polymer review

Mannich bases in polymer chemistry

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Mannich bases, the characteristic structure of which is $X-CH_2-N<$ (X = ketoalkyl, phenol, amide, phosphonic group, etc.), are widely employed as polymers or monomeric precursors of polymers in the production of substances with a large number of different applications in industry. This review covers the existing literature on Mannich bases involved in polymer chemistry on the basis of a classification of the polymeric structures which have been synthesized and describes their applications.

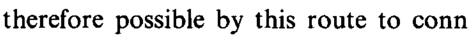
(**Keywords: Mannich bases; polymer synthesis; polymer functionalization**)

INTRODUCTION

The chemistry of Mannich bases has assumed a growing relevance, particularly in the last fifteen years, as a valid tool in the synthesis or chemical modification of polymeric molecules suitable for many different applications. Mannich bases have, in fact, come into use mainly as binders in electrophoretic coatings, flocculants in waste-water treatment and additives with various protecting actions for lubricating oils. Other interesting applications of such products are as polymeric antioxidants for plastics, ion-exchange resins, polymeric complexing agents etc.

The number of applications as well as the potential interest of Mannich bases lies in the versatility of their synthesis and on the wide range of reactions possible. The chemistry of such compounds has been extensively reviewed[1,2] and will be only briefly summarized here.

Mannich reaction implies the condensation of an H-active substrate with formaldehyde and an amine according to the scheme:

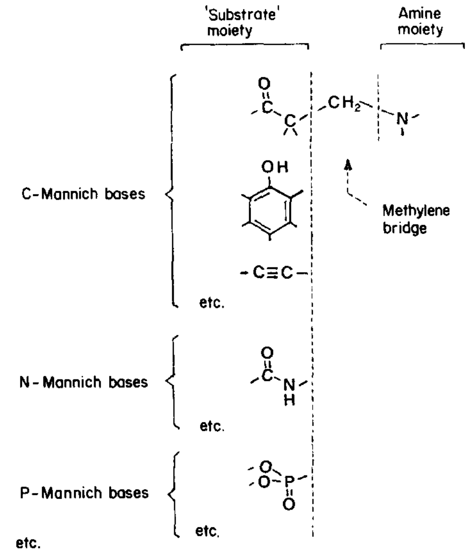


$$X-H + CH_2O + HN< \xrightarrow[(-H_2O)]{} X\frown N<$$

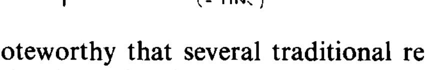
It is therefore possible by this route to connect two different molecular entities via a methylene bridge, thus affording a product with particular properties which can be exploited in a variety of applications.

The reactive hydrogen atom to be substituted by the aminomethyl group can, in fact, belong to a very wide series of different X–H compounds (from here on, 'substrates'), as demonstrated by the following examples.

The amine moiety, on the other hand, confers to the molecule typical basic properties such as the possibility of salt formation and nitrogen quaternization (with a consequent increase of hydrophilic power) and the capacity to speed up base-catalysed reactions.



Besides the behaviour due to the functions present in the substrate and amine moieties, Mannich bases also show peculiar properties which derive from their own structure. Of these, the possibility of amino group substitution by a nucleophilic reactant is an important aspect of our discussion, the reaction involved actually being an X-methylation of another H-active substrate:



$$X\frown N< + H-Y \xrightarrow[(-HN<)]{} X\frown Y$$

It is noteworthy that several traditional reactions of macromolecular chemistry involve Mannich base chemistry.

For instance, hardening of novolacs by hexamethylenetetramine[3] involves both aminomethylation and substitution reactions as well as a catalytic effect. Synthesis and chemical properties of Mannich bases are also present in the chemistry of aniline resins[4] and in the

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treatment of protein materials with formaldehyde, such as hardening of casein[5] or tanning hides (see also below). Moreover, Mannich bases have long been employed in the crosslinking of epoxy resins[6]. Finally, the synthesis of urea resins and related products, which uses an amidomethylation very similar to the Mannich reaction, may also be mentioned.

All these well known reactions, however, will be discussed here only in so far as their modern developments are concerned. The main subject of this review is Mannich bases which have been used more recently in other fields of polymer chemistry.

The polymeric structures which will be described are **a**–**h** in *Scheme 1*, where **a**–**e** are polymeric Mannich bases in which the characteristic aminomethyl group is present, and **f**–**h** are other polymers which are obtained with Mannich bases acting as precursors or polymerization assistant compounds (hardeners, accelerators etc.). The latter polymers do not usually contain aminomethyl groups, with only few exceptions, often due to reactions other than the Mannich reaction.

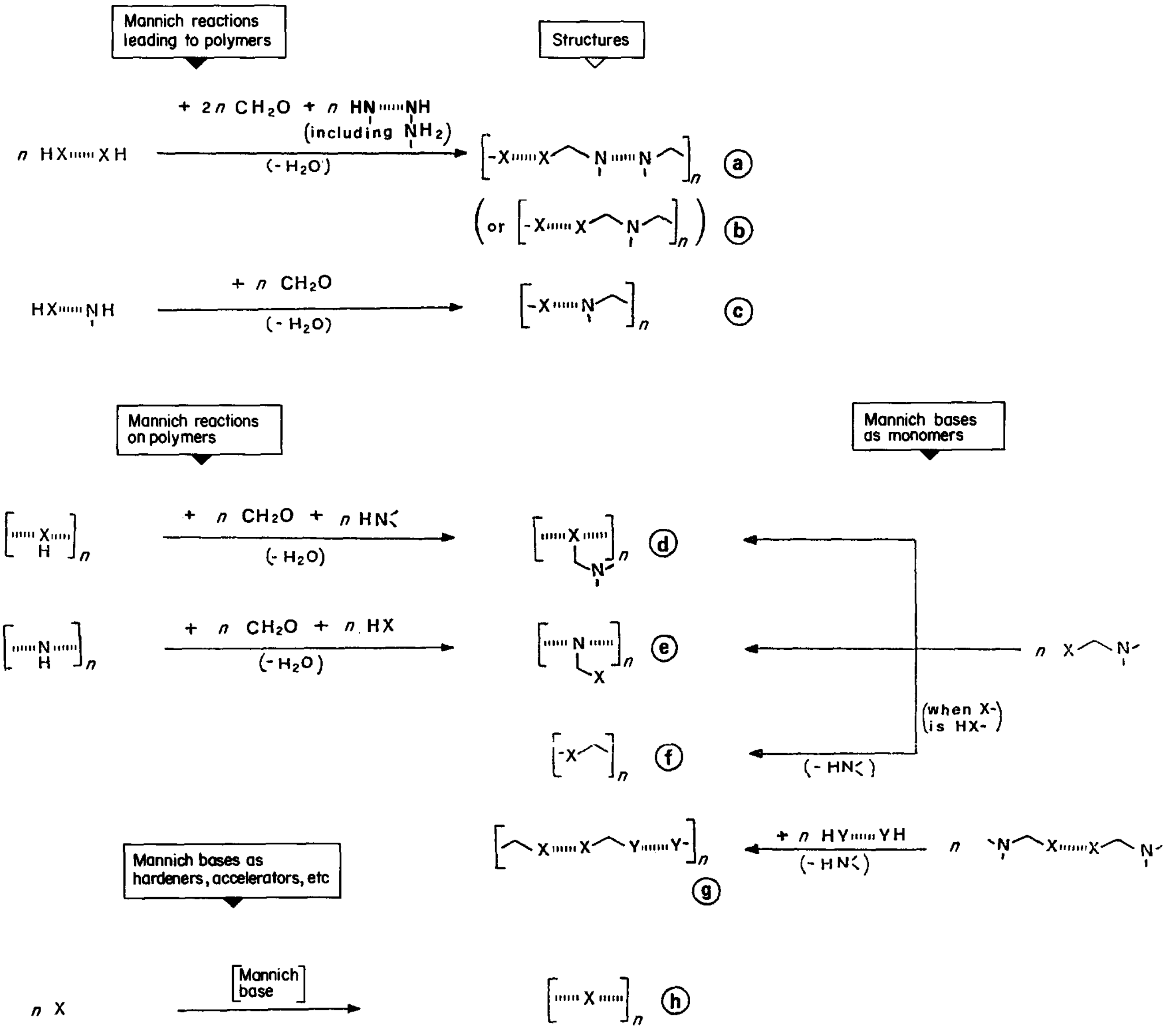
The first two main sections describe the application of Mannich reaction to, respectively, the synthesis of polymeric products **a**–**c** and to the functionalization of polymers leading to structures **d** and **e**.

This review then discusses the reactivity of Mannich bases as, respectively, monomers producing polymers **d**–**g**, and as hardeners, accelerators, etc., affording various structures **h**.

Other subjects not falling into the above Scheme are mentioned in a short Appendix, together with some indications on possible research lines, so far hardly studied, which could usefully be more closely investigated.

MANNICH REACTIONS LEADING TO POLYMERS

When the Mannich reaction is carried out between a ‘substrate’ containing at least two active hydrogen atoms and a bis-secondary amine (or a primary amine), a polycondensation takes place and a polymeric derivative is produced. Such polycondensation reactions can analogously occur also when both the amino group and an active hydrogen atom are present in the same



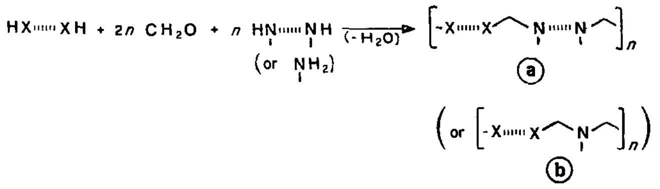
Scheme 1

monomeric molecule. These two groups of reactants will be discussed below.

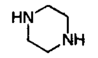
As the methylene bridge linking the amine and substrate moieties is part of the polymer backbone the possibility exists that polymer degradation occurs by deamination, or deaminomethylation, reactions which are both typically given by Mannich bases[1,2] (see Appendix).

Polymerization of bifunctional 'substrates' and amines

The polymeric Mannich bases here described are produced according to the following general Scheme:



The secondary bis-amines usually employed in the synthesis are piperazine **1** or 1,3-bis-piperidinopropane **2**.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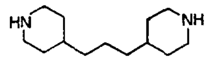
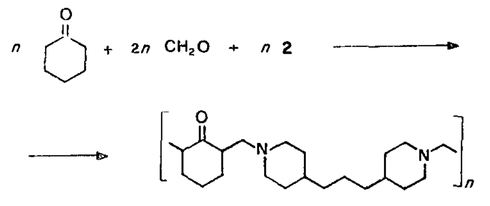

2

A number of substrates of the type HX···XH are used to give a large variety of polymeric products, such as aminoketone- (e.g. **3**), phenol-, acetylene- (e.g. **4**), *N*-amide- (e.g. **5**) derivatives and many others[7-15].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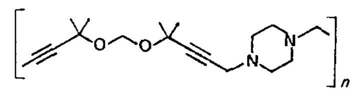
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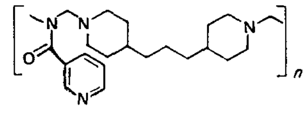
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Table 1 gives a more complete list of substrates and amines suitable for polymerization and indicates the likely position of attack by the aminomethylating reactant.

Products with analogous structures have been also obtained[16] using primary bis-amines, e.g. isophoronediamine, *m*-xylilendiamine etc., in the same molar ratios as above (substrate/formaldehyde/amine = 1:2:1). Since in these poly-Mannich bases (as for example **6**) secondary amino groups are present, they are successfully employed as hardeners for epoxy resins (see below).

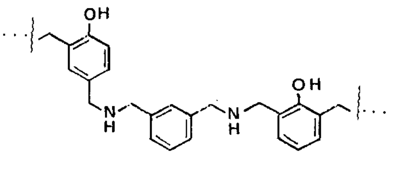
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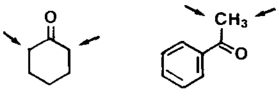
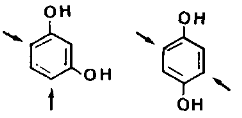
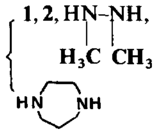
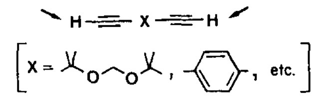
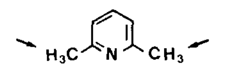
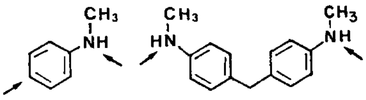
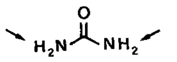
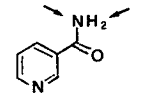
Table 1 'Substrates' and bifunctional secondary amines employed in the synthesis of polymeric Mannich bases

Substrates*	Amines	Refs.
For C-Mannich bases		
	1, 2	7, 8
		7, 9, 10
	1	11, 12
	1	9
	2	13
For N-Mannich bases		
	1	7–9, 14[a]
	1	15[b]
	2	13

*Arrows indicate the more likely position of attack by the aminomethylating agent

[a] Structures deriving from C-aminomethylation of the aromatic ring can also be formed

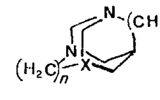
[b] As the aim of this work was to study the factors influencing the reaction between dimethylol-urea (or its corresponding methyl ether) and amine **1**, the expected polymer was neither isolated nor characterized

A second series of polymers includes products derived from various primary monoamines (**7**), or from ammonia under the form of hexamethylenetetramine and similar compounds (**8**), which can be considered useful preformed Mannich reagents.

R–NH$_2$

7

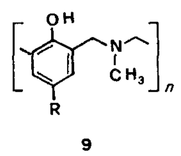
R = alkyl, hydroxyalkyl, carboxyalkyl or aryl group


8

n = 1, 2

X = N, P

In this case, also, polyketo-, polyphenol- (e.g. **9**), polyarylamino- (e.g. **10**), or polyamido-Mannich bases are produced[9,13,17-22].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R = C_{12-14} alkyl group

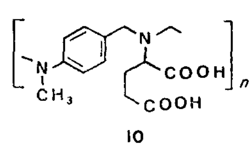
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Table 2 Bifunctional 'substrates' and primary amines employed in the synthesis of polymeric Mannich bases

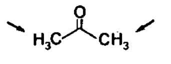
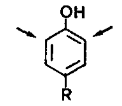
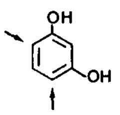
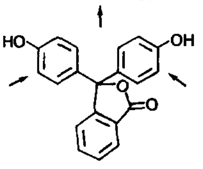
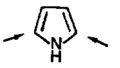
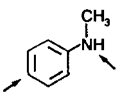
Substrates	Amines	Refs.
For C-Mannich bases		
	7	9, 13
 R=H	8	17
R=various alkyls	7	18, 19
	Hexamethylolmelamine	20
	Urea, guanidine, etc.	21
	7	9
For N-Mannich bases		
 (see note *a* in *Table 1*)	7	13
Urea and derivatives	8	17, 22

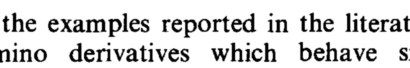
Table 2 lists substrates and amines employed in the synthesis of this series of polymers, which may in some cases be crosslinked derivatives.

Some of the examples reported in the Table for phenolic substrates are more properly considered amidomethylation reactions, as the starting compounds are urea, guanidine etc. Phenolphthalein is also included among the above phenolic substrates, and affords an interesting polymeric acid–base indicator[21].

Among the applications proposed for the polymeric Mannich bases described in this section, it is also worth mentioning the redox action of hydroquinone derivatives, which can be used as desulphurization agents[7], the vulcanization accelerating properties of some phenolic derivatives[18], and the combined antioxidant and dispersing actions of polymers **9** in lubricating oils[19]. Finally, the wrinkle recovery imparted by urea derivatives[22] to fabrics should be stressed.

Polymerization of monomeric 'substrates' containing the amino group

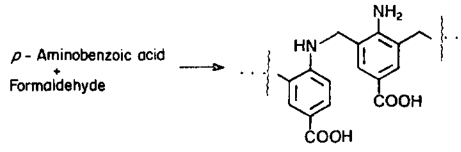
The polymerizations described in this section are carried out according to the following scheme:



ⓒ

All the examples reported in the literature deal with arylamino derivatives which behave simultaneously as amines and substrates undergoing *C*-aminomethylation on the activated sites of the aromatic ring. However, *N*-aminomethylation on the arylamine nitrogen atom presumably also occurs, as shown in the synthesis of aniline resins[4] as well as by the products with structure **10**, above. This implies that arylamino monomers may be expected to lead also to branched and crosslinked polymeric products.

p-Aminobenzoic acid is among the monomers employed leading to polymeric compound **11**, as has been reported[23].



11

Similar products deriving from *m*-aminophenol or from mixtures of arylamines with phenol have also been described[24,25].

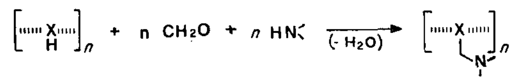
The properties of the resins mentioned in this section derive from their ionic character, complexing power and their ability to include into the polymer mass magnetizable metallic particles. Applications are wide, ranging from deodorants to magnetic tapes to supports for immobilized enzymes.

MANNICH REACTIONS ON POLYMERS

When Mannich aminomethylation is carried out with a polymeric substrate or a polymeric amine, grafting of amino- or X-groups on the polymer backbone will occur, and the two possibilities are described in the next two sections. The second section also deals with some examples of reaction between both polymeric substrate and amine, usually oligomeric poly(alkyleneamine), with consequent possibility of obtaining crosslinked derivatives.

Aminomethylation of polymeric 'substrate'

The reaction between a polymeric substrate and an amine occurs according to the scheme:



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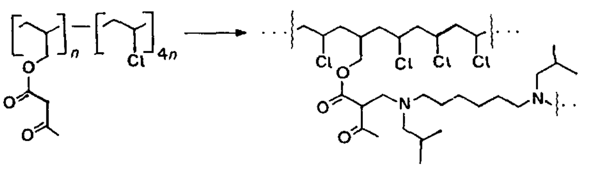
The substrate's H-active groups may already be present in the polymer molecule and thus available for reaction (see below); in other cases they must be introduced through a functionalization reaction before the aminomethylation is carried out (see below).

H-active groups present. Both C- and N-Mannich bases can be obtained by aminomethylation of a polymeric substrate.

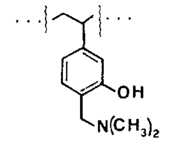
Among C-Mannich bases, only one example of a ketoamino derivative, given by reaction on the acetoacetic group of vinylchloride/allylacetoacetate copolymer, has been reported[26].



12

Product **12** is used in the composition of mixtures for the production of flame-resistant plastic foams, due to the presence of large halogenated parts in the molecule.

Other C-Mannich bases are phenolic and are usually obtained from poly(hydroxystyrenes). Poly(3-hydroxystyrene) affords products having structure **13**, which are then submitted to *N*-quaternization and finally to crosslinking with epoxy oligomers[27]. Poly(4-hydroxystyrene) is even more employed for aminoethylation, yielding Mannich bases **14**[28]. Derivatives **15** are also obtained with an increased degree of aminomethylation[28-30].



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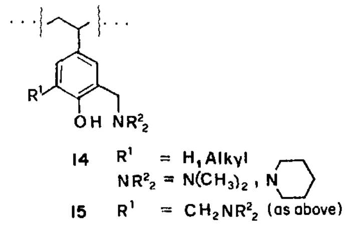


14 R¹ = H, Alkyl
$NR^2_2 = N(CH_3)_2$, N

15 R¹ = $CH_2NR^2_2$ (as above)

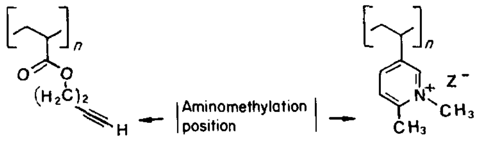
Many possibilities exist for modification of the ionic character of these polymers. This can be accomplished by aminomethylation of suitable carboxylated copolymers[31], or using carboxy amines, e.g. $HN(CH_2COOH)_2$ (ref. 32), by sulphonation of the polymeric Mannich base[33] or, finally, by quaternization of the amino group, mainly with alkyl halogenides[29,31,33].

Several interesting applications have been proposed for these products, such as electroconducting coatings for paper[29] etc. However, the most important is as flocculating agents[30] or ion-exchange resins, the latter in the case of crosslinked polymers[34].

Among polymers containing the phenol group, phenolformaldehyde resins have been aminomethylated with amino acids, thus giving products successfully employed as water-based coatings[35] (for these materials see also below).

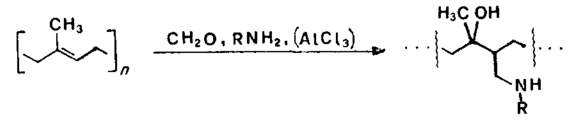
Finally, naturally occurring materials such as lignin and related products have been studied in order to obtain compounds with flocculating properties[36].

Other less common substrates which have been submitted to aminomethylation are polymethacrylates containing acetylenic groups as, for example, **16** (ref. 37) and poly(*N*-alkyl-2-methyl-5-vinylpyridinium) salts **17** (ref. 38), the site of attack being the acetylenic proton and, respectively, the methyl group in the α-position with respect to the pyridine nitrogen atom.



16 17

A particular *C*-aminomethylation reaction involving unsaturated hydrocarbons as substrates, has been applied to polyisoprene[39], with the formation of polyaminoalcohols **18**, as proposed by the authors. This would actually result from the addition of a methylolamine to the olefinic double bond instead of the substitution of an active hydrogen atom by the aminomethyl group (on the quite complex aminomethylation of alkenes, see the papers by Krieger, Manninen *et al.*[40]; see also the Appendix and refs. 230 and 231).

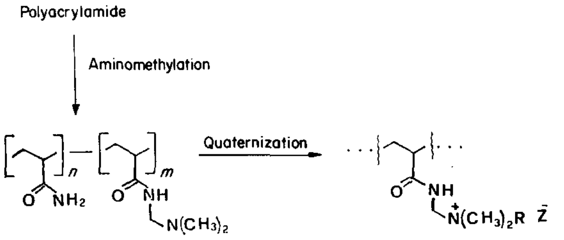


18

The N-Mannich bases deriving from polymeric substrates actually include only amide derivatives. This is not unexpected, as several very important classes of macromolecules, such as polyacrylamide, nylon and the proteins are polyamides. The relevance of polyacrylamides, known long ago[41], is demonstrated by the large number of papers and patents dealing with this subject[42-67].

Polyacrylamide and other analogous polymers are without doubt the most studied of the synthetic polymers, due to the various applications of the *N*-dimethylaminomethyl derivative. Besides polyacrylamide, several other substrates (polymethacrylamide[42-44], *N*-alkylpolyacrylamides[44] and acrylamide copolymers) and amines (various alkyl-, aryl- and alkanolamines[41-43,45-48]) are used for Mannich reaction.

The products obtained by aminomethylation of polyacrylamide should really be considered to be copolymers (see **19**) as the reaction yields can vary markedly and are usually less than 40%[42,47,49-51]. Yields above 80% have been reported in only a few cases[52,53]. Different reaction conditions have been investigated[42,43,45,48,50,54-60] in order to obtain better yields, to facilitate industrial production and to obtain more suitable materials. Thus, it has been observed that in aqueous solution the amount of aminomethylation increases with increasing pH, in the range 7.4–10[61], and mechanistic studies by ^{13}C n.m.r. have demonstrated that in such conditions the main aminomethylating agent is the methylene bis-amine $>N{-}CH_2{-}N<$[62].



19 20

The resulting Mannich bases have in some cases been treated with alkylating reagents[46,50,53,58] so that the quaternary ammonium salts **20** are obtained, with consequent further modification of both the ionic character and properties of the starting polyacrylamide.

The main applications of the above polymers are as flocculants[43,45-49,52,54,59,61,63] and dewatering agents[54,64]. They are also employed in the paper industry[49,53,63,64]. Studies have therefore been carried out on their technological properties in order, for example, to improve the stability of their solutions[65,66]. The flocculation mechanism has been investigated by also making use of isotopic tracers derived from $^{14}CH_2O$.[67]

Among polymeric N-Mannich bases, of prominent importance is the consistent group derived from acrylamide copolymers (*Table 3*).

Acrylamide random copolymers with acrylic acid and ester have been used also in ternary or quaternary systems, whereas graft copolymers are made using

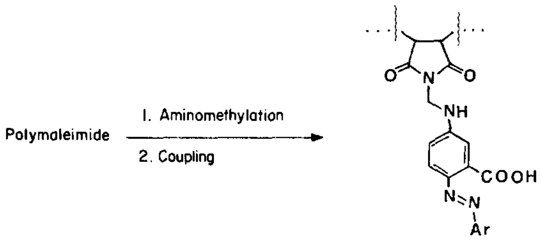
Table 3 Acrylamide copolymers submitted to Mannich reaction in order to produce aminomethylated products

Acrylamide copolymer	Amine reagent	Refs.
Random with acrylic acid	(Not indicated)	55
Random with styrene/acrylic acid	Dimethylamine	68
Random with styrene/ethylacrylate/hydroxyethyl-methacrylate	Dihydroxyethylamine	69
Graft on Vinal fibres	Dimethylamine or polyethylene-polyamine (see also text)	70
Graft on cellulose	Aniline	71
Graft on Xanthan gum	Dimethylamine	72

polyacrylamide or random copolymers of polyacrylamide[71] grafted onto synthetic hydroxy polymers (Vinal fibres) or natural macromolecules.

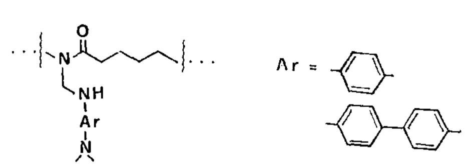
The above products are mainly employed for cationic electrophoretic coatings[69] (see also below), ion-exchange materials and, in the case of the water-soluble product derived from grafting with xanthan gum, as flocculants.

Polymaleimide has also been aminomethylated with aromatic amine[73] and then submitted to a coupling reaction with a diazo derivative, thus obtaining the azo dyes **21**, grafted on the polymeric chain, which are able to form coloured chelates and are also useful as pH indicators.



21

Other functionalization reactions of polyamides have been carried out mainly on Nylon 6 by the use of *p*-phenylenediamine[74] or benzidine[75] to give products **22**.



22

Finally, it is worth mentioning the condensation of the methylol groups $-\underset{|}{N}-CO-\underset{|}{N}-CH_2OH$ of urea oligomers with ethylenediamine. This reaction produces aminomethyl derivatives at the urea nitrogen atom, which improves the storage stability of the resin[76].

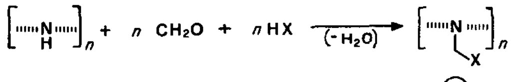
Aminomethylation following functionalization. Many examples exist of aminomethylation on substrates previously functionalized in order to make the Mannich reaction possible. *Table 4* lists such reactions, which lead to the polymeric derivatives **23–28**, which can subsequently be *C*- or *N*-aminomethylated at the indicated positions.

Polymer functionalization includes oxidation of polyolefins, addition to double bonds and acetal or ether formation from alcohols. The amino compounds employed in Mannich reaction can vary greatly according to the desired products.

Substrates **23**, after aminomethylation with hexamethylene-bisamine, are used as additives (detergents) for lubricating oils[77,78]. Substrates **24**, which will be discussed further below, are used in the paint industry; **25–27** are aminomethylated with ammonia, monomethylamine or dimethylamine in order to obtain animalization of the starting synthetic Vinal fibres to render them more suitable for dyeing[80]. Some have also been proposed as flocculants and additives for paper[81,82]. Finally, cellulose derivatives obtained from **28** show good complexing and ion-exchange properties[83].

Aminomethylation with polymeric amine

Mannich reactions with polymeric amines can be represented as follows:

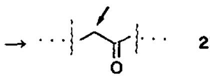
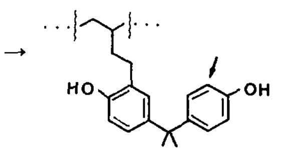
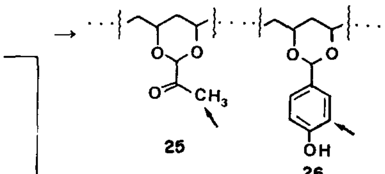
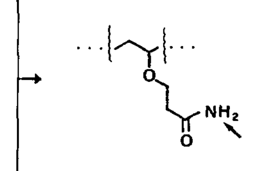
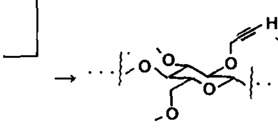


ⓔ

Few polymeric amines which have been submitted to this type of synthesis have been reported in the literature and, moreover, the reaction is mostly carried out on compounds with low molecular weight, the polyalkyleneamines usually employed having a degree of polymerization of only some units. The products obtained, however, are used for important applications, mainly as additives for lubricating oils.

A description of Mannich reactions with non-macromolecular and macromolecular substrates X–H now follows.

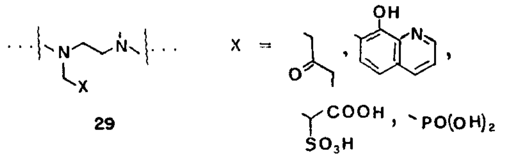
Table 4 Functionalization of polymers preceding Mannich aminomethylation

Starting polymer	Functionalized polymer*	Refs.
Ethylene/propylene copolymer	 23	77, 78
1,2-Polybutadiene	 24	79
Poly(vinyl alcohol)	 25 26	80
	 27	80–82
Cellulose or starch	 28	83

*Arrows indicate the likely position of attack

Non-macromolecular 'substrates'. Oligomeric poly(alkyleneamines), amino-polystyrenes and natural macromolecules are used for the Mannich reaction.

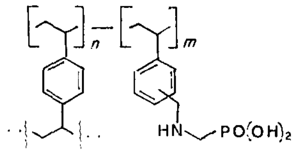
Products with structure **29** are derived from poly(ethyleneamine) and are obtained by reaction with ketones[84], phenols[85] and carboxy compounds[86,87]. A P-Mannich base afforded by phosphorous acid has also been reported[88].



29

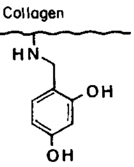
The ionic character and chelating properties of the above products have allowed several interesting applications to be proposed, such as desalting of petrol[86] or, with crosslinked polymers, the production of ion-exchange resins.

Aminomethylation with amino polymers having high molecular weight has been carried out between phosphorous acid and aminated chloromethylated styrene copolymers with divinylbenzene. The reaction gives P-Mannich bases (**30**), which show interesting selective sorption properties towards Cu^{2+}, In^{3+} and UO_2^{2+} ions[89].



30

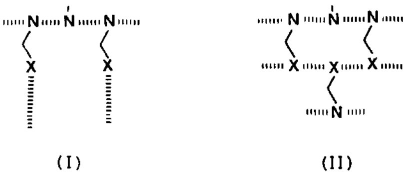
Natural macromolecules, such as collagen, have demonstrated the possibility of C-Mannich base formation making use of polyhydroxyphenols or their oligomeric derivatives as substrates[90-93]. Products with structures **31** are obtained, as confirmed by studies on model compounds[90,94].



31

Analogous behaviour has also been shown by particularly reactive carboxy substrates, such as malonic acid and acetoacetic acid derivatives and similar compounds[95,96]. Possible side reactions (cyclization, decarboxylation) as well as the ability to fix tanning metal ions have also been investigated[96].

Macromolecular 'substrates'. Both mono- and poly-functional polymeric substrates, Pol.-XH and $\left(\begin{array}{c}\text{--X--}\\ \text{H}\end{array}\right)_n$ are employed in the Mannich reaction with polymeric amines. The following scheme shows the structures, (I) and (II) respectively, which be obtained.



(I) (II)

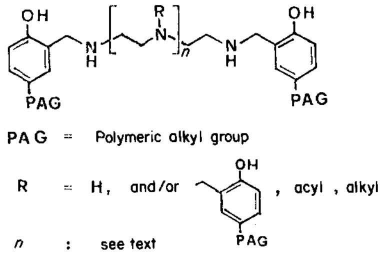
Structures (I) are the result of grafting, through formaldehyde, of the substrate and can be considered a particular case of graft copolymer synthesis. Structures (II) represent much more branched, even crosslinked, products.

The widely used additives for lubricating oils belong to the first group of products. They are obtained by aminomethylation of alkyl-phenols which usually have high molecular weight, the compatibility with the oil being conferred by the long hydrocarbon chain of such alkyl groups. Ashless detergent–dispersants which also possess antioxidant, anticorrosion and other properties are thus afforded. The large number of papers and patents (more than 40) published on this subject[97-142] confirms its relevance although, in our context, these products cannot be always considered as polymeric due to the sometimes low molecular weight of phenolic substrates or, as seen before, of the polymeric amine.

Polymeric substrates are usually obtained by phenol alkylation with polyenes (polypropylene, polybutenes). Other synthetic routes are sometimes adopted, such as condensation of polybutenyl succinic anhydride with an aminophenol derivative[99]. About two-thirds of the alkylphenols reported have a molecular weight of nearly 1000, the value of the residual part being smaller. In some cases, however, the possibility of aminomethylation of substrates with molecular weights up to 5000–10 000 (refs. 100–102) or even 100 000 (ref. 103) has been indicated.

The amine reactant is usually oligomeric poly(ethylene imine), with a degree of polymerization higher than 3, in some cases decamers being cited[104,105]. Some of the –NH– hydrogen atoms may be also substituted by acyl[106-109] or sometimes by alkyl groups[102].

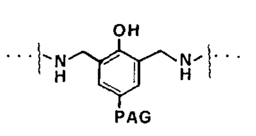
The reported[101,102,110,111] structures are like **32**, with phenol moieties at the ends of the polymeric chain, as the Mannich reaction should preferentially involve, for steric reasons, the terminal primary amino groups.



32

In most cases, therefore, R of the above formula is H; however, the possibility that more than two hydroxybenzyl groups are present in the molecule has been mentioned[101]. Patents usually report molar ratios of phenol/amine less than 2:1, in a few cases slightly greater[105,107,112,114] and only exceptionally[115,116] has a high value of such ratio been proposed. The technological reason for this is that the products obtained using a molar ratio 3:1 have been shown to be ineffective as ashless dispersants[116].

Examples of molar ratios of phenol/amine equal to one[103,116-118] or even less than one[104,119-121] are frequently reported, and the existence also of structures **33** is thus to be supposed. In this connection, as the ratio phenol/aldehyde is usually about 1:2 or less[103-105,118,120,121], the possibility that, under the described reaction conditions, dihydrooxazine structures **34** at the end of the polymeric chain are also present cannot be excluded (see ref. 2 and references therein).



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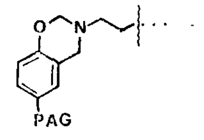


34

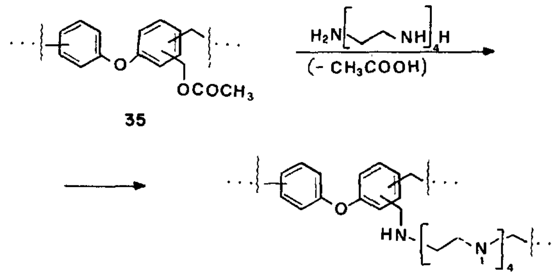
The importance of the above products has led to investigations of the possibility of modifications on the reactants or on the products of Mannich aminomethylation.

Some are classical[123] modifications of alkyl-phenols, introduced in order to improve their properties as, e.g. additives for oils, such as sulphurization, which links two phenoxy groups with sulphur bridges and can be carried out before[112,114,121,124–126] or after [100,119,127–130] the Mannich reaction. Also, treatment with ethylene oxide[100,132] usually produces phenol-ether derivatives bonded to oligomeric poly(ethylene glycol) chains and, in the case of these polymeric Mannich bases, presumably also involves the N–H groups of polyamine[6,16]. The above-mentioned presence of *N*-acyl groups in the polymeric chain usually derives from aminomethylation with an amine reactant bearing amide groups, although several other treatments have been made, e.g. with branched aldehydes[104,120,133], oxidation reagents[128,134–136], fatty acids[103,137,138], isocyanates[139] and others[113,117,121,125,131,140,142], which often do not allow the site of the molecule undergoing modification to be established easily.

Much less than those described above are the examples of Mannich reactions with polymeric polyfunctional substrates leading to more branched or crosslinked products having structure (II).

This is the case with a flocculating agent obtained from an acrylonitrile copolymer which, after hydrolysis, is aminomethylated with polyamine and finally crosslinked with further formaldehyde[143]. Such a product is presumably a polyacrylamide derivative similar to the polymers described above (see *Table 3* and ref. 70).

A patent on curing agents for epoxy resins[144] deals with an unusual case of aminomethylation on the polymeric substrate **35**, obtained from diphenylether, formaldehyde and acetic acid. The reaction with polyethyleneamine to give Mannich base **36** would actually occur on the acetylated methylol group of the substrate.



35

36

At the end of this section, the crosslinking with aldehyde (formaldehyde etc.) of protein macromolecules is worth mentioning: such products can in fact behave both as the amine reactant and the substrate[5].

Studies on the reaction between formaldehyde and collagen, based on model compounds, have demonstrated the importance of aldehyde concentration[145] and, above all, of pH[145–148]. It has also been observed that the number of methylene bridges formed for each collagen molecule (mol. wt about 10 000) is nearly 15[148], and the amino groups, in particular of lysine, hydroxylysine and histidine, could allow a Mannich reaction to occur[95]. The same papers make a number of comparisons between formaldehyde and glutaraldehyde behaviour, although the crosslinking action of the latter appears to follow much more complex reaction paths[149,150].

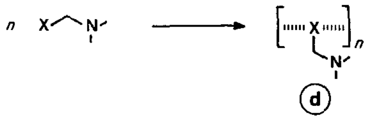
MANNICH BASES AS MONOMERS

When Mannich bases are employed as monomers in polymerization reactions, three different cases may take place according to whether the aminomethyl group $-CH_2-N<$ is involved or not in the polymerization.

The first two cases occur when the polymerization is due to functional groups present in the substrate or in the amine moiety: polymers with structures **d** or **e**, respectively, will thus be produced, as described below. However, this attribution cannot always be made confidently, particularly when active hydrogen atoms are simultaneously present in both parts of the molecule. In the third case the aminomethyl group is directly involved and polymerization takes place through amine substitution by a nucleophilic reagent.

Polymers with structure d

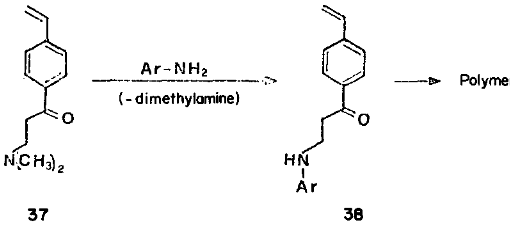
The polymerization of Mannich bases due to groups present in the substrate moiety, gives products in which pendant amino groups are bonded to the polymeric chain through the methylene bridge:



In agreement with the classifications usually adopted in macromolecular chemistry, these reactions can be differentiated into chain polyadditions and stepwise polymerizations.

Chain polyadditions. Styrene and vinylpyridine derivatives are included among the C-Mannich bases containing groups polymerizable by poly-addition.

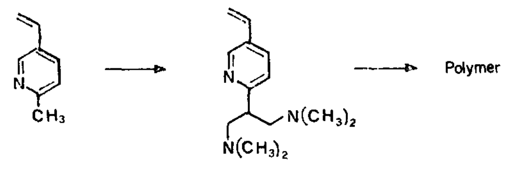
Keto base 37, which can be already considered a monomer of this kind, can be modified to give the arylamino derivative 38 through a substitution reaction, typically given by Mannich bases, and finally submitted to polymerization[151]:



37

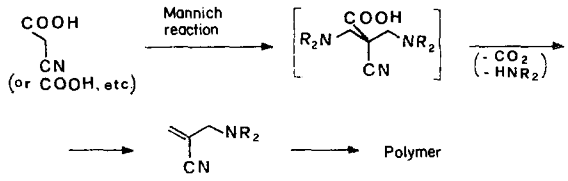
38

Vinylpicoline can afford *C*-aminomethylation on the methyl group[152] by a reaction largely dependent on variables such as contact time and reagent concentration, the bis-aminomethyl derivative **39** being produced in higher yields.



39

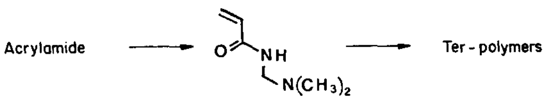
Acrylic aminomethyl monomers **40** are obtained by Mannich reaction on the appropriate malonic substrate under such conditions^{153} that simultaneous deamination and decarboxylation of the intermediate bis-Mannich base occurs (see also pp. 725, 726 of ref. 2):



40

Among N-Mannich bases, some polymerizable monomers have been studied for the applications already described. In particular, as the poly(*N*-aminomethylacrylamides) have been found to be quite interesting as polymeric flocculants, an alternative route to their synthesis through polymerization of a previously aminomethylated monomer has been investigated.

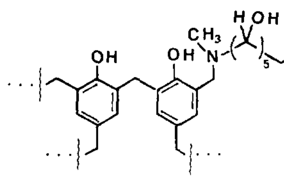
N-Dimethylaminomethylacrylamide **41** has thus been synthesized^{154} and then polymerized to ter-polymers which are employed in wastewater treatment^{155}.



41

Stepwise polymerizations. The more relevant class of monomers employed in step polymerizations is constituted by C-Mannich bases, mostly phenol derivatives.

N-Methyl-*N*-(2-hydroxyphenylmethyl)-D-glucamine (ref. 156), for example, when mixed with an approximately equimolar amount of phenol, gives crosslinked phenol resins (**42**), possessing very selective chelating properties towards, for example, H_3BO_3.

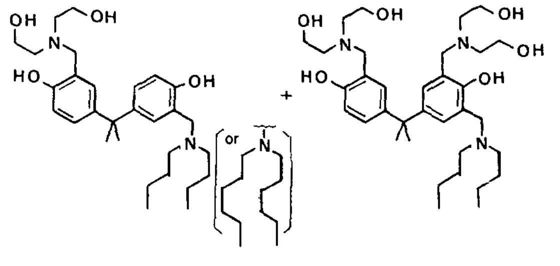


42

Important and extensive research$^{157-173}$ has been done on binders for electrophoretic coatings: these are usually constituted by aminomethylated oligomeric derivatives of phenols, which are applied to metals in an aqueous bath at neutral or slightly alkaline pH. Such ionic resin is frequently mixed with a non-ionic resin, the latter being selected for each application among the most various classes of polymers (epoxy, aminoresins, polyesters etc.)$^{69,157-163}$. A pigment is often also present in the above paints$^{159,164-166}$. The coated material is then baked and the consequent chemical modifications occurring on the aminomethyl groups are discussed below.

Scheme 2 summarizes the essential steps of the process, which is also proposed for impregnants and adhesives^{167}.

Mannich reaction on bisphenol A affords mixtures of aminomethylated products, such as **43**, from which an approximate indication can be drawn about the molecular ratios of the functional groups present in the mixture.

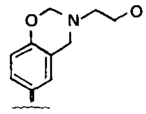


43

The above products are usually Mannich bases obtained from bisphenol A and hydroxyamines (mainly diethanolamine) mixed with other non-hydroxylated amines (e.g. dibutyl- or the more bulky dihexylamine$^{165,168-170}$).

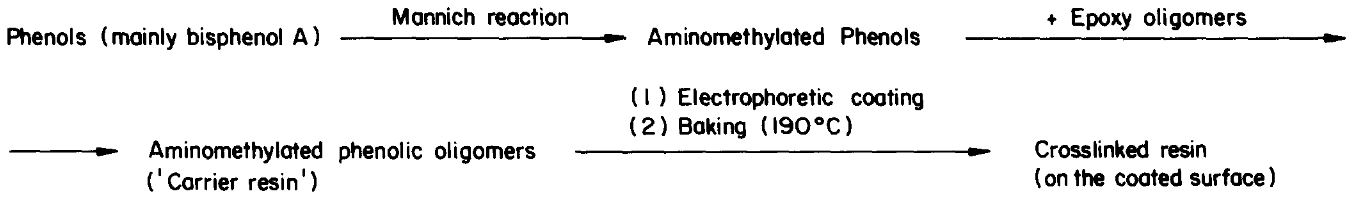
The substrate can be modified by inserting the bisphenol in a polymeric molecule (such as structure **24** in *Table 4*, see also ref. 79) or by totally or partially substituting bisphenol A by a mixture of phenol and alkylphenols$^{168-171}$.

Modification of the amine parts includes the use of primary amines such as ethanolamine^{171}, which could produce the dihydrobenzoxazine groups **44**, or the use of methoxyethylamine derivatives$^{157-161,164}$ (e.g. **45**).

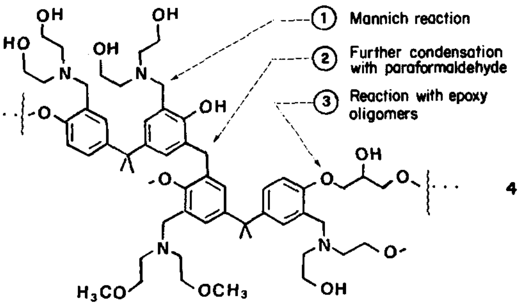


44

The above Mannich bases are then treated (*Scheme 2*) with epoxy oligomers (derived from bisphenol A or



Scheme 2



45

Scheme 3

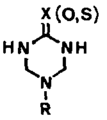
pentaerythritol) in such molar ratios that no more epoxy groups are present in the product.

An example of the more frequently investigated carrier resins can be represented by structure **45** (*Scheme 3*), in which another possibility of modification, i.e. further treatment with formaldehyde in order to increase the molecular size of the aminomethylated bisphenol, is also indicated.

Besides the hydroxyl group of phenol, the hydroxy groups of ethanolamine moieties might also be involved in the reaction with epoxide (see ref. 6) and in this case the resins produced would also contain structures **e**, discussed in the next section (e.g., the P-Mannich bases derived from alkanolamines and phosphonic esters of glycols).

Among the N-Mannich bases it is worth mentioning the cyclic ureides **46**, which are obtained by aminomethylation of urea (or thiourea) with primary amines[174]. Their well known importance as modifiers of formaldehyde resins is based on the possibility of easily predetermining steric hindrance or other features of the R group.

Cyanoguanidine can be analogously aminomethylated to give products **47**, which are employed in more or less complex formulations used in wastewater treatment and in the leather industry[175].



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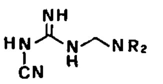
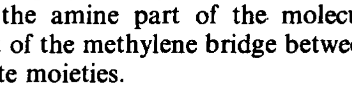


47

Polymers with structure e

This section describes monomeric Mannich bases which produce polymers by reaction of functional groups bonded to the amine part of the molecule, with no involvement of the methylene bridge between the amine and substrate moieties.



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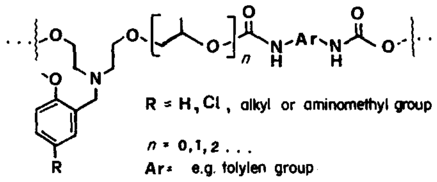
The Mannich bases used as reactive hardening agents for epoxy resins should also be considered in this section as, at the end of polymerization, their amino group is part of a polymeric chain. In this case, however, they should be considered as crosslinking agents rather than monomers and, moreover, the catalytic action represents a relevant feature of their behaviour. They will be therefore treated in the last main section of this review.

The examples here reported actually deal only with stepwise polymerization of C-, N- and also P-Mannich bases derived from alkanolamines. These latter products, mixed in some cases with other hydroxy compounds, are used as polyols in polyurethane synthesis.

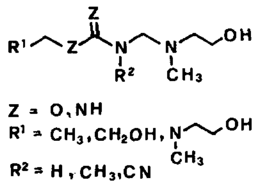
C-Mannich bases are phenolic derivatives of diethanolamine[176–180] and therefore the polyurethanes obtained are presumably represented by structures **48**; the expected urethane, isocyanurate etc. structures have been indeed confirmed by i.r., when molar ratios isocyanate/hydroxy group are sufficiently high (2:1)[179].



48

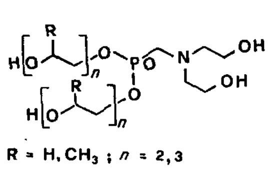
Modified products can be obtained by initial reaction of the phenolic Mannich base with propylene oxide; this implies $n \neq 0$ in structure **48** if reaction involves the ethanolamine hydroxy group as well as the phenolic group (see refs. 6 and 16). In other cases a mixture of epoxide (propylene oxide) and chlorendic anhydride has been employed[177] together with the use of halogenated phenols in order to improve the flame-retardant properties of the product.

N-Mannich bases also are consistently represented by a number of examples: carbamic acid derivatives[181,182], cyanoguanidine[183] or 3-aminopropionamide[182] derivatives aminomethylated with alkanolamines are used. Such molecules (see structures **49**) may also contain hydroxy groups or other active hydrogen functions besides the hydroxyethylamino groups, which can react with isocyanates.



49

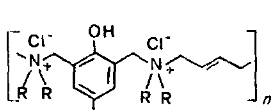
P-Mannich bases are prepared from phosphonic esters containing hydroxy groups[184,185]. The most representative structures are **50**, although modifications can be introduced by using piperazine in the place of diethanolamine, so that the molecular size is doubled.



50

The above polyols are used with the aim of conferring particular properties to the polyurethanes, mostly foams, that are produced. Mannich bases **49** appear mainly to improve the tackiness of polyurethane towards other materials[181,182] whereas P-derivatives **50** confer flame-retardant properties[184,185]. Such polyurethanes, besides plastic foams, are also proposed as impregnants, antistatic agents etc.[183]

An interesting example of polymerization involving the amine group of a Mannich base is given by the reaction between a chain extender (*trans*-1,4-dichloro-2-butene) and a phenolic bis-base: ionene polymers (e.g. **51**) used in water clarification are thus afforded[186].

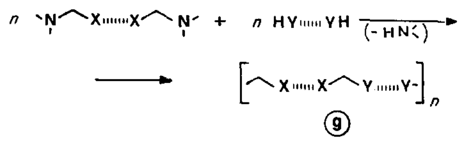


51

Polymerization using nucleophilic reagents

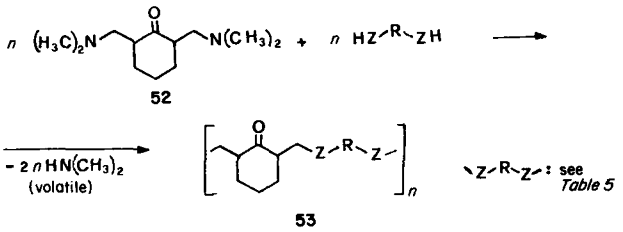
Mannich base polycondensations with nucleophile monomeric reactants, which occur with elimination of amine as byproduct, are described in this section. In order to obtain polymeric products through a repetitive and cumulative reaction, it is necessary that the Mannich base is at least bifunctional (A-A), as well as the nucleophilic species (B-B), or that both aminomethyl- and nucleophile groups are present in the same molecule (A-B).

Polycondensations using A-A and B-B monomeric species. The polycondensations here reported are step reactions given by couples of monomeric species A-A and B-B according to the scheme:



⑨

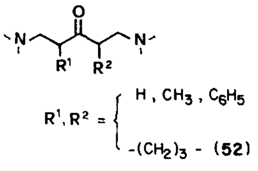
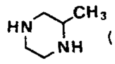
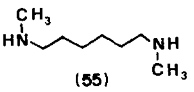
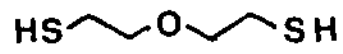
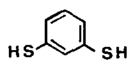
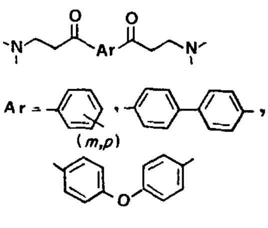
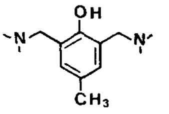
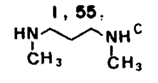
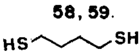
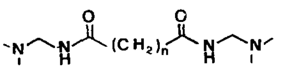
Various kinds of Mannich bases[187–198,200] ranging from ketonic to phenolic and to amidic derivatives (see **52**, leading to **53** and examples in *Table 5*) are suitable for the above reaction.



The amine moiety of the Mannich base is mostly constituted by the dimethylamino group, which gives a volatile species easily released as a byproduct of the reaction. The corresponding quaternary ammonium salts have been also employed in certain cases[195], and good results have been obtained by making use of the Mannich base hydrochloride in aprotic medium, since the condensation byproduct is an amine hydrochloride which is insoluble in the reaction medium and thus subtracted from equilibrium[199] (see reaction **61**→**62** below).

Nucleophile monomers so far employed are bis-amino and bis-thiol derivatives (*Table 5*).

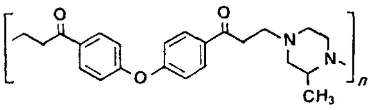
Table 5 Monomeric Mannich bases and nucleophiles employed in the synthesis of poly(β-aminoketones) and poly(β-ketothioethers)

	Nucleophile (HZ–R–ZH)			
	Bis-amines (Z=N)		Bis-thiols (Z=S)	
Mannich base[a]		Refs.		Refs.
 R¹,R² = H, CH_3, C_6H_5 -$(CH_2)_3$- (52)	Piperazine (I) I,  (54),  (55)	187 187, 189	H_2S (56) 56,  (57),  (58)  (59)	188 188, 190–192
	I, 54, 55	187, 189	56[b], 57, 58	191, 193, 194
	I, 55, [c]	195	58, 59, [d]	196
 n = 0,2,4,8	I,2,54, 55	197	59[d]	198

[a] Except otherwise indicated, amino group is $-N(CH_3)_2$
[b] With morpholine derived Mannich base[193]
[c] With Mannich base as N-Iodomethylate
[d] Macrocyclic products are also obtained (see text)

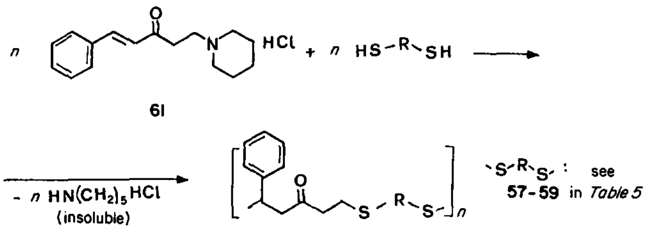
It should be observed that the same polymeric aminoderivatives may be directly obtained by Mannich synthesis (see first section) among a bifunctional substrate, formaldehyde and the suitable bis-amine, but the above exchange method gives much better results as regards reaction yields and degree of polymerization.

The bis-thiol reagent may vary from simple hydrogen sulphide to alkyl and aryl thiol derivatives. Most examples involve keto-Mannich bases, such as **52**, and diketo-Mannich bases, which afford, for example, the polymeric derivatives **60**. In order to get the corresponding poly(amino alcohols) the above poly(β-aminoketones) **60** were afterwards submitted to reduction[200], the latter reaction allowing multifunctional polymers to be obtained through the exploitation of another reactive property of keto Mannich bases.



60

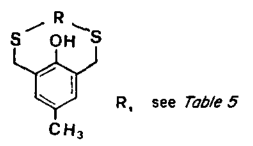
A particular case of polymerization has been found with unsaturated Mannich bases[199] such as the benzalacetone derivative **61**: here the bis-thiol monomer gives both the exchange reaction with the amino group and an addition reaction to the vinyl keto group, so that the polymeric derivative **62** is produced.



61

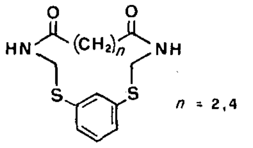
62

Phenolic Mannich bases are also suitable for polycondensation, the best results being given by Mannich base as the quaternary ammonium salt in reactions with bis-amines and as the free base in reactions with thiols. In the latter case, however, a competitive cyclization reaction also takes place and the polymeric product is always accompanied by variable amounts of macrocycle **63**, depending on the reaction conditions (reactant concentrations, catalyst, etc.) and the nature of the R group[196].



R, see *Table 5*

63



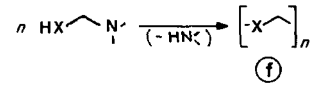
n = 2,4

64

N-Amidic bis-Mannich bases behave similarly, the polycondensation with bis-amines giving the expected polymeric products in high yield (*Table 5*), whereas the reaction with bis-thiols is strongly affected by the structure of amide derivative, which produces different relative amounts of polymer and cyclization product, only macrocycle **64** being obtained when n of the bis-base is 2 or 4. A polymer is produced with $n = 0$ or 8 (*Table 5*)[198].

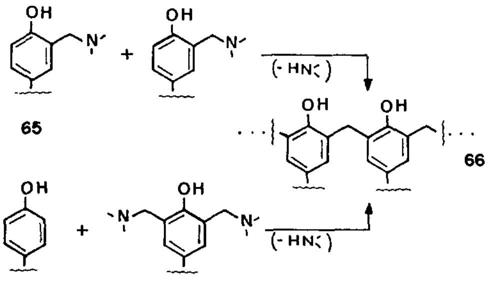
Applications of these S-polymers are worth mentioning: besides being used as resins[193], they have been tried as plastics stabilizers[188,192,194] because the polymeric structure makes their release from the stabilized compound more difficult. The antioxidant behaviour of polymer **62** (R = $-C_6H_4-$, *meta*) in the presence of hydroperoxide reagents has also been intensively studied[199].

Polycondensations using A-B type monomeric species. Polycondensations due to monomeric compounds of A-B type, i.e. with both the aminomethyl and nucleophile groups in the same molecule, occur as follows:



ⓕ

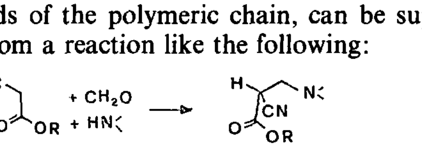
The above scheme includes the curing of paints described above as, after electrophoretic application, baking at 180–190°C (*Scheme 2*) causes crosslinking. Such crosslinking must take place in the case of, for example novolac hardening with urotropine[3] according to the scheme **65**→**66**, even if the reaction **67**+**68**→**66** also occurs.



65 66 67 68

Such behaviour on heating of compounds **65** is supported by the observation that baking causes the release of amine products[158,159,172]. To overcome this undesired effect, the use of particular amines in Mannich bases[171] or, even better, the addition to the painting medium of blocked isocyanates, which react with the released amines, has been introduced[158,172,173] and appears to conveniently solve the problem.

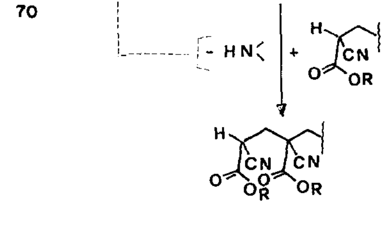
The same reaction scheme is followed by the oligomeric phenolic Mannich bases **69** which upon heating at 210°C release volatile dimethylamine and afford crosslinked resins[201].



69

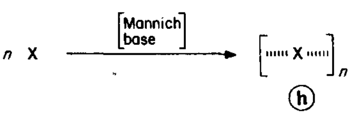
n = 0-4

Finally the preparation of polymers from cyanoacetic esters **70**, formaldehyde and secondary amine in catalytic amount[202] can be, at least formally, included in this section. The products obtained, which have a degree of polymerization of about 30 and aminomethyl groups at both ends of the polymeric chain, can be supposed to derive from a reaction like the following:



MANNICH BASES AS HARDENERS, ACCELERATORS, ETC.

This section describes Mannich bases employed as catalysts, vulcanization accelerators and hardeners. Such compounds can, in fact, behave either as catalytic agents, due to their basic nature, or they can enter into the macromolecular structure as crosslinking agents.



ⓗ

Both the above actions often occur in the hardening process and cannot be easily distinguished: tertiary amine derivatives are usually supposed to play a predominantly catalytic role, whereas the other amines participate in the reaction, with consequent insertion of the Mannich base, or its derivatives, into the macromolecule[6,16].

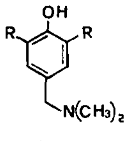
However, the matter is quite complex, especially if the various reaction possibilities of Mannich bases (deamination, deaminomethylation etc.[2]) as well as the number and nature of the products with which they can come into contact, are taken into consideration. It is therefore preferable first to describe these Mannich bases on the basis of their structure (*C*-, *N*- and *S*-aminomethyl derivatives) and then to treat successively their applications in macromolecular chemistry, together with some considerations, whenever possible, on the type of action they carry out.

C-Mannich bases

C-Mannich bases constitute the more consistent group in which polymerization accelerating agents derived from ketones[203–205] such as bis(dimethylaminomethylcyclohexanone) **52** are included. The use of a quaternary ammonium derivative of **52** has also been proposed, as this latter compound, which is unable to display any catalytic action, can decompose with the formation of tertiary amine, which is responsible for the catalysis[206].

A large amount of research has been carried out on phenolic Mannich bases which, according to the considerations made before, will distinguish between derivatives containing tertiary amino groups and those that do not.

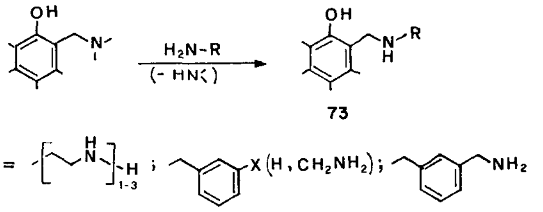
Among the former[6,207–217], the tris-aminomethyl derivative **71** is widely employed. The 2,6-di-tert-butyl derivative **72**[212–214], which is an important product widely patented for its antioxidant properties, besides acting as catalyst, is likely also to carry out a protective action towards the material to which it is added.



71 R = CH_2-$N(CH_3)_2$
72 R = $C(CH_3)_3$

Other tertiary Mannich bases are obtained from *p*-alkylphenols, bisphenol A, *β*-naphthol, etc.[207,215–217] The more frequently adopted amino group derives from dimethylamine, although products derived from amino acids[216] or macromolecular compounds obtained from hexamethylenetetramine[18] (see first section) are known.

Mannich bases containing primary or secondary amino groups are usually prepared through substitution of the tertiary amino group of a starting Mannich base by a suitable primary amine. This indirect method of synthesis is preferred, as it allows satisfactory control of product homogeneity[218–220]. The phenolic Mannich bases cited above, including the tris-aminomethyl derivative **71**, are used as the starting material for such reactions[218] and afford products **73**.



73

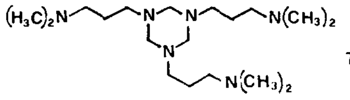
The tris-aminomethyl derivatives, in particular, which contain a very high number of amine hydrogen atoms, are expected to possess excellent crosslinking properties. In this respect, satisfactory performances have been obtained[16] by the polymeric Mannich bases previously described in this paper (e.g. product **6**, above).

Still among the C-Mannich bases, the base derived from ferrocene[221] and the undefined products obtained from shale tar[222] should be mentioned.

N-Mannich bases

This group of compounds includes methylene bis-amino derivatives obtained by condensation of formaldehyde with amines and/or ammonia, which can be considered also as 'Mannich reactants', such as compounds **8**[17,22], used either as monomers or as crosslinking agents.

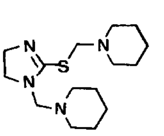
Methylene bis-piperidine and -pipecoline[223] or the hexahydrotriazine derivative **74**[224] are, on the contrary, employed as catalytic agents.



74

S-Mannich bases

Heterocyclic substrates[225–227] such as 2-mercaptobenzothiazole or 2-mercaptoimidazoline usually undergo *S*-aminomethylation, the latter compound giving the S,N-Mannich base **75**, due to reaction also of the ring nitrogen atom.



75

In this group of Mannich bases the products derived by reaction with carbon disulphide, formaldehyde and amine are also to be included[228].

These C-, N- and S-Mannich bases are mainly employed in the production of formaldehyde resins, epoxy resins, polyurethanes and in rubber vulcanization.

Hardening of formaldehyde resins is carried out with Mannich bases derived from cyclohexanone, acting as accelerators[203,204] (see **52**), whereas the methylene bis-amino derivatives like **8**[17,22] surely behave also as crosslinking agents.

Cyclohexanone derived Mannich bases are also employed in polyurethane synthesis; in particular, the corresponding quaternary ammonium derivatives allow release of trimethylamine to occur gradually[206].

Phenolic Mannich bases such as **71** and **72** are, however, much more frequently used[209–212,215–217], particularly for plastic foams, as they efficaciously catalyse, in particular, trimerization of isocyano group to isocyanurate. The correlation between catalyst basicity and the properties of the materials produced has been also investigated[212]. Other Mannich bases employed in polyurethane synthesis are obtained from ferrocene[221] or are methylene bis-amino derivatives[223,224], among which is the hexahydrotriazine **74**.

A very large number[16,207,208,210,218-220,222,223,229] of Mannich bases are employed as hardening agents for epoxy resins. These compounds are divided into two groups.

(1) There are tertiary amine derivatives presumably acting as polymerization initiators towards the epoxy group, and remaining partially bonded to the polymeric structure[6]: among them are some phenolic derivatives such as **71**[207,208] and the methylene bis-amines[223] already mentioned for polyurethanes.

(2) The second group are crosslinking primary and secondary amine derivatives possessing a reactive function, which are bonded to the macromolecule after hardening. It has not been excluded, however, that after crosslinking these compounds also act to some extent as initiators analogously to the above tertiary amines. Products **73**[218-220] and polymers as **6**[16] belong to this group.

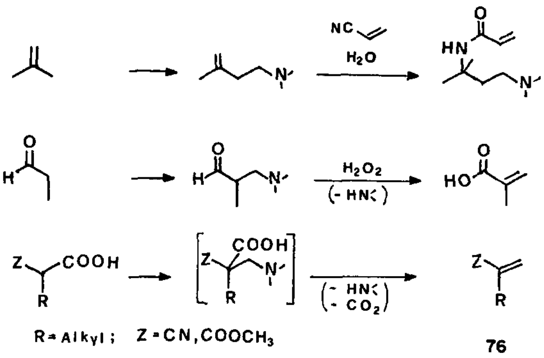
Finally, Mannich bases derived from cyclohexanone[205], phenols[18,213,214] and thiols[225-228] are employed as vulcanization accelerators for rubber (mainly neoprene). In this application also, the effectiveness of catalytic action has been attributed to dimethylamine formed by deamination of Mannich base, which is easily propagated through the mass of material[214].

APPENDIX

This last part is dedicated to some aspects of the chemistry of Mannich bases which, although not discussed in the preceding sections, is still related to polymer chemistry. This also allows us to highlight some possible research areas, so far scarcely explored, which could be worth closer investigation.

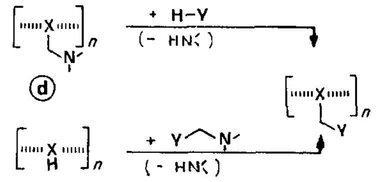
Due to their various reactivities[1,2], Mannich bases are convenient intermediates for preparing monomers, even sophisticated ones, suitable for polymer synthesis. Among the unsaturated monomers, acrylic derivatives from the well known deamination reaction[2] have been the most frequently studied[230-234] and *Scheme 4* shows some different routes to their synthesis.

Thus, Mannich base derived from isobutene (for alkene aminomethylation see the text and ref. 40) can give by Ritter reaction an acrylamidic monomer[230,231], whereas methacrylic acid is obtained in good yields by hydrogen peroxide oxidation, followed by deamination of the propionaldehyde Mannich base[232]. Moreover, deaminodecarboxylation of the Mannich bases obtained from malonic acid and methyl ester derivatives can afford various α-alkyl substituted acrylic monomers[233,234], among which a deuterated compound (**76**; $Z=COOCH_3$, $R=CD_3$) is also known[234]. In this regard, it is noteworthy that the Mannich reaction could permit isotopic atoms to be easily introduced into these molecules, e.g. in the $=CH_2$ group, which is originated by the reactant formaldehyde.

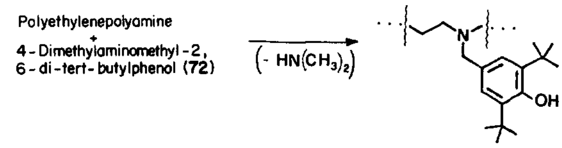


Scheme 4

Besides the deamination, substitution of Mannich base amino group, previously used for polymerizations leading to structures **f** and **g**, could be successfully adopted in new reactions, so as to graft $-CH_2Y$ groups onto a suitable polymeric substrate:



An example[235] of $-CH_2Y$ introduction into a polymer, although of quite low chain length, is actually given by the grafting of the antioxidant part of Mannich base **72** to the primary or secondary amino groups of a polyethylene polyamine:



As pointed out in the first section, when a deamination or a deaminomethylation occurs on polymers with structures **a–c**, polymer degradation takes place. This reaction can be usefully exploited, e.g. in pharmacological applications, in order to get a slow release of the drug[236]. On this basis, it should therefore be possible also to make use of such behaviour in systems such as **d** and **e** (*Scheme 1*) in which drug release would leave the polymeric matrix unchanged.

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