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Polymerisation of *N*-Vinylpyrroles

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Data on the polymerisation of *N*-vinylpyrroles, which have become readily available in recent years as a result of the discovery of their direct synthesis from ketoximes and acetylenes, are described systematically and surveyed. The characteristic features of their radical polymerisation and copolymerisation as well as their copolymerisation with electron-accepting monomers are examined and the mechanism and the unusual nature of the cationic polymerisation processes are discussed.
Attention is concentrated on new examples of the class of *N*-vinylpyrroles, their reactivity, and the structure of the polymers.
The bibliography includes 104 references.

CONTENTS

I.	Introduction	609
II.	Methods of synthesis of *N*-vinylpyrroles	609
III.	Radical polymerisation of *N*-vinylpyrroles	610
IV.	Copolymerisation of *N*-vinylpyrroles	612
V.	Copolymerisation of *N*-vinylpyrroles with electron-accepting monomers	613
VI.	Cationic polymerisation	614
VII.	Applications of poly-*N*-vinylpyrroles	615

I. INTRODUCTION

There has been a notable increase of interest in the chemistry of pyrroles in recent years. Two comprehensive monographs[1,2] and a review[3] have been published and the number of journal articles[2] dealing with various aspects of the chemistry of pyrrole derivatives has been increasing continually. This has been stimulated by a number of factors, for example, by the presence in natural objects of various pyrrole derivatives[1,2,4] such as antibiotics, pheromones, and toxins, as well as the discovery of new possibilities for the polymerisation of the pyrrole ring[5,6] and the employment of polypyrroles, which exhibit metal-like electronic conductivity, in the conversion of solar energy.[7-10]

N-Vinylpyrroles can be regarded as extremely interesting monomers for polymerisation and as starting compounds for organic synthesis, with the aid of which it is possible to obtain pyrrole-containing products. However, until recently these were regarded as unavailable and virtually unknown compounds.[1] Beside the evident practical value of poly-*N*-vinylpyrroles (in particular, these are potential semiconductors and photosensitive materials for electrophotography, holography, etc.), their synthesis and study were until recently held back by the difficulty of synthesising the initial monomers. The development of a new general method of synthesis of *N*-vinylpyrroles by the reaction of ketoximes with acetylene,[11,12] for which the name Trofimov reaction has been suggested,[13,14] has now led to virtually unlimited possibilities for the synthesis of monomers of this class.

The characteristic features of the polymerisation of *N*-vinyl monomers have been examined in monographs,[15,16] reviews,[17-20] and dissertations, for example, in Refs.21-23. However, they contain little information about the polymerisation of *N*-vinylpyrroles with the exception of a dissertation[21] in which a large section is devoted to this question. The polymerisation of *N*-vinylindoles has been studied to a much greater extent,[18,24,25] mainly in the systematic investigations of Skvortsova.[26-31]

N-Vinylcarbazole is the most reactive and the most thoroughly investigated monomer of the *N*-vinyl series[15,18] but neither indole nor carbazole are typical pyrroles.

The number of studies on the polymerisation of *N*-vinylcarbazoles which have been published is so large that an adequate survey of these is possible only in an independent review. This review is not therefore concerned with questions of the polymerisation of *N*-vinylcarbazole. It deals with the most significant aspects of certain contradictory features of the polymerisation of *N*-vinylpyrroles and *N*-vinylindoles taking into account the conclusions reached in earlier publications.

II. METHODS OF SYNTHESIS OF *N*-VINYLPYRROLES

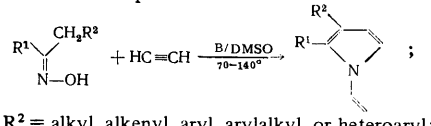
All the methods of synthesis of *N*-vinylpyrroles available until recently were based on the introduction of the vinyl group into compounds containing the pyrrole ring (see Refs.15-18 and the bibliography quoted therein).

NH-Heterocycles are usually vinylated directly with acetylene at elevated temperatures (150-200 °C) and pressures of 15-20 atm in the presence of basic catalysts.[15-18] One of the variants of the vinylation reaction is based on the use of vinyl acetate.[18]

The dehydration of *N*-β-hydroxyethyl derivatives, usually obtained from the corresponding heterocycles and oxiran to give the *N*-vinyl derivatives, takes place in the presence of potassium hydroxide at a reduced pressure and at elevated temperatures.[18]

The elimination of hydrogen halides from *N*-α- and *N*-β-haloethyl derivatives under the influence of bases is also used to synthesise *N*-vinyl monomers.[18]

The method of synthesis of *N*-vinylpyrroles based on the cyclisation of ketoximes with acetylene in a strong base—dimethyl sulphoxide (DMSO)—system has been developing most vigorously. *N*-Vinylpyrroles can be obtained by this reaction, by-passing the pyrroles themselves, from cheap and readily available compounds:[11,12]

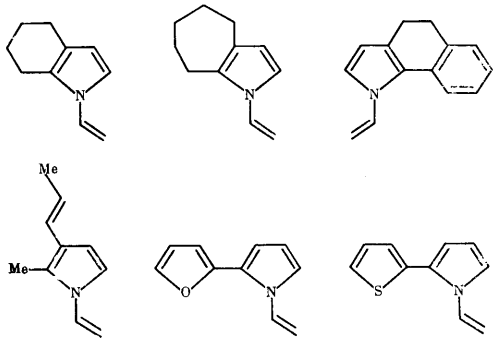


R^1, R^2 = alkyl, alkenyl, aryl, arylalkyl, or heteroaryl;
R^1-R^2 = $(CH_2)_n$, n = 3-5; B = strong base.

The yields of *N*-vinylpyrroles are 70-95% under the optimum conditions.

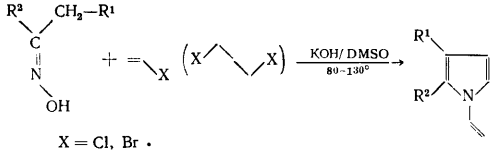
Even *N*-vinylpyrroles in which the initial pyrroles had been difficult to obtain previously by the usual methods or were completely unknown, for example, annelated pyrroles

derived from the oximes of cyclohexanone, suberone, and tetralones, or various alkenyl-, furyl-, and thienyl-pyrroles, became available together with simple alkyl- and aryl-substituted *N*-vinylpyrroles:[12,32-36]



Virtually all ketoximes containing at least one reactive methyl or methylene group in the α-position relative to the oxime functional group undergo this reaction.

A new effective procedure for the direct vinylation of pyrroles in a strong base–DMSO system has been developed.[37,38] *N*-Vinylpyrrole was obtained by this method in high yields under mild conditions at atmospheric pressure and temperatures in the range 80–100 °V (previously NH-heterocycles were vinylated under a pressure of 10–20 atm). Trofimov and co-workers[39-41] showed for the first time that the interaction of ketoximes with vinyl halides or halogenoethane in the same KOH–DMSO system also leads to *N*-vinylpyrroles:



X = Cl, Br .

Depending on the structure of the reactant and the conditions, this reaction can be directed towards the preferential formation of vinylated or non-vinylated pyrroles.[39-41]

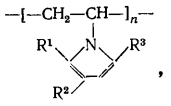
Thus effective, safe, and technologically viable methods of synthesis of *N*-vinylpyrroles, based on the use of cheap and readily available starting materials, namely ketoximes and ultimately ketones and also acetylenes, vinyl halides, and halogenoethane, have now been developed, which creates conditions for their wide-scale employment as monomers.

III. RADICAL POLYMERISATION OF *N*-VINYLPYRROLES

The study of the radical homopolymerisation of a series of *N*-vinylpyrroles has been undertaken.[21,42-44] Its aim was to seek the optimum conditions for the synthesis of the polymers, the analysis of their structure, and also the estimation of the reactivities of the monomers and the properties of the polymers.

It was established beforehand that hydrogen peroxide and benzoyl peroxide do not initiate the polymerisation of *N*-vinylpyrroles, but induce a deep colour in the monomers. It may be that the inertness of hydrogen peroxide under the given conditions is associated with the tendency of *N*-vinylpyrroles, indole, and some of their derivatives to oxidise.[45] The inability of benzoyl peroxide to initiate the polymerisation of certain vinyl monomers is usually explained by the rapid decomposition of the peroxide in the presence of these compounds[46] or by the addition of the products of its decomposition to the monomer, as happens for enamines,[47] ethyl vinyl sulphide,[48] and vinyl ethers.[49]

The homopolymers of substituted *N*-vinylpyrroles having the structure



where R^1 = H, Me, or Ph; R^2 = H or Me; R^3 = H or $COCF_3$; and $R^1 - R^3 = (CH_2)_4$, have been synthesised under conditions of radical initiation by azobisisobutyronitrile (ABIN).[42-44]

The occurrence of polymerisation involving the vinyl double bond has been demonstrated by ^{1}H NMR and infrared spectroscopic data. The absorption bands of the N–CH=CH_2 groups (at 582, 859, 946, 1582, and 1640 cm^{-1}) disappear from the infrared spectra of the polymers, but the characteristic bands of the pyrrole ring remain at 708, 1300, 1490, and 1540 cm^{-1}. The ^{1}H NMR spectra of the polymer contain no signals of the protons of the vinyl group (4.78 and 4.30 p.p.m.) and there are no significant perturbations in the resonance of the protons of the pyrrole rings, although a broadening of the signals characteristic of the polymers is observed.[42-44]

Solutions of the polymers in chloroform and carbon tetrachloride are intensely coloured, which is probably due to the ability of the test compounds to form charge-transfer complexes (CTC) with various halogens, hydrogen halides, and halohydrocarbons, which also happens for *N*-vinylindole[26] and *N*-vinylcarbazole.[20] The possibility of a formation of such complexes has been demonstrated in relation to poly-*N*-vinyl-4,5,6,7-tetrahydroindole.[44] When this polymer has been treated with a hot 1% aqueous HCl solution, its EPR spectrum contains a singlet with a width of 22 G, which can be due to centres of the CTC type (the concentration of unpaired electrons is 3×10^{17} spins g^{-1}). The appearance of a colour on prolonged contact with air justifies the hypothesis of the possible formation of complexes of these polymers with atmospheric oxygen. A freshly prepared polymer is virtually diamagnetic *in vacuo* (10^{-4} mmHg) and contains only traces of a paramagnetic admixture. Heating of the specimen at 150 °C for 5 h does not induce any changes in the EPR spectrum. However, when the polymer has been subjected to an analogous treatment in air after evacuation, its spectrum shows a low-intensity singlet with a width of about 10 g (the concentration of paramagnetic centres is 4.5×10^{16} spins g^{-1}).[44] Consequently the complex is formed precisely with oxygen and is not due to temperature-induced changes in the structure of the polymer leading to an expansion of the conjugation system. CTC of this type are readily decomposed on heating in a high vacuum. The intensity of the EPR signal then falls almost to zero.

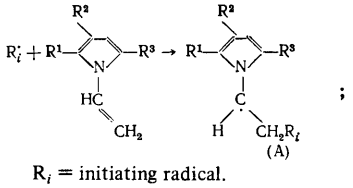
The results of the study of the polymerisation of *N*-vinylpyrroles justify their arrangement in the following sequence in terms of decreasing reactivity: 2-methyl-*N*-vinylpyrrole (I) > *N*-vinyl-4,5,6,7-tetrahydroindole (II) > 2,3-dimethyl-*N*-vinylpyrrole (III) > 2-phenyl-5-trifluoroacetyl-*N*-vinylpyrrole (IV) > 2-phenyl-*N*-vinylpyrrole (V).[42,43]

Conjugation between the pyrrole ring and the N-vinyl group has been demonstrated in *N*-vinylpyrroles by infrared[50] and ultraviolet[51] spectroscopy, NMR,[52,53] and the study of the relative basicities.[54]

According to ^{13}C NMR data,[52,53] the intensity of the $p-\pi$ conjugation in the *N*-vinyl group in the ground state of the series of compounds investigated falls in the sequence (II) ≥ (III) > (I) > (V) > (IV). Consequently the observed sequence of the monomers based on their reactivities in radical polymerisation is not associated directly with the effect of conjugation. Steric factors, namely the decreased probability of collisions with the growing radical and the

steric blocking of the active radical centre for the less compact monomers (III), (IV), and (V), apparently play an important role in the chain propagation stage.

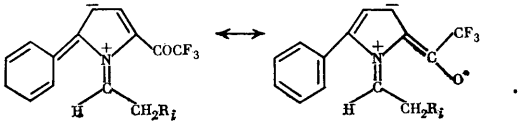
Another important factor influencing the character of the polymerisation should be the relative stability of the radical (A) responsible for chain propagation



(A)

R_i = initiating radical.

The stabilisation and may be the loss of reactivity of the radical (A) owing to the interaction with a neighbouring heteroatomic system will be more pronounced the greater the number of electron-donating substituents or substituents capable of conjugations are present in the ring, which has in fact been observed. Thus the unpaired electron in 2-phenyl-5-trifluoroacetyl-*N*-vinylpyrrole can be effectively distributed via a mechanism involving conjugation with participation of both substituents. For example, one may quote two of the large number of possible canonical structures:



Thus compounds (IV) and (V) should tend to form the most stable and perhaps also the least reactive radical, which in all probability explains their low reactivity in radical polymerisation.[44]

The kinetic parameters of the polymerisation of *N*-vinyl-4,5,6,7-tetrahydroindole have been estimated.[55] It has been established that polymerisation in bulk and in solution in benzene proceeds in the initial stages as a steady-state process at rates which depend on the concentrations of the reactants and the experimental temperature and is described by the equations

$$\lg V_0 = (-3.75 \pm 0.05) + (0.52 \pm 0.02) \lg[I],$$
$$\lg V_0 = (-5.22 \pm 0.02) + (0.98 \pm 0.03) \lg[M],$$

where [I] and [M] are the concentrations of the initiator of the monomer.

The kinetic reaction orders with respect to the monomer and the initiator have been determined together with the effective rate constant for the polymerisation K_{eff}, whose value proved to be virtually identical with K_{eff} for polymerisation in bulk found from the dependence of lg [M] on the reaction time. Thus the initial rate of polymerisation is described by a concentration dependence typical for the polymerisation of vinyl polymers with bimolecular termination of the kinetic chains.

The temperature dependence of the effective rate constant for the polymerisation in bulk is described satisfactorily by the Arrhenius equation

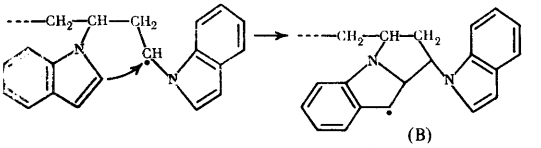
$$\lg K_{eff} = (9.5 \pm 0.4) - (4635 \pm 152) T^{-1}.$$

The effective activation energy and the pre-exponential factor are respectively 88.7 ± 2.9 kJ mol^{-1} and (3.0 ± 1.1) × 10^9 litre$^{1/2}$ mol$^{-1/2}$ s^{-1}. The average rate of initiation is 2.16×10^{-7} mol litre^{-1} s^{-1}.

According to kinetic calculations,[55] the comparatively low chain propagation rate constants in the radical polymerisation of *N*-vinyl-4,5,6,7-tetrahydroindole compared with other vinyl monomers, where the activation energies are approximately the same, are caused by the influence of entropy factors, namely by the steric hindrance induced by the presence of the bulky tetrahydroindole substituents.

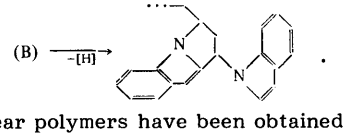
The average length of the kinetic chain ($\bar{\nu}$ = 42–107) greatly exceeds the experimentally observed length of the polymer chain ($\bar{P}$ = 20–33) for the same rate of initiation, which indicates a significant role of transfer processes in the termination of the growing chain. It was demonstrated by special experiments that there is no chain transfer to benzene. Another chain self-transfer constant obtained, which amounts to 1.49×10^{-2}, led to the conclusion that at 60 °C it is impossible to obtain polymers of *N*-vinyl-4,5,6,7-tetrahydroindole with $M_n > 10\,000$.[55]

A possible cause of the oligomeric character of the polymerisation products is intramolecular cyclisation of the macroradical as a result of the attack by the vinyl radical centre on a neighbouring pyrrole ring accompanied by its dearomatisation, the loss of hydrogen, and the subsequent chain transfer to the monomer analogous to that which occurs in the case of *N*-vinylindole:[56]

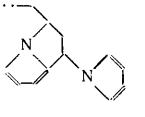


(B)

On the basis of the analysis of the ^{13}C NMR spectra using model compounds, it has been concluded[56] that the radical polymerisation of *N*-vinylindole involves partly the C(2)–C(3) bond of the indole ring and the formation of tricyclic condensed indoline structures, whose content in the polymer is about 25% judging from the intensity of the corresponding ^{13}C signals. Polycyclic radicals of type (B) should evidently exhibit a reduced reactivity as a consequence of stabilisation by the π-electron system and also the enhanced tendency towards chain termination as a result of the abstraction of a hydrogen atom and aromatisation:



The usual linear polymers have been obtained only for the *N*-vinyl derivatives of 2-methyl- and 2,3-dimethylindoles, i.e. compounds in which the 2-position has been substituted. As in the 3-methyl-*N*-vinylindole macromolecules, anomalous indoline structures have been detected in these polymers.[56] On the other hand, there are no anomalous signals in the ^{13}C NMR spectrum of poly-*N*-vinylpyrrole.[56] However, bearing in mind the limited sensitivity of the method, one cannot fully exclude the possibility that the polymer contains (albeit in the form of end fragments) small amounts of the corresponding bicyclic structures:



The formation of additional cyclic structures in the polymerisation of *N*-vinylpyrroles agrees with data obtained in the study of cyclopolymerisation as a phenomenon.[57] Intramolecular cyclisation of this kind can prove to be in a number of instances a thermodynamically more favourable process than intermolecular chain propagation reactions.

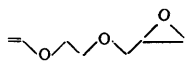
The maximum yield in the radical polymerisation of *N*-vinylindoles reaches 79% (for 2-methyl-*N*-vinylindole), while the minimum yield is 6% (for 2,3-dimethyl-*N*-vinylindole). The molecular weight of the polymers is 4000–10 100.[46]

Thus the reactivity of the monomers and the structure of the polymers formed depend strongly on the positions and numbers of the methyl groups in the pyrrole ring. However, in the series of *N*-vinylpyrroles (I)–(V), it is at present impossible to establish a clear-cut dependence of the reactivity of the monomers on their structure, because the structure is determined not only by different electronic and steric effects but also by the fundamental difference between the chain propagation and chain termination pathways.

IV. COPOLYMERISATION OF *N*-VINYLPYRROLES

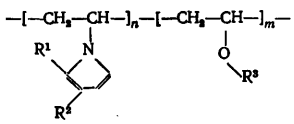
The majority of the known polymers obtained on the basis of monomers with pyrrole rings (mainly as part of the carbazole and indole systems) do not contain functional groups permitting a specific modification of their properties. Interesting possibilities of this kind have arisen from the copolymerisation of *N*-vinylpyrroles with vinyl compounds containing reactive groups such as the oxiran ring.

The copolymerisation of a series of substituted *N*-vinylpyrroles, namely 2-methyl-*N*-vinylpyrrole,[58,59] *N*-vinyl-4,5,6,7-tetrahydroindole,[60,61] and 2-phenyl-*N*-vinylpyrrole[58,59] with the glycidyl vinyl diether of ethylene glycol, called vinylox,[11] has now been investigated:



There are literature data showing that in some cases the copolymerisation of *N*-vinylindole[28] and *N*-vinylcarbazole[20] with various monomers entails the formation of the homopolymers of the initial compounds together with the copolymers. However, the character of the curves for the turbidimetric titration of the copolymerisation products indicates the formation of true copolymers in the given instance.[58,59] This conclusion is supported also by data obtained by fractionating the copolymers in which all the fractions show identical compositions close to that of the initial copolymer.[58,59]

The infrared and ^{1}H NMR spectra of the copolymerisation products confirmed the disappearance of the vinyl groups of the pyrroles and vinylox, the signals of the epoxy-groups in the pyrrole rings remaining unaltered.[58,61] Thus it has been shown that the copolymerisation involves the double bond of the vinyloxy- and *N*-vinyl groups:



R^1 = Me, Ph, $R^1 = R^3 = (CH_2)_4$, $R^3 = (CH_2)_3OCH_2CH{-}CH_2$ (O)

The copolymers are formed for any initial ratios of the monomers and are always enriched in pyrrole units. The initial composition is the main factor which determines the overall rate of reaction and the characteristics of the polymers.

A method for the determination of the content of pyrrole groups in the copolymers from ^{1}H NMR data has been developed in order to estimate quantitatively the composition of the copolymers.[62] The specific activity and polarity factors (see Table) have been determined from the quantitative estimation of the reactivities of *N*-vinylpyrroles within the framework of the *Q*–*l* scheme. The quantities $Q_2 = 0.021$ and $l_2 = -1.44$ for vinylox were used in the calculation.[63] The negative polarity of *N*-vinylpyrroles indicates the electron-donating character of the nitrogen atom in the radical formed. The quantities obtained within the framework of the *Q*–*l* scheme indicate a weaker conjugation (compared with the vinyloxy-group) between the double bond and the heteroatom.

It has been established in the course of partition chromatography that all the copolymers have a unimodal distribution and that their molecular weight is fairly homogeneous.[59]

The "copolymerisation limit", calculated by the method of Prokof'ev et al.[64] for the *N*-vinyltetrahydroindole and vinylox copolymers, is reached when the indole monomer has been consumed, regardless of the composition of the initial mixture, but the degree of conversion is determined by the initial composition.[66]

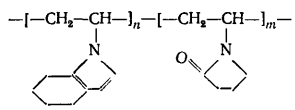
Calculation of the distribution of the copolymer units by the method of Gindin et al.[65] showed that, whatever the initial content of *N*-vinyl-4,5,6,7-tetrahydroindole, large blocks of the given monomer separated by one or two vinylox units predominate in the chain.

The copolymerisation constants (r) and the parameters of the specific activity (Q) and polarity (l) of *N*-vinylpyrroles.[62]

M_1	r_1	r_2	Q_1	l_1
2-Methyl-*N*-vinylpyrrole	6.5	0.05	0.024	−2.86
N-Vinyl-4,5,6,7-tetrahydroindole	5.2	0.06	0.020	−2 45
2-Phenyl-*N*-vinylpyrrole	3.4	0.32	0.013	−1.59

Note. M_1 = *N*-vinylpyrrole and M_2 = vinylox; $Q_2 = 0.21$ and $l_2 = 1.44$.[63]

A method has been developed for the preparation of the copolymers of *N*-vinyl-4,5,6,7-tetrahydroindole with *N*-vinylpyrrolidinone:[44,67]



The copolymerisation was carried out in a solvent or in its absence in the presence of ABIN and the yield of the copolymers reached 66–94%.

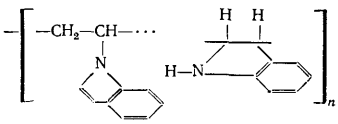
The possibility of using the absorption band of the carbonyl group of *N*-vinylpyrrolidinone at 1690 cm^{-1} for the quantitative determination of the composition of its copolymers was demonstrated previously.[68] The above method has been used also to estimate the composition of *N*-vinyl-4,5,6,7-tetrahydroindole copolymers.[44]

Under the conditions investigated, the maximum content of the tetrahydroindole fragments in the copolymers is 68% and the molecular weight diminishes with increasing fraction of the indole component from 20 000 to 2000. The use of benzene as the solvent reduces the molecular weight of the products without affecting significantly the composition of the copolymers.[44,67,69,70]

Like the *N*-vinyl-4,5,6,7-tetrahydroindole homopolymer, the copolymers are capable of forming complexes of the CTC type with atmospheric oxygen and hydrochloric acid.[44]

Studies[71–73] of the polymerisation of *N*-vinylindole and its 2- and 2,3-methylated analogues established that all the monomers readily polymerise under the influence of free radicals, cationic catalysts, radical-cations, and Ziegler–Natta catalysts and also thermally in the absence of catalysts.

Copolymers with indole, methylindole, indene, and coumarin with equimolar proportions of the monomeric fragments have been obtained under the conditions of thermal initiation:[71–73]



The yield of the polymers is 45% (indole)–78% (coumarin) and the intrinsic viscosity does not exceed 0.2 dl g^{-1}.

The attempts to synthesise the homopolymers of the above comonomers under identical conditions (thermopolymerisation at 150–200 °C) were unsuccessful.[71]

According to gel-chromatographic data, all the copolymers have a unimodal molecular weight distribution.[71] However, the structure of the copolymers has been demonstrated on the basis of infrared spectroscopic data.[71] The intensity of the bands of the indole ring (at 1539 and 714 cm^{-1}) in the infrared spectra of the copolymers is reduced, the band due to the N–H bond (at 3448 cm^{-1}) is present, and the characteristic frequencies of the C=C bond of *N*-vinylindole (at 1612 and 850–820 cm^{-1}) disappear.

The ^1H NMR spectra in deuteriobenzene yield a minimal amount of information as a consequence of the poor solubility of the copolymers but the ratio of the signal intensities of the aromatic and aliphatic protons confirmed the proposed structures.[71]

V. COPOLYMERISATION OF *N*-VINYLPYRROLES WITH ELECTRON-ACCEPTING MONOMERS

The copolymerisation of *N*-vinyl compounds with electron-accepting monomers usually leads to copolymers with a specific structure and properties and also yields interesting information about the formation of charge-transfer complexes and about their role in polymerisation processes. Unfortunately no information about the behaviour of simple *N*-vinylpyrroles in copolymerisation of this kind is as yet available in the literature. It has been stated[74,75] that the copolymerisation of *N*-vinylcarbazole with maleic anhydride is impossible, since the radical-ions formed as a result of the interaction of the monomers induce the kinetically more favourable homopolymerisation of *N*-vinylcarbazole. However, it was later shown that the copolymerisation of these monomers is possible in the presence of free-radical initiators, although some poly-*N*-vinylcarbazole is nevertheless always formed.[76]

A detailed study of the copolymerisation of *N*-vinylindole with maleic anhydride has been published recently.[77] The formation of alternating copolymers of *N*-vinylindole with the acceptor indicated had been published earlier,[51] but no structural characteristics of the products were indicated.

It has also been reported that *N*-vinylindole does not polymerise in acetonitrile at 40 °C in the presence of small amounts of maleic anhydride.[25] On the other hand, under the influence of free-radical initiators, *N*-vinylindole copolymerises with fumaronitrile and diethyl fumarate and the copolymers have a distinct alternating structure.[78–79] As a rule, the monomeric units of the acceptor predominate in the macromolecules of such copolymers as a result of side reactions involving the 3-position of the indole ring.

When *N*-vinylindole and maleic anhydride dissolve in chloroform, a pale-yellow colour appears, which indicates the electronic interaction of the monomers according to the data of Priola et al.[77] However, a distinct upfield shift of the signal of the protons of maleic anhydride is observed in its ^1H NMR spectrum when *N*-vinylindole is added. The shift has been attributed[77] to the reversible complex formation reaction between *N*-vinylindole and maleic anhydride. The equilibrium constant K_e, found[77] by Hanna's method,[80] is 0.25 litre mol^{-1} (in chlorform at 25 °C), which is extremely close to the value K_e = 0.28 litre mol^{-1} obtained for the maleic anhydride–indole system[81] (in chloroform at 20 °C). It is of interest that the same equilibrium constant (0.28) has been found[77] also for the *N*-methylindole–maleic anhydride system. This finding indicates complex formation mainly via the indole ring. Comparison[77] of the data obtained with the values of K_e for the copolymerisation of maleic anhydride with styrene, vinyl acetate, trimethylvinylsilane, ethyl vinyl ether, and ethyl vinyl sulphide leads to the conclusion that the electron-donating properties of *N*-vinylindole and styrene[82] in relation to maleic anhydride are similar and one can therefore expect alternating copolymers with the given acceptor, as for *N*-vinylindole, which is in fact observed in reality. If the copolymerisation is carried out in the absence of an initiator, then thermo- or photo-activation is required for the attainment of an acceptable degree of conversion.[77] Polymers obtained in the presence of free-radical initiators have comparatively high molecular weights (of the order of 56 000).

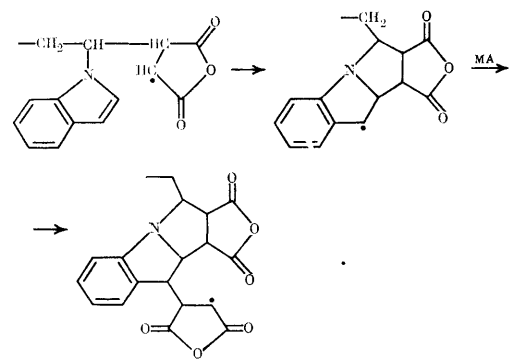
The spontaneous copolymerisation of *N*-vinylindole in the absence of free-radical initiators or Lewis acids suggests that the monomers can form CTC in the initiation stage.

The degree of conversion, the molecular weights, and the composition of the copolymers depend appreciably on the type of solvent in which the copolymerisation is carried out. Highly polar solvents such as acetonitrile or dimethylformamide promote the exclusive formation of the *N*-vinylindole homopolymer. This is explained by the fact that the equilibrium:

$$D + A \rightleftarrows [D \rightarrow A] \rightleftarrows [D^{+\cdot} A^{-\cdot}] \rightleftarrows D^{+\cdot} + A^{-\cdot},$$

where D is the monomer-donor and A the monomer-acceptor, is displaced to the right with increase in the ability of the solvent to solvate the ions.[77]

Analysis of the ^{13}C NMR spectra and the composition of the copolymers led to the conclusion[77] that the copolymerisation is complicated by cyclisation involving the 2-position in the indole ring and additional molecules of maleic anhydride (MA) in accordance with the scheme



The possibility of the participation of the C(2)–C(3) bond of the indole ring in copolymerisation with maleic anhydride has been confirmed by the synthesis of alternating copolymers of unsubstituted indole with the same comonomer-acceptor.[81]

The copolymerisation of maleic anhydride with methylindoles has also been investigated.[77] The fact that the composition of the copolymers does not change significantly as the composition of the initial mixture is varied is regarded as evidence in support of the mechanism of the alternating copolymerisation of *N*-vinylindole and its 2-, 2,3-, and 3-methyl derivatives. It is of interest that 2,3-dimethyl-*N*-vinylindole, for which reactions involving the C(2)–C(3) bond should be difficult, gives rise to 1:1 copolymers. On the

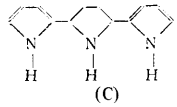
other hand, the dependences of the degree of conversion and of the intrinsic viscosity on the composition of the initial mixture are extremely complex and cannot be interpreted solely on the basis of the idea that the CTC formed undergoes homopolymerisation.

VI. CATIONIC POLYMERISATION

The cationic polymerisation of *N*-vinylpyrroles has been studied to a much lesser extent than the radical polymerisation. If one disregards the vinyl derivatives of carbazole and indole, then there exist apparently only two brief mentions of the polymerisation of pyrroles proper.[17,83] In one of these[83] *N*-vinylpyrrole and vinylindole were mentioned among a large number of vinylamines subjected to polymerisation in the presence of Lewis acids and their complexes with ether such as $ZnCl_2$, BF_3, $BF_3.OEt_2$, $AlBr_3$, $SnCl_4$, and $AlCl(Et_2)$. The polymerisation is carried out without a solvent or in an organic solvent, preferably an aromatic hydrocarbon or ether, in the temperature range from −100° to 100 °C and at a catalyst concentration of 10^{-3} mole per mole of the monomer.

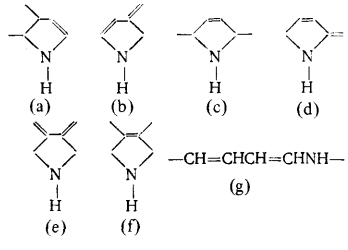
The synthesis of a specimen of poly-*N*-vinylpyrrole by the cationic polymerisation in the presence of $BF_3.OEt_2$, for comparison with the polymer obtained under the influence of an excess of CCl_4 (the polymers proved to be identical according to the infrared spectra), has been described.[25] The conditions of the cationic polymerisation and the yield are not quoted.

In general, bearing in mind the high sensitivity of the pyrrole ring to the action of various acid agents, one can hardly hope for the smooth polymerisation of *N*-vinylpyrroles under the conditions of cationic catalysis. In fact, the pyrroles and oligomers obtained under the influence of strong acids have been known for more than 100 years (quoted after Lamb and Kovachic[84]). In particular pyrrole was trimerised with the aid of HCl as early as 1888. Although different structures were attributed to the trimer formed,[84] only the formula (C), proposed in 1957,[85] satisfies all the available experimental data.

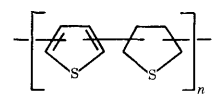


(C)

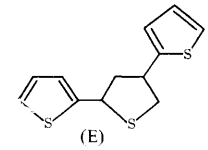
The polymerisation of pyrrole under the influence of trichloroacetic acid has been studied.[86] However, no data have been presented concerning the structure of the insoluble polymer formed. Later several non-aromatic structures (a)–(g) were proposed for the repeating units of the oligomer chain in the pyrrole oligomer obtained with the aid of the same catalyst:[87]



It is known that, on treatment with aluminium chloride or trifluoroacetic acid, thiophen is converted into a polymeric product whose characteristics are closest to formula (B):[88,89]



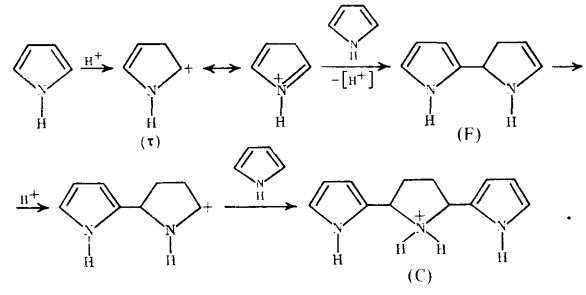
(D)



(E)

The liquid trimer (E) can be obtained by bringing thiophen into contact with phosphoric acid.[90,91] These data as well as the structure of the pyrrole trimer (C) justify the hypothesis that the chain formed in the oligomerisation of pyrrole under cationic conditions has alternating aromatic and non-aromatic structures by analogy with thiophen oligomers.

On the basis of ^{13}C and ^{1}H NMR, infrared and ultraviolet spectroscopic data, the results of mass-spectromatic studies, and the determinations of molecular weights, it has been recently confirmed[84] that the bulk of the pyrrole oligomer obtained in the presence of acids has the trimeric structure (C). The pyrrole ring is known to be protonated mainly in the 2-position.[1,2] This fact gives rise to certain difficulties when attempts are made to account for the formation of the trimer having the structure indicated. In order to obviate such difficulties, it is assumed[85] that, although the 2-protonated pyrrole does in fact predominate in the reaction mixture, its 3-protonated isomer is the more reactive electrophile. Protonation in the 3-position leads to the cation (τ) which in its turn reacts with pyrrole to form the dimer (F). Subsequent attack by its protonated form on the pyrrole ring leads to the protonated trimer (C):[84]



The positive charge on the nitrogen atom of the pyrrolidine ring lowers the reactivity of the neighbouring pyrrole rings with respect to the subsequent electrophilic attack. This is used to explain the relative stability of the trimer compared with other trimerisation products.[85]

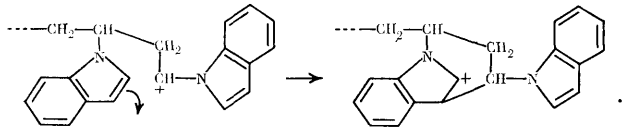
Together with the trimer (A), a coloured insoluble polymer, known for a long time as red pyrrole, is formed when pyrrole is acted upon by strong acids.[84] Its composition is variable, since it is continuously oxidised in air. In terms of its instability, it resembles the trimer. It has been suggested that the formation of "red pyrrole" can entail also ring opening.[84]

The involvement of the pyrrole ring in the formation of the macromolecule has been observed recently in the polymerisation of *N*-vinylindole and its methyl derivatives in the presence of $BF_3.OEt_2$.[56] As in radical polymerisation, the methyl groups in the pyrrole ring influence very significantly the yield, the molecular weight, and the structure of the polymers formed.

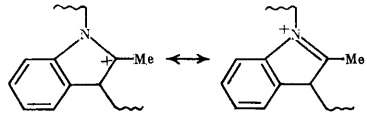
According to ^{13}C NMR spectroscopic data, cyclisation takes place in this case also, although its mechanism differs from that observed in radical polymerisation.[56] The character of the reactivity of the methyl derivatives of *N*-vinylindole is directly opposite to that noted for polymerisation in the presence of radical initiators. Among the methylated *N*-vinylindoles, the 2-methyl derivative gives rise to only

traces of a polymer, while the 3-methyl and 2,3-dimethyl-derivatives are very reactive and readily form polymers with a regular polyvinyl structure and there is no cyclisation side reaction.[56] The polymerisation of unsubstituted *N*-vinylindole leads to products with a partly cyclised structure where the molecular weight and degree of conversion are appreciably lower than for 3-methyl and 2,3-dimethyl derivatives.

It has been suggested[56] that in the cationic polymerisation of *N*-vinylindole the cyclisation reaction proceeds as a result of the attack by the growing cation on the C(3) carbon atom of the indole ring with formation of a six-membered ring in accordance with the following scheme:



The cause of the attack on the 3-position is the high electron density at this carbon atom, typical for indole compounds. All the electrophilic substitution reactions therefore usually proceed precisely in this position.[92] The very low reactivity of 2-methyl-*N*-vinylindole in cationic polymerisation can be explained by the fact that, as a result of intermolecular cyclisation, it forms a more stable tertiary cation, which should therefore be less reactive in the chain propagation stage:[56]



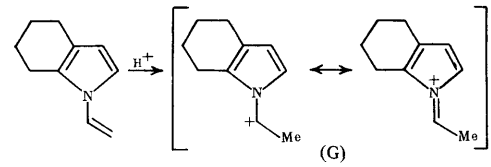
It is well known that, in the presence of halogens, hydrogen halides, alkyl halides, organochlorosilanes, and other electron acceptors, *N*-vinylindole polymerises via the double bond or produces polymeric charge-transfer complexes.[18,26,93,94]

According to Nomori et al.,[25] *N*-vinyl monomers can be arranged in the following sequence in terms of their reactivity towards polymerisation under the influence of electron acceptors: *N*-vinylcarbazole, *N*-vinylindole, *N*-vinylpyrrole. The ionisation potentials of these monomers decrease in the same sequence and hence the ease of their oxidation increases likewise, which is evidently inconsistent with the initiation mechanism postulating electron transfer as the key stage. At the same time, electron acceptors can be arranged in the following sequence in terms of their reactivity in polymerisation: dichlorodicyanobenzoquinone > *p*-chloranil > dichloro-*p*-benzoquinone > tetracyanoethylene > maleic anhydride. This sequence of electron acceptors is consistent with the sequence of the electron affinities and hence with the proposed polymerisation mechanism.

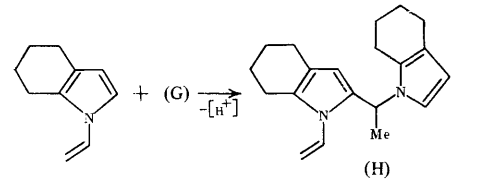
An *N*-vinylpyrrole polymer has been obtained in the presence of excess CCl_4 and the infrared spectrum of the product was consistent with the spectrum of the poly-*N*-vinylpyrrole synthesised in the presence of boron trifluoride etherate.[25]

It must be emphasised that the mechanism of polymerisation in the presence of carbon tetrachloride is not regarded as ultimately elucidated even for *N*-vinylcarbazole, despite the large number of studies devoted to this question.[20]

When *N*-vinyl-4,5,6,7-tetrahydroindole was acted upon by hydrochloric acid, a dimer, the product of electrophilic attack by the immonium cation on the pyrrole ring, was obtained together with the polymer:[95]



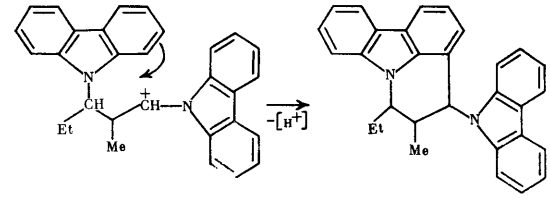
(G)



(H)

When hydrochloric acid is replaced by chlorotrimethylsilane, the yield of the dimer increases to 70%. This reaction leads to interesting possibilities for the synthesis of new *N*-vinylpyrroles.

Even the benzene fragments of the carbazole ring can be subjected to intramolecular attack by the growing cation. This has been demonstrated[22] for *N*-alkenylcarbazoles, which do not form high-molecular-weight products under the influence of acids (H_2SO_4 and $BF_3.OEt_2$), the main reaction being dimerisation. Thus the dimer of *N*-*trans*-propenylcarbazole gives rise to a cyclic product having the following structure:



VII. APPLICATIONS OF POLY-*N*-VINYLPYRROLES

Until recently, *N*-vinylcarbazole was the only widely available representative of the series of *N*-vinylpyrroles. A whole series of promising applications of this polymer have already been discovered: as insulating materials for the electrotechnical industry, particularly in high-frequency technology, and as components for the modification of synthetic rubbers.[15]

Poly-*N*-vinylcarbazole is one of the first and most vigorously investigated photosensitive polymeric systems, the interest in which is due primarily to their possible technological application in non-silver image recording processes—electrophotography, photothermoplastic recording, etc.[96,97]

The stream of publications on the properties and applications of *N*-vinylcarbazole is so great (see, for example, the relevant reviews[96-99]) that the problem indicated apparently requires special consideration and will not therefore be analysed in this article.

A photoconducting polymeric material has been obtained from the copolymers of *N*-vinylindole and its 2- and 3-methyl derivatives with *N*-vinylcarbazole or styrene.[72] These copolymers could be used as solutions or melts forming photosensitive layers for electrophotography.

The thermal copolymerisation of *N*-vinylindole with indole or other heterocyclic compounds having an endocyclic double bond leads to copolymers containing 2,3-indoline fragments in the main chain and indole rings in the side chain.[71-73] These polymers can also be used in electrophotography.

Poly-*N*-vinylpyrroles with high melting points have been synthesised in liquid SO_2 at −10° to −70 °C.[100]

Polyvinylindole has been investigated as a catalyst of photochemical polymerisation using its ability to form radical-ions.[101]

Polymers of *N*-vinylpyrroles having a stable colour have been described in patents.[102,103] The copolymers of *N*-vinyl-4,5,6,7-tetrahydroindole with vinylox sensitised by trinitrofluorenone are photosensitive and are capable of being hardened by polyamines like the usual epoxyresins.[61,66]

The study of the thermal stability of these copolymers by differential thermal analysis demonstrated the possibility of extending the temperature range of the use of the copolymers by introducing the indole component.[60]

In order to increase the assortment of reactive polymeric materials for the synthesis of medicinal drugs, a method has been developed for the preparation of the copolymers of *N*-vinyl-4,5,6,7-tetrahydroindole with *N*-vinylpyrrolidinone.[44,67] Water-soluble copolymers enriched in *N*-vinylpyrrolidinone exhibit an antisilicosis activity in model pneumoconiotic processes,[70] while the *N*-vinylpyrrolidinone homopolymer does not show such an activity.[104]

Products based on annelated pyrroles have been employed for the enrichment of polymetallic ores by flotation.[69] The polymeric flotation agent exhibits effective foam-producing properties when employed in amounts as low as 10 g per tonne of ore and the overall extraction of zinc and lead under these conditions reaches 175% [sic., Ed.], while under analogous conditions industrial foaming agents extract only 90% of the metals.[69]

Overall, the chemistry of *N*-vinylpyrroles is too new to compete successfully as regards practical applications with the chemistry of other pyrroles and even with that of *N*-vinylcarbazole. The examples quoted illustrate only the first advances achieved in the applied employment of *N*-vinylpyrroles.

Thus it follows from the literature data quoted that the chemistry of *N*-vinylpyrroles is developing very vigorously. At the same time some of its aspects have only been outlined for possible investigation. These include the cationic polymerisation whose key stage is the electrophilic substitution of hydrogen in the pyrrole ring by the immonium cation. This reaction can lead to new condensed polycyclic systems.

A characteristic feature of the present state of the chemistry of *N*-vinylpyrroles is the virtually complete absence of quantitative data concerning the polymerisation process and hence the absence of a clear-cut correlation between the structure of the monomers and their reactivity.

In the next few years one may expect the synthesis of new polyvinylpyrroles with properties of practical value both as a result of the use of new monomers of this series and as a result of the chemical modification of the highly reactive pyrrole ring in the polymers already known.

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