

Research Article

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Effect of Porogen Concentration on Surface Area and Porous Properties of Cross-linked Polymer Beads

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Abstract: Porous polymers were obtained and effect of cross-linkers (hydrophilic/hydrophobic), non-solvating porogens (n-butanol/n-hexanol) and their concentration on polymer properties were evaluated. Polymers revealed the increase in specific surface area (SSA) with increasing concentration of cross-linker (cross-link density) inversely SSA was decreased for greater concentration of non-solvating porogens. Importantly, MEH-100 [1:3 monomer:porogen (M:P) ratio] demonstrated the highest pore volume (PV) and pore size (PS) of 4.33 cc/g and 0.87 μm , respectively whereas MDH-100 (1:2 M:P) displayed the highest PV and PS of 3.56 cc/g and 0.68 μm , respectively.

Keywords: Cross-linked polymer beads; Porogens; Porosity; Specific surface area

1. INTRODUCTION

Over the last decade, cross-linked polymers with greater porosity have been received an increasing attention due to their interesting properties which make them for a wide range of applications in different fields [1–3]. Number of polymerization methods such as suspension, emulsion and dispersion were used to obtain the porous polymer. Emulsion polymerization technique can be used to obtain highly porous polymers. The major concern of emulsion polymerization method is that polymer synthesized by this technique has lack of strength, rigidity, stiffness and traces of surfactant remaining in the polymer can deteriorate the polymer properties. Suspension polymerization is the best technique to obtain the porous beaded polymer for the application as a solid-support. Several factors are attributing to the properties of beaded polymers [4,5]. Factors including monomer, cross-linker, cross-link density (CLD), type of porogen, porogen concentration, stirring speed, initiator and polymerization temperature are important parameters which decide the properties of polymer beads. Chemical parameters like cross-linkers and porogens are very crucial in controlling the properties of resulting polymers [6–9]. Due to inexpensiveness, methyl methacrylate polymer can become a versatile solid-support for entrapment of an enzyme which is important from technological view point.

Over the past few years, polymer resins were used in column chromatography [10–12] and main drawbacks of these resins are small pore size (PS) and low porosity which resulting into slow diffusion rate of mobile phase during passing through a stationary phase [13]. This problem can be eliminated to a

remarkable extent using non-solvating porogens. Porous polymers have potential applications consequently synthesis of polymer with large PS is an essential. Nowadays, different types of porogens are available to generate the porosity into the polymer beads. Porogens are classified in accordance to the type of porosity generated by the porogens into the polymers. Generally, porogens are classified into three main categories i.e. solvating (SOL), non-solvating (NONSOL) and polymeric (POLY) porogens [14,15]. Solvating porogens are well-known which offers high specific surface area (SSA) and low pore volume (PV) inversely non-solvating porogens generates the polymers with low SSA and greater PV. Poly porogens have the specific property to impart small SSA and PV. Obviously, solvating porogens are known to improve the SSA, whereas porosity can be improved by non-solvating porogens. Polymers were used as a solid-support to organic/inorganic entities like catalysts, reagents, substrates, scavengers and protecting groups [16–18]. Industrially, polymer-supported reactions are economical due to recyclable and reusable properties.

Rahman et al. [19] reported the toluene-n-heptane as a porogen for poly(glycidyl methacrylate-triallylisocyanurate-ethylene glycol dimethacrylate) terpolymer synthesis wherein they reported the SSA, PV and PS using a pair of porogen. In the present work, porous beaded polymers were obtained using a single non-solvating porogen instead of pair. This work is of specifically interested in obtaining the improved polymer properties such as SSA, PV and PS by employing hydrophobic non-solvating porogens. Despite of inexpensive, non-hazardous and ease of availability of hydrophobic alcoholic porogens, present work generates a ubiquitous porous polymer.

2. EXPERIMENTAL

2.1. Materials

Ethylene dimethacrylate (98%) and divinylbenzene (85%) were procured from Sigma-Aldrich. 2,2'-Azobisisobutyronitrile (99%) was received from SAS Chemicals, Mumbai. Poly(vinylpyrrolidone) K-90 powder (PVP, mol. wt.: 360,000 g/mol) was procured from Fluka, USA. Methyl methacrylate (99%), n-hexanol (98%) and methanol (99.8%) were purchased from Loba Chemie, Mumbai. n-Butanol (99%) was obtained from Merck, Mumbai, India. All chemicals were used as received.

2.2. Synthesis of cross-linked polymers by suspension polymerization

Polymer synthesis, purification, characterization techniques, monomer-cross-linker feed composition and FT-IR spectra were similar to our recently published work [20]. In the present work, poly(MMA-co-EDMA) and poly(MMA-co-DVB) having different CLDs (50, 100, 150 and 200%) were obtained varying monomer-cross-linker feed composition by suspension polymerization. Poly(MMA-co-EDMA) synthesized using n-butanol and n-hexanol porogens were abbreviated as **MEB** and **MEH** whereas poly(MMA-co-DVB) synthesized using n-butanol and n-hexanol porogens were abbreviated as **MDB** and **MDH**, respectively. Moreover, alcoholic porogens (n-butanol and n-hexanol) and their different monomer: porogen (M:P) ratio [1:1 (16 mL), 1:2 (32 mL) and 1:3 (48 mL)] were used for porous polymer synthesis.

3. RESULTS AND DISCUSSION

3.1. Specific surface area (SSA) determination

Number of properties such as SSA, PV, PS, porosity and morphology are significantly affects to the polymer efficiency. These properties can be controlled by proper selection of cross-linker, porogen

and their concentration [21,22]. Four polymer series (MEB, MEH, MDB and MDH) of methyl methacrylate monomer were synthesized by varying cross-linkers (EDMA/DVB), porogens (n-butanol/n-hexanol) and M:P ratios (1:1, 1:2 and 1:3) at four different CLDs (50, 100, 150 and 200%) using suspension polymerization. Further, effects of variation in reaction composition on SSA and porosity of cross-linked polymer beads were studied.

3.1.1. Effect of cross-linker and cross-link density

Type of cross-linker is substantially attributes to the physical properties of polymers. Ethylene dimethacrylate and divinylbenzene were used as a cross-linker whereas CLD was varied from 50 to 200%. In this work, polymer containing ethylene dimethacrylate cross-linker showed the greater SSA than polymer containing divinylbenzene as a cross-linker. This is mainly due to the basic structure of dimer of methyl methacrylate and ethylene dimethacrylate is almost similar, thus, miscibility of these two monomers is higher. On the contrary, miscibility of methyl methacrylate and divinylbenzene is lower due to different types of monomeric structures resulting into lower SSA. MEH series exhibited the greater SSA than MDH series in all M:P ratios (1:1, 1:2 and 1:3). The miscibility of ethylene dimethacrylate in water (1.086 g/L) is higher than miscibility of divinylbenzene (0.005 g/L) at 20°C, thus EDMA has more affinity toward aqueous phase for a longer period and forms smaller pores resulting into high SSA. In addition to type of cross-linker, effect of cross-linker concentration (CLD) was also evaluated. CLD also plays a pivotal role in cross-linked polymers because it not only affects the chemical composition of resulting polymer but also influences the physical properties. All four series demonstrated the increased SSA for increase in CLD at all M:P ratio [19]. Further, particular concentration of monomer and porogen pass through a critical value [23] at a particular CLD. As a result, all series revealed the increase in SSA from 50 to 150% CLD whereas SSA was decreased above 150% CLD for 1:3 (M:P) ratio (shown in **Figure 1** by a red arrow).

3.1.2. Effect of type and concentration of porogen

Undoubtedly, SSA and porous properties of beaded polymers are depending upon the type and concentration of porogens. In this work, polymers synthesized using n-butanol porogen exhibited much higher SSA compared to n-hexanol. This is due to the miscibility of n-butanol in water (80 g/L) is higher compared to n-hexanol (5.9 g/L) at 20°C, thus n-butanol remains in an aqueous phase for a longer period and forms smaller pores resulting into high SSA polymer. Moreover, poly(MMA-co-EDMA) exhibited the higher SSA with n-butanol than n-hexanol at 1:2 and 1:3 (M:P) ratio, inversely, SSA was decreased for MEB than MEH series at 1:1 (M:P) ratio. This is probably due to the fact that, cross-linker and porogen pass through a critical hydrophilic-hydrophobic concentration. Copolymer series MDB, MEH and MDH revealed the decrease in SSA with increase in porogen concentration because non-solvating porogen allows early-stage phase separation between aqueous and organic phase. Overall, poly(MMA-co-EDMA) displayed the higher SSA for n-butanol whereas poly(MMA-co-DVB) revealed the greater SSA for n-hexanol (1:2 and 1:3 M:P). This is due to decreased PS inside the nuclei of polymer beads resulting into smaller pores which generates higher SSA [8]. It was concluded that, SSA was increased with increasing CLD (concentration of cross-linker) whereas substantially decreased for increase in porogen concentration. SSA of four polymer series at four different crosslink densities is depicted in **Figure 1**.

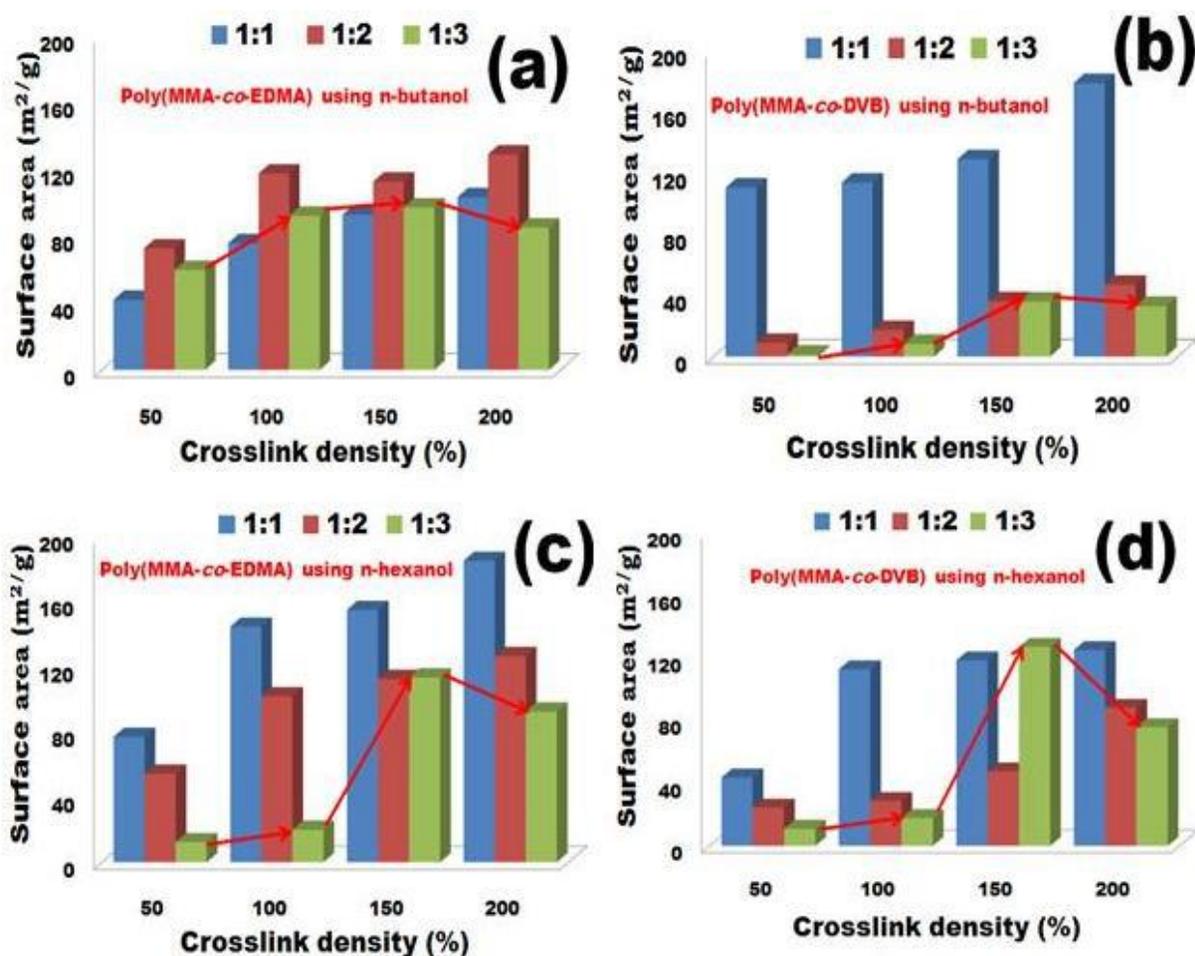


Figure 1. Specific surface area (SSA) of poly(MMA-co-EDMA) and poly(MMA-co-DVB) using n-butanol (a,b) and n-hexanol (c,d) porogens.

3.2. Effect of porogen and their concentration on porous properties

IUPAC classified the pores based on their width as micro, meso and macropores [24,25]. PV and PS are the most important properties of the porous polymer. Effect of porogens (type and concentration) on PV and PS were studied.

3.2.1. Pore Volume

Pore volume is a measure of void spaces in the beaded polymer whereas porosity is a fraction of the volume of voids over the total volume of the polymer matrix. First of all effect of porogen on pore volume was studied. Poly(MMA-co-EDMA) demonstrated the higher PV with n-hexanol compared to n-butanol porogen. This is probably due to the polarity difference in porogens. Indeed, n-hexanol is a less polar and less miscible with MMA-EDMA monomer system which leads toward porous polymer beads. In another, poly(MMA-co-DVB) revealed the higher PV with n-butanol compared to n-hexanol. This is again due to the more polarity of n-butanol and less miscibility with MMA-DVB monomer system resulting into porous poly(MMA-co-DVB) [26]. The effect of porogen concentration was also evaluated.

In this work, MEB, MDB, MEH and MDH series revealed the highest PV of 3.75, 3.64, 4.33 and 3.31 cc/g whereas PS of 0.44, 0.22, 0.87 and 0.466 μm using 1:3 (M:P) ratio, respectively. Notably,

poly(MMA-*co*-EDMA) illustrated the higher PV at 1:3 which was decreased for 1:2 and further for 1:1 (M:P) ratio with both (n-butanol/n-hexanol) porogens. This is because of higher concentration of hydrophobic alcoholic porogen in comparatively hydrophilic MMA-EDMA monomer system resulted into larger pores [27]. On the other hand, poly(MMA-*co*-DVB) displayed the greater PV at 1:2 (M:P) ratio which was decreased for change in M:P ratio of both (n-butanol/n-hexanol) porogens.

3.2.2. Pore Size

Application of the polymer is decided by PS of a polymer. Porous polymers are efficiently employed in pharmaceuticals, metal recovery, ceramics, biomedical, catalysis and metallurgy [28–32]. Indeed, solvating porogens have the property to generate more SSA and microporosity. On the contrary, non-solvating porogens have the property to generate lower SSA and macro or mega porosity into the polymer. PS demonstrated the similar observation like PV for both (n-butanol/n-hexanol) porogens. Porogen effect revealed that, poly(MMA-*co*-EDMA) and poly(MMA-*co*-DVB) have the larger PS with n-hexanol than n-butanol porogen at all M:P ratio. This is mainly due to the increased chain length of aliphatic porogen from C4 to C6 allows increase in PS [33]. The effect of porogen concentration was also examined. Poly(MMA-*co*-EDMA) exhibited the larger PS with both porogens at 1:3 (M:P) ratio due to increased concentration of hydrophobic porogen [24,34]. This observation was demonstrated by both (MEB and MEH) polymer series. In addition, poly(MMA-*co*-DVB) displayed the larger PS at 1:2 (M:P) ratio whereas change in M:P ratio leads toward smaller PS. Thus, poly(MMA-*co*-EDMA) and poly(MMA-*co*-DVB) revealed the maximum PV and PS at 1:3 and 1:2 M:P ratio, respectively because particular M:P concentration introduces the larger PS into the polymer beads. Recently, Costae et al. [35] reported the SSA, PV and PS of poly(MMA-*co*-DVB). However, polymer obtained in the present work by hydrophobic porogens is a paradigm of polymer porosity. Thus, aim of porous polymer synthesis was successfully achieved. PV and PS of polymers at 100% CLD using different cross-linkers, porogens and M:P ratios are depicted in **Figure 2**.

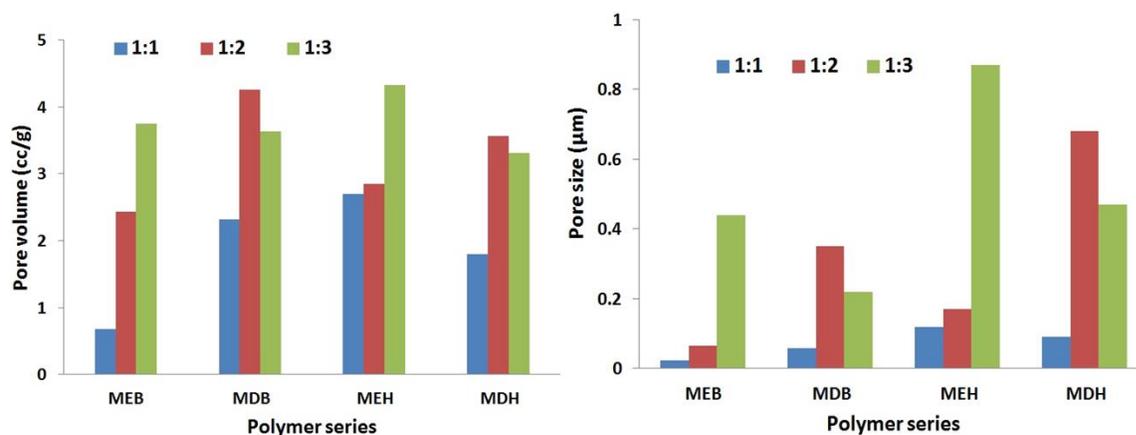


Figure 2. PV and PS of poly(MMA-*co*-EDMA) and poly(MMA-*co*-DVB) using n-butanol and n-hexanol porogens for 100% CLD at 1:1, 1:2 and 1:3 M:P ratio.

3.3. External morphology

Scanning electron microscopy (SEM) is the powerful tool to visualize the particle size and morphology of porous beads. SEM images of MEB were obtained for 100% CLD (1:1, 1:2 and 1:3 M:P ratio) at 200X and 10000X magnification. Lower (200X) and higher (10000X) magnification images

clearly demonstrated the uniform particle size and porous properties of the polymer beads, respectively.

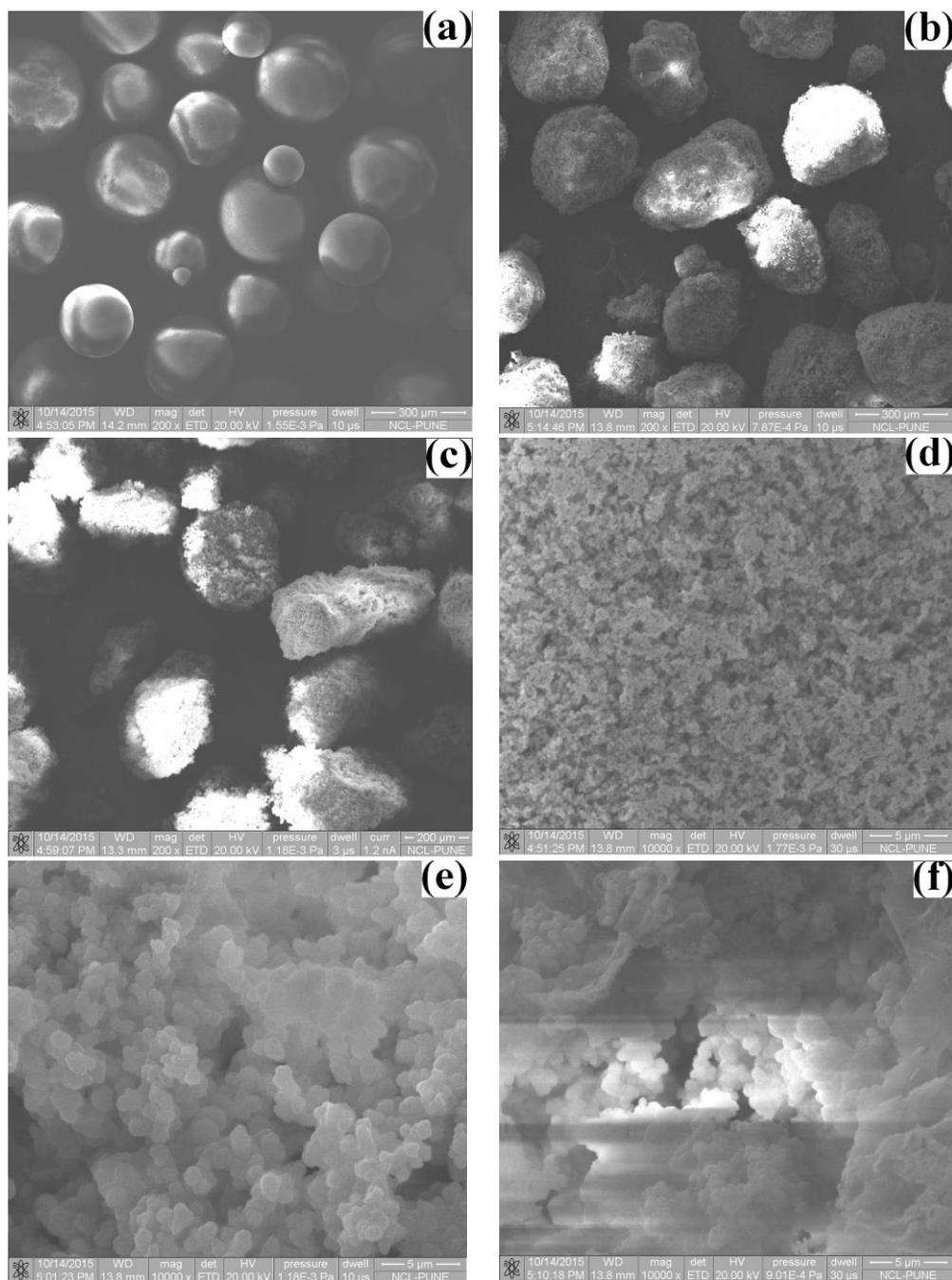


Figure 3. SEM images of MEB-100 (1:1, 1:2, 1:3 M:P) at 200X (a, b, c) and 10000X (d, e, f) magnification, respectively.

Interestingly, PV and PS of polymer beads were increased with increase in M:P ratio which can be visualized by SEM images (10000X magnification). SEM images of poly(MMA-co-EDMA) at 100% CLD for 1:1, 1:2 and 1:3 M:P ratios are represented in **Figure 3 a, b, c** (200X) and **Figure 3 d, e, f** (10000X).

4. CONCLUSIONS

In conclusion, greater concentration of non-solvating porogens is inversely functioning toward SSA and porosity of cross-linked polymer beads. Notably, higher concentration of non-solvating porogens leads toward greater porosity inversely small SSA. It is worth noting that, SSA was increased with increase in cross-link density (1:1 and 1:2 M:P) whereas decreased after 150% CLD (1:3 M:P) for all polymer series. Porous polymers were successfully obtained bearing high PV and large PS. In case of poly(MMA-co-EDMA), porous properties were increased for higher M:P ratio in the sequence of 1:1, 1:2 and 1:3. Poly(MMA-co-DVB) displayed highest PV (3.56 cc/g) and PS (0.68 μm) for 100% CLD (1:2 M:P) with n-hexanol and slight change in M:P ratio resulting into substantial decrease in porosity. SEM images (10000X) strongly support to porous morphology of polymer beads and clearly showed that PV and PS increased with increase in M:P ratio.

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The authors declare no conflict of interest

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