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Acetylene-Substituted Aromatic Polyamides: Curable Systems

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ABSTRACT: 2,6-Di-*n*-alkynyl-*p*-phenylenediamines were prepared from *p*-aminoacetanilide in a three-step synthesis. Low-temperature solution polycondensation in *N*-methyl-2-pyrrolidone of these novel monomers with 2,5-alkoxy-substituted terephthalic acid dichlorides yielded aromatic polyamides containing two acetylenic side groups per repeating unit. These polymers were highly soluble in common organic solvents, e.g., $CHCl_3$, toluene, and tetrahydrofuran (THF). The polymers were characterized by NMR, UV, and FTIR spectroscopy and DSC, TGA, and GPC measurements. Liquid-crystalline phases were not observed using DSC and the polarizing microscope. The polyamides were partially crystalline and showed no glass transition, as was verified by dielectric relaxation measurements. Curing of a transparent polymer film for several hours at 200 °C under an argon atmosphere resulted in an insoluble but still fully transparent film. This was due to inter- and intramolecular reactions of the acetylenic side chains. These reactions were followed by means of FTIR and UV spectroscopy.

Introduction

Stiff main-chain polymers, for example, fully aromatic polyesters and polyamides, are of interest because of their good mechanical and thermal stability. Many of the originally unsubstituted aromatic polyamide polymers proved to be infusible and also insoluble in common solvents. By introduction of lateral substituents,[1-9] it was possible to yield meltable polymers that were soluble in solvents such as chloroform, toluene, or tetrahydrofuran. Some of these substituted aromatic polyamides containing two, four, or six alkyl chains per repeating unit showed thermotropic, liquid-crystalline behavior.[5-12] In addition to overcoming the solubility and meltability problems, the introduction of lateral substituents offers the possibility to incorporate functional groups into fully aromatic polyamides. These reactive centers may allow the combination of the mechanical properties of stiff polymers with other properties such as ease of processing and curing, which facilitate their application. The introduction of a reactive center also may offer the possibility of further modifying an easily processable, soluble polymer by means of polymer analogue reactions after initial processing. This well-known principle is, for example, realized in the processing of formaldehyde resins by curing of fusible, soluble prepolymers in a mold to yield infusible resins. The first attempts to apply this principle to fully aromatic polyamides were realized by curing of aromatic polyamides containing phenylethnyl side groups fixed to a terephthalic acid moiety.[13] Heating of a pellet of the polymer for 16 h at 250 °C under a nitrogen atmosphere yielded a very stiff, thermally stable polymer.

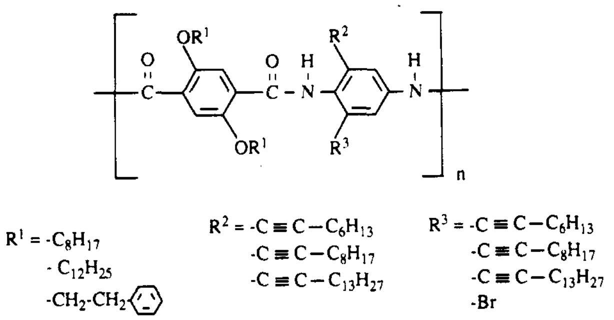

Figure 1. Formulas of the synthesized polyamides.

In connection with our investigations of highly substituted aromatic polyamides,[7-12] we synthesized alkyne-substituted polyamides of the structure shown in Figure 1.

This paper reports the synthesis, characterization, and curing experiments of these functionalized aromatic polyamides.

Results and Discussion

Monomer Synthesis. (a) **The disubstituted terephthalic acid dichlorides 3a–c** (see Table I) were synthesized using a modification of a literature procedure:[6]

Diethyl 2,5-dihydroxyterephthalate was alkylated twice by Claisen esterification with an excess of the correspond-

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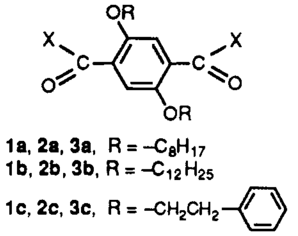
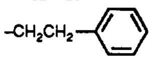
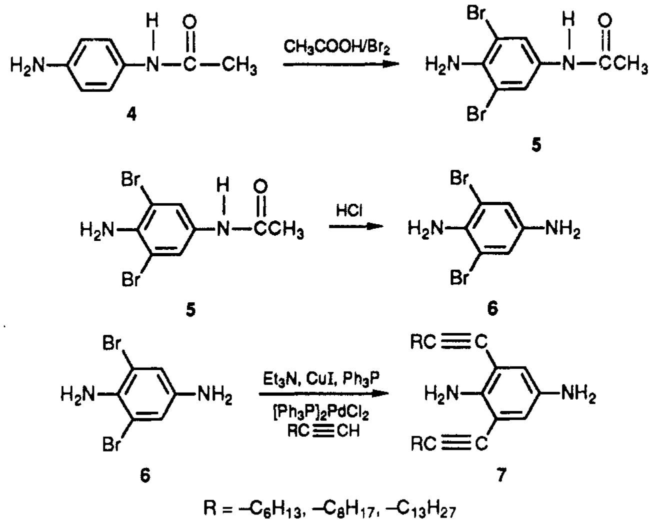
Table I
Yields and Melting Points of the Terephthalic Acid Derivatives



R =	X = -OC$_2$H$_5$ (1a-c) yield, %	-OC$_2$H$_5$ (1a-c) mp, °C	-OH (2a-c) yield, %	-OH (2a-c) mp, °C	-Cl (3a-c) yield, %	-Cl (3a-c) mp, °C
$-C_8H_{17}$	77	57[6]	97	126[8]	79	43[8]
$-C_{12}H_{25}$	97	50	94	129[8]	91	62[8]
	88	59	40	124	85	104

Scheme I
Synthetic Route to 2,6-Disubstituted *p*-Phenylenediamines



ing alkyl bromide to the diethyl 2,5-dialkoxyterephthalates **1a-c**. Saponification of **1a-c** with 30 wt % aqueous potassium hydroxide yielded the free 2,5-dialkoxyterephthalic acids **2a-c**. For the synthesis of diester **1c**, ethanol had to be added to the reaction mixture to enhance the solubility of **1c** in order to attain complete saponification to the diacid **2c**.

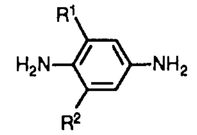
The diacyl chlorides **3a-c** were obtained by dissolving the free acids **2a-c** in a large excess of thionyl chloride and refluxing the solutions for several hours. Yields and melting points of the resulting products are given in Table I.

(b) **Alkyne-substituted *p*-phenylenediamines** were obtained according to the synthetic route shown in Scheme I.

Starting from *p*-aminoacetanilide (**4**), 3,5-dibromo-*p*-aminoacetanilide (**5**) was synthesized by bromination of **4** with a mixture of bromine and acetic acid.[14]

Because purification of either **4** or **5** was achievable only in small amounts and with great difficulty, the crude product **5** was used in the subsequent step. Cleavage of the acetyl group was achieved by refluxing the crude acetanilide **5** with a great excess of concentrated hydrochloric acid. The diamine **6** precipitated from the filtered reaction mixture on rendering the solution alkaline. Diamine **6** was purified by vacuum sublimation of the dried precipitate.

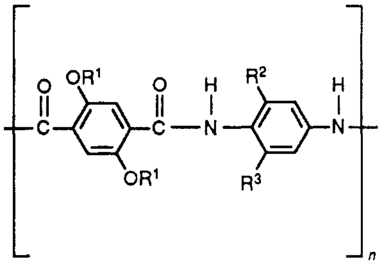
Table II
Yields and Melting Points of Alkyne-Substituted *p*-Phenylenediamines

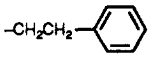
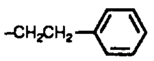
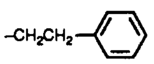


monomer	mp, °C	yield,[b] %
7a, $R^1 = R^2 = -C{\equiv}CC_6H_{13}$	[a]	60
7b, $R^1 = R^2 = -C{\equiv}CC_8H_{17}$	[a]	72
7c, $R^1 = R^2 = -C{\equiv}CC_{13}H_{25}$	37	51
8, $R^1 = -C{\equiv}CC_{13}H_{25}$ $R^2 = -Br$	60	15

[a] The product was obtained as oil. [b] For the last step in Scheme I.

Table III
List of the Polyamides 9-18



polyamide	$-R^1$	$-R^2$	$-R^3$
9		$-C{\equiv}CC_6H_{13}$	$-C{\equiv}CC_6H_{13}$
10		$-C{\equiv}CC_8H_{17}$	$-C{\equiv}CC_8H_{17}$
11		$-C{\equiv}CC_{13}H_{27}$	$-C{\equiv}CC_{13}H_{27}$
12	$-C_8H_{17}$	$-C{\equiv}CC_6H_{13}$	$-C{\equiv}CC_6H_{13}$
13	$-C_8H_{17}$	$-C{\equiv}CC_8H_{17}$	$-C{\equiv}CC_8H_{17}$
14	$-C_8H_{17}$	$-C{\equiv}CC_{13}H_{27}$	$-C{\equiv}CC_{13}H_{27}$
15	$-C_{12}H_{25}$	$-C{\equiv}CC_6H_{13}$	$-C{\equiv}CC_6H_{13}$
16	$-C_{12}H_{25}$	$-C{\equiv}CC_8H_{17}$	$-C{\equiv}CC_8H_{17}$
17	$-C_{12}H_{25}$	$-C{\equiv}CC_{13}H_{27}$	$-C{\equiv}CC_{13}H_{27}$
18	$-C_{12}H_{25}$	$-C{\equiv}CC_{13}H_{27}$	-Br

The 2,6-dibromo-*p*-phenylenediamine (**6**) was alkynylated to the *p*-phenylenediamines **7a-c** and **8** by use of the C-C coupling principle.[15-17] An aryl-alkynyl coupling can be achieved in high yields when aryl halogens react with monosubstituted acetylenic compounds in the presence of palladium(II) compounds. The reaction may be carried out with or without cuprous(I) salt catalysis and must be run in the presence of bases (for example, tertiary amines). Here a mixture of copper(I) iodide, triphenylphosphine, and bis(triphenylphosphine)palladium(II) chloride was used as a catalyst. From these compounds, the catalytic active species of tetrakis(triphenylphosphine)palladium(0) was formed.[17]

The crude products were purified by means of flash chromatography. The yields and melting points of the resulting monomers are given in Table II.

Polymer Synthesis and Characterization. The polyamides **9-18** (Table III) were synthesized via low-temperature solution polycondensation of the diamines **7a-c** and **8** with the terephthalic acid dichlorides **3a-c** in *N*-methyl-2-pyrrolidone. All polymers were easily soluble in chloroform, toluene, and tetrahydrofuran. This high solubility is due to the 4-fold alkyl substitution per repeating unit of the polyamides and probably to the incor-

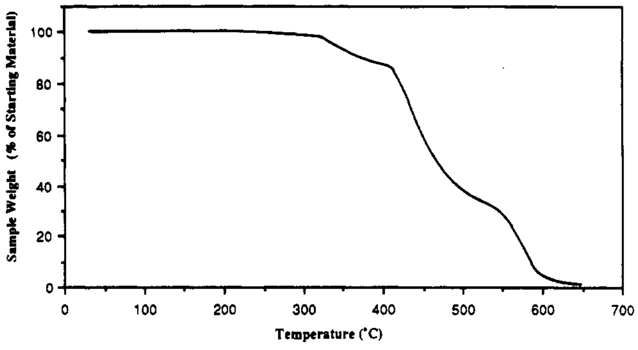


Figure 2. TGA plot of polyamide 17 (heating rate 10 K/min).

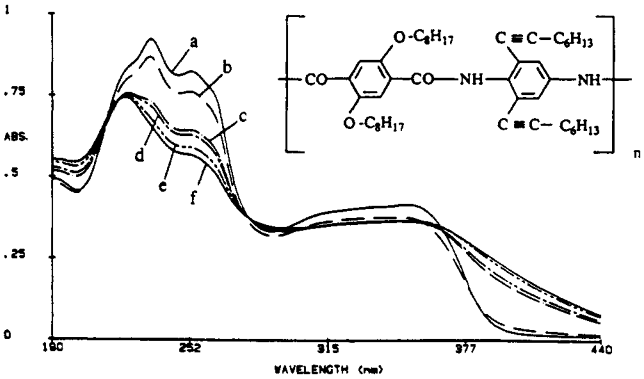


Figure 3. Dependence of the UV spectra of a cast film of polymer 13 on the time of curing at 200 °C: a, original film; b, 2 h at 200 °C; c, 6 h; d, 18 h; e, 30 h; f, 40 h.

poration of the unsymmetrical diamine monomers, which leads to the formation of internal copolymers corresponding to the two possible orientations of the substituted diamines. The polyamides were characterized by ^{1}H NMR and FTIR spectroscopy, elementary analysis, and GPC, TGA, and DSC measurements.

Curing Experiments. The polyamides 9–18 show a high thermal stability in thermogravimetric analysis. A significant weight loss only starts above 300 °C when heating polymer samples at a rate of 10 K/min under a nitrogen atmosphere (see Figure 2).

For the curing experiments, films of polymer 13 were cast from chloroform solutions on sodium chloride plates for FTIR spectroscopic investigations and on quartz plates for UV spectroscopy. The resulting films were heated for several hours at 200 °C under an argon atmosphere. After cooling to room temperature, UV and FTIR spectra were taken of the polymer films.

The resulting UV spectra are shown in Figure 3 and the FTIR spectra in Figure 4. At wavelengths longer than 370 nm the absorption increases with longer curing times. Simultaneously, the color of the sample changes from nearly colorless to yellow. Between 370 and 280 nm the absorption at first decreases but remains constant after 6 h of curing.

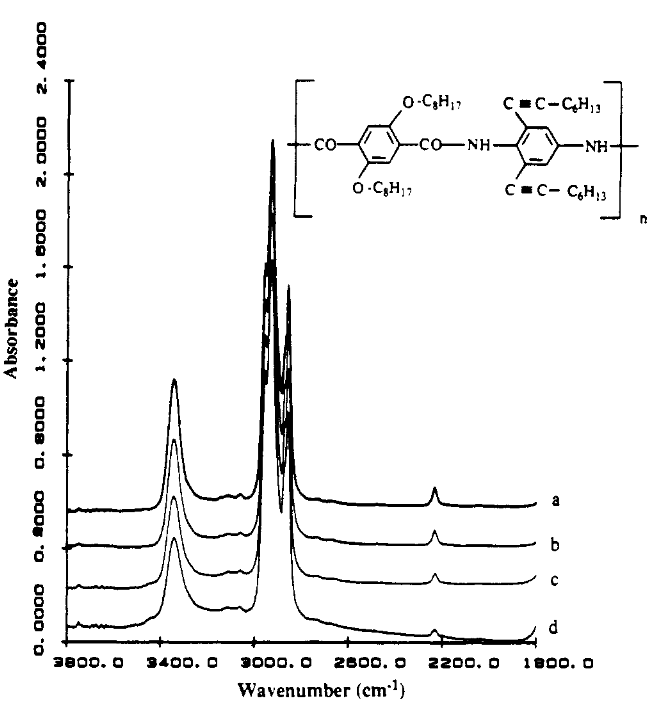


Figure 4. IR spectra of a cast film of polymer 13 cured at 200 °C: a, original film; b, 8 h; c, 18 h; d, 26 h.

Scheme II
Intramolecular Cyclization Reaction on Curing of Alkyne-Substituted Aromatic Polyamides

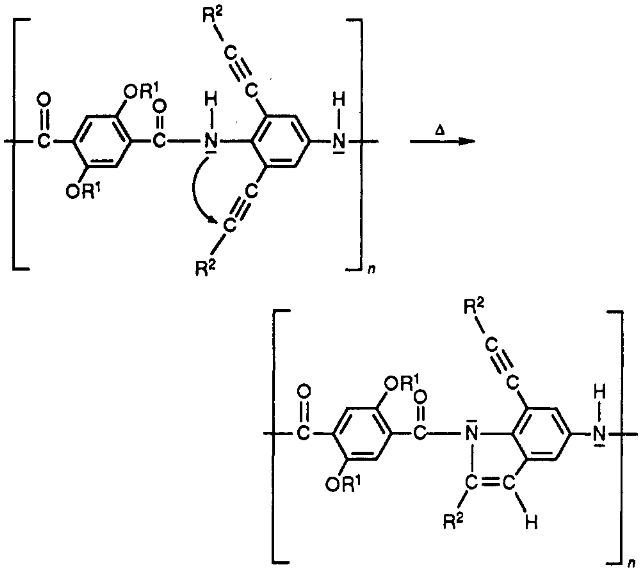


Table IV
Integrals of Characteristic IR Bands after Different Curing Times of a Cast Film of Polymer 13

	integral of the IR bands after different curing times			
IR band (cm^{-1})	0 h	8 h	18 h	26 h
NH (3343.7)	34.3	28.8	22.9	19.2
C≡C (2231.2)	1.81	1.43	0.91	0.52
C-H (2800–3000)	116.3	114.7	104.3	90.8

The behavior in the region between 280 and 210 nm is interesting. Here, a concerted reaction seems to be responsible for the decrease of the absorption. This is indicated by the appearance of two isosbestic points at 217 and 278 nm. The absorption in this region is due to the extension of the π-electron system of the polymer backbone and the alkyne side chains. The thermal treatment leads to a reduction of the conjugated system. This can be explained by an intramolecular cyclization reaction leading to the formation of indole units (see Scheme II). This process has been described for low molecular model compounds.[18] An intermolecular reaction of the acetylene units is also possible. This leads to a cross-linking of the polyamides. That this intermolecular process occurs is supported by their insolubility in organic solvents after curing. The high degree of cross-linking is also confirmed by the fact that the cured polymers show very broad (approximately 100 K) transitions in DSC, which is due to the melting of the alkyl side chains. The maxima of these transitions appear at the same temperatures as in the uncured polymers. The cured polymer films stay transparent. These temperature-induced

Table V
Sum Formulae, Elemental Analyses, Phase Transitions, and Molecular Weights of the Synthesized Polyamides 9–18

polyamide (formula of the repeating unit)		elem anal.				phase transition, K	M_n	M_w	polydispersity
		C %	H %	N %	Br %				
9 ($C_{46}H_{50}N_2O_4$)	calc	79.54	7.21	4.03		466.5	22 754	96 700	4.2
	found	78.87	7.19	4.36			(41 000)		
10 ($C_{50}H_{58}N_2O_4$)	calc	80.00	7.73	3.73		358.6	14 112	49 900	3.5
	found	78.74	7.92	3.36					
11 ($C_{60}H_{78}N_2O_4$)	calc	80.90	8.76	3.15		417.2	11 286	102 000	9.0
	found	80.03	8.90	3.19					
12 ($C_{46}H_{66}N_2O_4$)	calc	77.75	9.30	3.94		386.3	24 803	126 000	5.1
	found	76.30	9.36	3.66			(20 000)		
13 ($C_{50}H_{74}N_2O_4$)	calc	78.33	9.66	3.66		373.1	22 045	67 300	3.0
	found	77.64	9.97	3.58					
14 ($C_{60}H_{78}N_2O_4$)	calc	79.47	10.37	3.09		360.9	26 234	153 000	5.8
	found	79.14	10.32	3.14					
15 ($C_{54}H_{82}N_2O_4$)	calc	78.83	9.98	3.41		370.0	23 686	157 000	6.6
	found	78.11	10.21	3.24					
16 ($C_{58}H_{90}N_2O_4$)	calc	79.27	10.25	3.19		405.4	22 585	90 000	4.0
	found	79.21	10.24	3.05					
17 ($C_{68}H_{110}N_2O_4$)	calc	80.16	10.81	2.75		369.8	8 293	124 000	15
	found	79.70	11.02	2.86					
18 ($C_{53}H_{83}BrN_2O_4$)	calc	71.39	9.32	3.14	8.97	478.2	8 367	38 400	4.6
	found	72.19	9.64	3.21	8.73				

reactions can be described as nucleophilic attack of the amide nitrogen on the triple bond leading to the formation of an indole structure in the polymer backbone. A similar reaction can take place between two different polymer chains, yielding the described network structure of the cured polymer films. Thermally induced intermolecular reactions between alkyne groups may also account for some of the cross-linking.

The discussed mechanisms of the curing process were also followed by FTIR spectroscopy. The resulting IR spectra are shown in Figure 4.

On heating, the absorbances of the N–H bond at 3344 cm^{-1} and of the C–C triple bond at 2231 cm^{-1} decrease. This can be followed quantitatively by integration of the absorption bands as shown in Table IV.

On interpreting these data, one has to take into account that the intensity of an absorption band does not only depend on the content of the corresponding functional group but also very strongly upon the conjugation with other π-systems, as for example with the C–C triple bond.

The simultaneous decrease in intensity of the N–H band with the decrease in intensity of the absorption due to the C–C triple bond is consistent with both the intra- and the intermolecular reaction shown in Scheme II.

The curing experiments as described for the thin films were also performed with a powder of polymer **14**. This leads to a brittle, dark violet material with a metallic appearance. Powder conductivity measurements did not indicate that a conducting material resulted from curing. Due to the cross-linking, as described for the thin films, this cured polyamide was absolutely insoluble.

Experimental Part

Diethyl 2,5-Dialkoxyterephthalates 1a–c.[6] A total of 0.02 mol of diethyl 2,5-dihydroxyterephthalate and 0.4 mol of the corresponding alkyl bromide were dissolved in 100 mL of dry acetone. After addition of 0.3 mol of powdered K_2CO_3 and 0.004 mol of KI, the mixture was refluxed until no more starting material could be detected by TLC. The hot reaction mixture was filtered and the residue thoroughly washed with 100 mL of hot acetone. The acetone and the excessive alkyl bromide were distilled off the combined filtrates. The pale yellow residue, which solidified on cooling, was then recrystallized from ethanol to yield the pure diethyl 2,5-dialkoxyterephthalates **1a–c**.

^{1}H NMR of **1c** ($CDCl_3$, 400 MHz): δ 1.33–1.37 (t, J = 7 Hz, $-CH_3$; 6 H), 3.10–3.14 (t, J = 7 Hz, $-CH_2C_6H_5$; 4 H), 4.19–4.22 (t, J = 7 Hz, $-OCH_2CH_2-$; 4 H), 4.31–4.37 (q, J = 7 Hz, $-CH_2CH_3$; 4 H), 7.20–7.32 (m, ArH, $-C_6H_5$; 2 H + 10 H).

^{13}C NMR of **1c** ($CDCl_3$, 100.6 MHz): δ 14.24 ($-CH_3$), 35.79 ($C_6H_5CH_2-$), 61.25 ($-OCH_2CH_3$), 70.76 ($-OCH_2-$), 116.88–129.02 ($-CH_2CH_2C_6H_5$; C_{ar}H), 138.04 (C_{ar}COOEt), 151.61 ($C_{ar}OCH_2-$), 165.70 ($-C$OOEt).

2,5-Dialkoxyterephthalic Acids 2a–c.[6] A total of 0.014 mol of diethyl 2,5-dialkoxyterephthalates **1a–c** was refluxed for 4 h with a solution of 0.5 mol of KOH in 100 mL of water. The free acids **2a–c**, which precipitated on acidifying the reaction mixture with HCl, were collected by filtration and recrystallized from 120 mL of ethanol to yield the 2,5-dialkoxyterephthalic acids **2a–c** as white crystals. In the case of diethyl 2,5-bis[(2-phenylethyl)oxy]terephthalate (**1c**), a solution of 0.5 mol of KOH in a 1/3 mixture of ethanol/water was used instead of pure aqueous KOH to get complete saponification.

^{1}H NMR of **2c** ($CDCl_3$, 400 MHz): δ 3.08–3.19 (tt, J = 7 Hz, $-CH_2C_6H_5$; 4 H), 4.17–4.49 (tt, J = 7 Hz, $-OCH_2-$; 4 H), 7.20–7.36 (m, ArH, $-C_6H_5$; 2 H + 10 H).

^{13}C NMR of **2c** ($CDCl_3$, 100.6 MHz): δ 35.55 ($C_6H_5CH_2-$), 71.05 ($-OCH_2-$), 116.96–129.06 ($-CH_2CH_2C_6H_5$; C_{ar}H), 137.15 (C_{ar}COOH), 151.58 ($C_{ar}OCH_2-$), 164.85 ($-C$OOH).

2,5-Dialkoxyterephthalic Acid Dichlorides 3a–c. A total of 0.015 mol of the terephthalic acids **2a–c** was dissolved in 50 mL of thionyl chloride upon the addition of 3 drops of DMF. The mixture was stirred overnight and then refluxed for 4 h. Excess thionyl chloride was distilled off, and the solidified residue was recrystallized twice from dry hexane under an argon atmosphere to yield the dichlorides **3a–c** as yellow needles.

^{1}H NMR of **3c** ($CDCl_3$, 400 MHz): δ 3.1–3.2 (t, $-CH_2C_6H_5$; 4 H), 4.2–4.3 (t, $-OCH_2-$; 4 H), 7.2–7.35 (m, $-C_6H_5$; 10 H), 7.43 (s, ArH; 2 H).

^{13}C NMR of **3c** ($CDCl_3$, 100.6 MHz): δ 35.60 ($C_6H_5CH_2-$), 71.00 ($-OCH_2-$), 117.25–129.16 ($-CH_2CH_2C_6H_5$; C_{ar}H), 137.47 (C_{ar}COCl), 151.01 (C_{ar}COCl), 163.40 ($-C$OCl).

3,5-Dibromo-*p*-aminoacetanilide (5). Starting from *p*-aminoacetanilide (**4**), the dibromide **5** was obtained following the literature procedure of bromination with a mixture of bromine and acetic acid.[14]

2,6-Dibromo-*p*-phenylenediamine (6). A total of 18 g of the crude dibromide **5** were suspended in 150 mL of concentrated hydrochloric acid and refluxed for approximately 2 h, until no starting material could be detected by TLC. After the reaction had gone to completion, the mixture was diluted with a 4-fold amount of water. The residue was filtered off and washed thoroughly three times with 100 mL of 2 N HCl. The combined dark violet filtrates were rendered alkaline with aqueous KOH, whereupon the free diamine **6** precipitated and was filtered off. After drying, the crude diamine was purified by vacuum sublimation [100 °C (0.05 Torr)] to yield the 2,6-dibromo-*p*-phenylenediamine (**6**) as colorless plates.

2,6-Di-1-alkynyl-*p*-phenylenediamines 7a–c. The following reactions were carried out with the usual precautions for rigorous exclusion of air and moisture. The chemicals were purified prior to use. Triethylamine was refluxed with phthalic acid anhydride for 4 h and distilled over CaH_2. $Cu^{I}I$ was purified according to a literature procedure.[19] Triphenylphosphine was recrystallized first from methanol and then from hexane. All reactions were carried out under an argon atmosphere.

A total of 15 mmol of 2,6-dibromo-*p*-phenylenediamine (**6**) was suspended in 60 mL of dry triethylamine, and then 0.4 mmol of bis(triphenylphosphine)palladium(II) chloride, 1.6 mmol of $Cu^{I}I$, 4 mmol of triphenylphosphine, and 36 mmol of 1-alkyne were added. The reaction mixture was then heated to gentle boiling. The reaction was followed by TLC (solvent: $CHCl_3$/MeOH = 25/1). The disubstituted *p*-phenylenediamines **7a–c** can be recognized by their blue fluorescence on irradiation with UV light of 366-nm wavelength. When the dibromo-*p*-phenylenediamine (**6**) and the initially formed monosubstituted product had disappeared in the TLC, the reaction was stopped by adding 50 mL of diethyl ether. In a separating funnel an extra 50 mL of ether was added before washing the ethereal solution twice with water. The ether phase was dried with $MgSO_4$, and the diethyl ether was removed. The crude products were purified by flash chromatography with a $CHCl_3$/MeOH mixture (25/1).

^1H NMR of **7a** ($CDCl_3$, 400 MHz): δ 0.84–0.87 (t, J = 7 Hz, $-CH_3$; 6 H), 1.25–1.38 (m, $H_3C(CH_2)_2-$; 8 H), 1.38–1.50 (m, $-C{\equiv}CCH_2CH_2CH_2-$; 4 H), 1.50–1.65 (m, $-C{\equiv}CCH_2CH_2-$; 4 H), 2.3–2.4 (t, J = 7 Hz, $-C{\equiv}CCH_2-$; 4 H), 3.0–4.6 (sehr breit, $-NH_2$; 4 H), 6.6 (s, Ar*H*; 2 H).

^{13}C NMR of **7a** ($CDCl_3$, 100.6 MHz): δ 14.0 ($-CH_3$), 19.6–31.3 ($-(CH_2)_5-$), 77.0 ($ArC{\equiv}C-$), 95.6 ($ArC{\equiv}C-$), 109.4 ($C_{ar}C{\equiv}C-$), 119.1 ($C_{ar}H$), 136.7 ($C_{ar}NH_2$, ortho to the alkyne substituents), 142.3 ($C_{ar}NH_2$).

2-Bromo-6-pentadecynyl-*p*-phenylenediamine (8). The monosubstituted diamine **8** was obtained by stopping the alkylation reaction of dibromo-*p*-phenylenediamine (**6**) with pentadec-1-yne before complete conversion to the dialkynylated diamine **7c**. The products were separated by flash chromatography.

^{13}C NMR of **8** ($CDCl_3$, 100.6 MHz): δ 14.0 ($-CH_3$), 19.6–31.3 ($-(CH_2)_5-$), 76.8 ($ArC{\equiv}C-$), 109.3 ($C_{ar}C{\equiv}C-$), 118.46 ($C_{ar}H$, ortho to the bromine substituent), 119.85 ($C_{ar}H$, ortho to the alkyne substituent), 137.97 ($C_{ar}NH_2$, ortho to the alkyne substituent), 138.3 ($C_{ar}NH_2$).

Polyamides 9–18. For the low-temperature polycondensation of the monomers in *N*-methyl-2-pyrrolidone (2-NMP), the solvent was dried and purified by distillation over CaH_2 using a 75-cm column.

A solution (10 wt %) of the diamine monomer **7a–c** and **8** (0.8 mmol) in 2-NMP and a solution (10 wt %) of the acid chloride **3a–c** (0.8 mmol) in 2-NMP were injected with a syringe through a rubber septum in the nitrogen-purged reaction flask. The resulting solution was stirred for 2 days at 50 °C under a nitrogen atmosphere, and the polymers were isolated by precipitation in 150 mL of methanol. The dried precipitate was redissolved in 10 mL of chloroform and reprecipitated by addition to 150 mL of methanol. This purification procedure was repeated two more times to yield the polyamides as pale yellow solids.

Elemental analyses, yields, phase transitions (determined by DSC), and average molecular weights (GPC) of the synthesized polymers are given in Table V. The M_n values determined by GPC (Table V) were confirmed by vapor pressure osmometry for some of the polyamides (results in parentheses in Table V).

Methods and Materials. DSC measurements were performed with a Perkin-Elmer DSC-2c differential scanning calorimeter. The transition temperatures given in Table V represent the peak maxima of the 2nd heating curve (heating rate 10 K/min). TGA was performed with a Perkin-Elmer thermogravimetric analyzer TGS-2 (heating rate 10 K/min; nitrogen atmosphere). ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ using a 400-MHz FT NMR spectrometer Aspect 2000 (Bruker). Analytical GPC was performed in $CHCl_3$ with a Waters HPLC liquid chromatograph and a UV detector 440. Polystyrene was used as standard (M_n = 110 000, 50 000, 17 000, 4000; U = 1.04). Vapor pressure osmometry was performed with a Knauer vapor pressure osmometer in chloroform at 37 °C. FTIR spectra were recorded as cast films on NaCl plates using a Nicolet 5 DXC FTIR spectrometer. UV spectra were taken of films, cast from $CHCl_3$, on quartz plates with a Lambda 5 UV/vis spectrophotometer.

References and Notes

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Registry No. **1a**, 126297-17-4; **1b**, 126297-18-5; **1c**, 126297-21-0; **2a**, 107502-78-3; **2b**, 106107-76-0; **2c**, 126297-20-9; **3a**, 109424-57-9; **3b**, 103761-97-3; **3c**, 126297-19-6; **4**, 122-80-5; **5**, 84483-30-7; **6**, 29213-03-4; **7a**, 126297-22-1; **7b**, 126297-27-6; **7c**, 126297-29-8; **8**, 126297-23-2; **9** (copolymer), 126327-56-8; **9** (SRU), 126327-06-8; **10** (copolymer), 126297-28-7; **10** (SRU), 126327-08-0; **11** (copolymer), 126297-30-1; **11** (SRU), 126327-13-7; **12** (copolymer), 126327-57-9; **12** (SRU), 126327-07-9; **13** (copolymer), 126327-58-0; **13** (SRU), 126327-09-1; **14** (copolymer), 126327-59-1; **14** (SRU), 126327-14-8; **15** (copolymer), 126327-60-4; **15** (SRU), 126327-11-5; **16** (copolymer), 126297-31-2; **16** (SRU), 126327-12-6; **17** (copolymer), 126297-32-3; **17** (SRU), 126327-15-9; **18** (copolymer), 126297-33-4; **18** (SRU), 126327-10-4; diethyl 2,5-dihydroxyterephthalate, 5870-38-2; pentadec-1-yne, 765-13-9.