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Preparation of Macroporous Poly (vinyl alcohol-co-triallyl isocyanurate) Beads Bearing Aminocarboxylic Acid as Functional Groups by Suspension Polymerization

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Abstract: Macroporous poly (vinyl acetate-co-triallyl isocyanurate) beads were prepared with suspension polymerization method. The copolymer beads were then transformed into poly (vinyl alcohol-co-triallyl isocyanurate) by ester exchange reaction. Aminocarboxylic acids were immobilized on the copolymer beads by the esterification of hydroxyl groups with diethyllenetriaminepentaacetic bisanhydride. The weak acid exchange capacities, specific surface areas and mean pore diameters of the resultant resin beads were measured.

Keywords: Macroporous adsorption resin, suspension polymerization, poly (vinyl alcohol-co-triallyl isocyanurate), aminocarboxylic acid.

Polymeric adsorbents have been widely used for the extraction of natural products, wastewater treatment for pollution control, rare precious metal recovery and in biologic medical field such as hemoperfusion[1-3]. It is found that some polymeric anions such as sulfonated hydroxylethyl cross-linked chitosan[4,5], immobilized sulfonated dextran[6], crosslinked poly alcohol gel beads bearing taurine[7] and poly(acryl acid)[8] can selectively adsorb low density lipoprotein (LDL) from human plasma. The evidences, that the adsorption selectivity of LDL on these polymeric adsorbents is highly related with the existences of surface negative charges of the adsorbents, have been accumulated[6,9]. In order to clarify the effect of the density and ion intensity of the anions on surface of the polymeric adsorbents on the LDL adsorption selectivity and to develop novel high efficiency LDL adsorbents for hemapheresis, polymeric adsorbents bearing various carboxylic acids as functional groups are being prepared in our laboratory. The preparation and primary characterization of macroporous poly (vinyl alcohol-co-triallyl isocyanurate) beads are reported in this work.

Macroporous poly (vinyl acetate-co-triallyl isocyanurate) was synthesized using free-radical suspension polymerization technique. Mixture of butyl acetate and 200# gasoline was used as porogen. AIBN was used as initiator. In a typical experiment, a

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500 mL four-neck round bottom flask was loaded with 300 mL water containing 1.5% poly (vinyl alcohol) and 3% sodium chloride. Nitrogen was introduced into the reaction vessel and the solution stirred under nitrogen atmosphere. The temperature was raised to 40°C and the pre mix solution of 24 g vinyl acetate, 6 g triallyl isocyanurate, 15 mL butyl acetate, 15 mL 200$^{\#}$ gasoline and 0.3 g AIBN was added into the vessel with stirring. The temperature was raised to 65°C and sustained for 6 hours. Then the reaction mixture was heated to 75°C and remained at this temperature for 3 hour while stirring. The resultant beads were filtrated and washed with hot water and acetone. After extracted with acetone in a Wheaton Soxhlet extraction apparatus to removal the porogen, the resin beads were dried at 45°C under reduced pressure. The resultant copolymer was transformed into poly (vinyl alcohol-co-triallyl isocyanurate) as following process: 100 mL sodium hydroxide (3%wt) methanol solution and 20 g copolymer were added into a 250 mL three-neck flask. The temperature was sustained at 24°C for 24 hours while stirring. The resultant poly(vinyl alcohol-co-triallyl socyanurate) beads were collected by filtration and washed with water and ethanol and dried at 45°C under reduced pressure. 15g diethylenetriaminepentaacetic bisanhydride and catalytic quantity of 4-dimethyl amino pyridine was dissolved in 100 mL dry DMF, 5 g Poly (vinyl alcohol-co-triallyl isocyanurate) beads was added in the solution and swelled over night. The temperature of the reaction mixture was then raised to 60°C and sustained for 4 hours while stirring. After filtration, the copolymer beads were washed in turns with water, 0.1 mol/L sodium hydroxide, water, 0.1 mol/L hydrogen chloride solution, water and acetone and dried at 45°C under reduced pressure. Then, poly (vinyl alcohol-co-triallyl isocyanurate) beads bearing aminocarboxylic acid as functional groups were obtained.

The specific surface areas and mean pore diameters of the resultant copolymer beads were measured on a BET nitrogen adsorption apparatus (Micromeritics, ASAP 2010). The weak acid exchange capacity of the copolymer was determined with the method described in reference[10]. These results are listed in **Table 1** and **Table 2**. The results suggested that changing the polymerization conditions could alter the specific surface area, macro pore structure and the density of functional groups of the resultant copolymer beads. Practical Application of this novel polymeric adsorbent for LDL apheresis could be expected. Further investigations are in progress.

Table 1 Preparation and properties of poly(vinyl actate-co-triallyl isocyanurate) beads

Sample	Polymerization mixture (wt%)		Specific surface area (m^2/g)	Mean pore diameter (nm)
	Vinyl acetate	Triallyl isocyanurate		
1	42.5	7.5	28.0	25.0
2	40	10	29.7	20.9
3	37.5	12.5	42.5	20.0
4	35	15	46.8	21.2
5	32.5	17.5	58.2	19.3

Table 2 Weak acid exchange capacity of poly(vinyl alcohol-co-triallyl isocyanurate) beads bearing aminocarboxylic acid as functional groups

Sample	1	2	3	4	5
Crosslinking degree (wt%)	15	20	25	30	35
Weak acid exchange capacity (mmol/g)	3.06	2.58	2.34	2.06	1.98

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