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N–N BONDED POLYMERS

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1. INTRODUCTION

The extreme reactivity of hydrazine and its derivatives with oxidizers such as HNO_3 or N_2O_4, leading to spontaneous ignition, has been utilized in developing self-igniting (hypergolic) propellant systems. Hydrazine, monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH) have long been used as fuels in biliquid rockets.[1–3] For hybrid rocket propellants, solid fuels which ignite spontaneously on coming into contact with liquid oxidizers are preferred in order to give the motor on–off capability. Here again, solid derivatives of hydrazine or compounds with N–N bonds have been conceived as hypergolic fuels.[4–12] Indeed, several of these compounds have very short ignition delays (the elapsed time preceding ignition after the liquid oxidizer and the solid fuel come in contact), with white or red fuming nitric acid (WFNA or RFNA) when used in the powder form.

In practice, however, the fuel is used as a solid "grain", which has adequate mechanical strength, in hybrid motors. Hence, the powder material has to be processed using a polymeric binder for casting it into the desired grain shape. Conventional binders, such

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as carboxyl terminated polybutadiene (CTPB) or hydroxyl terminated polybutadiene (HTPB) used routinely in composite solid propellants, are unsuitable as they adversely affect the ignition delay (ID), making it intolerably long.[13] New binders, capable of imparting adequate mechanical strength without affecting the ID, are, therefore, required to process the powder fuel compositions for hybrid systems.

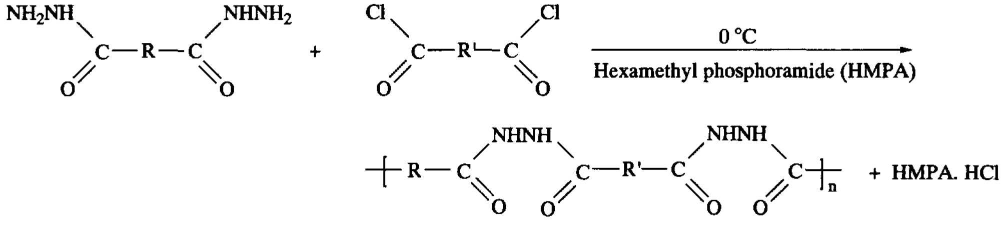
It is significant to note that a common feature of the spontaneously igniting systems mentioned above is that the fuels used are all based on compounds with N–N bonds. Assuming that the presence of N–N bonds in the backbone of the polymeric binder would make it more reactive with oxidizers like HNO_3 or N_2O_4, and could lead to ignition without affecting the ignition delay significantly, a search for new polymers with N–N bonds in the backbone was carried out. For use as binders, the N–N bonded polymers should, of course, in addition have suitable end groups and other favourable characteristics to impart adequate mechanical strength to the grain. A survey of the literature showed that apart from attempts made in the authors' laboratory,[13,14] hardly any work has been reported on N–N bonded polymers as propellant binders.

Hydrazine polymers have, however, received much attention over the years.[15–18] Several diverse applications[19–51] (Table 1) have been cited which include their use as adhesives, fibres and films, leather substitutes, permselective reverse osmosis membranes, chemotherapeutic antitumour agents, ion exchangers, etc. Of late, N–N bonded polymeric systems have been examined for their liquid crystalline properties. Because of the potential applications of liquid crystalline polymers[52–57] (Table 1), numerous papers reflecting a certain line of research relating to liquid crystallinity have appeared in recent years.[58–70] Specifically, these research works pertain to topics like synthesis of polymers containing mesogens in the main- or side-chain, theory, characteristics, structure, effects of substituents, copolymers, solvents and solution concentrations, etc.

In view of their interesting properties, a variety of N–N bonded polymers have been synthesized, although most of the work reported is patented. This report makes an attempt to put together the information available on polymers containing N–N bonds either in the polymer backbone or constituent heterocyclic rings, their synthetic routes, thermal characteristics and liquid crystalline properties, in an effort to design better N–N bonded polymeric systems.

2. POLYHYDRAZIDES

Polymeric hydrazides are prepared by condensing hydrazine or its derivatives with acyl halides, dicarboxylic acids, esters, anhydrides, polyacids and polymeric esters.[49,71–73] Aliphatic polyhydrazides, for example, have been prepared by a method of low temperature solution polymerization,[74–76] according to the following scheme:



SCHEME 1.

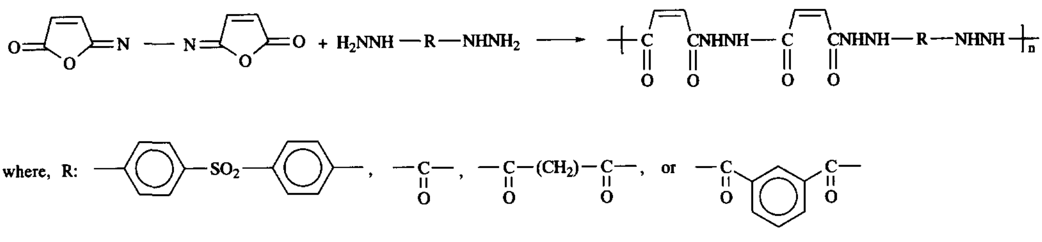
TABLE 1. N–N containing polymers and their useful characteristics

Hydrazine polymers	Useful properties	Ref.
Copolymers of hydrazine	Adhesives	19–21
Poly(*m*- or *p*-phenylene-4-phenyl 1,2,4-triazole)	Heat stable fibres and films	22, 23
Diphenylmethane diisocyanate-hydrazine–polypropylene glycol copolymer	As films on glass	24
Polyester–diisocyanate–hydrazine copolymer	Leather substitutes	25
Hexamethylene diisocyanate-hydrazine–polypropylene glycol polyurethane copolymer or diphenylmethane diisocyanate-ethylenediamine-hydrazine–poly(tetramethylene adipate). Aromatic polyamide hydrazide, *m*- or *p*-aminobenzoylhydrazide with iso- or terephthaloyl chloride	Microporous water permeable, high salt rejection reverse osmosis membranes	26–34
2,2′-polymethylene bis (phthalazinium salts)	Antitumour agent	35
Acrylonitrile homo- or copolymer, hydrazine treated, or epichlorohydrin–hydrazine copolymer. Cyclic maleic hydrazide condensed with CH_2O	As ion-exchangers with good capacity and selectivity	36–39
Polyisocyanate-polyether-hydrazine	Elastic, stable foams in upholstery	40
Poly(*p*-phenylene-1,3,4-oxadiazole-2,5-diyl)	Light, heat, weather resistant films	41
N-carbonimidoyl amidrazone	Heat and chemical resistance	42
Hydrazine-*p*-phenylenediamine-terephthaloyl chloride polymer	Heat resistant moldings and electrical insulators, and film forming properties	44
Dicarboxylic acid hydrazide condensed with urea	Thermally stable foams, moulding composites	45
$(RCOC{=}C)_2SiMePh$; R = Me/Ph condensed with hydrazine	Electrical conductance	46, 47
p-aminobenzoic acid-hydrazine–*p*-phenylenediamine-terephthalic acid or *p*-aminobenzoic acid-hydrazine–terephthalic acid copolymer	High modulus poly(amide–hydrazide) cords	48
Poly(Bu acrylate)–hydrazine hydrate condensate	For dressing fabrics	49
Aromatic diisocyanate–hydrazine copolymers	Coloured substance	50
Polymethylene bis(2,2-dimethylhydrazine)	Protects synthetic and natural rubber from the effects of O_3	51
Polyhydrazide, polyazine, heterocycle containing polymers	Liquid crystalline phase	52–57

Interfacial polymerization to polyhydrazides is best achieved in the presence of Na_2CO_3 as a catalyst.[77] Increased molecular weight (MW) and decreased yield have been observed upon dilution of the mixture. The yield is also reduced with increased temperature. Organic solvents influence polymeric properties; aromatic and chlorinated hydrocarbon solvents offer the best results related to MW and yield. The nature and properties of the polymer obtained depend upon the proportion of the reactants and functionality of the groups in the main chain.[77] For instance, a viscous substance is obtained by the reaction of diesters of higher dicarboxylic acids and hydrazine in a 1 : 2 mole ratio at 200°C.[78] Rubbery products are obtained when the polyester to hydrazine ratio is 1 : 0.5.[49] The solubility of *N*-alkyl substituted polyhydrazides obtained from aromatic dicarboxylic acids with hydrazine or its salts by alkylation in the presence of phosphorus-containing inorganic acids depends upon the number of hydrazide bonds in the main chain.[79]

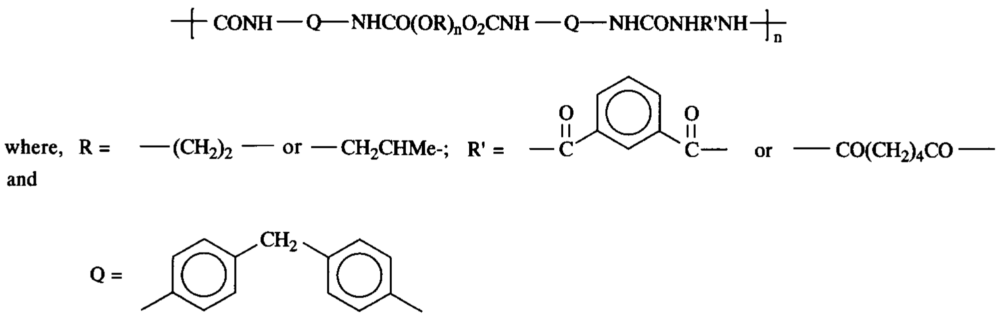
Simple hydrazides like $R(CH_2)_2CONHNH_2$ used in epoxy resin compositions have latent curability at low temperatures resulting in good storage stability.[80] In polymeric hydrazides, crosslinking occurs when the hydrazide groups are treated with multifunctional carbonyl compounds.[49] Introduction of units of hydrazine or sebacic acid dihydrazide into an unsaturated polyester chain by replacing a certain portion of a diol with an equivalent amount of a dihydrazide, during polymerization does not affect subsequent crosslinking with other vinyl monomers like styrene.[81]

Novel polyhydrazides synthesized by ring opening polyaddition of *N*,*N*′-bisisomaleimide with dihydrazides have also been reported.[82]



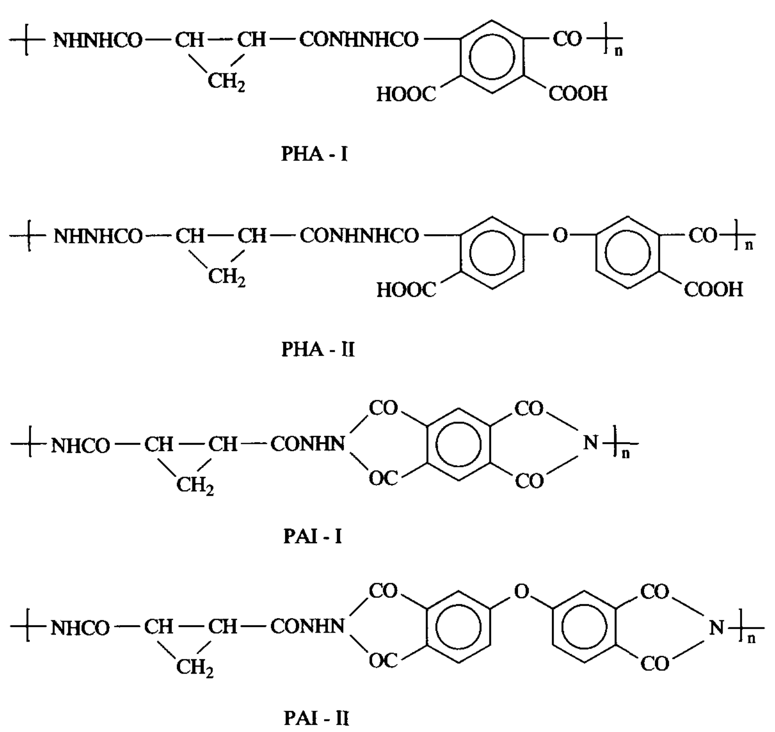
SCHEME 2.

Thermoplastic elastomers, such as a polypropylene glycol-4,4′-diphenylmethane diisocyanate–adipic acid dihydrazide copolymer, having both rigid and elastic segments in the chain have been obtained[83] by reacting oligomeric polypropylene glycol with diisocyanate and hydrazine or dihydrazide.



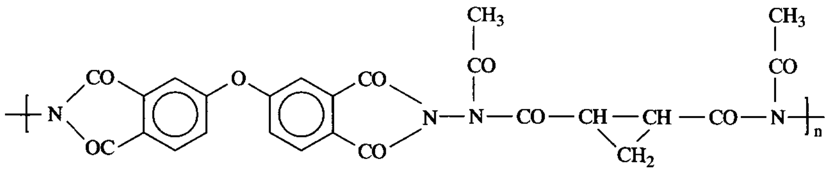
SCHEME 3.

Polyhydrazides undergo cyclodehydration. Polyhydrazido acids obtained by the reaction of *trans*-1,2-cyclopropanedicarboxylic hydrazide with pyromellitic or 3,3′-4,4′-diphenyl ether tetracarboxylic dianhydride in dimethylformamide (DMF), dimethylsulphoxide (DMSO), or *N*-methyl pyrrolidone (NMP), aprotic polar solvents, undergo cyclodehydration yielding the corresponding polyamidoimides.[84]



SCHEME 4.

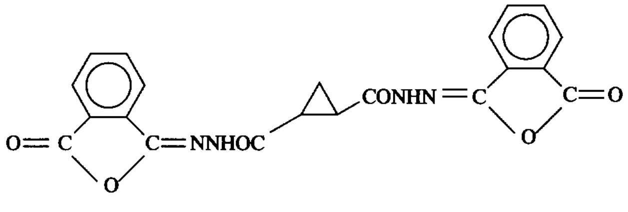
The plain optical rotatory dispersion curves obtained in the range of 350–590 nm for polymers in DMF solution have been used to characterize the cyclodehydration of polyhydrazido acids (PHA) to polyamidoimides (PAI). A polymer containing imide rings, with the following structure, whose optical activity is different from that of a polyamidoimide, has been identified by treating a DMF solution of PHA-II with a mixture of acetic anhydride (AA) and pyridine such that the molar ratio of AA to PHA-II exceeds 30. This polymer structure is reported to be confirmed by performing the thermal cyclodehydration which leads to the formation of PAI-II containing imide rings and by subsequent acylation of the amidoimide group.



SCHEME 5.

At the low molar ratio of AA to PHA-II of 4:6, partial imidization leads to a different polymer whose specific optical rotation value is intermediate between those of PHA and PAI. This suggests that the acylation rate of the amide group becomes significant at high concentrations of AA.

Cyclodehydration of the low MW amido acids results in the formation of both the imide and the isoimide (which subsequently rearranges to the imide). The predominance of one or the other path, and the isoimide rearrangement rate, depend on the amido acid structure and the nature of the dehydrating agent.[85,86] For polyamido acids, the possibility of isoimide intermediate formation during chemical cyclization has been studied to understand the nature of the intermediate product in the chemical cyclodehydration of PHA. Amidoisoimide is formed first, which later gets rearranged into amidoimide in the presence of the amido acid itself or nucleophilic agents such as acetic acid or acetate ion formed during cyclodehydration.



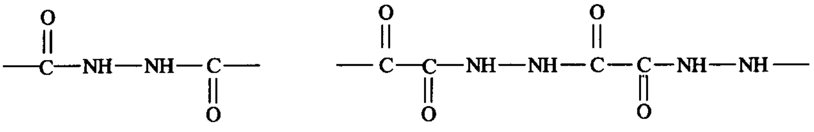
Isoimide structure

Scheme 6.

Polyhydrazides, in general, decompose at around 200–300°C. Study of thermal decomposition of aromatic/aliphatic polyhydrazides by pyrolysis/mass spectroscopy reveals that the primary decomposition processes are strongly influenced by structural factors.[87]

2.1. *Liquid crystalline polyhydrazides*

The liquid crystalline properties of polymers are generally exhibited either in solution or in the melt. Certain aromatic polyamides are well known to have the liquid crystalline (mesogenic) properties in solution (lyotropic).[55,63] This class of polymers exhibits transitions due to temperature changes similar to those of thermotropic liquid crystals. Polyhydrazides could be considered as polyamides with two amide groups being linked through carbonyl or imino units.[55]



$$-\overset{\overset{O}{\|}}{C}-NH-NH-\underset{\underset{O}{\|}}{C}-$$

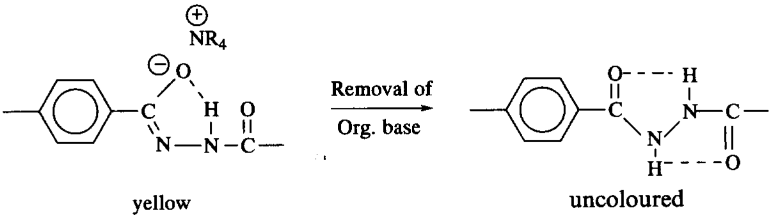
$$-\overset{\overset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-NH-NH-\overset{\overset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-NH-NH-$$

hydrazide group poly (oxalichydrazide) unit

Scheme 7.

Polyhydrazides with appropriate MW, structure and sufficient solubility exhibit liquid crystalline properties depending upon the nature of the units in the polymer. Polymeric hydrazides containing a substantial amount of aromatic units with the bonds linked coaxially or extended oppositely, have highly extended chains and yield liquid crystalline solutions in a variety of polar solvents. Poly(chloroterephthalic acid hydrazide) forms anisotropic solutions in 100% sulphuric acid.[52,88] However, the anisotropic solutions formed exhibit nematic–isotropic transitions or "gelation" with increasing temperature. For hydrazide copolymers, a mixture of fluorosulphonic acid and 100% sulphuric acid improves solubility and increases the range of formation of liquid crystalline solutions. This mixture of solvents also enables determination of the critical concentration of the copolymer as a function of the intrinsic viscosity at which liquid crystalline properties are exhibited.

In various aqueous organic bases, such as quaternary ammonium hydroxides (Me_4NOH, Et_4NOH) and also certain secondary aliphatic amines (piperidine), polyhydrazides form nematic liquid crystalline solutions. Solutions of polyhydrazides such as poly(terephthalic acid hydrazide) in organic bases are deep yellow. They have UV-visible absorption maxima at 370 nm, attributed to the association of the organic bases with the enol form of the hydrazide unit; the colour vanishes when the organic bases are washed out of the polymer.[55] It is also found that the addition of polar solvents, such as DMSO and tetrahydrofuran, causes the liquid crystalline solutions to become isotropic. However, in the bulk form, because of the anisotropy, they often appear turbid or opaque. Some hydrazide copolymers also form liquid crystalline solutions in organic bases.[89]



SCHEME 8.

2.2. *Liquid crystalline poly(amide hydrazide)s*

Para-linked poly(amide hydrazide)s have been prepared from 4-aminobenzhydrazide, oxalic dihydrazide and terephthalic dihydrazide by reacting with *p*-aromatic diacid chlorides. The high MW copolymers are soluble in sulphuric acid or a 1 : 1 mixture of fluorosulphonic acid and sulphuric acid, forming anisotropic solutions.[52,88]

Although the copolymer which forms high modulus, high tenacity fibres[90] from 4-aminobenzhydrazide and terephthalic acid, namely, poly(terephthaloyl 1,4-aminobenzhydrazide) forms an anisotropic solution in 100% sulphuric acid, it forms an isotropic dilute solution in DMSO solvent.[91–94] A more concentrated DMSO solution, however, is reported to exhibit anisotropic properties.[95]

Like the solutions of liquid crystalline polyhydrazides, poly(amide hydrazide)s containing oxalyl, terephthaloyl, chloroterephthaloyl and 2,5-pyridinedioyl units have been examined for their solubility and stability in sulphuric acid or sulphuric acid/fluorosulphonic acid mixtures, and also in a variety of other solvents. Although polymers with large fractions of *m*- or *o*-ring units have greater solubility, their solutions are not liquid crystalline.[52] Solution mesophase behaviour of block copolymers containing rigid units of poly(*p*-benzamide) and flexible units of the polyterephthalamide of *p*-aminobenzhydrazide in 80 : 20 proportion, respectively, has been investigated in dimethylacetamide solvent. Two phases appear to coexist. In addition to the fraction of the flexible component soluble in DMSO, attributed to oligomers and polymer units in the block copolymers, another fraction of a more complex isotropic phase also exists. As a consequence, there is no single anisotropic phase. However, the solubility of the flexible and isotropic phase is larger than that of the rigid homopolymer. Independent characterization of the DMSO-soluble fraction, of the insoluble residue, and of the sample isolated and recombined again do not show the properties of the original sample completely. This suggests the existence of a labile adduct between rigid and flexible components in the mesophase.[96]

3. POLYHYDRAZONES

A series of polyhydrazones with high nitrogen content has been prepared by condensing aliphatic or aromatic dibasic acid hydrazides

$$\left[\mathrm{NR(CH_2)_mNRN{=}CR'ZCR'{=}N} \right]_n$$

where $m = 2$ or 3, R = Et or Me, Z = $-CH_2-$ or $-(CH_2)_2-$ and R' = H or Me .

SCHEME 9.

with glyoxal, dialdehydes, diketones, diacidchlorides or acid anhydrides.[97–99] Both low and high molecular weight polymers have been obtained.[97,100] The reactions of poly(methyl vinyl ketone) with hydrazine and other amines have been investigated and it has been found that the reaction of the hydrazine with the polymer is affected by molecular volume and pK_b; generally, these reactions are observed to occur faster with hydrazine compared to other amines.[101] The thermal decomposition of polyhydrazones has not been investigated in detail. However, it has been found that the decomposition commences in the temperature range 180 to 240°C.[100]

4. POLYAZINES

Polyazines are generally obtained by the addition of hydrazine to carbonyl compounds,

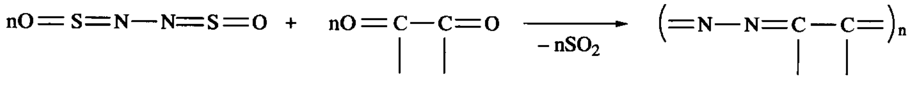
$$\mathrm{nO{=}CRArCR{=}O} + \mathrm{nH_2NNH_2} \xrightarrow[-2nH_2O]{} \left(\mathrm{{=}CRArCR{=}N{-}N{=}} \right)_n$$

where R = H or Me.

SCHEME 10.

Quinones, such as 1,2- or 1,4-naphthoquinone,[102] 9,10-phenanthrenequinone,[103] acenaphthenequinone[104] or diacetyl derivatives of benzene, biphenyl and ferrocene have been condensed with hydrazine hydrate.[105–109]

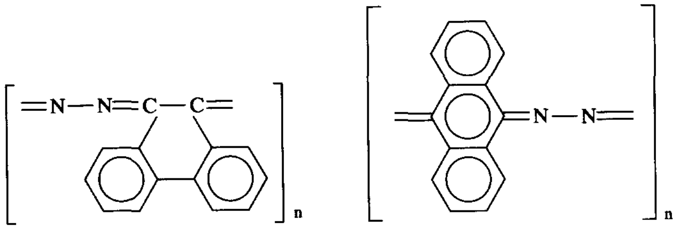
Polycondensation of diketones can also be carried out with N,N'-dithionylhydrazine in the presence of a catalyst.[103,105–109]



$$\mathrm{nO{=}S{=}N{-}N{=}S{=}O} + \mathrm{nO{=}C{-}C{=}O} \xrightarrow[-nSO_2]{} \left(\mathrm{{=}N{-}N{=}C{-}C{=}} \right)_n$$

SCHEME 11.

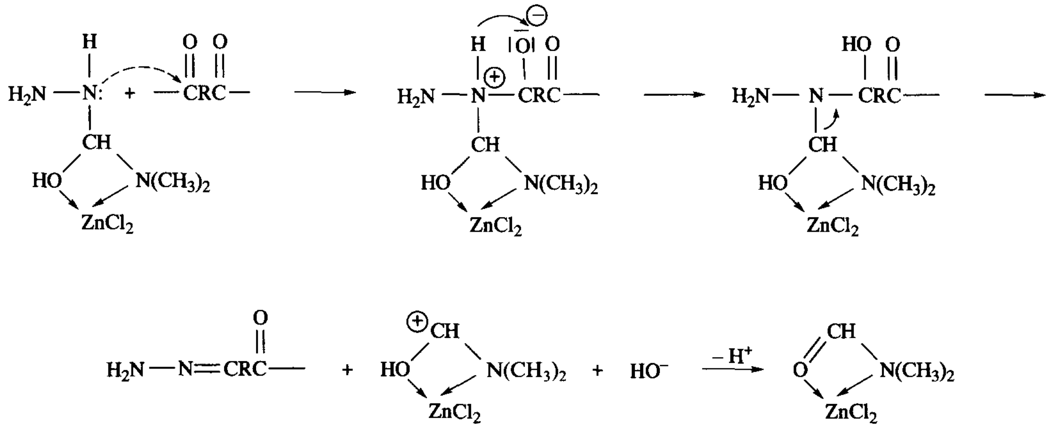
For example, polyphenanthrenequinone azines (PphQA) and polyanthraquinone azines (PaQA) have been prepared by this method.[110]



(PphQA) (PaQA)

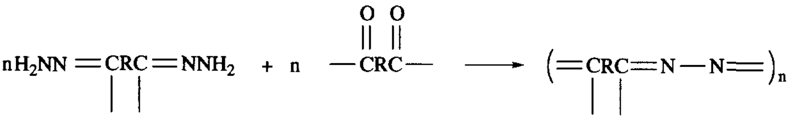
SCHEME 12.

Polycondensation of quinone with hydrazine hydrate in the presence of dimethylformamide as solvent, and $ZnCl_2$ as catalyst, is considered to proceed according to the following scheme[103]



SCHEME 13.

A dihydrazone thus formed undergoes polycondensation with the unconverted quinone and leads to the formation of polyazine

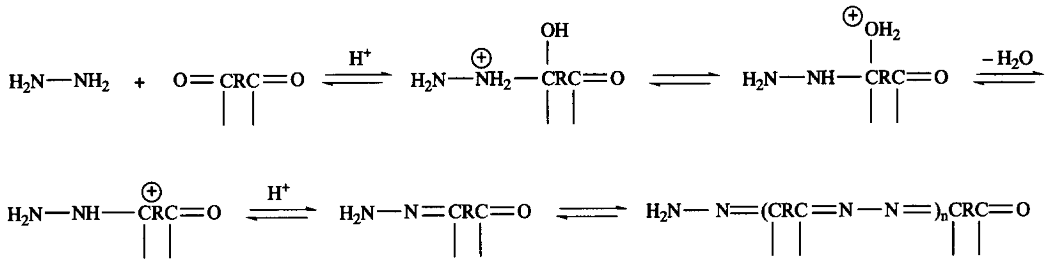


$$nH_2NN{=}\underset{|}{C}R\underset{|}{C}{=}NNH_2 + n\,-\overset{\overset{O}{\|}}{C}R\overset{\overset{O}{\|}}{C}- \longrightarrow \left({=}\underset{|}{C}R\underset{|}{C}{=}N{-}N{=}\right)_n$$

SCHEME 14.

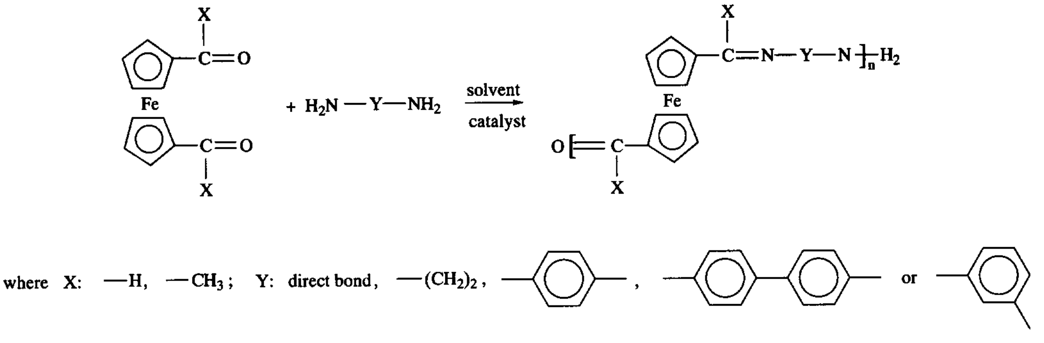
The polycondensation is also conceived to involve nucleophilic addition of hydrazine to the dicarbonyl component followed by the elimination of OH.[105] The initial nucleophilic addition to one of the carbonyl groups depends upon the electrophilicity of the carbonyl carbon which in turn is determined by the nature of the substituent and by the molecular symmetry (Scheme 15).

The general polycondensation reaction of 1, 1′-diacetyl ferrocene investigated using



SCHEME 15.

benzene as the solvent and *p*-toluenesulphonic acid monohydrate as the catalyst[107] is shown below:

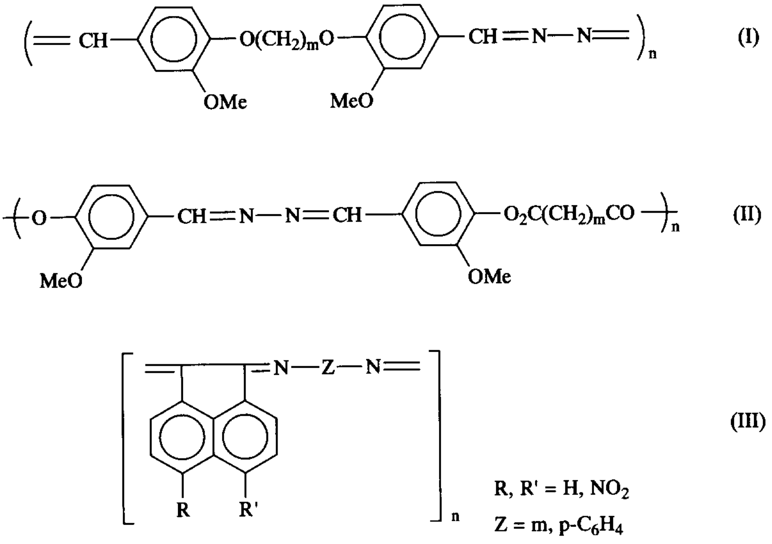


SCHEME 16.

Similarly, 2,4,6-tris(2-methoxy-4-formylphenoxy)-1,3,5-triazine, obtained by the interfacial polycondensation of vanillin with cyanuric chloride, condenses with hydrazine, forming polyazines.[111]

Polyazines obtained from compounds like *p*-diacetylbenzene, 4,4′-diacetylbiphenyl, etc., by using hydrazine hydrate or dithionylhydrazine, are without any branching and are terminated by carbonyl and amine groups.[105–108] Factors like temperature, reactant concentration and pH influence their formation. Increase in temperature and concentration of the reactants increases the yield and MW. However, a low molecular weight polymer is formed by polycondensation in HCl solution.[105] Since condensation is reversible, the presence of excess hydrazine in the mixture has some implication in determining the kind of terminal groups, MW and degradation pattern. In fact, increase in the MW induces resistance of the polyazine to hydrazinolysis.[105,108]

The thermal stabilities of polyazines containing ether (I) or ester (II) groups in the backbone have been determined. The azines have been found to be somewhat less stable compared to the polyazomethines (III).[102,106,112,113] Polyazines decompose around 260–300°C with rapid nitrogen elimination, followed by the formation of stable polyenes like stilbene units in the chain which decompose subsequently.[106,113] Polyazines of the derivatives of ferrocene decompose in the range 235–280°C, probably with the formation of a cyclic dimer.[107] Polymers prepared from hydrazine or disulphinyl hydrazine are less stable as compared to those obtained from aromatic amines; thermal degradative kinetics and calorimetric data have also been deter-



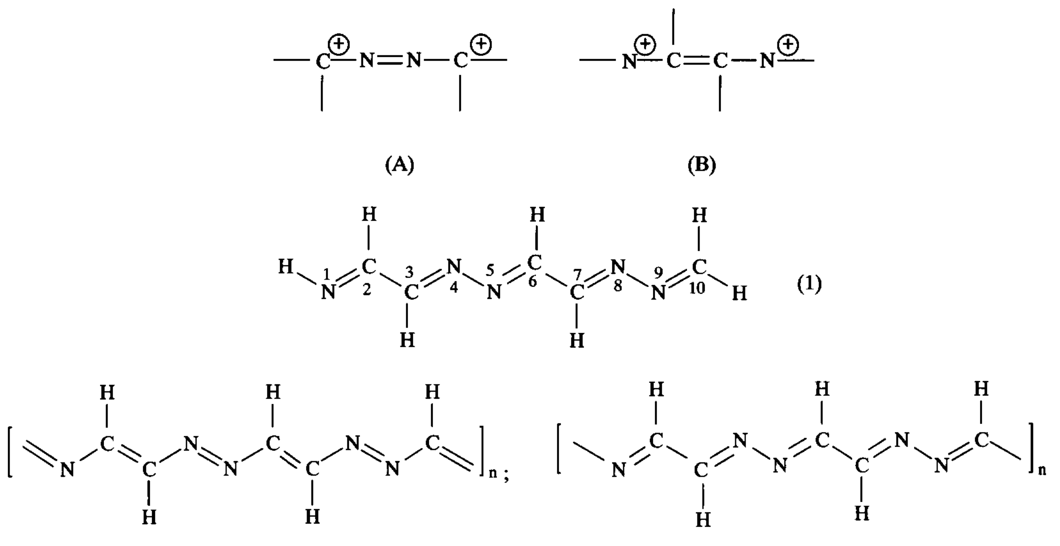
SCHEME 17.

mined.[84] Activation energy and order for the decomposition reaction have been reported.[113]

4.1. *Electrically conducting polyazines*

Synthesis, structural characteristics and chemical properties of electrically conducting polyazines have been studied.[114] Poly(phthalazine) prepared by anodic oxidation in acetonitrile solution containing Bu_4NBF_4, Bu_4NAsF_6 or $Et_4NPhMeSO_3$ exhibits electrical conductivity and has a fibrillar structure in the oxidized form. The effect of temperature on the electrical conductivity has also been determined.[115] Electrochemical impedance spectroscopy of the double layer capacitance and of the reactive resistance reveals certain kinetic parameters characteristic of the conjugated doped polymers containing heteroatoms. These are influenced by the physical and chemical structure of the polymers.[116]

Polyazine and permethylpolyazine, $(-N{=}C(CH_3){-}C(CH_3){=}N-)_n$, upon oxidative iodine doping, form nitrenium ion based bipolarons (dications) rather than polarons (radical cations) and the material becomes diamagnetic.[117] The two possible bipolaronic charge carrier structures, viz. carbenium ion (**A**) or nitrenium ion (**B**), are shown below. The presence of nitrenium is seen from ^{13}C and ^{15}N NMR chemical shifts, even though **A** ions are generally considered more stable than **B** ions. The presence of **B** implies oxidation of the more electronegative nitrogen in the polyazine, whereas the less electronegative carbon would be the preferred site of oxidation. In order to test the relative stabilities of **A** vs **B** in polyazine systems, quantum mechanical (semi-empirical and *ab initio*) calculations have been performed on oligomeric model compounds, such as the all *trans*-1,4,5,8,9-penta-aza-1,3,5,7,9-decapentaene (**1**); the calculations indicate that neither bipolarons nor nitrenium ions are formed upon oxidation. Therefore, in polyazines and similar polymers, the neutral polymer is envisioned to exist in two states, C and D, which are not degenerate, unlike in *trans*-polyacetylene, where these states are degenerate, leading to solitonic defects.

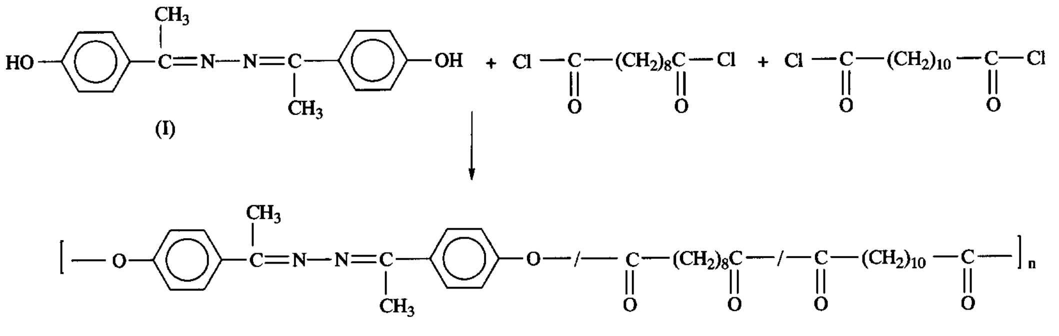


SCHEMES 18, 19 and 20.

4.2. *Liquid crystalline polyazines*

Thermotropic mesomorphism, known in simple organic compounds, has come to be known in polymeric liquid crystals as well, e.g. in liquid crystalline polyazines.[53] Thermotropic liquid crystalline polyazines containing mesogenic segments and flexible spacers in the main chain have been obtained.[54,118,119] The liquid crystalline poly(azine ether)s are of interest because of their thermal stability, especially their non-susceptibility to the thermally induced *trans*-esterification reaction in the melt, predominant in liquid crystalline polyesters.[120]

It has been observed[53,121] that semiflexible polyesters containing the 4-hydroxyacetophenone azine (I) mesogen, obtained via an interfacial polycondensation method, exhibit thermotropic nematic phase behaviour and have relatively low transition temperatures. However, the method does not yield polymer of sufficient molecular weight. Since the polymer is soluble in chlorinated solvents like chloroform, synthesis via a solution polycondensation route, shown in the scheme, has been attempted for obtaining polymer of controlled MW. The mesogen (I) is obtained by refluxing in ethanolic solution of hydrazine monohydrate and 4-hydroxyacetophenone in 0.45 : 1 mole ratio with a catalytic amount of HCl. The incorporation of



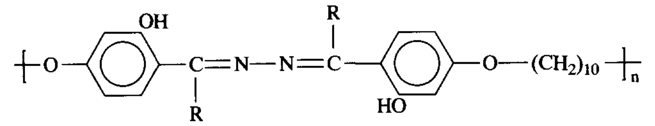
SCHEME 21.

different aliphatic spacers alters the melting temperature; significant decrease is observed for a 50 : 50 mole ratio of two different spacers, namely HOOC-$(CH_2)_8$-COOH and HOOC-$(CH_2)_{10}$-COOH.[122]

By varying the conditions of polymerization, attempts have been made to obtain polymers of sufficiently high MW.[53] When pyridine is used as an acid acceptor in large excess, dissolution of the mesogen diol (I) into a homogeneous solution is facilitated. However, a low MW polymer results and exhibits $MW/M_n > 3$ (this value otherwise is between 2 and 3). Although it is not clear why the pyridine-based system fails to yield high MW polymer, it is conceived that such could be due to some decomposition of the acid chloride during slow addition. Increasing the reaction temperature to 60°C does not improve the molecular weight significantly, although the polymer remains in solution throughout the polycondensation. However, a high MW polymer results upon scaling the reaction down to 20 mmol at 60°C. Immediate and efficient polymerization is observed when the acid chloride is added relatively quickly to Et_3N acid acceptor, with small amounts of *N*-methyl-2-pyrrolidone (NMP) to dissolve the diol; the solution becomes highly viscous and the product precipitates out. Addition of 4 mol% excess of the acid chloride mixture, surprisingly, results in relatively high MW polymer.

The first heating DSC curve of most of the poly(azine ether)s[53] with no indication of any glass transition temperature (T_g) suggests that they are highly crystalline. This higher degree of crystallinity of the polymers is presumably responsible for their poor solubility. A T_g of 25°C is observed only when the sample is heated a second time and cooled. Of the two endotherms which appear between 150 and 160°C, no significant change occurs with the first endotherm. Although its nature is not fully understood yet, it is attributed to crystal–crystal solid state polymorphism. The second endotherm (attributed to a crystal–nematic transition) and a nematic–isotropic transition which occurs at 250°C, are confirmed by hot stage microscopy. Although MW does influence these transitions, T_g of the polymer did not change appreciably with MW. The polymer possesses relatively good thermal stability, with the onset of thermal degradation occurring around 350°C. Less than 2% weight loss occurs upon heat treatment (> 1 h, 250–260°C) while the MW of the polymer decreases by less than 10%.

Several new mesogenic thermotropic poly(azine ether)s with the following structure are derived from substituted benzalazines[120,123]

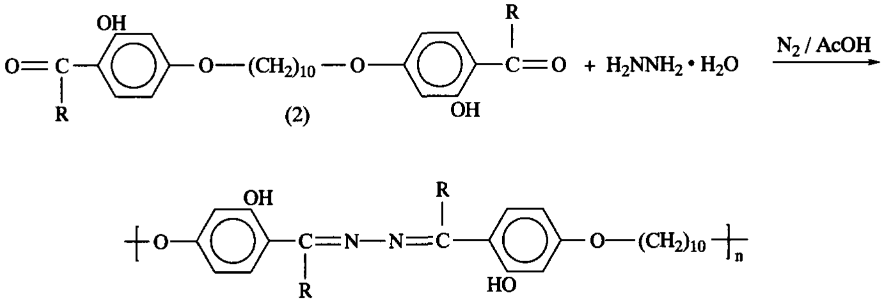


(1)

where R = H or $-CH_3$.

SCHEME 22.

mainly by polycondensation of mesogenic diphenols with α,ω-dibromoalkanes using phase transfer catalysts (PTC). Experiments have been carried out using monomers such as 2,4-dihydroxybenzaldehyde azine or 2,4-dihydroxyacetophenone azine and dibromodecane.[124,125] The method has been found to be unsuitable because the hydroxyl group in the *ortho*-position to the azine group is conceived to form a strong hydrogen bond with the nearest N atom of the central core, rendering it less active than the hydroxyl group in the 4-position.[123] In order to overcome this difficulty, solution polymerization of monomers (2) with hydrazine hydrate has been chosen as an alternative method which allows the formation of mesogenic units during the polymerization process.



where R = H or $-CH_3$.

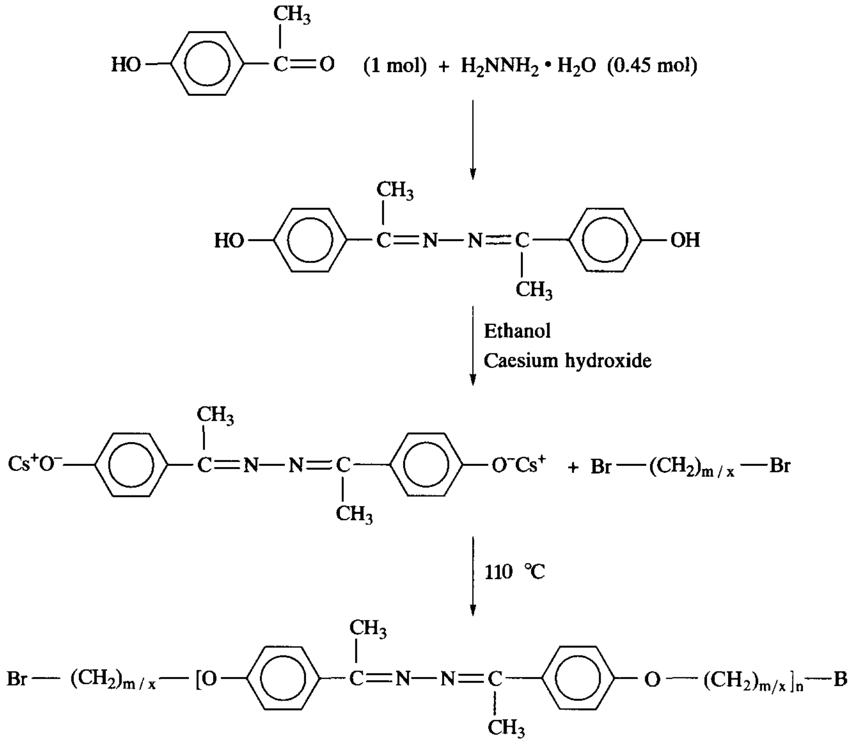
Scheme 23.

The solvent used in the polymerization process has a significant role and is important in that it must be miscible with hydrazine hydrate, dissolve the monomer and allow favourable reaction conditions, and the polymer must not precipitate with time. Ethanol and acetonitrile, having strongly polar character and high dielectric constants, are suitable solvents and serve to stabilize the carbocation which is an intermediate in the solvation reaction. The yield of polymer **1** ($R = H$) is 80–90% in ethanol and acetonitrile while it is 40–50% in 1,2-dimethoxyethane and DMF. The polymer **1** ($R = CH_3$) has a maximum yield of 40 to 50% in 1,4-dioxane and ethanol; in all other solvents a yield of about 20% is observed.[120]

All poly(azine ether)s show anisotropic properties except the ketone based polyazines synthesized in acetonitrile. The mesophases of all these polymers appear to be nematic by microscopy. Below the melting point there are often DSC peaks attributed to solid–solid transitions. The small weight loss is attributed to a loss of the terminal groups ($-C{=}N-NH_2$) and this explanation has enabled a determination of degree of polymerization (to be between 5 and 10) from DTG data.[120,123] Polyether **1** ($R{=}CH_3$), exceptionally exhibits different degrees of weight loss between 151 and 326°C without showing mesogenic properties.[120]

Recently, liquid crystalline poly(azine ether)s of sufficiently high MW have been synthesized more directly by Williamson polyetherification of diphenols from 4-hydroxyacetophenoneazine and 1,10-dibromodecane using liquid–liquid phase transfer catalysis (PTC). This procedure has been successful in polyether synthesis and is now a method of choice as a result of the limited solubility of the liquid crystalline polyether in the dipolar aprotic solvents employed in classical polyetherification.[126]

The direct procedure of preparing high MW polyesters by a heterogeneous route using dicarboxylate salts and dihaloalkanes has now been extended to prepare several polyethers and copolyethers of 4-hydroxyacetophenone azine with a homologous series of aliphatic flexible spacers, as shown in the following reaction scheme, which is a relatively simple and facile route.[127,128] Polymerization is effective at various reaction temperatures and the polymer solubility yields some control over MW. Thus, by varying the reaction temperature, and owing to the limited solubility of the polymer in NMP, polymers of different MW with well defined end groups have been prepared. Most of these reactions have been carried out at 110°C. ^{1}H NMR spectra, besides indicating the degree of polymerization in most polymers is above 60, suggest the predominance of alkyl bromide end groups. Polyethers containing a homologous series of flexible spacers had fibre forming capability. The effect of spacer lengths on the solubility and MW of the polyethers has also been studied.



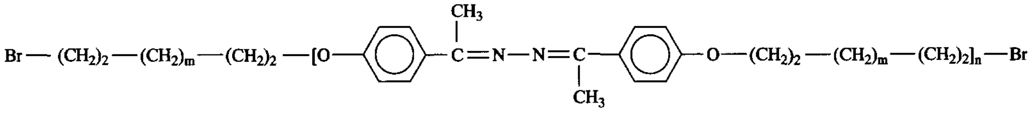
(Williamson etherification)

where $m/x = 5 - 12(1a - 1h)$.

SCHEME 24.

Copolyesters and copolyethers generally have lower melting temperatures than the corresponding homopolymers. The largest depression in the melting point is often achieved with an equimolar ratio of the two units. The copolymers, like the homopolymers, also have primarily electrophilic chain ends and contain a negligible quantity of caesium. Yields of both polyether and copolyether are about 94%, while MW of the copolyethers is higher than that of the homopolymers, increasing with the spacer length. Copolymers with spacers with odd numbers of carbon atoms have higher degrees of polymerization than those with spacers with even carbon atom numbers, thereby reflecting the higher solubility of the odd member combinations in the reaction medium.[127]

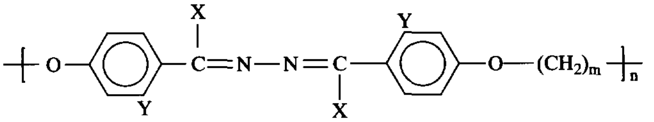
All of the above polyethers form anisotropic melts when cooled from the isotropic state during fibre spinning. Polyethers **1a** to **1d** ($m = 5$–8) which melt have no clear mesophase texture. However, a nematic threaded texture with considerable flow is observed for each of the polyethers synthesized in acetonitrile. Polyethers **1e** to **1g** have no distinct texture and become isotropic at T_m. The thermal transitions, including T_g, depend on the size of the flexible spacer, showing the classical even–odd behaviour. As in homopolymers, copolymers have also shown multiple endotherms during the DSC initial scan with no significant T_g, suggestive of their high crystallinity. All copolyethers are enantiotropic, showing anisotropy during both the heating and cooling scans. Copolyether **2e** with $m = 10$ exhibits monotropic mesomorphism. The mesophases, identified by microscopy, are found to be nematic.[127]



(2e)

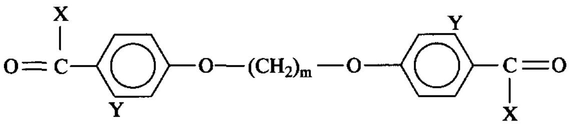
SCHEME 25.

Recently, four new mesomorpic poly(azine ether) series of thermotropic main chain liquid crystalline polymers with mesogenic units and flexible spacers connected by ether groups have been derived[54] from 4,4′-dihydroxybenzalazine, 4,4′-dihydroxy-α,α'-dimethylbenzalazine, 2,2′,4,4′-tetrahydroxybenzalazine, and 2,2′,4,4′-tetrahydroxy-α,α'-dimethlbenzalazine. Polymers in series I and II are prepared by PTC polycondensation while polymers in series III and IV can be synthesized by solution polymerization of monomers (A) with hydrazine hydrate. Characterization of their phase behaviour has been carried out by DSC and polarized light microscopy. When T_ms are below the decomposition temperature, polyethers in series I, II and IV, with the exception of $m = 6$, exhibit liquid crystalline behaviour whereas compositions in series III do not show mesomorphism. The mesophases of all these polymers appear to be nematic.[54]



where $m = 6, 8, 10, 12$; X, Y = H, H (I); X, Y = CH_3, H (II); X, Y = H, OH (III) and X, Y = CH_3, OH (IV).

SCHEME 26.



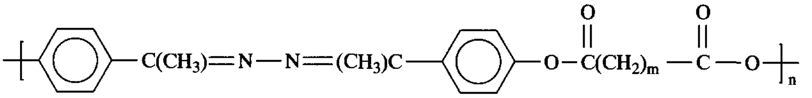
(A)

where $m = 6, 8, 10, 12$; X, Y = H, H (M-I); X, Y = CH_3, H (M-II); X, Y = H, OH (M-III); X, Y = CH_3, OH (M-IV).

SCHEME 27.

Rapid quenching of the molten polymers, preformed, does not induce any room temperature liquid crystalline properties due to the occurrence of crystallites, and therefore attempts have been made to synthesize polymers showing mesomorphic properties at room temperature either directly or after suitable modification.[128,129]

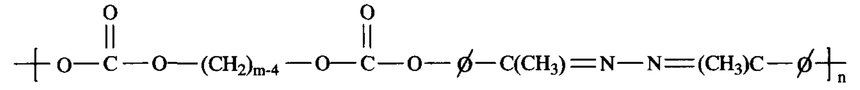
For example, polyaklanoates of 4,4′-dihydroxy-α,α′-dimethylbenzalazine exhibit thermotropic liquid crystalline behaviour. Disorder along the polymer chain is introduced by polymerizing 4,4′-dihydroxy-α,α′-dimethylbenzalazine with octanedioyl chloride and dodecanedioyl chloride in various molar proportions, such that the polymer becomes liquid crystalline at room temperature. Copolymers with the following formula, have been obtained by the reaction of 4,4′-dihydroxy-α,α′-dimethyl-benzalazine in alkaline solution with the appropriate mixtures of the diacylchlorides, following the procedure already described. The copolymer containing the two diacyl units in equimolar amounts turns out to be largely mesophasic at room temperature, after quenching. T_ms of the polymers range between 127 and 201°C.[129]



where $m = 6$ (75%), 10 (25%); 6 (50%), 10 (50%); 6 (25%), 10 (75%).

SCHEME 28.

Polymers having in the main chain alternating, rigid, highly conjugated aromatic groups and flexible aliphatic portions, which exhibit mesophasic properties, are reported.[130,131] In order to elucidate the influence of the relative lengths of the rigid conjugated units and the aliphatic spacers on the mesophasic properties, small changes in chain composition (i.e. change of groups to $O–C(O)–CH_2–$ in place of $O–C(O)–O$) have been studied and relationships have been established between the liquid crystalline behaviour of polymers and that of analogous low MW compounds. Polymers with the following structure have then been synthesized.[131] These semi-crystalline polycarbonates, which exhibit polymorphic behaviour both in the solid and in the liquid state, are prepared by the reaction of 4,4′-dihydroxy-α,α′-dimethylbenzalazine in alkaline aqueous solution with the appropriate bischloroformate, $Cl–C(O)–O–(CH_2)_{m-4}–O–C(O)–Cl$, in chloroform.



$$\left[O-\overset{\overset{O}{\|}}{C}-O-(CH_2)_{m-4}-O-\overset{\overset{O}{\|}}{C}-O-\emptyset-C(CH_3)=N-N=(CH_3)C-\emptyset\right]_n$$

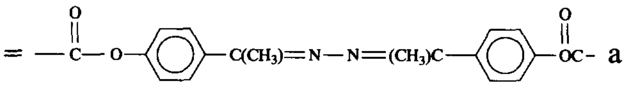
where $m = 10, 12, 14, 16$.

SCHEME 29.

The peculiar enantiotropic smectic behaviour of a class of azine copolymers with a nonperiodic structure has been described recently.[132,133]

$$\left[\left(\left(O-CH_2-CH_2\right)_2-OR\right)_m-\left(\left(O-CH_2-CH_2\right)_3-OR\right)_p\right]_n$$

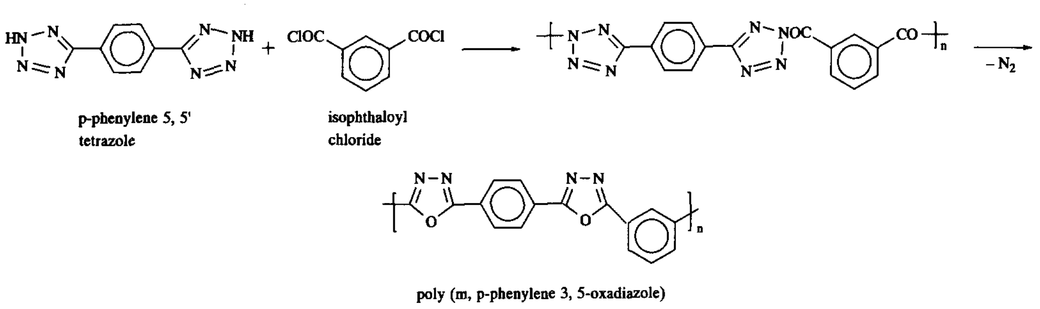
SCHEME 30.

Here R =  and m = 100−p = mole fraction × 100; p is in a random distribution, which may be compatible with the formula of a structurally periodic phase with no apparent segregation of homopolymer domains.[133] Mesogenic properties of this copolymer with m = 0 and 100 have been studied by DSC and XRD. Enantiotropic smectic mesomorphism is observed.[133]

The mesophasic behaviour of the polycarbonates[131] is clearly indicated by thermal analysis. The low temperature endotherm has been attributed to the melting of the semi-crystalline polymers. Its position decreases with increasing spacer length from 207 to 167°C. The high temperature endotherm corresponds to the isotropization of the mesophase. Its position also decreases from 257 to 197°C. XRD spectra of the liquid crystalline phases identify a nematic structure.

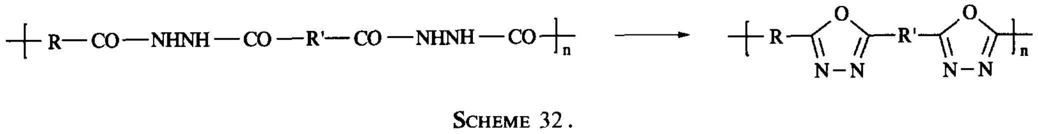
5. POLYOXADIAZOLES

Nitrogen-containing heterocyclic polymers are of practical importance on account of their high heat resistance and thermal stability.[134–136] These have been prepared by various methods. Preparative methods of a number of these polymers are given.[137] The generalized reaction for polyoxadiazole synthesis is as follows:



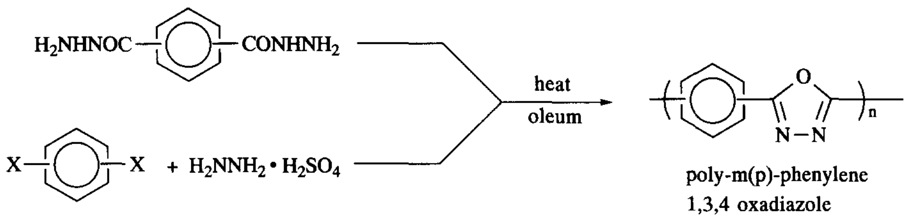
SCHEME 31.

The dihydrazides of adipic acid, azelaic acid and sebacic acid, when added to fuming sulphuric acid, give poly(aliphatic 1,3,4-oxadiazole)s. Similarly, addition of the aliphatic dihydrazine derivatives to isophthalic acid in fuming sulphuric acid gives polyoxadiazoles with alternating polymethylene and *m*-phenylene spacers.[138–140]



SCHEME 32.

Polycondensation of benzenedicarboxylic acids or their simple derivatives with hydrazine sulphate using a condensing agent forms poly(phenylene 1,3,4-oxadiazole)s.[139,141] The MW of poly(phenylene−1,3,4-oxadiazole) is controlled by varying oleum concentrations from 10 to 50%. The presence of an increased amount of oleum, beyond the required concentration, increases the viscosity of the polymer.[142] The mechanism of polymerization of hydrazine with benzenedicarboxylic acids in oleum has been examined; condensation of functional end groups of the oligomeric poly(1,3,4-oxadiazole) constitutes the first stage.[143] Polyoxadiazoles react further



where X = –COOH, –CONH$_2$, or –CN.

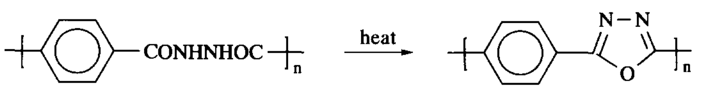
SCHEME 33.

with an alkyl sulphate containing < 4 carbon atoms in a medium containing > 80% sulphuric acid and form modified polymers.[144]

High strength and high modulus fibres, namely, poly-*p*,*p*′-terephthaloyl-*N*-methylhydrazide-co-1,3,4-oxadiazoles are prepared by high temperature polycondensation of terephthalic acid or dimethyl terephthalate with hydrazine and/or methylhydrazine sulphate in the presence of oleum.[145] The polymer formed is readily processed from sulphuric acid solutions. It is supposed that the polycondensation process is multistage and is associated with the various chemical conversions occurring under high temperature polycondensation and during extrusion of the reaction spinning solution into the coagulating medium. NMR studies reveal that the process involves several stages during the polycondensation, including saponification of dimethyl terephthalate and formation of oligo-1,3,4-oxadiazoles with reactive COOH and hydrazine end groups. These are followed by cyclocondensation, methylation of 1,3,4-oxadiazole fragments of the macromolecules with methyl hydrogen sulphate formed during the saponification and formation of *N*-methyl hydrazide fragments, and opening of the 1,3,4-*N*-methyloxadiazole ring during the precipitation of the polymer in aqueous sulphuric acid.[146] Therefore, it is realized that obtaining copolymers of a desired structure with a specific ratio of *N*-methyl hydrazide and 1,3,4-oxadiazole groups is linked with the nature and sequence of these conversions.

Polyoxadiazoles are also prepared by high temperature polymerization of dicarboxylic acids with dihydrazides in polyphosphoric acid. Polymers prepared in solution have the lowest heterogeneity. However, structural heterogeneity could be introduced in the formation of the polymer chain as well as in the cyclization steps.[147]

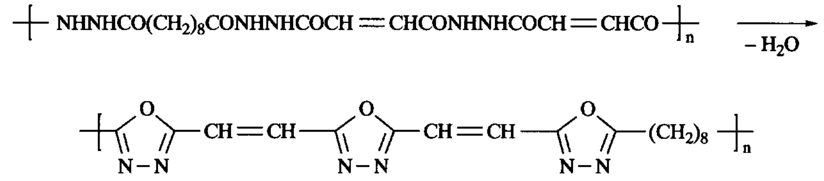
Yet another method of preparing polyoxadiazoles is by heating polyhydrazides. The cyclodehydration reaction[138–140] is represented as



SCHEME 34.

Poly(2,5-octamethylene-1,3,4-oxadiazole) and poly(vinylene-1,3,4oxadiazole) have been obtained by the cyclodehydration of sebacic acid polyhydrazide and *N*,*N*′-bis(isomaleimide) polyhydrazide respectively (Scheme 35).[148]

The thermodynamic behaviour of the polymer during the cyclodehydration process has been recognized to be very important. Analysis of thermodynamic data reveals that the physical state of the prepolymer is a dominant factor in the reaction. From the temperature dependence of the heat capacity of prepolymers and polyheteroarylenes (cyclized product) and the saturated water vapour pressure that prevails over the prepolymer during cyclization, the temperature range of the occurrence of the cyclo-

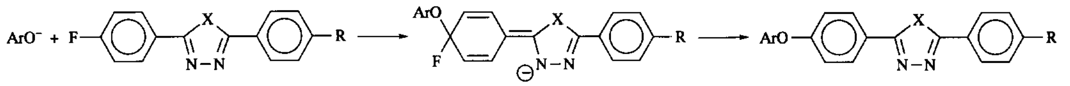


SCHEME 35.

dehydration process has been predicted. Furthermore, the degree of polymerization has been computed from the heats of combustion and cyclization of the prepolymers. This study has been useful in the synthesis of defect free, heat-resistant polyheteroarylenes by optimizing the temperature of cyclization.[149]

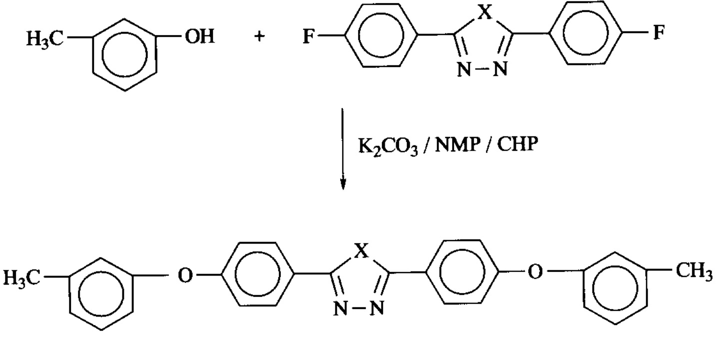
Thermal analysis data show that in hydrazine-isophthalic acid–terephthalic acid copolymer films and fibres, weight loss occurs with exothermic degradation between 470 and 520°C, depending upon polymer composition and is related to the degradation and conversion of the oxadiazole ring.[150] Thermogravimetric data indicate only minor weight loss below 450°C in air, but rapid weight loss occurs beyond that temperature for poly(*m*,*p*-phenylene-1,3,4-oxadiazole).[139] No change in their properties occurs up to about 200°C, and the polymer retains 60% or better of room temperature properties even at 300°C. There is little variation in thermal stability with increase in the MW of the polymer.[137] Poly(aliphatic 1,3,4-oxadiazoles) show abrupt weight loss $>380°C$.[151,152] The decomposition products of poly(1,3,4-oxidiazoles) containing carborane rings have been identified to consist of oligomers, benzene, PhCN, CO, CO_2, N_2, H_2, CH_4 and other volatile products.[153]

An activated halide displacement polymerization method has also been used to synthesize polyoxadiazoles. As in poly(aryl ether)s, generally prepared via the nucleophilic aromatic substitution of an activated aromatic dihalide with a bisphenoxide anion,[154–156] certain heterocycles can function as activating groups in these types of reactions.[157] The heterocyclic group, as assessed by ^1H NMR, seems to be an electron withdrawing group which stabilizes the negative charge developed through the formation of a stabilized intermediate (Meisenheimer complex) during the transformation to lower the activation energy for the process, as follows:



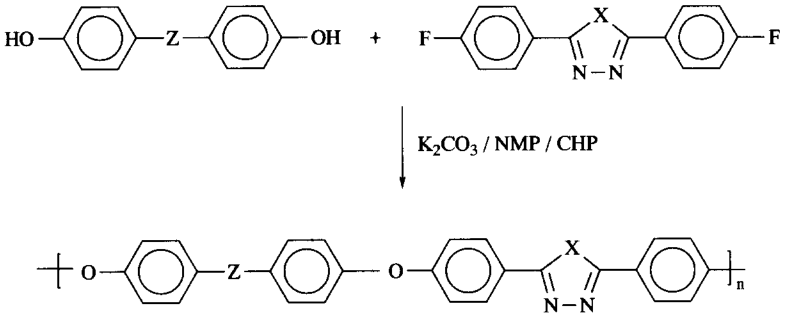
Meisenheimer Complex
SCHEME 36.

Several new polymers containing oxadiazole and triazole heterocyclic units have been synthesized from difluoro monomers in which the heterocycle functions as an activating group in the polymer-forming nucleophilic substitution reaction. Through the activated halide displacement polymerization process, oxadiazole and triazole heterocyclic rings have been incorporated in the backbone. The rationale and the feasibility of the oxadiazole/triazole activation and the suitability of halide displacement reactions as polymer forming reactions are also demonstrated by the model reactions of a monophenoxide derivative with both oxadiazoles and triazoles which lead to the expected products, shown below:[157]



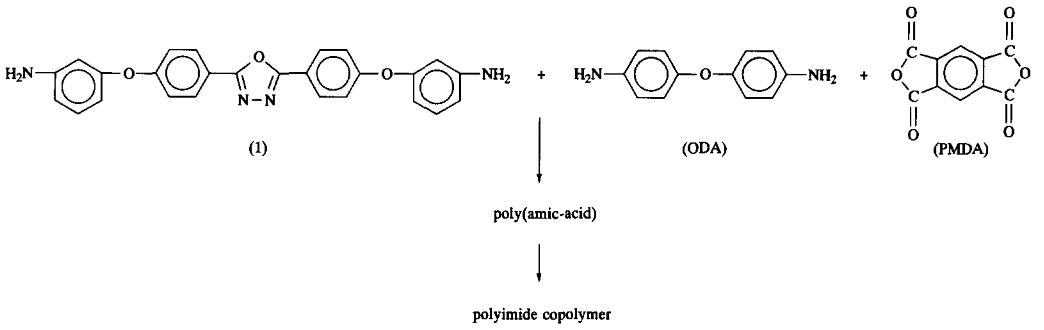
where X = O, N-ϕ and CHP is *N*-cyclohexyl-2-pyrrolidone.
SCHEME 37.

The polymerization of oxadiazole or triazole to high MW polymer is performed with the bisphenols and is shown in the following scheme:



where X = O, N ϕ ; Z = C(CH$_3$)$_2$, C(CF$_3$)$_2$.
SCHEME 38.

Rigid-rod high temperature polymers which have high modulus, low thermal expansion coefficient and exceptional thermal stability are less soluble than, and introduce processing difficulties unlike those of, the semi-rigid polyimides which are easily processed from solution. Combining the characteristics of both the rigid and semi-rigid structures in obtaining highly ordered materials, processable from a soluble precursor, is of importance.[158] In this regard, a number of imide copolymers with various heterocyclic systems, e.g. imide aryl ether oxadiazole, have been synthesized[159–162] by the heterocyclic activation of halides towards nucleophilic aromatic substitution using the monomer, 2,5-bis(4-aminophenoxy)-1,3,4-oxadiazole (1). The imide aryl ether oxadiazole copolymer is prepared through the poly(amic-acid) precursor via the standard polyimide synthesis,[158] as shown below:



SCHEME 39.

Polymerization of (**1**) with pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (ODA) yields copolymers. The copolymer is prepared such that the composition or weight percent of oxadiazole (**1**) ranges from 25 to 70%, relative to the wt% of PMDA and ODA or the polyimide component.

A comparative thermal analysis study of these copolymers and the PMDA/ODA polyimide has been made to assess the thermal stability by isothermal ageing at 400°C, and also to find the polymer decomposition rates at different temperatures. Incorporation of the oxadiazole-containing diamine affects the ordering in the copolymers containing different weight percentages of oxadiazole units, and diminishes the thermal stability substantially, while the decomposition temperature is observed to be lower, in the range of 445–465°C, compared to that observed (480°C) for PMDA/ODA polyimide copolymers. With the inclusion of both *m*-phenylene and aryl ether linkages, the copolymers exhibit T_gs in the range of 300°C; accordingly a large drop in the modulus is observed as oxadiazole composition in the copolymer increases.

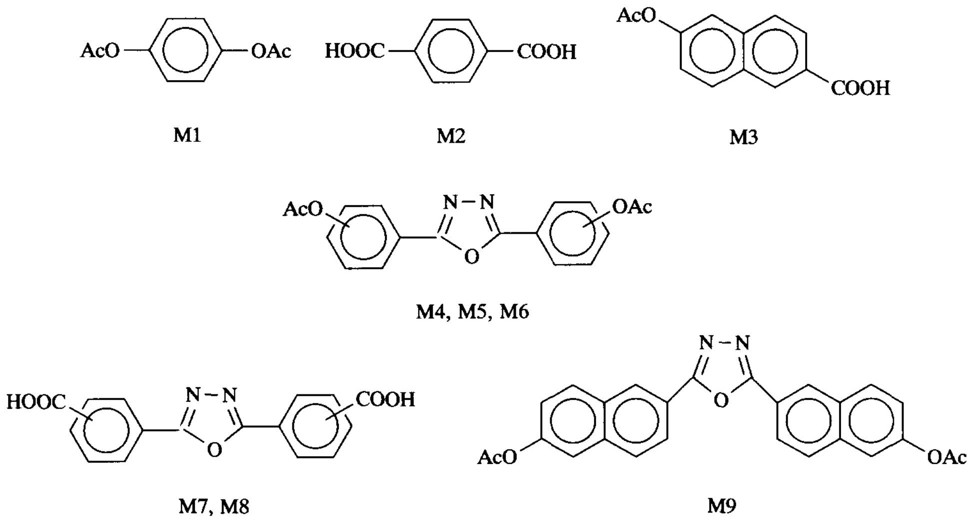
Crosslinkable heterocyclic polymers have been prepared by the polycondensation of tetracarboxylic anhydrides with diamines and treatment of the poly(amido acids) formed with unsaturated dicarboxylic anhydrides. The product possessed improved chemical resistance when the diamine monomers contained oxadiazole groups.[163]

5.1. *Liquid crystalline polyoxadiazoles*

It has already been mentioned that condensation polymers containing heterocyclic units and possessing outstanding strength and modulus are used predominantly as high temperature-resistant materials and fibres. It is interesting to note that in some instances heterocyclic units act as mesogenic moieties in polymers and impart liquid crystalline properties. Heterocyclic liquid crystalline polymers are highly desired for obtaining fibre of high tenacity and initial modulus because of the high orientation of the liquid crystalline lyotropic and thermotropic phases. Several heterocyclic polymers, such as aromatic polyesters containing rigid rod-like segments, form liquid crystalline solutions. Concentrated sulphuric acid solutions of poly(*p*-phenylene-1,3,4-oxadiazole) exhibit liquid crystalline properties, transition temperatures and optical anisotropy. Although some polymers yield lyotropic solutions, the solutions formed from poly(1,4-phenylene-1,3,4-oxadiazole) in solvents other than sulphuric acid[55] have been a subject of controversy as to whether they are lyotropic or not.

Thermotropic aromatic polyesters containing heterocyclic units in the main chain have been prepared by the melt polymerization method[164] which proceeds by the *trans*-esterification and polycondensation of monomers, such as 2,5-bis(4-hydroxyphenyl)-1,3,4-oxadiazole with terephthalic acid, 2,6-naphthalenedicarboxylic acid and 4-hydroxybenzoic acid in the presence of an active catalyst, $Sb_2O_3Zn(OAc)_2$. Post-polycondensation *in vacuo* increases the polymer MW while reduction in residual pressure and increasing the temperature from 270 to 300°C, increase the polycondensation rate significantly. Thermotropic polymers offer processing advantages over lyotropic polymers in terms of both cost and the range of products that can be fabricated. Consequently, much of attention has been directed towards the preparation of a polymer which exhibits a liquid crystalline melt at a processable temperature and is stable over a broad temperature range.

Usually, a polymer with high T_m is modified by introducing some disorder or disruption into the chain in order that the melting point (500–700°C) gets reduced to a sufficiently processable temperature (<350°C).[165–167] In fact, the copolyester (P_R) prepared[167] from hydroquinone diacetate (**M1**), terephthalic acid (**M2**) and two equivalents of 6-acetoxy-2-naphthoic acid (**M3**), in the ratio 25:25:50, is chosen as a reference and represented as $P_R{:}(M1)_1(M2)_1(M3)_2$. The effect of introducing various types of disruption into the copolyester (P_R) by total or partial replacement of the monomers has been studied by Brydon *et al.*[167] Several new copolymers have been prepared from oxadiazole containing diacetates M4 (=4,4′-diacetoxy); M5(=3,3′-diacetoxy); M6 (=3,4′-diacetoxy) and dicarboxylic acids M7 = 4,4′-COOH, M8 = 3,3′-COOH:



SCHEMES 40 and 41.

The modified polymers containing different groups have been identified and examined for fibre formation from a liquid crystalline melt, and other useful properties. The polymers obtained by the replacement of M1 in P_R by an oxadiazole containing diacetate include,

$$P1: (M4)_1(M2)_1(M3)_2$$

$$P2: (M5)_1(M2)_1(M3)_2$$

$$P3: (M6)_1(M2)_1(M3)_2$$

$$P4: (M4)_1(M2)_1(M3)_1$$

$$P5: (M4)_1(M2)_1(M3)_3$$

$$P6: (M4)_1(M2)_1(M4)_2.$$

These polymers, however, are not fibrous, although P6 is hard and coherent. Partial replacement of M1 by the oxadiazole containing diacetate leads to

$$P7: (M1)_{0.25}(M4)_{0.75}(M2)_1(M3)_2$$

$$P8: (M1)_{0.50}(M4)_{0.50}(M2)_1(M3)_2$$

$$P9: (M1)_{0.75}(M4)_{0.25}(M2)_1(M3)_2.$$

All of these are tough, fibrous and similar in appearance to P1. Replacement of both M1 and M2 by oxadiazole containing units leads to

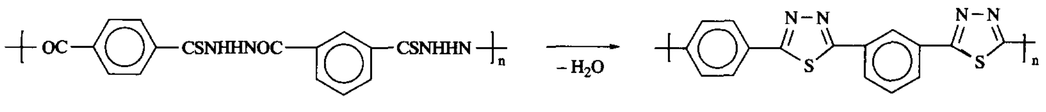
$$P10: (M4)_1(M7)_1(M3)_2$$

a polymer light in colour, hard, brittle and compact. Replacement of the M1 by the dinaphthyoxadiazole monomer M8 gives a polymer P11: $(M8)_1(M2)_1(M3)_2$, which has been studied in more detail. All of these polymers are soluble in trifluoroacetic acid/dichloromethane (30:70). Although all polymers had good thermal stability in air up to temperatures >400°C, their stability is less than that of the base polyester P_R as shown in TGA.

6. POLYTHIADIAZOLES

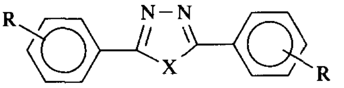
Polythiadiazoles are similar to polyoxadiazoles. A polythiadiazole has been prepared in the fibre form by cyclizing an aromatic polyoxathiahydrazine at 200–250°C (Scheme 42).[137]

Polythiadiazoles, MW ≈ 12000, containing units of structures shown below can be prepared from 1:1:1 molar mixtures of dialdehydes, hydrazine and sulphur.[168] Poly(*p*-



SCHEME 42.

phenylene-1,3,4-thiadiazole) has also been prepared by the polycondensation of dimethyltetrathioterephthalate with hydrazine in propylene carbonate.[169] Poly(azomethine) containing 1,3,4-thiadiazole rings in the backbone has been prepared by solution polycondensation of diamine (II) (R = 3-NH_2, 4-NH_2; X = O,S) with dialdehydes (III) (R = 3-CHO, 4-CHO; X = O,S). The thiadiazole-containing polyazomethines are highly crystalline as compared to those containing oxadiazole units. Wholly conjugated polymers are yellow powders, soluble in concentrated sulphuric acid and insoluble in common organic solvents.[170]



(II)

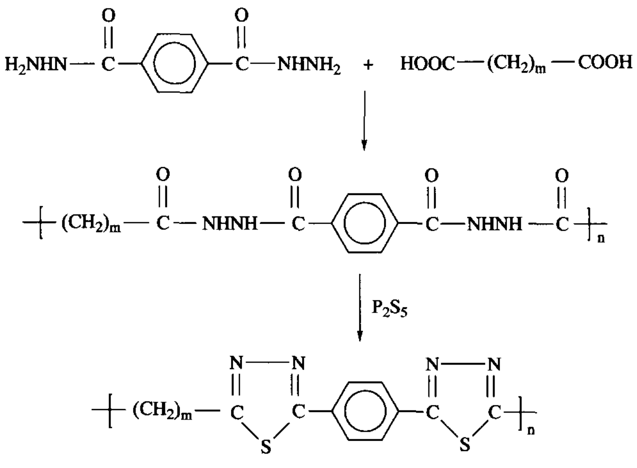
SCHEME 43.

Electrically conducting polymers containing 1,3,4-thiadiazole-2,5-diyl groups and also pyrrolediyl, thiophenediyl, furandiyl, phospholediyl, arsolediyl or stibolediyl groups are useful in antistatic packaging, sensors, mouldings, etc. 2,5-di-2-pyrrolyl-1,3,4-thiadiazole, obtained by condensing 2-pyrrolecarboxaldehyde with hydrazine hydrate and heating the resulting hydrazone with sulphur at 120°C, can be polymerized electrochemically in MeCN containing chloromethane and $PhSO_3H$ to a conducting polymer film.[171] In strong acids, the polymers are susceptible to hydrolysis and the solutions are electrically conducting. Doping with iodine leads to charge transfer complexes which show electrical conductivity owing to the extensive delocalization of H electrons along the polymer chain.[170]

Poly(thiadiazoles) decompose at temperatures $>220°C$.[170] The thermal properties of poly(*p*-phenylene-1,3,4 thiadiazoles) have been determined. They are stable at $<400°C$ in air and N_2. In fact thin films retain 92% of their original tenacity after ageing for 144 h at 300°C in both air and N_2.[137]

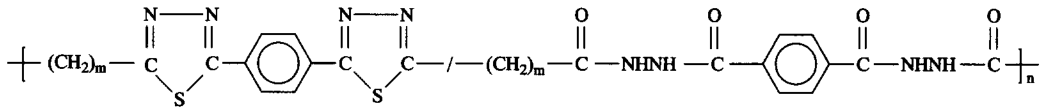
6.1. *Liquid crystalline polythiadiazoles*

A series of new thermotropic liquid crystalline polymers with 1,3,4-thiadiazole units

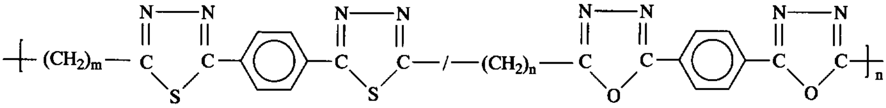


(1)

SCHEME 44a.



(2)



(3)

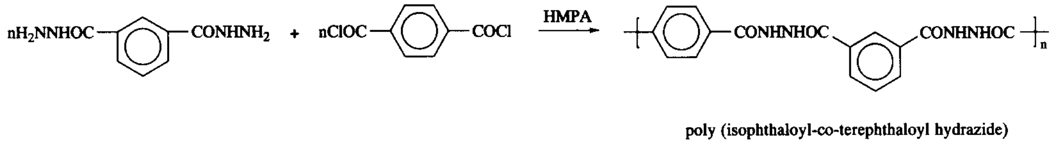
SCHEME 44b.

and aliphatic spacers in the main chain have been reported recently by Sato *et al.*[172] They are synthesized by the intramolecular cyclization of the precursor polyhydrazide with P_2S_5 in pyridine or a mixture of pyridine and NMP (pyridine/NMP volume ratio = 4:1) at 80 to 100°C; the precursor is prepared from terephthalcic dihydrazide and aliphatic dicarboxylic acids, as shown in the scheme. Polymer **1** is obtained without any scission of the backbone as shown by the viscosity which is almost the same as that of the precursor. IR and UV spectral data suggest that the intramolecular cyclization occurs incompletely owing to heterogeneous reactions and some unreacted hydrazide groups remain in the polymer chain, as shown in polymer **2**.

The DSC and DTA first heating scans of the above polymer, although not exhibiting a well defined T_g, show strong endothermic peaks in the range of 210 to 300°C. TGA shows a sluggish weight loss between 256 and 269°C followed by vigorous weight loss above 400°C. The weight loss at 210–300°C is attributed to the release of water from the unreacted hydrazide groups in the polymer chain accompanying cyclization, which is confirmed by the FTIR spectra before and after heating through the region containing the endothermic peaks. Upon heating, 1,3,4-oxadiazole rings are also formed in the backbone of polymer **3**, in addition to the thiadiazole rings. Second and third heating scans exhibit two endotherms at temperatures lower than the ones observed in the first scan. Polarizing microscopic observations suggest that the endotherms correspond to the melting (T_m) and isotropic phase (T_i) transitions. Both of these transitions decrease in temperature with increase in the spacer length. Between T_m and T_i, thiadiazole polymers form smectic phases.

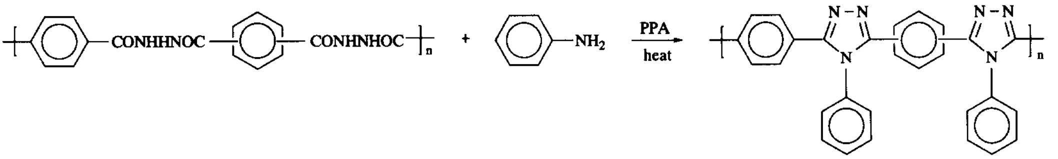
7. POLYTRIAZOLES

Linear poly(*m*,*p*-phenylene 4-phenyltriazoles) can be obtained by reacting aromatic diacid chlorides with isophthalic dihydrazide, using hexamethyl phosphoramide (HMPA) as a catalyst.[22,23,137,173–176]



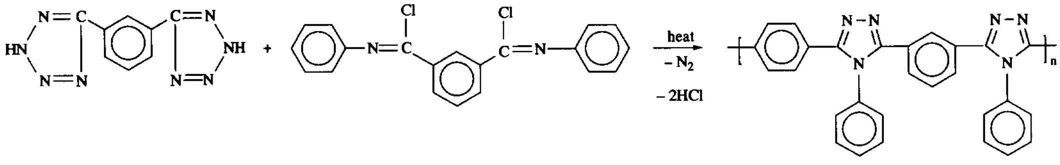
SCHEME 45.

The polyhydrazide formed is soluble and may be reacted in solution with aniline using phosphoric acid (PPA) as a catalyst under pressure to a low molecular weight, low viscosity polytriazole.[22]



SCHEME 46.

The reaction of bis(imide chlorides) with bistetrazoles affords the same polymer[174] and the reaction could be represented as follows,

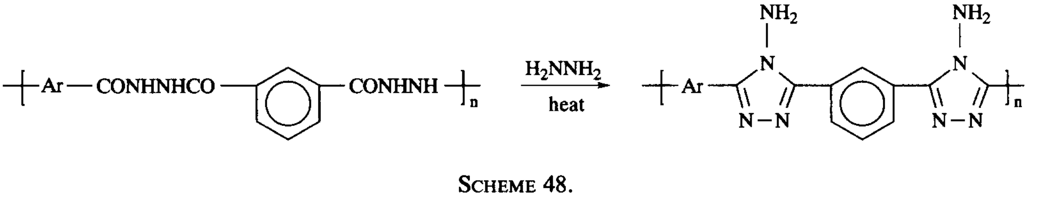


SCHEME 47.

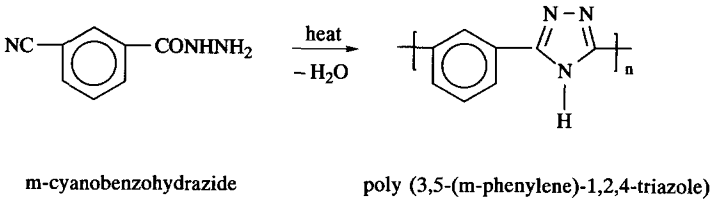
A more viscous polymer is obtained by the reaction between aromatic dihydrazide and hydrazine (Scheme 48).[173]

1,2,4-triazole polymers have been reported to form on treating nitriles with hydrazine in the presence of sulphur or sulphur compounds like mercaptoethanol, and subsequent heating. These can also be obtained directly by heating cyanobenzohydrazide (Scheme 49).[137, 177]

Similarly, poly(1,2,4-triazoles) have been prepared by the deamination of poly(4-amino-1,2,4-triazoles) with HNO_3.[173] Poly(4-amino-1,2,4-triazoles) suitable for casting purposes could be prepared by polycondensation of hydrazine and aliphatic



SCHEME 48.



Scheme 49.

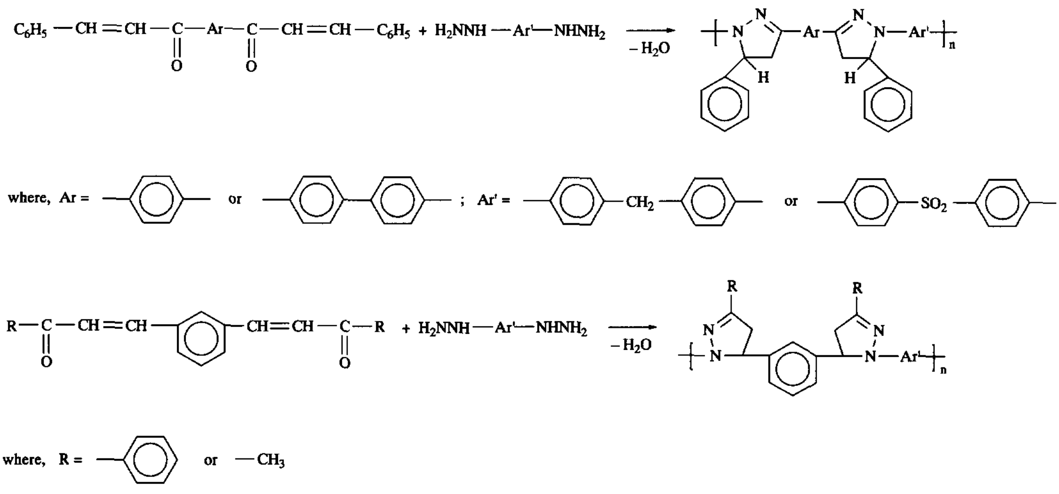
dicarboxylic acids or their esters.[176–179] This reaction is not accompanied by any exchange reactions leading to polyamide formation.[178,180]

Poly(3,5-(arylene)-1,2,4-triazoles) prepared by melt, solution and interfacial polycondensation are thermally stable.[181] The thermal stability of these polymers is enhanced to < 430°C by phenylation of the amino group.[22,23,173] The poly-(aminotriazoles) have melting points in the range of 150 to 340°C[175,176,179] and are not decomposed upon boiling with concentrated acids; the triazole nucleus is very stable to the hydrolytic action of the mineral acids.[182] Fibres from these types of polymers retain 30% of their room temperature strength at 300°C.[137] High nitrogen content polymers, with N/C ratio in the range 1 to 4.5 have been obtained by condensing formaldehyde and 4-amino-3,5-dihydrazino-1,2,4-triazole; they are stable, insensitive to impact and safe to handle, and are useful as binders in solid propellants.[183]

8. POLYPYRAZOLINES

Polypyrazolines have been synthesized from compounds containing two α,β-unsaturated carbonyl functions and aromatic dihydrazines. Much of the work has been carried out to synthesize thermally stable polyheterocycles, polyphthalazinones and polydihydropyridazinones.[184–187]

Pyrazolines are generally obtained by the reaction of α,β-unsaturated ketones with



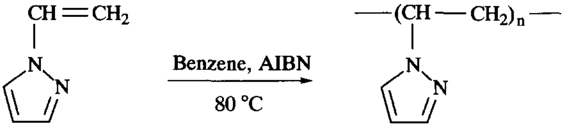
Scheme 50.

hydrazines.[188] By extension, polypyrazolines have been synthesized by reacting bifunctional intermediate compounds containing two α,β-unsaturated carbonyl functions with aromatic dihydrazines.

These polymers decompose exothermically between 200 and 280°C and have rather low thermal stability.[189]

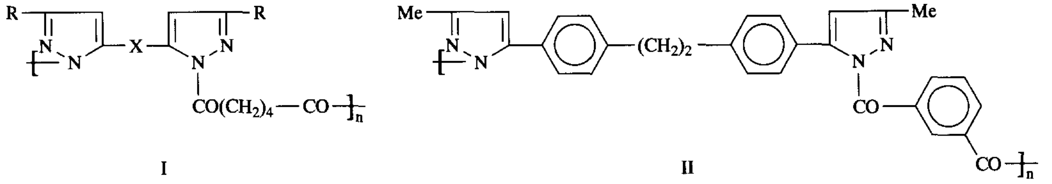
9. POLYPYRAZOLES

Synthesis, chemical and physicomechanical properties and potential uses of polymers containing pyrazole nuclei have been collated and reviewed.[190] Vinylpyrazoles are susceptible to polymerization on heating or distillation[191,192] and yield viscous liquid polymers.



SCHEME 51.

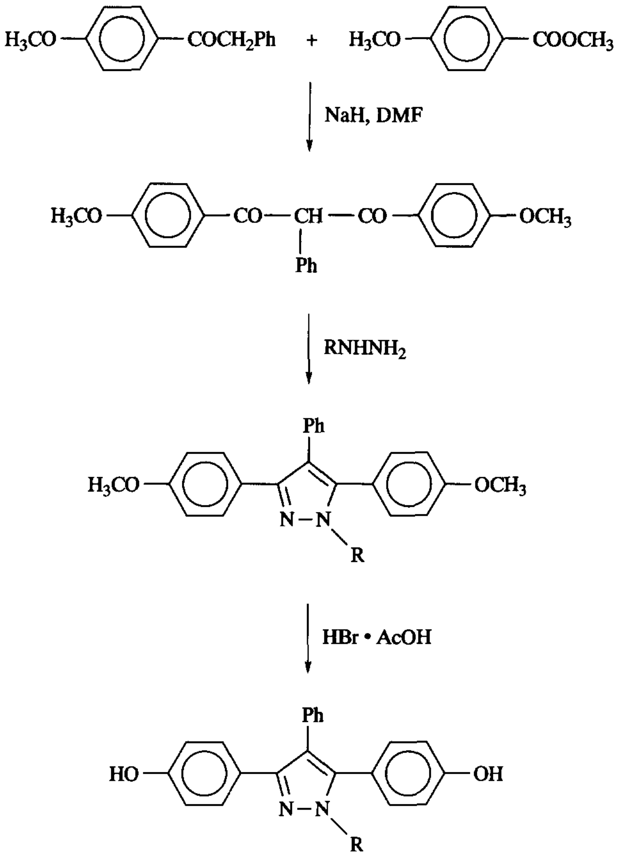
Polypyrazoles have also been obtained from polyhydrazones. For example, polypyrazoles I and II have been prepared by refluxing tetraketo compounds with dihydrazides of dicarboxylic acids to yield polyhydrazones which, upon heating, form relatively high melting point polypyrazoles.[193–196]



SCHEME 52.

The sodium enolates of aromatic bis-β-diketones, when condensed with the hydrochlorides of aromatic dihydrazides, form linear polymers which can be cyclized to polyazomethines containing aromatic units connected by $COCH_2C(R){=}NNH$ bridges. Chain extension coupled with cyclization of the bridging segments results upon further heating. Condensation then yields alternating aromatic and 1,5-pyrazole units.[196] Butadiene polymers obtained by oxidative coupling of 2-methyl-3-butyn-2-ol with glycerol α,β-diethyl ether or formal react with hydrazine hydrate to give polypyrazoles. These polypyrazoles are reported to be thermally stable polymers.[197]

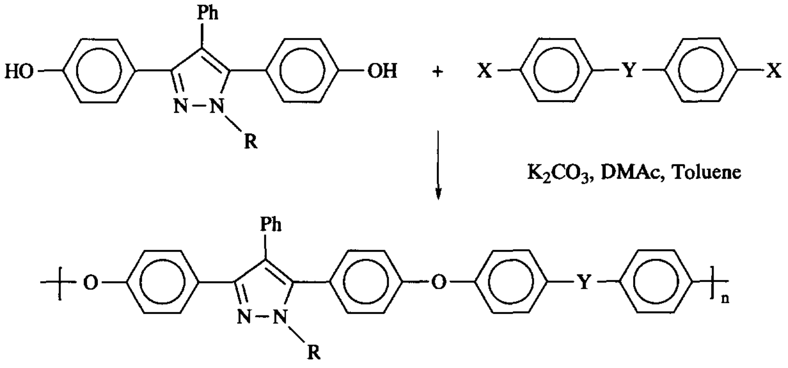
Synthesis of high MW poly (arylene ether pyrazoles) containing N–H and N–phenyl groups and with good solubility and mechanical and thermal properties has been reported.[198] Phenylated polypyrazoles with higher thermal stability and T_g can be synthesized by the aromatic nucleophilic displacement reaction of activated aromatic dihalides by bisphenolic pyrazole monomers. Bisphenols containing pyrazole groups, e.g. 3,5-bis(4-methoxyphenyl)-4-phenylpyrazole, have been prepared as shown in the scheme,



where R = H, Ph.

SCHEME 53.

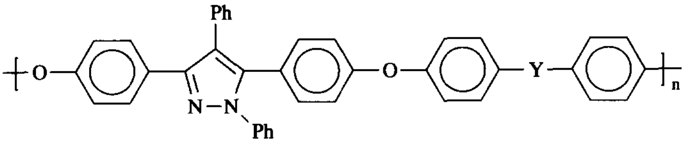
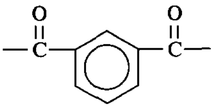
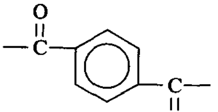
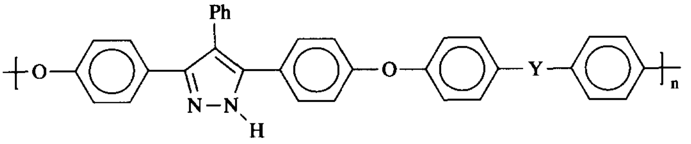
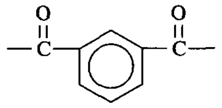
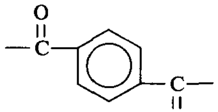
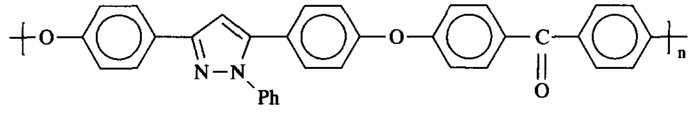
Poly(arylene ether pyrazoles) have been prepared by refluxing aromatic dihalides and pyrazole-containing bisphenols in DMAc with anhydrous potassium carbonate:



where R = H, Ph; X = Cl, F.

SCHEME 54.

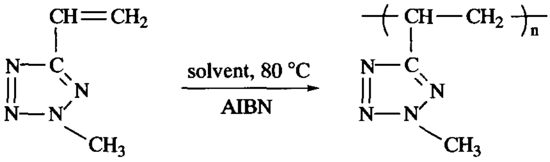
TABLE 2. Poly(arylene ether pyrazole)s

Polymer systems	Y	T_g
		196
	$-\overset{O}{\overset{\parallel}{C}}-$	205
		210
	$-\overset{O}{\overset{\parallel}{\underset{\underset{O}{\parallel}}{S}}}-$	243
		188
	$-\overset{O}{\overset{\parallel}{C}}-$	208
		200
	$-\overset{O}{\overset{\parallel}{\underset{\underset{O}{\parallel}}{S}}}-$	237
	–	206

The polymerization is carried out for 2–6 h during which the water formed is azeotropically distilled off using toluene. The fibrous polymer precipitates on pouring the viscous reaction mixture into an acetone/water mixture. Quantitative yields of medium to high MW phenylated poly(arylene ether pyrazoles) have been obtained. The polymer structures are shown in Table 2. Poly(arylene ether phenyl pyrazole)s containing phenyl groups on the pyrazole ring are white fibrous polymers. The phenyl groups enhance the T_g of the polymers, as expected, in the range of 196 to 243°C by about 5–10°C in comparison with the non-phenylated polymers. In contrast to aromatic dichlorides, use of aromatic difluorides results in premature gelation and the observed T_g (in the range of 188 to 237°C) decreases by about 20–30°C in comparison with the non-phenylated polymers. Similarly, the T_g of the polymers containing N–H linkages decreased by 20–30°C, while N–phenyl polymers showed an increase of 5–10°C in T_g relative to the previously prepared non-phenylated polymers. Mechanical properties like the critical strain release rate and critical stress intensity factor of compressed moulded specimens and adhesive specimens have been studied.

10. POLYTETRAZOLES

A number of vinyltetrazoles have been prepared and homopolymerized with organic peroxides and azo initiators, both in solution and emulsion systems[191,199–201] Poly(2-methyl-5-vinyl tetrazole) is used as an ingredient in igniter compositions and high energy propellants.[200] Other similar alkenyl and allyl tetrazoles are listed in Refs 191 and 201.

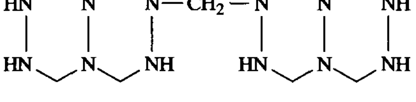


SCHEME 55.

11. N–N CONTAINING FUSED RING SYSTEMS

Fused ring polyaza systems containing six-membered heterocyclic triazine and tetrazine rings have been reviewed.[202,203] Poly(4-hydroxy-1,3,5-triazine-6-ones), suitable for the production of fibres, exhibit lactam–lactim tautomerism. The intermolecular hydrogen bridge formation in lactam-forming triazinone polymers has been studied by IR spectroscopy.[181] Polytriazines have been prepared from 2-butylamino-4,6-dichloro-1,3,5-triazine and 1,6-bis(2,2,6,6-tetramethyl-4-piperidylamino)-hexane, and also from 2,4-dichloro-6-(*N*-2,2,6,6-tetramethyl-4-piperidyl)butylamino-1,3,5-triazine and $H_2N(CH_2)_2NH_2$. Processing characteristics of triazine polymers and copolymers used as antioxidants in polyolefins have been examined. It is found that these antioxidants are resistant to extraction from the polyolefin by hot aqueous solutions of surfactants.[204]

Polymethylene(tetraformal trisazine) has been prepared from the monomer, namely, methylenebis(tetraformal trisazine) (MBTFT) and has been used as an N-rich additive for enhancing the performance of rocket propellants in terms of specific impulse, heat of formation, heat content and density.[205] MBTFT is prepared by treating hydrazine or tetraformal trisazine with 53% CH_2O in methanol. This mix-



(MBTFT)

SCHEME 56.

ture, when concentrated, is reported to form a polymer. Alternatively, the polymer may be prepared directly from CH_2O and hydrazine or tetraformal trisazine.

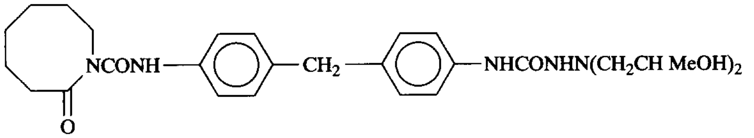
Diesters containing heterocyclic nuclei polymerize easily with hexamethylene diamine. The pyrazine nucleus, for example, is found to have the highest influence in imparting enhanced reactivity of the diesters to polymerization. This enhanced reactivity is attributed to the activity of the heteroatoms and not to the basicity.[206] The reactivity of polypyrazolylborates with metal complexes such as CpCo(CO)RI, where Cp is cyclopentadienyl and R is perfluoroalkyl, has also been studied.[207] Polymers such as poly(*N*-vinyl phenoxazine) and poly(*N*-vinyl phenothiazine),[208] having photoconductivity, high photosensitivity, elasticity and low softening point, are useful as electrophotographic materials. Photochromic properties of mesophasic side-chain liquid crystalline polymers containing spironaphthoxazine groups have been reported.[209]

12. N-N CONTAINING POLYURETHANES

A variety of linear, elastomeric, thermoplastic, high strength polymers have been obtained by chain extending diisocyanates or diisocyanate prepolymers based on polyesters,[210–212] polyethers,[212] polyester glycols or polyether glycols[33,213] with hydrazine or its derivatives. For example, a polyurethane prepolymer prepared from the polyester of adipic acid and 1,6-hexanediol by treating with methylenebis(4-phenyl isocyanate), when reacted with chain extenders such as semicarbazides, leads to a clear, viscous elastomer.

In another method of preparing linear, thermoplastic polyurethane polymers,[40,214–217] the reaction products of organic diisocyanates with hydrazine or dihydrazides are mixed with polymers such as polypropylene glycols, capable of reacting with hydrazine or its derivatives such as carbohydrazide, which act as chain extenders.

The functionality of groups in the main chain influences the properties of polymers containing hydrazine units.[215,218] Acyl chloride end groups in polyesters or polyethers react with hydrazine or its derivatives to give a high molecular weight polymer.[212] Oligourethanes with specific NH/NCO ratios yield better solubility,[218] low temperature flexibility,[219] light resistance,[25] etc. Piperazino-terminated polyamides, upon reacting with diisocyanates and hydrazine, yield block copolymers having good elasticity.[220] Caprolactam blocked isocyanate groups, shown below, and diols have been found to be useful for obtaining self-crosslinkable polyurethane elastomers.[221] Several of these polymers containing hydrazine, carbonyl, and imide groups have shown useful properties as adhesives,[19–21,222] rubbery and resinous materials,[223,224] fibres,[214] films[24] and ionomers.[218] For example, both allylhydrazine bisphenol A diglycidyl ether graft copolymer[20] and allylhydrazine pentaerythritol tetrakis (*β*-mercaptopropionate) copolymers have been used as adhesives curable both chemically and by irradiation.[19] The curing of epoxidized liquid polybutadiene with N_2H_4 and CS_2 leads to a



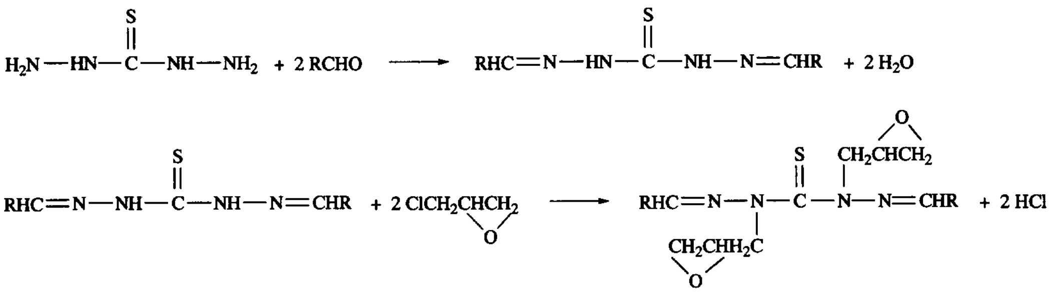
SCHEME 57.

hard thermosetting resin.[223,224] The hardness of the resin increases further when diethylene triamine is added to the mixture. Addition of a thiol, particularly ethanedithiol, cures liquid diene polymers of 1,3-butadiene, isoprene, etc., at 130°C within a few minutes to several hours. Dependent upon the amount of the thiol added, rubbery or resinous products are obtained. When polythiols are used, the curing process is accelerated substantially. Similar results have been observed when liquid polybutadiene is used along with N_2H_4 and CS_2 since polythiols will be formed *in situ*.[223,224] It thus appears that the proper choice of condensable monomers with hydrazine or its derivatives in certain proportions could lead to polymers with specific properties.

13. N-N CONTAINING EPOXY RESINS

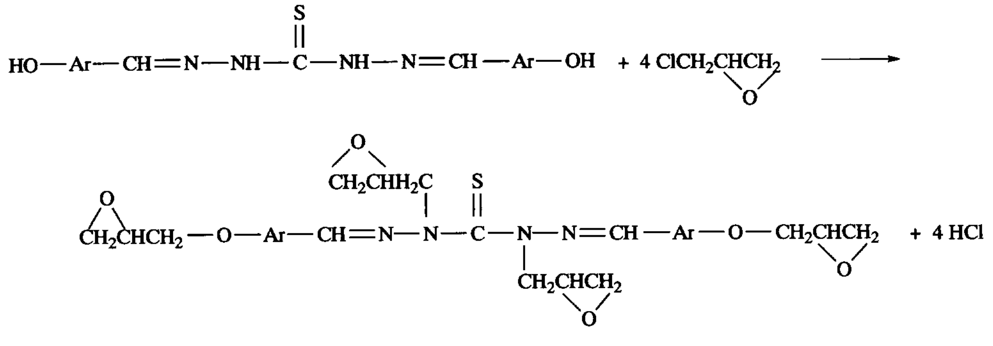
Preparation and properties of heterocyclic monomers such as triazines and triazoles containing epoxy groups, and their polymers, have been reviewed.[225] In order to prepare binders for hypergolic fuel compositions used in hybrid rockets, Jain *et al.*[14,226] synthesized new epoxy resins and studied the fuel grains cast with the resins as binders. The aim has been to develop hybrid rocket fuel grains which have short ignition delays with storable oxidizers, and at the same time have good mechanical strength.

The resins are prepared by glycidating bis-carbonohydrazones[226] and bis-thiocarbonohydrazones,[14] which in turn are obtained by reacting various aldehydes or ketones with carbohydrazide[227] or thiocarbohydrazides,[228] e.g.



Scheme 58.

The glycidation is carried out using an excess of epichlorohydrin at 80°C. The excess epichlorohydrin is subsequently distilled under vacuum. (If no base is added, the HCl



Scheme 59.

formed may react with epichlorohydrin to form 1,3-dichloro-2-propanol, which is likewise removed by vacuum distillation.)

Interestingly, tetraepoxy resins[14] could also be obtained by using the bis(hydroxybenzaldehyde) derivatives of carbo- and thiocarbohydrazides. In these cases, the glycidation additionally occurs at the hydroxy groups of the aldehyde, for example.

By using the general method as described above, several di- and tetraepoxy resins have been prepared. These include the diglycidyl ethers of acetonecarbonohydrazone (DGACH), furfural carbonohydrazone (DGFCH), furfural thiocarbonohydrazone (DGFTCH), butanonethiocarbonohydrazone (DGBuTCH), acetonethiocarbonohydrazone(DGATCH), benzaldehydethiocarbonohydrazone (DGBTCH) and the tetraglycidyl ethers of vanillincarbonohydrazone (TGVCH), vanillinthiocarbonohydrazone (TGVTCH), *o*-hydroxybenzaldehydethiocarbonohydrazone (TGoHBTCH) and *m*-hydroxybenzaldehydethiocarbonohydrazone (TGmHBTCH).

The resins have been characterized by IR and NMR spectra.[14] The physical characteristics and epoxy contents are given in Table 3. The resins are highly viscous liquids at room temperature; the viscosity falls steeply with increase in temperature. In general, the viscosities of difunctional and tetrafunctional resins do not differ much although the aromatic resins are more viscous than the aliphatic ones. Differential thermal analysis and thermogravimetry data show that isomerization of the epoxy groups to carbonyl groups accompanied by thermal polymerization and partial decomposition of the resins occur exothermically between 220 and 380°C. The thermal stability is affected by the surrounding atmosphere; the decomposition occurs at higher temperatures in He than in O_2.

The resins have been used as prepolymeric binders for solid fuel compositions and cured with amines or amino compounds. The cured resin grains, loaded with magnesium powder, ignite readily with white fuming nitric acid (WFNA) with sub-second delays and have tensile strengths of over 100 kg/cm^2. Fuel grains made with the difunctional carbonohydrazone resins give shorter ignition delays with WFNA as compared to those cast with the corresponding thiocarbonohydrazone resins.

In a similar study, diglycidyl ethers of vanillin azine (DGVAZ) and divanillylidene ethylenediamine (DGVED) and bisphenol A (DGBPA) have been prepared as viscous

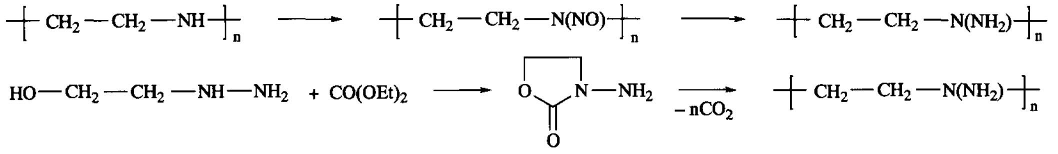
TABLE 3. Physical characteristics and epoxy content of epoxy resins based on biscarbonohydrazones and bisthiocarbonohydrazones

Resin	Colour	State	MW	Epoxy content groups/molecule	
				observed	calculated
DGACH	brown	viscous	282	1.94	2.0
DGFCH	brown	highly viscous	358	1.97	2.0
DGATCH	yellow orange	viscous	298	1.95	2.0
DGBTCH	brown	highly viscous	394	1.80	2.0
DGFTCH	brown	viscous	374	1.98	2.0
DGBuTCH	light brown	less viscous	326	1.95	2.0
TGVCH	brown	viscous	582	3.91	4.0
TGVTCH	brown	highly viscous	598	3.63	4.0
TGoHBTCH	brown	viscous	538	4.04	4.0
TGmHBTCH	brown	highly viscous	538	3.94	4.0

fluids flowable at elevated temperatures[13] and have been used to cast solid fuel compositions. The cast grains in the form of pellets have been examined for their ignition delay (ID) with WFNA, and compressed strengths. A comparison of the IDs show that, in general, the grains based on DGVAZ have better ignition characteristics, which in turn could be related to the presence of the N–N bond in the resin structure.

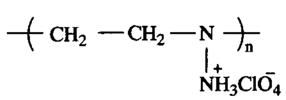
14. N–N CONTAINING ENERGETIC POLYMERS: ASSORTED STUDIES

A stable polymeric material $[N_2H_2(BH_2)_2]_n$ ($n = 11$–55) has been produced safely by heating N_2H_4–BH_3. It has been claimed to have potential application in rocket propellant systems; a procedure has been developed for obtaining $(NH_2\text{–}NH_3)_2B_{10}H_{10}$ and $(NH_2\text{–}NH_3)_2B_{12}H_{12}$.[229,230] A mixture of $(NH_2\text{–}NH_3)_2B_{10}H_{10}$ and $(NH_2\text{–}NH_3)_2B_{12}H_{12}$ readily ignites with vigorous, smooth combustion upon mixing with concentrated HNO_3.[231]



SCHEMES 60 and 61.

Nitrosation and reduction of polyethyleneimine is felt not to be a suitable route for obtaining poly(ethylene hydrazine) since commercial polyethyleneimine contains primary as well as secondary amino groups, and the primary sites would largely undergo deamination.[232] Poly(ethylene hydrazine), however, has been obtained as a low molecular weight elastomer by pyrolysis and thermal decarboxylation of 3-amino-2-oxazolidinone or its hydrochloride.[233] The polymer, on treatment with hydrazinium perchlorate, can be converted to:

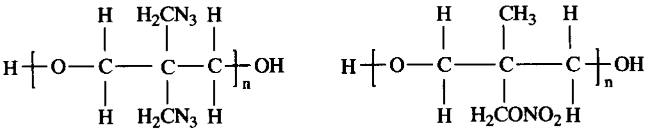


$$\left(CH_2-CH_2-\underset{\overset{|+}{NH_3ClO_4^-}}{N}\right)_n$$

SCHEME 62.

which is conceived as an oxidizing binder[234] for solid propellants. A high performance solid propellant may be prepared by masticating poly(ethylene hydrazine) with the dihydrazinium salt of decaborane and triaminoguanidinium monoborohydride at 70–100°C to form a viscous fluid-like plastic mass. The molten material is moulded, cooled and cast to produce a rubbery propellant grain. The propellant has a low autoignition temperature; it ignites and burns with low flame temperature at relatively low pressures to release energy through the formation of BN.[235] Amino-terminated polymer mixtures with magnesium undergo synergistic hypergolic ignition with red fuming nitric acid (RFNA) as an oxidizer. The ignition delay results for a hydrazine hydrate glyoxal copolymer/magnesium mixture using RFNA have been reported.[236]

Glycidyl azide polymers are emerging as an important class of energetic fuel binders useful in rocket propellants.[237–240] Void-free glycidyl azide polymer based propellants have been made by using deflagrating additives and a silane amine–expoxide.[237] Poly(epichlorohydrin-co-ethylene oxide) is dissolved in a solvent, heated and stirred



$H{+}O-C(H)(H)-C(H_2CN_3)(H_2CN_3)-C(H)(H){+}_n OH$ $\quad$ $H{+}O-C(H)(H)-C(CH_3)(H_2CONO_2)-C(H)(H){+}_n OH$

BAMO NMMO

SCHEME 63.

with sodium azide to obtain a glycidyl azide polymer. Hydroxyl terminated aliphatic polyethers with pendant alkenyl azide groups are prepared from metal azides with the polyethers in a poly(alkylene oxide–nonpolar liquid reaction medium.[238] Energetic prepolymers containing azide and/or nitrate ester groups, such as poly(3-nitratomethyl-3′-methyloxetane) (NMMO) and poly-3,3′-bis (azidomethyl) oxetane (BAMO) (MW 1800–3000) have also been prepared and characterized for potential use in advanced solid propellants, gun propellants and explosives.[239,240]

The reversible formaldehyde uptake of methyl methacrylate–divinylbenzene (DVB) copolymer treated with hydrazine[241] seems to be useful in the safe handling of an explosive polymeric system based on formaldehyde and hydrazine.[242] It is known that methyl methacrylate–DVB copolymer treated with hydrazine forms a resin which takes up formaldehyde by condensation with hydrazine residues but then releases the molecule in an acid medium. This reversibility depends upon the functionality and crosslink density. Incidentally, such a copolymer can take up and release formaldehyde to form an explosive polymeric solid with hydrazine in certain proportions in concentrated HNO_3. However, this activity of the copolymer remains to be explored.

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