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Cyclopolymerization. VI. Preparation and Properties of Crosslinked Polyamines by Cyclopolymerization

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ABSTRACT

Crosslinked polymer and copolymers containing tertiary amino groups were prepared from a number of allylamino monomers by cyclopolymerization. The effects of the initiator residue, reaction conditions, monomer structure, and degree of crosslinking on specific properties such as ion-exchange capacity, pKa, and range of nitrogen basicities were investigated.

INTRODUCTION

The theoretical considerations of the polymerization of diallyl compounds to give essentially linear saturated polymers have been discussed in earlier papers [1, 2]. This paper will be concerned with the use of cyclopolymerization reactions to produce commercially useful polymers with secondary or tertiary amine groups in the repeating unit.

Many of the applications for basic polyelectrolytes require an insoluble resin phase, for example in ion-exchange processes, and while such structures can be formed from diallylamino compounds under specific conditions, the yields are often low and the degree of crosslinking is

difficult to control [3]. This paper will therefore explain the method of forming suitable crosslinked polyamines in good yields by commercially acceptable methods with the control of specific polymer properties.

EXPERIMENTAL

Monomers

Triallylamine was obtained from the reaction of ammonia and allyl chloride [4] and purified by distillation.

Methyl, ethyl, propyl, and butyl diallylamines were prepared by reacting allyl chloride or bromide with the appropriate alkylamine [5].

1,4-Bis(diallylamino)butane and 1,5-bis(diallylamino)pentane were prepared by reduction of the corresponding amides [6], and 1,9-bis(diallylamino)nonane was prepared by the reaction of 1,9-di(p-toluene sulphonyl)nonane with diallylamine [7].

The remaining bis(diallylamino)alkanes, $(\text{allyl})_2\text{N}(\text{CH}_2)_n\text{N}(\text{allyl})_2$, with $n = 2, 3, 6, 7, 8, 10$ were prepared from the corresponding dibromoalkane with diallylamine by heating the mixture under reflux for 24 hr [7]. The purity of the product was assessed by GLC.

Initiators

2,2'-Azobisisobutyronitrile was obtained from Fluka and used without further purification.

2,2'-Azobisisobutyramidinium hydrochloride was prepared by the method of Dekking [8].

Polymerization of Triallylamine

Persulfate/Bisulfite Initiation

Triallylamine hydrochloride was prepared by the dropwise addition of concentrated hydrochloric acid to a stirred quantity of triallylamine cooled to 5° C. Addition was continued until a homogeneous solution of pH 5 was obtained.

N 100 ethyl cellulose (0.5 g) was dissolved in benzene (50 ml) and placed in a 250 ml flanged flask fitted with a lid, anchor stirrer, N₂ inlet tube, and tap.

Sodium metabisulfite (0.42 g) was dissolved in 15 ml of 70% triallylamine hydrochloride solution, and the resulting solution was added to the reaction vessel. After purging the dispersion with nitrogen, ammonium persulfate (0.6 g) was added with vigorous stirring. Stirring was continued for 1 hr, after which time the fine white polymer particles were filtered and washed with 1 M hydrochloric acid solution, followed by prolonged washing with 1 M sodium

hydroxide solution until no more chloride ion could be leached from the resin. The resin was finally rinsed with water to remove sodium hydroxide, and dried. The polymer was obtained in 78% yield.

2,2'-Azobisisobutyramidinium Hydrochloride Initiation

2,2'-Azobisisobutyramidinium hydrochloride (0.35 g, 1.3 mmole) was dissolved in 70% triallylamine hydrochloride solution (10 g, 40 mmole), and the solution was sealed in a test tube under nitrogen and heated at 60° C for 16 hr, by which time the mixture had polymerized to a firm gel.

The gel was transferred to a blender and macerated with 1 M hydrochloric acid. The solid cake obtained by filtration of the slurry was washed to remove linear polymer and converted to the free base form by treatment with 1 M sodium hydroxide. The yield of cross-linked polymer was 70%.

Transition Metal Redox Systems

A mixture of triallylamine hydrochloride solution (150 g of 70% solution, 0.61 mole) and aqueous titanium trichloride (2.7 ml of 14% solution) was dispersed in 1100 ml of petroleum ether (30-40° C) containing sorbitan monooleate (4.5 g).

The dispersion was purged with nitrogen for 10 min, and a 3% aqueous solution of hydrogen peroxide was added dropwise with vigorous stirring at such a rate as to maintain a gentle reflux. Peroxide addition was continued until the mixture turned orange, indicating the presence of excess peroxide. After a further period of 10 min the polymer beads were isolated and washed with 1 M hydrochloric acid until all color was removed. The yield of polymer (hydrochloride form) was 62 g (59%).

Polymerizations initiated by Ti^{3+} /hydroxylamine and Ti^{3+} /butyl hydroperoxide were carried out by similar procedures, giving yields of 42 and 46%, respectively.

Polymers from Diallylamino Compounds

The preparation of poly[bis(diallylamino)alkanes] and copolymers of bis(diallylamino)alkanes/(diallylamino)alkanes was carried out as for polytriallylamine using Ti^{3+} /hydrogen peroxide as the initiating system.

Measurement of Polymer Properties

Swelling Ratio (SR)

The swelling ratio of the polymer in acid and base forms was obtained by measuring the volume occupied by the resin in 0.1 M hydrochloric acid and 0.1 M sodium hydroxide solutions and expressing the results as a ratio.

Water Regain

The water regain of a resin was obtained by determining the weight of water retained per unit weight of resin in the acid form.

Titration Curves

Titration curves were constructed [9] by accurately weighing a number of samples of resin in the base form, adding various amounts of 0.1 M hydrochloric acid solution containing 1100 ppm sodium chloride and making up each sample to a standard volume with 1100 ppm sodium chloride. The samples were shaken for 24 hr, the resin was allowed to settle for 1 hr, and the pH of each solution was measured.

The ion-exchange capacity, pH at half-neutralization ($\text{pH}_{1/2}$) and the change in pH from 10 to 60% neutralization (ΔpH) of the resin were obtained from the titration curve.

DISCUSSION

Conventional crosslinking agents, such as divinylbenzene and ethylene glycol dimethacrylate, present problems when used as comonomers with diallylamines. First, the reactivity ratios of vinylic and allylic double bonds are often sufficiently different to give rise to variable distribution of crosslinks throughout the polymer. Second, the use of a nonbasic monomer lowers the overall base-capacity of the system (i.e., the number of amino groups able to act in ion-exchange capacity per unit weight resin), which is to be avoided if possible. A more desirable approach to the preparation of cross-linked polyamines is to use amine monomers with more than two allyl groups per molecule as the crosslinking agent. Two general systems were therefore considered: first, the use of triallylamine either alone or in conjunction with diallylamines; and second, the use of bisdiallylamines with or without diallylamines.

The diallylamine compounds, bisdiallylamine compounds, and triallylamine were all difficult to polymerize in their free base form,

but their salts, such as the hydrochloride, readily polymerized with the use of a variety of initiating systems. The greater ease of polymerization of salts probably reflects the ability of a positive nitrogen atom to direct radical attack away from itself [10]. Consequently, the formation of allylic radicals—which are well known chain-transfer and chain-terminating species—would be unlikely. Also the inhibiting effect of nitrogen lone-pair electrons is removed by salt formation. In the following discussion the hydrochloride salt of the monomer was used unless otherwise stated.

One of the most important properties of interest in the present study was the rate at which equilibrium, or near-equilibrium, conditions could be attained in ion-exchange reactions with the polymer. Fast ion exchange is best satisfied by small polymer beads. These can be prepared in laboratory quantities by grinding polymer prepared in bulk polymerizations, but for large-scale production, direct formation of the beads is obviously desirable. Therefore, while preliminary experiments were carried out in bulk, the major effort centered around the usefulness of the systems for dispersion polymerization.

Another property of interest was the variation in the basicity of the amine groups in the polymer. The aim of the work was to produce polymers with little variation in basicity, i.e., the polymers require flat titration curves, as this is an essential feature for use of the polyamines used in the thermal regeneration type of ion-exchange processes [9, 11].

The polymerization processes and polymers described in this paper are the subject of a patent application.

Polytriallylamine

Persulfate Initiators

Persulfate initiators have, in the past, been used to prepare polytriallylamine [12]. Polymers prepared by us, by a method similar to that reported, had desirable mechanical strength but were completely unsatisfactory for ion-exchange polymers in the present context; the titration curves did not have the necessary plateau shape, and the ion-exchange capacities of the resins were below the values found for polytriallylamines polymerized by gamma irradiation [13]. Similar results were obtained when the persulfate was dissociated by heat or used in conjunction with a reducing agent such as sodium metabisulfite (Fig. 1). We have related both the shape of the titration curve and the low ion-exchange capacity to the incorporation of initiator residues

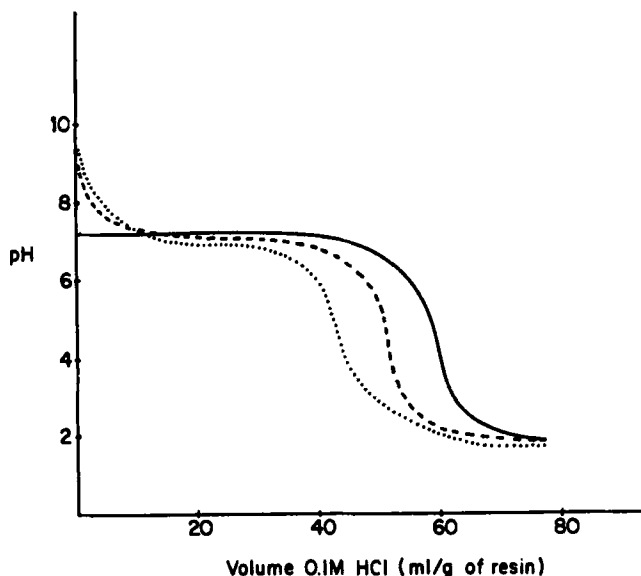


FIG. 1. Titration curves for polytriallylamine initiated by $(\text{NH}_4)_2\text{S}_2\text{O}_8/\text{Na}_2\text{S}_2\text{O}_5$ at various initiator concentrations: (—) 3.6 mole %; (- -) 4.5 mole %; (· · ·) 9.0 mole %.

in the polymer structure. The results in Table 1 show that as the sulfur analysis drops, the resins approach the ion-exchange properties required. However, even at 3.6% initiator concentration these polymers had unsatisfactory mechanical properties.

The capacity loss can be attributed to three factors. First, the large quantity of initiator required leads to a loss of ion-exchange capacity due to bound initiator fragments, such as sulfate (OSO_3^-) and sulfonate (SO_3^-) groups [14], increasing the amount of nonbasic material in the polymer. Second, the exchange sites near each strong acid initiator fragment will be lost by internal neutralization. Third, and less obvious, will be the loss of capacity due to the inaccessibility of some of the exchange sites because of the rigid polymer network. This last problem can be overcome by the use of a difunctional monomer and will be discussed later.

The pH at half-neutralization of these polytriallylamines was considerably less than that of analogous monomeric compounds. This phenomenon, which has been observed for other polyamines

TABLE 1. Polymerization of Triallylamine Hydrochloride with $(\text{NH}_4)_2\text{S}_2\text{O}_8/\text{Na}_2\text{S}_2\text{O}_5$ ^a

Initiator concn (mole %)	Yield (%)	Capacity (meq/g)	SR ^b	pH _{1/2}	ΔpH^c	Sulfur content (%)
3.6	78	5.9	1.3	7.3	0.0	2.6
4.5	76	5.0	1.2	7.2	0.5	3.2
9.0	99	4.2	1.1	7.0	1.2	3.7

^aTriallylamine concentration, 70% in water.

^bAcid/base swelling ratio.

^cChange in pH from 10% to 60% neutralization.

[9, 11], has been explained by postulating a lowering of the effective dielectric constant within the resin phase due to the introduction of nonpolar structures in the vicinity of the exchange sites.

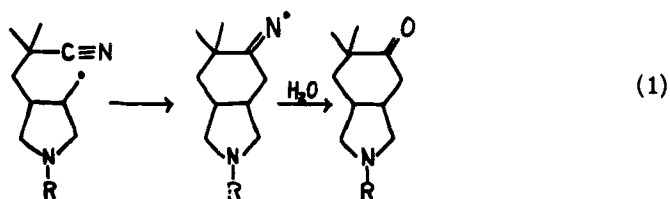
These results show the importance of the type and quantity of initiator used. We therefore conclude that for the present requirements the initiator fragments should ideally have the following specification: molecular weight as low as possible, to minimize capacity loss due to dilution; no charge, to eliminate internal neutralization; nonpolar structure so that all the amino groups are in similar nonpolar environments.

Initiators which fulfilled these requirements to various degrees were, therefore evaluated. All were noncharged but varied in polarity and molecular weight.

Azo Initiators

The radical derived from 2,2'-azobisisobutyronitrile (AIBN) satisfies the above specifications. However, polymerization of triallylamine with AIBN proved difficult because of solubility differences between the initiator and the monomer, and yields from polymerization initiated in this way were low. A further problem with AIBN is the backbiting reaction of the first-formed cyclic radical on the cyanopropyl residue [2]. This process leads to low molecular weight compounds and has the effect of reducing the number of radicals available for propagation [scheme (1)].

This problem of initiating polymerization in aqueous solutions was overcome by using azobisisobutyramidinium hydrochloride in



place of AIBN. All the polymers prepared by this method produced titration curves with excellent plateau shapes (Fig. 2).

The monomer concentration at which the polymerizations were carried out had little observable effect on the degree of crosslinking of the polymer and the yield of crosslinked polymer (Table 2). However, at low initial monomer concentration (less than 20% solids) only linear polymer was formed.

The dependence of the degree of crosslinking on the initial monomer concentration can be explained in terms of the length of the initially formed chains and the nature of the species formed during polymerization. In most free-radical polymerizations, at low monomer concentrations, chain-terminating processes are enhanced

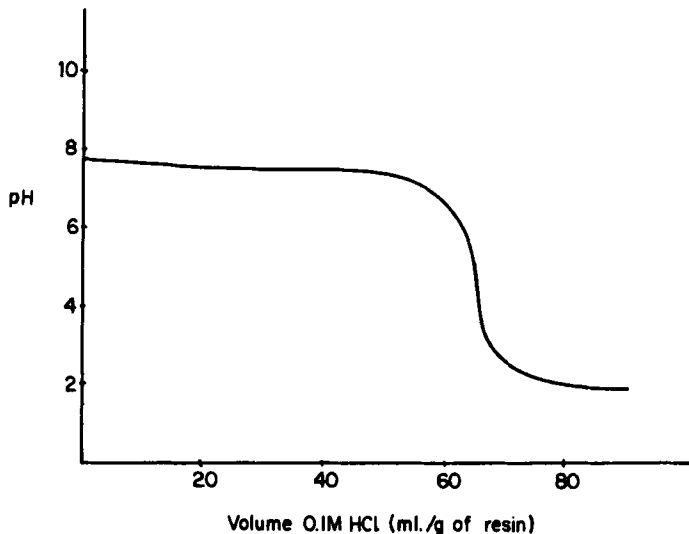
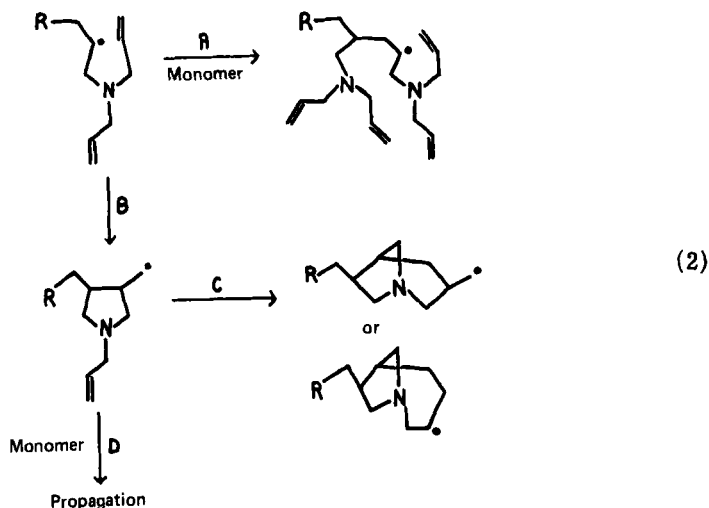


FIG. 2. A typical titration curve for polytriallylamine initiated by azobisisobutyramidinium dihydrochloride.

TABLE 2. Polymerization of Triallylamine Hydrochloride with 2,2'-Azobisisobutyramidium Hydrochloride in Water

Monomer concn (%)	Initiator concn (mole %)	Yield (%)	Capacity meq/g	SR	pH _{1/2}	ΔpH
70	3.2	63	6.5	1.4	7.5	0.2
70	4.5	69	6.3	1.6	7.6	0.2
60	3.2	68	6.3	1.5	7.4	0.5
60	4.5	77	6.4	1.4	7.4	0.6
50	3.2	72	6.3	2.0	7.7	0.8
50	4.5	77	6.6	1.6	7.7	0.8
30	3.2	68	7.0	2.0	8.0	1.0
30	4.5	72	7.6	2.0	8.1	1.2
15	3.2	Linear polymer				

relative to chain propagating processes and hence shorter chains are formed. In an idealized cyclopolymerization of triallylamine each unit in the polymer has one pendant allyl group. Therefore the longer the chain the greater is its functionality in terms of further radical attack, and the greater is the number of possible crosslinks per chain.



Another factor influencing the degree of crosslinking is the relative rates of the three competing reactions shown as scheme (2).

Reactions A and D are concentration-dependent; hence they are favored at high monomer concentrations. Reactions B and C are essentially monomer concentration-independent. Therefore high concentrations would lead to a more functional polymer chain resulting in more crosslinked or crosslinkable resin. Bicyclic structures caused by a similar type of radial attack in triallyl compounds have recently been observed by ESR techniques [15].

Transition Metal Initiators

While the azo initiator described above worked well in solution, the elevated temperatures required made dispersion polymerization difficult. Redox systems, which are technically less ideal initiating systems, were then tried as a possible compromise for commercial production. In general, these produce polar, noncharged radicals at low temperatures, which enables the polymerization to be carried out in dispersion with fewer problems than at elevated temperatures.

Three types of redox systems were used, namely Ti^{3+} /hydrogen peroxide, Ti^{3+} /hydroxylamine, and Ti^{3+} /t-butyl hydroperoxide. These systems have been reported to produce hydroxyl, amino, and methyl radicals, respectively [16, 17]. The best yields of crosslinked polymer were obtained when Ti^{3+} /hydrogen peroxide was used as the initiator. This observation is difficult to explain on purely chemical grounds as Rånby [18] has recently shown that the Ti^{3+} /hydroxylamine initiating species adds exclusively to the terminal carbon of allyl groups but that the Ti^{3+} /hydrogen peroxide species, while adding predominantly to the terminal carbon, also abstracts allylic hydrogen atoms. Allylic radicals would act as chain-terminating agents, and one would therefore expect Ti^{3+} /hydrogen peroxide to give a lower yield of product.

However, because the reactions are carried out in dispersions, the above considerations may be outweighed by such factors as the relative solubilities of the initiating system components in the monomer solvent and the dispersing phase and the rates of diffusion of initiator components into the monomer beads.

The nature of the transition metal-redox initiating system has little effect on the polymer structure in terms of the properties of interest to us (Table 3).

Polymers from Diallylamino Compounds

The broad general theory used to explain the polymerization of triallylamine hydrochloride suggests firstly cyclopolymerization,

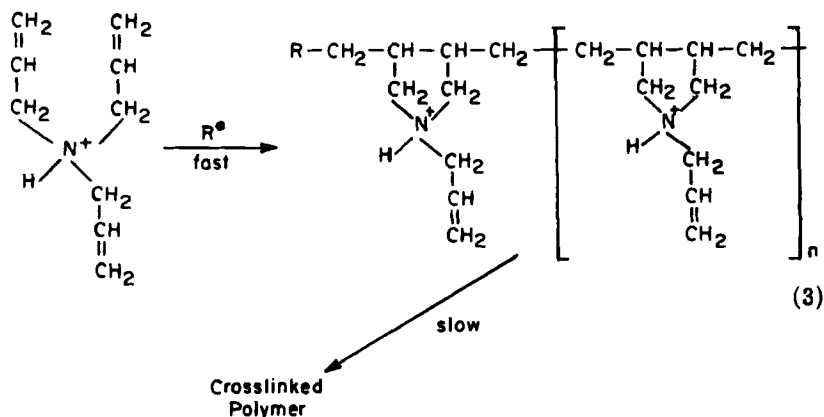
TABLE 3. Polymerization of Triallylamine Hydrochloride with Redox Initiators in Water

Monomer concn (%)	Initiator	Initiator concn (mole %)	Yield (%)	Capacity	SR	pH _{1/2}	ΔpH
70	Fe ²⁺ /H ₂ O ₂	0.7	43	6.7	2.2	7.8	0.3
70	Ti ³⁺ /H ₂ O ₂	5.6	65				
70	Ti ³⁺ /H ₂ O ₂	1.7	58	7.1	2.0	7.5	0.0
60	Ti ³⁺ /H ₂ O ₂	1.7	50	6.8	1.5	7.6	0.3
50	Ti ³⁺ /H ₂ O ₂	1.7	60	7.0	1.4	7.4	0.6
40	Ti ³⁺ /H ₂ O ₂	1.7	54	6.8	1.7	7.6	0.4
12 ^a	Ti ³⁺ /H ₂ O ₂	11.0	54	7.0	1.7	7.7	0.6
70	Ti ³⁺ /NH ₂ OH	1.7	42	7.0	1.3	7.7	0.0
70	Ti ³⁺ /tBuOOH	3.5	46	7.0	2.3	7.5	0.5

^aSolvent, 80% acetone.

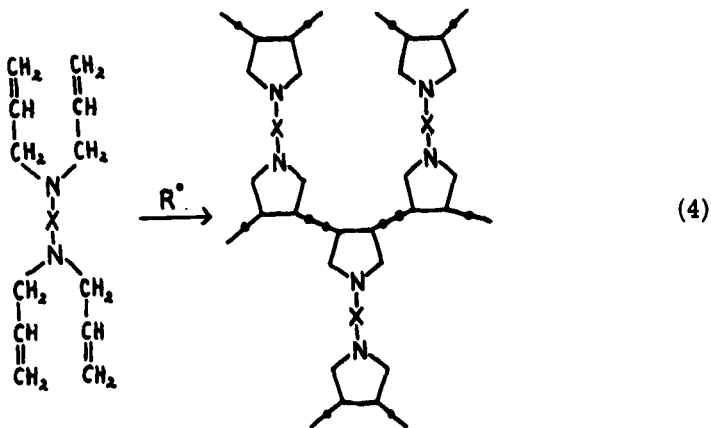
a relatively rapid reaction, and then a slow and incomplete crosslinking of some residual allyl groups.

Physical methods such as infrared spectroscopy and chemical techniques show that polytriallylamine has a large amount of residual unsaturation. Under certain conditions this unsaturation may lead to adverse reactions taking place during use of the polymer. Reactions



such as oxidation lead to a more polar and possibly charged polymer which no longer possesses the desired ion-exchange capacity or titration curve behavior.

The use of bis(diallylamino)compounds avoids the last slow step, and polymer formation is ideally a series of cyclopolymerizations.



Bis(diallylamino)alkanes of the general formula $(\text{allyl})_2\text{N}(\text{CH}_2)_n$ were prepared and polymerized by using Ti^{3+} /hydrogen peroxide as the initiating system (Table 4).

Titration curves for the polymers $n = 4$ to 10 (Figs. 3 and 4) exhibited flat plateaus similar to those observed for polytriallylamine. The pH at which the plateau occurred is related to the number of carbon atoms in the monomer unit, the larger the number of carbon atoms the lower the pH plateau. This is consistent with the theory previously put forward [11], relating the pK_a of polyamines to the polarity of the environment around the exchange sites and in the resin phase generally.

It has been shown for diaminoalkanes, where the amino groups are separated by less than five carbon atoms, that protonation of one amino group significantly lowers the pK_a of the other amino group due to electrostatic interactions [19]. Polymers from monomer with $n = 2$ or 3 behave as expected for systems in which there is considerable interaction between the amino groups. These polymers produce titration curves without distinct plateaus (Fig. 4).

TABLE 4. Polymerization of $(\text{Allyl})_2\text{N}(\text{CH}_2)_n\text{N}(\text{Allyl})_2$ with Ti^{3+} /Hydrogen Peroxide^a

Polymer	Yield (%)	Capacity	pH _{1/2}	ΔpH	Water regain
n = 2	64	b	b	b	1.39
n = 3	65	7.75	7.55	1.00	1.45
n = 4	63	7.13	7.90	0.60	1.61
n = 5	63	6.15	7.85	0.30	1.75
n = 6	64	6.13	7.65	0.30	1.86
n = 7	62	5.44	7.21	0.20	2.00
n = 8	61	5.42	6.90	0.15	2.17
n = 9	67	4.99	6.70	0.20	2.20
n = 10	58	4.32	6.58	0.25	2.44

^aInitial monomer concentration, 50% in water; initiator concentration, 8 mole %.

^bThe sloping curve obtained from this polymer made it impossible to measure accurately the capacity, pH_{1/2}, and ΔpH.

On the other hand, the flat plateau obtained from the pH titration of poly[bis(diallylamino)butane] (Fig. 4) was unexpected. A possible, but still tentative explanation is that the polymer chains are held in an extended position so that the effective N-N distance in the polymer is greater than that in solutions of the more flexible monomeric compounds and hence the electrostatic interaction is not so great.

Bis(diallylamino)methane did not polymerize under any of the conditions described, the monomer being recovered in all cases. This may be due to the difficulty of protonating both basic centers in the molecule, with the result that the close proximity of the free amine inhibits the polymerization of the neighboring diallylamino group.

Polymers prepared from bis(diallylamino)alkanes all contained large amounts of unsaturation. This is not unexpected for such highly functional systems where constraints on mobility after the initial stages of the reaction would make it difficult for all the

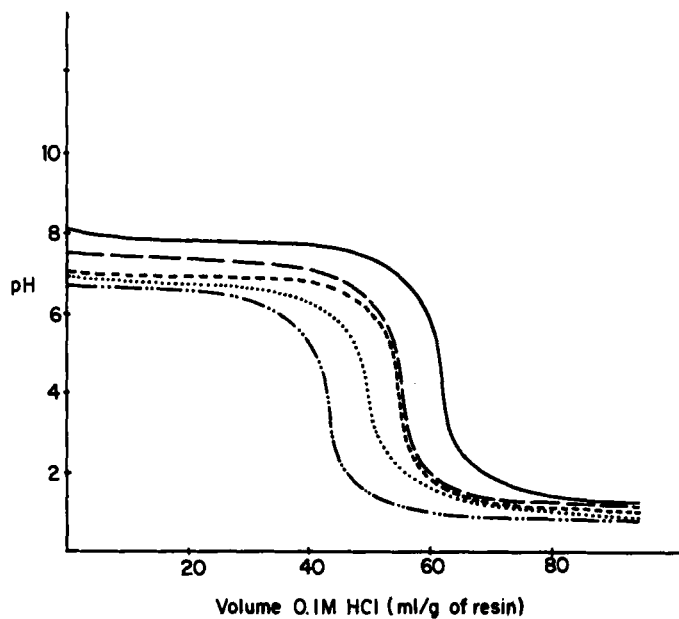


FIG. 3. Titration curves for polymers of $(\text{allyl})_2\text{N}(\text{CH}_2)_n\text{N}(\text{allyl})_2$ ($n > 5$).

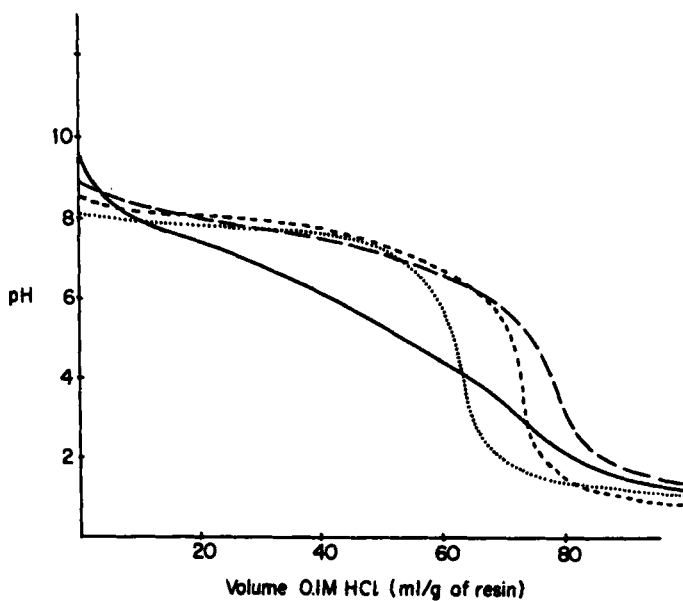


FIG. 4. Titration curves for polymers of $(\text{allyl})_2\text{N}(\text{CH}_2)_n\text{N}(\text{allyl})_2$ ($n < 6$).

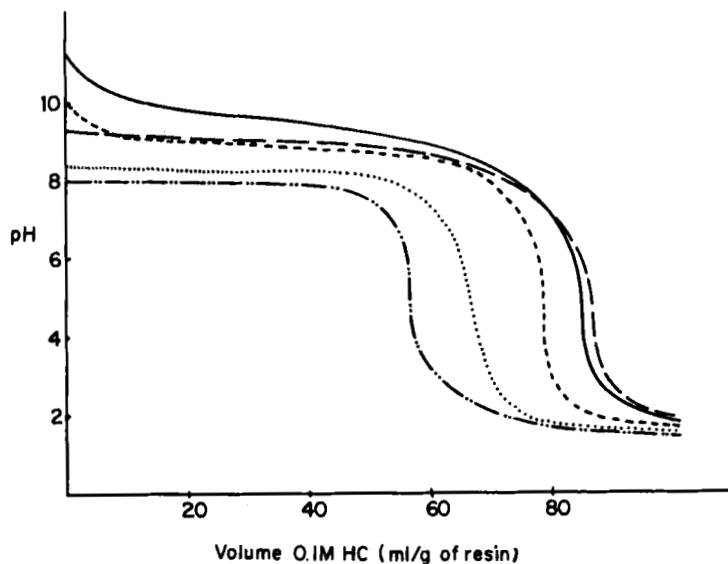


FIG. 5. Titration curves for diallylamino compounds/1,6-bisdiallyl-aminohexane copolymers.

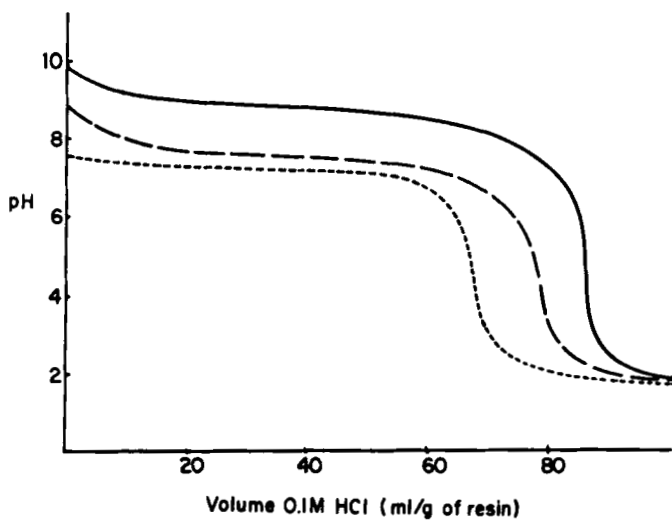


FIG. 6. Titration curves for methylallylamine (MeDAA)/1,6-bisdiallylaminohexane copolymers.

TABLE 5. Copolymers of Diallylamino Compounds and 1,6-(Diallylamino)hexane

Diallyl compound ^a	Bis(diallyl) compound concn (%)	Initiator concn (mole %)	Yield (%)	Capacity	SR	pH _{1/2}	ΔpH
DAA	10	6	53	8.4	2.1	9.3	0.8
DAA	20	6	42	7.4	—	8.4	1.3
MeDAA	10	6	56	8.4	3.0	8.8	0.4
MeDAA	28	4	52	7.8	1.5	7.6	0.6
MeDAA	61	4	65	6.5	1.1	7.2	0.3
EtDAA	10	6	50	7.8	3.1	8.9	0.3
EtDAA	20	6	48	7.1	—	8.7	0.4
PrDAA	10	6	52	6.7	2.7	8.3	0.0
BuDAA	20	6	55	5.5	2.5	8.0	0.1

^aDiallyl compounds: DAA, diallylamine; MeDAA, N-methyldiallylamine; EtDAA, N-ethyldiallylamine; PrDAA, N-(n-propyl)diallylamine; BuDAA, N-(n-butyl)diallylamine.

diallylamino groups to obtain the correct steric positions for further reaction.

The residual unsaturation can be reduced or eliminated by the addition of a less functional monomer to control the degree of crosslinking. Such a system, for example bis(diallylamino)/(diallylamino) copolymers, offers several advantages.

First, the crosslinking in these copolymers could be effectively controlled by varying the ratio of the two monomers, leading to polymers with ion-exchange capacities close to the theoretical values (Table 5, Figs. 5, 6).

It can be concluded that in order to have the maximum control over basicity properties of resins prepared from diallylamine compounds the preferred system is (diallylamino)alkane/bis(diallylamino)alkane copolymers. This particular system allows control of crosslinking, pK_a values, and ion-exchange capacity.

The preferred initiator system for polymerization of allylamine monomers on a large scale is Ti^{3+} /hydrogen peroxide, as this system gives high yields at low temperatures.

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