Preparation and Characterization of Porous Poly(methacrylic acid) Gel by Dispersion Polymerization

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ABSTRACT: Porous poly(methacrylic-co-glycidylmethacrylate) (MAA-GM) was prepared by dispersion polymerization using benzoyl peroxide as an initiator and methacrylate terminated phthalate glycol polyester as a steric stabilizer in polar organic medium (chloroform-ethanol mixture). The prepared poly(methacrylic acid) dispersion was crosslinked by glycidylmethacrylate oligomers. The crosslinked copolymer (MAA-GM) was base hydrolyzed using hydroxyl amine, sodium methoxide, and triethyl amine. The metal binding behavior of the prepared polymer was examined by means of atomic absorption spectrophotometer. The thermal stability of the prepared polymers was examined by thermal gravimetric analysis (TGA). © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1793–1798, 1999

Key words: dispersion polymerization; polymethacrylic acid gel; porous polymer; glycidylmethacrylate; metal polymer catalyst

INTRODUCTION

Gels are of great practical significance;¹ for example, gelatin gels are widely used in the food and photographic industries. Protein gels play a very important role in living organisms. Gels may be used as carriers for inorganic catalysts, because most of the support materials used for catalysts in polymer production are inorganic compounds. These materials introduce impurities into the polymer product and create polymer processing and quality problems. Gels may form when electrolytes are added to solutions of such polymers as cellulose acetate, methylmethacrylate, and methacrylic acid. Most porous polymeric materials are prepared by crosslinking polymerization with an inert component (diluent), which may be extracted after polymerization leaving holes in the polymer mass.²⁻⁵ In this article, we follow up the technique termed *interparticle crosslinking*⁶

to prepare poly(MAA) gel to be used as a carrier for inorganic metal catalysts.

EXPERIMENTAL

Methacrylic acid (MAA) and glycidylmethacrylate supplied by Redel de Haen and Aldrich, respectively, were purified by being passed through active alumina. Benzoyl peroxide reprecipitated from chloroform solution by methanol supplied by Sigma Chemical Company.

Preparation of Methacrylate Terminated Phthalate Glycol Polyester ⁷

The reaction mixture wt % (ethylene glycol 31.5, phthalic anhydride 51.8, methacrylic acid 6.0, trichloroethylene 9.94, *p*-toluene sulphonic acid 0.7) was heated under nitrogen in a stirred flask fitted with a reflux condenser and a Dean and Stark take-off to remove the water of esterification. After 6 h heating, the reaction temperature had

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Figure 1 Fourier transform infrared (FTIR) spectrum of the prepared methacrylate terminated phthalate glycol polyester.

risen from 107°C (initial reflux temperature) to 148°C.

Characterization of the Prepared Polyester

The prepared polymer was investigated by means of FT-IR. Figure 1 shows the characteristic peaks of the ordinary polyester. The solid content of the prepared polyester was determined and found to be 60%.

Dispersion Polymerization of Methacrylic Acid⁷

Polymerization was carried out in a 250 mL round bottom, three neck flask fitted with a mechanical stirrer, nitrogen inlet, and a condenser. The reaction was carried out at 70 + 1 and $80 + 1^{\circ}C$ (see Table I).

Table IReaction Ingredients of DispersionPolymerization of MAA

Ingredients	Concentration (wt %)			
Methacrylic acid	6			
Chloroform	75			
Ethanol	12			
Polyester	6.5			
Stabilizer				
Benzoyl peroxide	0.5			

The previously prepared polyester stabilizer was first dissolved in the chloroform mixture. Methacrylic acid was then introduced as one shot. Finally, benzoyl peroxide was added to initiate the polymerization. The polymerization was shown to be completed after ~ 180 min, where a good dispersion of poly(MAA) was obtained.



Figure 2 Conversion time curves: effect of ethanol concentration (\Box) 12.5 mL (+) 20 mL on the dispersion polymerization of methacrylic acid at 70°C.



Figure 3 Conversion time curves: effect of ethanol concentration (\Box) 12.5 mL, (+) 20 mL, on the dispersion polymerization of methacrylic acid at 80°C.

RESULTS AND DISCUSSION

Kinetics of Polymerization of MAA

Effect of Ethanol Concentration on Rate of Dispersion Polymerization of MAA

The dispersion polymerization of MAA was carried out at different concentrations of ethanol: 12, 20, 25, 30 wt %; whereas, the previous ingredients concentrations were kept constant. It was shown that the increase of alcohol concentration leads to a decrease in both the rate of polymerization reaction and the stability of the resulting dispersion (Figs. 2 and 3). The data are given in Table II, where it can be seen that the rate of polymerization reaction reaction decreased from 5.7×10^{-6} to 4×10^{-6} gmol/L s⁻¹ at 70°C and from 8.5×10^{-6} to 8×10^{-6} gmol/L s⁻¹ at 80°C, when the ethanol concentration was increased from 12 to 20 wt %.

Table IIEffect of Ethanol Concentration onthe Rate and Apparent Activation Energy ofthe Dispersion Polymerization Reaction

Alcohol Conc. (wt %)	Temperature (°C)	$\begin{array}{c} Reaction \\ Rate \times 10^6 \\ (gmol/L \; s^{-1}) \end{array}$	$\begin{array}{c} \text{Apparent} \\ \text{Activation} \\ \text{Energy} \\ E_a \; (\text{kJ/mol}) \end{array}$	
12	70	5.7		
12	80	8.5	39	
20	70	4.0		
20	80	8.0	70	



Figure 4 Scanning electron microscope graphs of poly(MAA-GM), magnification, (a) $\times 250$; (b) $\times 500$.

The apparent activation energy increased from 39 to 70 kJ/mol, when the alcohol concentration increased from 12 to 20 wt %. It was shown that the polymerization reaction does not proceed, even after 4 h of continuous stirring at high alcohol concentration (more than 20 wt %).

Crosslinking of the Particle Poly(MAA) Dispersion⁶

Preparation of the Crosslinker (Oligomers of Glycidylmethacrylate)

Glycidylmethacrylate monomer 10 mL was purified by being passed over active alumina. Benzoyl peroxide 0.1 g was dissolved in the monomer GM and then left for 24 h at room temperature in a closed flask under nitrogen atmosphere. The monomer changes into a slightly viscous solution of GM oligomers.

Crosslinking Process

Glycidylmethacrylate oligomers 10 mL was added to poly(MAA) dispersion, and the reaction mix-

Solvent for Absorption	Average Absorbed Mass of Solvent (g)	Swellability ^a %		
Benzene	0.65	325		
Toluene	0.62	310		
Chloroform	0.68	340		
Ethanol	0.60	300		
Dioxane	0.63	315		
Water	0.65	325		

Table	III	Swe	lling	Behavior	of the	Prepared
Resin	in	Polar	and	Nonpolar	Solven	nts

 $^{\rm a}$ Constant weight of polymer 0.2 g for all the swelling measurements.

ture was heated at 100°C under reflux condenser without stirring for 4 h. The polymer dispersion was changed into a solid mass, where it was subjected to freeze-drying conditions (-20° C, 10^{-4} atm) to remove the diluent mixture (chloroform–ethanol).

Scanning Electron Microscope

The polymer solid mass poly(MAA-GM) was crushed into small particles. A few particles were subjected to gold plating and then to a scanning electron microscope. Figure 4 shows the porous structure of different regions of the surface.

Base Hydrolysis of the Crosslinked Copolymer (MAA-GM)⁸

The crosslinked copolymer (MAA-GM) was subjected to base hydrolysis using triethylamine 20 mL, hydroxyl amine (5 g), and freshly prepared sodium methoxide as a base in methanol (100 mL). The reaction mixture was refluxed for 3 h. The resulting polymer was washed several times with methanol and finally dried at 40°C for 24 h. The base hydrolysis process changes the carboxylic and ester groups into hydroxamic groups -CONHOH, which have high affinity for metal ion absorption.

Swellability of the Porous Poly(hydroxamic acid) (Table III)

The data given in Table III show that the porous copolymer can absorb up to three times its original weight, and the swellability does not depend upon the polarity of the solvent.

Absorption of the Metal Ions by the Resin^{9–11}

The metal ion absorption capacity of the resin before and after base hydrolysis of poly(MAA-GM) was determined by the batch method. Accurately weighed resin samples (0.1 g) were equilibrated with 50 mL of 2000 ppm metal ion solutions in measuring flasks 50 mL each for 24 h. After reaching equilibrium, the amount of metal ions remaining in solution was determined by means of atomic absorption. The data are given in Table IV.

From Table IV, it is clear that the base hydrolysis of poly(MAA-GM) to poly(hydroxamic acid) raised the absorption capacity of the resin several times, which indicates that the metal chelation is predominantly on the lone pair of the nitrogen atom of the hydroxamic acid group —CONHOH.

Thermal Gravimetric Analysis (TGA)

Figures 5–7 show three thermal gravimetric analysis spectra of poly(MAA-GM), its base hydrolyzed form [poly(hydroxamic acid)], and its copper complex. The differential curves show that the poly(hydroxamic acid) is less thermally stable, weight loss 10.2%, than the original poly(MAA-GM), weight loss 5.64% of its original weight, which is attributed to the decomposition effect of the strongly basic hydrolyzing medium. The copper-polymer complex is the most thermally stable; that is, it loses 3.8 wt % of its original weight

Table IV Metal Ion Extracted % from 2000 ppm Before and After Hydrolysis

M^{n+}	cd^{2+}	Cr^{3+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Pd^{2+}	Na^+	Pb^{2+}
a	73	82	87	97	92	90	89	72	89
b	11	23	24	23	19	20.5	17.5	12	24

^a After hydrolysis.

^b Before hydrolysis.



Figure 5 Thermal gravimetric analysis of poly(MAA-GM).

at 200°C. This thermal stability enables the use of such metal-polymer complexes as a supporting material for catalyst and enzyme fixation.

Base Hydrolyzed Poly(MAA-GM) as a Catalyst Supporting Material⁶

The following procedures were used to support the prepared polymer with metal and metal oxide catalysts. 1.0 g of the porous poly(HYOX) is immersed in different salt solutions (5000 ppm) of (Cr, Fe, Co, Ni, Pd, Cd, and Cu) and stirred at room temperature for 1 h. After the polymer was turned to the characteristic color of the salt solution, it was filtered and dried at 60°C. The polymer was resuspended in ethanol. After that, 1.0 g of NaBH₄ was added to the suspension to reduce the metal ion M^{2+} , M^{3+} to the metallic state M^{0} . After 30 min, the polymeric material was turned to the metallic luster. The material was then left



Figure 6 Thermal gravimetric analysis of base hydrolyzed poly(MAA-GM).



Figure 7 Thermal gravimetric analysis of copper complex of the base hydrolyzed poly(MAA-GM).

in benzene for 3 days, after which, it was redried and kept in a vial as a metal-porous polymer catalyst to prepare the metal oxide-polymer catalyst. The above procedures were repeated, except that the reduction process was carried out in water instead of ethanol, where the material was turned black after a few minutes.

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