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Curable, Thermally Stable Poly(enaminonitriles)[1]

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ABSTRACT: Three new bis(1-chloro-2,2-dicyanovinyl) aromatic monomers have been synthesized. Vinylic nucleophilic substitution polymerization with 4,4′-diaminodiphenyl ether led to moderately high molecular weight poly(enaminonitriles) ($0.39 < [\eta] < 0.84$ dL/g, measured in dimethylformamide at 25 °C). The polymers exhibited excellent thermal stability, retaining 100% of their mass up to 400 °C under nitrogen. Evidence is presented for an intramolecular cyclization reaction occurring above 300 °C to form poly(4-aminoquinoline) repeat units. The cyclization reaction occurs without the emission of volatile byproducts. The dielectric constant of a representative polymer of this class was found to be approximately 8 before heat treatment and 5 afterward.

Introduction

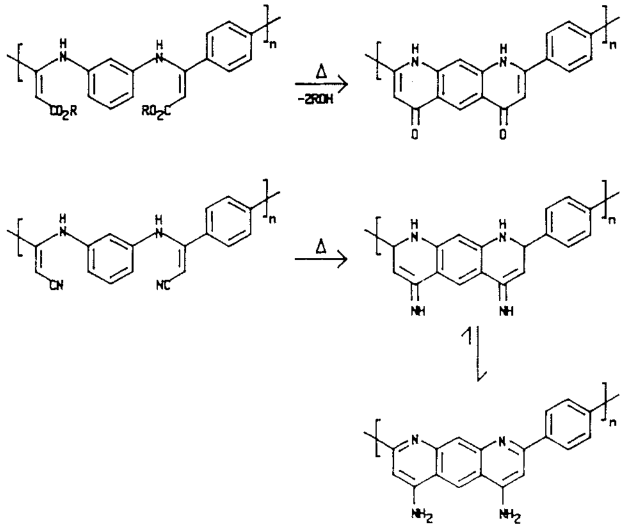
The production of thermally stable organic polymers has been the subject of many research efforts for the past 30 years. Interest has heightened recently because of growing applications of thermally stable polymers in the fields of aerospace and electronics. Of the wide variety of thermally stable polymers which have been synthesized,[2] most are aromatic, rigid rod polymers and therefore present great difficulties in processing because of their low solubilities and high glass transition or melting temperatures. Therefore, compromises have been necessary between thermal stability and processability. A common approach has been to synthesize a more flexible polymeric precursor which upon subsequent treatment ("curing") cyclizes intramolecularly to produce the final thermally stable, rigid rod polymer. Polyimides[3] are a familiar and successfully applied example of this approach.

The principal drawback to the curing reaction of polyimides and other similar polymers is the emission of a small molecule byproduct (usually water) in the process. The difficulties in removing the byproduct from the bulk polymer without causing voids has restricted the use of many polyimides to thin-film applications. Further difficulties in processing are encountered with polyimides because of the hydrolytic instability of the intermediate polyamic acid. In this paper we report on a class of new thermally and hydrolytically stable polymers which cure *without the emission of volatile byproducts.*

Earlier experiments in our laboratory[4] and elsewhere[5] showed that high molecular weight poly(enamino esters) could be produced by the condensation of bis(β-keto esters) with diamines. When aromatic diamines were employed, the polymers could be thermally cyclized with the concomitant expulsion of alcohol (the Conrad–Limpach reaction[6]) to produce thermally stable poly(4-quinolones). We decided to explore the possibility of performing a closely related cyclization reaction on poly(enaminonitriles) (Scheme I) which would occur by rearrangement to form poly(4-aminoquinolines).[7] Although similar acid-catalyzed cyclization reactions, involving nitriles are quite common, only one purely thermal, uncatalyzed example has been previously reported.[8] However, synthetic details are lacking in this paper.

Polymers containing the enamine linkage have been synthesized by any of three routes: (1) polycondensation of difunctional ketones bearing β-electron-withdrawing groups,[4,5,9] (2) poly Michael addition to activated diacetylenes,[10] and (3) displacement of leaving groups from activated diolefins (vinylic nucleophilic substitution).[11] We chose to employ the latter method using chloro*di*cyano ethylenes because such reactions are reported to proceed at rapid rates to high conversions with few side reactions.[12,13]

Scheme I



Wallenfels[14] has pointed out a useful analogy between the dicyanomethylidine group ($=C(CN)_2$) and the carbonyl oxygen atom. The two units have similar inductive and resonance effects, and many well-known reactions with carbonyl groups have been shown to have close parallels with the dicyanomethylidine group. If this analogy holds, then the monomers in this study can be likened to difunctional carboxylic acid chlorides.

Model Studies

To determine the conditions necessary to produce poly(enaminonitriles) and to provide well-characterized model compounds for comparison with the polymers, we attempted the synthesis of a number of model compounds.

Our initial studies dealt with α-hydroxy-β,β-dicyanoethylenes such as **1**. (NMR experiments indicated that **1** existed completely as its enol tautomer.) Enols like **1** are strongly acidic ($pK_a \simeq 1$) and form salts with amines.[15] The salt, **2**, of **1** with aniline was synthesized with the hope of forming the enamine **3** by dehydration, in analogy with the dehydration of amide salts used in the production of polyamides. Unfortunately, attempts to remove water by heating **2** in vacuo or by azeotropic distillation in benzene failed to produce the desired enamine. Instead, benzanilide and a partially hydrolyzed product (**4**) were obtained (Scheme II).

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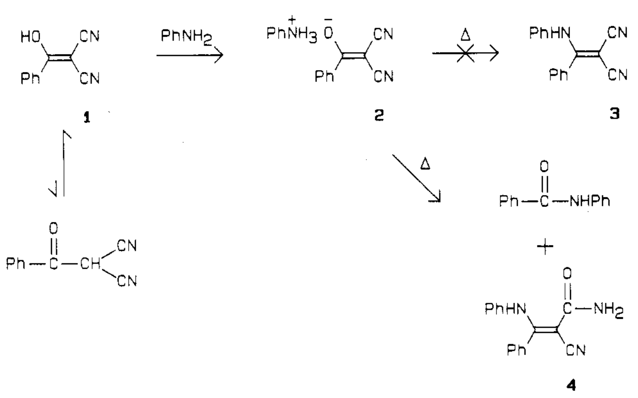
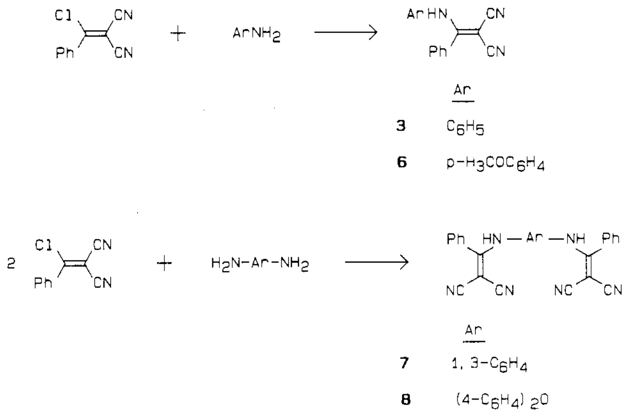
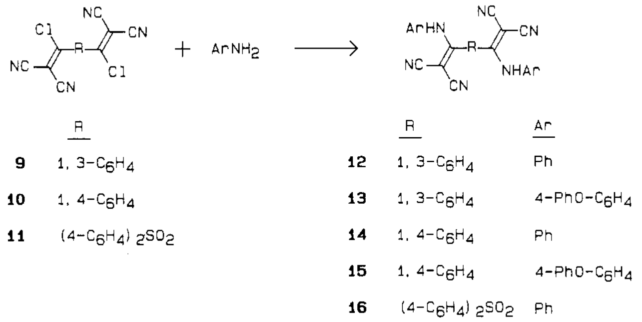
Scheme II



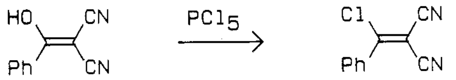
Scheme III



Scheme IV



Therefore, we synthesized the dicyanovinyl chloride **5** by reacting **1** with phosphorus pentachloride[16] in dry dichloromethane.



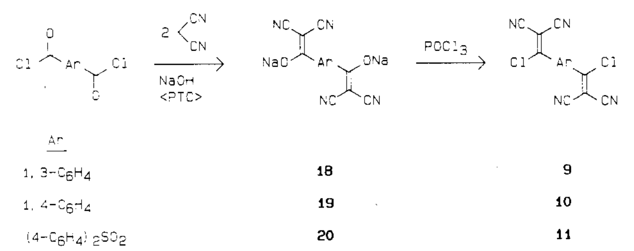
1 **5**

Reaction of **5** with aromatic amines or diamines was rapid and led to good yields of model enaminonitriles **3** and **6–8** (Scheme III). Similarly, the monomers **9–11** (see below) were reacted with aromatic amines to produce model enaminonitriles **12–16** (Scheme IV). The model enamines were stable to air and moisture and could be stored for months without decomposition.

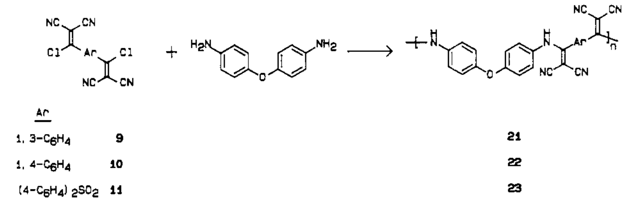
In addition, we measured the rate of reaction between **5** and aniline in acetonitrile at 30 °C by ultraviolet spectroscopy. The reaction was found to obey the following rate expression:

$$\frac{-\mathrm{d}[\mathbf{5}]}{\mathrm{d}t} = 2.40 \times 10^{-4}[\mathbf{5}][\text{aniline}] + 0.43 \times 10^{-4}[\mathbf{5}][\text{aniline}]^2\ \mathrm{M{\cdot}s^{-1}} \quad (1)$$

Scheme V

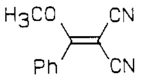


Scheme VI



This result indicates that there is a small, but significant, contribution from a mechanism which involves a second molecule of aniline. Comparison of our data with measurements on the same reaction using substituted compounds similar to **5**, carried out by Rappoport and coworkers,[13a,d] shows that the presence of para electron-withdrawing groups increases the reactivity of the dicyanovinyl chloride moiety. This effect may be caused by an increase in the partial positive charge on the carbon atom bearing the chlorine atom, rendering this position more electrophilic.

Our studies also demonstrated that chlorodicyanoethylene **5** is much more reactive with aromatic amines compared to methoxydicyanoethylene **17**.[17]



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Monomer Synthesis

Encouraged by the success of model reactions using **5**, we synthesized the corresponding difunctional compounds **9–11**. Compound **11** is a particularly attractive monomer because it contains an electron-withdrawing, rate-enhancing sulfone group para to the vinyl moiety. Each monomer was synthesized in two steps (Scheme V) as follows. The corresponding acid chloride was reacted with malononitrile under basic, phase-transfer conditions to provide the disodium salts of the bis enols. Reaction of the salts with phosphorus oxychloride produced the desired monomers. The highest yields were obtained when the salts were dried in a vacuum oven at 120 °C before use.

The disodium enolate salts were preferred to the enols themselves for several reasons. The salts were considerably easier to purify by recrystallization, and subsequent chlorination proceeded with higher yields and without byproduct formation.

Polymer Synthesis and Properties

Bis(chlorodicyanovinyl) monomers **9–11** were polymerized with 4,4′-diaminodiphenyl ether (oxydianiline, ODA) to produce poly(enaminonitriles) **21–23** (Scheme VI). In general, equimolar quantities of the desired monomer and ODA were mixed at room temperature in a polar, aprotic solvent such as *N*-methylpyrrolidone (NMP) or *N*,*N*-dimethylformamide (DMF) in the presence of 1 equiv of 4-(dimethylamino)pyridine as acid acceptor. The mixture immediately turned dark brown and then gradually

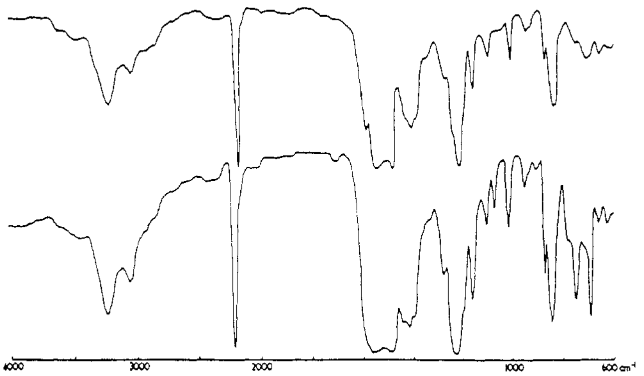


Figure 1. IR spectra of poly(enaminonitrile) 22 (thin film), upper, and model compound 15 (KBr pellet), lower.

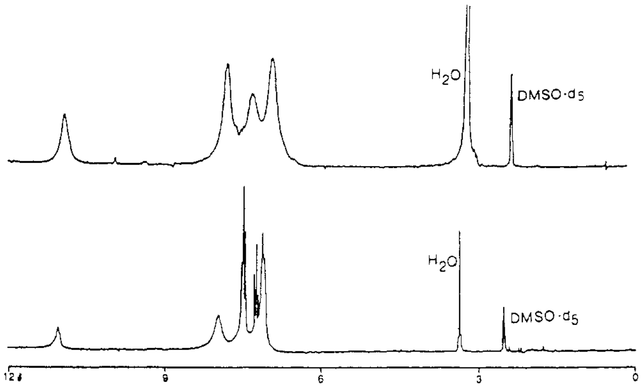


Figure 2. ^{1}H NMR spectra of poly(enaminonitrile) 22, upper, and model compound 15, lower, measured in DMSO-d_6 at 20 °C.

lightened. The solution was warmed (75–95 °C) overnight to ensure complete reaction, and the polymer was then precipitated in water.

The poly(enaminonitriles) were purified by reprecipitation and then were dried in a vacuum oven. The polymers were isolated as yellow-green powders. Elemental analyses of the polymers gave satisfactory results except for carbon, which was underestimated. Discrepancies here were probably caused by difficulties in fully combusting the highly thermally stable polymers.

Spectroscopic data for 21–23 closely matched data from model compounds which contained the same structural units. Figures 1–3 show the IR, ^{1}H NMR, and ^{13}C NMR spectra, respectively, for model compound 15 and the corresponding poly(enaminonitrile) 22.

Polymers 21–23 could be cast from DMF into tough (fingernail-creasable), transparent yellow films. An attempt to melt-press 22 at 225 °C into a film was unsuccessful.

The polymers appeared to possess moderately high molecular weights, judging from intrinsic viscosity measurements and gel permeation chromatography (GPC) (Table I). (The data are given for the individual polymerization batches which had the highest molecular weights.)

Despite its high intrinsic viscosity, polymer 22 seemed to contain a large amount of low molecular weight material by GPC, and, therefore, had a large polydispersity value. This effect may be an artifact of the GPC technique. Polymer 22 is the least soluble of the three polymers and may partially precipitate and redissolve during the GPC separation, leading to peak broadening.

All three polymers were soluble in DMF, DMSO, and NMP. Polymer 21 was also soluble in tetrahydrofuran (THF) and in 1,2-dimethoxyethane (DME) at room temperature. However, when the DME solution of 21 was heated to reflux, the polymer precipitated but then redissolved when the solution was cooled. Similarly, 23 was soluble in THF at room temperature, precipitated when the solution was heated to reflux, and then redissolved when the solution was cooled. This behavior may indicate the existence of lower critical solution temperatures for 21 in DME and 23 in THF. In contrast, polymer 22 displayed anomalous solubility behavior in THF and DME. Samples of 22 isolated by reprecipitation into methanol after synthesis were totally insoluble in THF and DME, both at room temperature or at the boiling point of these solvents. However, films of 22 cast from DMF were readily soluble in both THF and DME. Once dissolved, polymer 22 remained soluble in THF when the solution was heated to reflux but precipitated from boiling DME solution and did *not* redissolve on cooling.

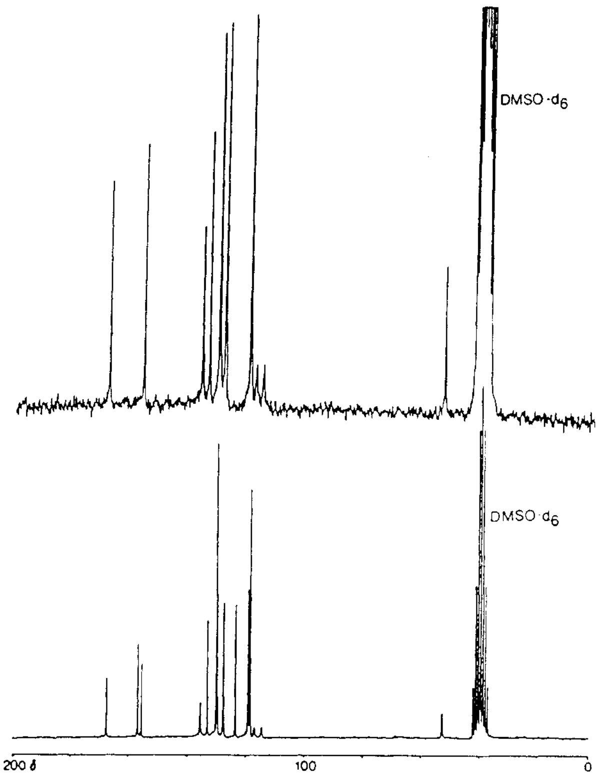


Figure 3. ^{13}C NMR spectra of poly(enaminonitrile) 22, upper, and model compound 15, lower, measured in DMSO-d_6 at 20 °C.

Table I
Intrinsic Viscosity (in DMF at 25.0 °C) and Apparent Molecular Weight Measurements by Gel Permeation Chromatography (in THF at 22 °C) for Poly(enaminonitriles) 21, 22, and 23[a]

polymer	[η], dL/g	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
21	0.39	11600	34400	2.96
22	0.84	6160	127000	20.5
23	0.68	3370	12600	3.76

[a] Polystyrene standards were used for GPC.

In addition, solution-cast films of 22 became cloudy and brittle when boiled for a few minutes in methanol and lost their solubility in THF and DME. These brittle films were still soluble in DMF. Boiling water or ethanol did not cause this change.

This unusual behavior may be caused by the development of partial crystallinity, under certain circumstances, in 22. Apparently, the crystalline samples have poorer solubility than the (presumably) amorphous materials, a behavior which has been commonly observed for other polymers. Films cast from DMF may be amorphous for kinetic reasons or because residual DMF acts as a plas-

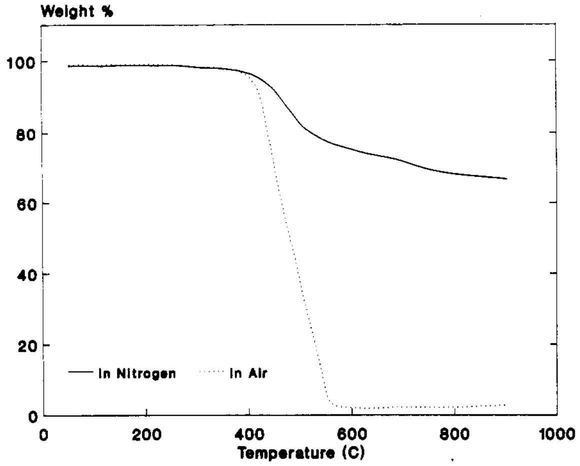


Figure 4. Thermogram for poly(enaminonitrile) **23** in air and in nitrogen. A heating rate of 10 °C/min was used.

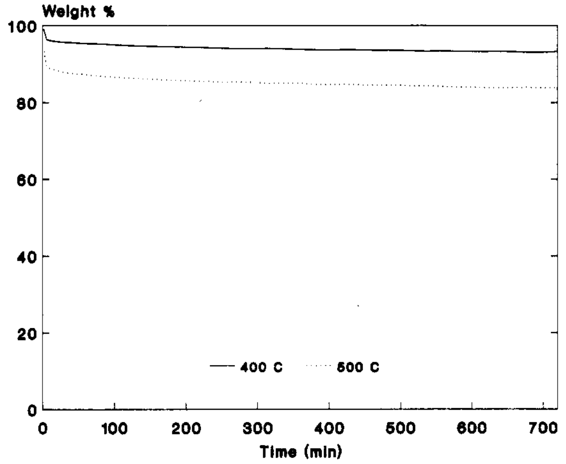


Figure 5. Isothermal aging TGA of poly(enaminonitrile) **21** at 400 and at 500 °C in nitrogen.

ticizer. This polymer may pass through a lower critical solution temperature in DME and precipitate as an insoluble, crystalline material. Methanol might extract traces of DMF from the film, promoting crystallization. X-ray analysis is required to clarify the cause of this behavior.

The three polymers exhibited excellent thermal stability, losing no mass below 400 °C in nitrogen and in air. The polymers decomposed completely in air above 500 °C but retained 70% of their original mass at 900 °C in nitrogen. A typical thermogravimetric trace is shown in Figure 4.

Isothermal aging studies, done at 400 and 500 °C under nitrogen, show a very slow mass loss over 12 h after the volatilization of oligomers from the sample (Figure 5). However, isothermal aging of **22** in air at 300 °C for 60 h caused the loss of 55% of the original mass of the sample. In this respect, **22** is inferior to Kapton polyimide film, which lost only 2% of its mass under the same conditions in a control experiment (Figure 6).

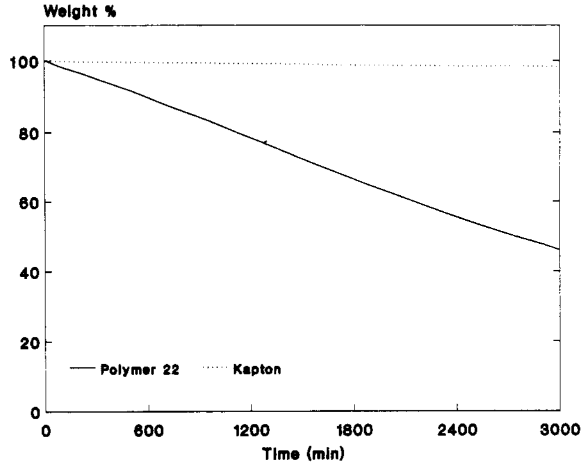


Figure 6. Isothermal aging TGA of poly(enaminonitrile) **22** and of Kapton polyimide at 300 °C in air.

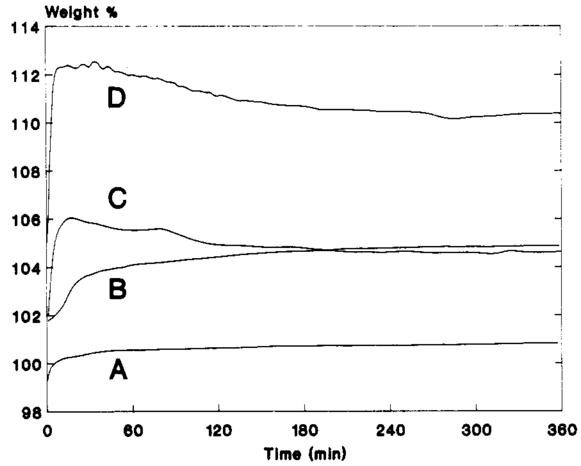


Figure 7. Water absorption at 40 °C in H_2O-saturated air for (A) **22** powder, (B) **22** film, (C) Kapton film, and (D) thermally cured **22** film.

Table II
Dielectric Measurements for Films of Poly(enaminonitrile) 22 Cast from DMF

test freq, Hz	capacitance, pF	ϵ	dissipation factor
	Before Heat Curing[a]		
10^1	474.5	8.452	0.0437
10^3	456.9	8.146	0.0106
10^4	448.5	7.996	0.0089
10^5	446.9	7.968	0.0145
	After Heat Curing[b]		
10^3	696.9	5.178	0.0042
10^4	689.9	5.126	0.0095
10^5	676.6	5.027	0.0368
10^6	658.7	4.894	0.2509

[a] Sample thickness 20.0 μm. Electrode area 1.27 cm^2; 24.0 °C.
[b] Sample thickness 7.5 μm. Electrode area 1.14 cm^2; 24.9 °C.

Samples of **22** were also compared to Kapton with respect to water absorption (Figure 7). In this experiment, samples of polymer were dried to constant weight at 110 °C under nitrogen in the TGA apparatus and then cooled to 40 °C and exposed to air saturated with water vapor. Kapton film absorbed approximately 4% of its weight in water, as did a solution-cast film of **22**. However, a powder sample of **22** (isolated by reprecipitation into methanol after synthesis) absorbed only 0.6% additional mass. The presence of crystallinity (see above) in the powder sample may be the cause of the lower water absorption. A sample of poly(enaminonitrile) **22** film which had been cured for 2 h at 300 °C (see below) was also tested and found to absorb 10.4% of its weight in water.

The dielectric constant of a film of poly(enaminonitrile) **22** was found to be near 8, an unusually large value (Table II). (For comparison, the dielectric constant of Kapton is approximately 3.6.[18]) This result is indicative of the large degree of charge separation within the enaminonitrile groups in the polymer, also observed in ^{13}C NMR spectra of polymers and model compounds (see above). The very large dielectric constant implies that a large degree of interaction of the molecular dipoles is present in the

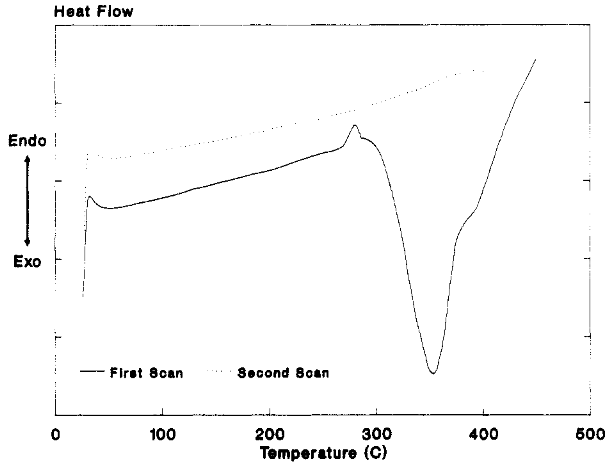


Figure 8. DSC traces for poly(enaminonitrile) **23** in nitrogen. A heating rate of 20 °C/min was used.

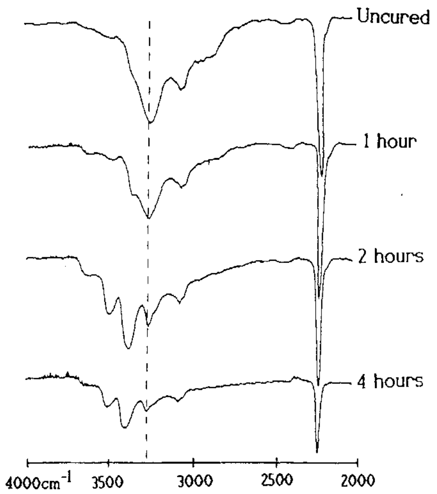


Figure 9. IR spectra of poly(enaminonitrile) **22** after various periods of curing at 400 °C under nitrogen.

polymer film. After heat treatment at 400 °C, the dielectric constant fell to approximately 5, presumably because some of the molecular dipoles are consumed in the cyclization process (see below).

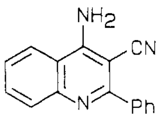
Glass transition temperatures were not detected by differential scanning calorimetry (DSC) for polymers **21**, **22**, and **23**. (Note: Film and powder samples of **22** gave identical DSC results.) However, very broad glass transitions were observed for these polymers between 200 and 250 °C by optical microscopy. Scratches were made in pieces of polymer film, and the loss of strain birefringence (caused by the scratches) was detected in this temperature range by using a hot-stage microscope with crossed polarizers. A small disturbance was detected by DSC for polymer **22** near 195 °C, which may be related to the onset of the glass transition.

DSC analysis did detect a broad, prominent exothermic transition for all three poly(enaminonitriles), starting near 300 °C and reaching maximum intensity near 350 °C. This peak was completely absent when the samples were cooled and rescanned. A typical calorimogram is shown in Figure 8.

Samples of polymers heated above 300 °C ("cured") changed color from yellow to orange, became slightly brittle, and were completely insoluble in solvents for the untreated polymer. (However, the cured polymer films retained some flexibility.) In addition, all three polymers displayed a gradual change in their IR spectra as they were heated (Figure 9). The enamine N–H stretching band at 3260 cm^{-1} disappeared and was replaced by *two* new bands at 3365 and 3480 cm^{-1}. At the same time, the nitrile band near 2210 cm^{-1} decreased to approximately half its original intensity. The IR spectrum of 4-amino-2-phenylquinoline-3-carbonitrile (**24**) (synthesized for comparison) showed the same bands found for the cured polymer.

Scheme VII

Ar	
1,3-C_6H_4	**21**
1,4-C_6H_4	**22**
(4-C_6H_4)$_2SO_2$	**23**



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The above data are consistent with a rearrangement, at least in part, of the enaminonitrile repeat unit into a 4-aminoquinoline (Scheme VII).

The insolubility of the cured polymers after heating in the solid state may be caused by the considerable stiffness of the rearranged chain or because of cross-linking. Two cross-linking mechanisms are conceivable. The same curing reaction which is postulated above might occur intermolecularly, or an amino group formed in the rearrangement may subsequently attack a cyano group on another polymer chain.

However, these cross-linking reactions cannot be the major curing processes, because they would lead to imino derivatives, which would only exhibit *one* N–H band in the IR, whereas *two* bands were actually observed, consistent with a primary amine function generated by the proposed cyclization reaction.

To demonstrate that curing of the poly(enaminonitriles) can occur without cross-linking and the consequent loss of solubility, a sample of polymer **23** was dissolved in molten diphenylsulfone (1.7% w/w) and heated to 340 °C for 30 min in a sealed tube under vacuum. Diphenyl sulfone was removed by washing the reaction mixture thoroughly with acetone, in which the polymer was insoluble. The IR spectrum of the polymer cured in this way exhibited the features discussed above, consistent with the proposed rearranged structure. (Bands were present at 3360 and 3450 cm^{-1} (primary amine), and the enamine and cyano bands had diminished in intensity compared with the spectrum of the starting material.) Most importantly, this material was *completely soluble* in DMSO, and its ^{1}H NMR spectrum showed no trace of the enamine NH absorption near 11.0 δ. Instead, a complicated multiplet between 7.5 and 8.4 δ was present. Clearly, this polymer can be cured without cross-linking by heating in dilute solution.

A similar experiment using **22** was unsuccessful because this polymer was insoluble in molten diphenyl sulfone.

The formation of the amino group may be the cause of the low thermal stability at 300 °C in air compared to polyimide, which lacks the easily oxidized NH group. Also, the hydrogen-bonding ability of the amino group may cause the absorption of a large amount of water by the cured polymer (see above).

On the other hand, the hydrolytic stability of the poly(enaminonitriles) prepared in this work is far superior to that of the polyamic acid precursors to polyimides. The stability of the enaminonitrile linkage was clearly demonstrated by an experiment with model compound **6**, which did not show any decomposition (by HPLC) after the compound was boiled in 50% aqueous acetonitrile for 6 days. As a further demonstration, poly(enaminonitrile) films can be boiled in water or soaked in 15% aqueous HCl without a significant loss of strength.

Experimental Section

Infrared (IR) spectra were recorded by using a Perkin-Elmer Model 298 spectrophotometer. Ultraviolet (UV) spectra were recorded with a Perkin-Elmer Model 552 spectrophotometer. Extinction coefficients are reported in parentheses in units of M^{-1} cm^{-1}. Nuclear magnetic resonance (NMR) spectra were obtained by using a Varian XL-200 spectrometer operating at 200 MHz for ^1H and 50.3 MHz for ^{13}C spectra. Some ^{13}C spectra were obtained on an IBM WP/SY 100 instrument operating at 25.1 MHz. Selected ^{13}C spectra were obtained by using the "attached proton test" (APT).[19] With this technique, the signals for carbon atoms bearing an even number of protons appear normal (denoted by ↑ after the observed shift), but inverted (denoted by ↓ after the observed shift). Mass spectra (MS) were obtained on a Hewlett-Packard Model 5987 integrated gas chromatograph–mass spectrometer. Ionization was done by 70-eV electron impact (EI) or methane chemical ionization (CI). Gel permeation chromatography (GPC) was done by using a series of five Waters Ultra-styragel columns (30 cm × 7.8 mm, cross-linked polystyrene), with average pore sizes of 10^6, 10^5, 10^4, 10^3, and 500 Å. Tetrahydrofuran (THF) was used as an eluent at 1.0 mL/min. Detection was by ultraviolet absorbance at 280 nm. Intrinsic viscosity measurements were performed by using Cannon-Ubbelohde viscometers at 25.0 °C. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on Perkin-Elmer System 7 instruments. Heating rates were 20 °C/min for DSC and 10 °C/min for TGA. Polymer dielectric constants were measured with a GenRad 1689 Precision RLC Digibridge. Sample thickness was measured with a Danatron digital electrogauge. Aluminum electrodes (2000 Å thick) were applied on both sides of the polymer film by vacuum deposition. The dielectric constant, ϵ, was calculated as follows:

$$\epsilon = \frac{(\text{capacitance in pF})(\text{thickness in } \mu\text{m})}{(\text{area in cm}^2)(885.4)} \qquad (2)$$

Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

The solvents toluene, dichloromethane, tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), and *N*-methylpyrrolidone (NMP) were dried and distilled according to literature procedures immediately prior to use. 4,4′-Diaminodiphenyl ether was recrystallized from THF and then sublimed at 175 °C at reduced pressure. 4-(Dimethylamino)pyridine was recrystallized from ethyl acetate.

(Hydroxyphenylmethylene)propanedinitrile (1). To a stirred mixture of toluene (200 mL), benzoyl chloride (28.1 g, 0.20 mol), and malononitrile (13.2 g, 0.20 mol) at 0 °C was added triethylamine dropwise. A precipitate and a brown oil separated from the solution. The mixture was stirred at 0 °C for 3 h then gradually warmed to room temperature. The precipitate was filtered, and the oil was separated. The filtrate was evaporated at reduced pressure to produce a small amount of brown oil. The combined oils were treated with 125 mL of ether and 100 mL of 5% HCl. The ethereal layer was separated and was washed repeatedly with saturated $NaHCO_3$. The combined bicarbonate extracts were carefully acidified to pH 4 (pH paper) with concentrated HCl, filtered to remove a byproduct of benzoic acid, and then further acidified with HCl to pH 2. The solid which formed was taken up in dichloromethane, the solution was dried ($MgSO_4$), and the solvent was removed at reduced pressure to give white, partially hydrated crystals, which were recrystallized from acetonitrile/benzene: mp 127–129 °C [lit.[15] 129–130 °C]; yield 39%. A small amount of the product was sublimed at 90 °C/0.5 mm to give a white solid, mp 96.5–98 °C, identified by ^1H NMR as the anhydrous product: IR (KBr) 3430 (OH), 2220 ($C\equiv N$) cm^{-1}; MS (EI), *m/e* 170 (M^+); ^1H NMR ($(CD_3)_2CO$) δ 6.48 (br s, 3 H, hydrated OH), 7.55–7.90 (m, 5 H, arom CH); ^{13}C NMR ($(CD_3)_2CO$) δ 63.2 (*C*($(CN)_2$)), [113.3, 115.0] ($C\equiv N$), [128.9, 129.5, 132.0, 113.7] (arom C), 184.3 (HOC=).

(Chlorophenylmethylene)propanedinitrile (5). To a stirred suspension of 4.00 g (21.3 mmol) of (hydroxyphenylmethylene)propanedinitrile (**1**) and 20 mL of dry dichloromethane was added dropwise at 23 °C a solution of 9.0 g (43.2 mmol) of phosphorus pentachloride in 200 mL of dichloromethane. The mixture was stirred at reflux for 16 h, and then dichloromethane and phosphorus oxychloride were removed at reduced pressure. The brown solid which remained was dissolved in a small amount of dichloromethane and flash chromatographed on silica gel eluting with dichloromethane. Evaporation of the eluate at reduced pressure afforded 2.95 g (73%) of a yellow solid which was further purified by recrystallization from chloroform/hexanes and sublimation at 60 °C/0.2 mm to produce a white solid: mp 70–72 °C [lit.[16] 72 °C]; IR (KBr) 2235 ($C\equiv N$) cm^{-1}; MS (EI), *m/e* 190 ($M^+ + 2$), 188 (M^+); ^1H NMR ($CDCl_3$) δ 7.4–8.1 (m); ^{13}C NMR ($CDCl_3$) δ 85.8 (=*C*($(CN)_2$)), [111.5, 111.7] ($C\equiv N$), [29.1, 129.2, 132.5, 134.4] (arom C), 167.4 (=CCl); UV (CH_3CN) 303 (15 100), 246 sh (4930), 237 (5300), 200 nm (13 400).

[(Phenylamino)phenylmethylene]propanedinitrile (3). A mixture of (chlorophenylmethylene)propanedinitrile (**5**, 0.951 g, 5.04 mmol), absolute ether (20 mL), and aniline (1.2 g, 12.5 mmol) was stirred for 10 min at 23 °C. The mixture darkened, and a white precipitate formed. The mixture was filtered, and the white precipitate was stirred for 2 h in 100 mL of water, refiltered, and dried to give 0.506 g (41%) of a white solid which was recrystallized from 95% ethanol: mp 183–4 °C [lit.[16] 182–4 °C]; IR (KBr) 3240 (NH), 2200 ($C\equiv N$) cm^{-1}; MS (CI), *m/e* 246 (M^+); ^1H NMR ($CDCl_3$) δ 6.8–8.1 (m, 10 H, arom CH), 8.3 (br s, 1 H, NH); ^{13}C NMR ($(CD_3)_2CO$) δ 56.3 (=*C*($(CN)_2$)), [114.9, 116.7] ($C\equiv N$), [126.0, 127.4, 129.6, 130.5, 132.6, 139.0] (arom C), 169.8 (vinyl C—N); UV (CH_3CN) 316 (13 000), 235 (10 100), 203 nm (20 100).

[((4-Methoxyphenyl)amino)phenylmethylene]propanedinitrile (6). A stirred solution of 0.866 g (4.59 mmol) of (chlorophenylmethylene)propanedinitrile (**5**) in 15 mL of dry dichloromethane was treated dropwise at 23 °C with a solution of *p*-anisidine (1.17 g, 9.52 mmol) in 25 mL of dichloromethane. The reaction mixture was stirred at room temperature for 3 h and then filtered. The filtrate was washed with 5% HCl (2 × 50 mL) and with water (2 × 50 mL), dried ($MgSO_4$), and concentrated at reduced pressure to produce 1.15 g (88%) of a crude solid. The product was recrystallized from absolute ethanol to form white crystals: mp 188–9 °C; IR (KBr) 3275 (NH), [2215, 2100] ($C\equiv N$) cm^{-1}; MS (EI), *m/e* 275 (M^+); ^1H NMR ($CDCl_3$) δ 3.69 (s, 3 H, CH_3), 6.7 (m, 4 H, anisidyl CH), 7.35 (m, 6 H, phenyl CH and NH); ^{13}C NMR ($CDCl_3$) δ 55.5 (OCH_3), 56.1 (=*C*($(CN)_2$)), 114.6 (CH ortho to O), [114.7, 115.2] ($C\equiv N$), [126.1, 129.0, 129.3, 129.9, 131.9] (arom C), 158.4 (arom C—O), 169.7 (vinyl C—N).

4,4′-Bis[(2,2-dicyano-1-phenylvinyl)amino]diphenyl Ether (8). A stirred solution of 0.535 g (2.67 mmol) of 4,4′-diaminodiphenyl ether and 0.649 g (5.31 mmol) of 4-(dimethylamino)pyridine in 45 mL of dry DMF at 0 °C under N_2 was treated dropwise with a solution of 1.00 g (5.32 mmol) of (chlorophenylmethylene)propanedinitrile (**5**) in 25 mL of DMF. The mixture was warmed slowly to room temperature and stirred under N_2 for 5 h. The product was precipitated by pouring the reaction mixture into 100 mL of water. The tan solid which separated was collected by filtration, washed thoroughly with water, and dried in vacuo over P_2O_5, producing 1.36 g (95%) of a crude solid. Recrystallization from methanol afforded 1.05 g (73%) of a light-tan solid, mp 275–7 °C. The melting point was raised to 277–9 °C after further recrystallization from CH_3CN: IR (KBr) 3240 br (NH), 2225 cm^{-1} ($C\equiv N$); MS (EI), *m/e* 504 (M^+); ^1H NMR ($(CD_3)_2SO$) δ 8–7.8 (br m, 18 H, arom CH), 10.9 (br s, 2 H, NH); ^{13}C NMR ($(CD_3)_2SO$) δ 52.1 (=*C*($(CN)_2$)), [114.6 br, 117.2 br] ($C\equiv N$), 118.8 (arom C ortho to O), [127.5, 128.6, 129.3, 131.8, 132.4, 133.3] (arom C), 155.2 (arom C—O), 168.6 (vinyl C—N).

1,3-Bis[(2,2-dicyano-1-phenylvinyl)amino]benzene (7). (Chlorophenylmethylene)propanedinitrile (**5**, 1.00 g, 5.30 mmol) was reacted with 0.29 g (2.7 mmol) of *m*-phenylenediamine in the presence of 0.65 g (5.3 mmol) of 4-(dimethylamino)pyridine in 45 mL of DMF by using the same procedure as for **15** (above). The crude product was recrystallized from nitrobenzene, washed thoroughly with absolute ethanol, and dried in vacuo over P_2O_5

to give 0.512 g (47%) of a tan powder: mp 287–9 °C; IR (KBr) 3250 br (NH), [2215, 2200] cm^{-1} ($C\equiv N$); MS (EI), *m/e* 412 (M$^+$); ^{1}H NMR (($CD_3)_2SO$) δ [6.87 (br m, 2 H), 7.06 (br m, 2 H)] (1,3-disubst arom CH), 7.51 (m, 10 H, phenyl CH), 10.94 (s, 2 H, NH); ^{13}C NMR (($CD_3)_2SO$) δ 54.1 (=*C*(CN)$_2$), [114.5, 116.6] ($C\equiv N$), [120.6, 122.6, 128.6, 128.9, 129.5, 131.5, 131.8, 138.4] (arom C), 168.3 (vinyl C—N).

1,3-Bis(2,2-dicyano-1-hydroxyvinyl)benzene, Disodium Salt (18). A two-phase mixture consisting of 123.2 g (0.607 mol) of isophthaloyl chloride and 80.2 g (1.21 mol) of malononitrile in 450 mL of dichloromethane with 27.6 g (0.121 mol, 0.10 equiv) of benzyltriethylammonium chloride in 100 mL of water was stirred and cooled in an ice bath. Five hundred milliliters of 6 N NaOH solution was added dropwise to the vigorously stirred reaction mixture over 3 h. The mixture was slowly warmed to room temperature, and stirring was continued for 18 h. The heterogeneous mixture was then filtered, and the precipitate was washed with 2-propanol and dried in air. The precipitate was recrystallized from water, producing 62.4 g (33%) of **18** as a tan powder: IR (KBr) 3400 br (possible hydrate), 2200 cm^{-1} ($C\equiv N$).

1,4-Bis(2,2-dicyano-1-hydroxyvinyl)benzene, Disodium Salt (19). Terephthaloyl chloride (150.0 g, 0.739 mol) and malononitrile (97.6 g, 1.48 mol) were condensed in the presence of 16.6 g (0.0728 mol, 0.05 equiv) of benzyltriethylammonium chloride by using the two-phase reaction procedure for **18**, above. The product was recrystallized from methanol/water to produce 98.4 g (43%) of **19** as a yellow powder: IR (KBr) 3450 br (possible hydrate), 2220 cm^{-1} ($C\equiv N$).

4,4′-Bis(2,2-dicyano-1-hydroxyvinyl)diphenyl Sulfone, Disodium Salt (20). Sulfonyldibenzoyl chloride[20] (31.8 g, 92.7 mmol) and malononitrile (12.9 g, 195 mmol) were condensed in the presence of 6.1 g (18.5 mmol, 0.1 equiv) of tetrabutylammonium bromide by using the two-phase reaction procedure for **18**, above. The product was extracted in a Soxhlet apparatus for 24 h with dichloromethane and then dried in a vacuum oven at 100 °C, leaving 40.4 g (98%) of **20** as a tan powder: IR (KBr) 3450 br (possible hydrate), 2204 cm^{-1} ($C\equiv N$).

1,3-Bis(1-chloro-2,2-dicyanovinyl)benzene (9). The bis enolate **18** (10.0 g, 32.7 mmol) was mixed with 50 mL of phosphorus oxychloride. After the initial vigorous reaction had subsided, the stirred mixture was heated at reflux for 30 min and then cooled. Excess $POCl_3$ was distilled at reduced pressure, leaving a dark-brown solid which was thoroughly extracted with dichloromethane. The extract was reduced, and the residue was flashed chromatographed (silica gel, CH_2Cl_2). Concentration of the eluate afforded a tan oil which gradually crystallized on standing. The product was distilled in a Kugelrohr apparatus at reduced pressure (220 °C/0.5 mm) and then recrystallized from chloroform/hexanes, producing 2.78 g (29%) of slightly yellow crystals, mp 125–7 °C. An analytical sample was obtained after two further recrystallizations from chloroform/hexanes: mp 127–9 °C; IR (KBr) 2235 cm^{-1} ($C\equiv N$); MS (EI), *m/e* 300 (M$^+$ + 2), 298 (M$^+$); ^{1}H NMR ($CDCl_3$) δ 7.80 (d t, 1 H), 8.08 (d, *J* = 1.6 Hz, 1 H), 8.14 (m, 2 H); ^{13}C NMR ($CDCl_3$, APT) δ 88.3↑ (=*C*(CN)$_2$), [110.7↑, 110↑] ($C\equiv N$), [129.3↓, 130.4↓, 133.5↓] (arom CH), 133.7 (unprotonated arom C), 164.4 (=C—Cl).

Anal. Calcd for $C_{14}H_4Cl_2N_4$: C, 56.22; H, 1.35; N, 18.73. Found: C, 56.01; H, 1.37; N, 18.67.

1,4-Bis(1-chloro-2,2-dicyanovinyl)benzene (10). Method A. Bis enolate **19** (10.0 g, 32.7 mmol) was reacted with 50 mL of phosphorus oxychloride under the same conditions as for **9**, above. The product was distilled in a Kugelrohr apparatus at 190–220 °C/0.1 mm to give 3.88 g (40%) of a tan product which was recrystallized twice from 1,2-dichloroethane/hexanes to obtain analytically pure material, mp 177–9 °C.

Method B.[21] A solution of 15 mL of phosphorus oxychloride in 20 mL of dichloroethane was placed in a three-necked flask fitted with a nitrogen inlet and outlet, a magnetic stirrer, a dropping funnel, and a condenser. The solid bis enolate **19** (10.0 g, 32.7 mmol) was added all at once, and vigorous stirring was begun. Heating with an oil bath was begun, and 25 mL of $POCl_3$ was added slowly over 1 h. The temperature of the mixture was maintained at 85 °C for 5 h. Solvent and excess $POCl_3$ were removed by distillation at reduced pressure. The solid yellow residue was extracted with dry dichloromethane and passed through a column of silica gel in a medium porosity fritted glass filter. The resulting light-yellow solution was concentrated on a rotary evaporator to give faintly yellow crystals which were purified by passage through a 15-cm column of silica gel with dichloromethane as the eluent. After removal of the solvent, 8.3 g (85%) of off-white crystalline solid was obtained: IR (KBr) 2225 cm^{-1} ($C\equiv N$); MS (EI), *m/e* 300 (M$^+$ + 2), 298 (M$^+$); ^{1}H NMR ($CDCl_3$) δ 8.00 (s); ^{13}C NMR ($CDCl_3$) δ 88.6 (=C(CN)$_2$), [110.7, 110.9] ($C\equiv N$), 129.6 (arom CH), 137.0 (unprotonated arom C), 164.4 (=C—Cl).

Anal. Calcd for $C_{18}H_4Cl_2N_4$: C, 56.22; H, 1.35; N, 18.73. Found: C, 56.00; H, 1.42; N, 18.91.

4,4′-Bis(1-chloro-2,2-dicyanovinyl)diphenyl Sulfone (11). A suspension of bis enolate **20** (10.0 g, 22.4 mmol), 50 mL of phosphorus oxychloride, and 75 mL of 1,2-dichloroethane was refluxed with stirring for 18 h. Solvent and excess $POCl_3$ were distilled at reduced pressure, leaving a brown solid. The solid was thoroughly extracted with boiling dichloromethane. The extract was concentrated, and the residue was flash chromatographed (silica gel, CH_2Cl_2). The eluate was evaporated at reduced pressure to leave 6.81 g (69%) of a yellow oil which quickly crystallized. Recrystallization from 1,2-dichloroethane produced 5.4 g (55%) of a yellow solid, mp 196–8 °C. An analytical sample was obtained after repeated recrystallization from 1,2-dichloroethane: IR (KBr) 2195 cm^{-1} ($C\equiv N$); MS (CI), *m/e* 441 (M$^+$ + 2), 439 (M$^+$); ^{1}H NMR ($CDCl_3$) δ [8.12 (d, 4 H, *J* = 8.5 Hz), 7.97 (d, *J* = 8.5 Hz, 4 H)] arom CH; ^{13}C NMR ($CDCl_3$) δ 88.8 (=*C*(CN)$_2$), [110.6, 110.8] ($C\equiv N$), [128.8, 130.1] (arom CH), 137.2 (arom. *C*—C—Cl), 145.0 (arom C—SO_2), 164.7 (=C—Cl).

Anal. Calcd for $C_{20}H_8Cl_2N_4O_2S$: C, 54.69; H, 1.84; Cl, 16.14; N, 12.75; S, 7.30. Found: C, 54.38; H, 2.13; Cl, 16.17; N, 12.61; S, 7.35.

1,3-Bis[2,2-dicyano-1-(phenylamino)vinyl]benzene (12). To a stirred solution of 0.95 g (3.2 mmol) of 1,3-bis(1-chloro-2,2-dicyanovinyl)benzene (**9**) in 25 mL of dry THF at 23 °C was added dropwise a solution of 1.33 g (14.3 mmol) of aniline in 25 mL of THF. The stirred mixture was heated at reflux for 18 h and then cooled and filtered. The filtrate was washed with a mixture of 25 mL of 10% HCl plus 25 mL of saturated NaCl and then twice with saturated NaCl. The organic layer was dried (Na_2SO_4), and the solvent was removed at reduced pressure to leave 1.31 g (100%) of a crude tan solid. Recrystallization from THF gave 0.85 g (65%) of **12** as a slightly yellow solid, mp 330.2–332.9 °C (dec, by DSC). An analytical sample was obtained after two more recrystallizations from THF: IR (KBr) 3240 br (NH), 2200 cm^{-1} ($C\equiv N$); MS (EI), *m/e* 412 (M$^+$); ^{1}H NMR (($CD_3)_2SO$) δ 7.0–8.0 (br m, 14 H, arom CH), 11.06 (br s, 2 H, NH); ^{13}C NMR (($CD_3)_2SO$, APT) δ 53.9↑ (=*C*(CN)$_2$), [114.5↑, 116.6↑] ($C\equiv N$), [125.2↓, 126.5↓, 128.8↓, 129.2↓, 131.1↓, 132.3↓] (arom CH), [132.4↑, 137.6↑] (unprotonated arom C), 167.2 (vinyl C—N).

Anal. Calcd for $C_{26}H_{16}N_6$: C, 75.71; H, 3.91. Found: C, 75.49; H, 3.95.

1,4-Bis[2,2-dicyano-1-(phenylamino)vinyl]benzene (14). 1,4-Bis(1-chloro-2,2-dicyanovinyl)benzene (**10**, 0.285 g, 0.953 mmol) in 25 mL of dry dichloromethane was treated dropwise with aniline (1.5 g, 16 mmol) with stirring at 23 °C. The mixture was stirred for 16 h at 23 °C and then filtered. The yellow solid thus obtained was dissolved in 15 mL of dimethyl sulfoxide, and the resulting solution was poured into 25 mL of water to precipitate the product. A yellow solid was filtered, washed with water, dried, and then recrystallized from THF to afford 0.293 g (75%) of **14** as a yellow powder: mp 353.2–356.2 °C (dec, by DSC); IR (KBr) 3450 br (NH), 2110 ($C\equiv N$) cm^{-1}; MS (EI), *m/e* 412 (M$^+$); ^{1}H NMR (($CD_3)_2SO$) δ 6.68 (br m, 10 H, phenyl CH), 7.5 (br s, 4 H, 1,4-disubst arom CH), 11.01 (br s, 2 H, NH); ^{13}C NMR (($CD_3)_2SO$) δ 53.2 (=*C*(CN)$_2$), [114.3 br, 116.6 br] ($C\equiv N$), [125.1, 126.8, 128.7, 129.8, 135.1, 137.5] (arom C), 167.1 (vinyl C—N).

4,4′-Bis[2,2-dicyano-1-(phenylamino)vinyl]diphenyl Sulfone (16). A solution of 1.00 g (2.28 mmol) of 4,4′-bis(1-chloro-2,2-dicyanovinyl)diphenyl sulfone (**11**) in 12 mL of dry DMF was treated dropwise with a solution of 2.0 g (21.9 mmol) of aniline in 12 mL of DMF over 20 min with stirring at 23 °C. The mixture was heated at 75 ± 5 °C for 18 h, cooled, and poured into 150 mL of vigorously stirred water. The precipitated product was collected by filtration, washed with water, and dried in air. Recrystallization from THF/hexanes afforded 1.03 g (82%) of **16** as a light-tan powder. An analytical sample was obtained by repeated recrystallizations from THF/hexanes: mp 315.6–319.4 °C (dec, by DSC); IR (KBr) 3240 br (NH), 2208 cm^{-1} (C≡N); MS (EI), *m/e* 552 (M^{+}); ^{1}H NMR ($(CD_3)_2SO$): δ 7.27 (br s, 10 H, aniline-derived CH), 8.03 (br AB quartet, 8 H, 1,4-disubst arom CH), 11.00 (br s, 2 H, NH); ^{13}C NMR ($(CD_3)_2SO$, APT): δ 53.1↑ (=*C*$(CN)_2$), [125.3↓, 127.1↓, 127.8↓, 128.7↓, 131.0↓] (arom CH), [137.2↑, 137.7↑, 142.8↑] (unprotonated arom C), 166.3↑ (=C—N) (the C≡N signals were too small to detect in this spectrum).

Anal. Calcd for $C_{32}H_{20}N_6O_2S$: C, 69.55; H, 3.65; N, 15.21; S, 5.80. Found: C, 69.18; H, 3.69; N, 14.74; S, 6.10.

1,3-Bis[2,2-dicyano-1-((4-phenoxyphenyl)amino)vinyl]benzene (13). 1,3-Bis(1-chloro-2,2-dicyanovinyl)benzene (**9**, 0.82 g, 2.7 mmol) was treated with 1.02 g (5.4 mmol) of 4-phenoxyaniline and 0.67 g (5.4 mmol) of 4-(dimethylamino)pyridine in 50 mL of dry DMF under the same conditions as for **16**, above. The product was purified by dry column chromatography on silica gel using ethyl acetate as eluent. A yellow band eluting at $R_f \cong 0.7$ was isolated, affording 0.81 g (50%) of a yellow powder. The solid was recrystallized from ethyl acetate/hexanes to afford 0.71 g (44%) of **13**: mp 245.0–248.4 °C (dec, by DSC) (a presumed solid phase transition was detected near 231 °C by DSC); IR (KBr) 3250 br (NH), 2215 (C≡N) cm^{-1}; MS (EI) *m/e* 596 (M^{+}); ^{1}H NMR ($(CD_3)_2SO$) δ 7.0–8.1 (br m, 22 H, arom CH), 11.05 (br s, 2 H, NH); ^{13}C NMR ($(CD_3)_2SO$, APT): δ 53.0↑ (=*C*$(CN)_2$), [118.3↓, 118.9↓] (arom CH ortho to oxygen), [23.4↓, 127.3↓, 129.0↓, 129.9↓, 130.4↓, 132.2↓] (arom CH), [132.6↑, 132.9↑] (unprotonated arom C), [155.0↑, 156.4↑] (arom CO), 167.3↑ (vinyl C—N).

Anal. Calcd for $C_{38}H_{24}N_6O_2$: C, 76.50; H, 4.05; N, 14.09. Found: C, 76.21; H, 4.17; N, 14.46.

1,4-Bis[2,2-dicyano-1-((4-phenoxyphenyl)amino)vinyl]benzene (15). 1,4-Bis(1-chloro-2,2-dicyanovinyl)benzene (**10**, 1.00 g, 3.34 mmol) was treated with 1.24 g (6.68 mmol) of 4-phenoxyaniline and 0.68 g (6.7 mmol) of triethylamine in 20 mL of dry NMP under the same conditions as for **16**, above. The product was recrystallized from THF, affording 1.08 g (54%) of **15** as a green–yellow powder: mp 332.3–335.0 °C (dec, by DSC); IR (KBr) 3245 br (NH), 2205 (C≡N) cm^{-1}; MS (EI) *m/e* 596 (M^{+}); ^{1}H NMR ($(CD_3)_2SO$) δ 6.8–7.7 (br m, 18 H, (arom CH derived from 4-phenoxyaniline)), 7.8 (br s, 4 H, 1,4-disubst benzene CH), 10.35 (br s, 2 H, NH); ^{13}C NMR ($(CD_3)_2SO$, APT) δ 52.6↑ (=$C(CN)_2$), [114.4↑, 116.8↑] (C≡N), [118.3↓, 119.0↓] (arom CH ortho to O), [123.5↓, 127.6↓, 129.8↓, 130.0↓] (arom CH), [132.0↑, 135.5↑] (unprotonated arom C), [155.3↓, 156.6↓] (arom C—N), 167.5 (vinyl C—N).

Anal. Calcd for $C_{38}H_{24}N_6O_2$: C, 76.50; H, 4.05; N, 14.09. Found: C, 76.40; H, 4.06; N, 13.99.

4-Amino-2-phenylquinoline-3-carbonitrile (24). [(Phenylamino)phenylmethylene]propanedinitrile (**3**, 25.1 mg, 0.245 mmol) dissolved in 10 mL of dichloromethane was treated dropwise with stirring at 23 °C with trifluoromethanesulfonic acid (1.0 mL), and the mixture was stirred at room temperature for 18 h. The mixture was made basic by the dropwise addition of 20% NaOH and extracted with three 25-mL portions of dichloromethane. The combined extracts were dried ($MgSO_4$), and the solvent was evaporated at reduced pressure to leave a crude tan solid. Recrystallization from aqueous ethanol gave **24** as a yellow powder: 19.3 mg (77%); mp 218.5–220 °C [lit.[8] 220 °C]; IR (KBr) [3450, 3360] (NH_2), 2197 (C≡N) cm^{-1}; MS (EI), *m/e* 245 (M^{+}); ^{1}H NMR ($CDCl_3$) δ 5.73 (br s, 2 H, NH), 7.2–8.1 (m, 9 H, arom CH).

Kinetic Measurements. The rate of reaction between freshly sublimed **5** and distilled aniline was measured by monitoring the change in UV absorbance at 360 nm of a solution of these compounds in dry acetonitrile at 30.0 °C. The product of the reaction, **11**, absorbed strongly at 360 nm (ϵ = 6300 M^{-1} cm^{-1}), but the starting materials had negligible absorbance. The solutions of **5** ranged in concentration from 2.51×10^{-3} to 5.02×10^{-3} M, and those of aniline ranged from 0.080 to 0.40 M (pseudo-first-order conditions).

In a typical experiment, 1.0 mL of a solution of **5** was mixed in a small test tube with 1.0 mL of aniline solution and then quickly transferred to a jacketed quartz UV cell, which was maintained at 30.0 ± 0.1 °C by using an external water bath and circulating pump. A solution containing the same concentration of aniline as the reaction mixture was used as a reference. The absorbance of the reaction solution increased smoothly with time, eventually approaching an equilibrium value, A_∞. The absorbance at time t, A_t, was read from the recorder chart, and plots of ln ($A_\infty - A_t$) were found to be linear to at least 95% reaction.

Poly[oxy-1,4-phenyleneimino(dicyanovinylidene)-1,3-phenylene(dicyanovinylidene)imino-1,4-phenylene] (21). To a stirred solution of 0.843 g (4.21 mmol) of 4,4′-diaminodiphenyl ether and 1.100 g (9.00 mmol) of 4-(dimethylamino)pyridine in 10 mL of dry NMP was added a solution of 1.258 g (4.21 mmol) of 1,3-bis(1-chloro-2,2-dicyanovinyl)benzene (**9**) in 10 mL of NMP at 23 °C. The mixture turned brown, and a precipitate appeared after a few minutes. The stirred mixture was heated under nitrogen for 18 h at 70 ± 5 °C, and the mixture turned green. The mixture was cooled and then poured into 150 mL of vigorously stirred water. The polymer precipitated as a fine, green–yellow powder which was isolated by centrifugation, dissolved in DMF, and reprecipitated into 300 mL of agitated methanol. The precipitate was isolated by centrifugation, washed with methanol, and dried in vacuo at 100 °C for 48 h to produce 1.19 g (66%) of **21** as a green powder: IR (thin film) 3245 br (NH), 2218 cm^{-1} (C≡N); ^{1}H NMR ($(CD_3)_2SO$) δ 6.6–8.2 (br m, 12 H, arom CH), 10.94 (br s, 2 H, NH); ^{13}C NMR ($(CD_3)_2SO$, APT) δ 52.9↑ (=*C*$(CN)_2$), 118.7↓ (arom CH ortho to oxygen), [127.4↓, 128.5↓, 132.1↓] (arom CH), [132.7↑, 133.1↑] (unprotonated arom C), 154.9 (C—O), 167.2 (vinyl C—N). The C≡N signals were barely visible above base-line noise as a broad, weak peak near 115 δ.

Anal. Calcd for $C_{26}H_{14}N_6O$: C, 73.23; H, 3.31; N, 19.71. Found: C, 71.32; H, 3.60; N, 19.91.

Poly[oxy-1,4-phenyleneimino(dicyanovinylidene)-1,4-phenylene(dicyanovinylidene)imino-1,4-phenylene] (22). 4,4′-Diaminodiphenyl ether (1.049 g, 5.24 mmol), 4-(dimethylamino)pyridine (1.280 g, 10.48 mmol), and 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene (**10**, 1.566 g, 5.24 mmol) were reacted according to the procedure for **21**, above. The crude polymer was twice reprecipitated from DMF into 500 mL of methanol agitated in a blender. The product was filtered, washed with methanol, and dried in vacuo at 100 °C for 48 h to produce 1.40 g (63%) of **22** as a yellow powder: IR (thin film) 3242 br (NH), 2216 cm^{-1} (C≡N); ^{1}H NMR ($(CD_3)_2SO$) δ 6.9–8.1 (br m, 12 H, arom CH), 10.95 (br s, 2 H, NH); ^{13}C NMR ($(CD_3)_2SO$, APT) δ 52.2↑ (=*C*$(CN)_2$), [114.3↑, 116.9↑] (C≡N), 118.8↓ (arom CH ortho to oxygen), [127.7↓, 129.7↓] (arom CH), [133.0↑, 135.5↑] (unprotonated arom C), 155.3↓ (C—O), 167.4 (vinyl C—N).

Anal. Calcd for $C_{26}H_{14}N_6O$: C, 73.23; H, 3.31; N, 19.71. Found: C, 71.36; H, 3.53; H, 20.02.

Poly[sulfonyl-1,4-phenylene(dicyanovinylidene)imino-1,4-phenyleneoxy-1,4-phenyleneimino(dicyanovinylidene)-1,4-phenylene] (23). 4,4′-Diaminodiphenyl ether (2.491 g, 12.44 mmol), 4-(dimethylamino)pyridine (3.051 g, 24.98 mmol), and 4,4′-bis(1-chloro-2,2-dicyanovinyl)diphenyl sulfone (**11**, 6.464 g, 12.43 mmol) in 30 mL of NMP were reacted according to the procedure for **21**, above. The crude polymer was twice reprecipitated from DMF into 250 mL of vigorously stirred methanol. The polymer, a fine, green–yellow powder, was isolated by centrifugation. After drying in vacuo at 140 °C for 24 h, 6.68 g (95%) of **23** was obtained: IR (thin film) 3455 br (NH), 2213 cm^{-1} (C≡N); ^{1}H NMR ($(CD_3)_2SO$) δ 6.7–8.2 (br m, 16 H, arom CH), 10.95 (br s, 2 H, NH); ^{13}C NMR ($(CD_3)_2SO$, APT) δ 52.2↑ (=*C*$(CN)_2$), [113.9↑, 117.1↑] (C≡N), 118.9↓ (arom CH ortho to oxygen), [128.0↓, 132.0↓] (arom CH), [132.7↑, 138.1↑] (unprotonated arom C), 143.0↑ (C—SO_2), 155.7↑ (C—O), 166.7 (vinyl C—N).

Anal. Calcd for $C_{32}H_{18}N_6O_3S$: C, 67.84; H, 3.20; N, 14.83; S, 5.66. Found: C, 66.17; H, 3.37; N, 14.38; S, 5.68.

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Registry No. **1**, 5515-36-6; **3**, 6123-68-8; **5**, 18270-61-6; **6**, 103229-96-5; **7**, 117371-47-8; **8**, 117371-48-9; **9**, 108090-23-9; **10**,

103134-51-6; **11**, 108090-21-7; **12**, 117371-51-4; **13**, 117371-52-5; **14**, 117371-53-6; **15**, 104156-79-8; **16**, 117371-54-7; **18**, 117371-49-0; **19**, 103229-97-6; **20**, 117371-50-3; **21** (copolymer), 108090-24-0; **21** (SRU), 117371-55-8; **22** (copolymer), 103134-52-7; **22** (SRU), 103083-29-0; **23** (copolymer), 108090-22-8; **23** (SRU), 117371-56-9; **24**, 70183-18-5; $PhNH_2$, 62-53-3; p-$H_3COC_6H_4NH_2$, 104-94-9; 3-$H_2NC_6H_4NH_2$, 108-45-2; 4,4′-$H_2NC_6H_4OC_6H_4NH_2$, 101-80-4; 3-$ClCOC_6H_4COCl$, 99-63-8; 4-$ClCOC_6H_4COCl$, 100-20-9; 4-$ClCOC_6H_4SO_2C_6H_4COCl$, 4462-61-7; H_2O, 7732-18-5; benzoyl chloride, 98-88-4; malononitrile, 109-77-3; 4-phenoxyaniline, 139-59-3.

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Spectroscopic Analysis of the Electric Field Induced Structural Changes in Vinylidene Fluoride/Trifluoroethylene Copolymers

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ABSTRACT: The electrical poling behavior of a uniaxially drawn random copolymer of 75 mol % vinylidene fluoride and 25 mol % trifluoroethylene has been examined by infrared spectroscopy at various temperatures. Vibrational assignments are clarified by examining the effects of annealing, orientation, temperature, and electric field on the spectrum. Bands sensitive to specific conformations are used as indicators of structural and orientation changes induced by an electric field. Intensity changes due to orientation demonstrate that the crystalline units are aligned in the draw direction by mechanical drawing, while molecular chains are rotated by the application of the electric field. Under a cyclic field of 2.2 MV/cm, the infrared intensity exhibits a hysteresis similar to that seen previously for PVDF. The shape of the hysteresis is sensitive to temperature with a large reversible intensity change observed above the Curie temperature. Below the Curie temperature bands show irreversible changes that suggest an improvement in chain packing and a disruption of long trans sequences by the applied field.

Introduction

Ferroelectric and piezoelectric polymers are a subject of great interest today. These materials exhibit lower piezoelectric activity than ferroelectrics such as quartz but can be processed easily and are light weight and flexible.[1] Polymers such as poly(γ-benzyl glutamate),[2] copolymers of vinylidene cyanide with vinyl acetate,[3] and methyl methacrylate[4] as well as the odd nylons[5] are known to be piezoelectric. Poly(vinylidene fluoride) (PVDF) has received much attention as it contains polar and nonpolar crystal phases which control the piezoelectric activity. The relative amounts of each phase can be altered by the application of a high strength electric field,[6] and studies have been reported on the structural change induced by poling and its field strength and temperature dependences.[7–10]

Our current interest is focused on PVDF and its copolymers with trifluoroethylene (TrFE). These copolymers have been the subject of much study since the addition of trifluoroethylene produces a trans structure similar to the β phase of PVDF and exhibiting greater piezoelectric activity.[11] In these materials a Curie phase transition is observed in which the planar trans ferroelectric phase containing ordered dipoles undergoes a solid–solid phase

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