Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Cyclopolymerization. XIII. Cyclopolymerization of Diallylaminomethylphenols

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To cite this Article Hodgkin, J. H. and Allan, R. J.(1977) 'Cyclopolymerization. XIII. Cyclopolymerization of Diallylaminomethylphenols', Journal of Macromolecular Science, Part A, 11: 5, 937 — 956
To link to this Article: DOI: 10.1080/00222337708061299
URL: http://dx.doi.org/10.1080/00222337708061299

J. MACROMOL. SCI.–CHEM., A11(5), pp. 937-956 (1977)

Cyclopolymerization. XIII.
Cyclopolymerization of Diallylaminomethylphenols

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ABSTRACT

New highly substituted benzyl diallylamino monomers were prepared from substituted phenols by use of the Mannich reaction. Their ability to cyclopolymerize as the free phenols and the structures and properties of the polymers formed were investigated.

INTRODUCTION

In the synthesis of highly functional polymers for use in areas such as chelating resins and polymeric drugs two major routes have been used [1]. One method has been the reaction of complex monomers in a step-growth type of polymerization; for example a phenol-formaldehyde condensation with monomers such as anthranilic acid and 8-hydroxyquinoline. The second, and commercially more favored

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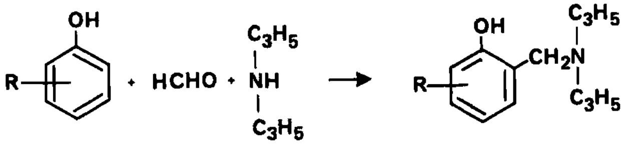
method, has been to attach complex groups to a preformed chain-growth polymer such as polystyrene. This requires a series of chemical reactions to be performed on a polymer with no way of removing side-reaction products. The resulting polymer is often far from a material with a single known structural unit.

A polymerization technique which has been less commonly used until recently [2] is the chain-growth polymerization of complex monomers. The reasons for avoiding this method include the difficulty of synthesizing monomers and the problem of chain-terminating groups in the complex structures. During earlier work on the cyclopolymerization of diallylamines [3, 4] we found a simple procedure for synthesizing and polymerizing highly functional monomers based on the diallylamine structure. Some of the materials produced appeared to have considerable promise as chelating polymer structures or polymeric drugs. This paper describes the synthesis of a series of diallylaminomethylphenols and their polymerization.

DISCUSSION

Monomer Synthesis

The monomers listed in Table 1 were all synthesized by the Mannich reaction, which in this case was the condensation of diallylamine, formaldehyde, and a phenol as shown in Eq. (1).

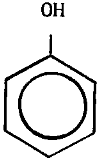
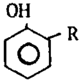
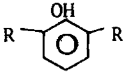
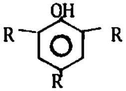
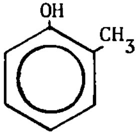
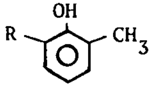
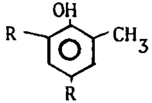


(1)

The conditions used were those normally encountered in previous work on the Mannich reaction [5, 6], with variations in time, temperature, and stoichiometry depending on the reactivity of the starting phenol and the degree of substitution required. These reactions, besides using cheap, readily available starting materials, gave a high yield of products.

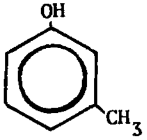
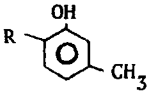
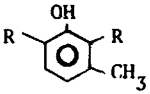
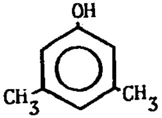
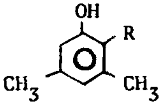
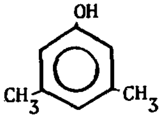
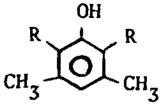
Table 1 lists the reaction conditions which led to different degrees of substitution ranging from mono- to tetrasubstituted products depending on the structure of the phenol. Although this product range caused

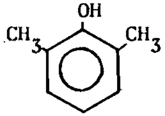
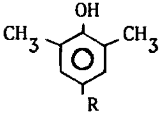
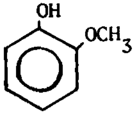
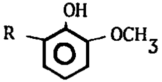
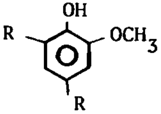
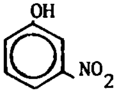
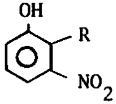
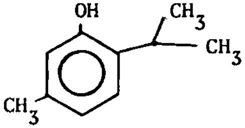
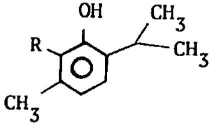
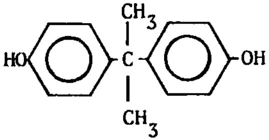
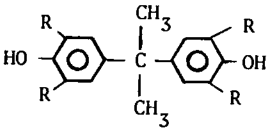
TABLE 1. Formation of Diallylaminomethylphenols

Starting phenol	Reaction conditions: Phenol/amine/formaldehyde mole ratio	Reaction conditions: Reflux time (hr)	Product R = $-CH_2N(CH_2-CH=CH_2)_2$		Yield (%)[a]	Purification properties[b]
	1/1.1/1.3	5		(I)	62	Colorless liquid, bp 130°C/0.4 Torr
	1/2.2/2.4	12		(II)	85	Viscous oil, bp 146-150°C/0.2 Torr
	1/5/5	50/125°C[c]		(III)	76	Chromatography, very viscous oil
	1/1.1/1.3	5		(IV)	85	Colorless oil, bp 128-130°C/0.2 Torr
	1/3/3	48/125°C[c]		(V)	83	Viscous oil bp 144-155°C/0.4 Torr

(continued)

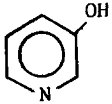
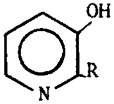
TABLE 1 (continued)

Starting phenol	Reaction conditions: Phenol/amine/formaldehyde mole ratio	Reaction conditions: Reflux time (hr)	Product R = $-CH_2N(CH_2-CH=CH_2)_2$		Yield (%)[a]	Purification properties[b]
	1/1.2/1.2	10		(VI)	95	Oil, bp 101-110°C/0.1 Torr
	1/2.5/2.5	40		(VII)	70	Chromatography, viscous oil
	1/1.2/1.2	12		(VIII)	95	Chromatography viscous oil
	1/3/3	40		(IX)	62	Chromatography, not distillable

	1/1.2/1.4	12		(X)	79	Viscous oil, not distillable
	1/1.1/1.1	3/60°C		(XI)	55	Distillation and chromatography, bp 130-132°C/0.3 Torr
	1/3/3	48/125°C[c]		(XII)	89	Chromatography, not distillable
	1/2.5/2.5	36		(XIII)	60	Bp 142-148°C/0.4 Torr
	1/1.2/1.4	12		(XIV)	88	Bp 108-113°C/0.2 Torr
	1/5/5.5	18		(XV)	90	Chromatography, viscous, nondistillable oil

(continued)

TABLE 1 (continued)

Starting phenol	Reaction conditions		Product R = $-CH_2N(CH_2-CH=CH_2)_2$	Yield (%)[a]	Purification properties[b]
	Phenol/amine/formaldehyde mole ratio	Reflux time (hr)			
	1/1.5/1.5	20	 (XVI)	75	Pale yellow oil, bp 88-92°C/0.2 Torr

[a] Where isomer mixtures were obtained, the yield was determined by NMR before complete isomer separation was achieved.

[b] Products purified by filtration through activated alumina and then distillation, unless otherwise specified.

[c] Reaction carried out in a sealed bomb.

some problems in the isolation of pure isomers, in general we were able to obtain high yields of a particular isomer by a combination of slight alterations to the reaction conditions and the use of different separation methods. For the less substituted phenols, column chromatography followed by high vacuum distillation was often sufficient. With the completely substituted structures, where the reaction could be forced to give one major derivative, repeated column chromatography yielded a pure product. However, some highly substituted intermediate compounds such as the mono-, di-, or trisubstituted 2,2-bis(4'-hydroxyphenyl)propane derivatives or the various 3-methoxyphenol derivatives have not yet been obtained in a pure form, and the reactions have not been recorded in Table 1.

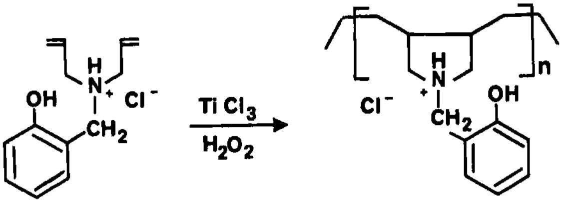
The structures of the monomers shown in Table 1 were determined by elemental analysis and infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy, with particular emphasis on the latter for distinguishing between the various possible isomers. Of greatest significance was the position of the benzylic methylene proton magnetic resonance signal. This was generally found at 3.70-3.80 ppm (from TMS) for a single diallylaminomethyl substituent placed ortho to a free phenolic group and between 3.70 and 3.60 ppm when there was a Mannich substituent on either side of the phenolic group. Where the diallylaminomethyl group was para to the phenolic group or ortho to an acetylated phenol [4], the chemical shift dropped to 3.50-3.40 ppm. Table 4 in the experimental section lists the spectroscopic and analytical figures for the monomers.

The range of phenolic compounds was chosen to give a variety of steric and electronic effects both in the Mannich reaction and the subsequent polymerization. For the Mannich reaction itself, electron-withdrawing groups and steric hindrance in the phenol structure reduce reactivity, whereas electron-donating groups enhance reactivity and often result in extra substitution. The latter is particularly true with the methoxyphenols where multisubstitution made the isolation of pure monomers difficult. Attempts at isolating useful products from dihydroxyphenols were even less successful for similar reasons. Accurate analytical figures were not obtained for the nitrophenol Mannich product (XIII), although NMR and IR spectra indicated it was the correct material. The problem with this monomer appears to be its instability to oxygen and heat.

Polymerization

Detailed studies of the kinetics and mechanisms of the cyclopolymerization of substituted diallylamino monomers together with the determination of the polymer backbone structures have been published previously by other members of this Division [7, 8]. Therefore these aspects of the work will not be considered in detail.

Previous efforts to polymerize the free phenolic diallylaminomethyl derivatives were unsuccessful [3], but our subsequent investigations have shown that the polymerization success is dependent on the absence of specific (but still unidentified) impurities in the monomers. All the monomers in Table 1 (except X) have been cyclopolymerized, as their hydrochloride salts, by use of free radical initiators to give polymers such as that shown in Eq. (2) for monomer I.



(2)

In the case of monomer X the inability to polymerize may either be due to unidentified impurities still present in the monomer or the fact that this is the only monomer without a diallylaminomethyl group placed ortho to the phenolic group. Some of the other monomers (XIII and XVI) have been polymerized in such low yield so far that characterizable samples of the polymers could not be obtained.

The mixtures of mono- and multisubstituted phenols obtained in many of the Mannich reactions have also been polymerized without separation of the isomers. In these cases removal of the low-boiling impurities by vacuum evaporation and subsequent filtration through an activated alumina column in benzene was generally sufficient purification. The results of these copolymer preparations are not reported because detailed polymer characterization was not possible.

The initiator system which gave consistently the best yields of polymer was the titanium trichloride-hydrogen peroxide redox system [3] in concentrated aqueous solutions, but other initiators including azobisisobutyronitrile in organic solvents have given good yields of polymers in a number of cases.

Monosubstituted Diallylaminomethylphenols. Although the polymerization method for the monosubstituted diallylaminomethylphenols differed little from that of the more highly substituted materials (see Experimental Section), the method for recovering pure polymer was different because the resulting polymers remained soluble in the aqueous acid solutions during polymerization. In the monosubstituted case the polymerized monomer solution was basified with ammonia and the resulting free base polymer extracted from the inorganic impurities with chloroform. It was then purified by repeated reprecipitations from this solvent by the addition of petroleum ether.

Table 2 gives the results of typical polymerization experiments for these monomers and also shows the analytical figures for the resulting polymers. The yields varied considerably with the different types of monomer and it appears that steric hindrance (in monomers XIV, VIII) and electron-withdrawing groups (monomers XVI and nitrophenol compound XIII) affected polymerization adversely. Another possible explanation, however, is the presence of impurities and other factors which could influence the initiation. For example, monomer XIV appeared to undergo a reverse Mannich reaction under acidic conditions to yield thymol, and monomers XIII and XVI gave dark green chelation products with the titanous chloride redox initiator. Polymer yield generally increased with increasing monomer concentration as long as adequate stirring could be maintained: the latter was a particular problem with monomer VIII which had a rather insoluble crystalline hydrochloride salt.

The products were all pale yellow to light brown, stable solids, soluble in chloroform, aqueous acids, and certain highly polar solvents such as dimethylformamide and dioxane but insoluble in alcohols, water, ether, and benzene. Although they often formed coherent films on evaporation of their chloroform solutions (probably due to crosslinking reactions) viscosity measurements in dioxane or chloroform solutions showed inherent viscosities of 0.08-0.02 dl/g only. Previous work had indicated the presence of some solvent/polymer interaction in these polymers which could be lowering the viscosities.

Since the purpose of this work was to obtain highly functional polymers with relatively perfect and known structures, detailed structural analysis was carried out by infrared, H, and ^{13}C-NMR spectrometry. Figure 1 gives examples of the ^{13}C-NMR polymer spectra. In all cases the purified polymers gave no evidence of end group structures which, considering the accuracy of the method previously used to determine end groups in such polymers [9] indicated an average of above 20-30 groups on the polymer chain. The polymers had the same cyclic structures previously found for N-substituted diallylamino polymers [3, 8] with about 80% cis five-membered rings and 20% trans five-membered rings along the main chain. No uncyclized allyl groups appear to remain on the polymer chain. The various functional groups attached to the polymer

TABLE 2. Homopolymerization of Mono(diallylaminomethyl) Monomers

Monomer	Conversion (%)		Analytical results[a] C (%)	H (%)	N (%)	Polymer properties
I	27	Calcd	76.81	8.43	6.57	White solid, mp 90-93°C
		Found	76.26	8.29	6.55	
IV	34	Calcd	77.38	8.81	6.45	Slightly yellow solid, mp 114-118°C
		Found	76.58	8.85	6.54	
VI	11	Calcd	77.38	8.81	6.45	White solid, mp 110-117°C
		Found	76.79	8.77	6.72	
VIII	7	Calcd	77.85	9.11	6.06	Cream solid, mp 128-135°C
		Found	76.61	8.76	5.68	
XI	15	Calcd	72.07	8.21	6.00	Cream solid, mp 109-114°C
		Found	71.56	8.08	6.40	
XIV	4	Calcd	78.69	9.73	5.40	White solid, mp 125-130°C
		Found	78.24	9.91	5.54	
XVI	3	Calcd	Not possible to purify			Yellow solid, mp 75-85°C
		Found				

[a] Calculated results are for polymers of infinite molecular weight.

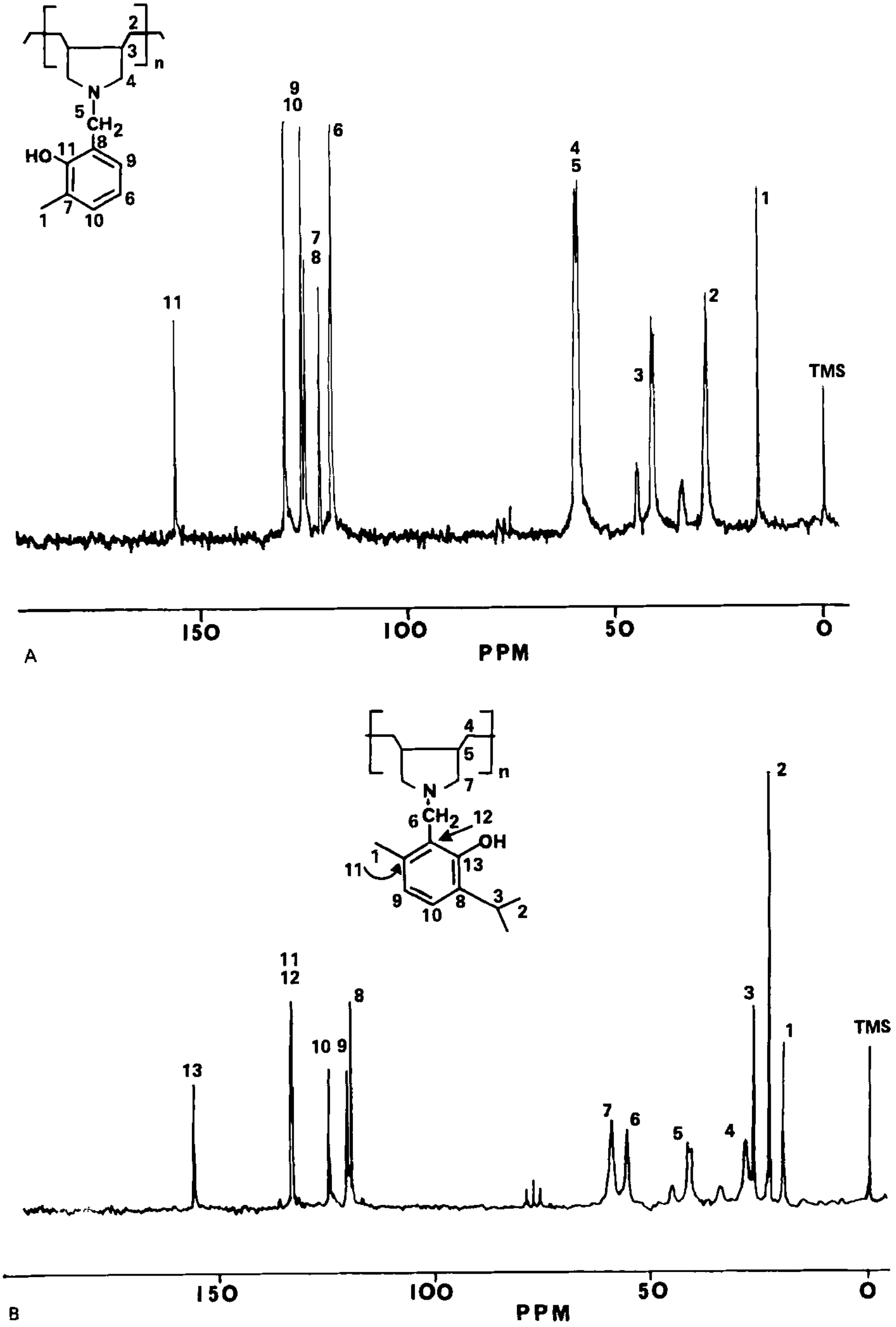
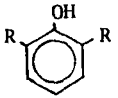
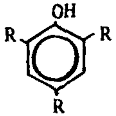
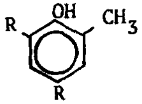
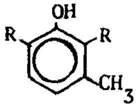
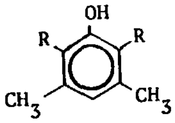
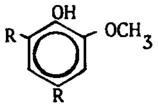
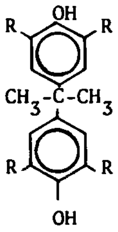


FIG. 1. Proton-decoupled natural-abundance ^{13}C-NMR spectra of cyclopolymerized monomers IV and XIV in $CDCl_3$.

TABLE 3. Homopolymerization of Multisubstituted Diallylamino Monomers

No.	Monomer R = $-CH_2-N(CH_2-CH{=}CH_2)_2$	Conversion (%)	Polymer analysis	C (%)	H (%)	N (%)	Polymer properties[a]
II		62	Calcd Found	76.88 75.21	9.03 8.58	8.97 8.48	Yellow, spongy, lightly crosslinked solid; low allyl groups
III		77	Calcd Found	76.91 75.22	9.32 9.12	9.97 9.61	Brittle yellow solid, highly crosslinked; high allyl groups
V		52	Calcd Found	77.25 75.93	9.26 9.12	8.58 8.09	Cream, spongy, lightly crosslinked solid; low allyl groups
VII		80	Calcd Found	77.25 75.49	9.26 9.27	8.58 8.02	Cream, highly crosslinked; low allyl groups
IX		19	Calcd Found	77.64 77.50	9.49 9.27	8.23 8.02	Yellow lightly crosslinked; high allyl group

XII		35	Calcd Found	73.64 71.73	8.83 8.46	8.18 7.81	Cream, highly crosslinked solid; low allyl groups
XV		42	Calcd Found	77.70 76.60	9.90 8.88	8.43 8.20	Brittle yellow solid, crosslinked; high allyl groups

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[a] Unreacted allyl groups determined by infrared spectroscopy.

via the nitrogen atom were unchanged by polymerization and shown by the sharpness of the individual ^{13}C peaks (e.g., Fig. 1) to be freely rotating and sterically unhindered by the main chain.

Multisubstituted Diallylaminomethylphenol Polymers. For many uses of highly functional polymers, crosslinked materials are required: for example, in ion-exchange or chelating resins. As there is considerable doubt whether diallylaminomonomers cyclocopolymerize with vinyl monomers [10, 11], multifunctional diallylaminomonomers with more than one cyclopolymerizable group were of great interest. The monomers, for example II, III, V, VII, IX, XII, XV are readily synthesized and on polymerization in the normal way (redox or free radical initiation of the hydrochloride salts) led to highly crosslinked resins. Due to the crosslinked nature of the polymers they were purified by continuous washing with 1 N hydrochloric acid to remove low molecular weight material and metallic impurities before being converted to the free base structure.

Table 3 gives the results of some polymerization experiments with these monomers. Although yields were generally much higher, the analytical results with these materials were not nearly as good as those obtained for the soluble polymers, but this was to be expected as the materials were hard to completely purify. The polymers were all light yellow spongy solids which strongly retained water and certain metal ions.

Detailed structural analysis of these polymers was complicated by their insolubility. Attempts to obtain ^{13}C spectra of the highly crosslinked materials were unsuccessful. Less crosslinked polymers from monomer II were synthesized by polymerization in more dilute solutions, but in this case the yields were low and the ^{13}C spectra showed that the resulting materials had a considerable amount of unreacted diallylamine groups. Infrared spectra of the polymers from highly substituted monomers e.g., Fig. 2 were similar to those obtained from the uncrosslinked materials of similar structure, except that as substitution increased so did the amount of unreacted diallylamine groups in the polymer. This was expected; in practice one would have to polymerize a mixture of mono- and multisubstituted monomer to obtain a crosslinked, saturated polymer.

Polymer Properties

This work showed that both soluble and crosslinked polymers containing complex structures with tertiary amine and phenolic groups could be synthesized by direct cyclopolymerization of easily prepared monomers. The very closely spaced weak acid (phenolic

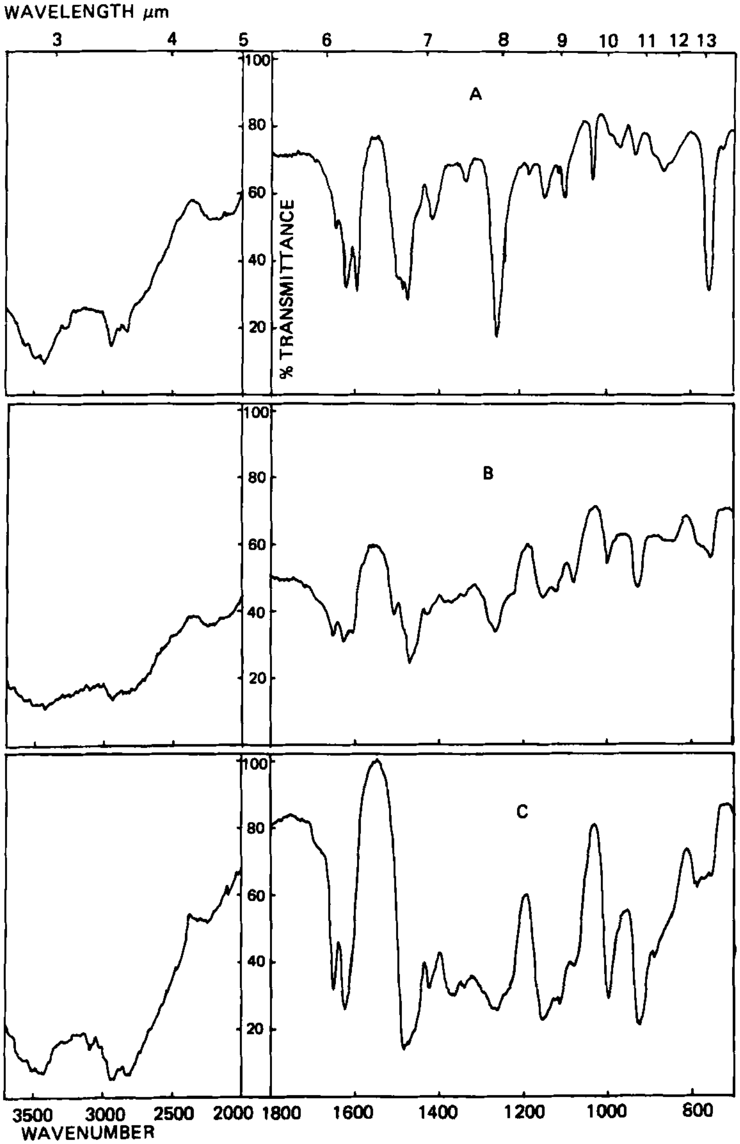

FIG. 2. Infrared spectra of cyclopolymerized monomers (A) I; (B) II; (C) III; as KBr disks.

groups) and basic (amine) groups on these polymers precluded their use as ion exchange resins but indicated some promise as chelating polymers. Preliminary studies with the polymers show that with cupric ion, some of them do form dark green chelated structures which are stable above pH 4. The only other ion which appears to complex with these resins below pH 8 is the mercuric ion. The resins with the greatest capacity are those synthesized from phenol (monomers I, II, and III); any other groups on the aromatic ring lower the capacity. This is especially so with the sterically, highly-hindered, resins such as those from monomer IX. Resins from the 3-nitrophenol and 3-hydroxypyridine monomers XIII and XVI have not been synthesized in sufficient quantity to test but are expected to be good chelating polymers. Later work has since given chelating polymers with slightly different structures which have a much greater chelating capacity and selectivity for Cu^{2+} copper and Hg^{2+} mercury ions, and these will be reported in a subsequent publication.

EXPERIMENTAL

Materials and Instrumentation

Diallylamine and the phenolic compounds were commercial materials of the highest available purity and were used without further treatment. The formaldehyde solution was BDH analytical reagent with 37-40% (w/v) formaldehyde and 11-14% (w/v) methanol.

The elemental analyses were carried out by the Australian Microanalytical Service, C.S.I.R.O., Melbourne. Infrared (IR) spectra were recorded on a Unican Sp 200 spectrophotometer in potassium bromide disks (for solids) and as thin films between sodium chloride plates (for liquids). Proton magnetic resonance (PMR) spectra of the monomers were recorded on a Varian HA 100 instrument and ^{13}C spectra on a Varian CFT/20. In both cases the chemical shifts (δ) are quoted in ppm from tetramethylsilane as the internal standard (Table 4).

General Preparation of Monomers

A mixture of the phenol and diallylamine in the molar quantities shown in Table 1 was mixed with a small amount of water ($\simeq$10%) in a flask equipped with a reflux condenser and dropping funnel. The mixture was cooled in ice and formaldehyde solution added dropwise

TABLE 4. Analysis and Spectral Results for Diallylaminomethyl Monomers

		Analysis				NMR (ppm)		
Compound		C (%)	H (%)	N (%)	Major IR peaks (cm^{-1})	Allyl	N-Methylene	Other[a]
I[b]	Calcd	76.81	8.43	6.89	3200 br(OH), 1642	5.8m (CH)	3.74s	6.86m (Ar)
	Found	77.06	8.14	6.99	990,930 (allyl)	5.18m (CH_2)	3.14d	-
II[b]	Calcd	76.88	9.03	8.97	3200 br(OH), 1642	5.8m (CH)	3.68s	6.90m (Ar)
	Found	76.96	8.84	9.06	998,931 (allyl)	5.15m (CH_2)	3.14m	
III	Calcd	76.91	9.32	9.97	2900 br(OH), 1649	5.8m (CH)	3.66s 3.05d	7.04m (Ar)
	Found	77.20	9.46	10.06	995,920 (allyl)	5.14m (CH_2)	3.46s 3.14d	
IV[b]	Calcd	77.38	8.81	6.45	3200 br(OH), 1615	5.8m (CH)	3.65s	6.75m (Ar)
	Found	77.50	9.06	6.52	990,929 (allyl)	5.12m (CH_2)	3.04m	2.26s (CH_3)
V	Calcd	77.25	9.26	8.58	2900 br(OH), 1648	5.85m (CH)s	3.72s 3.42s	6.97,6.76d (Ar)
	Found	77.30	9.56	8.33	992,920 (allyl)	5.16m (CH_2)m	3.15m 3.05m	2.20s (CH_3)
VI	Calcd	77.38	8.81	6.45	3000 br(OH),1620,	5.8m (CH)	3.69s	6.80d,6.58m (Ar)
	Found	77.61	8.99	6.60	1585,985,924 (allyl)	5.18m (CH_2)	3.13m	2.25s (CH_3)
VII	Calcd	77.25	9.26	8.58	3000 br(OH), 1642	5.85m (CH)	3.64 3.68s	6.99,6.58d (Ar)
	Found	77.45	9.38	8.64	994,920 (allyl)	5.12m (CH_2)	3.12m	2.16s (CH_3)
VIII	Calcd	77.88	9.15	6.06	3000 br(OH), 1620	5.8m (CH)	3.70s	6,44,6.52d (Ar)
	Found	78.05	9.17	6.11	1585,992,924(allyl)	5.2m (CH)	3.14m	2.15,2.20s (CH_3)
IX	Calcd	77.60	9.48	8.23	3000 br(OH), 1641	5.85m (CH)	3.64s	6.43s (Ar)
	Found	77.74	9.50	7.91	994,921 (allyl)	5.12m (CH_2)	3.08d	2.23s (CH_3)

(continued)

TABLE 4 (continued)

Compound		Analysis			Major IR peaks (cm $^{-1}$)	NMR (ppm)		
		C (%)	H (%)	N (%)		Allyl	N-Methylene	Other[a]
X[b]	Calcd[c]	54.81	5.22	12.20	3470 br(OH), 1641	5.8m (CH)	3.46s	6.90s (Ar)
	Found	54.96	5.35	12.51	1000,929 (allyl)	5.16m (CH_2)	3.07d	2.20s (CH_3)
XI	Calcd	72.07	8.21	6.00	3000 br(OH) 1650,	5.8m (CH)	3.76s	6.70m (Ar)
	Found	72.33	8.08	6.11	1252 (OCH_3), 990, 928 (allyl)	5.20m (CH_2)	3.17d	3.85s (OCH_3)
XII	Calcd	73.64	8.83	8.18	2900 br(OH) 1650	5.85m (CH)	3.74s, 3.46s	3.84s (OCH_3)
	Found	73.55	8.88	7.92	1605,1240 (OCH_3) 995,920 (allyl)	5.18m (CH_2)	3.16d, 3.07d	6.56d, 6.81d (Ar)
XIII	Calcd	62.88	6.50	11.29	2850 br(OH) 1618	5.9m (CH)	4.03s	7.2m (Ar)
	Found	Unstable			1535,1350 (NO_2) 995,930 (allyl)	5.2m (CH_2)	3.20d	7.6m (Ar)
XIV	Calcd	78.71	9.72	5.40	3000 (OH) 1648,	5.8m (CH)	3.77s	1.22d,2.19 (CH_3)
	Found	78.75	9.77	5.17	1582,993,927 (allyl)	5.16m (CH_2)	3.17d	3.2m(CH), 6.60, 7.00 (Ar)
XV	Calcd	77.69	9.09	8.43	3200 (OH) 1615	5.8m (CH)	3.64s	6.92s (Ar)
	Found	78.02	8.95	8.08	990,930 (allyl)	5.12m (CH_2)	3.10d	1.62s (CH_3)
XVI	Calcd	70.55	7.90	13.72	2900 (OH) 1648,	5.8m (CH)	3.98s	7.08d (Ar)
	Found	70.23	8.14	14.04	1580,995,928 (allyl)	5.22m (CH_2)	3.20d	8.00t (Ar)

[a] Phenolic OH peaks are not listed, as they are very variable and often broad.

[b] Data of Hodgkin and Solomon [3].

[c] Calculated for picrate salt.

with vigorous stirring. On completion of the formaldehyde addition the mixture was heated slowly to reflux, with a small amount of ethanol generally added to get a homogeneous solution. The Mannich base was recovered by basification of the solution with aqueous ammonia and extraction with chloroform. Purification was accomplished by chromatography or distillation, depending on the product.

General Preparation of Polymers

The monomer hydrochloride salt (0.05 mole) was prepared by slow addition of concentrated hydrochloric acid to the ice cold base and vacuum evaporation of excess acid and water. A solution of titanium trichloride (3 ml, 14%) was added to the salt in a two-necked flask containing a nitrogen inlet and a strong stirrer (magnetic for soluble polymers but mechanical for the insoluble materials). Hydrogen peroxide (5-10% solution) was then added dropwise to the cold solution (-5°C to -10°C) until the solution turned dark orange.

For soluble polymers, the product was isolated by basification with ammonia and continuous extraction with chloroform. The resulting extracts were dried with sodium sulfate, evaporated to dryness, and then triturated with petroleum ether to remove unchanged monomer and low molecular weight products. The polymers were purified by repeated precipitation from chloroform using petroleum ether.

For insoluble polymers the products were washed continuously with 1 N hydrochloric acid until the washings were colorless. The polymer hydrochloride network was then basified with ammonia and washed with distilled water to remove all inorganic residues and the polymer dried under vacuum.

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Accepted by editor December 24, 1976
Received for publication December 31, 1976