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The Reactions of Nitrile-containing Polymers

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The present review deals with chemical aspects of the reactions of polyacrylonitrile and related polymers, based on the reaction of the C≡N groups, the polymer-analogue transformations of polynitriles under the influence of water, alcohols, carboxylic acids, nitrogen-containing organic compounds, hydrogen sulphide, and other nucleophilic reagents, and the reaction of polynitriles with electrophilic reagents. Reactions undergone by the polymers but not by mononitriles, and reactions whose mechanisms are different for poly- and mononitriles, have been distinguished. The review cover the literature of the last 15 years. The bibliography contains 143 references.

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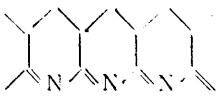
I. INTRODUCTION

As a consequence of the high and varied reactivity of the cyano-group, the properties of nitrile-containing polymers can be modified comparatively easily by treating these polymers with various reagents. A number of reactions of polynitriles, primarily reactions based on the hydrolysis of polyacrylonitrile (PAN), are widely used in industry. The reactions of nitrile-containing polymers have been reviewed in monographs[1,2] covering the literature for the period 1967–1970. In recent years, however, a large number of studies of fundamental importance have been carried out on the chemical transformations of macromolecular compounds containing nitrile groups. The present review is based mainly on papers published during this period. Of earlier work, only important studies not dealt with in Refs. 1 and 2 have generally been examined. The present review does not deal with work on the intramolecular reactions of the nitrile group with other functional groups to give heterocyclic compounds, since these reactions, which are used, in particular, to obtain heat-resistant polymers ("polyheteroarylenes"), were reviewed recently.[3]

The thermal treatment of polymers containing blocks consisting of nitrile-containing units leads to polymerisation at the CN groups to give polyazomethines (azapolyenes). This polymerisation can take place at the same time as the polymer-analogue reactions of polynitriles, and, as shown below, in a number of cases it precedes other transformations of the macromolecules. The present reivew begins with an examination of the influence of various reagents and functional groups (present in the original polymers or formed during thermal decomposition) on the polymerisation at the CN groups. The review does not examine the many studies of azapolyenes not concerned with the chemical nature of the observed conformations, studies of the thermal decomposition of CN-containing polymers at temperatures above 200–300 °C, or studies of the volatile products formed in the thermal decomposition of nitrile-containing polymers.

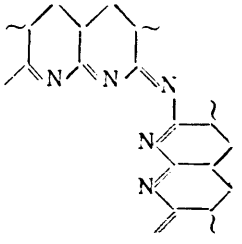
II. INTRA- AND INTERMOLECULAR REACTIONS OF CN GROUPS

Heating (100–200 °C) polymers rich in acrylonitrile and methacrylonitrile units leads to the intramolecular reaction of neighbouring nitrile groups to give sections with a ladder structure, for example:



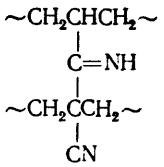
This reaction[1,2,4,5] continues to attract considerable attention, chiefly because it is a basic reaction in the degradation of nitrile fibres, accompanied by discolouration, and also because polymerisation at the CN groups of PAN is the first stage in the production of carbon fibres.

When PAN is heated, the intramolecular transformations are evidently accompanied by intermolecular reactions of the CN groups, leading to cross-linking of the polymer chains:[6,7]



The sections consisting of condensed rings are relatively short. They are formed by not more than 3–5 neighbouring units, and this is apparently related to the atactic structure of PAN.[6,8–11] The intermolecular reaction gives not

only N–C bonds, as shown above, but also C–C bonds:



Structure formation by the macromolecules during polymerisation makes the products insoluble. The ladder polymer based on polymethacrylonitrile (PMAN), after polymerisation at the CN groups, remains soluble in various solvents. This is related to the fact that PMAN does not contain relatively mobile α-hydrogen atoms, which in the case of PAN are responsible for the formation of intermolecular C–C bonds; steric factors also prevent intermolecular interaction.[1] When CN-containing polymers are heated to 200 to 250 °C, other processes accompanying structure formation, namely the rupture of polymer chains and the liberation of volatile degradation products, take place more intensively, and dehydrogenation or oxidative dehydrogenation leads to aromatisation of the condensed rings. The chains are broken much more easily in dimethyl sulphoxide (DMSO) solution than when the solid polymer is heated.[12] The slowest stage in the various successive transformations of PAN and similar polymers, however, is cyclisation, that is the rate of polymerisation at the CN groups determines the overall rate of the process.[13]

The presence of isotactic sequences in the PAN chain creates the most favourable conditions for the formation of polyconjugated systems. Increase in the concentration of these sequences is accompanied by an increase in the length of the conjugation chains in PAN subjected to thermal treatment.[5,14–16] An important part in the kinetics of the transformations of PAN is also played by the conformation of the polymer chain.[5]

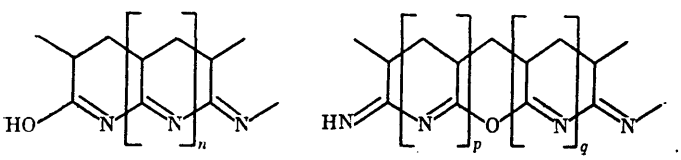
The treatment with nucleophilic reagents of polymers whose macromolecules contain blocks consisting of nitrile-containing units, or the introduction of nucleophilic functional groups into the macromolecules of these polymers, initiates polymerisation at the CN groups. A marked increase in the rate of formation of polycyclic structures in the thermal decomposition of nitrile-containing polymers is achieved in the presence of carboxyl groups.[1,17–26] When substituted acetic acids are added to PAN, intensive polymerisation at the CN group takes place even at 100 °C, and its rate increases with increase in p*K* for the acid. The rate of the process is also increased by hydrogen chloride.[27] The lower initial temperature of cyclisation in copolymers of acrylonitrile and vinylidene chloride, compared with PAN, is apparently due to the action of the hydrogen chloride liberated in the dehydrochlorination of the copolymer.[28] Strong discolouration in copolymers in which CN groups predominate is observed at 85 °C in the presence of benzenesulphonic acid.[19] Zinc chloride is an effective catalyst for the polymerisation.[29]

Derivatives of acids initiate the cyclisation and discolouration. In copolymers of acrylonitrile with esters of acrylic and methacrylic acids,[30] vinyl acetate,[25–31] acrylamide,[18,32] acrylamidoxime,[18] acrolein, and methyl vinyl ketone,[33] polymerisation at the nitrile groups is more rapid and begins at lower temperatures than in the case of PAN. The cyclisation of copolymers containing methyl acrylate or methyl methacrylate units is accompanied by the elimination of methanol. The temperature at which oligomerisation at the CN group starts in an inert atmosphere is lowered when PAN contains a small quantity of acrylothiamide units. In the presence of aqueous ammonia solution, thioamide groups initiate the reaction even at 90° and lower temperatures. Conditions have been found, in which partial polymerisation at the CN groups in the macromolecules of PAN fibres containing $CSNH_2$ groups gives fibres with a high heat resistance and an appreciable modulus of elasticity at increased temperatures.[34]

Polymerisation initiators include phenols,[35] alcohols,[20,21] imides,[1] and aliphatic amines.[1,17] In the polymerisation of the CN groups of PAN, initiated by trialkylamines, at the boiling point of the solvent (dimethylformamide (DMF), dimethylacetamide DMA), polymers with comparatively little structure formation, soluble in formic acid, are obtained. The characteristic viscosity of the polymers increases when phenols are used as co-initiators.[36] The rate of cyclisation of PAN is possibly also increased by ketimine groups[17] and by the amino-groups formed in enamines by the tautomeric transformation of N-substituted imino-groups ($\rangle CH-\overset{|}{C}=N- \rightleftharpoons \rangle C=\overset{|}{C}-NH-$).[24]

Polymerisation at the CN groups is also initiated by alkali metal hydroxides[12,37,38] and alkoxides,[20,39] including the polymeric compounds $NaO(CH_2CH_2O)_nNa$,[38,40] aqueous sodium carbonate solution,[19] potassium cyanide,[41] and other alkaline inorganic compounds. In the presence of bases, the reaction takes place at room temperature. Initiators with basic properties also bring about other reactions of polynitriles, in particular reactions ending in chain rupture.[37]

When PAN is heated in the presence of solutions of alkali metal hydroxides in DMSO, conjugated chains of two types are formed:[42]



Under the influence of organotin compounds (tributyltin methoxide, dibutyltin dimethoxide, etc.), polymerisation at the nitrile groups of PAN and PMAN takes place at 120 °C and 70 °C respectively.[43]

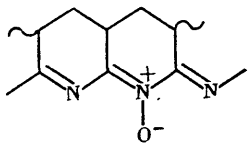
It was suggested[44] that polymerisation at the CN groups and discolouration of the polymer are initiated by β-ketonitrile groups present as defects in the PAN structure. It was later shown, however, that these groups have no significant influence on the transformations of PAN.[45]

Some authors have proposed a free-radical mechanism for the initiation of polymerisation at CN groups.[18,27,30,46]

In the absence of appreciable quantities of catalytically active impurities or structural defects, polymerisation at the CN groups may be preceded by intramolecular reactions involving the nitrile group and an α-hydrogen atom, whose products then directly initiate the polymerisation.[1,11,29] This suggestion is confirmed by the comparative stability to polymerisation of thoroughly purified PMAN, poly-α-phenylacrylonitrile, and other nitrile-containing polymers whose units do not contain mobile α-hydrogen atoms.[29]

Particular attention is being paid to the influence of atmospheric oxygen on the transformations of PAN.[9,22,47,48] It can now be taken as established that the presence of oxygen lowers the temperature threshold above which cyclisation, aromatisation, and structure formation in PAN take place.[8,22] The presence of oxygen also lowers the temperature of the start of dehydrocyanidation, intermolecular redistribution of hydrogen with the formation of

ammonia, and rupture of the polymer chains.[8,48] In addition, the reaction with oxygen leads to oxidative dehydrogenation of PAN.[8] According to Ref.44, the imino-groups in the conjugated chains are oxidised by atmospheric oxygen to give chromophoric nitrone groups, so that the colour of the polymers becomes more intense:



Carbonyl groups, which may also be formed by the hydrolysis of ketimine groups, also appear in PAN macromolecules during thermooxidative degradation.[8,12,24,44,45,49-51]

Since polymerisation at the nitrile groups is accompanied by discolouration of the polymer and a deterioration in its solubility, the use of stabilising reagents which suppress these processes may sometimes be of interest. Dienophiles (maleic anhydride, acrylamide, etc.) are effective PAN stabilisers.[52,53] The effect of these substances is based on a Diels–Alder reaction with the *cis*-azadiene sections of the polyconjugated chains;[53] this leads to rupture of the conjugated chain (a decrease in the intensity of the colour) and probably also to some extent prevents the growth of this chain. Dienophiles apparently have a stabilising action under the conditions of the thermal treatment of PAN, but do not influence the colour of the polymer which has previously been heated and kept in contact with air; they are also ineffective if the thermal treatment is combined with oxidation of the polymer, catalysed by various metal ions. This is explained by the appearance of $=\overset{+}{N}-\bar{O}$ groups in the macromolecules (see above).[53,54]

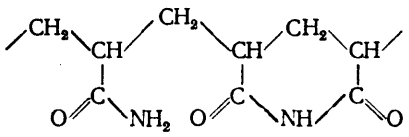
The temperature at which polymerisation of the CN groups of PAN begins is raised, and the extent to which these groups are involved in cyclisation is decreased, if small quantities of inert units (styrene, methylstyrenes, 2-vinylpyridine), dividing the polynitrile chain into relatively small blocks, are introduced into the macromolecules.[30] The inclusion of α-methylstyrene units in the macromolecules of PAN or the copolymer of acrylonitrile and vinyl acetate leads to an appreciable increase in the activation energy of the initial stage of the thermal degradation of the polymers.[55]

Intermolecular reactions involving polymerisation at the nitrile groups and trimerisation to give s-triazines can be used to harden oligomers and polymers containing infrequent (isolated) CN groups.[3]

III. HYDRATION AND HYDROLYSIS

The hydration and hydrolysis of the nitrile groups in polymers, as in low-molecular-weight compounds,[2] takes place chiefly in the presence of acids and bases.

Treatment with 75–95% sulphuric acid converts the nitrile groups of PAN into amide, imide, and carboxyl groups.[56] The structure and properties of the reaction product depend on the original H_2SO_4 concentration and the other reaction conditions.[39] In the presence of 70% sulphuric acid at room temperature, polymers with a high heat resistance, consisting of acrylonitrile and acrylamide units, were obtained. The nitrile units in these polymers are present in blocks. The polymers obtained from PAN in 80–90% sulphuric acid contain 25–30% units with amide groups and 75–70% units with imide groups:



An acrylomide homopolymer could not be obtained from PAN, because in the presence of sulphuric acid the amide groups in the 1,3-positions readily undergo cyclisation. However, in the copolymer of acrylonitrile and isobutylene with the 72 : 28 composition, in which the average length of the polyacrylonitrile blocks is ~3, imidisation is suppressed to a considerable extent; in the presence of 80% sulphuric acid, the nitrile groups are almost quantitatively converted into amide groups.[39]

Treatment of PAN with 65% nitric acid at −8 °C has been used to synthesise a polymer consisting chiefly of acrylonitrile and acrylamide units,[57] with a structure similar to that of the polymer obtained from PAN and 70% sulphuric acid.[39] The nitrile groups in PAN are also hydrated by the action of concentrated hydrochloric acid in DMF [58] and on prolonged treatment in an atmosphere of hydrogen chloride.[59,60]

The use of more dilute sulphuric acid than that indicated above, in the reaction of PAN or the copolymer of acrylonitrile and isobutylene, leads to hydrolysis of the nitrile groups, that is to the formation of carboxyl groups.[39,61] Treatment of PAN with 60% H_2SO_4 at 95 °C gave polymers partly or completely soluble in aqueous alkali solutions. The carboxyl groups increase the rate of hydrolysis of neighbouring nitrile groups.[39] According to Ref.61, PAN with an increased isotacticity undergoes racemisation under the conditions of hydrolysis with sulphuric acid; the concentrations of iso- and syndiotactic sequences in the product were equal.

The nitrile groups in copolymers of acrylonitrile with butadiene are hydrolysed in the presence of mixtures of zinc chloride and water at 140–170 °C.[62] This reaction takes place in the vulcanisation[63] of butadiene–nitrile rubber by zinc chloride and water. The cross-linking of the macromolecules is to a large extent due to the intermolecular addition of the carboxyl groups formed in the hydrolysis to the C=C double bonds to give ester groups.

In practice, the most important polymer-analogue transformation of PAN is its alkaline hydrolysis. The water-soluble polymers obtained by hydrolysing PAN and copolymers containing more than 50% acrylonitrile groups have found extensive application as thickeners, flocculants, and protective colloids, in the preparation of coatings for textile materials, in the dressing of leather, etc.[19,64-69] The hydrolysis of PAN is most frequently carried out at 90–100 °C by NaOH and an excess of water.[70,71] The hydroxides of other alkali and alkaline earth metals, sodium silicate, trisodium and tripotassium phosphates, and sodium sulphide are also used.[72-74] The alkaline hydrolysis of copolymers of acrylonitrile with vinyl acetate in the presence of DMF, DMSO, and DMA has been described.[75] The high-temperature (180–220 °C) hydrolysis of PAN has been carried out successfully in the presence of aqueous solutions of urea, which under these conditions is hydrolysed to ammonium carbonate, which is directly responsible for the conversion of the CN groups into $CONH_2$ and $COONH_4$ groups.[76] The product of the alkaline hydrolysis of PAN is usually an aqueous solution of the polymer. To obtain

the polymer as a powder, the hydrolysis of PAN is carried out using the stoichiometric quantity of water in the presence of propan-2-ol or various other water-soluble organic substances.[77,78]

The alkaline hydrolysis of PAN takes place in two stages. In the first, heterophase, stage, the colour of the polymer changes sharply from white through dark red to yellow. In the second, homophase, stage, the intensity of the colour of the reaction mixture decreases to pale straw-yellow.[79] The change in colour is due to the characteristic mechanism of hydrolysis of the polymers, which contain blocks with nitrile-containing units arranged in sequence. Although the hydrolysis of an isolated nitrile group begins with hydration to the amide group,[2] the hydrolysis of these polymers takes place (at least to an appreciable extent) with the intermediate formation of chromophoric polyazomethine sections, which are then hydrolysed to amide and carboxyl groups. This sequence of reactions in the alkaline hydrolysis of PAN is the reason for the high initial rate of this process, which is at least ten times the rate of hydrolysis of an isolated CN group.[80]

According to this hydrolysis scheme, the change in the colour of the reaction mass in the hydrolysis of copolymers of acrylonitrile depends on the distribution of the units of the comonomers in the macromolecules.[78,80] The colour is less intense in copolymers with low values of the average length of the acrylonitrile blocks. In the case of copolymers of acrylonitrile containing methyl acrylate and vinyl acetate groups, the process begins with the hydrolysis of the ester groups. The duration of the heterophase stage in the hydrolysis of these copolymers, and also copolymers with acrylic acid, is much shorter than that observed in the hydrolysis of the homopolymer of acrylonitrile. The presence of chemically inert and hydrophobic propylene units in copolymers with acrylonitrile, on the other hand, leads to an increase in the duration of the first stage of the hydrolysis.[80] The rate of the homogenisation of the reaction mixture in the alkaline hydrolysis of PAN is also increased in the presence of surface-active substances such as methylcellulose and polyvinyl alcohol.[79] With a deficit of NaOH (less than 50–60 mole % of the concentration of nitrile units in PAN) at 95 to 100 °C, the process stops at the first stage, that is a coloured water-insoluble polymer is obtained.[79]

An important characteristic feature of the alkaline hydrolysis of cyano-containing polymers, not observed in the case of low-molecular-weight nitriles, is the existence of a limiting degree of conversion.[79–81] For example, when PAN was heated (92–96°) for a long time in the presence of an equimolar (relative to the nitrile units) quantity of alkali, that is sufficient to convert all the nitrile groups into carboxylate groups, a polymer containing sodium acrylate and acrylamide units in the molar ratio 79 : 21 was obtained. Increase in the hydrolysis time above a definite limit, in spite of the presence of free alkali, did not lead to a further increase in conversion.[79] Increase in the excess of alkali and its concentration leads only to a slight increase in the limiting conversion of nitrile groups into carboxyl groups.[79,82] The concentration of amide groups in PAN subjected to alkaline hydrolysis decreases sharply with a marked increase in the reaction temperature. Thus when an equimolar quantity of NaOH is used, the limiting conversion of acrylonitrile units into sodium acrylate units is 94% at 170°, and almost 100% at 250°.[83] The explanation for the limitation of the degree of formation of carboxylate groups is that the accumulation of COO^- anions in the macromolecules during hydrolysis leads to an increase in the electrostatic repulsion between the polymer chains and the OH^- anions, as a result of which the effective rate constant of the hydrolysis decreases continuously to zero.[84–86] Increase in temperature makes it possible to overcome the electrostatic repulsion, but at 140 °C an increase in the degree of degradation (rupture) of PAN molecules is observed.[82]† The inclusion of negatively charged units in the macromolecule leads to additional limitation of the degree of hydrolysis of the CN groups. For example, a study of the alkaline hydrolysis of copolymers of acrylonitrile with sodium vinyl sulphonate established that with increase in the proportion of units of the second monomer in the copolymer, there is a slight decrease in the degree of hydrolysis of the acrylonitrile units with an increase in their degree of hydration.[89] The maximum degree of conversion of nitrile groups into carboxylate groups in copolymers of acrylonitrile with methyl acrylate (17 mole %) and acrylic acid (26 mole %) was comparatively low (72–70% at 92–96 °C), in spite of the fact that in the initial period the process took place readily.[80] The low degree of conversion in these cases is evidently related to the fact that there is electrostatic repulsion between the OH^- ions and COO^- groups formed both from acrylonitrile units and from methyl acrylate or acrylic acid units. On the other hand, the products of the hydrolysis of copolymers of acrylonitrile containing vinyl acetate units, which are hydrolysed to uncharged vinyl alcohol units, show a slightly higher limiting degree of hydrolysis of the CN groups, compared with the hydrolysis products of PAN.[80] Under the conditions of the alkaline hydrolysis of the copolymer of acrylonitrile and vinyl acetate, in which the nitrogen-containing units show limiting conversion, the units with ester groups are converted quantitatively into vinyl alcohol groups.[78]

In the case of copolymers of butadiene and acrylonitrile (in the mass ratio 82 : 18) [90] and acrylonitrile, butadiene, and styrene (ABC-copolymer,[91] in which the nitrile groups are mostly isolated, and also cyanoethylcellulose,[92] alkaline hydrolysis is analogous to the hydrolysis of low-molecular-weight mononitriles. Nevertheless, the limiting conversion of the CN groups in the hydrolysis of the ABC-copolymer is lower than in the hydrolysis of PAN, due to steric hindrance created by the branching of the macromolecules of the graft ABC-copolymer.[91] The rate of hydrolysis of the CN group is greater than that of the de-esterification of cyanoethylcellulose.[92]

In some studies the alkaline hydrolysis of PAN is combined with secondary transformations of the polymer. Thus a process has been developed for the direct esterification of PAN [93] by the reaction of the resulting carboxyl groups with dimethyl sulphate, and also for the synthesis of a polymer containing sodium acrylate and vinylimine units, by the Hofmann reaction of the amide groups.[94] The production of a polyampholyte, whose macromolecules contain COOH and NH_2 groups, from PAN, aqueous NaOH solution, and bromine, is explained by the fact that initially, the reaction with alkali gives carboxylate groups and polyconjugated sections $(-\underset{|}{C}=N-)_n$, which then react with hypobromite, undergoing transformations analogous to the Hofmann rearrangement.[95]

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†The macro-chains of PAN [87] and the copolymer of styrene with acrylonitrile[88] in the presence of potassium hydroxide or t-butoxide in DMSO are broken even at room temperature. The addition of monomers polymerising by an anionic mechanism (4-vinylpyridine, propylene oxide) leads to the formation of block copolymers.

Weakly acidic cation exchangers have been obtained by treating a polyacrylonitrile fibre, consisting of acrylonitrile, methyl acrylate, and itaconic acid units (92.2:6.3:1.5), with an alkaline hydrolysing agent and hydrazine hydrate as structure-producing agent.[96]

A recent paper[97] described the hydration of the CN groups of PAN in a neutral medium in the presence of manganese(IV) oxide or Raney copper as heterogeneous catalyst. In aqueous potassium thiocyanate solutions at 80 °C, up to 50% of the nitrile groups are converted into amide groups, with a simultaneous side reaction involving polymerisation at the CN groups.

Unlike mononitriles, PAN and PMAN react with water in the absence of specially added acids or alkalis. At a temperature of 230–250 °C and a pressure of 30–40 thousand atm, these polymers react with water, becoming water-soluble;[98] it was assumed that under these conditions the nitrile groups are hydrated quantitatively to give the corresponding carbo-chain polyamides. It was later found, however, that when heated in the presence of water, PAN undergoes hydrolysis, which takes place even at 160 °C and a pressure corresponding to the vapour pressure of the components of the reaction mixture.[99] This process, like the alkaline hydrolysis, begins with polymerisation at the nitrile groups,

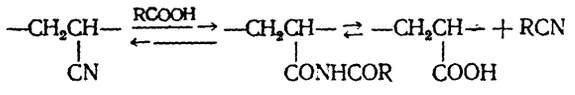
after which the $(-\overset{|}{C}=N-)_n$ blocks are hydrolysed to give amide and carboxyl groups.[100] The ammonia liberated catalyses both these reactions and the direct hydration of the nitrile groups to amide groups according to the usual scheme characteristic of low-molecular-weight compounds. The liberation of ammonia in the hydrolysis is responsible for the autocatalytic character of the process. Because of the high temperature of the process, hydrolysis is accompanied to a slight extent by rupture of the polymer chains. The limiting degree of hydrolysis of PAN by this method is high and is 60–65% at 200 °C; the remaining groups are acrylamide groups. The existence of a limiting degree of hydrolysis in this case is related to the reversible character of the hydrolysis of the amide groups in the absence of acids or alkalis.[101]

IV. OTHER ELECTROPHILIC REACTIONS

The CN groups in polynitriles react not only with water but also with other oxygen-containing compounds and with nitrogen- and sulphur-containing and other nucleophilic reagents.

The nitrile groups of copolymers of styrene and *p*-cyanostyrene are converted into ester groups in high yield by heating the copolymers with an excess of methanol and hydrogen chloride in tetrahydrofuran.[102] The reaction apparently involves the intermediate formation of orthoester groups. PAN undergoes direct esterification by methanol and sulphuric acid, and also of methanol, dimethyl sulphate, and catalytic quantities of sulphuric acid.[103] Like hydrolysis in the presence of sulphuric acid,[61] esterification is accompanied by racemisation.

The copolymer of styrene with acrylonitrile (in the molar ratio 61:39), in which the nitrile-containing groups are practically isolated, reacts at 160–220 °C with carboxylic acids according to the scheme



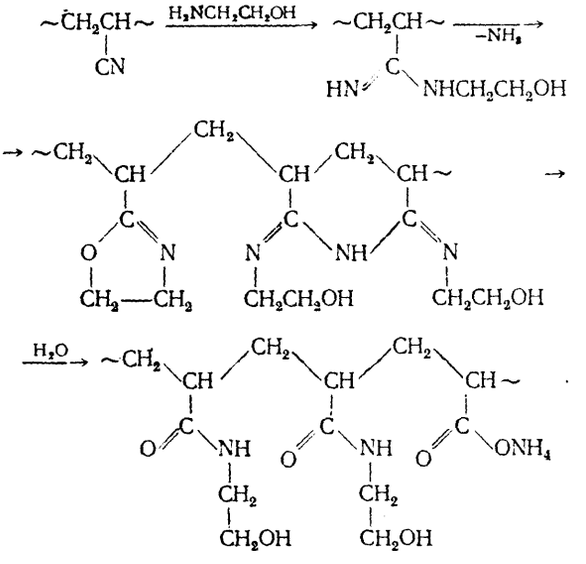
the copolymers obtained, up to 77% of the acrylonitrile units are converted into N-acylacrylamide and acrylic acid units. T_c decreases on going to polymers modified by acids with higher molecular weights.[104]

Copolymers of butadiene with acrylonitrile are vulcanised by dibasic carboxylic acids in the presence of anhydrous $ZnCl_2$, which accelerates the process and also directs the reaction of the CN and COOH groups towards the preferential formation of secondary amide bridges (-CONHCO-). The frost resistance of the vulcanisates obtained is greater than that of sulphur vulcanisates.[105]

In copolymers of methacrylic acid with methacrylonitrile, the intramolecular reaction of CN and COOH groups takes place even at 150 °C to give glutarimide units.[106] When the macromolecules contain polynitrile blocks, polymerisation at the CN groups takes place simultaneously, accompanied by discolouration of the polymer.[22,106] On heating, neighbouring carboxyl-containing groups give cyclic anhydride groups. Polymers containing imide heterocycles in the macromolecules have high vitrification temperatures.[39]

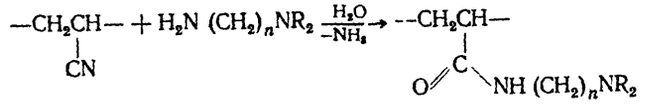
Polyacrylonitrile reacts with aniline on heating in the presence of metallic sodium or aluminium chloride to give polymers containing up to 30% N-phenylacrylamide units. The polymers isolated, which have a high proton-accepting power, also contained appreciable quantities of acrylic acid units.[107]

PAN reacts with an excess of 2-aminoethanol at 90 °C to give a water-soluble polymer.[108] The modification of PAN begins with the nucleophilic addition of 2-aminoethanol to the CN group and the formation of N-hydroxyethylamidine units. If these units are isolated, they subsequently undergo intramolecular condensation to give oxazoline fragments; neighbouring $-C(=NH)NHCH_2CH_2OH$ groups, however, as a result of condensation give N,N'-bis-(2-hydroxyethyl)glutarimidine fragments. The polymer obtained is easily hydrolysed, so that the modified units are converted chiefly into N-(2-hydroxyethyl)acrylamide and ammonium acrylate units:



Polyacrylonitrile, and also the copolymer of acrylonitrile and 5–10% vinyl acetate, in the presence of water at 115 to 120 °C reacts with an excess of N,N-dimethyl-1,3-diaminopropane or other primary–secondary primary–tertiary aliphatic diamines to give cationic polyelectrolytes, in which

dialkylaminoalkylacrylamide units predominate:[109]



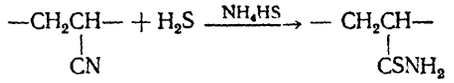
Similar transformations in these mild conditions are known for malono-, succino-, and glutaronitrile.[2] Since the mononitriles do not undergo these reactions, and polynitriles acquire a dark colour at the start of the reaction and the infrared spectrum indicates they contain C=N groups,[109] the ammonolysis–hydrolysis being considered, like alkaline hydrolysis, apparently begins with polymerisation at the C≡N groups, after which the polyconjugated sections of the macromolecules react with the amine and water.

Structured polymers have been obtained by treating PAN with hydrazine hydrate in DMF.[2,110] The cross-linking of the macro-chains is apparently partly based on the reaction of two nitrile groups with two hydrazine molecules to give 4-amino-1,2,4-triazole rings, containing macromolecular residues as substituents in positions 3 and 5.[2] Polyacrylonitrile fibres modified by treating with hydrazine are used as starting materials for further transformations,[111–114] in particular to obtain carbon fibres with good mechanical properties.[115] The modification of PAN and copolymers of acrylonitrile with aqueous solutions of hydrazine gives not only a three-dimensional network but also basic groups, which give the polymers chemisorption properties. Fibrous anion-exchangers obtained from copolymers of acrylonitrile with acrylic acid and hydrazine hydrate have a fairly high exchange capacity and are used in sorption processes.[116]

The reaction of PAN with hydroxylamine gives polyacrylamidoxime.[2,117] Polymer-analogue transformations of this polymer have been described.[118–120] Partial amidoximation of a polyacrylonitrile fibre at 90 °C has been used to obtain an anion-exchange and complex-forming fibrous sorbent.[121] The amidoximation of polyacrylonitrile chains grafted to cellulose fibres and to polypropylene has been carried out.[122]

In the reaction of PAN, copolymers of acrylonitrile and styrene or butadiene, and other CN-containing polymers, with dicyandiamide (100°, in mixtures of DMSO and methylcellosolve), more than 80% of the nitrile groups take part in the formation of 4-substituted, 2,6-diamino-s-triazine rings. The polymers obtained, containing triazine substituents in the macromolecules, have an increased thermal stability.[123]

Hydrogen sulphide adds on to the nitrile groups of PAN in DMSO or DMF in the presence of ammonium hydrogen sulphide or the salts of hydrogen sulphide with various secondary and tertiary amines as catalysts:[124]



The degree of thioamidation reaches 50–55% of the theoretical. The rate and the limiting degree of thioamidation increase with increase in the basic strength of the amine used as catalyst, and with increase in the reaction temperature. Increase in temperature, however, also increases the rate of side reactions. Thus in the reaction of PAN with hydrogen sulphide in the presence of ammonium hydrogen sulphide in DMF, more or less selective thioamidation is observed only at 0°, and at higher temperatures, amide and other functional groups are also formed.[124]

A polymer consisting of acrylonitrile and acrylothioamide units was also obtained by treating PAN with ammonium hydrogen sulphide alone in DMF. The polymer modified in this way retains its linear structure.[125] A modified polymer containing 7 mole % thioamide groups was used to obtain fibres.[126] Thioamide groups have been introduced into a prepared PAN fibre by treating it with aqueous solutions of ammonium[127] or sodium[128] sulphides, leading to a marked increase in the heat resistance and the stability of the fibre to repeated deformation at high temperatures. According to Ref.129, nitrile-containing fibres thioamidated with sodium sulphide solution have a high sorptive power with respect to the platinum group metals.

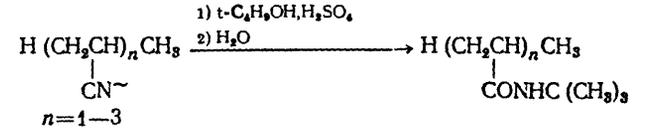
The addition of hydrogen sulphide to the nitrile groups of poly-α-chloroacrylonitrile has been described.[130] As in the polymerisation of the CN groups of PAN and in its alkaline hydrolysis, acrylic acid, methyl acrylate, and vinyl acetate units have an activating action on the thioamidation, whereas the rate of the thioamidation is decreased when the macromolecules contain styrene units.[131] Moreover, the initial effective rate constant for the thioamidation of the CN groups of PAN is 10–100 times that for the thioamidation of acetonitrile. This constant decreases rapidly, however, with increase in the degree of transformation of the CN groups.[132] Thus there is an analogy between thioamidation and various other reactions of polynitriles examined above. On this basis, and in view of the ability of thioamide groups to initiate polymerisation at the CN groups, it may be assumed that the thioamidation of polynitriles, like their alkaline hyrolysis, takes place at least partly via a stage involving the intra- and intermolecular cyclisation of CN-containing polymers.

The electrophilic reactions of nitrile groups in polymers also include reactions leading to the formation of a new C–C bond, for example the reaction of butadiene–nitrile rubber with resorcinol in the presence of HCl and $ZnCl_2$ (Hoesch synthesis), as a result of which up to 10% of the acrylonitrile units are converted into vinyl 2,4-dihydroxyphenyl ketimine units, and as a result of subsequent hydrolysis into vinyl 2,4-dihyroxyphenyl ketone units.[133] Polymers containing ketimine and ketone groups have also been obtained by the reactions of Grignard reagents with the copolymer of styrene and *p*-cyanostyrene,[102] and also PAN.[45]

V. NUCLEOPHILIC AND OTHER REACTIONS

In recent years it has been possible to carry out the polymer-analogue transformations of polynitriles using the most familiar nucleophilic reaction of CN groups, namely the Ritter reaction.

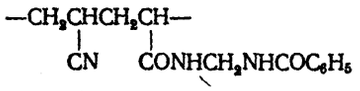
In the reaction of compounds which are low-molecular-weight models of PAN with t-butyl alcohol in tetramethylene sulphone in the presence of sulphuric acid at 25–40 °C, the nitrile groups are converted in high yield into N-t-butyl amide groups:



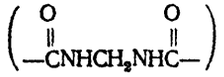
On going from the monomeric to the dimeric and trimeric models, the rate constant increases to a very slight extent that is in this reaction the neighbouring groups have no significant influence on the reactivity of the CN groups.[13] A study of the reaction of high-molecular-weight PAN with t-butyl alcohol under the same conditions established that the reaction has a limiting degree of transformation (abou 55%), which increases with increase in temperature and v decrease in the concentration or molecular weight of the original PAN. The polymer obtained has a much highe

than the original PAN, and the heat resistance of the modified polymer is determined by the degree of transformation of the nitrile groups.[135]

In tetramethylene sulphone in the presence of sulphuric acid, the CN groups of PAN undergo the Ritter reaction with N-hydroxymethylbenzamide, N-hydroxymethylphthalamide, and other N-hydroxymethyl-substituted amides and imides.[136] The polymers formed, for example

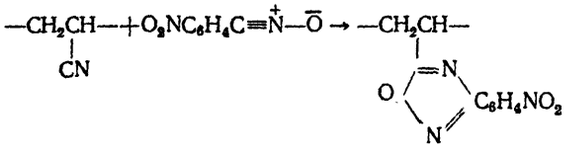


unlike the corresponding homopolymers obtained by radical polymerisation, for example poly(N-benzamidomethylacrylamide), show a greater tendency to undergo structure formation, and this is attributed, in particular, to the liberation of formaldehyde under the conditions of the polymer-analogue transformations and its reactions with the CN groups of different macromolecules to give methylene-bis-amide bridges



The vulcanisation of copolymers of butadiene, acrylonitrile, and vinylidene chloride at 142 °C under the influence of anhydrous zinc oxide is possibly based on the nucleophilic reactivity of the nitrile group.[137] The presence of ZnO leads to the partial dehydrochlorination of the vinylidene chloride units, and the $ZnCl_2$ (or $HZnCl_3$) catalyses the subsequent formation of the N–C bond as a result of the reaction of the nitrogen of the CN group with the carbon atom of another polymer chain having an increased electrophilic reactivity.

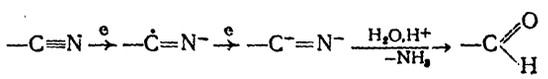
The 1,3-dipolar cyclo-addition of 4-nitrobenzonitrile oxide to the CN groups of copolymers of acrylonitrile with styrene and with vinylidene chloride, giving 1,2,4-oxadiazole heterocycles, was recently described:[138]



The syntheses were carried out in γ-butyrolactone by heating at 130 °C the copolymer with the chloride of 4-nitrobenzohydroxamic acid, which under these conditions undergoes dehydrochlorination to the nitrile oxide. The degree of conversion of the nitrile groups is 30–50%.

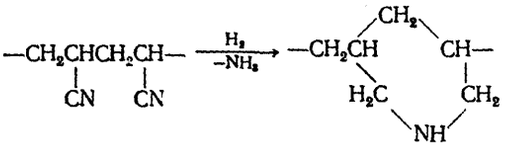
The reduction of the CN groups of polymers to aldimine or amino-groups has been described. The nitrile groups of carbo-chain polymers are partly reduced by tin(II) chloride in the presence of hydrogen chloride to aldimine groups, which on subsequent hydrolysis are converted into aldehyde groups (the Stephen reaction).[2] The use of this reaction to modify butadiene–nitrile rubber leads to an increase in the strength of the vulcanisates.[139]

The reduction of the nitrile groups in macromolecules by the radical-ions formed in the reaction of metallic sodium with naphthalene or hexamethylphosphoramide has been described. Aldehyde groups are produced in the polymers:[140]



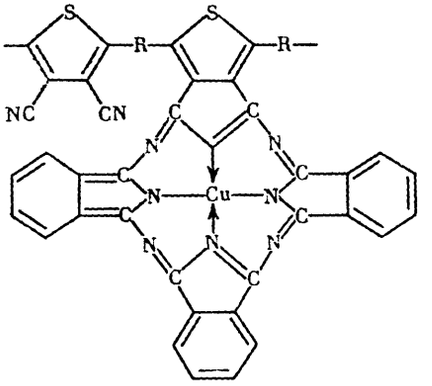
The intermediate products of this reaction initiate the graft polymerisation of styrene and methyl methacrylate, evidently an anionic mechanism.

In the presence of Raney nickel or other catalysts, the CN groups of PAN dissolved in DMF are partly hydrolysed (140–185 °C, 65–185 atm).[56,141] Since the CN groups occupy the 1,3-positions in the macromolecules, hydrogenation is accompanied by cyclisation, to give mainly piperidine rings:



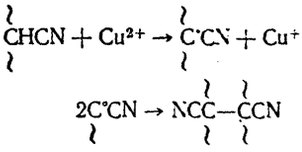
Acrylamide and acrolein units were also found in the modified polymer.

When hetero-chain polyamides whose chains contain 3,4-dicyanothiophene rings are heated (200–250 °C) with 1,2-dicyanobenzene and copper acetylacetonate, approximately 50% of the dicyanothiophene units are converted into phthalocyanine-like units:



The polymers obtained have an increased thermal stability.[142]

Butadiene–nitrile rubbers are cross-linked in the presence of copper(II) salts by a free-radical mechanism. The >CHCN group probably forms with Cu^{2+} a redox system in which there is one-electron transfer from the polarised CH bond to the cation, and the recombination of the radicals obtained leads to structure formation in the polymer:[143]



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The the reactions of nitrile-containing polymers can be divided into three groups. The first group consists of reactions taking place according to schemes familiar for low-molecular-weight nitriles. Because of the difference in the steric, polar, and other factors, the quantitative characteristics may differ considerably for the reactions of the low- and high-molecular-weight compounds. The second group also consists of reactions familiar for low-molecular-weight compounds, but in this case the transformations of the high- and low-molecular-weight compounds take place by different schemes. The third group consists of reactions which are specific for nitrile-containing polymers. The reactions of practical importance involving cyclisation and

polymerisation (third group) and various hydrolysis reactions (second group), for which reliable schemes for the transformations of the CN groups have been established, are now being studied in most detail, and methods for the control of these transformations have been developed. There is comparatively little published information, however, on the electrophilic reactions of polynitriles with various oxygen-containing (except water), nitrogen-containing, and other reagents, or on the nucleophilic reactions of polynitriles. In view of the reactivity of the CN group and the extensive use of compounds containing this group in synthetic organic chemistry, the possible applications of polynitriles as starting materials for the production of new polymers are far from exhausted. Since polynitriles are readily available, the detailed study of the known reactions of these polymers and the further extension of the range of reagents used for modification will undoubtedly produce promising results.

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