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## Synthesis of Cross-Linked Polyallylamines Which Are Resistant to Sulfite Attack

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### ABSTRACT

The effect of the type and amount of cross-linker, the monomer concentration, and the method of polymerization on the properties of some amine resins was studied. Resins were prepared by the free-radical initiated copolymerization of diallylamine or methyldiallylamine with a cross-linker such as 1,6-bis(N,N-diallylamino)hexane or triallylamine. Particular attention was given to controlling the factors responsible for the formation of pendant allyl groups in the resins since the presence of these groups is undesirable because they react with sulfite. Low monomer concentrations favored resins with low allyl content but the yield was also low. The best way of minimizing the number of pendant allyl groups is to use low levels of cross-linker. A resin with a very low pendant allyl group content, and therefore resistant to sulfite attack, was prepared from methyldiallylamine and 5 mol% 1,6-bis(N,N-diallylamino)hexane.

## INTRODUCTION

In common with other weak-base resins, the basic component of thermally regenerable Sirotherm resins is attacked by oxygen at the regeneration temperature, which usually exceeds 80°C [1]. ("Sirotherm" is an ICI Australia Limited trademark for thermally regenerable ion-exchange resins and associated plant.) In the use of polyallylamines as the basic component, it is essential to remove dissolved oxygen from the feed water to prolong resin life [1, 2]. To allow sodium sulfite to be used for deoxygenation of the feed water [3], it is necessary to synthesize polyallylamines which are free of unreacted double bonds, since it has been found that the residual double bonds react with sulfite [4]. This reaction results in the formation of sulfonate groups which significantly decrease the amine capacity of the resin and increase the slope of its titration curve [5]. The extent of reaction of sulfite with the double bonds can be obtained by sulfur analysis. In practice, the amount of sulfur introduced by reaction with sulfite should be less than ca. 0.5%.

This paper describes the preparation of resins from diallylamine (DAA) and methyldiallylamine (MDAA) cross-linked with 1,6-bis(N,N-diallylamine)hexane or triallylamine (TAA). Preparative variables include the type and amount of cross-linker used, monomer concentration, and polymerization method. The resins were evaluated for yield, capacity, swelling ratio and, in particular, the degree of unsaturation.

## EXPERIMENTAL

Polymers of diallylamine or methyldiallylamine cross-linked with 1,6-bis(N,N-diallylamino)hexane (hexa) were prepared by two different methods. In one method the monomers (as hydrochlorides) were polymerized in solution using the free radical initiator 2,2'-azobisisobutyramidinium dihydrochloride (amido). In the other method the polymers were prepared by suspension polymerization using a redox initiator system. The two methods may be exemplified by the following typical experiments.

Solution Polymerization of Diallylamine Hydrochloride (DAA) and Hexa

Solution polymerizations were carried out by degassing a mixture of DAA, hexa, and amido in water and then heating under nitrogen at 65°C for 48 to 88 h. Two mol% amido based on the total amount of amine was used. The mol% hexa was varied from 2 to 20% based on the total amount of amine. The resulting gel was stirred in a high-speed homogenizer with 2 N HCl and repeatedly washed either (1)

with 2 N HCl and then 0.001 N HCl to obtain the resin in the HCl form, or (2) with 2 N HCl, 0.3 N NaOH, and water to obtain the resin in the free base form and dried in vacuo at 50°C.

### Suspension Polymerization of DAA and Hexa (both as Hydrochlorides)

Ferrous sulfate heptahydrate (0.82 g, 5 mol% based on total amine) was dissolved in water (2.1 mL) by warming, anhydrous hexa (4.35 g), and aqueous DAA (10 mL of 67% solution) added with shaking and the pH adjusted to 3.5. This solution was saturated with nitrogen by either vacuum degassing and refilling the flask with nitrogen, or by bubbling nitrogen through the solution overnight, and added to a nitrogen-saturated solution of Span 80 (1.26 g) (a sorbitan monolaurate from the Atlas Powder Co., Delaware) in Shell X 2 (126 mL) and the mixture shaken vigorously. A slow stream of nitrogen was continuously bubbled through the mixture, which was cooled in an ice bath to 5°C with stirring at 100 rpm, and a mixture of 100 vol H<sub>2</sub>O<sub>2</sub> (0.36 mL), H<sub>2</sub>O (1.5 mL), X 2 (1.5 mL), and Span 80 (0.06 g) added dropwise at such a rate that the temperature remained at less than 7°C. The mixture was stirred at room temperature overnight, the X 2 decanted off, and the polymer washed twice by stirring with X 2 for 15 min and centrifuging and then transferred to a sintered glass column and dried by suction. The resin was washed successively with 2 N HCl (6 h), 0.3 N NaOH (overnight), water, and dried in vacuo to give 5.5 g (66%) of polymer.

### Reaction with Sulfite

The degree of unsaturation (or the amount of pendant allyl groups) was estimated by reaction with sulfite [4]. The pH of a 2% solution of Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> (100 mL) containing a sample of resin (0.32 g) was adjusted to 5 and the solution shaken for 24 to 72 h. The resin was washed with 2 N HCl and 0.001 N HCl and dried in vacuo. The resin was then analyzed for sulfur by the Australian Microanalytical Service. The lower this value, the more saturated is the resin.

### Swelling Ratio (s.r.)

The s.r. was used as an indication of the degree of cross-linking and is defined as the ratio of the volume of a quantity of resin in 0.1 N HCl to the volume of the same amount of resin in 0.1 N sodium hydroxide. The volumes were determined in a graduated centrifuge tube after centrifugation at low speed.

## RESULTS AND DISCUSSION

The preparation and properties of the resins are summarized in Tables 1 to 3.

TABLE 1. Preparation and Properties of PolyDAA Resins Cross-linked with Hexa

No.	Mole % hexa in initial solution (w/v %)	Monomer concentration (w/v %)	Method	s. r.	Yield (%)	Capacity (meq/g)		Theoretical capacity (meq/g)	Micro-analysis of polymer (free base) calculated (%)			Sulfite treatment	
						As free base	As HCl		N	O	% S as HCl	Capacity (meq/g) as free base	
1	20	66	Suspension	1.75	66	8.06	-	9.0	11.55	6.4	8.25	2.3	6.4
2	20	66	Solution	-	39	7.6	-	9.0	-	-	-	3.0	5.4
3	20	33	Suspension	2.6	54	7.75	-	9.0	11.26	5.0	8.0	2.4	5.8
4	20	33	Solution	2.1	60	7.6	-	9.0	-	-	-	2.1	6.1
5	10	66	Suspension	2.0	51	8.06	-	9.1 <sup>b</sup>	11.56	7.9	8.25	1.4	7.3
6	10	66	Solution	3.1	53	8.25	-	9.5	-	-	-	1.56	7.0

7	10	33	Suspension	3.0	27	8.2	-	9.3 <sup>b</sup>	-	12.02	6.8	8.6	1.0	7.6
8	10	33	Solution	4.1	66	8.1	-	9.5	-	-	-	-	1.5	7.0
9	5	64	Suspension	3.85	51	8.5	6.56	9.9	7.3	12.27	8.6	8.76	1.1	7.8
10	5	66	Solution	6.4	57	-	7.0	9.9	7.3	-	-	-	1.4	7.8
11	5	32	Suspension	-	<5 <sup>a</sup>	-	-	-	-	-	-	-	-	-
12	5	33	Solution	-	68	-	6.6	9.9	7.3	-	-	-	1.2	7.8
13	2.5	64	Suspension	5.5	44	8.63	6.5	10.1	7.4	12.72	6.9	9.08	0.7	8.75
14	2.5	82	Suspension	4.4	42	8.46	7.12	10.1	7.4	12.27	8.4	8.76	0.6	8.08
15	2.0	64	Suspension	6.2	49	8.48	-	10.1	7.4	11.3	9.5	8.11	0.4	8.7

<sup>a</sup> 4% was maximum yield obtained from three separate experiments.

<sup>b</sup> For 19 and 15% hexa, respectively (see Table 4).

TABLE 2. Preparation and Properties of PolyMDAA Resins Cross-linked with Hexa

No.	Mole % hexa in initial solution	Monomer concen- tration (w/v %)	Method	s.r.	Yield (%)	Capacity (meq/g)		Theoretical capacity (meq/g) free base	Sulfite treatment	
						As free base	As HCl		% S as HCl	Capacity (meq/g) as HCl
16	20	44	Suspension	3.3	73	8.3	6.4	8.3	1.0	-
17	12	70	Suspension	2.8	58	7.7	6.0	8.5	1.1	6.4
18	12	64	Suspension	2.4	64	7.0	-	8.5	0.8	-
19	12	50	Suspension	2.8	59	6.9	-	8.5	0.9	-
20	10	43	Suspension	5.4	56	7.8	-	8.6	0.5	6.3
21	10	49	Solution	4.4	68	8.6	6.5	8.6	0.8	-
22	5	75	Suspension	3.7	67	8.5	6.5	8.8	0.4	6.5
23	5	64	Suspension	3.5	80	8.8	6.7	8.8	0.2	6.5
24	5	80	Solution	6.0	55	8.5	6.5	8.8	1.0	6.3
25	5	64	Solution	5.4	68	8.4	6.4	8.8	1.1	6.4

TABLE 3. Preparation and Properties of PolyMDAA Resins Cross-Linked with TAA

No.	Mole % TAA in initial solution	Monomer concentration (w/v %)	Method	s.r.	Yield (%)	Capacity (meq/g)		Theoretical capacity (meq/g) free base	Sulfite treatment	
						As free base	As HCl		% S as HCl	Capacity (meq/g) as HCl
26	20	64	Suspension	2.6	71	-	6.3	8.6	3.5	6.0
27	10	64	Suspension	4.0	70	8.5	6.5	8.8	1.6	6.2
28	5	64	Suspension	6.0	66	8.4	6.5	8.9	1.0	6.4



### Yield of Resins

For polymerizations in solution the yield of polymer increased both as the amount of hexa in the initial solution and as the monomer concentration decreased. Thus the best yield (68%) for poly DAA resins was obtained using 5% hexa and a 33% monomer concentration. This anomalous trend in yields was not observed for suspension (redox) polymerizations. In the suspension polymerizations of DAA/hexa systems the maximum yield (66%) was obtained at the maximum hexa (20%) and maximum monomer (66%) concentrations used, a result which was expected. It was found that a negligible amount of polymer was formed with a 5% hexa and a 33% monomer concentration using the suspension system. The yield is more sensitive to the concentration of the solution than to the amount of hexa. Thus a 51% yield of polymer was obtained with only 5% hexa and a 64% monomer concentration but the yield was < 5% with a 32% monomer concentration.

### Capacity of Resins

The amine capacities of the resins were found to increase as the amount of hexa decreased, a result consistent with the theoretical prediction. The tables show that there is a difference between the theoretical capacity and the capacity measured by titration. The term "theoretical" capacity has to be qualified, because the values have been calculated assuming the polymer composition is the same as that of the monomers. This is reasonable only when the yield is high. A more realistic capacity may be calculated from the microanalytical nitrogen figure. When this is done there is a good correlation between the base capacity calculated from titration and that calculated from the microanalytical result (see, for example, Table 1, nos. 1, 3, 5, 7, and 9). A further reason for the difference between the theoretical value and that calculated from the microanalytical nitrogen figure is that the resin contains substantial amounts of oxygen derived from hydroxyl groups introduced from the redox initiator or from water.

### Swelling Ratio of Resins

The swelling ratios are a qualitative guide to the amount of cross-linking. In almost all cases it was found that resins prepared in solution had higher swelling ratios and therefore were less cross-linked than those prepared in suspension under similar conditions. Similarly all polymers (both solution and suspension) prepared using a 33% monomer concentration had higher swelling ratios than those prepared under similar conditions but using a 66% solution. As expected, the greater the mole % hexa in the initial solution the lower

the swelling ratio and therefore the greater the cross-linking in the polymer.

### Degree of Unsaturation of Resins

The sulfur analysis of sulfite-treated resins showed that solution polymerizations usually yielded polymers with greater amounts of unsaturation than a corresponding suspension polymerization. Similarly, the sulfur analysis of the sulfite-treated resins showed that the greater the amount of hexa in the initial solution the greater the amount of unsaturation in the polymer. Thus resins prepared using 20 mol% hexa were the most unsaturated and therefore lower levels of hexa are preferable. It was also found that a lower monomer concentration favored the formation of a less unsaturated polymer.

The capacities of the sulfite-treated resins are summarized in Tables 1 to 3. As expected, resins with the greater amount of hexa and hence the greater amount of unsaturation react with greater amounts of sulfite to give sulfonated resins having considerably diminished capacities.

Sulfonated Resin 9 was found to have a capacity of 7.8 meq/g. This compares with a theoretical capacity from nitrogen microanalysis of 8.0 meq/g. Figure 1 shows the titration curve for the resin before

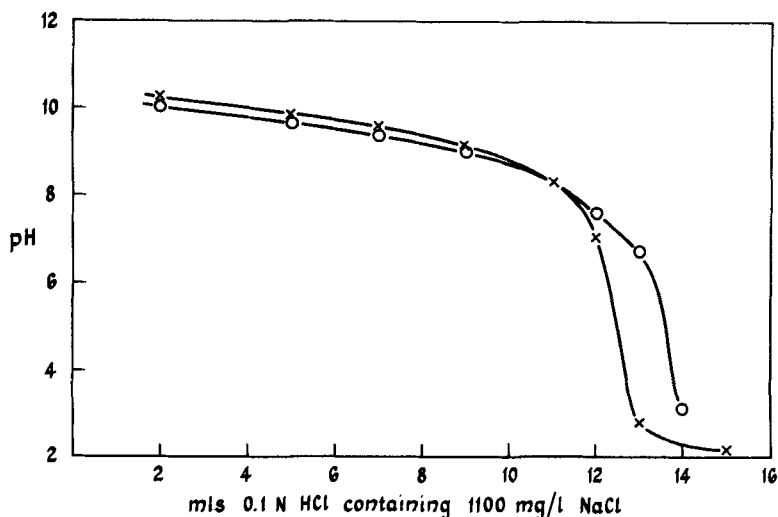


FIG. 1. Titration curve for Resin 9 (○) before reaction with sulfite and (×) after reaction with sulfite; 0.16 g of resin was used in each case.

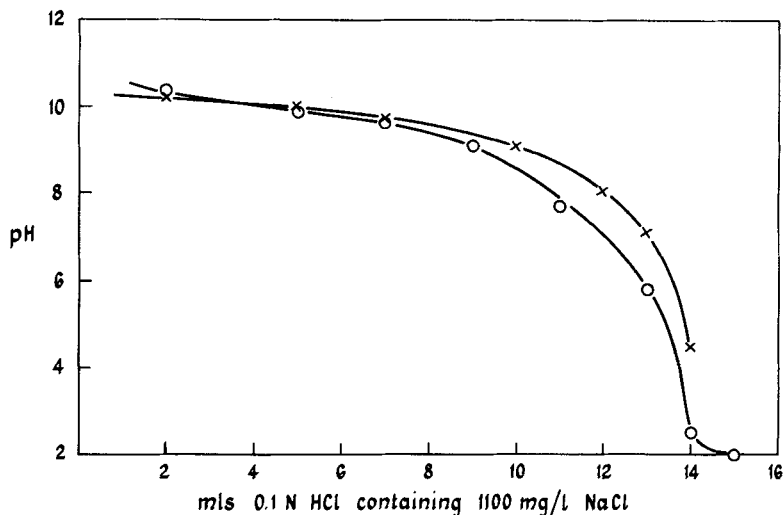


FIG. 2. Titration curve for Resin 15 (○) before reaction with sulfite and (×) after reaction with sulfite; 0.16 g of resin was used in each case.

and after sulfite treatment. It will be observed that the plateau feature is still retained and the small capacity reduction due to the weight increase caused by the sulfonate group still leaves a high capacity resin.

At very low levels of hexa (Resins 13, 14, and 15), where only 2.0 or 2.5% of hexa was present in the initial monomer solution, nearly 50% yields of polymer were obtained and all the hexa was incorporated in the polymer. Analysis of Resin 15 after treatment with sulfite showed that it contained only 0.4% sulfur and its titration curve was identical, within experimental error, to that of the untreated resin (Fig. 2). Thus Resin 15 should be suitable for use in the Sirotherm process where sulfite could be used as the oxygen scavenger.

A comparison of the results listed in Tables 1 and 2 shows that the properties of resins prepared from MDAA are similar to those of resins prepared from DAA. However, acceptable levels of unsaturation are achieved with higher levels of hexa in the initial solution (5% compared to 2.5%). The use of more hexa is an advantage since the resin then swells less. The titration curve of Resin 23 (Fig. 3) before and after reaction with sulfite shows the resins to be inert to sulfite.

Table 3 shows that similar trends are observed in the properties of resins prepared by cross-linking MDAA with triallylamine (TAA) rather than hexa. However, the use of a 5% level of TAA gives a resin with more unsaturation than does a 5% level of hexa.

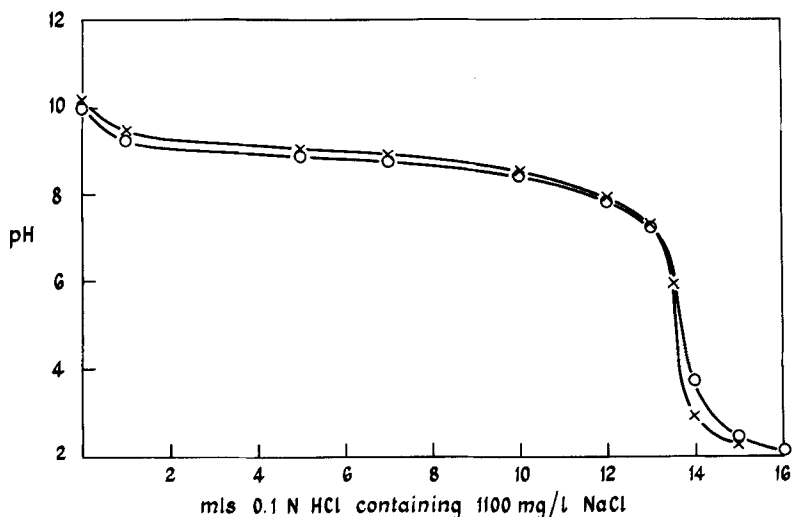


FIG. 3. Titration curve for Resin 23 (○) before reaction with sulfite and (×) after reaction with sulfite; 0.16 g of resin was used in each case.

### Resin Composition

The reactivities of DAA and hexa would be expected to be similar because of their similar structures and therefore a resin with a random distribution of DAA and hexa units would be anticipated. However, reactivity ratios were not measured because resin compositions could not be determined with sufficient precision. The determination of the composition of several resins was done as follows.

Since DAA is a secondary amine and hexa a tertiary amine, there are many potential ways of estimating the amount of one in the presence of the other when both are present in a copolymer. DAA, but not hexa, should react with, for example, isocyanates, isothiocyanates, and acetic anhydride, all of which have been used, with varying success, for determining secondary amines in the presence of tertiary amines. However, in the case of cross-linked copolymers there would be considerable doubt as to whether 100% reaction of the secondary amine could be achieved. Probably the reagent most likely to approach quantitative reaction is nitrous acid. In spite of the suggestion that secondary amines can be titrated with nitrous acid [6], we found that we were unable to achieve this even for simple amines such as diallylamine or piperidine. However, reaction did occur if the copolymer was stirred with excess nitrous acid to give a nitroso derivative. This derivative was analyzed for nitrogen and titrated

TABLE 4. Relationship between Amount of Hexa in the Initial Solution and the Amount of Hexa in PolyDAA Resins Cross-linked with Hexa

No.	Mole % hexa in initial solution	Mole % hexa in polyDAA from N analysis
1	20	23 <sup>a</sup>
3	20	34
5	10	19
7	10	15
9	5	8
13	2.5	6
14	2.5	7
15	2	5

<sup>a</sup>After nitrosation, the mole % hexa in polyDAA was calculated from the nitrogen microanalytical value to be 26 and by titration to be 15.

with acid. The composition was calculated from the results of the microanalysis and the amine (i.e., tertiary) capacity as determined from the acid titration. The results are given in Table 4. For Resin 1 the monomer solution initially contained 20% hexa and the polymer 26% hexa from the nitrogen analysis of the nitroso derivative and 15% hexa estimated from titration. The latter figure would be expected to be low because of the inaccessibility to the acid of some of the nitrogen atoms. Calculations showed that the amine composition of the resins in their free base form (but not as their hydrochlorides) could be obtained with reasonable accuracy merely from microanalytical figures and therefore it was finally decided to use this simpler procedure. Resin 1 was found to contain 23% hexa from microanalysis of the resin and 26% hexa from microanalysis of the nitroso derivative, which agrees within the experimental error. The microanalytical method assumed that the source of oxygen was water (it could also be OH from the initiator) and could not be used for amido-initiated resins because the initiator is also a source of nitrogen in the resin.

Although the results of the resin composition given in Table 4 are insufficient to draw firm conclusions, they suggest that a resin formed in 25% yield is likely to have 1.5 times the amount of hexa in the initial solution of monomers, a resin formed in 50% yield about 1.6 to 1.9 times the amount of hexa in the initial monomer solution and a resin

formed in 66% yield about 1.2 times the amount of hexa in the initial monomer solution. In other words, a resin formed in 50% yield contains all the hexa which was present in the initial solution of monomers. Tentative conclusions from these studies are that hexa polymerizes more readily than DAA. On the other hand, MDAA and hexa polymerize with about equal ease since better yields of cross-linked resin were obtained with MDAA/hexa systems. Under similar conditions, the yields of resin from MDAA/hexa systems are better than those from DAA/hexa systems, and the latter have higher contents of hexa.

### CONCLUSIONS

Resins which are low in unsaturation and therefore resistant to sulfite attack can be prepared from diallylamine and methyldiallylamine with bis(diallylamino) cross-linkers by the appropriate choice of polymerization conditions.

The method of polymerization has an influence on the residual unsaturation. The degree of cross-linking is less and the amount of unsaturation is greater for a solution than for a suspension polymerized resin. Thus suspension polymerization is preferred. These observations can be explained by assuming that both solution and suspension polymerizations under otherwise similar conditions of monomer concentration and amount of cross-linker yield polymers in which the amount of hexa is about the same but in the suspension polymerizations greater cross-linking is achieved by the hexa, thus reducing the amount of residual unsaturation.

The residual double bonds are associated with the amount of cross-linker in the resin and thus with the amount in the initial solution. As the amount of hexa is reduced, the capacity of the resin increases, and the cross-linking and the amount of unsaturation decrease. Thus, from the point of view of minimizing unsaturation, as little cross-linker as possible should be used. Of course, a level is eventually reached below which yields are too low and the degree of swelling becomes unacceptable.

In general, low degrees of cross-linking and low amounts of unsaturation are favored by low monomer concentrations. However, since the yield is more sensitive to the concentration of the solution than is the level of unsaturation, with only low yields being obtained at low concentrations, it is desirable to use high monomer concentrations and control the level of unsaturation by using low levels of cross-linker.

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