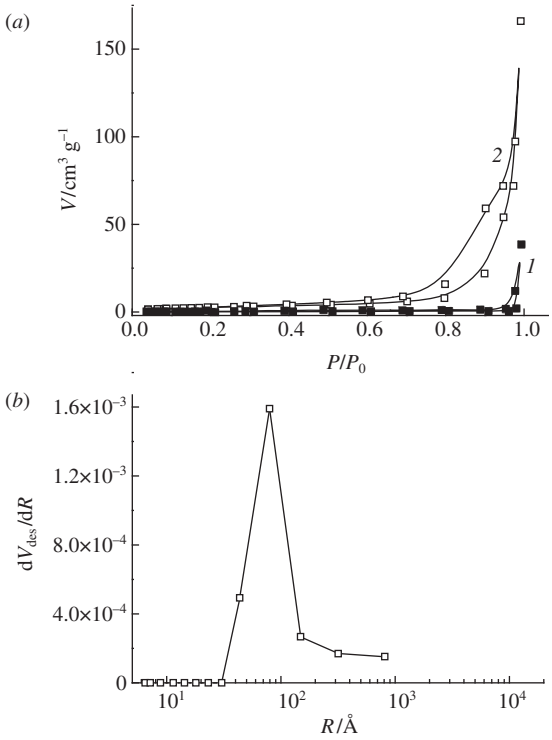

Figure 1 (*a*) Adsorption–desorption isotherms of network copolymers (*1*) **2** and (*2*) **4** after extraction, and (*b*) pore size distribution in copolymer **4**. *V* is the specific volume of nitrogen adsorbed (cm^3 g^{-1}); V_{des} is the specific volume of nitrogen desorbed (cm^3 g^{-1}) and *R* is the pore radius.

drawn to the narrow pore size distribution. Micropores are absent from network copolymer **4**. The sample contains mesopores with $d \leqslant 50$ nm and macropores. Different pore sizes in the copolymer are due to the separation of aggregated template macromolecules in phases of various sizes. Copolymer **2** had almost no porous structure ($S_{sp} < 1$ m^2 g^{-1}). The specific surface area of network copolymer **4** was higher ($S_{sp} = 9.8$ m^2 g^{-1}), and $V_{por} = 0.26$ cm^3 g^{-1}.

The porous structure of network copolymer **4** after the extraction of the template is confirmed by its end surface micrographs (Figure 2),‡‡ in which pores and channels of various sizes are clearly visible. Therefore, copolymer **1** is a blowing agent, and stable nanoscale pores appear after its removal from the polymer matrix.

Thus, a branched copolymer was proposed as a template with a blowing agent function to prepare a mesoporous network polymer of VP. Such VP–TEGDM network copolymers can be applied as the carriers of biologically active substances of prolonged action due to their amphiphilic nature, the presence of active sorption

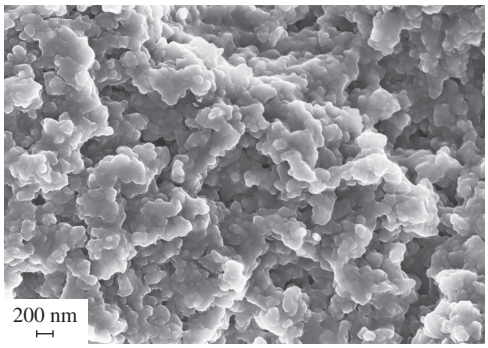

Figure 2 Surface micrograph of the VP–TEGDM copolymer after template extraction.

¶ Polymer samples were extracted with boiling isopropanol in a Soxhlet extractor for 10 h and then dried at room temperature and in a vacuum at 60 °C to constant weight.

†† The evacuated sample cell immersed in a liquid nitrogen bath ($T = 77$ K) run a certain amount of the adsorbate gas (N_2). The amount of nitrogen adsorbed and desorbed from the sample surface and in the pores was measured in equilibrium for each of the set values P/P_0 – relative pressure of nitrogen in the cell. These data we used to plot adsorption–desorption isotherms and to calculate specific surface S_{sp} using the Brunauer–Emmett–Teller equation (BET): $[W(P_0/P - 1)]^{-1} = (W_m C)^{-1} + [(C - 1)(W_m C)^{-1}](P/P_0)$, where *W* is the weight of nitrogen absorbed at given P/P_0; W_m is the weight of adsorbate at the surface monolayer (g); *C* is the parameter of BET equation describing the interaction of the adsorbent/adsorbate. The V_{por} value (the total pore volume) was determined by measuring the amount of nitrogen adsorbed at P/P_0 value close to 1, and the pore size distribution was plotted.[16] The error in the determination of V_{por} and S_{sp} did not exceed 7%.

‡‡ The electron microscopic images of the carbon-coated copolymer were obtained on a Zeiss LEO SUPRA 25 emission scanning electron microscope.

sites (N and O atoms) in the lactam ring of VP units, and nanoporous structure. The rate of releasing encapsulated low-molecular-weight compounds can be controlled by varying the physicochemical parameters of the polymer matrix (the chemical cross-linking density and porous structure) and the experimental conditions.

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Received: 27th September 2013; Com. 13/4212