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Valence band edges and optical band gaps of alternating substituted poly(phenylenevinylenes)

Mikkel Jørgensen (✉), Frederik C. Krebs

The Danish Polymer Center, RISØ National Laboratory, P.O. Box 49, 4000 Roskilde, Denmark

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Summary

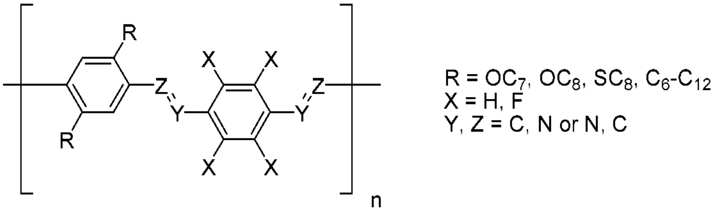
A collection of sixteen different PPV's with an alternating substituent pattern and three reference compounds MEH-PPV (poly(2-methoxy-5-ethylhexyloxy-1,4-phenylenevinylene)), CN-MEH-PPV (poly(2-methoxy-5-ethylhexyloxy-1,4-phenylenecyanovinylene)) and P3HT (poly(3-hexylthiophene)) were studied by ultraviolet photoelectron spectroscopy on gold substrates and by optical absorption spectroscopy in solution. Together these two techniques were combined to give a picture of the uppermost part of the electronic structure of these materials and allowed for a comparison based on the molecular substitution pattern under the same experimental conditions.

Introduction

Conducting polymers of the polyphenylenevinylene (PPV) type, shown in scheme 1, are still the subject of great interest as components of electronic devices such as field-effect transistors (FET's) [1-3], organic light emitting diodes (OLED's) [4] and photo voltaic devices [5-6]. A large number of differently substituted PPV's have been synthesised to tune the physical properties, such as their emission maxima, but also to be able to process them easily [7]. Many other properties have to be taken into account in choosing the polymer material for such applications. In most cases sandwich type structures are used with one or more layers of polymers in contact with metal or semiconductor electrodes. Evidently, controlling the relative positioning of electronic energy levels in the polymer materials with respect to the electrodes are crucial for the creation of operational devices. Energy levels, and especially those of the valence electrons, in thin films of polymers on metal substrates, can be measured using ultraviolet photoelectron spectroscopy (UPS) [8-11]. Using this technique a picture of the density of states of the uppermost orbitals are obtained from which the position of the HOMO can be defined with respect to the Fermi level of the substrate metal. The optical band gap can be measured from the absorption spectrum as the onset of the transition between the HOMO and the LUMO. Other methods such as cyclic voltammetry can also be used to measure the energy difference between the HOMO and LUMO [12]. Taken together, it is possible to construct a rough sketch of the uppermost part of the electronic structure [13].

During the last decade this has been done for some polymers such as poly-(9,9-dioctylfluorene) [8] and also some PPV's [10]. Tuning of the energy levels of polymers by attaching electron donating or withdrawing substituents through resonance or field effects have been investigated theoretically by Bredas et al. for PPV's [13]. It has also been realised practically in a series of poly(*ter*-phenylenevinylenes) [14] and poly(biphenylenevinylenes) [15] studied by us recently.

Although many differently substituted PPV's have been synthesised, a search through the literature revealed a preference for alkoxy substituents on the benzene rings and cyano groups on the vinylene groups. Less frequently, derivatives with aryl groups or silylated species have been reported [7]. In the present paper we have collected an extended series of PPV's with some new members to explore the ability to tune the energy levels in these materials measured by UPS.



Scheme 1. The materials studied using UPS and absorption spectroscopy

This series has long chain substituents on every second benzene ring as opposed to every benzene ring as is most commonly observed. The substituents include alkoxy, alkylthio and alkyl groups, fluoro substitution of the second benzene ring, cyano substitution on the vinylene groups and finally, imines instead of vinylenes. In previous papers we have described the preparation and characterization of the dialkyl-PPV's [16] and the poly(phenyleneimine) compounds [17].

The aim of this work was to make a qualitative experimental picture of the uppermost electronic structure for a range of PPV polymers as an aid to those constructing devices from these compounds.

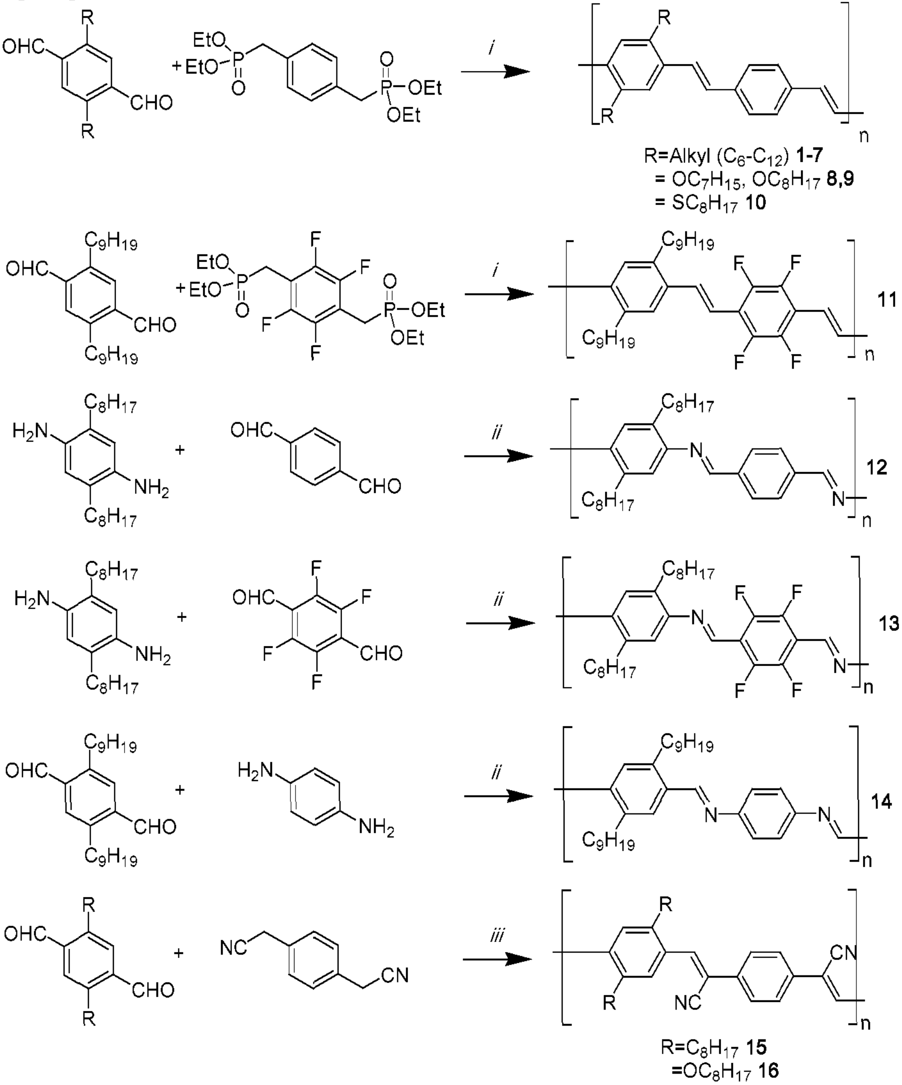
Experimental

Methods. The UV-VIS spectra were recorded in dry THF. The minimum energy cut-off was taken as the position at the low energy side where the absorbance was 10% of the maximum absorbance. This value was used as the optical band gap energy, E_g. The samples for ultraviolet photoelectron spectroscopy measurements (UPS) were prepared by spin coating a 1 mg mL^{-1} solution of the polymers in chloroform or chlorobenzene onto a freshly prepared (by sputtering) polycrystalline gold substrate. The samples were then dried in a vacuum oven at 50 °C for 24h. The photoelectron spectra were recorded at the ASTRID storage ring at Aarhus University, Denmark. The synchrotron beamline consists of an SX-700 monochromator and a hemispherical electron energy analyser. An ESCA (Electron Spectroscopy for Chemical Analysis) of the samples was recorded first to check the cleanliness of the area where the incident photons illuminated the sample and to analyse the atomic composition. The procedure employed in the analysis of the data has been reported [8,14].

Results and discussion

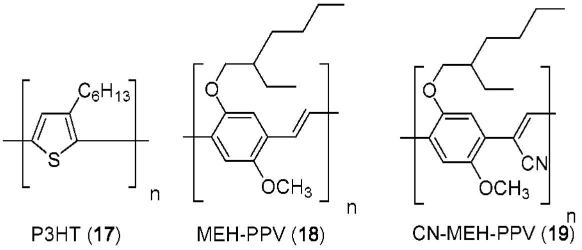
Synthesis. Preparation of the polymers is outlined in scheme 2. Three general condensation polymerisation reactions have been employed. The Horner-Emmons-

Wadsworth (HWE) reaction between a terephthaldehyde and a diphosphonate ester was used to prepare the range of dialkyl substituted PPV's **1-7** and the dialkoxy derivatives **8** and **9** and the alkylthio compound **10**. A fluorinated version of the diphosphonate ester was used to prepare the dialkyl fluoro PPV **11** [18].



Scheme 2. Synthesis of the PPV's investigated. i: HWE conditions (NaH in a mixture of 1,2 dichlorobenzene and diphenyl ether at reflux), ii: elimination of water in acetic acid at reflux, iii: potassium t-butoxide in THF at reflux.

The imine polymers **12**, **13** and **14** where synthesised using a terephthaldehyde and a diamine by water elimination in a high-boiling solvent with acid catalysis [17]. Finally, the Knoevenagel condensation was utilized to prepare the cyano substituted PPV's **15** and **16** [15]. Common to all these reactions is that two different monomers are used leading to PPV's with an alternating pattern of substitution.



Scheme 3. Set of reference polymers used in this study.

UV-VIS spectra. The solution UV-VIS spectra were recorded on the polymers dissolved in THF and the main data are presented in Table 1. One major transition peak was seen in all cases with a λ_{max} in the range 410 – 495 nm. In a few cases (compounds **13** and **16**) a smaller shoulder at longer wavelength was observed indicating the participation of another transition. Based on the molecular weight of the monomers an extinction coefficient ε_{max} of 10-45.000 M^{-1} cm^{-1} could be calculated in agreement with the expected $\pi-\pi^*$ transition. The optical band gap (E_g) was determined from the low energy onset (10% of λ_{max}). Values of 2-2.7 eV are found for the range of PPV's studied in accordance with known examples.

Table 1. UV-VIS data. Optical band gap: E_g, absorption maximum: λ_{max} and the molar extinction coefficient: ε. Compounds 13 and 15 showed two absorption peaks. Molecular weight (M_p) determined by SEC.

Compound	E_g	λ_{max} . (nm)	ε (M^{-1} cm^{-1})*10^{-4}	Molecular weight (M_p)
1	2.6	422	1.66	13.500
2	2.6	425	3.86	3.280
3	2.6	431	4.47	26.400
4	2.6	429	4.58	129.000
5	2.6	431	4.43	29.100
6	2.6	425	3.52	9.470
7	2.6	431	4.22	49.500
8	2.4	463	3.15	9.470
9	2.4	464	4.49	11.600
10	2.5	442	3.55	17.400
11	2.4	432	3.22	2.530
12	2.6	423	2.12	6.600
13	2.4	454 / 500	n.d.	1.865
14	2.7	410	2.42	n.d.
15	2.1	482 / 560	1.2	n.d.
16	2.2	464	1.1	n.d.
(17) P3HT	2.4	537	n.d.	87.000
(18) MEH-PPV	2.2	495	n.d.	100.000
(19) CN-MEH-PPV	2.5	431	n.d.	110.000

n.d. = not determined

The optical transition is broadened due to vibronic coupling, which is why the low energy onset is used.

Other methods for measuring the HOMO LUMO energy difference e.g. cyclic voltammetry [12] have equal uncertainties associated such as solvent and electrode dependencies. The outer limits are represented by compounds **16** at 2.1 eV and compound **14** at 2.7 eV. The low value for **16** is in part due to a broad shoulder in the spectrum and can be compared to the reference polymer CN-MEH-PPV that had an optical band gap of 2.5 eV. The main structural difference between them is the alternating substitution pattern of **16**. The rather high value found for compound **14** where the vinylene group has been replaced by an imine in this rather unknown type of polymers. A decreasing trend of E_g is observed going from the alkyl substituted PPV's **1-7** (2.6 eV), the alkylthio compound **10** (2.5 eV), the dialkoxy derivatives **8** and **9** (2.4 eV) and finally, to MEH-PPV (2.2 eV).

Ultraviolet photoelectron spectroscopy. UPS spectra of the polymers **1-16** and the reference compounds MEH-PPV, CN-MEH-PPV and the polythiophene P3HT were measured on thin films spin-coated on freshly prepared polycrystalline 5000 Å thick gold films (evaporated onto the sample holder by sputtering). The spectra where recorded using 50 eV radiation from a synchrotron and the important data have been summarised in table 2. A clean gold substrate was introduced first to establish the position of the work function Φ_{Au}. The low energy onset where photoelectrons begin to be observed is the Fermi level (E_F), which then serves as the zero binding reference level. This onset changes when a polymer film is applied on top of the gold layer corresponding to a higher binding energy called E_F^{VB} representing the electrons in the top of the HOMO (or valence orbitals). E_F^{VAC} is the energy difference between the Fermi level of the metal and the vacuum level of the polymer overlayer. The gold work function, Φ_F was determined to be 4.9 eV.

Table 2. Data from the photoelectron spectra the polymers **1-16** and reference polymers

Compound	E_F^{VB}	E_F^{VAC}	Cut-off	Δ	IP
1	0.8	3.9	45.3	-1.0	4.7
2	1.0	3.8	45.3	-1.2	4.7
3	0.7	4.1	45.3	-0.8	4.8
4	1.0	3.8	45.3	-1.2	4.7
5	0.8	4.0	45.3	-1.0	4.7
6	0.9	3.8	45.4	-1.1	4.7
7	0.8	4.0	45.3	-0.9	4.8
8	1.0	3.5	45.7	-1.5	4.4
9	0.6	4.3	45.5	-0.6	4.6
10	1.0	3.5	45.6	-1.5	4.4
11	2.0	2.4	45.6	-2.5	4.5
12	1.9	2.7	45.5	-2.3	4.6
13	2.5	1.9	45.7	-3.1	4.4
14	2.1	2.4	45.6	-2.5	4.5
15	1.8	2.7	45.6	-2.3	4.5
16	1.6	2.8	45.6	-2.1	4.4
(17) P3HT	0.6	3.7	45.8	-1.3	4.2
(18) MEH-PPV	1.0	3.5	45.6	-1.5	4.4
(19) CN-MEH-PPV	2.2	2.2	45.6	-2.7	4.4

It is well known that substitution can affect the electronic structure through resonance and field effects. Electron donating substituents decrease E_F^{VB} while electron attracting groups has the opposite effect. It is therefore not surprising that the alkoxy- and alkyl- substituted PPV's together with the poly-thiophene P3HT belong to the first group, while the fluorinated and cyano substituted PPV's together with the imine analogues (**12**, **13** and **14**) belong to the last. Changing substituents may also alter the geometry of the molecules through e.g. steric effects causing the π-conjugation of the backbone to either decrease or increase. Brédas and Heeger have published a theoretical investigation of these effects using a reasonably simple approach to calculate the band structure. They also conclude that changes in geometry may offset the results [13]. Normally, an offset of the ionisation potential (IP) relative to the vacuum level of gold in the instrument is observed. This offset (Δ) is computed as the difference $h\nu - (BE_{max} + \mathbf{E_F^{VB}}) - \Phi_{Au}$, where BE_{max} is the cut-off at high binding energy. This Δ is usually attributed to dipole layers at the polymer-vacuum interfaces. Typical values are in the range of a few eV as seen from Table 2. It is however notable that the larger values are found for the PPV's substituted with electron withdrawing substituents (**11**, **12**, **13** and **14**). A very large value of –3.1 eV is found in the case of polymer **13**, which has both fluorine substitution and imine groups in place of the ethylene bridges. These types of PPV's have not been studied using UPS previously. The film thickness is another factor that may influence the Δ value, since the dipoles possibly are larger for thicker films.

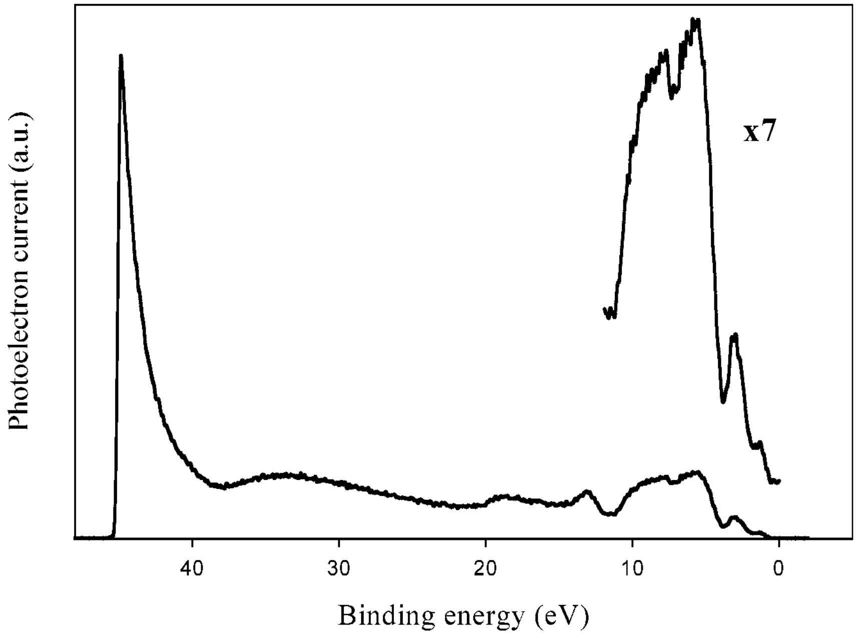


Figure 1. Ultraviolet photoelectron spectra of **3**. The incident photons had an energy of 50 eV and the binding energy scale is referenced to the Fermi level of gold. The secondary electron cut-off (BE_{max}) is seen as the left most edge, while the onset of the photoelectrons (E_F^{VB}) is seen to the right.

The UPS measurements giving the energy at the top of the valence band is combined with the optical band gap obtained from absorption spectroscopy to make a sketch of the upper part of the electronic structure shown in Figure 2. This graphical representation illustrates that it is indeed possible to tune the electronic properties over a wide range. The band gap is fairly constant in these compounds at about 2-2.5 eV while the position of the HOMO energy can be varied over nearly 2 eV.

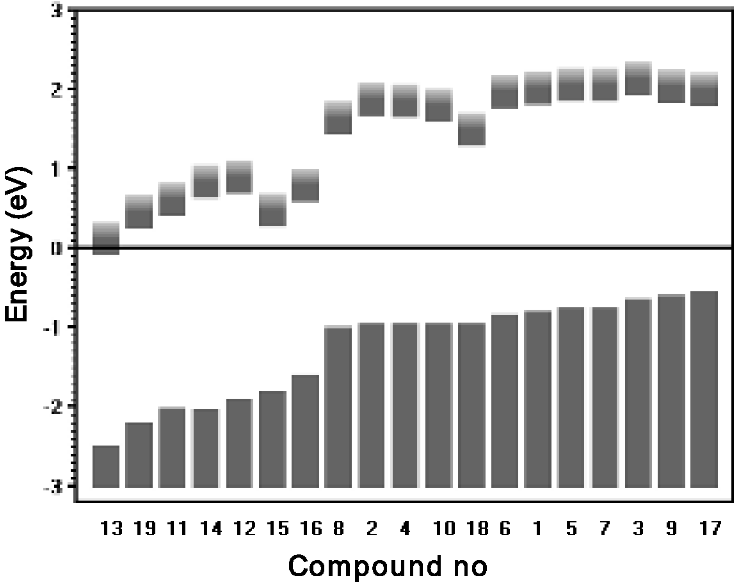


Figure 2. Sketch of the top most electronic structure of the polymers studied, arranged after increasing HOMO level. The order follows the pattern with PPV's having electron withdrawing substituents on the left, while the electron rich polymers are placed to the right. The zero level corresponds to the Fermi level of the gold substrate.

It must be remembered however, that the exact position of energy levels measured in the UPS experiments depend on the metal substrate used, since band bending occurs near the interface [19]. The alkyl compounds **1**-**7**, the alkoxy compounds **8**, **9** and MEH-PPV, the alkylthio compound **10** and the polythiophene P3HT constitutes a fairly homogeneous group with a high position of the HOMO-LUMO energy levels. Electron injection into the LUMO can be achieved with metal electrodes having a low work function such as calcium (ca. 3 eV or about 2 eV higher than the gold substrate used), while e.g. ITO (indium tin oxide) can be used for hole injection into the HOMO. MEH-PPV stands a little out in this series with a somewhat smaller band gap. This may be due to the presence of a higher number of electron donating substituents compared to e.g. **8** and **9**. Substitution with cyano groups at the vinylenes (**16** and CN-MEH-PPV), fluorination of one benzene ring (**11** and **13**) or replacement of the vinylene with imine groups (**12**, **13** and **14**) lowers the HOMO and LUMO energies considerably. Metals with higher work functions such as aluminium can then be used for electron injection. It is perhaps not surprising that having both imine substitution at the vinylenes and fluorinated benzene rings, as in compound **13,** results in the lowest energies. In short, figure 2 sums up the energy level range available to the PPV series at present. Electron donating substituents in general shift the positions of the energy levels up while electron withdrawing substituents act oppositely. It may also be stated that the same set of levels can be reached with differently substituted compounds.

Conclusions

A series of PPV's with an alternating substituent pattern is presented with two long chain groups connected to one benzene ring through carbon, oxygen or sulfur. The other benzene ring was in some instances fully fluorinated. The vinylene group was varied by substitution with cyano groups or replaced by imines. UPS measurements and absorption spectroscopy on the collected sixteen different PPV's together with three reference compounds MEH-PPV, CN-MEH-PPV and P3HT was used to construct a sketch of the uppermost part of the electronic structure. The optical band gap ranged between 2 and 2.7 eV while the highest occupied levels (the HOMO) varied between being 0.55 and 2.5 eV lower than the Fermi level of the gold substrate. Together with previous results this picture should aid the selection of PPV type polymers for use in electronic devices such as photo voltaic cells, FET's and OLED's.

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References

1. Huitema HEA, Gelinck GH, van der Putten JBPH, Kuijk KE, Hart CM, Cantatore E, Herwig PT, van Breemen AJJM, de Leeuw DM (2001) 414: 599.
2. Ho PKH, Kim J-S, Burroughes H, Becker SFY, Brown TM, Caclalli F, Friend RH (2000) Nature 404: 408.
3. Yang Y (1997) Mater. Res. Soc. Bull. 22: 16.
4. Friend RH, Gymer RW, Holmes AB, Burroughes JH, Marks RN, Taliani C, Bradley DDC, Dos Santos DA, Brédas J-L, Lögdlund M, Salaneck WR, (1999) Nature 397: 121.
5. Dittmer JJ, Marseglia EA, Friend RH (2000) Adv. Mater. 12: 1270.
6. Granström M, Petritsch K, Arias AC, Lux A, Andersson MR, Friend RH (1998) Nature 395: 257.
7. Kraft A, Grimsdale AC, Holmes AB (1998) Angew. Chem. Int. Ed. 37: 402.
8. Salaneck WR, Lögdlund M, Fahlman M, Greczynski G, Kugler T (2001) Materials Science and Engineering R34: 121. Greczynski G, Fahlman M, Salaneck WR, Johansson, N, dos Santos DA, Dkhissi A, Brédas J-L (2002) J. Chem. Phys. 116: 1700.
9. Kugler T, Lögdlund M, Salaneck WR (1999) Acc. Chem. Res. 32: 225.
10. Fahlman M, Beljonne D, Lögdlund M, Friend RH, Holmes AB, Brédas J-L, Salaneck WR (1993) Chem. Phys. Lett. 214: 327.
11. Veenstra SC, Heeres A, Stalmach U, Wildeman J, Hadziioannou G, Sawatsky GA, Jonkman HT (2002) Mat. Res. Soc. Symp. Proc. 708: 15.
12. Leuze M, Hohloch M, Hanack M (2002) Chem. Mater. 14: 3339.
13. Brédas J-L, Heeger AJ (1994) Chem. Phys. Lett. 217: 507.
14. Krebs FC, Jørgensen M (2002) Macromolecules 35: 7200.
15. Krebs FC, Jørgensen M (2002) Macromolecules 35: 10233.
16. Krebs FC, Jørgensen M (2003) Macromolecules 36: 4374.
17. Krebs FC, Jørgensen M (2003) Synth. Met. submitted.
18. Krebs FC, Jensen T (2003) J. Fluor. Chem. 120: 77.
19. Ishii H, Sugiyama K, Ito E, Seki K (1999) Adv. Mater. 11: 605.