Connective CC Double Bond Formation for the Synthesis of Donor- and Acceptor-Substituted Poly(*p*-phenylenevinylene)s

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ABSTRACT: A carbon−carbon bond formation through cation−anion coupling allows the synthesis of poly(*p*-phenylenevinylene)s (PPV) **1** and **2a**−**f**, which contain donor and acceptor groups in each vinylene unit. The crucial step in the double bond formation is the quantitative elimination of methanethiol at room temperature. In this work we describe the optimization of the molecular weight of polymers of structure types **1** and **2a**−**f** with regard to (i) solubility of the monomers and polymers and (ii) the reactivity and side reactions of the monomers. The simultaneous donor and acceptor substitution on the central double bond in PPV-analogous structures raises the question of the additivity of dipoles in each repeat unit of a conjugated polymer chain from the viewpoint of potential use in electrooptical applications. The sequence of donor and acceptor groups along the π-conjugated chain can be controlled by the choice of suitable monomers and is crucial for the alignment of the dipole components. The aggregation of polymers **1** and **2a**−**f**, observed in the GPC, makes it necessary to introduce MALDI-TOF mass spectrometry for the determination of the molecular weight of the donor- and acceptor-substituted polymers. The thermal properties are determined with regard to the high-temperature stability demanded for use in nonlinear optics (NLO).

1. Introduction

Here, we introduce a simple cation−anion coupling that allows donor- and acceptor-substituted vinylene units to be incorporated into the main chain of poly(*p*-phenylenevinylene)s.

This method has already been used by us for the "one-pot" construction of the oligomers **3a**−**g** (Chart 2).[1] The anions of type **5** are generated in situ from benzyl cyanide with sodium hydride in DMF at −60 °C (Scheme 1), whereby in the subsequent step suitable cationic components, for example, dibutyl[(methylthio)phenylmethylene]ammonium iodide (**8**) dissolved in DMF, are added to the reaction mixture. The key step of this reaction is the generation of the donor- and acceptor-substituted double bond at room temperature by elimination of methanethiol. The advantages of this new connective C−C double bond formation are the mild, but nevertheless quantitative, elimination and the ready accessibility of the monomers.

The simple availability of new π-systems with the unique combination of a conjugated chain and a high density of strong dipoles as well as conformative and configurative mobility encouraged us to extend the synthetic concept to the corresponding donor- and acceptor-substituted polymers.

We report on the selection of suitable monomers that allow us to build polymers **1** and **2a**−**f** with different sequences of donor and acceptor along the π-conjugated chain (see Chart 1). Optimization of the reaction parameters and the incorporation of solubilizing groups to increase the molecular weight are prominent in this work. We introduce matrix-assisted-laser-desorption-ionization/time-of-flight mass spectrometry (MALDI-TOF-MS) as a method for the determination of molecular weight and elucidate the problems in the conventional determination of molecular weight by GPC.

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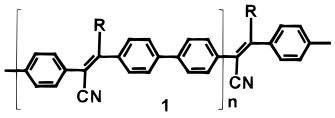
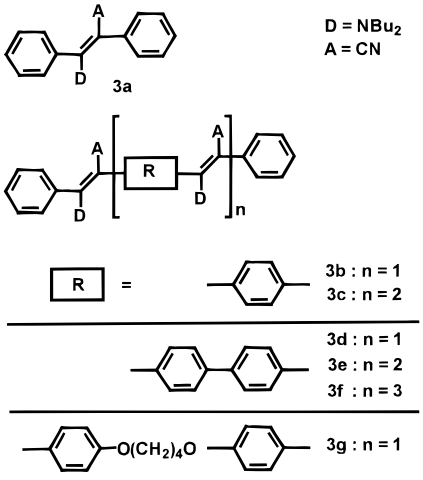
Chart 1. Donor- and Acceptor-Substituted Poly(*p*-phenylenevinylene)s 1 and 2a−f



	R	m
1	$-NBu_2$	
2a	$-NBu_2$	1
2b	$-N(2\text{-EtHex})_2$	1
2c	$-NBu_2$	2
2d	$-N$ OHex	1
2e	$-N$ O-2-EtHex	1
2f	$-N$ OHex	2

Chart 2. Donor- and Acceptor-Substituted Oligo(*p*-phenylenevinylene)s 3a−g



The thermal and optical properties as well as the processability of the donor and acceptor polymers are also investigated.

2. Synthesis

We applied two routes for the synthesis of donor- and acceptor-substituted polymers: (i) the AABB- and (ii)

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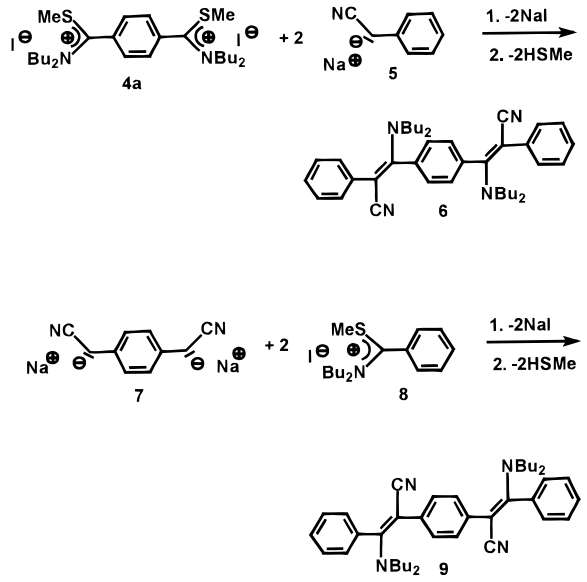
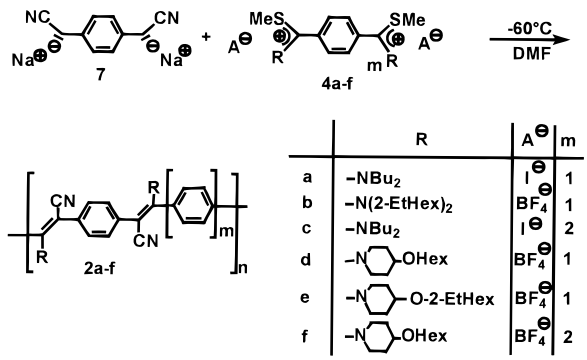
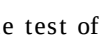
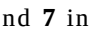
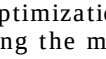
Scheme 1. Syntheses of Distyrylbenzenes 6 and 9 as Model Reactions for an AABB-Type Polycondensation (DMF, −60 °C → RT, 2 equiv of NaH)



Scheme 2. AABB-Type Polycondensation for the Synthesis of Polymers 2a−f (DMF, −60 °C → RT, 3 equiv of NaH)



	R	$A^{\ominus}$	m
a	$-NBu_2$	$I^{\ominus}$	1
b	$-N(2\text{-EtHex})_2$	$BF_4^{\ominus}$	1
c	$-NBu_2$	$I^{\ominus}$	2
d		$BF_4^{\ominus}$	1
e		$BF_4^{\ominus}$	1
f		$BF_4^{\ominus}$	2

the AB-type polycondensation. The test of the utility of the bifunctional monomers **4a** and **7** in an AABB-type polycondensation and the optimization of the reaction parameters took place using the model reactions outlined in Scheme 1. After deprotonation of benzyl cyanide (DMF, −60 °C, 2 equiv of NaH), coupling with *N*,*N*,*N*′,*N*′-tetrabutyl-*N*,*N*′-{*p*-phenylenebis[(methylthio)methylidyne]}bisammonium diiodide (**4a**) and elimination of methanethiol (−60 °C → room temperature (RT), the corresponding donor- and acceptor-substituted distyrylbenzene **6** was obtained.

After purification by precipitation of **6** from THF solution using petroleum ether, a yield of 93% could be achieved. The corresponding reaction of dianion **7** with dibutyl[(methylthio)phenylmethylene]ammonium iodide (**8**) led to a 93% yield of **9**. The reaction parameters optimized for the model reactions were then applied to the AABB-type polycondensation of monomers **4a** and **7** (Scheme 2).

In the determination of the molecular weight of the resulting polymer **2a** we faced several problems by applying conventional methods. For instance, gel permeation chromatography (GPC) with THF as eluent led to undefined, broad molecular weight distributions with molecular weights in a range from 100 000 to more than a million (polystyrene calibration). Accordingly, we subjected a homologous series of donor- and acceptor-substituted oligomers to GPC. The GPC trace for the oligomers **3a**,**d**,**e** showed definite peaks, which promised a possible calibration of the GPC column with the aid of higher oligomers. However, the elugramm of the tetramer **3f** itself showed high molecular weights, ranging from 3000 to 1 000 000. We considered aggregate formation for oligomers above the tetramer **3f** as the responsible factor for this finding. This idea will be underlined with the aid of optical investigations in section 3. Moreover, we investigated the homologous series of oligomers using GPC columns with different pore sizes and different solvents. And, in fact, we found a suppression of aggregation effects by applying GPC analysis in DMF (Figure 1). As summarized in Table 1, the number average molecular weights determined for these monodisperse compounds **3a**,**d**,**e**,**f** were at least by a factor of 1.7 too high. However, for polymers as for example **2c** (Figure 1), the shape of the GPC elugrams and polydispersities *D* of about 9 revealed intense adsorption effects on the column so that a reasonable evaluation was not possible. One explanation for the adsorption effects are polar interactions of the reactive end groups with the column materials. Even size exclusion chromatography at low polymer concentrations and upon adding a salt (LiBr) could not limit these adsorption effects.

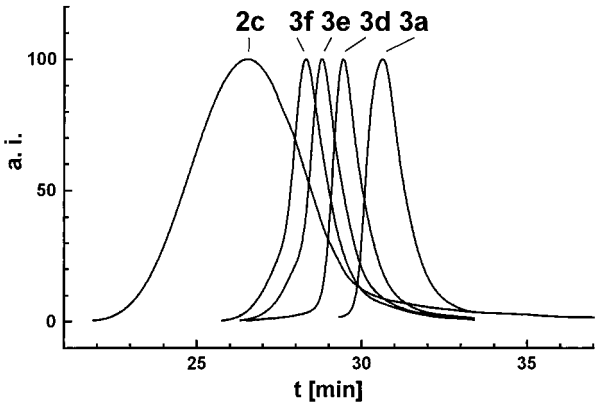


Figure 1. GPC investigation (DMF) of the homologous oligomers **1a**,**d**,**e**,**f** and polymer **2c**.

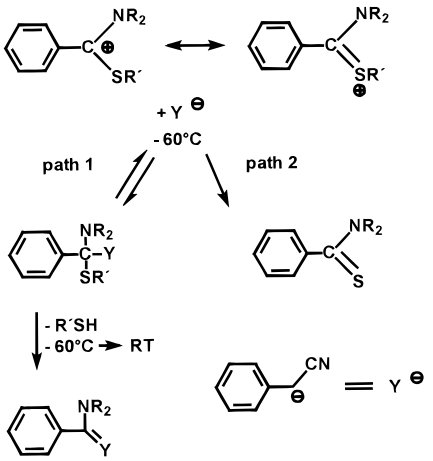
Table 1. GPC Data (DMF, 60 °C, UV Detector, Polystyrene Calibration) of 1a,d,e,f and 2c (M_w, M_n, Weight- and Number-Average Molecular Weight; *D*, Polydispersity; M_{calc}, Calculated Molecular Weight)

	M_n	M_w	*D*	M_{calc}	M_n/M_{calc}
3a	560	770	1.37	332	1.68
3d	1170	1630	1.39	663	1.76
3e	1740	2500	1.44	993	1.75
3f	2250	3290	1.46	1322	1.70
2c	1100	9500	8.6		

Aggregation effects also prevented a reasonable determination of the molecular weight by other common methods, such as vapor pressure osmosis and light scattering. Determination of molecular weights by viscosimetry in DMF, THF, and toluene did not help, because in the molecular weight range below 10 000 the increase of the viscosity after adding polymer to the solvent was too low to obtain usable data.

Efforts to determine the molecular weight by ^{1}H NMR end group analysis failed, since the broad signals of alkyl protons in the polymer, caused by mixtures of conformational and configurational isomers, cover the signals of the end group amide protons. In a further attempt, we applied ^{13}C NMR end group analysis. With

Scheme 3. Ambident Nature of the Cation Enabling Attack of the Nucleophile at the Carbon (Path 1, Kinetic Control) or at the Sulfur (Path 2, Thermodynamic Control)



the help of model compounds with corresponding end groups we were able to prove the occurrence of amide-, thioamide-, ammonium-, and cyanomethyl end groups. This result will be confirmed later by mass spectrometric investigation. However, a reasonable integration could not be applied because of the low intensity of the signals of the different possible end group carbons.

Due to the fact that aggregation effects did occur for all the donor- and acceptor-substituted polymers, we chose matrix-assisted-laser-desorption-ionization/time-of-flight (MALDI-TOF) mass spectrometry for an estimation of the molecular weights. The advantage of MALDI-TOF-MS is the possibility of determining the end groups of polymers and of comparison of the molecular weights resulting from the different polymerization reactions.[2] However, due to expected broad molecular weight distributions of the polycondensation products, we have to suppose that the real average molecular weights of the polymers are significantly higher than the measured ones.[3] Therefore, the following values of average molecular weights probably do not represent the actual state but help to compare the different polymerization results. We will discuss the exactness of this method later with the help of the calculated polydispersities.

By applying MALDI-TOF-MS, oligomers with up to five repetition units could be detected for **2a**. This result is surprisingly low if we take into consideration the yields of the oligomer synthesis. For the reaction of **4a** and **7**, the Carothers equation (4) would predict 28 phenylenevinylene repetition units. In light of these results, it is necessary to discuss possible side reactions as reasons for the limitation of the molecular weight. One problem is the ambident nature of the cationic reaction center. Hünig et al. could show in similar systems[5] that in addition to the desired C−C coupling, which is favored under kinetic control, attack of a nucleophile can also lead to dealkylation of the cation, resulting in the thermodynamically more stable carboxylic acid thioamide. On the basis of this work we postulated the two reaction paths shown in Scheme 3: path 1 corresponds to the desired reversible attack of the deprotonated benzyl cyanide at the carbon, which leads to the donor- and acceptor-substituted stilbene after heating to room temperature. We were able to suppress the undesired side reaction (path 2) at the level of the model reactions by choosing suitable reaction parameters, for example, low temperatures (−60 °C) and polar solvents (DMF).

^{1}H NMR experiments and field desorption (FD) mass spectrometry revealed that the end groups on both sides of the resulting chains in the polymerization reaction of **2a** still consist of cationic reaction centers and not of side products. Because of this, we had to consider insufficient solubility as the responsible factor for the restriction of molecular weight. To increase the solubility, we varied the dicationic component by changing the alkyl chain length. The dications can be easily synthesized starting from the corresponding carboxylic acid amide group (see Experimental Section). Therefore, we used dication **4b** with a branched 2-ethylhexyl group.

The model reaction of **4b** with the conjugate base of benzyl cyanide (**5**) results in a conversion of only 15% of the dication **4b**. It appears that shielding of the cationic reaction center by sterically demanding alkyl groups hinders the attack of the nucleophile. Therefore, we tried to improve the solubility by introducing 4,4'-biphenylylene instead of 1,4-phenylene units as aromatic building blocks. As reported in the literature,[6] the chain length of arylenevinylenes could be increased drastically by incorporation of twisted arylene (for example, biphenylylene) units that not only provide π-conjugation along the main chain but also lead to better soluble polymers with a less rigid structure. Another approach for increasing the solubility without shielding the cationic center includes the removal of the solubilizing alkyl groups from the cationic reaction center by introduction of a piperidino group. The combination of a twisted biphenylylene unit and the piperidino group modified at the 4-position in the case of monomer **4f** should give markedly improved solubility while maintaining the good conversion of the functional groups. After all, polymer **2c** could be prepared by the use of dication **4c** under the standard conditions mentioned above, whereby a weight average molecular weight (M_w) of 4300 and a number average molecular weight (M_n) of 2700 could be determined with the aid of matrix-assisted-laser-desorption-ionization/time-of-flight mass spectrometry. Monomer **4f** provided polymer **2f** with a weight average molecular weight of 6600 (M_n = 3900), which corresponds to 19 stilbene units along the chain. By varying the amount of DMF, we found that 1.3 mmol of **7** plus the appropriate dication in a total of 10 mL of DMF constitutes a compromise between sufficient solubility and an appropriate monomer concentration. No significant increase in molecular weight could be achieved at lower monomer concentrations, even when the reaction time was increased to 3 days.

With the help of MALDI-TOF mass spectrometry it is possible to prove the appearance of different end groups. The relative amounts of these end groups are influenced by the workup procedure. Treating polymers **1** and **2a**−**f**, dissolved in ethyl acetate, with water to remove the excess sodium hydride gives mainly carboxylic acid amide end groups. This result agrees with the literature[7] that quarternary salts of esters of thioimidic acids form amide and thiol upon basic hydrolysis. Workup by precipitation of the reaction product of **2a**−**f** and **1** from THF with petroleum ether leads mainly to the intact cation and few thioamide- or carboxylic acid amide groups. The MALDI-TOF mass spectrum of polymer **2c** treated with water is shown in Figure 2. The homologous mass peaks occur as $[MH]^+$ ions in

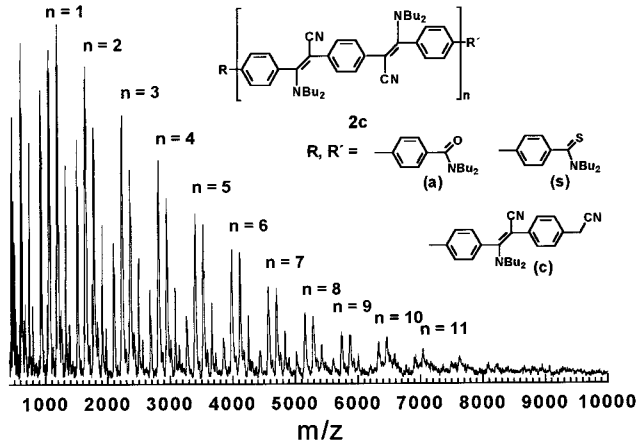


Figure 2. MALDI-TOF mass spectrum of polymer **2c**.

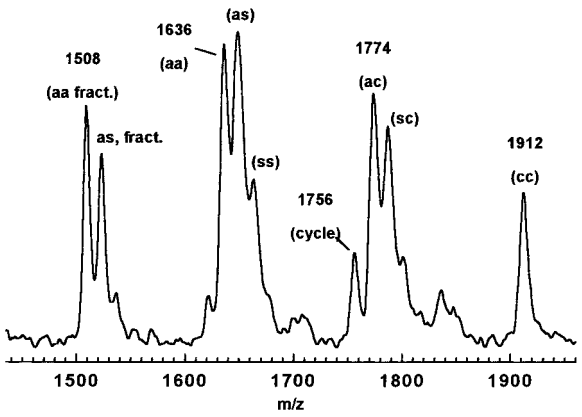


Figure 3. Expanded region of the MALDI-TOF mass spectrum displaying signals of **2c** with $n = 2$ and different end groups (amide (a), thioamide (s), cyanomethyl (c)).

groups of signals that belong to one chain length but different end groups. The peak-to-peak distance between the most intense signals of each series is 584 g/mol and corresponds to the calculated value for the repeat unit of **2c**. Figure 3 displays an expanded region of the spectrum with a group of signals representative of each chain length. The observed mass peak at 1636 g/mol belongs to the polymer chain with $n = 2$ and amide groups at both chain ends (aa). The signal at 1774 g/mol can be attributed to the corresponding chain but with one cyanomethyl end group (ac); the signal at 1912 g/mol corresponds to cyanomethyl end groups at both chain ends (cc). Apparently, fragmentation of dibutylamino groups occurs due to the MALDI-TOF-MS ionization technique, because an intensive peak occurs at 1508 g/mol, which corresponds to the polymer chain with $n = 2$ and amide groups at both chain ends after fragmentation of a $-NBu_2$ group. Due to this process we observe an overlap of signals of fragmentated chains with signals that correspond to thioamide end groups. Thus, the signals of chains with thioamide end groups at 1522 (as, fragment), 1648 (as), 1662 (ss), and 1786 g/mol (cs) appear at mass differences of about 14 and not exactly 16, compared to the signals of chains with amide end groups. The mass signal at 1756 g/mol could be attributed to a cyclic structure with $n = 3$.

Besides the molecular weight measurement of defined polymer chains, MALDI-TOF mass spectrometry can also be used for the characterization of the molecular weight distribution. The calculated polydispersities $D = M_w/M_n$ for the polymers **2c**−**f** (Table 2) lie between 1.53 and 1.72. This is a narrow distribution compared to an expected polydispersity of 2 for usual polycondensations.[4] This calculated, narrow molecular weight distribution could be explained by the inability of MALDI-TOF mass spectrometry to detect the high molecular weight fraction of a polydisperse polymer, as known from the literature.[3] However, in the case of polymers with narrow polydispersities this method is able to provide exact average molecular weights. To get reliable values for the polymer distribution, it would be necessary to combine GPC fractionation and MALDI-TOF mass spectrometry. In this case, MALDI-TOF-MS is used as an absolute detector to calibrate the GPC column.[3] As mentioned above, aggregation and adsorption effects of the measured polymers hamper the use of GPC. The polymers **1** and **2a**,**c**,**d**,**e**,**f** are characterized in Table 2, together with the molecular weight of one repeat unit and the weight (M_w) and number (M_n) average of the molecular weight determined by MALDI-TOF-MS.

Table 2. Weight- (M_w) and Number-Average (M_n) Molecular Weight, Determined by MALDI-TOF-MS, and the Calculated Polydispersity *D* for Polymers 1 and 2a,c,d,e,f

polymer	molecular weight of one repeat unit	M_w	M_n	D
1	330.3	3400	2200	1.55
2a	508.3	2100	1400	1.50
2c	584.8	4900	3200	1.53
2d	620.4	3800	2300	1.65
2e	676.4	3800	2200	1.72
2f	696.5	6600	3900	1.69

To investigate the reactivity of polymer chains with intact cationic end groups, a further attempt was made to increase the molecular weight of **2c** by way of a postpolymerization with dianion **7**: the dianion was generated separately with NaH, and another 5, 10, and 20% of **7** were subsequently added to polymer **2c** dissolved in 5 mL of DMF. With the aid of MALDI-TOF-MS we could determine after addition of 5% dianion only an increase in the molecular weight (M_w) from 4300 to 4900 (M_n: 2700−3200), whereby a further addition of dianion did not continue the polymerization.

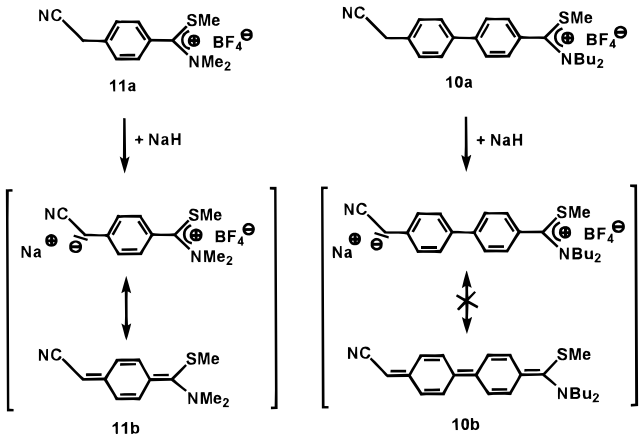
In a following approach, we tried to make use of the advantage of an AB-type polycondensation. Compared with an AABB-type polycondensation, the quality of the introduction of AB-type monomers lies in the availability of both functional groups within a single monomer unit, so that an ideal stoichiometry of 1:1 is guaranteed. In a first attempt, we synthesized the monomeric building block **11a** that contains a cationic and anionic function, separated through a phenylene ring. However, this compound did not undergo the desired head-to-tail addition to give donor- and acceptor-substituted PPV. Instead, it could be shown by ^{1}H NMR experiments that rather a *p*-quinodimethane form **11b** is adopted: Starting from 0.05 mmol of the colorless compound **11a** in an NMR tube at −50 °C in DMF-d_7, we added 1.5 equiv of sodium hydride. Immediately, the donor- and acceptor-substituted *p*-quinodimethane **11b** was formed, as shown in Table 3.

Characteristic for the quinoid structure of **11b** are the shifts to higher field of the signals that belong to the aromatic protons and the benzylic proton. Heating of the yellow reaction mixture in 15 °C steps to above room temperature showed no changes in the ^{1}H NMR spectrum, and on further heating, decomposition took place,

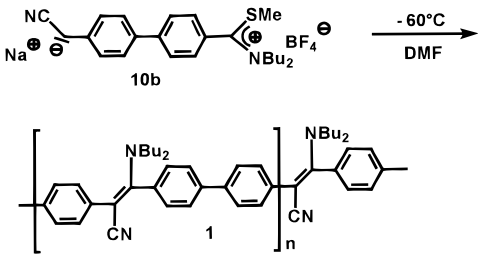
Table 3. ^{1}H NMR Data (DMF-d_6, 500 MHz, −50 °C) of 11a and 11b

^{1}H NMR (DMF-d_6, 500 MHz, 223 K)	compound **11a** δ (ppm)	*p*-quinodimethane **11b** δ (ppm)
aromatic H	8.01, 7.55 (dd (8.6 Hz), 4H)	7.29, 7.15, 6.42, 6.12 (2dd (J = 8.7 Hz), 4H)
benzylic H	4.45 (s, 2H)	3.25, (s, 1H)
$-N(CH_3)_2$	2.87 (s, 6H)	2.25 (s, 6H)
$-SCH_3$	2.45 (s, 3H)	2.23 (s, 3H)

Scheme 4. Formation of a Quinoid Resonance Structure of Monomer 11b in Contrast to Monomer 10b



Scheme 5. AB-Type Polycondensation for the Synthesis of Polymer 1 (DMF, −60 °C → RT, 1.5 equiv of NaH)



but no head-to-tail addition occurred. We will report elsewhere on the attempts to polymerize **11b** by using common *p*-quinodimethane polymerization routes.[8] Compared with the phenylene-bridged monomer, the biphenylylene-bridged system **10b** appeared more suitable: the quinoid resonance form does not contribute to its ground state because planarization of the biphenyl frame and the concomitant loss of two aromatic units are energetically unfavorable (Scheme 4).

After optimization of the reaction conditions, the highest molecular weight could be obtained by the reaction of 0.9 mmol of **10a** in 4 mL of DMF with 2 equiv of NaH with a reaction time of 48 h (Scheme 5) at −60 °C, resulting in a weight average molecular weight (M_w) of 3400 (M_n = 2200) for **1**, determined with the aid of MALDI-TOF-MS. A repeat unit here corresponds to one stilbene unit so that the AB-type polycondensation leads to chains with a parallel arrangement of dipoles ("acceptor−donor−acceptor−donor") when going from one vinylene unit to the neighboring one (Scheme 5).

In contrast, polymers made by the AABB-type polycondensation (Scheme 2) possess the sequence "acceptor−donor−donor−acceptor". The structures in Schemes 4 and 7 are simplified (all *E*) because we always find a mixture of *E*- and *Z*-isomers. The *E*/*Z*-isomerism has been investigated in the case of α-(dimethylamino)-β-cyanostilbene,[1] which represents a building block similar to a repetition unit of the polymers **1** and **2a**−**f**. The pure *E*-isomer of α-(dimethylamino)-β-cyanostilbene could be obtained in crystalline form.[1] When this crystal is dissolved in dimethylformamide at 15 °C, isomerization readily takes place, leading to a 57:43 equilibrium, as determined from the signal intensity of the *N*-methyl protons in the ^{1}H NMR spectrum. Because of the *E*/*Z*-configurational isomerism and also possible conformational mobility around the single bond between the phenylene and the vinylene units, we will not obtain rigid polymers with parallel aligned dipoles in solution and we cannot add up simply the single dipole moments. For the *E*- and *Z*-isomer of α-(dimethylamino)-β-cyanostilbene, AM1 calculations predict similar dipole moments (4.67 and 4.80 D, respectively[1]). Therefore, the effect of *E*/*Z*-isomerism on the permanent dipole moment of one donor and acceptor stilbene unit can be neglected, but how is the additivity of the dipoles along a polymer chain? For the donor- and acceptor-substituted oligomers **3a**,**d**,**e**,**f**, that represent parts of polymer **1**, the molecular dipole moments μ in solution have been measured:[1] an increase from 6.1 D for the stilbene **3a** to 9.4 D for the oligomer **3f** that has four stilbene subunits (**3d**, 7.1 D; **3e**, 7.9 D)[1] indicates even higher molecular dipole moments for **1**. Moreover, a single molecule with a dipole moment of 9.4 D in solution should lead to even higher macroscopic dipole moments in the bulk or in guest−host systems. The poling-induced alignment of dipoles in an amorphous polymer is further explained in section 3.

The question remains why the polymer made from the "cation−anion monomer" **10b** shows a significantly lower molecular weight than those resulting from an AABB-type polycondensation. While the ideal 1:1 stoichiometry should, in principle, be more favorable, the question of solubility is still the key issue. Obviously, polymer **1** shows a more regular structure since the biphenylylene units are incorporated as only aromatic building blocks with a regular distance of dipoles. Polymer **2c** is constructed in a less regular fashion since it contains an alternating sequence of phenylene and biphenylylene moieties. The former structure type appears more suitable for aggregate formation. As a consequence, a stronger restriction in molecular weight due to a lower solubility of aggregate particles can be expected. Moreover, the polymerization will be kinetically hindered because of the lower mobility of growing chains and a steric shielding of the reaction centers in the aggregates.[6]

Of course, an increase of solubility could have been achieved by the introduction of alkyl or alkoxy chains in the 2,5-positions of the phenylene units, as described in the literature.[9] However, the simplicity of the monomer synthesis would be lost and an additional torsion about formal single bonds of the individual subunits would affect the optical properties.

In section 3 we will show that a further increase of the chain length will not change the material properties of our polymers markedly.

3. Thermal and Optical Properties

Investigation of the optical properties can provide valuable information on the degree of conjugation along the main chain. Furthermore, it can offer additional evidence for the formation of aggregates and thereby

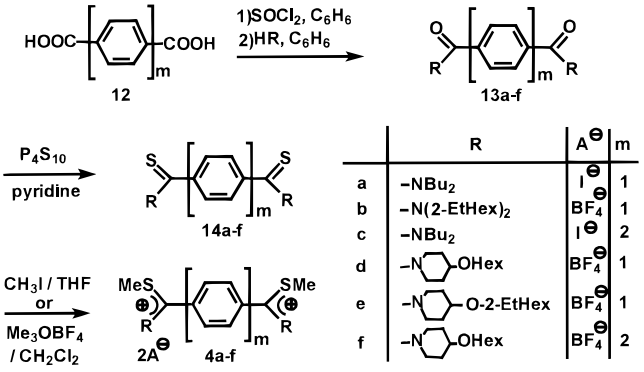
confirm the results observed by GPC: In the UV−vis spectra of the polymers **2a**−**f** (in chloroform solution and in the film), the longest wavelength absorption bands λ_{max} occur at 386 nm and absorption edges until 500 nm. Corresponding to the position of the absorption bands, the polymers possess weak, yellow color and do not absorb visible light above 500 nm. This is important for a possible application of these materials as optical waveguides.[10] A comparison of the polymer absorption spectra with the longest wavelength absorption maximum of the oligomers enables the determination of the effective conjugation length:[1] the stilbene **3a** shows an absorption maximum λ_{max} at 340 nm; when the chain length of the oligomers (**3d**, 370 nm; **3e**, 374 nm; **3f**, 378 nm) is increased, the longest wavelength absorption band converges to those of the polymers (**2a**−**f**, 386 nm; **1**, 380 nm). Compared with unsubstituted PPV, which possesses an effective conjugation length of 8−10 units,[11] the effective conjugation length of polymers **2a**−**f** and **1** is composed of 5−6 phenylenevinylene units so that a further increase in the molecular weight does not cause a change in the optical properties.

Measurements of fluorescence for polymers **1** and **2a**−**f** in solution (chloroform) reveal a weak emission between 400 and 500 nm. This is remarkable if we consider that the oligomers **3a**−**g** do not emit light,[1] since quenching of the fluorescence can be explained by the degree of rotational freedom about the central vinylene bond. This vinylene bond possesses σ-bond character, which opens channels for the nonradiating deactivation of the emission.[1] One possible explanation for the fluorescence of the polymers is that the aggregation can induce an immobilization of the vinylene unit by Coulomb interaction with the neighboring chain and, as a consequence, the nonradiating emission of energy is prevented.

Investigation of the thermal properties of the donor- and acceptor-substituted polymers **2a**−**f** and **1** is important to evaluate their applicability in nonlinear optical (NLO) devices. NLO properties arise from the noncentrosymmetry of NLO-active groups with permanent dipole moments, achieved by electric-field poling above the glass transition temperature (T_g) and "freezing in" the induced alignment by cooling below T_g under the applied electric field.

It is necessary to use thermally stable materials with high T_g's to obtain a good long-term stability of the poling-induced alignment since the state of frozen-in, aligned dipoles is thermodynamically unstable in the absence of the field.[12−14] The thermal properties of the polymers **1** and **2a**−**f** were carried out not only in the bulk but also in guest−host (polystyrene) systems by TGA (thermogravimetric analysis) and DSC (differential scanning calorimetry). The latter method reveals a continuous 5% degradation at 350 °C and a peak temperature of 425 °C. Depending on the substitution pattern, the polymers possess glass transition temperatures between 87 and 118 °C. Moreover, the polymers **1** and **2c**−**f** (and even oligomer **3f**) are film-forming and they show very good miscibility with matrix polymers. The good miscibility, for example, with polystyrene, in which up to 20 wt % of **2c**−**f** has been added, is reflected in the T_g of 86 °C (polystyrene: 105 °C). So we are able to obtain films of the polymers **1** and **2c**−**f** or of corresponding blends that possess the basic requirements for further investigation of NLO properties and orientational stabilities. We will report elsewhere on this work and on further optical and electrooptical investigation of these materials.

Scheme 6. Synthesis of the Dications 4a-f Starting from Terephthalic Acid (12)



4. Summary

In summary, a new polycondensation method, based on a simple cation−anion coupling has been introduced, which leads to the synthesis of soluble, film-forming, and thermally stable donor- and acceptor-substituted poly(*p*-phenylenevinylene)s **1** and **2a**−**f** under very mild reaction conditions. We describe the optimization of the polycondensation in terms of solubility of the polymers and reactivity of the monomers. The use of MALDI-TOF-MS made it possible to determine the end groups of the polymers and to compare the molecular weights of the materials **2a**−**f**, which result from the optimization of the polymerization parameters. We cannot exclude the possibility that the real molecular weights are higher than the measured ones because aggregation effects prevent the use of other analytical methods such as GPC for comparison. The degrees of polymerization of the polymers **1** and **2a**−**f** determined by MALDI-TOF-MS show a maximum of 10 (**2f** and **1**), which corresponds to 20 (**2f**) and 10 (**1**) phenylenevinylene units along the chain. The polymers **1** and **2**, resulting from an AB- or an AABB-type polycondensation, differ in the sequence of the donor and acceptor functions along the chain. This leads to a parallel arrangement of local dipole moments in the material obtained from AB-type polycondensation, while the AABB-type method produces an antiparallel arrangement.

We will report elsewhere on measurements of the dipole moments of the new polymers, on investigations into the aggregate structures, and on a determination of inter- and intramolecular dipole−dipole interactions.

5. Experimental Section

The terephthalic acid bis(thiodialkylamide)s **14a**−**f** were prepared from terephthalic acid (**12**) as described in the literature[15] (Scheme 6). The synthesis of 4-(alkyloxy)piperidine is also reported.[16]

General Procedure for the Preparation of the Dications 4a and 4c (Scheme 8). Terephthalic acid bis(thiodibutylamide) (**14a**) (4.00 g, 9.52 mmol) was placed in a 250 mL two-neck flask under an argon atmosphere and stirred for 48 h at room temperature with iodomethane (13.52 g, 95.22 mmol) in 60 mL of pyridine. The powdery reaction product **4a** was obtained after removal of the solvent under vacuum and recrystallization from THF (5.99 g, 90% yield).[17]

General Procedure for the Preparation of the Dications 4b,d,e,f. Terephthalic acid bis(thiobis(2-ethylhexyl)amide) (**14b**) (5.00 g, 7.75 mmol) was placed in a 250 mL two-neck flask under an argon atmosphere and stirred for 24 h at

room temperature with trimethyloxonium tetrafluoroborate (2.52 g, 17.05 mmol) in 100 mL of dichloromethane. The powdery reaction product **4b** was obtained after removal of the solvent under vacuum and recrystallization from THF (4.80 g, 73% yield).[15]

General Procedure for the Preparation of the Polymers 2a−f and 1. *p*-Xylylene dicyanide **(7)** (200 mg, 1.28 mmol) was dissolved in 5 mL of dry DMF under an argon atmosphere in a 250 mL flask. The mixture was cooled to −60 °C, 95% sodium hydride (97 mg, 3.84 mmol) was added under an argon flush, and the resulting mixture was stirred for 3 h at −60 °C. Subsequently, 1.28 mmol of the dication component **4a−f** dissolved in 5 mL of DMF was added and the mixture stirred at −60 °C for 24 h. The reaction mixture was then allowed to warm to room temperature overnight, and the solvent was removed under vacuum. The residue was taken up in ethyl acetate, washed with water, and dried over magnesium sulfate. After removal of the solvent by distillation, the residue was dissolved in 10 mL of THF and the polymer precipitated with petroleum ether.

2a. ^{1}H NMR ($CDCl_3$, 300 MHz), δ: 8.10−7.84, 7.84−7.08, 7.08−6.68, 6.68−6.45 (m (b), 8H, phenylene-H), 3.60−3.04, 3.04−2.57, 1.80−1.50, 1.50−1.18, 1.18−1.03, 1.03−0.50 (m (b), 36H, $-NBu_2$). ^{13}C NMR ($CDCl_3$, 75 MHz), δ: 143.3, 133.7, 133.4, 133.0, 124.9, 124.1, 124.0, 118.1, 117.8, 117.6, 100.8, 94.5, 81.1, 80.9, 80.7, 69.2, 35.5, 33.1, 32.0, 30.7, 27.0, 24.0, 15.5. UV spectrum (THF): λ_{max}, nm [ϵ_{max}, L/(mol cm)] = 386 (55 710). Anal. Calcd for $(C_{34}H_{44}N_4)_n$ (calcd without end groups): C, 80.27; H, 8.72; N, 11.01. Found: C, 81.20; H, 8.52; N, 10.30.

2c. ^{1}H NMR ($CDCl_3$, 300 MHz), δ: 7.96−6.65 (m (b), 12H, biphenylylene-H), 3.58−3.22, 2.93−2.58, 1.82−1.53, 1.50−1.18, 1.18−1.03, 1.03−0.75 (m (b), 36H, $-NBu_2$). ^{13}C NMR ($CDCl_3$, 75 MHz), δ: 171.4, 163.7, 161.2, 135.1, 134.7, 131.8, 131.7, 130.7, 129.7, 129.1, 129.0, 128.5, 128.3, 128.1, 127.9, 127.5, 127.3, 127.1, 123.8, 121.8, 117.6, 85.7, 51.7, 51.5, 51.3, 51.2, 30.1, 30.0, 20.1, 20.0, 13.6. UV spectrum (THF): λ_{max}, nm [ϵ_{max}, L/(mol cm)] = 386 (55 660). Anal. Calcd for $(C_{40}H_{48}N_4)_n$ (calcd without end groups): C, 82.15; H, 8.27; N, 9.58. Found: C, 82.99; H, 8.11; N, 8.99.

2d. ^{1}H NMR ($CDCl_3$, 300 MHz), δ: 8.05−7.83, 7.84−7.05, 7.05−6.85, 6.68−6.48 (m (b), 8H, phenylene-H), 3.45−3.30, 3.30−2.97, 2.97−2.55, 1.90−1.60, 1.60−0.95, 0.95−0.40 (m (b), 44H, piperidino/hexyl group). ^{13}C NMR ($CDCl_3$, 75 MHz), δ: 170.7, 163.7, 134.7, 138.6, 138.0, 137.2, 134.6, 134.5, 134.0, 133.5, 127.9, 127.7, 126.2, 67.8, 55.1, 48.4, 48.1, 32.2, 31.9, 29.7, 29.3, 27.0, 26.5, 23.2, 14.6; UV spectrum (THF): λ_{max}, nm [ϵ_{max}, L/(mol cm)] = 386 (54 800). Anal. Calcd for $(C_{40}H_{52}N_4O_2)_n$ (calcd without end groups): C, 77.38; H, 8.44; N, 9.02. Found: C, 78.11; H, 8.47; N, 8.77.

2e. ^{1}H NMR ($CDCl_3$, 300 MHz), δ: 8.10−7.90, 7.90−7.57, 7.57−7.13, 7.05−6.82, 6.63−6.53 (m (b), 8H, phenylene-H), 3.75−3.45, 3.45−3.15, 3.15−2.85, 2.85−2.50, 2.08−1.60, 1.55−0.95, 0.95−0.60 (m (b), 52H, piperidino/ethylhexyl-H). ^{13}C NMR ($CDCl_3$, 75 MHz), δ: 191.3, 169.5, 162.2, 160.9, 141.6, 139.0, 137.8, 137.1, 134.4, 133.2, 131.1, 130.6, 129.2, 128.2, 127.8, 126.9, 123.1, 122.9, 121.4, 119.1, 86.2, 85.1, 73.2, 71.2, 48.8, 48.3, 44.8, 44.3, 40.1, 39.9, 31.9, 31.0, 30.5, 29.6, 29.1, 27.3, 23.8, 23.0, 14.0, 11.0; UV spectrum (THF): λ_{max}, nm [ϵ_{max}, L/(mol cm)] = 386 (54 400). Anal. Calcd for $(C_{48}H_{68}N_4O_2)_n$ (calcd without end groups): C, 78.71; H, 9.28; N, 7.65. Found: C, 79.04; H, 8.89; N, 7.41.

2f. ^{1}H NMR ($CDCl_3$, 300 MHz), δ: 8.00−7.90, 7.78−7.40, 7.40−7.17, 7.05−6.92, 6.71−6.64 (m (b), 12H, biphenylylene-H), 3.76−3.71, 3.63−3.54, 3.54−3.16, 3.20−2.85, 2.85−2.71, 1.75−1.25, 1.25−1.03, 1.03−0.65 (m (b), 44H, piperidino/hexyl group). ^{13}C NMR ($CDCl_3$, 75 MHz), δ: 173.0, 170.0, 162.9, 162.6, 161.4, 161.1, 146.1, 145.9, 142.1, 135.9, 135.6, 134.4, 133.1, 130.7, 127.4, 123.4, 122.0, 86.1, 85.9, 84.6, 84.4, 73.7, 70.3, 48.9, 48.4, 40.2, 36.4, 32.1, 31.6, 31.4, 30.0, 29.9, 27.7, 25.8, 22.5, 14.0. UV spectrum (THF): λ_{max}, nm [ϵ_{max}, L/(mol cm)] = 386 (53 900). Anal. Calcd for $(C_{46}H_{56}N_4O_2)_n$ (calcd without end groups): C, 79.33; H, 8.10; N, 8.04. Found: C, 79.91; H, 7.78; N, 7.85.

1. ^{1}H NMR ($CDCl_3$, 300 MHz), δ: 8.01−6.76 (m (b), 8H, biphenylylene-H), 3.61−3.32, 2.95−2.65, 1.81−0.77 (m (b), 14H, $-NBu_2$). ^{13}C NMR ($CDCl_3$, 75 MHz), δ: 166.0, 165.5, 163.9, 142.0, 142.0, 136.8, 136.5, 136.4, 136.0, 132.1, 131.7, 131.6, 128.7, 128.5, 127.9, 127.8, 127.8, 119.8, 58.9, 58.9, 53.7, 53.4, 31.1, 31.0, 29.8, 29.6, 20.6, 20.6, 14.4, 14.4. UV-spectrum (THF): λ_{max}, nm [ϵ_{max}, L/(mol cm)] = 380 (52 020). Anal. Calcd for $(C_{23}H_{26}N_2)_n$ (calcd without end groups): C, 83.59; H, 7.93; N, 8.48. Found: C, 83.67; H, 7.90; N, 8.53.

Experimental Details for MALDI-TOF-MS. The mass spectrometry experiments were carried out with a Reflex MALDI-TOF mass spectrometer (Bruker). The device is equipped with a 337 nm nitrogen laser. The measurements took place in linear mode with an accelerating voltage of 35 kV. The mass spectrometer was calibrated externally by means of a polystyrene standard (M_n = 2500). 1,8,9-Trihydroxyanthracene, dissolved in THF, was employed as matrix and mixed with the samples, also dissolved in THF, so that a molar matrix:analyte ratio of about 500:1 was obtained. The samples prepared in this manner were allowed to crystallize in air on a metal support and were measured immediately.

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