Synthesis of Thermally Stable Polypyrazoles, Polypyrimidines, and other Heteroaromatic Polymers

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Synthesis of Thermally Stable Polypyrazoles, Polypyrimidines, and other Heteroaromatic Polymers

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by

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Introduction

As part of a continuing effort to prepare high performance - high temperature polymers for functional and structural applications, the reactions of aromatic dipropynones with aromatic dihydrazines, aromatic dithiols, and aromatic diamidines to provide polypyrazoles, polyenonesulfides, and polyprimidines respectively have been investigated. During the past year, it has been demonstrated that novel polypyrazoles and novel polyenonesulfides may be prepared by the proposed procedures. However, the preparation of polypyrimidines has not been achieved. The preparation and characterization of some novel polypyrazolones by reaction of aromatic dihydrazines with an activated diacetylenic diester has been achieved.

Technical Accomplishments:
 Polypyrazoles

Polymer Synthesis Polypyrazoles have been prepared from the reaction of the aromatic dipropynones with aromatic dihydrazines as shown below. A typical synthesis involved the reaction of stoichiometric amounts of an

\[
\text{Ph-C≡C-Ph} + \text{ClHNNH-Ar-NHHCl} \xrightarrow{\text{NEt}_3, m\text{-cresol}} \text{Ph-N-Ar-N-Ph}_n
\]

\[
\text{Ar} = \text{Ph} ; \text{PhCHPh} ; \text{PhSO}_2\text{Ph}
\]
aromatic dipropynone with an aromatic dihydrazine dihydrochloride at 75 - 85°C in m-cresol at a solids content of 15% (w/w) for 24 to 72 hours under a nitrogen atmosphere using triethylamine as the acid acceptor. Due to their hygroscopic nature, the dihydrazine dihydrochlorides were dried with heating under vacuum prior to use. Specific reaction conditions for the preparation of the various polymers have been reported. The resulting polymer solutions were poured into methanol in a high speed blender to isolate the polymers. The polymers were collected, washed repeatedly with methanol and dried under vacuum. Inherent viscosities ranged from 0.13 to 0.33 dL/g. The characterization and thermal properties of the polypyrazoles are presented in Tables 1 and 2.

Monomer Synthesis - The synthesis of the required aromatic dipropynones, 1,1'-(1,3-phenylene)bis(3-phenyl-2-propyn-1-one)(1,3-PPPO) and 1,1'-(1,4-phenylene)bis(3-phenyl-2-propyn-1-one)(1,4-PPPO) has been previously reported. Two H terminal dipropynones, 1,1'-(1,4-phenylene)-bis(2-propyn-1-one) (1,4-PPO) and 1,1'-(1,3-phenylene)bis(2-propyn-1-one) (1,3-PPO) have been prepared using the method reported for 1,4-PPO. The 1,3-PPO is a new compound.

The required aromatic dihydrazines, 4,4'-dihydrazinodiphenylmethane (4,4'-DHDPM), 3,3'-dihydrazinodiphenylmethane (3,3'-DHDPM), and 4,4'-dihydrazinodiphenylether (4,4'-DHDPE) were prepared by a modification of the procedure reported by Parkes and Morley. The corresponding diamine was dissolved in a 1:1 solution of concentrated hydrochloric acid and water and diazotized at 0°C with sodium nitrite. The diazonium salt was then reduced using stannous chloride in concentrated hydrochloric acid, collected and recrystallized from a 1% hydrochloric acid solution to give the dihydrazinedihydrochlorides in 10-40% yield. These compounds gave
satisfactory elemental analyses as the dihydrochlorides. The 4,4'-di-
hydrazinodiphenylsulfone (4,4'-DHDPS) was prepared by heating 4,4'-
dichlorodiphenylsulfone in refluxing excess hydrazine hydrate for 24
hours. The crude product was recrystallized from ethanol to give a 75%
overall yield, mp 195°C dec. [lit 5 195°C].

Polymer Characterization - Inherent viscosities ($\eta_{inh}$) were obtained
on 0.5% polymer solutions in chloroform at 25°C. Differential scanning
calorimetry (DSC) was performed at a heating rate of 20°C/min with the
glass transition temperature (Tg) taken at the inflection point of the $\Delta T$
versus temperature curve. Thermogravimetric analyses (TGA) were performed
on powder samples at a heating rate of 2.5°C/min in air and nitrogen.
Thermal data for the phenyl terminal and H-terminal polypyrazoles are
reported in Tables 1 and 2.

Results and Discussion

Prior to polymer synthesis, a series of model compounds were prepared
to serve as a guide to polymer synthesis and identification. The feasibil-
ity of the reaction of aromatic dipropyones with aromatic dihydrazines
as a facile route to polypyrazoles was successfully demonstrated by the
quantitative synthesis of a series of model compounds in relatively pure
form.

Low to moderate molecular weight polymers as evidenced by inherent
viscosities were readily prepared by the solution polymerization of
aromatic phenyl terminal dipropyones and aromatic dihydrazines. The
polymers could be dissolved in a mixture of m-cresol and toluene and
selectively precipitated by acetone to give higher molecular weight
fractions as evidenced by increased inherent viscosities, in one case as
high as 0.56 dL/g. The molecular weight of the as-prepared polymer was
limited presumably due to slight decomposition of the dihydrazine at the reaction temperature. Tough flexible transparent yellow films were formed from polymer fractions with an inherent viscosity of 0.40 dL/g by solution casting.

As presented in Table 1, the Tgs ranged from 225 to 261°C. No indication of crystallinity was observed. The temperature of 10% weight loss as determined by TGA ranged from 400 to 500°C in air and 470 and 512°C in nitrogen.

A typical synthesis of a hydrogen terminal polypyrrole shown below involved reacting stoichiometric amounts of a hydrogen terminal dipropynone with an aromatic dihydrazine in m-cresol at a solids content of 10% (w/v) for 2-4 hours under a nitrogen atmosphere. The reactions were started at low temperatures in an attempt to prevent the dihydrazine from adding twice to the same dipropynone. The reaction temperature was allowed to slowly increase to about 80°C. The resulting polymers were
soluble in most cases in DMAC and DMSO. One polymer (P2) was completely soluble only in conc. H₂SO₄. The inherent viscosities of the hydrogen terminal polypyrazoles ranged from 0.31 to 1.05 dL/g.

The polypyrazoles prepared from the terminal dipropynones (1,3 and 1,4 PPO's) required milder reaction conditions and less reaction time than those prepared from the phenylated dipropynones. Also, the inherent viscosities of the polymers prepared from the terminal dipropynones were higher. This can be attributed to two factors; the difference in reactivity between the terminal (more reactive) and the phenylated dipropynones, and the possibility of slight decomposition of the dihydrazines at the higher run temperatures and longer reaction times required for preparation of the phenylated polypyrazoles.

Proton magnetic resonance (¹H NMR), carbon-13 magnetic resonance (¹³C NMR) and infrared (IR) spectra for the polypyrazoles gave absorptions characteristic of those obtained for analogous model compounds. In the ¹³C NMR spectrum a resonance corresponding to the methine carbon in the pyrazole ring is observed at 105.1 ppm, [lit 105 ppm], this resonance appears as a doublet in the ¹³C single frequency off resonance spectrum supporting the proposed structure of the pyrazole ring.

The formation of the polypyrazoles is postulated to occur via Michael type addition of the hydrazine to the α,β-unsaturated acetylenic ketone followed by cyclization and loss of water in mild acidic media. This mechanism appears to be operative in our polymerization as evidenced by the isolation of uncyclized polymer in one case. Infrared spectroscopy of the uncyclized polymer revealed the absence of absorptions characteristic of a = C-H band at 3225 cm⁻¹ and a C = C band at 2105 cm⁻¹, and the presence of a N-H band at 3350 cm⁻¹, and a carbonyl band at 1640 cm⁻¹. The
open chain polymer was cyclized thermally and also by treatment with acid to the corresponding polypyrrole.

Conclusions

Low to moderate molecular weight polypyrroles were readily prepared from the cyclocondensation of aromatic dipropynones and aromatic dihydrazines. The polymers exhibited good thermal stability. A paper reporting the preparation and properties of the polypyrroles under NASA Grant NAGI-239 was presented at the national meeting of the American Chemical Society held in Chicago, Illinois, September 1985.

Polyenonesulfides

Introduction

The work reported herein concerns the polyaddition of 1,1'(1,3-phenylene)bis(3-phenyl-2-propyn-1-one)(1,3-PPPO) and 1,1'-(1,4-phenylene)-bis(3-phenyl-2-propyn-1-one)(1,4-PPPO) with a series of aromatic dithiols as a facile route to novel polyenonesulfides.

Technical Approach

The required nucleophilic and electrophilic monomers employed were prepared by known synthetic methods. Aromatic dipropynones were prepared as previously reported. Aromatic dithiols were readily prepared by reduction of aromatic disulfonyl chlorides with stannous chloride hydrate in acetic acid and dealkylation of dialkylthiobenzenes with sodium in liquid ammonia.

Model Compounds

Model enonesulfides were readily prepared by the piperidine catalyzed addition of thiophenol to mono- and dipropynones in alcohol or benzene as shown below.
Based on spectral evidence and results reported by previous investigators, only the (Z)-enonesulfide isomers were obtained. Results of thin layer chromatography (TLC) indicate the possible presence of the (E)-isomer in some cases. However, (E) isomers were not isolated during the course of this study.

**Polymer Preparation and Characterization**

Polyenonesulfides were obtained from the N-methylmorpholine catalyzed addition reaction of stochiometric amounts of pure aromatic dithiols to 1,3- and 1,4-dipropynones in m-cresol as shown below. The 20% (w/w) solids solutions were stirred at temperatures ranging from 25 to 40°C for 8-36 hours under a nitrogen atmosphere. As the reaction proceeded, a highly viscous solution of polyenonesulfide was obtained.
Structural and configurational assignments for the resulting enonesulfides and polyenonesulfides were based on analytical data, infrared, proton and $^{13}$C nuclear magnetic resonance spectroscopy. The inherent viscosities ($\eta_{inh}$) obtained from 0.5% polymer solutions in chloroform at 25°C ranged from 0.31 to 1.35 dL/g. DSC thermograms displayed well defined second order transitions in the range of 132-180°C. TGA results indicate a decomposition temperature of 331°C in air and 339°C in a nitrogen atmosphere for a typical polyenonesulfide.

Thermal properties of the novel polyenonesulfides prepared are presented in Table 3. Respectable mechanical properties were observed for the polyenonesulfides. Thin film properties representative of the polyenonesulfides were obtained for the polymer prepared from 1,3-PPO and
1,3-benzenethiol. The polyenonesulfide film exhibited the following properties: tensile strength, 11,300 psi @ 25°C, 7,540 psi @ 93°C; tensile modulus, 466,000 psi @ 25°C, 394,000 @ 93°C; and elongation to break, 3.0% @ 25°C, 14.5% @ 93°C. Polyenonesulfides do not display hydrogen bonding interactions and may exist as coiled atactic flexible chains. The uncoiling of the polymeric chains at elevated temperatures would account for the relatively high elongation to break. The observed difference in the tensile modulus and strength further supports the flexible structure of the polyenonesulfides.

Conclusions

In summary, easily fabricable polyenonesulfide polymers were readily prepared from the solution polyaddition of activated dipropynones (1,3- and 1,4-PPPO) with various aromatic dithiols. Additional evaluation of mechanical properties is currently being performed by the Polymeric Materials Branch of the NASA Langley Research Center. A paper reporting the preparation and characterization of polyenonesulfides has been accepted for presentation at the national meeting of the American Chemical Society to be held in New York, N.Y. in the spring of 1986.

Polypyrazolones

Introduction

The work reported in this section concerns the polyaddition cyclization of a diacetylenic diester, 1,4-phenylene-bis(3-ethyl propiolate) (1,4-PEP), with three aromatic dihydrazines.

Technical Approach

The required aromatic dihydrazines have been prepared under NAG1-239 as previously reported.¹
The diacetylenic diester, 1,4-phenylene-bis(3-ethyl propiolate) (1,4-PEP), has been prepared by a multi-step synthesis and the general method appears below. The sequence first involves the preparation of p-diethynylbenzene. Two methods with reasonable yield history have been used to date. A. S. Hay reported that the bromination of a 50% solution of p-divinylbenzene gave 1,4-bis(1,2-dibromoethyl) benzene. Debromination of the dibromide with potassium t-butoxide followed by filtration and sublimation gave a 71% yield of pure p-diethynylbenzene for the dehydrohalogenation step. An alternate method used by Takahashi and co-workers in 1980 involves the more costly palladium catalyzed ethynylation of dihalogenerated aromatic compounds. Aromatic diiodo and dibromo compounds undergo substitution of trimethylsilylacetylene with copper (I) iodide and bis(triphenylphosphine) palladium dichloride as co-catalysts. Base hydrolysis of the trimethylsilyl groups with sodium hydroxide gives pure p-diethynylbenzene in 88% yield.

Model Compounds

Ethyl phenylpropiolate and phenylhydrazine have been reacted in various solvent and temperature combinations to form isomeric mixtures of 1,3-diphenylpyrazol-5-one, and 2,3-diphenylpyrazol-5-one. The mode of addition of the phenylhydrazine to the acetylenic ester was evaluated. Equimolar quantities of ethyl phenylpropiolate and phenylhydrazine were reacted for 96 hours at room temperature in ethanol. The solvent was removed in vacuo to give a 96% crude yield of light yellow crystals, m.p. 134-135°C. Infrared analysis of the crude product showed the absence of an alkyne stretching band at 2200 cm⁻¹, indicating that the isolated product was composed only of cyclized material. This data is consistent
1. $\text{Br}_2$, CHCl$_3$, 0-5°C

\[ \text{BrCH}_2\text{CHBr} - \text{CHBrCH}_2\text{Br} \]

2. K$^+$ t-Bu, t-BuOH, Δ

\[ \text{HC=CH} - \text{C=CH} \]

3. 1. $\alpha$-BuLi,
2. CO$_2$,
3. H$_2$O$^+$

\[ \text{HOOC-} \text{C=C-} - \text{C=C-COOH} \]

4. abs. EtOH

\[ \text{EtOOC-} \text{C=C-} - \text{C=C-COOEt} \]
with the literature\textsuperscript{11} for 1,3-diphenylpyrazol-5-one, \textit{15}. Physical data for compound \textit{15} is summarized in Table 4.

The reaction of 1,4-PEP with phenylhydrazine in a 2:1 molar ratio in \textit{m}-cresol at 100°C gave an 83\% crude yield of \textit{3,3'(1,4-phenylene)bis(1-phenylpyrazol-5-one)}, \textit{17}. \textit{\textsuperscript{1}H NMR}, and \textit{\textsuperscript{13}C NMR} data are in agreement with previous model compound data and are included in Table 4.

\textbf{Polymer Preparation and Characterization}

Preliminary work has been conducted to determine the optimum reaction conditions for the polymerization of 1,4-PEP with various aromatic dihydrazines. Three novel polypyrazolones \textit{18, 19,} and \textit{20} have been prepared by the reaction of equimolar amounts of 1,4-PEP with 4,4'-dihydrazinodiphenyl sulfone, 4,4'-dihydrazinodiphenylmethane, and 4,4'-dihydrazinodiphenylether, respectively. These polymers have inherent viscosities in DMSO of 0.12, 0.44, and 1.05 dL/g respectively. The inherent viscosities of the polymer appear to increase as the relative nucleophilicity of the dihydrazines increase. The increase in nucleophilicity is due in part to the electron donating ability of the hinge atom in each dihydrazine in the order \textit{-O- > -CH\textsubscript{2}- > -SO\textsubscript{2}-}. The \textit{\textsuperscript{1}H NMR}, \textit{\textsuperscript{13}C NMR}, and infrared data for polymer \textit{19} compare favorably with data from the pyrazolone model compounds. Spectral data for polymer \textit{19} are shown in Table 4, and reaction conditions for the preparation of polypyrazolones are summarized in Table 5. Two polymer samples prepared as part of the pilot study have been submitted to the Polymeric Materials Branch of the NASA-Langley Research Center for preliminary evaluation.
Introduction

The work reported in this section concerns the attempted polymerization of 1,1'- (1,3-phenylene)bis(3-phenyl-2-propyn-1-one), (1,3-PPPO), 1,1'- (1,4-phenylene)bis(3-phenyl-2-propyn-1-one), (1,4'-PPPO), 1,1'- (1,3-phenylene)bis(2-propyn-1-one), (1,3-PPO), and 1,1'- (1,4-phenylene)bis(2-propyn-1-one), (1,4-PPO), with a series of aromatic diamidines as a route to polyprimidines.
Technical Approach

The required dipropynones and diamidines were prepared by known synthetic methods. The aromatic dipropynones were prepared as previously reported. The aromatic diamidines were prepared using the Pinner method by dissolving the appropriate dinitrile in methylene chloride saturated with hydrogen chloride and adding 3.0 molar equivalents of ethanol. The resulting imidate ester then subjected to ammonolysis in absolute ethanol saturated with anhydrous ammonia to yield the amidine hydrochloride. The diamidines prepared in this manner are 1,3-diamidinobenzene, 1,4'-diamidinobenzene, 4,4'-diamidinobenzophenone, 4,4'-oxydibenzamidine, 4,4'-benzamidine sulfone. Many of the necessary dinitriles were not commercially available and could not be efficiently prepared by the substitution of a diazonium group by cuprous cyanide. Instead they were prepared by substitution of the desired dihalide (either bromide or chloride) by cuprous cyanide in N-methyl-pyrrolidone.

Model Compounds

Model pyrimidines were prepared to study the proposed reaction. Benzamidine hydrochloride was reacted with 1,3-PPPO or 1,4-PPPO to form bis(2,6-diphenylated pyrimidines). Benzoylphenylacetylene was reacted with 1,3- or 1,4-benzamidine hydrochloride to form bis(4,6-diphenylated pyrimidines). Both sets of model pyrimidines were prepared in 2-propanol with enough sodium bicarbonate to neutralize the hydrochloride salt of the amidine. Based on spectral, stoichiometric, and thin-layer chromatographic evidence, the reaction proceeded in quantitative yield. Model compounds, Table 6, were characterized by elemental analysis and infrared spectroscopy.
Polymer Preparation and Characterization

Many attempts were made to polymerize the various diamidines and dipropynones. In the general procedure, an equimolar amount of each monomer was dissolved in freshly distilled solvent with concentrations between 5-20% (w/w) solids under a nitrogen atmosphere. The mixtures were stirred for 24-96 hours at temperatures ranging from 25-125°C. A variety of solvents and solvent mixtures were tried. m-Cresol, hexamethylphosphoramide (HMPA), dimethylformamide (DMF), piperidine, N-methylpyrrolidone, and polyphosphoric acid were used as solvents. As the polymerization proceeded the resulting oligomers precipitated before high molecular weight could be achieved. These products did not show glass transitions when subjected to thermal analysis nor would they dissolve in common organic solvents. Their infrared spectra were consistent with those of the model pyrimidines.
NASA-Langley - V.C.U. Interaction

During the course of the grant period, a close cooperative and collaborative relationship has been maintained with Paul M. Hergenrother, Senior Polymer Scientist, Polymeric Materials Branch, NASA-Langley. Approximately thirty polymer samples have been submitted to Paul Hergenrother for characterization which involved determination of both physical and mechanical properties.

John Connell, a Virginia Commonwealth University graduate student, has received support under NAGI-239 to spend one year in the Polymeric Materials Branch at NASA-Langley. Mr. Connell's duties involve the evaluation of thermal or mechanical properties of new polymers for end use applications. The student has had the opportunity to more fully characterize promising new high temperature polypyrroles as adhesives, composite matrices, films and coatings using equipment and instrumentation not available at V.C.U.

Personnel

The principal investigator devoted approximately 100% of his time during the summer and 35% of his time during the academic year to the project. The graduate research assistants listed below contributed to the research effort summarized in this report. Those contributing who received full or partial support under NAGI-239 were: J.W. Connell, E.W. Cooper, S.M. Andrews and R.O. Waldbauer.
Publications, Presentations and Patents

The research reported in the publications, presentations and patent application listed below was performed under NASA Langley Research Center Grant NAG1-239.

Papers Published:


Papers in Preparation:


Abstracts and Presentations:


Abstracts (continued)


Patent Application Pending:

EXPERIMENTAL

General

All melting points were determined on a Thomas Hoover melting point apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlabs, Inc., Atlanta, Georgia. Inherent viscosities were obtained on a 0.5% w/v solution (0.1000 g in 20 mL) at 25°C. Infrared (IR) spectra were obtained on a Perkin-Elmer 283 spectrophotometer as thin films, KBr discs and Nujol mulls. Proton and carbon nuclear magnetic resonance (\(^1\)H and \(^{13}\)C NMR) spectra were obtained on a JEOL FX90Q Fourier transform NMR spectrometer. Chemical shifts are reported in parts per million (\(\delta\)) downfield from internal tetramethylsilane (TMS). Differential scanning calorimetry (DSC) was performed in static air or a nitrogen atmosphere at a heating rate of 20°C/min using a DuPont model 990 thermal analyzer in combination with a standard DSC cell. The apparent glass transition (Tg) was taken at the mid-inflection point of the ΔT versus temperature curve after heating the sample to 300°C followed by quenching on a cold surface. Thermogravimetric analyses (TGA's) were performed on powdered samples using a Perkin-Elmer program temperature controller model UV-1 in combination with a heater controller and an autobalance model AR-2 at a heating rate of 2.5°C/min in both air and nitrogen. Solvents and starting materials obtained from commercial sources were purified as required. Triethylamine, m-cresol and phenyl hydrazine were distilled prior to use.

Propynones and Dipropynones

Benzoylphenylacetylene (BPA). Into a 2 L three-neck round bottom flask fitted with a nitrogen inlet and a mechanical stirrer was placed 2.7
M N-butyllithium in hexane (112 mL, 0.30 mol, Aldrich Chemical Co.) in tetrahydrofuran (THF) (200 mL). The solution was maintained below 5°C during dropwise addition of phenylacetylene (30.7 g, 0.30 mol, Aldrich Chemical Co.) in THF (50 mL). The solution was stirred an additional 5 min and then freshly distilled benzaldehyde (35.0 g, 0.33 mol) in THF (50 mL) was added dropwise over 10 min with stirring. Additional THF (200 mL) was added and the solution was then allowed to warm to room temperature while stirring was continued over 45 min. The reaction mixture was neutralized with 20% aqueous acetic acid (100 mL). The organic layer was then washed twice with water (200 mL and the solvent removed in vacuo (< 40°C) to give the racemic acetylenic alcohol. To a stirred solution of the crude acetylenic alcohol in acetone (200 mL) was added dropwise a solution of chromic anhydride (21.0 g, 0.21 mol) in sulfuric acid (18.1 mL) and water (60.5 mL), maintaining the temperature below 20°C. Stirring was continued an additional 30 min and then the reaction mixture was poured onto cracked ice (750 g). The crude BPA was collected by filtration, washed with water, and air dried: yield 36.8 g (59.5%); mp 42-44°C. Recrystallization from hexanes containing a small amount of toluene gave pure BPA, mp 45.5-47.5°C (lit. mp 46-48°C).

1,1'-(1,4-Phenylene)bis(3-phenyl-2-propyn-1-one) (1,4-PPPO). A solution of lithium phenylacetylide (0.41 mol) was prepared in THF (200 mL) as previously described. Terephthalaldehyde (25.0 g, 0.186 mol, Aldrich Chemical Co.) in THF (150 mL) was added dropwise over 10 min to the phenylacetylide solution while maintaining the temperature below 5°C. The reaction slurry was treated with additional THF (200 mL) and then allowed to warm to room temperature over 45 minutes. The reaction mixture was
neutralized with 20% aqueous sulfuric acid (100 mL) and the organic layer was washed twice with water (200 mL) and the solvent removed in vacuo (<50°C) to yield an oil. A solution of the oil in acetone (200 mL) was then treated dropwise over 15 min with chromic anhydride (26.0 g, 0.26 mol) in sulfuric acid (22.4 mL) and water (75.0 mL) while maintaining the temperature below 20°C. The solution was then allowed to warm to room temperature while stirring was maintained for 30 min. The reaction mixture was poured onto cracked ice (750 g) to isolate the crude product. After filtration and air drying, the 1,4-PPPO was dissolved in a minimal amount of hot chloroform and the solution was filtered through a 5 cm bed of silica gel (mesh size 60-200, Davison Chemical Corp.) to remove chromium salts. Removal of the solvent in vacuo provided the product. Recrystallization twice from methyl ethyl ketone gave pale yellow needles of pure 1,4-PPPO: yield 32.7 g (52.6%); mp 192.5-193.5°C (lit.16 mp 185-187°C).

1,1'-(1,3-Phenylene)bis(3-phenyl-2-propyn-1-one) (1,3-PPPO).

Impure 1,3-PPPO from isophthalaldehyde (25.0 g, 0.186 mol, Sigma Chemical Co.) was obtained using the procedure described for the preparation of 1,4-PPPO. Recrystallization of the crude product from 2-propanol/95% ethanol gave cream colored crystals of pure 1,3-PPPO: yield 28.5 g (45.7%); mp 119-121°C. IR (KBr) 2212 cm⁻¹ (C≡C), 1640 cm⁻¹ (C=O); ¹H NMR (CDCl₃) δ 9.13-7.24 (14H, m, Ar-H); ¹³C NMR 176.7 ppm (C=O), 94.2 ppm (C≡C-CO), 86.7 ppm (C≡C-Ph) Anal. Calcd. For C₂₄H₁₄O₂: C, 86.21%; H, 4.22%  Found: C, 86.08%; H, 4.27%.

1-Phenyl-2-propyn-1-one (PPO)

To a solution of 1-phenyl-2-propyn-1-ol (50.0 g, .378 mol, Farchan
Chemical Co.) in acetone (300 mL) was added dropwise a solution of chromic anhydride (26.5 g, 0.26 mol) in sulfuric acid (24 mL) and water (75 mL), while maintaining the temperature 0 to 10°C. Stirring was continued an additional 30 min. at room temperature and then the reaction mixture was poured onto cracked ice. The crude product was collected by filtration and washed with water. Recrystallization from hexanes gave off-white crystals of PPO in 82% yield, m.p. 47-49°C [Lit. m.p. 46-48°C].

1,1'-(1,4-Phenylene)bis(2-propyn-1-one) (1,4-PPO)

Into a flame-dried, 1L, three-neck, round bottom flask fitted with a mechanical stirrer, pressure equalizing dropping funnel, reflux condenser, and a nitrogen inlet and outlet was placed 12.0 g (0.50 g atoms) of fresh magnesium turnings and 300 mL of dry THF. Ethylbromide (60.0 g, 0.55 mole) was placed in the pressure equalizing dropping funnel and added dropwise to prepare the Grignard reagent. Under nitrogen, acetylene was bubbled into 250 mL of dry tetrahydrofuran (THF) in a flame-dried 2L three neck round bottom flask fitted with a pressure equalizing dropping funnel containing ethylmagnesium bromide, a magnetic stirrer, and gas inlet tube which protruded into the THF in the flask. The acetylene was purified by passing it through a solution of pyragallol in sodium hydroxide and then through concentrated sulfuric acid. After 10 minutes, a small portion (5-10 mL) of ethylmagnesium bromide was introduced, a froth of ethane appeared immediately which was easily distinguishable from the larger bubbles of acetylene. After the frothing subsided the addition of the ethylmagnesium bromide was continued in a portion-wise fashion until the total solution had been added.

To the solution of ethynylmagnesium bromide, terephthalaldehyde
(24.0 g), (0.179 moles) (Aldrich Chem. Co.) in 150 mL THF was added over a 15-20 minutes period. The reaction was flushed with nitrogen and allowed to stir at room temperature for 2 hr. The mixture was then hydrolyzed with 1.5 L of saturated ammonium chloride solution. The aqueous phase was extracted with three 200 mL portions of diethyl ether. The THF solution and ether extracts were combined and dried over anhydrous magnesium sulfate. The THF/ether was removed under vacuum to give the racemic dipropynol as an oil.

To a mechanically stirred solution of the dipropynol in acetone (200 mL), chromic anhydride (12.6 g, 0.126 mole) in sulfuric acid (12 mL) and water (36 mL) was added dropwise while maintaining the temperature 0 to 5°C. Stirring was continued an additional 30 min. and the reaction mixture was poured onto cracked ice. The crude product was collected by filtration, washed with water, and air dried to yield 19.69 g (60% yield) of 1,4-PPO, m.p. 197-200. Recrystallization from 1,4-dioxane gave pale yellow needles of pure 1,4-PPO. Yield 10.5 g (32%), m.p. 206-208°C (dec) [Lit.18 m.p. 208°C (dec)].

\[1,1'-(1,3-Phenylene)bis\text{-}(2\text{-propyn-1-one})(1,3\text{-PPO})\]

Crude 1,3-PPO from isophthalaldehyde (24.0 g, 0.18 moles, Sigma Chemical Co.) was obtained using the procedure described for the preparation of 1,4-PPO. Recrystallization of the crude product from benzene gave yellow crystals of pure 1,3-PPO: Yield 9.36 g (28.7%), m.p. 105-107°C. Infrared spectrum (IR) (KBr) showed absorptions characteristic of (C=C-H) at 3225 cm\(^{-1}\), (C=C) at 2105 cm\(^{-1}\), and (C=O) at 1640 cm\(^{-1}\). Anal. Calcd. for C\(_{12}\)H\(_6\)O\(_2\): C, 79.11%; H, 3.32%. Found: C, 79.06%; H, 3.34%. Both 1,3 and 1,4-PPO discolored slightly on exposure to air. High pres-
sure liquid chromatographic analyses of freshly recrystallized and discolored compounds showed no change in their chromatograms. In addition, there were no changes in the melting points or the $^1$H NMR and $^{13}$C NMR spectra. Elemental analyses of freshly recrystallized and discolored compounds were within experimental limits (± 0.3% of theoretical values).

**Dihydrazines**

4,4'-Dihydrazinodiphenyl ether (4,4'-DHDPE)

Into a 2 L three-neck round bottom flask fitted with mechanical stirrer, thermometer and dropping funnel was placed 4-aminophenyl ether (20.0 g, 0.10 mol, Aldrich Chemical Co.) dissolved in 150 mL concentrated hydrochloric acid and 100 mL of water. The reaction mixture is placed in a dry-ice acetone bath which can be raised and lowered to maintain the temperature below 0°C. The solution was cooled to -5°C and a solution of sodium nitrite (15.1 g, 0.22 mol, Aldrich Chemical Co.) in 50 mL of water was added dropwise while maintaining the temperature -10 to 0°C. Stirring was continued for an additional hour at 0°C and the diazonium salt was reduced using stannous chloride dihydrate (148.6 g, 0.66 mol, Aldrich Chemical Co.) in concentrated hydrochloric acid (300 mL) previously cooled to 0°C. The mixture was stirred overnight at room temperature and the solid was subsequently collected by filtration and dried in vacuo. The dihydrazine dihydrochloride was recrystallized from a 1% aqueous hydrochloric acid solution using charcoal to give white platelets. Yield 12.7 g (42%) of the dihydrazine dihydrochloride. Anal. Calcd. for $\text{C}_{12}\text{H}_{16}\text{N}_4\text{Cl}_2\text{O}$: C, 47.54%; H, 5.32%; N, 18.48%. Found: C, 47.61%; H, 5.33%; N, 18.44%. The melting point of the free base was 132-134°C.
4,4'-Dihydrazinodiphenyl methane (4,4'-DHDPM)

4,4'-DHDPM was prepared in 37% yield from 4,4'-methylene dianiline by the same procedure as described for the preparation of 4,4'-DHDPE. The melting point of the free base was 146-148°C [Lit.\(^{19}\) m.p. 141-143°C]. Anal. Calcd. for C\(_{13}H_{18}N_4Cl_2\): C, 51.83%; H, 6.02%; N, 18.60%. Found: C, 51.69%; H, 6.06%; N, 18.51%.

3,3'-Dihydrazinodiphenyl-methane (3,3'-DHDPM)

3,3'-DHDPM was prepared in 27% yield from 3,3'-methylene dianiline by the same procedure as described for 4,4'-DHDPE. The melting point of the free base was 65-67°C. Anal. Calcd. for C\(_{13}H_{18}N_4Cl_2\): C, 51.83%; H, 6.02%; N, 18.60%. Found: C, 51.74%; H, 6.06%; N, 18.54%.

These three dihydrazines, (4,4'-DHDPE, 4,4'-DHDPM and 3,3'-DHDPM) were stored and analyzed as their dihydrochloride salts due to the instability of the free bases for prolonged periods in air. Due to their hygroscopic nature they were dried **in vacuo** prior to use.

The free bases were prepared by dissolving the dihydrazine dihydrochloride in distilled water and adding ammonium hydroxide. The solid was collected, washed with water and recrystallized from 95% ethanol.

4,4'-Dihydrazinodiphenyl sulfone (4,4'DHDPS)

Into a 250 mL round bottom flask equipped with a water condenser was placed 4-chlorophenyl sulfone (10.0 g, 0.35 mol, Aldrich Chemical Co.), hydrazine hydrate (80 mL, Aldrich Chemical Co.) and a boiling chip. The mixture was refluxed for 24 hrs, cooled and the solid collected by filtration and air dried. The crude product was recrystallized twice from 95% ethanol using charcoal to give white needles. Yield 7.7 g (79%), m.p. 25°
198°C (dec) [Lit.\textsuperscript{20} m.p. 198°C (dec)].

Model Pyrazoles

1,1'-(4,4'-Oxydiphenylene)bis(3,5-diphenylpyrazole)

A solution of 4,4'-dihydrazinodiphenyl ether dihydrochloride (0.4944 g, 1.63 mmol), BPA (0.6721 g, 3.26 mmol) and triethylamine (0.363 g, 3.58 mmol) in 95% ethanol was heated at reflux under a nitrogen atmosphere for 24 hr. The solvent was removed \textit{in vacuo} and the crude material was heated in boiling water to provide a yellow solid (0.88 g, 89% yield), m.p. 138-143°C. Recrystallization from toluene gave yellow leaflets. Yield 0.68 g (69%), m.p. 149.5-151°C. \textsuperscript{1}H NMR (CDCl\textsubscript{3}), δ7.0-7.9 (30 H, m, Ar-H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}), 105.1 ppm (C-4 pyrazole ring), SFOR doublet. Anal. Calcd. for C\textsubscript{42}H\textsubscript{30}N\textsubscript{4}O: C, 83.14%; H, 4.98%; N, 9.23%. Found: C, 82.88%; H, 5.11%; N, 9.22%.

1,1'-(4,4'-Methylene-diphenylene)bis(3,5-diphenylpyrazole)

A solution of 4,4'-dihydrazinodiphenyl methane dihydrochloride (0.6150 g, 2.04 mmol), BPA (0.8411 g, 4.08 mmol) and triethylamine (0.45 g, 4.4 mmol) were used to prepare the title compound following the procedure described for the preparation of 1,4'-(4,4'-oxybisphenylene)bis-(3,5-diphenylpyrazole). The crude compound was obtained as a yellow solid (1.1 g), m.p. 137-141°C. Recrystallization from toluene gave pale white leaflets. Yield 0.84 g (67.6%), m.p. 141.5-143°C. \textsuperscript{1}H NMR (CDCl\textsubscript{3}), δ2.98 (2H, s, -CH\textsubscript{2}-), 7.0-7.9 (30 H, m, Ar-H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}) 40.9 ppm -CH\textsubscript{2}-, SFOR triplet, 105.1 ppm (C-4 pyrazole ring), SFOR doublet. Anal. Calcd. for C\textsubscript{43}H\textsubscript{32}N\textsubscript{4}: C, 85.40%; H, 5.33%; N, 9.26%. Found: C, 85.29%; H, 5.40%; N, 9.14%.
1,1'-(3,3'-Methylene-diphenylene)bis(3,5-diphenylpyrazole)

A solution of 3,3'-dihydrazinodiphenylmethane dihydrochloride (0.7240 g, 2.40 mmol), BPA (0.9897 g, 4.8 mmol) and triethylamine (0.539, 5.2 mmol) used to prepare the title compound as described above. The crude product was recrystallized from ethyl ether to give pale white platelets. Yield 0.93 g (64%), m.p. 145-147°C. Anal. Calcd. for C₄₃H₃₂N₄: C, 85.40%; H, 5.33%; N, 9.26%. Found: C, 85.24%; H, 5.35%; N, 9.23%.

3,3'-(1,4-Phenylene)bis(2,5-diphenylpyrazole)

A solution of 1,4-PPPO (1.32149, 3.95 mmol) and freshly distilled phenylhydrazine (0.9397 g, 8.69 mmol, Aldrich Chemical Co.) was heated at reflux in 95% ethanol for 24 hr. under a nitrogen atmosphere. The solvent was removed in vacuo to give 1.93 g (95% of crude product, m.p. 240-243°C. Recrystallization from ethanol gave pale yellow needles. Yield 1.60 g (78.7%), m.p. 246.5-247.5°C. [Lit.²¹ m.p. 247-248°C]. Anal. Calcd. for C₃₆H₂₆N₄: C, 84.02%; H, 5.09%; N, 10.89%. Found: C, 83.93%; H, 5.13%; N, 10.85%.

3,3'-(1,3-Phenylene)bis(2,5-diphenylpyrazole)

A solution of 1,3-PPPO (1.6234 g, 4.85 mmol) and freshly distilled phenylhydrazine (1.1524 g, 10.6 mmol) in 95% ethanol was refluxed for 24 hr under a nitrogen atmosphere. The crude product was recrystallized from 95% ethanol to give a yellow powder. Yield 1.77 g (71%), m.p. 237-238°C. [Lit.²² m.p. 237-238°C]. Anal. Calcd. for C₃₆H₂₆N₄: C, 84.02%; H, 5.09%; N, 10.89%. Found: C, 83.90%; H, 5.12%; N, 10.87%.
1,1'-(4,4'-Oxydiphenylene)bis(5-phenylpyrazole)

A solution of 4,4'-DHDPE (1.3502 g, 5.86 mmol), PPO (1.5253 g, 11.72 mmol) and 1 drop H$_2$SO$_4$ in 95% ethanol was refluxed for 24 hr. under nitrogen. The solvent was removed in vacuo to give 2.44 g (91.5%) of crude product. Recrystallization from toluene gave white crystals. Yield 2.06 g (77%), m.p. 198-200°C. Anal. Calcd. for C$_{30}$H$_{22}$N$_4$: C, 79.27%; H, 4.88%; N, 12.32%. Found: C, 79.37%; H, 4.91%; N, 12.27%.

1,1'-(4,4'-Methylenediphenylene)bis(5-phenylpyrazole)

A solution of 4,4'-DHDPM (1.2500 g, 5.47 mmol), PPO (1.4238 g, 10.94 mmol) and 1 drop H$_2$SO$_4$ in 95% ethanol was refluxed for 24 hrs under nitrogen. The solvent was removed in vacuo to give 2.22 g (89%) of crude product. Recrystallization twice from toluene gave white platelets. Yield 1.68 g (67%), m.p. 217.5-219°C. Anal. Calcd. for C$_{31}$H$_{24}$N$_4$: C, 82.27%; H, 5.34%; N, 12.38%. Found: C, 82.24%; H, 5.35%; N, 12.35%.

3,3'-(1,4-Phenylene)bis(2-phenylpyrazole)

A solution of 1,4-PPO (2.1175 g, 11.62 mmol), phenylhydrazine (2.7642g, 25.56 mmol, Aldrich Chemical Co.) and 1 drop H$_2$SO$_4$ was refluxed in 95% ethanol for 24 hr. under a nitrogen atmosphere. The solvent was removed in vacuo to give 3.95 g (93%) of crude product. Recrystallization twice from toluene gave off pale yellow crystals. Yield 2.82 g (67%), m.p. 241.5-243°C. Anal. Calcd. for C$_{24}$H$_{18}$N$_4$: C, 79.53%; H, 5.00%; N, 15.46%. Found: C, 79.48%; H, 5.03%; N, 15.39%.

3,3'-(1,3-Phenylene)bis(2-phenylpyrazole)

A solution of 1,3-PPO (2.2107g, 12.13 mmol) phenylhydrazine...
(2.8860g, 26.68 mmol, Aldrich Chemical Co.) and 1 drop H$_2$SO$_4$ was refluxed in 95% ethanol for 24 hours under a nitrogen atmosphere. The solvent was removed in vacuo to give 3.95g (90%) of crude product. Recrystallization twice from toluene gave white crystals. Yield 3.02g (70%), m.p. 153-154.5°C. Anal. Calcd. for C$_{24}$H$_{18}$N$_4$: C, 79.53%; H, 5.00%; N, 15.46%. Found: C, 79.51%; H, 5.07%; N, 15.42%.

**Polypyrazoles**

Poly 1,1'- (4,4'-Oxydiphenylene) (1,4-phenylene) bis(3-phenylpyrazole) P1

Into a 50 mL three neck round bottom flask equipped with a mechanical stirrer, thermometer and nitrogen inlet was placed 1,4-PPPPO (1.8763 g, 5.61 mmol) and 8 mL m-cresol. The solid slowly dissolved and 4,4'-DHDPE•2HCl (1.7009 g, 5.61 mmol) was added and washed in with 2 mL m-cresol, the system was flushed with nitrogen for 10 min. Triethylamine (TEA) (1.25 g, 12.34 mmol) was added and the reaction mixture was warmed to 75°C for 24 hr. under a stream of nitrogen. The polymer was isolated by pouring the reaction mixture into methanol in a high speed blender. The pale yellow polymer was collected by filtration heated in distilled water to remove any TEA-HCl, and heated in methanol to remove any residual m-cresol. The polymer was dried at 95°C for several hours to give 2.8 g (97% yield). The inherent viscosity ($n_{inh}$) of a 0.5% solution (0.1 g in 20 mL solvent) in chloroform at 25°C was 0.33 dL/g. Transparent yellow fingernail creasible films were cast from chloroform. IR (KBr) 1595 cm$^{-1}$ overlapped (C=C) and (C=N). $^1$H NMR (CDCl$_3$) $\delta$ 6.9-7.8 (24 H, m, aromatic H). $^{13}$C NMR (CDCl$_3$) 105.2 ppm (C-4 pyrazole ring), SFOR 103.8 and 106.5 ppm doublet.
Pol 1,1'-(4,4'-Oxydiphenylene)(1,3-phenylene)bis(3-phenylpyrazole) P2

Polypyrrole P2 was prepared as previously described for P1 from 1,3-PPPO (2.2182 g, 6.63 mmol), 4,4'-DHDPE·2HCl (2.0114 g, 6.63 mmol) and TEA (1.5 g, 14.8 mmol) in 17 mL m-cresol. The reaction was heated at 100°C for 24 hr. under nitrogen. The polymer was isolated and worked up as described for P1 to give 3.95 g (98% yield) of yellow polymer. The n_{inh} of a 0.5% solution in chloroform was 0.31 dL/g. Transparent yellow fingernail creasible films were cast from chloroform. IR (KBr) 1595 cm⁻¹ overlapped (C=C) and (C=N). ¹H NMR (CDCl₃) δ 6.7-7.8 (24 H, m, aromatic H). ¹³C NMR (CDCl₃) 105.1 ppm (C-4 pyrazole ring), SFOR 103.7 and 106.4 ppm doublet.

Pol 1,1'-(4,4'-Methylenediphenylene)(1,4-phenylene)bis(3-phenylpyrazole) P3

The polypyrrole P3 was obtained from 1,4-PPPO (1.3772 g, 4.11 mmol), 4,4'-DHDPM·2HCl (1.2406 g, 4.11 mmol) and TEA (0.92 g, 9.1 mmol) in 14 mL m-cresol as previously described for P1. The reaction was heated at 75°C for 24 hr under nitrogen. The polymer was isolated and worked up as previously described to give 2.4 g (97% yield) of yellow polymer. The n_{inh} of a 0.5% solution in chloroform was 0.20 dL/g. Transparent yellow brittle films could be cast from chloroform. IR (KBr) 1595 cm⁻¹ overlapped (C=C) and (C=N). ¹H NMR (CDCl₃) δ 3.9 (ZH, s, -CH₂-), 6.8-7.8 (24 H, m, aromatic H). ¹³C NMR (CDCl₃) 40.9 ppm (-CH₂-), SFOR 39.8, 40.9, 41.7 ppm triplet. 105.2 ppm (C-4 pyrazole ring), SFOR 103.9 and 106.6 ppm doublet.
Poly 1,1'-(4,4'-Methylenediphenylene) (1,3-phenylene)bis(3-phenylpyrazole) 

Poly 1,1'-(4,4'-Methylenediphenylene) (1,3-phenylene)bis(3-phenylpyrazole) 
P4

Polymer P4 was obtained from 1,3-PPPO (2.2944 g, 6.86 mmol), 4,4'-DHDPM-2HCl (2.0670 g, 6.86 mmol) and TEA (1.5 g, 15 mmol) in 20 mL m-cresol as previously described for P1. The reaction mixture was heated at 75°C for 24 hr. under nitrogen. The polymer was isolated and worked up as previously described to give 4.0 g (97% yield) of yellow polymer. The n_{inh} of a 0.5% solution in chloroform at 25°C was 0.23 dL/g. Transparent yellow brittle films were cast from chloroform. IR (KBr) 1595 cm\(^{-1}\) overlapped (C=C) and (C=N). \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 3.9 (2H, s, -CH\(_2\)-), 6.8-7.8 (24H, m, aromatic H). \(^13\)C NMR (CDCl\(_3\)) 40.8 ppm (-CH\(_2\)-), SFOF 39.8, 40.8, 41.6 ppm triplet. 105.1 ppm (C-4 pyrazole ring). SFOR 103.8 and 106.5 ppm doublet.

Poly 1,1'-(4,4'-Sulfonyldiphenylene) (1,4-phenylene)bis(3-phenylpyrazole) 
P5

Polymer P5 was obtained from 1,4-PPPO (1.1845 g, 3.54 mmol) and 4,4'-DHDPS (0.9860 g, 3.54 mmol) in 11 mL m-cresol as previously described for P1. The reaction mixture was heated to 120°C for 48 hr under nitrogen. The polymer was isolated and worked up as previously described to give 1.94 g (95% yield) of yellow polymer. The n_{inh} of a 0.5% solution in chloroform at 25°C was 0.15 dL/g. IR (KBr) 1595 cm\(^{-1}\) overlapped (C=C) and (C=N). \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 6.8-7.8 (24H, m, aromatic H). \(^13\)C NMR (CDCl\(_3\)) 103.8 ppm (C-4 pyrazole ring), SFOR 102.5 and 105.4 ppm doublet.
Poly 1,1'-(4,4'-Sulfonyldiphenylene) (1,3-phenylene)bis(3-phenylpyrazole) 
P6

Polypyrazole P6 was obtained from 1,3-PPPO (1.1016 g, 3.29 mmol) and 4,4'-DHDPS (0.9170 g, 3.29 mmol) in 12 mL m-cresol as previously described for P1. The reaction mixture was heated to 125°C for 48 hr under nitrogen. The polymer was isolated and worked up as previously described to give 1.8 g (96% yield) of yellow polymer. The \( \eta_{inh} \) of a 0.5% solution in chloroform at 25°C was 0.13 dL/g. IR (KBr) 1595 cm\(^{-1} \) overlapped (C=C) and (C=N). \(^1\)H NMR (CDCl\(_3\)) \( \delta \) 6.8-7.8 (24H, m, aromatic H). \(^1^3\)C NMR (CDCl\(_3\)) 103.9 ppm (C-4 pyrazole ring), SFOR 102.7 and 105.5 ppm doublet.

Poly 1,1'-(4,4'-Oxydiphenylene) (1,4-phenylene)bispyrazole P7

Into a 50 mL three neck round bottom flask equipped with a mechanical stirrer, thermometer and nitrogen inlet was placed 1,4-PPO (1.0218 g, 5.60 mmol), 22 mL m-cresol and 1 drop concentrated sulfuric acid. The solid dissolved at room temperature and the solution was cooled to 0°C. 4,4'-DHDPE (1.2913 g, 5.6 mmol) was added and rinsed in with an additional 22 mL m-cresol. The solution was kept at 0°C for 1 hr and then slowly allowed to warm to room temperature. The temperature was gradually increased to 80°C and held for 1 hr. The highly viscous solution was poured into methanol in a high speed blender to precipitate the polymer. The light brown polymer was collected by filtration, then heated in methanol to remove residual m-cresol, collected and dried at 95°C to give 2.05 g (98% yield). The \( \eta_{inh} \) of a 0.5% solution in concentrated sulfuric acid at 25°C was 1.05 dL/g. IR (KBr) 1595 cm\(^{-1} \) overlapping (C=C) and (C=N). Due to the insolubility of the polymer \(^1\)H and \(^1^3\)C NMR spectral data were not obtainable.
Poly 1,1'-("4,4'-Oxydiphenylene) (1,3-phenylene)bispyrazole P8

Polypyrazole P8 was prepared as previously described for P7 from 1,3-PPO (0.9543 g, 5.24 mmol), 4,4'-DHDPE (1.2072 g, 5.24 mmol) and 20 mL \textit{m}-cresol to give 1.94 g (99% yield) of yellow polymer. The $n_{\text{inh}}$ of a 0.5% solution in N,N-dimethylacetamide (DMAc) at 25°C was 0.51 dL/g. Transparent amber fingernail creasible films were cast from DMAc. IR (KBr) 1595 cm$^{-1}$ overlapped (C=C) and (C=N). $^1$H NMR (DMSO-d$_6$) $\delta$ 6.9-7.8 (16H, m, aromatic H).

Poly 1,1'-("4,4'-Methylenediphenylene) (1,4-phenylene)bispyrazole P9

Polypyrazole P9 was prepared as previously described for P7 from 1,4-PPO (0.9230 g, 5.06 mmol), 4,4'-DHDPM (1.1567 g, 5.06 mmol) and 35 mL \textit{m}-cresol to give 1.84 g (97% yield) of light brown polymer. The $n_{\text{inh}}$ of a 0.5% solution in concentrated sulfuric acid at 25°C was 0.54 dL/g. IR (KBr) 1595 cm$^{-1}$ overlapping (C=C) and (C=N). Due to the insolubility of the polymer, $^1$H and $^{13}$C NMR spectral data were not obtainable.

Poly 1,1'-("4,4'-Methylenediphenylene) (1,3-phenylene)bispyrazole P10

Polypyrazole P10 was prepared as previously described for P7 from 1,3-PPO (1.2342 g, 6.77 mmol) and 50 mL \textit{m}-cresol to give 2.43 g (96% yield) of yellow polymer. The $n_{\text{inh}}$ of a 0.5% solution in DMAc at 25°C was 0.33 dL/g. IR (KBr) 1595 cm$^{-1}$ overlapping (C=C) and (C=N). $^1$H NMR (DMSO-d$_6$) $\delta$ 3.9 (2H, s, \textit{-CH$_2$-}), 6.8-7.8 (16H, m, aromatic H).

Poly 1,1'-("4,4'-Sulfonyldiphenylene) (1,4-phenylene)bispyrazole P11

Polypyrazole P11 was prepared as previously described for P7 from 1,4-PPO (0.6824 g, 3.74 mmol), 4,4'-DHDPS (1.0426 g, 3.74 mmol) and 15 mL
m-cresol to give 1.54 g (97% yield) of light brown polymer. The \( n_{\text{inh}} \) of a 0.5% solution in DMAc at 25°C was 0.60 dL/g. Transparent brown brittle films were cast from DMAc. X-ray diffraction spectroscopy indicates slight crystallinity. IR (KBr) 1595 cm\(^{-1}\) overlapping (C=C) and (C=N). \(^1\)H NMR (DMSO-d\(_6\)) \( \delta \) 6.6-7.9 (16H, m, aromatic H). \(^{13}\)C NMR (DMSO-d\(_6\)) 109.4 ppm (C-4 pyrazole ring), SFOR 108.7 and 110.7 ppm, doublet.

**Poly 1,1'-(4,4'-Sulfonyldiphenylene) (1,3-phenylene)bispyrazole P12**

Polypyrazole P12 was prepared as previously described for P7 from 1,3-PPO (1.4566 g, 7.99 mmol), 4,4'-DHDPS (2.2254 g, 7.99 mmol) and 27 mL m-cresol to give 3.2 g (95% yield) of yellow polymer. The \( n_{\text{inh}} \) of a 0.5% solution in DMAc at 25°C was 0.31 dL/g. Brittle films were cast from DMAc. IR (KBr) 1595 cm\(^{-1}\) overlapping (C=C) and (C=N). \(^1\)H NMR DMSO-d\(_6\) \( \delta \) 6.6-7.9 (16H, m, aromatic H). \(^{13}\)C NMR (DMSO-d\(_6\)) 109.3 ppm (C-4 pyrazole ring), SFOR 108.2 and 110.5 ppm, doublet.

**Fractionation of Polypyrazole P1**

Into a 50 mL beaker was placed 1.0 g of polypyrazole P1, (\( n_{\text{inh}} \) in CHCl\(_3\) at 25°C was 0.33 dL/g) and 5 mL m-cresol. The mixture was warmed until the polymer dissolved and toluene (5 mL) was added. The polymer remained in solution and the mixture was allowed to cool to room temperature. Acetone was added dropwise until the mixture became cloudy. The turbid solution was allowed to stand for 24 hr. to yield a gummy precipitate. The solvent was decanted and the tacky polymer dried to give 0.33 g (33% recovery) of yellow polymer. The \( n_{\text{inh}} \) of this fraction of polypyrazole P1 in CHCl\(_3\) at 25°C was 0.40 dL/g.
Uncyclized Polymer

Into a 50 mL three neck round bottom flask equipped with a mechanical stirrer, thermometer, and nitrogen inlet was placed 1,4-PPO (1.7498 g, 9.6 mmol) and 15 mL m-cresol. After the solid dissolved 4,4'-DHDPS (2.6720 g, 9.6 mmol) was added and rinsed in with an additional 15 mL m-cresol. After 8 hr at ambient temperature, the highly viscous solution was poured into methanol in a high speed blender, filtered and dried at room temperature to give 4.3 g (97% yield) of bright yellow polymer. The $n_{inh}$ of a 0.5% solution in m-cresol at 25°C was 0.35 dL/g. IR (KBr) 3350 cm$^{-1}$ (N-H), 1640 cm$^{-1}$ (C=O).

This polymer was cyclized by both chemical and thermal methods. The polymer (1.0 g) was cyclized chemically by dissolving it in concentrated sulfuric acid and pouring the solution into ice water to give 0.90g (97% yield) of tan polymer. The $n_{inh}$ of a 0.5% solution in DMAc at 25°C was 0.43 dL/g. IR (KBr) 1595 cm$^{-1}$ overlapping (C=C) and (C=N).

The polymer (1.0 g) was dissolved in m-cresol (5 mL) and heated to 110-120°C for 3-4 hr under nitrogen. The polymer was isolated by pouring the solution into methanol in a high speed blender, filtered and dried to give 0.88 g (96% yield) of light tan polymer. The $n_{inh}$ of a 0.5% solution in DMAc at 25°C was 0.50 dL/g IR (KBr) 1959 cm$^{-1}$ overlapping (C=C) and (C=N). The IR spectrum of each polymer (chemically and thermally cyclized) were essentially identical and were very similar to those of other polypyrazoles.

Aromatic Dithiols

1,3-Dithiobenzene

The 1,3-dithiobenzene was obtained from Aldrich Chemical Co., and purified by vacuum distillation prior to use.
1,4-Dithiobenzene

Sodium (13.8 g, 0.6 mol) as slowly added to ethanol (95%, 180 mL) and allowed to react. Isopropylthiol (76.2 g, 0.6 mol) was slowly added dropwise to the sodium ethoxide solution at ice water temperature. After 2 hours the reaction mixture was then reduced to half the initial volume in vacuo. Sodium isopropylthiolate was precipitated from the reaction mixture with anhydrous diethyl ether (800 mL). The precipitate was filtered and dried overnight at room temperature in vacuo.

A solution of the 1,4-dichlorobenzene (7.35 g, 0.05 mol) and sodium isopropylthiolate (14.72 g, 0.15 mol) in HMPA (200 mL) were stirred under a nitrogen atmosphere at 80°C for 3 hours. The progress of the reaction was monitored by TLC. The reaction mixture was poured into a saturated sodium chloride solution (2000 mL) and extracted with diethyl ether (1 L). The organic layer was washed with water and dried over molecular sieves (4A), and the solvent was removed in vacuo. The p-di(isopropylthio) benzene residue was chromatographed on silica gel using a mixture of light petroleum (bp 40-60°C) and ethyl ether (98:2) as eluants. The product was purified by vacuum distillation, bp 169-171°C (18 mm). IR (KBr) 3063, 2970, 2950, 2870 cm⁻¹, 1456 cm⁻¹ (C=C, s), 1375, 1385, (isopropyl C-H, M); ¹H NMR (CDCl₃) δ 3.2 (2H, m, isopropyl C-H), δ 1.2 (12H, d, isopropyl CH₃).

The 1,4-di(isopropylthio) benzene (4.54 g, 0.02 mol) was suspended in liquid ammonia in a three-neck flask filtered with a dry ice-acetone condenser. The suspension was stirred under a nitrogen atmosphere as small pieces of sodium (1.83 g, 0.08 mol) was added until a blue color was permanent for 30 minutes (1.5 to 2 equivalents of sodium was necessary for each alkylmercapto group). Solid ammonium chloride was added to decompose the excess sodium, and the ammonia was permitted to evaporate overnight in.
a nitrogen atmosphere. The residue was dissolved in a mixture of ice-
water and excess hydrochloric acid (200 mL of HCl, and 200 g of ice). The
crude 1,4-dithiobenzene precipitate was purified by steam distillation and
the aqueous suspension of dithiol was filtered, and dried in vacuo, mp
97°C, (lit. 23 97.5-98.5°C). IR (KBr) 3060-3020 cm⁻¹ (C-H, w), 2560 cm⁻¹
(S-H, s), 1580 cm⁻¹ (C = C, m); ¹H NMR (CDCl₃) δ 3.2 (2H, s, S-H).

4,4'-Dithiodiphenyl

The title compound was prepared from 4,4'-dichlorodiphenyl as de-
scribed in the preparation of 1,4-dithiobenzene. Purification was ac-
complished by dissolving the crude 4,4'-dithiodiphenyl compound into a 5%
aqueous sodium hydroxide solution (500 mL) and filtering through a sin-
tered glass funnel into concentrated hydrochloric acid (300 mL). The
solid product was collected by filtration. This treatment was repeated
and the product was sublimed at 150-160°C, to give 4,4'-dithiodiphenyl, mp
179-180°C (Lit. 23 179-181°C). IR (KBr) 3060, 3020 cm⁻¹ (C-H, m), 2550
cm⁻¹ (S-H, m); ¹H NMR (CDCl₃) δ 7.2 (8H, s, ArH), 3.2 (2H, s, S-H).

4,4'-Disulfonyl Chloride Diphenylether

Diphenylether (42.0 g, 0.25 mol) was slowly added to chlorosulfonic
acid (100 ml, 1.52 mol) while stirring. After three hours, the reaction
mixture was poured into (2L) and the crude product was filtered. Re-
crystallization from high boiling ligroin (bp 90-120°C) gave colorless
needles of 4,4'-disulfonyl chloride diphenylether: yield 70.3 g (77%); mp
123-125°C(Lit. 24 mp 128-129°C).
4,4'-Disulfonyl Chloride Diphenylmethane

Diphenylmethane (42.0 g, 0.25 mol) was slowly added to chlorosulfonic acid (100 mL, 1.52 mol) while stirring. After three hours, the reaction mixture was poured into water (2L) and the crude product was filtered. A 69% (62.4 g) yield of the crude product was obtained and used without further purification; mp 90-109°C. 24

4,4'-Dithiodiphenylether

Stannous chloride (80.0 g, 0.35 mol) was added to glacial acetic acid (300 mL) while stirring. Hydrogen chloride gas was allowed to pass through the turbid mixture until a clear homogeneous solution was obtained. 4,4'-Disulfonyl chloride diphenyl ether (11.0 g, 0.03 mol) was then added and allowed to react for 30 minutes. The reaction mixture was then filtered into concentrated hydrochloric acid (300 mL) to decompose the stannic salt of the dithiol. The acidic mixture was extracted with petroleum ether (800 mL). The organic layer was dried over molecular sieves (4A) and the solvent was removed in vacuo. Recrystallization from petroleum ether gave white crystals of pure product: yield 3.82 g (57%), mp 100-102°C (Lit. 25 103-104°C). IR (KBr) 3060, 3020 cm⁻¹ (C=C,m). ¹H NMR (CDCl₃) δ 7.2 (8H, Q, Ar-H), 3.2 (2H, s, S-H).

4,4'-Dithiodiphenylmethane

The title compound was prepared by procedures described for the preparation of 4,4'-dithiodiphenylether. To a homogeneous solution (80.0 g, 0.35 mol), glacial acetic acid (300 mL) and hydrogen chloride, 4,4'-disulfonyl chloride diphenylmethane (11.0 g, 0.03 mol) was added.
The reaction mixture was stirred for 30 minutes and filtered into concentrated hydrochloric acid (300mL). The acidic mixture was extracted with petroleum ether (400 mL). The organic layer was dried over molecular sieves (4A) and the solvent was removed *in vacuo*. The clear white solid was further purified using a Kugelrohr distillation apparatus. After purification 1.52 g (22%) of the pure 4,4'-dithiodiphenylmethane was obtained; mp 63-65°C. IR (KBr) 3080, 3040, 2920 and 2850 cm⁻¹ (C-H, m), 2560 cm⁻¹ (S-H, m), 1600 cm⁻¹ (C=C). ¹H NMR (CDCl₃) δ 7.2 (8H, Q, Ar-H), δ 3.2 (2H, S, S-H), δ 3.9 (2H, s, CH₂).

**Model Enonesulfides**

*1,3-Diphenyl-3-phenylthio-2-propen-1-one*

The title enonesulfide model was prepared by procedures reported by Omar and Basyouni. ²⁶ To a solution of 1,3-diphenyl-2-propyn-1-one (BPA) (0.50 g, 2.42 mmol) and thiophenol (0.28 g, 2.42 mmol) in (10mL) methanol was added two drops of piperidine. The solution was allowed to react at room temperature for 15 minutes before the first appearance of crystals. After 24 hours, a near quantitative yield of the crude product was collected and dried (0.70 g, 2.21 mmol, 90%). Following recrystallization from methanol pure yellow crystals were obtained, mp 105-107°C (Lit. ²⁶ 105-107°C). IR (KBr) 3060 and 3020cm⁻¹ (C-H, w), 1635 cm⁻¹ (C = O, s), 1540 and 950 cm⁻¹ (C=C-, s), 1250 cm⁻¹ (C=O,s); ¹H NMR (CDCl₃) δ 7.0-8.1 (15 H, m, Ar-H, and 1H vinyl).

**Bis(1,3-diphenyl-2-propen-1-one)sulfide**

A solution of BPA (1.5 g, 7.3 mmol) and sodium sulfide nonahydrate (0.87 g, 3.6 mmol) in 60 mL of methanol was heated at reflux for 1 hour.
The solution was allowed to stand at room temperature for 24 hours before removal of the solvent in vacuo. A near quantitative yield (1.5 g, 3.4 mmol, 93%) of the crude enonesulfide product was obtained. Recrystallization from methanol provide pure crystals, mp 183-185°C. IR (KBr) 3060 and 3020 cm⁻¹ (C-H, w), 1640 cm⁻¹ (C = O,s), 1550 and 950 cm⁻¹ (C = C-,s), 1250 cm⁻¹ (C-O,s); ¹H NMR (CDCl₃) δ 7.0-8.1 (20 H, Ar-H and 2H vinyl).

1,3-Phenylen bis(3-phenyl-3-phenylthio-2-propen-1-one)

To a solution of 1,3-PPPO (0.72 g, 2.2 mmol) and thiophenol (0.48 g, 4.3 mmol) in 1-propanol (60 mL) was added 4 drops of N-methylmorpholine. The solution was heated at reflux for 4 hours and allowed to stand at room temperature for 24 hours. The solvent was removed in vacuo and a near quantitative yield (1.12 g, 2.0 mmol, 93%) of the crude enonesulfide product was obtained. Recrystallization from methanol, 1-propanol or a mixture of benzene and hexane gave pure yellow crystals, mp 174-175°C. IR (KBr) 3060 and 3020 cm⁻¹ (C-H, w), 1640 cm⁻¹ (C=O,s), 1535 and 970 cm⁻¹ (C=C-,s), 1235 cm⁻¹ (C-O,s); ¹H NMR (CDCl₃) δ 7.0-8.1 (24 H, Ar-H and 2H vinyl).

1,4-Phenylen bis(3-phenyl-3-phenylthio-2-propen-1-one)

To a solution of 1,4-PPPO (0.75 g, 2.2 mmol) and thiophenol (0.49 g, 4.5 mmol) in 1-propanol (60 mL) was added 4 drops of N-methylmorpholine. The solution was heated at reflux for 4 hours and allowed to stand at room temperature for 24 hours. The solvent was removed in vacuo and a near quantitative yield (1.20 g, 2.16 mmol) of the crude enonesulfide product was obtained. Recrystallization from methanol, 1-propanol or a mixture of benzene and hexane gave pure yellow crystals, mp 201-203°C. IR (KBr)
3060 and 3020 cm\(^{-1}\) (C-H, w), 1640 cm\(^{-1}\) (C = O, s), 1540 and 960 cm\(^{-1}\) (C = C-, s), 1250 cm\(^{-1}\) (C-O, s); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 7.0-8.1 (24 H, Ar-H and 2H vinyl).

**Polyenonesulfides**

Polyenonesulfides reported in this study were prepared according to the following general procedure. All polymerizations were carried out in a 100 ml three neck round bottom flask submersed in a constant temperature oil bath. The required dipropynones and aromatic dithiols were purified before polymerization by appropriate recrystallization techniques. The solvent, \(m\)-cresol and N-methylmorpholine catalyst used in these polymerizations were distilled before use. Approximately 3.8 mmole (20% solids) of each of the required electrophilic and nucleophilic monomers were placed in a flame dried three neck flask. To this mixture was added 7 ml of \(m\)-cresol. The reaction mixtures were slowly stirred under a nitrogen atmosphere as a catalytic amount (2-4 drops) of N-methylmorpholine was added. A constant temperature ranging from 25-40°C for 8-36 hours was maintained for all polymerizations reactions. As the monomers gradually dissolved, the solution changed from a bright yellow to an amber color and became highly viscous. The progress of polymerizations were monitored by inherent viscosity measurements, IR spectroscopy, or TLC. After 12 hours the highly viscous solutions were poured into a high speed blender containing methanol (200-400 mL) to precipitate the polyenonesulfide polymers. The solid fiberous polymers obtained were filtered, rinsed repeatedly with methanol and dried at room temperature. The yield of all polymerization reactions varied from 90 to 98%. Inherent viscosity and thermal data for ten polyenonesulfides are recorded in Table 3.
Model Pyrimidine

4,4'-(Phenylene)bis(2,6-diphenylpyrimidine)

In a 100 mL round bottom flask fitted with a reflux condenser, a solution of benzamidine hydrochloride (0.200g 0.598 mmol), 1,4-PPPO (0.230g 1.197 mmol) and sodium bicarbonate (0.110g 1.30 mmol) in 2-propanol (150 mL) was heated at reflux for 8 hours. During this time a white precipitate separated from solution. The reaction mixture was cooled to room temperature and a drop of the supernatant was subjected to thin-layer chromatography. Upon development of the plate no spots corresponding to unreacted starting materials were detected. The reaction mixture was then filtered and the precipitate was washed with water to remove any salt formed from the neutralization of benzamidine hydrochloride. The precipitate was dried and weighed to yield 0.315g (98%) of the dipyrimidine. Crystalization from dioxane gave the dipyrimidine as a white powder, mp 345-346.5°C.
REFERENCES


Table 1
Characterization of Phenylated Polypyrazoles

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Monomer</th>
<th>X</th>
<th>$\eta_{inh}, \text{dL/g}$</th>
<th>$T_g, \text{°C (DSC)}$</th>
<th>Air</th>
<th>Nitrogen</th>
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<tr>
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<td>-CH$_2$-</td>
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<td>452</td>
<td>480</td>
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<tr>
<td>P8</td>
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<td>-O-</td>
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<td>232</td>
<td>500</td>
<td>505</td>
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<tr>
<td>P9</td>
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<td>-SO$_2$-</td>
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<td>-</td>
<td>-</td>
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<td>P10</td>
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<td>-CH$_2$-</td>
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<td>400</td>
<td>480</td>
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<td>490</td>
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<tr>
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*Fractionated sample, film former
Table 2

Characterization of Unsubstituted Polypyrazoles

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Monomer</th>
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<th>( \eta_{inh} ) dL/g</th>
<th>Tg, °C (DSC)</th>
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<th>Nitrogen</th>
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<td>-</td>
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<td>*P5</td>
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<td>242</td>
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*Film former
<table>
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<tr>
<th>Polymer</th>
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<th>Reaction Time, h</th>
<th>Reaction Temp., ºC</th>
<th>η(inh) dL/g</th>
<th>Tg, ºC</th>
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<td></td>
<td>PPPO</td>
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<tr>
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<tr>
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<td>1,3B</td>
<td>22</td>
<td>40</td>
<td>1.35</td>
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<tr>
<td>III</td>
<td>1,3</td>
<td>1,4B</td>
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<td>1,4B</td>
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<tr>
<td>X</td>
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<td>4,4'DPM</td>
<td>36</td>
<td>30</td>
<td>0.75</td>
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</table>

a m-Cresol as solvent, 20% solids concentration (w/w)
b B=Benzene, BP=Biphenyl, PB=Phenoxybenzene, DPM=Diphenyl methane and PPPO=1,1'(phenylene)bis(3-phenyl-2-propyn-1-one).
c CHCl₃ solvent, 0.5% g/dL concentration (w/v).
d After heating to 300ºC in static air.
Table 4

Spectral Characterization of Model Compounds 15 and 17 and Polypyrazolone 19

![Chemical Structures](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yielda</th>
<th>H(N²)</th>
<th>H(C⁴)</th>
<th>C³</th>
<th>C⁴</th>
<th>C⁵</th>
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<td>15</td>
<td>96</td>
<td>11.8</td>
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<td>19</td>
<td>86</td>
<td>--</td>
<td>6.02</td>
<td>149.5</td>
<td>83.8</td>
<td>154.0</td>
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</table>

aCrude yield, in %
bAll spectra were obtained in DMSO-d6 and are reported in ppm.
cC⁴ proton appears as weak doublet
dC⁴ carbon appears as doublet in SFOR.
Table 5

Synthesis and Characterization of Polypyrazolones

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Diester</th>
<th>Dihydrazine</th>
<th>Reaction Time(^a), hr</th>
<th>Reaction Temp, (^\circ)C</th>
<th>(\eta_{inh}^b) dL/g</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>1,4-PEP</td>
<td>4,4'-DHDPS</td>
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<tr>
<td>19</td>
<td>1,4-PEP</td>
<td>4,4'-DHDPM</td>
<td>48</td>
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<td>20</td>
<td>1,4-PEP</td>
<td>4,4'-DHDPE</td>
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<td>50 - 100</td>
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</table>

\(^a\) m-cresol as solvent

\(^b\) DMSO solvent, 0.5% g/dL concentration (w/v)
Table 6  
Melting Points and Elemental Analysis for Model Pyrimidines

<table>
<thead>
<tr>
<th>Propynone</th>
<th>Amidine</th>
<th>Melting Points (°C)</th>
<th>Yield (%)</th>
<th>% Carbon</th>
<th>% Hydrogen</th>
<th>% Nitrogen</th>
</tr>
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<tbody>
<tr>
<td>1,3-PPPO</td>
<td>BA</td>
<td>260.5-262</td>
<td>93</td>
<td>84.54</td>
<td>4.92</td>
<td>10.31</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(84.73)(^b)</td>
<td>(4.86)</td>
</tr>
<tr>
<td>1,4-PPPO</td>
<td>BA</td>
<td>345-346.5</td>
<td>98</td>
<td>84.68</td>
<td>4.86</td>
<td>10.38</td>
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<tr>
<td>BPA</td>
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<td>BPA</td>
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<td>90</td>
<td>84.61</td>
<td>4.90</td>
<td>10.33</td>
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</tbody>
</table>

a. PPPO = 1,1'-(phenylene)bis(3-phenyl-2-propyn-1-one), BPA = benzoyl phenyl acetylene, BA = benzamidine, DAB = diamidinobenzene

b. Theoretical values in parenthesis are the same for all four model pyrimidines.