Effects of structural variations of platinum and palladium poly-ynes on third-order non-linearity

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We present the measurements of both the real and imaginary parts of the third-order hyperpolarizability (γ) for a series of platinum and palladium poly-ynes and related oligomers. The variation of γ with the number of polymer repeat units is also studied.

(Keywords: non-linear optics; third-order hyperpolarizability; non-linear refractive index; non-linear absorption; platinum poly-ynes; palladium poly-ynes)

INTRODUCTION

Transition metal poly-ynes have large third-order optical susceptibilities (χ^3) which are comprised of contributions from the real and imaginary parts of the third-order hyperpolarizabilities (γ' and γ'', respectively) of the polymer repeat units. The existence of very large two-photon transitions in the polymer ensures that the imaginary part of the hyperpolarizability is the dominant component of the third-order susceptibility. In previous studies[1–5], we have used third-harmonic generation, four-wave mixing, optical Kerr gate, self-focusing, and intensity-dependent absorption techniques to define the relationship between polymer structure and optical non-linearity. By varying the substituents on the benzene ring, or by varying the ring itself, we can manipulate the physical properties of the polymers to obtain materials which are well-suited for optical devices. Here, we present the results of recent measurements on a series of transition metal poly-ynes and oligomers, selected to show the effects of variations in polymer repeat unit structure on both the real and imaginary components of the hyperpolarizability.

EXPERIMENTAL

Infra-red spectra were taken on a Perkin Elmer 783 spectrometer. Ultraviolet (u.v.) spectra of methylene chloride solutions were recorded on a Perkin Elmer Lambda 5 spectrometer. Molecular weights (M_n) were determined by gel permeation chromatography on a Waters chromatograph with microstyragel (500 Å) and ultrastyragel linear columns using tetrahydrofuran (THF) as the mobile phase, a flow rate of 0.8 ml min^{-1} and a 254 nm u.v. detector. Columns were calibrated against polystyrene standards from Waters.

Diethynylarenes were synthesized from dibromoarenes using the procedure of Takahashi *et al.*[6]. All catalysts and dibromoarenes were used as received from Aldrich, Lancaster Synthesis or Pfaltz and Bauer, except for 1,4-dibromo-2-fluorobenzene which was vacuum-distilled prior to use. 1,4-Dibromo-2,5-diethylbenzene was synthesized according to literature methods. All diethynylarenes synthesized were purified by sublimation or recrystallization immediately before use in the polymerizations.

Trans-dialkynyl complexes of palladium and platinum were prepared by the method of Sonogashira *et al.*[7] and purified by recrystallization from ethanol.

Palladium and platinum polymers of the form $[-(PBu_3)_2M-C{\equiv}C-C_6H_4-C{\equiv}C-]_n$ (where M = Pt, Pd) were prepared by a condensation reaction similar to that of Takahashi *et al.*[8,9]. In a typical experiment, a mixture of *cis*- and *trans*-dichlorobis(tri-n-butylphosphine)Pt (II) (2.35 g, 3.5 mmol) in 150 ml cyclohexane is bubbled with carbon monoxide, with stirring, to convert all of the material to the *trans* form. This solution is then added to a deoxygenated solution of freshly sublimed *p*-diethynylbenzene (0.44 g, 3.5 mmol) in 200 ml piperidine. Cuprous iodide (10 mg, 0.05 mmol) is added under a nitrogen atmosphere. The reaction mixture is brought to reflux for 2–24 h under nitrogen pressure. After evaporation of the solvent, the residue is filtered by alumina column chromatography in a helium atmosphere. The filtrate is concentrated and purified by precipitation into a 10-fold excess of methanol. Polymers are stored at ~0°C.

Polymers of the form $[-(PBu_3)_2M-C{\equiv}C-C_6H_4-C{\equiv}C-C{\equiv}C-C_6H_4-C{\equiv}C-]_n$ are synthesized by an oxidative coupling procedure[10]. In a typical polymerization, oxygen is bubbled into a mixture of cuprous chloride (0.70 g, 7.1 mmol) and *N,N,N',N'*-tetramethylethylenediamine (0.96 g, 8.3 mmol) in 95 ml methylene chloride for 20 min at room temperature. A solution of *trans*-bis(tri-n-butylphosphine)bis(*p*-ethynylphenylethynyl)Pt (1.00 g, 1.2 mmol) in 70 ml methylene chloride is then added and stirred under nitrogen pressure for 1–12 h (shorter reaction times are used to prevent long chain lengths which present solubility problems). After evaporation of the solvent, the residue is filtered by alumina column chromatography in a helium atmosphere. The filtrate is then concentrated and purified

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by precipitation into a 10-fold excess of methanol.These polymers are also stored at ~0°C.

To determine the real part of the hyperpolarizability, γ', we have used the optical Kerr gate technique on 0.02–0.10 M polymer samples dissolved in deoxygenated spectral-grade THF. The experimental procedure is the same as that described in reference 5, except that wavelengths of both the pump and the probe beams were 1.064 μm to ensure that only truly off-resonant γ' values are obtained. This measurement yielded a ratio of γ' for the polymer to that for THF. Absolute γ' values were calculated assuming γ' for THF was 4.8×10^{-37} esu.

The standard intensity-dependent absorption technique, also described in reference 5, is used to evaluate γ''. All γ'' values presented here were measured with a 532 nm laser beam. Maximum experimental error is estimated to be 25%.

RESULTS AND DISCUSSION

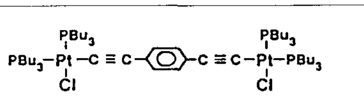
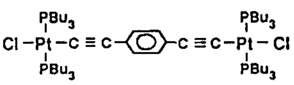
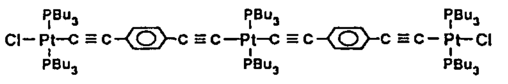
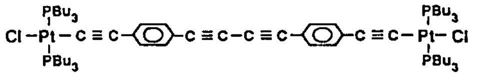
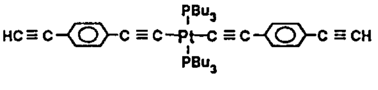
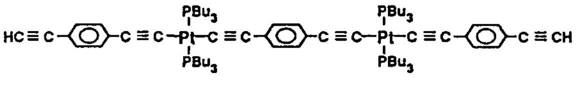
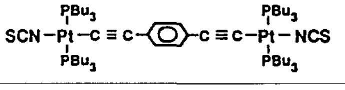
Within the concentration range measured (0.02–0.10 M), γ' values were found to be relatively invariant with sample concentration. The γ'' values however, were highly concentration dependent. This departure is currently under investigation. All values for γ'' presented here are for the lower range of stated concentrations.

Table 2 lists the γ' and γ'' values determined for a series of platinum poly-ynes with a single diethynylbenzene group in the polymer repeat unit. In earlier work[2], we noted that the principal contributors to the polymer repeat unit, $(PBu_3)_2PtCl_2$ and *p*-diethynylbenzene, have marginal optical non-linearity although mononuclear and binuclear platinum complexes constructed from $(PBu_3)_2PtCl_2$ and *p*-diethynylbenzene have substantial γ' and γ'' values. We previously found an additional modest increase in the hyperpolarizability values arising from the formation of polymers with repeat units analogous to the mononuclear complexes[2]. In this work, *Tables 1*, *2* and *4* show that the γ' values for the binuclear complexes **1b** and **3** are half those of the related repeat units in polymers **7** and **20**, respectively, thus confirming that linking a given structural unit with other units enhances hyperpolarizability. We are currently attempting to determine the number of repeat units required to achieve maximum non-linearity. Some of our initial data for complexes containing one to three platinums are presented in *Table 1*. Comparison of **1a** and **1b** shows the importance of having a *trans* arrangement of the phosphine ligands on the platinum metal centre. While γ' for the *trans* complex is only marginally improved over that for the *cis* isomer, the γ'' value for **1b** is significantly larger. Comparison of the γ'' value of **4** with the γ'' value for **7** suggests that there is a small interaction through platinum metal centres which enhances the non-linearity of the polymer repeat unit of **7**. Complex **4** is analogous to the repeat unit of polymer **7** but has a γ'' value only 40% that of γ'' for the polymer.

Linking two or three platinums is not sufficient to achieve the γ'' value per repeat unit for the analogous polymer **7**, as seen by reference to complexes **2** and **5**. While the γ'' values for these complexes are large, they represent γ'' for the entire molecule. When corrected for the number of platinums in the molecule, the resulting γ'' values per platinum–organic moiety are comparable to or less than the γ'' values for the simple units **1b** and **4**, respectively. This applies to the γ' values as well. In our study of the relationship between polymer chain length and non-linearity, we have seen that the longer polymers are relatively invariant in non-linearity per repeat unit, as demonstrated by the values for different chain lengths of polymer **11** (*Table 2*) and polymer **20** (*Table 4*). In each instance, doubling the number of linked units did not affect the γ' and γ'' values per repeat unit.

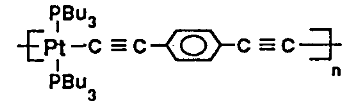
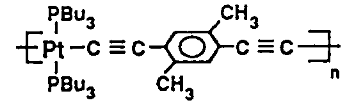
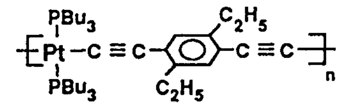
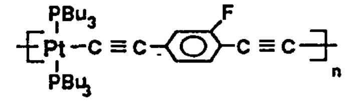
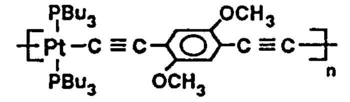
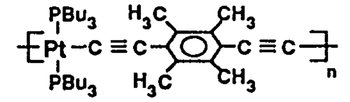
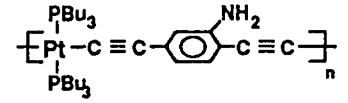
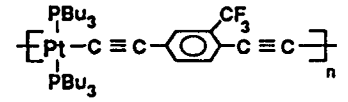
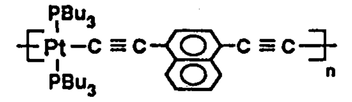
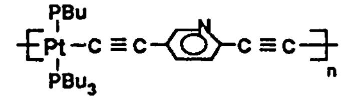
Comparison of complexes **1b** and **6** shows that

Table 1 Platinum complexes

No.	Sample	γ' (10^{-36} esu)[a]	γ'' (10^{-36} esu)[b]
1a	 *cis*	11	224
1b	 *trans*	19	827
2		45	1196
3		88	2167
4		53	759
5		66	1328
6		30	1134

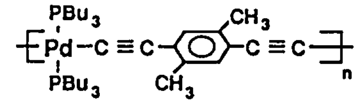
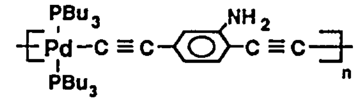
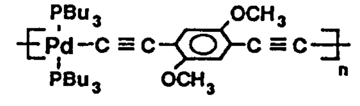
[a] Pump and probe at 1.064 μm
[b] Measured at 532 nm

Table 2 Platinum poly-ynes (one diethynylarene per repeat unit)

No.	Sample	*n*	γ' (10^{-36} esu)[a]	γ'' (10^{-36} esu)[b]
7		112	37	1906
8		26	29	1200
9		15	43	956
10		18	56	1260
11		111 105 62	48 65 43	1724 1330 1586
12		olig.	28	1324
13		76	18	1342
14		44	34	2148
15		62	19	2474
16		47, 35	33	2263

[a]Pump and probe at 1.064 μm
[b]Measured at 532 nm

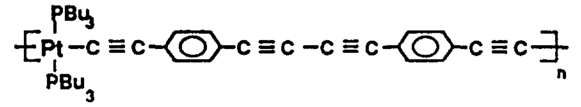
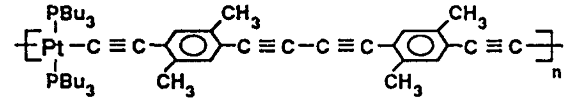
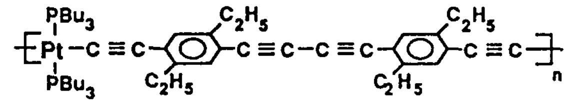
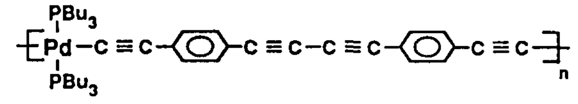
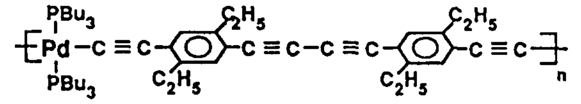
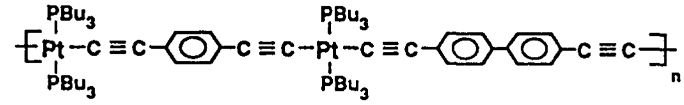
Table 3 Palladium poly-ynes (one diethynylarene per repeat unit)

No.	Sample	*n*	γ' (10^{-36} esu)[a]	γ'' (10^{-36} esu)[b]
17		4	19	1169
18		12	15	1753
19		67	22	2432

[a]Pump and probe at 1.064 μm
[b]Measured at 532 nm

end-group modification can be useful in enhancing non-linearity. Replacement of the chlorines of **1b** with the isothiocyanate group to form **6** gives a 50% increase in γ' and a 37% increase in γ''. Substituting diethynylbenzene groups for the chlorines to form **5** provides a three-fold increase in γ' while γ'' is increased by 60%. We intend to explore end-group modification of larger complexes as well as the polymers. Although

Table 4 Platinum and palladium poly-ynes (two diethynylarenes per repeat unit)

No.	Sample	n	γ' (10^{-36} esu)[a]	γ'' (10^{-36} esu)[b]
20		223 97	90 121	4558 4025
21		52, 38	116	2432
22		146	79	4933
23		olig. (5, 2)	66	2094
24		16	106	3490
25		66	–	4466

[a] Pump and probe at 1.064 μm
[b] Measured at 532 nm

we do not expect this to effect large changes in non-linearity for the polymers, this technique may be useful in altering the physical properties of the polymers.

Also of interest in *Table 1* is the effect of substituting two diethynylbenzenes for a single diethynylbenzene as seen by comparing complex **1b** with **3**. The increase in conjugation between the two metal centres leads to a four-fold increase in γ' and nearly a three-fold increase in γ''. The same result is seen with the metal polymers discussed below.

Our results in *Table 2* show the effects of adding substituents to the benzene ring in the polymer repeat unit. Polymers **8–13** include substituents considered to have electron-donating resonant effects with a benzene ring. For polymers **9–11**, the γ' values are, in general, slightly larger than the γ' value for the unsubstituted polymer, **7**. Polymer **8**, a xylene derivative, and polymer **12**, a durene derivative, have slightly lower or equivalent (within experimental error) γ' values. The γ' value for polymer **13**, however, is clearly smaller, which may be related to a weak interaction between the amino hydrogen and substituents on other polymer chains.

The $-CF_3$ group of polymer **14** is the only substituent having electron-withdrawing resonant effects in this series. The γ' for polymer **14** was essentially unchanged from that of polymer **7**. The effects of other electron-withdrawing substituents on the hyperpolarizability warrants further investigation.

Polymer **15**, with naphthalene substituted for benzene, shows a decrease in γ' compared to **7**, whereas the substitution of pyridine for benzene, polymer **16**, caused no significant change in γ'.

The results of substituting palladium for platinum on the γ' values can be seen in *Table 3*. All the γ' values for polymers **17–19** are reduced compared to their platinum analogues, polymers **8**, **13** and **11**, respectively. The similarity of γ' for polymers **17–19** suggests that they are less sensitive to ring substituent changes than platinum polymers. The palladium poly-ynes did not exhibit a dependence of γ' on chain length, giving similar values for oligomers ($n = 4$) and polymers ($n = 67$).

Table 4 lists platinum and palladium polymers with two diethynylbenzenes in the repeat unit. These γ' values are consistently larger, by a factor of 2 or more, than the analogous polymers in *Tables 2* and *3*. The addition of $-CH_3$ and $-C_2H_5$ groups in polymers **21** and **22** had very little effect on γ', as compared to the unsubstituted **20**.

An analogous determination of structural effects on non-linearity can be made for γ'', the imaginary part of the hyperpolarizability. Comparison of complex **1b** with polymer **7** and complex **3** with polymer **20** shows that linking polymer repeat units enhances γ'', as was the case with γ'. For polymers **7–13** however, all of the electron-donating substituents reduce γ'' values somewhat compared to the unsubstituted polymer **7**. Surprisingly, the electron-withdrawing $-CF_3$ unit raises γ'' slightly as does substitution of naphthalene and pyridine for benzene in polymers **15** and **16**. Substitution of palladium for platinum causes no change in γ'' for polymer **17** but produces modest increases for polymers **18** and **19**. With two diethynylbenzene units in the platinum polymer repeat unit, γ'' is more than double the value for the analogous single diethynylbenzene polymer (compare polymers **20**, **21** and **22** to **7**, **8** and **9**, respectively). We could not determine a trend for the palladium polymers **23** and **24** since we did not include the analogous single diethynylarene polymers in this study. However, the γ'' values for polymers **23** and **24** were as large or larger than the γ'' values for polymers **17**, **18** and **19**.

Substitution of biphenyl for one of the diethynylbenzenes in polymer **25** also gives a γ'' value that is more than double the γ'' value for the single diethynylbenzene repeat unit polymer (**7**) and is comparable to that for polymer **20**. Structurally however, polymer **25** differs in that it contains two platinums in its repeat unit whereas all of the other polymers in *Table 4* contain only one platinum per repeat unit. We must, therefore, compare γ''/platinum-organic unit for **25**, which is only slightly larger than the γ'' value for polymer **7**.

CONCLUSIONS

Linking a given structural unit with other units to form polymers increases non-linearity, although longer polymers do not achieve additional increases by further lengthening of the polymer chain. The non-linearity of the platinum and palladium poly-ynes is relatively insensitive to the nature of the substituents on the benzene ring in the polymer repeat unit. Increasing the number of diethynylarenes in the repeat unit from one to two enhances the non-linearity by a factor of 2 or greater. Higher non-linearity is expected from further increase in the number of diethynylarenes in each repeat unit.

The large γ values of the poly-ynes translate into large values for the macroscopic χ^3 as well, even in solutions with molarities of 0.05 M. For sample **23**, for example, the value of β, the two-photon absorption coefficient, is $6\ \mathrm{cm\ GW^{-1}}$ for a 0.064 M solution. This is bigger than the β for bulk ZnSe, for which a value of $5.5\ \mathrm{cm\ GW^{-1}}$ has been reported[11]. Since β is concentration dependent, we expect to increase χ^3 by several orders of magnitude upon switching from solutions to 100% polymer films. Free-standing, pure-polymer films of good optical quality are thus expected to be of considerable use in non-linear optical applications.

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