Macromolecules **2001,** *34,* 2129−2137

New Terthiophene Derivatives for Ultrahigh Molecular Weight Polyethylene-Based Absorption Polarizers

Nicola Tirelli,*,‡ Stefania Amabile,† Caterina Cellai,† Andrea Pucci,† Leonardo Regoli,† Giacomo Ruggeri,† and Francesco Ciardelli†

Department of Chemistry and Industrial Chemistry, University of Pisa, I-56126 Pisa, Italy, and Department of Materials, Institute of Biomedical Engineering, ETH-Zürich, CH-8044 Zürich, Switzerland

Received August 30, 2000; Revised Manuscript Received January 1, 2001

ABSTRACT: Several new terthiophene-based, highly anisotropic chromophores were synthesized and dispersed in ultrahigh molecular weight polyethylene (UHMWPE). The chromophores were axially oriented by drawing the polymer matrix and showed an extremely pronounced dichroic behavior. In a pseudo-affine deformation scheme the dyes did well approximate the ultimate properties in terms of molecular orientation; on the other hand, the observed thermochromism and other experimental evidence indicated the persistence of a phase segregation from the polymer matrix.

Introduction

In recent years a considerable effort has been devoted to the study of the optical properties of dichroic dyes dispersed in an oriented macromolecular matrix. The resulting absorption anisotropy can be used at the same time to study the chromophores orientation[1] and to produce linearly polarized light; in the last case, the polarizing efficiency depends, to a first approximation, on the possibility to transfer the axial orientation of the host to the low molecular weight guest; this depends on the characteristics of both host and guest.

It has been shown that the theoretical limiting properties of a polarizer can be approached by an appropriate combination of ultradrawable polymarts (e.g., polyolefins with drawing ratios >15, in particular UHMWPE) and highly anisotropic and strongly absorbing dyes;[2−5] a very good agreement with pseudo-affine deformation model predictions was often recorded.

The fundamentals of the characterization of UHMWPE-based polarizers and the calculation of their ultimate properties have extensively been discussed in the recent literature.[2]

The parameters regularly used for this characterization are dichroic ratio (R) and order parameter (S), which are directly related to molecular orientation of the dyes, and polarizing efficiency (PE) and single piece transmittance (T_{sp}), which define the polarizer performance. They are defined as follows:

$$R = A_{||}/A_{\perp}; \quad S = (R - 1)/(R + 2)$$

$$\mathrm{PE} = (T_{||} - T_{\perp})/(T_{\perp} + T_{||}); \quad T_{sp} = (T_{\perp} + T_{||})/2T_0$$

A and T indicate respectively absorbance and trasmittance, the subscripts $||$ and $\perp$ denote respectively the direction parallel or perpendicular to the drawing axis, and T_0 is the transmittance of the optical system without polarizer.

In the use of highly active dyes a general problem is that extended conjugation and high dipole moment enhance aggregation and phase separation phenomena; therefore, a limiting factor is the small guest concentrations that can be used.

Recently, linear low-density polyethylene (LLDPE) has also been used for dye dispersions,[6] with the advantage to decrease chromophores aggregation and to reach high dichroic ratios at moderate drawings.

In the present paper our aim was to (a) determine the possibility to compatibilize and orient in UHMWPE highly dichroic molecules, based on a linear rodlike conjugated core and bearing linear flexible chains at the molecule extremities; particularly, we have tried to qualitatively extrapolate the phase behavior of the guests from optical properties; (b) study the influence of chemical variations on the orientational behavior; (c) generate models of “neutral gray” polarizers, by mixing chromophores with appropriate absorption ranges.

Results and Discussion

Chromophore Synthesis. Using UHMW polyethylene as a host, three concepts should harmonize in the design of appropriate dichroic dyes: (a) their compatibility with polyethylene, (b) the presence of a rigid-rod-like absorbing core (for orientation), and (c) the high molar absorption, generally correlated to a high dipole moment. For the preparation of a “neutral gray” polarizer, dichroic dyes should be mixed together—hence the additional requirement that absorption maxima should match the fundamental colors.

These criteria have guided the design of several chromophores, whose key feature is a rigid-rod-shaped central part, based on a high dipole moment terthiophene unit, and linked to one or two long aliphatic chains (see Figure 1).

The terthiophene bridge was chosen because (a) it is linear and easy to end-functionalize and (b) the aromatic rings are not coplanar, and this helps in keeping low intermolecular interactions based on π-stacking. The introduction of terminal aliphatic groups increases the polyethylene compatibility and facilitates the molecular level dispersion of the dyes during the film drawing, even at moderately high chromophores load. A high

---

† University of Pisa.

‡ Institute of Biomedical Engineering.

* To whom all the correspondence should be addressed. E-mail tirelli@biomed.mat.ethz.ch.

10.1021/ma001518q CCC: $20.00

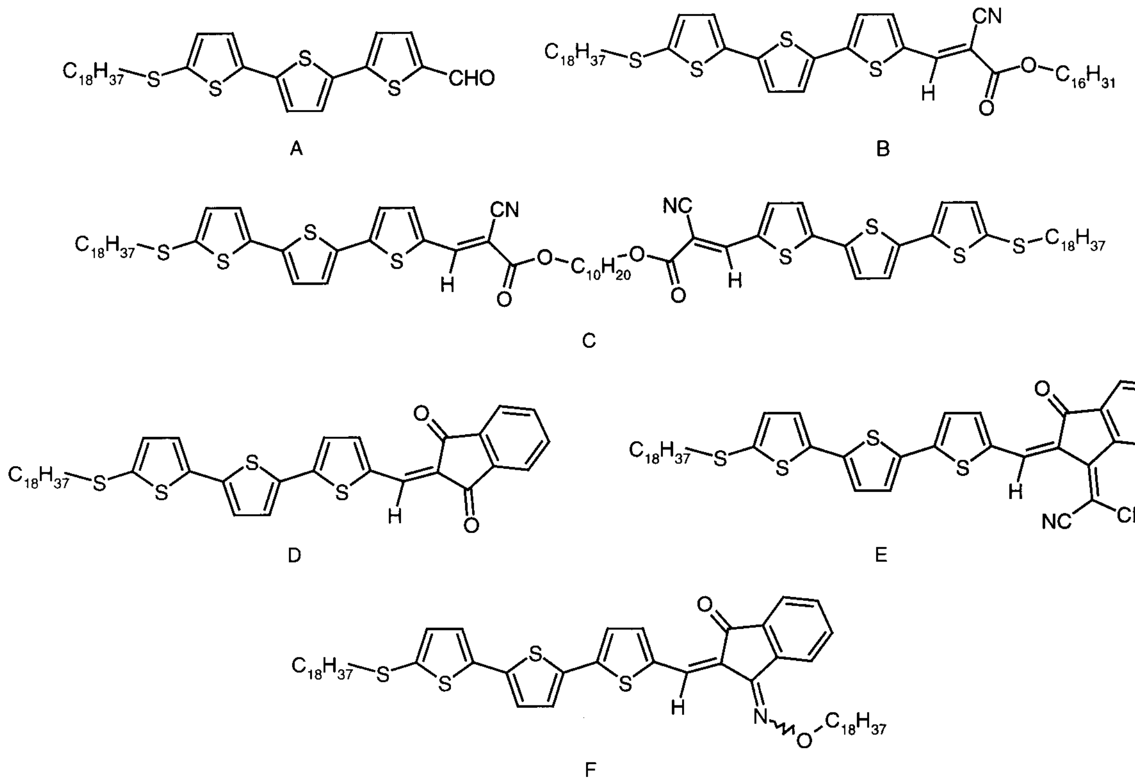

Figure 1. Structures of the terthiophene chromophores synthesized in this work.

aliphatic content is also necessary to reduce dipolar interactions: in fact, according to a fairly rough approximation (the two-level model), intense absorptions in the red or even infrared region of the spectrum are achieved through a decrease in energy of the first excited state (generally bearing a zwitterionic structure), which corresponds to high dipole moment structures. In this way, we have varied the chemical nature and the electron-withdrawing power of the group substituting the 2-position of the 5″-thioalkylterthiophene group: starting from the weakly electronegative aldehyde (A), we have prepared compounds containing the more polarized 2-cyano-2-carboxyvinyl (B, C) or 2-methyleneindan-1,3-dione (D, E, F), and where possible, we have introduced a second aliphatic chain.

A common synthetic path was used for all the compounds. Terthiophene was prepared according to a literature procedure,[7−9] using palladium catalysis to couple mono- and disubstituted thiophene derivatives; the core was then functionalized first with a thioether and later with an aldehyde, giving the dye A. The compounds B, C, D, E, and F were all obtained through Knoevenagel condensation of A with active methylene compounds; respectively, B with hexadecyl 2-cyanoacetate, C with 1,10-bis(2-cyanoacetate) decane, D with 1,3-indandione, E with 3-oxoindane-1-diyl-malononitrile, and F with 1,3-indandione mono(oxime octadecyl ether) (see Figure 2). The reactions with indandione derivatives followed a literature procedure.[10]

The *trans*-configuration of the double bond is confirmed by the ^{1}H NMR shift of the only vinylic proton (thermodynamic control of the Knoevenagel reaction).

The hexadecyl 2-cyanoacetate and the 1,10-bis(2-cyanoacetate)decane were synthesized from the corresponding alcohols, by direct esterification and azeotropic removal of water.

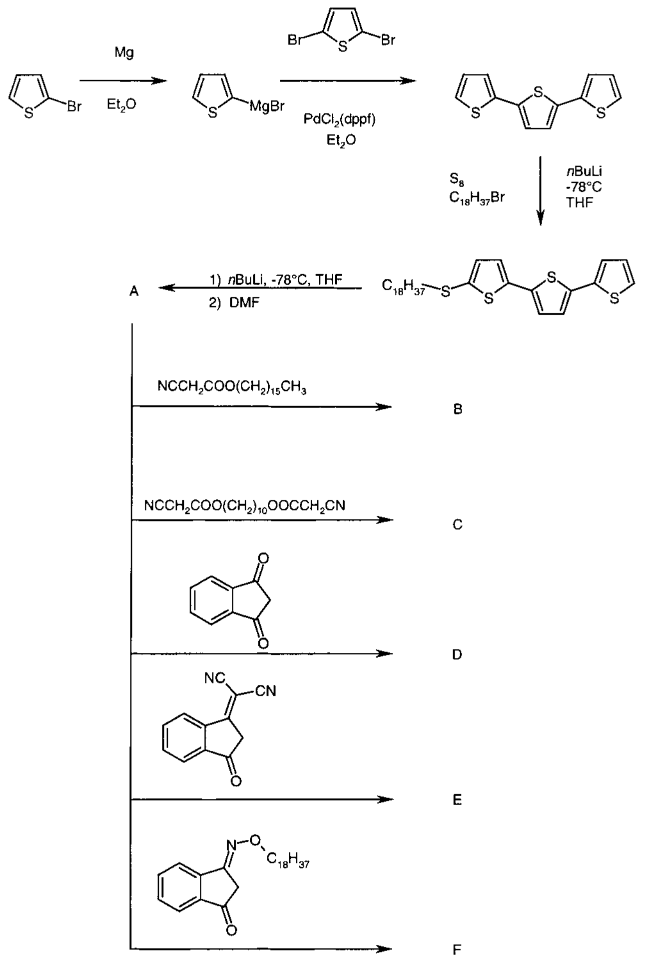

Figure 2. Synthetic paths followed in the dye preparation.

The 3-oxoindane-1-diyl-malononitrile was synthesized by Knoevenagel condensation of malononitrile on 1,3-indandione.[11] Direct functionalization of the carbonyl groups in chromophore D failed, due to the reversibility

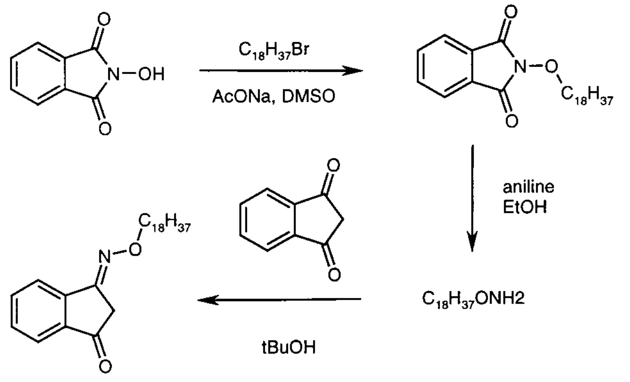

Figure 3. Preparation of the on the 1,3-indandione mono-oxime.

of thiophene–carbaldehyde–indandione linkage in the reaction conditions: chromophore A was recovered in good yields with traces of its adduct with malonitrile; the Knoevenagel is indeed an equilibrium reaction, and malononitrile is a better Knoevenagel acceptor than indandione.

The preparation of the 1,3-indandione mono(oxime octadecyl ether) was based on the Gabriel synthesis of the *O*-octadecylhydroxylamine (prepared using a literature procedure for the synthesis of hydroxylamine derivatives[12]), used then to produce the corresponding mono-oxime on 1,3-indandione (see Figure 3). This structure was chosen after the poor results obtained with other reagents for the introduction of a second aliphatic chain on that carbonyl group; in attempts to synthesize Schiff bases from aliphatic amines and in the Knoevenagel reactions with 2-cyanoacetates, only the formation of decomposition products was detected.

The preparation of the dye with two octadecyl chains from the 1,3-indandione bis(oxime octadecyl ether) failed, probably because of excessive sterical hindrance on the indandione methylene group. Also in this case, prolonged reaction times and high temperatures resulted only in the decomposition of the reagent mixture.

The above-described dyes always show a single melting point, both in the case of crystallization from solution and from the melt. The only exception is represented by the compound B: from the melt, it shows a first low-intensity melting at 85 °C, followed by the crystallization of most of the material and the final melting at 94 °C, the same melting temperature presented by the solution-crystallized material.

The UV–vis absorptions of the dyes are shown in Figure 4; the increase of the dipole moment, by increasing the electron-withdrawing strength of one substituent, allows to shift the absorption maximum up to more than 100 nm. By mixing chromophores with markedly different absorption ranges, one can enlarge the useful spectral window of the polarizer (neutral gray).

Film Preparation and Characterization. The polarizers were produced from solid-state drawn guest–host dispersions, obtained by casting of xylene solutions of UHMW polyethylene and dye, as described elsewhere for dispersions of low MW guests,[4,5] metal particles,[13] or polymers.[6] The dyes were dispersed singularly or mixed to produce a gray color, in concentrations varying from 1 to 3% w/w in the polymer. When mixed, the chromophores concentrations were adjusted on the basis of their extinction coefficients, to obtain the same absorbance for every dye and build a neutral gray polarizer.

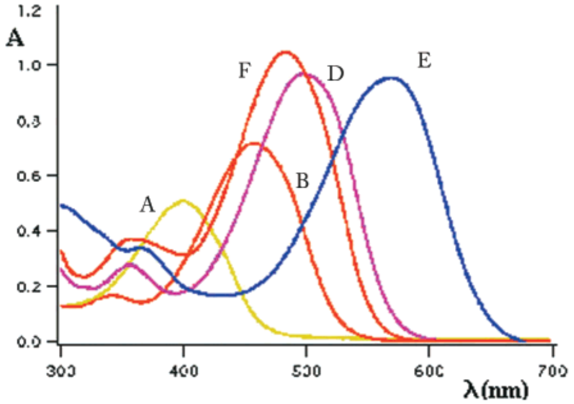

Figure 4. UV–vis spectra of the dyes: A (yellow curve), B (red), D (purple), E (blue), and F (dark red) in 2.0×10^{-5} M dioxane solution. The spectrum of C is identical to that of B, but with lower extinction coefficient.

The "as-casted" films showed always a distinct phase separation (see Figure 5a), except in the case of the mixtures for neutral gray polarizers. Melting peaks of the pure chromophores were recorded in the first heating scan of DSC analysis, where it was possible to clearly separate them from PE melting (Figure 6). On the other hand, the very small molar intensity of these transitions indicated that the dyes were mainly present in an amorphous phase. These transitions were no longer recorded after a first heating until 150 °C, which is close to the drawing conditions; this suggests that any bulky crystalline aggregate should disappear during drawing.

The analysis of film sections, performed by scanning electron microscopy (SEM) after freeze fracture, showed the chromophores to have a concentration peak on the film surface exposed to air (see Figure 5b), where the material shows the highest heterogeneity (see Figure 5c).

This phenomenon, caused by enrichment in chromophore of the solution during solvent evaporation, determines a heterogeneity in the film composition (along the direction normal to the film), which has to be taken in account for more sophisticated investigations. It has to be pointed out that the absorption values, recorded after drawing, are averaged along this direction.

After drawing, the films presented an extremely pronounced dichroism, for dispersions of pure chromophores, as in Figure 7, or of mixtures of them, as in Figure 8.

A summary of the optical properties presented by these polarizers is shown in Table 1. To make the comparison possible, the data are collected at the absorption maximum of each chromophore. Dichroic ratio values as high as 65 (mixture of A, B, and D) have been obtained; these figures place our systems at the top edge of the PE-dispersible dyes for polarizers applications.

A first overview of all the T_{sp} and PE data is given in Figure 8.

All the chromophores, except C, show a dependence of PE vs T_{sp} (Figure 9) close to the ultimate properties calculated for molecularly dispersed dyes with λ (drawing ratio) and $\epsilon_{\|}/\epsilon_{\perp} = \infty$, according to the pseudo-affine deformation scheme. This finding can be taken as an indirect proof of a good dispersion of the dyes.

Even with some exceptions, a general tendency to better orientation with increasing drawing ratio has

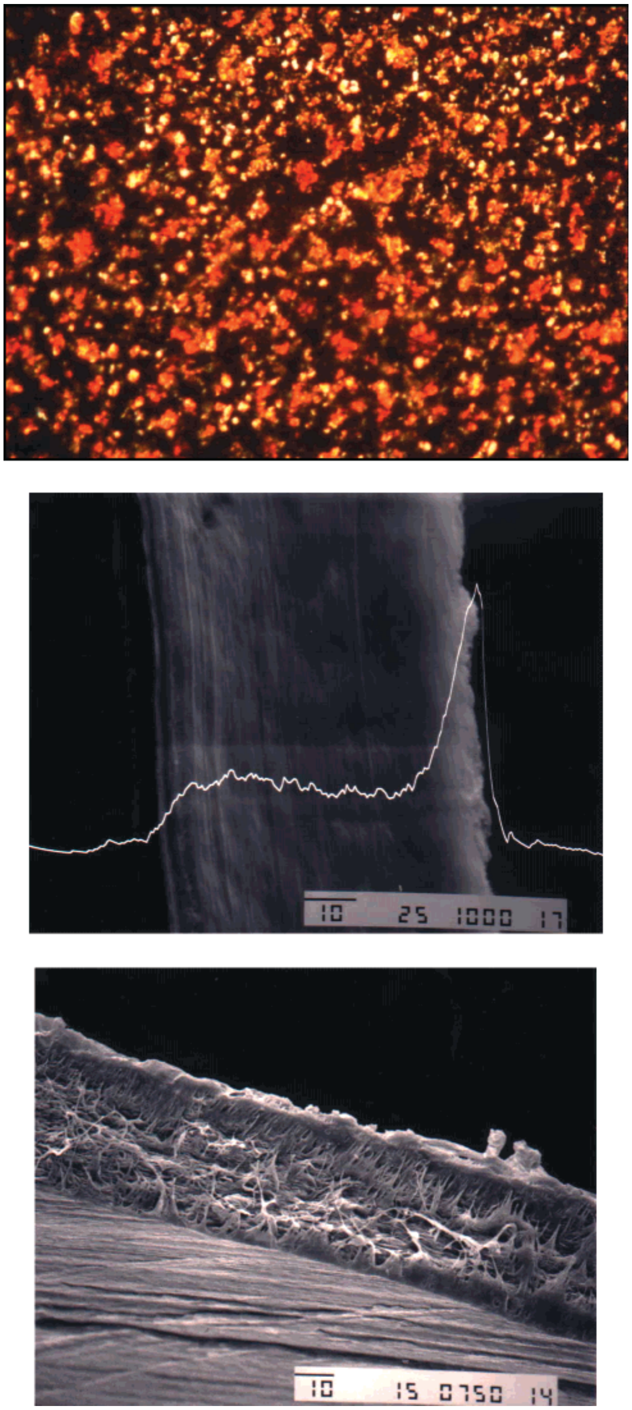

Figure 5. (a, top) Optical microscope picture of a dry chromophore B-containing UHMWPE film, before drawing. (b, middle) Sulfur concentration profile of a section of the same film. (c, bottom) A 750*SEM image of a section of the same film.

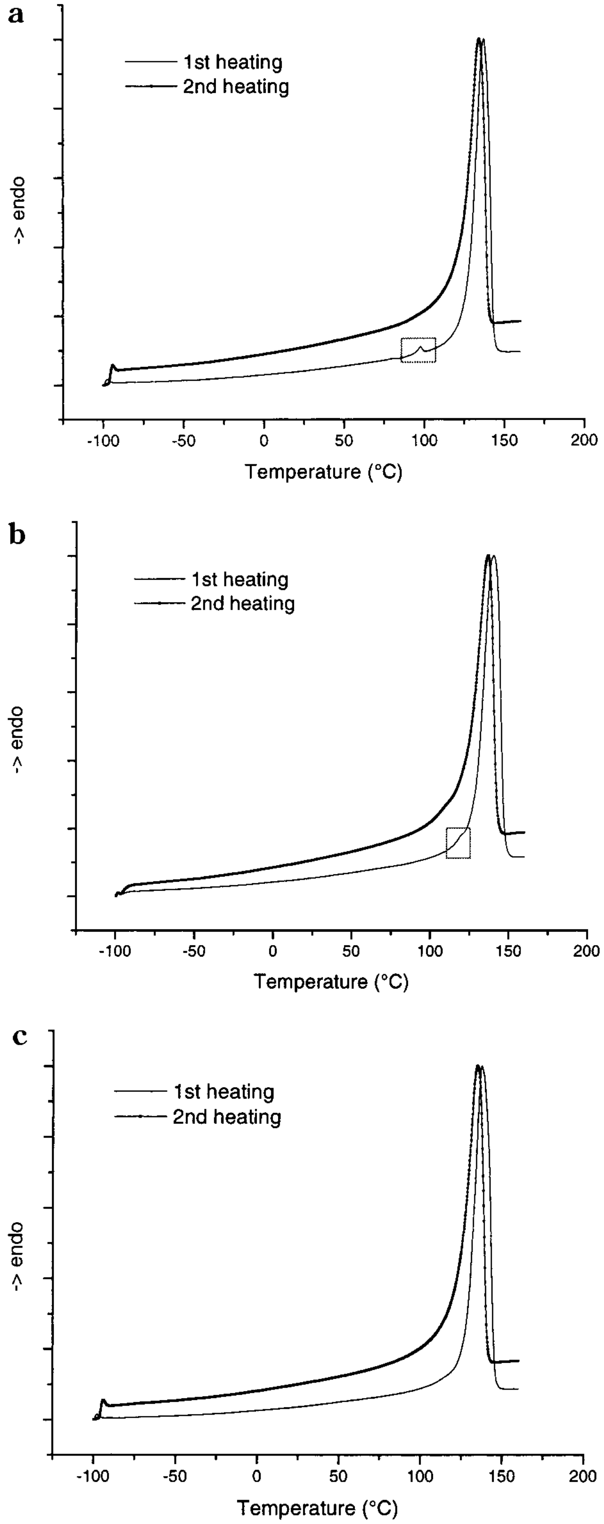

Figure 6. DSC first and second heating traces of (a) 1.4% w/w chromophore A film (peak separated from the PE melting), (b) 2.0% w/w chromophore B film (peak partially covered by the PE melting), and (c) 1.6% w/w mixture chromophore D film (peak falling under the PE melting).

been recorded (Figures 10 and 11); however, for some samples a maximum in orientation was shown at $\lambda = 30$. At high drawings (>10), low molecular weight chromophores tended not to purely follow the pseudo-affine scheme (which for example foresees a nonrealistic $R = 113$ at a drawing ratio of 20), because of nonperfect collinearity between transition moment and drawing direction and presence of aggregates. These two factors justify the presence of an asymptotic value but are λ-independent. On the contrary, when a maximum is recorded, it has likely to be ascribed to disorientation phenomena taking place at high λ, a behavior sometimes called “overdrawing”. To our knowledge, a satisfactory explanation has not yet been presented in the literature; this phenomenon could be linked to the nucleation of voids between polymer fibrils at very high drawings, with consequent randomization of the chromophores (in the form of either isolated molecules or, most likely, aggregates).

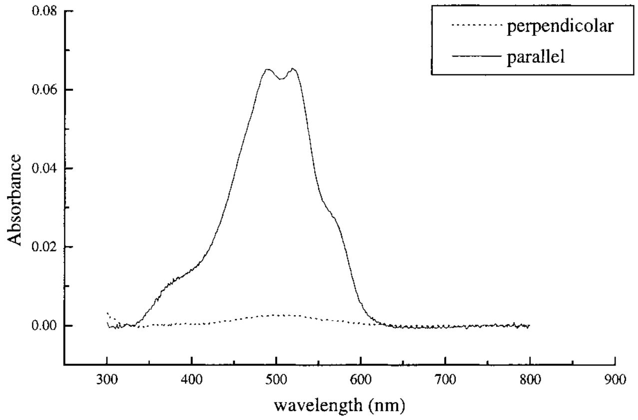

Figure 7. UV−vis spectra after drawing of a 1.6% w/w chromophore D film, drawing ratio = 30; light polarized parallel and perpendicular to the drawing axis.

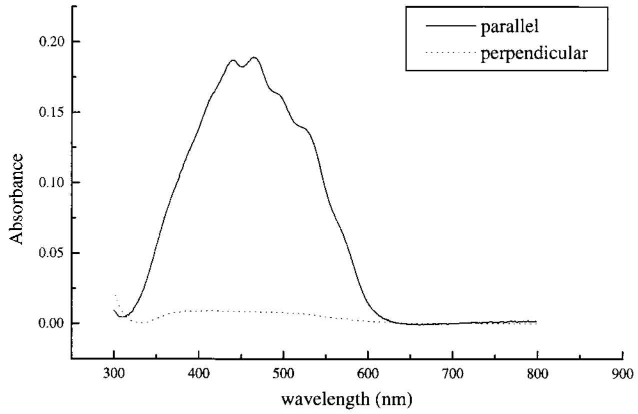

Figure 8. UV−vis spectra after drawing of a 2.5% w/w mixture M UHMWPE film, drawing ratio = 30; light polarized parallel and perpendicular to the drawing axis.

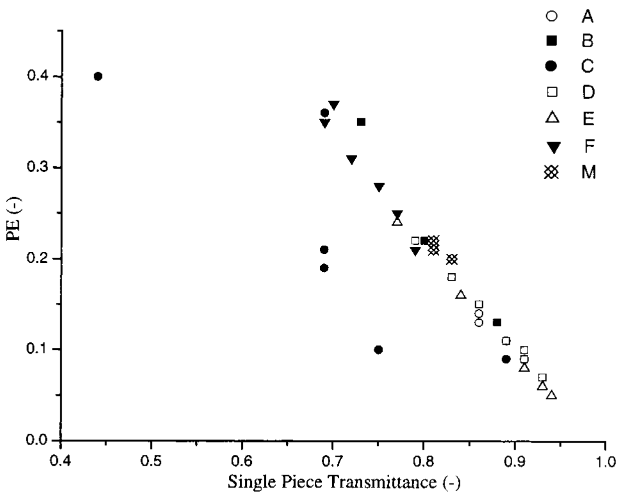

Figure 9. Polarizing efficiency vs single piece transmittance graphics for all the chromophores.

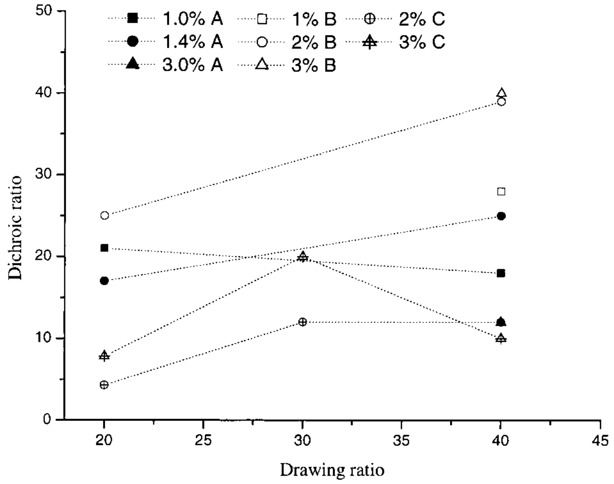

Figure 10. Dependence of dichroic ratio on draw ratio for samples containing chromophores A, B, and C.

Table 1. Polarizers Performance on Varying Chromophore Load and Drawing Ratio

chrom	concn (wt %)	drawing ratio	λ (nm)	R	S	PE	T_{sp}
A	1.0	20	400	21	0.87	0.11	0.89
A	1.0	40	400	18	0.85	0.14	0.86
A	1.4	20	400	17	0.84	0.11	0.89
A	1.4	40	400	25	0.89	0.09	0.91
A	3.0	40	400	12	0.79	0.13	0.86
B	1.0	40	440	28	0.90	0.13	0.88
B	2.0	20	440	25	0.89	0.22	0.80
B	2.0	40	440	39	0.93	0.35	0.73
B	3.0	40	440	40	0.93	0.13	0.88
C	2.0	20	426	4.3	0.52	0.40	0.44
C	2.0	30	426	12	0.78	0.21	0.69
C	2.0	40	426	12	0.78	0.19	0.69
C	3.0	20	426	7.8	0.69	0.36	0.69
C	3.0	30	426	20	0.86	0.10	0.75
C	3.0	40	426	10	0.76	0.09	0.89
D	1.0	20	490	29	0.90	0.09	0.91
D	1.0	40	490	26	0.89	0.07	0.93
D	1.6	20	490	24	0.88	0.18	0.83
D	1.6	30	490	29	0.90	0.10	0.91
D	1.6	40	490	17	0.84	0.11	0.89
D	2.0	20	490	26	0.89	0.07	0.93
D	3.0	20	490	26	0.89	0.15	0.86
D	3.0	40	490	15	0.83	0.22	0.79
E	2.0	20	555	12	0.79	0.24	0.77
E	2.0	30	555	16	0.83	0.16	0.84
E	2.0	40	555	19	0.85	0.05	0.94
E	3.0	20	555	13	0.79	0.24	0.77
E	3.0	30	555	18	0.85	0.08	0.91
E	3.0	40	555	30	0.9	0.06	0.93
F	2.6	20	476	14	0.81	0.35	0.69
F	2.6	30	476	19	0.85	0.37	0.70
F	2.6	40	476	15	0.82	0.25	0.77
F	3.9	20	476	12	0.77	0.31	0.72
F	3.9	30	476	14	0.81	0.28	0.75
F	3.9	40	476	10	0.76	0.21	0.79
M (A+B+D)	2.5	20	465	42	0.93	0.20	0.83
M (A+B+D)	2.5	30	465	65	0.96	0.22	0.81
M (A+B+D)	2.5	40	465	23	0.88	0.21	0.81

We have not been able to highlight a concentration dependence of the optical properties, at least in the range of concentrations of our samples.

The chemical structure influence on the orientation behavior, as given by the dichroic ratio values, is generally negligible. There are two exceptions: the chromophore C shows clearly lower values; indeed C, whose different behavior is evident also in Figure 8, can be considered a step toward a polymer-like structure; this can lead to a lower solubility in the PE phase and to bigger and less orientable aggregates.

In fact, it has been shown[6] that dichroic polymers may not follow the pseudo-affine deformation scheme in UHMWPE, most likely because of microphase separation. Where phase separation is less pronounced (in LLDPE[6]), the scheme is well followed.

The chromophore E has shown an unsatisfactory chemical stability: the drawn films present a second less intense absorption at 394 nm, whereas the maxi-

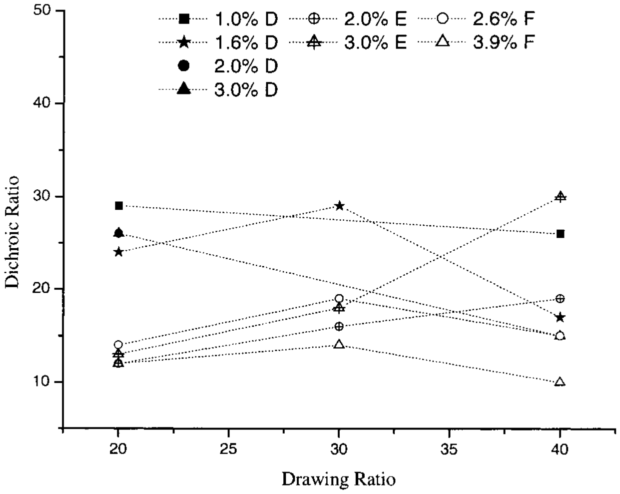

Figure 11. Dependence of dichroic ratio on drawing ratio for samples containing chromophores D, E, and F.

mum is always located at 567 nm. This decomposition can likely be ascribed to the influence of eventual PE additives: when UHMWPE was previously washed with dioxane, no chromophore degradation took place.

Among all the chromophores, analyzed alone or in mixture (samples M = chromophores A, B, and D mixed in equiabsorbing ratios), only F shows a distinct better polarizer performance (represented by the target of PE close to 1 and T_{sp} close to 0.5).

Attempts were done to prepare neutral gray polarizers by mixing different chromophores; A, B, and D together completely covered the spectral range between 350 and 550 nm (Figure 8), and the mixing did not decrease the dichroic ratios of the singular components.

The attempt to cover a more extended wavelength range, by mixing A, B, and E, resulted in a major decomposition of the chromophores mixture. This reaction must start from the already mentioned degradation of the dye E, even if TLC analysis showed that also the other components were involved: on the other hand, the mixtures M of A, B, and D did not show any degradation.

Influence of Aging on the Dichroism. Films containing the chromophore D at different concentrations and drawing ratios, analyzed immediately after drawing and 18 months after, did not show any significative differences in dichroic ratios.

Influence of Temperature on the Dichroism. Two phenomena contribute to a temperature dependence of the absorption properties of the chromophore dispersions in UHMWPE.

(A) At least some of the chromophores exhibit a thermochromic behavior: at a temperature close to the melting point of their bulky crystalline phases (93 °C for the dye B, 135 °C for the dye D), the absorption maxima shift even more than 50 nm (from red to yellow as reported for poly(3-alkylthiophenes)[14-16]). Thermochromism is well-known for oligo- and polythiophenes bearing lateral chains; it is generally interpreted as the result of a reduced conjugation in the main chain twisting, due to increased steric repulsion of side chains, and depends on the regiochemistry of the substitution.[16,17] On the contrary, unsubstituted thiophenes are believed to exhibit a thermochromic behavior caused by a change in intermolecular interactions.[18-20] In particular, it has been shown that terthiophene aggregates can be composed by cofacial almost planar molecules (with an internal dihedral angle up to 174°, compared to 147° of the isolated form); this determines an exciton splitting (Davydov splitting) in the first excited state and consequently a large blue shift in the first singlet−singlet transition.[18] The splitting should disappear upon the occurrence of crystalline rearrangement or melting. For oligothiophenes substituted in the 3- and 4-position, the possibility to obtain cofacial arrangements in the solid state is reduced, and weaker excitonic effects are observed; the thermochromic effect, if observed, is related mostly to the properties of the isolated molecule. The structure of our chromophores (no 3- or 4-substitution) suggests a behavior similar to the unsubstituted terthiophenes, that is, a thermochromic transition corresponding to a melting, and this is indeed confirmed by the occurrence of the color change in proximity of the melting point of the pure chromophores. This finding drives us to conclude that the dyes are likely present in form of aggregates, where terthiophene groups stack together in quasi-planar arrangements; in any case, more detailed investigations are envisaged.

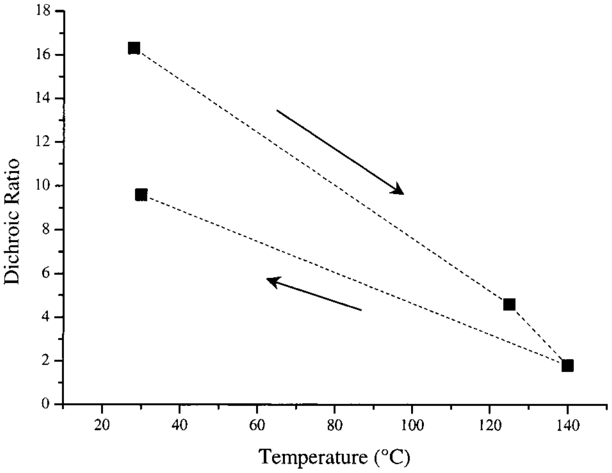

Figure 12. Temperature dependence of the dichroic ratio at 440 nm for a 2% w/w film of chromophore B, drawing ratio = 40.

Table 2. Fluorescence Dichroic Ratios (at Fluorescence Maxima) for Some Polarizers

sample (dye, concn, drawing ratio)	λ_{ecc} (nm)	R
B, 2% 20	450	2
B, 3% 40	450	3
D, 1.6%, 20	525	24
D, 1.6%, 40	525	29
M, 2.5%, 20	450	37
M, 2.5%, 40	450	32

(B) Heating the polarizers at 140 °C (that is, close to the UHMWPE melting), the dichroic ratio drops to almost zero, but it is partially recovered during the cooling (Figure 12).

This surprising phenomenon has been interpreted as an epitaxial crystallization of dye aggregates during cooling: according to this scheme, at 140 °C the PE macromolecules should present enough mobility to allow the dyes isotropization but still retain an axial orientation.

Fluorescence Dichroism. Our preliminary results show strong dichroism also in fluorescence. The results are shown in Table 2.

These data are intended only to show another possible application of these systems. A more rigorous study for rationalizing their emission properties is envisaged.

Conclusions

Polarizer Performance. Terthiophene-based dyes showed extremely high dichroic properties when dispersed in UHMW polyethylene. Although strongly phase separated in the undrawn films, after drawing they seem to be well dispersed in the polymeric material; moreover, the synthetic strategy allowed an easy variation of the spectral range covered by the chromophore absorption. The number of aliphatic chains did not play a significative role in the orientation behavior.

The studied polarizers are close to the ultimate properties in the case of low absorption. A more careful study has to be devoted to more concentrated samples, to obtain higher polarizing efficiencies.

Chromophore Morphology. The optical performance of the dyes suggests a behavior as "isolated" molecules. At the same time the occurrence of thermochromic transitions close to the melting points of the pure compounds suggests the presence of aggregates. Finally, the partial recovery of the linear dichroism observed for films heated at 140 °C indicates a template effect of the oriented PE fibrils, possibly a kind of epitaxial growth of chromophores aggregates. In our interpretation, the dyes do form aggregates in between the oriented fibrils after the film drawing; these aggregates can be oriented (submicrometer size) and are likely composed by anisotropically distributed molecules (hence the high dichroism).

The two thermal phenomena (thermochromism and dichroism recovery) could be advantageously exploited for producing optical switches, where both the absorption and the dichroic properties show a nonlinear temperature behavior.

The indications of the present work for the design of new dyes can be finally summarized in the following points: (a) For good dispersion at high chromophore load a low molar mass seems necessary: an oligomeric structure (dye C) did not improve the polarizing efficiency; amorphous dyes may reduce the formation of big aggregates. (b) High thermal stability of the red- or near-infrared-absorbing compounds ($\lambda_{max} > 550$ nm) is necessary. The indandione core is a promising structure, but more robust electron-acceptor groups have to be used.

Experimental Section

Materials. THF and dioxane were distilled on Na/K alloy. DMF was distilled on molecular sieves. Terthiophene was prepared according to literature procedure. UHMWPE: MW 3.6×10^6 g/mol, UH210, DSM, The Netherlands.

Physicochemical Characterization of Low Molecular Weight Compounds and Polymer Films. ^{1}H and ^{13}C NMR spectra were recorded with the help of a Varian Gemini-200 MHz spectrometer on 5−10% $CDCl_3$, DMSO-d_6, or acetone-d_6 solutions. FT-IR spectra were recorded with the help of a Perkin-Elmer 1330 spectrometer on films casted on KBr windows or on dispersions in KBr.

Mass spectra were recorded with the help of a VG 7070 E GC-MS double-focus spectrometer, directly on the solid products.

UV−vis spectra were recorded in dioxane solution with a Jasco Uvidec 510 spectrometer or on polymeric films (in polarized light) with a Perkin-Elmer Lambda 3B spectrometer.

Fluorescence spectra were recorded with the help of a SPEX Fluorolog 2 (F212 I) spectrometer, equipped with a Glan-Thomson polarizer.

The melting points and the optical microscope analysis were accomplished on a Reichert Polyvar optical microscope with crossed polarizers, equipped with a programmable Mettler FP 52 hot stage.

The scanning electron microscopy analysis was accomplished on a JEOL JSM T-300 microscope, equipped with an X-ray microanalysis facility.

DSC measurements were accomplished with a Perkin-Elmer DSC7 calorimeter, at a scan rate of 20 °C/min.

Thermogravimetric analyses were accomplished with a Perkin-Elmer TGA-7 under nitrogen flux, at a scan rate of 10 °C/min.

Film Preparation. A 0.5 g sample of UHMWPE and the appropriate quantities of chromophore(s) were dissolved in 75 mL of *p*-xylene at 125 °C, at first under stirring and then without until complete dissolution occurred; the solution is then cast on a cold glass or aluminum plate and slowly evaporated, first at room pressure and then at 20 mbar.

The polymeric films were manually drawn on a "hot shoe" (Kofler System) at 140 °C. The film roughness was diminished, using ultrapure silicon oil to reduce surface scattering between the films and the quartz slides used to keep them planar. In the analysis of the absorption data, the scattering contribution was corrected by the use of appropriate baselines.

5″-Thiooctadecyl-2,2′:5′,2″-terthiophene. 10.00 g (40 mmol) of terthiophene was dissolved in 40 mL of anhydrous THF, under dry argon atmosphere. At −78 °C (MeOH/liquid nitrogen bath) 25.15 mL of *n*-BuLi (1.6 M hexane solution) was added to the solution. The temperature was allowed to rise until 0 °C for 10 min, and then after cooling to −78 °C, 1.3 g (40 mmol) of sulfur was added. Again, the system was warmed to room temperature and after 1 h cooled to −78 °C. 13.43 g (40 mmol) of octadecyl bromide dissolved in 15 mL of THF was slowly dropped to the solution. After 20 h at room temperature, the reaction mixture was precipitated in water and the solid redissolved in THF and dried over Na_2SO_4. After solvent evaporation, the solid was extracted with boiling heptane and purified with chromatography on silica gel using ethyl acetate/hexane 9:1 as eluent; 12.73 g (yield 60%) of solid was recovered; mp = 83−87 °C.

^{1}H NMR ($CDCl_3$): $\delta = 0.8{-}0.9$ (t, 3H, C**H**$_3$); 1.0−1.7 (m, 32 H, −(C**H**$_2$)$_{16}$); 2.7−2.85 (t, 2H, ArS−C**H**$_2$−); 6.7−7.25 (m, 7H, aromatic C**H**) ppm.

^{13}C NMR ($CDCl_3$): $\delta = 14.1$ (**C**H$_3$); 22.7−29.7 (CH$_3$−(**C**H$_2$)$_{15}$−CH$_2$); 31.9 (−**C**H$_2$−CH$_2$−S); 36.9 (−CH$_2$−**C**H$_2$−S); 123.6 (terthiophene **C**5″); 123.7−127.8 (terthiophene **C**); 133.9 (terthiophene **C**5) ppm.

FT-IR: 680 (ν C−S); 790 (δ_{oop} C−H aromatic); 1580 (ν aromatic ring); 2848, 2918 (ν CH_2), 3070 (ν aromatic CH) cm^{-1}.

5″-Thiooctadecyl-2,2′:5′,2″-terthiophene-5-carbaldehyde (A). 5.61 g (11 mmol) of 5″-thiooctadecyl-2,2′:5′,2″-terthiophene was dissolved in 92 mL of dry THF under a dry argon atmosphere. At −78 °C 7.5 mL of *n*-BuLi (1.6 M hexane solution) and then 1.1 mL of dry DMF were added to the solution. The system was warmed to room temperature and stirred for 2 h. The reaction mixture was precipitated in water, and the solid dissolved in CH_2Cl_2 and dried over Na_2SO_4. After solvent evaporation, the solid was purified through chromatography on silica gel, using chloroform as eluent; 2.32 g (4 mmol, yield 37%) of yellow solid was recovered; mp = 116−118 °C.

^{1}H NMR ($CDCl_3$): $\delta = 0.8{-}1.0$ (t, 3H, C**H**$_3$); 1.1−1.5 (m, 30 H, −(C**H**$_2$)$_{15}$); 1.5−1.7 (m, 2H, ArS−CH$_2$−C**H**$_2$−); 2.7−2.9 (t, 2H, ArS−C**H**$_2$−); 7.0−7.4 (m, 5H, terthiophene C**H**), 7.6−7.7 (d, 1H, terthiophene C4−**H**), 9.9 (s, 1H, C**H**O) ppm.

^{13}C NMR ($CDCl_3$): $\delta = 14.1$ (**C**H$_3$); 22.7−29.7 (CH$_3$−(**C**H$_2$)$_{15}$−CH$_2$); 31.9 (−**C**H$_2$−CH$_2$−S); 36.9 (−CH$_2$−**C**H$_2$−S); 133.9 (**C**5″, terthiophene); 134.4−137.1 (**C,** terthiophene); 140.0 (**C**5, terthiophene); 182 (**C**HO) ppm.

FT-IR: 794 (δ_{oop} C−H aromatic); 1582 (ν aromatic ring); 1662 (ν CO); 2848, 2918 (ν CH_2), 3070 (ν aromatic CH) cm^{-1}.

TGA: Onset of the first decomposition peak $T = 310$ °C; 29% residual mass.

UV−vis: $\lambda_{max} = 399$ nm; $\epsilon = 25\,000$ mol cm^{-1}.

Hexadecyl 2-Cyanoacetate. The compound was synthesized according to a literature procedure:[21] yield 99%; mp = 50−51 °C.

^{1}H NMR (CDCl$_3$): $\delta = 0.7-1.0$ (t, 3H,C$\mathbf{H}_3$); 1.1−1.4 (m, 26 H, $-(\mathrm{C}\mathbf{H}_2)_{13}$); 1.5−1.8 (t, 2H, $-\mathrm{OCH_2}-\mathrm{C}\mathbf{H}_2-$); 3.4−3.5 (s, 2H, $\mathrm{NC}-\mathrm{C}\mathbf{H}_2-$); 4.1−4.3 (t, 2H, $-\mathrm{OC}\mathbf{H}_2-$) ppm.

1,10-Decylene Bis(2-cyanoacetate). Same procedure as for hexadecyl 2-cyanoacetate: yield 99%; mp 69−71 °C.

^{1}H NMR (CDCl$_3$): $\delta = 1.1-1.4$ (m, 6 H, $-(\mathrm{C}\mathbf{H}_2)$); 1.5−1.7 (t, 4H, $-\mathrm{OCH_2}-\mathrm{C}\mathbf{H}_2-$); 3.4 (s, 4H, $\mathrm{NC}-\mathrm{C}\mathbf{H}_2-\mathrm{COO}$); 4.1−4.2 (t, 4H, $-\mathrm{OC}\mathbf{H}_2-$) ppm.

^{13}C NMR (CDCl$_3$): $\delta = 24.3$ ($\mathrm{NC}-\mathbf{C}\mathrm{H_2}-\mathrm{COO}$); 25.1−28.6 ($-(\mathrm{C}\mathbf{H}_2)_8$); 28.8 ($\mathrm{OCH_2}-\mathbf{C}\mathrm{H_2}-$); 65.7 ($\mathrm{O}\mathbf{C}\mathrm{H_2}-\mathrm{CH_2}-$); 114.8 ($\mathbf{C}$N); 164.2 ($\mathbf{C}$OO) ppm. 31.9 ($-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{S}$); 36.9 ($-\mathrm{CH_2}-\mathbf{C}\mathrm{H_2}-\mathrm{S}$); 133.9 ($\mathbf{C}5''$, terthiophene); 134.4−137.1 ($\mathbf{C}$ terthiophene); 140.0 ($\mathbf{C}$5, terthiophene); 182 ($\mathbf{C}$HO) ppm.

Hexadecyl 2-Cyano-3-[(5″-thiooctadecyl-2,2′:5′,2″-terthien)-5-yl]propenoate (B). 0.089 g (0.17 mmol) of 5-formyl-5″-thiooctadecyl-[2,2′: 5′,2″]-terthiophene and 0.150 g (0.48 mmol) of hexadecyl 2-cyanoacetate were dissolved in 1 mL of dry dioxane, under dry argon atmosphere. 1 μL of piperidine and 10 μL of acetic acid were then added, and the solution was refluxed for 40 h and then stirred overnight at room temperature. During cooling, a red solid precipitated; it was filtered, redissolved in $\mathrm{CH_2Cl_2}$, washed with water until neutrality, and dried over $\mathrm{Na_2SO_4}$. After solvent evaporation, 0.108 g (0.11 mol, yield 71%) of red solid was obtained; mp = 94 °C.

^{1}H NMR (CDCl$_3$): $\delta = 0.8-0.9$ (t, 6H, $-(\mathrm{CH_2})_n-\mathrm{C}\mathbf{H}_3$); 1.1−1.5 (m, 56 H, $-(\mathrm{C}\mathbf{H}_2)_n-$); 1.5−1.8 (m, 4H, $-\mathrm{C}\mathbf{H}_2-\mathrm{CH_2}-\mathrm{S}-$ and $-\mathrm{C}\mathbf{H}_2-\mathrm{CH_2}-\mathrm{O}-$); 2.8 (t, 2H, $-\mathrm{C}\mathbf{H}_2-\mathrm{S}-$); 4.3 (t, 2H, $-\mathrm{C}\mathbf{H}_2-\mathrm{O}-$); 7.0−7.3 (m, 5H, terthiophene); 7.6 (d, 1H, terthiophene, *ortho* to the double bond); 8.2 (s, 1H, $-\mathrm{C}\mathbf{H}=$) ppm.

^{13}C NMR (CDCl$_3$): $\delta = 14.1$ ($\mathbf{C}\mathrm{H_3}-$); 22.7−30.0 ($\mathrm{CH_3}-(\mathbf{C}\mathrm{H_2})_n-$); 31.9 ($-\mathbf{C}\mathrm{H_2}-\mathrm{CH_2}-\mathrm{S}-$); 38.9 ($-\mathbf{C}\mathrm{H_2}-\mathrm{S}-$); 66.6 ($\mathrm{COO}-\mathrm{CH_2}-\mathbf{C}\mathrm{H_2}-$); 97.9 ($-\mathrm{COO}-\mathbf{C}\mathrm{H_2}-$); 115.4 ($-\mathbf{C}$N); 124.3−127.3 ($\mathbf{C}$, 3,2.2′,5′,2″-terthiophene); 133.7 (thioph$-\mathrm{CH}=\mathbf{C}$) 134.4−138.4 ($\mathbf{C}$, 4,3′,4′,3″,4″,5-terthiophene); 139.8 ($\mathbf{C}$, 5″-terthiophene); 145.8−145.9 (thioph$-\mathbf{C}\mathrm{H}=\mathrm{C}$); 162.9 ($-\mathbf{C}$OOR) ppm.

TGA: Onset of the first decomposition peak $T = 325$ °C; 28% residual mass.

UV−vis: $\lambda_{\max} = 457$ nm; $\epsilon = 36\,000$ mol cm^{-1}.

1,10-Decyl Bis(2-cyano-3-[(5″-thiooctadecyl-2,2′:5′,2″-terthien)-5-yl]propenoate (C). Same procedure as for chromophore B; purification through chromatography on silica gel, using chloroform as eluent: yield 47%; mp = 130−140 °C.

^{1}H NMR (CDCl$_3$): $\delta = 0.8-0.9$ (t, 3H, $-(\mathrm{CH_2})_n-\mathrm{C}\mathbf{H}_3$); 1.0−1.7 (m, 83 H, $-(\mathrm{C}\mathbf{H}_2)_n-$); 2.75−2.85 (t, 2H, $-\mathrm{C}\mathbf{H}_2-\mathrm{S}-$); 4.2−4.35 (t, 4H, $-\mathrm{C}\mathbf{H}_2-\mathrm{OOC}$); 6.9−7.65 (m, 12H, terthiophene); 8.2 (s, 1H, $-\mathrm{C}\mathbf{H}=$) ppm.

^{13}C NMR (CDCl$_3$): $\delta = 25.6-29.6$ ($-(\mathbf{C}\mathrm{H_2})_n$); 38.7 ($-\mathbf{C}\mathrm{H_2}-\mathrm{S}-$); 66.0 ($\mathrm{COO}-\mathrm{CH_2}-\mathbf{C}\mathrm{H_2}-$); 97.9 ($-\mathrm{COO}-\mathbf{C}\mathrm{H_2}-$); 115.4 ($-\mathbf{C}$N); 123.9−124.5 ($\mathbf{C}$, 3,2,2′,5′,2″-terthiophene); 133.2 (thioph$-\mathrm{CH}=\mathbf{C}$) 134.4−138.4 ($\mathbf{C}$, 4,3′,4′,3″,4″,5-terthiophene); 139.8 ($\mathbf{C}5''$, terthiophene); 145.8−145.9 (thioph$-\mathbf{C}\mathrm{H}=\mathrm{C}$); 162.9 ($-\mathbf{C}$OOR) ppm.

FT-IR: 788 ($\delta_{\mathrm{o.o.p}}$ C−H aromatic); 1662 (ν CO); 2222 (ν CN); 2848, 2918 (ν CH$_2$), 3070 (ν aromatic CH) cm^{-1}.

TGA: First decomposition peak $T = 347$ °C with 25% residual mass.

UV−Vis: $\lambda_{\max} = 458$ nm; $\epsilon = 28\,000$ mol cm^{-1}.

2-[(5″-Thiooctadecyl-2,2′:5′,2″-terthien)-5-methyliden]-1,3-indandione (**D**). Same procedure as for chromophore B; purification through two chromatographic steps on silica gel, using first chloroform and then hexane/chloroform 1:9 as eluents: yield 89%; mp = 135.5−136.3 °C.

^{1}H NMR (CDCl$_3$): $\delta = 0.8$ (t, 3H, $-\mathrm{C}\mathbf{H}_3$); 1.1−1.5 (m, 32H, $-(\mathrm{C}\mathbf{H}_2)_{16}-\mathrm{CH_2}-\mathrm{S}-$); 2.8 (t, 2H, $-\mathrm{C}\mathbf{H}_2-\mathrm{S}-$); 6.9−7.4 (m, 6H, terthiophene); 7.7−8.0 (m, 5H, $-\mathrm{C}\mathbf{H}=$ and indandione) ppm.

^{13}C NMR (CDCl$_3$): $\delta = 14$ ($\mathbf{C}\mathrm{H_3}-$); 22 ($\mathrm{CH_3}-\mathbf{C}\mathrm{H_2}-$); 28 ($-\mathbf{C}\mathrm{H_2}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{S}$); 29 ($-\mathbf{C}\mathrm{H_2}-\mathrm{CH_2}-\mathrm{S}$); 30 ($-(\mathbf{C}\mathrm{H_2})_{12}-$) 32 ($-\mathbf{C}\mathrm{H_2}-\mathrm{CH_2}-\mathrm{CH_3}-$); 39 ($-\mathbf{C}\mathrm{H_2}-\mathrm{S}$); 122−126 ($\mathbf{C}$, 3,2,2′5′,2″-terthiophene); 128 (thioph$-\mathrm{CH}=\mathbf{C}$); 132 (phenyl $\mathbf{C}$3 and $\mathbf{C}$6 of indandione, in β to the ketones); 134−136 ($\mathbf{C}$, 4,3′,4′,3″,4″-terthiophene); 137 ($\mathbf{C}$5, terthiophene); 139 ($\mathbf{C}5''$, terthiophene); 144 (phenyl $\mathbf{C}$4 and $\mathbf{C}$5 of indandione, in γ to the ketones); 150 (thioph$-\mathbf{C}\mathrm{H}=\mathrm{C}$) ppm. Carbonyl and $\mathbf{C}$1 and $\mathbf{C}$2 phenyl carbon atoms, in α to the ketones, cannot be distinguished from spectrum noise.

FT-IR: $\nu = 790$ (δ_{oop}C−H aromatic); 1588 (ν C=C); 1682 (ν C=O); 2850 (ν_{s} C−H); 2918 (ν_{as} C−H) cm^{-1}.

TGA: Onset of the first decomposition peak $T = 304$ °C; 48% residual mass.

UV−Vis: $\lambda_{\max} = 497$ nm; $\epsilon = 48\,500$.

3-Oxo-Δ$^{1,\alpha}$-indanmalonitrile. 1.32 g (20 mmol) of malonitrile and 6 μL of piperidine were dissolved in 400 mL of ethanol; heating at 60 °C, 1.04 g (0.71 mmol) of 1,3-indandione were added in small portions during 45 min. The reaction mixture was left for other 30 min at 60 °C, then 40 mL of water was added, and the precipitated solid was separated by centrifugation and extracted first with toluene at 50 °C and then with hexane. 0.84 g (0.43 mmol, yield 61%) of pale green solid was obtained; mp = 211.4−212.0 °C.

^{1}H NMR (C$_6$D$_6$): $\delta = 2.9$ (s, 2H, $-\mathrm{C}\mathbf{H}_2-$); 7.2−7.1 (m, 2H, phenyl C−$\mathbf{H}$ in γ to the C=O and C=C); 7.8−7.7 (m, 1H, phenyl C−$\mathbf{H}$ in β to the C=O); 8.5 (m, 1H, phenyl C−$\mathbf{H}$ in β to the C=C) ppm.

^{13}C NMR (C$_6$D$_6$): $\delta = 33.6$ ($-\mathbf{C}\mathrm{H_2}-$); 83.8 ($(\mathrm{NC})_2\mathbf{C}=\mathrm{C}-$); 108.0 ($-\mathbf{C}$N); 108.8 ($-\mathbf{C}$N); 123−124 (phenyl $\mathbf{C}$ in β to the C=O and C=); 133.0 (phenyl $\mathbf{C}$ in γ to the C=O and C=C); 164.5 ($\mathbf{C}=\mathrm{C(CN)_2}$); 196.3 ($\mathbf{C}$=O) ppm.

FT-IR (in Nujol dispersion): 788 (δ_{oop} C−H aromatic); 1574 (ν C−N); 1726 (ν C=O); 2222 (ν CN) cm^{-1}.

Mass spectrometry: molecular peak $m/z = 194$ (M$^+$).

3-Dicyano-methyliden-2-[(5″-thiooctadecyl-2,2′:5′,2″-terthien)-5-methyliden]-1,3-indandione (**E**). Same procedure as for chromophore B, but hexane/chloroform 2:8 was used as an eluent: yield 50%; mp = 135.5−137.0 °C.

^{1}H NMR (CDCl$_3$): $\delta = 0.9$ (t, 3H, $-\mathrm{C}\mathbf{H}_3$); 1.2−1.4 (m, 30H, $-(\mathrm{C}\mathbf{H}_2)_{15}-\mathrm{CH_2}-\mathrm{S}-$); 1.6 (m, 2H, $-\mathrm{C}\mathbf{H}_2-\mathrm{CH_2}-\mathrm{S}$); 2.8 (t, 2H, $-\mathrm{C}\mathbf{H}_2-\mathrm{S}-$); 6.8−7.3 (m, 5H, terthiophene); 7.4−7.8 (m, 5H, indandione); 8.6 (m, 1H, $\mathbf{C}5''$, terthiophene); 8.8 (s, 1H, thioph$-\mathrm{C}\mathbf{H}=\mathrm{C}$) ppm.

^{13}C NMR (CDCl$_3$): $\delta = 14$ ($\mathbf{C}\mathrm{H_3}-$); 22 ($\mathrm{CH_3}-\mathbf{C}\mathrm{H_2}-$); 28 ($-\mathbf{C}\mathrm{H_2}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{S}$); 29 ($-\mathbf{C}\mathrm{H_2}-\mathrm{CH_2}-\mathrm{S}$); 30 ($-(\mathbf{C}\mathrm{H_2})_{12}-$) 32 ($-\mathbf{C}\mathrm{H_2}-\mathrm{CH_2}-\mathrm{CH_3}-$); 38 ($-\mathbf{C}\mathrm{H_2}-\mathrm{S}$); 114 ($\mathbf{C}=\mathrm{C(CN)_2}$); 123.7 ($-\mathbf{C}$N); 124.7 ($-\mathbf{C}$N); 125−126 ($\mathbf{C}$, 3,2,2′5′,2″-terthiophene); 127 (thioph$-\mathrm{CH}=\mathbf{C}$); 133.5 (phenyl $\mathbf{C}$3 and $\mathbf{C}$6 of indandione, in β to the ketones); 134−136 ($\mathbf{C}$, 4,3′,4′,3″,4″-terthiophene); 137 ($\mathbf{C}$5, terthiophene); 139 ($\mathbf{C}5''$, terthiophene); 140 (phenyl $\mathbf{C}$4 and $\mathbf{C}$5 of indandione, in γ to the ketones); 146 ($\mathrm{C}=\mathbf{C}\mathrm{(CN)_2}$); 150 (thioph$-\mathbf{C}\mathrm{H}=\mathrm{C}$) ppm. Carbonyl, nitriles and $\mathbf{C}$1 and $\mathbf{C}$2 phenyl carbon atoms, in α to the ketones, cannot be distinguished from spectrum noise.

FT-IR: $\nu = 790$ (δ_{oop}C−H aromatic); 1590 (ν C=C); 1700 (ν C=O); 2850 (ν_{s} C−H); 2918 (ν_{as} C−H) cm^{-1}.

TGA: First decomposition peak at $T = 350$ °C with 30% residual mass.

UV−Vis: $\lambda_{\max} = 567$ nm; $\epsilon = 47\,500$.

***N*-Octadecyloxyphthalimide**. The compound was prepared according to a literature procedure[12] and purified through chromatography on silica gel, using chloroform as eluent: yield 61%; mp = 82.5−83.5 °C.

^{1}H NMR (CDCl$_3$): $\delta = 0.8$ (t, 3H, C$\mathbf{H}_3$); 1.2 (s, 30 H, $-(\mathrm{C}\mathbf{H}_2)_{15}$); 1.7 (t, 2H, $=\mathrm{N}-\mathrm{O}-\mathrm{CH_2}-\mathrm{C}\mathbf{H}_2-$); 4.2 (t, 2H, $=\mathrm{N}-\mathrm{O}-\mathrm{C}\mathbf{H}_2-\mathrm{CH_2}-$); 7.7 (m, 2H, aromatic C$\mathbf{H}$ in *meta* to the C=O groups), 7.8 (m, 2H, aromatic C$\mathbf{H}$ in *ortho* to the C=O groups) ppm.

^{13}C NMR (CDCl$_3$): $\delta = 13.9$ ($\mathbf{C}\mathrm{H_3}-$); 22.5 ($\mathrm{CH_3}\text{-}\mathbf{C}\mathrm{H_2}-$); 25.4 ($=\mathrm{N}-\mathrm{O}-\mathrm{CH_2}-\mathrm{CH_2}-\mathbf{C}\mathrm{H_2}$); 28.8 ($\mathrm{CH_3}-\mathrm{CH_2}-\mathrm{CH_2}-\mathbf{C}\mathrm{H_2}-$); 29.2 ($-\mathbf{C}\mathrm{H_2}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{CH_3}$); 29.3 ($=\mathrm{N}-\mathrm{O}-\mathrm{CH_2}-\mathrm{CH_2}-(\mathbf{C}\mathrm{H_2})_{10}$); 29.5 ($=\mathrm{N}-\mathrm{O}-\mathrm{CH_2}-\mathbf{C}\mathrm{H_2}-$); 31.8 ($-\mathbf{C}\mathrm{H_2}-\mathrm{CH_2}-\mathrm{CH_3}$); 70.4 ($=\mathrm{N}-\mathrm{O}-\mathbf{C}\mathrm{H_2}-$); 123.3 (aromatic $\mathbf{C}$ in *meta* to the C=O groups); 128.9 (aromatic $\mathbf{C}$=O groups); 134.0 (aromatic $\mathbf{C}$ in *ortho* to the C=O groups); 162.4 ($\mathbf{C}$=O) ppm.

FT-IR: 702 (δ_{oop} C−H aromatic); 950 (ν N−O); 1016 (ν C−O); 1466 (ν C−N); 1582 (ν aromatic ring); 1732 (ν CO); 2850, 2918 (ν CH$_2$) cm^{-1}.

Mass spectrometry: molecular peak $m/z = 415$ (M$^+$).

***O*-Octadecylhydroxylamine**. The compound was prepared according to a literature procedure[12] and purified in form hydrocloride through recrystallization from chloroform: yield 84%; mp = 126.0 °C.

^{1}H NMR ($\mathrm{CDCl_3}$): $\delta = 0.8$ (t, 3H, $\mathrm{C\mathbf{H}_3}$); 1.2 (s, 30H, $\mathrm{CH_3-(C\mathbf{H}_2)_{15}-}$); 1.8 (t, 2H, $\mathrm{-C\mathbf{H}_2-CH_2-O-N{=}}$); 4.0 (t, 2H, $\mathrm{-C\mathbf{H}_2-O-N{=}}$); 10.8–11 (3H, $\mathrm{O-N\mathbf{H}_3^+}$) ppm.

^{13}C NMR ($\mathrm{CDCl_3}$): $\delta = 13.5$ ($\mathrm{\mathbf{C}H_3-}$); 24.0 ($\mathrm{CH_3-\mathbf{C}H_2-}$); 25.0 ($\mathrm{{=}N-O-CH_2-CH_2-\mathbf{C}H_2-}$); 28.0 ($\mathrm{{=}N-O-CH_2-\mathbf{C}H_2-}$); 28.6 ($\mathrm{{=}N-O-CH_2-CH_2-CH_2-(\mathbf{C}H_2)_{16}}$); 30.9 ($\mathrm{-\mathbf{C}H_2-CH_2-CH_3}$); 74.1 ($\mathrm{{=}N-O-\mathbf{C}H_2-}$) ppm.

FT-IR: 920 (ν N−O); 1062 (ν C−O); 1474 (δ $\mathrm{-NH_3^+}$); 2980–2918 (ν $\mathrm{-NH_3^+}$ and ν C−H) $\mathrm{cm^{-1}}$.

1,3-Indandione Mono-O-octadecyloxime. 0.457 g (3 mmol) of 1,3-indandione was dissolved in 100 mL of dry *tert*-butyl alcohol under dry argon atmosphere. The solution was heated to the solvent reflux, while a solution of 0.99 g (3 mol) of *O*-octadecylhydroxylamine chloridrate in 40 mL dry *tert*-butyl alcohol was added dropwise in 7 h. The reflux was continued for 16 h; then, after evaporation of the solvent, the raw product was purified through chromatography on silica gel, using the mixture hexane/chloroform 7:1 as eluent. The first eluted product was the 1,3-indandione bis-*O*-octadecyloxime (0.270 g (0.396 mmol)), whose spectra are reported hereafter. The second fraction gave 0.590 g (1.4 mmol) of a solid composed by the two isomers (*E* and *Z* around the C=N bond) of 1,3-indandione mono-*O*-octadecyloxime. In fact, this fraction gave a single signal in the mass and NMR spectra but two spots in TLC analyses; mp = 72.3–73.9 °C.

^{1}H NMR ($\mathrm{CDCl_3}$): $\delta = 0.9$ (t, 3H, $\mathrm{C\mathbf{H}_3}$); 1.2 (s, 30H, $\mathrm{CH_3-(C\mathbf{H}_2)_{15}-}$); 1.7 (t, 2H, $\mathrm{-C\mathbf{H}_2-CH_2-O-N{=}}$); 3.3 (s, 2H, indandione methylene); 4.2 (t, 2H, $\mathrm{-C\mathbf{H}_2-O-N{=}}$); 7.4–7.9 (m, 4H, aromatic protons) ppm.

^{13}C NMR ($\mathrm{CDCl_3}$): $\delta = 14.1$ ($\mathrm{\mathbf{C}H_3-}$); 22.05 ($\mathrm{CH_3-\mathbf{C}H_2-}$); 25.8 ($\mathrm{{=}N-O-CH_2-CH_2-\mathbf{C}H_2-}$); 29.1 ($\mathrm{CH_3-CH_2-CH_2-\mathbf{C}H_2-}$); 29.3 ($\mathrm{-\mathbf{C}H_2-CH_2-CH_2-CH_2-CH_3}$); 29.5 ($\mathrm{{=}N-O-CH_2-CH_2-(\mathbf{C}H_2)_{10}}$); 31.0 ($\mathrm{{=}N-O-CH_2-\mathbf{C}H_2-}$); 37.4 ($\mathrm{\text{-}\mathbf{C}H_2-CH_2-CH_3}$); 75.8 ($\mathrm{{=}N-O-\mathbf{C}H_2-}$); 121.7–123.4 (phenyl **C**3 and **C**6 of indandione, in β to the ketones); 132.5–135.0 (phenyl **C**4 and **C**5 of indandione, in γ to the ketones); 138.3–145.0 (phenyl **C**1 and **C**2 carbon atoms, in α to the ketones); 151.7 ($\mathrm{\mathbf{C}{=}N}$); 199.02 ($\mathrm{\mathbf{C}{=}O}$) ppm.

FT-IR: 702 (δ_{oop}C−H aromatic); 916 (ν N−O); 1048 (ν C−O); 1466 (ν C−N); 1718 (ν C=O); 2914, 2848 (ν $\mathrm{CH_2}$) $\mathrm{cm^{-1}}$.

Mass spectrometry: molecular peak $m/z = 413$ ($\mathrm{M^+}$); 412 ($\mathrm{M} - 1$).

1,3-Indandione Bis-*O*-octadecyloxime. ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta = 0.8$ (t, 6H, $\mathrm{C\mathbf{H}_3}$); 1.2 (s, 60H, $\mathrm{CH_3-(C\mathbf{H}_2)_{15}-}$); 1.7 (t, 4H, $\mathrm{-C\mathbf{H}_2-CH_2-O-N{=}}$); 3.3 (s, 2H, indandione methylene); 4.2 (t, 4H, $\mathrm{-C\mathbf{H}_2-O-N{=}}$); 7.3 (m, 2H, aromatic protons); 7.7 (m, 2H, aromatic protons) ppm.

^{13}C NMR ($\mathrm{CDCl_3}$): $\delta = 13.9$ ($\mathrm{\mathbf{C}H_3-}$); 22. 5 ($\mathrm{CH_3-\mathbf{C}H_2-}$); 25.7 ($\mathrm{{=}N-O-CH_2-CH_2-\mathbf{C}H_2-}$); 29.3 ($\mathrm{CH_3-CH_2-CH_2-\mathbf{C}H_2-}$); 29.5 ($\mathrm{-\mathbf{C}H_2-CH_2-CH_2-CH_2-CH_3}$); 29.6 ($\mathrm{{=}N-O-CH_2-CH_2-(\mathbf{C}H_2)_{10}}$); 31.7 ($\mathrm{{=}N-O-CH_2-\mathbf{C}H_2-}$); 37.4 ($\mathrm{-\mathbf{C}H_2-CH_2-CH_3}$); 74.6 ($\mathrm{{=}N-O-\mathbf{C}H_2-}$); 121.3 (phenyl **C**3 and **C**6 of indandione, in β to the ketones); 130.2 (**C**4 and **C**5 of indandione, in γ to the ketones); 138.8 (phenyl **C**1 and **C**2 carbon atoms, in α to the ketones); 158.0 ($\mathrm{\mathbf{C}{=}N}$) ppm**).**

2-[(5″-Thiooctadecyl-2,2′:5′,2″-terthien)-5-methyliden]-1,3-indandione Mono-*O*-octadecyloxime (F). Same procedure as for chromophore B; purification through chromatography on silica gel, using using hexane/chloroform 2:8 as eluent: yield 34%; mp = 78.5–81.0 °C.

^{1}H NMR ($\mathrm{CDCl_3}$): $\delta = 0.9$ (t, 6H, $\mathrm{C\mathbf{H}_3}$); 1.2 (s, 60H, $\mathrm{CH_3-(C\mathbf{H}_2)_{15}-}$); 1.6 (m, 2H, $\mathrm{-C\mathbf{H}_2-CH_2-S}$); 1.8 (m, 2H, $\mathrm{-C\mathbf{H}_2-CH_2-O-N{=}}$); 2.8 (t, 2H, $\mathrm{-C\mathbf{H}_2-S}$); 4.3 (t, 2H, $\mathrm{-C\mathbf{H}_2-O-N{=}}$); 6.8–7.3 (m, 6H, terthiophene); 7.4–7.8 (m, 4H, indandione); 8.8 (s, 1H, $\mathrm{\mathbf{H}-C{=}C}$).

^{13}C NMR ($\mathrm{CDCl_3}$): $\delta = 13.9$ ($\mathrm{\mathbf{C}H_3-}$); 22.3 ($\mathrm{CH_3-\mathbf{C}H_2-}$); 25.8 ($\mathrm{{=}N-O-CH_2-CH_2-\mathbf{C}H_2-}$); 28.1 ($\mathrm{{=}N-O-CH_2-\mathbf{C}H_2-}$); 28.8 ($\mathrm{-\mathbf{C}H_2-CH_2-CH_2-S}$); 29.06 ($\mathrm{-\mathbf{C}H_2-CH_2-S}$); 29.1 ($\mathrm{-(\mathbf{C}H_2)_{12}-}$); 29.4 ($\mathrm{-(\mathbf{C}H_2)_{12}}$); 31.6 ($\mathrm{-\mathbf{C}H_2-CH_2-CH_3}$); 38.6 ($\mathrm{-\mathbf{C}H_2-\ S}$); 75.7 ($\mathrm{{=}N-O-\mathbf{C}H_2-}$); 120–124 (**C,** 3,2,2′5′,2″-terthiophene); 125.8 ($\mathrm{thioph-CH{=}\mathbf{C}}$); 129.7 (phenyl **C**3 and **C**6 of indandione, in β to the ketones); 133–136 (**C,** 4,3′,4′,3″,4″,5-terthiophene); 137.9 (**C,** 5″-terthiophene); 141.5 (phenyl **C**3 and **C**6 of indandione, in γ to the ketones); 148 ($\mathrm{thioph-\mathbf{C}H{=}C}$) ppm. Carbonyl, C=N, and **C**1 and **C**2 phenyl carbon atoms, in α to the ketones, cannot be distinguished from spectrum noise.

FT-IR: $\nu = 790$ (δ_{oop} C−H aromatic); 940 (ν N−O); 1072 (ν C−O); 1468 (ν C−N); 1696 (ν C=O); 2850, 2918 (ν $\mathrm{CH_2}$) $\mathrm{cm^{-1}}$.

UV−Vis: $\lambda_{\max} = 490$ nm; $\epsilon = 31\,000$.

Acknowledgment. We are very grateful to all the group of Polymer Technology at the Institute of Polymers of the ETH Zürich, in particular to Dr. Yvo Dirix and Dr. Andrea Montali for the help in measurements and above all to Dr. Cees Bastiaansen and Prof. Paul Smith, with whom the project has been started and thoroughly discussed.

References and Notes

(1) Borucki, B.; Otto, H.; Heyn, M. P. *J. Phys. Chem. B* **1998**, *102*, 3821.
(2) Bastiaansen, C.; Schmidt, H. W.; Nishino, T.; Smith, P. *Polymer* **1993**, *34*, 3951.
(3) Bastiaansen, C.; Schmidt, H. W.; Govert, L.; Smith, P. *Polym. Prepr.* **1993**, *34*, 776.
(4) Dirix, Y.; Tervoort, T.; Bastiaansen, C. *Macromolecules* **1995**, *28*, 486.
(5) Dirix, Y.; Tervoort, T. A.; Bastiaansen, C. *Macromolecules* **1997**, *30*, 2175.
(6) Eglin, M.; Montali, A.; Palmans, A. R. A.; Tervoort, T.; Smith, P.; Weder, Ch. *J. Mater. Chem.* **1999**, *9*, 2221.
(7) Ken, K.; Cai, Y.; Bedworth, P. W.; Marder, R. S. *Adv. Mater.* **1997**, *9*, 2.
(8) Hong, T.; Miller, L. L. *Chem. Mater.* **1995**, *7*, 1999.
(9) Carpita, A.; Rossi, R. *Tetrahedron* **1985**, *41*, 1919.
(10) Ionescu, M. V. *Bull. Soc. Chim. Fr.* **1929**, *23*, 210.
(11) Irick, G. *J. Chem. Eng. Data* **1971**, *16*, 118.
(12) Rougny, A.; Daudon, M. *Bull. Soc. Chim. Fr.* **1976**, *56*, 834.
(13) Dirix, Y.; Bastiaansen, C.; Caseri, W.; Smith, P. *Mater. Res. Soc. Symp. Proc.* **1999**, *559*, 147.
(14) Leclerc, M.; Fréchette, M.; Bergeron, J.-Y.; Ranger, M.; Lévesque, I.; Faid, K. *Macromol. Chem. Phys.* **1995**, *197*, 2077.
(15) Corish, J.; Feeley, D. E.; Morton-Blake D. A.; Bénière, F.; Marchetti, M. *J. Phys. Chem. B* **1997**, *101*, 10075.
(16) Yang, C.; Orfino, F. P.; Holdcroft, S. *Macromolecules* **1996**, *29*, 6510.
(17) Lévesque, I.; Leclerc, M. *Chem. Mater.* **1996**, *8*, 2843.
(18) DiCésare, N.; Belletête, M.; Leclerc, M.; Durocher, G. *J. Phys. Chem. A* **1999**, *103*, 803.
(19) DiCésare, N.; Belletête, M.; Marrano, C.; Leclerc, M.; Durocher, G. *J. Phys. Chem. A* **1999**, *103*, 795.
(20) DiCésare, N.; Belletête, M.; Leclerc, M.; Durocher, G. *Phys. Chem. Lett.* **1998**, 487.
(21) Tirelli, N.; Altomare, A.; Solaro, R.; Ciardelli, F.; Meier, U.; Bosshard, C.; Gunter, P. *J. Prakt. Chem.* **1998**, *340*, 122.

MA001518Q