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Poly(*p*-phenylene)s. Synthesis, Optical Properties, and Quantitative Analysis with HPLC and MALDI−TOF Mass Spectrometry

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ABSTRACT: A series of soluble low molecular weight poly(*p*-phenylene)s (PPP) has been synthesized by an excess polycondensation with the Suzuki coupling method. The reaction mixture therefore only contains oligomers of an odd number of phenylene units which are terminated by bromine atoms. The mixture has been preparatively separated into monodisperse fractions of the respective oligomers of up to 17 phenylene units. The absorption and emission spectra as well as the extinction coefficient of each fraction have been measured. On the basis of these data, the effective conjugation length can be estimated to be around 11 phenylene units. The fraction x_i of each oligomer in the reaction mixture has been calculated and quantified by analytical HPLC and MALDI−TOF mass spectrometry. The theoretically expected exponential decay of the fraction sizes with increasing length is found in the HPLC analysis; however, significant deviations are found if analyzed by MALDI−TOF mass spectrometry. Possible reasons for this deviation will be discussed.

Introduction

The outstanding properties of poly(*p*-phenylene) (PPP) make it potentially interesting for various areas of materials science. The rigidity of the polymer backbone, in combination with its conjugation of planar π-systems, make it promising as an electrically conducting material, for molecular composites, nonlinear optics, or electroluminescence.[1] However, the poor solubility of unsubstituted PPP and synthetic difficulties hindered a systematic investigation until solubility could be dramatically increased by attaching flexible side chains to the backbone serving as an “inherent” solvent.[2] Metal-catalyzed coupling reactions such as the Suzuki method for aromatic monomers finally opened the way to high molecular weight PPP.[3,4]

To establish structure−property relationships in conjugated polymers, monodisperse oligomers have often been used as model compounds.[5,6] Above a certain critical length the properties of the oligomers converge into the ones of the high molecular weight polymer. This is of particular interest with respect to the optical and electronic properties. The critical length above which absorption and emission spectra are identical with the high polymer has been defined as the “effective conjugation length” of the material.[5−7]

In contrast to the *p*-phenylene polymer, *p*-phenylene oligomers can be characterized by standard methods such as NMR or mass spectrometry. However, the relative differences of the oligomer properties decrease with increasing length so that a differentiation between two molecules, especially the separation into monodisperse fractions, is not easy.

Therefore, we chose a synthetic method that allows easy access to a mixture of oligomers with the structure of PPP which we call oligo(*p*-phenylene)s (OPPs). They are synthesized by excess polycondensation of AXA/BXB-type monomer systems and consist of only odd numbered phenylene units. Due to the larger molecular weight spacing of these oligomers, this mixture can more easily be separated into the respective oligomers by liquid chromatography. Monodisperse OPPs with defined end groups up to a length of 17 phenylene units have been isolated. Absorption and emission spectra as well as the extinction coefficient of each oligomer have been measured.

On the basis of these data, the elution diagram of the analytical high performance liquid chromatography (HPLC) of the oligomer mixture could be analyzed quantitatively with high accuracy. The obtained distribution was compared to the theoretically expected distribution and the distribution as determined by matrix-assisted laser-desorption ionization time-of-flight mass spectrometry (MALDI−TOF−MS) in order to check the suitability of MALDI−TOF−MS for a direct quantitative analysis of the molecular weight distribution of a *p*-phenylene-type oligomer. This is of particular interest, since it was shown previously, that MALDI−TOF analysis of a rigid rod PPP derivate deviates strongly from the normal MALDI mechanism.[8] The molecules have a significant absorption at the wavelength of the nitrogen laser (337 nm) normally used for MALDI analysis. This absorption causes radical ion formation as opposed to the cation attachment that normally occurs.[9] Thus, it is questionable how and to what extent the determination of the molecular weight distribution by MALDI−TOF mass spectrometry is affected by resonant absorption effects and fragmentation reactions.

In this paper we report on an exact comparison of molecular weight distribution data as obtained by MALDI−TOF mass spectrometry with data of high accuracy measured by oligomer-resolved HPLC to investigate the applicability of direct molecular weight determination by MALDI−TOF mass spectrometry and to elucidate the underlying processes.

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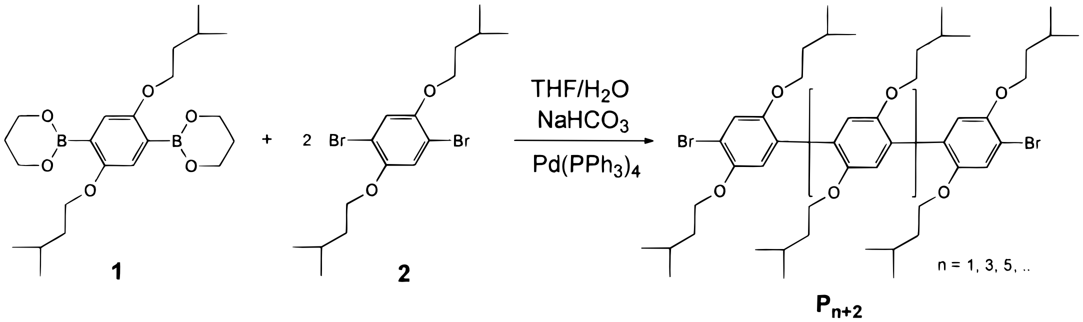

Figure 1. Chemical structure and synthesis of OPPs.

Results and Discussion

Synthesis. Since only a few "classical" organic reactions are known to generate a direct link between aromatic units, metal-catalyzed coupling reactions are commonly used for this purpose.[10,11] In particular, the palladium-catalyzed Suzuki reaction has been applied to couple aromatic bromides with aromatic boronic acids or esters. Since a large range of substituents on the aromatic monomers is tolerated and the reaction is nearly quantitative, the Suzuki method was used as a polymerization reaction yielding high molecular weight polymers.

For the oligomerization reaction in this study diboronic ester−phenylene monomer **1**[12] was reacted with a 2-fold excess of dibromophenylene monomer **2**[13] (see Figure 1). The synthesis of the monomers is described elsewhere.[14] Due to the large excess of the dibromide monomer **2**, only low molecular weight compounds with an odd number of phenylene units terminated by bromine end groups are expected in the reaction mixture.

The number average degree of polymerization $\overline{\mathrm{DP}}_\mathrm{n}$ of an excess polycondensation after complete reaction is given by[15]

$$\overline{\mathrm{DP}}_\mathrm{n} = \frac{1 + r_0}{1 - r_0} \qquad (1)$$

with r_0 being the ratio of the molar amounts of the monomers $r_0 = [\mathrm{AXA}]/[\mathrm{BXB}]$. BXB is the excess component, so that $r_0 < 1$. In this case, only oligomers with odd numbers of repeating units can be present in the reaction mixture after complete reaction. Here, 1 mol of AXA is reacted with 2 mol of BXB, so that r_0 is 0.5 and $\overline{\mathrm{DP}}_\mathrm{n} = 3$. The mole fractions x_i of each oligomer in the reaction mixture are[15]

$$x_i = \overline{\mathrm{DP}}_\mathrm{n} \times {r_0}^{i-1/2} \frac{(1 - r_0)^2}{1 + r_0} \qquad i = 1, 3, 5, ... \qquad (2)$$

Although a 2:1 ratio of the monomers might appear to be the optimum for the generation of the trimer, the resulting fraction of the trimer in the mixture after complete reaction is only $x_3 = 0.250$ according to eq 2. The fraction of the pentamer can be calculated to be $x_5 = 0.125$. Higher oligomers such as the heptamer ($x_7 = 0.062$), nonamer ($x_9 = 0.031$), and so on are also generated. One therefore expects an exponential decay of the fraction sizes of the oligomers with increasing length.

Due to the relatively large size differences of different oligomers, an analytical or preparative separation into the respective monodisperse oligomers is possible by chromatographic methods. Oligomers with a length of nine phenylene units can be separated by column chromatography in a solvent gradient of toluene and petrol-ether. The remaining higher oligomers can be washed from the column and separated by preparative HPLC. Monodisperse oligomers up to a length of 17 phenylene units could be isolated. Both the reaction mixtures and the separated oligomers have been characterized by NMR, analytic HPLC, and mass spectrometry. Properties of these materials, such as crystal structures and phase behavior, are reported elsewhere.[16−18]

Table 1. Absorption and Emission Maxima, Stokes Shift, and Extinction of the OPPs in CH_2Cl_2

oligomer	abs max (nm)	emission max (nm)	Stokes shift (eV)	max extinction (L/cm mol)
P1	302.1	390	0.925	5200
P3	323.9	396	0.697	18600
P5	327.7	401	0.692	29700
P7	333.1	403	0.646	50400
P9	335.0	403	0.625	68400
P11	335.6	403	0.618	80300
P13	336.0	404	0.621	
P15	336.4	404	0.617	
P17	336.2	404	0.619	89000

Optical Properties. The absorption and fluorescence maxima, the Stokes shifts, and the extinction coefficients of the oligomers **P1** to **P15** are summarized in Table 1. The absorption maximum in CH_2Cl_2 solution shifts from 302 nm for the monomer to 336 nm for the higher oligomers. Oligomers of a length of more than 11 phenylene units do not vary significantly from the polymer. The emission maximum in solution also shifts to lower energies from 390 nm for the monomer to 404 nm for the polymer. The extinction coefficients of the oligomers increase superlinearly with the length of the molecule. This is caused by a superposition of two effects: the number of phenylene units per molecule serving as a chromophore increases as well as the extinction per phenylene unit. The shift of the absorption maximum as well as the increasing extinction is visualized in Figure 2. The Stokes shift of the OPPs, here defined as the difference between the energies of the absorption and emission maximum, decreases with the size of the conjugated system.

In a plot of the energy of the absorption maximum vs $1/\mathrm{DP}_\mathrm{n}$ (DP_n being the number of phenylene units), a linear behavior is observed for the shorter oligomers. Above a length of about 11 phenylene units the absorption spectrum is identical with the polymer. The effective conjugation length can therefore be estimated to be in the range of about 11 phenylene units.

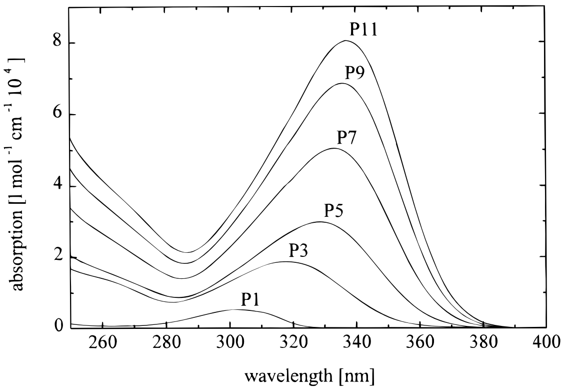

Figure 2. Absorption spectra of OPPs in CH_2Cl_2.

The maximum of the fluorescence for **P7** is already identical to the one for the polymer, even though the critical length above which the properties of the oligomers merge with those of the polymer in the absorption was 11 phenylene units. This deviation might be due to fact that the excited electronic states involved in the absorption and emission process lead to conformational changes of the conjugated system of different size. Absorption of a photon leads to an excited vibronic state of the excited singlet state S_1 which causes a local distortion of the conjugated system with the size of the conjugation length. This state relaxes into the vibronic ground state of S_1 very rapidly. The distortion of this vibronic ground state of S_1 might be less extended than the respective excited vibronic states. In this case, the emission of the heptamer must be identical to the one for the polymer, because the relaxation of the optical excitation takes place from the S_1 vibronic ground state. The experimental error of the absorption and emission maxima is, however, about 1 nm (0.01 eV). These statements have therefore to be confirmed with more exact measurements.

The extrapolation of energies of maximum absorption of various *p*-phenylene oligomers has recently been reported to be in the area of 20 phenylene units.[19] The systems investigated in this paper were, however, ladder systems in which adjacent phenylene units are forced into a planar conformation by chemical bridges both in the electronic ground and excited states. These systems cannot be compared with the *p*-phenylene oligomers described in this study, because the excitation energy of a large conjugated system depends not only on the electronic structure of the system, but also on the geometrical changes of the conjugated backbone at the transition from the ground state to the excited state. The extrapolated values calculated in ref 19 therefore cannot be compared with the effective conjugation length of about 11 phenylene units as determined in this investigation.

The Stokes shift of the oligomers decreases with increasing number of phenylene units. It reaches the value of the polymer at a length of about 11 phenylene units. This behavior is a consequence of the difference between the geometries of the ground and the excited state of these materials. The excited state of conjugated polymers tends to be more planar than the ground state.[20]

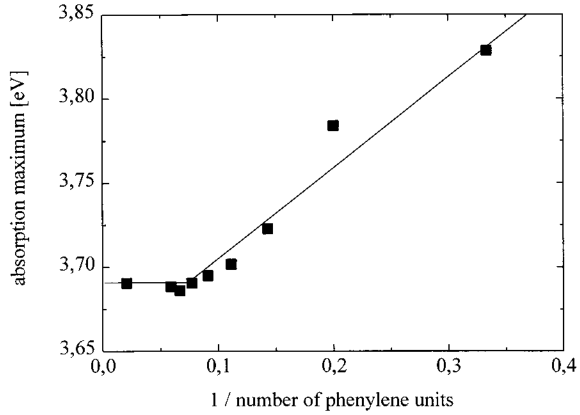

Figure 3. Kuhn plot of absorption maxima of OPPs.

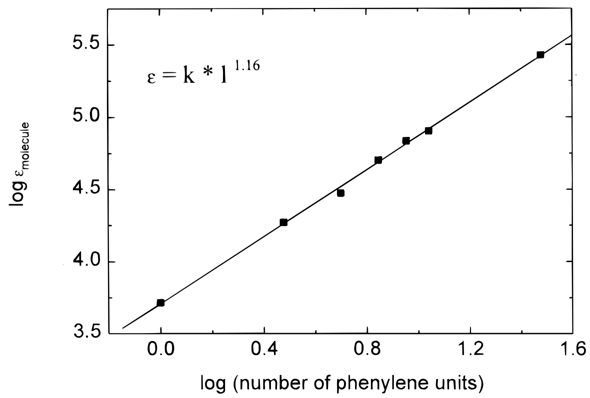

Figure 4. Extinction coefficients of OPPs.

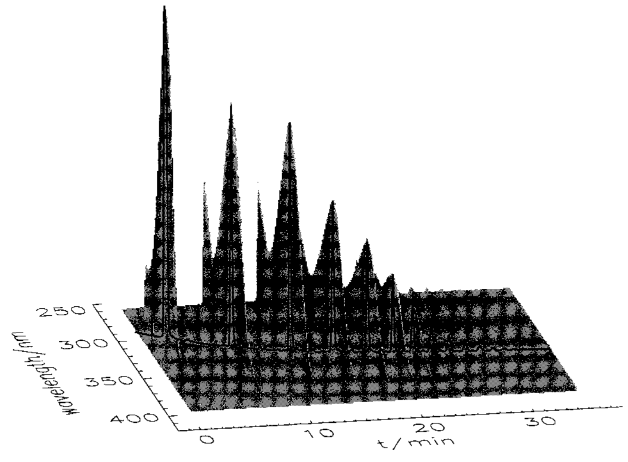

Figure 5. HPLC chromatogram as determined by the diode array detector. The trace line shows the one-dimensional chromatogram (Figure 6) constructed by following the absorption maxima.

The extinction of the OPPs are plotted vs the number of phenylene units in a log–log plot in Figure 4. The extinction per phenylene unit increases with the length of the conjugated system and reaches asymptotically the value of the polymer. This effect is caused by an increase of the oscillator strength with the size of the conjugated system. A linear regression in the log–log plot gives a slope of 1.16:

$$\epsilon \approx n^{\alpha} \quad \text{with} \quad \alpha = 1.16 \tag{3}$$

where ϵ is the extinction coefficient of an oligomer with n phenylene units. Similar power laws have been described in the literature with values for α of about 1.3.[21,22]

Quantitative Analysis by Analytical HPLC and MALDI–TOF–MS. HPLC. Figure 5 shows the two-dimensional chromatogram as determined by the diode

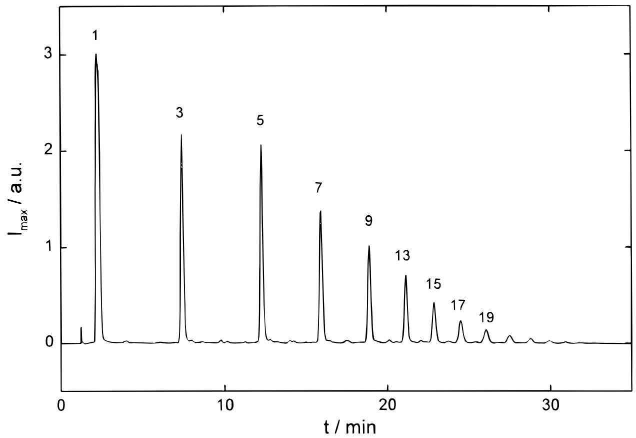

Figure 6. One-dimensional HPLC chromatogram taken from Figure 5 along a path through the absorption maxima (Int. vs *t*).

array detector in the spectral range of the oligomer absorption from 260 to 400 nm. The individual oligomer peaks are clearly baseline separated, and the shift of the absorption maximum is evident. For further data evaluation, a one-dimensional chromatogram was constructed, which compensates the wavelength shift by following the indicated path in the time−wavelength plane along the position of the absorption maxima (Table 1). Figure 6 shows the thus obtained chromatogram $I_{\mathrm{max}}(t)$, where the individual oligomer peaks are labeled with the respective number of phenylene units. After the chromatogram was enlarged at higher retention times, oligomers up to 31 phenylene units are found to be baseline separated. Due to the narrow peaks, the error introduced by the change of the absorption within a peak when following a curved path in the time−wavelength plane is negligible.

For a direct comparison with the MALDI−TOF spectra, the conversion of the chromatogram of Figure 6 into a frequency distribution as a function of molecular weight, $x(M)$, requires two steps: the construction of the calibration curve $M(t)$ and the conversion of the absorption intensities into a signal proportional to the number of OPP molecules. The first step is readily accomplished by plotting the molecular weights of the respective oligomers as a function of elution time t and approximating the data with a smooth curve, e.g., a polynomial. The data are then transformed according to

$$I(M) \propto I_{\mathrm{max}}(t)\left|\frac{\mathrm{d}M}{\mathrm{d}t}\right|^{-1} \tag{4}$$

The molecular weight dependence of the molar extinction coefficient for the transformation of $I(M)$ into the frequency distribution $x(M)$ is obtained from eq 3. Again, the errors introduced by approximating the discrete nature of the problem by continuous transformation functions are negligible.

The thus obtained frequency distribution is plotted in the upper part of Figure 7. The monomer peak, which contains the unreacted excess of the dibromo-phenylene monomer, is left out. The rapid decay of $x(M)$ with increasing chain length as predicted by eq 2 is obvious.

Starting with the trimer a quantitative evaluation is shown in Figure 8, where the peak areas are plotted as a function of the degree of polymerization (DP). Over more than 3 orders of magnitude the peak areas nicely follow an exponential decay, and from the straight line fit a slope of −0.133 is obtained, which translates to an intensity ratio of 1.86 for subsequent peaks. It should be noted that the monomer peak does not fit into the exponential decay. There is more unreacted monomer left over than expected from eq 2, with a ratio of 4.7 between the areas of the monomer and the trimer peaks.

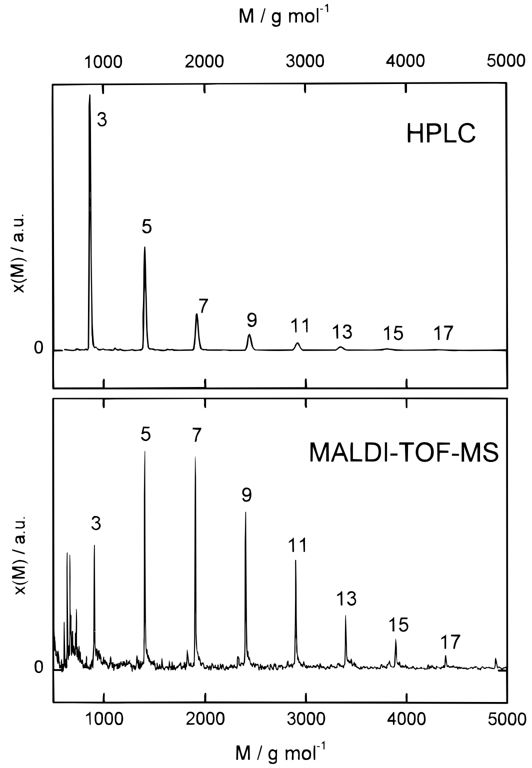

Figure 7. Oligomer distribution (mole fractions) as obtained by HPLC (top) and MALDI−TOF−MS (bottom).

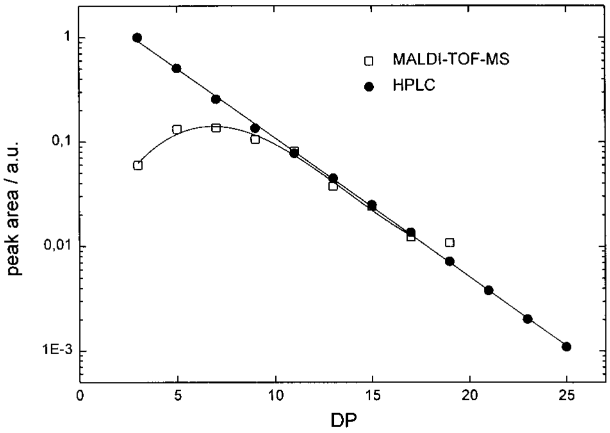

Figure 8. Comparison of polymer distributions determined by HPLC and MALDI−TOF−MS.Relative peak areas taken from the spectra in Figure 7 with straight line fit to the HPLC data.

MALDI−TOF−MS. Besides HPLC, mass spectrometry was employed, and the frequency distribution as obtained from MALDI−TOF−MS is shown in the bottom part of Figure 7. The general features of the distribution are comparable to the ones of the HPLC chromatogram: the oligomer peaks are found to be baseline separated at the expected positions, and there is virutally no signal between the major peaks. The additional intensity below the peak corresponding to three phenylene units stems from matrix material which is necessary for MALDI sample preparation.

Upon closer examination an additional peak family of low intensity, which hardly exceeds the baseline noise, can be found both in HPLC and MALDI–TOF–MS. From the MALDI–TOF–MS data, this peak can be attributed to molecules terminated by one bromine atom. These oligomers have been formed by side reactions during the Suzuki coupling reaction such as the substitution of bromine to hydrogen atoms. It should be noted that the MALDI–TOF–MS spectrum was taken after passing through the HPLC column and discarding material with elution times longer than 35 min. A MALDI–TOF–MS spectrum of the crude product shows small peaks for a series of oligomers in which one bromine end group has been changed to terphenylphosphonium cations.[23] These species are also side products of the Suzuki coupling reaction and amount to only a few percent.

A comparison of the spectra in Figure 7 reveals that there is no agreement between both methods as far as the peak areas are concerned. Contrary to HPLC, the peak areas from MALDI–TOF–MS do not decay monotonically and the highest intensity is found at seven phenylene units, as can be seen from the area plot in Figure 8. Interestingly, both techniques agree at approximately 11 phenylene units and above, where an identical slope is found in the semilogarithmic plot. This is approximately the chain length at which the absorption spectrum becomes identical to the one of the polymer (Figure 3) and which therefore has been identified with the effective conjugation length of 11 phenylene units. Unfortunately, the peak areas from mass spectrometry could only be determined up to a chain length of 19 phenylene units with sufficient accuracy. The higher order peaks vanish in the baseline noise. From the available data no unique answer is possible, as to whether the chain length dependences of the peak areas from HPLC and MALDI–TOF–MS become truely identical above 11 phenylene units, or whether the observed agreement is merely a coincidence within a limited range of DP.

One reason for the significant deviation of the mass spectrum observed for oligomers with up to 9 phenylene units can surely be attributed to the fact that the investigated PPP exhibits strong absorption (see Figure 2) at the wavelength of the desorption laser (337 nm) used for the MALDI measurements. Contrary to the normal soft ionization MALDI mechanism, where the analyte has no absorption at 337 nm and ionization usually takes place via cation attachment, the para-phenylene type polymer shows resonant absorption and accumulates excess laser power. This leads to the formation of radical ions by photoionization and causes fragmentation when the laser power exceeds the threshold for ion production.[8] Since the ionization efficiency in photoionization is correlated with the extinction coefficient at the excitation wavelength,[24,25] the signal intensity is not proportional to the number of molecules in the oligomer mixture. For this reason, the MALDI spectrum does not show a frequency distribution as expected and underestimates the lower homologues up to **P9**. As described above (optical properties), this is consistent with the observed superlinear increase of the extinction coefficients of the lower homologues up to **P9**. Remarkably, the peak areas of the higher oligomers **P11** up to **P19**, where the absorption maximum has already reached the value of the corresponding polymer, are in good agreement with the values measured by HPLC and show the expected frequency distribution at least for this limited region. Currently we have no exact model for the underestimation of the short chains in MALDI–TOF–MS. Since the intensities depend on the desorption and the ionization probabilities and on the detector response, the required model may be quite complex.

Conclusion

The excess polycondensation of AXA/BXB type monomers with the Suzuki coupling reaction opens an easy way to mixtures of defined oligo(*p*-phenylenes) that can be preparatively separated into monodisperse fractions of the respective oligomers of up to 17 phenylene units. The optical properties of the oligomers, such as absorption or emission spectra and the extinction coefficient, merge into the ones of the polymer at different sizes. The effective conjugation length can be estimated to be in the area of 11 phenylene units from an analysis of the absorption spectra, whereas the fluorescence spectra of the oligomers become identical to the polymer at lower number of phenylene units.

The fraction x_i of each oligomer in the reaction mixture can be calculated, if basic equations of polycondensation are applied. The expected exponential decay of the fraction sizes with increasing length of the oligomers is, in fact, observed, as demonstrated by analytical HPLC. This indicates that the Suzuki coupling reaction can be regarded as a pure polycondensation reaction.

The distribution of oligomers determined by MALDI–TOF–MS deviates significantly from the real distribution for the lower molecular weight compounds up to a length of about 9 phenylene units. This might be caused by the fact that the desorption and ionization efficiency increases superlinearly for the lower oligomers due to a superlinear increase of the corresponding extinction coefficients. The mass spectrometric data of oligomers with 11 and more phenylene units which have already reached the effective conjugation length as determined from the absorption spectra, are in good agreement with the HPLC data and thus show a frequency distribution. In this limited mass range, the desorption and ionization probability can be expected to be independent of chain length. It should be mentioned that the significant deviations of the mass spectrum in comparison to the calculated frequency distribution of the HPLC spectrum is not characteristic for MALDI–TOF mass spectrometry of oligomers. This has been shown by the MALDI–TOF measurement of polystyrene macromonomers and is in excellent agreement with data derived from isocratic and gradient HPLC measurements.[26] Moreover, the observed deviations of the lower OPPs are also independent of the well-known problems of MALDI–TOF MS which arise from the measurement of broad molecular weight distributions.[27–29] Contrary to the measurement of PPP they are responsible for the discrimination of the higher molecular weight homologues. We assume that the errors in measuring the low molecular weight PPPs arise mainly from the mechanism of desorption and ionization, which is unusual for MALDI analysis because of the resonant absorption behavior of the conjugated structures at 337 nm.

Finally, we have to conclude that the application of MALDI–TOF–MS for the determination of molecular weight distributions of OPPs should be used with care, particularly in the lower molecular weight range. This seems to be a general problem inherent in all oligomers with a significant absorption at the MALDI laser wavelength. Nevertheless, MALDI−TOF MS is an indispensable tool for the determination of the structure, endgroups and side reactions of the investigated oligo-(*p*-phenylenes).

Experimental Section

The extinction coefficients of the oligomers were measured from dichloromethane solutions on a Perkin-Elmer Lambda 9 UV/vis spectrometer. Photoluminescence spectra were obtained with a Fluorolog 2 Type F212, SPEX USA spectrometer with a Xe XBO 450W (Osram) lamp.

Analytical HPLC was carried out on a RP8 supersphere endcapped column (Merck, 125 mm × 4 mm). A three step solvent gradient from acetonitrile to dichloromethane has been used. The solvent composition changed linearly from 90% to 60% acetonitrile during the first 10 min, to 40% during the next 10 min, and finally to 20% during the last 20 min of the run. The measurements were recorded with a diode array detector HP 1050 in the range from 260 to 400 nm.

For preparative HPLC a RP18 column (250 mm × 20 mm) was used with a gradient of chloroform and acetonitrile. The solvent gradient changed linearly from 80% to 60% acetonitrile during the first 8 min and from 60% to 30% during the next 17 min.

The MALDI−TOF measurements were carried out with a Reflex I mass spectrometer (Bruker, Bremen, Germany), equipped with a 337 nm nitrogen laser. The spectra were recorded in the linear mode with the Bruker HIMAS detector at an acceleration voltage of 30 kV. The mass spectrometer was calibrated external with polystyrene standards (PSS, Mainz, Germany) before each measurement. The matrix 1,8,9-trihydroxyanthracene (dithranol) (Aldrich) and the samples were dissolved in THF and mixed at a mole ratio of approximately 1:500 (analyte:matrix). To avoid fragmentation in MALDI−TOF MS measurements of PPP samples, the laser power required for the desorption/ionization process was carefully adjusted slightly above threshold. The MALDI−TOF spectrum shown in this paper is smoothed and baseline corrected with the XMASS data processing program (Bruker).

Synthesis of Lower Molecular Weight Oligomers. A 100 mL Schlenk flask was charged with the aromatic diboronic ester **1** (500 mg, 1.195 mmol) and the aromatic dibromide **2** (976 mg, 2.390 mmol), $NaHCO_3$ (1.26 g, 15 mmol) connected to a reflux condenser and carefully flushed with argon. One after another, 15 mL dry THF, 15 mL degassed water, and the palladium catalyst ($Pd(PPh_3)_4$ (15 mg, 1 mol %) dissolved in 2 mL of THF were added. The mixture was then heated to 80 °C for 24 h with rigorous stirring. After cooling, the organic phase separated and the solvent was removed in vacuo. The mixture of oligomers was obtained as a colorless powder. The yield was not determined, because the experiment was carried out under nonoptimized conditions with reduced reaction times to avoid side reactions.

The separation of the oligomers was performed in two steps. First, the lower molecular weight compounds up to a length of nine phenylene units could be separated by column chromatography with a solvent mixture of toluene and petroleum ether (1:1 by volume). The amount of toluene was slowly increased to reach a 9:1 ratio of toluene/petroleum ether by volume. The remaining higher oligomers have been washed from the column with pure toluene and THF. The solvent was then evaporated in vacuo and the residue separated with a preparative HPLC column with a solvent gradient chloroform/acetonitrile. Monodisperse oligomers up to a length of 17 phenylene units have been isolated.

Characterization of Oligomers (Examples). OPP trimer (**2b**). Melting point: 105 °C. ^1H NMR ($CDCl_3$): $\delta = 7.18$ (s, 2H), 6.97 (s, 2H), 6.92 (s, 2H), 4.01 (t, 4H), 3.87 (m, 8H), 1.90 (m, 2H), 1.8−1.4 (m, 16H), 0.99 (d, 12H), 0.83 (dd, 24H) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 150.0$, 117.3, 102.5, 67.6, 38.0, 24.4, 22.5 ppm. IR (KBr): 2955, 2870, 1486, 1469, 1383, 1366, 1345, 1212, 1192, 1056, 1027, 967, 862 cm^{-1}. MS (field desorption): $m/e = 904.0$.

OPP pentamer. Melting point: 126 °C. ^1H NMR ($CDCl_3$): $\delta = 7.15$ (s, 2H), 7.02 (s, 4H) 6.97 (s, 2H), 6.92 (s, 2H), 4.00 (t, 4H), 3.88 (m, 16H), 1.89 (m, 2H), 1.8−1.4 (m, 28H), 0.98 (d, 12H), 0.86 (dd, 48H) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 150.0$, 117.3, 102.5, 67.6, 38.0, 24.4, 22.5 ppm. IR (KBr): 2955, 2870, 1486, 1469, 1383, 1366, 1345, 1212, 1192, 1056, 1027, 967, 862 cm^{-1}. MS (field desorption): $m/e = 1401.0$.

OPP heptamer. Melting point: 133 °C. ^1H NMR ($CDCl_3$): $\delta = 7.15$ (s, 2H), 7.02 (s, 8H) 6.97 (s, 2H), 6.92 (s, 2H), 4.00 (t, 4H), 3.88 (m, 24H), 1.89 (m, 2H), 1.8−1.4 (m, 44H), 0.98 (d, 12H), 0.86 (dd, 72H) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 150.0$, 117.3, 102.5, 67.6, 38.0, 24.4, 22.5 ppm. IR (KBr): 2955, 2870, 1486, 1469, 1383, 1366, 1345, 1212, 1192, 1056, 1027, 967, 862 cm^{-1}. MS (field desorption): $m/e = 1899.0$.

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