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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Hodgkin, J. H. and Solomon, D. H. (1976) 'Cyclopolymerization. VIII. The Synthesis of Allylamino Monomers by the Mannich Reaction and Their Polymerization', *Journal of Macromolecular Science, Part A*, 10: 5, 893 — 922

To link to this Article: DOI: 10.1080/00222337608061225

URL: <http://dx.doi.org/10.1080/00222337608061225>

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Cyclopolymerization. VIII. The Synthesis of Allylamino Monomers by the Mannich Reaction and Their Polymerization

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ABSTRACT

New diallylamino monomers were prepared from substituted phenol, aniline, and pyrrole derivatives by the Mannich Reaction. Their ability to form cyclic homopolymers and the structure and properties of these polymers were investigated.

INTRODUCTION

Basic resins are generally synthesized from crosslinked polystyrene by chloromethylation and then reaction with amino compounds. Such resins are commercially available (e.g., the Amberlite, Dow and Permutit anion resins) and have found very wide use as ion-exchange resins, films, surface coatings, etc. The preparation of specific basic resins by chemical modification of polystyrene suffers from several disadvantages: firstly problems can be encountered in directing substituents to the desired positions in the aromatic ring; secondly

effects normally associated with reactions on polymers (for example, the formation of nonremovable, side-reaction products and cross-linking) can also be a problem.

Some of these limitations would be removed if the basic polymer could be prepared direct from a suitably substituted basic monomer. This approach is common with aliphatic compounds; for example dimethylaminomethyl methacrylate and various allyl- and vinyl-substituted amines are commonly used as monomers to prepare polymers with alkylamino groupings. In the aromatic series there is a general lack of suitable monomers at commercially acceptable prices. In particular, the vinylic benzyl amines and other aromatic amines are not commonly available, but there have been indications that they could provide useful materials due to significant differences in their basicity when compared to aliphatic monomers [1].

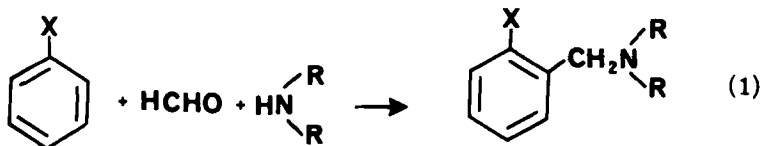
The Mannich reaction offers possibilities for the ready preparation of suitable benzylic amines at low cost. Some work has been carried out by using the Mannich reaction to prepare polymers by a polycondensation mechanism [2, 3], but the optimum yields of expected product in this type of reaction (60-80%) are not sufficient to give very satisfactory polymers. This disadvantage is not generally a problem with synthesis of unsaturated monomers, as they can be easily purified and subsequently polymerized.

This paper will discuss the synthesis, properties, and polymerization of a variety of benzylic and heteroaromatic diallylamines which can undergo free-radical cyclopolymerization. A subsequent paper will discuss the copolymerization of these monomers with various acidic monomers.

DISCUSSION

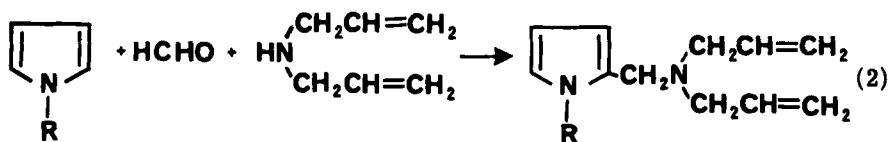
Synthesis of Monomers

The Mannich reaction is the condensation of ammonia or a primary or secondary amine, an aldehyde, and a compound capable of supplying one or more active hydrogen atoms [4, 5]. Compounds suitable for Mannich reactions are those with electron-rich centers such as phenols, tertiary aromatic amines, and certain heterocyclic compounds, and all three distinct types were included in our investigations. Equation (1) summarizes the general reaction scheme used for aromatic monomer preparation, where X is OH or NR₂ and R is an alkyl or allyl group (Multiple substitution into ortho and para positions can occur).



Many different, detailed, approaches to suitable basic monomers could be considered. The first of these is where the secondary amine provides the polymerizable group. In our work this was the diallylamino group which could then lead to cyclopolymerizable monomers. Another approach would be for the substituents on the aromatic ring to provide the polymerizable group. In this case X could be either a diallylamino group or a vinyl ester or vinyl ether group placed on the phenolic grouping after the use of the Mannich reaction. Pathways of the latter type were not pursued in the present work.

Another series of Mannich monomers studied was synthesized by use of electron-rich pyrrole heterocycles as shown in Eq. (2). Mono- or 2,5-disubstitution occurs, depending on reaction stoichiometry.

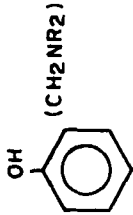
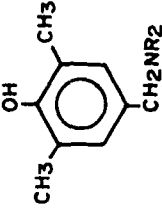
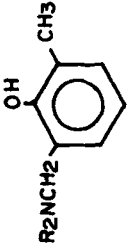
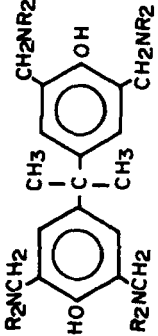


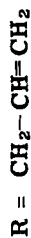
The Mannich reaction can be a high yielding reaction with cheap, readily available starting materials. However, the reaction is reversible and is accompanied by a number of common side reactions. This makes detailed reaction procedures quite important and very different depending on the starting materials. Some of the reasons for the variations have been explained by Thomson and Tramontini in their review articles [4, 5] but many are largely unknown. With our reactions no attempt was made to obtain the optimum conditions and, provided yields were above about 60% and the product was easily isolated in a pure form, no further refinement was undertaken.

Diallylaminomethyl Phenols

Diallylaminomethyl phenols were obtained in good yields by the general method used by Blicke [6] for phenolic compounds (Table 1).

TABLE 1. Reactions of Phenols with Diallylamine and Formaldehyde

Starting materials	Products	Yield (%)	Properties
Phenol + 1.5 mole of formaldehyde and amine		o ≈ 60 p < 10 di ≈ 20	o-substituted derivative Light colorless oil Bp 130° C/0.4 Torr
2,6-Dimethylphenol + 1 mole of formaldehyde and amine		69	2,6-disubstituted derivative Viscous colorless oil Bp 146-150° C/0.1 Torr
o-Cresol + 1 mole of formaldehyde and amine		75	Viscous colorless oil, Not distillable
Bisphenol A + 4 moles of formaldehyde and amine		70 tetra [+ lower substitution]	Viscous yellow oil Not distillable



With phenol and Bisphenol A, both multiple and monosubstituted derivatives were formed under most conditions. As the various isomers were often difficult to separate from each other, Table 1 includes only the type of experiments which led to products that could be obtained in a pure form. The resulting amines were all viscous oils which tended to decompose at higher temperatures. Some of the monosubstituted derivatives could be distilled under vacuum but the remaining products were separated by column chromatography.

Preliminary experiments indicated that these monomers would not readily polymerize or copolymerize. This was not entirely unexpected, as the Mannich reaction is reversible, and small amounts of the starting phenols, formaldehyde, or the diallylamine would be good polymerization inhibitors. However, the use of oxygen-substituted derivatives of the phenolic monomers was considered to be one solution to this problem. Since the Mannich reaction does not take place when the phenolic group is etherified or esterified, the derivatives were obtained after the diallylaminomethyl phenol formation was completed.

The derivative approach was typified by the acetylation of the phenolic groups. Careful treatment of the phenols with acetic anhydride gave good yields of their acetate derivative. Previous workers [7] had indicated that this reaction removed the dialkylamino grouping but detailed investigations showed that sufficient control of the reaction conditions (especially temperature) minimized the problem for the formation of this particular ester. Again, some difficulties were encountered with the separation and purification of some of the more highly substituted phenol acetate derivatives so these were not studied further at this time. They are, however, of great potential value for crosslinking polymers.

The acetate derivatives obtained (Table 2) were light oils that were easily purified by distillation and hence were much easier to characterize than the phenols. The structures were confirmed by PMR and analysis.

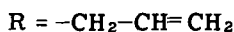
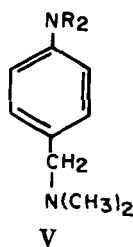
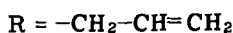
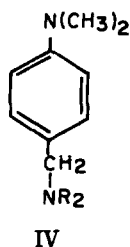
Substituted Anilines

Mioque and Vierfond [8] determined a useful procedure for the Mannich reaction on arylamines using aqueous-ethanolic solution and acetic acid catalyst. This method has been used by us to give quite good yields (>60%) of the monomers 1-dimethylamino-4-diallylaminomethylbenzene (IV) from dimethylaniline and 1-diallylamino-4-dimethylaminomethylbenzene (V) from diallylaniline.

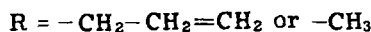
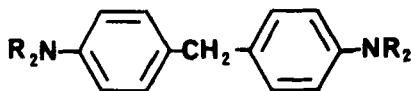
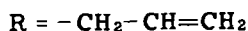
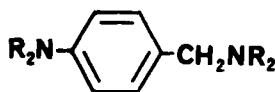
TABLE 2. Acetate Derivatives of Phenolic Mannich Bases

Starting phenol	Product		Acetylating conditions	Properties	Yield (%)
	No.	Structure			
2,6-Dimethylphenol	I		60° C/24 hr	Bp 120-122° C/0.3 Torr	77
o-Cresol	II		60° C/4 hr	Bp 94-95° C/0.2 Torr	81
Phenol	III		50° C/2 hr	Bp 118-120° C/0.75 Torr	69

R = $-\text{CH}_2\text{CH}=\text{CH}_2$



These two compounds illustrate two different methods of introducing the polymerizable diallylamino group. For crosslinkable resins it can be seen that an extension of these reactions could lead to a monomer with two different types of diallylamino group, such as VI.



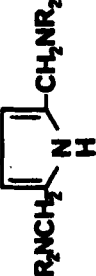


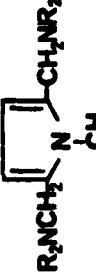


As found by the French workers [8], multiple substitution on the aromatic ring did not occur, and the use of forcing conditions just led to a higher yields of products such as VII.

Substituted Pyrroles

The pyrrole ring (like some other five-membered aromatic heterocycles) is extremely susceptible to electrophilic substitution in the α -positions; thus the Mannich reaction occurs very readily. The only problem is to contain the side reactions such as polypyrrole formation. By using the methods of Bachman and Heisey [9] which emphasize low temperatures and careful addition, the monomers shown in Table 3 were synthesized in high yield. Either mono- or disubstituted pyrrole derivatives were obtained by varying the reaction stoichiometry and the reagent addition sequences. The starting pyrrole XII was synthesized from potassium pyrrole and 1,4-dibromobutane by the method of Hobbs et al. [10] as a precursor for the highly crosslinkable monomer XIII.

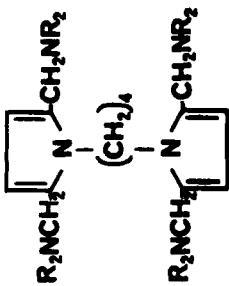
TABLE 3. Mannich Reaction with Pyrrole Derivatives

Starting pyrrole ^a	Product ^a		Yield (%)	Properties
	Structure	No.		
		VIII	74	Colorless oil [11] Bp 73°C/1 Torr
		IX	85	Viscous yellow oil Bp 107-108°C/0.5 Torr (decomp.)
		X	72	Colorless oil Bp 89-91°C/0.5 Torr
		XI	90	Yellow oil Bp 116-118°C/0.5 Torr

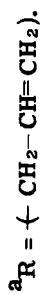
Very viscous yellow oil
Does not distill

70

XIII



XII



The monomers VIII and IX, having a free NH group, were susceptible to degradation by light, oxygen, and acids and had to be stored in sealed ampoules in a refrigerator. The other monomers were relatively stable, although they did darken on prolonged storage at room temperature. Again, all the monomer structures were confirmed by analysis and NMR spectra.

Synthesis and Properties of the Polymers

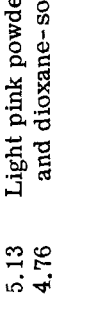
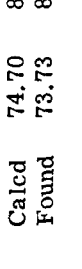
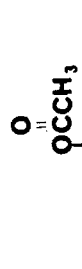
Of the monomers referred to above, only 2-diallylaminomethyl pyrrole VIII appears to have been synthesized previously [11]. Copolymers in this case were prepared with acrylonitrile and fumaronitrile but no homopolymerization attempts were reported.

A preliminary study with many different initiating systems, including Cobalt-60 and ultraviolet irradiation (with sensitizer species) as well as a series of chemically initiated, free-radical methods, of both the free base and various acidic salts was carried out. In most cases only low yields of partially polymerized products were obtained, where the reaction had occurred through the allyl groups. Under some conditions (especially in acidic solutions) the reverse Mannich reaction took place, and this led to phenol-formaldehyde type polymers or, with the pyrrole compounds, to large amounts of dark red polypyrrole [12]. Useful, homopolymeric species were obtained only from hydrochloric acid salts of the various amino monomers.

The preferred initiating system was found to be the $\text{TiCl}_3/\text{H}_2\text{O}_2$ redox initiation of aqueous solutions of the amine hydrochlorides [13]. Other redox systems, such as Fenton's reagent and TiCl_3 with organic peroxides, were tried but gave lower yields. Table 4 lists the polymers formed and their properties.

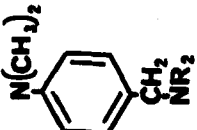
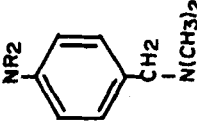
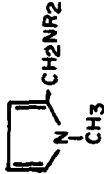
The monomers containing only one diallyl group gave predominantly soluble polymers which could be separated (by chloroform extraction of the basified solutions) from the inorganic ions and unchanged monomer present. However, there was a considerable variation in the ease of isolation of these materials, for example, the polymer from phenolic derivative III and to a lesser extent II held on strongly to the titanium ion. This was possibly due to the favorably placed polar groups on the benzene ring. To get higher polymer yields, the titanium could be removed as an insoluble complex with phenylphosphonic acid (under acidic conditions) before extraction of the polymer. Also noticeable with these two polymers was the considerable loss of acetyl groups during polymerization and work up unless temperatures were kept very low. With the monomers such as XI and XIII, containing more than one diallyl group, crosslinked products were obtained.

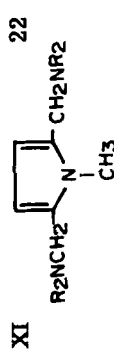
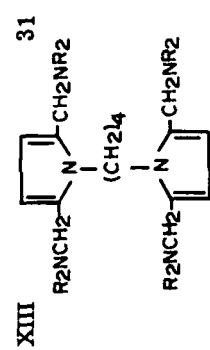
TABLE 4. Homopolymerization of Mannich Base Hydrochlorides

No.	Monomer Structure ^a	Polymer yield (%)	Analytical results ^b				Polymer properties
			Calcd Found	C (%)	H (%)	N (%)	
I		21	Calcd Found	74.70 73.73	8.48 8.25	5.13 4.76	Light pink powder, chloroform- and dioxane-soluble
II		23	Calcd Found	74.13 73.44	8.16 8.54	5.41 5.51	Colorless powder, chloroform- and dioxane-soluble
III		23	Calcd Found	73.47 73.35	7.76 7.97	5.71 6.22	Colorless powder, chloroform- and dioxane-soluble

(continued)

TABLE 4 (Continued)

Monomer		Polymer yield (%)	Analytical results ^b				Polymer properties
No.	Structure ^a		Calcd	Found	C (%)	H (%)	
IV		27	Calcd Found	78.21 78.09	9.63 9.30	12.16 11.78	Yellow solid; darkened slowly; chloroform- and dioxane-soluble
V		15	Calcd Found	78.21 77.35	9.63 8.85	12.16 11.02	Light brown, chloroform-soluble
X		20	Calcd Found	75.74 74.47	9.53 9.35	14.75 14.41	Brown, darkened slowly; chloroform- and dioxane-soluble

XI	 <p>22</p>	76.20 74.66	9.76 9.71	14.03 13.55	Brown, rubbery, insoluble solid
XIII	 <p>31</p>	76.87 75.75	9.67 9.54	13.45 12.54	Brown, rubbery, insoluble solid

^aR = -CH₂-CH=CH₂.

^bThe calculated analysis figures are for polymers of infinite molecular weight and cannot take into consideration endgroups or strongly bound inorganic impurities.

These were not soluble in acid and had to be filtered off as gelatinous, sticky solids, very difficult to purify. Once basified, these became more solid rubbery materials but any inorganic impurities remaining were strongly bound to the polymer.

The polymers from the phenol acetate derivatives were light pink or colorless solids stable to air and light, but the aniline- and pyrrole- substituted polymers were generally yellow to brown and tended to darken slowly on exposure to light. The monomers VIII and IX, which contained a pyrrole ring unsubstituted on the nitrogen atom, decomposed too readily under the acidic polymerization conditions to give a useful polymers so are not included in the list.

Attempts to obtain an indication of the molecular weights of these polymers by viscometry were unsuccessful due to the anomalous viscosity changes observed. In most cases the viscosity increases of polymer solutions were less or at the best very little more than those of similar monomers or model compounds.

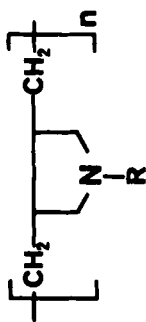
The polymer from monomer IV drastically decreased the viscosity of the solvent (dioxane), even at low concentrations; it is being further investigated to account for this property. Nuclear magnetic resonance (NMR) evidence, including both proton magnetic resonance (PMR) and ^{13}C NMR spectra, gives a minimum number of units of about 30 (MW \approx 6000) based on endgroup analysis.

Structure Determination

The solubility of the polymers containing one diallylamino group per unit is consistent with previous work [14, 15], which showed that cyclopolymerization occurs in this type of monomer. Infrared and PMR spectra (Table 5) confirmed the absence of significant amounts of unreacted allyl groupings and were consistent with an unbranched structure.

An interesting feature of the PMR spectra of these polymers was the high resolution of the peaks associated with hydrogen atoms attached to features on the aromatic rings. Figure 1 gives an example in the case of the polymer of compound I which, besides indicating the uniformity of this polymer structure, gives an idea of the freedom of rotation of this part of the polymer molecule. The PMR confirmed the relatively complete cyclopolymerization of these monomers and was able to give an indication between five- and six-membered ring formation in the cyclic structure e.g., structures XIV or XV for monomer I, the benzylic protons of the five-membered ring model compound XVI bring much closer to those of the polymer than the six-membered model XVII.

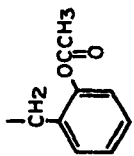
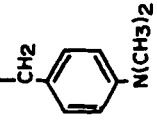
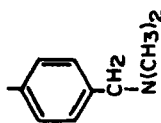
TABLE 5. PMR Spectra of Homopolymers

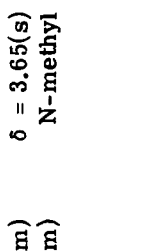
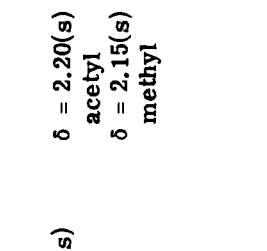
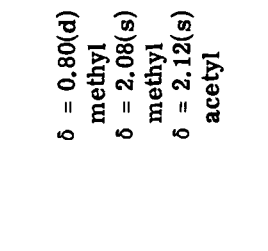
Chemical shifts δ (ppm from TMS, solvent CDCl_3)

Structure	Backbone	Ring- $\text{CH}_2\text{-N-}$	Benzylic	Aromatic	Additional protons
	$\delta = 0.82(\text{m})$ $\delta = 1.28$ (br.s)	$\delta = 3.02$ (br.s)	$\delta = 3.51(\text{s})$	$\delta = 7.02(\text{s})$	$\delta = 2.36(\text{s})$ acetyl $\delta = 2.19(\text{s})$ methyl
	$\delta = 1.23$ (br.s)	$\delta = 3.00$ (br.s)	$\delta = 3.52(\text{s})$	$\delta = 7.2(\text{m})$	$\delta = 2.32(\text{s})$ acetyl $\delta = 2.21(\text{s})$ methyl

(continued)

TABLE 5 (Continued)

Structure	Chemical shifts δ (ppm from TMS, solvent CDCl ₃)					Additional protons
	Backbone	Ring-CH ₂ -N-	Benzylic	Aromatic		
Polymers, R = 	$\delta = 1.22$ (br.s)	$\delta = 2.98$ (br.s)	$\delta = 3.80$ (br.s)	$\delta = 7.1(m)$ $\delta = 6.82(m)$	$\delta = 1.94(s)$ acetyl	
	$\delta = 1.22$ (br.s) $\delta = 2.10$ (br.s)	$\delta = 2.92$ (br.s)	$\delta = 3.50(s)$	$\delta = 6.71$ $\delta = 7.20$ AA' BB' multiplet	$\delta = 2.93(s)$ N-methyl	
	$\delta = 0.85(m)$ $\delta = 1.41$ (br.s)	$\delta = 3.00$ (br.s)	$\delta = 3.34(s)$	$\delta = 6.45$ $\delta = 7.20$ AA' BB'' multiplet	$\delta = 2.22(s)$ N-methyl	

<p>I</p> 	<p>$\delta = 1.22$ (br. s) $\delta = 2.08$ (br. s)</p>	<p>$\delta = 2.98$ (br. s)</p>	<p>$\delta = 3.60$(s)</p>	<p>$\delta = 6.05$(m) $\delta = 6.60$(m)</p>	<p>$\delta = 3.65$(s) N-methyl</p>
<p>XVI</p> 	<p>$\delta = 1.70$(m)</p>	<p>$\delta = 2.45$ (m)</p>	<p>$\delta = 3.48$(s)</p>	<p>$\delta = 7.00$(s)</p>	<p>$\delta = 2.20$(s) acetyl $\delta = 2.15$(s) methyl</p>
<p>XVII</p> 	<p>$\delta = 1.66$(m) $\delta = 0.86$(m)</p>	<p>$\delta = 2.76$ (m)</p>	<p>$\delta = 3.29$(s)</p>	<p>$\delta = 6.96$</p>	<p>$\delta = 0.80$(d) methyl $\delta = 2.08$(s) methyl $\delta = 2.12$(s) acetyl</p>

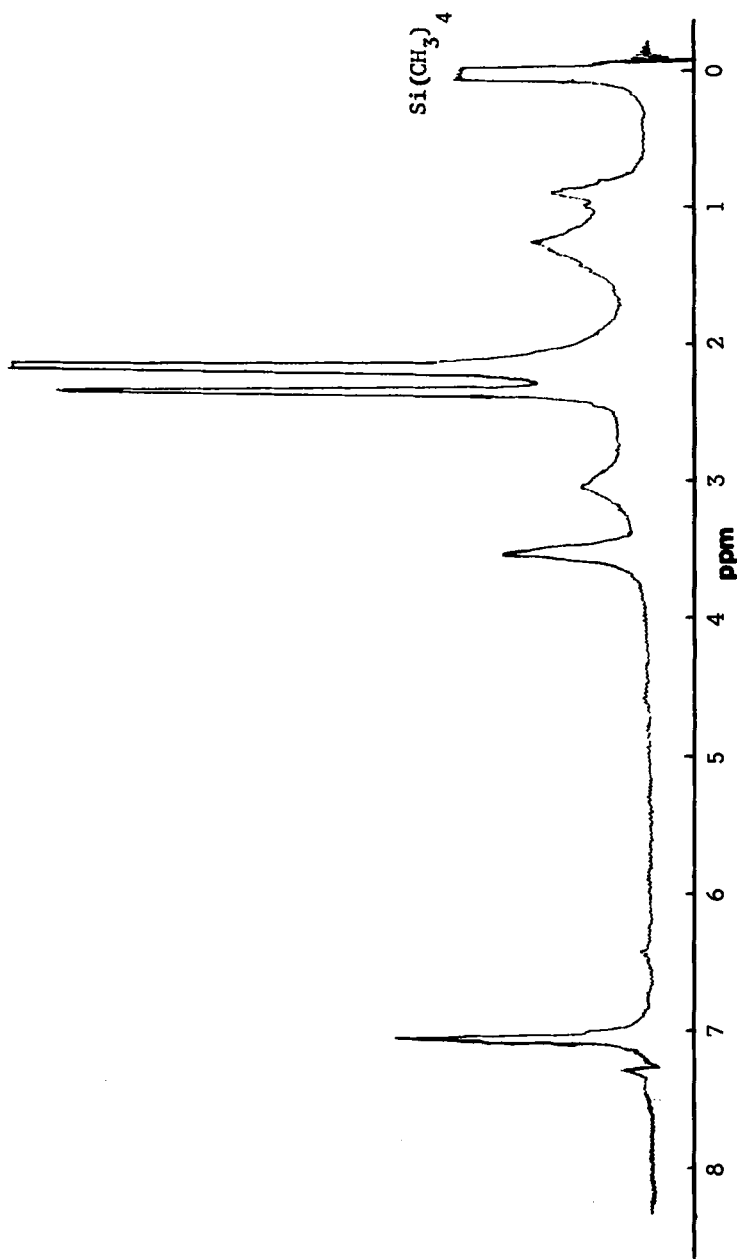
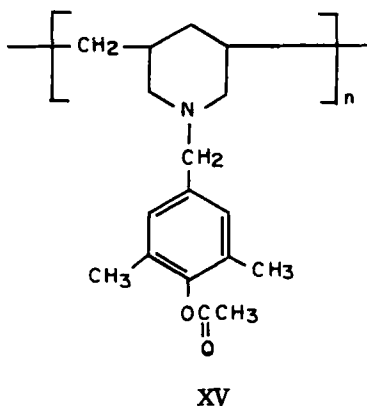
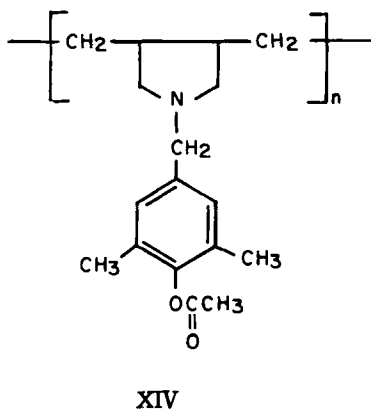


FIG. 1. Proton magnetic resonance spectra of homopolymer I in CDCl_3 .



^{13}C NMR spectra of this polymer (Fig. 2), together with the spectra of other model compounds synthesized via the Mannich reaction, confirmed the five-membered ring structure with predominantly ($> 80\%$) the *cis* isomer. A detailed analysis of the ^{13}C NMR spectra of these polymers and their model compounds will be reported in other papers in this series.

Titration Curves

The Mannich reaction was initially investigated as a cheap method of making benzylic amine resins, of the type produced by chloromethylating styrene and then basifying the product, but with much more homofunctional character. An important property of these resins was the shape of their titration curves, as Weiss et al. [16, 17] have shown that for polybases of this type the more heterofunctional units in the polymer the steeper the titration curve.

The data we obtained for the Mannich base polymers are shown in Figs. 3-5. Although not comparable to titrations of insoluble resins in completely aqueous systems [16], the system used by us (1:2 aqueous dioxane) allowed for greater polymer solubility and hence faster response to pH changes. The results for polymers V and VI were similar and showed the presence of the two different types of amino group in that pH changed fairly continuously throughout the titrations and no large pH plateaus were obtained. The polymers I-III show a somewhat more plateau-like titration shape because of their homofunctional nature; however, this plateau has been modified to varying degrees by associated polar, phenolic groups, an effect previously

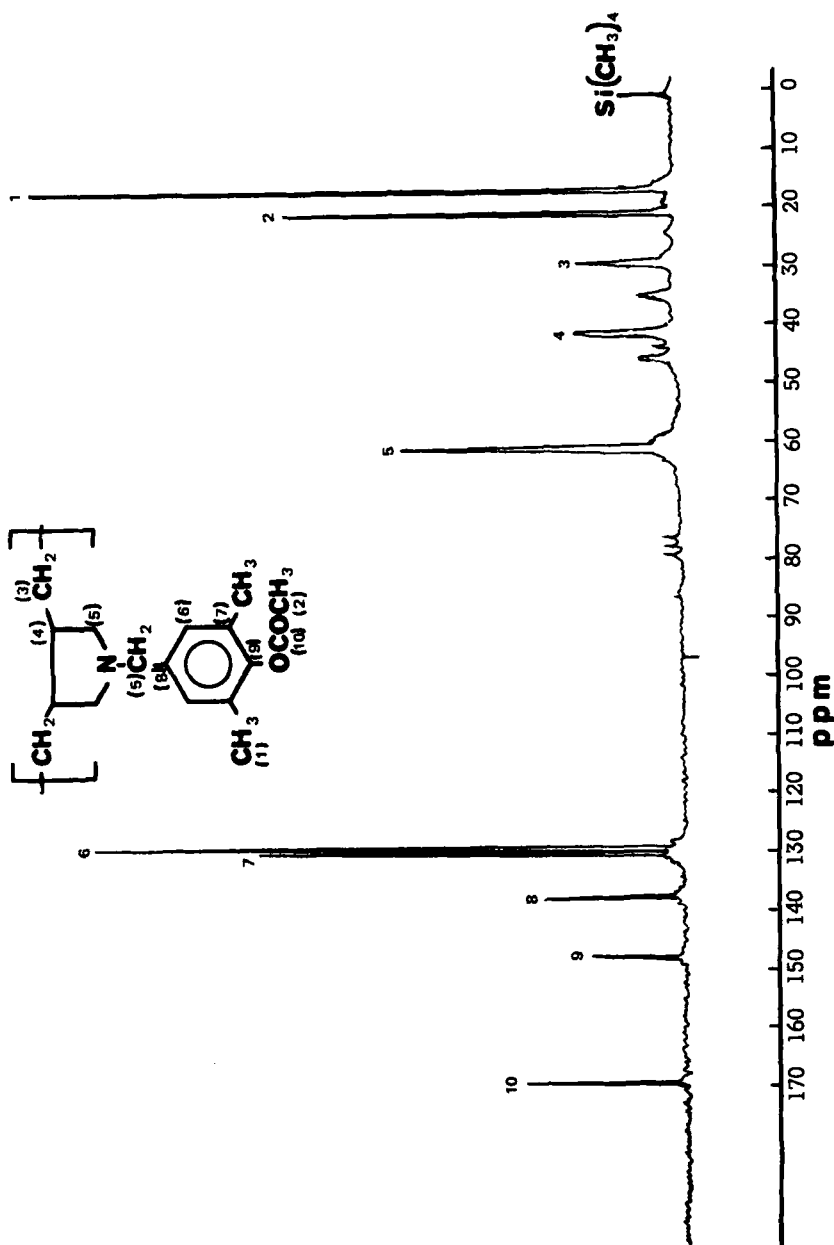


FIG. 2. Proton-decoupled natural-abundance ^{13}C NMR spectra of homopolymer I in CDCl_3 .

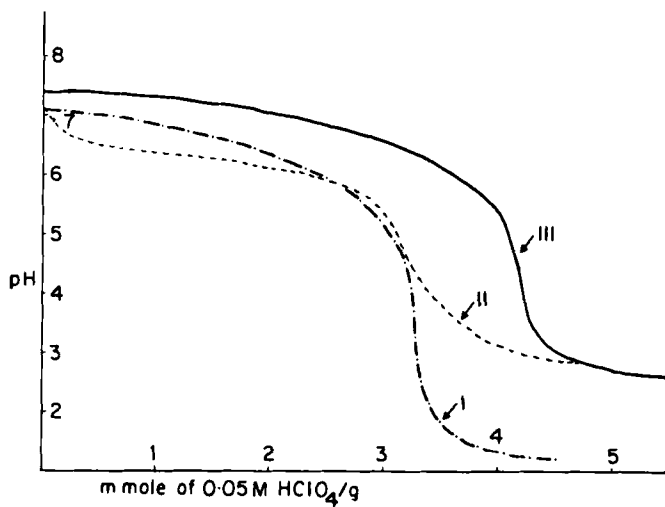


FIG. 3. Titration curves for homopolymers I, II, and III.

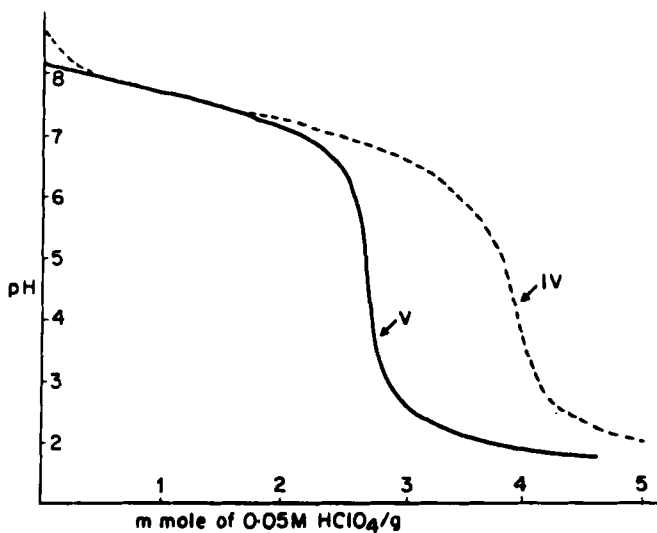


FIG. 4. Titration curves for homopolymers IV and V.

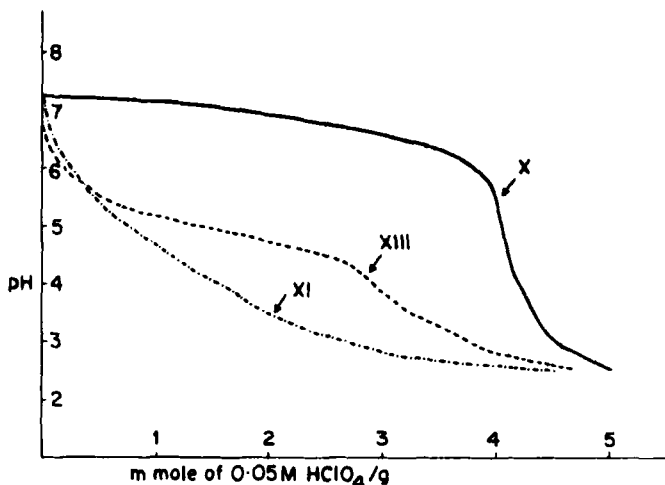


FIG. 5. Titration curves for homopolymers X, XI, and XIII.

noted [17]. The unusual curves for the crosslinked polymers XI and XIII were an indication of the incomplete neutralization of these gelled materials.

EXPERIMENTAL

Materials

Pyrrrole and N-methylpyrrrole were commercial reagents that were dried with potassium hydroxide and then distilled before use. Dimethylaniline was also purified by distillation. 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/w) methanol. Other reagents and solvents were purified by the usual methods. Diallylaniline was made by the method of Carnahan and Hurd [18].

Analyses

The elemental analyses were carried out by the Australian Micro-analytical Service, CSIRO, Melbourne. Infrared (IR) spectra were

recorded on a Unicam 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 HR 100 instrument. The chemical shifts (δ) are quoted as ppm from tetramethylsilane as the internal standard.

Phenolic Monomers

4-(Diallylaminomethyl)-2,6-dimethylphenol

A mixture of 12.7 g (0.1 mole) of 2,6-dimethylphenol and 9.7 g (0.1 mole) of diallylamine as a 25% aqueous solution was cooled at 20°C in a three-necked flask fitted with an electric stirrer, thermometer, and an addition funnel. The mixture was stirred while 10 g of aqueous formaldehyde was added dropwise over a period of 0.5 hr, the reaction mixture being maintained at 25-30°C. Stirring at this temperature was continued for 1 hr after completion of the addition. The addition funnel was then replaced by a reflux condenser, and the solution stirred and heated on a steam bath for 2 hr. To the hot solution was added 20 g of sodium chloride, and stirring and heating continued for 20 min. The organic layer was then extracted with ether, dried, and purified by column chromatography in benzene using aluminum oxide active (neutral) as the packing. The product, a light yellow oil (nondistillable) was obtained in 75% yield. Analysis. Found: C, 54.96%; H, 5.35%; N, 12.51%. Calculated for $C_{15}H_{21}NO \cdot C_6H_3N_3O_7$ as picrate salt, mp 170-171°C: C, 54.81%; H, 5.22%; N, 12.20%. IR: 3470 br (phenolic OH), 1641, 1000, 929 cm^{-1} (allylamino). PMR ($CDCl_3$): 2.20 (6H, singlet; methyl), 3.14 (4H, complex doublet; allylmethylene), 3.46 (2H, singlet; benzylic methylene), 5.16 (4H, multiplet; vinylmethylene), 5.8 (2H, multiplet; vinylmethine), 6.96 (2H, singlet; aromatic).

Other Phenolic Monomers

The other phenolic monomers and model compounds were obtained by similar procedures.

6-(Diallylaminomethyl)-2-methylphenol was obtained from o-cresol as a light yellow oil in 77% yield after purification by column chromatography in benzene and distillation, bp 103-106°C/0.1 Torr. Analysis. Found: C, 77.50%; H, 9.06%; N, 6.52%. Calculated for $C_{14}H_{19}NO$: C, 77.38%; H, 8.81%; N, 6.45%. IR: 3200 br (phenolic OH), 1642, 998, 931 cm^{-1} (allylamino). PMR ($CDCl_3$): δ 2.26 (2H, singlet; methyl), 3.04 (4H, doublet; allylmethylene), 3.65 (2H, singlet; benzylic methylene), 5.12 (4H, multiplet; vinylmethylene), 5.8 (2H, multiplet; vinylmethine), 6.75 (3H, ABC multiplet; aromatic).

2,2-Bis[2,6-di(diallylaminomethyl)5-hydroxyphenyl]propane was obtained from Bisphenol A as a viscous yellow oil in 73% yield after purification by column chromatography in benzene. Analysis. Found: C, 78.02%; H, 8.95%; N, 8.08%. Calculated for $C_{43}H_{50}N_4O_2$: C, 77.7%; H, 9.09%; N, 8.43%. IR: 3200 br. (phenolic OH), 1615, 990 cm^{-1} (allylamino). PMR ($CDCl_3$): δ 1.62 (6H, singlet; methyl), 3.10 (16H, doublet; allylmethylene), 3.64 (8H, singlet; benzylic methylene), 5.12 (16H, multiplet; vinylmethylene), 5.8 (8H, multiplet; vinylmethine), 6.92 (4H, singlet; aromatic).

Diallylaminomethylphenol derivatives were obtained as yellow oily mixtures of the tri-, di-, and monosubstituted products which could not be fully separated by chromatography or distillation. Exception was the monosubstituted ortho compound obtained in 60% yield when only 1.5 mole of diallylamine and formaldehyde were used per mole of phenol. The product was a colorless oil, bp 130°C/0.4 Torr. Analysis. Found: C, 77.06%; H, 8.14%; N, 6.99%. Calculated for $C_{13}H_{17}NO$: C, 76.81%; H, 8.43%; N, 6.89%. IR: 3200 br. (phenolic OH), 1642, 990, 930 cm^{-1} (allylamino). PMR ($CDCl_3$): δ 3.14 (4H, doublet; allylmethylene), 3.74 (2H, singlet; benzylic methylene), 5.18 (4H, multiplet; vinylmethylene), 5.8 (2H, multiplet; vinylmethine), 6.86 (4H, multiplet; aromatic).

The other separable product was the 2,6-di(diallylaminomethyl)phenol, which distilled as a colorless oil, bp 120°C/0.1 Torr in 20% yield when only 1.5 mole of diallylamine and formaldehyde was used per mole of phenol. Analysis. Found: C, 76.96%; H, 8.84%; N, 9.06%. Calculated for $C_{20}H_{28}N_2O$: C, 76.92%; H, 8.97%; N, 8.97%. IR: 3200 br (phenolic OH), 1640, 998, 932 cm^{-1} (allylamino) PMR ($CDCl_3$): δ 3.14 (8H, complex doublet; allylmethylene), 3.68 (4H, singlet; benzylic methylene), 5.15 (8H, multiplet; vinyl methylene) 5.8 (4H, multiplet; vinylmethine), 6.9 (3H, AB₂ multiplet), 7.32 (1H, singlet, phenolic OH).

4-(N-pyrrolidyl)-2,6-dimethylphenol was obtained from 2,6-dimethylphenol and pyrrolidine as a colorless solid in 88% yield and recrystallized from benzene as large needles, mp 124.5°C. Analysis. Found: C, 76.40%; H, 9.27%; N, 6.56%. Calculated for $C_{13}H_{16}NO$: C, 76.11%; H, 9.29%; N, 6.83%. IR: 3500 cm^{-1} br (phenolic OH). PMR ($CDCl_3$): δ 1.78 (4H, multiplet; pyrrolidine CH_2), 2.18 (6H, singlet; methyls) 2.55 (4H, multiplet; pyrrolidine CH_2N), 3.50 (2H, singlet; benzylic methylene), 6.90 (2H, singlet; aromatic), 6.06 (1H, singlet; phenolic OH).

4-[N(3-methylpiperidyl)]-2,6-dimethylphenol was obtained from 2,6-dimethylphenol and 3-methylpiperidine as a pink solid in 85% yield and recrystallized from benzene/petroleum ether as plates, mp 102-108°C, containing considerable solvent of crystallization.

Analysis. Found (after drying): C, 70.48%; H, 9.54%; N, 5.76%. Calculated for $C_{15}H_{23}NO$: C, 70.23%; H, 9.30%; N, 5.62%. IR: 3500 br (phenolic OH). PMR ($CDCl_3$): δ 0.80 (3H, doublet; methyl), 1.66 (9H, br. multiplet; piperidine methylene), 2.14 (6H, singlet; methyl), 2.78, (4H, br. multiplet; piperidine CH_2N), 3.29 (2H, singlet; benzylic methylene), 6.90 (2H, singlet; aromatic), 5.82 (1H, singlet; phenolic OH).

Phenol Acetate Monomers

In the synthesis of 4-(diallylaminomethyl)-,6-dimethylphenol acetate (I), 4-(diallylaminomethyl)-2,6-dimethylphenol (23.1 g, 0.1 mole) was dissolved in cold acetic anhydride (15 g, 0.15 mole) and gently warmed with stirring until the temperature reached 60° C. The solution was left at this temperature for 24 hr before 50 ml of cold water was added and then sodium carbonate solution slowly poured in with vigorous stirring (to minimize the foaming). When the solution had been completely basified it was extracted with ether and the resulting extracts dried with anhydrous sodium sulfate. On removal of the solvent the remaining brown oil was vacuum-distilled to yield a clear viscous oil of the expected product, bp 120–122° C/0.3 Torr (77% yield). Analysis. Found: C, 74.72%; H, 8.23%; N, 5.18%. Calculated for $C_{17}H_{23}NO_2$: C, 74.70%; H, 8.48%; N, 5.13%. IR: 1751 (acetate) 1639, 998, 926 cm^{-1} (allylamino). PMR ($CDCl_3$): δ 2.14 (6H, singlet; methyl), 2.28 (2H, singlet; acetyl), 3.08 (4H, complex doublet; allylmethylene), 3.47 (2H, singlet; benzylic methylene), 5.12 (4H, multiplet; vinylmethylene), 5.7 (2H, multiplet; vinylmethine), 7.06 (2H, singlet; aromatic).

The other phenol acetate monomers were obtained by the same procedure.

4-(Diallylaminomethyl)-2-methylphenol acetate (II) was obtained from the phenol as a light colorless oil after distillation under reduced pressure. Analysis. Found: C, 74.31%; H, 8.22%; N, 5.28%. Calculated for $C_{16}H_{21}NO_2$: C, 74.13%; H, 8.16%, N, 5.41%. IR: 1758 (acetate) 1642, 1002, 925 cm^{-1} (allylamino). PMR ($CDCl_3$): δ 2.14 (3H, singlet; methyl), 2.18 (3H, singlet; acetyl), 3.02 (4H, complex doublet; allylmethylene), 3.45 (2H, singlet; benzylic methylene), 5.12 (4H, multiplet; vinylmethylene), 5.7 (2H, multiplet; vinylmethine), 7.06 (3H, multiplet; aromatic).

2-(Diallylaminomethyl)phenol acetate (III) was obtained from the phenol as a light colorless oil after distillation under reduced pressure. Analysis. Found: C, 73.41%; H, 7.60%; N, 5.93%. Calculated for $C_{15}H_{19}NO_2$: C, 73.47%, H, 7.76%, N, 5.71%. IR: 1762 (acetate) 1642, 1000, 922 cm^{-1} (allylamino). PMR ($CDCl_3$): δ 2.15 (3H, singlet; acetyl), 3.02 (4H, complex doublet; allylmethylene), 3.48 (2H, singlet;

benzylic methylene), 5.12 (4H, multiplet; vinylmethylene), 5.7 (2H, multiplet; vinylmethine), 7.16 (4H, multiplet, aromatic).

4-(*N*-pyrrolidyl)-2,6-dimethylphenol acetate (XVI) was obtained from the phenol by the method used for compound I to give a viscous yellow oil, bp 110-112° C/0.3 Torr (73% yield). Analysis. Found: C, 70.44%; H, 8.54%; N, 5.42%. Calculated for C₁₅H₂₁NO₂: C, 70.28%; H, 8.55%; N, 5.66%. IR: 1762 cm⁻¹ (acetate). PMR (CDCl₃): δ 1.76 (4H, multiplet; pyrrolidine methylene), 2.10 (6H, singlet; methyl), 2.18 (3H, singlet; acetyl), 2.50 (4H, multiplet; pyrrolidine CH₂N), 3.49 (2H, singlet; benzylic methylene), 7.00 (2H, singlet; aromatic).

4-[*N*-(3-methylpiperidyl)]-2,6-dimethylphenol acetate (XVII) was obtained from the phenol by the method used for compound I to give a viscous yellow oil which was purified by chromatography on alumina (76% yield). Analysis. Found: C, 74.36%; H, 9.29%; N, 5.34%. Calculated for C₁₇H₂₃NO₂: C, 74.20%; H, 9.09%; N, 5.09%. IR: 1758 cm⁻¹ (acetate). PMR (CDCl₃): δ 0.80 (3H, doublet; methyl), 1.66 (9H, br. multiplet; piperidene methylene), 2.08 (6H, singlet; methyl), 2.12 (3H, singlet; acetyl), 2.78 (4H, br. multiplet; piperidine CH₂N), 3.29 (2H, singlet; benzylic methylene), 6.96 (2H, singlet; aromatic).

Aniline Monomers

4-(Diallylaminomethyl)-*N,N*-dimethylaniline (IV)

Formaldehyde solution (20 ml, 0.22 mole) was added slowly with stirring to diallylamine (19.5 g, 0.2 mole) in a 250-ml round-bottomed flask surrounded by an ice bath. Then both acetic acid (12 g, 0.2 mole) and dimethylaniline (24.2 g, 0.2 mole) were added slowly to ensure that the temperature remained below about 20° C, and finally enough ethanol was added to make a homogeneous solution. The mixture was then heated under a reflux for 30 hr before the ethanol was removed under reduced pressure. On cooling to below 10° C the solution was treated with cold 30% sodium hydroxide and extracted with ether. The ether extracts were dried with sodium sulfate and the solvent removed to yield a brown oil, which on vacuum distillation gave a 55% of the expected product as a light yellow oil, bp 114-116° C/1 Torr. Analysis. Found: C, 77.93%; H, 9.50%; N, 12.08%. Calculated for C₁₅H₂₂N₂: C, 78.21%; H, 9.63%; N, 12.16%. IR: 1643, 1002, 922 (allylamine), 1618, 808 cm⁻¹ (aromatic). PMR (CDCl₃): δ 2.92 (6H, singlet; *N*-methyl), 3.16 (4H, complex doublet; allylmethylene), 3.52 (2H, singlet; benzylic methylene), 5.15 (4H, multiplet; vinylmethylene), 5.8 (2H, multiplet; vinylmethine), 6.73, 7.24 (4H, AA', BB' multiplets, J_{AB} = 9 Hz; aromatic).

N,N-Diallyl-4-(dimethylaminomethyl)aniline (V)

This monomer was prepared in 69% yield from diallylaniline and dimethylamine by the same method as IV and was obtained as a light yellow oil, bp 108-111°C/0.7 Torr. Analysis. Found: C, 78.49%; H, 9.73%; N, 12.23%. Calculated for C₁₅H₂₂N₂: C, 78.21%; H, 9.63%; N, 12.16%. IR: 1642, 998, 928 (allylamine), 1618, 811 cm⁻¹ (aromatic). PMR (CDCl₃): δ 2.18 (6H, singlet; N-methyl), 3.28 (2H, singlet; benzylic methylene), 3.88 (4H, complex doublet; allylmethylene), 5.12 (4H, multiplet; vinyl methylene), 5.7 (2H, multiplet; vinylmethine), 6.63, 7.11 (4H, AA', BB' multiplets, J_{AB} = 9 Hz; aromatic).

Pyrrole Monomers2,5-Di-(diallylaminomethyl)pyrrole (IX)

Acetic acid (12 g, 0.2 mole) was added slowly with stirring to diallylamine (19.5 g, 0.2 mole) in a 250-ml round-bottomed flask surrounded by an ice bath. When the temperature had restabilized to 0-10°C, formaldehyde solution (20 ml) was slowly added. Pyrrole (6.7g, 0.1 mole) was then added dropwise with stirring as the temperature was kept between 0 and 5°C. On completion of the addition the solution was kept at 0-10°C for 24 hr and then basified with cold sodium hydroxide solution. The resulting brown oil was extracted with ether, dried with sodium sulfate, and the ether removed under vacuum at low temperature. The product was chromatographed on neutral alumina, with benzene as the eluting solvent to give a light brown oil in 85% yield. This could be distilled under vacuum to give a very low <15% yield of pure IX, bp 107-108°C/0.5 Torr, before the rest of the liquid polymerized into a red rubbery solid with the evolution of diallylamine. Analysis. Found: C, 75.47%; H, 9.59%; N, 14.65%. Calculated for C₁₈H₂₇N₃: C, 75.74%; H, 9.53%; N, 14.72%. IR: 3420 (NH), 1640, 1000, 925 cm⁻¹ (allylamine). NMR (CDCl₃): δ 3.03 (8H, doublet; allylmethylene) 3.52 (4H, singlet; pyrrole α-methylene), 5.12 (8H, multiplet; vinylmethylene), 5.75 (4H, multiplet; vinylmethine), 5.88 (2H, singlet; pyrrolic), 8.38 (1H, broad singlet; NH).

Other Pyrroles

2-Diallylaminomethylpyrrole (VIII) was synthesized as above for IX except that only a 0.1 mole quantity of each of the other reagents was used for each 0.1 mole of pyrrole and the reagent mixture was added to the pyrrole dropwise instead of the converse. The product

VIII was obtained in 67% yield as a colorless oil, bp 73° C/1 Torr. IR and PMR spectra were as described in the literature [11].

2,5-Di(diallylaminomethyl)-1-methylpyrrole (X) was synthesized as above for IX and was obtained in 87% yield from N-methylpyrrole. The product was a light yellow oil, bp 116-118° C/0.5 Torr. Analysis. Found: C, 76.40%; H, 9.85%; N, 13.50%. Calculated for $C_{19}H_{29}N_3$: C, 76.20%; H, 9.76%; N, 14.03%. IR: 1645, 1003, 927 cm^{-1} (allylamine). PMR ($CDCl_3$): δ 3.04 (8H, doublet; allylmethylene), 3.47 (4H, singlet; pyrrole α -methylene), 3.60 (3H, singlet; N-methyl), 5.16 (8H, multiplet; vinylmethylene), 5.75 (4H, multiplet; vinylmethine), 5.88 (2H, singlet; pyrrole).

2-(Diallylaminomethyl)-1-methylpyrrole (XI) was synthesized as above for VIII and was obtained in 64% yield from N-methylpyrrole. The product was a light yellow oil, bp 89° C/0.5 Torr. Analysis. Found: C, 75.64%; H, 9.37%; N, 14.62%. Calculated for $C_{12}H_{16}N_2$: C, 75.74%; H, 9.53%; N, 14.75%. IR: 1644, 1005, 931 cm^{-1} (allylamine). PMR ($CDCl_3$): δ 3.02 (4H, doublet; allylmethylene), 3.45 (2H, singlet; pyrrole α -methylene), 3.58 (3H, singlet; N-methyl), 5.12 (4H, multiplet; vinylmethylene), 5.75 (2H, multiplet; vinylmethine), 5.97 (2H, doublet; pyrrole β -hydrogen), 6.52 (1H, triplet; pyrrole α -hydrogen).

In synthesis of 1,4-di(-1-pyrrolyl)butane (XII), potassium (7.8 g, 0.2 mole) in freshly cut pieces was added (under a nitrogen atmosphere) to a solution of pyrrole (16.8 g, 0.25 mole) in 100 ml of dry tetrahydrofuran in a 1-liter three-necked flask. The mixture was heated with stirring under gentle reflux until all the potassium had disappeared. A further 100 ml of solvent was then added, and the temperature adjusted to 65° C as a solution of 1,4-dibromobutane (22 g, 0.1 mole) was added dropwise. The reaction mixture was stirred at this temperature for a further 8 hr and then cooled and filtered. The solid precipitate was washed with ether which was then added to the filtrate. The solid material was then dissolved in a small amount of water which was extracted with ether. This ether was then dried with sodium sulfate and the total solvent phases combined and evaporated down to leave a brown oily residue. This was vacuum distilled to give a yellow oil (83%), bp 97° C/0.1 Torr. IR: 3195 (pyrrole NCH_2), 1507, 1280, 1091, 727 cm^{-1} .

1,4-Bis-[2,5-bis(diallylaminomethyl)-1-pyrrolyl]butane XIII was synthesized as above for IX and was obtained in 78% yield from XII and purified by chromatography. The product was a viscous, non-distillable yellow oil. Analysis. Found: C, 77.20%; H, 9.45%; N, 13.60%. Calculated for $C_{40}H_{60}N_6$: C, 76.87%; H, 9.67%; N, 13.45%. IR: 3190 (pyrrole $N-CH_2$), 1647, 1004, 929 cm^{-1} (allylamine).

PMR (CDCl_3): δ 1.72 (4H, broad singlet; bridge methylenes), 3.01 (16H, doublet; allyl methylene), 3.44 (8H, singlet; pyrrole α -methylene), 4.07 (4H, broad triplet; pyrrole N-methylene), 5.09 (16H, multiplet, vinylmethylene), 5.75 (8H, multiplet; vinylmethine), 5.87 (4H, singlet; pyrrole).

Polymer Preparation

The most successful polymer preparation for all the monomers was as follows.

The monomer hydrochloride salt (0.05 mole) was prepared by the dropwise addition of concentrated hydrochloric acid to the stirred base at 0-10°C. Dilute acid (about 2 ml) was added to give a solution of pH 1-2, and then 4 ml of titanous chloride (14%) solution was stirred in. The mixture was stirred under nitrogen at temperatures between 5 and 45°C as a 10% solution of hydrogen peroxide was added dropwise until the mixture changed permanently to a strong orange color. After an additional 2 hr stirring the solution was basified with ammonium hydroxide solution and extracted with chloroform.

The chloroform extract was then dried with sodium sulfate and evaporated to dryness under vacuum to leave a brown oily residue. Trituration of this with petroleum ether removed all the unchanged monomer and low molecular weight material. The resulting polymers were purified by repeatedly dissolving in chloroform and reprecipitating with petroleum ether.

ACKNOWLEDGMENTS

The authors wish to thank Dr. S. Johns for the NMR spectra and Mr. R. Allan for technical assistance.

REFERENCES

- [1] D. Willis, H. A. J. Battaerd, G. A. Long, and D. E. Weiss, *Austral. Pat. Appl.* 45,081/72 (1972).
- [2] E. Tsuchida and T. Tomono, *J. Polym. Sci. Polym. Chem. Ed.*, **11**, 723 (1973).
- [3] T. Tomono, E. Hasegawa, and E. Tsuchida, *J. Polym. Sci. Polym. Letters Ed.*, **12**, 139 (1974).

- [4] B. B. Thomson, *J. Pharm. Sci.*, **54**, 715 (1968).
- [5] M. Tramontini, *Synthesis*, 703 (1973).
- [6] F. F. Blicke, in *Organic Reactions*, Vol. 1, Wiley, New York, 1942, pp. 303-341.
- [7] H. A. Bruson and C. W. MacMullen, *J. Amer. Chem. Soc.*, **63**, 270 (1941).
- [8] M. Miocque and J. M. Vierfond, *Bull. Soc. Chim. France*, 1970, 1896.
- [9] G. B. Bachman and L. V. Helsey, *J. Amer. Chem. Soc.*, **68**, 2496 (1946).
- [10] C. F. Hobbs, C. K. McMillin, E. P. Papadopoulos, and C. A. VanderWerf, *J. Amer. Chem. Soc.*, **84**, 43 (1962).
- [11] E. Tsuchida, T. Tomono, K. Honda, H. Nishishikawa, and E. Hasegawa, *J. Chem. Soc. Japan*, 1973, 1184.
- [12] K. Schofield, *Hetero-Aromatic Nitrogen Compounds—Pyrroles and Pyridines*, Butterworths, London, 1967.
- [13] B. Rånby, *J. Macromol. Sci.—Chem.*, **A6**, 904 (1972).
- [14] C. E. Schildknecht, *Allyl Compounds and their Polymers*, Interscience-Wiley, New York, 1973.
- [15] D. H. Solomon, *J. Macromol. Sci. Chem.*, **A9**, 95 (1975). and subsequent papers in this symposium.
- [16] D. E. Weiss, B. A. Bolto, R. McNeill, A. S. Macpherson, R. Sludak, E. A. Swinton, and D. Willis, *Austral. J. Chem.*, **19**, 561 (1966).
- [17] B. A. Bolto, R. McNeill, A. S. Macpherson, R. Sludak, D. E. Weiss, and D. Willis, *Austral. J. Chem.*, **21**, 2703 (1968).
- [18] F. L. Carnahan and C. D. Hurd, *J. Amer. Chem. Soc.*, **52**, 4586 (1930).