

# Hydroxy functionalized porous polymer particles derived from mixtures of hydrophilic and hydrophobic monomers<sup>\*</sup>)

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**Abstract:** Porous, hydroxy functionalized, polymer particles, having BET surface areas up to 146 m<sup>2</sup>/g, were synthesized by suspension polymerization of water in oil (w/o) emulsions. The emulsions were prepared by mixing polyoxyethylene sorbitan monooleate (Tween-80) solutions in water with a mixture of 2-hydroxyethyl methacrylate (HEMA), styrene (S) and divinylbenzene (DVB) dissolved in a mixture of cyclohexanol (CyOH) and octanol (OctOH). The resulting polymer particles were characterized by optical microscopy, scanning electron microscopy, infrared spectroscopy, and thermal gravimetric analysis. Nitrogen adsorption/desorption isotherms and particle size distribution were also determined. The influence of the organic porogen nature and the concentrations of divinylbenzene and Tween-80, the fraction of water in the w/o emulsions and the agitator rotation on the properties of the provided polymer particles were analyzed and discussed.

**Keywords:** 2-hydroxyethyl methacrylate, hydroxy functionalized porous polymer particles, suspension polymerization, w/o emulsion.

## Hydroksyfunkcjonalizowane porowate cząstki polimerowe otrzymane z mieszaniny hydrofilowych i hydrofobowych monomerów

**Streszczenie:** Nowe hydroksyfunkcjonalizowane porowate cząstki polimerowe o powierzchni właściwej 146 m<sup>2</sup>/g syntetyzowano metodą polimeryzacji suspensyjnej emulsji typu woda w oleju w/o. Emulsje otrzymano w wyniku zmieszania wodnych roztworów Tween-80 z mieszaniną metakrylanu 2-hydroksyetylu (HEMA), styrenu (S) i diwinylobenzenu (DVB) rozpuszczoną w mieszaninie cykloheksanolu (CyOH) i oktanolu (OctOH). Otrzymane polimery charakteryzowano metodami mikroskopii optycznej, skaningowej mikroskopii elektronowej, spektroskopii w podczerwieni i analizy termicznej (TGA). Wyznaczono także izotermy adsorpcji/desorpcji oraz rozkład wielkości ziaren uzyskanych na drodze polimeryzacji. Przeanalizowano wpływ natury porogenu, stężenia DVB i Tween-80 na charakterystykę otrzymanych cząstek.

**Słowa kluczowe:** metakrylan 2-hydroksyetylu, hydroksyfunkcjonalizowane porowate cząstki polimerowe, polimeryzacja suspensyjna, emulsja w/o.

Spherical polymer and composite particles with diameters in the nano- to microsize range, cross-linked or not cross-linked, porous or gel type, being additionally functionalized or without any reactive groups, have found numerous applications for decades. Depending on their features, they have been utilized, for instance,

for different synthetic (as matrices in solid phase organic synthesis, scavenging resins, specific polymeric reagents and supports for catalysts, including chiral ones) [1, 2], purification, separation and analytical purposes (e.g., as ion exchange resins, specific sorbents for solid phase extraction) [2], liquid chromatography [3–9], and the removal of toxic metal ions from waste water and sewage [10]. They are also commonly used in numerous biotechnological applications, e.g., for enzyme immobilization, separation of proteins and other bioactive molecules, drug delivery, in bioimaging and medicinal diagnostics and as matrices for cell culture and transplantation [11].

Heterogeneous polymerization techniques using the immiscibility of two or more liquids are usually applied for producing spherical polymer or composite particles [12]. The most common methods are suspension, dis-

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persion and precipitation polymerizations. By combining these methods or by using other special techniques, *e.g.*, Pickering emulsions [13], membrane/microchannel emulsification [14] or microfluidic polymerizations [15], particles with more complex architectures become accessible. Modern polymerization techniques are able to deliver, for instance, core-shell [12, 16], multihollow [12, 17–19] or Janus type particles [21, 22]. Additionally, by introducing additional, reactive, functional groups to the polymer structure, one can make the resulting particles capable of chemical post-modifications. As a result, the range of applications of polymer and composite particles constantly extends to new fields.

The simplest way of introducing additional functional groups to a polymer network is through the use of vinyl monomers providing extra functionalities. 2-Hydroxyethyl methacrylate (HEMA) is one of the popular monomers yielding polymers with easily modifiable functional groups (OH) [23] and tuned hydrophilicity. HEMA copolymers have also been utilized as carriers for enzyme and protein immobilization [24], as absorbents for chromatographic applications [25], and as scavengers for removing metal ions from solution [26, 27].

Since HEMA is readily soluble in water, its hydrophilicity causes problems with the proper stabilization of the dispersed phase during the course of suspension polymerization. The problems of solubility of HEMA in the continuous aqueous phase can be solved, at least partly, by salting out this phase with NaCl and MgCl<sub>2</sub> [28] and/or using Mg(OH)<sub>2</sub> (produced *in situ* from MgCl<sub>2</sub> and NaOH) or MgO as suspension stabilizers [29–32]. Horak *et al.* [33] established that the regular spherical particles of the HEMA polymers, cross-linked with ethylene glycol dimethacrylate (EGDMA), could be prepared using mixtures of cyclohexanol with octanol, decanol or butyl acetate as diluents of the monomers and polyvinylpyrrolidone (PVP, 1 wt %) as a suspension stabilizer. Toluene [34] or cyclohexane [35] turned out to be other effective diluents for performing suspension copolymerization of HEMA with vinyl monomers.

Gel type, spherical particles of terpolymers of HEMA with styrene and divinylbenzene (DVB) or interchangeably with ethylene-, diethylene- or triethylene glycol dimethacrylate [23], and also with 1,4-butanediol or 1,6-hexanediol dimethacrylate [36], were also produced in our laboratory using a 4 : 1 w/w cyclohexanol-octanol mixture. The post-modified HEMA gels were then utilized for catalytic purposes [36].

Continuing our previous studies, we decided to modify the procedure described previously in [23] to prepare porous, hydroxyl functionalized, spherical polymer particles based on HEMA, styrene and DVB. To achieve our goal, we introduced aqueous solutions of Tween-80 (polyethylene glycol sorbitan monooleate, an emulsifier) to an organic phase composed of the monomers and the same diluent set as used previously. This makes it possible to obtain water in oil emulsions thanks to the compatibility between Tween-80 and HEMA. The emulsions

were then used as a dispersion phase for suspension polymerization. Herein, we discuss the results of the performed experiments.

## EXPERIMENTAL PART

### Materials

Chemicals: benzoyl peroxide (BPO), polyoxyethylene sorbitan monooleate (Tween-80), cyclohexanol (CyOH), octanol (OctOH) used for synthesis of the new polymer particles were commercially available from Aldrich, Merck, Fluka or Avantor and used as received, unless otherwise stated. Styrene (S, >99 % Aldrich) and divinylbenzene (DVB, 80 %, Fluka) were purified by extraction with 5 wt % NaOH in 20 wt % NaCl solution before use. 2-Hydroxyethyl methacrylate (HEMA, 97 %, Aldrich) was distilled under reduced pressure.

### Polymer particle synthesis – general procedure

The water-in-oil emulsions (w/o emulsions) used as the dispersed phase in suspension polymerization were prepared in 20 cm<sup>3</sup> vials by mixing a solution of Tween-80 in water with a solution of the monomers (HEMA, S and DVB) and BPO in an organic solvent. CyOH or OctOH alone, or their mixtures of 4:1, 2:1, 1:1, 1:2 or 1:4 (w/w) were applied as diluents for the monomers and initiator. The mixtures were stirred at 7000 rpm for 5 min using an emulsifier to obtain a series of the w/o emulsions.

The continuous phase was prepared by dissolving polyvinylpyrrolidone K90 (PVP, 2 wt %) in deionized water.

The polymerization reactions were performed under an argon atmosphere in a 250 cm<sup>3</sup> cylindrical reactor equipped with a heating coat, mechanical stirrer, reflux condenser, and a dropping funnel. The w/o emulsions prepared, as described above, were dispersed in the continuous phase at room temperature. The reaction mixture was stirred at 350 rpm (runs 1–16) or 500 rpm (run 17) for 2 hrs at 70 °C and then for 6 hrs at 80 °C. The reaction mixtures were then cooled and a washing procedure was applied to remove the diluents and any unreacted monomers from the polymer products. The reactor contents were first diluted with an excess of demineralized water. Then, the polymer particles were isolated by decanting or filtering out. Washes with water were repeated several times before transfer of the particles to a Soxhlet apparatus to extract the residuals of the monomers and diluents with acetone for 8 hrs. Finally, the polymer particles were dispersed in methanol and left in this solvent overnight. The final products were isolated by filtration and dried under a reduced pressure at 40 °C. Their yields amounted to 40–60 %.

The experimental details on the composition of the w/o emulsions and suspension polymerization conditions are presented in Table 1.

**Table 1.** Suspension polymerization conditions

Entry	Dispersed phase (w/o emulsion) composition						Emulsion stability, min
	Oil phase in w/o emulsion				Tween-80 wt %	Water to oil phase, v/v	
	Monomers, mol %			Monomer diluent			
	HEMA	DVB	S	CyOH to OctOH ratio, w/w			
1	20	3	77	1 : 4	10	10 : 90	60
2	20	6	74	1 : 4	10	10 : 90	60
3	20	10	70	1 : 4	10	10 : 90	60
4	20	15	65	1 : 4	10	10 : 90	60
5	20	40	40	1 : 4	10	10 : 90	60
6	20	10	70	1 : 2	10	10 : 90	> 120
7	20	10	70	1 : 1	10	10 : 90	> 120
8	20	10	70	2 : 1	10	10 : 90	> 120
9	20	10	70	0 : 1	10	10 : 90	60
10	20	10	70	1 : 0	10	10 : 90	> 120
11	20	10	70	1 : 4	15	10 : 90	75
12	20	10	70	1 : 4	5	10 : 90	45
13	20	10	70	1 : 4	2	10 : 90	20
14	20	10	70	1 : 4	10	5 : 95	95
15	20	10	70	1 : 4	10	20 : 80	10
16	20	10	70	1 : 4	–	–	–
17*	20	10	70	1 : 4	10	10 : 90	60

Suspension polymerization conditions: an initiator – BPO, 1 wt %; a suspension stabilizer – PVP, 2 wt %; ratio of the monomers to diluent – 1 : 1 (v/v); agitator rotation – 350 rpm, \*500 rpm.

### Methods of testing

– Analysis of the particle size distribution and their average diameters was performed using a Mastersizer 2000E instrument (Malvern Instruments Ltd.). Samples of the polymer particles were sonicated for 5 min before each measurement.

– The particle morphology was studied using a Motic SMZ-143 stereomicroscope (Motic Co.) equipped with a digital camera (NIKON Colpix 4500) and a VEGA3 scanning electron microscope (Tescan Orsay Holding).

– The adsorption-desorption isotherm of nitrogen at 77 K (-196.15 °C) was determined using a 3Flex surface area and porosity analyzer (Micrometrics) equipped with a VacPrep 061 sample preparation system (Micrometrics). The samples were degassed at 393 K (119.85 °C) under vacuum for 24 hrs (until a pressure of 0.13 Pa was reached) before performing the analyses. The specific surface area, total pore volume and micropore volumes and area were determined.

– Pore size distribution was determined based on the BET, Barret-Joyner-Halenda (BJH) and t-plot (Harkins and Jura equation) methods.

– FT-IR spectra were recorded using a Nicolet 8700 spectrometer (Thermo Scientific) and KBr pellets.

– TGA analysis was performed using a TGA/DSC 1 analyzer (Mettler Toledo). Samples of the polymers were heated from 25 to 600 °C (10 °C/min) in a nitrogen atmosphere (50 cm<sup>3</sup> N<sub>2</sub>/min).

– The emulsion stability was assessed visually by observation of the time for the breakdown of an emulsion.

### RESULTS AND DISCUSSION

To obtain porous polymer particles bearing OH groups capable of post-modifications, we decided to use emulsions obtained from the above mentioned hydrophilic (2-hydroxyethyl methacrylate) and hydrophobic monomers (styrene and divinylbenzene), cyclohexanol or octanol, or their mixtures, benzoyl peroxide (an initiator), and a water soluble emulsifier (Tween-80) (Fig. 1). It was expected that water emulsified within the monomer phase would act as an extra porogen under suspension polymerization conditions.

It is well-known that the formation of water in oil emulsions is facilitated by surfactants with a HLB factor between 3 and 6 [37]. However, this rule may not be fulfilled for multicomponent mixtures since the solubility of the particular ingredients in such systems may be different from that in binary systems of surfactant/oil or surfactant/water. The latter binary system might be expected, in particular, for systems containing components of different hydrophobicity or hydrophilicity.

Further factors influencing the emulsion formation are the ratios of water and organic phases, electrolyte concentration or temperature [37].

In our experiments, the organic phase consisting of the monomers and diluents mentioned above was used in ex-

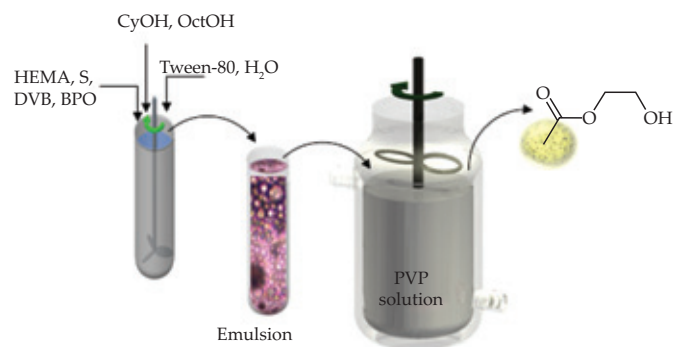


Fig. 1. General scheme of suspension polymerization of the w/o emulsions

cess in relation to the water phase. As a result, the w/o macroemulsions were obtained using a hydrophilic non-ionic surfactant, polyoxyethylene sorbitan monooleate (Tween-80, HLB = 15.0). Probably, the compatibility of polyoxyethylene moieties present in the molecules of Tween-80 with 2-hydroxyethyl methacrylate facilitated the extraction of the latter from water to the monomer solution and, as a result, the w/o macroemulsions were able to form.

The stability of the w/o emulsions depended on many factors, *e.g.*, Tween-80 concentration and amounts of water and of organic components (monomers and diluents) used in the experiments (Table 1). For instance, the system consisting of 5 wt % Tween-80, 10 vol % water and 1 : 4 w/w cyclohexanol-octanol (CyOH-OctOH) ratio (Entry 12) was stable for at least 45 min. An increase of Tween-80 quantity from 2 to 15 wt % extended the time of emulsion stability from 20 (Entry 13) to 75 min (Entry 11). Furthermore, a decrease in water fraction to 5 vol % (Entry 14) prolonged the emulsion stability above 95 min while the use of 20 vol % water (Entry 15) resulted in a dramatic reduction of the stability. An improvement in emulsion stability was also observed when the amount of cyclohexanol in relation to octanol was increased (Entries 6–8).

As mentioned, the high hydrophilicity of HEMA usually causes problems with the proper stabilization of the dispersed phase in the course of suspension polymerization. Thus, it might have been expected that the attempts of polymerization of the w/o emulsions containing this hydrophilic monomer and two other hydrophobic monomers and also organic solvents of different polarity must reveal various problems.

It was found that the ratio of the dispersed phase to the continuous one equal to 1 : 4 v/v and 1 wt % PVP, *i.e.*, the polymerization parameters applied in our previous work [23], turned out to be improper for the polymerization of the w/o emulsions obtained as described above. Particles characterized by a regular spherical shape could be obtained when the ratio of the w/o emulsion to the continuous phase and the PVP concentration were fixed to 1 : 10 v/v and 2 wt %, respectively. Experiments with two other suspension stabilizers, poly(vinyl alcohol) (PVA) and gum arabic (GA), were also performed, but they failed to yield promising results. Particles of ir-

regular non-spherical shape were mostly produced.

Different behaviors of the resulting particles were observed when the composition of the w/o emulsion was changed. The particles produced at 1 : 2 (Entry 6) and 1 : 4 w/w (Entry 3) ratios of cyclohexanol to octanol, or with octanol alone did not sink to the reactor bottom after complete polymerization when DVB was used in the amount of 10 mol % or more. A decrease in DVB concentration to 6 (Entry 2) or 3 mol % (Entry 1) resulted in the production of particles which that were classically „sinkable” in a water medium. These types of particles were also produced when an excess of cyclohexanol in the mixture with octanol (Entry 8) or cyclohexanol alone (Entry 10) were applied as a monomer diluent, independently of DVB quantity in the monomer composition.

The atypical behavior of the particles prepared using octanol alone or using mixtures containing an excess of octanol was probably caused by encapsulating large quantities of this solvent inside polymer particles in the course of the phase separation; the density of octanol at 25 °C is equal to 0.827 g/dm<sup>3</sup>. Probably, this process was promoted by the hydrophobic surfactant, Tween-80, present in the dispersed phase.

The use of CyOH and OctOH in the ratio of 1 : 1 w/w and of 10 mol % of DVB (Entry 7) resulted in the formation of “mixed type” particles. The particles prepared from the w/o emulsion consisting cyclohexanol alone or cyclohexanol in excess behaved in the classical way. They had a gel nature, similarly to the HEMA polymers described in [23], and they could be separated by sedimentation during washing with water after completed polymerization. The gel nature of the particles could be directly recognized in view of their transparency [38].

The formation of gel particles by suspension copolymerization of HEMA and ethylene glycol dimethacrylate was also observed by Horak *et al.* [33]. This finding was explained by the thermodynamic compatibility of cyclohexanol and polyHEMA. As a result, no phase separation was observed inside the particles during polymerization. Probably, the relatively high solubility of cyclohexanol in water was also a reason for the inactivity of the microdroplets of water, which were dispersed in the monomer solution with the help of Tween-80 as a porogen under suspension polymerization conditions.

It was observed that an increase in stirring rate from 350 to 500 rpm (Entry 17) intensified the mass transfer between the dispersed and continuous phase and, as a result, two types of particles, “sinkable” and “unsinkable”, were produced simultaneously, even in the presence of 1 : 4 w/w CyOH-OctOH mixture.

The photos taken with a stereomicroscope equipped with a digital camera revealed that the polymer particles increasingly became more milky with higher octanol fractions in the mixture with cyclohexanol (Fig. 2). This finding pointed to an increase in the porosity of the particles [38]. A role of octanol as an effective porogen in the preparation of the HEMA-EGDMA copolymers was

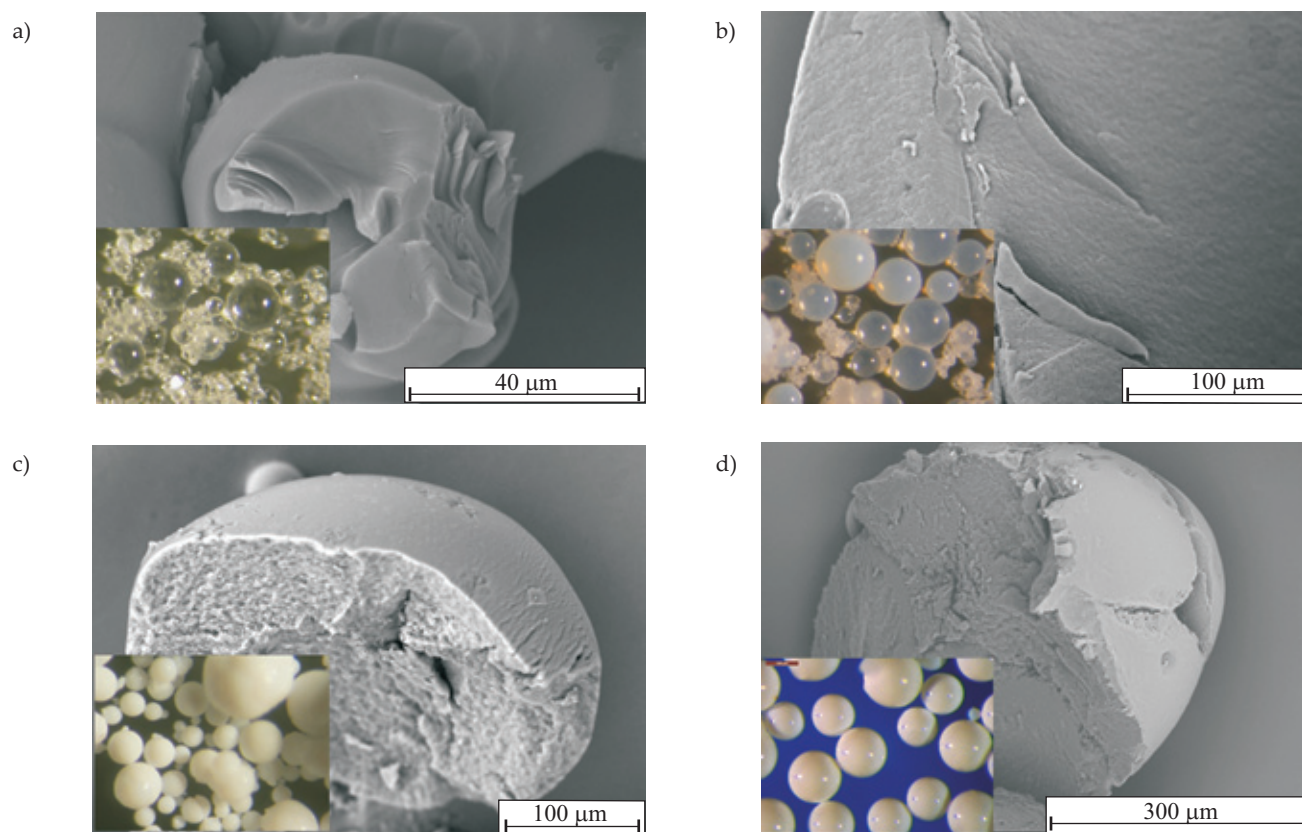


Fig. 2. The stereomicroscope photographs (small) and SEM images (large) of the polymer particles synthesized using different monomer diluents: a) CyOH, b) CyOH : OctOH 1 : 1 w/w, c) CyOH : OctOH 1 : 4 w/w, d) OctOH

also emphasized by Horak *et al.* [33]. They observed an increase in particle porosity when the amount of octanol in the diluent mixture was increased.

Based on the optical microphotographs, a tendency to agglomerate smaller particles could be concluded, in particular when cyclohexanol was used in excess.

The morphology of the polymer particles was also studied using scanning electron microscopy (Fig. 2). The SEM images showed the glassy nature of the particles obtained using 3 mol % DVB (Fig. 2a) typical for the weakly cross-linked gels. This finding corresponds to the conclusion resulting from the optical microphotographs. The surface of the particles became rougher and rougher with a diminished quantity of octanol in the diluent mixture. This corresponded with the „milky” appearance of the particles observed using an optical stereomicroscope.

FT-IR spectra recorded for the synthesized particles proved that the terpolymerization of HEMA, S and DVB occurred under the applied reaction conditions. The absorption bands at the ranges characteristic of hydroxyl ( $\nu_{\text{OH}} - 3450 \text{ cm}^{-1}$ ) and ester groups ( $\nu_{\text{C=O}} - 1727 \text{ cm}^{-1}$  and  $\nu_{\text{C-O}} - 1020 \text{ cm}^{-1}$ ), on the one hand, and aliphatic and aromatic hydrocarbon groups ( $\nu_{\text{C-H}} - 3080-2850 \text{ cm}^{-1}$  and  $\delta_{\text{C-H}} - 1600-1450 \text{ cm}^{-1}$ ), on the other hand, were observed in the obtained spectra.

The measurements of particle size distribution using a laser particle size analyzer revealed that the polymer

particles characterized by the greatest size dispersity were produced using cyclohexanol or octanol alone (Table 2, Fig. 3a). No logical dependence between the particle size distribution and the ratio of cyclohexanol and octanol was observed when the mixed monomer diluents were used, and in the case of experiments performed using different quantity of water in w/o emulsions. The dispersity of the particles increased with decreasing concentrations of Tween-80 (Fig. 3b) and decreased with a smaller quantity of the cross-linking monomer (DVB) (Fig. 3c). The dispersity of the polymer particles depended strongly on the applied stirrer rotation rate. An increase in the rate from 350 to 500 rpm resulted in a clear reduction of particle dispersity (Fig. 3d). The size of the particles, however, was then reduced as well.

The amount of water in the w/o emulsion only slightly influenced the particle size distribution and the average particle size (Fig. 3e).

The nitrogen adsorption-desorption isotherms of the particles were also studied. Figure 4 presents the isotherms obtained for the polymer particles prepared using different diluent compositions. The isotherms of type II, characteristic of nonporous or macroporous solids according to the IUPAC classification [39], were collected for the particles obtained using octanol alone or for the emulsions consisting of octanol in excess. The shape of the hysteresis loops in these cases indicated the presence of slit pores within the particles.

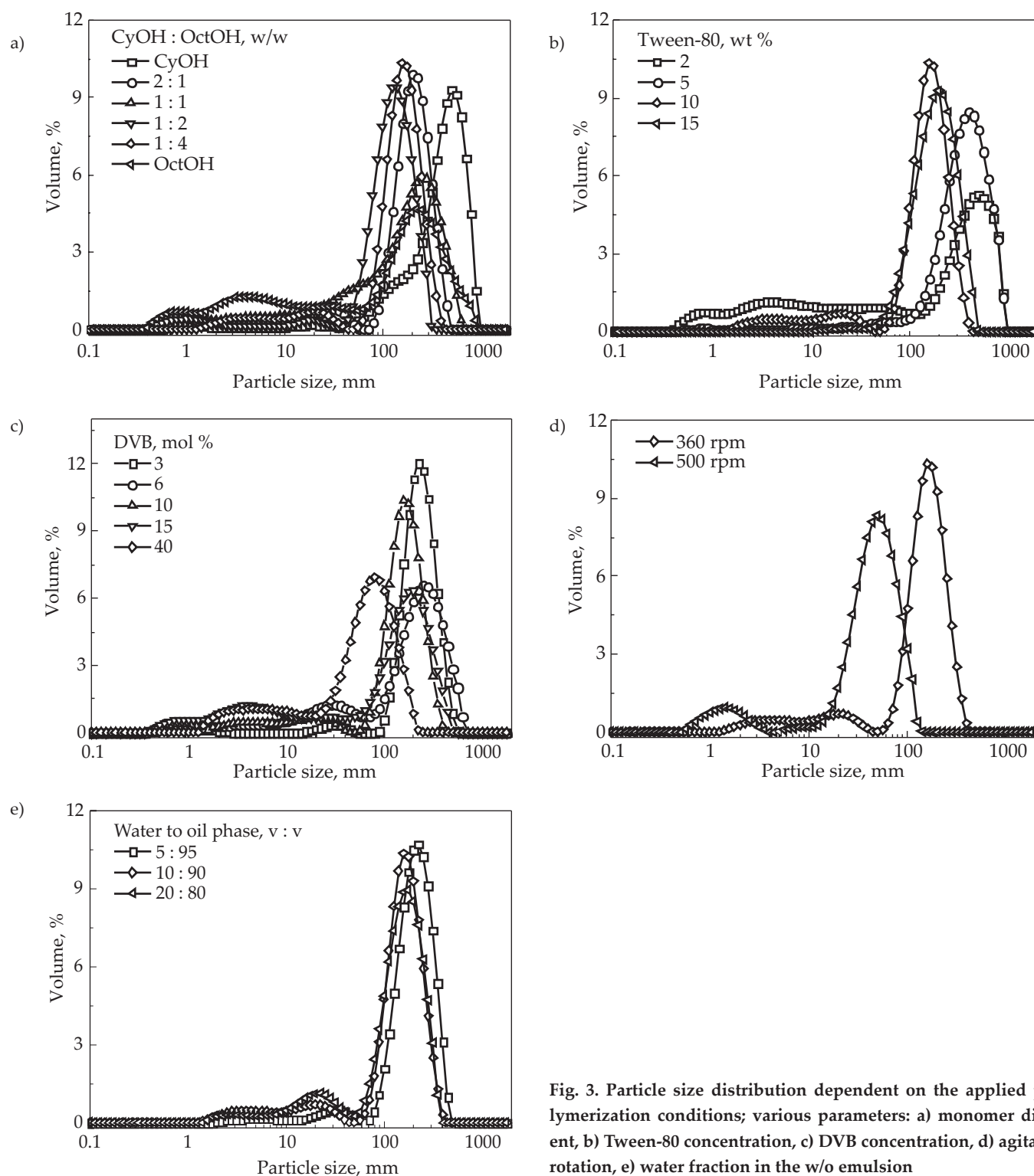


Fig. 3. Particle size distribution dependent on the applied polymerization conditions; various parameters: a) monomer diluent, b) Tween-80 concentration, c) DVB concentration, d) agitator rotation, e) water fraction in the w/o emulsion

The results of the performed measurements proved that the porosity of the particles increased with higher fractions of octanol in the diluent mixture (Table 2). As a result, the BET surface area ( $S_{\text{BET}}$ ) of the particles increased from 0.4  $\text{m}^2/\text{g}$  for 1 : 1 w/w CyOH : OctOH ratio to 47.3  $\text{m}^2/\text{g}$  for the ratio of 1 : 4. At the same time, the BJH adsorption cumulative volume of the pores ( $V_p$ ) increased dramatically. Furthermore, an increase in the BJH adsorption average pore diameter ( $D_p$ ) could also

be observed when octanol was used in excess. However, the use octanol alone did not result in a further increase in  $S_{\text{BET}}$  and, quite the opposite, caused its lowering to 33.6  $\text{m}^2/\text{g}$ . Simultaneously, the average pore diameter decreased by about three times, from 17 to 5.2 nm.

Figure 5 presents the pore size distributions observed for the particles prepared using different diluent compositions. Similar profiles of the distribution could be observed for particles obtained using an excess of octanol or

Table 2. Characteristics of the provided polymer particle

Entry	Particle size, $\mu\text{m}$			Major fraction		$S_{\text{BET}}$ $\text{m}^2/\text{g}$	$D_p$ nm	$V_p$ $\text{cm}^3/\text{g}$
	min	max	average	diameter range $\mu\text{m}$	vol. %			
1	0.4	632	238	89–632	95.4	–	–	–
2	0.4	710	206	71–710	73.7	–	–	–
3	1.6	448	162	56–448	87.3	47.3	17.0	0.158
4	0.4	564	140	56–564	69.5	70.1	17.2	0.254
5	1.4	252	67	20–252	80.1	146	7.9	0.289
6	0.4	356	131	45–356	91	7.7	21.3	0.046
7	0.4	710	175	100–710	67.4	0.4	5.8	$3 \cdot 10^{-4}$
8	0.4	564	200	80–564	80	–	–	–
9	0.4	1002	149	64–1002	62.9	33.6	5.2	0.020
10	0.7	1002	436	112–1002	91.3	–	–	–
11	1.8	1002	215	32–503	74.2	34.2	16.8	0.159
12	0.5	1002	382	100–1002	92.9	38.0	14.3	0.152
13	0.4	1002	246	105–1002	58.6	–	–	–
14	2.2	502	217	71–502	94	25.1	5.2	0.015
15	1.8	399	157	50–399	84.8	17.7	5.2	0.010
16	400	> 1000	–	–	100	–	–	–
17*)	0.6	159	48	10–159	90	18.6	21.1	0.110

\*) Agitator rotation – 500 rpm.

octanol alone. The measurements of nitrogen adsorption-desorption isotherms revealed the presence of micro-, meso- and macropores inside the particles. A different profile of the pore size distribution was found for the particles obtained using 1 : 1 w/w CyOH : OctOH ratio.

A decrease in the volume fraction of water in the dispersed phase from 10 to 5 % resulted in lowering the BET surface area from 44.6 to 25.1  $\text{m}^2/\text{g}$ . At the same time, the volume ( $V_p$ ) and diameter ( $D_p$ ) of the pores decreased about ten and threefold, respectively. These findings seem to prove that water molecules dispersed in the monomer solution took part in creating the porous struc-

ture of the polymer particles. It was also found that the increase of water fraction from 10 to 20 vol % resulted in lowering  $S_{\text{BET}}$  (even below the value observed for 5 vol %),  $V_p$  (from 0.158 to 0.010  $\text{cm}^3/\text{g}$ ) and  $D_p$  (from 17.0 to 5.2 nm). Probably, too much water in the dispersed phase resulted in transferring hydrophilic organic components, HEMA and cyclohexanol, to the continuous phase and, in consequence, may have changed the suspension polymerization conditions. The relatively high solubility of cyclohexanol in water during suspension polymerization was reported by Horak *et al.* [33]. Despite the noted changes in  $S_{\text{BET}}$ ,  $V_p$  and  $D_p$ , the observed profiles of the particle size

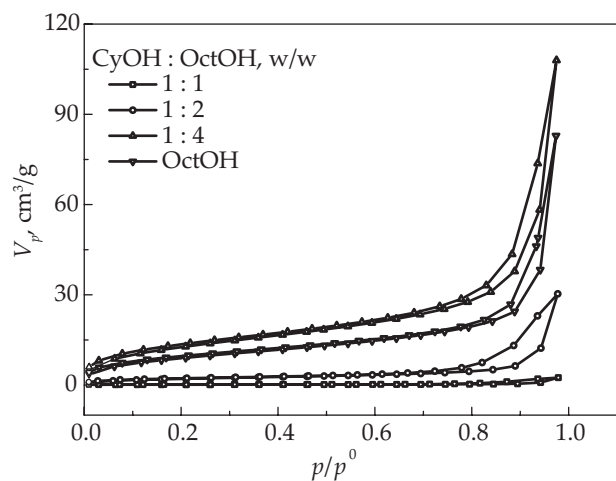


Fig. 4. Nitrogen adsorption-desorption isotherms dependent on the composition of the monomer diluents

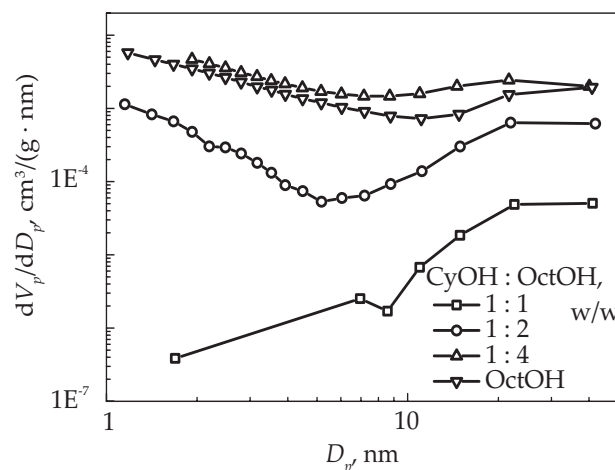


Fig. 5. Pore size distribution dependent on the composition of the monomer diluents

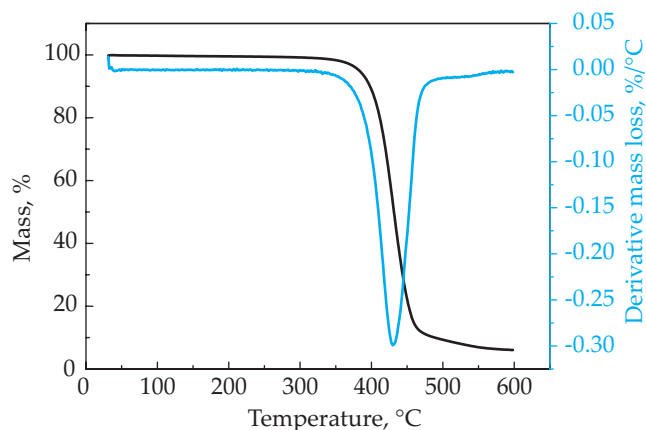


Fig. 6. TGA thermal curves recorded for terpolymer 20 % HEMA – 10 % DVB – 70 % S (Entry 3)

distribution remained very similar, independently of the initial quantity of water in the dispersed phase.

The use of cyclohexanol in excess resulted in the formation of gel type polymer particles.

The BET surface area of the particles increased about four times after increasing the DVB fraction in the monomer mixture from 10 to 40 mol %. Simultaneously,  $V_p$  increased by about two times and  $D_p$  decreased by half.

No significant influence of the concentration of Tween-80 on the values of  $S_{BET}$ ,  $V_p$  and  $D_p$  was observed, however, 2 wt % of Tween-80 turned out to be insufficient to achieve a spherical shape of polymer particles during suspension polymerization.

The effect of the stirring rate on  $S_{BET}$  and  $V_p$  values was also noted. An increase in rotation from 350 to 500 rpm resulted in decreasing the latter parameters by about 2.5 and 1.5 times, respectively. Simultaneously, the average pore size ( $D_p$ ) increased by more than 20 %.

The thermal stability of the polymer particles was analyzed. The polymer samples were heated to 600 °C under a nitrogen atmosphere. No degradation was observed up to about 300 °C. The maximal degradation rate of the particles was noted at 430 °C (Fig. 6).

To check the accessibility of OH groups inside the porous particles for potential post modifications, selected polymer samples were treated with phenyl chloroformate in  $\text{CH}_2\text{Cl}_2$  at ambient temperature for 24 hrs, similarly as done in the case of the gel type HEMA resins in our previous work [23]. The changes in the FT-IR spectra in the ranges of OH and C=O stretches proved that the OH groups were able to react with phenyl chloroformate, thus yielding carbonates (Fig. 7). The formation of the carbonate moieties resulted in a lower intensity of the absorption band at  $3450\text{ cm}^{-1}$  ( $\nu_{\text{OH}}$ ) and the appearance of a new band at  $1769\text{ cm}^{-1}$  ( $\nu_{\text{C=O}}$  carbonates).

Using a method described previously [23], the loading of hydroxyl groups introduced with HEMA moieties to the polymer particles in the course of the suspension po-

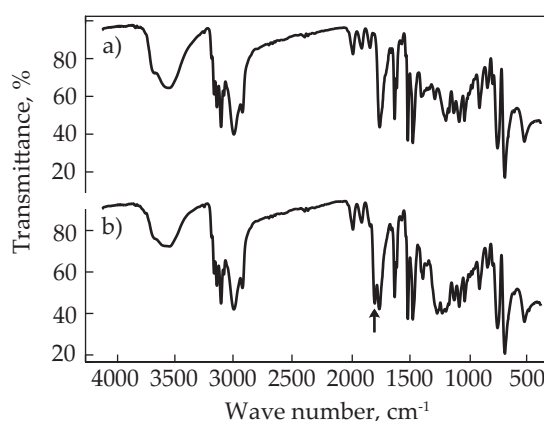


Fig. 7. Comparison of the FT-IR spectra of: a) 20 % HEMA – 10 % DVB – 70 % S (Entry 6), b) the product of its modification with phenyl chloroformate

lymerization of the w/o emulsion consisting of the mixture of 20 mol % HEMA, 70 mol % S and 10 mol % DVB was assessed. Loading amounted to about 1.5 mmol/g.

The possibility of chemical post modification of the porous HEMA particles and the number of modifiable OH groups make the obtained polymer particles interesting from the point of view of their further potential applications, for instance, as supports for transition metal ion catalysts or as chromatographic sorbents.

## CONCLUSION

A new synthetic route leading to porous hydroxyl functionalized polymer particles, based on the compositions of hydrophilic (HEMA) and hydrophobic (S and DVB) monomers and solvents of different polarity (cyclohexanol and octanol) was developed. The w/o emulsion composed of the monomers and diluents mentioned above and water solutions of Tween-80 was used as a dispersed phase in suspension polymerization instead of the classical monomer phase. By tuning the w/o emulsion composition, porous polymer particles were obtained, which are characterized by the BET surface area equal to  $146\text{ m}^2/\text{g}$  and by particle diameters in the range of 20–250  $\mu\text{m}$  (80 %).

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