

Polymer-supported redox catalysts for polymerization

A. E. Poornanandhan, P. Rajalingam and Ganga Radhakrishnan*

Polymer Division, Central Leather Research Institute, Madras 600 020, India

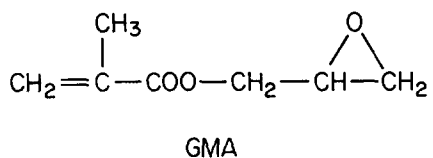
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Crosslinked poly(glycidyl methacrylate) has been functionalized by ethanolamine and subsequently by xanthation. The xanthate based beads were used for anchoring Fe^{2+} ions, after which they have been used in conjunction with H_2O_2 as a redox catalyst system for aqueous polymerization of acrylamide. The polymer beads were characterized for percentage modification at subsequent stages by elemental analysis, Fourier-transform infra-red spectroscopy and pore size distribution. The efficiencies of polymerization with the polymer-supported catalyst and with a conventional system were compared with respect to the yield and molecular weight.

(Keywords: polymer support; redox catalyst; glycidyl methacrylate beads; functionalization; epoxy groups; polyacrylamide)

INTRODUCTION

Solid-phase peptide synthesis, introduced by R.B. Merrifield in 1963, is the starting point in the field of functional polymers. Subsequently, large numbers of functional polymers have been prepared using mainly styrene and divinylbenzene¹. Many workers have developed various functional polymers that could be used as polymer-supported reagents for organic synthesis²⁻⁴, catalysts for various reactions⁵⁻⁸, ion exchangers^{9,10}, chromatographic column materials¹¹, immobilization of enzymes¹², biomedical applications^{13,14}, etc. Many of these functional polymers can be prepared by suspension polymerization of functionalized monomers or post-chemical modification of polymer beads. Recently, some monomers other than styrene have been used in the preparation of these functional polymers¹⁵⁻¹⁷.



Glycidyl methacrylate (GMA) can be used for the preparation of functional polymers owing to its reactive glycidyl ether functional group, which can be modified with various reagents¹⁸. The reaction of the glycidyl ether group with amine¹⁹ has been well studied and the final product is a tertiary amine attached to the primary carbon of the glycidyl group. Glycidyl methacrylate is used in the graft copolymerization of various monomers²⁰ as well as in copolymerization processes. No reports on the modification of the glycidyl group and further

application as redox catalysts have been found in the literature. So we attempted to prepare a redox catalyst using a modified glycidyl methacrylate- H_2O_2 system and to apply it as a catalyst for free-radical polymerization of vinyl monomers, especially with a view to preparing polymers without metal-ion contamination.

EXPERIMENTAL

Materials

Doubly distilled water was used throughout the reactions. Glycidyl methacrylate (Fluka) was distilled under vacuum and the middle fraction was used. Divinylbenzene (DVB; Aldrich), benzoyl peroxide (BPO; Fluka), poly(vinyl alcohol) (PVA) of molecular weight 125 000, calcium sulfate and sodium hydroxide (SD Fine Chem, India; AR) were used as received. Acrylamide (SD Fine Chem, India; AR) was recrystallized from methanol before use. Acetone, methanol, chloroform, dichloromethane (SD Fine Chem, India; AR) were used after distillation after removing the water by standard procedures. Carbon disulfide, ethanolamine (SD Fine Chem, India; AR) and ethyl acetate (IDPL, India; AR) were used after distillation.

Instruments

Infra-red spectra of all polymers were recorded with a Nicolet 20DXB FTi.r. spectrophotometer using the KBr pellet technique. Thermogravimetric analysis was done using a Du Pont 951 t.g.a. unit with a 990 Thermal Analyzer. Optical micrographs were taken with a Reichert-Jung Thermogalan Optical Microscope and attached Asahi Pentax Camera at 100× magnification. Surface area and pore size distributions were measured using a Carlo-Erba Strumentazione Sorpt meter 1800. C, H and N were estimated using a Carlo-Erba Strum-DP200 elemental analyser.

* To whom correspondence should be addressed

Estimation of iron content of the beads

Estimation of iron in the polymer was done after treatment as follows. First, 0.10 g polymer was charred in a silica crucible on a bunsen burner. The remaining non-volatile part of the polymer was digested in 2.0 ml concentrated nitric acid (five times) by heating on a hot plate and then dissolved in water. The solution was made up to 100 ml in a standard flask. This solution was used for estimating the iron content by the inductively coupled argon plasma (i.c.p.) spectroscopy technique.

Suspension polymerization of GMA-DVB (PG beads)

A 1000 ml three-necked round-bottomed flask fitted with a gas inlet, an overhead anchor-type Teflon stirrer and a water condenser was charged with 156 ml water, 94 ml 1.6% aqueous solution of poly(vinyl alcohol) and 0.1 g calcium sulfate. Nitrogen gas was purged into the mixture and stirred for 30 min at 35–40°C in a thermostatic water bath. Appropriate volumes of purified monomer and crosslinker were taken in 100 ml beaker and 2% initiator (BPO) with respect to total volume of the monomers and required amount of toluene were transferred into the beaker. After completely dissolving the initiator, the mixture was transferred into the reaction flask. Stirring the contents of the flask at 35–40°C for another 30 min, the temperature of the thermostatic water bath was increased up to $80 \pm 1^\circ\text{C}$ and constantly stirred for 24 h at this temperature. After cooling the flask to room temperature, the contents were poured into 1 litre of water. The top portion of the contents was decanted after stirring with a glass rod and allowing for settlement. This process was repeated until the decanted portion was clear and colourless. The product, crosslinked poly(glycidyl methacrylate) (PG) beads, were filtered in a sintered crucible and washed successively with water, acetone, ethyl acetate, dioxane, chloroform and dichloromethane to remove suspension stabilizer, unreacted monomer and oligomers. The washed product was dried under vacuum at 60°C for 24 h. The beads were then sieved using standard test sieves. The 100–200 and 200–400 mesh (BSS) sizes were collected for further work. I.r.: 1731 cm^{-1} , ester carbonyl stretch; 907 cm^{-1} , epoxy stretch. Elemental analysis: C, calc. = 59.145, obs. = 60.778; H, calc. = 7.090, obs. = 7.209.

Modification of PG beads by ethanolamine (PGE beads)

Poly(glycidyl methacrylate), crosslinked with 10% divinylbenzene (based on monomer volume), 200–400 mesh (BSS), 5.0 g, was taken in a ground-jointed conical flask and swollen in 30.0 ml chloroform. To this, 25.0 ml ethanolamine was added dropwise and stirred using a magnetic stirrer cum heater at 40°C for 6 h. After completion of the reaction, the contents were diluted with chloroform and filtered in a sintered crucible. After washing several times with chloroform, the product (PGE) was dried under vacuum at room temperature for 24 h. I.r.: 445 cm^{-1} , N–H and O–H stretch; 1567 cm^{-1} , N–H bend; 905 cm^{-1} , epoxy stretch. Elemental analysis: C, calc. = 53.188, obs. = 48.167; H, calc. = 8.431, obs. = 7.003; N, calc. = 6.892, obs. = 3.053.

Modification of PGE beads by CS_2/NaOH (PGEX beads)

First, 5.0 g of PGE was taken in a ground-jointed conical flask. To this approximately 0.1 mol of

1:1 mol ratio of CS_2/NaOH in water was added and fitted with a water condenser, stirred on a magnetic stirrer at 39–40°C for 6 h. The product (PGEX) was filtered, washed with CS_2 , dichloromethane and dried under vacuum at room temperature for 24 h. I.r.: 3416 cm^{-1} , N–H stretch; 1120 cm^{-1} , C=S stretch; 902 cm^{-1} , epoxy stretch. Elemental analysis: C, calc. = 39.857, obs. = 44.025; H, calc. = 5.351, obs. = 5.792; N, calc. = 4.648, obs. = 3.253.

Anchoring of Fe^{2+} on PGEX beads by ferrous sulfate (PGEXF beads)

First, 2.0 g of PGEX beads in 25.0 ml of water was taken in a conical flask. An exactly weighed (2.0 g) amount of ferrous sulfate was added to the conical flask and stirred for 6 h at room temperature. After filtering the product (PGEXF), the filtrate was collected. The product was thoroughly washed with water and dried under vacuum at room temperature for 24 h. The washings were added to the filtrate and estimated for unreacted ferrous sulfate with standard potassium permanganate solution. Amount of ferrous ion in 1 g of PGEXF beads was estimated by the i.c.p. technique and given as 0.03202 g. This agrees with the titrated value.

Polymerization of acrylamide by PGEXF– H_2O_2 redox system

Three polymerization tubes (A, B, C) were taken and charged with 2.0 g of acrylamide, and 25.0 ml aqueous H_2O_2 (2.2934×10^{-5} mol) was pipetted into the three tubes. Then, 2.2934×10^{-5} mol of ferrous sulfate was added to tube A, and 0.04 g of PGEXF beads equivalent to 2.2934×10^{-5} mol of Fe^{2+} was added to tube B. The third tube C was kept as a blank without ferrous sulfate or PGEXF beads. All the tubes were immersed in a water bath, after flushing N_2 gas for 3 min, maintained at 43°C and stirred using a magnetic stirrer. After 48 h the contents of each flask were poured into methanol separately. Polyacrylamide was precipitated with tubes A and B, while with C no polymerization was observed under the conditions employed. The precipitates were then redissolved in water and reprecipitated with methanol. Purified products from A and B give brown and white coloured products respectively. The molecular weights of the polyacrylamides obtained from tubes A and B were estimated using an Ubbelohde viscometer in 1 M sodium nitrate solution at 30°C. The limiting viscosity number or intrinsic viscosities of A and B products are 1.8304 and 5.7069 dl g^{-1} respectively. The K and α values used in the Mark–Houwink equation are $K = 3.73 \times 10^{-4}$ and $\alpha = +0.66$. The molecular weights estimated are $A = 3.91 \times 10^5$, $B = 2.19 \times 10^6$. Yields of the reaction for A and B are 55.0% and 85.0% respectively.

RESULTS AND DISCUSSION

Suspension polymerization of glycidyl methacrylate with divinylbenzene as crosslinker was carried out using PVA as suspension stabilizer and toluene as porogene. Use of porogene improves the porosity of the resulting poly(glycidyl methacrylate) beads. Various degrees of crosslinked PG beads were prepared by varying the GMA and DVB feed percentages. The percentage of crosslinking was taken as the percentage of DVB added

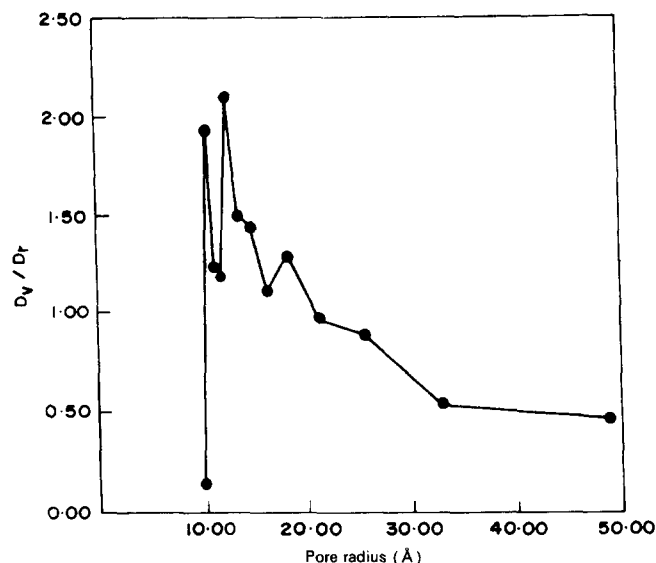
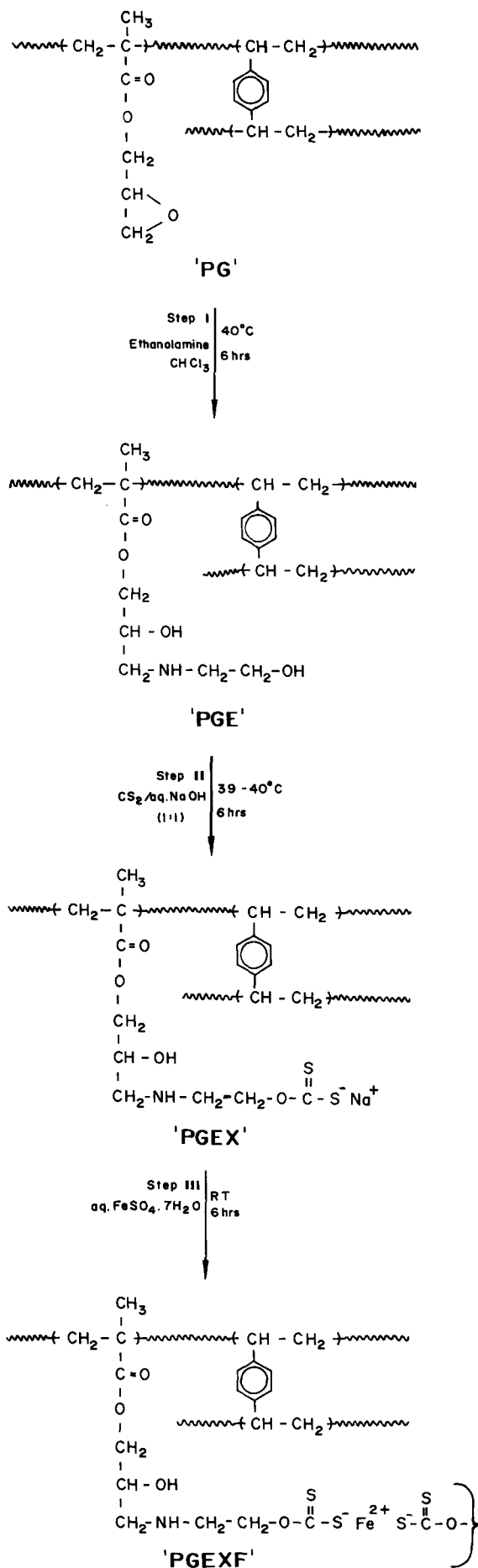


Figure 1 Pore size distribution curve of PG beads

in suspension polymerization. Beads were sieved to get various sizes of PG beads using standard test sieves. Polymer beads having 200–400 mesh (BSS) were collected and the total specific surface area and pore size distribution of the beads measured. The total specific surface area of the beads is $26.476 \text{ m}^2 \text{ g}^{-1}$. A plot of derivative of desorption volume/derivative of pore radius (D_v/D_r) versus pore radius forms the pore size distribution curve, and it is given for PG beads in Figure 1.

The polymer-supported redox catalyst system with H_2O_2 was based on the polymer-anchored Fe^{2+} system. In the first step, the glycidyl group of poly(glycidyl methacrylate) is modified with ethanolamine. Further modification of the alcoholic group of PGE beads with CS_2/NaOH reagent gives xanthate. Xanthates are capable of complexing with metal ions. All the modifications were confirmed by infra-red spectroscopy. Various steps involved in these reactions are given in Scheme 1.

Percentage conversions of the above reactions were 44.3 and 110.4 for steps I and II respectively. The values were calculated from C, H and N analysis data. The calculated molecular weight of PGE was taken as the molecular weight of the polymer containing the secondary amine, which was formed in the epoxide opening reaction. The molecular weight of PGE was calculated making an assumption that only secondary amine was formed in epoxide opening reaction with ethanolamine. This may be due to the rigid nature of the polymer, which hinders the reaction between secondary amine and epoxide group to form a tertiary amine²¹. The presence of secondary amine was confirmed from the FTi.r. spectrum. As the reaction was carried out in the swollen state, some tertiary amine may also be formed on the surface of the bead. This could be the reason for the error in the calculated molecular weight of PGE. Similarly, the small peaks of the parent compound appear in the infra-red spectrum of the products, indicating that the conversions are not 100%. Good agreement between calculated and observed values for PG beads shows the intactness of the glycidyl ether group upon suspension polymerization. Higher conversion of PGE to PGEX can be explained if we take into account that the alcoholic



Scheme 1

groups, which formed in epoxide opening reaction with ethanolamine, participate in the xanthate formation. The calculated molecular weight of PGEX is based on the reaction of one of the OH groups of ethanolamine added to PG beads and CS₂. The higher value of %C and lower value of %N estimated may be due in part to other OH groups also being substituted with CS₂. To study the thermal stability of these polymers, thermogravimetric analysis is carried out. From the thermograms, it is observed that all the polymers are stable up to 200°C. The small weight loss at 100°C may be due to water. The initial decomposition temperatures of PG, PGE, PGEX and PGEXF are 280, 240, 250 and 225°C respectively. Percentage degradation of the polymers at different temperatures are given in Table 1.

Morphological changes on the polymer beads are followed with optical micrographs. It is seen from the

micrographs (Figure 2) that there is no fracture of the beads during the series of chemical modifications.

Polymerization of acrylamide using polymer-supported catalysts PGEXF-H₂O₂, Fe²⁺-H₂O₂ were carried out in three polymerization tubes (A, B, C) in N₂ atmosphere at 43°C. The molecular weights of the resulting polymers were determined using an Ubbelohde viscometer at 30°C in 1 M NaNO₃ solution. It was observed that the molecular weight of polyacrylamide obtained from B is approximately five times higher than that of A. This may be due to the slow release of ·OH radicals owing to the diffusion-controlled process of the heterogeneous PGEXF-H₂O₂ system giving less ·OH radicals compared to the Fe²⁺-H₂O₂ system. As a result, there will be less ·OH radicals in the PGEXF-H₂O₂ system compared to the Fe²⁺-H₂O₂ system for corresponding concentrations. Therefore the PGEXF-H₂O₂ system leads to higher molecular weight polymer than the Fe²⁺-H₂O₂ system. It is also noticed that the yield of the polymer is higher for B compared to A. This may be due to the higher efficiency of polymer-supported catalysts. It is also interesting to notice that the polymer-supported catalyst gives a white coloured precipitate, while the conventional catalyst gives only a brown coloured precipitate, probably due to contamination of the polymer with Fe²⁺ ions. By using the polymer-supported redox catalyst, it is possible to get pure product, free from contamination of other reagents present in the reaction medium.

Table 1 Percentage weight loss of the polymer beads

Polymer	Temperature (°C)								
	50	100	150	200	250	300	350	400	450
PG	0.8	2.0	2.4	2.8	3.6	28.0	72.0	86.0	88.0
PGE	1.2	8.4	9.2	9.6	12.4	24.0	46.0	68.0	77.6
PGEX	0.8	10.8	12.4	12.8	15.2	24.8	42.0	54.0	66.0
PGEXF	0.8	6.0	6.8	7.2	14.0	31.2	46.4	57.2	66.0

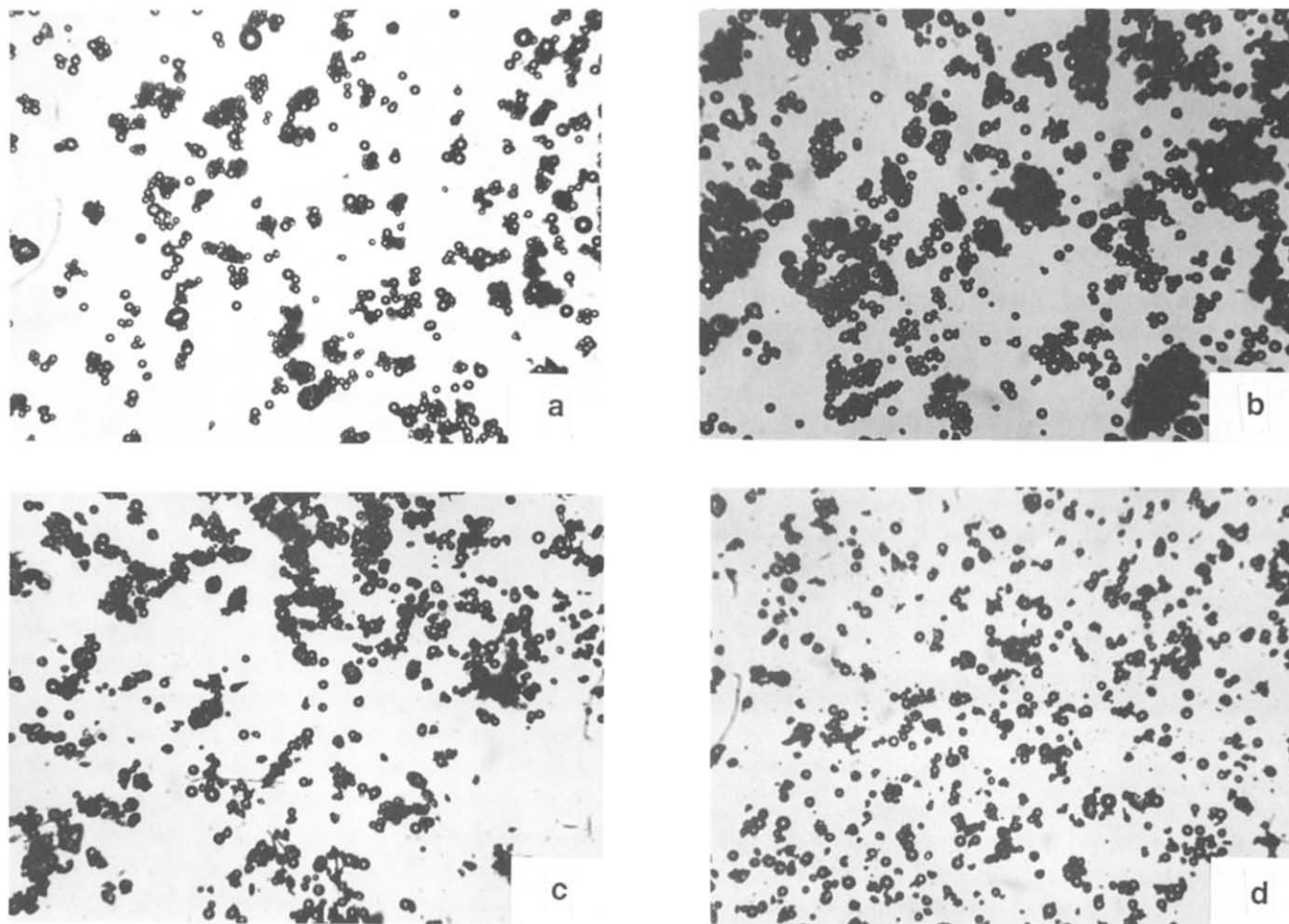


Figure 2 Optical micrographs of (a) PG, (b) PGE, (c) PGEX and (d) PGEXF beads at 100 × magnification

CONCLUSIONS

Poly(glycidyl methacrylate) beads are prepared with various degrees of crosslinking as well as various sizes. Modification of PG with ethanolamine, CS_2/NaOH and Fe^{2+} gives polymer-supported redox catalysts with H_2O_2 for radical polymerization of vinyl monomer. FTi.r. analysis, t.g.a. and elemental analysis are carried out and optical micrographs are taken for all the beads. PG beads are characterized for their specific surface area as well as pore size distribution. PGEXF catalyst gives higher conversion as well as higher molecular weight product. Presently we are using the PGEXF catalysts to polymerize vinyl monomers that are not soluble or miscible with aqueous systems.

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