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Synthesis and Photopatterning of Fluorene Based Reactive Mesogens

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Summary: In this paper we report the synthesis, characterisation and photopatterning of polydisperse fluorene oligomers. The oligomers were synthesised using the Yamamoto coupling. The molecular weights of the oligomers and as a consequence the nematic-isotropic transition temperatures were tailored by an endcapping reaction. With the endcapping species we introduced reactive acrylate functionalities. Subsequent photocrosslinking through a test mask led to the formation of fluorescent microstructures with a resolution of 1 μm.

Keywords: endcapping; fluorene oligomers; photolithographie; photopolymerization; reactive mesogen

Introduction

Semiconducting organic materials have gained interest in the last years due to their applications in displays, electronics, or sensors. Especially organic light-emitting diodes (OLEDs) are currently emerging as promising technology for flat panel displays and large area lighting.[1,2] In view of the mentioned applications patterning techniques for the production of pixelated devices are of particular interest. Various cost-efficient printing techniques are used for structuring.[3] The accessible resolutions are sufficient for displays, but the main problem is the spatial separation of the red, green and blue droplets in the printing process. Thus pre-patterned substrates have to be used in many cases. An alternative method is the vapour deposition of small molecules using shadow masks, which is relatively expensive and shows a poor scalability to larger substrates.[4] Conventional photolithography techniques optimized for inorganic materials are difficult to apply to organic materials. It was shown that classic photoresist techniques can only be transferred to structure organic compounds with major modifications, e.g. as lift-off techniques,[5] which limits their applicability in OLED manufacturing.

Thus an attractive approach is the direct photochemical crosslinking of the semiconducting material itself, for example by the introduction of photocrosslinkable moieties.[6,7] By light induced crosslinking the material becomes insoluble and can simultaneously be patterned, comparable to a negative photoresist. It is very important that during the crosslinking procedure the chemical structure of the material is not modified, which sometimes requires low processing temperatures and using inert atmospheres to avoid degradation processes.[8] In this study we report the synthesis of novel polydisperse oligofluorenes carrying photopolymerisable acrylate groups. The molecular weight of the oligofluorenes is tuned by using an endcapper, which terminates the reaction in a controlled way.[9,10] To obtain well defined oligomers the endcapping process has to be quantitative, which was proven by Maldi-ToF and elemental analysis. Here, the acrylate groups are introduced directly with the endcapping species in a Yamamoto reaction. In many publications the acrylate functionalisation is performed after the polymerisation of a precursor monomer, which is more difficult particularly with

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regard to a desired full conversion of the OH– groups into acrylates.[11,12] Here we demonstrate, that the Yamamoto coupling tolerates acrylate moieties and the acrylates tolerate the reaction conditions without any side reactions. So well-defined oligomers were obtained directly and subsequent photopatterning using standard photoinitiators resulted in patterns with a minimum resolution of 1 μm.

Experimental Part

Materials

All chemicals and reagents were purchased from Aldrich. Sec-BuLi was used as received from Acros. *N,N*-dimethylaniline, absolute toluene, and dimethylformamide (DMF) were purchased from FLUKA. Ethanol (EtOH) and toluene were distilled and tetrahydrofuran (THF) was distilled over potassium prior to use. The photoinitiators were used as received from Ciba.

Synthesis of 2-Bromo-7-(6-(2-tetrahydropyranyloxy)-hexyl)-9,9-di-(2-ethylhexyl)-fluorene (2)

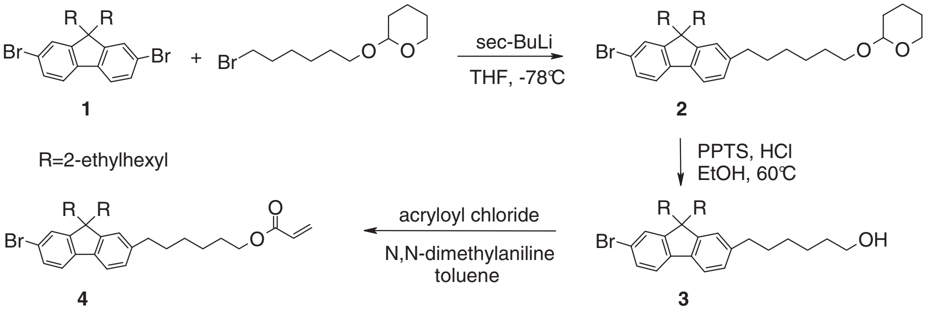
9.4 g (12.1 mmol) of compound **1** (see Scheme 1) were dissolved in 250 ml absolute THF and cooled to −78 °C. The solution was stirred for 5 min before 14.5 ml (18.9 mmol) sec-BuLi were added via a syringe. After stirring for 5 min 5 g (18.9 mmol) 2-(6-bromohexyloxy)tetrahydro-2*H*- pyran were added dropwise. The solution was stirred and allowed to warm up over night. The product was extraced with ether and the organic phase was washed with water and dried with Na_2SO_4. The crude product was purified by column chromatography using hexane/ethylacetate 18:1 as eluent. A transparent oil with 43% yield was obtained.

^{1}H-NMR (250 MHz, $CDCl_3$). δ (ppm): 7.4–7.6 (m, 4H), 7.1–7.2 (m, 2H), 4.5 (d, 1H), 3.8 (m, 2H), 3.4 (m, 2H), 2.6 (t, 2H), 1.9 (d, 4H), 1.4 (m, 6H), 0.4–1.0 (m, 32H). IR (cm^{-1}): 2956, 2928, 2855 (CH stretch); 1454, 1378 (CH deformation); 1136, 1120 (CH_2-O); 813 (CH aromatic). m/z = 654 (M^+).

Synthesis of 2-Bromo-7-(6-hydroxyhexyl)-9,9-di-(2-ethylhexyl)-fluorene (3)

A solution of 2.7 g (4.08 mmol) **2** and 0.1 g p-toluenesulfonic acid pyridinium salt (PPTS) in 200 ml EtOH was prepared. 5 drops HCl (conc.) were added and the mixture was heated to 60 °C under stirring for 2 h. The EtOH was evaporated and 80 ml dichloromethane (CH_2Cl_2) and 80 ml water were added to the product mixture. After stirring for 5 min the phases were separated. The water phase was washed with CH_2Cl_2 and the combined organic phases were washed with water. Purification by column chromatography with hexane/THF 10:1 as eluent yielded 99% of **3** as transparent oil.

^{1}H-NMR (250 MHz, $CDCl_3$). δ (ppm): 7.4–7.6 (m, 4H), 7.1–7.2 (m, 2H), 3.6 (d, 2H), 2.6 (t, 2H), 1.9 (t, 4H), 0.4–1.0 (m, 38H). IR (cm^{-1}): 3355 (OH); 2957, 2928, 2855 (CH



Scheme 1.
Synthesis of the reactive endcapper 2-Bromo-7-(6-acryloyloxy-hexyl)-9,9-di-(2-ethylhexyl)-fluorene **4**.

stretch); 1455, 1378 (CH deformation); 813 (CH aromatic). m/z = 568 (M^+).

Synthesis of 2-Bromo-7-(6-acryloyloxy-hexyl)-9,9-di-(2-ethylhexyl)-fluorene (4)

A solution of 2.04 g (3.58 mmol) **3**, 0.035 g (0.16 mmol) 2,6-di-tert-butyl-p-cresol (BHT) and 0.5 ml (3.93 mmol) *N,N*-dimethylanilin in 150 ml toluene was prepared. 0.36 g (3.93 mmol) acryloylchloride were added dropwise under argon and the mixture was stirred at 50 °C for 14 h. The solvent was evaporated and the crude product was purified by column chromatography using hexane/ethylacetate 10:1 and medium pressure chromatography using hexane/ethylacetate 20:1 as eluents. A transparent oil was obtained in 65% yield.

^{1}H-NMR (250 MHz, $CDCl_3$). δ (ppm): 7.4–7.6 (m, 4H), 7.1–7.2 (m, 2H), 6.4 (d, 1H), 6.1 (dd, 1H), 5.8 (d, 1H), 4.1 (t, 2H), 2.6 (t, 2H), 1.9 (d, 4H), 1.4 (m 6H), 0.4–1.0 (m, 32H). IR (cm^{-1}): 2957, 2928, 2854 (CH stretch); 1725 (C=O); 1637 (C=C); 1455, 1378 (CH deformation); 1189 (C–O); 813 (CH aromatic); 753 (C–H double bond). m/z = 624 (M^+). Anal. Calcd for $C_{38}H_{55}BrO_2$ (623.76): C, 73.17; H, 8.89; Br, 12.81; O, 5.13. Found: C, 73.26; H, 8.86; Br, 12.75; O, 5.05.

Synthesis of α,ω-Bis(6-acryloyloxy-hexyl)-oligo(9,9-di(ethylhexyl)- fluorene-2,7-diyl) (5a-e)

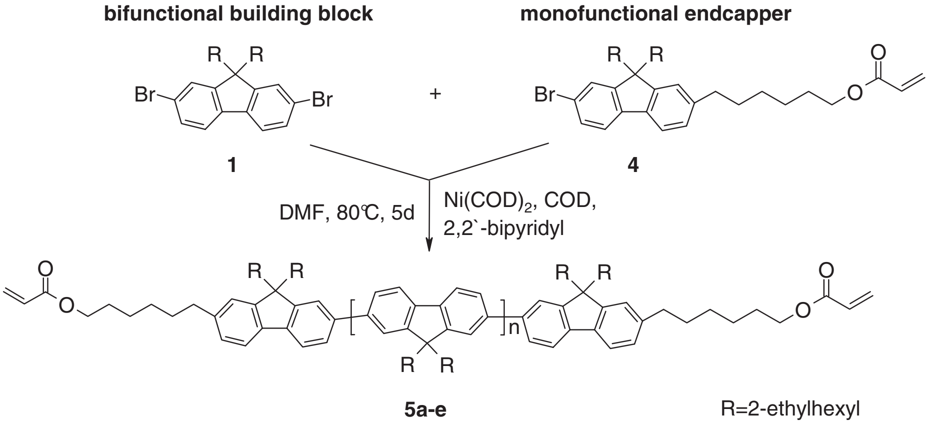
The synthesis of **5e** with a ratio of monomer **1** to endcapper **4** of 1:3 is described in detail:

A schlenk flask was charged with 0.8 g (2.91 mmol) nickeldicyclooctadiene, 0.36 ml (2.91 mmol) cyclooctadiene, 0.45 g (2.91 mmol) 2,2′-bipyridyl and 20 ml dry DMF under argon. The mixture was degassed by 3 freeze-thaw cycles before it was heated to 80 °C for 30 min under stirring. 0.21 g (0.38 mmol) **1** and 0.71 g (1.14 mol) **4** were weighed into a separate flask under argon. 30 ml dry toluene were added and the mixture was degassed by 3 freeze-thaw cycles. Subsequently the monomer mixture was added to the catalyst mixture using a cannula. The reaction mixture was stirred at 80 °C for 5 days in the dark. Afterwards it was poured into 140 ml methanol/HCl(conc.) 1:1 and stirred at room temperature for 2 hours. The organic phase was separated from the HCl phase which was then washed with Et_2O. The combined organic phases were washed with water and the solvent was evaporated. The crude product was filtered over a small alumina (neutral) column using toluene as eluent, then washed with alkaline EDTA solution (5%), reprecipitated twice from THF into methanol and dried in vacuum yielding 0.22 g (40%) of **5e** as pale yellow oil (Table 1).

^{1}H-NMR (250 MHz, $CDCl_3$). δ (ppm): 7.4–7.7 (m, 18H), 7.1–7.2 (m, 5H), 6.4 (d, 2H), 6.1 (dd, 2H), 5.8 (d, 2H), 4.1 (t, 4H), 2.7 (t, 4H), 2.5 (dd, 14H), 1.7 (m, 9H), 1.4 (m, 10H), 0.4-1.0 (m, 118H). IR (cm^{-1}): 2963, 2928, 2855 (CH stretch); 1726 (C=O); 1659 (C=C); 1470 (CH deformation); 1194 (C–O); 810 (CH aromatic); 742 (C–H double bond). M_n(GPC, polystyrene calibration) = 1900 g/mol. Anal. Calcd for $C_{134}H_{190}O_4$ (1865.01): C, 86.30; H, 10.27; O, 3.43. Found: C, 85.17; H, 10.53; O, 3.10.

Characterization

^{1}H-NMR spectra were recorded on a Bruker AC 250 spectrometer in $CDCl_3$ at 250 MHz with tetramethylsilane as reference. The IR spectra were recorded using a Bio-Rad Digilab FTS-40. Mass spectra were obtained by a Finnigan MAT 8500 (70eV) with MAT 112S Varian. The molecular weights were determined by a Waters size exclusion chromatography system (GPC) for oligomers (analytical columns: crosslinked polystyrene gel, length 2 × 60 cm, width 0.8 cm, particle size 5 μm, pore size 100 Å, eluent THF (0.5 ml/min, 80 bar), polystyrene calibration). The Maldi-ToF spectra were obtained by a Bruker Reflex III with highmass detector. The fluorescence spectra were recorded on a SHIMADZU RF-5301 PC spectrofluorometer with 90 ° detection. The emission spectra were obtained at ambient temperature from thin films spin coated (1000 rpm, 4 wt%) from xylene solutions on glass substrates. The liquid crystalline behaviour was exami-



Scheme 2.
Synthesis of α,ω-Bis(6-acryloyloxy-hexyl)-oligo(9,9-di(ethylhexyl)-fluorene-2,7-diyl) **5a-e** via endcapping reaction.

ned by a polarisation microscope Nikon Diaphot 300 with a Mettler FP 90 hotstage from films that were obtained by drop casting from CH_2Cl_2 solutions. The irradiation experiments were performed using a Xe-Hg- mixgas lamp Ushio UXM 200H. The microstructures were examined with a fluorescence microscope Leica DMR-SP with selective filter systems (excitation 340–380 nm, dichromatic mirror 400 nm, suppression filter LP 420 nm).

Results and Discussion

Synthesis

Compound **1** was synthesised by the alkylation of 2,7-dibromofluorene as described in literature.[13] The reactive endcapper **4** was synthesised in 3 steps. The first step is the selective alkylation of 9,9-di(2-ethylhexyl)-2,7-dibromofluorene **1** with 1 equivalent 2-(6-bromohexyloxy)tetrahydro-2H-pyran. The resulting THP-protected fluorene **2** is then deprotected using PPTS in EtOH which leads to the formation of the corresponding alcohol **3**. The last step is the esterification of compound **3** with acryloyl chloride to the acryloylfluorene **4** (see Scheme 1).

The polydisperse reactive mesogens **5a-e** were obtained in a 1-step reaction shown in Scheme 2. The Yamamoto reaction of the bifunctional monomer **1** and the monofunctional endcapper **4** leads to the oligomeric mixtures **5a-e** with different molecular weights. The coupling was performed using Ni(COD)$_2$ and 2,2′-bipyridyl in a mixture of dry DMF and dry toluene.[14] The chemical structures were validated by GPC, Maldi-ToF, ^{1}H-NMR, and IR spectroscopy.

The molecular weights of the fluorene oligomers **5a-e** were determined by GPC and are shown in Table 2.

Table 1.
Molar amounts of dibromo compound **1** and endcapper **4** and the resulting yields.

	ratio **1:4**	n_1 [mmol]	n_4 [mmol]	yield [%]
5a	2:1	0.32	0.16	55
5b	3:2	0.34	0.23	60
5c	1:1	0.24	0.24	50
5d	1:2	0.47	0.94	40
5e	1:3	0.38	1.14	40

Characterization

The molecular weight of the oligomers decreases from 4100 g/mol to 1900 g/mol with increasing amounts of endcapper **4**. The molecular weight distributions of **5a-e** can be seen in Figure 1.

The GPC scans in Figure 1 show one homologous series of oligomers. The lowest

Table 2.
Molecular weights, degrees of polymerisation, and isotropic-nematic transition temperatures $T_{i,n}$ of **5a-e**.

	ratio **1**[a]:**4**[b]	M_n(GPC)[c] [g/mol]	M_w(GPC)[c] [g/mol]	P_n(GPC)	$T_{i,n}$ [°C][d]
5a	2:1	4100	6500	9.7	–
5b	3:2	3800	5600	8.9	250
5c	1:1	3100	4400	7.1	190
5d	1:2	2000	2500	4.3	85
5e	1:3	1900	2200	4.1	65

[a] Bifunctional building block;
[b] Endcapper;
[c] Polystyrene calibration;
[d] Determined with polarisation microscopy.

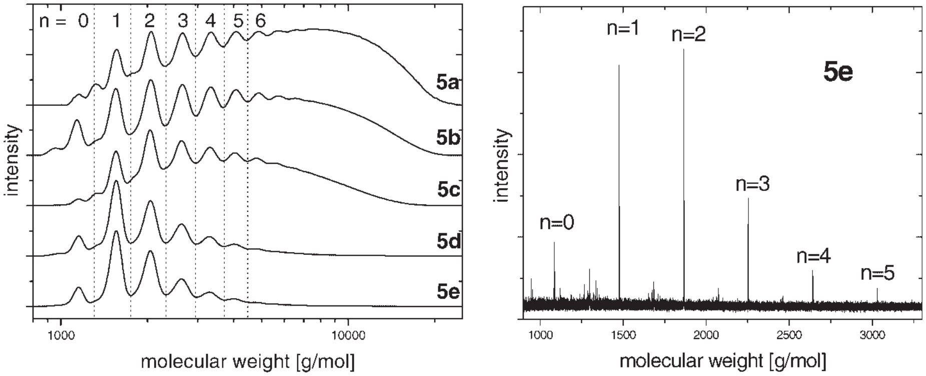
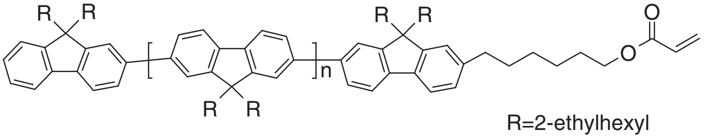


Figure 1.
left: GPC scans of the oligomers **5a-e** (polystyrene calibration), n refers to Scheme 2. *right*: Maldi-ToF spectrum of **5e**, recorded with 2,2′-p-phenylene-bis(5-phenyloxazole) (POPOP) as matrix material.

molecular weight compound in the mixtures is the dimeric species with a molecular weight of 1089 g/mol (n = 0) and the resolution of the oligomer GPC goes up to the octamer (n = 6). The lowest molecular weight mixture **5e** mainly consists of the trimeric species (n = 1). With an increasing amount of bifunctional monomer **1** the intensity of the high molecular weight part increases and in mixture **5a** the polymeric part becomes dominant. Furthermore shoulders next to the oligomer signals appear from mixture **5c** on and the intensity of these shoulders increases with a decreasing amount of endcapper. Maldi-ToF spectra were recorded to investigate the completeness of the endcapping process (Figure 1). The Maldi-ToF spectrum in Figure 1 shows one homologous row of oligomers from the dimer on. Between the oligomer signals other small signals appear which can be assigned to decomposition products in the Maldi process. This was proven by Maldi-ToF experiments with purified monodisperse fluorene compounds. Maldi-ToF spectra of **5a-c** show additional signals



Scheme 3.
Mono-endcapped fluorene oligomers found in mixtures **5a-c**.

which are assigned to the oligomers carrying only one acrylate group (Scheme 3). These one-arm compounds were only found in the high molecular weight mixtures from **5c** on which matches well with the results from GPC, where the one-arm compounds appear as small peaks in-between the main peaks of the oligomers. Thus the Maldi-ToF spectra reveal that the endcapping process is not complete, when the amount of endcapper **4** is reduced. The endcapping reaction is only complete if enough endcapper is provided. Compared to our results with the fluorene endcappers without acrylate groups [9] here the reactivity of the monobromo compound with alkylacrylate groups attached in position 7 is reduced drastically. The low reactivity of the endcapper is also reflected in the ratios of bifunctional building block to endcapper **(1:4)** and the resulting molecular weights. With the alkylacrylate endcapper a ratio of 3:2 gives a molecular weight of 3800 g/mol, whereas with the non functionalised endcapper from reference [9] the same molecular weight is obtained with a much higher ratio of 5:1.

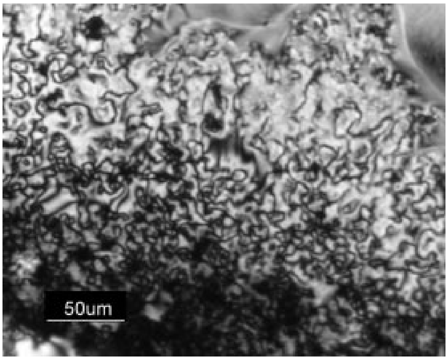


Figure 2.
Nematic Schlieren texture of **5b** observed upon cooling with 10 °C/min between crossed polarisers; picture taken at 25 °C.

Thermal Properties

All mixtures exhibit nematic mesophases and the transition temperatures strongly depend on the molecular weights (Table 2). The clearing temperatures were determined with polarisation microscopy and could be tuned in a broad temperature range from 250 °C for **5b** to 65 °C for **5e**. $T_{i,n}$ of the highest molecular weight mixture **5a** could not be determined due to thermal decomposition starting at 300 °C. Upon cooling no crystallisation is observed and stable nematic glasses are formed (Figure 2).

Photopolymerization

The photopolymerization experiments were carried out in the nematic phase of the reactive mesogens to achieve a high mobility of the acrylate groups in order to minimize the reaction time. Therefore the mixtures **5d** and **5e** seemed to be most suitable, because they contain only oligomers with two acrylate side arms and their nematic phases are at low temperatures, which prevent a thermal polymerisation. Thin films of the photocrosslinkable bisacrylates **5d** and **5e** with 1 wt% photoinitiator (Irgacure 819, Ciba Geigy) and 0.5 wt% stabiliser (BHT) were prepared

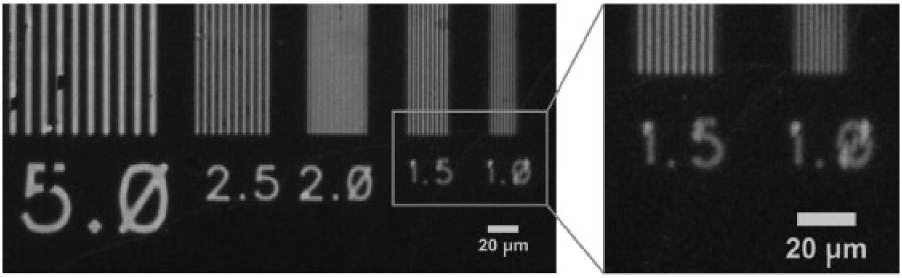


Figure 3.
Microstructures of a thin film of **5d** (+1 wt% irgacure 819, 13 min exposure time at 60 °C); picture taken under a fluorescence microscope.

from xylene solutions (4 wt%, thickness 40 nm). The films were heated into the nematic phase (25 °C below $T_{i,n}$) and annealed for 20 min under inert atmosphere. Subsequently the crosslinking was achieved by exposure to UV light using a Xenon-mercury lamp where the photoinitiator gives rise to the formation of radicals. After that the films were developed in THF to wash away the residual monomer.

The exposure and development process was optimized to avoid oxidation processes and to obtain well resolved structures. 10–15 minutes were found to be the optimal irradiation time to get highly crosslinked films. Fluorescent oligofluorene microstructures were formed by irradiation through a μm size mask and subsequent development for 10s in THF (Figure 3). A minimum resolution of 1 μm could be obtained.

Conclusion

In this paper we presented the direct synthesis of novel photopolymerisable oligomeric fluorene oligomers. The conversion of bromine groups in the Yamamoto coupling is complete, if enough endcapper is provided and well defined oligomeric mixtures are obtained. The molecular weight decreases with an increasing amount of endcapper. All mixtures exhibit nematic mesophases, the transition temperatures strongly depend on the molecular weight and were tuned in the range of 65 °C–250 °C. Subsequently photopolymerisation experiments were carried out and under optimised conditions irradiation through a μm-sized mask resulted in the formation of well resolved fluorescent 1 μm structures.

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