The Raman Spectra of Different Ladder Type Poly(*p*-phenylenes) and Ladder Type Oligo(*p*-phenylenes)

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Summary: We report on Raman spectra of ladder type oligo(*p*-phenylenes) of different chain lengths (5LOPP and 7LOPP) and make a comparison to the Raman spectrum of the corresponding polymer, ladder type poly(*p*-phenylene) (LPPP). For a better understanding of the vibrational behavior of LPPP, several LPPPs with different substituents (methyl, allyl, *n*-butyl, 1-adamantyl) were investigated. The recorded Raman spectra of these LPPPs show significant changes in the interring CC stretching regions. An experimental analysis of the frequencies, intensities and line-shapes of significant modes is given in dependence on the substituents and chain lengths.

Introduction

The class of ladder type poly(*p*-phenylene)s (LPPP)[1,2] and oligo(*p*-phenylene)s (LOPP)[3] are in the focus of intensive investigations among the family of conjugated materials because of their high potential for optoelectronic applications like polymer light emitting diodes (PLEDs),[4] light-emitting electrochemical cells (LECs)[5] and organic lasers.[6,7] To further elucidate the photophysics of this class of materials LOPPs with different chain lengths and LPPPs with different substituents were synthesized which allow the study of the influence of these parameters on the optical and electronic properties. Increasing the effective conjugation length going from a 5 phenyl ring oligomer to a polymer results in a red shift of the absorption and emission spectra, while different substituents at the methine bridge can influence the interchain correlation which also affects the luminescence properties.

Raman spectroscopy is a powerful tool to study structural changes, as well as changes in the electronic properties. To reveal the interplay of structure and photophysics in this class of materials we have studied the Raman spectra of LPPPs with different

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substituents[2, 8, 9] (Figure 1a) and LOPPs with different chain lengths (5LOPP shown in Figure 1b, 7LOPP has the according structure to 5LOPP).

Material

The interring bridges which are added to poly(*para*-phenylene) (PPP) result in a planarization of adjacent phenyl rings, which also leads to a red shift of the electronic spectra.[10] To increase chemical stability of the introduced bridge as well as to increase inter-chain separation different substituents were attached on the position R_x in LPPP (Figure 1a). A methyl substituent on this position results in the mLPPP. The synthesis of LPPP and mLPPP are reported in Ref. 1 and Ref. 2, 8 respectively. The other substituted ladder polymers described in Figure 1a follow the same routes of syntheses.[9] The LOPPs are synthesized as described in Ref. 3.

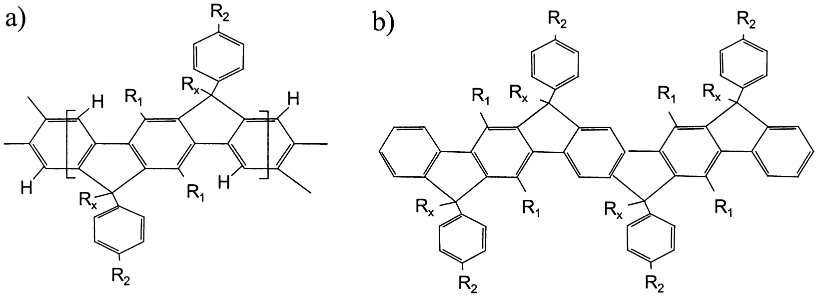


Figure 1. Chemical structure for various ladder type *p*-phenylene systems:
a) ladder type poly(p-phenylene)s (M_n, M_w from GPC, PS calibration):
LPPP: $R_1 = C_6H_{13}$, $R_2 = C_{10}H_{21}$, $R_x = H$ (M_n: 12000, M_w/M_n: 1.83);
mLPPP: $R_1 = C_6H_{13}$, $R_2 = C_{10}H_{21}$, $R_x = CH_3$ (M_n: 55000, M_w/M_n: 2);
allyl-LPPP: $R_1 = C_6H_{13}$, $R_2 = C_{10}H_{21}$, $R_x = (\text{-}CH_2\text{-}CH{=}CH_2)$ (M_n: 14000, M_w/M_n: 1.89);
n-butyl-LPPP: $R_1 = C_6H_{13}$, $R_2 = C_{10}H_{21}$, $R_x = CH_3(CH_2)_3$ (M_n: 11500, M_w/M_n: 2.04);
1-adamantyl-mLPPP: $R_1 = C_6H_{13}$, $R_2 = C_{10}H_{16}$, $R_x = CH_3$ (M_n: 10500, M_w/M_n: 1.81).
b) ladder type oligo(*p*-phenylene): 5LOPP: $R_1 = C_6H_{13}$, $R_2 = C(CH_3)_3$, $R_x = H$.

Experiment

Raman measurements were performed on films (3 μm thickness) of the polymers and oligomers drop casted from a chloroform solution. The Raman spectra of the polymers with different substituents were recorded with a Renishaw Raman Spectrometer 2000 at HeNe Laser excitation (633nm). To investigate the chain length dependence a Dilor OMARS 89 triple-spectrometer with the 647 nm line of a Krypton Laser was used.

The main Raman modes

The vibrational behavior of LPPPs should be considered in relation to that of poly(p-phenylene) (PPP). The spectra are dominated by a few significant vibrations located at the polymer backbone. The three strongest modes assigned to the conjugated skeleton in PPP are: aromatic CC stretching (1595 cm^{-1}), interring CC stretching (1285 cm^{-1}) and CH bending (1222 cm^{-1}).[11] For LPPP the symmetry lowers from the idealized plane PPP with D_{2h} to point group C_{2h}, and for ladder oligomers (LOPP) to C_{2h} and to C_{2v} for odd and even numbers of rings, respectively. The aromatic CC stretching mode splits in two strong modes and the four strongest modes in the Raman spectrum are related to A_g (C_{2h}) or A_1 (C_{2v}) vibrations and related to the three main modes in PPP.

The influence of different substituents

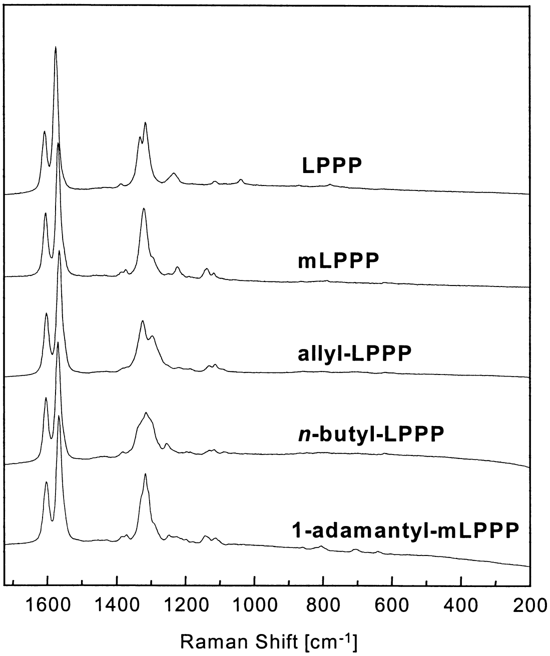


Figure 2. Raman spectra of LPPP with different substituents.

The recorded Raman spectra with different substituents R_x and R_2 are shown in Figure 2. The substituents on the methine bridge mostly affect the Raman spectra in the interring CC stretching region (around 1300 cm^{-1}):

The most significant difference between LPPP and mLPPP is one missing mode at around 1317 cm^{-1} in mLPPP. Together with theoretical calculations[12] we found that the additional mode in LPPP has to be assigned to the strong intermix of the bending motion of the hydrogen on the methine bridge with the interring vibration, whereas the motions of the methyl-group do not resonate with the interring mode.[13] When substituting R_x with a more complex molecule, such as *n*-butyl, or allyl, one can observe further changes of the line shapes with a partly recovered double peak structure. Again this we interpret as an intrinsic coupling of side group vibrations in resonance with the interring vibration. As a comparison, also the substitution with 1-adamantyl on the R_2 place of mLPPP is shown in Figure 2. The spectrum is very similar to that of mLPPP which demonstrates the much weaker interaction of the more separated R_2 chain with the interring vibration and goes conform with theoretical calculations[13].

In contrast to the interring modes the aromatic modes are almost unaffected, their line positions are stable within a range of 6 cm^{-1}. Further differences are observed in the CH bending/interring CC stretching region around 1232 cm^{-1} for all polymers.

The influence of different chain lengths

The Raman spectra with increasing chain length are shown in Figure 3. Following aspects dominate the spectra:

The intensities of the Raman modes change significantly with the chain length. Those modes which are attributed to vibrations of the conjugated backbone are getting more intense with increasing chain length. We have signed the main modes from ν_1 to ν_{10} in Figure 3, and have shown the intensity increase in Figure 4a on ν_2, as an example. The three modes which are attributed to interring CC stretching (ν_4,ν_5,ν_6 around 1333 cm^{-1}, 1315 cm^{-1} and 1295 cm^{-1}) are well resolved in the oligomers, whereas in the polymer ν_6 is close to ν_5 and can be observed only at low temperature and high spectral resolution.[13] The line shifts of the main modes due to increasing chain length are rather weak (about 4 cm^{-1} in average). The greatest shift with increasing chain length is observed for the mode ν_3 at 1398 cm^{-1} (5LOPP) which shifts down to 1389 cm^{-1} for LPPP (downshift of 9 cm^{-1}). This usual behavior of vibrations is due to the quantum mechanical nature of "particles in the box" which generally scale with 1/n. As Figure 4b shows, also ν_3 reflects this behavior. Due to this linear 1/n function we can estimate from the change in line width between 5LOPP and LPPP a relevant width of chain length distribution in LPPP, drawn as an estimated error bar in Figure 4a and b.

The errors in Raman intensity and Raman frequency are estimated with ±20% and ±1 cm^{-1}, respectively.

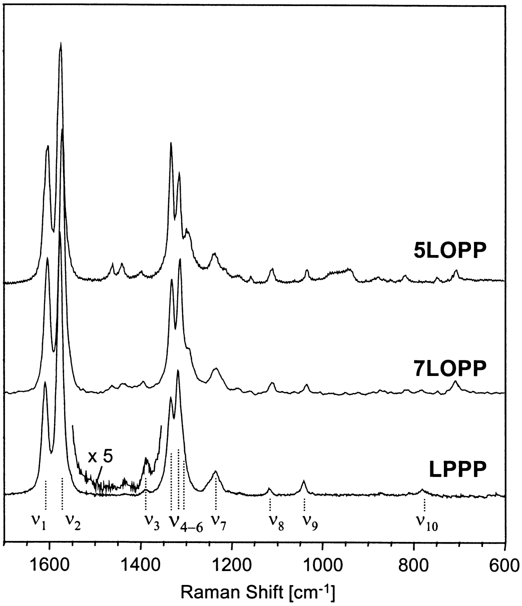
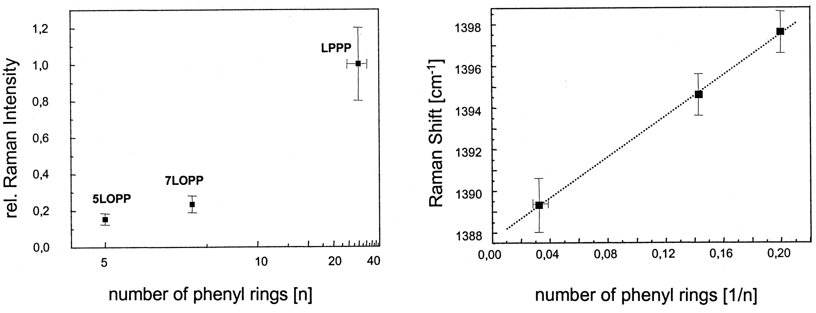


Figure 3. Raman spectra of ladder type oligomers and polymer (R_x = H).



a) b)

Figure 4. a): Relative Raman intensities for the aromatic mode ν_2, normalised to LPPP; b): Line position of ν_3.

Conclusion

In conclusion we find that different substituents at the methine bridge strongly affect the mode structure located in the region of the interring CC stretching modes because of a general sensibility of these modes to structural changes of side chains located at the methine bridge. The average molecular weight of mLPPP is significantly longer than all the other ladder polymers. However, because of the 1/n law of vibrational frequencies and the expected saturation of Raman intensities at long chains, the differences in the Raman spectra between 130 (mLPPP) and around 30 phenyl rings for all the other polymer, are neglectable small compared with the influence of the side chains. With increasing chain length fewer modes significantly rise in Raman intensity and become the characteristic main modes of the polymer. This offers one possible way to characterize the quality of a sample in a sense of average chain length.

The mostly pronounced line dispersion of ν_3 gives an additional intrinsic tool to characterize the chain length distribution. The line positions in general are weakly affected by the chain length, which indicate a rather small (or in someway compensated) renormalization of the vibrational modes with the conjugated system.

The LPPP has a different side chain on the R_2 place compared to the LOPPs, but this influence of the R_2 on the main backbone modes should be neglectable small.

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