Rigid-Rod Fully Aromatic Polyamides with Controlled Constitution: Synthesis and Some Properties

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ABSTRACT: The theory of constitutional isomerism in polycondensates was applied to rigid-rod fully aromatic polyamides. Polymers from terephthalic acid chloride and 2,6-dichloro-*p*-phenylenediamine, nitro-*p*-phenylenediamine, and methoxy-*p*-phenylenediamine with varying constitutional order ranging from ordered head-to-head/tail-to-tail constitution to statistical constitution were obtained in a one-stage synthesis. Constitutional order was calculated by using the relevant kinetic reaction parameters and monomer feed rates and also determined in some cases by ^{1}H NMR spectroscopy. A significant dependence of the solubility of the polymers on the constitutional order was found.

Introduction

Rigid-rod fully aromatic polyamides, usually containing only para-substituted aromatic moieties, represent a class of polymers of exceptional technological importance. Fibers obtained from nematic solutions of these polymers (aramids) are at present employed in a variety of applications where high mechanical strength and thermal resistance are required.[1] In some cases substituted fully aromatic polyamides are used.[2,3] However, introduction of substituents on the monomers, such that monomeric units become symmetrically nonequivalent, gives rise to constitutional isomerism of the resulting polymers. The effects of constitutional isomerism on these materials have not been investigated so far, nor have fully aromatic polyamides with well-defined constitutional regularity been synthesized to the present. In fact, the constitutional regularity of such fully aromatic polyamides is usually unknown. On the other hand, significant effects of constitutional isomerism on various macroscopic properties, such a crystallinity and solubility have been observed in several cases and can be expected to appear in these materials.[4,5]

The theory of constitutional isomerism in polycondensates as described in the preceding paper[6] is applied here to rigid-rod fully aromatic polyamides with substituted 1,4-phenylene moieties. In order to quantitatively describe the structural regularity in the chain, we used the parameter s, as defined previously:[6,7] s = probability for two adjacent, nonsymmetric units to point in the same direction, $0 \leq s \leq 1$. For details on this definition and related issues, see the preceding paper and references cited therein.[6]

Choice of Monomers

General Considerations. Maintaining all the advantageous properties of the best fully aromatic polyamides while being able to fully control the constitutional regularity in a one-step synthesis requires careful selection of the type of substituted monomer. The substituted monomers must meet two basic requirements: First, any softening of the amide linkage must be avoided; the rigidity of the amide bond is, together with the geometric persistence of the chains, the cause for the rigid-rod character of the fully aromatic polyamides, which in turn is the basis of their desirable properties. Second, substitution should lead to a marked difference in reactivity between the two reaction sites of the monomer. Computer modeling of the polymerization reaction indicated that r ($r = k_{aX}/k_{bX}$, see previous paper) should not exceed about 0.01 if control of the constitutional regularity over a satisfactory range of values for s should be possible. The latter objective could be met by substituting one of the nitrogens of the diamine monomer; however, reports of a substantial softening of the amide bonds made this seem impractical.[8-10] As substituted *p*-phenylenediamine monomers are generally more readily available and easier to synthesize than the corresponding terephthalic acids, we limited ourselves to substituted diamine monomers.

Kinetic Parameters. Two ratios of reaction rate constants determine largely the constitutional regularity of the polycondensates: r and g. The parameter r defines the reactivity ratio, k_{aX}/k_{bX}, of the slower reacting amino function relative to the faster reacting amino group. Approximate values were determined by competitive amidation of an excess of the diamine with benzoyl chloride, after rapid mixing. The quantitative ratio of the products reflects the kinetic ratio, r, of the functional groups. The reaction system was chosen as close as possible to polymerization conditions; the same solvent system (NMP/THF 10:1) and reaction temperature as in the polymerization was used (NMP stands for 1-methyl-2-pyrrolidone and THF for tetrahydrofuran). Benzoyl chloride was predissolved in THF and added rapidly to a solution of the amine in NMP. The product mixture was analyzed by using ^{1}H NMR spectroscopy with the following approximation. Schematically

$$\text{XabX} + \text{Yc} \rightarrow \text{XabX} + \text{cabX} + \text{Xabc} + \text{cabc} + \text{XY}$$

(X = –H, Y = –Cl, ab = $-NHC_6H_2RR'NH-$, c = $-OCC_6H_5$, so that XabX = diamine, Yc = benzoyl chloride, cabX & Xabc = monoamides, cabc = diamide, XY = HCl, and R and R′ designate the substituents to the ring: –H, –Cl, $-NO_2$, and $-OCH_3$). It can be shown that

$$r = \ln([\mathrm{B}]/[\mathrm{B}]_0)/\ln([\mathrm{A}]/[\mathrm{A}]_0) \quad (1)$$

$$r = \ln(1 - [\mathrm{P_b}]/[\mathrm{B}]_0)/\ln(1 - [\mathrm{P_a}]/[\mathrm{A}]_0) \quad (2)$$

where [A] and [B] are the concentrations of free amino groups on the unsubstituted and substituted termini of the 1,4-phenylene moieties, respectively, and $[\mathrm{P_a}]$ and $[\mathrm{P_b}]$ are the concentrations of the amide groups from the corresponding amino functions. The subscript zero indicates a concentration at the start of the reactions.

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Of course $[A]_0 = [B]_0$. For small extends of reaction the following approximation holds

$$r \approx [P_b]/[P_a] \tag{3}$$

The parameters g_a and g_b relate to the symmetric monomer. Parameter g_a defines the ratio of the reaction rate constants of the second reacting functional group on the symmetric monomer after the first functional group has reacted with an -aX group (the faster reacting group) to that of the first functional reacting group. The definition of g_b is analogous to that of g_a. Approximate values for these parameters were determined as follows: terephthalic acid chloride was reacted with ca. 0.5 equiv of (monofunctional) substituted aniline, the reaction was quenched after about 5 min with aqueous ammonia, and the resulting product mixture of unreacted, single-reacted, and double-reacted terephthalate was analyzed quantitatively by using ^{1}H NMR in a manner analogous to the above determination of r.

One absolute rate constant is also required for the specification of feed rates. k_{aX} is the rate constant of the faster reacting diamine group with the first acyl chloride group of terephthalic acid chloride. Values for k_{aX} were estimated experimentally by reacting benzoyl chloride with the corresponding substituted aniline, reacted under polymerization conditions. Pseudo-first-order reaction conditions were chosen by using a large excess of benzoyl chloride compared to the substituted aniline. In a typical experiment 10^{-4} mol of benzoyl chloride was added as a pure liquid to 100 mL of a 2×10^{-2} M solution of diamine in NMP/THF (10:1) with 5% LiCl w/w. The solution was shaken thoroughly, and the absorption at 520 nm was measured as a function of time. Kinetic constants for the reaction were calculated from the equation

$$k_{aX}[Yc]\,(t_i - t_1) = \ln\,(D_1 - D_\infty)/(D_i - D_\infty) \tag{4}$$

where [Yc] is the concentration of benzoyl chloride, t_1 is the time when measurement of absorption was started, D_1 is the absorption at time t_1, D_∞ is the absorption at the end of the reaction and D_i is the absorption at the time t_i. The values thus obtained were corrected for the effect of the additional -COCl group in the YccY monomer and the additional $-NH_2$ group in the XabX monomer using Hammet's equation with the following parameters:[11,12]

$$\sigma(-NH_2) = -0.66, \quad \sigma(-COCl) = 0.69, \quad \mu = -3.44$$

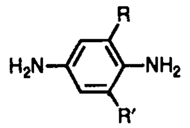
This procedure reduces, of course, the accuracy of the final values of k_{aX} in a manner not easily quantifiable. We conclude that values obtained are correct within $^1/_2$ an order of magnitude. This uncertainty is of little consequence for our results, however.

We report here on polymers from three different diamines: 2,6-dichloro-*p*-phenylenediamine, nitro-*p*-phenylenediamine, and methoxy-*p*-phenylenediamine. Table I shows the substituted monomers that were used with the kinetic characteristics determined as described above.

Polymerizations

The polymerization reaction must meet two basic requirements: (i) constitutional isomerism in the product must be fully controllable and (ii) sufficiently high molecular weight must be obtained to permit fiber spinning. Control of constitution requires effective control of the monomer feed rates; to this end, only homogenous reaction systems were considered. As the reaction system described in the literature yielding high molecular weight fully aromatic polyamides are all heterogeneous, we developed a new modification for our purposes. Terephthalic acid chloride was used as monomer for its high reactivity toward amines.

Table I
Kinetic Data for the Reaction Systems Investigated



substituent					
R	R′	$r \times 10^2$	k_{aX}, L mol^{-1} s^{-1}	g_a	g_b
-Cl	-Cl	9.2	2.9	0.50	0.10
$-NO_2$	-H	8.7	1.3×10^{-3}	0.57	0.25
$-OCH_3$	-H	9.0	4.0×10^3	0.60	0.25
estimated error		±5%	±50%	±5%	±5%

As with all amidation reactions the choice of solvent was found to be critical for obtaining high molecular weight polymers. Several amides were tested as solvents for their high solvating power and their ability to bind hydrochloric acid, which is formed in the reaction. Best results were obtained by using *N*-ethylpyrrolidone (NEP). The other amides tested were *N*-methylpyrrolidone (NMP), tetramethylmethylphosphoramide (TMMP), and hexamethylphosphoramide (HMP), which gave all lower molecular weight polymers. This could be attributed to a side reaction of these amides with terephthalic acid chloride, which has been reported before.[13] Decomposition experiments of terephthalic acid chloride in the solvents considered showed that this reaction was slowest in NEP. Use of a solvent mixture of NEP/THF (tetrahydrofuran) further markedly slowed down the reaction of the acid chloride with the solvent. A ratio of NEP/THF of about 10:1 by volume proved to be optimal. Increasing the amount of THF lead to precipitation of the polymers in an early stage of the reaction, while reducing it increased the side reaction. A possible explanation for this behavior is a preferential solubilization of the acid chloride by THF, which "protects" the monomer from reacting with NEP. Addition of dry lithium chloride to the reaction solution from the beginning of the reaction also increased the polymers' molecular weights.

In order to minimize decomposition of the acid chloride, it was predissolved in pure THF and added to a solution of diamine in NMP with about 5% w/w LiCl. The overall monomer concentration also turned out to be an important factor for achieving high molecular weights. Concentrations used in the syntheses lie probably close to the optimal values. Increasing the concentration causes the formation of unstirrable gels or even precipitation of the polymers very early in the course of the reaction, while reducing the concentration diminishes the polymerization rate considerably. In both cases side reactions become more prominent compared to the polymerization, decreasing the molecular weights.

Characterization and Properties

Determination of Constitutional Regularity, *s*. Expected values for the structural order parameter, *s*, were calculated by the methods described in ref 6 for all polymers synthesized using the kinetic parameters summarized in Table I and the monomer feed rates applied. Figure 1 shows curves as calculated values of *s* as a function of feed rates of terephthalic acid chloride to the reaction mixture for the poly(2,6-dichloro-1,4-phenyleneterephthalamide) (dichloro polymer, CP), poly(nitro-1,4-phenyleneterephthalamide) (nitro polymer, NP), and poly(methoxy-1,4-phenyleneterephthalamide) (methoxy poly-

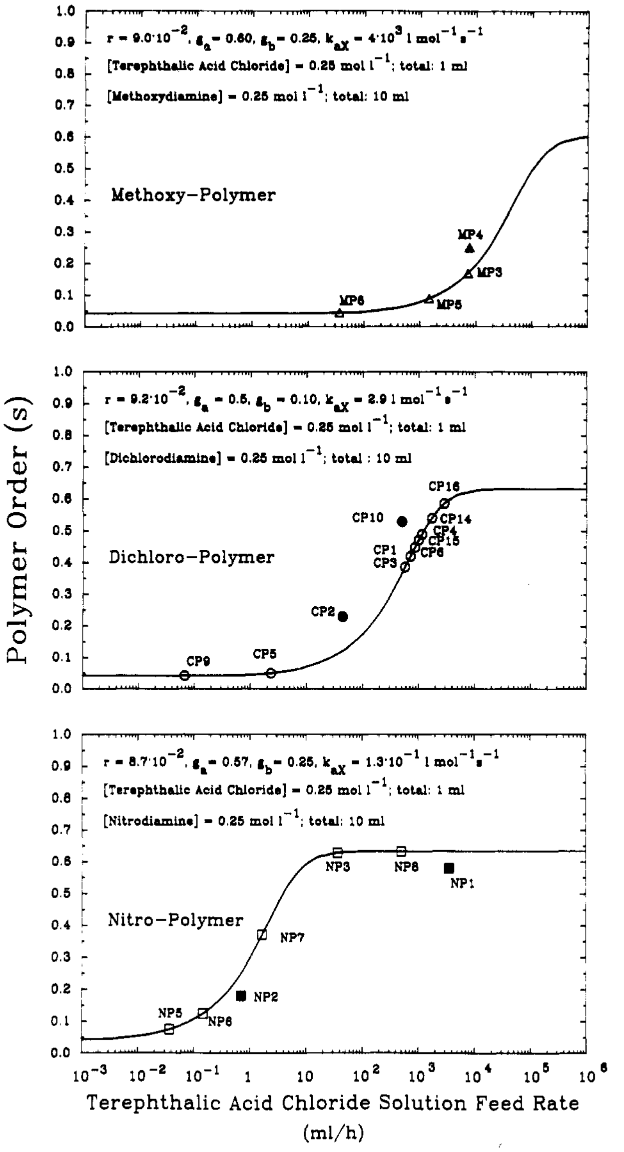


Figure 1. Polymer order, s, versus feed rate of terephthalic acid chloride, YccY, to diamine, XabX. Open symbols represent calculated values of s; filled symbols represent values determined by ^{1}H NMR spectroscopy.

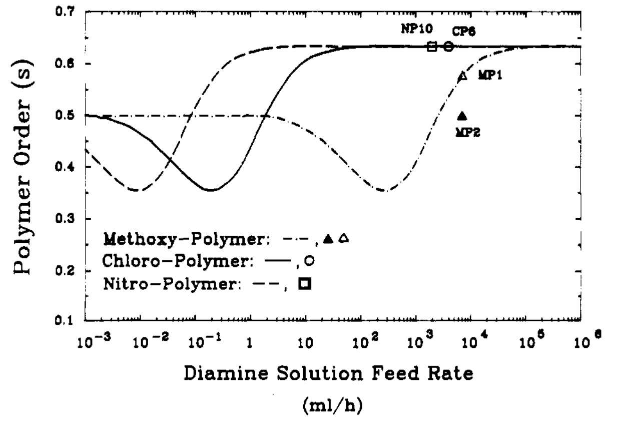


Figure 2. Polymer order, s, versus feed rate of diamine solution. Open symbols represent calculated values of s; filled symbols represent values determined by ^{1}H NMR spectroscopy.

mer, MP) compounds synthesized. Figure 2 shows calculated values of s as a function of the monomer feed rate for the inverted addition mode in which the diamine solution is added to the terephthalic acid solution. This addition mode is only feasible with fast addition rates as the polymer formed is only slightly soluble in THF-rich solvent mixtures. For the lower molecular weight polymers s could be determined directly by using ^{1}H NMR. Figure 3 shows the 360-MHz ^{1}H NMR of a methoxy polymer together with spectra of the "trimeric" model compounds. In the amide region four peaks can be observed. Comparison with the spectra of the "trimeric" model compounds indicates that the peaks correspond to the three possible, distinguishable substructures -acca-, -accb-, and -bccb- present in the polymer. Peak integration yielded estimates for the values of the parameter s. All polymers synthesized are indicated in Figures 1 and 2 by symbols; in all cases, open symbols represent values for s estimated from the feed rates, while filled symbols indicate values for s determined by NMR.

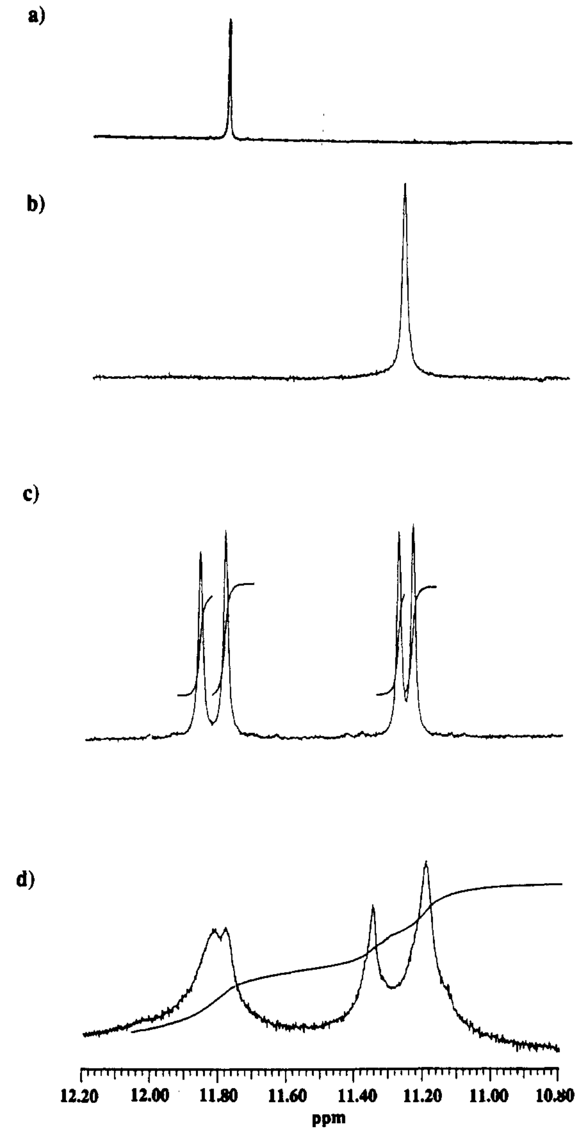


Figure 3. 360-MHz ^{1}H NMR, amide region in dimethyl-d_6 sulfoxide at 80 °C: (a) *N,N'*-bis(2,6-dichlorophenyl)benzene-1,4-diamide (1), (b) *N,N'*-bis(3,5-dichlorophenyl)benzene-1,4-diamide (2), (c) mixture of 1 and 2 and *N*-(2,6-dichlorophenyl)-*N'*-(3,5-dichlorophenyl)benzene-1,4-diamide, (d) polymer CP2.

Molecular Size Properties. Solution viscometry experiments were performed on all polymers synthesized in order to obtain information about their molecular weight. Size-exclusion chromatography experiments allowed us to draw conclusions about the molecular weight distribution of the polymer samples. In essence, these experiments show that the polymers obtained exhibit M_w/M_n ratios close to the expected theoretical value of 2, which

Table II
Polymer Characteristics

polymer code	constitution[a]	viscosity[b] $(\ln \eta_{rel})/c$, dL/g	M_w/M_n[c] (SEC)	M_n[d] (VPO)	elem anal. C	H	N	Cl
Poly(methoxy-1,4-phenyleneterephthalamide) (MP)								
MP1	N*	1.9	2.1	5600	67.09	4.61	10.23	
MP2	N*, $s = 0.5$	0.50	2.02	1840	67.55	4.45	10.29	
MP3	R	0.89	1.55	3900	68.65	4.12	10.11	
MP4	I, $s = 0.3$	1.92	2.2	5500	67.88	4.11	11.12	
MP5	R	2.48	2.2	6000	66.88	4.07	11.13	
MP6	R	3.12			67.51	4.13	10.89	
				theoretical	67.16	4.51	10.44	
Poly(2,6-dichloro-1,4-phenyleneterephthalamide) (CP)								
CP1	N	0.50	1.4	2000	54.43	2.66	9.13	24.02
CP2	I, $s = 0.23$	0.48	1.5	1800	54.22	2.12	9.18	23.22
CP3	N	3.51	2.1	7700	54.43	2.25	9.13	22.08
CP4	N	4.51			54.89	2.22	9.17	23.19
CP5	N	1.12	1.6	3700	54.14	2.78	9.11	23.18
CP6	N*	0.77	1.55	2700	54.78	2.12	9.89	23.09
CP9	R	1.86	1.9	4900	54.77	2.66	9.18	22.09
CP10	N, $s = 0.53$	0.51	1.67	1700	54.11	2.79	9.12	23.74
CP13	R	3.82			54.49	2.67	9.13	23.18
CP14	N	5.68			54.76	2.11	9.14	22.49
CP15	N	3.54	2.1	7900	54.43	2.78	9.11	23.09
CP16	N	2.49	2.1	5700	55.13	2.91	9.87	22.22
				theoretical	54.75	2.63	9.12	23.09
Poly(nitro-1,4-phenyleneterephthalamide) (NP)								
NP1	N, $s = 0.52$	0.50	1.6	1800	58.71	3.16	14.23	
NR2	R, $s = 0.18$	0.62	1.7	2100	58.45	3.13	14.22	
NP3	N	2.55	2.1	6200	59.21	3.18	14.84	
NP5	R	1.72	1.8	5100	59.11	3.46	14.19	
NP6	R	2.49			59.20	3.15	14.00	
NP7	I	2.65			58.21	3.38	14.86	
NP8	N	3.55			59.59	3.11	14.12	
NP10*	N	2.97	2.1	7100	58.81	3.58	14.34	
				theoretical	59.37	3.20	14.84	

[a] Where possible, actual s measurements are listed, else the codes N, I, and R refer to nonregular ($s \approx 0.50$), intermediate ($0 < s < 0.5$), and regular ($s \rightarrow 0$) polymers, respectively, and are assigned on the basis of monomer feed rates. The polymers marked with an asterisk were obtained by rapid addition of the diamine monomer to the terephthalic acid chloride monomer; in all other cases the terephthalic acid chloride was added to the diamine. [b] All viscometry experiments were performed at $c = 0.05 \pm 0.005$ g/dL in 96% sulfuric acid at 25 ± 0.1 °C in a constant-temperature water bath with a size 200 Cannon–Fenske viscometer. [c] Size-exclusion chromatography (SEC) experiments were performed on a Model 2133 Hewlett Packard apparatus using three silica gel columns with pore sizes of 100, 1000, and 10 000 Å. Dimethylformamide (DMF) was used as solvent. SEC experiments could only be performed on those samples sufficiently soluble in DMF. Molecular weight distributions (M_w/M_n ratios) were calculated according to the method used by Collins et al.[14] A universal calibration curve was determined by using polystyrene standards, and M_w values were then calculated with values for the Mark–Houwink constants K and a for poly(p-phenyleneterephthalamide) published by Arpin and Strazielle.[15] Other experiments, not reported here, indicate that the Mark–Houwink exponents a for these polymers are very similar to the one for poly(p-phenyleneterephthalamide). [d] VPO experiments were performed on a Wescan Model 233 using DMF as solvent at 90 °C. The osmometer was calibrated with sucrose acetate and "monodisperse" polystyrene standards in DMF at 90 °C. Generally only the sufficiently soluble, low molecular weight samples were analyzed.

confirms the assumption that the polymerization conditions are homogeneous. On some samples vapor phase osmometry (VPO) experiments were also performed, giving values for the number-average molecular weight, M_n. In Table II the results of these experiments together with elemental analysis data of the samples are summarized.

Solubilities and Thermal Behavior. Solubilities of the polymers (i.e., the maximum amount of sample giving an apparently homogeneous solution) synthesized were measured by suspending a sample in the solvent for 2 days at constant temperature and determining the amount dissolved thereafter. In two cases the viscosities of the polymer dissolved and the residues was measured and compared to the viscosity of the original sample to test for decomposition or preferential dissolution of lower molecular fractions, but no significant difference could be found. In Figure 4 the solubility values obtained are shown with the corresponding inherent viscosities for the polymers synthesized. As expected the solubility depends on the molecular weight of the polymers with samples having higher molecular weight exhibiting lower solubilities compared to analogous samples with lower molecular weight. In addition, a marked increase in solubility with decreasing order, s, in polymers with similar molecular weight can be observed. This can be rationalized by assuming better packing of the ordered chains in the solid state.

Thermal properties of a regular and a nonregular methoxy polymer and dichloro polymer were evaluated by differential scanning calorimetry (DSC). Polymer samples were dried at $T = 150$ °C and $p < 1$ mmHg for 2 days prior to the experiments. Samples were scanned under a nitrogen atmosphere at 10 °C/min up to 500 °C. All scans gave essentially straight base lines; no signs of degradation could be observed. Structural isomerism does not affect the thermal behavior of the polymers, at least in the temperature range observed.

Conclusions

It has been illustrated by the synthesis of poly(2,6-dichloro-1,4-phenyleneterephthalamide), poly(nitro-1,4-phenyleneterephthalamide), and poly(methoxy-1,4-phenyleneterephthalamide) that constitutional isomerism in fully aromatic polyamides prepared in a one-stage polycondensation reaction with nonsymmetric monomers can

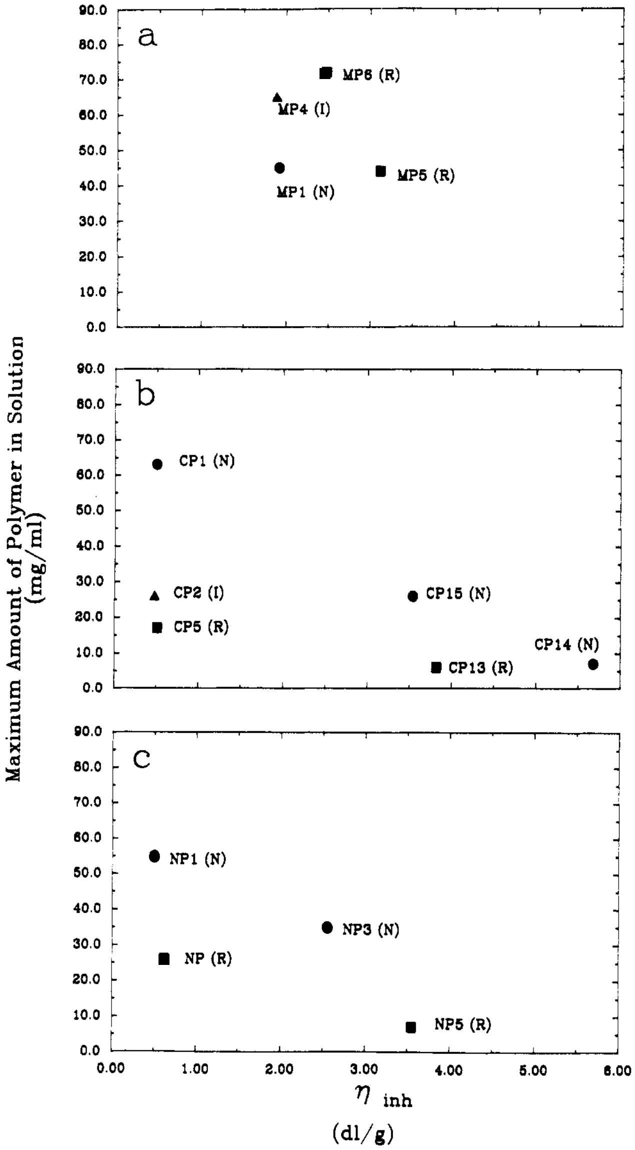


Figure 4. Maximum amount of polymer in solution versus inherent viscosity ($\eta_{inh} = (\ln \eta_{rel})/c$ at $c = 0.5$ g/dL) for the polymer systems investigated: (a) poly(methoxy-1,4-phenyleneterephthalamide) in NMP containing 5% w/w LiCl at 80 °C; (b) poly(2,6-dichloro-1,4-phenyleneterephthalamide) in NMP containing 5% w/w LiCl at 80 °C; (c) poly(nitro-1,4-phenyleneterephthalamide) dissolved in DMF containing 5% w/w LiCl at 80 °C. Data points are labeled as in Table II. Constitutional regularity is indicated by the following: N, nonregular; I, intermediate; R, regular (i.e., of the head-to-head/tail-to-tail type).

be controlled over a continuous range. Given a particular system, constitutional regularity can be controlled between limits set by the reaction kinetics through the mode of addition and feed rates of the monomers. The range of constitutional regularity achieved spans values for highly regular head-to-head/tail-to-tail polymers ($s \rightarrow 0.005$) and polymers with a moderate excess of head-to-tail structure ($s \approx 0.65$). In several cases the constitutional regularity (i.e., the parameter s) was determined experimentally by ^{1}H NMR spectroscopy and was found to be in agreement with predictions. The thermal behavior of the substituted, fully aromatic polyamides seems to be independent of constitutional regularity and falls within the ranges found for similar polymers by other researchers. Characterization of the polymers prepared revealed that, as expected, solubility decreased with increasing molecular weight and also that solubility is strongly influenced by the constitutional regularity. This effect is apparently independent of the polymer/solvent system.

Investigations of the solution behavior of these polymers will be reported in a subsequent paper.

Experimental Section

Purification of Monomers. The monomers used were all available commercially but required further purification before use. After the compounds were purified all manipulations were carried out in an argon atmosphere by using a VAC/ATMOSPHERES glovebox and vacuum-line techniques to avoid contamination with air moisture.

Benzoyl chloride (Fluka Chemicals Co., puriss. p.a.) was used without further purification. Purity was checked by ^{1}H NMR; no impurities could be detected.

Terephthalic acid chloride, reagent grade (Fluka Chemicals Co.), was purified by double sublimation at 85 °C at $p = 30$ mmHg. Purity was checked by melting point (137 °C) and ^{1}H NMR.

Nitro-*p*-phenylenediamine (Aldrich Chemical Co.; 1.2 g of raw material) was chromatographed on an ACE Glass 60 cm × 4.5 cm prep-scale column packed with Kieselgel 60 obtained from EM Science. As the solvent system, acetone/dichloromethane (3:2) was used. The main fraction was then sublimed at 100 °C and $p < 1$ mmHg. About 500 mg of monomer with a melting point of 138.5 °C was thus obtained.

2,6-Dichloro-*p*-phenylenediamine, reagent grade (97%; Polyscience Chemical Co.), was purified by double sublimation at 85 °C and $p < 1$ mmHg. Purity was checked by melting point (125 °C) and ^{1}H NMR.

Methoxy-*p*-phenylenediamine. The compound was purchased from Aldrich Chemical Co. in its sulfate form. A total of 750 mg of material was converted into the free amine by reacting them with 1 equiv of potassium hydroxide in water. After the water was evaporated, the material was dried for about 1 day in a desiccator at room temperature and $p = 30$ mmHg and subsequently sublimed at 110 °C and $p < 1$ mmHg. Purity was checked by melting point (157 °C) and ^{1}H NMR. The monomer is very sensitive to light and air.

Polymerizations. In the following some typical polymerizations are described. All manipulations were carried out under inert gas by using vacuum-line technique. The solvents were refluxed over calcium hydride for 2 days and then distilled twice.

Polymer NP10, Immediate Mixing. A total of 530 mg (2.61 mmol) of terephthalic acid chloride was dissolved in 1 mL of THF containing ca. 150 mg of dried LiCl (vacuum oven dried for 24 h at 90 °C) and added to a solution of 0.4 g (2.61 mmol) of nitro-*p*-phenylenediamine dissolved in 5 mL of *N*-ethylpyrrolidone (NEP) containing ca. 150 mg of LiCl at 0 °C under vigorous stirring. After 15 min the temperature was raised to about 20 °C. After about 5 h the solution formed an unstirrable gel. At that point another 5 mL of NEP was added, and the solution was stirred mechanically for another 3 days at room temperature. The solution was then precipitated into a cold water bath under vigorous stirring; the precipitate was thereafter suspended in water at 80 °C for 40 min and then dried in a vacuum oven at 75 °C for 1 day. A total of 700 mg of brown-red material (95% of theoretical yield) was thus obtained. ^{1}H NMR (400 MHz): δ 10.8–11.0 (br), 10.3–10.5 (br), 7.0–8.8 (br m). ^{13}C NMR (67.5 MHz, with LiCl): δ 163.5, 161.0, 135, 136, 134, 125–130 (m), 117–120 (m).

Polymer NP11, Constant Addition. A total of 400 mg (1.97 mmol) of terephthalic acid chloride was reacted with 302 mg (1.97 mmol) of nitro-*p*-phenylenediamine in a completely analogous way to the reaction described above with the following exceptions: The terephthalic acid chloride solution was transferred to a 5-mL syringe with a glass Luer-Lock tip connected to a 10-cm-long Teflon tube. The syringe was placed on a Sage syringe pump (Model 235), and the Teflon tube was lowered inside the nitro-*p*-phenylenediamine solution. During the entire addition time (about 4 h), the reaction temperature was maintained at room temperature.

Polymer CP3, Immediate Mixing. A total of 410 mg of 2,6-dichloro-*p*-phenylenediamine (2.32 mmol) was reacted with 1 equiv of terephthalic acid chloride analogously to the synthesis of polymer NP10. The reaction yielded after purification 712 mg of off-white material (85% of theory). ^{1}H NMR (360 MHz, with LiCl): δ 11.0 (br s), 10.8 (br s), 9.5 (br), 7.0–8.0 (br m). ^{13}C NMR (67.5 MHz, with LiCl): δ 165.5, 165.0, 139, 136, 134, 125–130 (m), 119–121 (m).

Polymer MP5, Immediate Mixing. A total of 400 mg (2.90 mmol) of methoxy-*p*-phenylenediamine was reacted with 1 equiv of terephthalic acid chloride analogously to the synthesis of polymer NP10. The reaction yielded, after purification, 660 mg of material (78% of theory). Purification of this compound is particularly important as even small residual amounts of unreacted monomer catalyze decomposition of the polymer. ^{1}H NMR (300 MHz, with LiCl): δ 10.60 (br s), 9.34 (br s), 8.25 (s, 1 H), 8.05 (m, 2 H), 7.81 (m, 2 H), 7.56 (s, 1 H), 3.89 (s, 1 H). ^{13}C NMR (75.47 MHz, with LiCl): δ 164.50, 152.20, 137.90, 136.7, 128.9, 128.1, 125.3, 122.1, 112.1, 104.7, 55.7.

Model Compounds for NMR Peak Assignments. In the following a synthesis for one model compound is described. The other models were obtained analogously.

***N,N′*-Bis(2-nitrophenyl)benzene-1,4-diamine**: 500 mg (3.62 mmol) of 2-nitroaniline was added at once to 0.5 mol equiv (768 mg) of terephthalic acid chloride in about 10 mL of NEP at room temperature. The reaction mixture was stirred for another 2 h at room temperature and was then poured into 150 mL of cold water. The precipitate formed was filtered off and then recrystallized from DMSO. A total of 333 mg (82% of theory) was thus obtained. ^{1}H NMR (200 MHz, with LiCl): δ 10.94 (2 H, s), 8.13 (4 H, br s), 8.04 (2 H, d, J = 8 Hz), 7.50–7.78 (4 H, m), 7.40–7.53 (2 H, m). ^{13}C NMR (50.32 MHz, with LiCl): δ 165.13, 144.36, 136.45, 133.99, 131.51, 128.76, 126.37, 125.03. Mp: 275 °C.

Important data on some other models synthesized are shown below, some of the species were not isolated as pure compounds and mp's, etc., were not obtained.

***N,N′*-Bis(3-nitrophenyl)benzene-1,4-diamide**: ^{1}H NMR (200 MHz, with LiCl): δ 11.8 (2 H, s), 9.0 (2 H, br), 8.48 (2 H, dd, J_1 = 8.6 Hz, J_2 = 2 Hz), 8.30 (4 H, 3), 7.89 (2 H, dd, J_1 = 8.4 Hz, J_2 = 2 Hz), 7.63 (2 H, t, J = 8.4 Hz). ^{13}C NMR (50.32 MHz, with LiCl): δ 165.46, 147.99, 140.69, 136.77, 129.83, 128.29, 126.99, 118.89, 115.01. Mp: 388 °C dec.

***N*-(2-Nitrophenyl)-*N′*-(3-nitrophenyl)benzene-1,4-diamide**: ^{1}H NMR (200 MHz, with LiCl): δ 11.9 (1 H, s), 10.8 (1 H, s).

***N,N′*-Bis(2-methoxyphenyl)benzene-1,4-diamide**: ^{1}H NMR (200 MHz, with LiCl): δ 10.20 (2 H, s), 8.18 (4 H, s), 7.62 (2 H, dd, J_1 = 8.5 Hz, J_2 = 2 Hz), 7.10–7.31 (4 H, m), 6.98 (2 H, dt, J_1 = 8.5 Hz, J_2 = 2 Hz), 3.98 (6 H, s). ^{13}C NMR (50.32 MHz, with LiCl): δ 164.7, 159.3, 140.1, 137.4, 129.4, 127.6, 112.5, 109.3, 106.0, 54.9. Mp: 250 °C.

***N,N′*-Bis(3-methoxyphenyl)benzene-1,4-diamide**: ^{1}H NMR (200 MHz, with LiCl): δ 11.30 (2 H, s), 8.3 (4 H, s), 7.72–7.80 (2 H, m), 7.6–7.7 (2 H, m), 7.28 (2 H, t, J = 8 Hz), 6.70 (2 H, dd, J_1 = 9 Hz, J_2 = 2 Hz). ^{13}C NMR (50.32 MHz, with LiCl): δ 164.2, 152.3, 136.6, 127.6, 126.4, 126.2, 125.4, 120.0, 111.5, 55.7.

***N*-(2-Methoxyphenyl)-*N′*-(3-methoxyphenyl)benzene-1,4-diamide**: ^{1}H NMR (200 MHz, with LiCl): δ 11.35 (1 H, s), 10.25 (1 H, s).

***N,N′*-Bis(2,6-dichlorophenyl)benzene-1,4-diamide**: ^{1}H NMR (200 MHz, with LiCl): δ 10.82 (2 H, s), 8.17 (4 H, s), 7.60–7.65 (4 H, m), 7.38–7.47 (2 H, m). ^{13}C NMR (50.32 MHz, with LiCl): δ 164.5, 136.3, 134.1, 133.0, 129.5, 128.5, 127.9, 48.5. Mp: 355 °C.

***N,N′*-Bis(3,5-dichlorophenyl)benzene-1,4-diamide**: ^{1}H NMR (200 MHz, with LiCl): δ 10.99 (2 H, s), 8.11 (4 H, s), 7.92 (4 H, d, J = 1.9 Hz), 7.37 (2 H, t, J = 1.9 Hz). ^{13}C NMR (50.32 MHz, with LiCl): δ 165.1, 141.4, 137.2, 134.0, 127.7, 123.0, 118.8, 48.5. Mp: 360 °C.

***N*-(2,6-Dichlorophenyl)-*N′*-(3,5-dichlorophenyl)benzene-1,4-diamide**: ^{1}H NMR (200 MHz, with LiCl): δ 11.04 (1 H, s), 10.87 (1 H, s).

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References and Notes

(1) Reisch, M. S. *MRS Bull.* **1987**, *Nov 16/Dec 31*, 22.

(2) Morgan, P. W. *Macromolecules* **1977**, *10*, 1381.

(3) Kwolek, S. L. U.S. Patent, 3,671,542, 1972.

(4) Pino, P.; Lorenzi, G. P.; Suter, U. W.; Casartelli, P. G.; Steinmann, A.; Bonner, F. J.; Quiroga, J. A. *Macromolecules* **1978**, *11*, 624.

(5) Steinmann, A.; Arber, A.; Schmucki, M.; Suter, U. W.; Lorenzi, G. P.; Pino, P. *Int. Symp. Macromol. Chem., Strasbourg, Prepr. 1*, **1981**, *103* and references cited therein.

(6) Gentile, F. T.; Meyer, W. R.; Suter, U. W., preceding paper in this issue.

(7) Suter, U. W.; Pino, P. *Macromolecules* **1984**, *17*, 2248.

(8) Tsvetkov, V. N.; Koton, M. M.; Shtennikova, I. N.; Lavrenko, P. N.; Peker, T. V.; Okatova, O. V.; Novakowskii, V. B.; Nosova, G. I. *Polym. Sci. USSR* **1979**, *21*, 1883.

(9) Preston, J. *J. Polym. Sci., Polym. Chem. Ed.* **1966**, *4*, 529.

(10) Preston, J.; Krigbaum, W. R.; Asrar, J. *Copolymerization and Polymers with Chain-Ring Structures*; ACS Symposium Series 195; American Chemical Society: Washington, DC, 1982; p 351.

(11) *Handbook of Organic Chemistry*: McGraw-Hill Book Co.: New York, 1987.

(12) The values used are an average of the values obtained by using the kinetic data on amidation reactions of benzoyl chloride with aromatic amines published by: Verkataraman, H. S.; Hinshelwood, C. *J. Chem. Soc.* **1960**, 4977.

(13) Herlinger, H.; Hoerner, H. P.; Druschke, F.; Knoell, H.; Haiber, F. *Angew. Macromol. Chem.* **1973**, *29/30*, 229.

(14) Collins, E.; Bares, M.; Billmeyer, H. *Experiments in Polymer Science*; John Wiley & Sons: New York, 1973.

(15) Arpin, M.; Strazielle, C. *Polymer* **1977**, *18*, 591.

Registry No. NP (copolymer), 76523-09-6; NP (SRU), 26098-26-0; MP (copolymer), 76523-08-5; MP (SRU), 76558-77-5; CP (copolymer), 64925-43-5; CP (SRU), 37357-28-1; $\mathrm{O_2NC_6H_4}$-*o*-$\mathrm{NHCOC_6H_4}$-*p*-$\mathrm{CONHC_6H_4}$-*o*-$\mathrm{NO_2}$, 750-11-8; $\mathrm{O_2NC_6H_4}$-*m*-$\mathrm{NHCOC_6H_4}$-*p*-$\mathrm{CONHC_6H_4}$-*m*-$\mathrm{NO_2}$, 34062-85-6; $\mathrm{O_2NC_6H_4}$-*m*-$\mathrm{NHCOC_6H_4}$-*p*-$\mathrm{CONHC_6H_4}$-*o*-$\mathrm{NO_2}$, 130954-42-6; $\mathrm{MeOC_6H_4}$-*m*-$\mathrm{NHCOC_6H_4}$-*p*-$\mathrm{CONHC_6H_4}$-*m*-OMe, 6957-81-9; $\mathrm{MeOC_6H_4}$-*m*-$\mathrm{NHCOC_6H_4}$-*p*-$\mathrm{CONHC_6H_4}$-*o*-OMe, 130954-43-7; $\mathrm{ClCOC_6H_4}$-*p*-COCl, 100-20-9; *N,N′*-bis(3,5-dichlorophenyl)terephthalamide, 130954-44-8; *N*-(2,6-dichlorophenyl)-*N′*-(3,5-dichlorophenyl)terephthalamide, 130954-45-9; 2-nitroaniline, 88-74-4; nitro-*p*-phenylenediamine, 5307-14-2; 2,6-dichloro-*p*-phenylenediamine, 609-20-1; methoxy-*p*-phenylenediamine, 5307-02-8; *N,N′*-bis(2,6-dichlorophenyl)terephthamide, 130954-46-0; benzoyl chloride, 98-88-4.