Poly(arylazophosphonate)s: A New Polymer Class with Arylazophosphonate Units in the Main Chain

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ABSTRACT: Poly(arylazophosphonate)s are synthesized from bifunctional diazonium salts and bifunctional phosphoric diesters by interfacial polycondensation at the interface water/organic solvent. The azo unit is formed via N−P coupling during the polycondensation reaction in satisfying yield and selectivity. Fifteen new polymers were synthesized and characterized by common methods such as ^{1}H, ^{13}C, and ^{31}P NMR, FTIR, UV/visible spectroscopy, and DSC and GPC measurements. According to first laser ablation experiments as well as film forming properties and thermal and photochemical behavior, poly(arylazophosphonate)s seem to be suitable materials for ablation with XeCl* excimer lasers.

Introduction

Polymers suitable for laser ablation lithography must combine a number of properties to fulfill all requirements which are necessary for practical application. The greatest challenge is the combination of good film-forming properties and photochemical sensitivity with sufficient thermal and photochemical stability. For this reason the polymers should contain highly sensitive chromophores with excellent absorbance behavior in the main chain, which can be fragmented by a selective wavelength of the excimer laser, in the case of a commercially available XeCl* excimer laser at 308 nm.

Azo-derived functional groups combine both properties, due to good absorption behavior at $\lambda_{max} = 308$ nm and spontaneous fragmentation by photochemical activation into nitrogen and other volatile products.[1] The azo-containing groups are sensitive to various stimuli (e.g. light or heat) and respond to these stimuli in a well-defined manner. Therefore azo-containing groups are useful for breaking units in the polymer chain (Figure 1).

In earlier works the successful application of the concept has already been demonstrated with poly(triazene)s containing three connected nitrogen atoms in the backbone. As a result of their high thermal stabilities combined with favorable photolytic sensitivities, triazene polymers are suitable materials for laser-induced microimaging.[2,3] Besides poly(pentazadiene)s[4] and poly(hexazadiene)s,[5] which have been prepared and intensely investigated, heteroatom-containing azopolymers, such as poly(diaryldiazosulfide)s, also showed promising photo- and thermosensitive properties.[6,7]

A new class of polymers with azo-derived functional groups are poly(arylazophosphonate)s. Arylazophosphonates (**3**) have been well-known for almost 40 years. The first synthesis was described in 1958 by F. Suckfüll and H. Haubrich.[8] These compounds contain the arylazo group Ar−N=N− adjacent to the phosphate group $PO(OR)_2$. The synthesis was carried out by N−P coupling of aromatic diazonium salts with diesters of the phosphoric acid (Scheme 1).[8,9] Arylazophosphonates (**3**) can be isolated as red oils or as crystalline solids and were synthesized in a great variety with several substituents R^1, R^2, and R^3.[8,10−12]

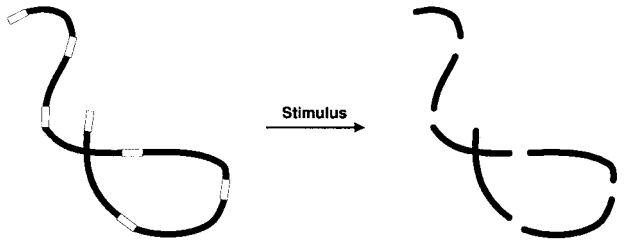
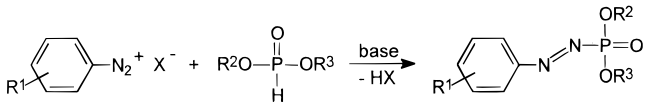


Figure 1. Fragmentation of an azo groups containing polymer chain by a defined stimulus (e.g. light or heat).

Scheme 1. Synthesis of Arylazophosphonates via N−P Coupling



1 **2** **3**

Synthesis

For the preparation of polymers with arylazophosphonate units in the main chain, two strategies can be followed.

Indirect Method. Monomers containing preformed arylazophosphonate units are converted into polymers via common polycondensation reactions. The advantage consists of the structural diversity and the resulting properties, due to the large variety of polycondensation methods. It is essential that the arylazophosphonate units tolerate functional groups such as hydroxy, carbonic acid, isocyanate, etc. Otherwise, the protected version of the reactive groups or polymer reactions must be used.

Direct Method. Alternatively, the arylazophosphonate units can be formed during the polycondensation from monomers containing the groups for the N−P coupling, e.g. reaction of bifunctional diazonium salts (**4**) with bifunctional phosphoric diesters (**5**) according to Scheme 2. The advantage of this route is the one-step preparation, resulting in regular structures, high molecular masses, and products with good film-forming properties. However, yield and selectivity of the N−P coupling must be high.

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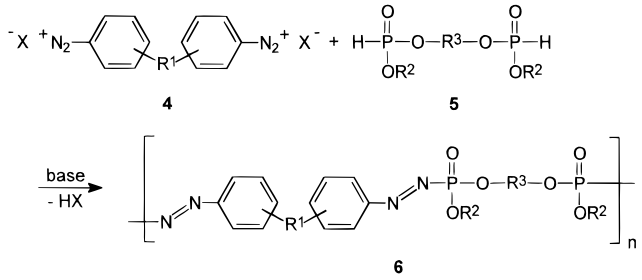
Scheme 2. Synthesis of Poly(arylazophosphonate)s via Interfacial Polycondensation of Bifunctional Diazonium Salts and Bifunctional Phosphoric Diesters



Applying the N−P coupling technique (direct method), poly(arylazophosphonate)s were prepared via interfacial polycondensation[13,14] as shown in Scheme 2.

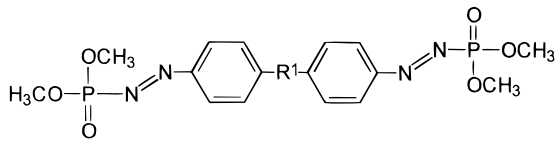
Model Compounds

To get a better insight into the course of the N−P coupling two selected model compounds (**7** and **8**) were synthesized (Figure 2). In addition, it was necessary to study and collect specific analytical data for this functional group, since those were scarcely available from the literature. Some arylazophosphonate-containing compounds have been previously described but were unsatisfactorily characterized.[8−12] The structure of the polymers can be proved by comparison of the analytical data of the model compounds with the analytical data of the polymers.

Since selectivity and rate of the N−P coupling reaction were high (yields were found about 90%), this reaction type seemed to be suitable for polycondensation reactions. This indicates that the formation of the azophosphonate unit via N−P coupling is fast and selective enough for the polyreaction. The model compounds contain structural elements that are very similar to those in the polymers. As expected, polar groups in the aromatic moiety and rigid spacers serve to increase the melting point.

Monomer Synthesis

Bifunctional aromatic diazonium salts can be prepared from bis(amine)s via double diazotization in mineral acid at a temperature of about 0 °C.[15] The diazotization of aromatic bis(amine)s such as 1,4-diaminobenzene is quite difficult and leads to side products.[16] The degree of side reactions is reduced when amine functions are not located at the same aromatic system. Therefore, three different bis(amine)s, varying



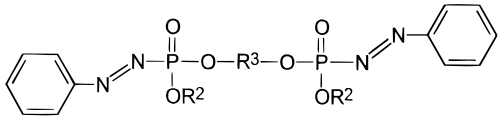
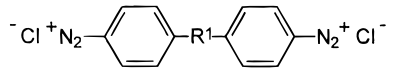


Figure 2. Structures of the synthesized low molecular mass model compounds (R^1 = −, O, CO; R^2 = Me, Et; R^3 = $(CH_2)_2$, $(CH_2)_6$, $(CH_2)_2O(CH_2)_2$, CH_2-*c-hex*-CH_2, CH_2-*p-ph*-CH_2).

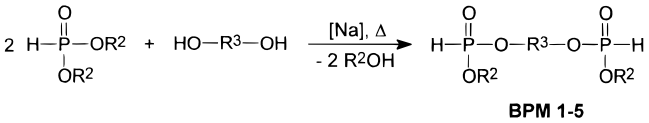
Table 1: Structure of Bifunctional Aromatic Diazonium Salt Monomers DSM 1 through DSM 3



monomer	bisamine	R^1
DSM 1	Benzidine[a]	
DSM 2	4,4′-Diaminodiphenyl ether	O
DSM 3	4,4′-Diaminobenzophenone	CO

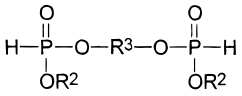
[a] Biphenyl structure.

Scheme 3. Synthesis of Bifunctional Phosphite Monomers BPM 1 through BPM 5



BPM 1-5

Table 2. Data for the Bis(phosphite) Monomers BPM 1 through BPM 5



bis(phosphite)	R^2	R^3	yield,[a] %	ref
BPM 1	Et	$(CH_2)_2$	53	19
BPM 2	Me	$(CH_2)_6$	76	19
BPM 3	Me	$(CH_2)_2O(CH_2)_2$	72	19
BPM 4	Me	CH_2-*c-hex*-CH_2[b]	56	this work
BPM 5	Me	CH_2-*p-ph*-CH_2[c]	42	this work

[a] After purification by distillation (yields of the crude product >95%). [b] 1,4-Disubstituted cyclohexyl (mixture of isomeres: trans/cis = 3/1). [c] 1,4-Disubstituted *p*-phenyl.

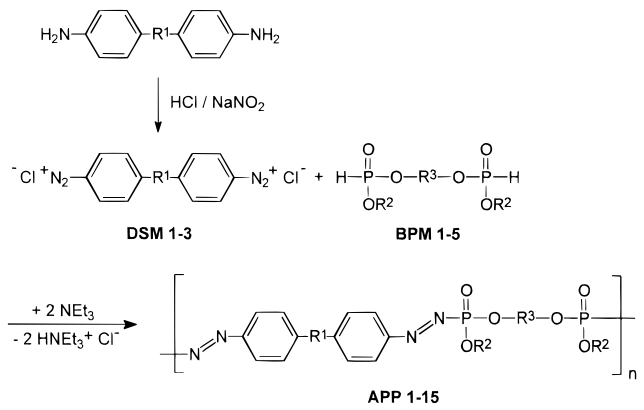
in their linking units R^1, were favored for this reaction as listed in Table 1. All bifunctional aromatic diazonium salt monomers **DSM 1**, **DSM 2**, and **DSM 3** were prepared as chlorides and were used directly in aqueous solution for the polycondensation.

Bifunctional phosphoric diester (bis(phosphite)s) monomers must contain two −O−PO(OR)−H groups for linear polycondensation via N−P coupling. An easy synthetic approach for those monomers is the transesterification of commercially available dialkyl phosphites with diols as shown in Scheme 3.[17−19]

The transesterification succeeds by using an excess on dialkyl phosphites. Otherwise, side reactions such as cyclization or oligomerization become dominant.[20−22] For the transesterification reaction of the bifunctional phosphite monomers **BPM 1** through **BPM 5**, exclusively primary diols were used. Secondary and tertiary diols are not reactive in this process.[23]

Due to aqueous reaction conditions during the interfacial polycondensation aliphatic groups OR^2 were favored over aromatic groups OR^2 due to their lower tendency of hydrolysis (Table 2).[23] Most bifunctional phosphite monomers in Table 2 were prepared at temperatures of about 140 °C without any solvent. The crude products could be isolated nearly quantitatively and were purified by distillation before they were used for polycondensation. Variation of the linking unit R^3 should yield valuable information about the structure−property relationships of the resulting polymers. Therefore diols with flexible units (**BPM 1**, **BPM 2**, and **BPM 3**) and diols with rigid units (**BPM 4** and **BPM 5**) were applied for the synthesis of the poly(arylazophosphonate)s **APP 1** through **APP 15**.

Scheme 4. Synthesis of Poly(arylazophophonate)s via N−P Coupling of Bifunctional Phosphoric Diesters and Bifunctional Diazonium Salt Monomers



The bifunctional phosphoric diester monomers are colorless viscous fluids and show a high solubility in organic solvents such as chloroform, dichloromethane, tetrachloromethane, and toluene. Their extremely low solubilities in water make them suitable for interfacial polycondensation with water-soluble bifunctional diazonium salt monomers.

Polymer Synthesis

Polymer synthesis was carried out by interfacial polycondensation of the described bifunctional phosphoric diesters and bifunctional diazonium salts of commercially available bis(amine)s at 0 °C. Fifteen new polymers, **APP 1** through **APP 15,** were prepared by systematically combination of both monomer types (Scheme 4).

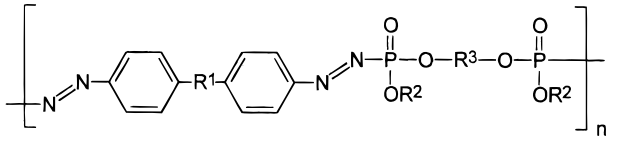
The bifunctional diazonium salt monomers **DSM 1**, **DSM 2**, and **DSM 3** were prepared in aqueous solution and used in situ for polycondensation. The bisphosphite monomers **BPM 1**, **BPM 2**, **BPM 3,** and **BPM 4** were dissolved in tetrachloromethane while toluene was used for **BPM 5** as solvent. Both monomers were used in very high concentrations in order to realize high reaction rates. Intensive stirring is necessary for high yields by interfacial polycondensation, due to the permanent renewal of the interface water/organic solvent.[13] The polycondensation was started after thorough mixing of both phases by adding the base triethylamine. The polymeric crude product contains, in addition to the target compound, unsoluble parts, produced by free radical interlinking reactions. Since the poly(arylazophosphonate)s are soluble in chloroform or dichloromethane they can be separated from the unsoluble parts by solvent extraction. The polymers were obtained in yields from 26 to 85% with molar masses $\bar{M}_n$ up to 15 500 g/mol (Table 3).

Results and Discussion

The polymers were characterized by ^{1}H, ^{13}C, and ^{31}P NMR, FTIR, and UV/visible spectroscopy. The characterizing data were compared with those from model compounds.

Polymer Films. Film-forming properties of the polymers **APP 1** through **APP 15** are excellent. Homogeneous films in thicknesses between 1 and 200 μm coated on several substrates with different geometric dimensions (glass, quartz, silicon) could be easily prepared by casting or spin coating and subsequent drying at moderate temperatures. According to the primitive thumbnail test, adhesion on the substrat and inherent mechanical stability were satisfying.

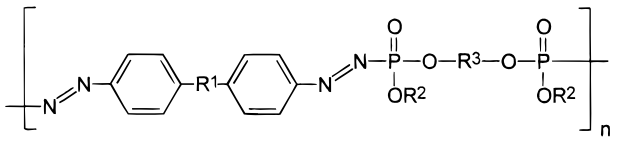
Table 3. Structure and Synthetic Data of the Polymers APP 1 through APP 15



polymer	R^1	R^2	R^3	yield,[a] %	$\bar{M}_n$,[b] g/mol	$\bar{M}_w/\bar{M}_n$
APP 1		Et	$(CH_2)_2$	56	10800	2.0
APP 2	O	Et	$(CH_2)_2$	85	8800	3.3
APP 3	CO	Et	$(CH_2)_2$	33	11100	2.7
APP 4		Me	$(CH_2)_6$	80	14400	2.7
APP 5	O	Me	$(CH_2)_6$	41	10600	3.4
APP 6	CO	Me	$(CH_2)_6$	43	6800	2.2
APP 7		Me	$(CH_2)_2O(CH_2)_2$	40	3600	2.0
APP 8	O	Me	$(CH_2)_2O(CH_2)_2$	41	8600	2.3
APP 9	CO	Me	$(CH_2)_2O(CH_2)_2$	26	5400	2.7
APP 10		Me	CH_2-*c-hex*-CH_2[c]	60	6700	2.1
APP 11	O	Me	CH_2-*c-hex*-CH_2[c]	46	15500	2.7
APP 12	CO	Me	CH_2-*c-hex*-CH_2[c]	41	6900	2.1
APP 13		Me	CH_2-*p-ph*-CH_2[d]	67	11700	2.9
APP 14	O	Me	CH_2-*p-ph*-CH_2[d]	50	14400	2.5
APP 15	CO	Me	CH_2-*p-ph*-CH_2[d]	48	7800	2.5

[a] After 2-fold reprecipitation. [b] Determined by GPC (in $CHCl_3$, polystyrene standard). [c] 1,4-Disubstituted cyclohexyl (mixture of isomeres: trans/cis = 3/1). [d] 1,4-Disubstituted *p*-phenyl.

Table 4. Glass Transition Temperature T_g and Absorption Maxima $\lambda_{max}^{\pi\rightarrow\pi^*}$ of the Polymers APP 1 through APP 15



polymer	R^1	R^2	R^3	T_g, °C	$\lambda_{max}^{\pi\rightarrow\pi^*}$, nm
APP 1		Et	$(CH_2)_2$	43	354
APP 2	O	Et	$(CH_2)_2$	22	343
APP 3	CO	Et	$(CH_2)_2$	33	304
APP 4		Me	$(CH_2)_6$	37	354
APP 5	O	Me	$(CH_2)_6$	25	342
APP 6	CO	Me	$(CH_2)_6$	31	303
APP 7		Me	$(CH_2)_2O(CH_2)_2$	22	355
APP 8	O	Me	$(CH_2)_2O(CH_2)_2$	32	343
APP 9	CO	Me	$(CH_2)_2O(CH_2)_2$	33	304
APP 10		Me	CH_2-*c-hex*-CH_2[a]	58	354
APP 11	O	Me	CH_2-*c-hex*-CH_2[a]	50	342
APP 12	CO	Me	CH_2-*c-hex*-CH_2[a]	52	304
APP 13		Me	CH_2-*p-ph*-CH_2[b]	48	356
APP 14	O	Me	CH_2-*p-ph*-CH_2[b]	50	344
APP 15	CO	Me	CH_2-*p-ph*-CH_2[b]	48	305

[a] 1,4-Disubstituted cyclohexyl (mixture of isomeres: trans/cis = 3/1). [b] 1,4-Disubstituted *p*-phenyl.

Thermal Analysis. The polymers **APP 1** through **APP 15** have been investigated concerning the glass transition temperature T_g (Table 4). As expected, a dependence of T_g on the rigidity of the linking unit R^3 is apparent. Flexible polymer units (**APP 1** through **APP 9**) generated from bisphosphite monomers **BPM 1** through **BPM 3** result in a low glass transition temperature between 20 and 40 °C. In contrast, rigid polymer units (**APP 10** through **APP 15**) increase the

glass transition temperature from 50 to 60 °C. The different flexible units of the bifunctional diazonium salt monomers R^1 did not show any systematic influence on T_g.

Photochemical Behavior. Model compounds and all poly(arylazophosphonate)s exhibit a red color. The absorption does not depend on bisphosphite linking unit R^3. However, the linking unit R^1 between the aromatic systems in the bifunctional diazonium salt monomers has a strong effect on the absorption maxima (Table 4). Because of the wide absorption for the $\pi \rightarrow \pi^*$ transition the n $\rightarrow \pi^*$ transition at about 500 nm could not be detected.

Summary and Conclusion

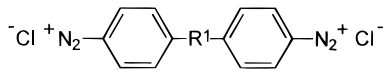
By application of the N−P coupling technique, fifteen new poly(arylazophosphonate)s were synthesized by interfacial polycondensation from bifunctional diazonium salts and bifunctional phosphoric diesters. To obtain polymers with high molecular weights—which are essential for film-forming properties—yield and selectivity of the N−P coupling must be high. Variation of the monomers during the polyreaction leads to a great variety of polymers with different structures. Glass transition temperatures (T_g) were found to be in the range 20−60 °C. The poly(arylazophosphonate)s were coated on several substrates in thicknesses between 1 and 200 μm. The polymers are red and show absorption maxima between 303 and 356 nm. Because of their excellent film-forming properties and absorption behavior poly(arylazophosphonate)s are suitable materials for laser ablation experiments with XeCl* excimer lasers (308 nm). A variety of ablated structures have been generated by irradiation of the polymer films with a commercially available pulsed XeCl* excimer laser. The results are promising.[24] Macro experiments (holes with 105 μm diameter) indicate remarkable structures with sharp edges, clear contours, and flat bottoms. Moreover, various structures with micrometer dimensions were generated by micro experiments and were characterized by means of REM. The images possess a very good optical resolution and indicate that poly(arylazophosphonate)s are suitable materials for micromechanical applications.

Experimental Section

Materials. Aromatic diamines, dialkyl phosphites, and diols were used as received. All solvents were purified by using rectifying columns and the crude products of the bifunctional phosphite monomers were purified by distillation before use. The bifunctional diazonium salt monomers were prepared in the dark at temperatures near 0 °C.

Equipment. For the NMR spectra a Bruker ARX 300 was used to record the ^{1}H NMR (300.13 MHz), ^{13}C NMR (75.47 MHz), and ^{31}P NMR (121.51 MHz) spectra at 300 K. Tetramethylsilane (TMS) was used as internal reference for the ^{1}H and ^{13}C NMR spectra. For the ^{31}P NMR spectra, triphenyl phosphite ($P(OPh)_3$) was used as an external reference (δ = +126.9 ppm referring to H_3PO_4). H_3PO_4 was not added to avoid intersections of the H_3PO_4 signal and the signal for the phosphorus-containing compounds expected in the same range. ^{13}C and ^{31}P NMR spectra were proton decoupled. Molecular weights were obtained by GPC analysis using a Waters system: pump 510 equipped with an UV detector 486 (254 nm) and a RI detector 410; Ultrastyragel columns (500, 10^3, 10^4, 10^5 Å) with the system calibrated vs polystyrene standards. The samples were eluted with tetrahydrofuran and chloroform, flow rate 0.5 mL/min. Elemental analysis was performed by the Microanalytisches Laboratorium, Organische Chemie of the Technische Universität München. For the thermoanalysis a DSC 7 from Perkin-Elmer and a PL-STA 1500 from Polymer Laboratories were applied (STA: Simultaneous thermal analysis). T_{max} indicates the temperature with maximal enthalpy of decomposition and $T_{5\%}$ the temperature after 5% of mass reduction. The scanning rate was 10 K/min in all cases. The FTIR spectra were performed with a Bruker IFS 55 and for the UV/visible spectra a CARY 3 from Varian was used.

Preparation of Bifunctional Diazonium Salt Monomers DSM 1 (R^1 = −), DSM 2 (R^1 = O), and DSM 3 (R^1 = CO).



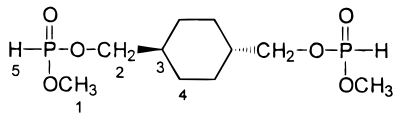
DSM 1 - DSM 3

A 10 mmol sample of the aromatic amine is dissolved in 50 mmol of concentrated hydrochloric acid and cooled to 0 °C. Only a small amount of water is added to completely dissolve the hydrochloride at 0 °C. The mixture is cooled at about 5 °C while a solution of 20 mmol of sodium nitrite in 5 mL of water is added; the temperature should be kept below 5 °C. Finally, the mixture is stirred at about 5 °C for 30 min. The solutions of the obtained bifunctional diazonium salt monomers are used in situ for polycondensation without further characterization.

Preparation of Bifunctional Phosphite Monomers BPM 1 through BPM 5. The monomers **BPM 1** through **BPM 3** were synthesized according to ref 19. **BPM 4** and **BPM 5** were prepared according to the following route:

A 300 mmol sample of the diol (1,4-benzenedimethanol or 1,4-cyclohexanedimethanol) and 1800 mmol of dimethyl phosphite (3 times excess) are put into a flask at room temperature and are purged with nitrogen for 10 min. As a catalyst, approximately 10−15 mmol of sodium metal is added to the reaction mixture, which is heated to 140 °C so the methanol set free and is removed by distillation. As soon as the distillation of the methanol is complete, the temperature is reduced to 70 °C, and the excess of dimethyl phosphite is removed under vacuum. The crude product can be isolated nearly quantitatively and is purified by distillation.

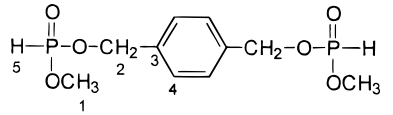
Characterization of Bifunctional Phosphite Monomer BPM 4.



BPM 4

Yield: 50.4 g (56%). ^{1}H NMR ($CDCl_3$, δ in ppm): 1.1−1.9 (m, 20H, H3/H4), 3.78 (d, 12H, H1, $^3J_{H,P}$ = 12.0 Hz), 3.91 (m, 4H, $H2_{trans}$), 4.00 (m, 4H, $H2_{cis}$), 6.79 (d, 4H, H5, $^1J_{H,P}$ = 696.8 Hz). ^{13}C NMR ($CDCl_3$, δ in ppm): 24.7 (s, $C4_{cis}$), 28.3 (s, $C4_{trans}$), 35.8 (d, $C3_{cis}$, $^3J_{C,P}$ = 6.1 Hz), 38.3 (d, $C3_{trans}$, $^3J_{C,P}$ = 6.1 Hz), 52.0 (d, C1, $^2J_{C,P}$ = 5.6 Hz), 68.2 (d, $C2_{cis}$, $^2J_{C,P}$ = 6.4 Hz), 70.4 (d, $C2_{trans}$, $^2J_{C,P}$ = 6.3 Hz). ^{31}P NMR ($CDCl_3$, δ in ppm): 8.3. FTIR spectroscopy, $\tilde{\nu}$ in cm^{-1} (film): 3482 (m, ν(O−H)), 2931 (s, ν(C−H)), 2855 (s, ν(C−H)), 2425 (m, ν(P−H)), 1452 (s, δ-(C−H)), 1258 (s, ν(P═O)), 1038 (s, ν(P−OC)). Boiling point: 165 °C at 2 Pa. Refraction index: n_D^{20} = 1.4678. Anal. Calcd for $C_{10}H_{22}O_6P_2$: C, 40.01; H, 7.39. Found: C, 38.63; H, 7.40.

Characterization of Bifunctional Phosphite Monomer BPM 5.



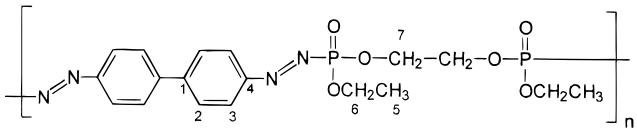
BPM 5

Yield: 53.0 g (60%). ^{1}H NMR ($CDCl_3$, δ in ppm): 3.74 (d, 6H,

H1, $^3J_{H,P}$ = 12.0 Hz), 5.13 (d, 4H, H2, $^3J_{H,P}$ = 9.6 Hz), 6.86 (d, 2H, H5, $^1J_{H,P}$ = 704.3 Hz), 7.43 (s, 4H, H4). ^{13}C NMR ($CDCl_3$, δ in ppm): 52.0 (d, C1, $^2J_{C,P}$ = 6.0 Hz), 66.8 (d, C2, $^2J_{C,P}$ = 5.4 Hz), 128.3 (s, C4), 136.2 (d, C3, $^3J_{C,P}$ = 5.9 Hz). ^{31}P NMR ($CDCl_3$, δ in ppm): 8.1. FTIR spectroscopy, $\tilde{\nu}$ in cm^{-1} (film): 3544 (w, ν(O−H)), 2933 (s, ν(C−H)), 2856 (s, ν(C−H)), 2425 (m, ν(P−H)), 1452 (s, δ(C−H)), 1259 (s, ν(P═O)), 1039 (s, ν-(P−OC)), 836 (m, δ(C−H)). Boiling point: 170 °C at 2 Pa. Refraction index: n_D^{20} = 1.5045. Anal. Calcd for $C_{10}H_{16}O_6P_2$: C, 40.83; H, 5.48. Found: C, 39.77; H, 5.47.

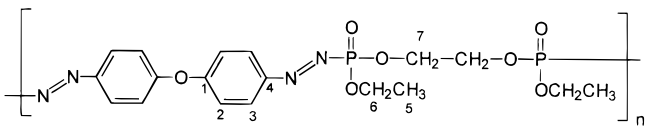
Polycondensation of Poly(arylazophosphonate)s AAP 1 through AAP 15. The freshly prepared diazonium salt solution (10 mmol) is filled into a flask and cooled to 0 °C. The unstirred aqueous solution will be underlayed with a precooled solution of 10 mmol of the corresponding bisphosphite monomer **BPM 1** through **BPM 4** dissolved in tetrachloromethane (in the case of the solution of **BPM 5** (in toluene) the aqueous solution will be overlayed). After intensive stirring for 30 s, the interfacial polycondensation is started by adding 50 mmol of precooled triethylamine. The mixture turns red, and the polymer precipitates immediately. The mixture is stirred for 30 min under ice cooling. The remaining diazo groups are destroyed by adding 1 g of dimethyl phosphite and continued stirring for 20 min. The polymer is separated from the reaction mixture by centrifugation. Watersoluble compounds are removed by stirring in 150 mL of water and subsequent isolation of the polymer. The polymer is dissolved almost completely in chloroform (unsoluble parts are removed by filtration) and precipitated in 300 mL of tetrachloromethane. Finally, the polymer is separated and dried under vacuum.

Characterization of AAP 1 (R^1 = −), AAP 2 (R^1 = O), and AAP 3 (R^1 = CO).



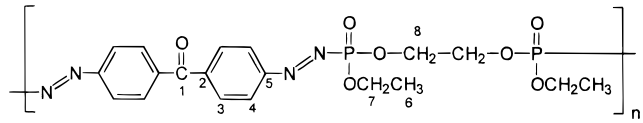
APP 1

Yield: 2.53 g (56%). ^{1}H NMR ($CDCl_3$, δ in ppm): 1.2−1.3 (m, $H5_{end}$), 1.3−1.6 (m, 6H, H5), 4.0−4.2 (m, $H6_{end}$), 4.2−4.5 (m, 4H, H6), 4.5−4.8 (m, 4H, H7), 7.6−7.8 (d, 4H, H2, $^3J_{H,H}$ = 8.2 Hz), 7.8−8.1 (d, 4H, H3, $^3J_{H,H}$ = 8.2 Hz). ^{13}C NMR ($CDCl_3$, δ in ppm): 16.4 (d, C5, $^3J_{C,P}$ = 5.8 Hz), 65.3 (d, C6, $^2J_{C,P}$ = 6.7 Hz), 67.0 (d, C7, $^2J_{C,P}$ = 6.2 Hz), 123.9 (s, C2/C3), 128.2 (s, C2/C3), 145.1 (s, C1), 153.7 (d, C4, $^3J_{C,P}$ = 54.0 Hz). ^{31}P NMR ($CDCl_3$, δ in ppm): −1.5. UV/visible ($CHCl_3$): $\lambda_{max}^{\pi\rightarrow\pi^*}$ = 354 nm. DSC (10 K/min): T_g = 43 °C; T_{max} = 205, 225 °C. STA (10 K/min): $T_{5\%}$ = 182 °C. GPC ($CHCl_3$): $\bar{M}_n$ = 10 800 g/mol; $\bar{M}_n$ = 21 600 g/mol; $\bar{M}_w/\bar{M}_n$ = 2.0. Anal. Calcd for $(C_{18}H_{22}N_4O_6P_2)_n$: C, 47.80; H, 4.90; N, 12.39. Found: C, 47.79; H, 4.83; N, 11.39.



APP 2

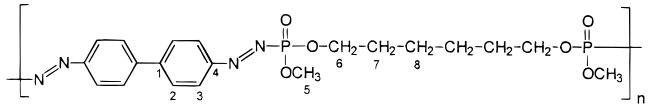
Yield: 3.99 g (85%). ^{1}H NMR ($CDCl_3$, δ in ppm): 1.2−1.3 (m, $H5_{end}$), 1.3−1.5 (m, 6H, H5), 4.1−4.2 (m, $H6_{end}$), 4.2−4.4 (m, 4H, H6), 4.4−4.6 (m, 4H, H7), 7.0−7.2 (d, 4H, H2, $^3J_{H,H}$ = 8.8 Hz), 7.8−8.0 (d, 4H, H3, $^3J_{H,H}$ = 8.8 Hz). ^{13}C NMR ($CDCl_3$, δ in ppm): 16.4 (d, C5, $^3J_{C,P}$ = 6.0 Hz), 65.2 (d, C6, $^2J_{C,P}$ = 6.6 Hz), 66.8 (d, C7, $^2J_{C,P}$ = 6.7 Hz), 119.5 (s, C2/C3), 125.7 (s, C2/C3), 150.4 (d, C4, $^3J_{C,P}$ = 53.8 Hz), 161.0 (s, C1). ^{31}P NMR ($CDCl_3$, δ in ppm): −2.0. UV/visible ($CHCl_3$): $\lambda_{max}^{\pi\rightarrow\pi^*}$ = 343 nm. DSC (10 K/min): T_g = 22 °C; T_{max} = 207 °C, shoulder. STA (10 K/min): $T_{5\%}$ = 185 °C. GPC ($CHCl_3$): $\bar{M}_n$ = 8800 g/mol; $\bar{M}_w$ = 29 400 g/mol; $\bar{M}_w/\bar{M}_n$ = 3.3. Anal. Calcd for $(C_{18}H_{22}N_4O_7P_2)_n$: C, 46.16; H, 4.73; N, 11.96. Found: C, 46.25; H, 4.82; N, 11.20.



APP 3

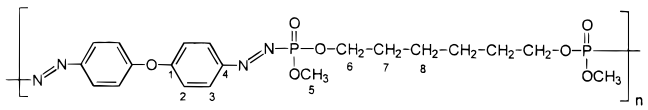
Yield: 1.59 g (33%). ^{1}H NMR ($CDCl_3$, δ in ppm): 1.2−1.3 (m, $H6_{end}$), 1.3−1.5 (m, 6H, H6), 4.1−4.3 (m, $H7_{end}$), 4.3−4.5 (m, 4H, H7), 4.5−4.8 (m, 4H, H8), 7.9−8.2 (m, 8H, H3/H4). ^{13}C NMR ($CDCl_3$, δ in ppm): 16.4 (d, C6, $^3J_{C,P}$ = 5.7 Hz), 65.6 (d, C7, $^2J_{C,P}$ = 6.7 Hz), 67.0 (d, C8, $^2J_{C,P}$ = 6.2 Hz), 123.1 (s, C3/C4), 131.0 (s, C3/C4), 141.0 (s, C2), 155.4 (d, C5, $^3J_{C,P}$ = 54.0 Hz), 194.5 (s, C1). ^{31}P NMR ($CDCl_3$, δ in ppm): −2.2. UV/visible ($CHCl_3$): $\lambda_{max}^{\pi\rightarrow\pi^*}$ = 304 nm. DSC (10 K/min): T_g = 33 °C; T_{max} = 206, 229 °C. STA (10 K/min): $T_{5\%}$ = 196 °C. GPC ($CHCl_3$): $\bar{M}_n$ = 11 100 g/mol; $\bar{M}_w$ = 29 900 g/mol; $\bar{M}_w/\bar{M}_n$ = 2.7. Anal. Calcd for $(C_{19}H_{22}N_4O_7P_2)_n$: C, 47.51; H, 4.62; N, 11.66. Found: C, 46.84; H, 4.59; N, 10.94.

Characterization of AAP 4 (R^1 = −), AAP 5 (R^1 = O), and AAP 6 (R^1 = CO).



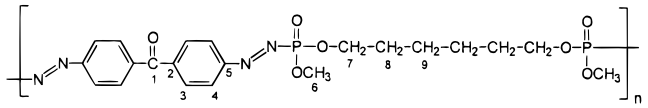
APP 4

Yield: 3.84 g (80%). ^{1}H NMR ($CDCl_3$, δ in ppm): 1.3−1.6 (m, 4H, H8), 1.6−1.9 (m, 4H, H7), 3.7−3.8 (d, $H5_{end}$), 3.9−4.1 (d, 6H, H5, $^3J_{H,P}$ = 10.8 Hz), 4.1−4.4 (m, 4H, H6), 7.7−7.9 (d, 4H, H2, $^3J_{H,H}$ = 8.5 Hz), 7.9−8.2 (d, 4H, H3, $^3J_{H,H}$ = 8.5 Hz). ^{13}C NMR ($CDCl_3$, δ in ppm): 25.0 (s, C8), 30.4 (d, C7, $^3J_{C,P}$ = 5.4 Hz), 55.1 (d, C5, $^2J_{C,P}$ = 6.7 Hz), 68.8 (d, C6, $^2J_{C,P}$ = 6.7 Hz), 123.9 (s, C2/C3), 128.2 (s, C2/C3), 145.1 (s, C1), 153.7 (d, C4, $^3J_{C,P}$ = 53.5 Hz). ^{31}P NMR ($CDCl_3$, δ in ppm): −1.2. UV/visible ($CHCl_3$): $\lambda_{max}^{\pi\rightarrow\pi^*}$ = 354 nm. DSC (10 K/min): T_g = 37 °C; T_{max} = 199 °C, 219 °C. STA (10 K/min): $T_{5\%}$ = 195 °C. GPC ($CHCl_3$): $\bar{M}_n$ = 14 400 g/mol; $\bar{M}_w$ = 38300 g/mol; $\bar{M}_w/\bar{M}_n$ = 2.7. Anal. Calcd for $(C_{20}H_{26}N_4O_6P_2)_n$: C, 50.00; H, 5.46; N, 11.66. Found: C, 49.35; H, 5.55; N, 10.46.



APP 5

Yield: 3.73 g (41%). ^{1}H NMR ($CDCl_3$, δ in ppm): 1.4−1.6 (m, 4H, H8), 1.7−1.9 (m, 4H, H7), 3.7−3.8 (d, $H5_{end}$), 3.9−4.1 (d, 6H, H5, $^3J_{H,P}$ = 9.8 Hz), 4.1−4.2 (m, 4H, H6), 7.1−7.2 (d, 4H, H2, $^3J_{H,H}$ = 8.7 Hz), 7.9−8.2 (d, 4H, H3, $^3J_{H,H}$ = 8.7 Hz). ^{13}C NMR ($CDCl_3$, δ in ppm): 25.0 (s, C8), 30.4 (d, C7, $^3J_{C,P}$ = 5.8 Hz), 55.1 (d, C5, $^2J_{C,P}$ = 6.7 Hz), 68.8 (d, C6, $^2J_{C,P}$ = 6.8 Hz), 119.5 (s, C2/C3), 125.6 (s, C2/C3), 150.8 (d, C4, $^3J_{C,P}$ = 54.2 Hz), 161.0 (s, C1). ^{31}P NMR ($CDCl_3$, δ in ppm): −0.4. UV/visible ($CHCl_3$): $\lambda_{max}^{\pi\rightarrow\pi^*}$ = 342 nm. DSC (10 K/min): T_g = 25 °C, T_{max} = 205 °C, 218 °C. STA (10 K/min): $T_{5\%}$ = 195 °C. GPC ($CHCl_3$): $\bar{M}_n$ = 10 600 g/mol; $\bar{M}_w$ = 35600 g/mol; $\bar{M}_w/\bar{M}_n$ = 3.4. Anal. Calcd for $(C_{20}H_{26}N_4O_7P_2)_n$: C, 48.39; H, 5.28; N, 11.29. Found: C, 48.13; H, 5.28; N, 10.34.

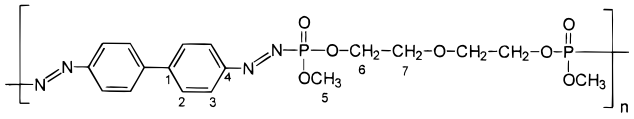


APP 6

Yield: 2.19 g (43%). ^{1}H NMR ($CDCl_3$, δ in ppm): 1.3−1.6 (m, 4H, H9), 1.6−1.9 (m, 4H, H8), 3.7−3.8 (d, $H6_{end}$), 3.9−4.1 (d,

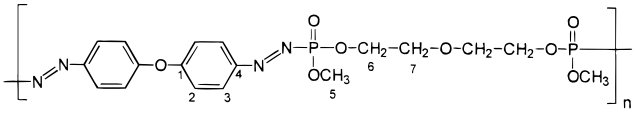
6H, H6, $^3J_{H,P}$ = 10.6 Hz), 4.2−4.4 (m, 4H, H7), 7.8−8.2 (m, 8H, H3/H4). ^{13}C NMR ($CDCl_3$, δ in ppm): 25.0 (s, C9), 30.3 (d, C8, $^3J_{C,P}$ = 5.7 Hz), 55.3 (s, C6, $^2J_{C,P}$ = 6.8 Hz), 68.9 (d, C7, $^2J_{C,P}$ = 6.7 Hz), 123.0 (s, C3/C4), 131.0 (s, C3/C4), 141.0 (s, C2), 155.2 (d, C5, $^3J_{C,P}$ = 53.8 Hz), 194.6 (s, C1). ^{31}P NMR ($CDCl_3$, δ in ppm): −0.8. UV/visible ($CHCl_3$): $\lambda_{max}^{\pi\rightarrow\pi^*}$ = 303 nm. DSC (10 K/min): T_g = 31 °C, T_{max} = 196 °C, 224 °C. STA (10 K/min): $T_{5\%}$ = 211 °C. GPC ($CHCl_3$): $\bar{M}_n$ = 6800 g/mol; $\bar{M}_w$ = 15 400 g/mol; $\bar{M}_w/\bar{M}_n$ = 2.2. Anal. Calcd for $(C_{21}H_{26}N_4O_7P_2)_n$: C, 49.61; H, 5.15; N, 11.02. Found: C, 49.57; H, 5.05; N, 10.21.

Characterization of AAP 7 (R^1 = −), AAP 8 (R^1 = O), and AAP 9 (R^1 = CO).



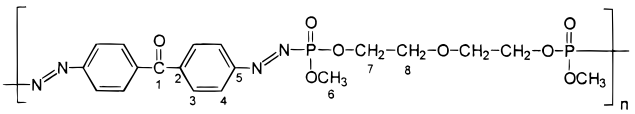
APP 7

Yield: 1.87 g (40%). ^{1}H NMR ($CDCl_3$, δ in ppm): 3.7−3.9 (m, 4H, H7), 3.9−4.1 (m, 6H, H5), 4.3−4.6 (m, 4H, H6), 7.7−7.9 (d, 4H, H2, $^3J_{H,H}$ = 8.3 Hz), 7.9−8.1 (d, 4H, H3, $^3J_{H,H}$ = 8.3 Hz). ^{13}C NMR ($CDCl_3$, δ in ppm): 55.2 (d, C5, $^2J_{C,P}$ = 6.0 Hz), 67.6 (d, C7, $^3J_{C,P}$ = 6.6 Hz), 70.2 (d, C6, $^2J_{C,P}$ = 5.7 Hz), 123.9 (s, C2/C3), 128.2 (s, C2/C3), 145.1 (s, C1), 153.8 (d, C4, $^3J_{C,P}$ = 53.8 Hz). ^{31}P NMR ($CDCl_3$, δ in ppm): −0.8. FTIR spectroscopy $\tilde{\nu}$ in cm^{-1} (film): 3005 (m, ν(C−H)), 2957 (w, ν(C−H)), 2904 (w, ν(C−H)), 1597 (m, ν(C═C)), 1489 (w, ν(C═C)), 1458 (m, δ(C−H)), 1266 (s, ν(P═O)), 1032 (s, ν(P−OC)), 830 (m, δ-(C−H)). UV/visible ($CHCl_3$): $\lambda_{max}^{\pi\rightarrow\pi^*}$ = 355 nm. DSC (10 K/min): T_g = 22 °C; T_{max} = 198, 220 °C. STA (10 K/min): $T_{5\%}$ = 188 °C. GPC ($CHCl_3$): $\bar{M}_n$ = 3600 g/mol; $\bar{M}_w$ = 7200 g/mol; $\bar{M}_w/\bar{M}_n$ = 2.0. Anal. Calcd for $(C_{18}H_{22}N_4O_7P_2)_n$: C, 46.16; H, 4.73; N, 11.96. Found: C, 45.88; H, 4.67; N, 11.20.



APP 8

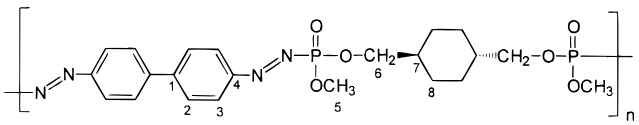
Yield: 1.99 g (41%). ^{1}H NMR ($CDCl_3$, δ in ppm): 3.8−3.9 (m, 4H, H7), 3.9−4.1 (d, 6H, H5, $^3J_{H,P}$ = 10.5 Hz), 4.3−4.6 (m, 4H, H6), 7.1−7.2 (d, 4H, H2, $^3J_{H,H}$ = 8.2 Hz), 7.9−8.0 (d, 4H, H3, $^3J_{H,H}$ = 8.2 Hz). ^{13}C NMR ($CDCl_3$, δ in ppm): 55.2 (d, C5, $^2J_{C,P}$ = 6.8 Hz), 67.5 (d, C7, $^3J_{C,P}$ = 6.8 Hz), 70.2 (d, C6, $^2J_{C,P}$ = 5.7 Hz), 119.5 (s, C2/C3), 125.7 (s, C2/C3), 150.8 (d, C4, $^3J_{C,P}$ = 54.4 Hz), 161.0 (s, C1). ^{31}P NMR ($CDCl_3$, δ in ppm): −0.4. FTIR spectroscopy $\tilde{\nu}$ in cm^{-1} (film): 3003 (m, ν(C−H)), 2956 (w, ν(C−H)), 2866 (w, ν(C−H)), 1582 (s, ν(C═C)), 1489 (s, ν-(C═C)), 1462 (s, δ(C−H)), 1242 (s, ν(P═O)), 1044 (s, ν(P−OC)), 837 (m, δ(C−H)). UV/visible ($CHCl_3$): $\lambda_{max}^{\pi\rightarrow\pi^*}$ = 343 nm. DSC (10 K/min): T_g = 32 °C; T_{max} = 202, 219 °C. STA (10 K/min): $T_{5\%}$ = 193 °C. GPC ($CHCl_3$): $\bar{M}_n$ = 8600 g/mol; $\bar{M}_w$ = 19 400 g/mol; $\bar{M}_w/\bar{M}_n$ = 2.3. Anal. Calcd for $(C_{18}H_{22}N_4O_8P_2)_n$: C, 44.64; H, 4.58; N, 11.57. Found: C, 44.91; H, 4.71; N, 11.84.



APP 9

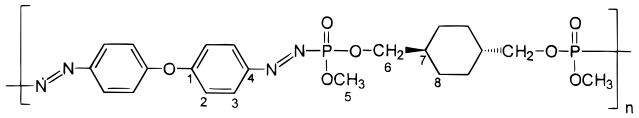
Yield: 1.29 g (26%). ^{1}H NMR ($CDCl_3$, δ in ppm): 3.7−3.9 (m, 4H, H8), 3.9−4.1 (d, 6H, H6, $^3J_{H,P}$ = 10.7 Hz), 4.3−4.6 (m, 4H, H7), 7.8−8.1 (m, 8H, H3/H4). ^{13}C NMR ($CDCl_3$, δ in ppm): 55.4 (d, C6, $^2J_{C,P}$ = 6.6 Hz), 67.8 (d, C8, $^3J_{C,P}$ = 6.8 Hz), 70.1 (d, C7, $^2J_{C,P}$ = 5.9 Hz), 123.1 (s, C3/C4), 131.0 (s, C3/C4), 141.2 (s, C2), 155.3 (d, C5, $^3J_{C,P}$ = 53.7 Hz), 195.2 (s, C1). ^{31}P NMR ($CDCl_3$, δ in ppm): −1.3. FTIR spectroscopy $\tilde{\nu}$ in cm^{-1} (film): 3002 (m, ν(C−H)), 2957 (w, ν(C−H)), 2903 (w, ν(C−H)), 1661 (m, ν(C═O)), 1598 (m, ν(C═C)), 1503 (w, ν(C═C)), 1470 (m, δ(C−H)), 1274 (s, ν(P═O)), 1037 (s, ν(P−OC)), 833 (m, δ(C−H)). UV/visible ($CHCl_3$): $\lambda_{max}^{\pi\rightarrow\pi^*}$ = 304 nm. DSC (10 K/min): T_g = 33 °C; T_{max} = 193 °C, 225 °C. STA (10 K/min): $T_{5\%}$ = 199 °C. GPC ($CHCl_3$): $\bar{M}_n$ = 5400 g/mol; $\bar{M}_w$ = 14 300 g/mol; $\bar{M}_w/\bar{M}_n$ = 2.7. Anal. Calcd for $(C_{19}H_{22}N_4O_8P_2)_n$: C, 45.98; H, 4.47; N, 11.29. Found: C, 46.68; H, 4.54; N, 10.79.

Characterization of AAP 10 (R^1 = −), AAP 11 (R^1 = O), and AAP 12 (R^1 = CO).



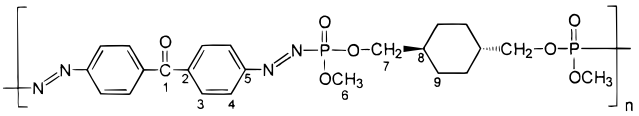
APP 10

Yield: 3.04 g (60%). ^{1}H NMR ($CDCl_3$, δ in ppm): 1.0−2.1 (m, 20H, H7/8), 4.02 (d, 12H, H5, $^3J_{H,P}$ = 10.5 Hz), 4.12 (m, 4H, $H6_{trans}$), 4.21 (m, 4H, $H6_{cis}$), 7.80 (d, 8H, H2, $^3J_{H,H}$ = 8.2 Hz), 8.05 (d, 8H, H3, $^3J_{H,H}$ = 8.2 Hz). ^{13}C NMR ($CDCl_3$, δ in ppm): 24.7 (s, $H8_{cis}$), 28.2 (s, $H8_{trans}$), 36.0 (s, $H7_{cis}$), 38.5 (s, $H7_{trans}$), 55.2 (d, C5, $^2J_{C,P}$ = 6.8 Hz), 70.6 (s, $H6_{cis}$), 73.4 (s, $H6_{trans}$), 123.9 (s, C2/C3), 128.2 (s, C2/C3), 145.1 (s, C1), 153.7 (d, C4, $^3J_{C,P}$ = 53.6 Hz). ^{31}P NMR ($CDCl_3$, δ in ppm): −1.2. UV/visible ($CHCl_3$): $\lambda_{max}^{\pi\rightarrow\pi^*}$ = 354 nm. DSC (10 K/min): T_g = 58 °C; T_{max} = 213 °C, shoulder. STA (10 K/min): $T_{5\%}$ = 193 °C. GPC ($CHCl_3$): $\bar{M}_n$ = 6700 g/mol; $\bar{M}_w$ = 14 300 g/mol; $\bar{M}_w/\bar{M}_n$ = 2.1. Anal. Calcd for $(C_{22}H_{28}N_4O_6P_2)_n$: C, 52.18; H, 5.57; N, 11.06. Found: C, 51.14; H, 5.54; N, 10.25.



APP 11

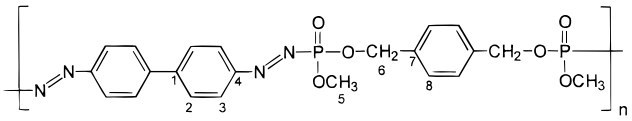
Yield: 2.40 g (46%). ^{1}H NMR ($CDCl_3$, δ in ppm): 1.1−2.1 (m, 20H, H7/8), 4.00 (d, 12H, H5, $^3J_{H,P}$ = 10.6 Hz), 4.11 (m, 4H, $H6_{trans}$), 4.17 (m, 4H, $H6_{cis}$), 7.20 (d, 8H, H2, $^3J_{H,H}$ = 8.8 Hz), 8.00 (d, 8H, H3, $^3J_{H,H}$ = 8.8 Hz). ^{13}C NMR ($CDCl_3$, δ in ppm): 24.7 (s, $H8_{cis}$), 28.2 (s, $H8_{trans}$), 36.0 (s, $H7_{cis}$), 38.5 (s, $H7_{trans}$), 55.1 (d, C5, $^2J_{C,P}$ = 5.5 Hz), 70.6 (s, $H6_{cis}$), 73.4 (s, $H6_{trans}$), 119.5 (s, C2/C3), 125.6 (s, C2/C3), 150.7 (d, C4, $^3J_{C,P}$ = 54.0 Hz), 161.0 (s, C1). ^{31}P NMR ($CDCl_3$, δ in ppm): −1.0. UV/visible ($CHCl_3$): $\lambda_{max}^{\pi\rightarrow\pi^*}$ = 342 nm. DSC (10 K/min): T_g = 50 °C; T_{max} = 215 °C, shoulder. STA (10 K/min): $T_{5\%}$ = 198 °C. GPC ($CHCl_3$): $\bar{M}_n$ = 15 500 g/mol; $\bar{M}_w$ = 42 300 g/mol; $\bar{M}_w/\bar{M}_n$ = 2.7. Anal. Calcd for $(C_{22}H_{28}N_4O_7P_2)_n$: C, 50.58; H, 5.40; N, 10.72. Found: C, 49.53; H, 4.23; N, 10.45.



APP 12

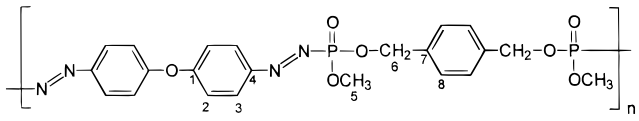
Yield: 2.19 g (41%). ^{1}H NMR ($CDCl_3$, δ in ppm): 1.0−2.3 (m, 20H, H8/9), 4.04 (d, 12H, H6, $^3J_{H,P}$ = 10.5 Hz), 4.11 (m, 4H, $H7_{trans}$), 4.20 (m, 4H, $H7_{cis}$), 8.01 (m, 16H, H3/H4). ^{13}C NMR ($CDCl_3$, δ in ppm): 24.7 (s, $H9_{cis}$), 28.2 (s, $H9_{trans}$), 35.8 (s, $H8_{cis}$), 38.4 (s, $H8_{trans}$), 55.4 (d, C6, $^2J_{C,P}$ = 5.6 Hz), 71.0 (s, $H7_{cis}$), 73.7 (s, $H7_{trans}$), 123.0 (s, C3/C4), 131.0 (s, C3/C4), 141.0 (s, C2), 155.0 (d, C5, $^3J_{C,P}$ = 53.7 Hz), 195.3 (s, C1). ^{31}P NMR ($CDCl_3$, δ in ppm): −3.0. UV/visible ($CHCl_3$): $\lambda_{max}^{\pi\rightarrow\pi^*}$ = 304 nm. DSC (10 K/min): T_g = 52 °C; T_{max} = shoulder, 224 °C. STA (10 K/min): $T_{5\%}$ = 202 °C. GPC ($CHCl_3$): $\bar{M}_n$ = 6900 g/mol; $\bar{M}_w$ = 14 400 g/mol; $\bar{M}_w/\bar{M}_n$ = 2.1. Anal. Calcd for $(C_{23}H_{28}N_4O_7P_2)_n$: C, 51.69; H, 5.28; N, 10.48. Found: C, 51.40; H, 5.22; N, 10.01.

Characterization of AAP 13 (R^1 = −), AAP 14 (R^1 = O), and AAP 15 (R^1 = CO).



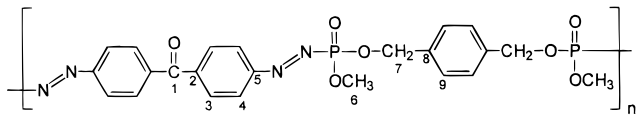
APP 13

Yield: 3.35 g (67%). ^{1}H NMR ($CDCl_3$, δ in ppm): 3.6−3.8 (m, $H5_{end}$), 3.9−4.1 (d, 6H, H5, $^3J_{H,P} = 10.7$ Hz), 5.0−5.2 (m, $H6_{end}$), 5.2−5.4 (d, 4H, H6), 7.3−7.6 (s, 4H, H2, $^3J_{H,H} = 8.3$ Hz), 7.7−7.9 (d, 4H, H2, $^3J_{H,H} = 8.3$ Hz), 7.9−8.1 (d, 4H, H3, $^3J_{H,H} = 8.3$ Hz). ^{13}C NMR ($CDCl_3$, δ in ppm): 55.2 (d, C5, $^2J_{C,P} = 6.7$ Hz), 69.7 (d, C6, $^2J_{C,P} = 6.3$ Hz), 123.9 (s, C2/C3), 128.2 (s, C2/C3/C8), 128.4 (s, C2/C3/C8), 136.2 (s, C7), 145.1 (s, C1), 153.7 (d, C4, $^3J_{C,P} = 54.1$ Hz). ^{31}P NMR ($CDCl_3$, δ in ppm): −0.5. UV/visible ($CHCl_3$): $\lambda_{max}^{\pi\rightarrow\pi^*} = 356$ nm. DSC (10 K/min): $T_g = 48$ °C; $T_{max} = 184$ °C, shoulder. STA (10 K/min): $T_{5\%} = 185$ °C. GPC ($CHCl_3$): $\bar{M}_n = 11\,700$ g/mol; $\bar{M}_w = 34\,100$ g/mol; $\bar{M}_w/\bar{M}_n = 2.9$. Anal. Calcd for $(C_{22}H_{24}N_4O_6P_2)_n$: C, 52.81; H, 4.43; N, 11.20. Found: C, 52.58; H, 4.57; N, 10.73.



APP 14

Yield: 2.58 g (50%). ^{1}H NMR ($CDCl_3$, δ in ppm): 3.6−3.8 (m, $H5_{end}$), 3.8−4.0 (d, 6H, H5, $^3J_{H,P} = 10.6$ Hz), 5.0−5.2 (m, $H6_{end}$), 5.2−5.4 (d, 4H, H6), 7.1−7.2 (d, 4H, H2, $^3J_{H,H} = 8.7$ Hz), 7.3−7.5 (s, 4H, H8), 7.8−8.0 (d, 4H, H3, $^3J_{H,H} = 8.7$ Hz). ^{13}C NMR ($CDCl_3$, δ in ppm): 55.1 (d, C5, $^2J_{C,P} = 6.8$ Hz), 69.5 (d, C6, $^2J_{C,P} = 6.3$ Hz), 119.5 (s, C2/C3), 125.7 (s, C2/C3), 128.3 (s, C8), 136.2 (d, C7, $^3J_{C,P} = 5.9$ Hz), 150.7 (d, C4, $^3J_{C,P} = 54.5$ Hz), 161.1 (s, C1). ^{31}P NMR ($CDCl_3$, δ in ppm): −1.0. UV/visible ($CHCl_3$): $\lambda_{max}^{\pi\rightarrow\pi^*} = 344$ nm. DSC (10 K/min): $T_g = 50$ °C; $T_{max} = 172$ °C, 182 °C. STA (10 K/min): $T_{5\%} = 186$ °C. GPC ($CHCl_3$): $\bar{M}_n = 14\,400$ g/mol; $\bar{M}_w = 35\,800$ g/mol; $\bar{M}_w/\bar{M}_n = 2.5$. Anal. Calcd for $(C_{22}H_{24}N_4O_7P_2)_n$: C, 51.17; H, 4.29; N, 10.85. Found: C, 50.68; H, 4.40; N, 10.58.



APP 15

Yield: 2.54 g (48%). ^{1}H NMR ($CDCl_3$, δ in ppm): 3.7−3.8 (m, $H6_{end}$), 3.8−4.1 (d, 6H, H6, $^3J_{H,P} = 10.5$ Hz), 5.0−5.2 (m, $H7_{end}$), 5.2−5.5 (m, 4H, H7), 7.3−7.5 (s, 4H, H9), 7.7−8.1 (m, 8H, H3/H4). ^{13}C NMR ($CDCl_3$, δ in ppm): 55.4 (d, C6, $^2J_{C,P} = 6.5$ Hz), 69.8 (d, C7, $^2J_{C,P} = 6.3$ Hz), 123.1 (s, C3/C4), 128.4 (s, C9), 131.0 (s, C3/C4), 136.1 (s, C8), 141.0 (s, C2), 155.5 (d, C5, $^3J_{C,P} = 53.9$ Hz), 195.5 (s, C1). ^{31}P NMR ($CDCl_3$, δ in ppm): −1.2. UV/visible ($CHCl_3$): $\lambda_{max}^{\pi\rightarrow\pi^*} = 305$ nm. DSC (10 K/min): $T_g = 48$ °C; $T_{max} = 191$ °C, 205 °C. STA (10 K/min): $T_{5\%} = 198$ °C. GPC ($CHCl_3$): $\bar{M}_n = 7800$ g/mol; $\bar{M}_w = 29900$ g/mol; $\bar{M}_w/\bar{M}_n = 2.5$. Anal. Calcd for $(C_{23}H_{24}N_4O_7P_2)_n$: C, 52.28; H, 4.20; N, 10.60. Found: C, 51.16; H, 4.29; N, 9.55.

References and Notes

(1) Rau, H. *Angew. Chem.* **1973**, *85*, 248.
(2) Stebani, J.; Nuyken, O.; Lippert, Th.; Wokaun, A. *Makromol. Chem. Rapid Commun.* **1993**, *14*, 365.
(3) Lippert, Th.; Wokaun, A.; Stebani, J.; Nuyken, O.; Ihlemann, J. *Angew. Makromol. Chem.* **1993**, *206*, 97.
(4) Baindl, A.; Lang, A.; Nuyken, O. *Macromol. Chem. Phys.* **1996**, *197*, 4155.
(5) Nuyken, O.; Scherer, C.; Voit, B. *Macromol. Chem. Phys.* **1996**, *197*, 1101.
(6) Nuyken, O.; Lang, A.; Stasko, A.; Wokaun, A. *Angew. Makromol. Chem.* **1995**, *228*, 73.
(7) Nuyken, O.; Lang, A. *Angew. Makromol. Chem.* **1995**, *230*, 129.
(8) Suckfüll, F.; Haubrich, H. *Angew. Chem.* **1958**, *70*, 238.
(9) Bock, H. *Angew. Chem.* **1965**, *77*, 469.
(10) Suckfüll, F.; Haubrich, H. DB Patent 1008313, 1955.
(11) Lewis, E. S.; Nieh, E. C. *J. Org. Chem.* **1973**, *38*, 4402.
(12) Levin, Ya. A.; Valeeva, T. G.; Gozman, I. P.; Gol'dfarb, E. I. *Zh. Obsh. Khim.* **1985**, *55*, 1290.
(13) Morgan, P. W. *Condensation polymers: by interfacial and solution methods*; Springer: Berlin, 1980; p 32.
(14) Millich, F.; Carraher, C. E. *Interfacial synthesis*; M. Dekker: New York, 1977.
(15) Zollinger, H. *Diazo Chemistry I*; Verlag Chemie: Weinheim, Germany, 1994.
(16) Ladenburg, A. *Ber. Dtsch. Chem. Ges.* **1876**, *9*, 219.
(17) Oswald, A. A. *Can. J. Chem.* **1959**, *37*, 1498.
(18) Petrov, K. A.; Nifant'ev, É.E.; Gol'tsova, R. G. *Zh. Obsh. Khim.* **1963**, *33*, 1485.
(19) Zavalishina, A. I.; Sorokina, S. F.; Nifant'ev, É. E. *Zh. Obsh. Khim.* **1968**, *38*, 2271.
(20) Vogt, W.; Balasubramanian, S. *Makromol. Chem.* **1973**, *163*, 111.
(21) Pretula, J.; Penczek, S. *Makromol. Chem.* **1990**, *191*, 671.
(22) Penczek, S.; Pretula, J. *Macromolecules* **1993**, *26*, 2228.
(23) Sasse, K. In *Methoden der organischen Chemie (Houben-Weyl)*; Thieme: Stuttgart, Germany, 1965; Vol. XII/2, p 20.
(24) Nuyken, O.; Scherer, C.; Nobis, M. N.; Ihlemann, J. *Polym. Mater. Sci. Eng.* **1997**, *76*, 206.

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