Second-Order Nonlinear Optical Active Calix[4]arene Polyimides Suitable for Frequency Doubling in the UV Region

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A new type of soluble calix[4]arene-based polyimides was prepared by reaction of bis(3-aminopropyl) dipropyl functionalized tetranitrocalix[4]arenes with hexafluoroisopropylidene diphthalic anhydride. Spin-coating of these polymers and subsequent electric field poling results in films that are highly transparent above 410 nm and exhibit high and thermally stable second harmonic generation coefficients. These properties make these materials very suitable for frequency-doubling applications in the UV region (820−410 nm).

Introduction

Sources of laser light of short wavelength ($\lambda < 500$ nm) are of considerable interest for various applications, such as optical sensing and data storage. The first examples of blue lasers have been reported recently, but practical applications are still hampered by technical problems.[1] Alternatively, blue laser light may be obtained by second harmonic generation of light from readily available red diode lasers. This process requires materials of high transparency in the UV region and with appreciably, stable second-order nonlinear optical (NLO) coefficients.[2]

Currently considerable research is directed to the development of polymeric materials with high NLO coefficients, especially for electrooptical applications.[3,4] Polymeric materials have the advantage over crystalline (inorganic) materials of easier processability, e.g., thin films can be prepared by spin-coating on flat substrates, such as silicon wafers, allowing implementation in microelectronic circuits. The required noncentrosymmetric alignment of the NLO chromophores in these materials is generally obtained by electrical poling. The first examples in this field are polymers in which the NLO chromophores are dissoluted in a polymer matrix (the so-called solid-solution approach).[5] However, high concentrations of NLO-active chromophores in the polymer are prohibited by the occurrence of segregation or centrosymmetric crystallization, giving rise to a decrease of the second-order NLO activity. Furthermore, high concentrations of chromophore can lower the glass transition temperature of the polymer, resulting in an earlier thermal relaxation of the noncentrosymmetrical structure.

A more promising approach to obtain stable NLO materials is to bind the NLO chromophores covalently to the polymer chain or in the polymer network.[3,6] This method allows a higher chromophore density in the material than the solid-solution approach and the restricted motional freedom of the chromophores, especially in polymers with high glass transition temperatures, imposes a lower tendency for relaxation. However, the development of NLO-active polymers with high glass transition temperatures (T_g > 150 °C) that are still processable, i.e., are soluble in organic solvents commonly used for spin-coating, is not straightforward. A strategy to overcome the processability problem is to use in the spin-coating process a soluble prepolymer that can afterward be further polymerized by UV or thermal curing. Suitable for these purposes are for example polyamic acid prepolymers functionalized with NLO-active groups. After thermal curing these prepolymers yield insoluble and transparent polyimides with a high T_g.[3,7]

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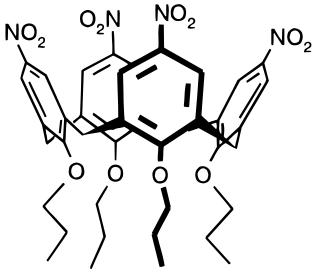
Also certain aromatic imide linkers have been successfully used in NLO-functionalized polyimides to improve the solubility without decreasing the T_g.[8,9] For example Yu et al. reported NLO-active polyimides functionalized with (dialkylamino)-*p*-nitro- or *p*-sulfonyl-(aza-)stilbene chromophores, that have stable frequency-doubling coefficients of 10−27 pm/V (d_{33} values, corrected for dispersion).[7b,c,d,9] Such polymers may have considerable interest for application in electrooptical switching but are less suitable for generation of blue laser light (λ = 410 nm) because of the substantial overlap of the generated second harmonic with the absorption band of the chromophores (λ_{max} = 370−450 nm).

Previously, we have found that calix[4]arenes[10] substituted with electron-donating propoxy groups at the lower rim and electron-accepting nitro groups at the upper rim exhibit high second-order hyperpolarizabilities ($\beta_z = 30 \times 10^{-30}$ esu at 1064 nm), and are virtually transparent above 400 nm.[11] Moreover, due to the relatively high dipole moment (μ = 13.8 D) these molecules can be efficiently poled in an electrical field. Poled neat films of (tetranitrotetrapropoxy)calix[4]arene exhibit high frequency-doubling coefficients d_{33} that are stable at room temperature but lose most of their NLO activity at high temperatures (>80 °C).[11,12] It was expected that covalent incorporation of the calix[4]arenes in a polymer matrix of high glass transition temperature would considerably stabilize the noncentrosymmetric alignment, obtained after poling.



In this paper the synthesis and physical characterization of a class of polyimides in which nitrocalix[4]arenes have been incorporated in the main chain as the NLO-active groups are reported. These polymers form thermally stable and highly transparent NLO materials, which makes them especially suitable for frequency doubling in the UV region.[13]

Experimental Section

Synthesis. Melting points were determined with a Reichert melting point apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Brucker AC 250 spectrometer in $CDCl_3$ (unless stated otherwise) using residual solvent protons or Me_4Si as internal reference. Mass spectra were recorded with a Finnigan MAT 90 spectrometer using *m*-nitrobenzyl alcohol (NBA) as a matrix. Infrared spectra were recorded with a Jasco A-100 infrared spectrophotometer and absorbance spectra were measured on a Hewlett-Packard 8452A diode array spectrophotometer. Elemental analyses were carried out with a Model 1106 Carlo-Erbu Strumentazione element analyzer. THF was freshly distilled from Na/benzophenone ketyl, hexane (petroleum ether, bp 60−80 °C), and CH_2Cl_2 from K_2CO_3. DMF was dried over molecular sieves (4 Å) for at least 3 days. NMP was distilled from $CaCl_2$ and stored over molecular sieves (4 Å). NaH was a 55−65% dispersion in mineral oil and was washed three times with *n*-hexane prior to use. Other reagents were reagent grade and were used without further purification. Flash column chromatography was performed with silica 60 (0.040−0.063 mm, 230−400 mesh) from E. Merck. All reactions were carried out in an argon atmosphere.

5,11,17,23-Tetra-*tert*-butyl-25,27-dipropoxy-26,28-bis(3-phthalimidopropoxy)calix[4]arene (2). To a well-stirred suspension of 0.42 g (17.44 mmol) of NaH in 100 mL of DMF was added 4 g (5.46 mmol) of 5,11,17,23-tetra-*tert*-butyl-25,27-dipropoxycalix[4]arene (**1**) in small portions. After 30 min, 7.8 g (29.07 mmol) of *N*-(3-bromopropyl)phthalimide dissolved in 20 mL of DMF was added dropwise in 1 h. Subsequently the mixture was stirred for 20 h at 70 °C. After cooling to room temperature and addition of 10 mL of H_2O, the DMF was removed by evaporation. The residue was taken up in CH_2Cl_2 (200 mL), washed with 1 N HCl (2 × 50 mL) and brine (2 × 50 mL). After drying over $MgSO_4$ the organic layer was concentrated in vacuo. Flash column chromatography (SiO_2, CH_2Cl_2/hexane, 1:1) or, if possible, recrystallization from CH_2Cl_2/MeOH gave pure **2** as a white powder in 67% yield, mp 241−243 °C (CH_2Cl_2/MeOH). ^{1}H NMR δ 7.83, 7.70 (2m, 8H, ArH-pht), 6.93, 6.56 (2s, 8H, *o*-*tert*-butyl ArH), 4.06, 3.90, 3.70 (3t, 12H, J = 7 Hz, OCH_2 and NCH_2), 4.36 and 3.10 (ABq, 8H, J = 14 Hz, $ArCH_2Ar$), 2.51 (quintet, 4H, J = 7 Hz, CH_2CH_2N), 1.88 (sextet, 4H, J = 7 Hz, CH_2CH_3), 1.20, 0.91 (2s, 36H, *tert*-butyl CH_3), 0.85 (t, 6H, J = 7 Hz, CH_2CH_3); ^{13}C NMR δ 168.27 (C=O), 153.99, 152.9 (ArC−O), 144.70, 143.99 (ArC−*t*-Bu), 134.82, 132.66, 132.28 (ArC−CH_2 and ArC−C=O), 133.75, 125.24, 124.60, 123.11 (ArC−H calix and ArC−H Pht), 77.38, 72.54 (O−CH_2), 35.44 (N−CH_2), 33.94, 33.64 ($C-(CH_3)_3$), 31.60, 31.27 ($C-(CH_3)_3$), 31.15 (CH_2−Ar), 29.77 (CH_2-CH_2N), 23.48 (CH_2-CH_3), 10.45 (CH_3); FAB-MS *m/z* 1107 (M^-, calcd 1106.6). Anal. Calcd for $C_{72}H_{86}N_2O_8$: C, 78.09; H, 7.83; N, 2.53. Found: C, 78.32; H, 7.98; N, 2.58.

5,11,17,23-Tetranitro-25,27-dipropoxy-26,28-bis(3-phthalimidopropoxy)calix[4]arene (3). To a solution of 3 g (2.71 mmol) of **2** in 60 mL of CH_2Cl_2 was added 2.4 mL (31 mmol) of trifluoroacetic acid. Subsequently 2.3 mL (55 mmol) of nitric acid (100 %) was added in portions upon which the mixture turned purple-black. After 10 min the reaction mixture was poured into icewater and diluted with 50 mL of CH_2Cl_2. The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL), and the combined organic layers were washed with brine (3 × 50 mL), dried over $MgSO_4$, and concentrated under reduced pressure. Recrystallization from CH_2Cl_2/MeOH afforded pure **3** in 98% yield, mp 169−171 °C (MeOH). ^{1}H

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NMR δ 7.83, 7.73 (2m, 8H, ArH-pht), 7.49, 7.61 (2s, 8H, *o*-$\mathrm{NO_2}$-ArH), 4.13, 3.95, 3.84 (3t, 12H, *J* = 7 Hz, $\mathrm{OCH_2}$ and $\mathrm{NCH_2}$), 4.52 and 3.40 (ABq, 8H, *J* = 14 Hz, $\mathrm{ArCH_2Ar}$), 2.28 (quintet, 4H, *J* = 7 Hz, $\mathrm{C}\mathit{H}_2\mathrm{CH_2N}$), 1.88 (sextet, 4H, *J* = 7 Hz, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 0.97 (t, 6H, *J* = 7 Hz, $\mathrm{CH_3}$); ^{13}C NMR δ 168.16 ($\mathrm{C{=}O}$), 161.50 (ArC−O), 142.99, 142.82 (ArC−$\mathrm{NO_2}$), 135.61, 135.21 (Ar*C*−$\mathrm{CH_2}$), 131.91 (Ar*C*−$\mathrm{C{=}O}$), 134.23, 124.14, 123.93, 123.30 (ArC−H calix and Pht), 78.00, 73.52 (O−$\mathrm{CH_2}$), 34.82 ($\mathrm{CH_2N}$), 31.17 ($\mathrm{CH_2}$−Ar), 29.59 ($\mathit{C}\mathrm{H_2{-}CH_2N}$), 23.34 ($\mathit{C}\mathrm{H_2{-}CH_3}$), 10.16 ($\mathrm{CH_3}$); FAB-MS *m/z* 1062.9 ($\mathrm{M^-}$, calcd 1062.3). Anal. Calcd for $\mathrm{C_{56}H_{50}N_6O_{16}}$: C, 63.27; H, 4.74; N, 7.91. Found: C, 62.93; H, 4.79; N, 8.05.

5,11,17,23-Tetranitro-25,27-dipropoxy-26,28-bis(3-aminopropoxy)calix[4]arene (4). A suspension of 1.11 g (1.05 mmol) of **3** in 20 mL of THF and 80 mL of EtOH was refluxed for 3 h after addition of 1.0 g (19.4 mmol) of hydrazine hydrate. Upon cooling of the now clear orange solution, a white precipitate was formed. This precipitate was filtered off, the filtrate was concentrated in vacuo and taken up into 100 mL of $\mathrm{CH_2Cl_2}$. After addition of 50 mL of 1 N NaOH the mixture was stirred during 30 min. After separation the organic layer was washed with 1 N NaOH (2 × 25 mL) and brine (2 × 25 mL) and dried over $\mathrm{MgSO_4}$. Evaporation of the solvent afforded **4** as a yellow powder in 93% yield, mp 209−211 °C ($\mathrm{CH_2Cl_2}$). ^{1}H NMR δ 7.46, 7.66 (2s, 8H, ArH), 4.07, 3.98 (2t, 8H, *J* = 7 Hz, $\mathrm{OCH_2}$), 4.51 and 3.40 (ABq, 8H, *J* = 14 Hz, $\mathrm{ArCH_2Ar}$), 2.87 (t, 4H, *J* = 7 Hz, $\mathrm{C}\mathit{H}_2\mathrm{NH_2}$), 2.01 (quintet, 4H, *J* = 7 Hz, $\mathrm{C}\mathit{H}_2\mathrm{CH_2N}$), 1.98 (sextet, 4H, *J* = 7.5 Hz, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 1.38 (br s, 4H, $\mathrm{NH_2}$), 1.00 (t, 6H, *J* = 7 Hz, $\mathrm{CH_3}$); ^{13}C NMR δ 161.35 (ArC−O), 142.84 (ArC−$\mathrm{NO_2}$), 135.64, 135.18 (Ar*C*−$\mathrm{CH_2}$), 124.21, 123.81 (ArC−H), 77.68, 74.07 (O−$\mathrm{CH_2}$), 38.80 ($\mathrm{CH_2{-}NH_2}$), 33.66 ($\mathit{C}\mathrm{H_2{-}CH_2NH_2}$), 31.14 (Ar−$\mathrm{CH_2}$), 23.24 ($\mathit{C}\mathrm{H_2{-}CH_3}$), 10.08 ($\mathrm{CH_3}$); FAB-MS *m/z* 804.2 ($[\mathrm{M + H}]^+$, calcd 803.8); IR (KBr) 1355 and 1530 ($\mathrm{NO_2}$), 3420 ($\mathrm{NH_2}$) $\mathrm{cm^{-1}}$; UV−vis ($\mathrm{CHCl_3}$) $\lambda_{\max} = 292$ nm, $\epsilon = 24 \times 10^3$ L $\mathrm{mol^{-1}\,cm^{-1}}$. Anal. Calcd for $\mathrm{C_{40}H_{46}N_6O_{12}{\cdot}1.7H_2O}$: C, 57.62; H, 5.97; N, 10.08. Found: C, 57.41; H, 5.68; N, 9.72. Karl Fischer titration calcd for $\mathrm{1.7H_2O}$: 3.68. Found: 3.72.

Polymerization. The calix[4]arene polyamic acid prepolymer (**6**) was obtained by stirring a solution of 30 mL of dry NMP, 3.0 g (3.74 mmol) of calix[4]arene diamine **4** and 1.66 g (3.74 mmol) of hexafluorodisopropylidene diphthalic anhydride (6FDA, **5**) for 14 h under argon. The reaction mixture was used in subsequent polyimidization reactions. IR (KBr) 3450 (br, NH and OH), 1680 (COOH), 1730 ($\mathrm{C{=}O}$ amide), 1530 and 1360 ($\mathrm{NO_2}$), 760 ($\mathrm{CF_3}$) $\mathrm{cm^{-1}}$.

Tetranitrocalix[4]arenepolyimide (7a): Thermal Polyimidization. A solution of polyamic acid prepolymer **6** in NMP and 10 vol % of *o*-dichlorobenzene was refluxed (190−200 °C) for 11 h. Water formed in the imidization was removed with a reverse Dean−Stark apparatus. The reaction mixture was poured into 300 mL of dry ice cooled EtOH under vigorously stirring. The resulting precipitate was filtered off, dissolved in THF (20 mL) and poured into hexane (200 mL). Again filtering off the precipitate and subsequently washing with diisopropyl ether (3 × 50 mL) afforded polymer **7a** as a gray powder. ^{1}H NMR (THF) δ 8.0−7.0 (m, 8H + 6H, *o*-$\mathrm{NO_2}$-ArH and ArH−phthalimido), 4.2−3.5 (br m, 8H + 4H, $\mathrm{OCH_2}$ and $\mathrm{CH_2}$−Pht), 4.4 and 3.4 (2 × br s, 8H, $\mathrm{ArCH_2Ar}$), 2.2 (br s, ?H, $\mathrm{C}\mathit{H}_2\mathrm{NH{-}C{=}O}$), 2.0−1.3 (m, 4H + ?H, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$ and $\mathrm{C}\mathit{H}_2\mathrm{CH_2N}$), 0.9 (br s, 6H, $\mathrm{CH_3}$); UV−vis ($\mathrm{CH_2Cl_2}$) $\lambda_{\max} = 290$ nm, $\epsilon = 21 \times 10^3$ L $\mathrm{mol^{-1}\,cm^{-1}}$.

Tetranitrocalix[4]arenepolyimide (7b): Chemical Polyimidization. To a solution of poly(amic acid) prepolymer **6** in NMP was added 1.4 g of $\mathrm{Ac_2O}$, 0.5 g of pyridine, and 1.05 g of toluene. After stirring at 60 °C for 20 h, workup was carried out as described for **7a**. Pure polymer **7b** was obtained as a white powder. ^{1}H NMR ($\mathrm{CD_2Cl_2}$) δ 8.0−7.3 (m, 8H + 6H, *o*-$\mathrm{NO_2}$ArH and ArH-pht), 4.2−3.8 (br m, 8H + 4H, $\mathrm{OCH_2}$ and $\mathrm{CH_2}$−Pht), 4.48 and 3.36 (br ABq, 8H, *J* = 14 Hz, $\mathrm{ArCH_2Ar}$), 2.29 (br m, 4H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2N}$), 1.89 (sextet, 4H, *J* = 7.5 Hz, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 0.93 (t, 6H, *J* = 7 Hz, $\mathrm{CH_3}$); IR (KBr) 1780 ($\mathrm{C{=}O}$, asym stretch), 1720 (Ar−$\mathrm{C{=}O}$), 1355 and 1530 ($\mathrm{NO_2}$), 1385, 1150 and 729 (imide ring) $\mathrm{cm^{-1}}$; UV−vis ($\mathrm{CH_2Cl_2}$) $\lambda_{\max} = 292$ nm, $\epsilon = 20 \times 10^3$ L $\mathrm{mol^{-1}\,cm^{-1}}$.

Film Preparation, Poling, and Measurements. Poled films were prepared at 20 and 50% relative humidity in a clean room with dust class 100. A solution of **7a** or **7b** in cyclopentanone (5−10 and 25% w/w for thin and thick films, respectively) was spun on Pyrex glass (2 s, 200 rpm; >40 s, 1000−2000 rpm), yielding films with thicknesses in the range 0.3−2 μm. These films were oriented at 150−230 °C for 15 min by corona poling (25 μm tungsten wire at a film distance of 10 mm, corona voltage 9 kV, current 10 μA). The corona field was switched on after the poling temperature was reached. The films were allowed to cool to room temperature while the voltage was maintained. The orientation parameter $\cos^3\theta$ of the films was calculated as described in ref 13 and varied between 0.2 and 0.3. The SHG efficiencies of the films were measured with a Q-switched Nd:YAG laser at 1064 nm fundamental wavelength, using α-quartz as a reference (d_{11} = 0.51 pm $\mathrm{V^{-1}}$).

Instrumentation. GPC analyses were performed with a Waters apparatus equipped with a PL-MIX column (Polymer Laboratories, UK) using DMF (HPLC grade)/LiBr/HOAc 99/0.5/0.5 as eluent. This eluent was used to avoid partial adsorption of the polyamic acid groups to the gel. A mixture of polystyrenes (PL-mix-C of Polymer Laboratories UK) was used as reference.[9b] TGA was performed on a Hi-Res TGA 2950 thermogravimetric analyzer (TA Instruments). Samples were heated under nitrogen from 20 to 600 °C with a heating rate of 20 °C/min. DSC was performed on a Perkin-Elmer DSC7 calorimeter with heating rates of 20 or 30 °C.

Results and Discussion

Synthesis of Calix[4]arene-Based Polymers.[14] To enable the covalent incorporation of the NLO active calix[4]arene in a polyimide chain, it was necessary to modify the tetrapropoxytetranitrocalix[4]arene with two amino functionalities. Therefore the diamino functionalized derivative **4** was synthesized (Scheme 1). The starting compound 5,11,17,23-tetra-*tert*-butyl-25,27-dipropoxycalix[4]arene[10,15] (**1**) was alkylated with *N*-(3-bromopropyl)phthalimide in DMF using NaH as the base, affording 5,11,17,23-tetra-*tert*-butyl-25,27-dipropoxy-26,28-bis(3-phthalimidopropoxy)calix[4]arene (**2**) in 67% yield. Subsequent *ipso* nitration with a mixture of trifluoroacetic acid (TFA) and 100% $\mathrm{HNO_3}$ gave 5,11,17,23-tetranitro-25,27-dipropoxy-26,28-bis(3-phthalimidopropoxy)calix[4]arene (**3**) in 98% yield.[16] The protecting phthalimido groups were then removed with hydrazine, yielding 93% of the tetranitrocalix[4]arene diamino monomer (**4**).

For the solubility of polyimides the structure of the dianhydride linker is very important. We have selected the hexafluoroisopropylidene diphthalic anhydride unit (6FDA, **5**) as this linker is known to yield polyimides of good solubility with still high T_g.[8,17] Furthermore 6FDA

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(14) Only two examples of polymers with covalently bound calix[4]arenes (non-NLO active) have been described in the literature. A calix[4]arene methacrylate oligomer with an average molecular weight of 6.7 kDa (ca. 6 calix[4]arene units) has been prepared by McKervey et al. (Harris, S. J.; Barrett, G.; McKervey, A. *J. Chem. Soc., Chem. Commun.* **1991**, 1224). The same monomethacrylate calix[4]arene tetraester monomer has been incorporated in a methacrylate functionalized polysiloxane in our group (Brunink, J. A. J.; Lugtenberg, R. J. W.; Brzózka, Z.; Engbersen, J. F. J.; Reinhoudt, D. N. *J. Electroanal. Chem.* **1994**, *378*, 185−200) for application as an ion-selective membrane on chemically modified field effect transistors. Glass transition temperatures were not reported for both polymers, but because of the flexibility of the polymer backbones the T_g's will be too low to obtain thermally stable NLO films after incorporation of NLO active calix[4]arenes.

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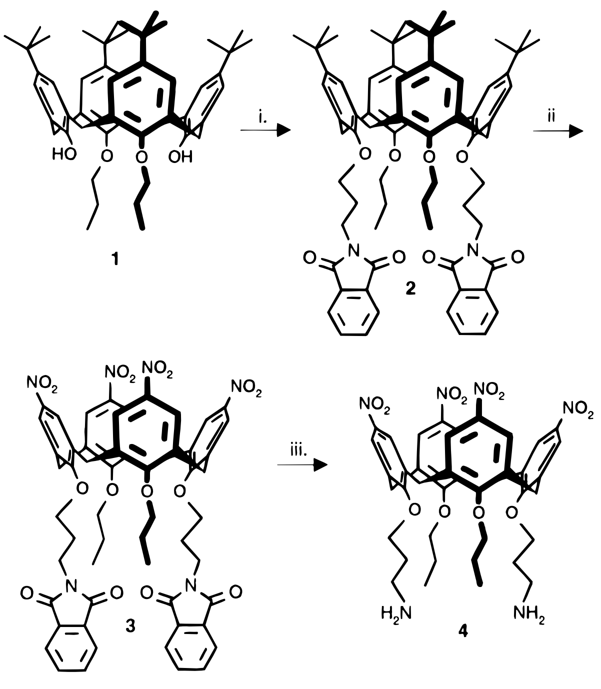
Scheme 1. Synthesis of Calix[4]arene Diamine Monomer 4[a]

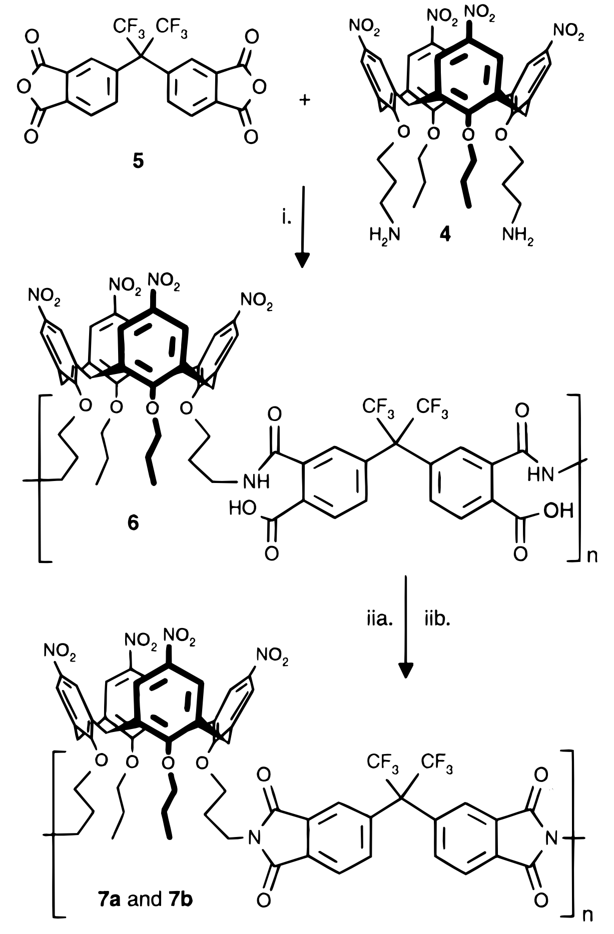


[a] (i) NaH, *N*-(3-bromopropyl)phthalimide, DMF, 20 h, 70 °C. (ii) TFA, 100% HNO_3, CH_2Cl_2, 10 min, room temperature. (iii) $H_2NNH_2 \cdot H_2O$, THF, EtOH, 4 h, reflux.

derived polyimides can yield transparent and low birefrigent films after spin-coating.[8,17] Poly(amic acid) prepolymer **6** was prepared by reacting calix diamine **4** and dianhydride **5** in dry *N*-methyl-2-pyrrolidinone (NMP) (Scheme 2). Subsequently, two routes to imidization of the polymer were investigated. A thermal imidization to polyimide **7a** was performed in *o*-dichlorobenzene by the azeotropic removal of water at 190 °C.[8,18] Chemical imidization to polyimide **7b** was achieved by reaction of polyamic acid **6** in NMP with acetic anhydride, using pyridine as an organic base.[8,19]

Polymer Characterization. Polyamic acid **6** and polyimides **7a** and **7b** were characterized by IR and ^{1}H NMR spectroscopy. Polyamic acid **6** exhibits a typical amide carbonyl absorption at 1730 cm^{-1} and a broad carboxylic carbonyl absorption at 1675 cm^{-1}. The thermally imidized polymer **7a** shows typical absorptions for a polyimide ring at 729, 1150, and 1385 cm^{-1} and the asymmetric and symmetric aromatic imide carbonyl stretch absorptions at 1780 and 1720 cm^{-1}.[20] In addition major peaks at 1730 and 1675 cm^{-1} were apparent, indicating the presence of considerable amounts of unreacted amic acid groups. In the infrared spectrum of the chemically imidized polymer **7b** only the typical absorptions for a polyimide ring and the aromatic imide carbonyl stretch absorptions, as given above, are present. The presence of the unreacted amic acid groups in polymer **7a** is also indicated by the poor solubility of this polymer. Like polyamic acid **6**, polymer **7a** is soluble only in polar solvents such as THF or DMSO, whereas polymer **7b** is well soluble in a variety of organic solvents. The complete imidization in **7b** can also be concluded from the ^{1}H NMR spectrum where the signal of the methylene group linked to the amino group has shifted from 2.9 ppm in the calix[4]arene diamino monomer (**4**) to 3.8 ppm after imidization. This shift of 0.9 ppm is in accordance with data reported in the literature.[20] Due to broadening and overlap of peaks, the different amide and carboxylic acid resonances of **6** and **7a** are difficult to assign.

Scheme 2. Polymerization[a]



[a] (i) NMP, 14 h, room temperature. (iia) *o*-dichlorobenzene, 11 h, 190−200 °C. (iib) Ac_2O, pyridine, toluene, 14 h, 60 °C.

Gel permeation chromatography (GPC) gave molecular weights (M_w) of 43 and 56 kDa for **7a** and **7b**, respectively, which indicates that an average of ca. 40 and 50 calix[4]arene units are connected. Both polymers have a rather similar molecular weight distribution of 1.95 and 1.91, respectively.

It is known that the glass transition temperatures of polyimides are usually high (200−400 °C) and difficult to measure in differential scanning calorimetry (DSC).[21] For **7a** a large uptake of heat from 190 °C (the thermal imidization temperature) to 240 °C is observed during the first heating run (Figure 1) which can be attributed to further imidization. The second DSC run of **7a** is similar to the DSC runs of **7b** and shows a minor phase transition at 238 °C. This probably reflects the T_g of the fully imidized polymer. Also a thermal gravity analysis (TGA) of **7a** points to further imidization upon initial heating, since a loss of weight of 1.12% was

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(18) Jou, J.-H.; Huang, P.-T. *Macromolecules* **1991**, *24*, 3796−3803.

(19) Beuhler, A. J.; Wargowski, D. A. United States Patent No. US005317082A, 1994.

(20) Yang, S.; Peng, Z.; Yu. L. *Macromolecules* **1994**, *27*, 2638−2640. Peng, Z.; Yu, L. *Ibid.* 5858−5862.

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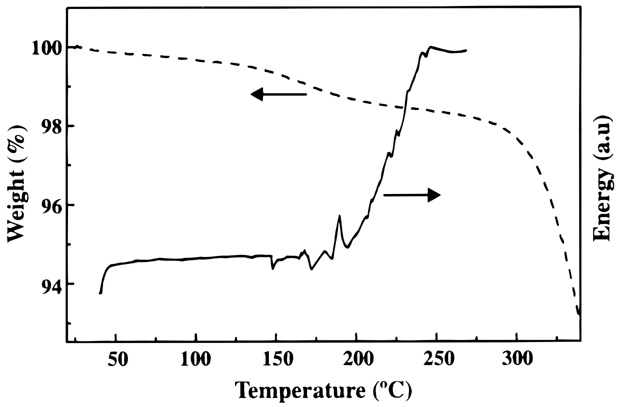

Figure 1. DSC curve (solid line) and TGA curve (dashed line) of **7a**.

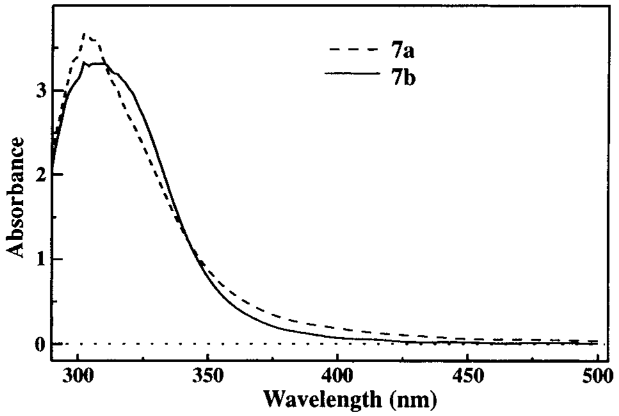

Figure 2. UV−vis spectra of thin films of **7a** and **7b** (before poling).

observed between 130 and 240 °C (Figure 2), corresponding to 0.76 equiv of water. Above 300 °C the polymer starts to decompose.

(Non-)linear Optical Properties. Oriented thin films of **7a** and **7b** were prepared on glass substrates by spin-coating from cyclopentanone solution, followed by electric field poling. The calixarene imide polymers give smooth, physically stable, and highly transparent films of thicknesses ranging from 0.2 to 2.2 μm, depending on the spinning speed and the concentration of the cyclopentanone solution. Films that were obtained earlier[11] from pure (tetranitrotetrapropoxy)calix[4]arene were only 0.3 μm thick, fragile, and gave scattering of light. The transparency of films of **7a** and **7b** is illustrated by the absorption spectra shown in Figure 2. Because of the low λ_{cutoff} values of 410 and 450 nm, respectively, off-resonance frequency doubling from 1064 to 532 nm or even from 820 to 410 nm is possible.[22]

Important for the practical use of NLO-active polymers is their long-term stability. Therefore various poling and curing conditions were investigated after films were poled for 15 min, at 150, at 230, or at 150 °C after 2 h of thermal curing at 150 °C. The frequency-doubling coefficient d_{33} (1064 nm) of the thus obtained films of **7a** and **7b** varied between 2.3 and 4.0 pm V^{-1}.[23]

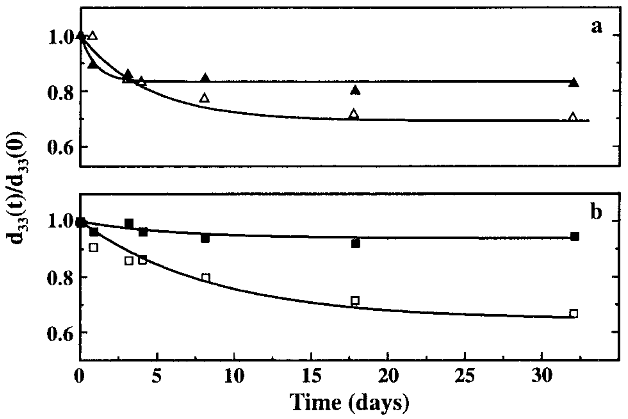

Figure 3. Stability of frequency doubling coefficient d_{33} of differently prepared films of **7a** stored at room temperature (solid symbols) and at 80 °C (open symbols). (a) 30 min thermally cured at 230 °C and poled at 230 °C; (b) poled at 150 °C.

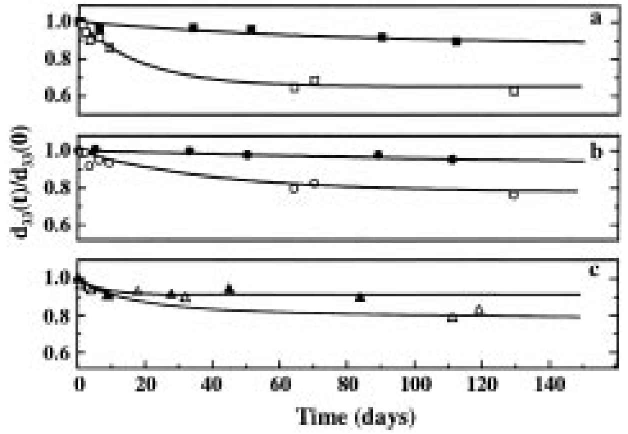

Figure 4. Stability of frequency-doubling coefficient d_{33} of differently prepared films of **7b** stored at room temperature (solid symbols) and at 80 °C (open symbols): (a) poled at 150 °C; (b) poled at 230 °C; (c) 2.5 h thermally cured at 150 °C and poled at 150 °C.

Table 1. Molecular Weights and Glass Transition Temperatures of 7a and 7b

polymer	M_w (kDa)	M_n (kDa)	polydispersity	T_g (°C)	$\lambda_{\max}$ (nm)	λ_{cutoff} (nm)
7a	43.2	22.1	1.95		290	450
7b	56.1	29.3	1.91	238	292	410

Figures 3 and 4 show the stability of the frequency-doubling coefficient d_{33} for the films of **7a** and **7b** prepared under different poling conditions and stored at room temperature or at 80 °C. Films stored at room temperature all show a stable NLO activity after an initial decay of 15% or less (Figures 3 and 4). When stored at 80 °C, the film of **7a** which was cured and poled at 230 °C shows a stable NLO activity of 2.3 pm/V after an initial decay of 30% (Figure 3a). The film poled at 150 °C, however, shows a decay of more than 30%

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(22) Noordman et al. have shown that with neat films of (tetranitrotetrapropoxy)calix[4]arene frequency doubling from 820 to 410 nm is possible with efficiencies up to 0.23% over a path length of 6 mm in a Cerenkov-type device.[13a] Efficiencies of that order of magnitude and higher (2 orders of magnitude is feasible[13a]) should also be obtainable with the polymer films **7a** and **7b** since the absorption properties of these films are, as expected, similar to or even better than the neat calix[4]arene films used in the Cerenkov-type devices. Noordman et al. have also studied noncritically-phase-matched second harmonic generation using calix[4]arene−SiO$_x$N$_y$ planar waveguides.[13b] In this work they show that frequency doubling to 450 nm with a maximal efficiency of 0.9% is possible when using a fundamental peak power of 500 W. Furthermore an optical loss of 1 dB/mm was observed at 458 nm. On the basis of the results obtained for these planar calix[4]arene−SiO$_x$N$_y$ waveguides, it is shown by calculations that normalized efficiencies of 7.5% W^{-1} (corrected for nonuniformity and absorption) could be obtained in a 10 mm long device by using a 5 μm *channel* waveguide instead of a *planar* waveguide.

after 30 days, and even after this period no stable value is reached (Figure 3b). Thus, to obtain stable films of **7a**, thermal curing prior to the poling process is essential. This thermal curing promotes further imidization and rigidification of the polymer, thereby prohibiting the relaxation of the aligned calixarenes in the polymer matrix.

All films of **7b** are stable at 80 °C after some initial decay has occurred (Figure 4). Poling close to the glass transition temperature or extensive thermal curing prior to poling is advantageous for the NLO stability of films of **7b** as is shown by the relative NLO activity curves in Figure 4.

Conclusions

Calix[4]arene polyimides of high processability have been synthesized by reaction of bis(3-aminopropoxy)dipropoxytetranitrocalix[4]arenes with hexafluoroisoproylidene diphthalic anhydride. After spincoating, the calix[4]arene chromophores in these polymers can be efficiently poled, yielding highly transparent (>400 nm) NLO active films. Both thermally (**7a**) and chemically (**7b**) imidization of the polyamic acid prepolymer **6** yields polyimides of high thermal NLO stability when treated under the proper poling conditions. This makes these calix[4]arene polyimides promising for frequency-doubling applications.

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(23) The d_{33} values in these polymers are two to three times lower compared to the value of 7.3 pm V^{-1} for films of *neat* (tetranitrotetrapropoxy)calix[4]arene.[11] This can be attributed to the 20% lower chromophore density caused by the presence of the polyimide linker and to the lower degree of alignment of the chromophores caused by the restricted rotational freedom of the covalently linked NLO active calix[4]arenes in the polymer ($\cos^3 \theta < 0.3$ in the polyimide films and 0.6 in neat films). The use of calix[4]arene derivatives with higher β values such as tetrakis(*p*-nitrostilbene)tetrapropoxycalix[4]arene can potentially further enhance the SHG efficiency as neat films of these compounds have d_{33} values of 25−40 pm V^{-1}.[11,12]