Soluble, Rigid-Rod Polyimides with Dye-Containing Side Groups via a Novel Precursor Route

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ABSTRACT: Soluble, rigid-rod precursor polyimides were prepared via Pd-catalyzed copolycondensation of 3,6-diphenoxy-*N,N'*-bis(4-bromo-2,5-didodecylphenyl)pyromellitic diimide, 3,6-diphenyl-*N,N'*-bis(4-bromo-2,5-didodecylphenyl)pyromellitic diimide, and 2,5-didodecylbenzene-1,4-diboronic acid. From these precursors, soluble, dye-containing polyimides were obtained by nucleophilic substitution of the phenoxy side groups for (a) 4-hydroxyazobenzene, (b) 4'-nitro-4-hydroxyazobenzene, (c) 4-[(4-nitrophenyl)azo]-1-naphthol ("magneson II"), and (d) 2,3'-dimethyl-4-[(2-hydroxy-1-naphthyl)azo]azobenzene ("sudan red B"), respectively. An almost quantitative exchange was achieved in the case of the sterically less demanding dyes (a and b); a low conversion was observed for the bulky dyes (c and d). Throughout, no evidence for chain degradation or other side reactions during the substitution reaction was found by analyzing the products by high-field NMR spectroscopy and membrane osmometry.

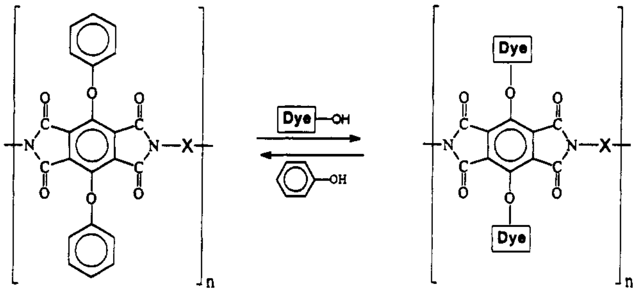
Introduction

The synthesis of soluble, well-defined rigid-rod polymers with dye-containing pendant groups has been developed into an important objective in polymer chemistry during recent years.[1] This increasing interest stems mainly from the expectation that these materials would display good properties for their use in optical devices. In order to prepare such polymers, direct routes starting from dye-containing monomers have serious limitations which are associated with the low chemical and thermal stability of many dyes, and/or the reduced reactivity of these monomers themselves. The second way to prepare the desired materials consists of introducing the dye functionalities into an appropriate soluble precursor polymer. Since unsubstituted rodlike polymers are insoluble, measures are required to increase the solubility in order to implement this second path. A much higher solubility can be achieved by attaching flexible side chains to the rodlike polymer backbones.[2] Using these side-chain-substituted polymers as precursors, dyes should be introducible into these macromolecules in a well-defined manner. In the case of phenoxy-substituted polyimides, the nucleophilic substitution at the pyromellitic diimide moiety may open up an efficient way to soluble, dye-containing rigid-rod polymers, as shown in Scheme I. This conversion is known to occur under mild conditions via a Meisenheimer complex,[3] and a variety of polyimides and dye derivatives should be stable under the required reaction conditions.

Recently, we reported on a novel Pd-catalyzed polycondensation method[4] which opens up an efficient access to soluble, rigid-rod polyimides **3a,b** of homogeneous molecular structure and high molecular weight (Scheme II).

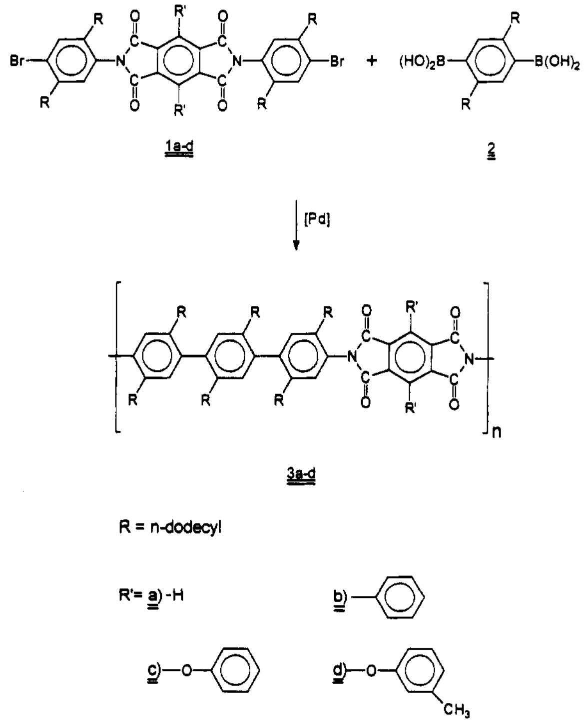
The developed synthetic strategy allows the imide structures to be already built up during the monomer synthesis. Consequently, the low yields known for imidizations involving 3,6-disubstituted pyromellitic dianhydrides[5] do not affect the polycondensation process here. Hence, that route is well suited for synthesizing polyimides with substituted pyromellitic diimide units and should be, in particular, an efficient method for preparing precursor polyimides such as **3c** or **3d**, the possible precursors in conversions according to Scheme I. As we were interested in exploring the potential of the nucleophilic substitution reaction for introducing dye functionalities into rigid-rod polyimides, appropriate precursor polyimides were prepared and their homogeneous conversion into dye-containing polyimides was studied. In

Scheme I[a]



[a] X = aromatic or aliphatic moiety.

Scheme II



the present paper, we give an account of the synthetic aspects and the structural eludication of the first soluble, rigid-rod polyimides with azo dye pendant groups.[6]

Experimental Section

Reagents and Analyses. Chemicals and solvents used were purchased from Aldrich and Fluka Chemical Co. and used as received. 3,6-Diphenyl-*N*,*N*′-bis(4-bromo-2,5-didodecylphenyl)pyromellitic diimide (**1b**),[4b] 2,5-didodecylbenzene-1,4-diboronic acid (**2**),[7] and 2,5-didodecyl-4-bromoaniline (**5**)[4b] were synthesized as described previously. 3,6-Diphenoxypyromellitic dianhydride (**4**)[8] and $Pd(PPh_3)_4$[9] were prepared according to the literature. Methods and techniques were as previously described.[4] The assignment of the absorptions in the ^1H and ^{13}C NMR spectra was made according to the numbering given in Figures 1 and 2, respectively.

3,6-Diphenoxy-*N*,*N*′-bis(4-bromo-2,5-didodecylphenyl)pyromellitic Diimide (1c). A mixture of 2,5-didodecyl-4-bromoaniline (**5**) (5.0 g, 9.8 mmol), phenol (50 g, 0.42 mol), and isoquinoline (4 mL) was heated up to 70 °C. 3,6-Diphenoxypyromellitic dianhydride (**4**) (2.0 g, 4.9 mmol) was added in small portions within 1 h. After complete addition, toluene (10 mL) was added and the water formed was removed azeotropically by distillation. After 12 h the reaction was complete. The reaction mixture was cooled down to about 50 °C and poured into acetone (200 mL). The precipitate was isolated by filtration, washed with acetone, and dried in vacuo. Recrystallization from dimethylformamide (DMF) resulted in the pure compound **1c** (5.5 g, 81%) as yellow-orange crystals: mp 198 °C; ^1H NMR ($C_2D_2Cl_4$, 363 K) δ 7.46 (s; 2H, H^3), 7.31 (dd; 4H, H^{12}), 7.09 (t; 2H, H^{13}), 7.03 (d; 4H, H^{11}), 6.92, 6.90 (2s; 2H, H^6), 2.61, 2.25 (2m; 8H, α-CH_2), 1.53 (m; 8H, β-CH_2), 1.25 (m; 72H, $CH_2CH_2(CH_2)_9CH_3$), 0.88 (t; 12H, CH_3); ^{13}C NMR ($C_2D_2Cl_4$, 363 K) δ 162.02 (s; C^9), 158.53 (s; C^{10}), 145.70 (s; C^7), 141.05 (s; C^5), 139.89 (s; C^2), 133.96 (d; C^6), 131.38 (s; C^8), 130.01 (d; C^3), 129.67 (d; C^{12}), 128.24 (s; C^1), 125.97 (s; C^4), 123.79 (d; C^{13}), 116.02 (d; C^{11}), 35.67, 31.91, 30.98, 29.63, 29.51, 29.35, 22.67 (7t; CH_2), 14.08 (q; CH_3).

3,6-Bis(3-methylphenoxy)-*N*,*N*′-bis(4-bromo-2,5-didodecylphenyl)pyromellitic Diimide (1d). Method A. Imide **1d** was prepared according to the procedure given for diimide **1c** from 2,5-didodecyl-4-bromoaniline (**5**) (5.0 g, 9.8 mmol), isoquinoline (4 mL), 3,6-diphenoxypyromellitic dianhydride (**4**) (2.0 g, 4.9 mmol), and toluene (10 mL) using *m*-cresol (50 mL, 0.478 mol) instead of phenol. Recrystallization from DMF resulted in the pure compound **1d** (5.3 g, 77%).

Method B. 3,6-Diphenoxy-*N*,*N*′-bis(4-bromo-2,5-didodecylphenyl)pyromellitic diimide (**1c**) (2.4 g, 1.73 mmol) was refluxed in a mixture of *p*-xylene (80 mL), *m*-cresol (18 mL, 0.173 mol), and isoquinoline (3 mL). After 12 h, the reaction mixture was poured into acetone (200 mL). The precipitate was removed by filtration, washed with acetone, and dried in vacuo. Recrystallization from DMF resulted in the compound **1d** (2.2 g, 90%) as yellow-orange crystals: mp 196 °C; ^1H NMR ($C_2D_2Cl_4$, 363 K) δ 7.46 (s; 2H, H^3), 7.16 (dd; 2H, H^{14}), 6.90 (m; 6H, H^{11}, H^{13}, H^{15}), 6.76, 6.74 (2s; 2H, H^6), 2.32 (s; 6H, aryl-CH_3), 2.62, 2.28 (2m; 8H, α-CH_2), 1.55, 1.41 (2m; 8H, β-CH_2), 1.25 (m; 72H, $CH_2CH_2(CH_2)_9CH_3$), 0.88 (t; 12H, $(CH_2)_{11}CH_3$); ^{13}C NMR ($C_2D_2Cl_4$, 363 K) δ 162.08 (s; C^9), 158.48, 158.45 (2s; C^{10}), 145.62, 145.59 (2s; C^7), 140.99 (s; C^5), 140.04 (s; C^{12}), 139.85, 139.82 (2s; C^2), 133.90, 133.78 (2d; C^6), 131.40, 131.35 (2s; C^8), 130.02, 129.98 (2d; C^3), 129.19 (d; C^{14}), 128.21 (s; C^1), 125.93 (s; C^4), 124.57 (d; C^{13}), 116.94, 116.90 (2d; C^{11}), 112.30 (d; C^{15}), 35.66, 31.90, 29.63, 29.51, 29.41, 29.34, 22.67 (7t; CH_2), 21.46 (q; aryl-CH_3), 14.10 (q; $(CH_2)_{11}CH_3$).

Precursor Copolyimide 6c ($x = 0.5$, $y = 0.5$). A mixture of imide **1b** (1.5000 g, 1.1098 mmol), imide **1c** (1.5355 g, 1.1098 mmol), and 2,5-didodecylbenzene-1,4-diboronic acid (**2**) (1.1134 g, 2.2196 mmol) was refluxed for 5 days in the heterogeneous system of toluene (80 mL) and aqueous Na_2CO_3 (1 M, 80 mL) in the presence of $Pd(PPh_3)_4$ (0.0256 g, 0.0222 mmol). The polymer was precipitated by pouring the whole reaction mixture into acetone (400 mL). The precipitate was filtered off, washed with acetone (100 mL) and dilute hydrochloric acid (1 M, 100 mL), and dried in vacuo (P_4O_{10}). The solid obtained was extracted with chloroform in a Soxhlet apparatus to remove inorganic impurities. The obtained solution was concentrated to about 50 mL. Polymer **6c** was precipitated by pouring this solution into acetone (200 mL). The slightly orange-brown polymer **6c** (3.3 g, 92%) was filtered off and freeze-dried from benzene: ^1H NMR ($C_2D_2Cl_4$, 363 K) δ 7.54 (m; 10H, H^{11}, H^{12}, H^{13}) 7.36 (m; 4H, $H^{12'}$), 7.00, 7.08, 7.11, 7.15 (4m; 12H, H^3, H^6, $H^{3'}$, $H^{6'}$, $H^{3''}$, $H^{6''}$, $H^{11'}$, $H^{13'}$), 2.36 (m; 24H, α-CH_2), 1.44 (m; 24H, β-CH_2), 1.24 (m; 216H, $CH_2CH_2(CH_2)_9CH_3$), 0.87 (t; 36H, CH_3); ^{13}C NMR ($C_2D_2Cl_4$, 363 K) δ 165.00, 164.84 (2s; C^9), 162.72 (s; $C^{9'}$), 158.79 (s; $C^{10'}$), 145.71 (s; $C^{7'}$), 143.31 (s; C^1, $C^{1'}$, $C^{4'}$, $C^{1''}$), 140.31 (s; C^{10}), 139.29, 139.58 (2s; C^5, $C^{5''}$), 137.42 (s; C^2, $C^{2'}$, $C^{5'}$, $C^{2''}$), 134.82 (s; C^8, $C^{8'}$), 131.35 (s; C^7), 131.86, 130.35, 129.96, 128.98 (4d; C^3, C^6, $C^{3'}$, $C^{6'}$, $C^{3''}$, $C^{6''}$, C^{12}, $C^{12'}$, C^{13}), 128.25 (s; C^4, $C^{4''}$), 127.94 (d; C^{11}), 123.99 (d; $C^{13'}$), 116.09 (d; $C^{11'}$), 32.83, 32.06, 31.39, 31.06, 30.78, 30.29, 29.80, 29.46, 22.78 (9t; CH_2), 14.15 (q; CH_3).

Precursor Copolyimide 6d ($x = 0.5$, $y = 0.5$). Copolyimide **6d** was prepared by polycondensation of a mixture of imide **1b** (0.2918 g, 0.216 mmol), 2,5-didodecylbenzene-1,4-diboronic acid (**2**) (0.2167 g, 0.432 mmol), and imide **1d** (0.3048 g, 0.216 mmol) in the heterogeneous system of toluene (40 mL) and aqueous Na_2CO_3 (1 M, 40 mL) in the presence of $Pd(PPh_3)_4$ (5.0 mg, 0.0043 mmol). After workup according to the procedure given for polyimide **6c**, polymer **6d** (0.7 g, 99%) was obtained as an orange, fibrous material: ^1H NMR ($C_2D_2Cl_4$, 363 K) δ 7.54 (m; 10H, H^{11}, H^{12}, H^{13}), 7.32 (m; 2H, $H^{12'}$), 7.16, 7.11, 7.07, 7.01, 6.92, 6.81 (6m; 10H, H^3, H^6, $H^{3'}$, $H^{6'}$, $H^{3''}$, $H^{6''}$, $H^{11'}$, $H^{13'}$, $H^{15'}$), 2.36 (m; 24H, α-CH_2), 2.27 (s; 6H, aryl-CH_3), 1.45 (m; 24H, β-CH_2), 1.25 (m; 216H, $CH_2CH_2(CH_2)_9CH_3$), 0.87 (t; 36H, CH_3); ^{13}C NMR ($C_2D_2Cl_4$, 363 K) δ 165.00, 164.84 (2s; C^9), 162.79 (s; $C^{9'}$), 158.76 (s; $C^{10'}$), 145.62 (s; $C^{7'}$), 143.35 (s; C^1, $C^{1'}$, $C^{4'}$, $C^{1''}$), 140.32 (s; C^{10}), 140.04 (s; $C^{12'}$), 139.31, 138.95 (2s; C^5, $C^{5''}$), 137.43 (s; C^2, $C^{2'}$, $C^{5'}$, $C^{2''}$), 134.82 (s; C^8, $C^{8'}$), 131.38 (s; C^7), 131.88, 130.35, 129.61, 129.00, 128.55 (5d; C^3, C^6, $C^{3'}$, $C^{6'}$, $C^{3''}$, $C^{6''}$, C^{12}, C^{13}, $C^{14'}$), 128.25 (s; C^4, $C^{4''}$), 127.92 (d; C^{11}), 124.74 (d; $C^{13'}$), 116.93 (d; $C^{11'}$), 112.75 (d; $C^{15'}$), 32.85, 32.07, 31.47, 30.80, 29.82, 29.47, 22.79 (7t; CH_2), 21.62 (q; aryl-CH_3), 14.16 (q; CH_3).

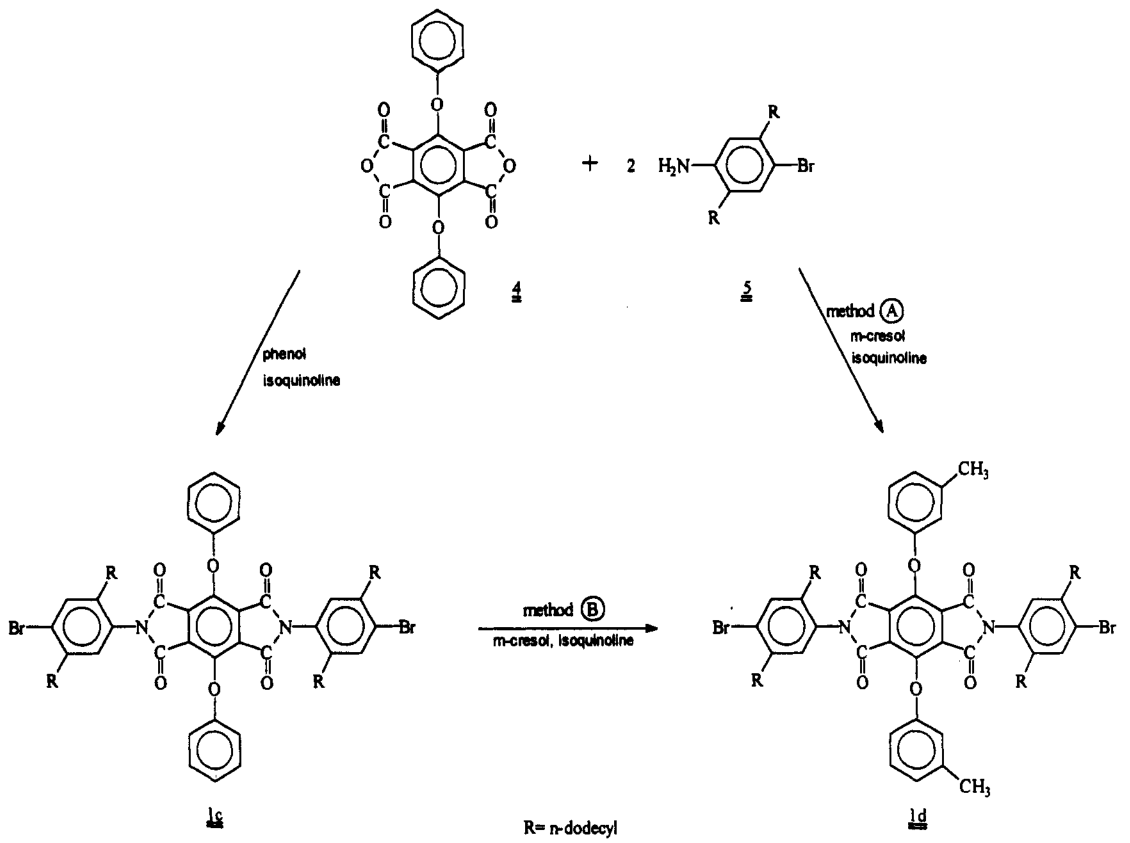
Nucleophilic Displacement Reactions. (A) Copolyimide 6d from Precursor 6c. Polyimide **6c** (0.5 g, 1 equiv) was refluxed in a mixture of *m*-cresol (33.36 g, 0.3085 mol, 1000 equiv), isoquinoline (2 mL), and *p*-xylene (50 mL) for 12 h. The whole reaction mixture was poured into acetone (200 mL), and the precipitate was isolated by filtration. To remove last traces of *m*-cresol, the raw product was extracted with acetone in a Soxhlet apparatus for 12 h. Finally, the polymer itself was extracted with chloroform, precipitated in acetone, and freeze-dried from benzene as described for polymer **6c**. The yield was 0.45 g (90%) of an orange fibrous material.

(B) Copolyimides 6e–h; General Procedure. Polyimide **6c** (0.1 g, 1 equiv) or polyimide **6d** (0.1009 g, 1 equiv) was treated in a mixture of isoquinoline (2 mL) and *p*-xylene (50 mL) with a dye derivative **7** (1.234 mmol, 20 equiv) under reflux for 12 h. The whole reaction mixture was poured into acetone (200 mL). The precipitate was isolated by filtration. After drying of the solid in vacuo, the raw product was extracted with acetone in a Soxhlet apparatus to recycle the unreacted dye. Finally, the polymer itself was extracted with chloroform, precipitated in acetone, and freeze-dried from benzene. Intensively colored polymers **6e–h** were obtained throughout.

(C) Copolyimide 6e. Yield: 0.95 g (95%); ^1H NMR ($C_2D_2Cl_4$, 363 K) δ 7.97, 7.85 (2m; 8H, $H^{12'}$, $H^{15'}$), 7.53, 7.42, 7.38 (3m; 16H, H^{11}, H^{12}, H^{13}, $H^{16'}$, $H^{17'}$), 7.19, 7.15, 7.09, 7.00 (4m; 14H, H^3, H^6, $H^{3'}$, $H^{6'}$, $H^{3''}$, $H^{6''}$, $H^{11'}$), 2.37 (m; 24H, α-CH_2), 1.44 (m; 24H, β-CH_2), 1.23 (m; 216H, $CH_2CH_2(CH_2)_9CH_3$), 0.86 (t; 36H, CH_3); ^{13}C NMR ($C_2D_2Cl_4$, 363 K) δ 165.09, 164.99 (2s; C^9), 162.63 (s; $C^{9'}$), 160.44 (s; $C^{10'}$), 153.17 (s; $C^{14'}$), 149.40 (s; $C^{13'}$), 145.51 (s; $C^{7'}$), 143.55 (s; C^1, $C^{1'}$, $C^{4'}$, $C^{1''}$), 140.35 (s; C^{10}), 139.33, 139.10 (2s; C^5, $C^{5''}$), 137.46 (s; C^2, $C^{2'}$, $C^{5'}$, $C^{2''}$), 134.80 (s; C^8, $C^{8'}$), 131.90, 130.36, 129.70, 129.21 (4d; C^3, C^6, $C^{3'}$, $C^{6'}$, $C^{3''}$, $C^{6''}$, C^4, $C^{4''}$, C^{12}, C^{13}, $C^{16'}$, $C^{17'}$), 130.99 (s; C^7), 127.94 (d; C^{11}), 124.92 (d; $C^{12'}$), 123.02 (d; $C^{15'}$), 116.57 (d; $C^{11'}$), 32.85, 32.06, 31.47, 30.80, 29.81, 29.46, 22.79 (7t; CH_2), 14.16 (q; CH_3).

(D) Copolyimide 6f. Yield: 0.97 g (97%); ^1H NMR ($C_2D_2Cl_4$, 363 K) δ 8.31 (m; 4H, $H^{16'}$), 8.02, 7.97, 7.95 (3m; 8H, $H^{12'}$, $H^{15'}$), 7.54 (m; 10H, H^{11}, H^{12}, H^{13}), 7.35, 7.23, 7.15, 7.10, 7.09, 7.01 (6m;

Scheme III



14H, H^3, H^6, $H^{3'}$, $H^{6'}$, $H^{3''}$, $H^{6''}$, $H^{11'}$), 2.39 (m; 24H, α-CH_2), 1.44 (m; 24H, β-CH_2), 1.23 (m; 216H, $CH_2CH_2(CH_2)_9CH_3$), 8.86 (t; 36H, CH_3); ^{13}C NMR ($C_2D_2Cl_4$, 363 K) δ 165.09, 164.85 (2s; C^9), 162.62 (s; $C^{9'}$), 161.25 (s; $C^{10'}$), 155.72 (s; $C^{14'}$), 148.65 (s; $C^{13'}$), 144.55 (s; $C^{7'}$, $C^{17'}$), 143.34 (s; C^1, $C^{1'}$, $C^{4'}$, $C^{1''}$), 140.31 (s; C^{10}), 139.50, 138.95 (2s; C^5, $C^{5''}$), 137.43 (s; C^2, $C^{2'}$, $C^{5'}$, $C^{2''}$), 134.82 (s; C^8, $C^{8'}$), 131.31 (s; C^7), 131.87, 130.34, 129.69, 128.99 (4d; C^3, C^6, $C^{3'}$, $C^{6'}$, $C^{3''}$, $C^{6''}$, C^4, $C^{4''}$, C^{12}, C^{13}), 127.94 (d; C^{11}), 125.69 (d; $C^{12'}$), 124.83 (d; $C^{16'}$), 123.51 (d; $C^{15'}$), 116.73 (d; $C^{11'}$), 32.84, 32.06, 31.47, 30.79, 29.81, 29.46, 22.78 (7t; CH_2), 14.15 (q; CH_3).

(E) Copolyimide 6g. Yield: 0.95 g (95%) of nearly unchanged precursor polyimide **6c** (5–10% substitution, NMR).

(F) Copolyimide 6h. Yield: 0.95 g (95%) of nearly unchanged precursor polyimide **6c** (5–10% substitution, NMR).

Results and Discussion

Monomer Synthesis and Model Reactions. A soluble precursor polyimide with phenoxy-substituted pyromellitic diimide units was the central intermediate for synthesizing the desired dye-containing rigid-rod polyimides according to Scheme I. 3,6-Diphenoxy-*N,N'*-bis(4-bromo-2,5-didodecylphenyl)pyromellitic diimide (**1c**) was considered to be a suitable starting material for the Pd-catalyzed synthesis[4] according to the route shown in Scheme II. It was prepared by reacting 3,6-diphenoxypyromellitic dianhydride (**4**) with 2 equiv of 4-bromo-2,5-didodecylaniline (**5**) in a mixture of phenol, isoquinoline, and toluene under reflux (Scheme III).[4] A single recrystallization from DMF resulted in the pure diimide **1c** as a yellow-orange crystalline mass with 81% yield. Its purity was checked by ^1H NMR spectroscopy and estimated to be better than 98%.

In addition to compound **1c**, the corresponding cresoxy-substituted imide **1d** is a suitable monomer, too. Compound **1d** was prepared analogously to compound **1c**, but using *m*-cresol instead of phenol (Scheme III, method A). Here, simultaneous to the imidization process, the phenoxy substituents of dianhydride **4** were replaced by *m*-cresoxy groups. This exchange occurs via the same nucleophilic substitution[3] which is planned for converting the precursor polyimides. As this exchange reaction is an equilibrium process, a large molar excess of *m*-cresol was used. Only traces of the corresponding phenoxy-substituted imide derivative **1c** were then found in the product mixture (NMR). Repeated recrystallization from DMF resulted in the pure compound **1d** in 77% yield.

The molecular structures of monomers **1c** and **1d** were established on the basis of their ^1H and ^{13}C NMR spectra. The given signal assignment (see Experimental Section and Figure 1) is based on the comparison with the spectra of compounds **1a** and **1b** (Scheme II),[4] use of tabulated increments,[10] and DEPT measurements (for ^{13}C NMR spectra; DEPT: distortionless enhancement by polarization transfer). In the ^1H as well as in the ^{13}C NMR spectra, the number of resonances throughout corresponds to the number of nonequivalent hydrogen and carbon atoms of imides **1c** and **1d**, respectively. Further signals attributable to impurities were not found, neither in the ^1H nor in the ^{13}C NMR spectra.

In order to develop suitable reaction conditions for the planned nucleophilic substitution at the polyimides, model experiments were performing using the conversion **1c** → **1d** (Scheme III, method B), varying reaction time and composition of the reaction mixture. The reactions were monitored by analyzing samples of the product mixtures by NMR. The well-resolved absorptions of the phenoxy and cresoxy substituents in the ^1H as well as in the ^{13}C NMR spectra allow an estimation of the extent of substitution achieved under the respective conditions.

As expected from the synthesis of imide **1d** via method A, imide **1d** was also formed by refluxing imide **1c** in a mixture of *m*-cresol, isoquinoline, and *p*-xylene. An almost quantitative exchange was ensured in that equilibrium reaction when a large excess of *m*-cresol was used.

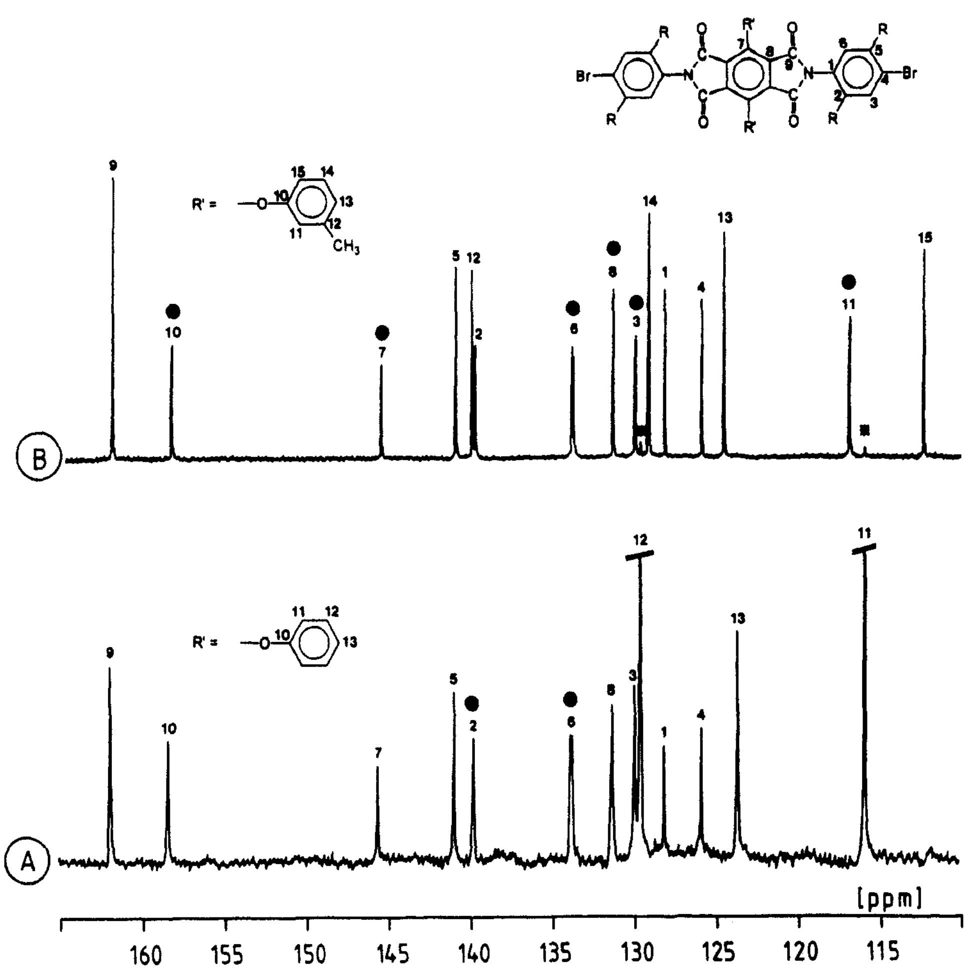


Figure 1. Aromatic regions of the ^{13}C NMR spectra of imide **1c** (panel A) and of imide **1d** (panel B). The latter was made from imide **1c** by nucleophilic substitution according to method B (Scheme III). Spectra were recorded in $C_2D_2Cl_4$ at 363 K.

The NMR spectra obtained from these model compounds are also of importance for the interpretation of those of the planned polyimides. For that reason, the aromatic region of a representative ^{13}C NMR spectrum of an imide **1d**, made by method B (Figure 1B), is discussed here in more detail together with the spectrum of an imide **1c** (Figure 1A). In the given example, a hundredfold molar excess of *m*-cresol was used for the synthesis of imide **1d**.

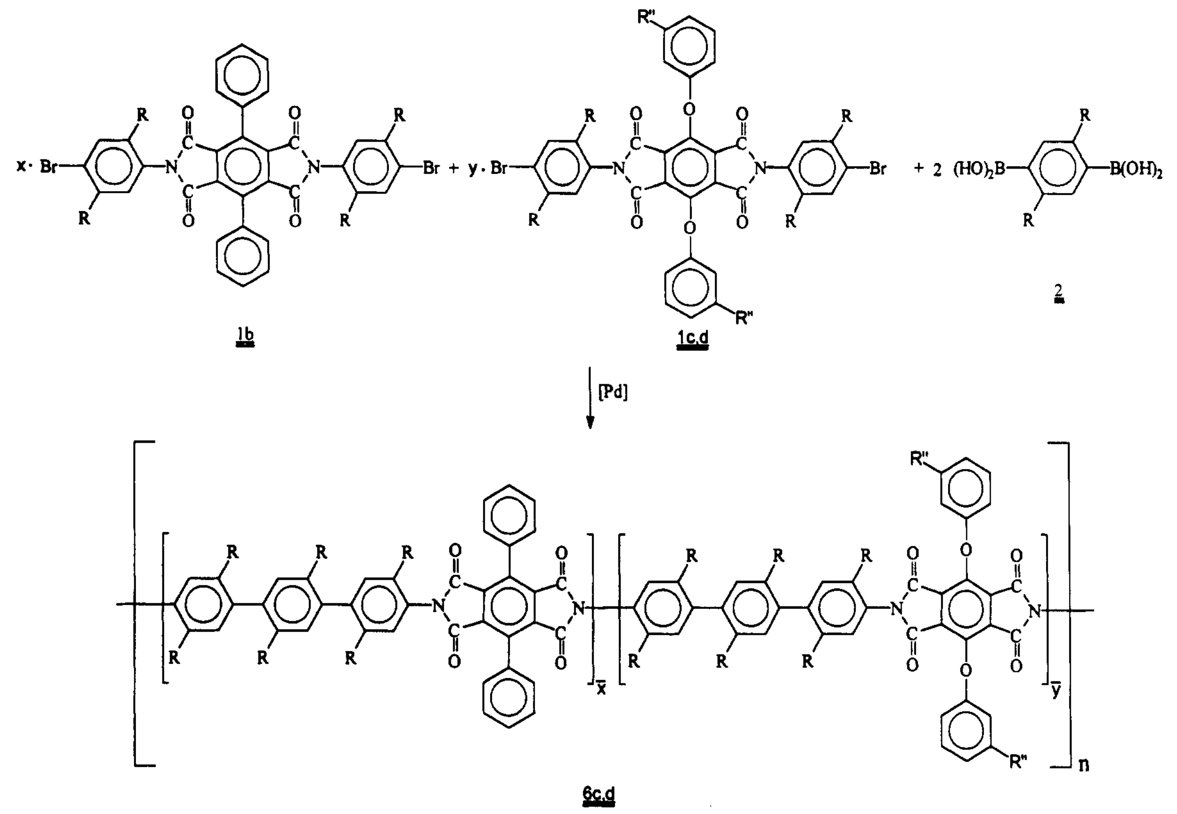
As one can see from these spectra, the nucleophilic displacement process, **1c** → **1d** resulted in an almost complete disappearance of the signals of the carbons C^{12}, C^{13}, and C^{11} of the phenoxy substituents at 129.67, 123.79, and 116.02 ppm, respectively. Only very small absorptions in Figure 1B at 116.02 and 129.67 ppm (assigned by asterisks) point toward the remaining phenoxy groups. On the other hand, an equivalent appearance of characteristic signals at 140.04, 129.19, 124.57, 116.92, and 112.30 ppm, which correspond to the cresoxy substituents, unambiguously verifies the success of the exchange process. The evaluation of the NMR spectra for the given example indicates <5% of remaining phenoxy substituents in the product **1d**. By prolonging the reaction time and increasing the excess of *m*-cresol, a further decrease of phenoxy groups in the product could be achieved. A nearly 100% yield of pure imide **1d** was obtained when a thousandfold excess of *m*-cresol was used.

The formation of different atrop isomers of the monomers **1c** and **1d** is manifested in both cases by narrow splitting of definite absorptions in the proton and carbon spectra,[4] assigned by circles (●) in Figure 1. The lack of additional signals pointing toward the formation of side products demonstrates that the conversion **1c** → **1d** proceeds selectively and without side reactions under all reaction conditions tested. This medium should therefore also be suitable for introducing dye derivatives into precursor polyimides.

Synthesis of Precursor Polyimides. First, precursor polyimides **3c** and **3d** with two phenoxy or cresoxy substituents in each pyromellitic diimide moiety were synthesized. According to Scheme II, equimolar amounts of imide **1c** (or **1d**) and 2,5-didodecyl-1,4-benzenediboronic acid (**2**) were polycondensed in the heterogeneous system of water (Na_2CO_3) and toluene in the presence of catalytic amounts of $Pd(PPh_3)_4$.[4] Polyimides **3c** and **3d**, respectively, were recovered as orange, fibrous materials in virtually 100% yield. Rather unexpectedly, the solubility of the obtained polyimides **3c** and **3d** was very low.[11] Even at elevated temperatures, polymers **3c** and **3d** only swelled in solvents like toluene, chloroform, or 1,1,2,2-tetrachloroethane, which are, on the other hand, excellent solvents for polyimides **3a** and **3b** described earlier.[4] ^1H NMR spectra could only be recorded for the products in highly diluted solutions. These spectra indicate the formation of polyimides **3c** and **3d** of regular structure. However, a detailed structure proof by ^{13}C NMR or the determination of the degrees of polycondensation ($\overline{DP}$'s) achieved was not possible so far. In addition, readily soluble, structurally well-defined precursor polymers were required for further conversion. Consequently, it was necessary to look for other precursor polyimides having a significantly higher solubility than polyimides **3c** and **3d**.

Because the phenyl-substituted polyimide **3b** is known to be highly soluble in many organic solvents, an improved solubility was expected for statistical copolyimides **6**

Scheme IV



R= n-dodecyl R''= c) H , d) CH_3

(Scheme IV). Hence, copolyimides **6c** and **6d** were synthesized by copolycondensation of mixtures of phenyl- and phenoxy-substituted imide monomers **1b** and **1c** (or **1d**) with the corresponding amount of diboronic acid **2** under the same reaction conditions as used for the synthesis of polyimides **3**. Equimolar amounts of monomers **1b** and **1c** (or **1d**) ($x = 0.5, y = 0.5$) were used in the majority of polymerizations. In some further polymerizations, monomer **1b** was used in a 9-fold excess ($x = 0.9, y = 0.1$) with respect to monomer **1c** (or **1d**). In all cases, yellow-orange, fibrous polymers were obtained in nearly 100% yield.

Without exception, copolymers **6c** and **6d** show a much higher solubility than the corresponding homopolymers **3c** and **3d**. Furthermore, copolymers **6** ($x = 0.9, y = 0.1$) show a somewhat higher solubility than copolymers **6** ($x = 0.5, y = 0.5$). Nevertheless, all copolymers **6** readily dissolved in chloroform, 1,1,2,2-tetrachloroethane, or *o*-dichlorobenzene. Thus, their molecular structures could be established on the basis of high-resolution ^1H and ^{13}C NMR spectra [for copolymers **6** ($x = 0.5, y = 0.5$), see Experimental Section and Figure 2A]. The correct number of resonances was found throughout. The observed chemical shifts agree with the δ values calculated from tabulated increments[10] and those expected from the spectra of homopolymer **3b**[4b] as well as from those of monomers **1c** and **1d**, respectively. A full signal assignment could be made. The narrow splitting of some of the absorptions is due to the presence of atrop isomers within the polymer chains. Their observation was expected because of the use of monomers **1** as isomer mixtures. The lack of further absorptions corresponding to chain end groups and/or structural irregularities points toward the formation of structurally homogeneous, high molecular weight copolyimides **6c** and **6d**.

As all copolymers **6** readily dissolve in common organic solvents, their molecular masses were determined by membrane osmometry. Measurements in *o*-dichlorobenzene at 50 °C gave $\overline{M_n}$ values of 17 000–25 000 for polyimides **6c** and **6d** ($x = 0.5, y = 0.5$), corresponding to $\overline{\mathrm{DP}}$'s of 11–16. In polycondensations using the 9-fold excess of monomer **1b**, polyimides **6c** and **6d** ($x = 0.9, y = 0.1$) having $\overline{M_n}$ values of up to 41 000 were obtained, corresponding to $\overline{\mathrm{DP}}$'s of about 26. The higher $\overline{M_n}$ values of the latter presumably originate in their higher solubility in the reaction mixture due to the greater portion of phenyl-substituted pyromellitic diimide units in these polymers.

Conversion of Precursor Polyimides. In the final step, the phenoxy groups of precursor polyimide **6c** had to be replaced by dye substitutents by nucleophilic substitution. In order to achieve as low a thermal exposure of the dye components as possible, the lowest possible conversion temperature was first looked for. In a trial experiment, **6c** → **6d**, polyimide **6c** was treated under reflux in a mixture of isoquinoline and a 100-fold molar excess of *m*-cresol, but using the lower boiling toluene instead of *p*-xylene. According to the NMR analysis of the obtained product, almost no substitution took place under these conditions. On the other hand, when *p*-xylene was used, the substitution occurred much faster. More than 95% of the phenoxy pendant groups were replaced by *m*-cresoxy substituents after 12 h. ^1H as well as ^{13}C NMR spectra show only very weak absorptions pointing toward remaining phenoxy substituents in the product **6d**. As a representative example of the efficiency of the reaction, Figure 2B shows the aromatic region of the ^{13}C NMR spectrum of a polyimide **6d** obtained from this procedure.

After testing the exchangeability of the phenoxy substituent bond at the precursor polyimide **6c**, the substitution reaction was applied to introduce the desired dye substituents into the polyimide backbone. It was necessary to have one free phenolic hydroxy group and a sufficient thermostability in the appropriate dyes. On the basis of these considerations, four azo dyes were selected for further

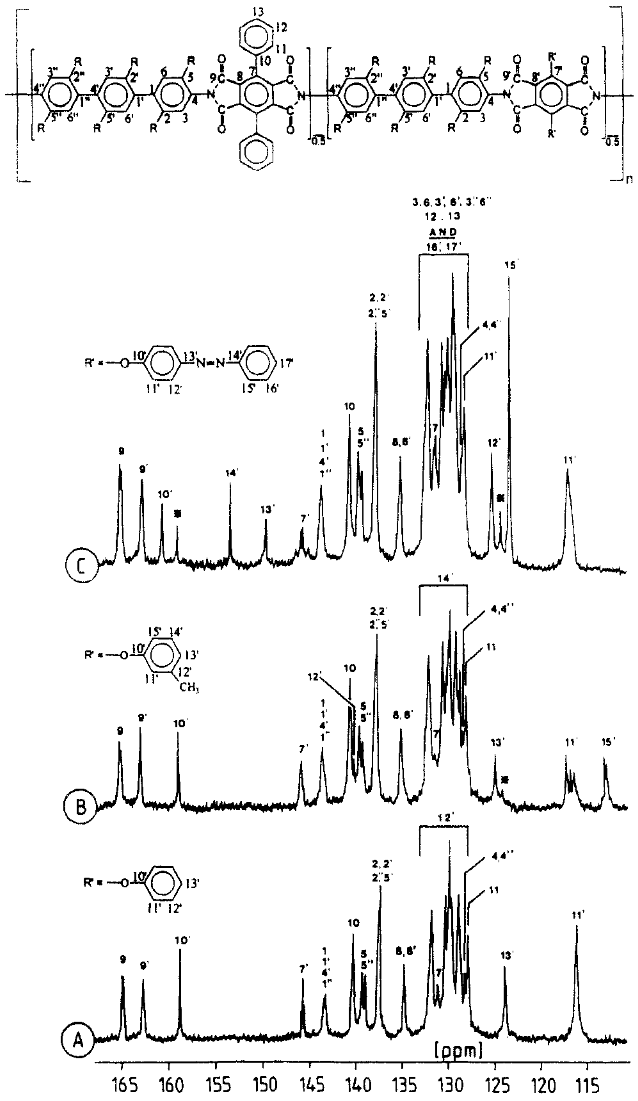


Figure 2. Aromatic regions of the ^{13}C NMR spectra of precursor polyimide **6c** (panel A) and of polyimides **6d** (panel B) and **6e** (panel C). Polyimides **6d** and **6e** were made by nucleophilic substitution according to Scheme V. Spectra were recorded in $C_2D_2Cl_4$ at 363 K.

investigations, namely, 4-hydroxyazobenzene (**7e**), 4'-nitro-4-hydroxyazobenzene (**7f**), 4-[(4-nitrophenyl)azo]-1-naphthol ("magneson II", **7g**), and 2,3'-dimethyl-4-[(2-hydroxy-1-naphthyl)azo]azobenzene ("sudan red B", **7h**). According to Scheme V, precursor polyimide **6c** was treated under the successfully tested conditions with a 20-fold excess of the dye component **7**.

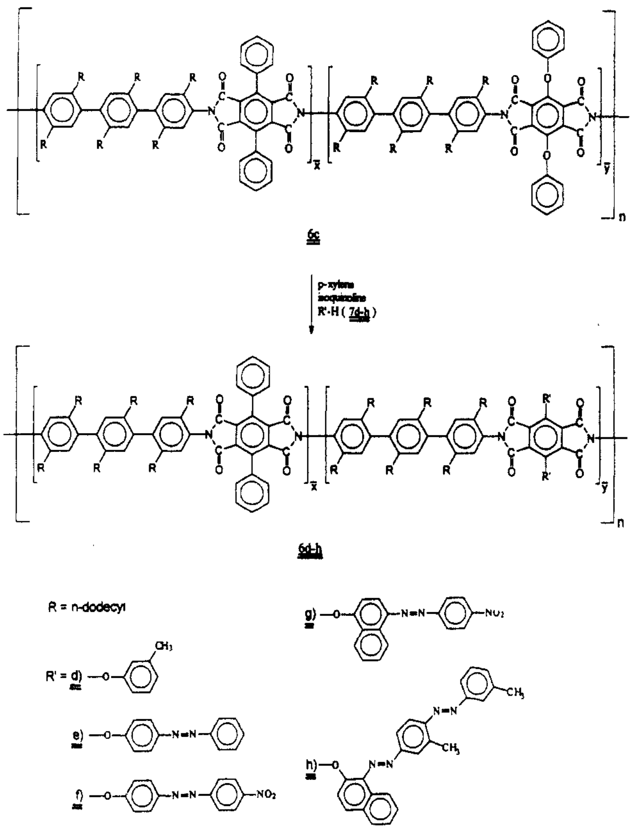
After refluxing the mixtures for about 12 h, the resulting polymers were isolated with an almost quantitative yield. After further purification,[12] intensively colored polyimides were obtained throughout which readily dissolved in the same solvents as the precursor polyimide **6c**. Their molecular structures and their composition could thus be examined by NMR spectroscopy. According to these investigations, only a very low degree of substitution (5–10%) was achieved in the case of the bulky dyes **7g** and **7h**. Almost unchanged polyimide **6c** was recovered from these reactions. Even prolongation of the reaction time did not lead to a significantly higher conversion. On the other hand, more than 90% of the phenoxy groups were exchanged in the case of the sterically less demanding dyes **7e** and **7f**. Here, in the ^{1}H as well as in the ^{13}C NMR spectra, the characteristic absorptions of the dye substituents were unambiguously identified. Besides these resonances, only very weak absorptions of remaining phenoxy substituents were observed. As a representative example, the aromatic region of the ^{13}C NMR spectrum of polyimide **6e** is shown in Figure 2C.

As one can see from this spectrum and the given signal assignment, all absorptions can unambiguously be assigned to carbon atoms of the repeating units of the polyimide **6e**. Small absorptions, which are identified by asterisks, correspond unambiguously to imide units with remaining phenoxy groups. This portion of phenoxy groups was somewhat higher (about 10%) in the case of the dye-substituted polyimides **6e** and **6f** because the nucleophilicity of the phenolates **7e** and **7f** is considerably reduced due to their electron-withdrawing diazo groups. In addition, an excess of only 20-fold of the dye component was used in these conversions. The limited solubility of the dyes in the reaction mixture was responsible for that change in the procedure. However, an almost quantitative exchange of the phenoxy groups could be achieved here as well by a second conversion.

Throughout, no evidence for chain degradation, cross-linking processes, or decomposition of the dye derivatives was found in the NMR spectra. Nevertheless, in order to confidently exclude degradation during the substitution process, the $\overline{DP}$'s of the dye-containing polyimides **6e,f** were determined by membrane osmometry and compared with the $\overline{DP}$'s of the precursor polyimides **6c** used for their preparation. In a typical experiment, the precursor polyimide **6c** showed a $\overline{M}_n$ of 17 200 ($\overline{DP} \approx 11$), and the obtained polyimide **6e** a $\overline{M}_n$ of 16 400 ($\overline{DP} \approx 10$, calculated for 100% conversion). Thus, these osmometric measurements also indicate that degradation processes during the displacement reaction can be excluded.

UV–Vis Spectroscopy. The incorporation of the dye-containing pendent groups into polyimides **6** is reflected not only by their NMR but also by their UV–vis spectra. Figure 3 depicts two series of these spectra recorded in chloroform at room temperature. In Figure 3A, the

Scheme V



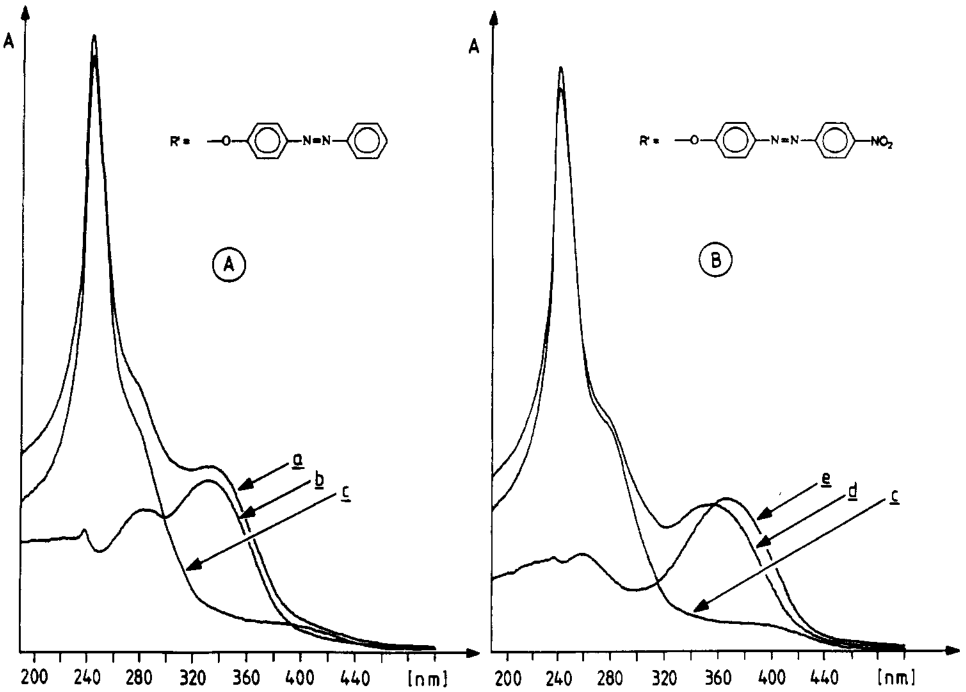


Figure 3. UV–vis spectra of polyimides **6e** (panel A, spectrum a) and **6f** (panel B, spectrum d) together with the spectra of precursor polyimide **6c** (spectra c) and of the dyes **7e** (spectrum b) and **7f** (spectrum e). All spectra were recorded in chloroform at room temperature.

spectrum of polyimide **6e** (a) is shown together with those of the dye **7e** (b) and the precursor polyimide **6c** (c). Figure 3B shows the corresponding spectra of polyimide **6f** (d), dye **7f** (e), and polyimide **6c** (c).

The absorption of the monomeric azo derivative **7e** at λ_{max} = 335 nm remains almost unchanged when this dye is attached to the polyimide **6e**. On the other hand, the corresponding absorption of the dye **7f** at λ_{max} = 336 nm suffers a hypsochromic shift of about 12 nm when this dye is attached to the polymer backbone of polyimide **6f**. In this case, the long-wave absorption appears at λ_{max} = 354 nm. The reasons for this different absorption behavior as well as the prospective nonlinear optical properties of polyimides **6e** and **6f** are presently under investigation.

Conclusion

We have shown that the findings of this study clearly demonstate the practicability of transforming soluble, well-defined rigid-rod precursor polyimides into those with dye-containing pendant groups. By varying the composition of the precursor copolymers as well as by varying the excess of hydroxy compound used for the substitution reaction, a predetermined amount of dye functionalities can be introduced into the polymers. In the light of these results, this nucleophilic substitution reaction can be considered as an efficient method for introducing a variety of aromatic hydroxy derivatives into phenoxy-substituted polyimides. It is intended to widen the scope of the nucleophilic substitution reaction with the aim of preparing further attractively functionalized polyimides.

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(11) This dramatical loss of solubility of polyimides **3c** and **3d** in comparison to polyimides **3a** and **3b** could be caused by intermolecular electronic interactions which are stronger in the case of aryl ether-substituted pyromellitic diimide units; see: Wilson, D.; Stenzenberger, H. D.; Hergenrother, P. M. *Polyimides*; Chapman and Hall: New York, 1990. The formation of chemically cross-linked structures during the polycondensation is unlikely.

(12) The used excess of dye components **7** could be recycled almost quantitatively in all cases by workup of the obtained solutions.