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The Further Cross-Linking of Polydiallylamines with Dihalo Compounds

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ABSTRACT

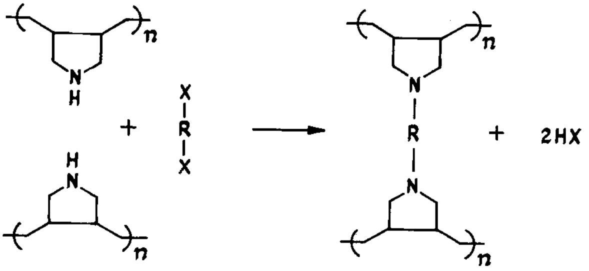
Highly swollen ion-exchange resins result from the polymerization of diallylamine in the presence of 2 mol% of a bis-diallylamino compound as the cross-linking reagent. It is shown that post cross-linking with a dihalo compound is an acceptable method for decreasing the swelling propensity of the resins. The secondary amino groups are then converted to tertiary types, although there is some formation of quaternary ammonium groups which is detrimental in ion-exchange resins which are to be regenerated thermally. The aromatic compound α,α'-dichloro-p-xylene is more suitable than the less rapidly reacting aliphatic compound $Br(CH_2)_4Br$ and the even slower reacting reagent $Cl(CH_2)_4Cl$. However, satisfactory products are obtained with the use of $Br(CH_2)_6Br$. The additional cross-linking of the polydiallylamine results in a lowering of the basicity level by one to two orders of magnitude, with the electron-withdrawing aromatic product exhibiting the greatest effect. Better pH buffering properties are usually obtained when the product is subsequently treated with hot alkali, which transforms any quaternary ammonium groups present to tertiary amino types.

INTRODUCTION

Weakly basic ion-exchange resins may be prepared by polymerizing diallylamine in the presence of a cross-linking agent of the bisdiallylamino type [1]. Such resins are useful in the Sirotherm (an ICI Australia Limited trademark for thermally regenerated ion-exchange resins and associated plant) desalination process which employs a mixture of weakly basic and weakly acidic insoluble polymers which may be regenerated with hot water rather than chemicals, as in conventional ion exchange [2]. The degree of cross-linking of the polydiallylamine (PDAA) resin is kept as low as possible to minimize residual unsaturation, which would react with the sulfite used in feed water deoxygenation. Deoxygenation is essential to prolong resin life by avoiding oxidation of amino groups under thermal regeneration conditions.

Because of the low level of cross-linking, the resins are very soft and swell greatly in dilute acid, which makes the preparation of the desired amphoteric composite resin beads from them extremely difficult. The composite resins contain the basic resin in microparticle form together with an acidic resin comprised of microparticles of cross-linked poly(acrylic acid) and a binder of poly(vinyl alcohol). Acidic conditions are employed in the formation of the composite beads when the poly(vinyl alcohol) is cross-linked with a dialdehyde [3].

Additional cross-linking of the basic PDAA resin without accompanying unsaturation should be possible by reacting the secondary amino groups with a dihalo compound as depicted in



(1)

If all the secondary amino groups react in this manner, a product containing only tertiary amino forms is obtained. Tertiary amine resins are preferred for the best operation of thermally regenerable systems, and the presence of amino groups of the one level of basicity is also desirable [2].

The aim of the present study was to determine whether common dihalo compounds could be used to toughen diallylamine resins and reduce their swelling propensity, and still yield a resin which was suitable for incorporation into an amphoteric composite bead which has optimum performance in the operation of processes based on regeneration with hot water [3]. The dihalo compounds selected were α,α'-dichloro-p-xylene, 1,6-dibromohexane, 1,4-dibromobutane, and 1,4-dichlorobutane.

RESULTS AND DISCUSSION

The starting resin was a PDAA resin cross-linked with 2 mol% of 1,6-bis(N,N-diallylamino)hexane and prepared by dispersion polymerization with a redox initiator [1]. It consisted of finely divided soft particles which adhered to one another very firmly when the polymer was dried. The swelling behavior of the resins was exemplified by the volume of 1 g of the dry, free base form of the resin when swollen in 0.1 N HCl. For the resin to be useful for making amphoteric composite beads, this volume should not exceed 8 mL; for the starting PDAA resin the value was 45.6 mL.

The results of experiments with the four dihalo compounds are shown in Table 1. The % NH which could react indicates the proportion of secondary amino groups present in the resin which is available to react with the amount of dihalo compound added. The expected capacity is the basic capacity of the resin, expressed in meq/g of dry free base form, which has been calculated from the anticipated final polymer composition. It is higher than the capacity found experimentally because the cross-linked network in the resin prevents access to all the basic sites. The titration curves of the resins were measured to determine the suitability of the products for use in a thermal regeneration process. Best results are obtained when the resin has a high buffering capacity, an estimate of which is provided by the gradient of the titration curves between the points of 30 and 70% neutralization (ΔpH). The smaller this value, the flatter the titration curve and the higher the buffering action of the resin.

For up to 50% reaction of the NH groups the resin can act as its own absorber for the HCl or HBr formed in the reaction, as in (1). The acid will react with and be held by the unreacted NH groups rather than by the newly formed tertiary amino centers which are of lower basicity. Hence for higher conversions it was necessary to add an acid sink such as pyridine or solid sodium carbonate to take up the acid released.

Pyridine in methanol is the best combination for acid adsorption, although solid sodium carbonate in methanol or ethanol were used also. This was determined using 1,4-dibromobutane as the cross-linker (Table 1, Nos. 13, 16, and 17). Similar results were obtained with 1,6-dibromohexane (Nos. 8 and 10).

TABLE 1. Properties of 2% Cross-Linked Resins Reacted with Dihalo Compounds in Refluxing Methanol for 20 h

No.	% NH which could react	Expected capacity, meq/g free base	Found capacity, meq/g free base	Volume of 1 g free base resin in HCl, mL	ΔpH, 30-70% Neutralization
		α,α'-Dichloro-p-xylene			
Starting resin	Nil	10.1	8.6	45.6	0.95
1	50	8.2	6.8	-	-
2[a]	75	7.4	5.8	5.6	0.85
3[b]	100	6.7	6.4	4.7	0.75
4[b]	125	-	6.1	4.4	0.90
4H[c]	125	-	6.4	4.5	0.38
5[d]	50 + 50% MeI	-	6.5	11.2	1.95
6[d]	25	9.1	7.6	10.9	1.20
7[d]	50	8.2	6.6	4.5	0.50
		1,6-Dibromohexane			
8[b]	50	8.5	7.6	6.3	1.40
9	50	8.5	7.1	8.6	1.20
10[a]	50	8.5	7.1	8.4	0.85
		1,4-Dibromobutane			
11[b]	25	9.6	7.5	12.5	2.15
12[b]	50	9.0	6.6	11.5	2.04
13[b]	75	8.5	5.9	11.9	1.75
13H[c]	75	8.5	6.6	4.9	0.50
14	50	9.0	6.7	15.6	-
15	75	8.5	6.5	35.6	1.90
16[a]	75	8.5	5.6	27.5	-
17[e]	75	8.5	5.8	18.1	-

(continued)

TABLE 1 (continued)

No.	% NH which could react	Expected capacity, meq/g free base	Found capacity, meq/g free base	Volume of 1 g free base resin in HCl, mL	ΔpH, 30-70% Neutralization
		1,4-Dichlorobutane			
18	50	9.0	6.2	48.1	-
19[b]	50	9.0	7.1	12.5	2.15
19H[c]	50	9.0	7.3	-	2.13
20[b]	75	8.5	6.7	10.9	1.95
21[b]	100	8.0	6.5	10.6	1.95
21H[c]	100	8.0	6.8	-	1.70

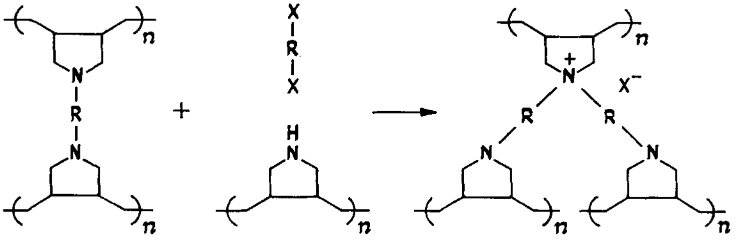
[a] Plus sodium carbonate.
[b] In pyridine/methanol, 4:1 v/v.
[c] After treatment in refluxing 2 N NaOH for 48 h.
[d] Original resin 5% cross-linked.
[e] In ethanol plus sodium carbonate.

α,α'-Dichloro-p-xylene

The results in Table 1 show that, of the compounds studied, this material is the most effective cross-linking agent as judged from the reduced swelling behavior shown in the second last column. The reaction is essentially complete after 3 h. An increase in the amount of cross-linker decreases the ease of swelling, but at the expense of capacity (Nos. 6 and 7).

An increase in the amount of α,α'-dichloro-p-xylene cross-linker has a strong effect on the overall basicity of the product resin. It lowers the levels of the curves as shown in Fig. 1; the parallel reduction in base capacity is evident from the end-points of the titration curves. At the same time it improves the gradient of the titration curve (50 vs 25% NH reacted), although the effect falls off as the potential % NH reacted increases to 75 (see also Table 1), Nos. 6 and 7; also 2, 3, and 4).

Further reaction of the dichloro compound with the tertiary amino centers already formed is possible, yielding quaternary ammonium groups as shown in



(2)

The presence of these is undesirable because of the new level of basicity introduced, which steepens the gradient of the titration curve. Also, quaternary ammonium groups take no part in the thermally reversible equilibrium [3]. It is possible that quaternary ammonium groups could be formed prior to all the secondary amino groups being converted to the tertiary form. Such a resin would contain a great variety of functional groups of varying levels of basicity, which is contrary to the aims of the present work.

The titration behavior of the products made with % NH reacted levels above 50 suggests that the formation of quaternary ammonium

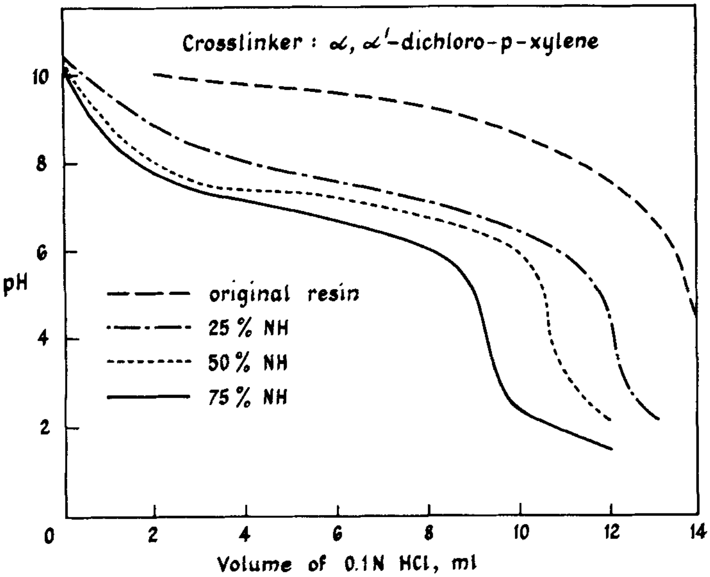


FIG. 1. Titration curves of resins made by reacting PDAA with α,α'-dichloro-p-xylene.

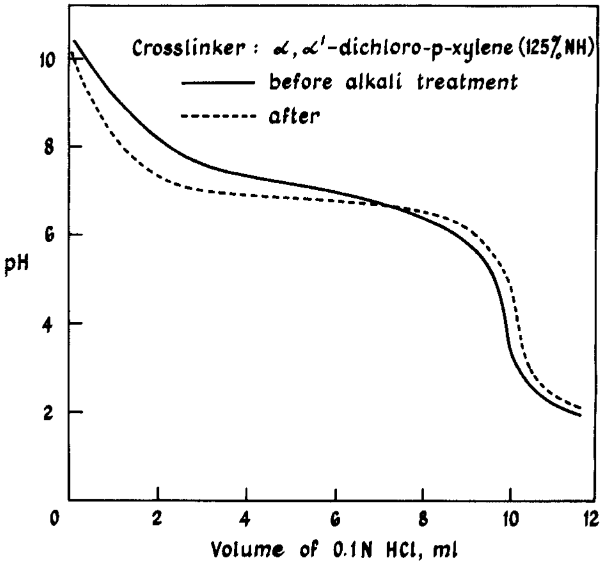
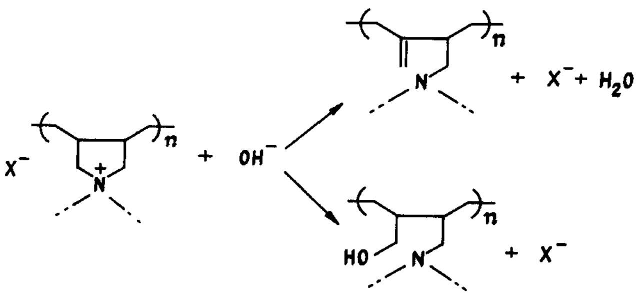


FIG. 2. Titration curves of Resin No. 4 before and after treatment of the resin to degrade quaternary ammonium groups.

centers is taking place. This is clearly so when the % NH reacted is above 100. Experiments were performed to see if the strongly basic quaternary ammonium groups could be converted to the weakly basic tertiary amino forms by treating the resins with boiling 2 N NaOH under nitrogen for 48 h. The titration curves of the resins determined before and after such treatment are shown in Fig. 2. The gradient after treatment is the lowest of all the cases studied (Table 1, Nos. 4 and 4H). A Hofmann degradation is clearly taking place, and the resulting polymer may have a number of possible structures [4], as shown in



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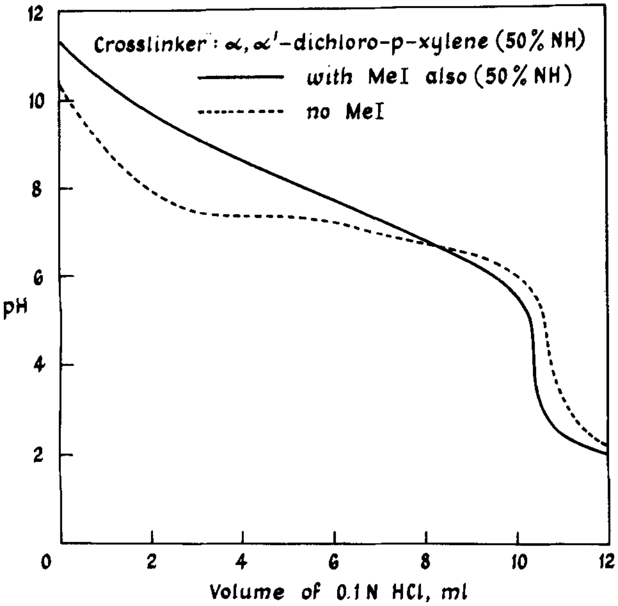


FIG. 3. Titration curves of Resins Nos. 7 and 5 showing the effect of further reaction with methyl iodide.

However, reaction of the alkali-treated resin with sulfite, which is used as a method of measuring the unsaturation present in the resin [7], showed that the top reaction in (3) is not the major pathway. After reaction with sulfite, sulfur analysis indicated that resin No. 13 contained only 0.2 meq/g of double bonds.

The 50% NH product (Table 1, No. 5), after the additional crosslinking step, was reacted with methyl iodide with the intention of converting any unreacted secondary amino groups to the tertiary form. However, many strongly basic quaternary ammonium groups were formed, as evidenced by the higher level of the titration curve shown in Fig. 3. These had a detrimental effect on the slope of the curve.

1,6-Dibromohexane

At the 50% NH level, experiments were carried out under various conditions, mainly to determine the best acid absorber (Table 1). Again, the highest bulk density was achieved using pyridine. The values are not as low as those obtained in the preceding section, but practical resins are possible. Although the titration curves are similar as shown in Fig. 4, they display higher levels of basicity.

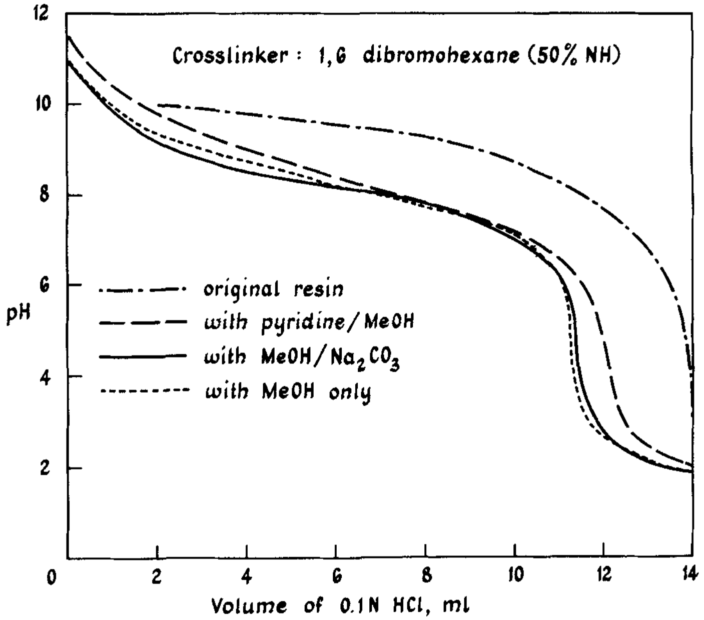
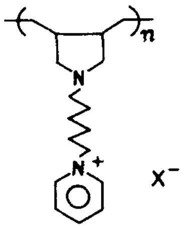


FIG. 4. Titration curves of resins made by reacting PDAA with 1,6-dibromohexane with and without the presence of acid absorbers during the reaction.

This aspect will be discussed further when the titration behavior resulting from the use of the four types of cross-linker is compared.

The trend in ΔpH in this series suggests that the use of sodium carbonate gives the best results, and pyridine the worst, as regards the homofunctionality of the product. The presence of pyridinium groups at the pendant end of the proposed cross-linker as shown in (4) cannot be discounted. Hot caustic soda treatment of the products was not attempted.



(4)

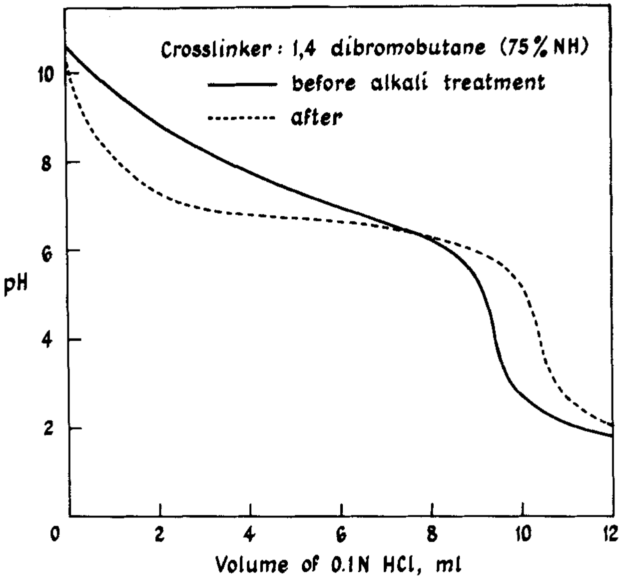


FIG. 5. Titration curves of Resin No. 13 before and after treatment of the resin with boiling alkali.

1,4-Dibromobutane

The swelling properties of the resins are markedly inferior to those of the resins described earlier, and no practical resins could be obtained, with the possible exception of an alkali-treated product (No. 13H in Table 1). A check on the bromide ion produced indicated that 80% reaction had occurred versus essentially complete reaction in the preceding studies. As already mentioned, an acid absorber is beneficial in reducing swelling with pyridine in methanol being the most effective (No. 13 vs 15, 16, and 17). The titration curves have considerable slope, indicating the presence of a mixture of basic functionalities. A very great improvement results on treatment of the resin with hot alkali, as shown in Fig. 5 (cf. Nos. 13 and 13H in Table 1).

1,4-Dichlorobutane

This dichloro compound gave results analogous to those obtained with the more reactive 1,4-dibromobutane, except that without the presence of an acid absorber the resin obtained was soft and bulky and almost impossible to handle (No. 18). Even with pyridine present the swelling could not be reduced to an acceptable level. The titration curves of the products were also unsatisfactory, and were very

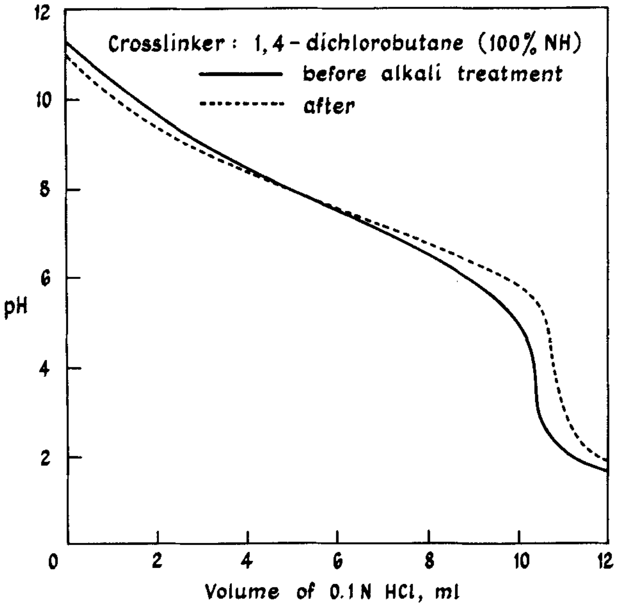


FIG. 6. Titration curves of Resin No. 21 before and after treatment of the resin with boiling alkali.

little improved by first treating the resin with hot alkali (Nos. 19 and 19H; also 21 and 21H, as depicted in Fig. 6). The high swelling of the products, especially in the absence of an acid sink (No. 18), indicates that the cross-linking reaction is far slower with this reagent.

Comparison of Basicity Levels

The basicity of the original PDAA resin is greatly lowered by the introduction of the additional cross-links, as can be seen from Figs. 1 and 4. Using the pH value at half neutralization ($pH_{\frac{1}{2}}$) as a measure of the level of basicity, it can be seen that this is decreased by 1 to 2 units, depending on the nature of the cross-linker. The values obtained are at the levels required in thermal regeneration systems [2]. Data on basicity levels are compiled for a number of the modified resins in Table 2, together with the ΔpH gradient values.

For the example in which the aromatic cross-linker was utilized, the $pH_{\frac{1}{2}}$ of the PDAA is lowered by 2.2, with a further lowering to a total of 2.6 units when hot alkali treatment is employed to degrade the very strongly basic quaternary ammonium groups which were

TABLE 2. Titration Behavior of 2% Cross-Linked PDAA Resins Reacted in Methanolic Pyridine with Dihalo Compounds

No.	% NH which could react	Dihalo compound[a]	$pH_{\frac{1}{2}}$ in 1100 mg/L NaCl	ΔpH 30-70% Neutralization
-	Nil	-	9.4	0.95
4	125	A	7.2	0.90
4H[b]	125	A	6.8	0.38
7[c]	50	A	7.3	0.50
9[d]	50	B	8.3	1.20
8	50	B	8.4	1.40
12	50	C	7.8	2.04
13	75	C	7.4	1.75
13H[b]	75	C	6.7	0.50
19	50	D	8.3	2.15
19H[b]	50	D	8.2	2.13

[a] A: α,α'-dichloro-p-xylene; B: 1,6-dibromohexane; C: 1,4-dibromobutane; D: 1,4-dichlorobutane.

[b] After treatment in refluxing 2 N NaOH for 48 h.

[c] No pyridine present, and initial resin 5% cross-linked.

[d] No pyridine present.

introduced (Nos. 4 and 4 H). The flattening of the curve has already been remarked upon. A similar basicity is obtained for an initially 5% cross-linked PDAA resin after reaction with a lesser amount of the dihalo compound (No. 7).

Much smaller decreases in $pH_{\frac{1}{2}}$ result when the cross-links are of an aliphatic type, the values for 50% NH reaction ranging from 1.0 to 1.6 for hexamethylene and tetramethylene (Nos. 8, 12, and 19). This is in accord with the electron-withdrawing character of the aromatic p-xylylene bridge, and parallels the pK_a values observed for simple amines. Thus for N-substituted pyrrolidines the pK_a values vary as follows [5]:

Pyrrolidine	11.3
N-Benzylpyrrolidine	9.5
N-n-Butylpyrrolidine	10.4

When the dibromo compounds are used as the additional cross-linking reagent, the product in the tetramethylene case has a lower $pH_{\frac{1}{2}}$ by 0.6 units (Nos. 12 and 8). This is in line with its lower concentration of basic groups at 6.6 vs 7.6 meq/g (Table 1). In comparisons of resins of similar structure, those having the lower concentration of basic groups always exhibit less basic behavior [6]. For the same % NH reacted, the tetramethylene product should have the higher capacity; that this has not occurred suggests that more side reactions are taking place. This is in accord with the higher ΔpH, which indicates a larger quaternary ammonium content.

A comparison of the products in the tetramethylene series obtained from the use of the dibromo or dichloro compounds clearly shows that the latter yields a more basic resin, and that this is also in line with the respective basic capacities of 6.6 and 7.1 meq/g (Tables 1 and 2, Nos. 19 and 12).

Degradation of the quaternary ammonium sites to tertiary amino forms also causes the expected base weakening in the tetramethylene resins, although the effect is minimal in the dichloro case (Nos. 13 and 13H; 19 and 19H). Contrary to what is found for all the other cases, the ΔpH is barely changed in the dichloro example, which is difficult to explain.

EXPERIMENTAL

The PDAA resins cross-linked with 1,6-bis(N,N-diallylamino)-hexane (usually 2 mol%) were made as before [1]. Further cross-linking with dihalo compounds was carried out on the free base form of the resin swollen in methanol. For example: α,α'-dichloro-p-xylene (0.45 g, 2.6 mmol) dissolved in methanol (20 mL) was added to the free base resin (1 g, 5.2 meq) swollen in methanol (15 mL), in a small flask equipped with a condenser and a magnetic stirrer. It was heated under reflux (under a partial vacuum, to exclude air) for 20 h. The cross-linked resin (No. 7) was collected on a sintered glass funnel, rinsed in boiling methanol and dried at the pump. The high yield of resin (1.45 g) indicated essentially complete reaction of the dichloroxylene. When the resin was extracted with 2 $\underline{N}$ sodium hydroxide three times, 88% of the added chloro groups were recovered from the washings as chloride ion. A subsequent reaction showed 90% conversion (by chloride determination) in 3 h.

When the resin was further treated to convert quaternary ammonium centers to the tertiary amino species, it was refluxed in caustic soda (1 g of resin in 25 mL of 2 $\underline{N}$ sodium hydroxide) under nitrogen for 48 h.

The method of determining the basic capacity and titration behavior was as described in earlier work [6]. The titration curves were determined for slurries of the resin in 1100 mg/L sodium chloride solution at 20°.

The reaction of bisulfite with a resin to determine its unsaturation content was carried out according to the method of Eppinger and Jackson [7].

CONCLUSIONS

The swelling of PDAA resins may be satisfactorily reduced by reacting them with a further cross-linking reagent, the most effective compounds found being α,α'-dichloro-p-xylene and 1,6-dibromohexane. The modified resins then exhibit basicity levels appropriate for a thermal regeneration system, with the two preferred systems giving levels differing by one order of magnitude. The resins produced have adequate total base capacities; they contain an acceptable concentration of tertiary amino groups. The buffering properties are not sufficient unless a treatment with hot alkali is first carried out to degrade strongly basic quaternary ammonium groups (introduced in a side reaction) to the weakly basic tertiary amino form.

The physical strength of the basic resin is improved to the extent that the additionally cross-linked products can even be employed as the binder to hold active matrix resins together [8].

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REFERENCES

[1] B. A. Bolto, K. H. Eppinger, and M. B. Jackson, J. Macromol. Sci.–Chem., A17(1), 153 (1982).
[2] B. A. Bolto and D. E. Weiss, Ion Exchange and Solvent Extraction, Vol. 7 (J. A. Marinsky and Y. Marcus, eds.), Dekker, New York, 1977, p. 221.
[3] B. A. Bolto, K. H. Eppinger, A. S. Macpherson, R. V. Siudak, D. E. Weiss, and D. Willis, Desalination, 13, 269 (1973).
[4] E. Baumann, J. Chem. Eng. Data, 5, 376 (1960).
[5] D. D. Perrin, Dissociation Constants of Organic Bases in Aqueous Solution, Butterworths, London, 1965.
[6] D. E. Weiss, B. A. Bolto, R. McNeill, A. S. Macpherson, R. Siudak, E. A. Swinton, and D. Willis, Aust. J. Chem., 19, 561 (1966).
[7] K. H. Eppinger and M. B. Jackson, J. Macromol. Sci.–Chem., A14, 121 (1980).
[8] M. B. Jackson, Am. Chem. Soc. Polym. Prepr., 20, 624 (1979).