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H. A. J. Battaerd^a; R. Siudak^b

^a Central Research Laboratories ICIANZ Ltd., Victoria, Australia ^b Chemical Research Laboratories CURO Division of Applied Chemistry, Melbourne, Australia

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Synthesis and Ion-Exchange Properties of Surface Grafts

H. A. J. BATAERD

*Central Research Laboratories
ICI ANZ Ltd.
Ascot Vale
Victoria, Australia, 3032*

and
R. SIUDAK

*Chemical Research Laboratories
CSIRO Division of Applied Chemistry
Melbourne, Australia, 3001*

SUMMARY

The synthesis of ion-exchange resins consisting of an inert nucleus with a thin shell of active material grafted to the surface is described. The shell carrying the exchange function is substantially uncross-linked. The exchange properties of such resins are characterized by fast equilibration. Rate curves and properties for several types of ion-exchange structures are described.

INTRODUCTION

Reactive polymers such as ion-exchange resins consist of a cross-linked framework carrying reactive groups. The structure of such resins represents a compromise between the physical and exchange properties required [1]. Cross-linking, for instance, which is introduced to give the resin insolubility and the desired stability, influences, sometimes adversely, such important properties as rate of exchange and selectivity. It was thought that by

applying grafting techniques it might be possible to produce a resin with an inert core, possessing the required mechanical strength, and an outer shell of reactive resin, which would not have to be cross-linked.

The techniques for achieving surface grafts were developed for the treatment of fibers to impart washability, dye retention, abrasion resistance, etc. [2].

Ion-exchange resins based on the proposed principle and described in this paper have been given the name of "shell grafts."

Due to the restriction of active sites to a thin surface layer and to the absence of cross-links in this layer, equilibration between shell adsorbent and solution takes place very quickly. The active layer represents only a small part of the whole bead and this means that the shell resin can possess only a relatively small exchange capacity. Therefore its usefulness will be restricted to applications where high capacities are not required, but where a rapid approach to equilibrium is necessary. This is the case, for instance, in multistage ion-exchange processes and chromatography, where rapid equilibration is essential for sharp separation.

Work on a chromatographic application has been published by Parrish [3] who used shell-type resins for the separation of organic acids and bases. The advantages of shell resins for use in counter-current separation processes were described by Weiss [4] as early as 1953.

Rates of equilibration of ion-exchange resins could be improved by such means as reducing the particle size or reducing the degree of cross-linking of the resin. However, both methods have serious disadvantages such as excessive pressure drops over beds of fine particles and excessive swelling when the cross-linking is too low.

Shell resins do not depend on small particle size for fast rates and, as they have a nonreactive and impermeable core, they show very little swelling, even though the surface layer is not cross-linked.

PREPARATION OF SHELL RESINS

Substrates

For the work described in this paper the following substrates were used:

- 1) Clear polyethylene (PE) beads, density 0.919, MFI 7 (see Fig. 1)
- 2) Polyethylene beads loaded with 16.6% w/w rutile titanium dioxide (see Fig. 2)
- 3) Polytetrafluoroethylene (PTFE) powder, agglomerate size 25-500 μ (see Fig. 3).

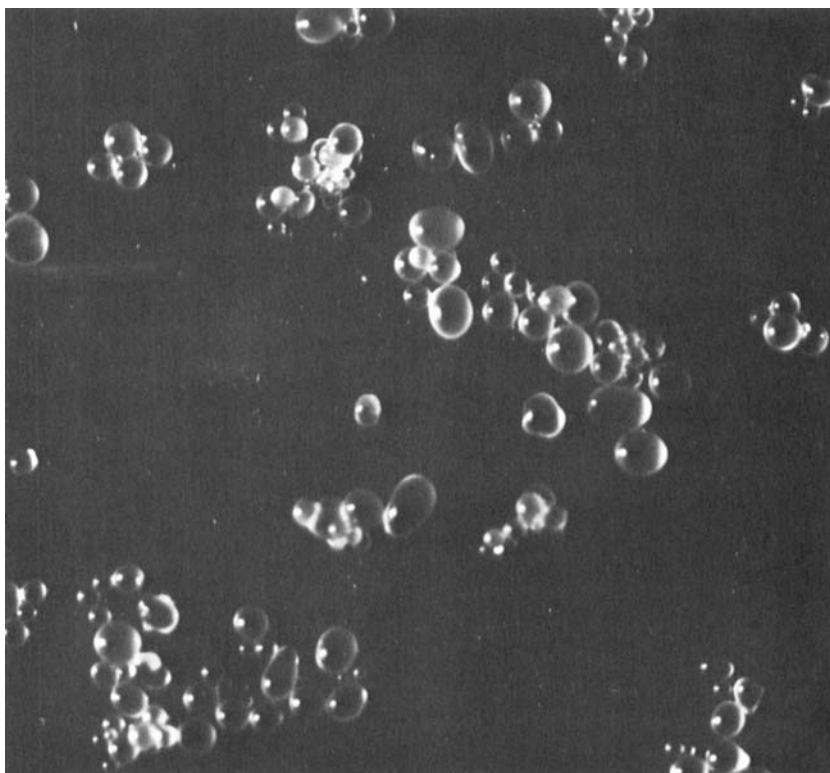


Fig. 1. Clear polyethylene beads, density 0.919, MFI 7.

The beads 1) and 2) were prepared from polyethylene powder by a method developed at ICIANZ Central Research Laboratories [5].

The use of irregular particles was soon abandoned, based on rate measurements, and spherical polyethylene powders were used instead. It was thought initially that it might be advantageous to cross-link the polyethylene beads to increase strength and insolubility. For this purpose beads were swollen in commercial divinyl benzene solution (54% DVB in a mixture of ethylvinylbenzene and diethylbenzene) and irradiated to 2 Mrad with cobalt 60γ rays, thereby insolubilizing 99.8% of the divinyl benzene (DVB). Beads so treated were insoluble above 5% w/w of DVB, but they were also porous and consequently this approach was discontinued (see Fig. 4).

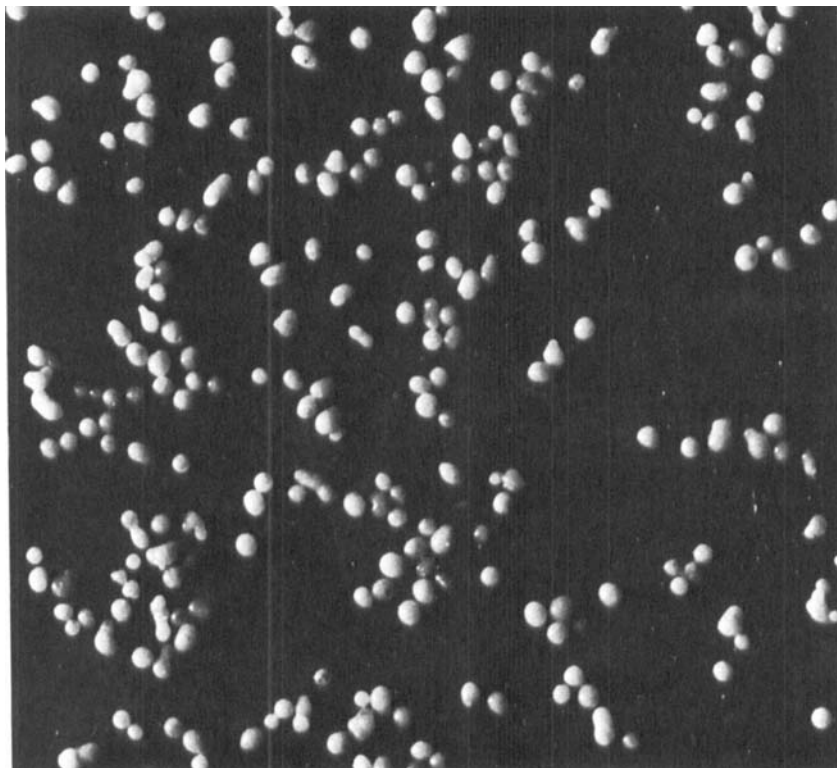


Fig. 2. Polyethylene beads, loaded with 16.6% w/w rutile titanium dioxide.

Conditions for Surface Grafting

In earlier work at the ICIANZ Research Laboratories it was established that, provided conditions for grafting were carefully chosen, a positive surface graft could be achieved [6, 8]. Such a system was used by Catt, Niall, and Tregear [8] for styrene and polytetrafluoroethylene film (see Fig. 5).

A number of other similar systems have now been developed [7]. The general rules contained in Table 1 apply to the selection of suitable systems, particularly for radiation initiation.

The system polyethylene-acrylic acid illustrates some of these conditions. Acrylic acid was grafted onto polyethylene beads by flushing them with nitrogen saturated with acrylic acid vapor at 35°C, while irradiating with cobalt-60 γ rays at a dose rate of 0.3 Mrad/hr.

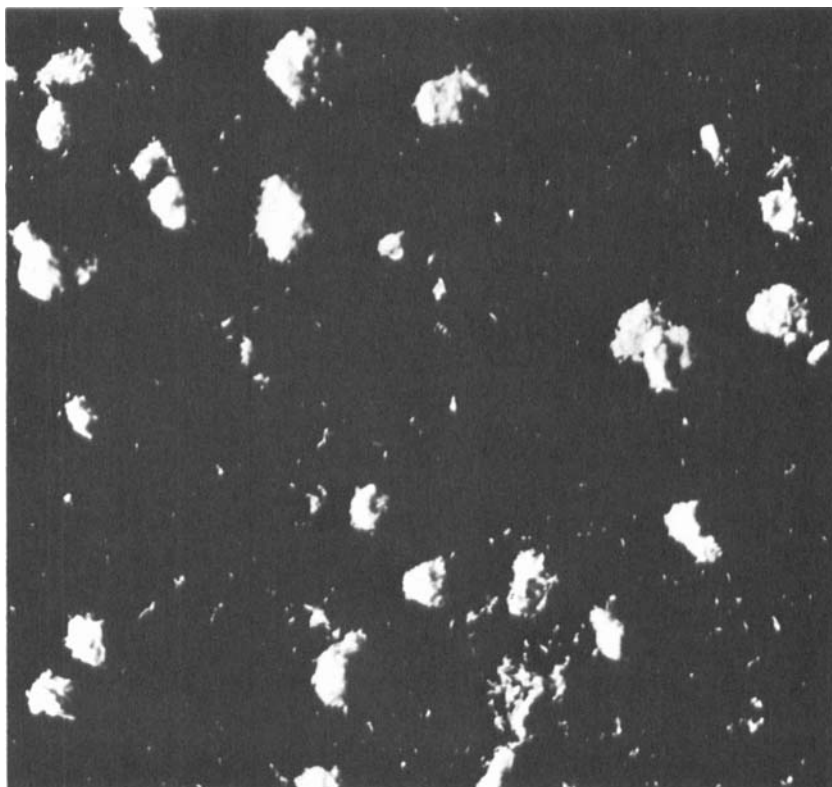


Fig. 3. Polytetrafluoroethylene powder, agglomerate size 25-500 μ .

The weight increase of the beads as a function of dose is plotted in Fig. 6. The increase in weight has been taken as representing the graft achieved since very little, if any, extractable homopolymer was formed.

Acrylic acid was also grafted onto beads from a 1-in-3 by volume mixture of acrylic acid in methanol, inhibited with 1% copper sulphate.

The beads formed by the first method are designated RLNB 858/179, and by the latter method Specpol 24.

To establish that a surface graft had taken place, beads of RLNB 858/179 were charged with cupric ions. A cross section of a bead so treated showed a well-defined boundary between the inert core and the grafted shell (see Fig. 7). Similar cross sections were scanned with an electron beam microprobe. The results confirmed the sharp boundaries found by visual observation (see Fig. 8).



Fig. 4. Cross section of crosslinked polyethylene beads, showing porosity.

The graft stands up to continuous cycling with 0.1 N sodium hydroxide and sulfuric acid, and it was not destroyed by prolonged boiling in 20% sodium hydroxide solution. The kinetics of sodium ion uptake and regeneration with acid show little change after 1000 adsorption/regeneration cycles (Figs. 9 and 10). To date resin samples have stood up to 5000 such cycles without a significant loss of capacity. It is therefore reasonable to assume that the shell is attached to the core by chemical rather than by physical bonds.

Many other systems have been investigated [6, 7]. It may be of interest to discuss briefly the system polyethylene-g-styrene.

Surface grafts have been achieved from the vapor in a fluidized bed or from a solution of the monomer in methanol. Shell formation was demonstrated by visual microscopy of sections of beads. In this case, however, the shells have to be converted subsequently by chemical means to introduce

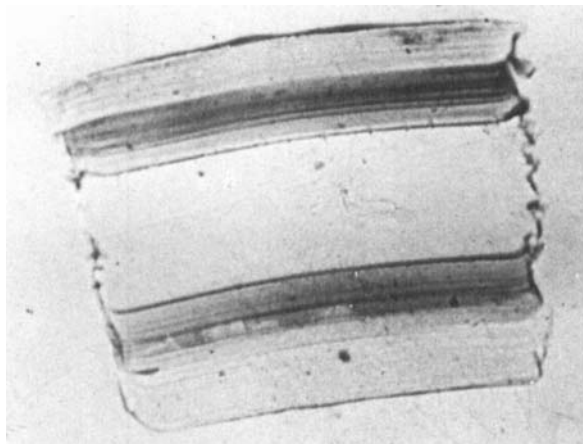


Fig. 5. Surface graft of styrene on PTFE film. Cross section of a 0.25 mm film.

Table 1. Conditions Necessary for the Formation of Surface Grafts

I.	System Selection Selection of substrate and monomer depending on their relative susceptibility to incident irradiation.
II.	Low Solubility of Monomer in Substrate Use of poor solvents.
III.	Solubility of Monomer in Its Polymer
IV.	Slow Diffusion of Monomer into Polymer <ol style="list-style-type: none"> a. Low temperature. b. Crystallinity of substrate. c. High rates of monomer consumption. d. Low monomer concentration.
V.	Factors Influencing Site of Initiation of Monomer <ol style="list-style-type: none"> a. Level of incident energy. b. Crystallinity.

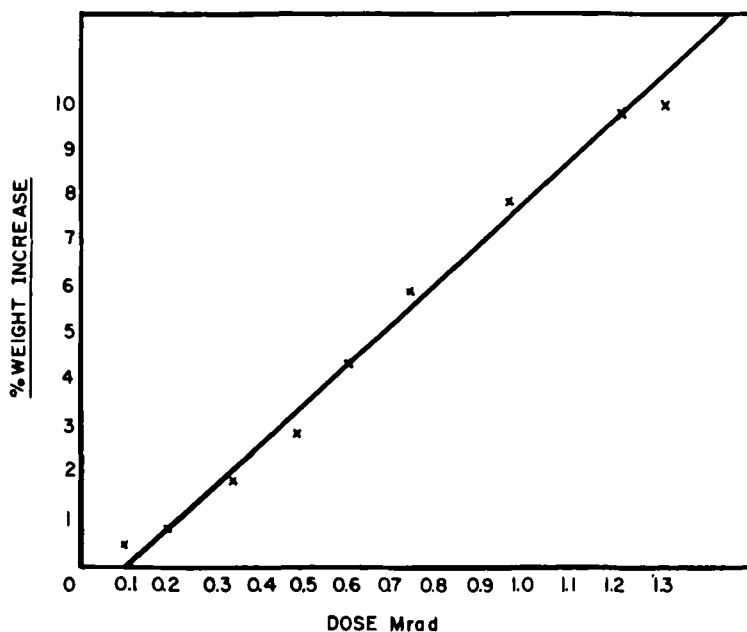


Fig. 6. Per cent weight increase of polyethylene beads, grafted with acrylic acid vapor in nitrogen at 37°C, as a function of irradiation dose.

ion-exchange groups. The usual path of chloromethylation and amination may lead to cross-linking [1]. Two resins were prepared by this method, using diethylamine and ammonia, respectively, and were compared with a conventional resin (Table 2). While the results showed some improvement in rates, it would appear that, for weak base resins at least, there is a case for an approach by direct grafting of monomers or a reduction in the number of chemical steps by using monomers other than styrene.

Unfortunately, with few exceptions, many N-vinyl compounds do not graft readily, notable exceptions being monomers such as N-alkylamino methacrylates and N-vinyl pyridines [2].

In Table 3 the kinetic properties of a direct graft of dimethylaminoethyl methacrylate and polyethylene beads are given.

To avoid the chloromethylation step mentioned above, a graft was prepared [7] from vinyl chloroethyl ether and aminated by treatment with diethylamine. An acrolein graft [7] was also prepared and transformed into a primary amine by the Leuckart-Wallach reaction. The polymer so formed can best be described as polyethylene-g-(acrolein-co-allylamine)

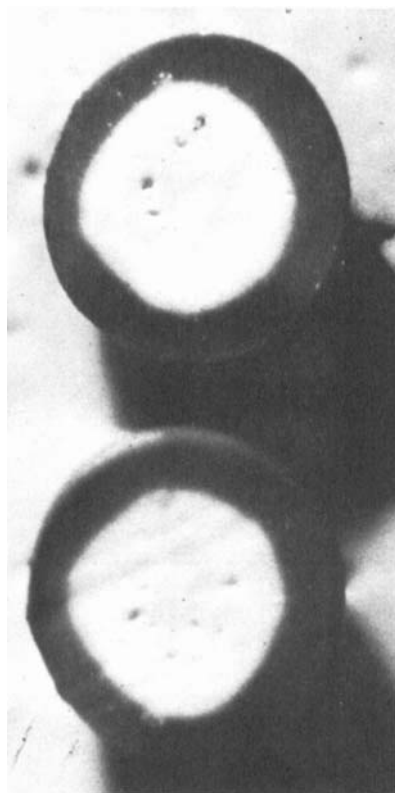


Fig. 7. Cross section of bead from RLNB 858/179 charged with cupric ions.

since only a certain proportion of the aldehyde groups can be converted. Rates achieved with the latter two polymers are given in Table 2.

ION-EXCHANGE PROPERTIES OF SHELL GRAFT RESINS

Figure 11 shows adsorption rates obtained with a polyacrylic acid-type shell adsorbent and a commercial gel-type carboxylic acid resin (Zeokarb 226, Permutit Co., London).

The shell adsorbent shows a very much faster rate, but the actual equilibrium uptake of Zeokarb 226 is approximately ten times that of the shell resin. However, in a column of conventional standard-bead resin, operating at cycle times much shorter than the equilibration time, the resin will use

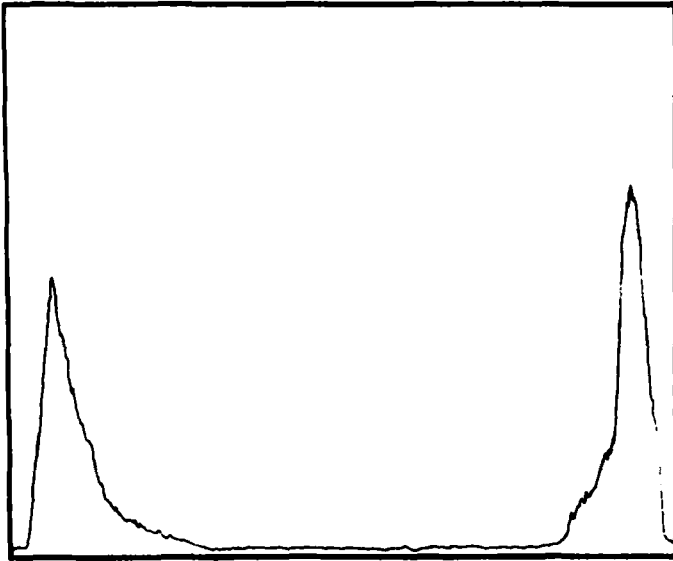


Fig. 8. Electron beam microprobe scan of a bead cross section from RLNB 858/179.

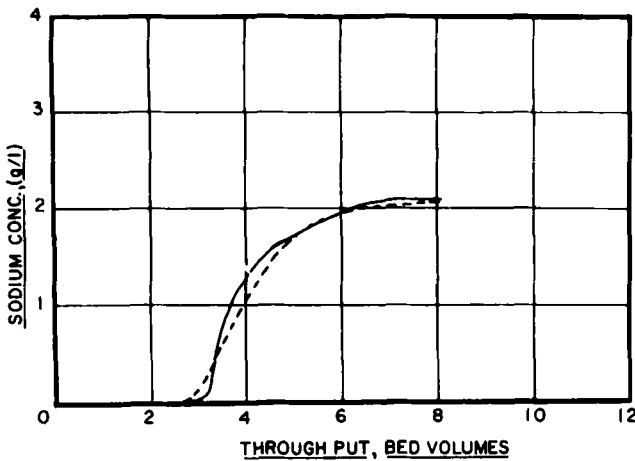


Fig. 9. Adsorption kinetics of Specpol 24 (Polyethylene-g-acrylic acid) after 100 (- -) and 1000 (-) cycles. Adsorption: feed, 0.099 N NaOH, 0.29 BV/min.

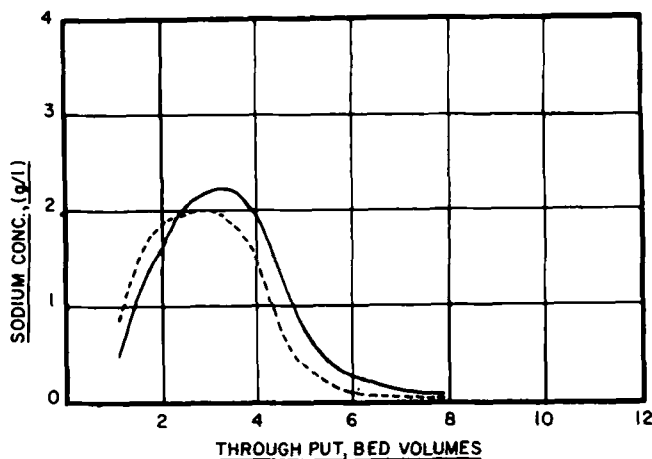


Fig. 10. Desorption kinetics of Specpol 24 (Polyethylene-g-acrylic acid) after 100 (- -) and 1000 (-) cycles. Regeneration: feed, 0.102 N H₂SO₄, 0.29 BV/min.

Table 2. Weakly Basic Copolymers Used in Shell Adsorbents

Structure of shell	Equilibrium capacity (meq/g)	% Equilibrium capacity reacted after			
		1 min	5 min	10 min	60 min
$\sim\text{C}-\text{C}\sim$ $\text{CH}_2-\text{N}-(\text{C}_2\text{H}_5)_2$	4	2.5	7.5	10	20
$\sim\text{C}-\text{C}\sim$ CH_2-NH_2	1.32	38	52	63	95
$\sim\text{C}-\text{C}\sim$ CH_2-NH_2	1.31	5	26	35	80

Table 3. Weakly Basic Copolymers Used in Shell Adsorbents

Structure of shell	Equilibrium capacity (meq/g)	% Equilibrium capacity reacted after		
		5 min	10 min	60 min
$\begin{array}{c} \text{CH}_3 \\ \\ \sim\text{C}-\text{C}\sim \\ \\ \text{COOC}_2\text{H}_4\text{N}(\text{CH}_3)_2 \end{array}$	0.68	50	90	95
$\begin{array}{c} \sim\text{C}-\text{C}-\text{C}-\text{C}\sim \\ \quad \\ \text{C}=\text{O} \quad \text{CH}_2 \\ \quad \\ \text{H} \quad \text{NH}_2 \end{array}$	1.6	90	95	96
$\begin{array}{c} \sim\text{C}-\text{C}\sim \\ \\ \text{O} \\ \\ \text{C}_2\text{H}_4-\text{N}(\text{C}_2\text{H}_5)_2 \end{array}$	2.1	63	85	90

only a fraction of its full capacity. On reversal of each cycle a time lag will occur before the direction of ion diffusion has achieved constancy. This problem is practically nonexistent with shell adsorbents since these resins reach a state of near-equilibrium very quickly.

Figure 12 shows that cross-linking the shell has little effect on the initial rate, but seems to retard a later stage of the reaction.

Of the two different methods used for the synthesis of shell grafts, the vapor-phase graft method seems, in general, to result in resins with faster equilibration rates than those obtained using the solution graft method (Fig. 13).

The different types of anion shell adsorbents examined are listed, together with their total exchange capacities and per cent equilibrium at-

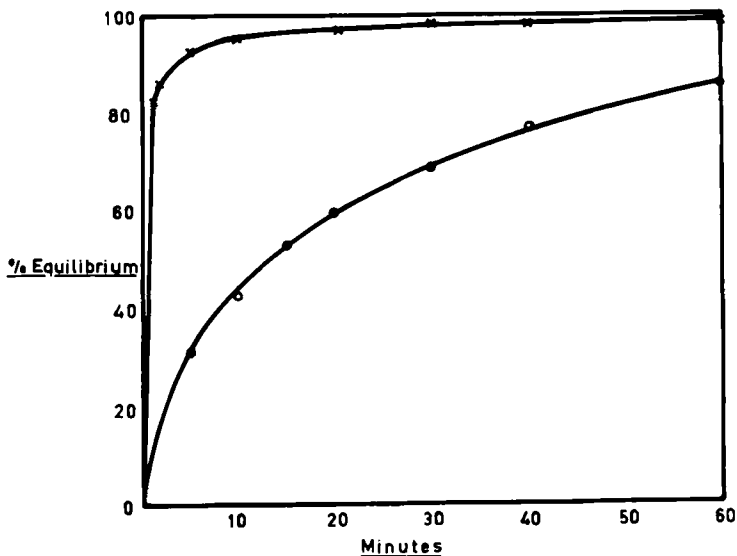


Fig. 11. Rates of Na^+ ion uptake from 0.05 N NaOH solution. (X) Shell graft resin RLNB 858/179 [PE (TiO_2)/acrylic acid]. Capacity 0.86 meq./g. Bead size 22-36 mesh. (O) Zeokarb 226 (Permutit Co., London) Capacity 9.8 meq./g. Bead size 14-52 mesh.

tained after different time intervals, in Tables 2 and 3. The first resin is a commercial resin, Deacidite G (Permutit Co., London), which has been included for comparison. This is an essentially homofunctional, weakly basic anion exchanger, based on cross-linked polystyrene, with diethylamino functional groups.

Tables 2 and 3 illustrate the vast difference between adsorption rates of the various shell grafts and the commercial resin. The polyacrolein-type shell showed the most noteworthy result with a value of 90% equilibrium achieved after only 5 min. These figures show that the use of shell adsorbents could result in a considerable improvement over conventional ion-exchange resins in processes where rate of exchange, rather than total capacity, is of importance.

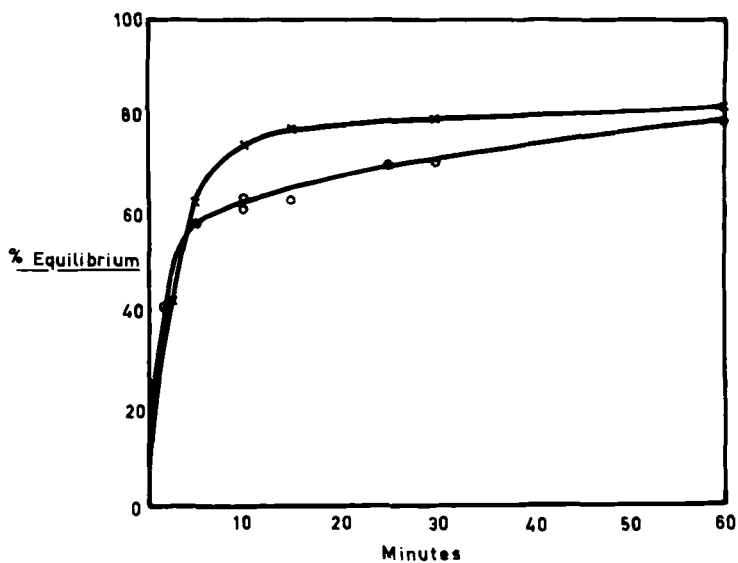


Fig. 12. Effect of cross-linking on rates of Na^+ ion uptake. (X) Specpol 2 (PE/acrylic acid, not cross-linked). Capacity 2.1 meq./g. (O) Specpol 3 [PE/acrylic acid, cross-linked (3% DVB)]. Capacity 1.4 meq./g.

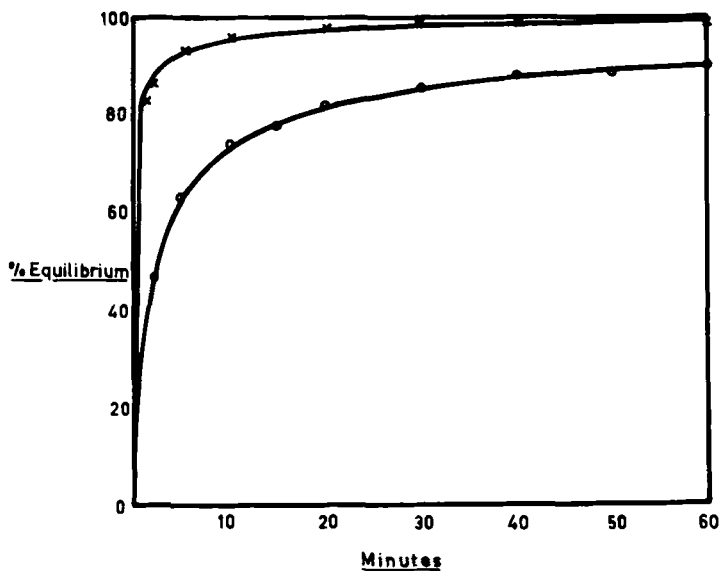


Fig. 13. Effect of method of preparation on rates of Na^+ ion uptake. (X) RLNB 858/179. [PE (TiO_2)/acrylic acid, prepared by vapor-phase graft method.] Capacity 0.86 meq./g. (O) Specpol 24 (PE/acrylic acid, prepared by solution graft method). Capacity 1.0 meq./g.

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