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Preparation of Magnetic Amine Resins by Polymer Modification

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ABSTRACT

Weak acid ion exchangers prepared by graft polymerization of acrylic acid on cross-linked PVA microbeads containing magnetic iron oxide were converted to strong or weak base resins by reaction with glycidyltrimethylammonium chloride or with epichlorohydrin and diethylamine, respectively. Capacities up to 2.6 meq/g were obtained, but the products were susceptible to alkaline hydrolysis. Comparable resins prepared by grafting substituted methacrylic esters hydrolyzed more slowly, indicating that hydrolysis occurred at the ester linkage.

INTRODUCTION

The advantages of fine magnetic ion exchangers over conventional resins have been described previously [1, 2], as has the preparation of such resins by graft polymerization [1]. Since the number of monomers which could be grafted to magnetic poly(vinyl alcohol) (PVA) substrates was limited, attempts have been made to broaden the range of magnetic ion exchangers by modification of the grafted polymers. These attempts were briefly outlined before [1], and two procedures for converting graft polyacrylamide to weakly basic structures—the Hofmann degradation and the Mannich reaction with formaldehyde and diethylamine—have been described in more detail [2]. The present paper gives details of further modification reactions carried out on polymers grafted to magnetic substrates.

EXPERIMENTAL

Modification reactions were carried out on a resin prepared by grafting acrylic acid on < 100 μm beads of PVA 100% cross-linked with glutaraldehyde and containing 70% w/w of γ-Fe_2O_3. The resin had a capacity of 6.12 meq/g. 5-10 g lots were refluxed in an organic solvent with glycidyltrimethylammonium chloride (GMAC) [a gift of Shell Chemical (Aust) Pty Ltd] or epichlorohydrin and diethylamine (LR grades). The magnetic beads were then separated, washed with water, and air-dried. The extent of conversion was determined by microanalysis (performed by the Australian Microanalytical Service) and by $AgNO_3$ titration of chloride eluted from the products by 2 M $NaNO_3$ solution. The results shown in Tables 1 and 2 are based on microanalysis for nitrogen.

Strong base resins were also prepared by quaternization of poly-4-vinylpyridine (PVP) grafts with butyl bromide. Resins were heated with excess butyl bromide in DMF for 16-30 h at 50°C under nitrogen.

RESULTS AND DISCUSSION

Strong Base Resins

Strong base monomers have previously been prepared by esterification of methacrylic acid with GMAC [3] or epichlorohydrin and trimethylamine [4, 5]. The magnetic poly(acrylic acid) (PAA) grafts

TABLE 1. Esterification of Polyacrylic Acid Graft with Glycidyltrimethylammonium Chloride

mmol PAA	mmol GMAC	mL 1-PrOH	Time (h)	Capacity (meq/g)
61.2	61.2	75	4	0.88
61.2 (Na^+)	61.2	75	4	1.18
31.1 (Na^+)	30.6	75	8	0.40
31.1 (Na^+)	153	100	4	0.64

TABLE 2. Reaction of Polyacrylic Acid Graft with Epichlorohydrin and Diethylamine

mmol PAA	mmol epi	mmol DEA	Solvent	Capacity (meq/g)
48.0	28.5	49.0	20 mL 1-PrOH	0.76
44.5	35.5	49.0	20 mL 1-PrOH	1.00
61.2	61.3	61.5	75 mL 1-PrOH	1.52
61.2	61.3	61.5[a]	75 mL 1-PrOH	1.04
61.2[a]	61.3	61.5	75 mL 1-PrOH	1.06
61.2	61.3	61.5	75 mL dioxane	1.03
61.2	61.3	61.5	75 mL DMF	1.04
61.2	61.3	61.5[b]	75 mL 1-PrOH	1.12
55.4	364	566	200 mL 2-PrOH	0.50
55.4	454	716	200 mL 2-PrOH	1.42
61.2	648	715	200 mL 1-PrOH	2.62
61.2	61.3	575	75 mL 1-PrOH	0.39

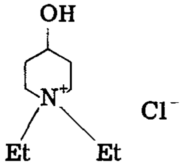
[a] Added after 2 h.
[b] In excess HCl.

were similarly esterified with GMAC as set out in Table 1. Complete conversion of a resin with a carboxyl capacity of 6.12 meq/g would give a strong base resin of capacity 3.18 meq/g (as chloride). It can be seen that the extent of esterification was low, that the sodium salt of the weak acid reacts more rapidly, as would be expected of the more nucleophilic carboxylate anion, and that, surprisingly, using excess GMAC or increasing the reaction time from 4 to 8 h caused a decrease in the product capacity.

Quaternization of magnetic PVP grafts gave strong base resins with capacities up to 0.74 meq/g (as hydrochloride) and degrees of quaternization up to 70-80%. However, as reported previously [1], the PVP grafts were found to be highly unstable under alkaline conditions, and this approach was not pursued further.

Weak Base Resins

Weak base resins were prepared by reacting the same PAA grafts with epichlorohydrin and diethylamine (DEA) as set out in Table 2. This reaction would be expected to proceed via the azetidinium intermediate [6-11]



since formation of this species proceeds rapidly under milder conditions than the reaction of epichlorohydrin with carboxylic acids [12].

Stoichiometric amounts of the reagents gave a capacity of 1.5 meq/g after 4 h in refluxing propanol, indicating that the carboxyl group reacts more rapidly with the azetidinium intermediate than with the epoxide ring of GMAC. However, the reaction of the carboxyl group with the intermediate is still the rate-determining step, for delayed addition of either the amine or the carboxylic resin (with the total reaction time still 4 h) resulted in a reduced yield of weak base. Higher boiling solvents were not advantageous. Although conversion of the carboxyl to the carboxylate group would be expected to accelerate the reaction, the yield of amine resin suffered in the presence of excess DEA, presumably because the azetidinium salt is converted [10, 11] to the diamine, $Et_2NCH_2CH(OH)CH_2NEt_2$. However, with both epichlorohydrin and DEA in excess, the capacity approached the theoretical limit of 2.82 meq/g.

Stability

The stability of the resins prepared as described above was questionable because of the possibility of hydrolysis at the ester linkage (and at the quaternary nitrogen atom in the case of the GMAC esters). Stability tests were therefore carried out, resin samples being shaken in a 2% NaOH, 10% NaCl solution, and the remaining capacity being determined at intervals. Figure 1 shows results for the strong and weak base resins compared with two strong base resins prepared by grafting 2-hydroxy-3-methacryloyloxypropyltrimethylammonium chloride ($CH_2{:}C(CH_3)COOCH_2CH(OH)CH_2N(CH_3)_3^+Cl^-$) and 2-methacryloyloxyethyltrimethylammonium methosulfate ($CH_2{:}C(CH_3)COOCH_2CH_2N(CH_3)_3^+CH_3OSO_3^-$). The poor stability of the modified products can be attributed to the greater ease of hydrolysis of acrylic as compared to methacrylic esters. (Smets and coworkers found rate constants for the high temperature hydrolysis of acrylic acid-methyl acrylate copolymers [13] to be 2-4 times greater than those for hydrolysis of comparable methacrylic acid-methyl methacrylate copolymers [14] under similar conditions. Gaetjens and Morawetz [15] found a somewhat larger α-substituent effect in the rapid hydrolysis at 25° of copolymers containing p-nitrophenyl ester groups.) This indicates that hydrolysis of the strong base resins occurs at the ester linkage rather than at the

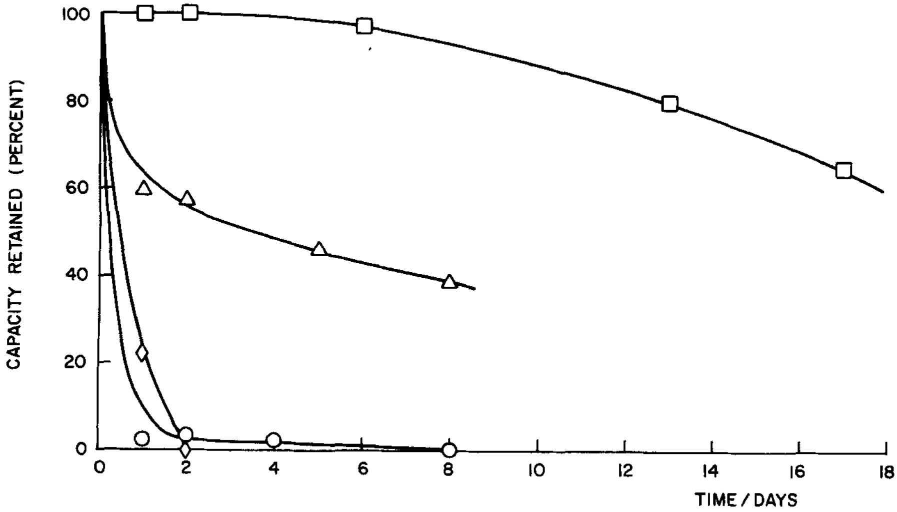


FIG. 1. Alkaline hydrolysis of magnetic shell graft resins. Resins shaken in 2% NaOH/10% NaCl solution. 2-Hydroxy-3-methacryloyloxypropyltrimethylammonium chloride graft, 4 g/50 mL (□); 2-methacryloyloxyethyltrimethylammonium methosulfate graft, 2 g/50 mL (△); GMAC ester, 2 g/50 mL (◇); and epichlorohydrin-DEA product, 2 g/50 mL (○).

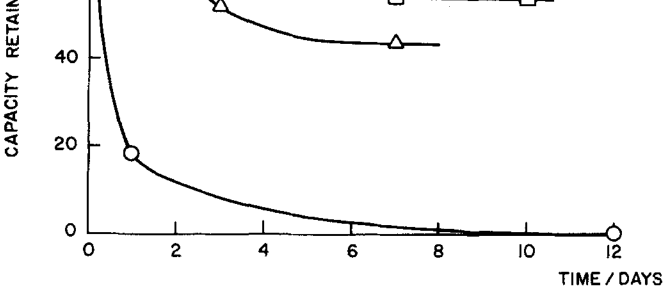


FIG. 2. Alkaline hydrolysis of magnetic shell graft resins. Hofmann product, 2 g/50 mL 2% NaOH/10% NaCl (□); Mannich product, 1 g/50 mL 2% NaOH/10% NaCl(○); and original polyacrylamide graft, 3 g/40 mL 1 M NaOH solution (△).

quaternary nitrogen. A similar conclusion was reached by Holata et al. [16] for soluble polymethacryloyloxyethyltrimethylammonium hydroxide.

Figure 2 compares the hydrolysis of modified and unmodified polyacrylamide grafts [1, 2]. (The hydrolysis of the unmodified graft was followed by determination of evolved ammonia.) The apparent plateau reached by graft polyacrylamide at ca. 50% hydrolysis indicates that alkaline hydrolysis does not involve scission of whole graft chains from the substrate. The initial rate was much faster in 2 M NaOH than in 1 M, but again a plateau was reached. Similar behavior has been reported for soluble polyacrylamide [17-20] and for polyacrylamide grafted to 60-100 nm polystyrene beads [21]. Weak base resins prepared from graft polyacrylamide via the Hofmann and especially the Mannich route [2] were also labile under alkaline conditions.

None of the products described here was deemed to have adequate stability for use as an ion exchanger.

CONCLUSIONS

Esterification with GMAC of PAA grafted to magnetic composite beads was incomplete under the conditions employed. Esterification with epichlorohydrin and DEA approached complete conversion when a large excess of both reagents was used. This reaction proceeds via an azetidinium intermediate which reacts more rapidly with carboxyl groups than does the epoxy group of GMAC. Both products rapidly lost capacity under alkaline conditions; hydrolysis of the quaternary ammonium ester was traced to the ester linkage. Previously described weak base resins prepared by modification of polyacrylamide grafts also suffered rapid capacity loss under alkaline conditions.

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