polymer reviews

Recent progress in carbazole based polymers

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This review highlights the recent developments in carbazole based polymer systems which have taken place along three main directions: (a) syntheses of homopolymers, copolymers, copolycondensates and copoly(step) polymers containing pendant carbazole units linked to the main chain directly or through flexible units; (b) chemical modification of these polymer systems to cation radical complexes, nuclear substituted polymeric materials, ion-exchange resins, charge-transfer complexes, copolymeric materials containing donor–acceptor units; and (c) syntheses of polymer systems containing carbazole units in the main chain such as polyamides, polyimides, polyarylates, polysulphones, polymeric azo-dyes, polysiloxanes, polyquinone and miscellaneous carbazole-incorporated polymer systems. These polymers of tailored chemical structures exhibit outstanding and interesting thermal, electrical, photoelectrical, ion-exchange and other physico-chemical properties, which have been discussed and rationalized in the light of the structural characteristics of these polymer systems.

Keywords Carbazole; stereo-block; photoconductivity; hole-carrier mobility; chemical modification; charge-transfer complex

INTRODUCTION

Recently carbazole based polymer systems have received considerable attention which is amply justified in view of the unusual electrical, photoelectric, thermal and other relevant properties of these materials. Penwell et al.[1] have reviewed (1978) the developments in polymerization and structure–property relations of polymer systems based on poly(N-vinylcarbazole) (PNVC) alone.* The object of this review is to highlight the versatile developments and expansion in the broad field of carbazole based polymer systems which display outstanding physico-chemical, thermal, electrical and photoelectrical properties. The review brings to focus the major advances accomplished during the years 1971–1981 in the chemistry of polymer systems based on pendant carbazole units and those containing carbazole units in the main chain including also their chemical modifications and property manifestations. Some work on the conventional polymerization and copolymerization of N-vinylcarbazole (NVC) which does not bring to light any new feature related to either the catalyst or polymer properties, has not been brought under the purview of this review article.

POLYMERS BASED ON PENDANT CARBAZOLE UNITS

Homopolymers

It is well known that NVC is a very reactive monomer towards radical, cationic and charge-transfer polymerizations. The recent developments (1978) in the homopolymerization of this monomer have been reviewed by Penwell et al.[1] More recently, the stereoregular polymerization of NVC by the

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* Tazuke et al. (Encyclopedia of Polymer Science and Technology, 1971, **14**, 281) reviewed the literature on synthesis and property evaluation of PNVC and NVC based copolymers.

homogeneous catalyst systems, $CoCl_2$–quinoline/pyridine–$ZnEt_2$ in toluene, has been described by Biswas and Mishra[2,3]. PNVC obtained from these systems shows partial solubility in methyl ethyl ketone (MEK). The general glass transition of the insoluble and soluble fractions are more or less similar but the d.t.a. of the insoluble part reveals a sharp endothermic peak at 485°C which is otherwise absent in MEK soluble fraction or aprotonic acid initiated PNVC. ^{13}C-n.m.r. spectra for the insoluble fraction show a triplet at δ (ppm) 49.3, 49.7 and 50.63 assigning stereoblock configuration to PNVC. The rate of polymerization is second order in NVC and proportional to $[ZnEt_2]^2[CoCl_2$–ligand$]$ up to a certain concentration following thereafter to a limiting value. The polymerization is initiated through the complex (*Scheme I*):
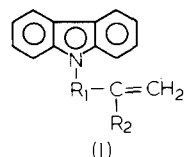
Scheme I
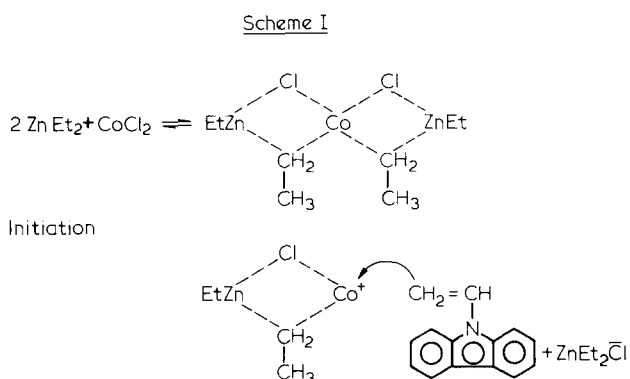
The X-ray diffraction pattern is similar although somewhat less sharp (pyridine system > quinoline system) as compared with that for PNVC reported by Crystal[4]. The photoconductive and dielectric properties of such stereoblock PNVCs might be different from those for atactic PNVCs. However, preliminary investigations[5] appear to endorse this notion; detailed studies are in progress.

Other reported homopolymerizations of NVC such as plasma (Simionescu et al.[6]) and molecular sieve (SK-500 and 13X) (Biswas et al.[7-9]) initiated polymerizations are probably more significant from the point of view of new initiator development.

Some interesting N-substituted carbazoles[10] involving polymerizable terminal vinyl groups have been synthesized (see *Table 1*) and polymerized by conventional free-radical polymerization initiator, (AIBN) except the monomer (b) which undergoes cationic polymerization with initiator $BF_3.OEt_2$.

Table 1

No	N—R₁—	R₂
a	N—CH₂—⬡—	H
b	N—(CH₂)₂—O—	H
c	N—(CH₂)₂—OOC—	H
d	N—CH₂NHCO—	H
e	N—CH₂NHCO—	CH₃
f	N—CH₂—CH—CH₂—OOC— / OH	H
g	N—CH₂—CH—CH₂—OOC— / OH	CH₃
h	N—CH₂—CH—CH₂—HN—⬡ / OH	H
i	N—CH₂—CH—CH₂—HN—⬡— / OH	H
j	N—(CH₂)₂—COO—(CH₂)₂—OOC—	H
k	N—(CH₂)₂—COO—(CH₂)₂—OOC—	CH₃

The relative distance of the pendant carbazole units from the backbone significantly influences the properties of these polymers. Thus, a separation by a flexible chain with 5–8 C and O atoms imparts a low T_g, and so the polymers of (j) and (k) with the longest chains are of soft appearance even at room temperature. Again, the polymers bearing flexible units with terminal carbazole moieties such as polymers of (c–f) provide films different from that of PNVC. Recently, Ledwith et al.[11] have reported some novel nuclear as well as N-substituted carbazole- containing methacrylate polymers, (2a–2c) and (3a, 3b), which are susceptible to photochemical

a.	R=CH₂
b.	R=CH₂CH₂
c.	R=CH₂COOCH₂CH₂

(2)

(3)

a. 2-isomer
b. 3-isomer

degradation causing both scission of the chain backbone and diminution of carbazole chromophore fluorescence. Comparison of the absorption and emission spectra of these polymers shows that appreciable emission occurs only in the case of (3a). Excimer emission from (3a) is weakest in polar fluid solvents and strongest in a rigid glassy matrix. Luminescence decay measurements in the presence and absence of anthracene quencher suggest that down-chain energy migration is virtually absent in the sterically unhindered polymers, (2a–2c) and (3b), and this is confirmed by steady-state analysis of collisional quenching.

The cationic polymerization of a particularly significant model monomer, β-N-carbazolylethyl vinyl ether (*Table 1*, 1b), has been reported by four groups[10,12-14]. Electronic transport properties and photoconductivity in the polymer, poly(β-N-carbazolylethyl vinyl ether) (PβNCEVE), observed by Turner and Pai[14] signify that PβNCEVE has a hole carrier mobility similar to PNVC at comparable field strengths even though the carbazole units are extended from the backbone. This conclusion by Turner and Pai[14] contradicts the earlier observations by Okamoto et al.[12] claiming much lower hole mobility in PβNCEVE. However, the measurements of charge carrier mobility by Turner et al. are more direct than the steady state technique used earlier[12] and consequently, they reflect the inherent electronic transport properties of PβNCEVE. This leads us to a conclusion that the attachment of the photoactive groups directly to the polymeric backbone for increased interactions is not necessarily valid as proposed by Okamoto et al.[12]. Furthermore, the molecular dispersions of N-isopropylcarbazole in bisphenol A based polycarbonate, at much lower carbazole concentrations than the same in PNVC, exhibits hole mobilities equivalent to PNVC at equivalent field strength[15]. From these results, it appears that the position of the carbazole units relative to the polymer backbone is not important.

Tazuke et al.[16] have reported the synthesis and polymerization of various carbazole monomers (4). The

(4)
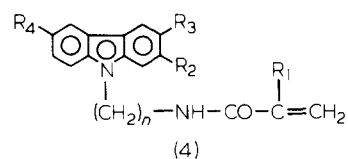
n = 2–3,
R = H, CH₃, halogen,— COOR,—OAC,
R = H, —NO₂,
R₃R₄ = H, halogen, CH₃,—CHO,—CH₂OH,—CPh₃.

polymerizations of these monomers have been conducted in the presence of AIBN. In general, these polymers are found to exhibit photoconductivity. Particularly, the polymers of (4) with ($R_1 = R_2 = R_3 = R_4 = H$, $n = 3$) and ($R_1 = CH_3$, $R_2 = R_3 = R_4 = H$, $n = 3$) show good conductivity and film formation properties. The polymer with ($R_1 = R_2 = R_3 = R_4 = H$, $n = 1$) reported by two groups[10,17], forms a good film and is useful for photoelectric semiconductors. It has been suggested by Tazuke et al.[18] that the polymer containing pendant system trans-1,2-di-N-carbazolylcyclobutane group, prepared from the monomer (5), on composition with a sensitizer 2,4,7-trinitrofluorenone (TNF), forms a more effective and flexible film than PNVC composed with
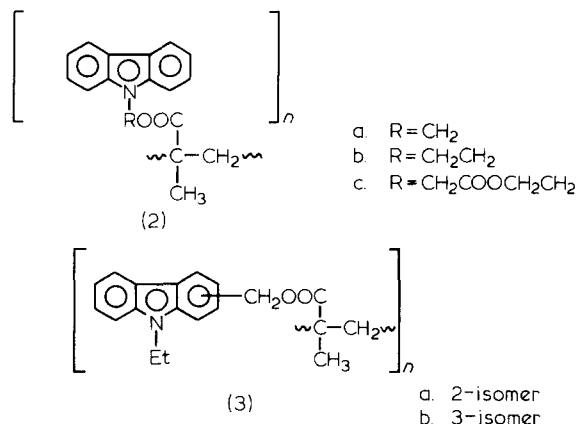
TNF. However, both the former and the latter exhibit comparable photoconductivity.


(5)
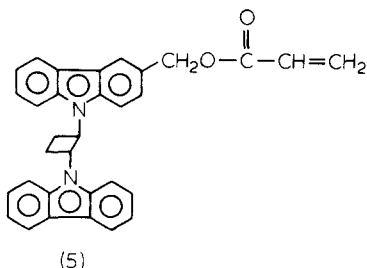
Vinyl polymers containing pendant carbazole units have been the model polymers for studying the electrical properties due to more efficient electron migration compared to the conventional vinyl polymers. Williams *et al.*[19] have suggested that the polymers (6a) and (6b) exhibit electrical carrier mobility which varies as the

a. 2-isomer
b. 3-isomer

(6)
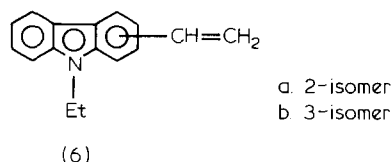
square root of the electric field over the range of fields examined and is not directly related to the observed variations in n.m.r. chemical shifts resulting from inter-ring shielding effects. The polymer (6a), which shows the overall largest upfield shift of the aromatic protons, exhibits a mobility of 1.4×10^{-6} cm^2 V^{-1} s^{-1} at a field of 4×10^5 V cm^{-1} and polymer (6b) which exhibits the smallest shielding effect, has a mobility of 2.4×10^{-8} cm^2 V^{-1} s^{-1} at equivalent fields. Notably, PNVC exhibits an intermediate degree of shielding with a mobility of 1.4×10^{-7} cm^2 V^{-1} s^{-1}. It has been further suggested that polymer (6a) accumulates the largest amount of trapped charge.

Recently, some photoconductive polymers, polydiacetylenes, based on monomers (7) containing carbazole units have been reported by Yee[20,21]. The

(7)
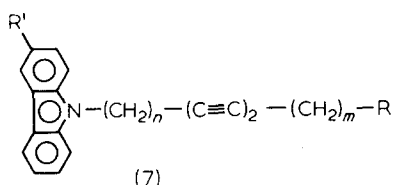
$m, n = 0-10$;
R = H, -OH, N-Carbazolyl carbamate;
R' = H, Cl, Br, -NO

polymerization of these monomers has been carried out by γ-irradiation or by thermal annealing. The polymer (7) with $(m = n = 1,$ R' = H, R = N-carbazolyl) shows significant photoconductivity with a peak at ~370 nm in the action spectra involving photoconduction onset at ~2.3 eV. In general, the photoconduction onset in all the cases is blue-shifted with respect to optical absorption, a result which is consistent with the excitonic assignment for the lowest energy optical transition in the polydiacetylenes.

Simionescu *et al.*[22] have recently reported the syntheses of five novel vinyl monomers containing 3-vinylic moiety substituted carbazole units, viz. N-(9-ethyl-3-carbazolyl)-maleimide, 9-ethyl-3-carbazolyl acrylamide, 9-ethyl-3-

carbazolyl methacrylamide, 9-ethyl-3-hydroxy-methylcarbazolyl acrylate, and 9-ethyl-3-hydroxymethyl-carbazolyl methacrylate, which subsequently have been subjected to homopolymerization in presence of AIBN. As anticipated[22], the polymers would be capable of forming charge-transfer complexes and possess characteristic structure–photoconducting property relations as well.

Copolymers

The copolymerization of vinylcarbazole monomers with conventional comonomers has recently been extensively studied; however, some interesting copolymerizations between N-vinylcarbazole (NVC) and some specific comonomers (*Table 2*) afford materials with distinctive photoconductive, electrical and thermal properties relative to those of the conventional copolymers and homopolymers based on pendant carbazole units. In general, these materials have been obtained through free-radical (AIBN) copolymerization (see *Table 2*) in dry benzene at ambient temperature. In a few cases, cationic copolymerization techniques have been employed (*Table 2*) using aprotonic acid initiators, e.g. $AlCl_3$, $ZnCl_2$, $SnCl_4$.

Characteristics of the copolymer systems. Limburg and Seanor[23] have studied the photoconducting behaviour of N-vinylphthalimide (NVP) copolymer for different compositions of NVP/NVC. A sufficient enhancement in photocurrent for the copolymer relative to PNVC is observed. The observed enhancement in the photocurrent is primarily due to absorption in the charge-transfer band, which extends well into the visible wavelength. The photoconductivity of the copolymer is maximum at 25 mol% of NVP and 75 mol% of NVC. With increase in the concentration of NVP (50/50, NVP/NVC), the diminution of photoconductivity in the copolymer is observed, which is due to the fact that the distribution of the donor (carbazole units) and acceptor groups (phthalimide units) is random and with increasing NVP concentration, some of the phthalimide groups are not involved in charge-transfer complexing. Seanor[24] has

Table 2 Copolymerization involving vinylcarbazoles

Comonomers	Copolymerization process	Reference
NVC/p-nitrostyrene	(a) Photoirradiation	31
	(b) Thermal/AIBN	
3-Vinyl-N-ethylcarbazole/styrene	Free-radical	64
3-Vinyl-N-methylcarbazole/ styrene	"	64
3-Methyl-NVC/styrene	"	32, 65
NVC/N-vinylphthalimide	"	1, 23
NVC/vinylferrocene	"	25
NVC/4-vinylpyridine	"	26
NVC/5-nitroacenaphthene	"	26
NVC/m-nitrostyrene	"	26
NVC/styrene	"	32, 33
NVC/N-vinylpyrrolidone	Cationic	27, 34
NVC/N-propenylcarbazole	"	34
NVC/1-vinylnaphthalene	Free-radical	28, 29
β-N-Carbazolylethyl vinyl ether/ maleic anhydride	"	14
β-N-Carbazolylethyl vinyl ether/ N-substituted maleimide	"	14
NVC/divinylbenzene	Cationic	30

NVC: N-vinylcarbazole

studied the hole mobility in NVC/NVP copolymer. The effective hole mobility in this copolymer system decreases with an increase in NVP concentration.

Pittman *et al.*[25] have reported that vinylferrocene copolymer exhibits higher dark conductivity and lower photoconductivity than PNVC. In fact, both are essentially insulators. The copolymers based on 4-vinylpyridine, 5-nitroacenaphthene and *m*-nitrostyrene (*Table 2*) are found to exhibit appreciable photoconductivity[26]. Solutions of these copolymers containing benzophenone and benzoin ethyl ether in pyridine, on exposure to u.v. light, show a photo-current/dark current ratio of 600. However, a decrease of photocurrent in the copolymers[27] based on styrene and *N*-vinylpyrrolidone (*Table 2*) relative to PNVC is attributed to the interruption effect of the comonomer component on the overlap of the π-electrons of the carbazolyl group creating disturbance in carrier migration. As reported by Yokoyama *et al.*[28], the carrier photogeneration mechanism for 1-vinyl-naphthalene/NVC copolymer involves triplet–triplet annihilation which causes delayed fluorescence of the carbazole chromophore. The photocurrent and the delayed fluorescence are increased by the introduction of a few mole per cent of naphthalene units. Moreover, the photocurrent has a quadratic dependence upon the illumination light intensity in high fields. Pertinently, as observed by Cabaness *et al.*[29], 1-vinylnaphthalene/NVC copolymer exhibits monomer emission at 360 nm and low-energy excimer or exciplex emission at 408, 442 and 450 nm. The ratio of the intensities of the emissions at 408 and 360 nm increases linearly with NVC content in the range 25–34%.

Turner and Pai[14] have recently reported the electronic transport properties of the copolymers based on *β-N*-carbazolylethyl vinyl ether, (8a–8f). These copolymers

(8)
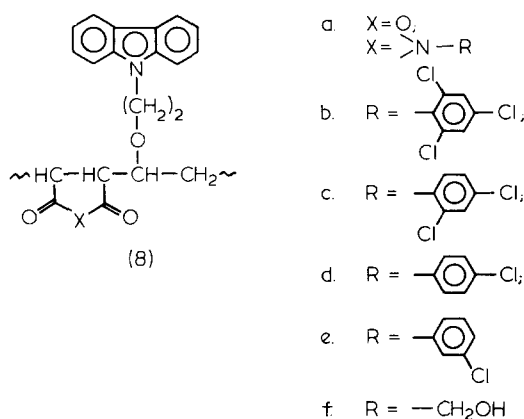
a. $X = O$,
$X = N-R$

b. $R = $ (with Cl substituents)

c. $R = $ (with Cl substituents)

d. $R = $ (with Cl)

e. $R = $ (with Cl)

f. $R = -CH_2OH$

exhibit hole mobility in the range from $<10^{-8}$ to $>5 \times 10^{-8}$ cm^2 V^{-1} s^{-1} at a field of 7.5×10^5 V cm^{-1}. The copolymer from *N*-(2,4,6-trichlorophenyl)maleimide shows highest hole mobility and that from *N*-(4-chlorophenyl)maleimide exhibits lowest hole mobility at the equivalent field strength. The charge carrier transport in these cases is dominated by deep bulk trapping which is thought to be inherent in the copolymers.
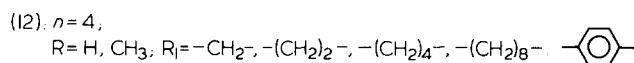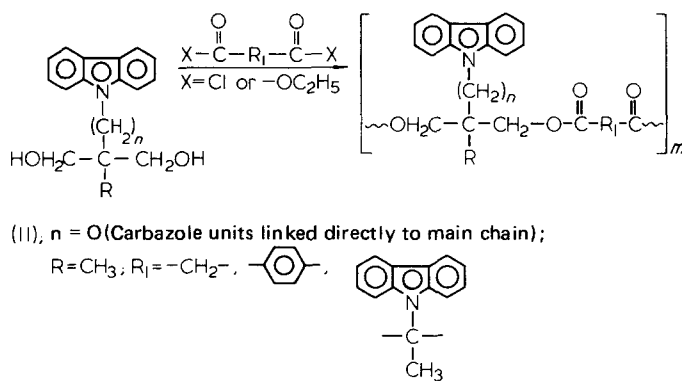
Thermal properties. More recently, Biswas and Mishra[30] have reported the distinctive thermal characteristics for the copolymer obtained from NVC and divinylbenzene (*Table 2*). The copolymer retains its fundamental chemical structure up to the temperature

400°C and thereafter undergoes weight loss at sufficiently slow rate (weight losses 2 and 22% at 440 and 540°C, respectively) in air. The copolymer exists in the form of intra- and intermolecular crosslink matrices, (9) and (10), as evident from the initial thermal stability temperature and swelling characteristics.

(9)

(10)
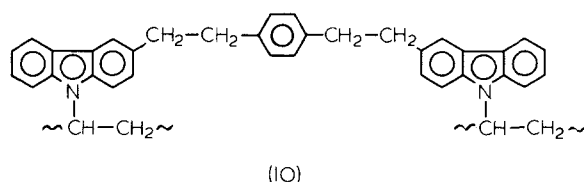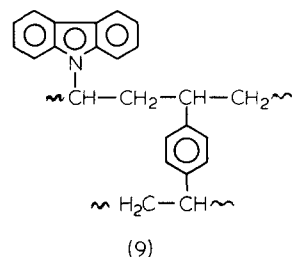
Copolycondensates

Aiming at a wider choice of polymer structures for studying charge-transfer interactions and better solubility of polymer in less polar solvents, a series of preparations of polyesters containing carbazole units linked directly to the backbone or by a polymethylene chain of appropriate length has been reported by Tazuke *et al.*[35–38] Polyesters (11) and (12) have been prepared by polycondensation of carbazole based diols with diethyl malonate, diethyl terephthalate, diethyl 2-*N*-carbazolyl-2-methyl malonate, succinoyl chloride, adipoyl chloride and sebacoyl chloride.

(11), n = 0 (Carbazole units linked directly to main chain);
$R = CH_3$; $R_1 = -CH_2-$,

(12): n = 4;
$R = H, CH_3$; $R_1 = -CH_2-, -(CH_2)_2-, -(CH_2)_4-, -(CH_2)_8-$

G.p.c. analyses indicate that the polyesters (11) consist of 2 to 5 repeating units (oligomeric products) and polyesters (12) consist of at least 10 repeating units. In all these cases, steric factors in the diol monomers determine the ease of the condensation polymerization. I.r. spectra of the polymers indicate the existence of a small amount of hydroxyl groups attributable to the end groups. The absorption spectra of the polymers (12) are identical in the wavelength region between 220 and 360 nm indicating the absence of specific interactions between the carbazole units. This is due to sufficient spacing between the

neighbouring carbazole units linked to the main chain through flexible methylene units.

Thermal stability of the copolycondensates based on pendant carbazole units constitutes a unique feature of these polymers. Biswas et al.[39,40] have recently reported a novel thermally stable copolycondensate (NVCF) synthesized from NVC and furfural. The synthesis was conducted with various furfural concentrations and it was concluded that, with increase in the furfural concentration, gelling time increases; however, beyond the optimum concentration, the condensation ceases completely. NVCF retains its fundamental chemical structure up to a temperature of 300°C and thereafter experiences a weight loss of around 50% at 600°C. Overall thermal and gelling properties of NVCF signify that it has a densely crosslinked matrix structure.

*Copoly(step) polymers**

An interesting step-reaction polymerization[41] of N-(6-hydroxy-5-hydroxymethyl hexyl) carbazole and hexamethylene diisocyanate without a catalyst produces a high molecular weight polyurethane (13a) soluble in common solvents such as DMF, chloroform, anisole. When ethylene diisocyanate is used instead of the former, the resulting polymer (13b) becomes less soluble. Notably, the polymer (13a) is found to be effective for the spectroscopic investigations.

(13)

a R=-(CH₂)₆-
b R=-(CH₂)₂-
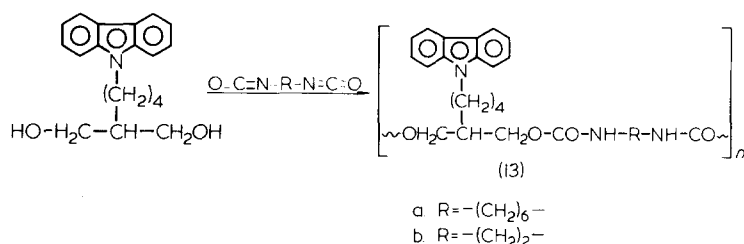
## CHEMICAL MODIFICATION OF POLYMERS BASED ON PENDANT CARBAZOLE UNITS

Polymers containing pendant carbazole units show various properties by subjecting them to chemical modification through reactions involving cation radical complex formation, charge-transfer complex formation, side chain displacement and nuclear substitution. In fact, the chemically modified polymers exhibit improved electrical, photoconductive and thermal properties relative to the conventional homo- and copolymers, and show some novel properties such as ion-exchange properties, which may be of specific technical use. The behaviour of these polymers is generally governed by their reactivity which is indirectly related to their structures and the nature of the functional moieties linked to the pendant systems.

Cation radical complexes

The mechanism of semi- and photoconductance occurring in PNVC based materials has received considerable attention. More recent investigations[42-46] conclude that the charge migration in the semi- and photoconductive PNVC based materials is controlled by

* Nomenclature: Polymers prepared by step-reaction polymerization (Ref. F. W. Billmeyer, Jr. Textbook of Polymer Science, Wiley–Interscience, New York, 1971, p. 257).

a hopping mechanism between traps. These various studies suggest that doped PNVC provides an efficient matrix for hole and/or electron migration. For producing more efficient conductive polymers, a possibility of introducing unpaired electrons by the formation of cation radicals in NVC polymers has been surveyed by Block et al.[47]. in fact, such a possibility was established synthetically by Ledwith et al.[48,49] through generation of stable cation radicals by an oxidative dimerization of carbazoles.

Cation radical complexes[47] of NVC polymers have been prepared by an oxidative crosslinking of the polymers through pendant carbazole units using tris-(p-bromophenyl) ammoniumyl hexachloroantimonate (V) as oxidant. In all the cases, the addition of oxidant results in the immediate formation of the characteristic green colour of the polymeric carbazylium cation radical (14) (Scheme II). The oxidation process involves three

Scheme II

(14)

X = H or Cl
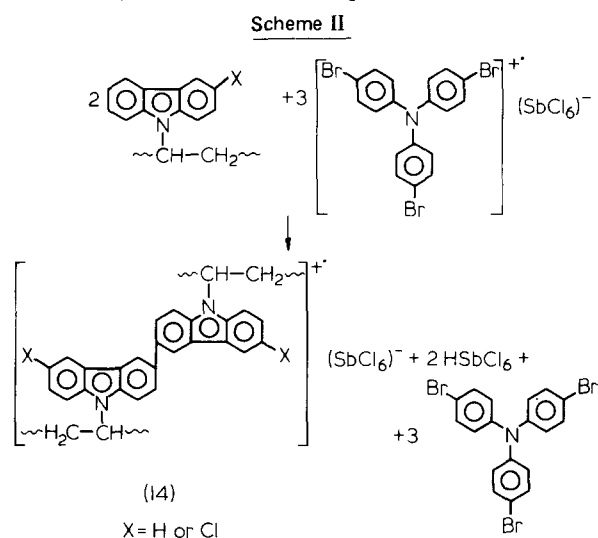
electron-transfer processes with pendant carbazole ring dimerization via the 3-position with respect to the heteroatom. In fact, the oxidation results in intermolecular crosslinking and, therefore, causes gelation in the presence of a sufficient amount of oxidant.

Electrical properties. The introduction of cation radicals by oxidation of PNVC provides materials[47] of significant semiconductivity (σ) up to $\sim 10^{-5}$ ohm^{-1} cm^{-1} at 293 K. The values of σ are synthetically adjustable in the range 10^{-5}–10^{-12} ohm^{-1} cm^{-1} by varying the concentrations of PNVC and oxidant. The increase in the mole fractions of cation radicals enhances the value of σ and reduces the activation energies for conductance. PNVC cation radical polymers with very high cation radical contents exhibit negligible loss of conductivity with time.

Photoconductive properties. PNVC cation radical complex (14) on illumination with visible radiation develops a photocurrent[47] and particularly, at lower mole fraction (x) of cation radicals ($<4 \times 10^{-3}$), exhibits significant photoconductivity. Inclusion of cation radicals into PNVC at low concentration introduces a large number of states which act as traps or recombination centres. At the low levels of light intensity attainable and at the higher temperatures, the hole and electron demarcation levels which energetically separate the role of trap state from recombination centre, are well removed from the conduction (electron migration) or valence (hole migration) bands. These leave a large population of states

acting as traps in the forbidden gap. In fact, at moderate temperatures, the attainable level of photocurrent is first order with respect to light intensity (lux), which implies[47] that there is a wide distribution of levels (in energetic terms) throughout the forbidden zone. However, at much lower temperatures, this order dependence is not maintained. Moreover, the wavelength response for the complex is essentially panchromatic in the region 400–600 nm indicating a close similarity in photoresponse and lamp emission power. Notably, both the photo- and semiconductivities in this case show similar activation energies.

Poly(nuclear substituted N-vinylcarbazole)

Chemical modification of PNVC through appropriate substitution in the active 3- and/or 6-positions of the pendant carbazole units produces polymers with distinct electrical and photoconductive properties and improved thermal properties relative to those of the unmodified polymer (PNVC).

Modified PNVC by Friedel–Crafts reaction. Biswas *et al.*[50,51] have recently reported that PNVC undergoes typical Friedel–Crafts acylation reactions with phthalic anhydride and benzoyl chloride in the presence of $AlCl_3$ producing polymers (15a, 15b). The reaction of PNVC

a. R = COOH
b. R = H

(15)
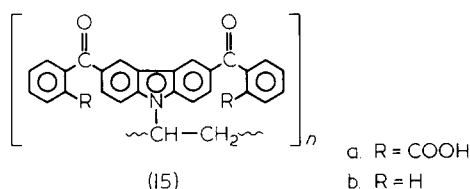
with furfural[39,40] in the presence of $AlCl_3$ is also an example of a Friedel–Crafts reaction. In this case, the polymer is modified to a network structure containing intra- and intermolecular crosslinking as a result of substitution of furfural or polyfurfural (formed in the medium) in the pendant carbazole rings linked to the same chain or different chains of the polymer. Increase in the concentration of furfural results in increased crosslinking in the end product.

Furfural based PNVC is thermally stable up to 400°C and experiences a weight loss of around 60% at 600°C suggesting a sufficiently improved thermal stability relative to that for the unmodified polymer (PNVC: 100% weight loss at 600°C).

Modified PNVC by Schotten–Baumann reaction. More recently, Biswas and Das[52] have reported a novel chemically modified polymer (16), poly(N-vinylcarbazole-3,6-diphthalimide) [P(NVC-DPI)], which has been

(16)
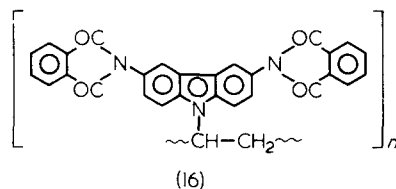
synthesized through the Schotten–Baumann reaction between poly(N-vinylcarbazole-3,6-diaminehydrochloride) prepared by nitration of PNVC followed by reduction, and phthaloyl chloride in the presence of alkali under selective experimental conditions.

The modified polymer (16) exhibits remarkably enhanced thermal stability[52] and attractive electrical and photoconductive characteristics[53] relative to those of the unmodified polymer (PNVC) as is evident from *Table 3*. The permittivity of the polymer (16) far exceeds the limiting value of insulation which is a characteristic nature of the unmodified polymer (PNVC), and ultimately, the polymer (16) exhibits specific conductivity and current (in dark), both 10^5 times higher, and a 10^7 times higher photocurrent than PNVC. This occurs due to the fact that the incorporation of the strongly polar phthalimide groups (acceptors) in the pendant carbazole units (donors), displaying efficient electron migration throughout the pendant systems, favours the polymer being involved in the formation of charge-transfer complexes which in turn behave distinctively under an electric field as well as under illumination with visible radiation.

Modified PNVC by chloromethylation reaction. Chloromethylation reactions[54] modify PNVC through substitution of chloromethyl groups at 3- and/or 6-positions of the pendant carbazole units. The various chloromethylating agents such as monochlorodimethyl ether, formaldehyde/HCl_{gas}, paraformaldehyde/HCl_{gas} and catalysts such as $FeCl_3$, $ZnCl_2$, $SnCl_2$, have been employed for these reactions. In fact, monochlorodimethyl ether and $ZnCl_2$ are found to be highly effective reagents for this modification. In spite of this, the reaction time is an important parameter in the chloromethylation of PNVC. In the early stages of the reaction, the substitution level increases with time and reaches the optimum value (step I). Further increase of reaction time causes crosslinking of the polymer (step II) parallel with the chloromethylation and in the later stage, crosslinking formation becomes dominant.

Step I :

(17)

Step II :

(18)
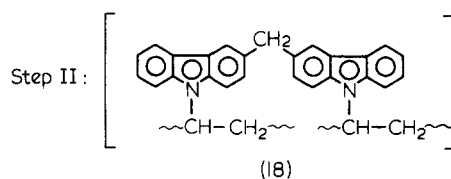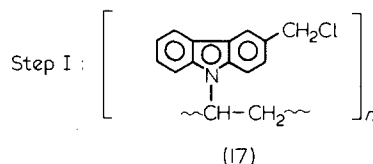
The chloromethylated polymer exhibits excellent thermal stability showing practically no weight loss up to temperatures around 400°C.

Modified PNVC by halogenation. According to Griffiths *et al.*[55] and Pielichowski *et al.*[56–58], incorporation of halogens (Cl,Br,I) in PNVC modifies the polymer through the electronic structure of the pendant carbazole units and the interchain structure involving pendant group overlap. This modification brings about a characteristic variation in the charge generation and charge transport which, in fact, affect the tacticity, electrical and photoconductive properties of the modified polymer.

The effects of bromine substitution in the 3- and/or 6-positions of the pendant carbazole units of PNVC on the

Table 3 Thermal, electrical and photoconductive characteristics of P(NVC–DPI) and PNVC

| Polymer | % Weight loss at 600°C | Electrical characteristics* at 100 kHz | | Photoconductive characteristics[†] at room temperature | | |
		ϵ'/tan δ at 30°C	ϵ'/tan δ at 140°C	σ_D (ohm^{-1} cm^{-1})	I_D (amp)	I_{Ph} (amp)
P(NVC–DPI)	36	20.05/0.0083	18.57/0.0099	5×10^{-11}	5×10^{-6}	1.05×10^{-5}
PNVC[‡]	100	4.96/0.0027	3.73/0.0036	4.2×10^{-16}	4.2×10^{-11}	5×10^{-12}

* ϵ': permittivity; tan δ: dielectric loss
[†] σ_D: specific conductivity in dark; I_D: dark current; I_{Ph}: photocurrent
[‡] Data taken from Biswas and Das[53], and Block et al.[47]

Table 4 Ion-exchange capacities and thermal stabilities of cation-exchange resins

| Cation-exchange resin | Ionogenic group | Capacity (m. equivalent/g) | Thermal stability: temperature (°C) giving | | Reference |
			10% weight loss	50% weight loss	
Sulphonated PNVC	$-SO_3^-H^+$	4.50	100	500	86
Phosphorylated PNVC	$-PO_3^{2-}(H^+)_2$	3.20	140	—	85
Sulphonated (phthalic anhydride based PNVC)	$-SO_3^-H^+$	4.73	180	590	50
Sulphonated (furfural based PNVC)	$-SO_3^-H^+$ $-COO^-H^+$	4.40	125	425	39
Phosphorylated (furfural based PNVC)	$-PO_3^{2-}(H^+)_2$	5.12	310	565	40
Sulphonated poly[NVC-3,6-bis(4-keto-1-naphthol)]	$-SO_3^-H^+$ $-COO^-H^+$ $-OH$ (phenolic)	5.12	110	495	51
Sulphonated (NVC-divinylbenzene copolymer)	$-SO_3^-H^+$	4.90	110	300	87
Sulphonated (NVC-furfural copolycondensate)	$-SO_3^-H^+$ $-COO^-H^+$	4.62	110	295	39
Phosphorylated (NVC-furfural copolycondensate)	$-PO_3^{2-}(H^+)_2$	5.18	425	590	40

structure and the electrical and photoconductive properties have been extensively studied by Griffiths et al.[55]. Pertinently, X-ray diffraction studies reveal that this substitution interferes with the interchain interactions in the polymer eliminating the usual degree of chain parallelism and destroying the ability to crystallize. The photogeneration and the drift mobility of the charge carriers indicate, however, that in the modified polymer the majority carrier (hole) generation is reduced by a factor of 2 and the mobility is reduced by more than an order of magnitude relative to the unmodified polymer (PNVC). Furthermore, the photoconductivity, using either hole or electron transport, decreases in bromine substituted PNVC, which, however, contradicts the earlier view of Inami et al.[59,60] proposing an increased photoconductivity on bromination of PNVC. It is felt, however, that the measurement techniques used by Inami et al.[60] do not lead to unambiguous material properties. Moreover, it is difficult to assess the influences of the electronic structure of the pendant units and the bulk chain conformation on the photoconductive properties of the brominated polymer separately. Notably, 3,6-dibromo-N-vinylcarbazole polymer exhibits excimer phosphorescence[61] in solid solution in the 77 K phosphorescence spectrum.

Pochan et al.[62,63] have studied the dielectric relaxation behaviour of poly(3-chloro-N-vinylcarbazole) and investigated the effect of sorbed oxygen on them. The chlorinated polymer exhibits only β- and γ-relaxations; however, unmodified PNVC shows α, β, γ and δ-relaxations in the temperature interval $-180°$ to $+240°C$. The oxygen sorption experiment indicates that oxygen associates itself with the carbazole units *via* electronic interaction and, consequently, an off-axis

dipole is induced in the carbazole moieties by the sorbed oxygen producing dielectric active motion about the axis of symmetry of the carbazole units.
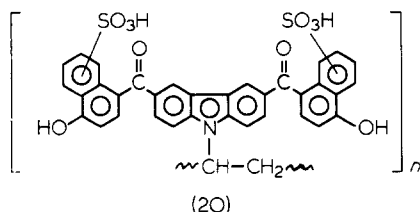
Ion-exchange resins

For production of heat-resistant, flame-retardant and chemically stable ion-exchange resins, some specific homopolymers and copolymers containing pendant carbazole (unsubstituted/substituted) units have been employed. These polymers have been subjected to chemical modifications through conventional organic reactions such as sulphonation, phosphorylation, chloromethylation followed by amination etc., resulting in the formation of ion-exchange resins.

Cation-exchange resins. PNVC, phthalic anhydride[50]/furfural[39,40] based PNVC polymers, NVC-divinylbenzene copolymer (*Table 2*) and NVC-furfural copolycondensate[39,40] have been converted into cation-exchange resins (*Table 4*) through incorporation of the sulphonic acid ($-SO_3H$) and phosphonic acid ($-PO_3H_2$) groups to the pendant systems existing in the polymeric matrix. Notably, in course of sulphonation, phthalic anhydride based PNVC polymer undergoes cyclization[50] through free carboxylic acid groups ($-COOH$) to form a polyquinonic structure (19) along with nuclear substitution of $-SO_3H$ groups, and the furfural based

(19)
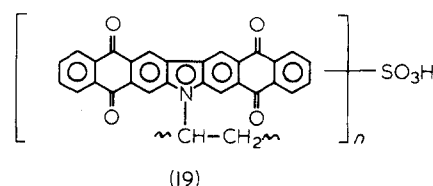
NVC and PNVC polymers suffer cleavage[39] owing to oxidation of the secondary alcoholic groups of the crosslinking agent, polyfurfural, causing creation of additional weak ionogenic $-COOH$ groups along with strong ionogenic $-SO_3H$ groups in the polymeric matrix (*Table 4*). More recently, an interesting polyfunctional cation-exchange resin (20) has been reported by Biswas and Das[51] through chemical modification of PNVC to poly(NVC-3,6-dicarboxylic acid) followed by condensation with 1-naphthol in presence of sulphuric acid which acts as a condensing catalyst as well as a sulphonating agent.

(20)

Sulphonated resins exhibit ion-exchange capacities in the range 4.50–5.12 milli equivalent/g, and weight losses of 10 and 50% in the temperature ranges 100°–180°C and 295°–590°C, respectively as presented in *Table 4*. Ion-exchange capacities of the phosphorylated resins compare well with those of sulphonated resins; however, the phosphorylated PNVC resin shows a comparatively lower capacity. Furthermore, the thermal stability of the phosphorylated (furfural based PNVC and NVC) resins are remarkably high as compared with others (*Table 4*).

Anion-exchange resins. The copolymers based on NVC/styrene, 3-methyl-NVC/styrene, 3-vinyl-*N*-ethyl-carbazole/styrene and 3-vinyl-*N*-methylcarbazole/styrene, (*Table 2*), have been specifically employed for the synthesis of anion-exchange resins[32,64,65]. These copolymers on chloromethylation[32,64,65] with mono-chlorodimethyl ether in the presence of $ZnCl_2$ followed by quaternization with tert-alkylamines, e.g. $(CH_3)_3N$, produce strong-base quaternary ammonium groups, $-N^+(CH_3)_3$, in the polymeric matrix leaving chloride ions free as anion-exchangers. The resins exhibit ion-exchange capacities in the range 3.6–3.8 milli equivalent/g.

Charge-transfer complexes

One of the most significant means of enhancement of the electrical and photoconductive properties in polymeric materials is perhaps through chemical modification of polymers involving charge-transfer (CT) complex formation. The electron transfer in the CT complexes invariably results in the appearance of new, broad and structureless absorption bands in the visible or ultraviolet spectrum and is often accompanied by perturbations of the absorption bands of the parent polymer molecule. The dipole-moment, conductivity and the optical properties of the CT complexes are different from those of the parent molecules.

Polymeric systems form ground-state as well as excited-state CT complexes. One of the important factors in these CT complexes is the overlap of the orbitals involved which is indirectly related to steric effects. The latter may well place serious limitations upon the extent to which conductivity can be enhanced by CT complex formation. In general, polymers can form three types of CT complexes[66]: (a) polymeric donor + monomeric acceptor, (b) polymeric donor + polymeric acceptor, and (c) polymeric acceptor + monomeric donor.

In fact, there is practically no information on the complex of type (c) particularly with carbazole units in the polymeric chain.

(a) Polymeric donor–monomeric acceptor systems. Polymers containing pendant carbazolyl groups (donors) linked directly or through flexible side-chain units to the backbone combine with monomeric acceptors through three types of CT interactions[36], viz. (a) 1:1 interaction involving each donor group and each monomeric acceptor molecule, (b) sandwich-like interaction in which each acceptor molecule is located in between two donor groups and (c) interaction through participation of more than two donor groups aggregated around each acceptor molecule. The relative effectiveness of these three modes of donor–acceptor interactions is governed by the nuclear substituent of the pendant system, the nature of the polymeric backbone and the side-chain structure. For correlating the structure of polymers with the different modes of CT complex formation, various homopolymers, copolymers and copolycondensates containing pendant carbazole (substituted/unsubstituted) units have been employed. In general, PNVC appears to be the most thoroughly studied[1] homopolymeric donor system, the CT interaction of which with various monomeric acceptors (TNF, TCNQ, TCNE, halogenoquinones, etc.) has been examined and their electrical and photoconductive properties have been evaluated[1]. Pertinently, the CT complex of PNVC:TNF (2,4,7-trinitrofluorenone) is the most important and common material for use as a photoconductive layer in xerography and related techniques[67–69]. The mixture of PNVC and TNF (1:1 molar ratio) contains three structural components, i.e. a complex PNVC:TNF, uncomplexed carbazole units of PNVC and free TNF molecules, which make the interpretation of the electrical properties rather ambiguous in terms of a simple model. New photosensitive materials have since been developed[56–58] through CT complex formation between the low molecular weight acceptors and thermally stable chemically modified PNVC donors containing halogen substituents in the pendant carbazole rings, viz., poly(3-chloro-*N*-vinylcarbazole) (P3ClNVC), poly(3,6-dichloro-*N*-vinylcarbazole (P3,6ClNVC), poly(3-bromo-*N*-vinylcarbazole) (P3BrNVC), poly(3,6-dibromo-*N*-vinylcarbazole) (P3,6BrNVC), poly(3-iodo-*N*-vinylcarbazole) (P3INVC), and poly(3,6-diiodo-*N*-vinylcarbazole) (P3,6INVC). Introduction of halogen substituents into 3- and/or 6-positions of the carbazole rings of PNVC causes formation of complexes with TNF showing much greater complexing enthalpy. Within the temperature range 268–303 K, ΔH values for the complexes increase in the following sequence[57]:

$$\Delta H_{P3ClNVC} < \Delta H_{P3,6ClNVC} < \Delta H_{P3BrNVC} < \Delta H_{P3INVC}$$
$$< \Delta H_{P3,6BrNVC}.$$

However, the entropy increments decrease in the same sequence. In comparison with the PNVC:TNF complex, each of these complexes shows a higher degree of complex formation[57] and increased stability, and exhibits more regular structure. Significantly, all the CT complexes formed from the halogenated PNVCs and TNF have similar charge-transfer energy values.[57]

Thermal properties. CT complexes of halogenated PNVCs and TNF exhibit endothermic and exothermic effects.[57] The endothermic effect is due to a thermal dissociation of complexes and the melting of the acceptor TNF. The temperature ranges of these endothermic effects lie considerably below T_g of the parent polymer (donor matrix) in the complex, and therefore, the structural changes of the complexes reflected by the endothermic effect are caused mainly by TNF molecule. Notably, the temperatures of the maximum endothermic effect of the complexes of monosubstituted polymers are lower than those of disubstituted ones with the same halogen substituent.

Electrical properties. The halogen substituents play an important role[58] over the dark conductivity of the complexes of halogenated PNVCs and TNF. The dark conductivity at room temperature for all complexes of the monosubstituted polymers (P3ClNVC:TNF, P3BrNVC:TNF, P3INVC:TNF) is greater than that for the PNVC:TNF complex. However, the conductivity for complexes with disubstitution (Cl,Br,I in 3- and 6-positions, respectively, in the carbazole rings of PNVC) is lower than that for PNVC:TNF complex, but higher than the conductivity for pure TNF. It reveals that the introduction of the halogen atom/atoms strongly affects the potential barrier between the substituted pendant carbazole unit of the polymer and the acceptor molecule (TNF). This influence may be rationalized in terms of the kind of substitution (mono- or di-substitution), the electron affinity of the substituent (Cl,Br,I), the changed ionization potential connected with electron affinity of the carbazole units of the polymer matrix in the complex, and the change of electron density which is transported between localized states (localized on the TNF molecules).

Pielichowski and Starzyk[58] have suggested that the halogenated PNVCs:TNF CT complexes exhibit also very interesting photoconductive properties.

CT complex formation between the polyesters (11) containing pendant carbazole units linked directly to the backbone and the acceptor molecule TNF has been reported by Tazuke *et al.*[36] As is experienced[36] from the strong excimer fluorescence, the carbazole units of PNVC are tightly packed and, consequently, the accommodation of bulky acceptor TNF is somewhat difficult in the space between the adjacent carbazole units, which results in lower stability constant value for the complex; however, the space between the carbazolyl groups is about 5 Å for the polyester (11) [R_1 =carbazole (N) – $\overset{}{C}$–CH_3][36], which is suitable for complexing with TNF molecule. In the other polyesters (11) (R_1 = –CH_2– and –*p*-benzene)[36], the distance between the carbazolyl groups is too large to hold a TNF molecule, and, therefore, the absence of both intra- and intermolecular interactions reflects on the small values of stability constant for the complexes. The former polyester possessing weak interactions between the carbazolyl groups as indicated by weak excimer emission favours the formation of sandwich-like complexes.

As pointed out in the preceding discussion (Tazuke *et al.*[35,36]), the adequate space between the carbazolyl groups in the polymeric matrix for accommodating TNF molecule results in the increase of the stability constant value for the CT complex. Therefore, the flexible side-chains (chain of methylene groups) connecting the carbazolyl groups to the backbone of the polymers, polyesters (12), would facilitate CT complex formation with TNF. The stability constant value for this system increases[37] with decreasing length of the main chain repeating units separating the pendant carbazolyl groups, which results in stronger excimer emission[35], and with increasing degree of polycondensation which reflects the ease of aggregation of the carbazolyl groups around TNF.

More recently, Tazuke *et al.*[41] have reported CT complex formation between the polyurethanes (13) containing pendant carbazole units linked to the backbone through flexible methylene groups and TNF. It has been observed that the complex formation increases with higher local concentration of the carbazolyl groups which in fact manifests in the high molecular weight of the polyurethanes, a trend more or less consistent with the situation in the polyester cases. The polyurethane complexes are enthalpically less favoured but the entropy of these complexes, however, overcompensates the enthalpic disadvantage because of low entropy state due to restricted mobility of the pendant chromophores caused by the intra- and intermolecular hydrogen bond formation[41] in the parent polymers.

The vinyl polymers (1) (*Table 1*) containing pendant carbazole units linked to the backbones through flexible side-chain other than methylene groups have also been reported[10] to form CT complexes with TNF. Notably, the absorption spectra of these complexes do not show any distinct CT band; however, their CT absorptions spread over most of the visible region.

(b) Polymeric donor–polymeric acceptor systems. A critical study[38] has been made over the CT complexes formed between the polymeric donors (21) (polyesters containing pendant carbazole units linked to the backbone through flexible methylene groups) and the strongly electron accepting polymers (22) (polyurethanes bearing pendant trinitrofluorenone units). The complex

Polymeric donors (polyesters):
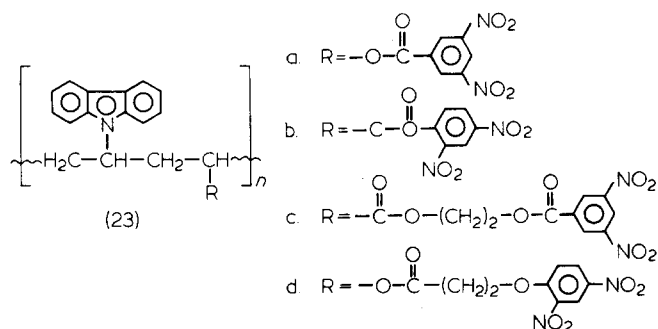

(21)
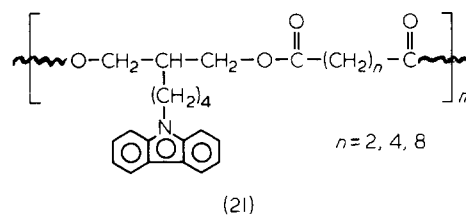
Polymeric acceptors (polyurethanes):

(22)
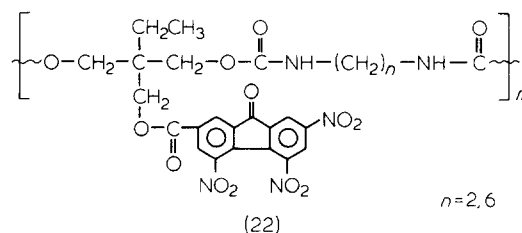
formation depends on the degree of polycondensation ($\overline{DP}$) as well as on the structure-matching of the donor and acceptor polymers. With increasing $\overline{DP}$, the solubility of the polymeric donor–acceptor mixture tends to decrease due to strong CT complex formation between a polymeric donor–acceptor pair of matched structure.

Copolymer containing donor–acceptor units

Recently, Chang *et al.*[70] have reported novel

syntheses of NVC copolymers, (23a–23d), in which electron accepting groups (dinitrophenyl) have been incorporated into the polymer backbone through reactions of NVC–vinylalcohol copolymer prepared by alkaline hydrolysis of NVC–vinylacetate copolymer, and NVC–acryloyl chloride copolymer with the appropriate acid chlorides and hydroxy compounds containing dinitrophenyl groups, respectively.

(23)

a. $R = -O-\overset{O}{\underset{}{C}}-$ (NO$_2$)(NO$_2$)

b. $R = -\overset{O}{\underset{}{C}}-O-$ (NO$_2$)

c. $R = -\overset{O}{\underset{}{C}}-O-(CH_2)_2-O-\overset{O}{\underset{}{C}}-$ (NO$_2$)(NO$_2$)

d. $R = -O-\overset{O}{\underset{}{C}}-(CH_2)_2-O-$ (NO$_2$)(NO$_2$)

Owing to intramolecular charge-transfer complex formation through interactions between the pendant carbazole units (donors) and the dinitrophenyl groups (acceptors) linked to the same polymer backbone, these materials are particularly expected to exhibit photoconductive properties[70]. The copolymer (23a) has nearly the same resistance–capacitance time (*RC* time) as PNVC doped with 10% *p*-chloranil. Notably, the addition of *p*-chloranil to this copolymer does not improve the photoresponse, but rather slows it down. However, the copolymer (23b) shows a very poor photoresponse as compared with (23a). In fact, this difference occurs due to presence of a carbonyl group attached to the dinitrophenyl unit in the copolymer (23a), which makes it a stronger electron acceptor than (23b). This investigation has been further extended[70] for studying the effect of side-chain length and flexibility on the photoresponse. Copolymer (23c) containing flexible side-chains exhibits 10% increased absorbance compared with PNVC and shows an *RC* time which is comparable with that for *p*-chloranil doped PNVC but much lower than that of the copolymer (23a). Notably, the copolymer (23d) containing flexible side chain shows no photoresponse. This anomalous behaviour of (23d) is responsible[70] for the non-existence of carbonyl group adjacent to the dinitrophenyl unit as there is in the case of (23c). It emphasizes that the increase in the flexibility and the length of the segments holding the dinitrophenyl groups to the polymer main chain does not improve the photoresponse. Chang *et al.*[70] have also reported that NVC–vinyl alcohol copolymer on modification through chemical reaction with *p*-chloranil instead of doping affords a photoconductive material (24) whose photoresponse is stronger than that for undoped PNVC, but somewhat inferior to that of PNVC doped with *p*-chloranil.


(24)
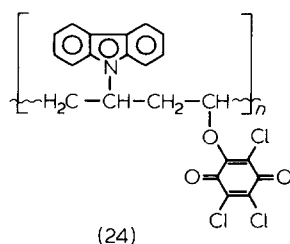
POLYMERS CONTAINING CARBAZOLE UNITS IN THE MAIN CHAIN

Polyamides

A series of polyamides (25), containing carbazole units in the main chain, has been reported by Tazuke *et al.*[71] The polymers have been synthesized by low temperature solution polycondensation of 3,6-diamino-*N*-ethylcarbazole with various diacid chlorides, viz. succinoyl, glutaroyl, adipoyl, suberoyl and sebacoyl dichlorides.


(25)   *n* = 2, 3, 4, 6, 8
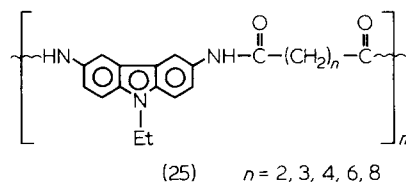
As reported[71], a polyamide with carboxylate end groups is much more stable than that with amine end groups. Apparently, the amine group attached to electron donating carbazole unit is susceptible to oxidation. These polyamides are polymeric electron donors[71] in which the donor units (carbazole) are arranged with regular intervals. Pertinently, studies on donor–acceptor interactions between the polyamides and the acceptor molecule, 1,3,5-trinitrobenzene (TNB), reveal[71] that the complexes exhibit higher stability constant values as compared with the case of the monomeric model compound, *N*-ethyl-3,6-bis(propionoyl-amino)carbazole (26). However, there is no regularity in the sequence of

(26)
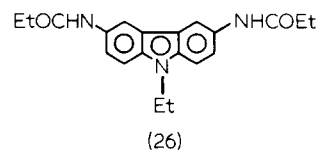
stability constants in respect of the number of methylene units separating two carbazole groups. There is a possibility that donor units in the polymer molecules might be located in such a way that each donor unit could cooperate to form a donor–acceptor complex. In fact, no specific interactions between the carbazole units could, however, be detected[71] by fluorescence spectroscopy.

Recently, synthesis of some thermally stable aromatic polyamides, (27a–27e), based on carbazole units has been reported[72] through polycondensation of *N*-ethylcarbazole-3,6-diacid chloride with various aromatic diamines, viz., *m*-phenylene diamine, *p*-phenylene-diamine, benzidine, 4,4′-diaminodiphenylmethane and 2,7-diaminofluorenone.

(27)

a. $R = $ (naphthyl) ;

b. $R = $ (phenyl) ,

c. $R = $ (biphenyl) ,

d. $R = $ (diphenylmethane) ,

e. $R = $ (fluorenone)
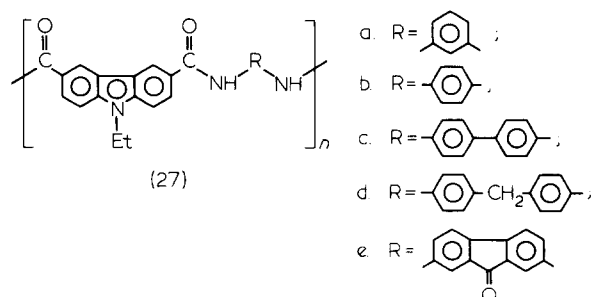
Thermal stability of these polyamides, depending on the structure of the diamine unit, increases[72] in the following order: (d) and (e) < (b) < (c) < (a).

Polyimides

Most of the polyimides known at present have been obtained from carbocyclic aromatic monomers, but of late polyimides based on heterocyclic monomers have received considerable attention[73]. Biswas and Das[74,75] have reported some polyimides (28a–28c) based on carbazole units in the main chain. These polymers have

(28)

a. R = H[75],

b. R = CH₃–,[74]

c. R = ⟨O⟩–CH₂–,[75]
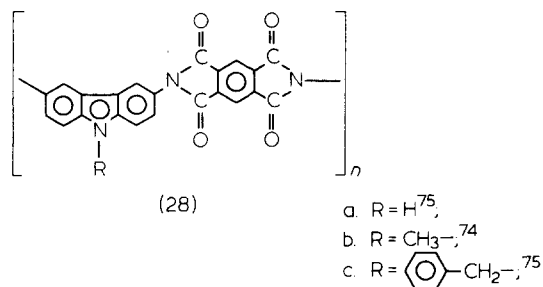
been synthesized by a two-stage process involving polycondensation of the diamine monomers, e.g., 3,6-diamino carbazole and N-substituted 3,6-diamino carbazoles with pyromellitic dianhydride in polar organic solvents resulting in the formation of pre-polymers [poly(amic acids)] which, on thermo-cyclodehydration, produce insoluble and infusible polyimides. The pre-polymers have been employed also for the preparation of polyimide films. The symmetrical distribution of heteroatomic effect on the active sites of the diamine monomers, which, in addition with large π-electron systems involved in carbazole rings, facilitates the interaction between the carbazole monomers and dianhydride molecules through carrier solvent molecules causing the formation of pre-polymers with excellent yields and moderate viscosities.

Despite this fact, the incorporation of the hydrocarbon substituents to heteroatom in diamine carbazole monomer brings about a characteristic variation of thermal and electrical properties.

Thermal properties. Thermal stability of the polyimides (up to temperature 450°C) depends on the size of the N-substituents, and decreases in the following order: (c)>(b)>(a); however, at higher temperature, the polymers (28b) and (28c) suffer cleavage of N-substituents as experienced[74,75] from exothermic effects. The higher thermal stability of (28c) possibly results from the presence of bulky N-substituent and intermolecular electronic interactions involving $-CH_2C_6H_5$ groups.

Electrical properties. All the polyimides are good insulators. Their permittivity and dielectric loss, depending on the structure of the N-substituents, increases in the following sequence: (a)<(b)<(c), which is, in fact, well consistent with the increasing order of the polarity of the substituents.

Polyarylates

Recently, Biswas and Das[76,77] have reported a new range of insulating polyarylates (29a–29c) containing carbazole units in the backbone. In general, the polyarylates have been synthesized by low temperature solution polycondensation of N-methylcarbazole-3,6-diacid chloride with various diphenols, viz., resorcinol, bisphenol A, phenolphthalein, in presence of acceptor catalytic reagent, pyridine.


(29)
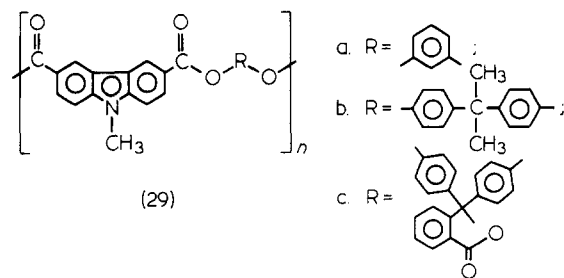
Thermal properties. In general, the polymers retain their fundamental chemical structures up to the temperature range 260°–300°C. However, the overall thermal stabilities of these polymers decrease in the following order: (29a)>(29c)>(29b). The cardo-polyarylate (29c) possessing bulky phthalide groups hinders the molecular rotation with respect to sp³-hybridized carbon causing segmental motion to occur at higher temperature, and thereby resulting in higher thermal stability relative to (29b). However, in the polymer (29a), the carbon atoms in the main chain are sp²-hybridized, resulting in delocalization of π-electrons throughout the chain causing rigidity in the molecule and thereby increasing the bond energy in the polymer, which in consequence reflects an enhanced thermal stability in (29a) as compared to others.

Dielectric properties. The polymer (29c) is found to exhibit higher permittivity relative to other polymers (*Table 5*). Moreover, all the polymers behave like insulators as evident from the permittivity and the dielectric loss values presented in *Table 5*. In general, permittivity of the polymers decreases with increasing temperature; however, the dielectric loss under this condition increases owing to electrical conduction in the polymer molecules at higher temperatures.

Polysulphones

Some thermally stable polysulphones[78] (30) have been synthesized through polycondensation of 3,6-carbazoledisulphonyl chloride with aromatic compounds such as benzene, toluene, diphenyl ether, etc., in presence of $AlCl_3$, $FeCl_3$ or polyphosphoric acid. The compound sodium-3,6-carbazoledisulphonate also has been

(30)
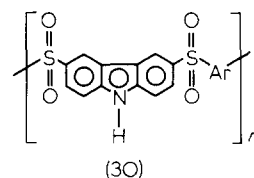
reported[78] to produce these polymers in presence of polyphosphoric acid. In general, polysulphones (30) are

*Table 5* Dielectric properties of polyarylates (29) *

Frequency (kHz)	Temperature (°C)	Permittivity/dielectric loss		
		(29a)	(29b)	(29c)
100	40	3.17/0.0038	3.20/0.0030	4.41/0.0076
1000	40	2.92/0.0095	2.74/0.0042	4.16/0.0017
10000	40	2.50/0.0082	2.56/0.0059	4.01/0.0050
100	70	2.55/0.0073	2.80/0.0068	4.02/0.0056
100	100	2.10/0.0099	2.67/0.0073	3.25/0.0131
100	150	– /0.0158	2.13/0.0100	2.01/0.0140

* Taken from the data of Biswas and Das[76,77]

found to retain their chemical structures up to the temperature range 310°–355°C. Interestingly, 3,6-carbazoledisulphonyl chloride produces[78] also soluble polysulphonamides and polysulphonates on polycondensation with diamines such as *m*-phenylenediamine etc., and diols such as ethylene glycol etc., respectively.

Polymeric azo-dyes

Azo-dyes have so far been synthesized[79] reportedly from coaltar constituents, e.g., quinoline, pyridine and a variety of aromatic hydrocarbons. More recently, Biswas and Das[80] have synthesized a carbazole (a coaltar byproduct) incorporated polymeric azo-dye (31) by

(31)
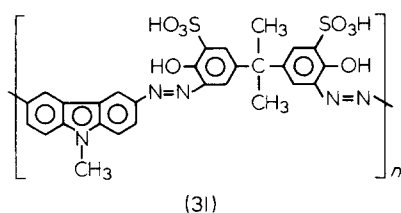
diazotization of carbazole derivative, *N*-methylcarbazole-3,6-diamine, and subsequent coupling reaction with 2,2-bis(4-hydroxyphenyl-3-sulphonate-Na)-propane prepared from bisphenol A.

The dye is sensitive to inorganic acids developing different colours which are, in fact, due to internal salt formation[80] with acids; however, the deepening of the colour is due to resonance among charged canonical structures (32). Furthermore, it is diamagnetic in nature possessing a magnetic susceptibility constant value 0.45×10^{-6}.


(32)
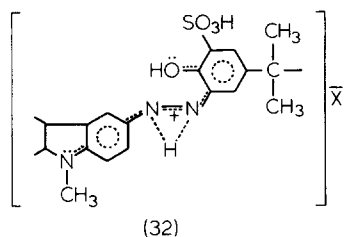
Electrical properties. The volume conductivity (σ) and the dielectric loss for the polymer are found[80] to be in the ranges 0.96–2.23×10^{-6} ohm^{-1} cm^{-1} and 0.165–0.192, respectively, under the electric field over a frequency range 300 Hz–30 kHz at 25°C. It is evident from σ values that the polymer possesses semiconductivity which, in fact, occurs under the influence of orientational polarization in presence of external electric field as well as due to intra- and intermolecular hydrogen bonding established in the molecular chains containing strong polar groups, viz., $-N=N-$, SO_3H and phenolic OH. It is suggested[80] that the transport of charge through hydrogen bonds is of considerable importance in determining the electrical properties. The electron mobility is more facilitated in the hydrogen-bonded network matrix causing higher conductivity of the polymer. However, this effect is more pronounced when the polymer is composed[80] with polyvinyl alcohol to produce coloured flexible film. The resulting conductivity of the film (of the order of 10^{-6} ohm^{-1} cm^{-1}) is 10^3 times higher than that of polyvinyl alcohol. The enhancement is more reasonable in the sense that the polymer (31) combines with another polymer,

polyvinyl alcohol, containing secondary hydroxyl groups through van der Waal's forces acting to hold them together, causing thereby the formation of sufficiently stable hydrogen-bonded network structure.

Polysiloxanes

Recently, synthesis of two interesting polymers (33a, 33b) containing silane and carbazole units in the main chain has been reported[81] through polycondensation of bis(diethylamino)methyl phenyl silane with 2,7-bis(hydroxymethyl phenyl silyl)-*N*-methylcarbazole and 2,7-bis(hydroxydiphenyl silyl)-*N*-methylcarbazole, respectively.
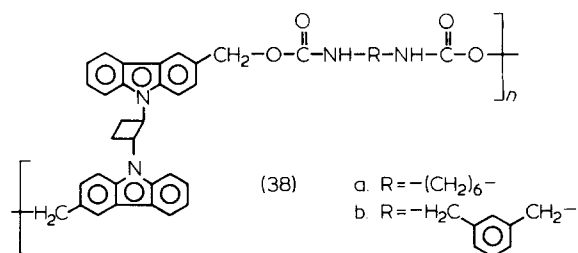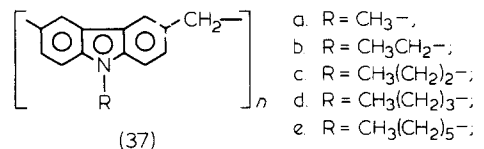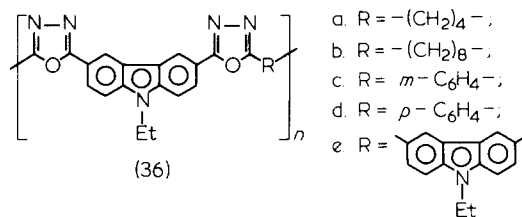

(33)
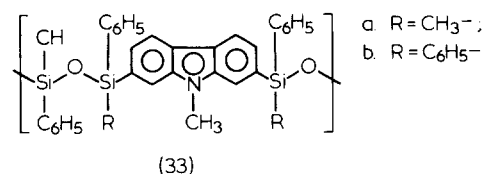
Polyquinone

A heat-resistant ladder polyquinone[82] (35) based on carbazole units has been synthesized through two-step process: (a) Friedel–Crafts reaction between carbazole and pyromellitic dianhydride in presence of AlCl$_3$, and (b) thermal cyclodehydration of the resulting poly(keto acid) (34) at temperature 280°–300°C.

(34) (35)
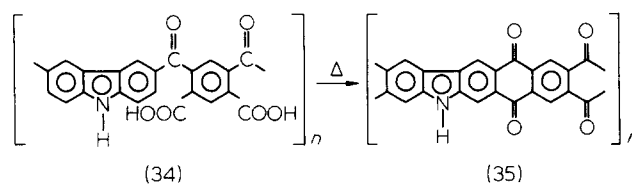
The polymer (35) has been reported[82] to exhibit paramagnetic, semi- and photoconductive properties.

Miscellaneous carbazole polymers

Some interesting polymers containing carbazole units in the main chain are listed below:

(36)

a. R = $-(CH_2)_4-$;
b. R = $-(CH_2)_8-$;
c. R = $m-C_6H_4-$;
d. R = $p-C_6H_4-$;
e. R =

(37)

a. R = CH_3-;
b. R = CH_3CH_2-;
c. R = $CH_3(CH_2)_2-$;
d. R = $CH_3(CH_2)_3-$;
e. R = $CH_3(CH_2)_5-$;

(38)

a. R = $-(CH_2)_6-$
b. R = $-H_2C$ — CH_2-

Poly-1,3,4-oxadiazoles[83] (36a–36e) have been obtained by dehydrocyclization of polyhydrazides prepared by polycondensation of N-ethylcarbazole-3,6-diacid chloride with dihydrazides of the corresponding dicarboxylic acids (R$<^{COOH}_{COOH}$). The polymers (36a–36e) possess initial thermal stability[83] up to the temperature range 370°–400°C. The carbazole polymers[84] (37a–37e) which have been prepared through reaction of a series of N-alkylcarbazoles with formaldehyde, are expected to show photoconductivity. Two novel photoconductive polymers (polyurethanes) (38a, 38b) have been recently reported by Tazuke *et al.*[18]. The main component which is responsible for the photoconductive behaviour of the polymers (38a, 38b) is *trans*-1,2-di-N-carbazolylcyclobutane unit which is, in fact, an effective donor unit for producing a good photoconductive composition with TNF molecule.

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