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NEW BLUE CROSSLINKABLE POLYMERS FOR ORGANIC LIGHT EMITTING DEVICES

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ABSTRACT

Here, we report on new blue electroluminescence (EL) crosslinkable polymers containing fluorene/phenylene alternating repeating units. Additionally, they contain polymerizable oxetane groups attached through flexible hexyloxy chains to phenylene units of the polymer backbone. The copolymers were synthesized *via* Pd-catalyzed Suzuki coupling reactions. The copolymers obtained were found to be soluble and easily processable from common organic solvents such as chloroform or toluene and have been characterized by ^{1}H and ^{13}C NMR spectroscopy, FT-IR spectroscopy and elemental analysis. The degree of polymerization has been determined by gel permeation chromatography (GPC). The thermal properties of the copolymers have been characterized by differential scanning calorimetry (DSC). The optical properties of the polymers were investigated in solution by UV/VIS spectroscopy. The polymers were photo-crosslinked in spin-coated thin films to yield insoluble networks.

Key Words: Conjugated polymers; Crosslinkable polymers; Multilayer light emitting devices; Oxetane.

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INTRODUCTION

Due to their potential applications in large-area flat-panel displays, polymer light-emitting devices (pLEDs) have attracted attention [1-5]. There is still an urgent need to design efficient blue-emitting polymers for full-color displays. High HOMO-LUMO gap polymers are required for blue light emission. Polyfluorenes have emerged as the most attractive blue-emitting polymers. The first blue-emitting polymer LED was made by Yoshino *et al.* [6] using poly(9,9-dihexylfluorene). Recently, the preparation of high molecular weight polyfluorene homopolymers and statistical random copolymers by nickel(0)-mediated polymerization of fluorene-based monomers has been reported [7-10]. Also Pd-catalyzed couplings between various 9,9-disubstituted or 9-monosubsituted 2,7-dibromofluorenes and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dialkylfluorenes was used to prepare well-defined poly(2,7-fluorene) derivatives [11].

In order to construct very efficient light-emitting devices multilayer structures are needed [12-15]. To build these structures two methods are popular. The more common one is the preparation by vacuum deposition. This method is limited to substrates with low molecular weight and excellent thermal stability. In addition, it requires a huge instrumental expanse, and is therefore connected with high fabrication costs. An alternative method to fabricate organic thin films is the preparation from solution, e.g. by spin-coating. Here, the production costs are reduced, large areas can be coated easily, and the molecular weight of the materials is not limited. The most important issues for solution casting are solubility and film-forming properties of the materials. However, by the preparation of multilayer devices exclusively by spin-coating from solution, one must ensure that the already coated layers are not partially dissolved by the solvent used in one of the following processing steps.

In order to make preparation methods from solution suitable for fabrication of multilayer organic light-emitting devices (OLEDs), the solubility of the layers must be reduced after their deposition. The conversion of a soluble precursor polymer into an insoluble form was realized in the case of unsubstituted PPV [1]. Another approach is the crosslinking of, monomers or pre-polymers containing polymerizable moieties either as side groups, end groups, or in the main chain of the polymers [16-22].

In this paper, we present the preparation of novel crosslinkable copolymers based on a fluorene/phenylene alternating main chain with oxetane side chains, which can be photo-polymerized in bulk following a cationic mechanism to form linear polyethers. The main advantages of the oxetane-groups are high rates of polymerization, high conversions, and low shrinkage during the crosslinking process [23]. Previously, we reported the synthesis of crosslinkable oxetane-functionalized low-molecular-weight triarylamines [19, 20], as well as crosslinkable hole-transport polymers containing triarylamines moieties in the main chain and crosslinkable oxetane side groups [21]. We present the synthesis of a novel oxetane-functionalized monomer containing two bromo functional groups (A_2-type monomer), which can be polymerized in an A_2B_2-type polycondensation by palladium-catalyzed Suzuki-coupling [24-28] with various fluorene bis(boronic ester)s (B_2-type monomer) to form a conjugated main chain. We attached the oxetane groups as crosslinkable moieties to the rigid polymer backbone by a flexible alkoxy spacer.

EXPERIMENTAL

Materials

All chemicals were purchased from Aldrich and used without further purification. The 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene (**10**) and the 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**11**) were prepared as described in the literature [11].

Instrumental

^{1}H NMR (300 MHz) and ^{13}C NMR (60 MHz) spectra were obtained on a Bruker ARX 300 spectrometer in deuterated chloroform solutions (298 K) relative to tetramethylsilane (TMS) as internal standard. Number-average (M_n) and weight-average (M_w) molecular weights were determined by gel permeation chromatography in chloroform by UV-VIS detector (254 nm) versus polystyrene standards. Differential scanning calorimetric measurements were performed on a Perkin Elmer DSC7 with a heating rate of 30 K/min. Elemental analysis were carried out by the micro-analytical laboratory of the 'Anorganisch-chemisches Institut' of the TU München. UV/VIS spectra were recorded on a Varian, Cary 3 spectrometer. FT-IR spectroscopy was carried out on a BRUKER IFS 55 spectrometer.

Synthesis

3-(6-Bromohexyloxymethyl)-3-ethyloxetane (2)

To a solution consisting of 105 g 50% NaOH, 100 mL hexane and 1.3 g tetrabutylammoniumbromide 9.3 g (80 mmol) 3-ethyl-3-hydroxymethyloxetane **1** and 58.5 g (240 mL) 1,6-dibromohexane were added. The mixture was refluxed for 5 hours. After cooling down to room temperature it was diluted with 200 mL water and extracted three times with 150 mL diethylether. The combined organic layers were dried with anhydrous magnesium sulfate and the solvent was removed on a rotary evaporator. The resulting liquid was purified by distillation. The product was obtained as colorless liquid in the yield of 67% (b.p.: 105°C/$4 \cdot 10^{-1}$ mbar).

IR (film): 3471, 2797, 2936, 1730, 1638, 1459, 1376, 1270, 1242, 1118, 1059, 980, 828, 644, 561 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 4.66 –OC**H**$_2$– oxetane (d, *J* = 5.9, 2 H), 4.59 –OC**H**$_2$– oxetane (d, *J* = 5.7, 2 H), 3.74 –OC**H**$_2$– (s, 2 H), 3.67 –OC**H**$_2$– (t, *J* = 6.5, 2 H), 3.62 –C**H**$_2$–Br (t, *J* = 6.9, 2 H), 2.08 –C**H**$_2$– (quint., *J* = 6.7, 2 H), 1.95 –C**H**$_2$CH$_3$ (quart., *J* = 7.4, 2 H), 1.81 –C**H**$_2$– (quint., *J* = 6.5, 2 H), 1.73-1.55 –C**H**$_2$– (m, 4 H), 1.10 –C**H**$_3$ (t, *J* = 7.4, 3 H). ^{13}C NMR ($CDCl_3$) δ = 78.95 –O**C**H$_2$– oxetane; 73.84, 71.73 –O**C**H$_2$–; 43.80 **C**$_q$; 34.19, 33.10, 29.73, 28.33, 27.14, 25.74 –**C**H$_2$–; 8.57 –**C**H$_3$.

Elemental analysis: $C_{12}H_{23}BrO_2$ (279.21) Calcd.: C 51.62 H 8.30
Found: C 51.99 H 8.60

2,5-bis[3-(6-Hexyloxymethyl)-3-ethyloxetane]-1,4-dibromphenyl (4)

7.23 g (27 mmol) 2,5-dibromohydroquinone [29] was dissolved in a solution of potassium hydroxide in ethanol (2 equivalents KOH per phenolic hydroxy group). 22.47 g (80 mmol) **2** was added and this solution was heated to reflux. After 12 hours, the mixture was cooled to room temperature and the precipitate formed was filtered off and washed with methanol. The organic solvents were removed on a rotary evaporator. The liquid product was purified by silica-gel column chromatography using hexane/ethylacetate (2/1) as the eluent. The pour product was obtained as yellow viscous liquid after vacuum distillation in the yield of 48% (b.p.: 240°C/1·10^{-4} mbar).

IR (film): 3472, 2935, 2862, 1637, 1493, 1463, 1361, 1269, 1212, 1113, 1063, 980, 829, 433 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.31 =C**H**– (s, 2 H), 4.68 –C**H**$_2$– oxetane (d, *J* = 5.9, 4 H), 4.6 –C**H**$_2$– oxetane (d, *J* = 5.9, 4 H), 4.18 =HC–OC**H**$_2$– (t, *J* = 6.3, 4 H), 3.76 –OC**H**$_2$–C$_q$ (s, 4 H), 3.70 –OC**H**$_2$– (t, *J* = 6.3, 4 H), 2.08-1.60 –C**H**$_2$– (m, 20 H), 1.11 –C**H**$_3$ (t, *J* = 7.4, 6 H). ^{13}C NMR ($CDCl_3$) δ = 150.49 =H**C**–O–; 118.90, 111.55 arom. **C**H; 78.99 –O**C**H$_2$– oxetane; 73.87, 71.83, 70.57 –O**C**H$_2$–; 43.83 **C**$_q$; 29.86, 29.47, 27.16, 26.24, 26.17 –**C**H$_2$–; 8.60 –**C**H$_3$.

Elemental analysis: $C_{30}H_{48}O_6Br_2$ (664.51) Calcd.: C 54.22 H 7.28
Found: C 53.66 H 6.80

Copolymer (12)

0.6822 g (1.026 mmol) of **4**, 0.6021 g (1.026 mmol) of **10**, 5 mL of 2 M solution of potassium carbonate and 14 mL of toluene were charged into a 100 mL Schlenk-flask under nitrogen atmosphere. The mixture was degassed via several freeze-pump cycles and kept under nitrogen. 0.024 g (0.02 mmol, 2 mol% with respect to monomers) of $Pd(PPh_3)_4$ in 1 mL of toluene were then added. The resulting mixture was degassed once more and then heated to 80°C for four days under vigorous stirring in the exclusion of light. After the mixture had cooled to room temperature, the polymer was precipitated by a dropwise addition of the whole mixture into 300 mL of methanol. The precipitate formed was removed by filtration and washed with 100 mL water and 100 mL acetone. The polymer was redissolved in chloroform and filtered through a teflon-membrane filter. The polymer was recovered by precipitating into methanol. The solid material was washed for 24 hours in a Soxhlet apparatus using acetone and dried in vacuum at room temperature. The yield was 64%.

IR (KBr): 3416, 2960, 2828, 2857, 1617, 1510, 1461, 1377, 1261, 1206, 1102, 1024, 980, 801 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.74-7.36 =C**H**– (m, 6 H), 7.05 =C**H**– (s, 2 H), 4.36 –OC$\mathbf{H}_2$– oxetane ring (d, *J* = 5.7, 4 H), 4.29 –OC$\mathbf{H}_2$– oxetane ring (d, *J* = 5.7, 4 H), 4.00-3.79 –OC$\mathbf{H}_2$– (m, 4 H), 3.46-3.33 –OC$\mathbf{H}_2$– (m, 8 H), 1.76-0.59 –C$\mathbf{H}_2$– and –C$\mathbf{H}_3$ (m, 52 H). ^{13}C NMR ($CDCl_3$) δ = 149.49, 138.84, 136.05, 130.34, 127.73, 126.99, 126.15, 123.41, 118.24, 115.82 arom. **C**; 77.57 –O**C**H_2– oxetane; 72.47, 70.46, 68.80 –O**C**H_2–; 54.06 fluorene $\mathbf{C}_q$; 42.04 oxetane $\mathbf{C}_q$; 39.51, 30.68, 29.35, 28.57, 28.45, 25.73, 24.93, 24.82, 22.97, 21.70 –**C**H_2–; 13.04, 7.20 –**C**H_3.

Elemental analysis:	$(C_{55}H_{80}O_6)_n$	$(837.23)_n$	Calcd.:	C 78.90	H 9.63
			Found:	C 76.95	H 9.59

Copolymer (13)

Following the procedure described for the copolymer **12**, 0.5404 g (0.8132 mmol) of **4**, 0.5225 g (0.8132 mmol) of **11**, 4 mL of 2 M solution of potassium carbonate, 12 mL of toluene, 0.019 g (0.016 mmol, 2 mol% with respect to monomers) of $Pd(PPh_3)_4$ were used. The yield was 96%.

IR (KBr): 3455, 2926, 2854, 1637, 1509, 1460, 1376, 1260, 1204, 1107, 1028, 980, 821 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.73-7.40 =C**H**– (m, 6 H), 7.05 =C**H**– (s, 2 H), 4.36 –OC$\mathbf{H}_2$– oxetane (d, *J* = 5.7, 4 H), 4.29 –OC$\mathbf{H}_2$– oxetane (d, *J* = 5.7, 4 H), 3.99-3.82 –OC$\mathbf{H}_2$– (m, 4 H), 3.46-3.33 –OC$\mathbf{H}_2$– (m, 8 H), 1.67-0.72 –C$\mathbf{H}_2$– and –C$\mathbf{H}_3$ (m, 60 H). ^{13}C NMR ($CDCl_3$) δ = 149.49, 138.84, 136.07, 130.33, 127.76, 126.97, 126.17, 123.44, 118.28, 115.81 arom. **C**; 77.57 –O**C**H_2– oxetane; 72.48, 70.47, 68.79 –O**C**H_2–; 54.05 fluorene $\mathbf{C}_q$; 42.41 oxetane $\mathbf{C}_q$; 39.49, 30.81, 29.34, 28.59, 28.45, 25.74, 24.94, 24.83, 23.03, 21.61 –**C**H_2–; 13.07, 7.20 –**C**H_3.

Elemental analysis:	$(C_{59}H_{88}O_6)_n$	$(893.30)_n$	Calcd.:	C 79.33	H 9.93
			Found:	C 77.99	H 9.85

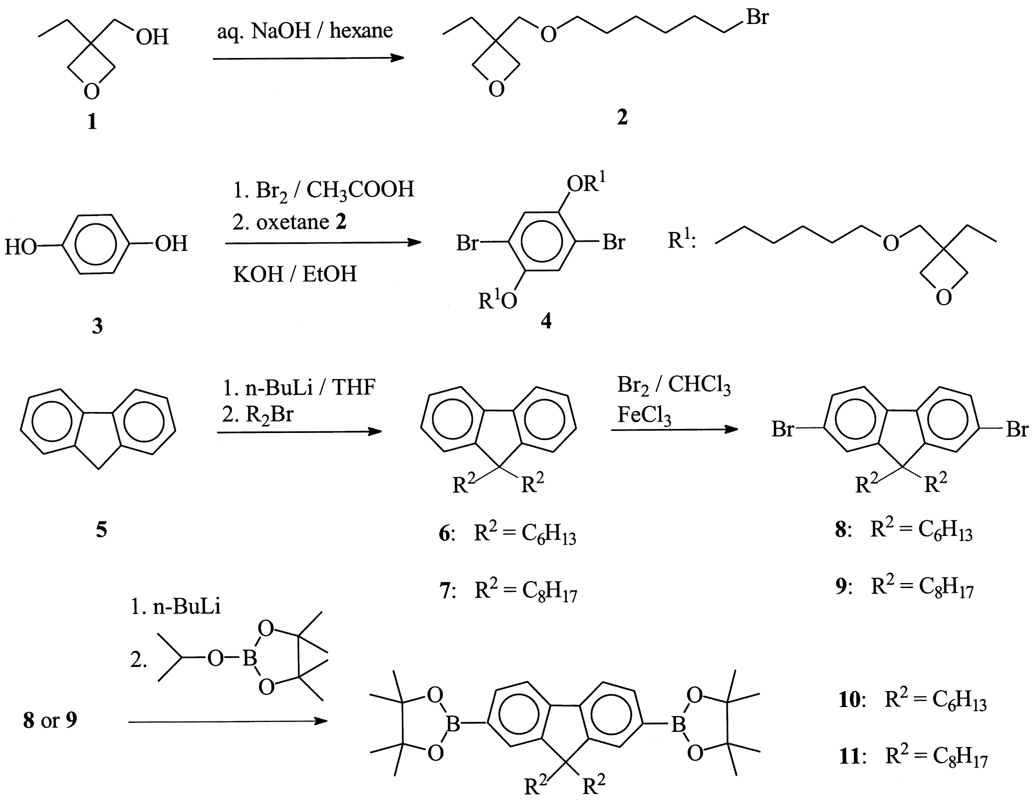
RESULTS AND DISCUSSION

To obtain copolymers as described above we first needed the oxetane-functionalized monomer. Such a monomer should fulfill the following requirements: 1) aromatic character, 2) bromo groups in *para*-position, 3) crosslinkable oxetane groups linked through flexible side chains. Along these lines, we constructed the oxetane-functionalized monomer **4** as shown in Scheme 1. First the ether **2** was prepared by a two phase reaction of 3-ethyl-3-hydroxymethyloxetane **1** with 1,6-

dibromohexane. Through this reaction, flexible alkyl spacer are introduced in order to enable the mobility of the oxetane groups. Therefore, a decrease in the glass-transition temperature of the polymers is expected which results in an increasing diffusional mobility of the polymerizable group. This should guarantee a high conversions in the crosslinking reaction [20]. Bromination of the hydroquinone **3** involved the synthesis of the 2,5-dibromohydroquinone which reacted finally with the ether **2** under formation of target comonomer **4**. With this reaction, **4** is obtained in 48% yield after purification by column chromatography followed by vacuum distillation. The comonomers **10** and **11** are easily accessible in three steps starting from fluorene and were prepared as described previously [11]. Different lengths of alkyl side chains attached in the 9-position of the fluorene were chosen because this was expected to influence the solubility and mobility of the resulting polymers.

The Suzuki polycondensation method was applied to polymerize the oxetane-functionalized comonomer **4** with the 9,9-dialkylsubstituted fluorene comonomers **10** or **11**, respectively. These reactions were carried out in a slightly modified version of the standard procedure given by G. Wegner *et al*. [30]. In the reaction, tetrakis(triphenylphosphine)palladium (0) is usually used as the catalyst, aqueous sodium carbonate as base, and THF as organic solvent. In the initial experiment, we employed a two-phase system of equal amounts of THF and water as the reaction medium for the coupling of the comonomers **4** and **10**. After 48 hours, at a temperature of 80°C under exclusion of light polymeric material precipitated from the reaction mixture. A similar result was obtained for the reaction mixture of toluene/water (ratio 2:1) in the polycondensation reaction of the monomers **4** and **11**. Only 11% of the product was extracted with chloroform in the case of the solvent ratio 1:1 (monomers **4** and **10**) and the value of 37% was obtained for the solvent ratio 2:1 (monomers **4** and **11**). For more details, see Table 1. Complete extraction could not be achieved by using other organic solvents such as toluene, methylene chloride or chlorbenzene. The higher amount of extractable material in the later case can be due to the fact that the monomer **11** has longer alkyl chains attached at the 9-position of the fluorene. Our explanation of the results described above is that during the polycondensation reaction the polymer chains bearing oxetane groups have been partially crosslinked resulting in a completely insoluble fraction. Although the exact mechanism of the side reactions is not yet well understood. Due to the insolubility, the structure of these materials could not be proved.

The reaction conditions had to be further modified to achieve acceptable results in terms of yields on the soluble polymer. We used a mixture of toluene and distilled water in the ratio 3:1 as reaction medium. Under these reaction conditions, the polymers remain in solution during the reaction time what means that side reactions were hindered. A decrease in the relative amount of water resulted in a increasing amount of soluble polymer, as can be seen in Table 1. This approach allows the construction of processible polymers in high yields. The resulting conjugated copolymers are strictly of an alternating type with well-



Scheme 1. Synthesis of comonomers (**4**, **10** and **11**).

defined blocks of crosslinkable oxetane-units linked to each other by one alkyl-substituted fluorene unit. These copolymers both show a very good solubility in common organic solvents (chloroform, toluene, THF). The good solubility enables solution characterization and renders them processable into thin films by means of spin-coating.

Characterization

The molecular weights and absorption characteristics of the copolymers as well as the glass-transition temperatures (T_g) are summarized in Table 1. The good solubility of the copolymers prepared here permits their characterization by gel permeation chromatography in chloroform using polystyrene standards. A polydispersity (M_w/M_n) of around 3 was calculated, which is consistent with a polycondensation reaction. The Suzuki-coupling led to copolymers with degrees of polymerization 33, as shown in Table 1.

Table 1. Results of the Polycondensation-Polymer Properties

Polymer	Reaction mixture	Yield [a] / %	$\bar{M}_n$ [b]	$\bar{M}_w$ [b]	*PDI*	$\overline{DP}$ [c]	T_g [d]/ °C
12a	THF/H_2O (1:1)	11	14100	42000	2.98	32	—
13a	toluene/ H_2O (2:1)	37	17800	55000	3.07	40	—
12	toluene/ H_2O (3:1)	64	13700	34300	2.49	33	89
13	toluene/ H_2O (3:1)	96	14900	60600	4.07	33	77

[a] Given for the soluble fraction.

[b] Given in g·mol^{-1} determined by gel permeation chromatography in chloroform by UV-VIS detector (254 nm) versus polystyrene standards.

[c] Degree of polymerization calculated from $\bar{M}_n$ according to comonomer composition.

[d] Glass transition temperatures as determined by DSC (30 K/min).

The structure of the copolymers has been confirmed by ^{13}C and ^{1}H NMR spectroscopy. The copolymers exhibit alternating repeat units. The ^{1}H NMR spectra show rather broad signals typical of polymeric materials. Additionally, the ^{1}H NMR spectra of the alkoxy substituted copolymers show a singlet at about 7.05 ppm. This signal corresponds to the two protons of alkoxy-substituted phenylene rings. The characteristic signals of the oxetane ring are found to be at 4.36 and 4.29 like a doublets. All signals show correct integral ratios (for a detailed data list see the Experimental section).

The thermal properties of the polymers were examined by differential scanning calorimetry (DSC); glass transition temperatures (T_g) were found to be 89°C for **12** and 77°C for **13**. As expected, the lower T_g for the polymer **13** is due to longer side chains attached to fluorene unit.

Using UV/VIS spectroscopy, we have studied the optical properties of the new copolymers in dilute solution of dichloromethane. The absorption maxima are positioned at 370 nm what is 18 nm blue-shifted compared to high molecular weight poly(9,9-dihexylfluorene) with an absorption maximum at 388 nm in tetrahydrofuran [31] (Figure 1). For a comparison, the absorption maximum of the analogous copolymer with hexyl side chains attached to the phenylene ring is positioned at 325 nm [9].

The result obtained is expected since the absorption properties are related to the π-conjugated system which is hardly influenced by the presence of the side chains. Fluorene derivatives are interesting since they contain a rigid planar biphenyl unit and the substitution at the 9-position provides the possibility of improving the solubility of polymers without significantly increasing the steric interactions in the polymer backbone. On the other side, the inclusion of lateral flexible chains on the poly(*p*-phenylene) backbone has the drawback that the additional substituents twist the substituted phenylene rings considerably out of plane. Due to the increase of the twist angle between the *para*-linked aryl units the absorption maximum will be shifted to a lower wavelength. The conjugation that means overlap of the π-orbitals will be severely diminished. In our case, the increased twist angle between oxetane-substituted phenylene unit and fluorene unit due to increased steric interactions in the repeating moiety causes a blue-shift of the absorption maxima compared to the fluorene homopolymer.

The proof-of-principle is demonstrated using polymers **12** and **13**. We prepared films of about 100 nm thickness by spin-coating from chloroform solution onto glass substrates. Crosslinking experiments were performed in the presence of 5% by weight of the [(4-Phenylthio)phenyl]diphenylsulfonium hexafluoroantimonate as photo-initiator [32, 33] under irradiation with UV light at room temperature. The conversion rates were monitored by the real time FT-IR-spectroscopy [34]. Results of these measurements are shown in Figure 2. About 77% of oxetane groups were converted after 10 minutes in the case of the polymer **12**, and about 90% in the case of the polymer **13**. It should be mentioned that these results are sensitive on the choice of the integration parameters of the out-of-plane vibration band at 980 cm^{-1} (out-of-plane vibration characteristic for the oxetane group) and can be interpreted just as the relative comparison of the corresponding compounds. Crosslinking experiments at higher temperatures are in progress.

CONCLUSION

The extension of the concept of crosslinkable materials for preparation of multilayer devices by spin-coating has been introduced. Novel crosslinkable blue electroluminescent polymers containing fluorene/phenylene alternating units in the main chain and crosslinkable oxetane side groups were presented. They were obtained *via* Pd-catalyzed Suzuki coupling reaction. The key structure was the novel oxetane-functionalized dibromophenylene-monomer **4**. The polymers were

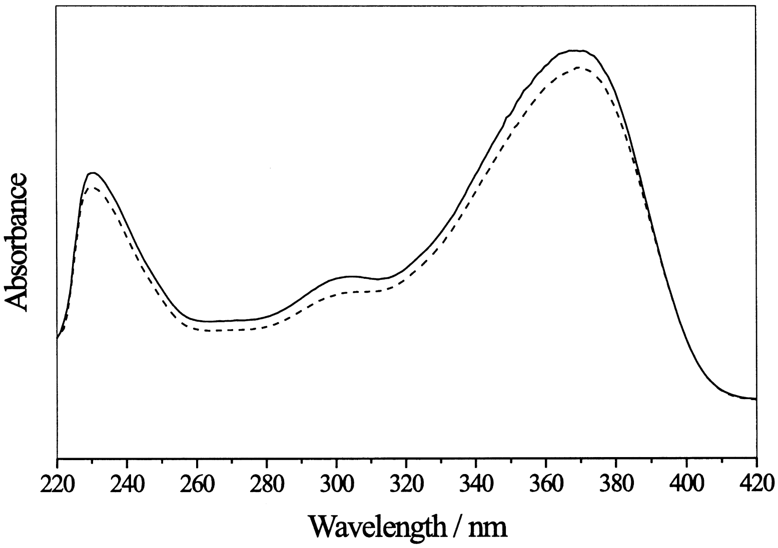
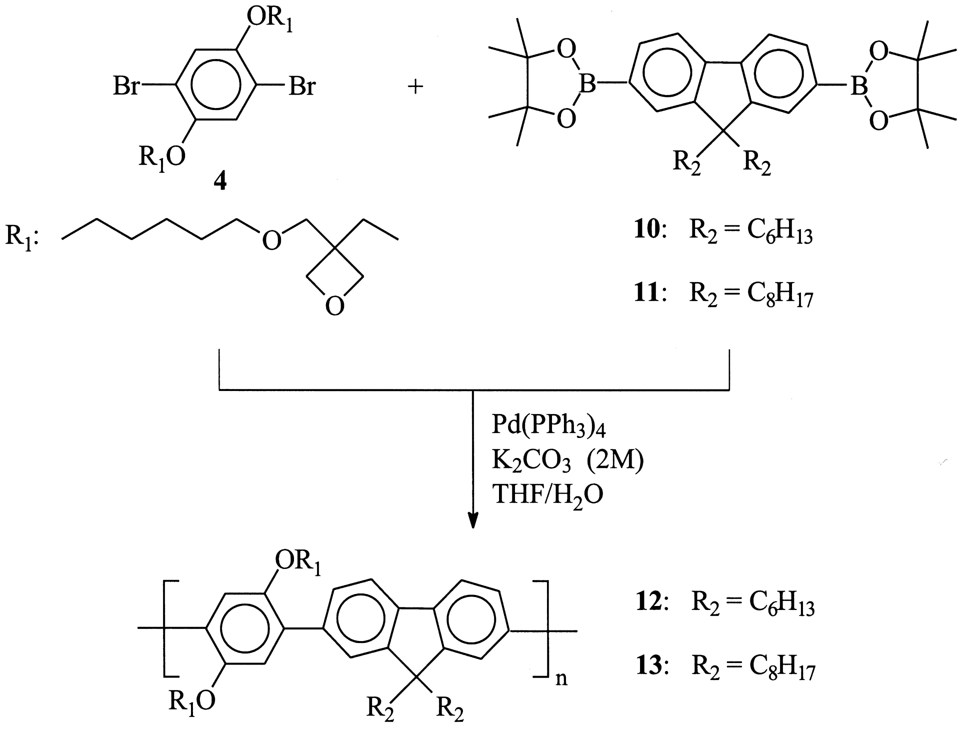


Figure 1. Normalized absorption spectra of copolymers in dichloromethane; (**12** --), (**13** —).



Scheme 2. Synthesis of copolymers (**12** and **13**).

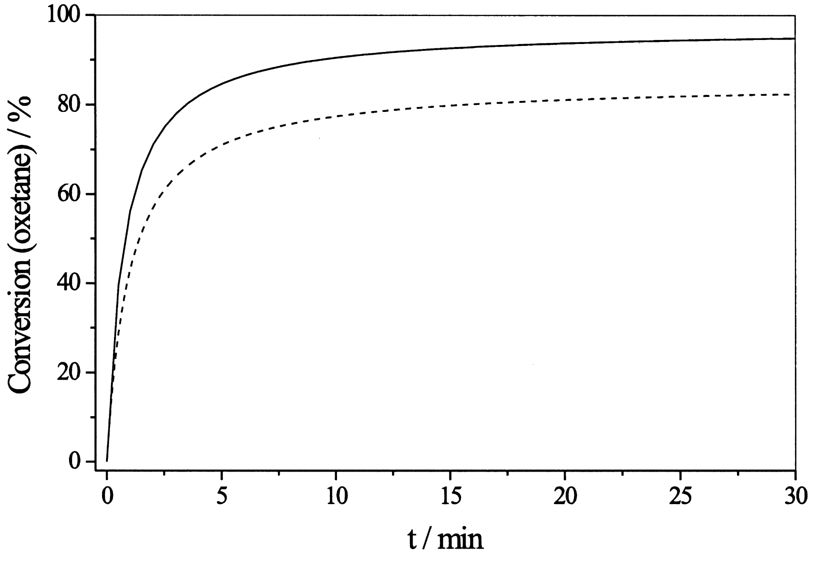


Figure 2. Time dependence of the conversion of the oxetane groups monitored during the UV-irradiation (100 mW/cm^2) of the polymers **12** -- and **13** — (films of about 100 nm thickness spin-coated from chloroform solutions) using the real time FT-IR spectroscopy (intensity of the oxetane band at 980 cm^{-1}) initiated with triarylsulfonium salt (5% by the weight) at room temperature.

photocrosslinked in bulk to yield insoluble networks. Using the real time FT-IR spectroscopy the conversion of the oxetane groups during the crosslinking reaction was monitored.

Further work will aim to vary the degree of functionalization with oxetane groups. Furthermore, we plan to prepare polyfluorenes with oxetane groups attached at 9-position of the fluorene monomer. Further investigations of organic light emitting devices (OLED)s incorporating these materials are in progress.

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