



Role of aliphatic hydrocarbon content in non-solvating porogens toward porosity of cross-linked microbeads



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ABSTRACT

Megaporous spherical acrylate copolymer beads were synthesized by suspension polymerization using non-solvating porogens. Non-solvating porogens with higher aliphatic hydrocarbon content generated megaporous morphology with lower surface area. Surface area increased and inversely megaporosity was decreased with decrease in the aliphatic hydrocarbon content of porogen. Megaporosity (5.47 μm) and pore volume of 5.52 cm^3/g was obtained with n-decanol. Thermal property of copolymer is a function of type (rigidity/flexibility/elemental composition) and concentration (cross-link density) of monomer and cross-linker. Copolymer containing rigid cross-linker (divinylbenzene) had better thermal stability over copolymer with flexible cross-linker (ethylene dimethacrylate). Further, higher concentration of rigid cross-linker or lower concentration of flexible cross-linker enhanced the thermal stability. Porous polymers are potentially recognized as a solid support for solid-phase synthesis.

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1. Introduction

Porous polymers have generated increased commercial attention in the past 2 decades due to their applications in the fields of enzyme immobilization, catalysis, adsorbents, chromatography, and separation science [1,2]. The porous properties such as surface area, pore volume, pore size, and morphology of polymers depend on the various physico-chemical parameters such as monomer, porogen, cross-link density (CLD), stirring speed, and polymerization temperature [3,4]. Different porogens such as organic solvents, inorganic and polymeric materials are examined to obtain porous materials [5]. In general, organic porogens are low molecular weight solvents, inorganic porogens are solutions of potassium chloride, sodium chloride, and sodium bicarbonate [6], whereas homopolymer like polyethylene glycol or polypropylene of different molecular weight are used as polymeric porogen.

In 2012, Rahman et al. [7] reported that toluene–n-heptane as a non-solvating porogen in terpolymer synthesis wherein pore volume and pore size increased with concentration of porogen. Aliphatic alcohols with carbon number ranging from 4 to 12 are known as hydrophobic porogens [8]. Hydrophobicity of the porogen substantially affects the properties like surface area, pore

volume, and pore size of the beaded microsphere. Indeed, large pore volume (megaporous) and small surface area is the characteristic property of the non-solvating porogens [9]. Porous polymers have advantages over other porous material like silica or zeolites. Zeolite has the greater density, is brittle, and more expensive than porous organic polymers [10]. Macro and megaporous copolymer beads have potential applications in solid-phase synthesis [11], solid-phase extraction [12], combinatorial chemistry [13], and mostly for immobilization of an enzyme which can be used for organic synthesis, functional group transformation [14,15], chiral resolution [16], and ring opening polymerization [17]. Different types of immobilization techniques such as covalent, ionic, adsorption, and entrapment are available to anchor the enzymes [18]. However, entrapment and adsorption techniques are widely used due to large structure property of an enzyme. Thus, porous material containing more pores and greater pore volume are the better candidates for entrapment of enzymes.

Recently, Todorovic et al. [19] synthesized a methyl methacrylate copolymer for enzyme immobilization. They reported the highest pore volume of 3.25 cm^3/g . In 2007, Chen et al. [20] showed the pore size of polystyrene in the range of 0.03–0.1 μm for *Candida Antarctica* Lipase B (CALB) adsorption. In this study, non-solvating porogens i.e. cyclohexanol, n-octanol, and n-decanol were examined to obtain megaporous beaded copolymers. We have obtained much higher porosity (megaporous) with acrylate copolymer using a single non-solvating porogen.

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2. Experimental section

2.1. Materials

Ethylene dimethacrylate (98%) and divinylbenzene (85%) were procured from Sigma–Aldrich, India; azobisisobutyronitrile (99%) was purchased from SAS Chemicals, Mumbai, India, and poly(vinylpyrrolidone) K90 powder (PVP, mol. wt.: 360,000 g/mol) was procured from Fluka, USA. Methyl methacrylate (99%), cyclohexanol (99%), n-octanol (99%), n-decanol (99%), methanol (99.8%), and acetone (99.5%) were procured from Loba Chemie, India. All chemicals were used as received.

2.2. Synthesis of copolymers by suspension polymerization

The aqueous phase was prepared by dissolving the protective colloid poly(vinylpyrrolidone) in deionized water (1 wt%). Moreover, organic phase was prepared by mixing monomer (MMA), cross-linker (EDMA/DVB), initiator (AIBN), and pore generating solvent (cyclohexanol/n-octanol/n-decanol) in a nitrogen atmosphere at room temperature. Copolymer synthesis was conducted in a double-walled cylindrical glass reactor. The reactor was equipped with a thermostat, mechanical stirrer, and a condenser. The prepared aqueous phase was added to the reactor as a continuous phase. Subsequently, the prepared organic (discontinuous) phase was slowly added to the reactor containing aqueous (continuous) phase with continuous stirring at 300 rpm under nitrogen atmosphere. The reaction temperature was raised to 70 °C and maintained for 3 h. Thus, copolymer beads obtained were thoroughly washed with water, methanol, and finally with acetone. These beads were dried at 60 °C under reduced pressure. The copolymers obtained by suspension polymerization were further purified by soxhlet extractor [21]. Poly(MMA-co-EDMA) and poly(MMA-co-DVB) of differing cross-link densities (CLDs) were synthesized. Poly(MMA-co-EDMA) obtained were abbreviated as **MEC** (MMA–EDMA–cyclohexanol), **MEO** (MMA–EDMA–n-octanol), and **MEDe** (MMA–EDMA–n-decanol) series. Poly(MMA-co-DVB) series were abbreviated as **MDC** (MMA–DVB–cyclohexanol), **MDO** (MMA–DVB–n-octanol), and **MDDe** (MMA–DVB–n-decanol). The CLD defines the percent moles of cross-linking agent (ethylene dimethacrylate/divinylbenzene) relative to the moles of methyl methacrylate. Monomer-cross-linker feed composition of poly(MMA-co-EDMA) and poly(MMA-co-DVB) at different CLDs and reaction conditions are reported in Table 1.

2.3. Characterisation

Synthesis of copolymers was confirmed by FT-IR spectrometer (Perkin Elmer, USA). The sample was mixed with potassium bromide (KBr) to make pellets for FT-IR study. Surface area of copolymer beads was determined using a surface area analyzer (NOVA 2000e Quantachrome instruments, Boynton, FL-33426) by BET (nitrogen adsorption) method. Pore volume and pore size was

determined by a mercury porosimetry (Quantachrome, automated mercury intrusion porosimeter, PM-60-7). Mercury porosimetry was carried out for the samples of poly(MMA-co-EDMA) and poly(MMA-co-DVB) for 100% CLD. However, samples dried at 80 °C under reduced pressure for 6 h were used for pore size and pore volume determination using mercury porosimetry by nitrogen adsorption–desorption method. Morphology was observed by scanning electron microscopy (Quanta 200 3D dual beam ESEM, Netherland) wherein electron source for ESEM was thermionic emission tungsten filament.

3. Results and discussion

In 1963, Merrifield et al. [22] invented the solid-phase chemistry for the applications of supported materials such as catalyst, reagent, substrate, scavenger, protecting group, photosensitizer, and enzyme in solid-phase synthesis. The solid/insoluble support for solid-phase synthesis may be organic (polymer), inorganic (silica/metal oxide/mixed metal oxide/zeolites), or organic–inorganic hybrid (metal-organic framework). Further, study of the physical properties like surface area, pore volume, pore size, and surface morphology of solid-support is essential to correlate the obtained properties.

3.1. Fourier transform infra-red spectroscopy

Synthesis of copolymer was confirmed by FT-IR spectroscopy (KBr, cm^{-1}). Poly(MMA-co-EDMA) revealed peak at 2952 due to the presence of aliphatic C–H str, 1732 assigned to C=O str and 1474 corresponds to C–H vib ($-\text{CH}_2-$). Moreover, the peak at 1455 is due to C–H bend ($-\text{CH}_2-$), 1389 corresponds to C–H bend ($-\text{CH}_3-$), and 1267 attributes to C–O–C antisym str. Poly(MMA-co-DVB) revealed the peak at 2991 corresponds to aromatic C–H str., 2950 assigned for aliphatic C–H str, and 1731 for C=O str. Moreover, peak at 1468 is assigned to C–H vib ($-\text{CH}_2-$), 1451 corresponding to C–H bend ($-\text{CH}_2-$), and 1386 ascribed to the C–H bend ($-\text{CH}_3$). Furthermore, the peak at 1239 is assigned to C–O–C antisym str, 905 is assigned to the *para* disubstituted benzene ring [23], 841 is ascribed to the aromatic C–H out-of-plane bend. FT-IR spectrum of poly(MMA-co-EDMA) and poly(MMA-co-DVB) are represented in Fig. 1.

3.2. Surface area determination

Six series of methyl methacrylate copolymers were obtained by varying cross-linkers, CLD, and porogens to evaluate the effect of different parameters on the properties of cross-linked microbeads. For this, non-solvating, hydrophobic porogens were selected to obtain megaporous polymer. Cyclohexanol as porogen generated surface area in the range 94–300 m^2/g (MEC series) and 94–244 m^2/g (MDC series). Copolymers obtained using n-octanol had surface area in the range of 3–11 m^2/g (MEO series) and 3–33 m^2/g (MDO series). Further, copolymers obtained using n-

Table 1
Monomer–cross-linker feed composition.

Monomer system	Units	Cross-link density (%)					
		25	50	75	100	150	200
MMA:EDMA	mol	0.104:0.026	0.080:0.040	0.065:0.048	0.054:0.054	0.041:0.062	0.033:0.066
	g	10.448:5.171	7.990:7.910	6.469:9.605	5.434:10.759	4.117:12.227	3.314:13.122
MMA:DVB	mol	0.113:0.028	0.090:0.045	0.075:0.056	0.064:0.064	0.050:0.075	0.041:0.082
	g	11.298:3.672	9.030:5.871	7.520:7.334	6.443:8.378	5.008:9.769	4.096:10.653

Reaction conditions: Batch size – 16 mL; AIBN – 2.5 mol%; stirring speed – 300 rpm; reaction time – 3 h; reaction temp. – 70 °C; outer phase – H_2O ; protective colloid – poly(vinylpyrrolidone); concentration of protective colloid – 1 wt.%; porogen – cyclohexanol, n-octanol, and n-decanol; porogen concentration – 48 mL (1:3 v/v).

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