

Highly luminescent poly[(*m*-phenylenevinylene)-*co*-(*p*-phenylenevinylene)] derivatives synthesized via metathesis condensation (ADMET)

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Dedicated to Prof. Dr. Klaus Hummel on the occasion of his 70th birthday

Abstract

In this paper, we report on the synthesis of poly(phenylenevinylene)s containing *m*-linked phenylene groups in order to reduce the length of conjugation, which is an important tool to influence the color of photo- and electroluminescence.

Various substituted and unsubstituted divinylbenzenes and 4,4'-divinylbiphenyl were synthesized as monomers. These were polymerized via diene metathesis condensation, acyclic diene metathesis (ADMET), using the fluorinated Schrock-type initiator [Mo(=NAr)(=C(H)CMe₃)(OCMe(CF₃)₂)₂]; (Ar = 2,6-diisopropyl-phenyl). The neat poly(phenylenevinylene)s suffer from a very low solubility. To overcome this problem, substituents were introduced into the monomers, and copolymerization was performed with *exo,exo*-norbornene-2,3-dioldiacetate. The polymers were characterized by ¹H-NMR, FT-IR, UV/VIS and GPC analysis. Photoluminescence (PL) spectra were taken and used to evaluate the photophysical properties of the oligomers and copolymers, which showed solid-state PL-quantum efficiencies of up to 52%. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Poly(*m,p*-phenylenevinylene)s; ADMET; Conjugated polymers; Photoluminescence; Quantum efficiencies; Metathesis polymerization

1. Introduction

Conjugated polymers and oligomers have been investigated intensively because of their optical and optoelectronic properties. These properties make them interesting for applications in various devices such as light emitting diodes [1–4], photodiodes [5,6], photovoltaic

cells [7,8], or optically pumped lasers [9–13]. Depending on the HOMO–LUMO energy gap of the polymer, it is possible to fabricate devices that emit any color from the UV to the IR region [14–16]. The energy gap can be influenced by the type of the main chain of the polymer itself, by introduction of electron withdrawing or donating substituents or by variation of the conjugation length [14–22]. The conjugation of poly(*p*-phenylenevinylene) (PPV) or poly(*p*-phenylene) (PPP) derivatives can be interrupted either by saturated bridges [17] or by *ortho*- or *meta*-linkages [18,21,22]. This leads

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to a hypsochromic shift of the UV/VIS absorption and the photoluminescence (PL) emission spectra.

The interruption of the conjugation also affects the PL quantum efficiency. This efficiency increases as the formed excitons are hindered to migrate to quenching sites [18,21]. It is very important to improve the PL efficiency of the polymers to make the resulting optoelectronic devices suitable for commercial use. On the basis of a simple spin statistics argument, an upper limit for the internal EL quantum efficiency of 25 % of the solid state PL efficiency is estimated [23].

One of the most promising and best-investigated classes of conjugated polymers is PPV and its derivatives. Several ways to synthesize these polymers have been described in the past.

Examples of these methods are:

a two-step synthesis via precursor routes [1,24,25],
dehydrohalogenation [26],
the Wittig [21,22] or the Heck [27–29] condensation,
ring opening metathesis polymerization (ROMP) [25,30,31], and
acyclic diene metathesis (ADMET) [30,32,33].

As mentioned above, tailoring the conjugation length leads to control of color and also to higher PL-quantum efficiencies [18–22]. It has already been shown that ROMP is well suited for the synthesis of well-defined block copolymers containing PPV blocks of different segment lengths [31]. Using two difunctionalized monomers “A” and “B,” the Wittig and Heck reaction can lead to alternating copolymers where the comonomers form the repeating unit “AB” [18,21,22], while other condensation methods yield statistical copolymers.

On the other hand, it has been reported that via the Heck route prepared PPVs contain more or less defects due to formation of 1,1-vinylidene moieties [29]. The Wittig route leads to a

high amount of *cis*-vinylene units [21]. In addition, the reaction conditions required by some of the above mentioned methods are quite harsh, sometimes they require high temperatures. Therefore, we chose the metathesis condensation reaction for the polymer synthesis using a highly active carbene initiator of the Schrock type $[Mo(=NAr)(=C(H)CMe_3)(OCMe(CF_3)_2)_2]$; (Ar = 2,6-diisopropylphenyl). In this way, we were able to synthesize copolymers containing *m*-linkages by ADMET. *Exo,exo*-norbornene-2,3-dioldiacetate, 4,4'-divinylbiphenyl and various substituted and unsubstituted divinylbenzene molecules were used as monomers. A broad range of copolymers was synthesized.

2. Experimental

2.1. General aspects

The FT-IR spectra were obtained on a BOMEM M 100 FT-IR spectrometer, 1H -NMR on a Bruker B-Hs 90 90 MHz or on a Varian Gemini at 200 MHz, ^{13}C -NMR at 50 MHz. UV/Vis spectra were performed with a HP 8452A diode array spectrophotometer. PL spectra were taken with a high-resolution apparatus consisting of a Jobin Yvon HR649 monochromator, a Hamamatsu R 643-02 photomultiplier and a 1000-W Xe-lamp in combination with a Jobin Yvon H10DUV monochromator, MS with a Kratos Profile mass spectrometer and gel permeation chromatograms were detected with a Waters 410 differential refractometer (two PL gel 5 μ Mixed-C columns, chloroform as the eluent, 1-ml/min flow rate, room temperature, calibration with narrow distributed polystyrene standards bought from PSS Mainz).

Toluene, tetrahydrofuran and diethylether were dried over Na/K and distilled under an argon atmosphere; CH_2Cl_2 was dried over CaH_2 and distilled under inert gas. DMF was dried

over a molecular sieve 3 Å under inert gas and distilled under reduced pressure. Pyridine was dried over a molecular sieve 3 Å.

The following chemicals were purchased from Fluka: terephthalaldehyde, isophthalaldehyde, methyltriphenyl phosphonium bromide, 2,6-di-*t*-butyl-4-methyl-phenol (BHT), 4,4'-dibromobiphenyl, sodium hydride, copper cyanide, 2,4-dibromophenol, lithium aluminium hydride, dimethylaminopyridine. Diisobutylaluminium hydride and 3,5-dibromobenzoic acid were purchased from Aldrich, and potassium carbonate was purchased from Merck.

2.2. Synthesis of the monomers

The vinylic monomers were synthesized from the corresponding aldehydes in Wittig reactions following methods described in literature [34]. The purity of the monomers was determined by GC measurements (Hewlett Packard Series 6890 Gas Chromatograph with FID, HP 5 Column (30 m × 0.25 mm × 0.25 μm), He was the carrier gas. The polymerization solutions contained 1–5 BHT (stabilizer). The polymerization was not affected in any case by this substance. 4,4'-Diformylbiphenyl and the substituted isophthalaldehydes were obtained from the bromo-compounds in three step reactions analogous to previously published procedures for the preparation of dialkyl- and dialkoxy-terephthaldehydes [26,27] (Schemes 1 and 2).

2.2.1. 1,4-Divinylbenzene (DVB 1) **1**

Prepared from terephthalaldehyde; for details see Ref. [34]; yield: 78%, colorless liquid: ¹H-NMR (CDCl₃): 7.35 (s, 4H, arom), 6.75 (dd, 2H, α-vinyl), 5.77 (dd, 2H, *cis*-β-vinyl), 5.27 (dd, 2H, *trans*-β-vinyl) ppm; ¹³C-NMR (CDCl₃): 137.17, 136.54, 126.46, 113.83 ppm; FT-IR (NaCl): 3083/3035 (CH-stretch vinyl + arom.), 1626/1509 (C=C stretch), 1120 (CH in plane, *p*-subst. arom.), 996/913 (CH out of plane, terminal vinyl), 846 (CH out of plane, *p*-subst. arom.), 668, 447 cm⁻¹; MS (EI): *m/z* = 130 (M⁺, 100%), 115 (29%), 77 (10%), 63 (10%), 51 (16%), 40 (6%).

2.2.2. 1,3-Divinylbenzene (DVB 2) **2**

Prepared from isophthalaldehyde; for preparation details see Ref. [34]; yield: 82%, colorless liquid: ¹H-NMR (CDCl₃): 7.51 (s, 1H arom.), 7.37 (m, 3H, arom.), 6.80 (dd, 2H, α-vinyl), 5.80 (dd, 2H, *cis*-β-vinyl), 5.29 (dd, 2H, *trans*-β-vinyl) ppm; ¹³C-NMR (CDCl₃): 137.88, 136.81, 128.77, 125.61, 124.33, 113.83 ppm; FT-IR (NaCl): 3080/3050 (CH-stretch vinyl + arom.), 1632/1600/1509 (C=C stretch), 1120 (CH in plane, *m*-subst. arom.), 990/905 (CH out of plane terminal vinyl), 801/702 (CH out of plane *m*-subst. arom) cm⁻¹; MS (EI): *m/z* = 130 (M⁺, 100%), 115 (35%), 102 (6%), 77 (12%), 63 (10%), 51 (17%), 40 (12%).

2.2.3. 4,4'-Dicyanobiphenyl **3**

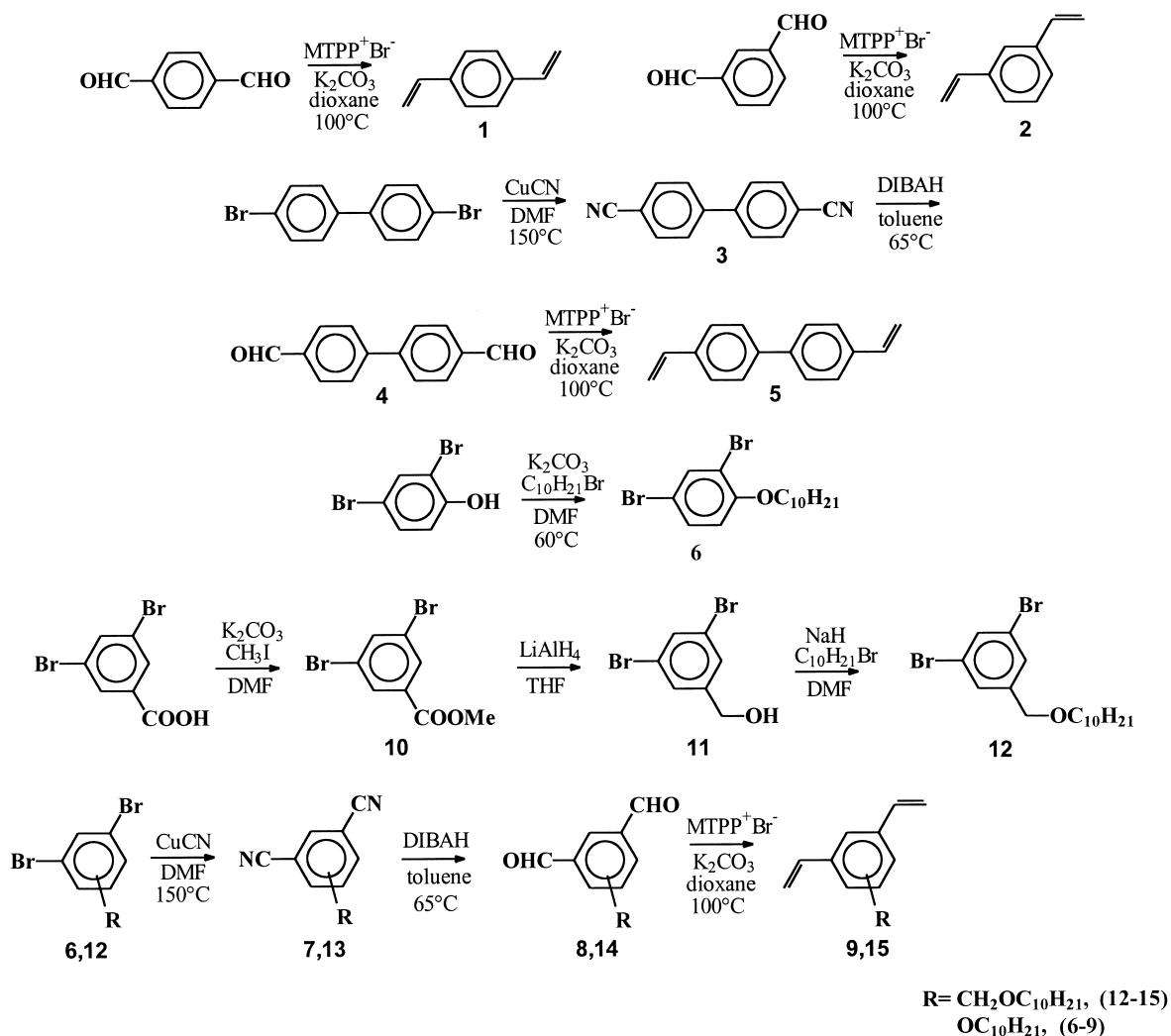
Prepared from 4,4'-dibromobiphenyl; for details see Ref. [32]; yield: 47%, white solid: ¹H-NMR (CDCl₃): 7.81 (d, 4H arom.), 7.72 (d, 4H, arom.) ppm; FT-IR (KBr): 3072/3034 (CH-stretch arom.), 2224 (CN stretch), 1602/1490 (C=C stretch arom.), 1186/1121 (CH in plane arom.), 818 (CH out of plane *p*-subst. arom.) cm⁻¹; MS (EI): 204 (M⁺, 100%), 177 (7%).

2.2.4. 4,4'-Diformylbiphenyl **4**

Prepared from **3**; for details see Ref. [32]; yield: 63%, white flat crystals: ¹H-NMR (CDCl₃): 10.10 (2H, aldehyde), 8.01 (d, 4H arom.), 7.82 (d, 4H, arom.) ppm; FT-IR (KBr): 2827/2740 (CH stretch aldehydes), 1683 (C=O stretch), 1600/1561 (C=C stretch arom.), 1387,1312, 1211/1006 (CH in plane, *p*-subst. arom.), 1168, 820 (CH out of plane *p*-subst. arom.), 659, 549 cm⁻¹; MS (EI): *m/z* = 210 (M⁺ 100%), 181 (7%), 152 (53%), 104 (7%), 76 (20%).

2.2.5. 4,4'-Divinylbiphenyl (DVBi) **5**

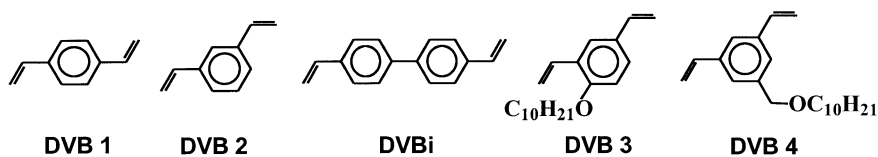
Prepared from **4**; for details see Ref. [34]; yield: 76%, white solid: ¹H-NMR (CDCl₃): 7.61 (d, 4H arom.), 7.47 (d, 4H, arom.) 6.81 (dd, 2H, α-vinyl), 5.83 (dd, 2H, *cis*-β-vinyl), 5.32 (dd,



Scheme 1. Monomer synthesis.

2H, *trans*- β -vinyl) ppm; ¹³C-NMR (CDCl₃): 140.13, 136.74, 136.47, 127.10, 126.76, 114.02 ppm; FT-IR (KBr): 3085/3034/3002 (CH stretch vinyl + arom.), 1624/1497 (C=C

stretch), 993/903 (CH out of plane terminal vinyl), 830 (CH out of plane arom.) cm⁻¹; MS (EI): m/z = 206 (M⁺, 100%), 189 (9%), 178 (12%), 103 (7%), 89 (6%), 76 (7%).



Scheme 2. Synthesized monomers.

2.2.6. 2,4-Dibromo-1-decyloxybenzene **6**

Prepared from 2,4-dibromophenol; for details see Ref. [35]; yield: 94%, colorless liquid: $^1\text{H-NMR}$ (CDCl_3): 7.65 (d, 1H arom.), 7.31 (dd, 1H, arom.) 6.72 (d, 1H, arom.), 3.95 (t, 2H, $-\text{OCH}_2-$), 1.82 (m, 2H, methylene), 1.31 (m, 14H, methylene), 0.89 (t, 3H, methyl) ppm; FT-IR (NaCl): 3065 (CH stretch arom.), 2933/2862 (CH stretch alkyl), 1579/1560 ($\text{C}=\text{C}$ stretch arom.), 1469 (CH deformation methylene), 1391 (CH deformation methyl), 1266/1048 ($\text{C}-\text{O}$ stretch), 870/801 (CH out of plane 1,2,4- subst. arom), 696, 637 cm^{-1} ; MS (EI): $m/z = 394$ (M^+ , 4%), (392 (M^+ , 7%), 390 (M^+ , 4%), 252 (100%), 172 (8%), 85 (14%), 69 (28%), 55 (52%), 43 (27%).

2.2.7. 2,4-Dicyano-1-decyloxybenzene **7**

Prepared from **6**; for details see [32]; yield: 86%, white solid: $^1\text{H-NMR}$ (CDCl_3): 7.82 (s, 1H, arom.), 7.72 (d, 1H, arom.), 7.03 (d, 1H, arom.), 4.14 (t, 2H, $-\text{OCH}_2-$), 1.85 (m, 2H, methylene), 1.22 (m, 14H, methylene), 0.91 (t, 3H, methyl) ppm; FT-IR (KBr): 3112/3088/3056 (CH stretch arom.) 2950/2920/2859 (CH stretch aliph.) 2229 (CN stretch), 1604/1568/1505 ($\text{C}=\text{C}$ stretch arom.), 1469 (CH deformation methylene), 1304, 1292, 1070, 976, 924, 840 (CH-out of plane arom.), 511, 408 cm^{-1} ; MS (EI): $m/z = 284$ (M^+ , 4%), 140 (17%), 85 (53%), 71 (61%), 57 (100%), 43 (76%).

2.2.8. 1-Decyloxy-2,4-diformylbenzene **8**

Synthesized from **7**; for details see Ref. [32]; yield: 70%, white solid: $^1\text{H-NMR}$ (CDCl_3): 10.51 (s, 1H aldehyde), 9.94 (s, 1H, aldehyde), 8.33 (d, 1H, arom.), 8.10 (dd, 1H, arom.), 7.13 (d, 1H, arom.), 4.19 (t, 2H, $-\text{OCH}_2-$), 1.90 (q, 2H, methylene), 1.61–1.18 (m, 14H, methylene), 0.91 (t, 3H, methyl) ppm; $^{13}\text{C-NMR}$ (CDCl_3): 190.25 (aldehyde), 188.72 (aldehyde), 165.63/135.64/131.89/129.46/124.87/113.16 (arom.), 69.44 ($-\text{O}-\text{C}-$), 31.92/29.56–28.95/26.00/22.72/14.16 (aliph.) ppm; FT-IR (KBr): 3078/3000 (CH stretch arom.), 2952/2916/2850 (CH stretch aliph.), 1685

($\text{C}=\text{O}$ stretch aldehyde) 1604/1503 ($\text{C}=\text{C}$ stretch arom.), 1469 (CH deformation methylene), 1287, 1250 (CO stretch), 832 (CH-out of plane arom.), 690 cm^{-1} ; MS (EI): $m/z = 290$ (M^+ , 54%), 149 (100%), 85 (34.5%), 71 (40%), 57 (85%), 43 (83%).

2.2.9. 1-Decyloxy-2,4-divinylbenzene (DVB **3**) **9**

Synthesized from **8**; for details see Ref. [34]; yield: 80%, colorless liquid: $^1\text{H-NMR}$ (CDCl_3): 7.53 (d, 1H, arom.), 7.28 (dd, 1H, arom.), 6.82 (d, 1H, arom.), 7.06 (dd, 1H, α -vinyl), 6.68 (dd, 1H, α -vinyl), 5.80 (dd, 1H, *cis*- β -vinyl), 5.64 (dd, 1H, *cis*- β -vinyl), 5.28 (dd, 1H, *trans*- β -vinyl), 5.15 (dd, 1H, *trans*- β -vinyl), 4.00 (t, 2H, $-\text{OCH}_2-$), 1.83 (q, 2H, methylene), 1.6–1.2 (m, 14H, methylene), 0.90 (t, 3H, methyl) ppm; $^{13}\text{C-NMR}$ (CDCl_3): 156.23/136.39/131.80/130.09/126.78/126.69/124.48/114.49/111.93/111.71 (arom. + vinyl), 68.53 ($-\text{O}-\text{C}-$), 31.97/29.77/29.63/29.44/29.39/29.34/26.18/22.75/14.17 (aliph.) ppm; FT-IR (CaF): 3080 (CH stretch arom. + vinyl), 2926/2848 (CH stretch aliph.), 1635/1603/1501 ($\text{C}=\text{C}$ stretch arom. + vinyl), 1463 (CH deformation methylene), 1249/1119 (CO stretch) 991/900 (CH out of plane terminal vinyl), 814 (CH-out of plane arom.), 724 (CH_2 rocking) cm^{-1} ; MS (EI): $m/z = 286$ (M^+ , 26%), 146 (100%).

2.2.10. 3,5-Dibromomethylbenzoate **10**

Prepared from 3,5-dibromobenzoic acid; for details see Ref. [35]; yield: 93%, yellowish solid: $^1\text{H-NMR}$ (CDCl_3): 8.11 (d, 2H, arom.), 7.83 (t, 1H, arom.), 3.90 (s, 3H, methyl) ppm; FT-IR (KBr): 3112/3030 (CH stretch arom), 2950 (CH stretch methyl), 1725 ($\text{C}=\text{O}$ stretch ester), 1556 ($\text{C}=\text{C}$ stretch arom.), 1448 (CH deformation methyl), 1424 (CH deformation methylene), 1272/1130 (COC sym. stretch), 971 (CH out of plane, arom.) 887 (CH out of plane, arom.), 763, 739, 669 cm^{-1} ; MS (EI): $m/z = 296$ (M^+ , 41%), 294 (M^+ , 86%), 292 (M^+ , 45%), 265 (48%), 263 (100%), 261 (51%), 237 (17%), 235 (34%), 233 (17%), 154 (13%), 75 (56%).

2.2.11. 3,5-Dibromobenzylalcohol **11**

Prepared from **10**; for details see Ref. [35]; yield: 73%, white solid: $^1\text{H-NMR}$ (acetone- d_6): 7.55 (s, 1H, arom.), 7.50 (s, 2H, arom.), 4.61 (m, 2H, Ar- CH_2O -), 2.82 (s, 1H, alcohol) ppm; FT-IR (KBr): 3475–3200 (OH stretch), 3073 (CH stretch arom), 2929/2898/2842 (CH stretch aliph.), 1585/1556 (C=C stretch arom.), 1420 (CH deformation methylene), 1203, 1100, 1032, 852 (CH out of plane arom.), 744, 688 (ring deformation) cm^{-1} ; MS (EI): $m/z = 268$ (M^+ , 35%), 266 (M^+ , 76%), 264 (M^+ , 41%), 185 (62%), 157 (39%), 77 (100%), 51 (20%).

2.2.12. 1,3-Dibromo-5-decyloxymethylbenzene **12**

Prepared from **11**; for details see Ref. [35]; yield: 62%, colorless liquid: $^1\text{H-NMR}$ (CDCl_3): 7.57 (t, 1H, arom.), 7.42 (d, 2H, arom.), 4.43 (s, 2H, aliph.), 3.46 (t, 2H, $-\text{OCH}_2-$), 1.60 (q, 2H, methylene), 1.41–1.21 (m, 14H, methylene), 0.89 (t, methyl) ppm; $^{13}\text{C-NMR}$ (CDCl_3): 142.92/133.02/129.08/122.96 (arom.), 71.31/71.08 ($-\text{O}-\text{C}-$), 31.96/29.71–29.38/26.20/22.74/14.18 (aliph.) ppm; FT-IR (CaF): 3089/3063 (CH stretch arom.), 2948/2853 (CH stretch aliph.), 1587/1557 (C=C stretch arom.), 1471 (CH deformation methylene), 1424 (CH deformation Ar- CH_2-O), 1352 (CH deformation methyl), 1198, 1112 (CO stretch), 848 (CH out of plane arom) 741 cm^{-1} ; MS (EI): $m/z = 406$ (M^+ , 1%), 406 (M^+ , 3%), 406 (M^+ , 1%), 266 (76%), 250 (100%), 185 (6%), 169 (25%), 83 (25%), 43 (21%).

2.2.13. 1,3-Dicyano-5-decyloxymethylbenzene **13**

Prepared from **12**; for details see Ref. [32]; yield: 55%, white solid: $^1\text{H-NMR}$ (CDCl_3): 7.85 (s, 3H, arom., not resolved), 4.55 (s, 2H, Ar- CH_2O -), 3.51 (t, 2H, $-\text{OCH}_2-$), 1.65 (m, 2H, methylene), 1.21 (m, 14H, methylene), 0.90 (t, 3H, methyl) ppm; FT-IR (KBr): 3078 (CH stretch arom.), 2956/2919 (CH stretch aliph.), 2854 (CH stretch aliph.), 2237 (CN stretch),

1597 (C=C stretch arom.), 1486, 1469 (CH deformation methylene), 1361 (CH deformation methyl), 1258, 1158/1123 (CO stretch), 882 (CH out of plane arom.), 716 (CH-out of plane arom.), 680 cm^{-1} ; MS (EI): $m/z = 298$ (M^+ , 9%), 159 (34%), 141 (100%), 83 (48%), 69 (35%), 55 (31%), 43 (27%).

2.2.14. 1-Decyloxymethyl-3,5-diformylbenzene **14**

Prepared from **13**; for details see Ref. [32]; yield: 53%, white-yellowish solid: $^1\text{H-NMR}$ (CDCl_3): 10.10 (s, 2H, aldehydes), 8.26 (s, 1H, arom.), 8.12 (s, 2H, arom.), 4.61 (s, 2H, Ar- CH_2O -), 3.50 (t, 2H, $-\text{OCH}_2-$), 1.65 (m, 2H, methylene), 1.21 (m, 14H, methylene), 0.90 (t, 3H, methyl) ppm; FT-IR (KBr): 3053/3028 (CH stretch arom.), 2951/2920/2853 (CH stretch aliph.), 2804/2748 (CH stretch, aldehydes), 1698 (C=O stretch), 1609/1587 (C=C stretch arom), 1463 (CH deformation methylene), 1366 (CH deformation methyl), 1294, 1135/1104 (CO stretch), 1018, 889 (CH out of plane arom.), 693 (ring deformation), 548 cm^{-1} ; MS (EI): $m/z = 304$ (M^+ , 2%), 166 (42%), 148 (100%), 83 (54%), 69 (34%), 55 (38%), 41 (36%).

2.2.15. 1-Decyloxymethyl-3,5-divinylbenzene (DVB 4) **15**

Prepared from **14**; for details see Ref. [34]; yield: 71%, colorless liquid: $^1\text{H-NMR}$ (CDCl_3): 7.36 (d, 1H, arom.), 7.31 (s, 2H, arom.), 6.73 (dd, 1H, α -vinyl), 5.79 (dd, 1H, *cis*- β -vinyl), 5.28 (dd, 1H, *trans*- β -vinyl), 4.51 (s, 2H, Ar- CH_2O -), 3.48 (t, 2H, $-\text{OCH}_2-$), 1.64 (q, 2H, methylene), 1.61–1.19 (m, 14H, methylene), 0.90 (t, 3H, methyl) ppm; $^{13}\text{C-NMR}$ (CDCl_3): 139.49/138.15/136.88/125.10/123.71/114.42 (arom. + vinyl), 72.90/70.87 ($-\text{O}-\text{C}-$), 32.16/30.02/29.88/29.83/29.75/29.59/26.47/22.94/14.38 (aliph.) ppm; FT-IR (NaCl): 3086 (CH stretch vinyl + arom.) 2923/2843 (CH stretch aliph.), 1620/1592 (C=C stretch arom. + vinyl), 1458 (CH deformation methylene), 1356 (CH deformation

methyl), 1108 (CO stretch), 998/907 (CH out of plane terminal vinyl), 869 (CH out of plane arom), 720 (CH₂-rocking) cm⁻¹; MS (EI): m/z = 300 (M⁺, 6%), 144 (100%), 129 (11%).

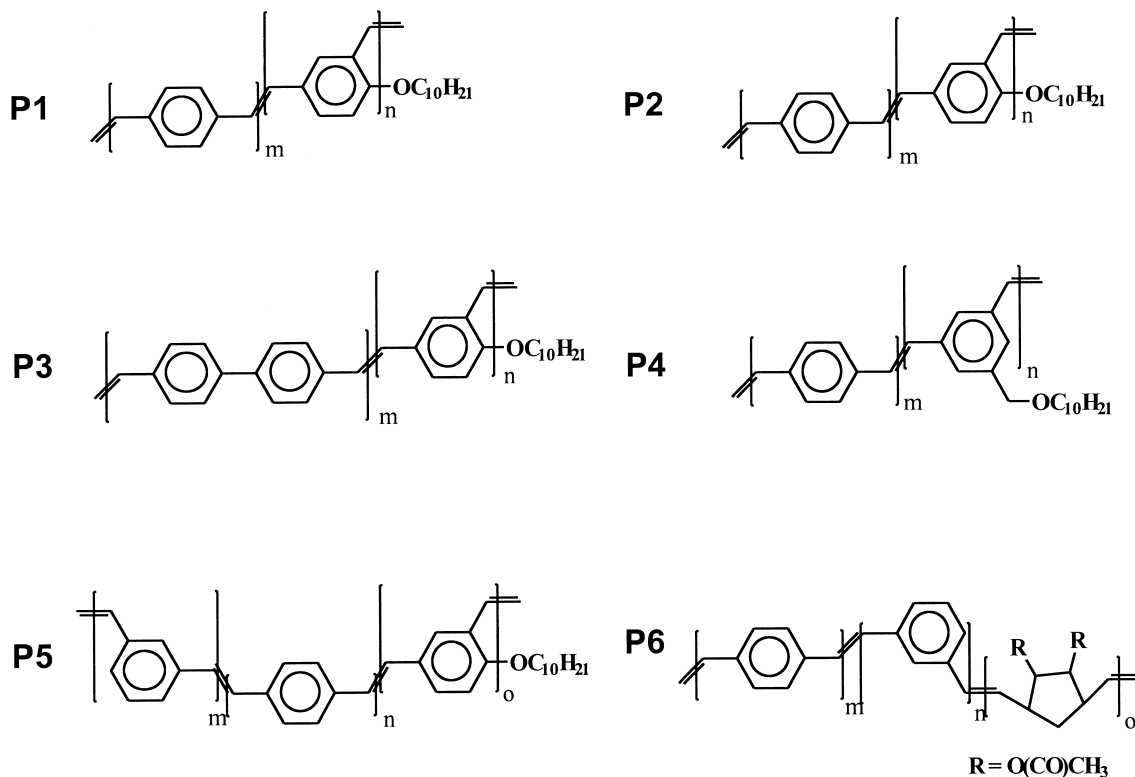
2.2.16. *Exo,exo*-bicyclo[2,2,1]hept-5-enyl-2,3-dioldiacetate **16**

Prepared from *exo,exo*-bicyclo[2,2,1]hept-5-en-2,3-diol; for details see Ref. [36]; yield: 93%, white solid: ¹H-NMR (CDCl₃): 6.08 (d, 2H, olefin), 4.65 (d, 2H, ring pos. 5,6), 2.75 (m, 2H, ring pos. 1,4), 2.01/1.99 (s, 6H, methyl), 1.95 (m, 1H, ring pos 7), 1.70 (m, 1H, ring pos 7') ppm; FT-IR (KBr): 3071 (CH stretch olefin), 2987 (CH stretch methyl) 1743 (C=O stretch

ester), 1374 (CH deformation, methyl), 1254 (CO stretch), 1061 (COC asym stretch), 722 (CH-out of plane *cis*-olefin) cm⁻¹.

2.3. Synthesis of the polymers **P1–P6**

The polymerizations were carried out at room temperature in a N₂-glove box using 1.5-ml dichloromethane (**P1–P5**) or toluene (**P6**) as the solvent for 250 mg of the monomers. The reaction vials were kept open in order to remove the ethylene, which is formed during ADMET reactions as a byproduct. The usual molar ratio initiator/monomer ratio was 1/50. Higher amounts of initiator were necessary in polymer-



(The polymers were synthesized using the following monomer ratios:

P1: DVB 1 : DVB 3 = 1:2

P2: DVB 1 : DVB 2 = 1:1

P3: DVBi : DVB 3 = 1:2

P4: DVB 1 : DVB 4 = 1:1

P5: DVB 1 : DVB 2 : DVB 4 = 1:1:1

P5: DVB 1 : DVB 2 : NbAc₂ = 2:4:1)

Scheme 3. Synthesized polymers.

izations including **DVB 3** as a comonomer. This fact will be discussed later. The reactions were stopped by adding benzaldehyde in a Wittig-like reaction. For purification the polymers were repeatedly precipitated by dropping the solution (CH_2Cl_2) into methanol. The yields of the soluble fractions were between 22% and 32% (Scheme 3).

2.3.1. Poly[(1,4-phenylenevinylene)-co-(1-decyloxy-2,4-phenylenevinylene)] **P1**

$^1\text{H-NMR}$ (CDCl_3): 7.75–6.65 (arom., vinylene, terminal vinyl ($\alpha\text{-H}$)), 5.90–5.55 (terminal vinyl (*cis*- $\beta\text{-H}$)), 5.35–5.10 (terminal vinyl, (*trans*- $\beta\text{-H}$)), 3.9 ($-\text{OCH}_2-$), 1.81–1.25 (methylene), 0.85 (methyl) ppm; FT-IR (NaCl): 3018 (CH stretch arom) 2923/2851 (CH stretch aliph.), 1623/1598/1498 ($\text{C}=\text{C}$ stretch vinylene + arom.), 1466 (CH deformation methylene), 1251/1110 (CO stretch), 1023, 963 (CH out of plane *trans*-vinylene), 807 (CH-out of plane arom.) cm^{-1} .

2.3.2. Poly[(1,4-phenylenevinylene)-co-(1-decyloxy-2,4-phenylenevinylene)] **P2**

$^1\text{H-NMR}$ (CDCl_3): 7.75–6.65 (arom., vinylene, terminal vinyl ($\alpha\text{-H}$)), 5.90–5.55 (terminal vinyl (*cis*- $\beta\text{-H}$)), 5.35–5.1 (terminal vinyl, (*trans*- $\beta\text{-H}$)), 3.90 ($-\text{OCH}_2-$), 1.80–1.25 (methylene), 0.85 (methyl) ppm; FT-IR (CaF): 3017 (CH stretch arom.) 2925/2853 (CH stretch aliph.), 1631/1598/1500 ($\text{C}=\text{C}$ stretch arom.), 1466 (CH deformation methylene), 1252/1110 (CO stretch), 1026, 964 (CH out of plane *trans*-vinylene), 903 (CH out of plane terminal vinyl), 809 (CH out of plane arom.), 731 (CH_2 rocking) cm^{-1} .

2.3.3. Poly[(4,4'-biphenylenevinylene)-co-(1-decyloxy-2,4-phenylenevinylene)] **P3**

$^1\text{H-NMR}$ (CDCl_3): 7.75–6.65 (arom., vinylene, terminal vinyl ($\alpha\text{-H}$)), 5.90–5.61 (terminal vinyl (*cis*- $\beta\text{-H}$)), 5.35–5.09 (terminal vinyl (*trans*- $\beta\text{-H}$)), 3.91 ($-\text{OCH}_2-$), 1.79–1.25

(methylene), 0.85 (methyl) ppm; FT-IR (CaF): 3016 (CH stretch arom.), 2924/2856 (CH stretch aliph.), 1624/1599/1497 ($\text{C}=\text{C}$ stretch vinylene + arom.), 1466 (CH deformation methylene), 1252/1103 (CO stretch), 1015, 965 (CH out of plane *trans*-vinylene), 904 (CH out of plane terminal vinyl), 808 (CH-out of plane arom.), 733 (CH_2 rocking) cm^{-1} .

2.3.4. Poly[(1,4-phenylenevinylene)-co-(1-decyloxymethyl-3,5-phenylenevinylene)] **P4**

$^1\text{H-NMR}$ (CDCl_3): 7.52–7.25 (arom.), 7.15–7.08 (*trans*-vinylene), 6.84–6.67 (terminal vinyl, ($\alpha\text{-H}$)), 5.88–5.75 (terminal vinyl (*cis*- $\beta\text{-H}$)), 5.34–5.25 (terminal vinyl, (*trans*- $\beta\text{-H}$)), 4.58/4.55 ($\text{Ar}-\text{CH}_2-\text{O}$), 3.58–3.49 ($\text{O}-\text{CH}_2-\text{R}$), 1.61–1.19 (methylene), 0.88 (methyl) ppm; FT-IR (NaCl): 3067/3023 (CH stretch arom.), 2921/2850 (CH stretch aliph.), 1629/1592/1510 ($\text{C}=\text{C}$ stretch vinylene + arom.), 1456 (CH deformation methylene), 1359 (CH deformation, methyl), 1156/1105 (CO stretch), 962 (CH out of plane *trans*-vinylene), 904 (CH out of plane terminal vinyl), 844 (CH out of plane arom.), 691 (ring deformation, arom.), 540 cm^{-1} .

2.3.5. Poly[(1,3-phenylenevinylene)-co-(1,4-phenylenevinylene)-co-(1-decyloxymethyl-3,5-phenylenevinylene)] **P5**

$^1\text{H-NMR}$ (CDCl_3): 7.52–7.25 (arom.), 7.15–7.08 (*trans*-vinylene), 6.84–6.67 (terminal vinyl, ($\alpha\text{-H}$)), 5.88–5.75 (terminal vinyl (*cis*- $\beta\text{-H}$)), 5.34–5.25 (terminal vinyl (*trans*- $\beta\text{-H}$)), 4.58/4.55 ($\text{Ar}-\text{CH}_2-\text{O}$), 3.58–3.49 ($\text{O}-\text{CH}_2-\text{R}$) 1.60–1.20 (methylene), 0.8 (methyl) ppm; FT-IR (NaCl): 3072/3023 (CH stretch arom.), 2922/2851 (CH stretch aliph.), 1625/1594/1511 ($\text{C}=\text{C}$ stretch vinylene + arom), 1456 (CH deformation methylene), 1360 (CH deformation, methyl), 1104 (CO stretch), 962 (CH out of plane *trans*-vinyl), 904 (CH out of plane terminal vinyl), 844/691 (CH-out of plane arom), 538 (ring deformation) cm^{-1} .

2.3.6. Poly[(1,3-phenylenevinylene)-co-(1,4-phenylenevinylene)-co-(*exo,exo*-norbornenylenediol-2,3-diacetate)] **P6**

$^1\text{H-NMR}$ (CDCl_3): 7.7–7.3 (arom), 7.13 (*trans*-vinylene), 6.95–6.6 (terminal vinyl, (α -H)), 6.45–6.2, 5.9/5.7 (terminal vinyl, (*cis*- β -H)), 5.5–5.3, 5.35/5.2 (terminal vinyl (*trans*- β -H)), 5.05 (cyclopentane H_2 , H_3), 3.0/2.5 (cyclopentane H_1, H_4), 2.05 (methyl), 1.6–1.2 ppm; FTIR (NaCl): 3020 (CH stretch arom.), 2932/2837 (CH stretch aliph.), 1742 (C=O stretch ester), 1595/1510 (C=C stretch arom.), 1370 (CH deformation, methyl), 1239 (CO stretch), 960 (CH out of plane *trans*-vinylene), 902 (CH out of plane terminal vinyl), 798 (CH out of plane arom.), 692 (ring deformation, arom.), 538 cm^{-1} .

3. Results and discussion

As previously mentioned, polymers consisting of only unsubstituted conjugated units suffer from a very poor solubility. To solve this problem, copolymerization with *exo,exo*-2,3-norbornenylenediol diacetate, or introduction of alkoxyethyl groups into the phenylene moieties was done. Various combinations of divinylbenzene derivatives (**DVB 1–DVB 4**) and 4,4'-divinylbiphenyl (**DVBi**) were copolymerized via ADMET. The Schrock-type hexafluoro initiator [$\text{Mo}(=\text{NAr})(=\text{C}(\text{H})\text{CMe}_3)(\text{OCMe}(\text{CF}_3)_2)_2$] with (Ar = 2,6-diisopropylphenyl) was chosen as it is one of the fastest of the molybdenum initiators. Improvements in the solubility due to copolymerization of unsubstituted divinylbenzenes with *exo,exo*-norbornene-2,3-dioldiacetate

were rather limited. The best solubility obtained in connection with this polymer (**P6**) was around 10 mg/ml (in CHCl_3).

There were still insoluble fractions observed in connection with all polymers. The yields of soluble fractions were between 22% and 32%.

Copolymerizations with **DVB 3** proceeded very slowly. As a possible explanation Thorn-Csanyi et al. suggested, that the oxygen in the *ortho* position to the vinyl group coordinates at the Mo atom of the catalyst and stabilizes the catalytic intermediates [33] (see Fig. 1).

This problem could be overcome by adding high amounts of initiator, 8–10 mol% instead of 2% (which was used for the other reactions), and long reaction times (68 h). However, the polymers showed rather broad sometimes bi- or even multimodal distributions, which on the other hand improved the film forming properties. The polymerization rate of monomer mixtures containing **DVB 4** is much higher, **P4** and **P5** started to precipitate from solution after only half an hour.

3.1. Characterization

The polymers were all greenish-yellow solids, which exhibited an intensive luminescence in solution. Their structures were determined by FT-IR and $^1\text{H-NMR}$ spectroscopy.

Due to the irregular polymer structures, which was caused by the more or less statistical incorporation of the different divinylbenzene molecules, the $^1\text{H-NMR}$ spectra of all the polymers showed a variety of signals in the aromatic region. Detailed interpretation was very difficult because of that.

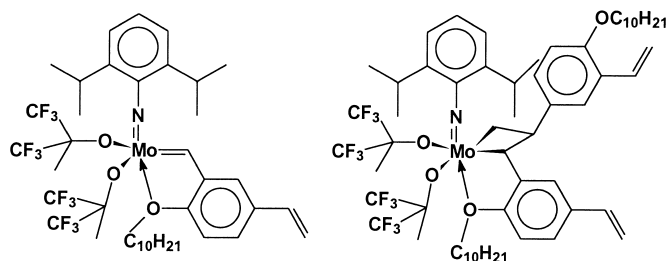


Fig. 1. Stabilization of the catalytic intermediates by coordination of the *o*-oxygen at the molybdenum atom.

The $^1\text{H-NMR}$ of **P1**, **P2** and **P3** showed signals at about 7.45–7.35 and 7.15–7.05 ppm, which corresponded to those of the *trans*-vinylene protons of alkoxy-PPV [33] and the unsubstituted analogs. No peaks were detected at 6.7–6.1 ppm, which could be attributed to *cis*-vinylene bonds. Jacobs et al. reported chemical shifts for the *cis*-vinylene protons of 6.64 and 6.55 ppm in *cis,cis*-2,5-dimethoxy-1,4-bis[2-(2,4,5-trimethoxyphenyl)ethenyl]benzene, and of 6.69 and 6.58 for the *cis,trans*-isomer [37]. Also, **P4** and **P5** did not show any signals of *cis*-vinylene protons, which should be expected near 6.6 ppm according to the reference spectrum of *cis*-stilbene. The *trans*-vinylene protons were observed at about 7.1 ppm again.

These results corresponded to those of earlier published PPV prepared via the ADMET route, where *trans*-configuration was reported [30,32,33].

Polymer **P6** — where ADMET condensation was combined with the ring opening poly-

merization of a norbornene compound — showed resonances at 5.5, 5, 3, 2.65, 2.05 and 1.6–1.2 ppm. These signals were also found in the poly-*exo,exo*-2,3-norbornylenediacetate homopolymer [38]. This is typical of block formation, which was caused by the kinetics of the reaction. Typical $^1\text{H-NMR}$ signals corresponding to the norbornenylene derivative (marked with N, Fig. 2) had vanished already after 4 min of reaction time; until this time, only a small conversion of the divinylbenzenes had occurred. Thus, at the beginning of the polymerization, only polynorbornene was formed, without significant incorporation of the diene compound, then the condensation of the divinylbenzenes led to further elongation of the chains connecting some of the chains, which might explain the multimodal distribution (see below).

The IR spectra of all the polymers showed strong bands corresponding to *trans*-vinylene CH-out of plane vibrations at about 960–965 cm^{-1} . In the region between 670 and

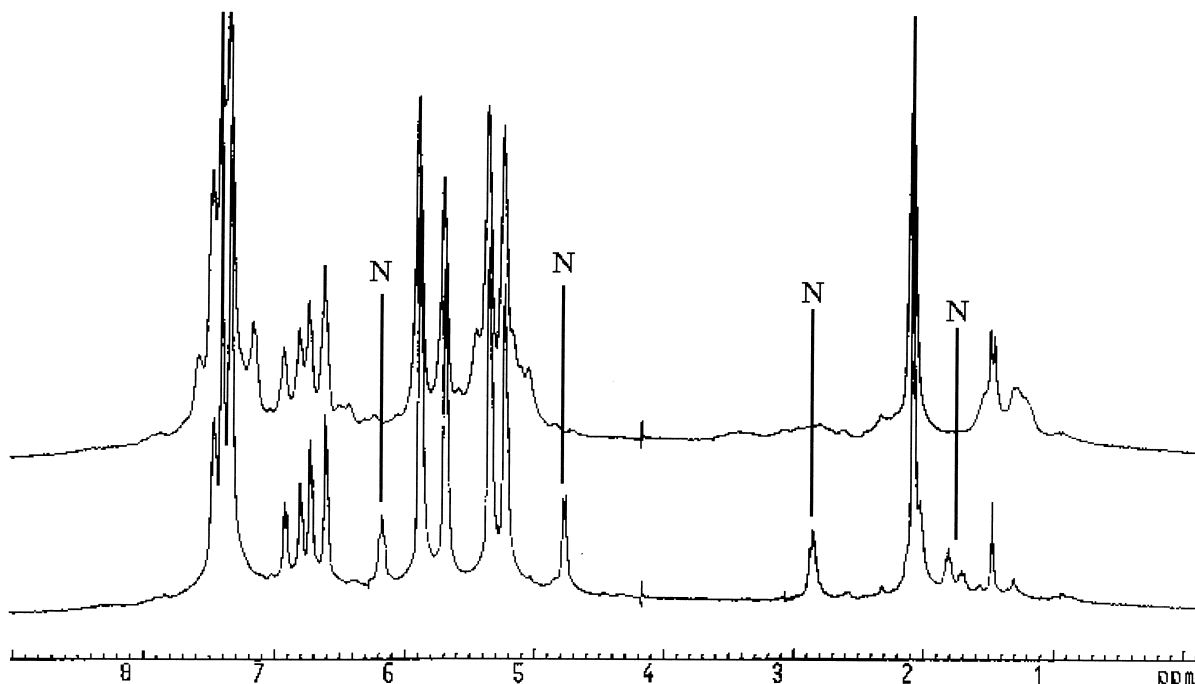


Fig. 2. $^1\text{H-NMR}$ spectra of the monomer mixture used for the synthesis of **P6** (lower graph) and after 4 min of polymerization time (upper graph).

730 cm^{-1} , where the *cis*-vinylene CH-out of plane band was expected, bands caused by ring deformations of *m*-substituted aromatic rings at 690–695 cm^{-1} were found (**P4–P6**). Weak bands at 720–730 cm^{-1} caused by CH_2 -rocking vibrations also occurred (**P1–P5**).

GPC analyses (Fig. 3) showed the polymers to consist of multimodal distributions. **P1**, **P2**, and **P3** exhibited very similar chromatograms, each consisting of a fraction of a molecular weight (M_n) of about 20 000–25 000 g mol^{-1} . The molecular weight of the main fraction was determined to be about 1800–2400 g mol^{-1} . The distributions of the polymers containing **DVB 4** are narrower than those which were observed with polymers synthesized from **DVB 3**. The degree of polymerization of **P5** was lower compared to **P4**. This was due to the higher amount of unsubstituted monomer, the incorporation of which reduced the solubility,

thus causing a precipitation already at low molecular weight.

The copolymer containing norbornene-2,3-dioldiacetate consisted of a small fraction with a number average of 68 000 g mol^{-1} , a relatively broad distributed fraction with 3600 g mol^{-1} and an oligomeric fraction with about 600 g mol^{-1} . A possible explanation for this fact can be that the incorporation of the norbornenylenedioldiacetate was far from being statistical. Monomodale molecular weight distribution would be expected on statistical incorporation of all the monomers. Block formation occurred due to the higher reactivity of the norbornene derivative — a result confirmed by the earlier mentioned measurements of the kinetics of the reaction. In addition, one has to take into account that a vinyl group stops the growth of a polymer chain. Only if the second vinyl group also reacted with a growing chain, a coupling of

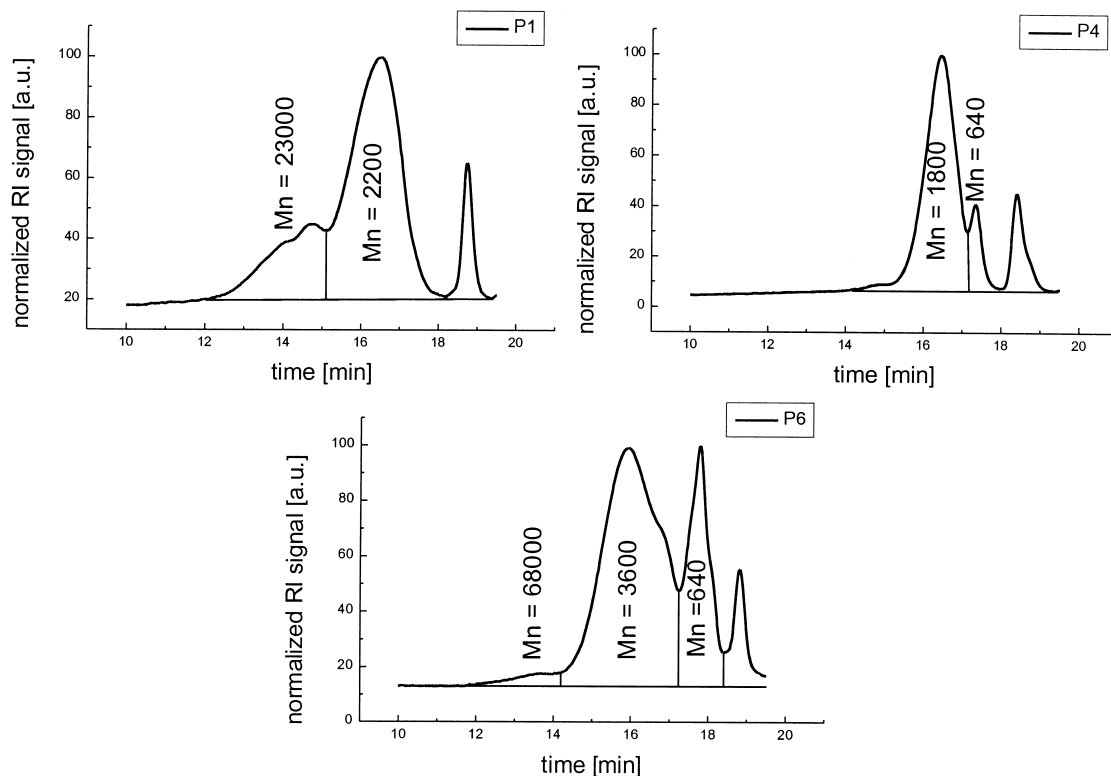


Fig. 3. GPC-chromatograms of **P1**, **P4** and **P6**.

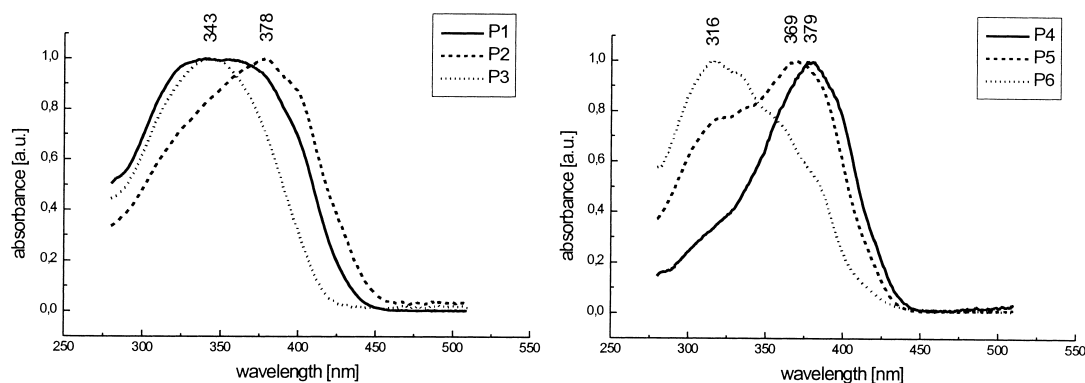


Fig. 4. UV/VIS spectra of the polymers (solution in CH_2Cl_2).

these chains was possible causing a doubling of the molecular weight. If a slow condensation with another diene took place, this did not contribute very much to the elongation of the chain. So, this might have led to the multimodal polymer distribution. Two-dimensional liquid chromatography measurements and/or preparative GPC followed by a spectroscopic investigation of the fractions would give additional information. Such investigations are underway.

3.2. UV/VIS and PL spectra

The UV/VIS absorption (Fig. 4, measured in CH_2Cl_2) and of the PL emission spectra (Fig. 5, thin films on quartz plates) showed dependence on the conjugation lengths within the

polymers. Increasing the ratio of *m*-vinyl over the *p*-vinyl monomer led to a blueshift of the emission and absorption bands meaning that the conjugation length was shortened. **P1** (monomer ratio **DVB 1:DVB 3** = 1:2) absorbed and emitted at shorter wavelengths than the chemically similar **P2**, which was polymerized from a monomer ratio of **DVB 1:DVB 3** = 1:1. The absorption band of **P5** showed a hypsochromic shift compared to that of **P4**. An exception were the solid state emission spectra of **P4** and **P5**, which exhibited only non-significant differences. However the λ_{max} values of the emission spectra of these polymers obtained from the solutions differ by 30 nm (Fig. 6).

Reduction of the λ_{max} of absorption and emission was also observed on replacing phenylene (**P1**) by biphenylene (**P3**) moieties.

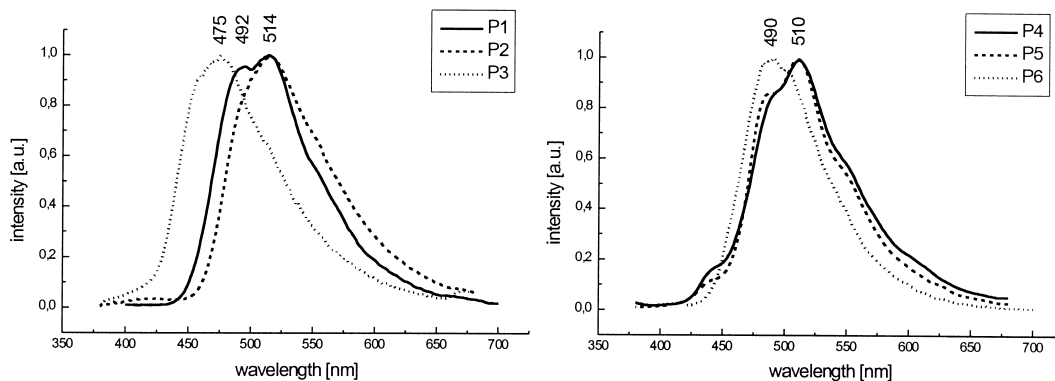


Fig. 5. Photoluminescence spectra (thin films).

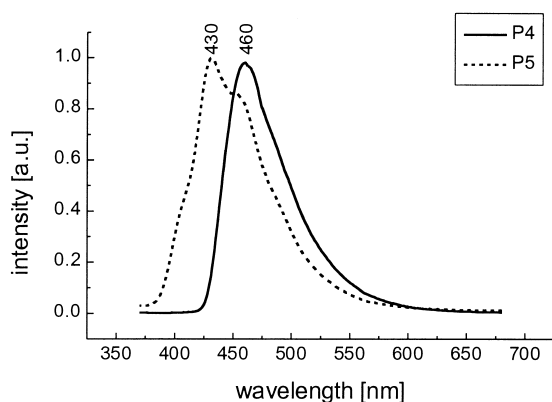


Fig. 6. Photoluminescence spectra of **P4** and **P5** (solution in CH_2Cl_2).

As each single chromophore contributes to the UV/VIS absorption of the molecules, the structure of the spectra is directly connected with the distribution of the different conjugated segments. Due to this fact, it is possible to conclude from the spectra that **P3** had segments with shorter maximum conjugation length than **P1** and **P2**. This matched with the results of the PL measurements, where the emission should occur from these sites.

The solid state emission maxima ranged from 475 nm for **P3** to about 510–515 nm for **P1**, **P2**, **P4**, **P5**. The λ_{max} of **P6** lied at 490 nm. The colors observed were bluegreen (**P3**) and green (**P1**, **P2**, **P4**–**P6**).

PL-quantum efficiency measurements of the films (on quartz plates) have been performed using an integrating sphere according to the method described by Liu et al. [39]. The polymers revealed quantum efficiencies of up to 52%. (**P1**). Other values were 51% (**P6**), 32% (**P5**), 28% (**P4**). **P3** and **P2** exhibited quantum efficiencies of about 20%.

4. Conclusions

The Schrock type initiator $[\text{Mo}(=\text{NAr})(=\text{C}(\text{H})\text{CMe}_3)(\text{OCMe}(\text{CF}_3)_2)_2]$; ($\text{Ar} = 2,6$ -diisopropylphenyl) polymerizes divinylbenzene compounds in an ADMET condensation poly-

merization to the *trans*-isomers with high selectivity. This was proven by FTIR and $^1\text{H-NMR}$ spectroscopy. The UV/VIS absorption and the PL bands showed a dependence on the ratio of the *m*-divinyl over the *p*-divinyl comonomer and therefore on the length of the conjugated segments.

The PL efficiencies of the synthesized copolymers reached pretty high levels (up to 52%), making the materials very interesting for their application in LEDs. But there are still some improvements to be made in connection with solubility. It is necessary to use only substituted divinylbenzene comonomers in order to achieve higher molecular weights and an increased processability of the polymers. As *ortho*-alkoxy substituted divinylbenzenes were converted very slowly due to coordination of the oxygen at the molybdenum atom of the catalyst, it is recommendable that the substituent is alkyl if in *o*-position or is placed in *m*-position if being an alkoxy group.

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