Synthesis and Characterization of Novel Thermally Stable Polypyrazoles[1]

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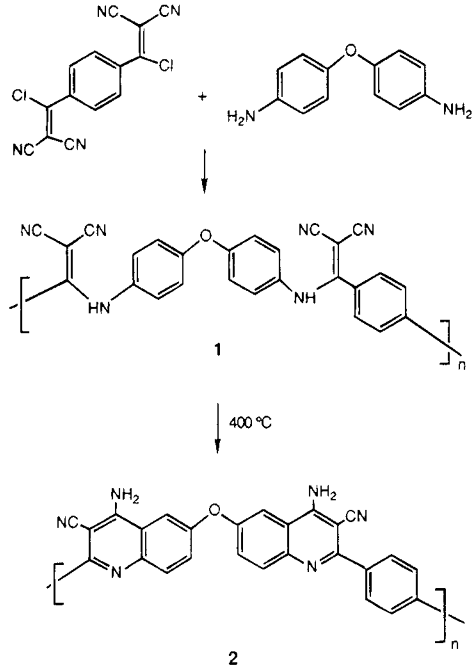
ABSTRACT: Bis-electrophilic monomers containing 1-chloro-2,2-dicyanovinyl moieties were reacted with dihydrazines, employing a vinylic nucleophilic substitution reaction, to prepare high molecular weight and processable polypyrazoles. All five polymers synthesized by this route exhibited excellent thermal stability. The polymers were fully characterized by spectroscopic methods, by solution viscosity measurements, and by thermal analysis techniques. These polypyrazoles exhibited excellent thermal stability in both nitrogen and air. Condensation of isophthalic dihydrazide with one of the bis-electrophilic monomers led to a polypyrazole in which N-1 of the pyrazole moiety was benzoylated. This polymer showed poorer thermal stability than that of the pyrazoles derived from the dihydrazines.

Introduction

The growing need for novel polymers possessing excellent thermal stability by the electronics and aerospace industries has provided researchers with the impetus that led to the discovery of a variety of thermally stable polymers.[2] The structural requirements for such polymers include incorporation of chemical bonds of high dissociation energy, the presence of functional groups in the polymer backbone that cross-link upon heating, and inflexible chains. Aromatic moieties in a molecule normally endow the polymers with superior thermal stability. Because the most common mechanism for the degradation of the polymers is oxidative in nature, incorporation of heterocyclic units further improves the thermal stability by increasing the char yield at very high temperature. Unfortunately, polymers possessing these structural features are difficult to process because of their low solubilities in common organic solvents and high glass transition or melting temperatures. These conflicting trends often lead to a processability–thermal stability tradeoff.

A common approach to solve the problem of processability is to synthesize a more flexible prepolymer which upon subsequent treatment ("curing") cyclizes intramolecularly to produce the final thermally stable, rigid-rod polymers. Polyimides[3] are a familiar and successfully applied example of this approach. The principal drawback of this approach to the curing reaction of polyimide and other similar polymers is the emission of volatile molecules which are trapped in the bulk of high molecular weight polymer. The difficulties in removing these small molecules from the bulk polymer without causing voids have restricted the use of many polyimides to various thin-film applications. Moreover, the intermediate poly(amic acid) (prepolymer) suffers from poor hydrolytic stability. We, therefore, reasoned that the presence of suitable, regiochemically disposed functional groups in a prepolymer which can undergo intramolecular cyclization by structural rearrangement will yield cured polymer *without emission of volatile byproducts*. Recent work[4] from our laboratory has demonstrated the successful application of this approach to the preparation of several new polymers employing a vinylic nucleophilic substitution reaction.

Scheme 1. Synthesis and Curing of Poly(enaminonitrile)



One of the first polymers synthesized, based on the rationale presented above, was poly(enaminonitrile) **1** (Scheme 1) which cyclized, in part, to poly(aminoquinoline) **2** upon heating.

It was thought that the reaction of a bis(chlorovinylidene cyanide) monomer with a dihydrazine monomer might lead to a poly(enhydrazinonitrile) **24** which could be thermally cyclized to a polypyrazole (Scheme 8). A review of the literature showed a precedent[5] for the synthesis of a pyrazole moiety by vinylic nucleophilic substitution reaction of alkylidenemalononitrile, bearing a suitable leaving group, with a hydrazine nucleophile (Scheme 4). However, no polypyrazoles had been synthesized, by this route, prior to this work.

Polypyrazoles have been synthesized by cycloaddition[6] of bis(nitrilimines), bis-sydnones, and bisazides to bis-acetylenes. They were also synthesized by polycondensation of dihydrazine with tetracarbonyl compounds,[7]

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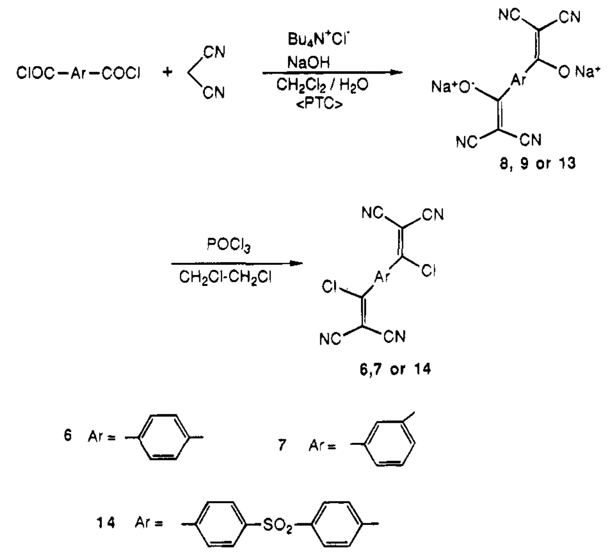
Scheme 2. Synthesis of Monomers 6, 7, and 14



Scheme 3. Synthesis of Intermediates 11 and 12

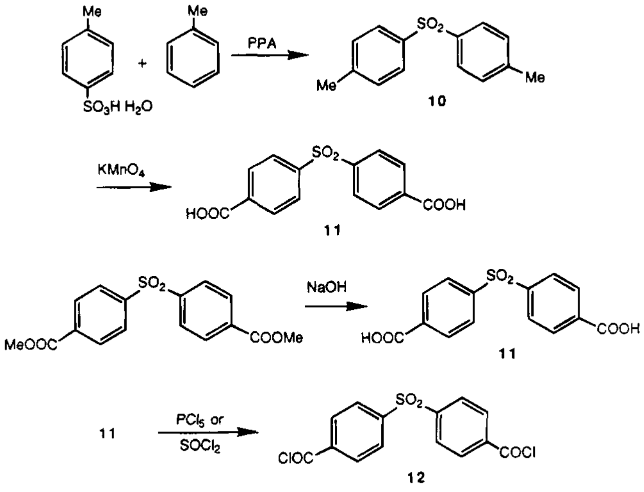
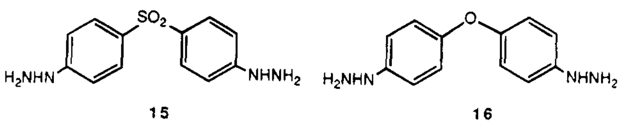
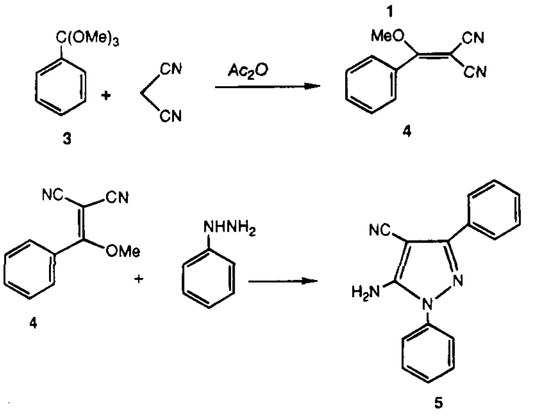


Chart 1. Structures of Monomers 15 and 16



Scheme 4. Synthesis of Model Compound 5



bis(β-substituted vinyl ketones),[8] and aromatic dipropynones.[9]

Monomer Synthesis

Monomers **6** and **7** were first synthesized (Scheme 2) with some modifications of the previously reported procedure.[4a] Another more reactive monomer 4,4′-bis(1-chloro-2,2-dicyanovinyl)diphenyl sulfone (**14**) was also synthesized by a similar procedure. 4,4′-Sulfonylbis(benzoyl chloride) (**12**), required for the condensation with malononitrile, was synthesized following the reactions shown in Scheme 3. In the first method 4-toluenesulfonic acid monohydrate was reacted[10] with toluene in poly(phosphoric acid) to give 1,1′-sulfonylbis(4-methylbenzene) (**10**) which was then oxidized[11] to 4,4′-sulfonylbis(benzoic acid) (**11**) using alkaline potassium permanganate.

In the later stages of the work it was found that the dicarboxylic acid **11** can be easily synthesized in quantitative yield by the base-catalyzed hydrolysis of commercially available 4,4′-sulfonylbis(methylbenzoate). 4,4′-Sulfonylbis(benzoic acid) (**11**) was converted to 4,4′-sulfonylbis(benzoyl chloride) (**12**) either by reaction with refluxing thionyl chloride in the presence of a catalytic amount of pyridine or by heating it with solid phosphorus pentachloride and phosphorus oxychloride. 4,4′-Sulfonylbis(benzoyl chloride) (**12**) obtained from the later reaction gave better yields of 4,4′-bis(2,2-dicyano-1-hydroxyvinyl)phenyl sulfone disodium salt (**13**) when reacted with malononitrile under phase-transfer catalysis conditions. Bisenolate **13** was reacted with phosphorus oxychloride to give the desired monomer **14**.

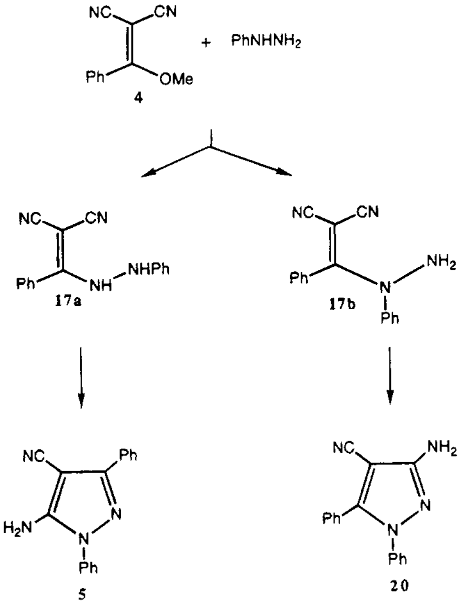
Two dihydrazine monomers **15** and **16** (Chart 1) were synthesized by a previously reported procedure.[12] Bis(4-hydrazinophenyl) sulfone (**15**) was synthesized by aromatic nucleophilic substitution with hydrazine hydrate on bis(4-chlorophenyl) sulfone. Bis(4-hydrazinophenyl) ether (**16**) was synthesized by diazotization of bis(4-aminophenyl) ether followed by *in situ* reduction of the resultant diazonium salt with $SnCl_2$/HCl. This dihydrazine was obtained as the dihydrochloride and was purified by crystallization from 1% HCl. It was converted *in situ* to free dihydrazine during the polymerization to prevent oxidation of this sensitive molecule.

Synthesis of Model Compounds

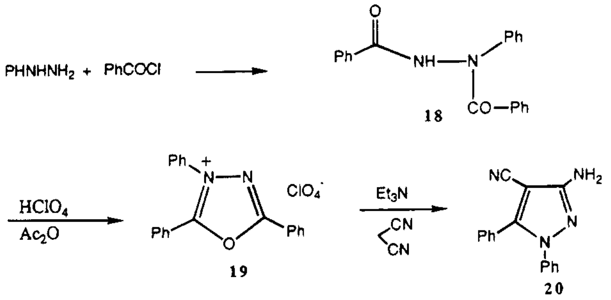
It was deemed useful to study the chemistry of the reaction of a hydrazine nucleophile with an alkylidenemalononitrile. Hence, 3-methoxy-3-phenyl-2-cyanopropenenitrile (**4**) was reacted with phenylhydrazine, following a general procedure,[5] to give 1,3-diphenyl-4-cyano-5-aminopyrazole (**5**; Scheme 4). Compound **4** was synthesized[13] by acetic anhydride-mediated condensation of malononitrile with trimethyl orthobenzoate (**3**).[14] In the synthesis of **5**, it was observed that the reaction was extremely rapid. This fact indicated that this reaction may be well suited for polymerization, but it also led to the concern that the reaction might be so rapid that selectivity and regiochemical control might be lost, yielding two different regioisomers, namely, **5** and **20**, via intermediate enhydrazinonitriles **17a** and **17b**, respectively (Scheme 5).

Literature reports for the synthesis of both **5** and **20** do not give any spectral data. Hence, 1,5-diphenyl-3-amino-4-cyanopyrazole (**20**) was synthesized by the literature procedure[15] (Scheme 6). *N,N′*-Dibenzoylphenylhydrazine[16] (**18**), synthesized from benzoyl chloride and phenylhydrazine, was reacted with perchloric acid in acetic anhydride to give, in almost quantitative yield, 2,3,5-triphenyl-1,3,4-oxadiazolium perchlorate (**19**),[15a]

Scheme 5. Reaction Pathways to Isomers 5 and 20



Scheme 6. Synthesis of Model Compound 20

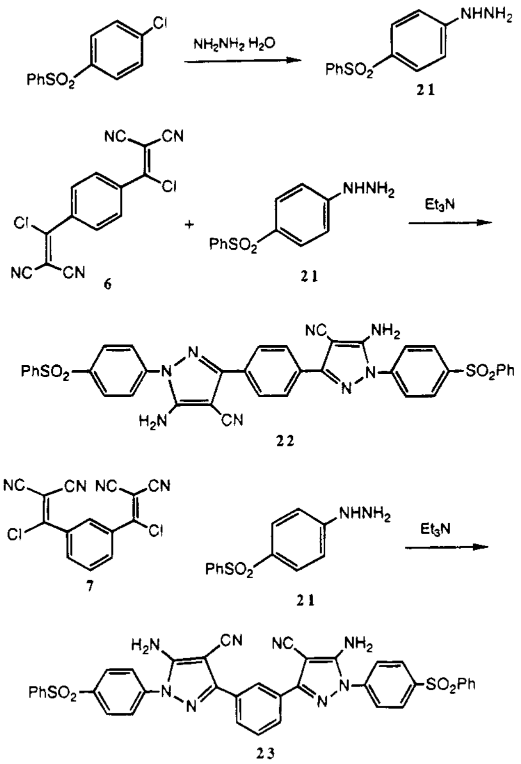


which was reacted with malononitrile in the presence of triethylamine to give the desired pyrazole **20**.^{15b} Comparison of the spectral data for **5** and **20** indicated that the pyrazole obtained from vinylic nucleophilic substitution reaction has the regiochemistry shown for **5**. Pyrazole **5** also serves as a model compound for the polypyrazoles prepared in this work. Two additional model compounds **22** and **23**, more closely resembling the structural repeat unit of the polypyrazole, were synthesized by the reaction of 4-hydrazinophenyl phenyl sulfone (**21**) with **6** and **7**, respectively (Scheme 7). 4-Hydrazinophenyl phenyl sulfone (**21**) was synthesized by a procedure similar to the synthesis of dihydrazine **15** from 4-chlorophenyl phenyl sulfone and hydrazine hydrate.

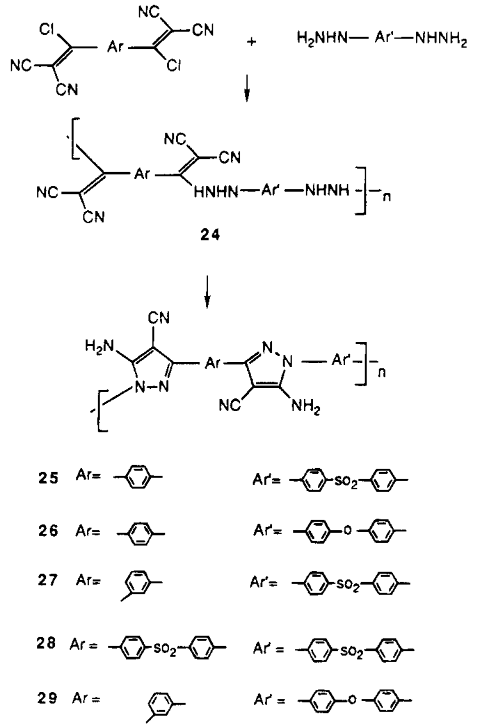
Synthesis and Characterization of Polypyrazoles

Bis(chlorovinylidene cyanide) monomers **6**, **7**, and **14** were reacted with either **15** or **16** as shown in Scheme 8 to give polypyrazoles **25**–**29**. It was hoped that it would be possible to isolate poly(enhydrazinonitriles) **24**, but further reaction continued and only polypyrazoles were obtained as the final products.

Scheme 7. Syntheses of Model Compounds 22 and 23



Scheme 8 Synthesis of Polypyrazoles



A typical polymerization procedure involved condensation of equimolar amounts of both monomers in polar, aprotic solvents such as *N*-methylpyrrolidinone (NMP) in the presence of 1 equiv of 1,4-diazabicyclo[2,2,2]-octane (DABCO) as an acid acceptor. After initial mixing at 0 °C, the reaction mixture was warmed to room temperature and stirred at ~ 70 °C for 24 h to attain a higher degree of polymerization. The viscous polymer solution, after cooling to room temperature, was poured into vigorously stirred water to precipitate the polymers. The polymer was purified by reprecipitation from solution in a polar aprotic solvent, such as *N*,*N*-dimethylformamide (DMF), *N*-methylpyrrolidinone, and *N*,*N*-dimethylacetamide (DMAc), into water or methanol, or it was washed with methanol in a Soxhlet apparatus. The polymers were dried *in vacuo* at 70–80 °C for 24–48 h. In some cases complete removal of absorbd solvent in the polymer sample could not be achieved.

Table 1. Viscosities of Polymers 25–29

polymer	[η]	polymer	[η]
25	1.62[a]	**28**	0.46
26	1.70[b]	**29**	0.25
27	0.35		

[a] Inherent viscosity in dL/g at a concentration of 0.31 g/dL in concentrated sulfuric acid at 25 °C. [b] Inherent viscosity in dL/g at a concentration of 0.42 g/dL in concentrated sulfuric acid at 25 °C.

Table 2. Thermogravimetric Analyses of Polymers 25–29

polymer	50% wt loss [temp °C (air)]	residual wt % [1000 °C (N_2)]	% wt retained[a] [300 °C (air)]
25	600	60	92
26	500	60	92
27	505	54	85
28	505	52	56
29	620	54	92

[a] After 24 h.

Spectral data of all the polymers closely matched those of the model compounds. All five polymers possess moderate to high molecular weights as judged from the viscosity values in Table 1. They were soluble in polar, aprotic solvents such as NMP, DMF, DMAc, and dimethyl sulfoxide (DMSO). Tough transparent films could be cast from the solutions of the polymers in these solvents by evaporation. The films of polymers **25**, **26**, and **28** were fingernail-creasable. In the case of polymers **27** and **29**, thick films were somewhat brittle as compared to the flexibility of films of the other polymers. This brittleness may be caused by the relatively lower molecular weight of these polymers.

Differential scanning calorimograms of these polymers do not show glass transitions or any other transitions. When these polymers were heated *in vacuo* or in air above 150 °C, they became insoluble in common organic solvents but were soluble in sulfuric acid. When IR spectra of polymer **25** were recorded before and after heating, they were virtually identical. In a separate experiment, in the case of polymer **25**, optical microscopy using a hot-stage microscope indicated a broad glass transition (100–300 °C) and some degree of crystallinity after heating. The decrease in solubility after heating could also result from increased crystallinity. Thermogravimetric analyses (TGA) in a dynamic atmosphere of air and nitrogen and isothermal aging studies at 300 °C in air showed that the polymers possessed moderate to excellent thermal stability (Table 2). Figure 1 shows the TGA and isothermal aging scans for polymer **26**. The differences in the thermal stability of different polymers may rationalized as follows.

From the data in Table 2, it is clear that the 50% weight loss temperature for polymer **25** is higher than that for polymer **26**. The presence of ether oxygen atoms in conjugation with the aromatic backbone makes polymer **26** more electron-rich as compared to polymer **25** where the sulfone group makes the aromatic backbone electron-deficient. Because the mechanism for polymer degradation, when the polymer is heated in the air, is likely to be oxidative in nature, polymer **26** is more prone to oxidation and degradation than polymer **25**. The structures of polymer **25** and **27** differ in the fact that polymer **25** possesses 1,4-entrainment coming from the bis(1-chloro-2,2-dicyanovinyl)benzene monomer, while polymer **27** possesses 1,3-entrainment. Consequently, better packing of chains and hence a higher degree of crystallinity is expected in polymer **25**. This fact probably leads to the somewhat higher stability of polymer **25** over **27**. It should also be noted that polymer **25** possesses higher molecular weight than polymer **27**. Polymer **28** shows the worst thermal stability of all five polypyrazoles. The presence of two sulfone linking groups per repeat unit in polymer **28** results in a significant decrease in the catenation of aromatic carbon atoms in this polymer as compared to polymers **25–27** and **29**. This decrease in catenation may be responsible for the lower thermal stability of polymer **28** in comparison with the other polymers described in Table 2. Both polymers **26** and **29** contain ether oxygen atoms in the repeat unit but differ in the fact that polymer **26** has 1,4-entrainment in the polymer backbone while polymer **29** has 1,3-entrainment. Polymer **29** shows a somewhat better thermal stability than polymer **26**. The possible explanation for the better thermal stability of **29** may be due to the fact that the oxygen linkage in the *meta* position in **29** will result in a decrease in the electron enrichment of the aromatic backbone by electron donation from oxygen, while in the case of **26**, electron donation from ether oxygen atoms will be delocalized through a *para* aromatic linkage. Thus, the relative "electron deficiency" of polymer **29** will make it more stable toward oxidative degradation in comparison with **26**. An interesting feature of the thermal behavior of polymer **29** to be noted is that it shows an unusually high 50% weight retention temperature as compared to the other polymers.

Synthesis and Characterization of Model Compounds and Polymers Derived from Hydrazides. As discussed earlier, in the case of the synthesis of polypyrazoles **25–29**, it was not possible to isolate poly(enhydrazinonitriles) (intermediate **24**) that subsequently cyclized to give polypyrazoles under the conditions used in this work. It was reasoned that by reaction of a hydrazide nucleophile in place of the hydrazine nucleophile with chlorovinylidene cyanide monomers it might be possible to isolate the enhydrazidonitrile which might be sufficiently deactivated at the nitrogen atom bearing a carbonyl group toward intramolecular cyclization to give polypyrazole under the conditions employed for the synthesis of polypyrazoles **25–29**. Therefore, phenylhydrazide was reacted with chlorophenylmethylidenedinitrile[17] in an attempt to isolate the adduct **30** which could be cyclized to give pyrazole derivative **31** (Scheme 9). This reaction was carried out under conditions similar to the synthesis of **5**. The reaction product isolated was found to be **31** and not **30**. The structure of the product was determined on the basis of IR, mass spectral, proton NMR, and carbon NMR data. If compound **30** were isolated, the carbon NMR spectrum should show two nitrile peaks, but only one nitrile peak at 113.98 ppm was observed. Moreover, in the case of **30** two downfield peaks corresponding to an enamine hydrogen atom and an amide hydrogen atom would be expected at 9.0–11.0 ppm in the proton NMR spectrum. Instead, only one peak at 8.14 ppm is observed. Another model compound **32** was also synthesized by reaction of phenylhydrazide with monomer **6**.

One polymer, **33**, was synthesized from 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene (**6**) and isophthalic hydrazide as shown in Scheme 10. During the course of polymerization, the solution became very viscous (a thick paste), and hence it was diluted with additional solvent. Upon stirring the reaction mixture overnight, it became turbid as polymer precipitated from solution. This polymer was insoluble in common organic solvents.

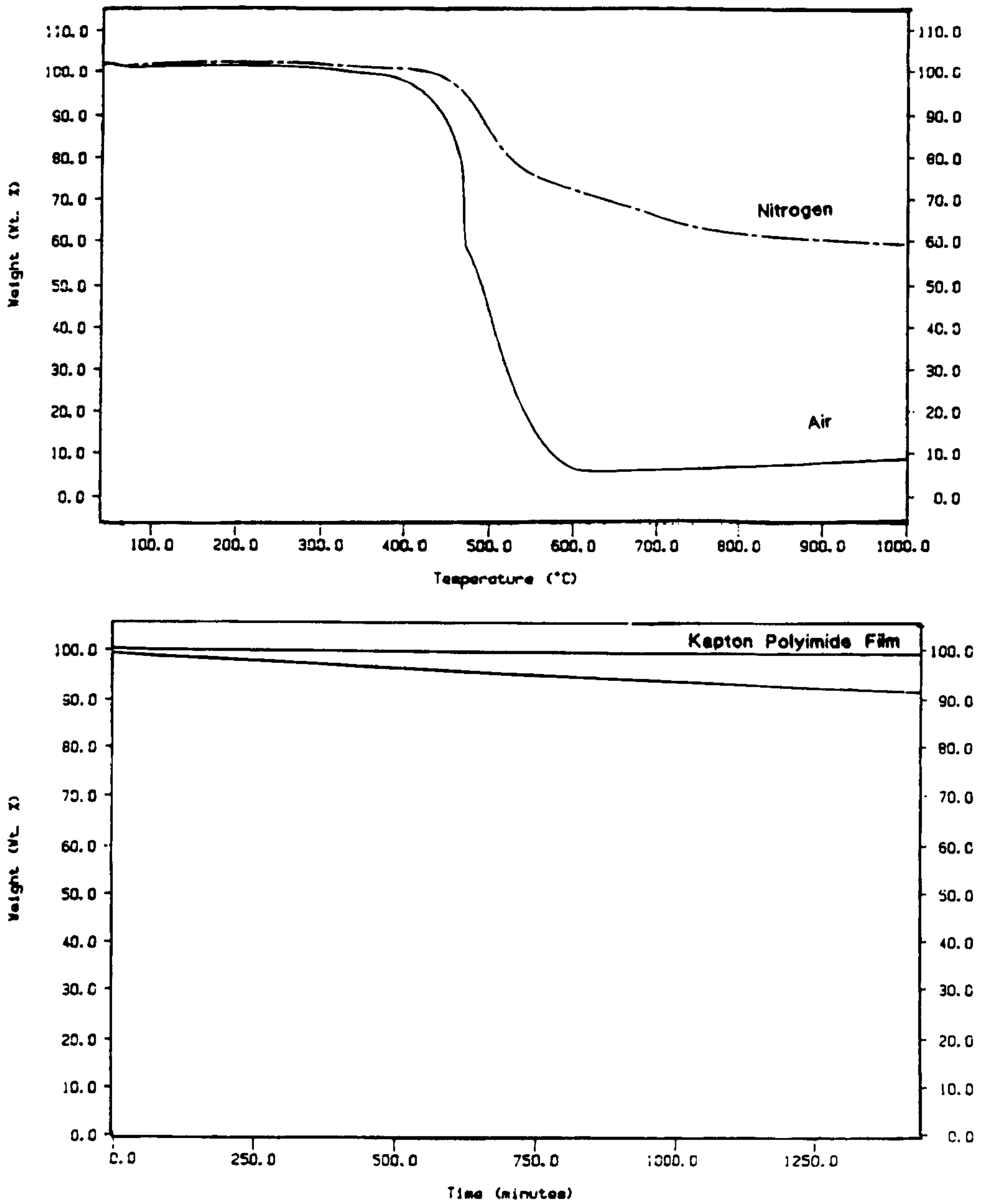
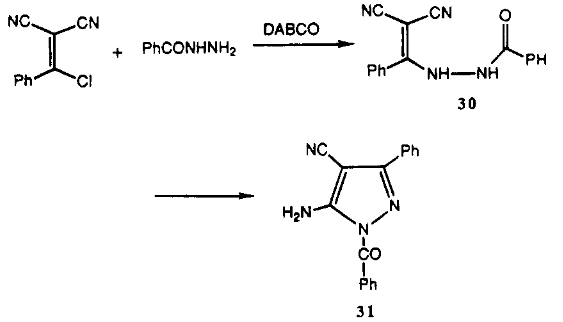
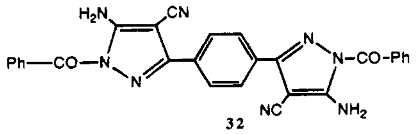


Figure 1. Thermogram for polypyrazoles **26** in air and in nitrogen (top) and isothermal aging of polypyrazole **26** and Kapton at 300 °C (bottom).

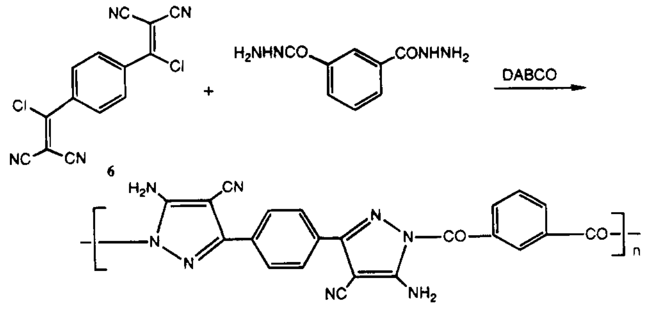
Scheme 9. Synthesis of Model Compound 31





32

Scheme 10. Synthesis of Polymer 33



The polymer was also insoluble in acids such as formic acid and methanesulfonic acid but was soluble in concentrated sulfuric acid. A solution of polymer was made in sulfuric acid (0.5 g/dL) by stirring the polymer in sulfuric acid overnight. The inherent viscosity was found to be 0.05 dL/g at 25 °C. Such a low viscosity value indicated that the polymer had probably degraded under these conditions. The IR spectrum of the polymer matched well with the spectrum of the model compound **32** as shown in Figure 2.

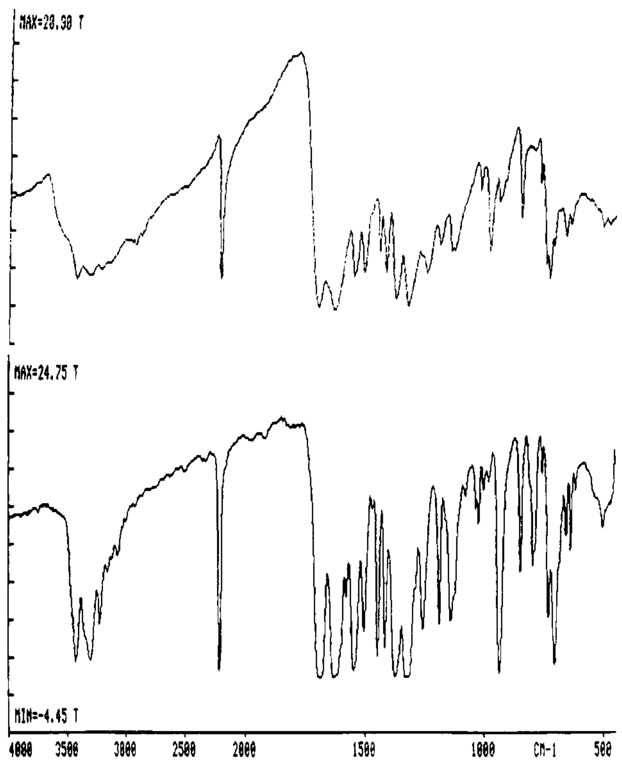


Figure 2. FTIR spectra of polymer **33** (top) and model compound **32** (bottom).

Thermogravimetric analysis (Figure 3a) of polymer **33** indicated that polymer was less thermally stable than polypyrazoles **25**–**29**. In the case of polypyrazole **33** the 1-position of the pyrazole moiety is connected to a benzene ring via a carbonyl group. A literature report[18] showed that there was a serious loss in the thermal stability of polypyrazoles, unsubstituted at the 1-position, when they were reacted with benzoyl chloride to give polypyrazoles with an *N*-benzoyl substituent. In the case of polymer **33**, if degradation takes place at the N–CO– bond, the effect can be extremely detrimental because it can lead to chain cleavage. A differential scanning calorimogram of polymer **33** (Figure 3b) showed an exothermic peak at 305 °C which did not reappear when the sample was rescanned. This exothermic peak may result from an, as yet, unidentified intermolecular reaction.

However, it should be noted that there is also a possibility of reaction between amino and nitrile groups. The differential scanning calorimogram of model compound **32** also showed an exotherm at 316 °C which did not reappear upon rescanning. A detailed study of the curing reaction(s) of such systems is currently underway.

Experimental Section

A. Instrumental Methods. Unless otherwise specified, all melting points were determined on a Thomas/Hoover melting point apparatus using open capillary tubes and are uncorrected. In some cases the melting points were also determined using differential scanning calorimetry.

Infrared (IR) and Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer Model 298 spectrophotometer and a Perkin-Elmer Model 1800 Fourier transform infrared spectrometer, respectively. The positions of the absorption bands are reported in reciprocal centimeters. The bands are denoted by s (strong), w (weak), or br (broad). Ultraviolet (UV) spectra were obtained from solutions in quartz cells (1 cm path length) on a Perkin-Elmer Lambda 4C spectrophotometer interfaced with a Perkin-Elmer Model 7500 computer. The wavelengths of maximum absorption, λ_{max}, are reported in nanometers, and the extinction coefficients are given in parentheses. NMR spectra were recorded on a Varian Model XL-200 spectrometer operating at 200 MHz for ^{1}H and 50.3 MHz for ^{13}C spectra. Some ^{13}C spectra were also obtained on an IBM Model WP/SY 100 spectrometer operating at 25.1 MHz. In all ^{1}H NMR experiments the chemical shifts are recorded in ppm from tetramethylsilane as an internal standard when $CDCl_3$ was used as a solvent and from hexamethyldisiloxane in the case of all other solvents. The data are reported as follows: shift (multiplicity, coupling constant, integration). Abbreviations used to report multiplicity are s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), m (complex multiplet), and br (broad). In all ^{13}C NMR spectra the chemical shifts are reported in ppm. The solvent peaks (in the case of DMSO-d_6 a peak at 39.5 ppm and in the case of $CDCl_3$ a peak at 77.0 ppm) were used as reference. All ^{13}C NMR spectra were obtained using broadband decoupling. In some cases ^{13}C NMR spectra were obtained using the attached proton test (APT).[21] Mass spectra were obtained on a Hewlett-Packard Model 5987 integrated gas chromatograph–mass spectrometer. All sample introductions were made via the direct insertion probe (DIP). Ionization was done by 70 eV electron impact (EI) or methane or isobutane chemical ionization (CI). FAB mass spectra were obtained on a VG 70E mass spectrometer using 2-nitrobenzyl alcohol. The molecular ion is represented as M^+. The peaks corresponding to various fragments are reported as *m/e* (assignment, % relative intensity).

Intrinsic viscosities of the polymer solutions were measured in a Cannon–Ubbelohde viscometer at 25 °C. The polymer solutions for the viscosity measurements were filtered through a 0.45-μm filter (ACRODISC CR, Gelman Sciences).

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on Perkin-Elmer System 7 analyzers interfaced with a Perkin-Elmer 7500 computer. The samples for DSC were encapsulated in an aluminum pan, and an empty aluminum pan was used as a reference. Unless otherwise noted, heating rates were 10 °C/min for DSC and TGA.

Elemental analyses were performed by Galbraith Laboratories, Inc., P.O. Box 51610, Knoxville, TN 37950-1610, and Robertson Laboratory, Inc., 29 Samson Avenue, P.O. Box 761, Madison, NJ 07940. The presence of thermally stable structural moieties in the compounds under discussion leads to carbonaceous residues, causing low carbon values to be obtained in some instances.

B. Solvents and Reagents. Reagent-grade *N*-methylpyrrolidinone (Aldrich) was stirred with anhydrous barium oxide for 24 h, filtered, and fractionally distilled under reduced pressure. The distillate was stirred overnight with anhydrous barium oxide, filtered, redistilled under reduced pressure, and stored over freshly activated Type 5A molecular sieves. (The molecular sieves (Aldrich) were activated by heating evenly in a round-bottomed flask while being constantly flushed with nitrogen. The molecular sieves were heated until no water vapor could be seen condensing on the cool wall of the flask.) Methylene chloride and 1,2-dichloroethane were dried by fractional distillation over P_2O_5. Malononitrile was purified by distillation over P_2O_5 under reduced pressure. 1,4-Diazabicyclo[2.2.2]octane (DABCO) was purified by sublimation at ~40 °C ($P < 1$ Torr). Triethylamine was dried by distillation over calcium hydride and was stored over KOH pellets. Bis(4-aminophenyl) ether was recrystallized from ethyl acetate followed by sublimation *in vacuo* at ~170 °C. Isophthalic hydrazide (American Tokyo Kasei) was recrystallized from water and dried thoroughly prior to use in polymerization. Phenylhydrazide, 4-chlorophenyl phenyl sulfone, and 4-chlorophenyl sulfone were obtained from Aldrich Chemical Co. and were used as received. Hydrazine hydrate (Aldrich, Fisher) was used as received. Isophthaloyl and terephthaloyl chloride either were prepared by reaction of the corresponding dicarboxylic acids with thionyl chloride in the presence of a catalytic amount of pyridine or were used as received (Aldrich, Kodak). Thionyl chloride, $POCl_3$, PCl_5, and $AlCl_3$ were reagent-grade chemicals and were used without

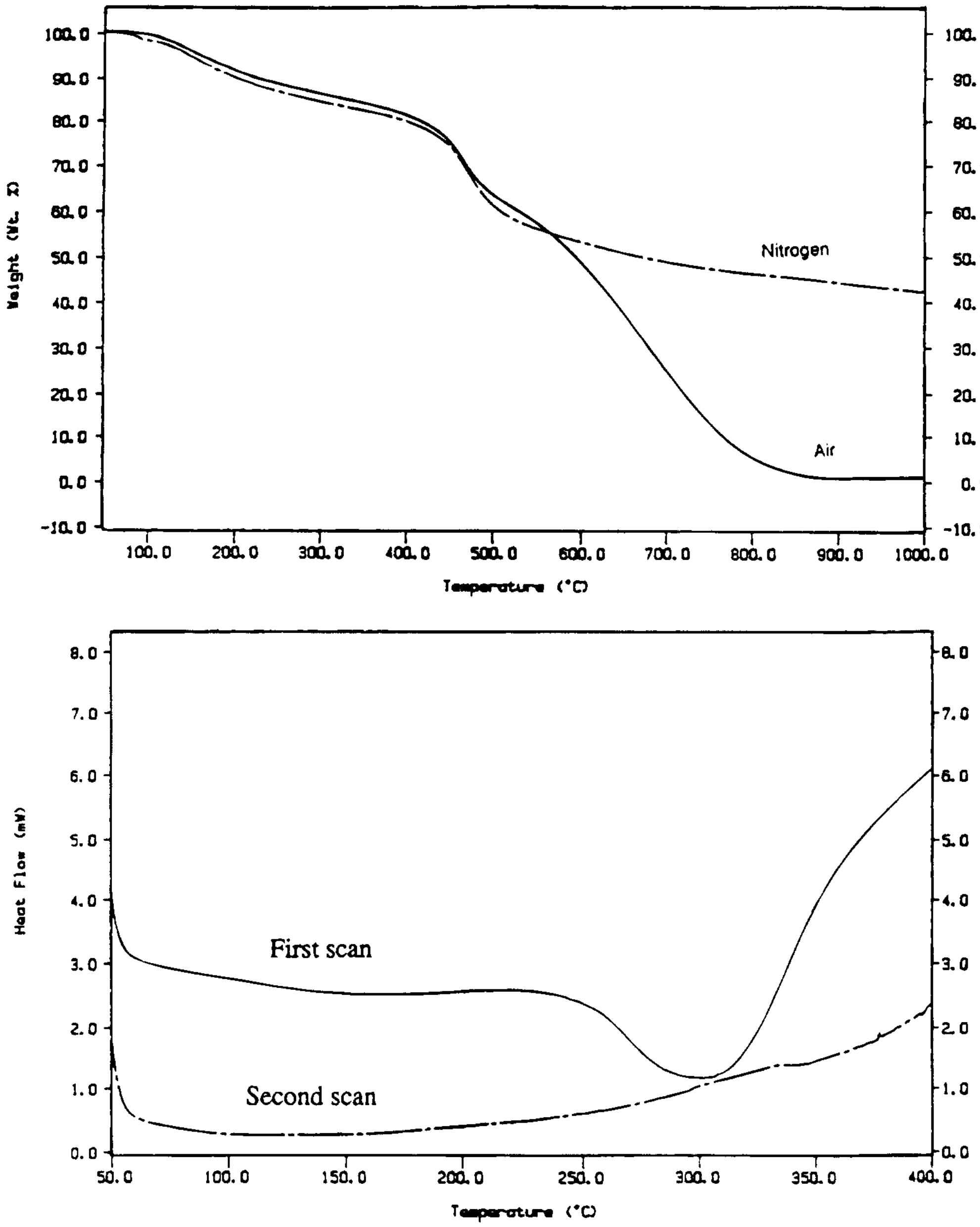


Figure 3. Thermogram (a, top) and differential scanning calorimogram (b, bottom) of polymer **33**.

purification. 4,4′-Sulfonylbis(methylbenzoate) (Aldrich) was technical grade and was used without purification.

C. Syntheses. Trimethyl orthobenzoate (3).[14] The reaction of benzotrichloride with sodium methoxide yielded pure trimethyl orthobenzoate in 55.12% yield. IR: 3062, 3038 (b), 2840 (s), 1488 (m), 1445 (s), 1311, 1395 (s), 1265 (b), 1060, 920 (s), 770 (s), 705 (s), 665(s) cm^{-1}. MS (CI/positive ion): *m/e* 151 (M−OMe, 100), 105 (M−Ph, 38). ^{1}H NMR (CDCl$_3$): δ 3.14 (s, 9H), 7.3−7.7 (m, 5H).

3-Methoxy-3-phenyl-2-cyanopropenenitrile (4). This compound was prepared in 60% yield following a general literature procedure.[13a] Mp: 92−93 °C (lit.[13a] mp 93−94 °C). MS (CI/positive ion): *m/e* 185 (M$^+$ + 1, 100), 171 (13), 105 (10). ^{1}H NMR (CDCl$_3$): δ 3.93 (s, 3H), 7.50−7.7 (m, 5H).

1,3-Diphenyl-4-cyano-5-aminopyrazole (5). This compound was prepared[5] from **4** and phenylhydrazine in 49% yield. Mp: 171−172 °C (lit.[18] mp 172−173 °C). IR (KBr): 3470, 3362, 2210, 1625, 1510, 1490, 1450, 770, 710, 698, 670 cm^{-1}. MS (CI/positive ion): *m/e* 261 (M$^+$ + 1, 100). ^{1}H NMR (CDCl$_3$): δ 4.71 (s, 2H), 7.4−8.0 (m, 10H). ^{13}C NMR (CDCl$_3$): δ 75.0 [*C*−CN], 115.0 [C−*C*N], 118.0, 124.2, 126.4, 127.9, 128.8, 129.3, 129.29, 132.0) [aromatic *C*], 137.0 [*C*−Ph], 151.08 [*C*−NH$_2$].

1,1′-Sulfonylbis(4-methylbenzene) (10).[10] A 250-mL three-necked, round-bottomed flask, equipped with a mechanical stirrer and a reflux condenser, was charged with a mixture of 4-toluenesulfonic acid monohydrate (7.6 g, 0.04 mol), toluene (3.68 g, 0.04 mol), and poly(phosphoric acid) (120 g). The mixture was stirred with a mechanical stirrer, and the reaction mixture was heated at 80−100 °C for 16 h. The hot reaction mixture was poured into ice water (400 mL). The colorless precipitate was filtered, washed with water, and dried overnight on a fritted funnel followed by drying in a vacuum oven (P < 1 Torr) at 60 °C. The reasonably pure product (6.85 g, 69.7%) thus obtained was further purified by crystallization from 95% ethanol. Mp: 150−152 °C (lit.[19] mp 153 °C). ^{1}H NMR (CDCl$_3$): δ 2.36 (s, 6H), 7.26 (d, J = 7.8 Hz, 4H), 7.79 (d, J = 8.2 Hz, 4H).

4,4′-Sulfonylbis(benzoic acid) (11). Method A. A 500-mL three-necked, round-bottomed flask, equipped with a mechanical stirrer, a reflux condenser, and an addition funnel, was charged with 4,4′-sulfonylbis(4-methylbenzene) (**10**) (10.00 g, 40.65 mmol), potassium hydroxide (8.0592 g, 143.66 mmol), and pyridine (25.2 mL). The reaction mixture was heated to boiling, and a solution of potassium permanganate (58.93332 g, 372.9 mmol) in water (252 mL) was added dropwise over a period of 12 h. (Note: All the potassium permanganate did not dissolve in 252 mL of water, and the undissolved portion was added in solid form.) The reaction mixture was stirred and refluxed for 48 h, cooled to room temperature, mixed with a small amount of Celite, and filtered to remove manganese dioxide, and then washed with water (150−200 mL). The combined washings and filtrate were concentrated to 350 mL and acidified with 10% HCl to yield a colorless precipitate of the desired acid. The precipitate was digested for 0.5 h at 40−45 °C, filtered, washed with 300 mL of water, and dried *in vacuo* ($P < 1$ Torr) at room temperature. The solid thus obtained was dissolved in, and precipitated from, an aqueous sodium hydroxide solution (approximately 8−10% w/v) with hydrochloric acid. The precipitate was thoroughly dried in a vacuum oven using a vacuum pump at 100 °C for 36 h (7.3007 g, 58.7%). The IR spectrum of the product was identical with the literature spectrum.[20]

Method B. A mixture of 4,4′-sulfonylbis(methylbenzoate) (200.00 g, 0.59 mol) and aqueous sodium hydroxide (3 N, 1 L) were heated at boiling for 24 h. The reaction mixture was cooled and filtered, and the filtrate was acidified with 50% HCl. A thick colorless precipitate was obtained, filtered, washed with water (2 L), and dried first on the fritted funnel and then over phosphorus pentoxide *in vacuo* ($P < 1$ Torr) at room temperature (181.5 g, 99.05%). The IR spectrum of the product was identical with the literature spectrum.[20]

4,4′-Sulfonylbis(benzoyl chloride) (12). Method A. A mixture of 4,4′-sulfonylbis(benzoic acid) (**11**) (180.00 g, 0.58 mol) and thionyl chloride (450 mL) was refluxed in the presence of a catalytic amount of pyridine (1−1.5 mL) for 24 h. The reaction mixture was cooled and some light yellow solid crystallized which was filtered (solid A). The filtrate was concentrated to obtain more solid (solid B). Both solids (A and B) were combined and crystallized from trichloroethylene to give pure product (144.5 g, 71.61%). Mp: 153 °C (lit.[19] mp 154 °C).

Method B. A 1-L round-bottomed flask, equipped with a reflux condenser bearing a Drierite drying tube, was charged with 4,4′-sulfonylbis(benzoic acid) (**11**) (189.5 g, 0.61 mol) and mixed intimately with phosphorus pentachloride (129.02 g, 0.61 mol). The flask was heated in an oil bath to 100−110 °C. After about 2 h, droplets of liquid phosphorus oxychloride started appearing on the wall of the flask. Heating was continued overnight with occasional shaking. Some more liquid was produced during the course of the reaction. Some phosphorus oxychloride (just enough to turn the solid reaction mixture into a thick slurry so that the mixture could be stirred) was added to the reaction flask. The reaction was continued for 24 h at 135−140 °C. Phosphorus oxychloride was distilled under reduced pressure, and the residue was crystallized from trichloroethylene to yield colorless diacid chloride (127.4 g, 60%). Mp: 153−154 °C (lit.[19] mp 154 °C).

4,4′-Bis(2,2-dicyano-1-hydroxyvinyl)diphenyl Sulfone Disodium Salt (13). A slightly modified workup of the previously reported procedure[4a] led to the better yield of the product. Also, the use of a reaction kettle instead of a round-bottomed flask facilitated the removal of the crude product at the end of the reaction. A 3-L reaction kettle, equipped with a mechanical stirrer, an addition funnel, and a reflux condenser, was charged with 4,4′-sulfonylbis(benzoyl chloride) (**12**) (127.4 g, 0.3714 mol), malononitrile (51.681 g, 0.782 mol), and methylene chloride (1600 mL). The contents in the reaction kettle were vigorously stirred and cooled to 0 °C using an ice bath. Benzyltriethylammonium chloride (24.43 g, 0.074 mol) in water (150 mL) was added to the reaction kettle. An aqueous sodium hydroxide solution (6 N, 1001.5 mL) was added dropwise to the cold reaction mixture over a period of 10−12 h. The reaction mixture was then stirred at room temperature for 3−4 h. The thick yellow precipitate which formed was filtered, dried, extracted in a Soxhlet apparatus with methylene chloride, and dried (solid A). The water layer from the filtrate was separated and concentrated to give some more solid (solid B), which was filtered and washed thoroughly with methylene chloride. Solids A and B were combined and dried at 150 °C *in vacuo* ($P < 1$ Torr) for 48 h (129.99 g, 78.46%). IR (KBr): 3440 (b), 2195 (s), 1590−1520 (b), 1445, 1400, 1381, 1288, 1160, 1098, 1012 (w), 849 (w), 785 (w), 760, 700, 670 cm^{-1}.

Bis(4-hydrazinophenyl) Sulfone (15).[12] The reaction of 4-chlorophenyl sulfone and hydrazine hydrate (80 mL) gave the desired dihydrazine in excellent yield. The crude product was crystallized twice from ethanol to give monomer grade dihydrazine in 83.5% yield. Mp: 197−198 °C (litl[12] mp 198 °C). ^{1}H NMR (DMSO-d_6): δ 4.12 (s, 4H), 6.71 (d, J = 8.9 Hz, 4H), 7.44 (d, J = 8.8 Hz, 4H), 7.54 (s, 2H). ^{13}C NMR (DMSO-d_6): δ 108.21, 126.17 [aromatic C−H], 126.66 [C−$\mathrm{SO_2}$], 153.33 [C−$\mathrm{NHNH_2}$].

Bis(4-hydrazinophenyl) Ether Dihydrochloride (16). The reaction was carried out according to the literature procedure,[12] and the crude product was recrystallized from 1% HCl (49.1% yield). The crystalline product sometimes looked like shiny flakes or crystalline powder. It should be pointed out that *absolutely no* heat should e applied while drying under vacuum because the compound tended to decompose upon heating while being dried. This monomer was stored as its hydrochloride and was freshly recrystallized and dried just prior to polymerization.

***N,N′*-Dibenzoylphenylhydrazine (18).**[16] The reaction of phenylhydrazine and benzoyl chloride gave the desired product in 90.1% yield. Mp: 178−179 °C (lit.[16] mp 177−178 °C). MS (EI): m/e 316 (M^+, 5.5), 194 (11.7), 105 ($\mathrm{PhN_2^+}$, 100), 77 (Ph, 68.2). ^{1}H NMR (DMSO-d_6): δ 7.1−7−7 (m, 15H), 11.45 (s, 1H).

2,3,5-Triphenyl-1,3,4-oxadiazolium Perchlorate (19).[15a] *N,N′*-Dibenzoylphenylhydrazine (**18**) (4.0 g, 12.65 mmol) was suspended in acetic anhydride (20 mL). To this stirred mixture was added, dropwise, perchloric acid (2 mL), with the temperature of the reaction mixture being maintained at room temperature. In about 4−5 min, a colorless solid started precipitating. The reaction mixture was stirred for 2 h more; the solid was filtered, washed repeatedly with diethyl ether, and dried *in vacuo* (5.024 g, 99.6%). IR (KBr): 3200 (m), 3060 (m), 1680 (m), 1612 (s), 1595 (s), 1552 (s), 1485, 1450, 1335, 1290, 1085, 770 (s), 715 (s), 685 (s), 625 (s), cm^{-1}.

1,5-Diphenyl-3-amino-4-cyanopyrazole (20).[15b] To the stirred suspension of 2,3,5-triphenyl-1,3,4-oxadiazolium perchlorate (**19**) (3.985 g, 0.01 mol) in acetonitrile (15 mL) were added malononitrile (0.75 g, 0.011 mol) and dry triethylamine (3.0 g, 4.13 mL). The resulting reaction mixture was stirred for 3 h and poured into water (30−40 mL), and the solid that precipitated was collected, washed with acetonitrile, and dried to give the desired pyrazole (0.998 g, 38.23%). Crude product was further purified by crystallization from acetonitrile. Mp: 199 °C (lit.[15b] mp 198−199 °C). IR (KBr): 3390, 3310, 3200, 2220, 1675, 1590, 1550, 1525, 1495, 1445, 1400, 1400, 1290, 965, 910, 760, 700 cm^{-1}. MS (CI/positive ion): m/e 261 (M^+ + 1, 1870). MS (EI): m/e 260 (M^+, 100), 259 (40). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 4.26 (s, 2H), 7.2−7.4 (m, 10H). ^{13}C NMR ($\mathrm{CDCl_3}$): δ 81.74 [C−CN], 114.18 [C−CN], 125.04, 127.14, 128.07, 128.92, 129.01, 129.08, 129.96 [aromatic C], 147.17 [C−Ph], 156.6 [C−$\mathrm{NH_2}$].

4-Hydrazinophenyl Phenyl Sulfone (21). 4-Chlorophenyl phenyl sulfone (10.00 g, 39.6 mmol) and hydrazine hydrate (80 mL) were refluxed for 24 h. The reaction mixture was cooled, and the precipitate was filtered and dissolved in 5% HCl. Any insoluble solid was filtered. The solution was made basic to litmus with sodium acetate, and the precipitated hydrazine was washed with water and recrystallized from ethanol (4.292 g, 43.7%). Mp: 197−199 °C. IR (KBr): 3339 (s), 3283 (s), 1584, 1515, 1446, 1348, 1292, 1149, 1102, 1070, 996, 964, 814, 731, 717, 689, 587 (w), 564, 502 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 4.19 (s, 2H), 6.75 (d, J = 8.95 Hz, 2H), 7.45−7.56 (m, 5H). ^{13}C NMR (DMSO-d_6) (APT): δ108.19 (carbon atoms ortho to $\mathrm{NHNH_2}$ and meta to the sulfone group), 123.45 [C−$\mathrm{SO_2}$, para to $\mathrm{NHNH_2}$], 124.37 [carbon atoms meta to $\mathrm{SO_2}$ in the phenyl ring], 127.09, 127.32 [carbon atoms meta to $\mathrm{SO_2}$], 130.47 [carbon atoms para to $\mathrm{SO_2}$ in the phenyl ring], 141.31 [C−$\mathrm{SO_2}$], 153.98 [C−$\mathrm{NHNH_2}$].

Model Compounds 22 and 23. The syntheses and the partial characterization data were reported in an earlier paper.[1] Complete characterization data are given below. None of these model compounds melted but decomposed at a temperature higher than 350 °C (observed by TGA).

Compound 22. FTIR (KBr): 3400−3200, 2220, 1635, 1595, 1560, 1515, 1320−1295 (m), 1160, 1110, 985, 845, 695 cm^{-1}. MS (FAB m/e 723 (M^+ + 1, 35), 613 (27), 460 (100). ^{1}H NMR (DMSO-d_6): δ 7.10 (s, 4H), 7.60−7.68 (m, 6H), 7.83 (d, J = 9

Hz, 4H), 7.91 (s, 4H), 7.95−7.99 (dd, J = 8.1, 1.7 Hz, 4H), 8.08 (d, J = 9 Hz, 4H). ^{13}C NMR (DMSO-d_6): δ 71.92 [C−CN], 114.95 [C−CN], 124.64, 126.34, 127.36, 128.65, 129.75, 131.44, 133.82, 139.57, 140.72, 150.30 [aromatic C], 141.32 [C−C_6H_4], 152.32 [C−NH_2]. Calcd for $C_{38}H_{26}N_8O_4S_2$: C, 63.14; H, 3.62; N, 15.50. Found: C, 62.88; H, 3.64; N, 15.45.

Compound 23. FTIR (KBr): 3450−3000, 2220, 1635, 1595, 1560, 1520, 1500, 1450, 1410, 1320, 1310, 1160, 1105, 845, 750, 685 cm^{-1}. λ_{max} (ϵ) (NMP): 268.9 (45 798), 255.7 nm (40 191 M^{-1} cm^{-1}). FAB (MS): m/e 723 (M$^+$ + 1, 100), 583 (20). ^{1}H NMR (DMSO-d_6): δ 7.08 (s, 4H), 7.31−7.68 (m, 7H), 7.81 (d, J = 8.7 Hz, 4H), 8.28 (m, 1H). ^{13}C NMR (DMSO-d_6): δ 70.26 [C−CN], 112.96 [C−CN], 121.83, 122.78, 124.99, 125.51, 126.99, 127.52, 129.47, 131.92, 137.76, 138.90, 148.73 [aromatic C], 139.48 [C−C_6H_4], 151.57 [C−NH_2]. Calcd for $C_{38}H_{26}N_8O_4S_2$: C, 63.14; H, 3.62; N, 15.50. Found: C, 62.88; H, 3.98; N, 15.24.

Poly[(5-amino-4-cyano-1*H*-pyrazole-1,3-diyl)-1,4-phenylenesulfonyl-1,4-phenylene)] (25). This polymer was synthesized according to the previously described procedure.[1] FTIR (film): 3420−3200, 2220, 1635, 1595, 1555. 1520, 1430, 1410, 1320, 1300, 1160, 1105, 985, 850, 760, 600 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 7.11 (s, 4H), 7.83−7.91 (m, 4H), 8.13 (d, J = 8.5 Hz, 4H). ^{13}C NMR (DMSO-d_6): δ 71.95 [C−CN], 114.93 [C−CN], 124.772, 126.37, 129.00, 131.43, 139.26, 150.34 [aromatic C], 141.56 [C−C_6H_4], 153.30 [C−NH_2].

Poly[(5-amino-4-cyano-1*H*-pyrazole-1,3-diyl)-1,4-phenylene-(5-amino-4-cyano-1*H*-pyrazole-3,1-diyl)-1,4-phenyleneoxy-1,4-phenylene)] (26). A dry 50-mL reaction kettle was fitted with a mechanical stirrer, an addition funnel with a nitrogen inlet, and a reflux condenser connected to a mineral oil bubbler. The assembly was charged with bis(4-hydrazinophenyl) ether dichloride (**16**) (1.100 g, 3.63 mmol), 1,4-diazabicyclo[2.2.2]octane (DABCO) (0.8955 g, 7.260 mmol), and dry *N*-methyl-2-pyrrolidinone (8 mL). To this solution, stirred under nitrogen and cooled to 0 °C, was added, dropwise, a solution of 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene (**6**) (1.0854 g, 3.6286 mmol) in dry NMP (8 mL). The color of the reaction mixture changed to dark brown and then to light yellow (ca 5−10 min). Stirring was continued, and the reaction mixture was allowed to warm to room temperature (1 h). At this point the reaction mixture became very viscous (almost a paste), and it was diluted with additional NMP (15 mL). The reaction mixture was then gradually heated to 70 °C, stirred at that temperature for 16 h, and cooled to room temperature, and polymer was precipitated by pouring the reaction mixture into vigorously stirred water. The precipitated polymer was filtered and dried. A small portion of the polymer was dissolved in DMF and a flexible film was cast. The rest of the polymer was extracted in a Soxhlet apparatus for 24 h using methanol and dried at 200 °C *in vacuo* (P < 1 Torr) for about 5 h (1.5410 g, 84.2%). The latter treatment rendered the polymer almost insoluble in polar aprotic solvents in which it was soluble prior to drying. FTIR (film): 3400−3200 (m), 2220, 1670, 1630, 1560, 1520, 1500, 1240, 1165, 840, 620 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 6.83 (s, 4H), 7.20 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 8.9 Hz, 2H), 7.92 (s, 4H). ^{13}C NMR (DMSO-d_6): δ 69.25 [C−CN], 113.44 [C−CN], 117.65, 124.68, 124.91 [aromatic protonated C], 129.78, 130.96, 151.27 [aromatic quaternary C], 147.50 [C−C_6H_4], 154.15 [C−NH_2].

Poly[(5-amino-4-cyano-1*H*-pyrazole-1,3-diyl)-1,3-phenylene-(5-amino-4-cyano-1*H*-pyrazole-3,1-diyl)-1,4-phenylenesulfonyl-1,4-phenylene)] (27). Bis(4-hydrazinophenyl sulfone (**15**) (1.8595 g, 6.68 mmol.), 1.4-diazabicyclo[2.2.2]octane (DABCO) (0.7500 g, 6.68 mmol), and 1,3-bis(1-chloro-2,2-dicyanovinyl)benazene (**7**) (2.000 g, 6.68 mmol) were reacted in dry NMP according to the procedure for **25**, above. The reaction mixture was cooled to room temperature and poured into vigorously stirred water. The precipitated polymer was filtered and dried. A small portion was dissolved in DMF, and a clear film was cast from the solution. The rest of the polymer was extracted in a Soxhlet apparatus using methanol and dried *in vacuo* (P < 1 Torr) at 150 °C for 10 h (3.3211 g, 98.5%). FTIR (film): 3400−3200, 2220, 1670, 1635, 1595, 1560, 1520, 1500, 1410, 1325, 1298, 1160, 982, 850, 800, 760, 640 cm^{-1}. λ_{max} (ϵ) (NMP): 269.4 (24931), 256 (21529). ^{1}H NMR (DMSO-d_6): δ 7.10 (s, 4H), 7.59 (t, J = 7.6 Hz, 1H), 7.83−7.93 (m, 4H), 8.13 (d, J = 8.5 Hz, 2H), 8.31 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 70.21 [C−CN], 112.89 [C−CN], 121.79, 122.86, 125.07, 127.13, 127.53 [aromatic protonated C], 129.41, 137.41, 148.71 [aromatic quaternary C], 139.58 [C−C_6H_4], 151.54 δ [C−NH_2].

Poly[(5-Amino-4-cyano-1*H*-pyrazole-1,3-diyl)-1,4-phenylenesulfonyl-1,4-phenylene-(5-amino-4-cyano-1*H*-pyrazole-3,1-diyl)-1,4-phenylenesulfonyl-1,4-phenylene)] (28). A dry 100-mL three-necked, round-bottomed flask was fitted with a mechanical stirrer, an addition funnel with a nitrogen inlet, and a reflux condenser connected to a mineral oil bubbler. The assembly was charged with bis(4-hydrazinophenyl) sulfone (**15**) (0.9501 g, 3.417 mmol), 1,4-diazabicyclo[2.2.2]octane (DABCO) (0.3833 g, 3.417 mmol), and dry *N*-methyl-2-pyrrolidinone (NMP) (12 mL). To this solution, stirred under nitrogen and cooled to 0 °C, was added, dropwise, a solution of 4,4′-bis(1-chloro-2,2-dicyanovinyl)phenyl sulfone (**14**) (1.50 g, 3.417 mmol) in dry NMP (7 mL). The color of the reaction mixture changed to dark brown and then to light yellow (ca. 2 min). The reaction mixture was allowed to warm to room temperature (~2 h) and stirred at room temperature for 5 h followed by stirring at ~70 °C for 24 h. The reaction mixture was cooled to room temperature and poured into vigorously stirred water to precipitate the polymer which was filtered, washed with plenty of water on the frit, dried, and reprecipitated into water from a solution in NMP. The precipitated polymer was again filtered, extracted in a Soxhlet apparatus using methanol, and dried *in vacuo* (P < 1 Torr) at 70−80 °C for 48 h (2.0153 g, 91.57%). FTIR (film): 3400−3200 (m), 2216 (s), 1628, 1591, 1557, 1514, 1455, 1423, 1405, 1385, 1323, 1156, 1107, 1074, 1014, 985, 847, 753, 712, 687 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 7.17 (s, 4H), 7.82 (d, J = 8.6 Hz, 4H), 7.98−8.14 (m, 12H). ^{13}C NMR (DMSO-d_6): δ 72.40 [C−CN], 114.23 [C−CN], 124.74, 126.86, 127.84, 128.79, 135.44, 141.01, 141.77, 149.08 [aromatic C], 139.55 [C−C_6H_4], 153.44 [C−NH_2].

Poly[(5-amino-4-cyano-1*H*-pyrazole-1,3-diyl)-1,3-phenylene-(5-amino-4-cyano-1*H*-pyrazole-3,1-diyl)-1,4-phenyleneoxy-1,4-phenylene)] (29). A dry 100-mL three-necked, round-bottomed flask was fitted with a mechanical stirrer, an addition funnel with a nitrogen inlet, and a reflux condenser connected to a mineral oil bubbler. The assembly was charged with bis(4-hydrazinophenyl) ether dihydrochloride (**16**) (1.5200 g, 5.01 mmol), 1.4-diazabicyclo[2.2.2]octane (DABCO) (1.1257 g, 10.02 mmol), and dry *N*-methyl-2-pyrrolidinone (10 mL). To this solution, stirred under nitrogen and cooled to 0 °C, was added, dropwise, a solution of 1,3-bis(1-chloro-2,2-dicyanovinyl)benzene (**7**) (1.50 g, 5.01 mmol) in dry NMP (10−11 mL). The color of the reaction mixture changed to dark brown and then to light yellow (ca. 2 min). The reaction mixture was allowed to warm to room temperature (~2 h) and stirred at room temperature for 5 h followed by stirring at ~70 °C for 24 h. The reaction mixture was cooled to room temperature and poured into vigorously stirred water to precipitate the polymer which was filtered, washed with plenty of water on the frit, and dried (1.7689 g, 77.35%). The polymer was further purified by precipitation into water/methanol (50/50 v/v) from a solution in NMP. The precipitated polymer was in the form of a fine suspension which was centrifuged at 7000−8000 rpm for 3 h to separate the solid. The polymer thus obtained was dried at 60−70 °C *in vacuo* (P < 1 Torr) for 24 h. A clear, flexible film was cast from a solution in NMP. FTIR (film): 3420−3070 (b), 2216 (s), 1896 (w), 1617, 1301, 1221, 1167, 1102, 1012, 984, 907, 838, 806, 698 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 6.81 (s, 4H, NH_2), 7.1−8.3 [aromatic C−H with fine splitting, 12H, 7.19 (d, J = 8.8 Hz), 7.56 (d, J = 8.6 Hz), 7.84 (s), 7.88 (d), 8.30 (s)]. ^{13}C NMR (DMSO-d_6): δ 69.27 [C−CN], 113,35 [C−CN], 117.68, 121.67, 124.94, 127.39, 128.16, 129.87, 130.92, 147.78, 151.26, 154.12 (C−NH_2).

1-Benzoyl-3-phenyl-4-cyano-5-aminopyrazole (31). To a stirred solution of phenylhydrazide (0.7222 g, 5.30 mmol) and DABCO (0.2972 g, 2.65 mmol) at 9 °C was added chlorophenylmethylidenedinitrile[17] (1.0 g, 5.30 mmol). The reaction mixture turned brown and then quickly changed to yellow, and a solid precipitated. The reaction mixture was allowed to warm to room temperature (1 h) and then stirred at 60−70 °C overnight. The reaction mixture was cooled to room temperature and poured into water. The solid was filtered and dried (1.2334 g, 80.73 %). Proton NMR indicated that the crude product was almost pure. An analytical sample was obtained by crystallization from methanol. Mp: 208−210 °C. FTIR (KBr): 3440, 3305, 3230, 2225, 1690 (b), 1640, 1605, 1550, 1500, 1452, 1385, 1335, 1259, 1185, 1132, 1077, 945−932 (d), 800, 790, 775, 730, 707, 698, 658 cm^{-1}. MS (CI/positive ion): *m*/*e* 289 (M$^+$ + 1, 100). ^{1}H NMR (DMSO-d_6): δ 7.4−8.05 (m, 10H, aromatic C−*H*), 8.14 (s, 2H, −N*H*$_2$). ^{13}C NMR (DMSO-d_6): δ 71.05 [*C*−CN], 113.98 [−*C*N], 126.33, 127.63, 128.53, 129.75, 129.87, 130.54, 131.85, 132.58. 151.69, 157.18 (*C*−NH$_2$), 169.03 [>*C*=O]. Anal. Calcd for $C_{17}H_{12}N_4O$: C, 70.81; H, 4.20; N; 19.43. Found: C, 70.95; H, 4.47; N, 19.35.

3,3′-(1,4-Phenylene)bis(1-benzoyl-5-amino-4-cyanopyrazole) (32). A 50-mL three-necked flask, equipped with a magnetic stirring bar, a nitrogen inlet, and a reflux condenser attached to a mineral oil bubbler, was charged with a solution of DABCO (0.3700 g, 3.342 mmol) and phenylhydrazide (0.9103 g, 6.686 mmol) in dry NMP (20 mL). The reaction flask was cooled to 0 °C using an ice bath and a solution of 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene (**6**) (1.0 g, 3.34 mmol) in approximately 10 mL of dry NMP. The reaction mixture turned brown and then quickly turned light yellow, and a yellow solid precipitated. The reaction mixture was allowed to warm to room temperature, stirred at 60−70 °C for 12 h, cooled to room temperature, and poured into 100 mL of an ice−water mixture. A light yellow solid was obtained and was filtered, washed with water, redissolved in hot NMP, and reprecipitated into water. The precipitate, almost colorless, was washed with hot water and cold methanol, and dried *in vacuo* ($P < 1$ Torr) (1.3195 g, 79.25%). IR (KBr): 3435, 3300, 3212, 2218, 1680, 1635, 1550, 1450, 1417, 1375, 1325, 1255, 1186, 1138, 985, 850, 795−785 (b), 730, 703 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 7.4−8.05 (m, 10H, phenyl *H*), 7.89 (s, 4H, phenylene *H*), 8.15 (s, 4H, −N*H*$_2$). ^{13}C NMR (DMSO-d_6) (125 °C): δ 71.24 [*C*−CN], 113.4 [*C*N], 126.58, 127.43, 130.31, 131.20, 131.60, 132.373, 150.73, 157.06 [*C*−NH$_2$], 168.78 [−*C*=O].

Poly[(5-amino-4-cyano-1*H*-pyrazole-1,3-diyl)-1,4-phenylene-(5-amino-4-cyano-1*H*-pyrazole-3,1-diyl)carbonyl-1,3-phenylenecarbonyl] (33). A dry 50-mL reaction kettle was fitted with a mechanical stirrer, an addition funnel with a nitrogen inlet, and a reflux condenser connected to a mineral oil bubbler. The assembly was charged with isophthaloylhydrazide (1.1685 g, 6.017 mmol), 1,4-diazabicyclo[2.2.2]octane (DABCO) (0.6750 g, 6.0 mmol), and dry *N*-methyl-2-pyrrolidinone (NMP) (10 mL). To this solution, stirred under nitrogen and cooled to 0 °C, was added, dropwise, a solution of 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene (**6**) (1.8 g, 6.0 mmol) in dry NMP (6.3 mL). The color of the reaction mixture changed to dark brown and then to light yellow (ca 5−10 min). Stirring was continued, and, in a few minutes, the reaction mixture became very viscous (almost a paste) and it was diluted with 10 mL of NMP. The reaction mixture was warmed to room temperature and stirred overnight. The yellow polymer precipitated, was separated, washed with water, and dried *in vacuo* ($P < 1$ Torr) at room temperature. The polymer was found to be insoluble in polar aprotic solvents such as DMF, NMP, DMAc, DMSO, DMAc (saturated with LiCl), NMP (saturated with LiCl), diglyme, nitrobenzene, and methanesulfonic acid but is soluble in concentrated sulfuric acid. The IR spectrum of the polymer matches well with those of the model compounds. FTIR (KBr): 3424, 3305, 2215 (s), 1698, 1631, 1549, 1508, 1443, 1416, 1373, 1321, 1240, 1186, 1136, 977, 740, 726, 658, 636, 502 cm^{-1}.

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References and Notes

(1) Preliminary communication: Moore, J. A.; Mehta, P. G. *Macromolecules* **1988**, *21*, 2644.

(2) (a) Hergenrother, P. M. In *Encyclopedia of Polymer Science and Technology*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Kroschwitz, J. I., Eds.; Wiley-Interscience: New York, 1986; Vol. 7, p 639. (b) Cassidy, P. E. *Thermally Stable Polymers*; Marcel Dekker: New York, 1980.

(3) Mittal, K. L. *Polyimides*; Plenum: New York, 1984; Vols. 1 and 2.

(4) (a) Moore, J. A.; Robello, D. R. *Macromolecules* **1989**, *22*, 1084 and references cited therein. (b) Moore, J. A.; Mehta, P. G. *Polym. Mater. Sci. Eng.* **1989**, *60*, 74. (c) Kim, S. Y. Ph.D. Thesis, Rensselaer Polytechnic Institute, Troy, NY, 1989.

(5) Dickinson, C. L.; Williams, J. K.; McKusick, B. C. *J. Org. Chem.* **1964**, *29*, 1915.

(6) (a) Stille, J. K.; Harris, F. W. *J. Polym. Sci., Polym. Chem. Ed.* **1968**, *6*, 2317. (b) Stoicescu-Crivat, L.; Bruma, M. *Rev. Roum. Chim.* **1967**, *12* (10), 1245. (c) Stille, J. K.; Harris, F. W. *J. Polym. Sci.* **1966**, *B4*, 333. (d) Stille, J. K.; Gotter, L. D. *J. Polym. Sci. Polym. Chem. Ed.* **1969**, *7*, 2492. (e) Stille, J. K.; Harris, F. W. *J. Polym. Sci., Polym. Chem. Ed.* **1968**, *6*, 2317. (f) Stille, J. K.; Harris, F. W. *J. Polym. Sci., Polym. Chem. Ed.* **1968**, *6*, 2331. (g) Gilliams, Y.; Smets, G. *Makromol. Chem.* **1969**, *128*, 263.

(7) (a) Shaeffer, J. P.; Bertram, J. L. *J. Polym. Sci.* **1966**, *B3*, 95. (b) Neuse, E. W. *Macromolecules* **1968**, *1*, 171.

(8) (a) Ueda, M.; Funayama, M.; Kawaharasaki, N.; Imai, Y. *Makromol. Chem.* **1981**, *182*, 837. (b) Imai, Y.; Nakjima, T.; Ueda, M. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 2161.

(9) Connell, J. W.; Bass, R. G.; Sinsky, M S.; Waldbauer, M. O.; Hergenrother, P. M. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, (9) 2531.

(10) (a) Graybill, B. M. *J. Org. Chem.* **1967**, *32*, 2931. (b) Burton, H.; Praill, P. F. G. *J. Chem. Soc.* **1955**, 887.

(11) Reddy, T. A.; Srinivasan, M. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 2987.

(12) (a) Connell, J. W.; Bass, R. G.; Sinsky, M. S.; Waldbauer, M. O.; Hergenrother, P. M. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 2531. (b) Tokunga, D.; Hattori, T.; Kubo, T. *Chem. Abstr.* **1957**, *52*, 112911.

(13) (a) Jones, R. G. *J. Am. Chem. Soc.* **1952**, *74*, 4889. (b) Sato, J. L.; Perez, M. A. *Synthesis* **1981**, 955. (c) Dornow, A.; Schlesse, E. *Chem. Ber.* **1958**, *91*, 1830.

(14) DeWolfe, R. H. *Synthesis* **1974**, *3*, 153.

(15) (a) Boyd, G. V.; Dando, S. R. *J. Chem. Soc., Part C* **1970**, 1397. (b) Boyd, G. V.; Dando, S. R. *J. Chem. Soc., Part C* **1971**, 225.

(16) Franzen, H. *Chem. Ber.* **1909**, *42*, 2465.

(17) We thank Mr. Robert P. Reeves for synthesizing chlorophenylmethylidenedinitrile by a procedure described in ref 4a.

(18) Bracke, W. *J. Polym. Sci., Polym. Chem. Ed.* **1972**, *10*, 983.

(19) Meyer, H. *Justus Liebigs Ann. Chem.* **1923**, *433*, 327.

(20) Standard Spectra Collection, Sadtler Research Laboratories, Grating IR spectrum 27449.

(21) Patt, S. L.; Schoolery, J. N. *J. Magn. Reson.* **1982**, *46*, 535.

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