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Regularly Alternating Copoly(amide−enaminonitriles)

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ABSTRACT: Regularly alternating copolymers of aromatic amide and enaminonitrile groups were synthesized by solution polycondensation of diamines containing preformed amide or enaminonitrile groups with *m*- or *p*-bis(1-chloro-2,2-dicyanovinyl)benzene or aromatic diacid chlorides, respectively. Most of the copolymers were high molecular weight materials ($[\eta]_{DMF} = 1.0-3.1$). The copolymers were soluble in proton-accepting solvents and showed high glass transition temperatures in the range 262−320 °C. The enaminonitrile groups underwent curing between 300 and 350 °C, as do homopoly(enaminonitriles). The thermal stability (air and nitrogen) of the copolymers was good to excellent. In general, the predominantly para-substituted copolymers showed lower thermal stability than the corresponding homopoly(enaminonitriles) and Kevlar, while higher thermal stability was exhibited by the meta-substituted copolymers when compared to Nomex.

Introduction

The limited processability of aromatic polyamides (aramids) is a consequence of high melting temperatures and poor solubility in simple, nonaggressive solvents. Various approaches have been applied to obtain processable, thermally stable, and high molecular weight polymers. Oishi et al.[1] have reported fluorinated aramids which have improved T_g but lowered thermal stability. Substitution of the aromatic ring with methyl, phenyl, or phenoxy groups,[2] the use of comonomers with angular structures or ether linkages,[3] and N-alkylation or N-phenylation[4] have been used to improve the processability of aramids, but at the expense of lowered thermal stability. The increase in solubility was attributed to a change from a rigid-rod to a more flexible structure.[5] Introduction of substituents interferes with the trans-configuration of the amide bond, and a more flexible polymer structure is obtained because of the corresponding increase in cis-configurations available to the amide linkage.

Based on the useful analogy made by Wallenfels that the dicyanomethylene group ($=C(CN)_2$) and the carbonyl oxygen atom exert similar inductive and resonance effects,[6] our approach to improve the solubility properties of aramids has been to replace the amide groups ($-NH-C=O$) with enaminonitrile groups ($-NH-C=C(CN)_2$) in the polymer backbone. The latter group is expected to undergo resonance interactions similar to those of the amide bond in aramids, and in the absence of substituents on the phenyl ring or N-substitution, the rigidity of the polymer backbone for poly(enaminonitriles) is expected to be retained. Higher molecular weight polymers are also possible as a result of the expected improvement in solubility. Poly(enaminonitriles), PEANs, are hydrolytically stable, have good film-forming properties, and show good to excellent thermal properties. In contrast to aramids such as Kevlar, high molecular weight PEANs have been reported that are soluble in solvents such as DMF, DMSO, NMP, DMAC, pyridine, and di- and triglymes.[7] Further, PEANs can be cured thermally without evolution of volatile products to give insoluble polymers. The solubility of PEANs in many organic solvents has been attributed to the introduction of the rather bulky and polarizable dicyanovinylidene group, in place of oxygen atoms in amide groups, with the apparent consequence of reducing crystallization and/or very strong hydrogen bonding interactions in the polymers. As a result, unlike the very strongly self-associated amide NH protons in aramids, the enamine hydrogen atoms are able to form hydrogen bonds with other proton-accepting functional groups to give soluble polymers. The role of hydrogen bonding as the basis of solubility of PEANs has been established by studying the solubility properties of polymers that do not contain an enaminonitrile proton, poly(piperazine−enaminonitriles),[8] where the latter show reduced solubility in solvents such as those listed above.

Although the thermal stability of PEANs is good to excellent, the thermooxidative stability and glass tran-

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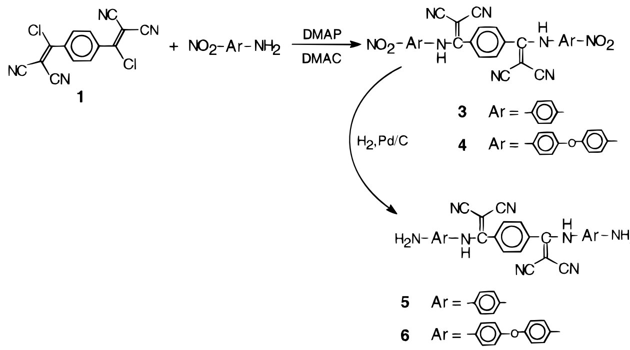
Scheme 1



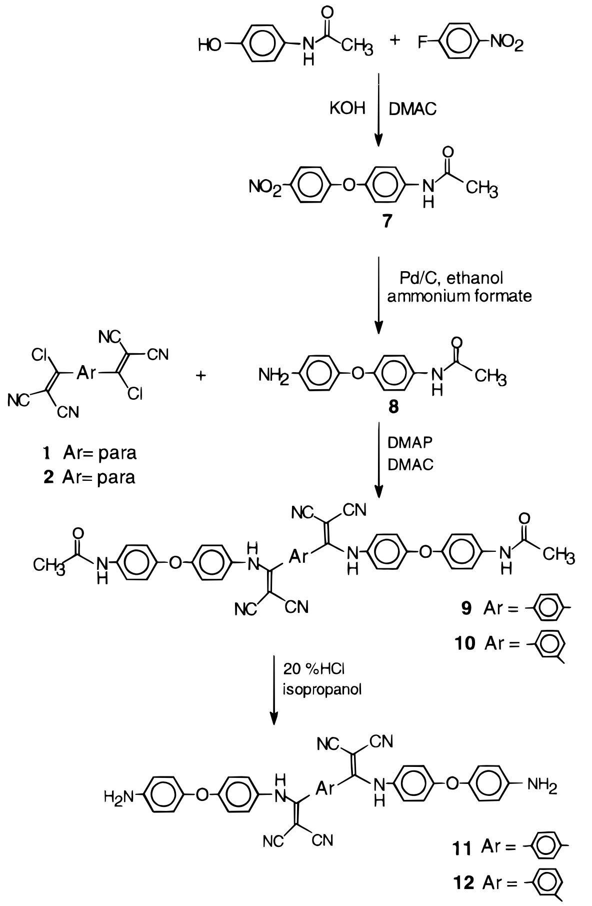
sition temperatures could be improved. To achieve this goal, incorporation of amide groups by copolymerization was investigated with the intention of, at least, retaining good solubility. This work reports the synthesis and characterization of regularly alternating aromatic copolymers that contain both amide and enaminonitrile groups in the polymer backbone. Gong and co-workers have reported the synthesis of polyurethanes[9] and polyarylates[10] containing thermally curable enaminonitriles in the main chain. Although the polymers they describe were low molecular weight materials, the enaminonitriles were thermally curable and showed good thermal stability. Copolyamides containing enaminonitrile segments have been reported by Mikroyannides.[11] These modified polymers showed improved solubility in common organic solvents and enhanced heat resistance compared to poly(benzamides). However, relatively low molecular weight polymers were reported, with inherent viscosities ranging between 0.12 and 0.18 dL/g for a polymer solution of 0.5 g/dL in 98% H_2SO_4 or DMF.

Results and Discussion

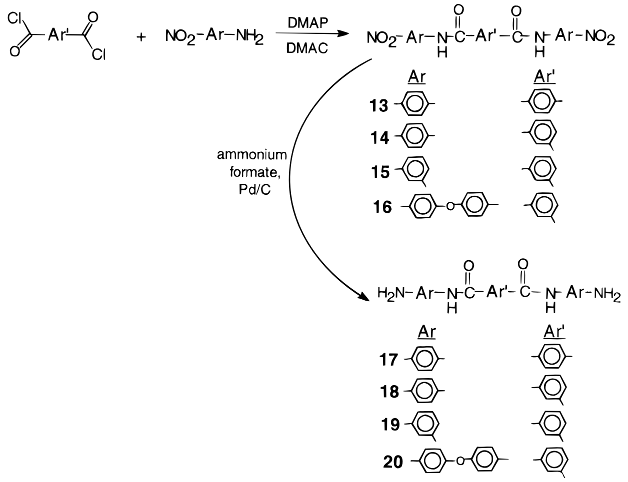
Monomer Synthesis. The synthesis of diamines containing preformed enaminonitrile groups was initially attempted because of the improved solubility expected when carbonyl groups are replaced with dicyanovinylidene groups. Synthesis of several diamines was attempted, as outlined in Scheme 1. There were several difficulties with this approach. Complete reduction of the dinitro compounds was difficult because the palladium catalyst became coated by reactant/products. Separation of the dinitro and diamine compounds was made difficult because of their poor solubility in low boiling solvents, and the similar solubility properties of the two compounds. An alternative approach to the dinitro compounds was synthesis of acetylated derivatives **9** and **10** (Scheme 2). Two diamines, **11** and **12**, were successfully synthesized but in low yields (25%), after separation of side products. The side products were possibly caused by the acidic conditions used at reflux over 24−48 h for complete hydrolysis of the acetyl group. Cyano groups are known to undergo hydrolysis to COOH under aqueous acidic conditions at elevated temperatures. Separation of the diamines was achieved by column chromatography. However, the synthesis of the diamines via the acetylated derivative was time consuming, and separation by chromatography was tedious.

The cost in time and materials (monomers **1** and **2**) to synthesize diamines containing enaminonitrile groups via dinitro compounds and acetylamino derivatives led to the synthesis of diamines that instead contained preformed amide groups. Several such diamines have been used successfully in polymerizations, despite their relative insolubility in lower boiling solvents.[12] A series of diamines (**17**−**20**) containing preformed amide groups was synthesized, as outlined in Scheme 3. Another set of bis(nitro) compounds (**21** and **22**) was prepared by condensation of *m*- or *p*-nitrobenzoyl chloride with 4,4′-diaminodiphenyl ether, followed by reduction to give the diamines[13] (Scheme 4).

Scheme 2

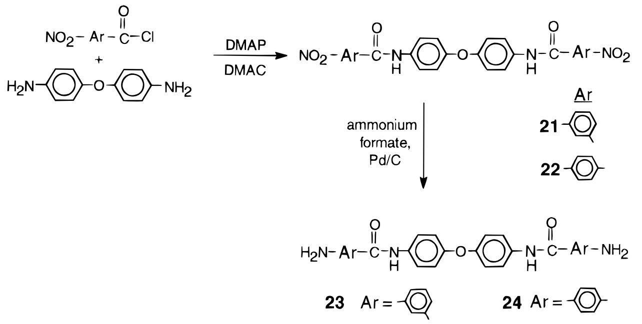


Scheme 3

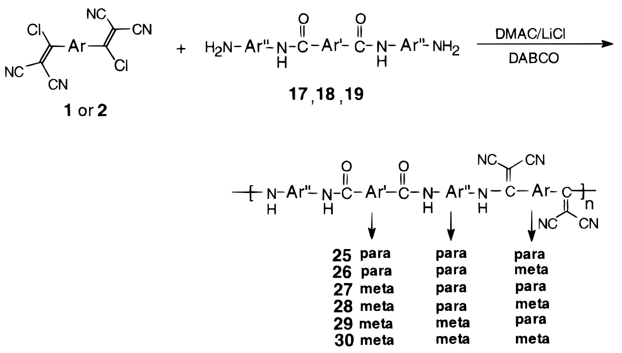


Polymer Synthesis and Characterization. The first set of regularly alternating copolymers (**25**−**30**) contained no flexible oxygen linkages (Scheme 5) and thus can be compared to aramids such as poly(*m*-phenyleneisophthalamide) (DuPont's Nomex) and poly(*p*-phenyleneterephthalamide) (DuPont's Kevlar). The next series of regularly alternating copolymers (**31**−

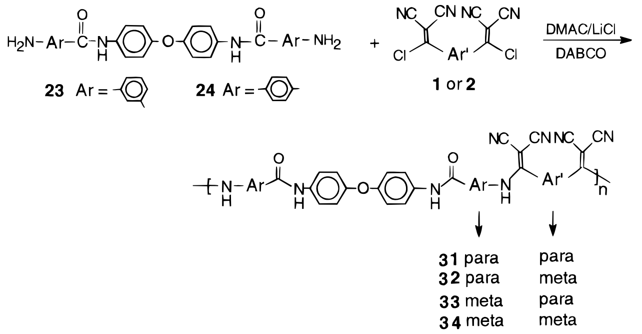
Scheme 4



Scheme 5

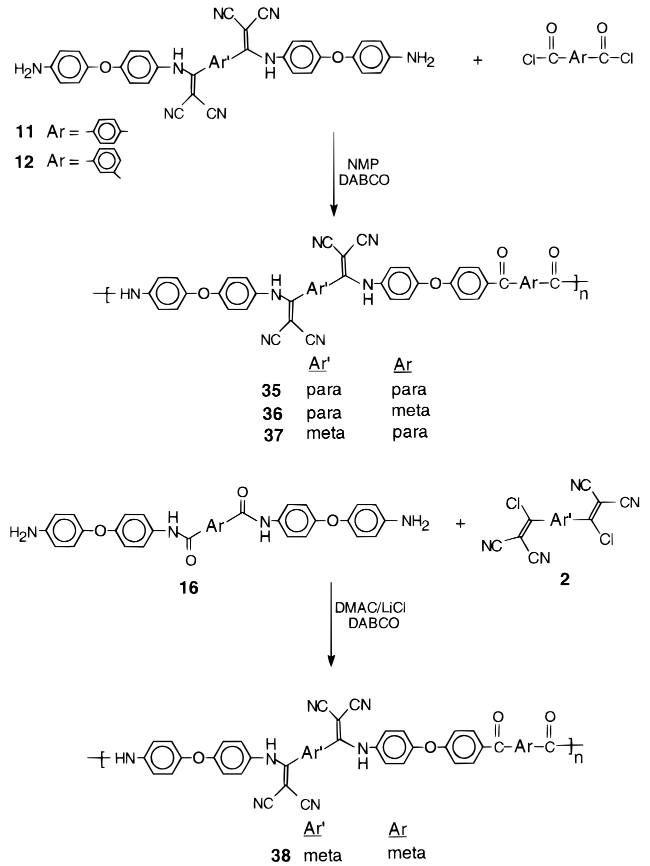


Scheme 6

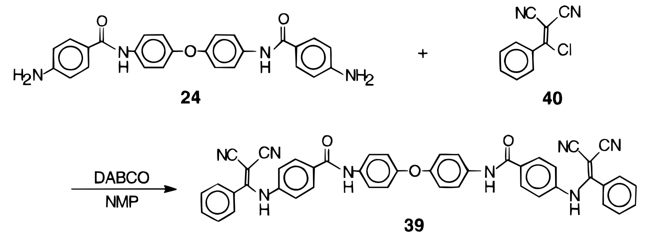


34)[13] contained one ether linkage per repeat unit (Scheme 6) and two ether linkages per repeat unit (**35**−**38**) (Scheme 7). Several model compounds were synthesized to confirm the polymer structures. A representative example (**39**) is shown in Scheme 8. The spectral data of model compound **39** are consistent with the spectral data of polymer **31**, as shown in Figures 1−3. The ^{1}H NMR spectra show some differences between model compound **39** and polymer **31**. The proton resonances for the terminal phenyl rings (a) of **39** are found between 7.45 and 7.70 ppm, while the ortho protons of the dicyanovinylidene-substituted benzene ring (b) of polymer **31** are found at ∼7.83 ppm, overlapping peaks at 7.74 ppm (protons c) and 7.91 ppm (protons d). The protons, b, for polymer **31** are flanked by two dicyanovinylidene groups and are expected to be shifted downfield relative to the proton resonances for the terminal phenyl rings of **39**, which are adjacent to only one dicyanovinylidene group. The assignments of the ^{1}H NMR spectra were also confirmed by heteronuclear multiple-quantum coherence-bilinear rotational coupling (HMQC) and total correlation spectroscopy (TOCSY) NMR experiments.[14]

Scheme 7



Scheme 8



Two additional copolymers (**40** and **41**) were obtained by condensation of a nonsymmetrical diamine, 4,4′-diaminobenzanilide,[15] with monomers **1** and **2** (Scheme 9). This diamine lacks symmetry, and the reactivities of the two amino groups are expected to be different, giving either head-to-head or head-to-tail arrangements in the polymer structure. Predominantly ordered polymers, as determined by ^{1}H NMR spectroscopy, were obtained by the slow addition of monomer **1** or **2** to a solution of the nonsymmetrical diamine. The detailed NMR analysis of these polymers will be reported in a future publication.[16]

The characterization data for polymers **25**−**41** and some homopolymers are given in Table 1. All the polymers formed clear yellow, fingernail-creasable films, except for polymers **25**, **35**, and **40**, which were yellow but showed some cloudiness, possibly because of some crystallinity. A film of **25** was somewhat brittle. Most of the copolymers are high molecular weight materials with intrinsic viscosities between 1.0 and 3.1 dL/g; the rest gave moderate molecular weight materials with intrinsic viscosities between 0.4 and 0.76 dL/g. End groups were detected for polymer **25** by ^{1}H NMR spectroscopy, and on the basis of the repeat unit to end group ratio, a number average molecular weight of 11 440 was calculated for the polymer. Using a polydispersity of 2.1, as determined by GPC, a weight average molecular weight of 24 000 was calculated. This result was inconsistent with a result of M_w = 10 000,

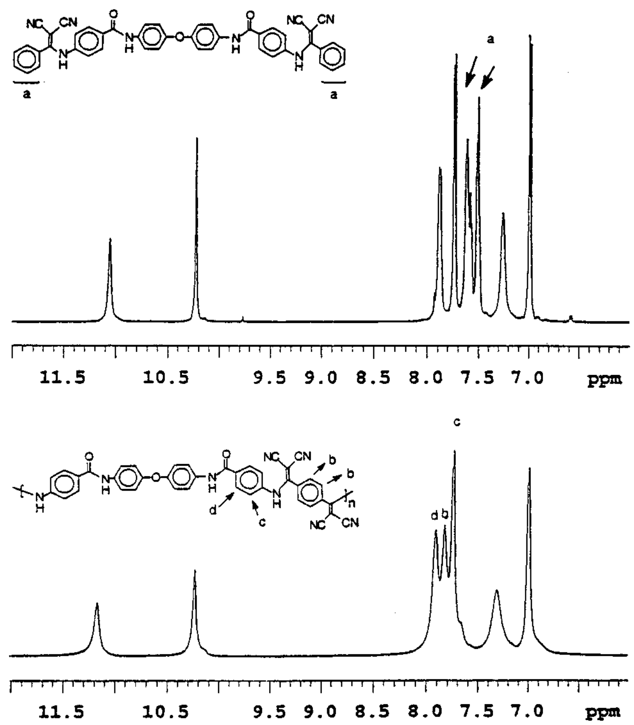


Figure 1. ^{1}H NMR (room temperature) spectra of model compound **39** (top scan) and polymer **31** (bottom scan).

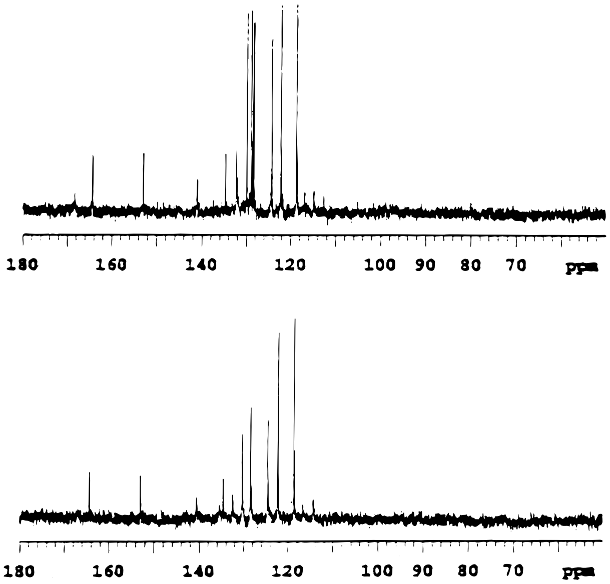


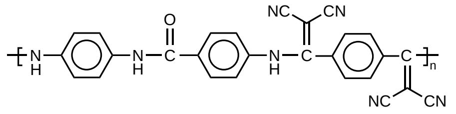
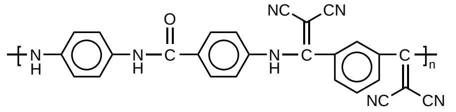
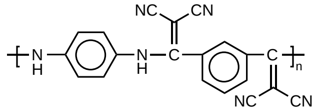
Figure 2. ^{13}C NMR spectra of model compound **39** (top scan) and polymer **31** (bottom scan).

as determined by gel permeation chromatography (GPC) for polymer **25**. The apparent difference in the weight average molecular weight of **25** by GPC and end group calculations is possibly a result of the difference in the hydrodynamic volume of polymer **25** and the PEO standards used in the molecular weight calibration. Polymer **25** is basically a rigid rod, while PEO is a flexible polymer. The number average molecular weight by GPC and end group calculations for polymer **26** were comparable because of the presence of the more flexible meta linkage in this polymer. A comparison of T_g values of **25** and **26**, indeed, shows a significant decrease by approximately 60 °C upon introduction of a meta linkage into polymer **25**.

A comparison of T_g values versus percent of para linkages per repeat unit of the copolymers is shown in Figure 4. In general, introduction of flexible ether linkages reduces T_g values (compare curves a and b). For the series of polymers with no flexible ether linkages, an increase of meta linkages in the polymer chain lowers T_g values, as expected. In the series of polymers with two ether linkages per repeat unit (curve c), there appears to be only a small decrease in T_g values with increasing meta substitution. However, the apparent indifference to meta substitution possibly reflects differences in the molecular weights of the polymers in question (the intrinsic viscosity of the all para polymer, **34**, is lower than that of the all meta polymer, **38**). On the other hand, polymers **35** and **37**, which have comparable intrinsic viscosities, also show similar T_g values. It is possible that in the presence of two ether linkages per repeat unit, polymer flexibility is not changed significantly with meta substitution and, consequently, T_g values are not affected.

Despite the lower molecular weight of **25**, a high T_g value of 330 °C was obtained. However, at these temperatures, the polymer may undergo some intra- and intermolecular curing reactions, similar to those reported for PEANs (see Scheme 10), and an enhancement in the glass transition temperature may be a reflection of a stiffer backbone caused by intramolecular cyclization or the influence of cross-linking. The curing processes are observed in the differential scanning calorimogram (DSC), Figure 5, as a broad irreversible exothermic peak, ranging between 325 and 400 °C. An FTIR spectrum of the polymer after these curing processes shows some changes in the NH region and a reduction in the intensity of the CN band that are consistent with the proposed curing processes (Figure 6). While the band at $\sim$3200 cm^{-1} is labeled as NH for the cured sample, previous studies on PEANs have reported the appearance of NH_2 groups with a corresponding decrease in the CN band intensity.[7] In the copolymers, the presence of NH_2 groups is difficult to observe because, in addition to enaminonitrile NH groups, amide NH groups are also present in this region. The film used for determining T_g values was insoluble at the end of the TMA measurements, indicating possible cross-linking of the polymer. The enhancement in T_g values from curing processes also applies to polymers **27** and **31**, which showed T_g values of 321 and 310 °C, respectively. These T_g values are comparable to Kevlar. It is interesting to note that high T_g values are possible even with the presence of one flexible linkage per repeat unit (a meta linkage for polymer **27** and an oxygen linkage for polymer **31**). Further, the presence of a meta linkage at the amide-substituted benzene ring (an isophthaloyl unit in **27**) causes a smaller decrease in the T_g value compared to the placement of a meta linkage at a dicyanovinylidene-substituted benzene ring, as in polymer **26**. In polymer **40**, a T_g value was not detected, presumably because it is high and may be obscured by the curing processes. In general, high T_g values were obtained for the copolymers containing predominantly para substitution. The all para (**25**) and all meta (**30**) copolymers show T_g values similar to Kevlar and Nomex, respectively. Two general comments can be made about the T_g values of the copolymers. First, high glass transition temperatures are observed for all the copolymers, ranging between 262 and 330 °C. Secondly, the T_g values of the copolymers are similar to those of the corresponding aramids and PEANs.

Table 1. Characterization Data for Polymers 25−41 and Some Homopolymers

polymer	Ar″	Ar′	Ar	T_g (°C) TMA[a]	$[\eta]$,[b] dL/g	$10^4 M_w$	PD[c]	film[d]
25	para	para	para	330	0.76	10.9	2.1	Y, C
26	para	para	meta	268	0.62	7.9	2.2	F, Y
27	para	meta	para	321[e]	1.0			F, Y
28	para	meta	meta	294	1.7	33.2	2.8	F, Y
29	meta	meta	para	270	3.1	>40.0	3.63	F, Y
30	meta	meta	meta	262	2.1	>40.0	2.42	F, Y
31		para	para	310	1.76	24.1	3.2	F, Y
32		meta	para	297	1.79	22.8	2.4	F, Y
33		para	meta	283	2.32	22.8	4.1	F, Y
34		meta	meta	274	0.95	16.8	2.3	F, Y
35		para	para	276	0.62	4.5	3.4	F, Y, C
36		para	meta	264	0.40	4.5	3.2	F, Y
37		meta	para	272	0.60	5.7	2.1	F, Y
38		meta	meta	268	1.38			F, Y
40				none seen	2.1	>40.0	4.1	Y, C
41				280	1.1	22.3	2.3	F, Y
Kevlar				>300	4.8[e]			
Nomex				270	1.0[e]			
PEAN				287	0.55			

[a] Second runs reported. [b] Intrinsic viscosity at 25.00 °C in DMF. [c] PD = polydispersity by GPC (M_w/M_n). [d] F = flexible and fingernail-creasable. C = cloudy, Y = yellow. [e] Inherent viscosity done in concentrated sulfuric acid.[30]

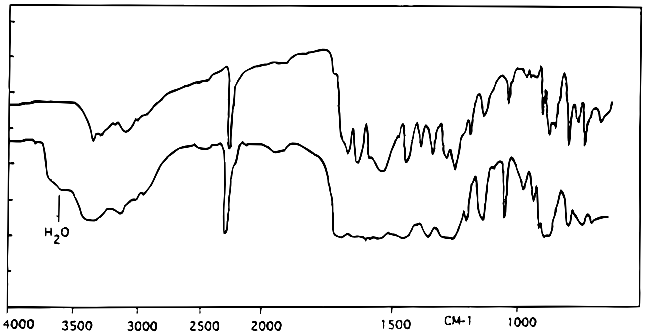
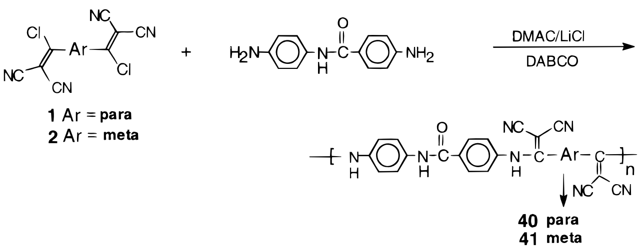


Figure 3. FTIR spectra of model compound **39** (top scan) and polymer **31** (bottom scan).

Scheme 9



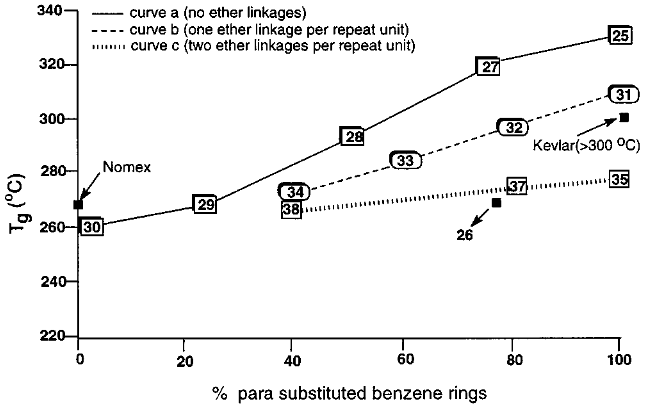
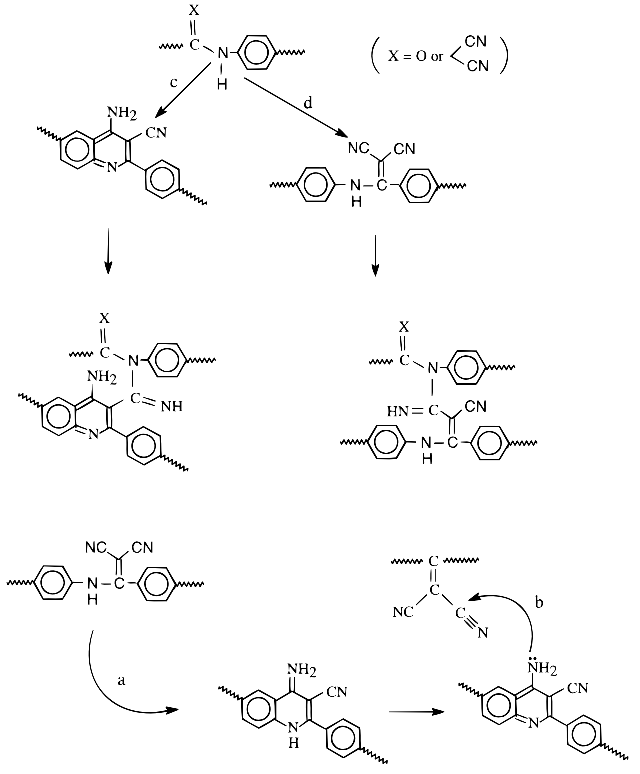


Figure 4. T_g values versus percent of para linkages per repeat unit of copolymers **25**−**38**.

Kevlar 49 is reported to absorb an appreciable amount of moisture, 8%, despite its crystalline morphology,[17] and the water sorption capacity of polyamides, such as Nylon 6 and 66, has been related to the number of amide linkages in the polymer chain.[18] PEAN homopolymers with enaminonitrile groups, considered to be equivalent to amide groups, were reported to absorb less moisture (1−4%). This result is not unexpected because, compared to the oxygen atom (sp^2) of the amide group, the nitrogen lone pair electrons (sp) of the cyano group are poorer electron donors and are less likely to undergo hydrogen-bonded interactions with water. Upon exposure to a 100% humidity environment, the dried copolymers showed an absorption of 0.5−2.5% of moisture. Introduction of amide groups in the copolymers did not increase the amount of water absorbed compared to poly(enaminonitriles).

Copolymer Solubility. Unlike aramids, regularly alternating aromatic poly(amide−enaminonitriles) which contain up to 50% of amide linkages retain the desirable solubility properties of PEANs. The copolymers are soluble in polar aprotic solvents (NMP, DMF, DMAC, DMSO) and pyridine, among others. The solubility in THF (Table 2) appears to be correlated with the degree of flexibility of the copolymer chain. Polymers containing the more rigid para linkages (**25**, **40**, **31**) are insoluble in THF, while polymers containing more than two meta linkages per repeat unit are soluble. The presence of two ether linkages per three phenyl groups introduces sufficient flexibility in the polymer chain to make even the para-linked polymer (**35**) soluble in THF. Decreasing the number of ether linkages to one for every

Scheme 10. Proposed Curing Processes of Enaminonitrile Groups



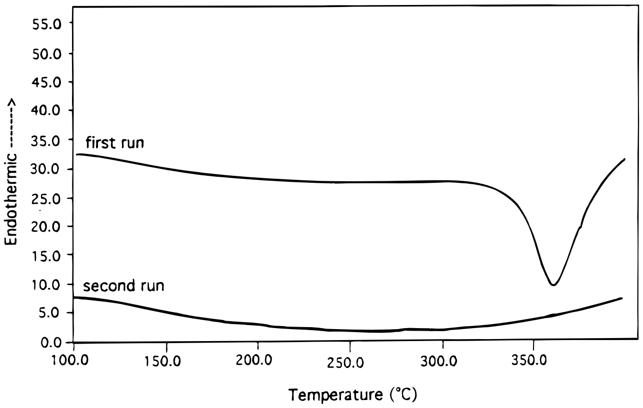


Figure 5. Differential scanning calorimogram of polymer **25**.

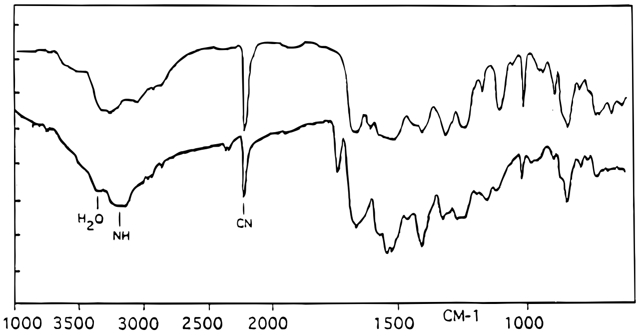


Figure 6. FTIR spectra of polymer **25** before curing (top scan) and after curing (bottom scan).

five phenyl groups reduces the solubility of polymers **32** and **33** in THF, even when there are meta linkages present. The high molecular weights of the latter polymers may lower the solubility of the polymers in THF. All the copolymers are soluble in diglyme with the exception of the two para-linked polymers, **40** and **31**.

The polymers which showed solubility in THF and diglyme became cloudy when heated, indicating the occurrence of lower critical solution temperature (LCST) behavior. PEANs have also been reported to show similar LCST behavior in "glyme" and THF solvents.[3b] Upon cooling, the copolymer solutions became clear (reversible phase separation), with the exception of polymer **40**. In the case of polymers showing partial solubility, the filtrate was heated to detect LCST behavior. For copolymer **40**, heating of the filtrate rendered it cloudy and the solution remained cloudy upon cooling (irreversible phase separation). The irreversible phase separation may be caused by the development of crystallinity during phase separation.

Thermal Properties. The thermal properties of copolymers **25**−**41** and some homopolymers are shown in Table 3. Previous results for PEAN homopolymers showed a modest improvement in thermal stability with the introduction of meta linkages.[3b,19] The reason for the enhancement in thermal stability with the introduction of a more flexible meta group is not readily apparent in PEANs. For polyamides, the converse was observed, where meta linkages decreased thermal stability. The latter observation is consistent because a more flexible backbone is expected to weaken or lower intermolecular hydrogen-bonded interactions, as compared to a rigid-rod para-substituted polymer, leading to lowered thermal stabilities. In the case of the copolymers, most exhibited good thermal stabilities with 10% weight loss occurring between 445 and 480 °C. Copolymers **27**, **35**, and **40** showed slightly improved thermal stabilities. A possible explanation for the lower thermal stabilities of the predominantly para polymers, **25** and **26**, is the observation of resonances in the ^{1}H NMR spectra corresponding to end groups. The thermal stabilities of aromatic amide model compounds have been reported to be influenced by end groups.[20] Lowered thermal stability was observed in the presence of amino or carboxylic acid end groups, with the latter being more detrimental to thermal stability. Carboxylic acid and amino end groups were postulated to reduce thermal stabilities by inducing acidolysis or aminolysis of the amide bond. Figures 7 and 8 show thermogravimograms of **25**, **27**, **31**, **35**, Kevlar, and Nomex. In general, except for **35**, all the copolymers showed onsets of degradation in a fairly narrow range of temperatures which were lower than that for Kevlar but higher than that for Nomex. The predominantly para-substituted copolymers have lower thermal stabilities than the corresponding aramids, but meta-substituted copolymers, for example **30**, exhibited higher thermal stabilities (air and nitrogen) than Nomex (meta substituted). The latter trend is consistent with the general observation of a modest improvement in thermal stability when the dicyanovinylidene groups are meta substituted on the benzene ring.

As seen in Figure 8, after accounting for solvent loss, copolymer **35** shows a broad and gradual weight loss that is coincident with the sharper onset of degradation of Kevlar. The enhanced thermo-oxidative stability of copolymer **35** relative to **25** and **31** is surprising because the latter polymers are also para-substituted and contain zero and one ether linkage per repeat unit, respectively. The lower thermal stability of **25** is explainable because of its lower molecular weight; the presence of a larger number of end groups, detectable by ^{1}H NMR spectroscopy, may contribute to an earlier onset of degradation. The presence of crystallinity in **35** is a

Table 2. Solubility Properties of Copolymers in THF and Diglyme[a]

solvent	25	26	27	28	29	30	31	32	33	34	35	36	37	38	40	41
THF	I	s*	ss, f*	s*	s*	s*	I	I	I	s*	s*	s*	s*	s*	I	s*
diglyme	s*	s*	s*	s*	s*	s*	ss, f*	s*	s*	s*	s*	s*	s*	s*	ss, f	s*

[a] I, insoluble; ss, partial solubility; s*, soluble, shows phase separation upon heating (reversible); f*, filtrate shows phase separation upon heating (reversible); f, filtrate shows phase separation but remains cloudy upon cooling (irreversible).

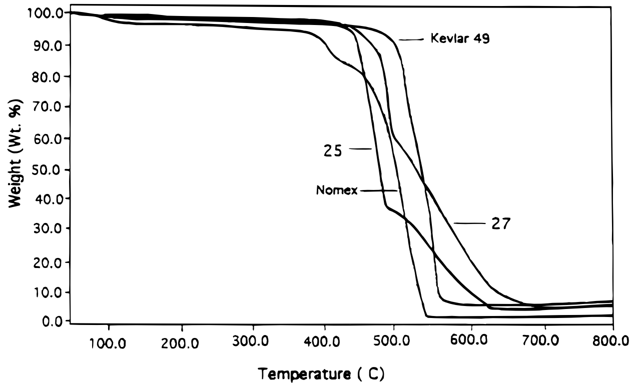


Figure 7. Thermogravimograms in air of polymers **25** and **27**, Kevlar 49, and Nomex.

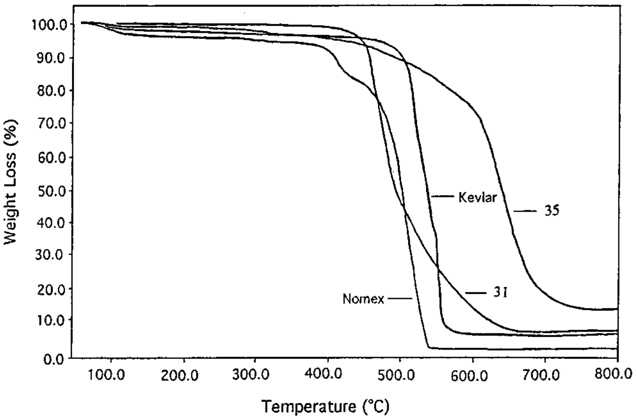


Figure 8. Thermogravimograms in air of polymers **31** and **35**, Kevlar 49, and Nomex.

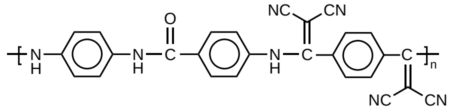
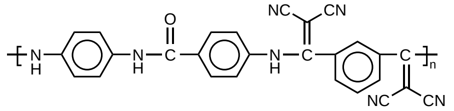
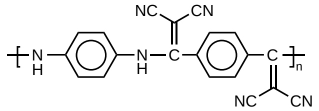
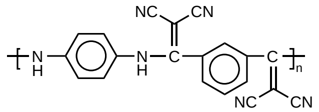
likely reason for its enhanced stability. The film of **35** was slightly cloudy, possibly indicating some degree of crystallinity, while **31** was apparently amorphous because it formed a clear film.

The thermal stability of most of the copolymers in nitrogen is good to excellent, with 10% weight loss seen between 500 and 540 °C (Figure 9). This range was lower than that observed for Kevlar, but higher than that for Nomex. Polymers **29**, **30**, and **40** exhibited higher thermal stabilities than the rest of the copolymers. The enhanced thermal stability of **40** is not surprising because it contains no ether or meta linkages. After the initial loss of residual solvent (~300 °C), **29** and **30** showed thermal stabilities that are noticeably ehanced by ~100 °C, relative to polymers **25**−**28**. The repeat units of **29** and **30** have three and four meta linkages, respectively, and both polymers have higher molecular weights than polymers **25**−**28**. It is not clear whether meta substitution and/or higher molecular weights are the reasons for the improved thermal stability in nitrogen. A possible correlation between thermal stability and degree of cross-linking can be postulated to explain the improved thermal stability in nitrogen for polymers containing enaminonitrile groups. In nitrogen, significant amounts of cross-linking may occur during the curing process before degradation of the polymer takes place, leading to an enhancement in thermal stability. A greater amount of cross-linking is conceivable for meta-substituted polymers because of their higher molecular weights (longer chains will correspond to a higher degree of entanglements). In air, degradative processes could possibly preempt cross-linking because the initially formed primary amines from intramolecular curing are oxidizable. As a result, the thermo-oxidative stabilities of PEANs and copolymers are lower than corresponding polyamides.

A weight loss of 20−30% at 700 °C (N_2) was observed for the copolymers, except for **29**, **30**, and **40** which gave lower values of 15−18%. These weight losses are less than observed for Kevlar and Nomex but higher than PEANs. The weight loss is apparently correlated with the number of enaminonitrile groups; a higher char yield is obtained with an increasing number of these functions in the polymer. A higher degree of cross-linking is possible with a greater number of enaminonitrile groups, and through cross-linking the number of volatile fragments evolved during degradation is possibly decreased, leading to a higher char yield.

Previous results on isothermal aging studies conducted at 300 °C in air for 2 h have shown substantial weight losses for PEAN (~30%) as compared to Kapton (2−3%).[21] Several copolymers were selected for isothermal aging studies to determine if a lower weight loss is possible when carbonyl groups are included in the backbone of PEANs. Isothermal aging studies were done between 300 and 320 °C for 24 h in nitrogen and air, and the results are reported in Table 4. Variable results were observed for studies in air. Polymers **30** (all meta substituted) and **31** (all para substituted with one ether linkage per repeat unit) showed fairly large weight losses (24−31%). The all-para-substituted polymers with zero and two flexible ether linkages per repeat units, **25** and **35**, respectively, showed smaller weight losses of ~12%. The lower weight losses of **25** and **35**, relative to polymers **30** and **31**, possibly result from the absence of any flexible linkages (meta substitution or oxygen) in polymer **25** and the possible presence of crystallinity observed for **35**. Isothermal aging of the copolymers in nitrogen resulted in small weight losses (1−2 weight %), and FTIR spectra showed a decrease in the intensity of the CN band (2200 cm^{-1}). The FTIR spectra for copolymer **25**, untreated and isothermally treated, and an isothermally cured PEAN are shown in Figure 10. The spectral changes of copolymer **25** upon isothermal aging are consistent with those observed for an isothermally cured PEAN. Thus, isothermal aging in nitrogen leads to curing of the copolymers. These cured copolymers were further treated isothermally in air to determine if the cured samples could be more heat resistant than untreated copolymers. Polymer **30** showed the same weight loss, whether untreated or cured, but the weight loss of polymer **31** was reduced by half when a cured sample was used, indicating greater heat resistance was possible if the copolymer was cured prior to isothermal aging in air. The appearance of the cured samples (isothermal aging in nitrogen) provides a possible answer for the difference in behavior of polymers **30** and

Table 3. Thermal Properties of Copolymers 25−41 and Some Homopolymers

	Ar″	Ar′	Ar	10 wt % loss, air (°C)	10 wt % loss, N_2 (°C)	wt % loss, in N_2 at 700 °C
25	para	para	para	453	533	25
26	para	para	meta	473	541	20
27	para	meta	para	495	527	20
28	para	meta	meta	461	523	25
29	meta	meta	para	469	621	15
30	meta	meta	meta	461	661	15
31		para	para	453	504	29
32		para	para	452	511	25
33		para	meta	481	510	28
34		meta	meta	445	533	25
35		para	para	520	501	27
36		para	meta	462	515	30
37		meta	para	454	514	25
38		meta	meta	447	504	30
40				490	550	18
41				467	520	20
Kevlar[a]				506	550	56
Nomex[a]				420	536	46
PEAN				477	566	14
PEAN				525	578	14

[a] Kevlar 49 and Nomex 450 (supplied by Dupont) were used for the thermal studies.

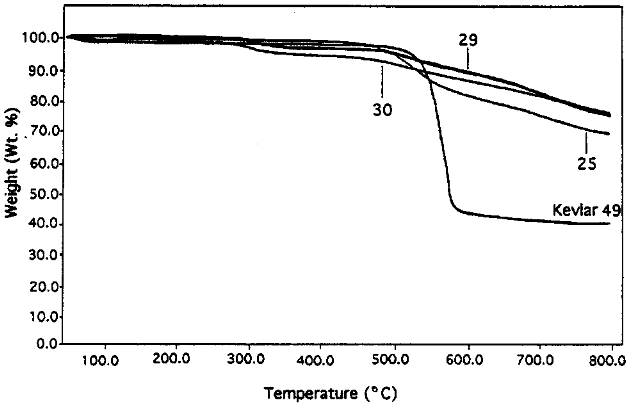


Figure 9. Thermogravimograms in nitrogen of polymers **25**, **29**, **30** and Kevlar 49.

Table 4. Isothermal Aging Data for Selected Copolymers at 300−320 °C for 24 h

polymer	weight loss (%), N_2	weight loss (%), air	appearance of cured polymer	weight loss (%) in air of cured polymer
25	2	13	brown	6−10
30	1	24	brown-black	23
41	2	31	yellow-brown	15
35	2	11	dark brown	12
1,4 PEAN	1.5	28	dark brown	31
Kevlar[a]		5		
Nomex[a]		12		

[a] Kevlar 49 and Nomex 450 (supplied by DuPont) were used for the isothermal aging studies.

31. Cured polymer **31** was a mustard-colored sample, while polymer **30** appeared to be degraded because of its brown-black appearance. Thus, curing of **30** is also accompanied by degradation processes during isothermal heating in nitrogen for an extended period of time. Overall, weight losses comparable to that for Nomex can be attained for the copolymers if they are cured, without degradation, prior to isothermal aging in air.

Conclusions

Poly(amide−enaminonitriles) synthesized here were generally high molecular weight materials that could be cast into flexible yellow films. All the polymers were soluble in polar aprotic solvents, and most were soluble in diglyme. The polymer solutions are stable and do not gel or precipitate, unlike Nomex solutions, which are often metastable. Solubility in THF was variable and depended on the degree of flexibility of the polymer backbone, with ether linkages and/or meta substitution promoting solubility of the polymers. The presence of amide groups in the copolymers did not increase the absorption of moisture, relative to PEANs. The copolymers exhibited excellent thermal stabilities, showing 10% weight losses between 450 and 495 °C and 505 and 545 °C in air and nitrogen, respectively. With the exception of copolymer **35**, the thermal stability of the predominantly para-substituted copolymers was generally lower than the corresponding aramid and poly(enaminonitrile) homopolymers. With meta-substituted polymers, the copolymers displayed higher thermal stabilities than the corresponding aramid polymers. All the copolymers exhibited broad irreversible exothermic transitions between 300 and 350 °C, indicative of curing of enaminonitrile groups without emission of any volatile byproducts. Several copolymers, which are predominantly para substituted, showed T_g values >300

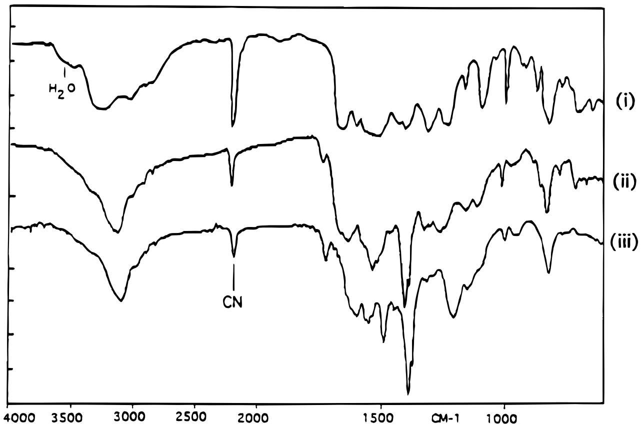


Figure 10. FTIR spectra of (i) uncured polymer **25**, (ii) polymer **25** cured isothermally in nitrogen, and (iii) poly(enaminonitrile) homopolymer cured isothermally in nitrogen.

°C, which are comparable to the reported T_g value of Kevlar. In general, the T_g values of the copolymers are similar to the T_g values of the corresponding PEAN and polyamide homopolymers.

The copolymers retained 70−75% of their mass at 700 °C in nitrogen over a period of 24 h. The amount of char formed is higher than that for aramids but lower than that for PEAN, and the results are consistent with the generation of a higher char residue from polymers containing greater numbers of enaminonitrile groups.

Isothermal aging studies of the copolymers at 300−320 °C in air for 24 h showed weight losses of 24−31%, but lower values of 10−13% for a copolymer exhibiting some degree of crystallinity. Smaller weight losses were observed for some of the copolymers (10−15%) that were first cured by heating at 300 °C in nitrogen.

It is apparent from the above results that alternating copolymers of aromatic amide and enaminonitrile units can be synthesized as high molecular weight materials that have high glass transitions comparable to aramids and, in addition, are soluble in polar, aprotic solvents. While an apparent enhancement in the thermal stability of the meta-substituted copolymers was observed, the para-substituted copolymers showed lower thermal stabilities than the corresponding homopolymers.

In conclusion, regularly alternating copolymers of aromatic amide and enaminonitrile groups were successfully synthesized as high molecular weight materials, which showed good to excellent thermal stabilities and high T_g values and retained the desirable solubility properties of PEANs.

Experimental Section

Characterization. All melting points were determined by differential scanning calorimetry. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. The presence of charred residue from thermally stable structural moieties in the compounds analyzed has been observed to cause incorrect low carbon values to be obtained. Infrared (IR) and Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer Model 298 spectrophotometer and a Perkin-Elmer Model 1800 Fourier transform infrared spectrophotometer, respectively. Nuclear magnetic resonance (NMR) spectra were recorded on either a Varian XL-200 (200 MHz ^{1}H; 50.3 MHz ^{13}C) or Varian 500 (500 MHz ^{1}H; 125 MHz ^{13}C) spectrometer. The NMR shifts were recorded as parts per million (ppm) and are referenced to residual solvent resonances. Peak assignments for ^{1}H and ^{13}C spectra were made on the basis of calculated values[22] and comparison to previously reported data on similar structures, and where needed, NMR experiments of heteronuclear multiple-quantum coherence-bilinear rotational decoupling (HMQC)[23] for ^{1}H−^{13}C and total correlation spectroscopy (TOCSY)[23] for ^{1}H−^{1}H were used. FAB-MS (fast atom bombardment mass spectra) were obtained on a VG 70E mass spectrometer at the Polaroid Corp., Cambridge, MA. Gel permeation chromatography (GPC) was performed using a VISCOTEK Model 200 GPC with refractive index and viscosity detectors. A series of three Waters Ultrastyragel columns (cross-linked polystyrene) with average pore sizes of 10^3, 10^4, and 10^5 Å were used. DMF containing 0.01 M $LiNO_3$ was used as the eluent at a flow rate of 0.8 mL/min. A calibration curve was obtained with narrow molecular weight poly(ethylene oxide) standards. Viscosity measurements were made at 25.00 °C with a Cannon-Ubbelohde viscometer (75E 198). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on Perkin-Elmer System 7 instruments interfaced with a Perkin-Elmer Model 7500 computer. Thermal studies were conducted at a heating rate of 20 °C/min. Thermomechanical analysis (TMA) was performed on a Perkin-Elmer TMA 7 instrument interfaced with an IBM PS 2/model 55 SX computer. The extension probe was used to measure glass transition temperatures on polymer films under helium flow. Polymer films (1−1.2 mil thick) were cast from a solution of 0.08−0.1 g of polymer in 7−9 mL of DMF; the solvent was removed under vacuo (2−3 Torr) at room temperature, followed by heating at ~80 °C for 48 h and finally at ~95 °C for another 24 h.

Materials. Dimethylacetamide (DMAC), dimethyl sulfoxide (DMSO), and *N*-methylpyrrolidone (NMP) were stirred over anhydrous barium oxide for 48 h and distilled under reduced pressure. Dichloroethane and dichloromethane were stirred over calcium hydride and fractionally distilled. Tetrahydrofuran (THF) and dimethylformamide (DMF) were purchased from Aldrich as HPLC grade solvents. 4-(Dimethylamino)pyridine (DMAP) and 1,4-diazabicyclo[2.2.2]octane (DABCO) were sublimed under reduced pressure. Aniline and malononitrile were distilled prior to use. 4,4′-Diaminobenzanilide was obtained from Nobel Chemicals, Inc. and purified by column chromatography (silica gel, ethyl acetate). The remaining reagents were used as received from Aldrich.

4-Acetamido-4′-nitrodiphenyl Ether (7). 4-Acetamidophenol (50.00 g, 331.1 mmol) was dissolved in 200 mL of DMAC in a 1 L three-necked flask, which was fitted with a magnetic stirrer, a nitrogen inlet, and a Dean-Stark trap attached to a water-cooled condenser. To the flask, were added 200 mL of toluene and 18.5 g of 99.99% KOH pellets. The reaction mixture was heated to reflux, and 7 mL of water was removed azeotropically (Dean-Stark trap). Heating was continued until ~200 mL of toluene had been removed. The dark brown solution was cooled to ~40 °C. 1-Fluoro-4-nitrobenzene (34.95 g, 248 mmol) was added, and the reaction mixture was heated between 150 and 160 °C for 2 h. A yellow solid was obtained after the addition of 800 mL of 1 N NaOH to the cooled reaction mixture, and the product was air-dried for 5 days (60.6 g, 89.8%). The yellow solid was washed in ethyl acetate and purified by recrystallization from ethanol, mp 151−152 °C (lit.[24] 153 °C). ^{1}H NMR (DMSO-d_6): 2.04 (s, 3H, CH_3), [7.07, 7.22] (dd, 4H ortho to O, J = 9.3, 9.0 Hz, respectively), 7.67 (d, 2H ortho to NH−C=O, J = 9.0 Hz), 8.22 (d, 2H ortho to NO_2, J = 9.25 Hz), 10.06 ppm (s, 1H, amide H).

4-Acetamido-4′-aminodiphenyl Ether (8). **7** (20.00 g, 73.5 mmols) was dissolved in 200 mL of anhydrous ethanol in a dried 500 mL three-necked flask, equipped with a nitrogen inlet, a magnetic stirrer, and a water-cooled condenser. To the mixture was added 10% palladium/carbon (1.50 g), followed by anhydrous ammonium formate (20.00 g, 298 mmol) in a single portion. The reaction mixture was stirred for 1 h at room temperature, then heated between 50 and 60 °C for 6−7 h, and stirred for 18 h at room temperature. The catalyst was removed by gravity filtration, and addition of water to the filtrate gave an emulsion. An oily layer separated upon standing and formed a solid, mp 134 °C[25] by DSC, which was dried in vacuo (2−3 Torr) at 50 °C over P_2O_5 for 48 h (16.60 g, 93.3%). ^{1}H NMR (DMSO-d_6): 4.90 (s, 2H, NH_2), 6.66 (d, 2H ortho to NH_2), [7.75, 8.00] (dd, 4H ortho to O), 7.25 ppm (d, 2H ortho to NH−C=O).

1,4-Bis[2,2-dicyano-1-((4-(4-(acetylamino)phenoxy)phenyl)amino)vinyl]benzene (9). A dried 300 mL three-necked flask was equipped with a nitrogen inlet, a magnetic stirrer, and a water-cooled condenser connected to a mineral oil bubbler. The flask was charged with **8** (10.000 g, 41.3 mmol), DMAP (5.04 g, 41.3 mmol), and 200 mL of NMP. **1**[3,7,19] (6.178 g, 20.66 mmol) in $\sim$10 mL of NMP was added to the flask at room temperature. The reaction mixture changed to dark brown and gradually became yellow and cloudy. The reaction mixture was heated for 48 h at 70−75 °C and, upon cooling, was added to water to give a yellow precipitate. The crude product was air-dried and purified by recrystallization from NMP/acetone (13.05 g, 89.0%), mp 340 °C (DSC). MS (FAB): *m*/*e* 710 (M^+, 97). FT-IR: [3236, 3184] (NH), 3044 (br, aromatic C—H stretch), 2214 (CN), 1627 ($C{=}O$), 1522, 1500, 1402, 1370, 1230, 1014, 832 cm^{-1}. ^1H NMR (DMSO-d_6, 60 °C): 2.01 (s, 6H, CH_3) 6.92 (d, 8H ortho to O, $J = 8.8$ Hz), 7.2 (br, s, 4H meta to O), 7.54 (d, 4H meta to O, $J = 8.8$ Hz), 7.75 (s 4H ortho to $C{=}C(CN)_2$), 9.76 (s, 2H, amide H), 10.76 ppm (br, s, 2H, enaminonitrile H). ^{13}C NMR/HMQC (DMSO-d_6, 60 °C): ppm [169.0, 167.8] ($C{=}O$ and $C{=}C(CN)_2$), [156.0 151.0] (C—O), [135.2 (possibly two peaks), 132.5] (tertiary aromatic), 129.5 (C ortho to $C{=}C(CN)_2$), [127, 120.6] (C meta to O), [118.2, 118.8] (C ortho to O), [114.1, 116.6] (CN), 52.5 (wk, $C(CN)_2$), 23.8 (CH_3).

1,4-Bis[2,2-dicyano-1-((4-(4-aminophenoxy)phenyl)amino)vinyl]benzene (11). A dried 300 mL three-necked flask was fitted with a dropping funnel, a magnetic stirrer, and a reflux condenser. The flask was charged with **9** (3.28 g, 4.62 mmol) and 75 mL of 2-propanol. The reaction mixture was heated to reflux, and 50 mL of aqueous 20% HCl was added dropwise. The reaction mixture was refluxed for 48 h to obtain a homogeneous solution. The hot solution was filtered, cooled to room temperature, and neutralized with concentrated ammonium hydroxide to give a yellow precipitate. The yellow solid was filtered, washed with water and methanol, and air-dried overnight (2.21 g, 76.3%). The crude product was washed with acetonitrile/benzene (50/50) solution and purified by recrystallization from THF/chloroform. The product was dried in vacuo (0.2 Torr) at 100 °C over P_2O_5 for 48 h, melting point 304 °C (DSC, with decomposition). Alternatively, the diamine was purified by column chromtography (silica gel, eluting with progressively increasing solvent polarity (from 30 to 80% ethyl acetate/hexane). For best results, the diamine was coated on silica gel and applied to the top of the column prepared with 30% ethyl acetate/hexane as solvent. Fractions of 50 mL were collected and tested by TLC (silica gel, 75% ethyl acetate and visualized by short wavelength UV light and iodine). The diamine was present at $\sim 0.5 R_f$; byproducts and starting material were detected at R_f values of 0.75, 0.6, 0.4, and 0.2−0.3. MS (FAB): *m*/*e* 627 ($M^+ + 1$, 31). FT-IR: [3306, 3222] (NH_2), 2212 (CN), 1734, 1602, 1550, 1500, 1400, 1232, 834 cm^{-1}. ^1H NMR (DMSO-d_6, 65 °C): {(4.85, very broad singlet, 4H, NH_2); sharper peak at 22.0 °C (5.1 ppm)}, 6.58 (d, 4H ortho to NH_2, $J = 8.5$ Hz), [6.72, 6.80] (dd, 8H ortho to O, $J = 8.8$, 8.2, respectively), 7.14 (d, 4H ortho to $NH{-}C{=}C(CN)_2$, $J = 7.4$ Hz), 7.73 (s, 4H ortho to $C{=}C(CN)_2$), 10.5 ppm {(very broad singlet, 2H, enaminonitrile H); sharper peak at 22 °C (10.80 ppm)}. ^{13}C NMR (DMSO-d_6): 167.3 ($C{=}C(CN)_2$), 157.6 (C—O para to NH), 145.5 (possibly two overlapping peaks; $C{-}NH_2$ and C—O para to NH_2), [136.0, 131.4] (C—NH and $C{-}C{=}C(CN)_2$), 129.6 (C ortho to $C{=}C(CN)_2$), 127.2 (C ortho to NH), 120.6 (C meta to NH_2), 116.7 (C meta to NH), 114.8 (C ortho to NH_2), [114.5, 117.2] (CN), 52.0 ppm (wk, $C(CN)_2$). Anal. Calcd for $C_{38}H_{26}N_8O_2$: C, 72.77; H, 4.15; N, 17.88. Found: C, 72.25; H, 4.73; N, 16.37.

4-Amino-4′-nitrodiphenyl Ether. A 1 L three-necked flask was fitted with a magnetic stirrer, reflux condenser, and a dropping funnel. The flask was charged with **7** (13.00 g, 47.8 mmol) and ethanol (200 mL), and 20% HCl (240 mL) was added in 20 mL portions. The reaction mixture was refluxed for 3 h and then cooled to room temperature and neutralized with 4 N NaOH. The yellow precipitate was filtered out, washed well with water, and dried in vacuo (2−3 Torr) at 50 °C over P_2O_5 for 72 h (10.86 g, 98.7%), mp 137 °C (lit.[26] 134−135 °C). ^1H NMR spectroscopy showed only the product. ^1H NMR (DMSO-d_6): 5.15 (s, 2H, NH_2), 6.62 (d, 2H ortho to NH_2, $J = 8.8$ Hz), 6.84 (d, 2H meta to NH_2, $J = 8.6$), 7.00 (d, 2H meta to NO_2, $J = 9.3$ Hz), 8.19 ppm (d, 2H ortho to NO_2, $J = 9.1$ Hz). ^{13}C NMR (DMSO-d_6): 164.7 (C—O para to NO_2), 146.8 (C—O para to NH_2), 143.7 ($C{-}NO_2$), 141.5 ($C{-}NH_2$), 126.2 (C ortho to NO_2), [121.6, 116.2] (C ortho to O), 115.0 ppm (C ortho to NH_2).

***N,N*′-Bis(4-nitrophenyl)terephthalamide (13).** *p*-Nitroaniline (10.00 g, 72.5 mmol), DABCO (8.12 g, 72.5 mmol), and 200 mL of DMAC were mixed in a 500 mL, three-necked flask equipped with an argon inlet, a magnetic stirrer, and a water-cooled condenser. Terephthaloyl chloride (7.35 g, 36.2 mmol) was added as a solid to the yellow solution. The reaction mixture became cloudy, and the flask was warm to the touch. The reaction mixture was stirred at room temperature for 10 h, followed by heating between 75 and 80 °C for an additional 18 h. The cooled reaction mixture was added to 1 L of water to give a yellow precipitate, which was washed twice with water and then four times with methanol. The yellow solid was dried in vacuo (2−3 Torr) for 48 h over P_2O_5 at 90 °C (13.2 g, 90%). The crude product was purified by recrystallization from hot DMAC, followed by recrystallization from DMSO, mp 385 °C (DSC) (lit.[27] 367−368 °C, lit.[28] 353−355 °C, lit.[29] 291−293 °C). IR (KBr): [3408, 3322, 3288, 3266] (multiple bands of NH), 3122 (aromatic CH), 1662 ($C{=}O$), 1614, 1596, 1542 (NO_2), 1504, 1410, 1332 (NO_2), 1306, 1270, 1256, 1178, 1114, 894, 852 (C—N stretch), 752 cm^{-1}. ^1H NMR (DMSO-d_6, 70 °C): 8.07 (d, 4H, H meta to NO_2, $J = 9.3$ Hz), 8.14 (s, 4H, H ortho to $C{=}O$), 8.26 (d, 4H, H ortho to NO_2, $J = 9.3$ Hz), 10.8 ppm (br, 2H, NH). ^{13}C NMR (DMSO-d_6): 165.4 ($C{=}O$), 145.1 ($C{-}NO_2$), 142.8 (C—NH), 137.1 ($C{-}C{=}O$), 127.9 (C ortho to carbonyl group), 124.5 (C ortho to NO_2), 120.3 ppm (C meta to NO_2).

***N,N*′-Bis((4-(4-nitrophenoxy)phenyl)amino)isophthalamide (16).** A dried 500 mL three-necked flask was equipped with a nitrogen inlet, a magnetic stirrer, and a water-cooled condenser connected to a mineral oil bubbler. The flask was charged with 4-amino-4′-nitrodiphenyl ether (3.00 g, 13.04 mmol), DABCO (1.46 g, 13.0 mmol), and 100 mL of NMP. Isophthaloyl chloride (2.15 g, 7.2 mmol) was added as a solid to the flask, and the reaction mixture became cloudy yellow. The reaction mixture was heated for 24 h at 60 °C and, upon cooling, was added to water to give a yellow precipitate which was filtered out and washed well with methanol. The product was dried in vacuo (2−3 Torr) over P_2O_5 at 100 °C for 48 h (3.60 g, 94%), mp 216 °C (DSC). FT-IR: [3380, 3268] (br, NH), [3078, 3112] (possibly aromatic C—H stretch), [1658, 1646) (br, $C{=}O$), 1608, 1588, 1510 (br), 1487, 1406, 1344, 1242 (br), 1198, 1166, 1112, 1014, 880, 848, 748 cm^{-1}. ^1H NMR (DMSO-d_6, 60 °C): 7.13 (d, 4H meta to NO_2, $J = 9.0$ Hz), 7.19 (d, 4H meta to NH), 7.69 (t, 1H meta to $C{=}O$, $J = 7.5$ Hz), 7.91 (d, 4H ortho to NH), 8.16 (d, 2H para to $C{=}O$, $J = 7.5$ Hz), 8.23 (d, 4H ortho to NO_2, $J = 9.1$ Hz), 8.56 (s, 1H ortho to both $C{=}O$), 10.42 ppm (br, s, 2H, amide H). ^{13}C NMR (DMSO-d_6, 60 °C): 164.9 ($C{=}O$), 163.0 (C—O para to NO_2), 150.0 (C—O para to NH), 142.2 ($C{-}NO_2$), [136.4, 135.1] (C—NH and $C{-}C{=}O$), 130.4 (C para to $C{=}O$), 128.4 (C meta to $C{=}O$), 127.0 (C ortho to both $C{=}O$), 125.9 (C ortho to NO_2), 122.4 (C ortho to NH), 120.5 (C meta to NH), 117.1 ppm (C_3). Anal. Calcd for $C_{32}H_{22}N_4O_8$: C, 65.08; H, 3.73; N, 9.49. Found: C, 64.89; H, 3.85; N, 9.40.

***N,N*′-Bis(4-aminophenyl)terephthalamide (17).** **13** (8.50 g, 21 mmol) and 150 mL of DMAC were placed in a dried 500 mL three-necked flask, equipped with a nitrogen inlet, a magnetic stirrer, and a water-cooled condenser. To the mixture was added 10% palladium/carbon (1.50 g), followed by the addition of anhydrous ammonium formate (9.0 g, 143 mmol) in a single portion. The reaction mixture was stirred at room temperature for 3 h and then at 50−55 °C for 3 h, followed by 48 h at room temperature. The suspension was filtered to give a light yellow filtrate. Upon addition of water to the filtrate, only a small amount of product was recovered. The filtered catalyst, which appeared green (possibly coated with product), was air-dried for 2 days and washed with three 15 mL portions of warm DMSO. Addition of water to the DMSO filtrate gave a yellow precipitate (5.50 g, 76%). The crude product was purified by recrystallization from DMF and dried in vacuo (1−2 Torr) at 100 °C over P_2O_5 for 72 h, mp 310 °C (DSC, with decomposition) (lit.[27] 312 °C, lit.[11b] 275−277 °C). FT-IR (KBr): 3384 (NH), [3306, 3266] (NH_2), 1652 (C=O), 1604, 1540, 1514, 1430, 1322, 1258, 1118, 1016, 864, 826, 710 cm^{-1}. ^{1}H NMR (DMSO-d_6): 4.95 (s, 4H, NH_2), 6.54 (d, 4H, H ortho to NH_2, J = 8.6 Hz), 7.38 (d, 4H, H meta to NH_2, J = 8.6 Hz), 8.01 (s, 4H, central aromatic H), 9.99 ppm (s, 2H, NH). ^{13}C NMR (DMSO-d_6): 164.1 (*C*=O), 145.1 (*C*−NH_2), 137.6 (*C*−C=O), 128.0 (C para to NH_2), 127.5 (C ortho to C=O), 122.4 (C meta to NH_2), 113.8 ppm (C ortho to NH_2).

1,1′-Oxybis(4-((3-nitrobenzoyl)amino)benzene) (21). 4,4′-Diaminodiphenyl ether (5.10 g, 25.6 mmol) and DMAP (5.72 g, 51.1 mmol) were dissolved in 100 mL of DMAC in a 500 mL three-necked flask, equipped with a nitrogen inlet, a magnetic stirrer, and a water-cooled condenser. 3-Nitrobenzoyl chloride (9.48 g, 51.1 mmol) was added to the reaction mixture as a solution in 20 mL of DMAC. The reaction mixture changed to a dark yellow and appeared cloudy. The reaction mixture was stirred at room temperature for 13 h, followed by heating at 80 °C for 48 h. The cooled reaction mixture was precipitated in 1 L of distilled water and filtered, and the crude product was washed with methanol and acetone. The product was dried at 100 °C for 4 days in vacuo (2−3 Torr) over P_2O_5 to give 11.6 g (91%), mp 173 °C (DSC). FT-IR (KBr): [3288, 3270] (NH), 3120 (aromatic C−H), 1656 (C=O), 1528 (NO_2), 1500, 1404, 1352 (NO_2), 1320, 1254, 1220, 840, 716 cm^{-1}. ^{1}H NMR (DMSO-d_6): 7.04 (d, 4H ortho to O, J = 8.0 Hz), 7.7−8.0 (m, 6H (protons meta to O; proton meta or para to NO_2)), 8.3−8.6 (t, 4H (protons para to C=O; proton meta or para to NO_2)), 8.78 (s, 2H ortho to both NO_2 and C=O), 10.59 ppm (s, 2H, amide H). ^{13}C NMR (DMSO-d_6): 163.2 (C=O), 153.3 (C−O), 147.9 (C−NO_2), 136.4 (*C*−C=O), [134.4, 134.3] (C para to NO_2, C−NH), 130.3 (C meta to NO_2), 126.3 (C para to C=O), [122.4, 122.5] (C ortho to both NO_2 and C=O; C ortho to NH), 118.8 ppm (C ortho to O). Anal. Calcd for $C_{26}H_{18}N_4O_7$: C, 62.65; H, 3.64; N, 11.24. Found: C, 62.86; H, 3.64; N, 11.31.

1,1′-Oxybis(4-((3-aminobenzoyl)amino)benzene) (23). **21** (7.70 g, 15.5 mmol) and 100 mL of DMAC were placed in a dried 500 mL three-necked flask, equipped with an argon inlet, a magnetic stirrer, and a water-cooled condenser. To the mixture was added 10% palladium/carbon (1.00 g), followed by anhydrous ammonium formate (7.7 g, 115 mmol) in a single portion. The reaction mixture was stirred at room temperature for 6 h. The catalyst was removed by gravity filtration, and water was added to the light-brown filtrate to precipitate the product. Thee crude product was dried overnight at 100 °C in vacuo (2−3 Torr) over P_2O_5 to give a white solid (6.04 g, 89.2%), which was purified by recrystallization from DMF/ethanol and dried in vacuo (2−3 Torr) at 100 °C over P_2O_5 for 5 days, mp 232 °C (DSC). FT-IR (KBr): [3424, 3340, 3264] (NH_2, NH), 1638 (C=O), 1602, 1528, 1500, 1408, 1322, 1258, 1234, 830 cm^{-1}. ^{1}H NMR (DMSO-d_6): 5.30 (s, 4H, NH_2), 6.72 (d, 2H para to NH, J = 8.0 Hz), 6.97 (d, 4H ortho to O, J = 6.9 Hz), 7.04 (d, 2H para to NH_2, J = 7.8 Hz), 7.07 (s, 2H ortho to both NH_2), 7.12 (t, 2H meta to NH_2, J = 7.9 Hz), 7.74 (d, 4H ortho to NH), 10.07 ppm (s, 2H, amide H). ^{13}C NMR (DMSO-d_6): 164.4 (*C*=O), 152.8 (C−O), 148.9 (C−NH_2), 136.1 (*C*−C=O), 135.0 (C−NH), 128.9 (C meta to NH_2), 122.0 (C ortho to NH), 118.7 (C ortho to O), 116.9 (C para to C=O), 114.8 (C para to NH_2), 113.1 ppm (C ortho to both NH_2 and C=O). Anal. Calcd for $C_{26}H_{22}N_4O_3$: C, 70.75; H, 4.99; N, 12.99; O, 10.88. Found: C, 70.45; H, 5.34; N, 12.85; O, 10.95.

1,1′-Oxybis[4-((4-((2,2-dicyano-1-phenylvinyl)amino)benzoyl)amino)benzene] (39). A dried 100 mL three-necked flask was fitted with a nitrogen inlet, a magnetic stirrer, and a water-cooled condenser. **24** (0.500 g, 1.14 mmol), DABCO (0.128, 1.14 mmol), and NMP (15 mL) were added to the flask. (1-Chloro-2,2-dicyanovinyl)benzene (0.4292 g, 2.28 mmol) was added as a solid to the reaction mixture at room temperature. The reaction mixture was stirred at room temperature for 18 h, followed by heating to 70−80 °C for 6 h. The cooled reaction mixture was precipitated in water, filtered, and washed with methanol, and the yellow precipitate was dried in vacuo (2−3 Torr) at 100 °C over P_2O_5 for 24 h (0.611 g, 72.0%). The crude product was recrystallized from acetone. The product was difficult to purify; some diamine was detected by NMR that could not be separated from the starting products. No melting point was obvserved up to 350 °C by DSC; decomposition occurred by 350 °C. MS (FAB): *m/e* (no molecular ion peak was observed). FT-IR (KBr): [3350, 3220] (NH_2, NH), 2218 (CN), 1600, 1554, 1504, 1446, 1416, 1218, 846 cm^{-1}. ^{1}H NMR (DMSO-d_6): 6.99 (d, 4H ortho to O, J = 7.8 Hz), 7.24 (s, 4H ortho to NH), 7.45−7.70 (m, 10H (protons ortho, meta and para to C=C(CN)$_2$), 7.74 (d, 4H meta to O, J = 6.8 Hz), 7.88 (s, 4H ortho to C=O), 10.21 (s, 2H, amide H), 11.03 ppm (s, 2H, enamine H). ^{13}C NMR (DMSO-d_6): 168.4 (*C*=C(CN)$_2$), 164.4 (*C*=O), 153.0 (C−O), 141.1 (*C*−NH−C=C-(CN)$_2$), 134.7 (*C*−NH-C=O), 132.4 (C para to C=C(CN)$_2$), 132.0 (*C*−C=C(CN)$_2$ or *C*−C=O, possibly both are overlapping), 130.0 (C ortho to C=C(CN)$_2$), 129.0 (C meta to C=C(CN)$_2$), 128.4 (C ortho to C=O), 124.4 (C meta to C=O), 122.2 (C meta to O), 118.7 (C ortho to O), [116.7, 114.9] ppm (CN), not observed (*C*−CN).

Typical Procedure for Polymerizations (Polymer 29). (Detailed procedures for the preparation of the remaining polymers are reported in the Supporting Information.)

A 50 mL three-necked flask was equipped with a nitrogen inlet and outlet connected to a mineral oil bubbler, a water-cooled condenser, and a magnetic stirrer. The glassware was flame-dried under a flow of nitrogen, and cooled to room temperature. **15** (0.800 g, 2.312 mmol), DABCO (0.259 g, 2.31 mmol), and a 2.4% LiCl solution in DMAC (15 mL) were added to the flask. The clear brown solution was cooled to 4−8 °C in an ice bath. Monomer **1** (0.6913 g, 2.31 mmol) was added slowly as a solid in small increments over a period of ∼$^1/_2$ h. The viscosity increased slowly to give a hazy yellow soltion, and an additional 3 mL of solvent was added. The reaction mixture was allowed to reach room temperature, and an additional 10 mL of solvent was added gradually as the viscosity increased. The reaction mixture was stirred at room temperature for 2 h, followed by heating at 70−75 °C for an additional 20 h, cooled to room temperature, and precipitated dropwise in 900 mL of vigorously stirred water. The polymer particles were filtered, air-dried overnight, redissolved in ∼75 mL of DMF, and reprecipitated into vigorously stirred water. The fibrous polymer was dried in vacuo (3−4 Torr) at 100 °C over P_2O_5 for 3 days to give 1.18 g (89%). A yellow, fingernail creasable film was obtained from the polymer solution in DMF. T_g (TMA, second run, 10 °C/min) = 270 °C. FT-IR (film): 3264 (br, NH), 3070 (aromatic H), 2216 (CN), 1654 (br, C=O), [1576−1508] (br), [1490−1420] (br), 1308, 1244, 1100, 1000, 846, 788, 718, 692, 662 cm^{-1}. ^{1}H NMR (DMSO-d_6, 60 °C): 6.92 (br, s, 2H para to NH−C=O), 7.30 (br, 2H meta to NH−C=O), 7.61 (d, 2H para to NH−C(CN)$_2$), 7.64 (t, 1H meta to C=O), 7.83 (s, 4H ortho to C=C(CN)$_2$), 7.92 (s, 2H ortho to both NH), 8.14 (d, 2H para to C=O), 8.52 (s, 1H ortho to both C=O), 10.45 (s, 2H, amide H), 10.95 ppm (s, 2H, enamine H). ^{13}C NMR (DMSO-d_6, 60 °C): 166.7 (*C*=C(CN)$_2$), 165.1 (*C*=O), [139.5, 137.7] (C−NH), [135.5, 135.0] (C−C=C(CN)$_2$, *C*−C=O), 130.5 (C para to C=O), 129.7 (C ortho to C=C(CN)$_2$), 128.8 (C meta to NH), 128.4 (C meta to C=O), 126.9 (C ortho to both C=O), 120.5 (C para to NH−C=O), 118.6 (C para to NH−C=C(CN)$_2$), 116.6 (C ortho to both NH), 114.0 (CN), 53.2 ppm (*C*(CN)$_2$).

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Supporting Information Available: Detailed experimental procedures, NMR chemical shift assignments, and FTIR peak listings for **10**, **12**, **14**, **15**, **18**, **19**, **20**, **22**, **24**−**38**, **40**, and **41** (28 pages). Ordering information is given on any current masthead page.

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