

Charge Transfer Interactions in Polyesters with a Donor-(σ -Bridge)-Acceptor Moiety in the Repeating Unit

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ABSTRACT: Two high molecular weight linear polyesters were investigated to gain insight in how the photophysics of electron donor-(σ -spacer)-electron acceptor (D σ A) compounds are affected by incorporation into a polymer. They were prepared by condensation of either adipoyl or sebacoyl chloride with a diol that was functionalized with an *N,N*-dialkylaniline donor, a cyclohexyl type σ -spacer, and a 1,1-dicyanovinyl acceptor. The solubility, which is very low, and the thermal properties of the polyesters are dictated by physical crosslinking as a consequence of interchain donor-acceptor interactions. Charge transfer (CT) absorption and emission are observed, which involve CT between D σ A moieties of different chains rather than CT processes within a single D σ A unit. As a result, the photophysics of the D σ A units in the polyesters differs strongly from that of similar D σ A compounds in solution. Upon swelling the polymers with THF, the CT fluorescence disappears partly. Analogous polymers containing only an *N,N*-dialkylaniline donor display dual fluorescence; one band reflects local emission, while the other is attributed to excimer emission. © 2004 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 42: 4775–4784, 2004

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INTRODUCTION

The photophysics of (electron donor)-(σ -spacer)-(electron acceptor) compounds (D σ A) has been studied extensively.¹ Upon photoexcitation of either the donor or the acceptor, photoinduced electron or charge transfer (CT) can take place, producing a highly dipolar excited state D⁺ σ A⁻, even when the “insulating” hydrocarbon spacer is rigid. Most studies have focused on isolated com-

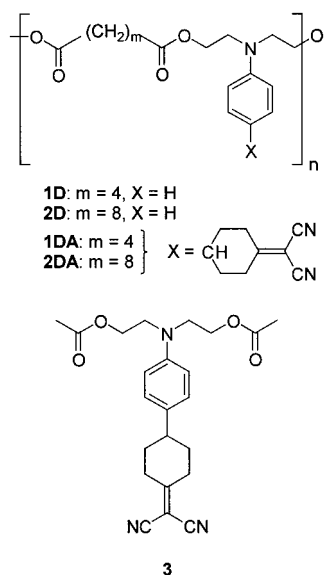
pounds, that is, molecules in dilute solution or in the gas phase. These studies not only provided fundamental insight in the factors that influence the charge separation and recombination processes, but also disclosed attractive optical and optoelectronic features. Therefore, D σ A compounds have been shown or proposed to function as active unit in (opto)electronic devices² such as electroluminescent³ or rectifying systems.^{4,5}

To be suitable candidates for application in (opto)electronic devices, D σ A compounds generally should maintain their photophysical properties upon incorporation in materials such as polymers. Whether this is indeed the case is largely unknown since, as far as we are aware, reports on polymers incorporating rigid or semirigid D σ A units are scarce.⁶ It should be realized that a high

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Scheme 1. Compounds under study.

concentration of D σ A units such as are found in polymers may lead to intermolecular photophysical processes that are not accessible for isolated D σ A chromophores.^{7,8} Among these are transport of excitation energy⁹ and excimer formation.^{7,10} Moreover, electron donating and accepting groups have the tendency to interact intermolecularly in the ground state, resulting in the formation of charge-transfer complexes.^{11,12} Formation of these complexes may not only affect the behavior of the D σ A chromophores, but also the properties of the material as a whole.

The objective of this study is to gain insight in how the steady-state photophysics of semirigid D σ A moieties are influenced by incorporation into a polymer. Hereto we report on the synthesis and (photophysical) properties of polyesters **1DA** and **2DA** (Scheme 1), which contain D σ A moieties in the repeating unit. The electron donor is an *N,N*-dialkylanilino moiety and the electron acceptor is a 1,1-dicyanovinyl group. Photoinduced charge separation and recombination processes in a variety of compounds containing this donor-acceptor combination and a σ - or σ - π - σ -bridge have been extensively investigated by us^{13–15} and others.¹⁶ For model compound **3** it was shown by the presence of a weak intramolecular CT absorption band that the four- σ -bond bridge relays a weak through-bond interaction between the donor and acceptor.¹⁵ Furthermore, in polar as well as nonpolar solvents, photoinduced intramolecular electron transfer appeared to take place in near quan-

titative yield.¹⁷ The resulting charge-separated state is fluorescent in nonpolar and medium polarity solvents, but not in polar solvents like THF.

Polyesters **1DA** and **2DA** were designed to study the effects of possible aggregation on the photophysics of D σ A units. To associate these effects as closely as possible with the nature of chromophores containing both an electron donor and an electron acceptor, we also investigated the properties of polyesters **1D** and **2D**. In the repeating unit of these materials only the donor moiety is present, which may give rise to interchromophore photophysical processes, but not to specific donor-acceptor interactions.

EXPERIMENTAL

General

All glassware was silanized by treatment with Me₃SiCl. Adipoyl chloride (Acros) and sebacoyl chloride (Aldrich) were carefully distilled under vacuum, giving colorless material. Pyridine (which had been stored on 4Å molsieves) was boiled with CaH₂ under reflux and then distilled in a N₂ atmosphere. CH₂Cl₂ was distilled from P₂O₅. 2,2'-(Phenylimino)diethanol (**5a**) was obtained from Acros and was twice crystallized from diethyl ether (57 mg mL⁻¹; boiling point to -20 °C) under N₂. The purity was monitored with TLC (hexane:ethyl acetate 1:1 v/v). MeCN was distilled from CaH₂. All reactions (including the work-up) were carried out in a N₂ atmosphere and with dry solvents.

Molecular weights were determined relative to polystyrene standards by means of size exclusion chromatography (SEC) with THF as eluant and performed using a Thermo Separation Products Spectra Series P200 pump, a Spectra System UV2000 absorption detector of the same manufacturer ($\lambda = 254$ nm), and an Alltech Jordi-Gel DVB Mixed Bed column (length 300 mm; I. D. 7.8 mm). The elution curves were analyzed with Spectra-Physics GPC/PC v1.00 software. Differential scanning calorimetry (DSC) thermograms were obtained on a Mettler DSC 12E or DSC 821E instrument at heating and cooling rates of 3 K min⁻¹. Thermogravimetry was performed at a heating rate of 20 K min⁻¹ with a Perkin-Elmer TGS-2 apparatus equipped with an AR-2 autobalance or a TA instruments SDT 2960 simultaneous DSC-TGA apparatus under N₂. Prior to thermal analysis by DSC or thermogravimetry, samples

were dried in vacuum for at least 3h. Solution NMR spectra were recorded on a Bruker AC 300 spectrometer operating at 300.13 MHz for ^1H -NMR and at 75.47 MHz for ^{13}C -NMR. Samples were dissolved in CDCl_3 . Chemical shifts (in ppm) are referenced to internal TMS (0 ppm) in the case of ^1H -NMR and to external TMS in the case of ^{13}C -NMR. ^{13}C CP/MAS NMR spectra were recorded at 75.47 MHz on a Varian Unity Inova spectrometer equipped with a 7 mm CP/MAS probe. Polymers were packed in a silicon nitride rotor (together with KBr as filler material) and spun at 6000 Hz. A cross polarization contact time of 0.5 ms was used. Spectra were averaged from 4844 (**1DA**) or 26,136 (**2DA**) FIDs, and a line broadening factor of 100 Hz was applied. Chemical shifts are given relative to TMS; external adamantane (δ 29.2 and 38.3 ppm) was used as secondary chemical shift reference. IR spectra were measured at 4 cm^{-1} resolution on a Perkin-Elmer FT-IR 2000 spectrometer equipped with a Golden Gate single reflection diamond ATR accessory or a Perkin-Elmer Spectrum One FT-IR spectrometer equipped with a Perkin-Elmer Universal ATR Sampling Accessory. The spectra are corrected for the wavelength dependence of the penetration depth of the IR light in the sample.

For the investigation of the photophysical properties of **1D** and **1DA**, the fractions with the highest molecular weight were used. UV-Vis absorption and fluorescence spectroscopy were performed using equipment described elsewhere.^{18,19} Samples for solid state UV-Vis spectroscopy were obtained either by dissolving the polymer in CH_2Cl_2 , sprinkling it over KBr, grinding and drying under vacuum (**1D**, **2D**), or by swelling the polymer in CH_2Cl_2 , followed by grinding with KBr and drying under vacuum (**1DA**, **2DA**). Fluorescence spectra of solid **2D** and **3** were obtained from films on quartz substrates. For **1DA**, **2DA**, and **1D** a piece of polymer was held in the excitation bundle by means of a needle. Swelling was accomplished by keeping a piece of polymer in the swelling solvent overnight. Next, the polymer was pushed into a 0.5 mm cuvette filled with a small amount of the same solvent. Care was taken to assure that the excitation beam was completely intercepted by polymer, so that only fluorescence of the solid material was monitored. All fluorescence spectra of solid samples were collected in front face geometry.

Synthesis

The synthesis and purification of monomer **5b** have been reported previously.¹⁵ The procedure²⁰ for melt polycondensation that gave low molecular weight **1DA** is described in the Supplementary Material.

General Procedure for Solution Polycondensation²¹

To an ice-cooled stirred solution of the appropriate carboxylic acid chloride (~ 3 mmol) in CH_2Cl_2 (6 mL) was added an equimolar amount of diol. To the solution (or suspension, in the case of diol **5b**) were added dropwise 4 equivalents of pyridine (~ 12 mmol). A white precipitate formed immediately, and an orange color developed that largely disappeared in some hours. The mixture was stirred for 7 days at room temperature under exclusion of light. Subsequently, the polymer was precipitated by dropwise addition of the reaction mixture to a vigorously stirred sixfold volume of dry MeCN under N_2 . Stirring was continued for 30 min after precipitation. Low molecular weight fractions of $M_w = 1000$ – 2000 , presumably corresponding to cyclic oligomers, were generally detected by SEC in this stage. To completely remove this low molecular weight material, the precipitation procedure was repeated twice (using 6 mL of CH_2Cl_2 and 36 mL of dry MeCN each time).

Polymer 1D

Three polymerizations were performed, employing **5a** and 0%, 1%, and 3% excess of adipoyl chloride. These gave colorless film-forming polymers (yields: 50, 52, and 40%) with relative M_w values of 98.0×10^3 (M_w/M_n 2.8), 94.9×10^3 (M_w/M_n 2.7), and $137 \times 10^3\text{ g mol}^{-1}$ (M_w/M_n 2.7), respectively. ^1H -NMR: δ 1.55–1.65 (m, 4H, $-\text{CH}_2-$), 2.24–2.31 (m, 4H, $-\text{H}_2\text{C}-\text{COO}-$), 3.59 (t, $J = 6.3$ Hz, 4H, $-\text{N}-\text{CH}_2-$), 4.23 (t, $J = 6.3$ Hz, 4H, $-\text{O}-\text{CH}_2-$), 6.68–6.77 (m, 3H, Ar-H), 7.18–7.24 (m, 2H, Ar-H), in accordance with literature data.²² ^{13}C -NMR: δ 24.2 ($-\text{CH}_2-$), 33.7 ($-\text{H}_2\text{C}-\text{COO}-$), 49.5 ($-\text{N}-\text{CH}_2-$), 61.3 ($-\text{O}-\text{CH}_2-$), 112.2 (Ar, ortho), 117.1 (Ar, para), 129.4 (Ar, meta), 147.3 (Ar, ipso), 173.1 (C=O). IR (ATR): ν 2947, 2868, 1726 (C=O), 1597, 1504, 1459, 1380, 1355, 1227, 1162, 1135, 1076, 988, 745, 692. T_g -10.1 °C (M_w 98.0×10^3), -9.4 °C (M_w 94.9×10^3), -9.2 °C (M_w $137 \times 10^3\text{ g mol}^{-1}$).

Polymer 1DA

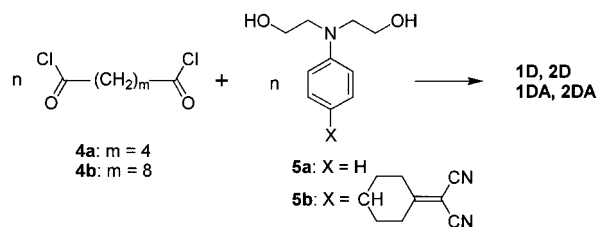
SEC (THF) of the very viscous to gel-like reaction mixture gave a relative M_w of $180 \times 10^3 \text{ g mol}^{-1}$ ($M_w/M_n = 4.6$) for the high molecular weight peak. A cyclic oligomer fraction was present as well. The crude reaction mixture was diluted with CH_2Cl_2 (25 mL) and precipitated in MeCN (85 mL). The precipitate was reprecipitated using CH_2Cl_2 (20 mL) and MeCN (100 mL). The polymer obtained in this way was stirred with MeCN (100 mL), isolated by decantation of the supernatant, and dried under reduced pressure. Analysis of the supernatant indicated that low molecular weight fractions had been completely removed. The resulting reddish rubber-like material was insoluble in CH_2Cl_2 (swells), CHCl_3 (swells), THF (swells), benzene, toluene, ethyl acetate, and MeCN. ^{13}C -NMR (CP/MAS): δ 24.7, 34.1, 41.3, 49.6, 60.9, 82.5, 112.4, 132.2, 146.9, 173.5; see Figure S2 (Supplementary Material) for assignment. IR (ATR): ν 2937, 2863, 2230 ($\text{C}\equiv\text{N}$), 1726 ($\text{C}=\text{O}$), 1612, 1595, 1519, 1444, 1381, 1231, 1164, 1136, 1078, 987, 819. T_g 54 °C.

Polymer 2D

This polymer was prepared from **5a** and 3% excess sebacoyl chloride and was obtained as a colorless material. The yield was not accurately determined since the polymer was not thoroughly dried, but is estimated to be $\sim 40\%$. M_w $84 \times 10^3 \text{ g mol}^{-1}$ (M_w/M_n 4.8). ^1H -NMR: δ 1.29 (b, 8H, $-\text{CH}_2-$), 1.59 (b, 4H, $-\text{CH}_2-$), 2.27 (bt, 4H, $-\text{H}_2\text{C}-\text{COO}-$), 3.66 (bt, 4H, $-\text{N}-\text{CH}_2-$), 4.27 (bt, 4H, $-\text{O}-\text{CH}_2-$), 6.82 (m, 1H, Ar-H), 6.89 (m, 2H, Ar-H), 7.20–7.30 (m, 2H, Ar-H). ^{13}C -NMR: δ 24.7 ($-\text{CH}_2-$), 29.0 ($-\text{CH}_2-$), 29.0 ($-\text{CH}_2-$), 34.0 ($-\text{H}_2\text{C}-\text{COO}-$), 51.8 ($-\text{N}-\text{CH}_2-$), 60.4 ($-\text{O}-\text{CH}_2-$), 114.9 (Ar, ortho), 121.6 (Ar, para), 129.7 (Ar, meta), 173.5 ($\text{C}=\text{O}$); because of line broadening a signal of the ipso aromatic carbon atom could not be detected. IR (ATR): ν 2929, 2855, 1730 ($\text{C}=\text{O}$), 1598, 1505, 1462, 1381, 1162, 990, 746, 693. T_g -29 °C.

Polymer 2DA

This polymer was prepared from **5b** and 3% excess of sebacoyl chloride. SEC in THF of the reaction mixture gave a relative M_w of $310 \times 10^3 \text{ g mol}^{-1}$ (M_w/M_n 4.0) for the high molecular weight fraction. Three reprecipitations from MeCN gave material that was largely insoluble. Two consecutive treatments consisting of stirring and heat-



Scheme 2. Polycondensation of **1D**, **2D**, **1DA**, and **2DA**. Conditions: pyridine, CH_2Cl_2 .

ing in THF resulted in dissolution of material with M_w of 17×10^3 (M_w/M_n 2.1) and $34 \times 10^3 \text{ g mol}^{-1}$ (M_w/M_n 2.0). UV-Vis and fluorescence studies were performed on material that was not soluble in THF. Estimated yield (not thoroughly dried) $\sim 30\%$. ^{13}C -NMR (CP/MAS): δ 29.2, 62.0, 126.5, 131.7, 145.3, 173.2. IR (ATR): ν 2927, 2855, 2231 ($\text{C}\equiv\text{N}$), 1729 ($\text{C}=\text{O}$), 1614, 1520, 1454, 1382, 1231, 1163, 1066, 817. T_g : see below.

RESULTS AND DISCUSSION

Synthesis and Characterization

A first approach to obtain polymer **1DA** consisted of a melt polycondensation at 100 °C of monomer **5b**¹⁵ with adipoyl chloride **4a** (Scheme 2). This provided polymeric material with $M_w = 9.5 \times 10^3 \text{ g mol}^{-1}$ (SEC; $M_w/M_n = 1.38$), equivalent to about 20 repeating units. This low degree of polymerization is most probably caused by the inhomogeneous nature of the polymerization medium. It appeared that HCl, instead of evolving during the polymerization under vacuum, protonated the dialkylaniline functionality. This led to an almost instantaneous solidification of the reaction mixture. The deprotonated polymer was soluble in THF and CHCl_3 , which allowed positive identification of its structure with solution ^1H and ^{13}C -NMR spectroscopy and UV-Vis absorption spectroscopy.

Polymerization in solution as recently described by Kricheldorf et al.²¹ gave high polymer and appears to be a convenient procedure for the preparation of polyesters containing amino groups. Thus, reaction of **5a** with adipoyl chloride **4a** and sebacoyl chloride **4b** (Scheme 2) afforded high molecular weight **1D** (M_w of up to 1.37×10^5 , $M_w/M_n = 2.7$) and **2D** ($M_w = 8.40 \times 10^4$, $M_w/M_n = 4.8$), respectively. These materials were reasonably soluble in solvents like THF, chloroform, and benzene. Polymers **1DA** and **2DA** were obtained

from reaction of **5b** with **4a** and **4b**, respectively. Upon isolation of the high molecular weight fraction of **1DA** and **2DA** by reprecipitation, a tough rubber-like substance was obtained that could not be redissolved in any common organic solvent. This thwarted SEC of these fractions. SEC of the reaction mixtures revealed the presence of both high molecular weight ($M_w = 1.80 \times 10^5$, $M_w/M_n = 4.6$ for **1DA** and $M_w = 3.10 \times 10^5$, $M_w/M_n = 4.0$ for **2DA**) and low molecular weight fractions of $M_w = 1000$ to 2000 . The latter fractions presumably consist of cyclic oligomers.

THF swells **1DA** to a multiple of its initial volume; the polymer takes up about 400% of its own mass. With benzene limited swelling, about 30%, was observed. Polymer **2DA** is somewhat more susceptible to swelling than **1DA**. In benzene it takes up 60% of its own mass, while in THF the mass increases to 500%. Low molecular weight fractions of **2DA** proved to be slightly soluble in THF. The insolubility and swelling characteristics of the donor-acceptor polyesters are in line with what has been observed for copolymers with pendent electron donor and acceptor groups.²³ The solubility of these copolymers reaches a minimum for a 1:1 donor-acceptor ratio and is maximal (compared to good swelling) in polar solvents such as THF, at elevated temperatures. Inter- and intramolecular ground state CT complexes were held responsible for the solubility characteristics of the mixed copolymers.²³ It is likely that they cause the insolubility of **1DA** and **2DA** as well. Although intrachain interactions also play a role, the large solubility difference between donor-acceptor and donor-only polymers is best rationalized by accumulative interchain CT interactions involving the $D\sigma A$ units.

Infrared spectroscopy and NMR spectroscopy (either in solution or the solid state) and UV-Vis absorption spectroscopy confirmed the expected structure of the polymers. Attenuated total reflectance (ATR) FT-IR spectra of all polyesters (Figure S1, Supplementary Material) show the characteristic ester C=O stretch vibration at 1726 – 1730 cm^{-1} and expected aromatic substitution patterns in the region 900 – 650 cm^{-1} . Furthermore, a C \equiv N stretch vibration at 2230 or 2231 cm^{-1} is discernible in the spectra of **1DA** and **2DA**. Hence, all expected functionalities are present.

In the ^{13}C CP/MAS NMR spectrum of high molecular weight **1DA** (Figure S2, Supplementary Material), all signals anticipated on the basis of the solution spectrum of low molecular weight

1DA as obtained by melt polycondensation are present. The only exception is the signal of the C = C(CN)₂ carbon atom C10. This signal is located at 183.7 ppm for both low molecular weight **1DA** and **3**. In the case of high molecular weight **1DA**, it presumably has either a very small intensity due to the applied cross polarization time or is strongly broadened. The ^{13}C CP/MAS NMR spectrum of **2DA** is similar to that of **1DA**.

Thermogravimetric analysis (TGA, Figure S3, Supplementary Material) in an N₂ atmosphere revealed a small weight loss for **1DA** and **2DA** that sets in between 100 and 140 °C. It is believed that this is due to a small amount of volatiles that were left in the polymer, despite prolonged drying under vacuum. This is confirmed by DSC (see below) and by the fact that for **3** weight loss sets in at 230 °C, well above 100 °C. Full decomposition of **1DA** and **2DA** begins at about 300 °C. At that temperature the weight loss of **1D** and **2D** sets in as well. Whereas decomposition of **1D** and **2D** results in volatile products only, **1DA** and **2DA** leave residues of 40 and 14%, respectively. This residue must consist of material originating from the dicyanovinyl acceptor.

Differential scanning calorimetry (DSC) of **1D** in the range -40 to 150 °C revealed a glass transition with a midpoint at -9 °C. This transition was reproducibly followed by a relaxation process, while at higher temperatures some weak and indistinct features arose. Upon repeated heating and cooling of **1DA** in the range -20 to 150 °C, a glass transition at 54 °C developed. A second, less pronounced transition at 87 °C is visible in the DSC thermograms. The origin of this transition is unknown at present. Upon heating polyester **2D**, a reproducible glass transition at -29 °C is observed (Supplementary Material, Figure S4), also accompanied by a subsequent relaxation process. The glass transition of donor-acceptor polymer **2DA** is situated at higher temperatures. In three consecutive heating runs, the glass transition increased from 9 °C (pristine sample) via 24 to 31 °C. Although this irregularity might be caused by degradation, no sign of decomposition of **2DA** (and **1DA**) was detected by means of ATR FT-IR spectroscopy after several DSC heating-cooling cycles. These observations are consistent with the idea that traces of solvent were present, as was already suggested by TGA.

The presence of only glass transitions in the DSC curves shows that all polyesters are amorphous. The trends in the glass transition temperatures are readily interpreted in terms of chain

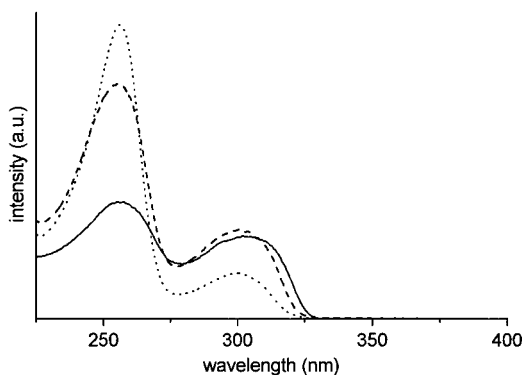


Figure 1. UV spectra with ordinate in Kubelka–Munk units of donor polymers **1D** (solid line) and **2D** (dashed line) as dispersion in KBr. A spectrum of **2D** in CH_2Cl_2 (dotted line) is given for comparison. The spectrum of **1D** in CH_2Cl_2 is virtually indistinguishable from that of **2D** (see Table 1).

flexibility and chain-chain interactions. Donor-acceptor polymers have higher glass transition temperatures than the donor polymers of equal main chain length (by some 60 °C) since interchain CT interactions between the aniline donors and the dicyanovinyl acceptors are operative. This is supported by the result that T_g of **2DA** is lower than that of **1DA**, that is, T_g decreases with reduced density of CT contacts. The larger flexibility of the main chain, which contains more methylene units in the case of **2DA**, is, however, also likely to contribute. This effect is without much doubt responsible for the difference in T_g of **1D** and **2D**.

Photophysical Properties

Electronic absorption spectra of donor polymers **1D** and **2D** were obtained from solutions in CH_2Cl_2 and dispersions in KBr. The spectra are shown in Figure 1, while absorption maxima are compiled in Table 1.

Both in solution and in the solid state, the UV spectra of the donor polymers are typical of *N,N*-dialkylanilino chromophores.¹⁸ The position of the maxima, near 256 and 300 nm, is not affected by the aggregation state of the polymer. This indicates that no ground state interchromophore complexes (either inter- or intrachain) are present. However, differences in intensities seem to exist as the relative intensity of the 256 nm band is much smaller in the solid state than in solution. Since in solution the 256 and 300 nm transitions are equally intense as those of other *N,N*-dialkylanilines,¹⁸ we attribute the reduced

Table 1. Absorption Maxima λ_{max} (in nm) of Materials under Study. Molar Absorption Coefficients (Units $10^3 \text{ M}^{-1}\text{cm}^{-1}$) Are Given in Parentheses

Compound	Matrix	λ_{max}
1D	KBr	256, 303
	CH_2Cl_2	256.5 (13.2), 300.0 (2.00)
2D	KBr	256, 301
	CH_2Cl_2	256.0 (12.2), 300.0 (1.90)
1DA	KBr	257, 306, 350
2DA	KBr	261, 337
3	KBr	257, 305
	CH_2Cl_2	257.5 (26.2), 303.5 (2.53) ¹⁵

signal at 256 nm in the solid materials to increased scattering contributions in the 200–280 nm wavelength interval.

UV-Vis spectra of KBr dispersions of the donor-acceptor polymers and compound **3** (which is an oil) are depicted in Figure 2. Also shown is a solution spectrum of **3** in CH_2Cl_2 ,¹⁵ which is also composed of typical *N,N*-dialkylanilino transitions at 257.5 and 303.5 nm. In addition to these absorptions, for **3** dispersed in KBr an absorption tail extending to 400 nm is present. An intermolecular CT absorption located at a similar position was found for crystals of 2-[4-(1-phenylpiperidin-4-yl)cyclohexylidene]malononitrile, (**6**),¹⁹ which is a compound with an identical acceptor and also an *N,N*-dialkylanilino donor. Single crystal X-ray diffraction has shown that the donor and acceptor moieties in **6** form an intermolecular cofacial 1:1 donor-acceptor complex. It is thus highly likely that interchromophore CT complexes exist in the liquid state of **3** as well.

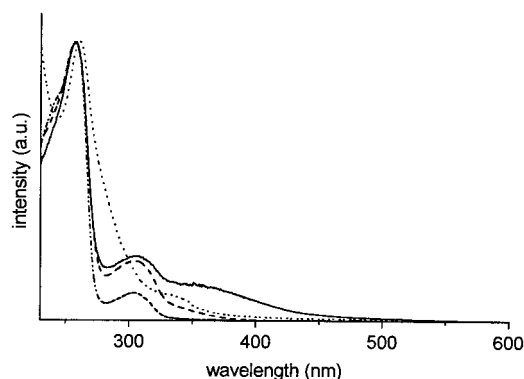


Figure 2. UV-Vis absorption spectra with ordinate in Kubelka–Munk units of dispersions of **1DA** (solid line), **2DA** (dotted line), and **3** (dashed line) in KBr along with a solution spectrum of **3** in CH_2Cl_2 (dash dot dot).

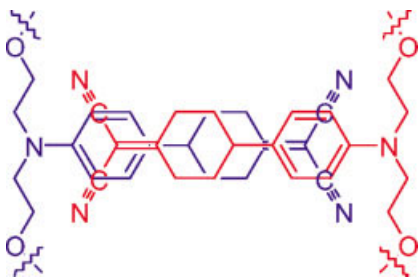


Figure 3. Proposed mode of D σ A aggregation in polyesters **1DA** and **2DA**.

The UV-Vis spectrum of **1DA** is markedly different from that of **3** in solution at wavelengths longer than 330 nm. It exhibits a fairly strong absorption at about 350 nm that tails to 500 nm. By analogy with **3** and **6**, this is attributed to (one or more) inter-D σ A CT absorptions. This term covers both CT absorptions between D σ A units in a single polymer chain and between D σ A units in different chains. Based on the DSC results and the solubility properties, it is likely that CT interactions between different chains dominate. The 350 nm band is more intense than that of **3** and low molecular weight **1DA** (KBr matrix, not shown), whose spectra are very similar to each other. The spectrum of **2DA** exhibits a broad feature of unknown origin at short wavelengths (which gains intensity upon going down to 200 nm), the 255–260 nm absorption, and an inter-D σ A CT absorption. The maximum of the latter is found at 337 nm, which is a somewhat shorter wavelength than in the case of **1DA**, but close to a weak shoulder present in the spectrum of the KBr dispersion of **3**. Moreover, in comparison to the intensity of the 300 nm absorption, the relative intensity of the inter-D σ A CT absorption seems to be substantially larger for **1DA** than for **2DA**. These results imply that the CT interactions in **2DA** are less strong than in **1DA**. This is in line with the expectation that when the density of D σ A units is reduced, there is less opportunity for donor-acceptor contact.

In Figure 3 a structure of the D σ A aggregates responsible for the CT absorption is proposed. This geometry is based on the solid state packing mode of compound **6** (see above).¹⁹ It reveals that upon complexation of two D σ A chromophores two CT interactions arise, which readily accounts for the impact that the introduction of the D σ A units has on the thermal and solid state properties of the polyesters.

Fluorescence spectra of the donor polymers in dilute benzene solution and in their neat form are

shown in Figure 4. In solution the spectra display characteristic emission from the S₁ state of an *N,N*-dialkylaniline. Although the maxima (both at 330 nm) are positioned at a somewhat short wavelength, there is little substantial difference with, for example, 4-cyclohexyl-*N,N*-dimethylaniline, which fluoresces in the region 335–340 nm.¹⁸ In contrast, in their neat form, polymers **1D** and **2D** exhibit dual fluorescence. The typical *N,N*-dialkylaniline S₁ emission is accompanied by a broad band with a maximum around 460 nm. Since the 460 nm emission is completely absent in benzene solution, even when the concentration is as high as 0.07M monomer units (**1D**), it is a typical solid state phenomenon. This renders it likely that the emission is due to excimer formation,⁷ that is, in the excited state a fluorescent dimer of the aniline-type chromophores is formed. The finding that the 460 nm emission is less intensive for the polymer with the smaller concentration of aniline chromophores is consistent with this interpretation. Since the aniline moieties in **1D** and **2D** are not expected to undergo significant diffusion within the excited state lifetime of ~ 2 ns,¹⁸ the ground state geometry must be conducive to the formation of the excimeric species.²⁴ It is unfortunately not possible to distinguish between intra- and interchain complexation.

For solid **1DA** a quite intense, broad fluorescence is observed with a maximum at approximately 550 nm (Fig. 5).²⁵ Local *N,N*-dialkylani-

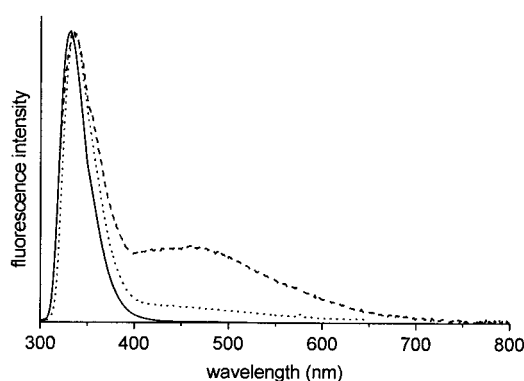


Figure 4. Normalized fluorescence spectra of **1D** in benzene (solid line) and of neat **1D** (dashed line) and **2D** (dotted line). The spectrum of **2D** in benzene is similar to that of **1D**. Note that for the neat materials, the 335 nm bands look narrower at the short wavelength side than they actually are because of self-absorption and that real maxima may be slightly hypsochromically shifted. Excitation wavelength 280 nm.

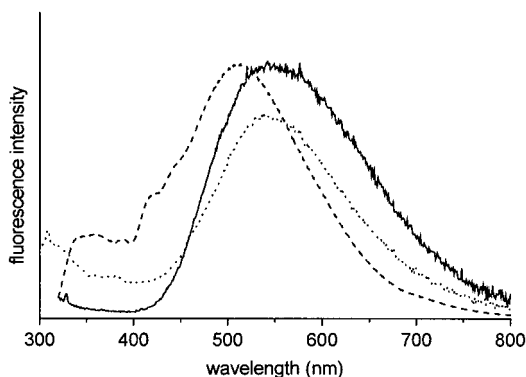


Figure 5. Fluorescence spectra of solid **1DA** (solid line), solid **2DA** (dashed line), and neat **3** (dotted line). Intensities are arbitrarily scaled. Excitation wavelength 280 nm.

line S_1 emission is completely absent. In combination with the appearance of the 550 nm band, this strongly suggests that CT emission is seen. CT fluorescence with a maximum at a comparable position is observed for neat **3**. The fluorescence spectrum of solid **2DA** is somewhat different. A broad emission is also present, but the maximum is situated at 515 nm. Furthermore, some local-like emission in the wavelength interval 300–400 nm is observed. Although fluorescence quantum yields could not be determined, visual inspection revealed that the fluorescence of **1DA** and **2DA** is very bright.

In principle, the broad emission of **1DA**, **2DA**, and **3** can be of both inter- and intra- $D\sigma A$ nature. However, with quantum yields ranging from 0.019 to 0.056 in solvents of different polarity, intra- $D\sigma A$ CT fluorescence of **3** is weak.¹⁵ Although the fluorescence quantum yield in general depends on the environment of a fluorophore, the difference in intensity is so large that it strongly suggests that the bright fluorescence of **1DA** and **2DA** is of inter- $D\sigma A$ nature. Interestingly, torsional motion around the dicyanovinyl $C=C$ bond is one of the factors thought to be responsible for the small fluorescence quantum yield of **3**.¹⁵ Deactivation along this dark decay channel is likely to be suppressed in **1DA** and **2DA** since in a tight face to face CT complex such as proposed in Figure 3, rotation about the $C=C$ bond must be hampered. In this context it is relevant to note that crystals of **6** are strongly luminescent as well. Incorporation of the $D\sigma A$ fluorophores into a polymeric material thus has the effect that the fluorescence, although different in nature, becomes much brighter.

It is conspicuous that for **1DA**, CT emission is the only radiative excited state decay process that is revealed by fluorescence. For comparison: intra- $D\sigma A$ emission of molecular compounds of the type studied here is often accompanied by some local emission. The observation of only inter- $D\sigma A$ emission indicates that formation of the inter- $D\sigma A$ CT-state is very efficient and rapid. Since once again diffusion during the lifetime of excited states is ruled out, the majority of emitting species must already be involved in ground state CT complexes. One should, however, realize that the inter- $D\sigma A$ emission is so intense that it might obscure other emission signals. A small contribution of intra- $D\sigma A$ CT fluorescence to the emission spectrum can, therefore, not be excluded. This is corroborated by the observation of a small amount of local-like emission for **2DA**. Here the chromophore density might be so low that a number of $D\sigma A$ units do not form an intermolecular CT complex. These uncomplexed chromophores then give both local N,N -dialkylaniline emission and the weak intra- $D\sigma A$ fluorescence. This is in agreement with a less prominent CT absorption band for **2DA**.

The influence of swelling with benzene and THF on the fluorescence of **1DA** and **2DA** was also investigated (Fig. 6). Although benzene was found above to induce only a limited extent of swelling, its presence nevertheless leads to spectral changes. The maximum of the CT emission of **1DA** shifts from 550 to 615 nm, while that of **2DA** shifts from 515 to 600 nm. Although it is not clear whether these differences between **1DA** and **2DA**

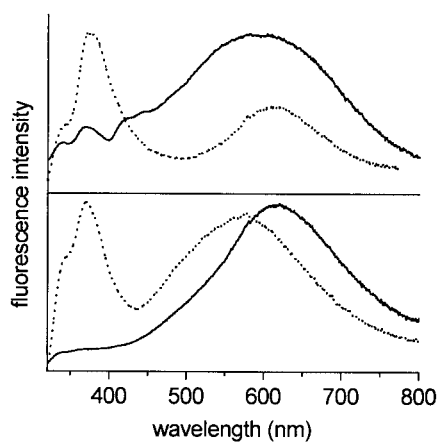


Figure 6. Fluorescence spectra of **1DA** (bottom) and **2DA** (top) swollen with benzene (solid lines) and swollen with THF (dotted lines). Intensities are arbitrarily scaled. Excitation wavelength 290 nm.

are significant, it is evident that relaxation of the CT state occurs as a consequence of swelling with benzene. As intramolecular CT fluorescence of **3** in benzene has its maximum at 508 nm,¹⁵ it is clear that the chromophores are not fully solvated and that inter-D σ A emission is still observed. Hence, benzene stabilizes the polar inter-D σ A CT state.

A larger change in the appearance of the fluorescence spectra of **1DA** and **2DA** is seen upon going to the good swelling agent THF. For both polyesters local-like emission becomes visible. The maximum emission is, however, situated near 375 nm instead of near the typical value of 335–340 nm, which suggests that the emitting state is different. The exact nature of this state is difficult to assess since specific solvation by the polymer matrix and conformational changes of the D σ A moiety¹⁷ can play a role. Along with the appearance of local-like emission, the remaining portion of the CT emission shifts to longer wavelengths. Maxima are situated at 570 and 610 nm for **1DA** and **2DA**, respectively. Thus, here as well, relaxation of the inter-D σ A CT complex is accomplished. The fact that in the bad swelling agent benzene, only shifted CT emission is present, while in the good swelling agent THF, both local-like and shifted CT emission are observed, suggests that upon swelling, first the photoinduced CT state is stabilized and eventually the (ground state) CT contacts are disrupted. It should be realized that in the isolated chromophores, intra-D σ A charge transfer can occur. However, in THF intra-D σ A fluorescence is too weak to be detected.

CONCLUSION

The results presented here show that it is not straightforward to incorporate D σ A chromophores in polymeric materials. As previously indicated by polymeric systems based on other types of photoactive units,^{7–10} properties of molecular D σ A compounds cannot be simply extrapolated to polymeric properties. As evidenced by the comparison with the donor polymers **1D** and **2D**, the presence of both an electron donor and an electron acceptor is essential herein. Thus, while **1D** and **2D** are soluble in common organic solvents, D σ A polymers **1DA** and **2DA** are insoluble. This is explained by the occurrence of intra- and, in particular, inter-D σ A CT interactions. The polyesters are physically crosslinked by these CT

interactions, which dictate the solid state and thermal properties. The presence of CT interactions is confirmed by the presence of inter-D σ A CT bands in the absorption spectrum of the donor-acceptor polyesters. These bands could be readily assigned by analogy with the absorption spectra of closely related molecular D σ A compounds with a well-defined solid state packing motif.¹⁹

Interchromophore interactions dominate the fluorescence behavior of the polymers. In addition to local donor emission, the photoexcited donor polymers display red-shifted, broad fluorescence bands that presumably reflect excimer formation of the aniline moieties. Fluorescence also reveals large differences between polymeric and molecular D σ A chromophores. Whereas D σ A compounds give weak intra-D σ A fluorescence, the CT fluorescence of **1DA** and **2DA** is of inter-D σ A nature and much more intensive. It is likely that in the polymeric environment, one of the mechanisms responsible for nonradiative decay, namely, rotation along the dicyanovinyl double bond, is suppressed. Swelling in THF of **1DA** and **2DA** results in partial disappearance of the broad CT emission and the simultaneous rise of local-like fluorescence. These findings are explained by stabilization and break-up of the inter-D σ A CT states, respectively.

It is of interest to compare the inter-D σ A interactions in **1DA** and **2DA** to chromophore-chromophore interactions in polymers containing D π A functional units, that is, units in which the donor and acceptor are separated by a π -system. A large number of these materials are known in the nonlinear optics literature^{26,27}; frequently donor-acceptor substituted stilbenes and azobenzenes are used. An explicit comparison is not straightforward since polymer types are different, the topology (side chain, main chain, T shape) differs, and often copolymers have been studied. Nevertheless, we have the impression that particularly interchain interactions are stronger in the D σ A polymers **1DA** and **2DA** than in D π A polymers. This is suggested by the fact that D π A polymers are often reasonably soluble.²⁸ There are indeed indications that intrachain rather than interchain effects are operative in polymers with donor-acceptor azobenzene side groups.²⁹

Interactions between D π A moieties are predominantly electrostatic in nature.^{29,30} The dipole moments of the D σ A units in **1DA** and **2DA** are, however, small as the ground state donor-acceptor mixing is weak. Thus, intermolecular CT in-

teractions become much more important in the aggregation of $D\sigma A$ chromophores. These are relatively strong, since the absence of substantial donor-acceptor mixing also brings about that the dialkylanilino and dicyanovinyl groups preserve their full electron donating and accepting power, respectively. It is, finally, noteworthy that interchromophore CT absorptions such as are revealed by Figure 2 are not likely to be observed for $D\pi A$ polymers, as their UV/Vis spectra are dominated by strong intrachromophore CT absorptions.

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REFERENCES AND NOTES

- Wasielowski, M. R. *Chem Rev* 1992, 92, 435.
- Petty, M. C.; Bryce, M. R.; Bloor, D. *An Introduction to Molecular Electronics*; Edward Arnold: London, 1995.
- Verhoeven, J. W.; Goes, M.; Hofstraat, J. W. *International Patent* WO0065881, 2000.
- Aviram, A.; Ratner, M. A. *Chem Phys Lett* 1974, 29, 277.
- Metzger, R. M. *J Mater Chem* 1999, 9 2027.
- One of the few examples is provided by polymers incorporating donor-acceptor substituted norbornadiene moieties, which are able to store light energy by means of a reversible photoinduced isomerization reaction; Kawashima, N.; Kameyama, A.; Nishikubo, T.; Nagai, T. *J Polym Sci Part A: Polym Chem* 2001, 39, 1764.
- Guillet, J. *Polymer Photophysics and Photochemistry*; Cambridge University Press: Cambridge, 1985.
- Photophysics of Polymers*; Hoyle, C. E.; Torkelson, J. M., Eds. ACS Symposium Series 358; American Chem Society: Washington, DC, 1987.
- Ghiggino, K. P.; Yeow, E. K. L.; Haines, D. J.; Scholes, G D; Smith, T. A. *J Photochem Photobiol A* 1996, 102, 81.
- Fehervari, A. F.; Kagumba, L. C.; Hadjikyriacou, S.; Chen, F.; Gaudania, R. A. *J Appl Pol Sci* 2003, 87, 1634.
- Simionescu, C. I.; Grigoraş, M. *Prog Polym Sci* 1991, 16, 907.
- Müller-Dethlefs, K.; Hobza, P. *Chem Rev* 2000, 100, 143.
- Hoogesteger, F. J.; van Walree, C. A.; Jenneskens, L. W.; Roest, M. R.; Verhoeven, J. W.; Schuddeboom, W.; Piet, J. J.; Warman, J. M. *Chem Eur J* 2000, 6, 2948.
- Oosterbaan, W. D.; Koper, C.; Braam, T. W.; Hoogesteger, F. J.; Piet, J. J.; Jansen, B. A. J.; van Walree, C. A.; van Ramesdonk, H. J.; Goes, M.; Verhoeven, J. W.; Schuddeboom, W.; Warman, J. M.; Jenneskens, L. W. *J Phys Chem A* 2003, 107, 3612.
- Oosterbaan, W. D.; van Gerven, P. C. M.; van Walree, C. A.; Koeberg, M.; Piet, J. J.; Havenith, R. W. A.; Zwikker, J. W.; Jenneskens, L. W.; Gleiter, R. *Eur J Org Chem* 2003.
- Scherer, T.; Hielkema, W.; Krijnen, B.; Hermant, R. M.; Eijkelhoff, C.; Kerkhof, F.; Ng, A. K. E.; Verleg, R.; Tol van der, E. B; Brouwer, A. M.; Verhoeven, J. W. *Recl Trav Chim Pays-Bas* 1993, 112, 535.
- In the nonpolar solvent cyclohexane, evidence was found for conformational contraction of the charge-separated state, resulting in a compact charge-transfer (CCT) conformer (see ref. 15). The bridge separating the donor and acceptor should thus be viewed as being semi-rigid.
- Oosterbaan, W. D.; Koeberg, M.; Piris, J.; Havenith, R. W. A.; van Walree, C. A.; Wegewijs, B. R.; Jenneskens, L. W.; Verhoeven, J. W. *J Phys Chem A* 2001, 105, 5984.
- Oosterbaan, W. D.; Havenith, R. W. A.; van Walree, C. A.; Jenneskens, L. W.; Gleiter, R.; Kooijman, H.; Spek, A. L. *J Chem Soc, Perkin Trans 2* 2001.
- Ballauff, M. *Makromol Chem Rapid Commun* 1986, 7, 407.
- Kricheldorf, H. R.; Rabenstein, M.; Maskos, M.; Schmidt, M. *Macromolecules* 2001, 34, 713.
- Dworczak, R.; Fabian, W. M. F.; Kieslinger, D.; Junek, H. *Dyes Pigm* 1997, 34, 13.
- Simionescu, C. I.; Bârboiu, V.; Grigoraş, M. *J Macromol Sci-Chem* 1985, A22, 693.
- He, Z.; Hammond, G. S.; Weiss, R. G. *Macromolecules* 1992, 25, 1568.
- This emission is observed upon excitation between 260 and 450 nm.
- Burland, D. M.; Miller, R. D.; Walsh, C. A. *Chem Rev* 1994, 94, 31.
- Moerner, W. E.; Silence, S. M. *Chem Rev* 1994, 94, 127.
- A few examples of soluble $D\pi A$ polymers, of which the structure can roughly be compared with that of **1DA** and **2DA**: Tsutsumi, N.; Matsumoto, O.; Sakai, W.; Kiyotsukuri, T.; *Macromolecules* 1996, 29, 592; Shen, Y.; Qiu, L.; Li, Z.; Zhang, X.; Zhao, Y.; Zhai, J.; Delaire, J.A.; Nakatani, K.; Atassi, Y. *J Mater Sci* 1999, 34, 1513.
- Brown, D.; Natansohn, A.; Rochon, P. *Macromolecules* 1995, 28, 6116.
- Harper, A. W.; Sun, S.; Dalton, L. R.; Garner, S. M.; Chen, A.; Kalluri, S.; Steier, W. H.; Robinson, B. H. *J Opt Soc Am B* 1998, 15, 329.