

# Raman and i.r. spectroscopic investigation of aromatic 1,3,4-oxadiazole polymers and oligomers

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The molecular structure of poly(*p*-phenylene-1,3,4-oxadiazole) (POD) is investigated using i.r. and Raman spectroscopy. Both methods reveal characteristic differences for the  $\alpha$ - and  $\beta$ -POD forms that are most obvious in the spectral region between 1500 and 1650  $\text{cm}^{-1}$ . The spectra for dimer and tetramer compounds already show the same features as found for longer chains. Based on molecular modelling calculations these differences are assigned to *cis* and *trans* conformations of the main chain segments. High pressure measurements show a linear shift of the Raman lines and support the result of the thermodynamic stability of the *trans* conformation. © 1997 Elsevier Science Ltd. All rights reserved.

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## INTRODUCTION

Poly(1,3,4-oxadiazole)s have received considerable interest for the production of high performance materials due to their high thermal stability in oxidative atmosphere and specific properties determined by the structure of the 1,3,4-oxadiazole rings<sup>1</sup>. It has been shown that from the spectral and electronical points of view, the oxadiazole cycle is similar to a *p*-phenylene structure, which is known to be highly thermoresistant. Also, it does not contain any hydrogen atoms, it lacks tension, it does not have any possibilities of rearrangement and it has structural symmetry<sup>2</sup>. Besides their excellent resistance to high temperature, poly(oxadiazoles) have many desirable characteristics such as good hydrolytic stability, high glass transition temperature, low dielectric constant, and tough mechanical properties. Some poly-oxadiazoles have semi-conductive properties, other structures can be electrochemically doped and thus made conductive, and other have liquid crystalline properties, which makes them very attractive for a wide range of high performance applications<sup>3–6</sup>.

However, aromatic polyoxadiazoles often exhibit poor solubility in many solvents, and they are frequently processed from sulfuric acid solutions<sup>7</sup>. Recently, it was shown that poly(arylene-1,3,4-oxadiazole)s are soluble in

an aprotic solvent system consisting of a nitroalkane and a Lewis acid<sup>8</sup>. This solvent system was described for the first time by Jenekhe *et al.* for aromatic heterocyclic rigid rod polymers such as poly(benzoxazole)s or poly(benzimidazole)s<sup>9</sup>. Poly(*p*-phenylene-1,3,4-oxadiazole) (POD) is soluble in nitromethane, nitroethane or nitrobenzene containing a Lewis acid.  $\text{AlCl}_3$  and  $\text{FeCl}_3$  can be used as a Lewis acid. Two molecules of the salt are required per oxadiazole unit in the main chain if  $\text{AlCl}_3$  is used. This is an indication that interactions exist between the nitrogen atoms of the oxadiazole ring and the Lewis acid molecules<sup>10</sup>. The new solvent system has allowed the development of new possibilities for processing aromatic poly(oxadiazole)s into fibres, films or membranes.

By processing POD from dilute solutions in concentrated sulfuric acid, two structures distinguishable by X-ray diffraction can be obtained depending on the coagulation condition<sup>11</sup>. The  $\beta$ -form is caused by 'hard' coagulation conditions characterized by a predominantly two-dimensional order. The crystallization behaviour of POD in the coagulation process was studied by Calandrelli *et al.*<sup>12</sup>. 'Soft' coagulation creates the  $\alpha$ -structure distinguished by a relatively high degree of three-dimensional order.

Systematic i.r. spectroscopic investigations of thin POD films have shown that there are significant differences between the  $\alpha$ - and the  $\beta$ -forms. A sharp single band at 1568  $\text{cm}^{-1}$  was observed for samples of the

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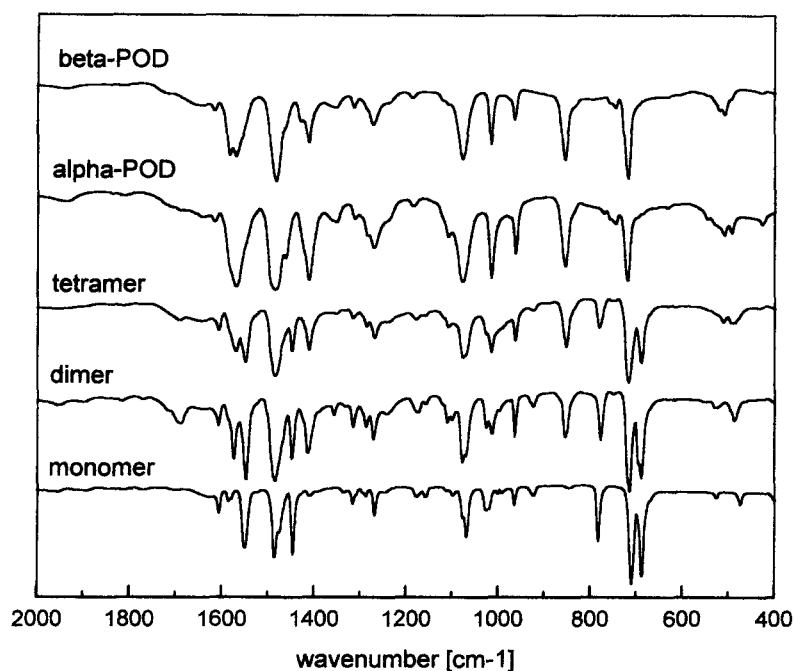


Figure 1 I.r. spectra of *p*-phenylene-1,3,4-oxadiazole oligomers and polymers

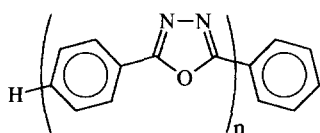
$\alpha$ -form, the  $\beta$ -form shows a strong absorption band at  $1584\text{ cm}^{-1}$ . Also, the conversion from the  $\beta$ -form to the  $\alpha$ -form in POD films by treatment with 75% sulfuric acid can be easily observed by the increasing intensity of the i.r. band at  $1568\text{ cm}^{-1}$ <sup>13</sup>.

It is important to point out that the  $\alpha$ -POD is formed directly by coagulation from nitroalkane/Lewis acid mixtures<sup>8</sup>. Probably by complexing the oxadiazole unit with two  $\text{AlCl}_3$  molecules a certain preorder in the arrangement of the polymer chains is realised and remains in the following steps of the coagulation and the removal of  $\text{AlCl}_3$ .

Because the  $\alpha$ -modification leads to higher tenacities of fibres there is a practical interest to form it directly by the coagulation process and to understand both the molecular and supramolecular structures and their relation to the polymer properties. In this paper, Raman and i.r. spectroscopic investigations on  $\alpha$ - and  $\beta$ -POD are described and compared with those of corresponding monomers and oligomers of the same chemical structure. In addition, molecular modelling results are used to explain the i.r. spectroscopic data. Raman spectra of aromatic 1,3,4-oxadiazole oligomers and polymers are not known yet. High pressure Raman experiments are performed in order to investigate the influence of volume change onto the molecular vibrations of both POD forms.

## EXPERIMENTAL

### Materials



1.  $n = 1$  2,5-diphenyl-1,3,4-oxadiazole (DPO)
2.  $n = 2$  dimer

3.  $n = 4$  tetramer
4.  $n > 100$  poly(*p*-phenylene-1,3,4-oxadiazole) (POD)

DPO **1** is synthesized by chemical cyclization of dibenzoyl hydrazine as described in ref. 14:  $F_p$ :  $142^\circ\text{C}$  (Lit.:  $F_p$ :  $143^\circ\text{C}$ ). The synthesis of the dimer **2** follows the procedure outlined in ref. 15:  $F_p$ :  $322^\circ\text{C}$  (Lit.:  $F_p$ :  $323$ – $324^\circ\text{C}$ <sup>16</sup>). The method described in ref. 17 is applied for the synthesis of the tetramer **3**. According to the literature **3** decomposes before melting above  $340^\circ\text{C}$ . POD **4** is synthesized by direct polycondensation of terephthalic acid with hydrazine sulfate in fuming sulfuric acid (33 wt% free  $\text{SO}_3$ ) as described in ref. 18. The inherent viscosity in conc. sulfuric acid is  $3.2\text{ dl g}^{-1}$ . The  $\alpha$ -POD was prepared by precipitation of the polymer from nitromethane/ $\text{AlCl}_3$  solution into ethanol whereas the  $\beta$ -POD was isolated by precipitation of the polymer from sulfuric acid solution into water, as described in ref. 13.

In all compounds the i.r. bands typical for the 1,3,4-oxadiazole ring at  $1550$  and  $965\text{ cm}^{-1}$ <sup>19,20</sup> are observed. Whereas the absorption bands of monosubstituted benzene rings are observed for DPO **1** the other substances show typical bands of *para* substituted phenylene rings at  $1412$ ,  $1112$ ,  $1015$  and  $860\text{ cm}^{-1}$ <sup>21–23</sup> (Figure 1).

Solid-state- $^{13}\text{C}$  n.m.r. investigations show a significant peak at  $165\text{ ppm}$  for all compounds which is characteristic for the carbon atoms in the 1,3,4-oxadiazole ring.

### Raman spectroscopy

Room temperature Raman measurements were performed using a He–Ne laser ( $632.8\text{ nm}$  wavelength) for excitation. The laser light was focused to a small spot of less than  $10\text{ }\mu\text{m}$  diameter so that in the crystalline samples (monomer and dimer) the spectra are collected from single crystals. A triple Raman spectrometer system with a CCD detector (T 64000, Instruments SA) was used for dispersing and recording the scattered light.

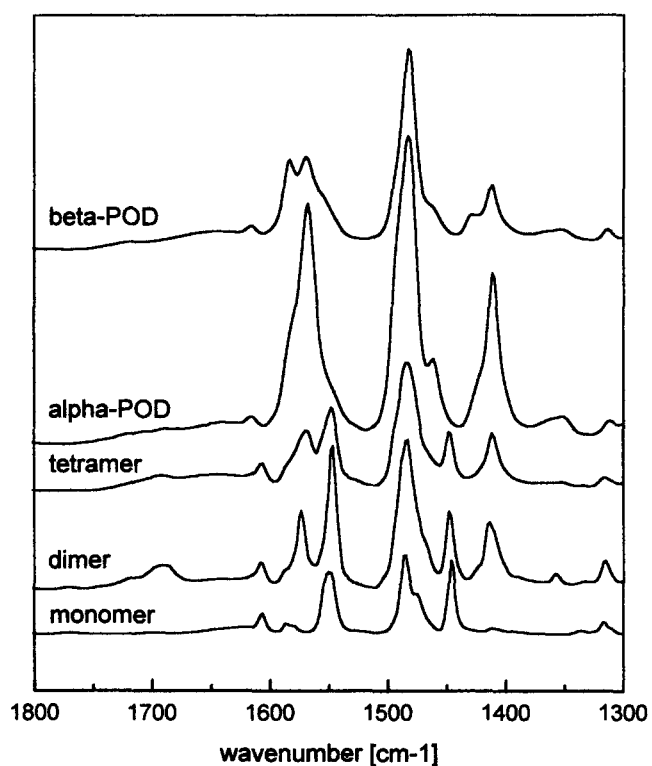


Figure 2 Infra-red bands in the region between 1300 and 1800  $\text{cm}^{-1}$

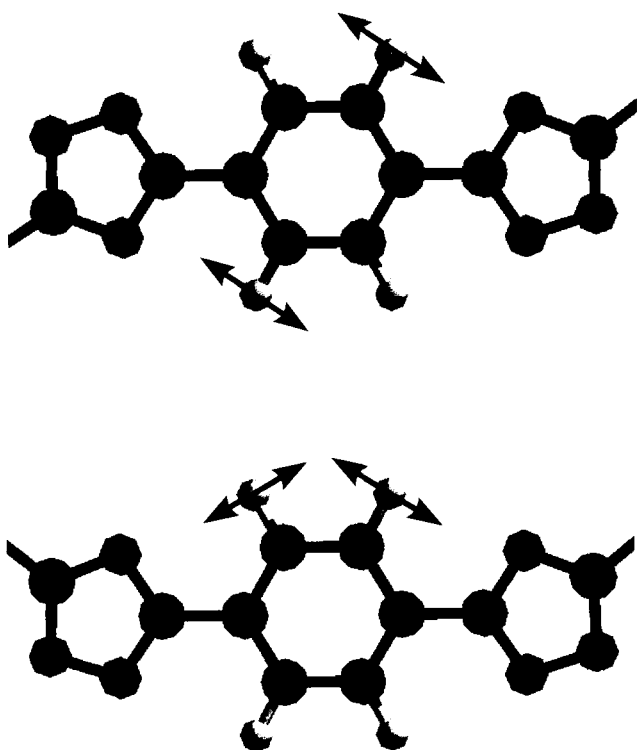


Figure 3 *Trans* and *cis* conformations in the oxadiazole dimer

With a typical width of the entrance slit of  $100\ \mu\text{m}$  a resolution of about  $2\ \text{cm}^{-1}$  was achieved. Raman spectra were measured in the range from 8 to  $2000\ \text{cm}^{-1}$ , which includes the low-energy lattice modes and the relevant skeletal molecular vibrations.

#### High pressure measurements

High pressure was generated using the gasketed diamond anvil cell technique (for a review of this technique see, e.g., ref. 24). The sample chamber was formed by a hole of  $200\ \mu\text{m}$  diameter drilled into a steel gasket which was preindented to a thickness of  $100\ \mu\text{m}$ . A small piece of the sample material (typical size  $50\ \mu\text{m}$ ) was prepared together with a  $20\ \mu\text{m}$  chip of  $\text{SrFC1:Sm}^{2+}$  for *in situ* pressure determination. The latter pressure luminescence sensor was used instead of the standard ruby gauge in order to increase the precision of pressure measurement<sup>25</sup>. A mixture of methanol/ethanol as the pressure transmitting medium guarantees a hydrostatic pressure distribution.

#### Infra-red spectroscopy

Infra-red transmission spectra were recorded in the range from  $4000$  to  $400\ \text{cm}^{-1}$  using a Nicolet Magna 550 FTIR-spectrometer with a resolution of  $4\ \text{cm}^{-1}$ . The samples 1–3 were prepared as KBr pellets while the polymers 4 were investigated as free standing films.

#### Molecular modelling

Molecular simulations were performed using the VIBRATE module of POLYGRAF. The model parameters were taken from a modified DREIDING force field which results from an optimization of simulated data in comparison with experimental X-ray data of crystalline 1,3,4-oxadiazole derivatives<sup>26</sup>. The modifications concern the valence angles and charges prescribed to the atoms. The valence angles of the atoms in the 1,3,4-oxadiazole ring are changed in such a way that the ring is kept unstressed and in plane. Other changes of the molecular backbone are proved to be negligible in the frequency range of interest. The partial charges for the atoms are taken from a MOPAC calculation using AM1 Hamiltonian. The calculated charges as well as the chosen valence angles correspond to values given by El-Azhary<sup>20</sup> for an unsubstituted 1,3,4-oxadiazole ring.

## RESULTS AND DISCUSSION

#### *I.r. spectroscopy and molecular modelling*

From previous investigations<sup>12,13</sup>, it was not clear if the different i.r. spectra of the  $\alpha$ - and  $\beta$ -POD are caused by conformational effects or by the influences of the supramolecular structure like crystalline lattices. In ref. 13 it was assumed by the authors that the different positions of oxadiazole frequencies are due to the different conformations of the macromolecules.

In order to obtain more detailed information a comparison was made between the spectra of monomer 1, dimer 2, tetramer 3 and those of POD 4. As shown in Figure 2 the i.r. band of the monosubstituted phenyl ring at  $1446\ \text{cm}^{-1}$  is characteristic for the monomer DPO and decreases with increasing number of repeating units in the range dimer, tetramer and polymer. This is caused by the fact that in these molecules the phenyl ring is only the end group of the chain and thus their molecular weight portion decreases. Consequently, the POD spectra show the phenylene ring bands at  $1412$ ,  $1112$  and  $1015\ \text{cm}^{-1}$ , but do not show the phenyl ring band. The band at  $1487\ \text{cm}^{-1}$  is also a phenyl ring vibration but nearly independent of the type of substitution<sup>21</sup>.

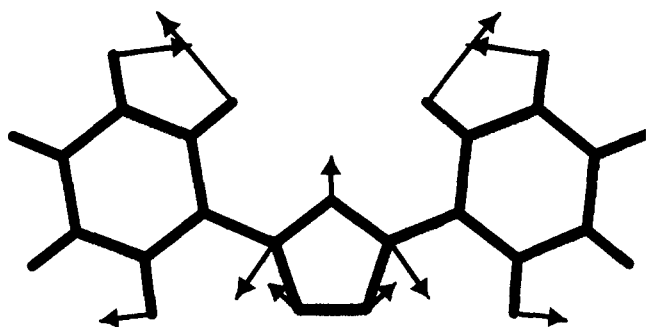


Figure 4 Normal modes of DPO

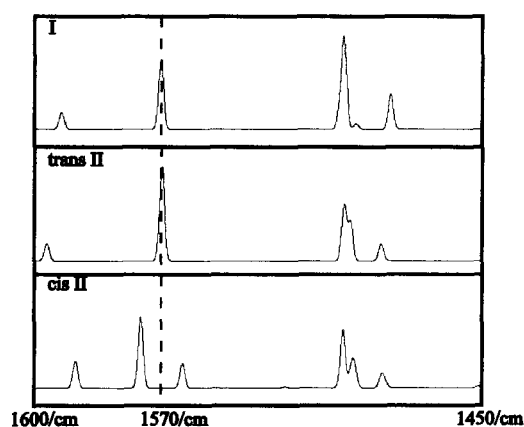


Figure 5 Simulated i.r. spectra for DPO, *cis* dimer and *trans* dimer, respectively

The DPO **1** spectrum is dominated by the oxadiazole band at  $1550\text{ cm}^{-1}$ . Compared with the monomer an additional absorption band appears at  $1570\text{ cm}^{-1}$  in the spectra of the oligomer compounds **2** and **3**<sup>27</sup>. According to ref. 13 this band is assigned to the oxadiazole ring and dominates the spectrum of the  $\alpha$ -POD whereas the absorption band at  $1584\text{ cm}^{-1}$  is more pronounced in the spectrum of the  $\beta$ -POD. But, it should be mentioned here that this band also appears as shoulder in the spectrum of the  $\alpha$ -POD as well as in the spectra of the oligomers.

In order to explain the differences in the i.r. spectra molecular simulations were performed for both DPO **1** and the dimer **2**. It is assumed that these differences may be attributed to different conformational arrangements of the neighbouring oxadiazole rings as shown in Figure 3 for the dimer **2**<sup>28</sup>.

Figure 4 shows a typical normal mode for DPO **1** in the frequency range around  $1570\text{ cm}^{-1}$ . A doubling and shift occur for bands related to oxadiazole ring vibrations in the oligomers when all motions take place in the plane of the molecule. In Figure 4 the arrow starting at an atom shows the direction and by its length the amplitude of the movement of this atom involved in the normal mode.

Besides the atomic motions of the oxadiazole ring, the great vibrational amplitude of the hydrogen atoms at the adjacent phenylene rings close to the oxygen side of the oxadiazole ring deserves special attention. The vibration of this proton determines the coupling of two of these modes localized at neighbouring oxadiazole rings in the chain. For the pair in *trans* conformation these strongly moving hydrogen atoms are on opposite

sides of the same phenylene ring. Hence, their mutual interaction is small, the splitting of the oxadiazole ring vibrations is negligible and a model spectrum for a *trans* dimer is very similar to this one of the monomer. In the *cis* conformation the two vibrating protons are on neighbouring sites of the phenylene ring. A strong charge interaction of the two protons results in a remarkable splitting of the oxadiazole ring vibration and in two well separated i.r. absorption bands as shown in Figure 5.

Due to the known difficulties in describing the charge distribution in classical models the agreement between simulated and experimental spectra is only qualitative. The number of bands and their mutual position is well reproduced in our simulation. Since the difficulties increase remarkably by changing to the polarization sensitive Raman spectra a comparison with experimental data requires a more sophisticated treatment as, for example, for the nonsubstituted oxadiazole ring<sup>20</sup>.

Comparing the energies for dimers in *trans* and *cis* conformations, it turns out that the *trans* conformation is energetically favoured but the difference is small. Therefore, at ambient temperatures the dimer **2** is a mixture of molecules having *cis* or *trans* conformations, and i.r. absorption bands originating from both conformations are observed in the spectra. According to the molecular modelling results we suggest that the i.r. band at  $1570\text{ cm}^{-1}$  is due to the dimers in *trans* conformation, whereas the bands at  $1550$  and  $1584\text{ cm}^{-1}$  represent contributions from the *cis* conformation. Although,

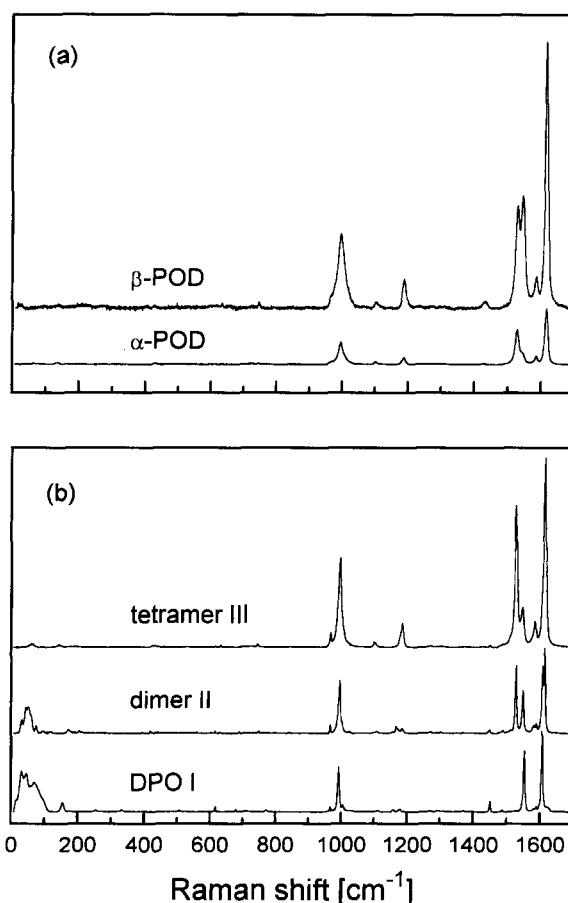


Figure 6 Raman spectra of *p*-phenylene-1,3,4-oxadiazole oligomers (b) and polymers (a)

a phenyl ring vibration is expected at  $1582\text{ cm}^{-1}$ <sup>21-23</sup> an additional assignment of the band at  $1584\text{ cm}^{-1}$  to an oxadiazole ring vibration cannot be ruled out. Thus, this band would represent a superposition of both excitations.

Contrary to ref. 13, from these results it follows that *cis* and *trans* conformations are present in both POD modifications. A higher content of *trans* conformation leads to a more linear chain which can be arranged more easily in the higher ordered  $\alpha$ -form. In contrast, a higher content of *cis* conformation disturbs the three-dimensional packing of the macromolecules and the less ordered  $\beta$ -form results. Thus, the difference between the i.r. spectra of  $\beta$ - and  $\alpha$ -POD is really caused by different conformations. This conclusion is supported by the fact that the i.r. spectra of stretched foils of  $\beta$ -POD are not identical with those of a  $\alpha$ -POD. Thus, the supramolecular structure does not influence the i.r. region discussed above.

#### Raman spectroscopy

Figure 6a shows the Raman spectra of  $\alpha$ -POD and  $\beta$ -POD below  $1700\text{ cm}^{-1}$ . The basic differences between both spectra appear in the frequency range near  $1540\text{ cm}^{-1}$  where the Raman active vibration of the oxadiazole ring is expected<sup>20,23,29</sup>.  $\alpha$ -POD shows a sharp intense peak at  $1527\text{ cm}^{-1}$ , whereas in  $\beta$ -POD two Raman lines at  $1530$  and  $1544\text{ cm}^{-1}$  can easily be distinguished. Comparing the Raman excitations at lower frequencies ( $1000\text{ cm}^{-1}$ ,  $1200\text{ cm}^{-1}$ ) there are only minor differences for the spectra of  $\alpha$ - and  $\beta$ -POD. However, the linewidths in the  $\beta$ -form are larger than those in  $\alpha$ -POD, indicating a higher amount of disorder.

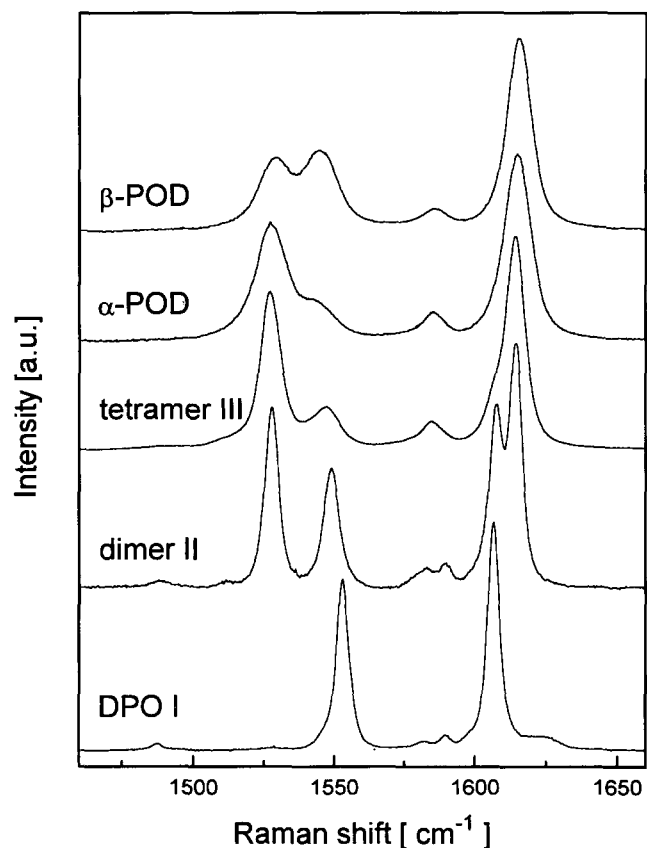


Figure 7 Raman excitations for oxadiazoles in the region between  $1400$  and  $1700\text{ cm}^{-1}$

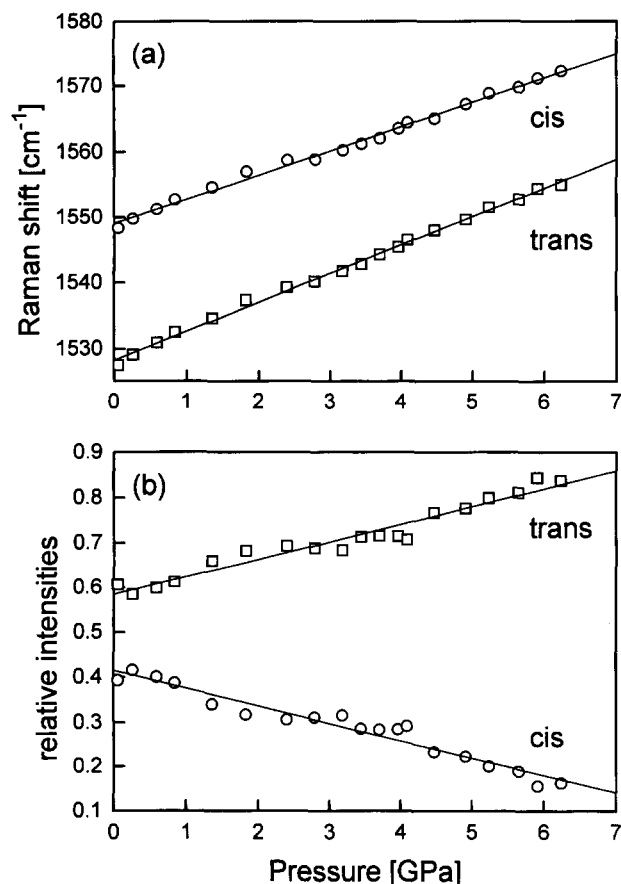


Figure 8 Influence of the hydrostatic pressure on the Raman shift of the lines characteristic for *cis* and *trans* conformations of dimer 2 (a) and on the relative intensities of these bands (b)

In order to obtain further insight into the conformational differences of  $\alpha$ - and  $\beta$ -POD we considered the corresponding vibrational spectra of oligomers 1–3 which are shown in Figure 6b. The monomer 1 and the dimer 2 form crystalline modifications as indicated in the Raman spectra by the excitation of lattice phonons below  $100\text{ cm}^{-1}$  which has been proven by X-ray investigations showing a high degree of crystallinity. These strong excitations are missing in the spectra of the tetramer and the polymers. The interesting range between  $1500$  and  $1650\text{ cm}^{-1}$  in the Raman spectra is shown in more detail in Figure 7. The monomer spectrum exhibits only one sharp Raman active oxadiazole ring vibration at  $1552\text{ cm}^{-1}$ . This band is well separated from the strong phenyl ring vibration at  $1606\text{ cm}^{-1}$ . The formation of a dimer molecule results in the splitting of both fundamental ring vibrations. The separation of the

Table 1 Zero pressure frequencies  $\nu_0$  ( $\text{cm}^{-1}$ ) and pressure coefficients  $d\nu/dp$  ( $\text{cm}^{-1}\text{ GPa}^{-1}$ ) of the most intensive Raman excitations between  $1500$  and  $1700\text{ cm}^{-1}$  for the dimer and the polymers of DPO

		Dimer	$\alpha$ -POD	$\beta$ -POD
Oxadiazole ring, <i>trans</i> conformation	$\nu_0$	1528	1528	1530
	$d\nu/dp$	4.4	5.3	5.9
Oxadiazole ring, <i>cis</i> conformation	$\nu_0$	1549	—	1546
	$d\nu/dp$	3.7	—	4.3
Phenyl ring	$\nu_0$	1609	—	—
	$d\nu/dp$	7.4	—	—
Phenylene ring	$\nu_0$	1616	1615	1616
	$d\nu/dp$	3.8	4.5	4.5

phenyl ring vibration into two peaks ( $1608$  and  $1615\text{ cm}^{-1}$ ) can be understood by the contribution of the phenylene ring vibration which is slightly higher in frequency. Since the number of phenylene rings increases with the chain length the corresponding vibration is expected to determine the spectrum of the higher oligomers. In the tetramer spectrum the intensity of the phenyl ring vibration is already small and contributes only as a small shoulder near  $1608\text{ cm}^{-1}$  to the spectrum.

The strong splitting of the oxadiazole ring vibration in the dimer spectrum ( $1528$  and  $1549\text{ cm}^{-1}$ ) cannot be explained by two different species of rings within one dimer molecule. However, depending on the *trans* or *cis* conformation there exist two different molecular structures of the dimer (Figure 3). Since the energy difference between the two structures is small it is expected that at room temperature there is a mixture of molecules in the *trans* and *cis* conformations. The dipole moments of the rings are almost parallel in the *cis* and antiparallel in the *trans* conformation. From the previous discussion it follows that due to the large value of this dipole moment a strong dipole-dipole interaction and a corresponding influence on the frequency of the oxadiazole ring vibration has to be assumed. This results in a different frequency shift for the *trans* and *cis* conformations and in a splitting of the Raman line by about  $20\text{ cm}^{-1}$ . With increasing chain length the *trans* conformation is energetically favoured. This is indicated by the relative change in intensities of both lines comparing the spectra of the dimer, the tetramer and  $\alpha$ -POD. In  $\beta$ -POD the intensity ratio of the vibrations of oxadiazole rings in the *trans* and *cis* conformations is opposite. There are more *cis* conformations along the chain than in  $\alpha$ -POD. Because of the higher energy of the *cis* conformations and the larger volume of the  $\beta$ -chain this structure is metastable. This is supported by the observed conversion into  $\alpha$ -POD if  $\beta$ -POD is treated with 75% sulfuric acid<sup>13</sup>. Thus, the Raman results correspond very well with those of i.r. spectroscopy.

#### High pressure measurements

The variation of thermodynamic parameters like temperature or pressure can be very useful to investigate the stability of *trans* and *cis* conformations in the oxadiazole oligomers and polymers. Of special interest is the change of the ratio of *trans* and *cis* conformations which can be determined from the Raman intensities of the corresponding oxadiazole ring vibrations. An excellent candidate for this investigation is the dimer since both oxadiazole ring vibrations at  $1528$  and  $1549\text{ cm}^{-1}$  and the phenylene ring vibration at  $1616\text{ cm}^{-1}$  are well separated and of high intensity.

The application of hydrostatic pressure results in an increase of the molecular vibration frequencies. For the most intensive Raman excitations (phenylene and oxadiazole ring vibrations) this shift is linear with pressure. The value of about  $4\text{ cm}^{-1}\text{ GPa}^{-1}$  is comparable with the pressure coefficients of Raman lines in other heterocyclic organic compounds and polymers. Figure 8a shows the linear pressure shift of the two oxadiazole ring vibrations. The pressure coefficients for the *trans* and *cis* conformations are  $4.4$  and  $3.7\text{ cm}^{-1}\text{ GPa}^{-1}$ , respectively. The larger coefficient for the *trans* conformation indicates that the ring vibration is more

sensitive with respect to a volume change if the dipole orientation is antiparallel. This is in accordance with the large frequency shift of  $24\text{ cm}^{-1}$  of the oxadiazole ring vibration in the *trans* conformation compared with the isolated ring in the DPO monomer.

The relative intensities of the Raman excitations as a function of pressure resulting from the *trans* and *cis* conformations are shown in Figure 8b. With increasing pressure the *trans* conformation is preferred with respect to the *cis* conformation. The change of intensities is reversible if the pressure is released. Therefore, we conclude that increasing pressure (or decreasing volume) favours the *trans* orientation. This can be explained by a qualitative thermodynamic consideration. Since the *cis* molecule occupies a slightly larger volume than the *trans* molecule the free enthalpy difference  $\Delta G$  between both conformations increases with pressure. Assuming a statistical (Boltzmann) distribution of *trans* and *cis* molecules this increase of  $\Delta G$  results in a decrease of the amount of *cis* conformations.

High pressure experiments have been performed also for the polymeric  $\alpha$  and  $\beta$  forms of POD. The results for the typical Raman excitations in the frequency range between  $1500$  and  $1700\text{ cm}^{-1}$  are summarized in Table 1. The phenylene ring vibrations of both conformations show the same zero pressure frequencies and pressure shifts. Differences are observed in the pressure dependence of the vibration frequencies of the oxadiazole rings. The pressure coefficient of the corresponding vibration in  $\beta$ -POD is about 10% larger than in  $\alpha$ -POD (see Table 1). Comparing these results with the phonon energies of the dimer it is obvious that the zero pressure frequencies are almost identical but the pressure coefficients are appreciably higher in the polymers. This general tendency holds for the oxadiazole as well as the phenylene ring vibrations. The larger pressure shift may be explained by the higher compressibility of the polymers. The dimer DPO forms a crystalline structure which is less compressible than the noncrystalline polymeric material. Therefore, we expect a stronger pressure dependence of the molecular vibrations in the polymer as shown in Table 1.

## CONCLUSIONS

It is shown that the two different modifications of poly(*p*-phenylene-1,3,4-oxadiazole) can be distinguished by both i.r. and Raman spectroscopy. The differences are clearly marked in the spectral region between  $1500$  and  $1650\text{ cm}^{-1}$ . The characteristic oxadiazole ring vibration at  $1552\text{ cm}^{-1}$  observed for the monomer splits into two lines with considerable shift for the dimer, higher oligomers and polymers, respectively. This splitting may be understood by the occurrence of the *cis* and the *trans* conformations, where a different involvement of hydrogen atoms adjacent to the oxadiazole ring results. This is confirmed by molecular modelling calculations.

Application of pressure results in a linear shift of the fundamental oxadiazole and phenylene ring vibrations. The oxadiazole ring vibrations slightly differ for the  $\alpha$  and  $\beta$  forms. The evaluation of the relative intensities between the lines assigned to the *trans* or *cis* conformations supports the assumption also resulting from the modelling that  $\alpha$  is the thermodynamically stable form though the difference to the  $\beta$ -form is small.

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