the alkyne to the alkene.[9] No absorbances for Si–O–Pd moieties were discernible. However, considering the percentages of Pd in the sample, these could be obscured by the large Si–O absorbances in the 1200–800 cm^{-1} region. Thermogravimetric analysis (TGA) showed 7% weight loss on heating (20 °C/min) to 900 °C. Oven-dried (110 °C, 24 h) samples showed <4% weight loss on heating to 900 °C, which confirms the high degree of cross-linking in the system. Powder X-ray diffraction analysis (XRD) showed no diffraction pattern, signifying that the particles are too small and dispersed to allow a significant repeating unit for the crystallinity determination.[12] However, by doubling the palladium loading, we observed a broad signal (again due to high metal dispersion) for Pd(0) at 2.25 Å. Certainly, further analysis is in order to ensure that smaller, amorphous, or oxide-coated metal salts are not present. No palladium oxide at 2.64 Å or any other Pd crystalline forms were observed. Scanning electron microscopy (SEM) studies using energy-dispersive analysis with X-rays (EDX) indicated that the deposition of palladium is uniform throughout several regions of the polymer studied. Transmission electron microscopy (TEM) showed that the particles were generally on the order of 15 Å in size and uniformly dispersed (Figure 1). A few larger particles, up to ~80 Å, were also detected. A particle size distribution (based on 120 particles) is shown in Figure 2. During the SEM and TEM analysis, much charging of the material occurred. In some samples, particles of palladium in the xerogel were rapidly converging to form larger particles while viewing under the TEM probe. This type of insulator charging during electron field bombardment has recently been addressed.[13]

Finally, in an effort to form sol–gel-derived material containing palladium(0) with no Si–H residue, we have developed a method involving the use of palladium(II) acetate (0.05 equiv), triethoxysilane (0.25 equiv), and tetraethoxysilane (2.5 equiv) in THF/water to afford xerogels that are free from any residual Si–H moiety by FTIR analysis. This is complementary to our system using triethoxysilane and an alkyne for removal of the Si–H residue as discussed previously.

Analysis of the porosity and metal surface area as well as further use of this method for heterogeneous catalyst preparation is being done. Use of this method for the deposition of other metals and mixed-metal composites is currently under investigation for $\chi^{(3)}$ NLO enhancements on monolithic xerogels containing conjugated organic oligomers.

Acknowledgment. We thank the Department of Health and Human Services, Biomedical Research Support Grant, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their generous support. We are grateful to Dr. N. Watabe and Dana Dunkelberger of the University of South Carolina Electron Microscopy Center and Professor Willard Sharp of the Department of Geology for their assistance. Additionally, we thank Dr. C. Le Gressus of the French Atomic Energy Commission, Materials Division, for helpful suggestions on the insulator charging mechanisms. The scanning electron microscopy was purchased with a grant from the National Science Foundation (BIR-8805143).

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Reviews

Ladder Polymers: Recent Developments in Syntheses, Characterization, and Potential Applications as Electronic and Optical Materials

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This review covers the syntheses and characterization of ladder polymers exhibiting significant π-electron conjugation. Special emphasis is placed upon discussion of electrical, magnetic, and optical properties and upon the difficulties associated with the synthesis of highly defined structures. Insight is provided into overcoming the problem of polymer solubility that has plagued early research involving ladder polymers.

Introduction

It is well-known that polymers with extensive π-electron conjugation exhibit unusual physical properties.[1,2] Since the observation of metallic conductivities for polyacetylene samples doped with electron donors or acceptors, π-electron polymers have been the focus of an impressive re-

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search effort. Recently, a number of such polymers have been observed to exhibit large, ultrafast nonlinear optical (NLO) responses; this observation has spurred scientists to explore the potential application of such materials for the development of optoelectronic devices ranging from optical computers to sensor protection elements.[3-6] Electrical and nonlinear optical properties of such polymers are dramatically affected by the π-electron correlation (or coherence length), which is in turn determined by the effectiveness of p-orbital overlap along the polymer backbone.[7-12] Thus, polymer conformation and ultrastructure will be a concern in designing polymers for optimum π-orbital overlap and electroactivity. For linear conjugated polymers such as polyacetylene and polythiophene, it is very difficult to realize a long-chain polymer in a planar configuration where adjacent p orbitals will be collinear. On the other hand, optimum orbital overlap is obviously realized with the planar configuration of a ladder polymer; therefore, electron delocalization in the ladder polymer is enhanced. Theoretical calculations of the third-order susceptibility of conjugated polymers, such as polydiacetylene, indicate a strong relationship between $\chi^{(3)}$ and the delocalization of π-electron clouds:

$$\chi^{(3)} \propto D^6/(E_F d)^3$$

where D is a delocalization parameter, d the interatomic spacing, and E_F the Fermi energy.[8b,c] It can be seen that large electron delocalization will enhance the optical nonlinearity of the polymer, and hence conjugated ladder polymers are good candidates for NLO studies.

Another factor influencing the technological utility of a conjugated π-electron polymer is the environmental stability of the polymer. Most of the linear electroactive polymers, such as polyacetylene, poly(*p*-phenylene), polythiophene, etc., are unstable in air, and their electronic properties rapidly degrade with the interruption of π-electron delocalization associated with air oxidation.[1-5] Ladder polymers, in contrast, possess a high resistance to mechanical, thermal, and chemical degradation as is evident from both theoretical calculation and experiments.[13]

Unfortunately, ladder polymers have problems associated with their special structures; the most serious of these being that of poor solubility, particularly in organic solvents. This is especially true for ladder polymers with delocalized π-electrons because of strong interaction between the π-electron clouds of adjacent polymer chains. For example, theoretical calculations on poly(benzimidazobenzophenanthroline) (BBL) have shown that the interchain π–π interactions to be even stronger than intrachain chemical bonds.[14] This intrinsic insolubility greatly inhibits characterization and the processing of ladder polymers. For the former, powerful techniques of high-resolution nuclear magnetic resonance (NMR), gel permeation chromatography (GPC), etc., cannot be used. Poor solubility obviously inhibits processing of polymers into optical quality films, but the consequences of poor solubility are particularly far reaching for asymmetric polycondensations where solubility problems can result in low molecular weights (i.e., products may be better described as oligomers than polymers) and incomplete condensation can result in a variety of structures (i.e., various amounts of open-chain and fully fused ring materials).

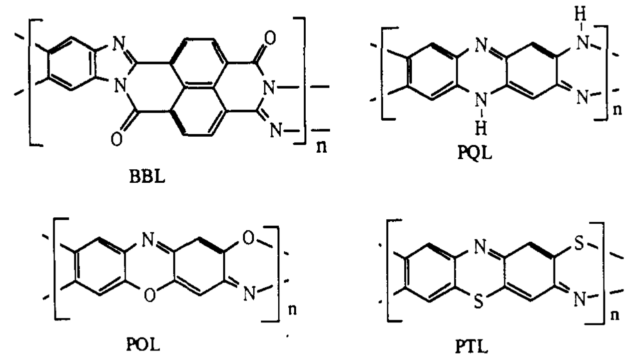

Figure 1. Structures of ladder polymers.

Despite problems deriving from poor solubility, research efforts on ladder polymers have continued on a modest scale. Three research avenues have, in general, been pursued. First, the electrical, optical, and magnetic properties of some known ladder polymers, e.g., BBL,[15,16] poly(1,6-dihydropyrazino[2,3-*g*]quinoxaline-2,3,8-triyl-7-(2*H*)-ylidene-7,8-dimethylidene) (PQL), poly(2*H*,11*H*-bis[1,4]oxazino[3,2-*b*:3′,2′-*m*]triphenodioxazine-3,12-diyl-2,11-diylidene-11,12-bis[methylidene]) (POL), poly-(2*H*,11*H*-bis[1,4]triazino[3,2-*b*:3′,2′-*m*]triphenodithiazine-3,12-diyl-2,11-diylidene-11,12-bis[methylidene]) (PTL),[15,17] etc., have been studied (see Figure 1). Progress has been made in doping these materials to obtain highly conductive materials.[15,17] Second, the problem of improving the processibility of ladder polymers has been addressed by two approaches: ladder structures have been derivatized with suitable side groups to destabilize the interchain interaction (thus improving the processibility), and ladder polymers have been prepared by thermal treatment of a soluble precursor polymer. Interchain interactions decrease dramatically as the molecular interaction distance decreases; thus, the introduction of reasonably bulky side groups into a ladder structure will improve the solubility of ladder polymer. Our research has combined these two approaches.[18-20] Derivatized ladder polymer precursors have been synthesized, processed into thin films, and then thermally treated to obtain ladder polymer films that showed very large third-order NLO susceptibilities. Another approach is that reported by Jenekhe et al.,[21] who demonstrated that a reversible formation of electron donor–acceptor complexes of rigid-chain polymers (including

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Table I. Calculated Ionization Potentials (IP), Band Widths (BW), and Bandgaps (E_g)

polym	IP, eV	BW, eV	E_g, eV	ref
polyacene	6.0	5.3	0.2	31
	5.8	5.9	0.0	30
poly(pyridinopyridine)	8.7	3.9	2.9	31
PANP	8.7	4.3	3.0	30
poly(pyrazinopyrazine)	8.1	4.4	0.0	31
	8.1	5.1	0.0	29
poly(perinaphthalene)	4.0	4.4	0.3	25

ladder polymers as BBL and PQL) with Lewis acids (such as $GaCl_3$, $AlCl_3$, and $FeCl_3$, etc.) allows dissolution in organic solvents to form viscous solutions that can be processed by conventional methods. Finally we note ladder polymer films can also be prepared by electrochemical polymerization of special monomers[22,23] and by vapor-phase polymerization and deposition.[24,25]

In this review, we review the progress in ladder polymer studies, mainly focusing on the ladder polymers with potential electroactivities and special optical properties. The first section surveys theoretical work on ladder polymers and provides insight into the basis of their interesting electroactivity. The second section reviews the synthesis and characterization of conjugated ladder polymers. In reading the first two sections the reader should exercise caution in attaching great significance to the hypothetical ladder structures discussed. The real structures are likely more complicated than can be ascertained from available data. This situation will be addressed in detail in the conclusion section.

Electronic Structures of Ladder Polymers: Theoretical Studies

Conjugated ladder polymers have attracted the attention of theoreticians because of their special structure. Since most of the ladder polymers have very complicated electronic structures, only a few ladder polymers have been investigated using first-order Hückel molecular orbital theory,[25,31] extended Hückel molecular orbital theory (EHMO),[26,27] and valence effective Hamiltonian (VEH) theory.[28-31] Table I lists values calculated for ionization potential, bandgap, and bandwidth for some selected ladder polymers by using VEH theory.

Polyacene (see Scheme I) is the most theoretically investigated ladder polymer although it has not been synthesized in a well-defined structure. A simple Hückel theory calculation[26] indicated a zero bandgap for polyacene and hence predicted a metallic behavior. Kivelson et al.[32] predicted, using a nearest-neighbor model, that polyacene has a Fermi surface lying at the edge of the Brillouin zone but that an accidental degeneracy between the valence bands and conduction bands makes it metallic. They predicted that polyacene would be a material that may possess interesting condensed-phase properties including high-temperature superconductivity and ferromagnetism. On the other hand, an EHMO[26] calculation showed that the degeneracy at $k = \pi/a$ is slightly split due to the inclusion of non-nearest-neighbor interactions. VEH calculations by Bredas[30] indicated IP, BW, and E_g values as shown in Table I, and a zero bandgap was also predicted. However, VEH calculations by Kao et al.[31] revealed a bandgap of 0.2 eV by using the MOMM (molecular-orbital-based molecular mechanics methods) optimized geometry of polyacene. These results seem to be consistent with an extrapolated value of 0.5 eV from oligomers (benzene, naphthalene, etc.) to polymers.

Poly(pyridinopyridine) (pyrolyzed poly(acrylonitrile), PANP, see Scheme VI) can be viewed as an analogue of polyacene in which all of the C–H positions along one edge of polyacene have been replaced by nitrogen. A semiempirical extended Hückel theory predicted that the top of the valence band in PANP is largely composed of nitrogen lone-pair orbitals. The bandgap was predicted to be 1.03 eV.[27] VEH calculations, however, gave rise to larger bandgaps, i.e., values of 2.9–3.0 eV have been obtained.[30,31] VEH calculations also indicated that the highest occupied band is a π-band with a very large (4.3 eV) width and the nitrogen lone-pair band is located 0.85 eV below the top of the highest occupied π-band. This is in contrast to the results obtained from EHMO calculations.[27] According to bandgap predictions, it appears unlikely that conductivities as high as 5 S/cm may be obtained on PANP.[33]

Further substitution of C–H groups in PANP by N produces poly(pyrazinopyrazine) (see Scheme X). VEH calculations[29] showed that the σ-nitrogen lone-pair band is wide (5.1 eV) due to the contribution from $2p_y$ orbitals on both N and C. The lone-pair orbital becomes the highest occupied band. It was predicted that the first occupied energy band, which is a π-band, overlaps the lone-pair band. As a result of these calculations, paracyanogen is predicted to be metallic; EHMO calculations showed similar trends.[27] But experimental measurements so far on paracyanogen observe only semiconductivity.[34] This discrepancy has been attributed to the low molecular weight of paracyanogen polymers synthesized so far.

Poly(perinaphthalene) (PPN, see Scheme V) has also been studied by using VEH theory.[25] The bandgap was predicted to be 0.3 eV, which is much lower than that found in *cis*-polyacetylene (*cis*-PA). It was argued that for an isolated chain with a planar geometry, contributions to the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) come only from the atoms on the periphery of the chain, and PPN can be considered as formed by two interacting *cis*-polyacetylene chains. The interaction between the two *cis*-polyacetylene subunits in PPN provokes the splitting of the original *cis*-PA HOMO and LUMO band, resulting in a much smaller bandgap than in *cis*-PA. An ionization potential of the order of 4.0 eV and a HOMO bandwidth of ca. 4.4 eV were also predicted.[25]

Synthesis and Characterization of Ladder Polymers

Synthesis of ladder polymers has been carried out by two different routes. The first route employs a two-step procedure in which a soluble precursor is synthesized and

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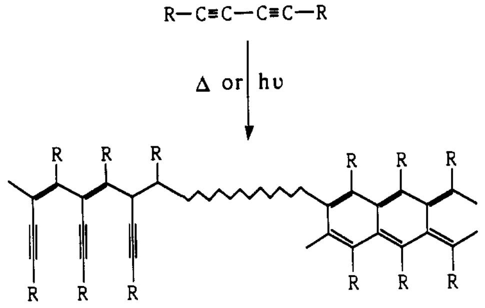
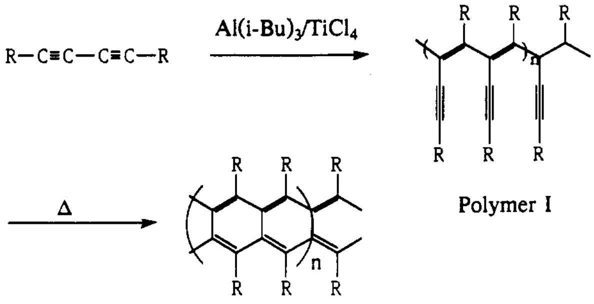
Scheme I



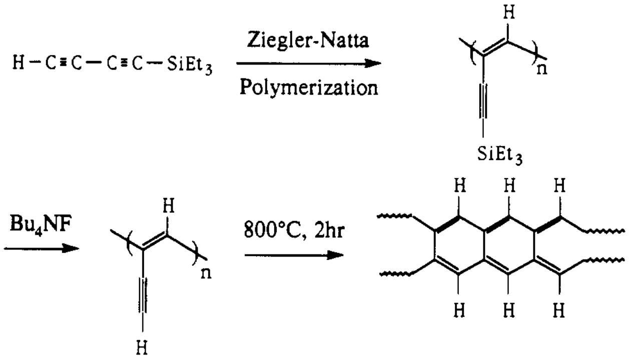
Scheme II



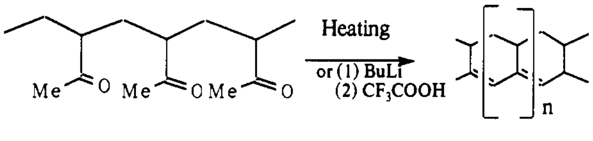
subsequently converted to a ladder polymer. This route leads to materials in desired forms such as thin films, but the ladder structures are usually less complete because of statistical effects and side reactions in the solid-state reaction. Another route is a direct one-step reaction in solution or the molten state, in which the ladder polymers obtained are usually in the form of powders and are difficult to process. In this section, we will review the synthesis and characterization of ladder polymers with conjugated π-electron systems. Excellent reviews on ladder polymers covering early literature have been prepared by Bailey,[35] Overberger and Moore,[36] Dewinter.[37]

I. Ladder Polymers Containing Only Carbon and Hydrogen. (1) Polyacene. Polyacene-type polymers can be prepared in multifunctional polycondensation reactions by different methods.[38-43] Butadiyne undergoes spontaneous polymerization when its vapor is left in contact with an inert plastic film, such as poly(tetrafluoroethylene) (see Scheme I).[38-40] After 5 weeks in contact with butadiyne vapor, a colored coating was observed that darkened further on heating. The final product was paramagnetic with a free electron *g* value and a line width of 10 G. A spin density of 8 × 10^{19} spin/g was observed. Infrared (IR) absorption at 885 cm^{-1} was tentatively assigned to the acene unit C–H vibration. Pendant acetylene group absorptions in the IR spectrum were also detected. The detailed chemistry involved is not completely certain. Scheme I leading to a polymer containing acene ladder segments and polyene segments was postulated.

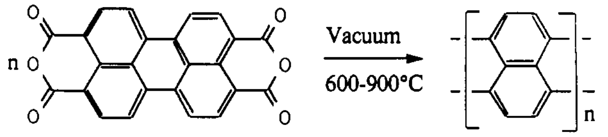
Scheme III



Scheme IV



Scheme V



Another route to polyacene is via polymer precursors of substituted diacetylenes (see Scheme II).[41] The diacetylene monomer undergoes polymerization by a Ziegler–Natta (ZN) catalyst. A conjugated linear polymer with acetylene pendant can be obtained, which can be thermally or chemically (by Friedel–Craft catalysts) converted into a black insoluble powder. Both heat and Friedel–Craft catalysts convert the initial polymer into the same product. UV–vis and IR spectra showed a further cyclization reaction, and the structure of polymer II was proposed to account for a fraction of the product obtained. But the chemistry involved in cyclization is complicated, and no definite structural information has been obtained. Both pristine and thermally treated polymers have paramagnetic centers. Polymer I has a line width of 3.6 G and a *g* value of 2.0021. Its spin concentration is about 5 × 10^{18} spins/g. Upon thermal treatment, the spin concentration increases to 4 × 10^{19} spins/g. The absorption spectrum showed a red shift after thermal treatment. But the conductivity of the polymer is low, ca. 10^{-14} S/cm. These results seem to indicate cross-linking in the polymer.

Recently, a slightly different procedure has been used to obtain polyacene.[42] (Triethylsilyl)butadiyne has been polymerized by using Ziegler–Natta catalyst, and the polymer obtained was desilylated by Bu$_4$NF to obtain a conjugated polymer with pendant acetylene (see Scheme III). This can be thermally treated to form a highly conductive material with a conductivity of 0.78 S/cm. The structure of the final material has been assigned to polyacene.

(2) Poly(dihydroacene). In 1938, Marvel and Levesque[44] studied the cyclization of poly(methyl vinyl ketone). When the polymer was heated to 300 °C, water was given off. The pyrolysis product was a red, glassy, fusible solid. Chemical analysis showed that segments with a ladder type structure were formed, and the condensation was governed by statistics, only 86% of the ketone units participating in the condensation (see Scheme IV). Ap-

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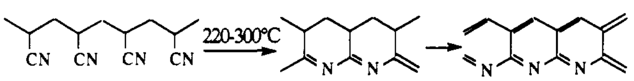
Scheme VI



parently, the group initially coupled at random to form rings.

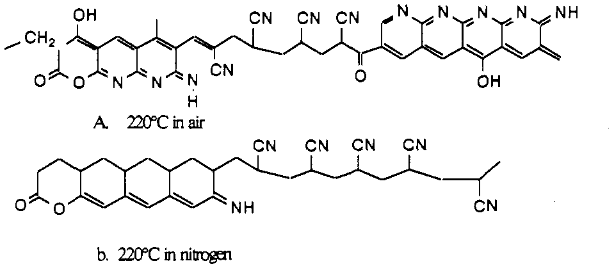
This ladder polymer can also be prepared by intramolecular condensation of poly(methyl vinyl ketone) catalyzed by LiBu and followed by dehydration using CF_3COOH (see Scheme IV).[45] The final product is a dark brown solid.

(3) Poly(perinaphthalene) (PPN). When 3,4,9,10-perylenetetracarboxylic dianhydride is pyrolyzed in an evacuated system, a highly conducting material can be obtained (see Scheme V).[24] Elemental analysis and infrared and Raman spectroscopies indicate a ladder type structure polymer, poly(perinaphthalene).[24,25] Conducting films or conducting ribbons can be produced by different synthetic procedures.[24,25,46–49] These materials are chemically and environmentally stable and have a density of 1.758 g/mL. The films showed metallic ($\sigma_{RT}/\sigma_{4K} = 2$) and semiconductor behavior depending on the reaction temperature.[24] Pellets of PPN gave room-temperature four-point probe conductivities ranging from 10^{-2} S/cm at a T_p (pyrolysis temperature) of 530 °C to 15 S/cm at a T_p of 800 and 900 °C.[25] The conductivities of PPN samples prepared at various temperature were unchanged upon exposure to compensating agents, such as NH_3 or benzoquinone, suggesting that the observed conductivities are intrinsic and not due to some impurity. EPR spectra showed a moderately strong line at $g = 2.0025$ with peak-to-peak line widths of 3–7 G at room temperature. When the starting dianhydride is mixed with niobium pentachloride and subjected to the pyrolysis, mirrorlike films can be obtained, containing niobium with no chlorine. Conductivity measurements showed these films to be superconducting with an onset T_c of 12 K. When boric acid was mixed with starting monomer, a p-type semiconductor film was obtained. When doped with zinc metal, an n-type semiconductor film resulted.

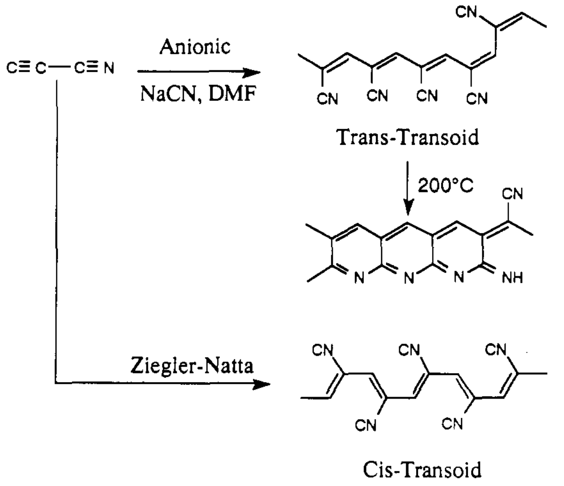
II. Polymers Containing Heteroatoms Other Than C and H. (4) Poly(pyridinopyridine) (PANP). When poly(acrylonitrile) (PAN) is heated both under inert atmosphere and in air, the polymer develops a red color that has been ascribed to the formation of thermally stable ladder polymer segments with C═N and C═C conjugation through additional polymerization of cyano group -CN (see Scheme VI).[50–57]

The material obtained in air has aromatic heterocycles carrying hydroxyl groups, while those treated under inert atmosphere possess hydrogenated heterocycles containing C═N conjugations. The molecular structures produced by oxidative treatment are more thermally stable.

Scheme VII



Scheme VIII



Oxygen plays an important role during the oxidative treatment. IR and elemental analysis showed that oxygen exists in hydroxyl and carbonyl groups.[54,58] The possible chemical structures of Scheme VII have been proposed for oxidized and unoxidized ladder polymers.[54,59]

PAN is an insulator; however, as the heat treatment time increases, the electrical conductivity of the polymer increases. Electrical conductivities as high as 5 S/cm^{-1} have been obtained in oxidized samples.[33] The increase in electrical conductivity has been attributed to thermal conversion of the PAN polymer to a conjugated structure and eventually to a doubly conjugated ladder structure. IR spectra showed that the sudden increase of electrical conductivity is correlated to the formation of conjugated C═C and C═N bonds (1600, 1300 cm^{-1}).[33]

Pyrolyzed PAN has been observed with p-type or n-type semiconductivity by controlling the influence of oxygen.[60] It was found that the sample's thermal electromotive force (emf) changes its sign, i.e., samples with p-type conductivity in air are found to have n-type conductivity after heating in vacuo. The reason is not clear, but it is assumed that the desorption of oxygen causes the transition of the hole producing (p-type) semiconductor into electronic (n-type) materials and hence the change of the emf sign.

Cyanoacetylene can be polymerized into linear polymers at low temperature by anionic, Ziegler–Natta, and metathesis polymerization catalysts (see Scheme VIII).[61,62]

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(59) Bailey, J. E.; Clarke, A. J. *Nature* **1971**, *234*, 529.

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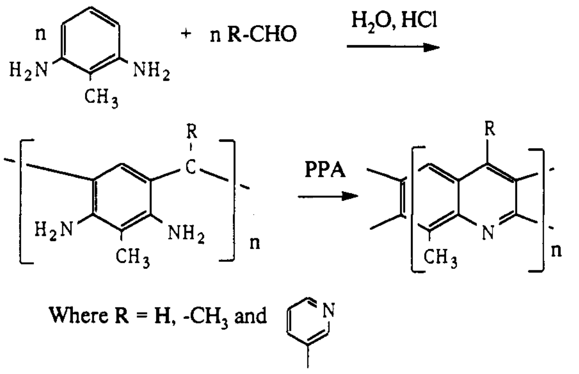
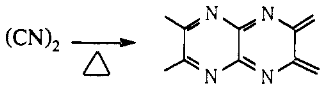
Scheme IX



Scheme X

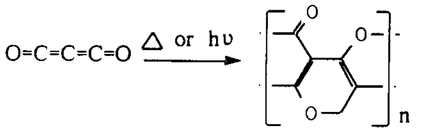


The polymers are brown to black amorphous powders, soluble in polar organic solvents. The molecular weights are of the order of several thousands. The ZN polymer has a high cis–transoid structure, and the nitrile group is hard to cyclize because of the long distance between nitrile groups (see Scheme VIII). Polymers obtained by anionic polymerization are rich in trans–transoid structure and can be cyclized as indicated by the disappearance of the 2210-cm^{-1} band in the IR spectrum when the polymer is heated at 200 °C.[61,62] The final polymer is insoluble, and a ladder structure with segments like PANP was proposed (see Scheme VIII). Both polymer and prepolymer are EPR active. The cyclized polymer can be heavily doped by iodine, and a room-temperature conductivity of 1×10^{-3} S/cm has been obtained.

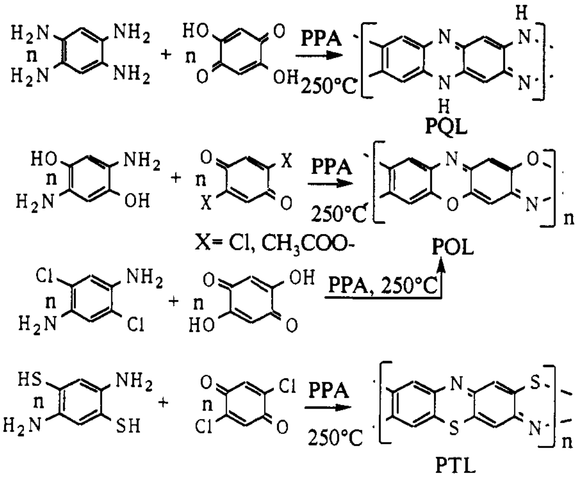
(5) **Poly(1-methylcyclohexa-1,3-diene-2,3-diyl-5,6-diylidene-5-methylidyne-6-nitrilo).** Ruan and Litt[64-67] have utilized the reaction of diaminotoluene with aldehydes in acidic aqueous solution to synthesize polymers that can be treated in strong acidic media such as poly(phosphoric acid) (PPA) to carry out further reactions (see Scheme IX). These polymers have very low molecular weight. For polymers with R = H, the highest intrinsic viscosity is 0.15 dL/g. Postcyclization in PPA media produces intractable powders; IR, UV, and X-ray diffraction spectra support the formation of ladder structures. It was found that when the initial polymer was treated at 250 °C in PPA, on average only 50% of the closed rings were oxidized and one ring in every six repeat units was still open. As the condensation temperature increases, the content of nitrogen in the final product decreases and impurity contamination increases. These polymers can be doped by $NO^+PF_6^-$ or I_2 to conductivities of 2.4×10^{-2} S/cm. However, low molecular weight and intractability of these materials exclude them from practical application.

(6) **Paracyanogen (poly(pyrazinopyrazine)).** When the compounds from which cyanogen can be formed such as mercuric cyanide, silver cyanide, oxamide, iodine cyanide, etc.,[34,68-70] are heated, a dark brown to black powder polymer can be obtained. The structure of this material is very complicated, but evidence has been given for the existence of some ladder units as shown in Scheme X. This material is soluble in concentrated sulfuric acid. Dilution by water causes precipitation of polymers. It will decompose into cyanogen in alkaline solutions. Electrical measurements suggest semiconductor properties.[34]

Scheme XI



Scheme XII



(7) **Poly(carbon suboxide).** Carbon suboxide can undergo polymerization initiated by heat or light. A reddish brown solid can be obtained, which is called "red coal".[71-79] Polymerization can also be performed in cyclohexane solution by using Et_3N and pyridine as catalysts. Poly(carbon suboxide) thin films with controlled thickness can be formed by deposition from a gaseous monomer. Spectroscopic, chemical, and X-ray diffraction analysis suggested a ladder type structure with a *cis*-polyacetylene type conjugated backbone (see Scheme XI).[61-77] This polymer is photosensitive and paramagnetic. A spin concentration as high as 2×10^{19} spins/g has been detected at a polymerization temperature of 105 °C. The paramagnetism follows the Curie–Weiss law. A g value of 2.0045 ± 0.0002 has been measured. The ^{13}C coupling constant from the selectivity labeled polymer indicates π-electron delocalization over the ladder structure. Photopolymerization of the monomer gives this polymer the potential of image formation by selective irradiation of a monomer layer.[78,79]

(8) **PXL** (PQL, POL, and PTL; the definition of the

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(64) Ruan, J. Z.; Litt, M. H. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 285.

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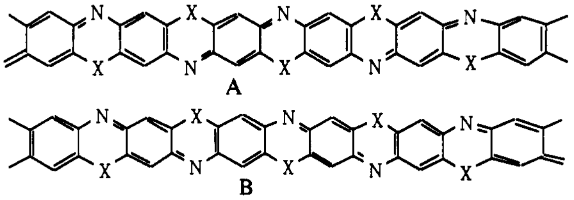
(79) Yang, N. L.; Snow, A. W.; Haubenstock, H.; Bramwell, F. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 1909.

Scheme XIII



acronym is given in the Introduction and Scheme XII): PXL is another class of ladder polymers developed by Stille et al.[80-83] Tetrafunctional monomers, such as aromatic tetraamines and 2,5-disubstituted quinone, have been used in the synthesis of these ladder polymers in an acidic medium such as polyphosphoric acid (see Scheme XII).

When tetraaminobenzene (TAB) reacts with 2,5-dihydroxy-*p*-benzoquinone in PPA or hexamethylphosphoramide (HMP), a quinoxaline type ladder polymer is obtained that is soluble in 1,2-dichloro-1,1,2,2-tetrafluoroethane.[80-83] A polymer obtained by using the same starting materials and PPA as solvent showed an inherent viscosity of 1.45 dL/g in HMP at 0.3 wt %. This polymer is thermally stable up to 520 °C.[83] When 1,4-dihydroxy-2,5-diaminobenzene polymerizes with 2,5-dichloro-*p*-benzoquinone in a two-step reaction, POL type ladder polymers can be prepared.[80] These ladder polymers have poor solubility in common organic solvents. The thermal stability of these ladder polymers is very poor: a slow decomposition starts at ca. 275 °C under nitrogen, which could be the indication of incomplete cyclization and low molecular weight. POL can also be prepared from 2,5-dichloro-*p*-phenylenediamine and 2,5-dihydroxy-*p*-benzoquinone in PPA at 250 °C.[17]

When 2,5-diamino-1,4-benzenedithiol reacts with 2,5-dichloro-*p*-benzoquinone in PPA at 250 °C, PTL can be obtained.[17] All of these polymers are black insoluble materials.

The structures of PXL type ladder polymers are very interesting because these materials are capable of supporting bond alternation defects (solitons/polarons/bipolarons; the conceptual descriptions of these terms are given in ref 1) upon chemical doping.

Structures A and B are degenerate, i.e., they have the same ground-state energies (see Scheme XIII). These materials are paramagnetic. EPR and ENDOR (electron and nuclear double resonance) measurements indicate a finite delocalization of the π-electron along the ladder backbone.[84]

Electrical conductivity measurements indicate conductivities of 4×10^{-6} and 1×10^{-8} S/cm for PTL and POL, respectively.[15,17] These values, which are unusually high for conjugated organic polymers, could arise from the contribution of contamination by impurity residues such as PPA, etc. PTL can be doped either by p-type dopants such as AsF_5 or n-type dopants such as potassium in naphthalene to increase the conductivity by 2–5 orders of magnitude.[17]

POL and PQL films can be prepared by electropolymerization of *o*-phenylenediamine and *o*-aminophenol in acidic solutions on basal-plane pyrolytic graphite and on In–Sn oxide conducting glass electrodes by applying anodic potentials.[22,23] A brownish orange thin film showed a conductivity of 4.0×10^{-7} S/cm at 298 K. The IR spectra showed some evidence of ladder units; absorption at 1645 cm^{-1} due to C=N stretching and absorption at 1050 and 1235 cm^{-1} due to C–O–C stretching have been observed. But a strong absorption around 3420 cm^{-1} due to NH_2 stretching suggests that the polymer has a large portion of open-chain structures or that the molecular weight is relatively low. TGA (thermal gravimetric analysis) showed that this material is stable only to 300 °C, which also indicates an incomplete cyclization. PQL can be prepared by electropolymerization of phenylenediamine under similar conditions. An incompletely cyclized polymer with low thermal stability has been obtained in the form of thin films.

Scheme XIV

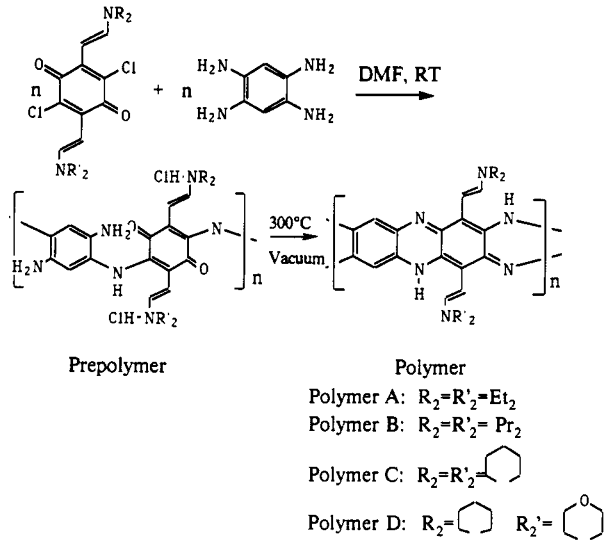


Table II. ESR Measurements of Ladder Polymers

	prepolym		polym	
	A	B	A	B
ΔH, G	9.00	10.05	6.3	8.75
g	2.00515	2.00510	2.0034	2.00298

Sita and Marvel prepared polymeric materials from TAB by oxidation followed by thermal treatment.[85] The final polymer was a black solid, and a structure containing ladder segments was proposed based on elemental analysis results.

(9) Derivatized PQL Ladder Polymers.[18-20] Dichloroquinone monomers derivatized with (dialkylamino)vinyl substituents were prepared via a Mannich type reaction from chloranil, actaldehyde, and dialkylamine in toluene.[18,19] These quinone monomers were reacted with tetraaminobenzene to prepare prepolymers. The prepolymer solution was then used to cast films that can be thermally treated at 300 °C to obtain final polymer films. FTIR, elemental analysis, and NMR results indicate that the final polymers containing ladder type segments as shown in Scheme XIV. Viscosity measurement of prepolymers in DMF at 25 °C gave intrinsic viscosities of 1.4, 0.30, 0.25, and 0.15 dL/g for prepolymers A–D, respectively. This indicates that as the size of side group increases, the molecular weight of the polymer decreases.

UV–vis spectra of these polymers showed a lower band energy edge at 1.56 eV compared with that of the prepolymer at 1.79 eV in MSA solutions, which implies that the polymer systems have more extended π-electron conjugation. TGA of these polymers showed very high ther-

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(80) Stille, J. K.; Freeburger, M. E. *J. Polym. Sci. A-1*, **1968**, *6*, 161.

(81) Stille, J. K.; Mainen, E. *J. Polym. Sci., Polym. Lett.* **1966**, *4*, 39.

(82) Stille, J. K.; Mainen, E. L.; Freeburger, M. E.; Harris, F. M. *Polym. Prepr.* **1967**, *8*, 244.

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(84) Dalton, L. R.; Thomson, J.; Nalwa, H. S. *Polymer* **1987**, *28*, 543.

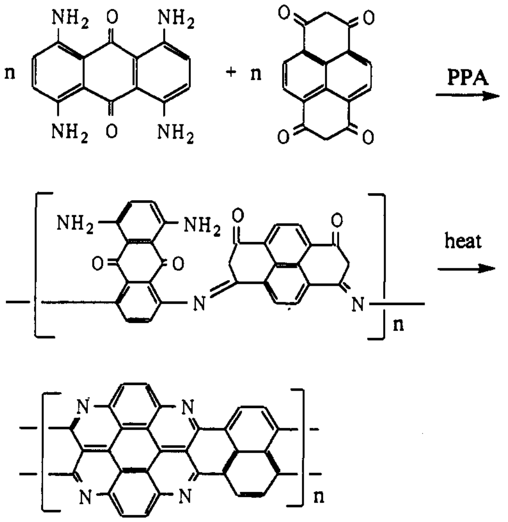
(85) Sita, J.; Marvel, C. S. *J. Polym. Sci. A-1* **1967**, *7*, 3203.

Table III. Optical Properties of Ladder Polymers[a]

property	polym sample A	B	C	D
n	1.96 ± 0.02	1.92 ± 0.02	1.92 ± 0.02	1.92 ± 0.02
α, 10^4 cm^{-1}	2.32 ± 0.16	2.54 ± 0.18	1.88 ± 0.31	4.08 ± 0.24
$\chi^{(3)}_{1111}$, 10^{-10} esu	9.78 ± 3.0	8.90 ± 2.5	7.40 ± 2.1	15.5 ± 5.1
$\chi^{(3)}_{1221}$, 10^{-10} esu	1.8 ± 0.5	1.9 ± 0.5	1.6 ± 0.5	3.0 ± 0.9
$\chi^{(3)}_{T}$, 10^{-10} esu	3.8 ± 1.2	4.4 ± 1.2	3.8 ± 1.2	7.7 ± 2.0
$\chi^{(3)}_{1111}/\alpha$, 10^{-14} esu cm	3.23	3.50	3.93	3.80

[a] $\chi^{(3)}_{ijlk}$'s are the tensorial components of the third-order susceptibilities and $\chi^{(3)}_{T}$'s are the thermal contributions to the third-order NLO processes.[19,20]

Scheme XV



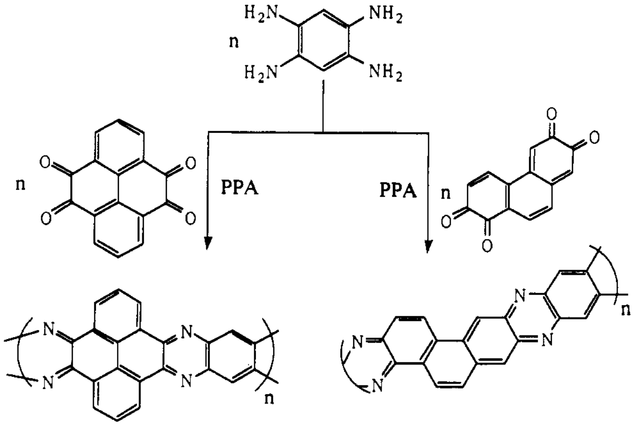
mal stabilities. The polymers with (diethylamino)vinyl substituents are stable up to 690 °C.

Both prepolymers and polymers are EPR active (Table II). In the prepolymers, the g values shift significantly from that of the free electron (2.0023), as might be expected for quinone radicals. The g values of the polymers are identical with those of underivatized ladder polymers reported in ref 80 and are near the free electron value, implying significant electron delocalization. Line width (ΔH) changes from prepolymer to polymer also imply a greater electron delocalization in the latter.

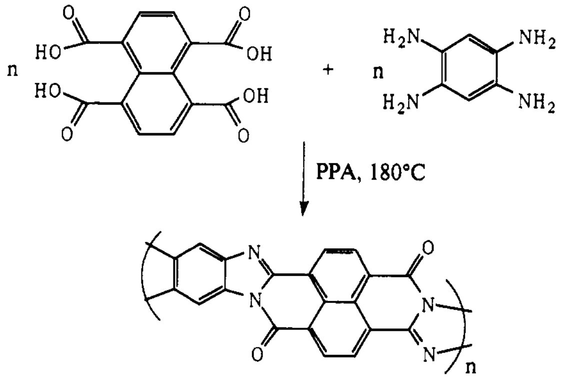
These polymers exhibit large third-order nonlinear susceptibilities (see Table III). It can be seen that these polymers have very high $\chi^{(3)}/\alpha$ values (where $\chi^{(3)}$ is the third-order nonlinear optical susceptibility and α is the optical absorption coefficient). All these materials showed identical results, which implies that different substituents on the amine have a minor influence on NLO properties as long as we maintain the ladder structure with aminovinyl derivatization. It should be noted that a significant resonant contribution exists in these ladder polymer systems at the wavelength at which the degenerate four-wave mixing (DFWM) measurements were taken.[19,20]

(10) Ladder Graphite Structure Polymer. Marvel et al. synthesized a thermally stable polymer with a structure resembling that of graphite by the condensation of 1,4,5,8-tetraaminoanthraquinone and 1,3,6,8-tetraketo-1,2,3,6,7,8-hexahydropyrene in PPA (see Scheme XV).[86,87]

Scheme XVI



Scheme XVII



The prepolymer as shown in Scheme XV with an open-chain structure was soluble in methanesulfonic acid. The final polymer with a closed-ring structure, which was obtained by heating the prepolymer having an inherent viscosity of 0.4 dL/g at 0.3 wt %, was insoluble even in strong acids. Elemental analysis indicated that a high degree of cyclization was achieved. The final polymer is thermally stable up to 550 °C under nitrogen. The prepolymer can be solubilized by treating it in a reducing mixture consisting of potassium hydroxide and sodium dithionite in aqueous DMAc solution. Small brittle films can be cast from the methanesulfonic acid solution of the prepolymer. Conductivity measurements indicated conductivities of 2×10^{-4} and 3×10^{-5} S/cm for ladder polymer and prepolymer, respectively.[88] This small conductivity difference was attributed to the structural similarity of the two polymers. The presence of fused aromatic rings and hydrogen bonding between the amine hydrogens and keto oxygen atoms in the prepolymer may produce a nearly planar arrangement similar to that of the ladder polymer.

Tetraketo monomers have been used in polymerization with tetraamino compounds in acidic media such as PPA and *m*-cresol (see Scheme XVI).[82,83] The polymers obtained had good solubilities in aprotic solvents, such as HMP, and excellent thermal stabilities. These polymers have similar thermal stability and can be stable up to 460 °C in air and 680 °C under nitrogen.

(11) BBL. BBL type ladder polymers (first developed by Van Deusen et al.[89]) are synthesized from dianhydrides and tetraamino monomers in strong acidic media such as

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(86) Hurley, S. A.; Dutt, P. K.; Marvel, C. S. *J. Polym. Sci. A-1* **1972**, *10*, 1243.

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PPA (see Scheme XVII). The synthesis of this type of ladder polymer is actually an extension of dye synthesis.[89-95] BBL is completely soluble in MSA and can be cast into films (density ca. 1.3 g/cm^3) that are dark with an intense golden luster. A 0.3-mm film cast from an MSA solution near 60 °C under reduced pressure (0.05 Torr) was found to have an initial modulus of 1.1×10^6 psi. Tensile strength averaged 16 600 psi with elongation at rupture of 2.9%. This ladder polymer is thermally stable up to 550 °C in air and 700 °C under nitrogen. It is a semicrystalline polymer with a layered structure in two-dimensional arrays. X-ray and IR analyses revealed a compact interchain packing in solution as molecular aggregates and in the bulk after precipitating from solution.[96]

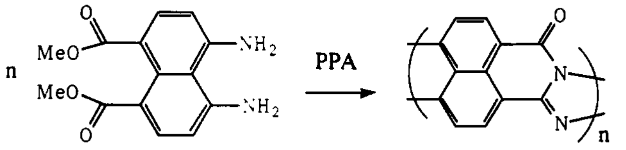
Pristine BBL is an insulator (ca. 10^{-12} S/cm). Doping with SO_3 or H_2SO_4 vapor as opposed to AsF_5 and BF_3 produces conductive complexes.[15,97] These doped films retain their flexibility but swell considerably. Unusually high dopant concentrations were determined (6–8 dopants/polymer unit) by measuring weight uptake of the sample. The high dopant content and swelling during doping were attributed to intercalation of dopant into the layered structure of the polymer. Films of BBL can be donor-doped with both potassium vapor (300–500 °C) and potassium naphthalide in THF. The latter process gives complexes with conductivity as high as 1 S/cm.

Electron spin resonance (ESR) measurements have been performed on pristine and thermally annealed thin films of BBL.[98] Both samples gave a strongly anisotropic signal, suggesting a highly planar polymer backbone. It was found that thermal treatment considerably affects the spin susceptibility and electrical conductivity of BBL films. Thermally annealing the BBL films to a high temperature, T_0, increases the spin susceptibility for $T_0 < 850$ K. However, annealing to $T_0 > 900$ K results in a dramatic reduction in the spin susceptibility and a dramatic increase in the conductivity. A room-temperature in-plane conductivity of 1 S/cn of annealed samples (900 K) has been observed, which has been attributed to a phase transition to a fully condensed, cross-linked aromatic structure.[98]

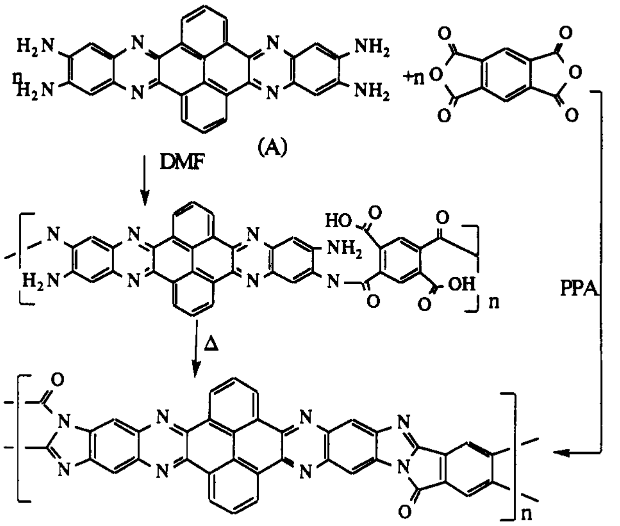
The electrochemical reactivity of the BBL polymer film has been examined by using cyclovoltametry, coulometry, and spectroelectrochemistry.[16] In contact with an aqueous $(Bu_4N)_2SO_4$ buffer, BBL voltammetry exhibits two redox steps, corresponding to the sequential reduction of the unprotonated and the protonated forms of BBL connected by a pK_a = 2.2.

BBL can be doped by ion implantation[99] using boron, argon, and krypton implantation. As the concentration of implanted impurities increased, the gold–yellow pristine BBL films gradually turn black and then silver–gray with metallic luster. BBL can be doped to conductivities as high as 224 S/cm at a dose of 4.0×10^{16}/cm^2 while retaining the mechanical properties of pristine films. Spatially selective implantation creates regions of conducting lines in an insulating matrix, which suggest the potentials of microelectronic device applications for this ladder polymer.

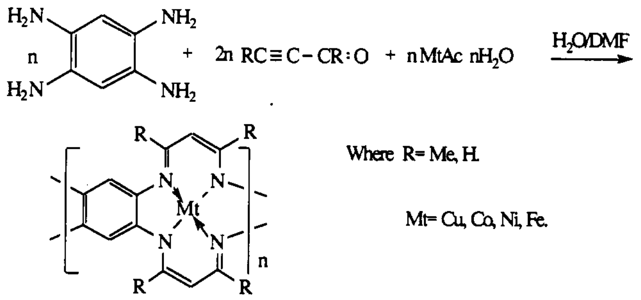
Scheme XVIII



Scheme XIX



Scheme XX



Nonlinear optical properties of BBL film have been studied via DFWM measurements.[18,100] It was found that pristine BBL film has a $\chi^{(3)}$ value of 2×10^{-9} esu at a wavelength of 532 nm with a linear absorption of 18.3 μm^{-1}.[18] When the measurements were performed at a wavelength of 1064 nm, a $\chi^{(3)}$ value of 9.1×10^{-11} esu has been observed, and after electrochemical doping, the $\chi^{(3)}$ value increased to 1.2×10^{-10} esu.[100]

(12) Analogues of BBL. The analogues of BBL, with 1,4,5,8-tetraaminonaphthalene, tetraaminobenzene, and 1,2,4,5-benzenetetracarboxylic anhydride as monomers, have been synthesized by Marvel[95] and Arnold[101,102] via an open-chain precursor. These polymers have low molecular weights and are thermally stable to 500 °C.

Arnold[101,102] reported a self-condensation of AB type monomer, dimethyl-4,5-diaminonaphthalene-1,8-dicarboxylate (DMDANDC), in PPA media to obtain a BBL analogue ladder polymer (see Scheme XVIII). The

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polymer had a inherent viscosity of 0.25 dL/g in MSA at 0.3% and was thermally stable up to 450 °C in air and 600 °C under nitrogen.

Another interesting tetraamino monomer was made from the condensation of 1,2,6,7-tetraketopyrene and 1,2-diamino-4,5-(*p*-toluenesulfamido)benzene followed by detosylation in H_2SO_4.[103] This tetraamino monomer has been polymerized with pyromellitic acid and 1,4,5,8-naphthalenetetracarboxylic acid to produce ladder polymers (see Scheme XIX). The comparison of IR spectra of polymer and model compound supports the formation of ladder segments in polymer. A soluble open-chain precursor has been synthesized from reaction of the tetraamino monomer with pyrromellitic dianhydride in DMAC with an intrinsic viscosity of 1.0 dL/g. A yellow thin film can be cast from prepolymer solution and then thermally treated to obtain a polymer with cyclized ladder segments.

III. Metal-Containing Ladder Polymers.[104-106] Ladder type polymeric tetraaza(14)annulene metal chelates have been prepared from propynal aldehydes, tetraaminobenzene, and transition-metal salts (see Scheme XX). The structures of the products were determined by IR spectroscopy. The dark-colored polymers are insoluble in organic solvents, and their molecular weights are unknown. These polymer have high thermal stabilities. They start to decompose under nitrogen at ca. 700 K and have 10% weight loss at 1070 K.

The Co- and Cu-containing chelates showed high activities as catalysts for the oxidation of ethylbenzene to acetophenone. For all of these chelates, the electrical conductivity is low, with conductivities of ca. 10^{-9}–10^{-12} S/cm. This can be understood from X-ray diffraction investigations that showed that the delocalization of π-electrons is concentrated on the six-membered propane-1,3-diiminato chelate ring. Intramolecular charge transfer is inhibited, and hence the charge carriers cannot be transported through the polymer chains.

IV. Polymers with Alternating Rigid Ladder and Flexible Chain Units. As with other conjugated polymers, the poor solubility of the conjugated ladder polymers has presented a difficult problem. Theoretical studies show that in polyconjugated systems, π-electron delocalization is limited by electron–phonon and electron–electron interaction.[7-9] Consequently, the third-order NLO response will increase as the conjugation length increases for short conjugation length and then begin to saturate to some finite length. For example, in polyene systems, theory predicts that after 15 double bonds, the third-order susceptibility begins to saturate.[9] These results suggest that in order to have a large optical nonlinearity, it is not necessary to have a large conjugated system within the polymer. Incorporation of finite chain length NLO-active units into processible polymers will provide materials with NLO properties similar to those found in extended conjugation polymers. On the basis of this observation, we have synthesized copolymers incorporated with PQL ladder unit and flexible chain segments (see Scheme XXI).[107]

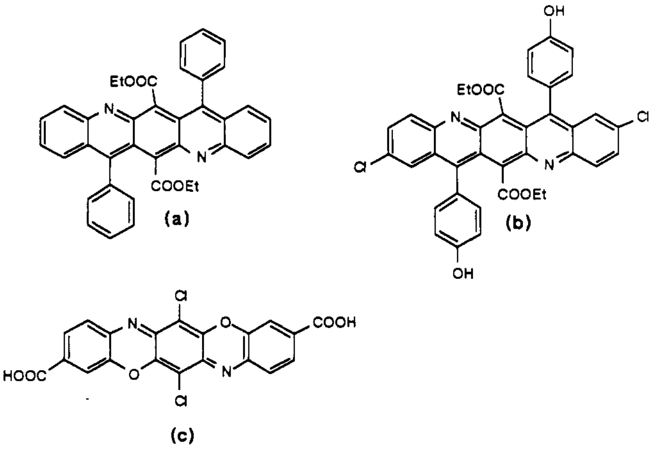
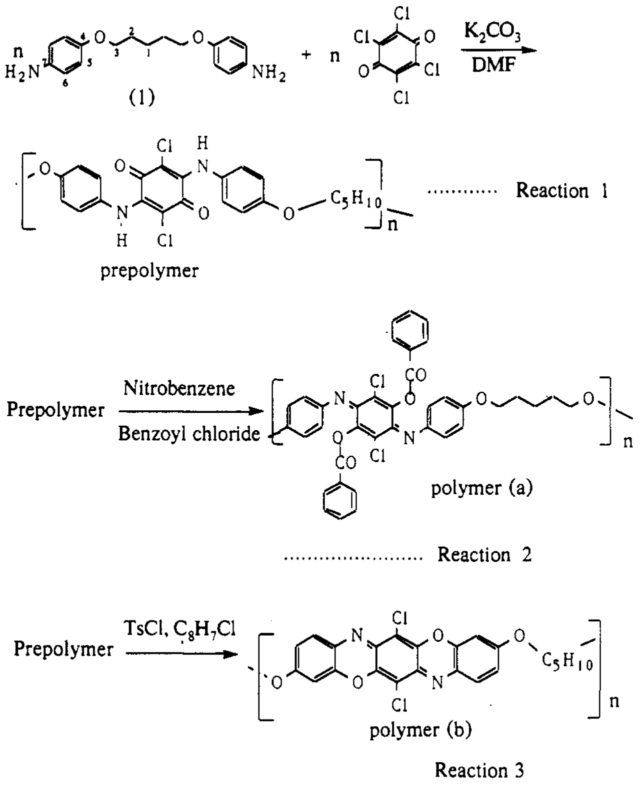


Figure 2. Structures of ladder units incorporated into copolymers.

Scheme XXI



This copolymer has a clearly defined optical bandgap, good processibility, and relatively high thermal stability (T_{dec} = 400 °C). Degenerate four-wave mixing (DFWM) measurements reveal unusually large optical nonlinearity: $\chi^{(3)}$ values as high as 4.5×10^{-9} esu for polymer a, an open-chain version of triphenodioxazine, have been observed. Similar signal amplitude has been observed for polymer b. Recently this work has been expanded to different type of ladder units. Structures as shown in Figure 2 have been incorporated into polymers with flexible chain segments.[108,109] These small ladder-type molecules and their corresponding copolymers show large NLO effects via DFWM measurements. Although this synthetic approach cannot be used to prepare extended ladder polymers, it provides a way to utilize the unusual optical properties of ladder polymer and yet realize the solubility necessary to permit the preparation of optical-quality thin films. This scheme can be extended to permit the preparation of not only modified polyethers but also poly-

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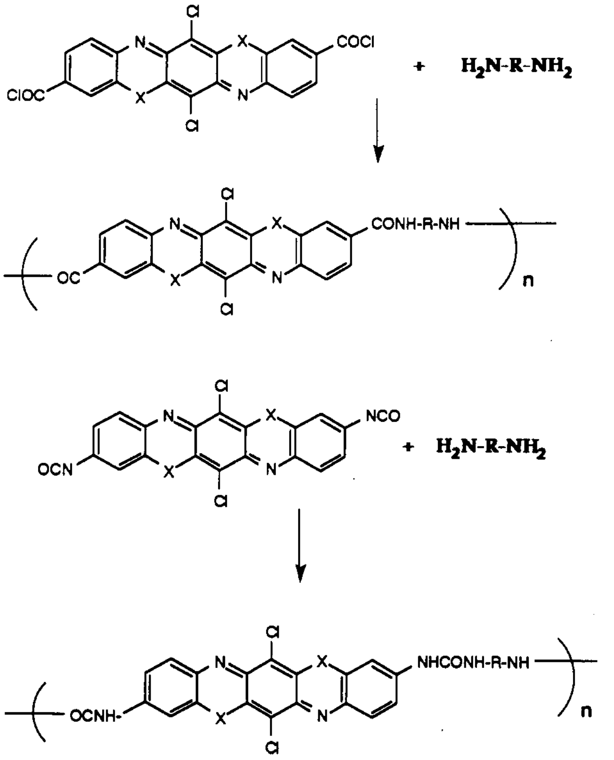
Scheme XXII



imides/amides, polyurethanes, etc. Scheme XXII shows a few of these examples.[109]

Conclusion

The majority of the ladder polymers have been synthesized by polycondensation under vigorous reaction conditions. The complexities of the reactions prevent the achievement of perfect ladder structures. Acidic reaction media such as PPA can corrode the glassware and thus introduce silicon contamination, which is hard to eliminate. When multifunctional monomers are used, side reactions such as cross-linking are difficult to avoid. Poor solubility of the ladder oligomers in reaction media prevents further propagation and leads to precipitation from reaction media. Low molecular weight materials are then often obtained. All of these effects have been reflected in elemental analysis results of ladder polymers. Few, if any, ladder polymers reported have acceptable results for elemental analysis. These effects (imperfection, low molecular weight and contamination) have profound influences on their thermal stabilities and other physical properties such as electrical conductivities. Therefore, one should be especially careful in the physical measurements and their explanations. For example, unusually high electrical conductivities in a ladder polymer should be viewed with caution since the impurity contamination may make the dominant contribution to electrical transport properties in these materials.

Although there are many problems associated with ladder polymers, the electronic, optical, and structural properties of the materials described herein makes them still attractive. A perfect ladder structure may not be synthesized in the near future, but polymers with extended ladder units have shown some important characteristics such as high conductivity and optical nonlinearity. We expect that research on ladder polymers will continue to grow. There are two aspects to which one should pay more attention. The first aspect is the chemistry of synthesis. It can be seen from this review that the traditional route might not be powerful enough to synthesize processible, conjugated ladder polymers. New synthetic schemes should be developed. A successful example is the work by Schlueter although the ladder polymer is not conjugated.[110] The second aspect is the characterizations of the ladder polymers. To gain more insight into the physical properties of the ladder polymer, structural information is crucial. As mentioned above, most of the existing ladder polymers are ill-defined, largely owing to the poor solubilities of these materials. To get more information of their structures, advanced analytical techniques should be used, such as solid-state NMR.

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