

# Preparation of High Capacity Weak Base Poly(methyl methacrylate)–Ethylene Glycol Dimethylacrylate Copolymer Anion Exchange Resin by Modification Using $\text{NO}_x$

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**ABSTRACT:** Macroporous poly(methyl methacrylate)–ethylene glycol dimethylacrylate (PMMA–EGDM) resin (resin 1) was prepared by suspension polymerization and gelatin was found to be the key component deciding the size of particles. To prepare aminated macroporous weak base PMMA–EGDM exchanger, resin 1 was nitrated using  $\text{NO}_2$  gas with a minor amount of  $\text{NO}$  (termed  $\text{NO}_x$ ). The modified PMMA–EGDM resin (resin 2) was reduced to  $\text{NH}_2$  groups and the exchange capacity of the weak base anion exchange resin (resin 3) was determined. Regression analysis of  $\text{NO}_x$  consumption versus time and the exchange capacity  $Q$  versus time data suggested a second-order kinetics for the modification reaction and these are reported. We examined the effect of duration of nitration on the exchange capacity of resin 3. It was found that it first increased with the increase

in the extent of nitration, reaching a broad maximum of 4.8 meq/g of wet resin with 78% moisture for about 8 h of nitration, and decreasing for longer nitration times as a result of polymer degradation. These results were compared with commercial resin, which had an exchange capacity of 1.68 meq/wet g with 43% moisture content. To assess the salvation ability of the modified PMMA–EGDM resin, consistent with the literature, we devised three stages of removing moisture. Experiments suggest that the high capacity of the modified PMMA–EGDM resin may be attributed to this increased salvation ability. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1991–1999, 2003

**Key words:** crosslinking; copolymers; anion exchangers; PMMA resins; solvation

## INTRODUCTION

Exchangers are insoluble solid materials that carry cations, anions, and/or chelating functional groups, and among these, organic exchangers (crosslinked polymer gels) are the most important. Their exchanging properties are obtained by (1) polymerizing functional monomers, (2) grafting an already prepared polymer with a functional polymer, or (3) modifying crosslinked polymers through chemical reaction with materials that provide necessary functional groups. The polymer most commonly used commercially is styrene–divinyl benzene copolymer (PS–DVB, with DVB content of 8–25%) because it can easily be functionalized as a result of its excess of phenyl rings.<sup>1–5</sup> To prepare an anion exchange resin, this copolymer is normally chloromethylated (i.e., introducing  $\text{CH}_2\text{Cl}$  group) by reacting with chloromethyl methyl ether. Acrylate and methacrylate polymers are important membrane materials for liquid and gas separation because of their stability and hydrophilic nature, although they have not been adopted as exchangers

because they cannot be modified without some degree of degradation. In this study we propose a nitration scheme to modify poly(methyl methacrylate)–ethylene glycol dimethylacrylate (PMMA–EGDM) copolymer without loss of the resin's mechanical strength, and show that the weak base exchanger, thus formed, has an exchange capacity considerably greater than that of available commercial anion exchangers.

The nitration of aliphatic hydrocarbons (and polymers such as PMMA–EGDM copolymer) is conventionally done by using nitric acid at temperatures between 250 and 400°C,<sup>6</sup> which because of their low reactivity, occurs satisfactorily for methane and ethane. For higher alkanes and polymers, however, there is cracking or depolymerization because of the cleavage of the C–C bonds. In this study, we report a gas phase nitration scheme of macroporous PMMA–EGDM copolymer, using a mixture of  $\text{NO}$  and  $\text{NO}_2$  gases (sometimes termed  $\text{NO}_x$ ) at a relatively low temperature (120°C), and this was not previously reported in the literature. For the purpose of anion exchanging, the aminated resin can be easily formed by reduction with hydrazine hydrate. To assess the efficacy of this gas-phase reaction, we determined its anion exchange capacity and compared it with commercially available resins [e.g., the chloride form of

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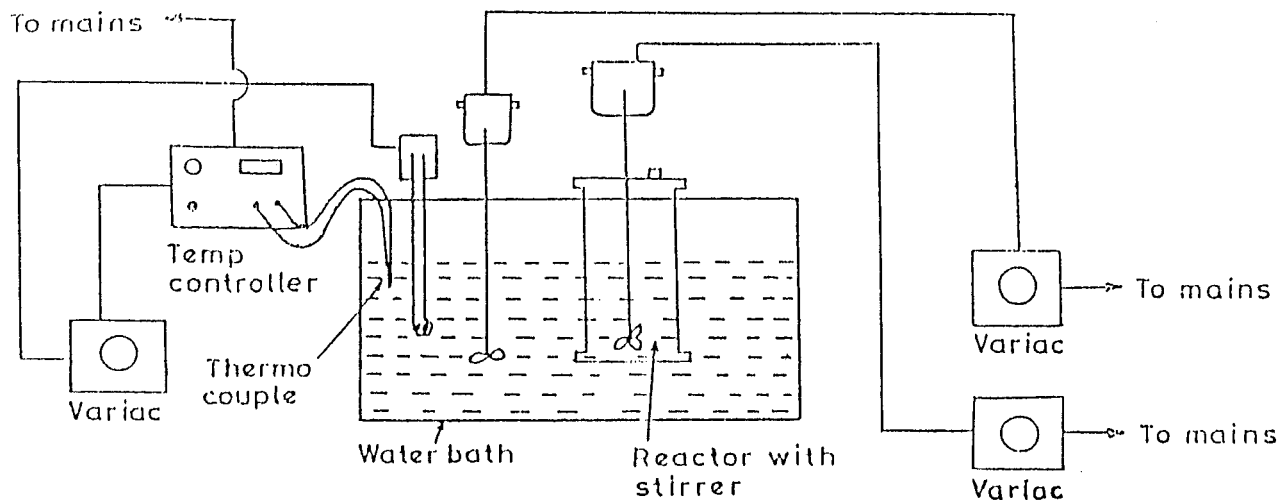


Figure 1 Experimental setup for the preparation of PMMA-EGDM resin.

PS-DVB anion exchangers from Dow Chemicals (Midland, MI)]. We found that the exchange capacity of our resin was about five times greater than that of commercial resins, indicating the high efficiency of the gas-phase nitration scheme. In addition, the original PMMA-EGDM resin was brittle, hard, and hydrophobic; however, the modified resin did not lose its strength, was not brittle, and was highly hydrophilic, retaining as much as 78% moisture.

## EXPERIMENTAL

### Preparation of macroporous PMMA-EGDM copolymer resin

The macroporous PMMA-EGDM resin (size, 1 mm) was prepared by the process of suspension polymerization using methyl methacrylate and ethylene glycol dimethacrylate by following the recipe previously reported.<sup>7-9</sup> The recipe for the preparation of PMMA-EGDM resin used in this work consisted of two phases. The organic phase consisted of methyl methacrylate (MMA, 280 g, 2.8 mol), ethylene glycol dimethacrylate (EGDM, 80 g, 0.41 mol), azobisisobutyronitrile (AIBN, 4 g, 0.025 mol), and toluene (200 mL, 2.18 mol). The second, aqueous phase consisted of calcium carbonate (8 g, 0.08 mol), sodium sulfate (48 g, 0.34 mol), gelatin (0.031 g), and distilled water (900 mL). These were mixed and, under agitation, polymerized for 4 h at 60°C and subsequently for 3 h at 95°C in the experimental setup shown in Figure 1. It was observed that particles started to adhere and form a large lump when the gelatin content was reduced below 0.031 g. However, for the gelatin content beyond this value, the resin particles do not adhere and it was found that 0.031 g of gelatin produced a resin of 1 mm particle size.

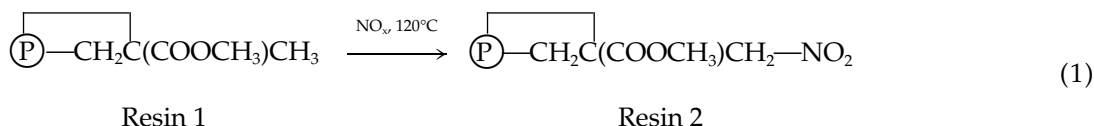
### Gas phase nitration of PMMA-EGDM resin using NO<sub>x</sub>

Direct gas-phase nitration of PMMA-EGDM resin occurred efficiently in the presence of NO<sub>2</sub> with a small amount of NO and was carried out in a 2.5-L reaction bottle. This reaction vessel was equipped with an aluminum cap with a 1.2-mm opening at the top for injecting the gas, which was closed by a silicon rubber septum. By use of the method of Vogel<sup>10</sup> and Cotton and Wilkinson,<sup>11</sup> NO<sub>2</sub> with a minor amount of NO (termed NO<sub>x</sub>) was generated in a 1.5-L two-neck round-bottom flask by reacting sodium nitrite (NaNO<sub>2</sub>, 10 g, 0.14 g-mol) with sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, sp. gr. 1.18, 25 mL) in the presence of ferrous sulfate (FeSO<sub>4</sub>, 5 g, 0.072 g-mol). The reaction occurred at room temperature and the flask was equipped with a rubber septum for withdrawing NO<sub>x</sub> with a 100-mL syringe.

The scheme of nitration was similar to that described in the literature<sup>12-14</sup> and about 1.5 g of PMMA-EGDM resins were introduced into the reaction vessel placed in an oven maintained at the desired reaction temperature. A small needle was used to puncture the silicone rubber septum of the reactor so as to allow a thermal equilibrium with the oven without developing pressure in it. The gas inside the bottle expanded as a result of heating and escaped through the needle; after this, the needle was removed and the vessel was taken out and allowed to cool at room temperature. This created a slight vacuum inside the vessel on cooling so that when NO<sub>x</sub> was introduced into the bottle, at the reaction temperature, the total pressure remained at about 1 atm. After feeding the required amount of gas mixture, the vessel was again kept in the oven maintained at the reaction temperature. After com-

pletion of nitration the vessel was removed from the oven and allowed to cool to room temperature. If we

represent PMMA-EGDM by resin 1 below, its nitration can be written as

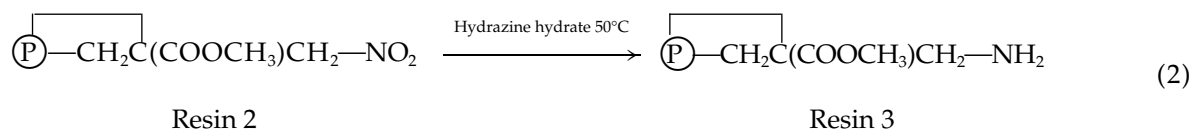


The methyl ester groups are known to be stable and are less likely to undergo modification. For this reason, the nitration of (O=C-OCH<sub>3</sub>) is not shown in eq. (1).

#### Amination of PMMA-EGDM resins

To reduce the NO<sub>2</sub> functional group to amine groups on the surface of PMMA-EGDM resins, 1.5 g of resin

2 was heated with 50 mL hydrazine hydrate at 60°C in a conical flask for 4 h. The resin's color changed from pale yellow to golden yellow after the amination reaction, and is shown in Figure 2. Again, the chemical changes taking place on the resin can be represented by



#### Characterization of resin 2

Resins 1 to 3 were characterized both chemically and instrumentally by standard techniques available to confirm the modifications. To carry out the characterization, we first performed an elemental nitrogen detection test and determined the amount of NO<sub>x</sub> consumed as a function of time during the nitration.

Elemental spot test for nitrogen detection in PMMA-EGDM resin

To detect nitrogen in resin 2, the Lassaigne element spot detection test was slightly modified. In this element nitrogen detection test, the polymer resin is fused with metallic sodium to form sodium cyanide. The entire contents were washed with water and 2–3 mL of this filtrate solution was poured into a test tube containing 0.1–0.2 g of powdered ferrous sulfate crystals. The mixture was then heated gently with shaking; then, without cooling, dilute sulfuric acid was added to dissolve the metallic hydroxides. The Prussian blue color of the formed mixture confirmed the presence of nitrogen.

Determination of exchange capacity of resin 3

We determined the exchange capacity of resin 3 by the following two procedures. The titration method, although simpler, underestimated the results.

*Titration method.* This method, based on the fact that all amine groups react with HCl to yield an ammonium salt, is convenient and quick. The procedure

consists of placing about 1.5 g of aminated resin in a conical flask and heating it with 50 mL of 0.1N HCl for 4 h. The reaction mass was then filtered and the filtrate contained unconsumed HCl, which was titrated with 0.1N NaOH to determine the chlorine ion intake by the aminated resins. This technique was always found to give lower values compared to those obtained by the gravimetric method.

*Gravimetric method.* The method of determining the exchange capacity of resin 3<sup>15</sup> is the gravimetric method, consisting of the following two steps.

1. *Regeneration:* In this step, the mixed acid is first prepared by mixing 18.1 mL of H<sub>2</sub>SO<sub>4</sub> (sp. gr. 1.84) with 27.5 mL of HCl (sp. gr. 1.19) in 500 mL of distilled water. The mixture is brought to a total volume of 1000 mL using distilled water. After this, the test water is prepared by diluting

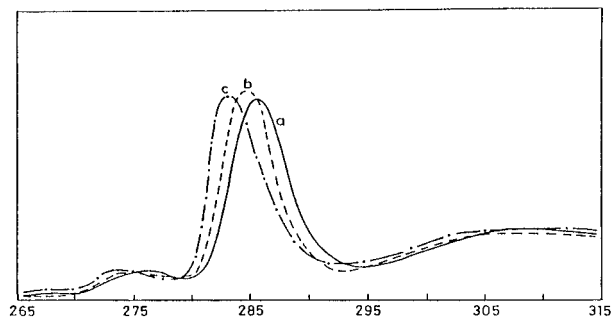


Figure 2 ESCA analysis for C 1s energy of (a) unmodified resin 1, (b) nitrated resin 2, and (c) aminated resin 3.

the mixed acid with distilled water to a 1% concentration. This test water is then added to resin 3 in a quantity of 100 mL/g and kept for 24 h. After this the resin is filtered and washed with distilled water until the filtrate becomes neutral, which is concluded by observing whether the color of methyl orange changes from orange red to orange yellow. This way we obtain resin that is free from the mixed acid.

2. *Determination of exchange capacity:* The regenerated resin obtained from step 1 is then mixed with 0.1N NaNO<sub>3</sub> solution (8.5 g in 100 mL distilled water) and kept for another 24 h. Then the reaction mass is filtered and the filtrate is added to 1.7 g of AgNO<sub>3</sub> with 2–3 drops of HNO<sub>3</sub> and the entire mass is kept for 24 h. The chlorine ions present in the filtrate form AgCl, which is precipitated. This precipitate is removed and weighed and the capacity of aminated resin is calculated.

#### Bond energy determination through ESCA analysis

The instrument used in this study was an ESCA VG MK.II apparatus (VG Scientific, UK). To determine the binding energy of different elements present in PMMA-EGDM resins, the sample was first baked for 8–10 h at 100°C. This operation was performed to obtain a clean surface and was necessary whenever the vacuum of the sample is broken or changed or the sample is changed. After sufficient baking, the sample was introduced to sample-holding track/tray in the main chamber by a sample-transport mechanism. Our sample was in the form of 1 mm size resin and the vacuum inside the system was maintained at 10<sup>-9</sup> mmHg. Survey scans were taken in the two regions of 0–500 and 500–1000 eV, respectively. According to the survey scan and depending on the nature of modifications carried out, various peaks of different elements were obtained. In our case the elements scanned were carbon, nitrogen, and oxygen. This gave rise to their respective peaks along with their binding energy regions in the survey scans. Thereafter, to analyze the binding energy of a particular element and its shift from its standard value, a sample depth scan was taken individually for carbon in the range of 275–325 eV, for oxygen in the range of 525–575 eV, and for nitrogen in the range of 400–450 eV. The entire analysis was carried out for blank, nitrated, and aminated resins 1–3.

## RESULTS AND DISCUSSION

This study is divided into nine sections that deal with (1) the formation of resins by suspension polymerization, (2) the chemical characterization of the nitrate and amine functional groups in the resin, (3) the time

and temperature effects of nitration, and (4) the solvation effect of the modification. These are discussed below.

#### Suspension polymerization of crosslinked macroporous resin

Crosslinked macroporous PMMA-EGDM copolymer resin in the form of 1 mm diameter beads were prepared according to the recipe given in the literature for suspension polymerization of PS-DVB resin particle formation. Experiments show that in this recipe, the particle size of the PMMA-EGDM resin is greatly affected by the amount of gelatin used. In addition, there is a critical concentration below which cohering particles start to form large lumps and the entire reaction mass become sticky in nature. It was found that a gelatin content of 0.031 g is the optimum value to obtain the desired particle size.

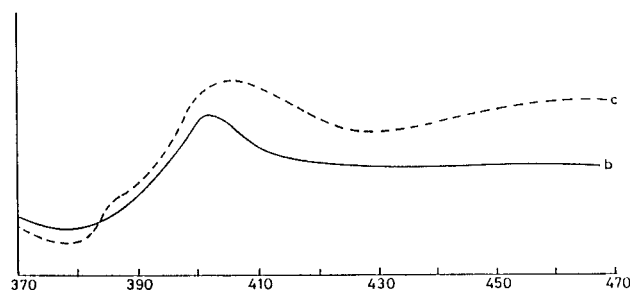
#### Nitration of PMMA-EGDM resin

By use of the procedure described earlier, resin 1 was prepared so that its average particles were large, with a size between 1 and 1.5 mm, by keeping the amount of gelatin as 0.031 g in the recipe. Resins of uniform size were separated by sieving, and these in turn were subjected to nitration. To allow a large amount of gas, we chose to work with a relatively large glass reactor (2.5 L) to accommodate the NO<sub>x</sub> without significantly increasing the reactor pressure at the reaction temperature. The silicone rubber septum facilitates introduction of the gas mixture of a known amount of NO<sub>x</sub>. To carry out the reaction smoothly, a large oven was used that could accommodate at least six reaction vessels at a time.

The effect of different reaction parameters on the extent of nitration was examined by varying the temperature, the amount of the gas feed, and the time of reaction. For each set of reactions, the amount of consumed NO<sub>x</sub> was determined by adding 100 mL of distilled water to the reactor to dissolve the remaining NO<sub>x</sub> followed by vigorous shaking. This procedure converts the residual gas within the reaction into nitric acid.<sup>11–14</sup> After this the polymer resin was separated and the filtrate consists of the HNO<sub>3</sub> solution, which is a pale yellow color. This solution was titrated with 0.1N NaOH to determine the strength of HNO<sub>3</sub> in water, and the consumed NO<sub>x</sub> was determined by the known data of the initial amount of NO<sub>x</sub> introduced into the reaction bottle. The polymer resin was then washed, dried, and kept in a dessicator, and the nitrated resin 2 was observed to have a change of color, from white to golden yellow.

#### FTIR analysis of modified resins

Functional groups present in resins 1, 2, and 3 after the reaction were determined instrumentally by FTIR (PE



**Figure 3** ESCA analysis for N 1s bond energy of (a) unmodified resin 1, (b) nitrated resin 2, and (c) aminated PMMA-EGDM resin 3.

1600; Perkin Elmer Cetus Instruments, Norwalk, CT). The resin was first ground into a fine powder and mixed with potassium bromide. The pellets (1 cm in size) were prepared by means of a hydraulic press, and samples of blank, nitrated, and aminated resins 1, 2, and 3 were used to determine FTIR spectra. There was a characteristic sharp peak at  $140\text{ cm}^{-1}$  for nitrated resin 2, which confirmed the presence of the NO<sub>2</sub> group. In resin 3 there was a strong absorption near  $3100\text{--}3200\text{ cm}^{-1}$ , which confirmed the presence of the NH<sub>2</sub> group, with the simultaneous disappearance of the peak at  $1400\text{ cm}^{-1}$  attributed to NO<sub>2</sub>.

#### Elemental analysis through ESCA

To determine the binding energy of the different elements present in PMMA-EGDM resin, we carried out an ESCA analysis, the results of which are shown in Figures 2 and 3. In the range of 275–325 eV for carbon, a peak of C 1s in Figure 2 for carbon is observed at 284.2 eV in resin 1, which was expected. Thereafter, the nitrated resin 2 was scanned and a peak was observed at 295.3 eV for C 1s. There was a shift of 1.1 eV, which confirmed the change in carbon binding energy. We then scanned nitrogen N 1s in the range of 400–450 eV for resins 2 and 3. A characteristic peak of nitrogen at 407 eV was present in the nitrogen range of 395–410 eV, as shown in Figure 3. The scan of resin 2 shows the nitrogen N 1s peak at 450 eV, and there is a decrease in the binding energy for aminated resin 3, which confirms the presence of the bond between carbon and nitrogen.

#### Determination of NO<sub>x</sub> consumed during the reaction

The unreacted NO<sub>x</sub> was determined by dissolving it in distilled water with vigorous shaking. The HNO<sub>3</sub>, which is a pale yellow color, was titrated with 0.1N NaOH to determine the strength of HNO<sub>3</sub>, and in this way the amount of consumed NO<sub>x</sub> was determined. In this study we examined the NO<sub>x</sub> consumption during the nitration reaction with both time and temperature.

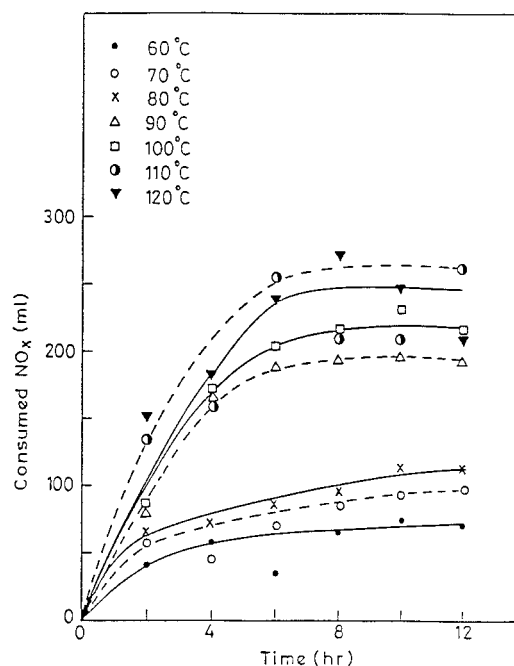
The results are plotted in Figure 4, where it may be observed that on increasing the time and temperature, the NO<sub>x</sub> consumption first increases and then attains an asymptotic value for each temperature. At lower temperatures, the NO<sub>x</sub> reacted to the PMMA-EGDM resin is of a lesser amount. We found that 120°C was the optimal temperature, and only after 9 h of reaction time was the resin observed to degrade. The NO<sub>x</sub> consumption decreases drastically because at this temperature, polymer degradation occurs by affecting the sites of reaction of polymer for the NO<sub>x</sub>.

#### Reproducibility of experimental data

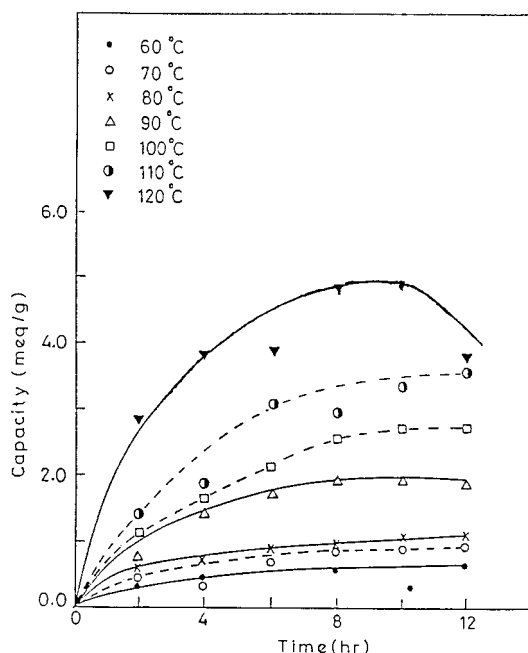
To demonstrate the reproducibility of the experimental results, we carried out the gas-phase nitration of PMMA-EGDM resin at 120°C for various reaction times (<9 h when the degradation of resin is negligible). The resultant nitrated resin 2 was aminated to form resin 3 and its exchange capacity was determined. The resin was subjected to regeneration cycles for at least nine times. Repeated experimentations revealed that the amount of NO<sub>x</sub> consumed was reproducible to within 40%, and that the exchange capacity *Q* was determined within 6%. In the regeneration cycle, however, *Q* is reproducible within 5%.

#### Exchange capacity of resin 3

To study the effect of time of nitration of the resin, the reaction was carried out for 9 h and samples were taken on an hourly basis. For this purpose, nine reac-



**Figure 4** Effect of time and temperature on NO<sub>x</sub> consumption of PMMA-EGDM resin.



**Figure 5** Effect of time and temperature on exchange capacity of resin 3.

tor bottles were placed in an oven maintained at the desired temperature. One reactor bottle was withdrawn every hour; the reacted  $\text{NO}_x$  within the bottle was determined and the results are plotted in Figure 4. On increasing the time of reaction, the color of the modified resin 1 changed gradually from white to pale yellow and brown to the naked eye. To examine the formation of nitrate groups in resin 2, it was converted to resin 3 and the capacity of the latter is shown in Figure 5.

In Figure 5 we examine the dependency of the exchange capacity of resin 3 with the duration of nitration (<9 h when the resin degradation is negligible), carried out at  $120^\circ\text{C}$ . We observe a maximum exchange capacity of 4.8 meq/g of wet resin after 8 h of nitration. A commercially available anion exchange resin is the chloromethylated PS-DVB copolymer, the quaternized form of which has the following structure:



and has an exchange capacity of 1.68 meq/g of wet resin (moisture  $\sim 43\%$ ). Compared to this resin, resin 3 has a capacity about five times this value.

It is recalled that 300 mL (13.39 mol) of  $\text{NO}_x$  was completely consumed per gram of the resin in the nitration reaction. If it is assumed that there is only one  $\text{NH}_2$  group on the repeat unit of resin 3, the anion exchanging group in resin 3 would be  $\text{NH}_3^+\text{Cl}^-$ . In this resin the molecular weight of the repeat unit  $[-\text{CH}_2-$

$\text{C}(\text{COOCH}_3)\text{CH}_2\text{NH}_2^+\text{Cl}^-]$  would be 150.5 and would provide one exchangeable chloride ion. Let us assume that  $N_0$  is the number of repeat units of polymer chain. Because resin 3 is a network, in the limit  $N_0$  should be infinity; however, for a real chain let us assume this to be some large number. For this ensemble of chains, its molecular weight is  $150.5N_0$  and it gives  $N_0$  exchangeable chloride groups. In other words, on a dry basis, it should give a capacity of  $N_0/(150.5N_0)$  or 6.64 meq/dry gram, a value that is independent of chain length. We have already observed that 13.39 mmol of  $\text{NO}_x$  is completely reacted to each gram of the resin, and in Figure 5, we observe that the maximum capacity reached is 4.8 meq/g of wet resin. Later, we show that the equilibrium moisture content of the resin is 78%, which means that on a dry basis, the capacity would be  $4.8/0.22$  or 21.82 meq/g of dry resin. This suggests that a capacity of 21.82 meq/dry gram of resin can be explained only by multiple nitration of a given repeat unit. Second, the resin reported in this work has a low surface area, which indicates that most of the modification reaction must have occurred within the polymer gel phase, with negligible reaction on the surface.

#### Determination of rate constant

In the process of modifying PMMA-EGDM resins, we carried out their gas-phase nitration as the first step, followed by their amination. We discussed the chemistry of reaction in a preceding section, and using  $\text{NO}_x$  conversion data, we are now ready to determine the kinetics of the nitration reaction. Experimental results show that the  $\text{NO}_x$  intake during the nitration reaction increases asymptotically as the time of nitration increases.

In the previous section, we showed that the nitration of polymer chains in resin 2 occurs within the gel medium. It may be likely that the  $\text{NO}_x$  under reaction conditions forms active species that diffuse into the gel giving the modification reaction. This suggests that the overall nitration reaction, discussed earlier, is a multistep process and its mathematical analysis would be complex. In the Appendix we assumed first-, second-, and third-order kinetics for the gas-phase consumption of  $[\text{NO}_x]$  versus  $t$  data, as well as capacity  $Q$  versus  $t$  data, and carried out a linear regression analysis using a  $y_{\text{model}} = ax_t + b$  type equation. Given that at  $t = 0$ , the conversion of  $\text{NO}_x$ , as well as  $Q$ , is strictly zero,  $b$  in this relation is identically equal to zero. We have computed the following:

$$S_r = \sum_{i=1}^n (y_i - y_{i,\text{model}})^2 \quad (3a)$$

**TABLE I**  
**Results of Regression Analysis of Consumption of NO<sub>x</sub> Versus Time**  
**and Exchange Capacity Versus Time**

Model type	Value of reaction order	Best-fit rate constant
Gas model 1	First-order	$k_1 = 233.54 \exp(-3182.77/T)$
Gas model 2	Second-order	$k_2 = 1.536 \times 10^{-5} \exp(-3689.9/T)$
Gas model 3	Third-order	$k_3 = 1.20 \times 10^{-8} \exp(-4249.5/T)$
Solid model 1	First-order	$k_{Q1} = 3.613 \exp(-994.3/T)$
Solid model 2	Second-order	$k_{Q2} = 0.104 \exp(-623.6/T)$
Solid model 3	Third-order	$k_{Q3} = 8.076 \times 10^{-6} \exp(-403.52/T)$

$$S_i = \sum_{i=1}^n (y_i - \bar{y})^2 \quad (3b)$$

$$\bar{y} = \frac{1}{n} \sum_{i=1}^n y_i \quad (3c)$$

and  $S_t > S_r$  implied that there is clustering of data and  $y = \bar{y}$  is a better representation of data compared to a line passing through the origin. The results of regression analysis are presented at the end of every model described in the Appendix (and summarized in Table I). This shows that in the first-order kinetic model there is clustering of data and, by increasing the order to the second- and third-order kinetic model, the fit of the data improves considerably, as seen from the values of coefficient of correlation  $r$ . We found the reverse trend when we started to fit the capacity  $Q$  versus  $t$  data. On increasing the order of the kinetic model, the coefficient of correlation  $r$  decreases. Because we have already established that all NO<sub>x</sub> molecules appear as nitrate groups in resin 2, it is expected that the kinetic order of both conversion of NO<sub>x</sub> versus  $t$  and  $Q$  versus  $t$  should have the same order. This means that the regression analysis suggests the second-order kinetic model.

### Equilibrium water content of resin 3

Ion exchangers<sup>1,4</sup> usually absorb water and swell because of their solvation ability. This swelling occurs until equilibrium is attained. We adopted the following experimental procedure<sup>12-14</sup> to determine this and to assess the solvation ability of resins 2 and 3, prepared in this study.

1. *Saturation of polymer resin with moisture:* Approximately 1.5 g of resin, which was already dried in a dessicator for at least 6 months, is weighed and placed in a standard joint conical flask. This resin is refluxed with 100 mL of distilled water for 4 h. The resin is separated and dried from the water adhering to it by use of filter papers.

2. *Oven drying:* The surface-dried resin is once again weighed, which is the wet mass of the resin. To assess how strongly water is solvated by the resin,<sup>6</sup> we carried out drying in two stages. In the first stage, the resin is placed in an oven maintained at  $105 \pm 2^\circ\text{C}$  for 4 h, after which the weight is determined. The mass of water lost by this procedure is termed shell 1 moisture.
3. *Vacuum drying:* In the second stage of drying, the resin from the oven is subjected to vacuum drying at  $100^\circ\text{C}$  for 24 h at 750 mmHg vacuum. The mass of the moisture lost by this procedure is termed shell 2 moisture.
4. *Vacuum drying for 6 months at ambient temperature under P<sub>2</sub>O<sub>5</sub>:* The resin obtained from stage 2 drying is stored in a vacuum dessicator for 6 months. The moisture lost this way is termed shell 3 moisture.

The first two stages of drying were chosen so that the commercial chloromethylated resin would completely lose its moisture. The unmodified resin loses the absorbed water completely after the first stage of drying, whereas the commercial form [strong base anion exchange resins from Dow Chemicals (obtained by chloromethylation)] loses 11.4% absorbed water after the first stage and the remaining 32.13% is lost by second-stage drying. The unmodified resin 1 retains 9.35% as shell 1 moisture, which is less than that of the commercial resin. This has no shell 2 or shell 3 moistures.

The results for shell 1, shell 2, and shell 3 moistures for resin 3 are plotted in Figure 6 as a function of duration of nitration. We observe that shell 1 and shell 2 moisture first increase with time of nitration, but after about 5 h, they decrease, to reach an asymptotic value for extended reaction times. However, shell 3 moisture continued to increase, eventually reaching an asymptotic value. Coincidentally, the time at which shell 1 and shell 2 moistures decrease is also the time at which the maxima occur in the exchange capacity, and the total moisture content is almost independent of the time of nitration.

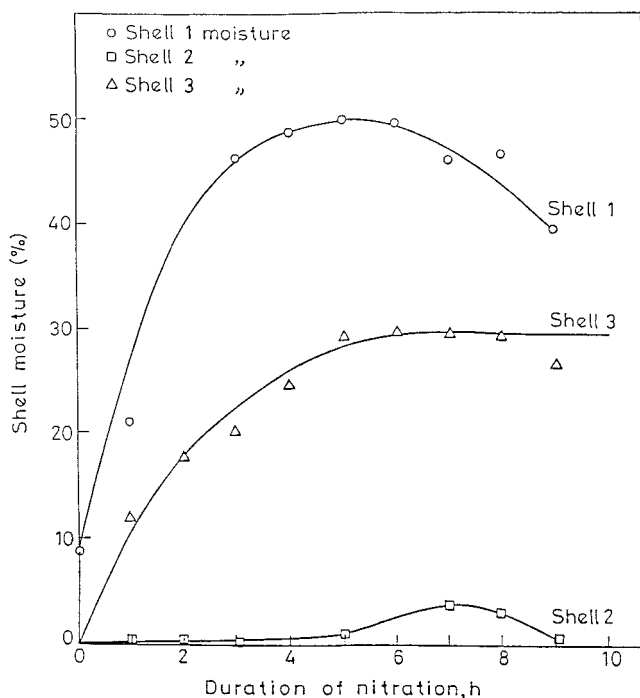


Figure 6 Effect of duration of nitration on different percentages of shell moisture for resin 3.

### CONCLUSIONS

In this study we developed a new method for nitration of PMMA-EGDM resin. The consumption of  $\text{NO}_x$  was determined by dissolving unreacted gas in water, and analysis of the exchange capacity of resin 2 shows that every molecule of  $\text{NO}_x$  reacted, appearing as an amine group in the resin. In addition, we showed that the high capacity of the resin can occur only when there is more than one exchanging site on every repeat unit of the polymer. After regression analysis of the kinetic data of the consumption of  $\text{NO}_x$  and the exchange capacity versus reaction time, the assumption of second-order kinetics gave the best results.

We investigated the effect of duration of nitration on the exchange capacity of a weak base anion exchanger, resin 3. We found that for short duration, the exchange capacity increases but decreases slightly for extended times. To assess the solvation ability of resin 3 prepared in this study, we devised three stages of drying, that produced shell 1 to shell 3 moistures. Shell 1 and shell 2 moistures are those characteristic of corresponding chloromethylated resins of the same mass. For the modified resins, shell 1 and shell 2 moistures increased for short times of nitration; however, they decreased after about 5 h of nitration, to attain a lower asymptotic value. The shell 3 moisture continued to increase, indicating that the solvation ability of this resin increases with the duration of nitration and is likely to be responsible for the high exchange capacity observed.

### APPENDIX

#### Linear regression analysis of experimental data of $\text{NO}_x$ consumption versus time and data on exchange capacity of resin 3 versus time

For the data of conversion of  $\text{NO}_x$  versus time ( $t$ ), we sought to determine the order  $n$  of the reaction in the following expression:

$$\frac{dC_A}{dt} = kC_A^n$$

We now examine the first-, second-, and third-order kinetics (or,  $n = 1, 2$ , and  $3$ ) and integrate the above equation to obtain the following. We then carried out the regression analysis of the data of consumption of  $\text{NO}_x$  versus  $t$  to determine the rate constants at different temperatures. We subsequently determined their temperature dependency by another regression analysis and report the results below for every model.

1. Gas model 1 (for  $n = 1$ )

$$-\ln(1 - X_A) = k_1 t$$

$$\text{Best-fit rate constant } k_1 = 233.54 \exp(-3182.77/T)$$

2. Gas model 2 (for  $n = 2$ )

$$\frac{X_A}{1 - X_A} = k_2 C_{A0} t$$

$$\text{Best-fit rate constant } k_2 = 1.536 \times 10^{-5} \exp(-3689.9/T)$$

3. Gas model 3 (for  $n = 3$ )

$$\frac{2X_A - X_A^2}{(1 - X_A)^2} = 2k_3 C_{A0}^2 t$$

$$\text{Best-fit rate constant } k_3 = 1.20 \times 10^{-8} \exp(-4249.5/T)$$

In the above expressions,  $A_0$  is the conversion of  $\text{NO}_x$ , which is strictly zero at  $t = 0$ . This implies that in the regression line  $A_0 = 0$ , and the number of data points that we have taken is 10.

The analysis of experimental data of  $\text{NO}_x$  conversion versus  $t$  was carried out for different gas models. For the first-order model, the variable  $S_r$  is less than  $S_t$ , which means that data clustering around the mean give less total error. Thus, we conclude that the assumption of first-order kinetics is a poor one. The assumption of second-order kinetics shows that for four out of nine temperatures studied,  $S_r > S_t$ . As opposed to this, for  $n = 3$ , such a condition does not



occur and the correlation coefficient for the data is >60%.

For solid-phase kinetic studies for exchange capacity  $Q$  versus  $t$  data, we assumed that every molecule of NO<sub>x</sub> reacted appears in NH<sub>2</sub> groups within the resin. In view of this, the integrated first-, second-, and third-order kinetics models can be expressed by replacing  $X_{\text{NO}_x}$  with  $Q/Q_\infty$  to obtain the following models.

1. Solid model 1

$$-\ln\left(1 - \frac{Q}{Q_\infty}\right) = k_1 t$$

Best-fit rate constant  $k_{Q1} = 3.613 \exp(-994.3/T)$

2. Solid model 2

$$\frac{Q/Q_\infty}{1 - Q/Q_\infty} = k_2 Q_\infty t$$

Best-fit rate constant  $k_{Q2} = 0.104 \exp(-623.6/T)$

3. Solid model 3

$$\frac{\left(\frac{Q}{Q_\infty}\right)(2 - Q/Q_\infty)}{(1 - Q/Q_\infty)^2} = 2k_3 Q_\infty^2 t$$

Best-fit rate constant  $k_{Q3} = 8.076 \times 10^{-6} \exp(-403.52/T)$

In the above expressions  $Q_\infty$  is the asymptotic exchange capacity (at  $t = \infty$ ).

The experimental data on exchange capacity  $Q$  was analyzed for different kinetic models. A careful exam-

ination of results reveals that in these models,  $S_t > S_r$ , which implies that it is possible to determine the best line passing through the origin. However, for first-order solid model 1, except for  $T = 120^\circ\text{C}$ , the correlation coefficient  $r$  was >75%. As the kinetic order  $n$  increases, results show that the fit becomes poorer. The second-order fit for both sets of data appear to give optimal results. The regression analysis data yield rate constants that are given along with the above-mentioned models.

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