Ultrafast Optical Kerr Effect of Conjugated Silver Phenylacetylide Complex Oligomer

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Abstract: Silver phenylacetylide oligomer was found to exhibit prominent third-order nonlinear optical property, with susceptibility $\chi^{(3)}$ of 2.4×10^{-14} esu (10^{-4} mol/L in 1:1 dimethyl sulfoxide/$CHCl_3$ mixed solution) and second-order hyperpolarizability γ of 5.18×10^{-32} esu *via* heterodyned ultrafast optical Kerr effect measurement. It existed mainly as 1:1 complex oligomers and polymers as characterized by mass spectroscopy and elemental analysis etc.

Keywords: Silver phenylacetylide, conjugated complex, optical Kerr effect.

Conjugated polymers with large third-order optical nonlinearity have been focused for their promising potentials for advanced materials applications[1]. Recently, investigations of transition metal with organic ligand systems have been greatly intensified due to the d-electrons incorporated in the conjugated system, which are expected to enhance the hyperpolarizability. Phenylacetylene and the metal phenylacetylides play important roles in formation of unique coordinated clusters[2], but it seems that the study of metal phenylacetylides, particularly of the silver phenylacetylides is extremely far from being commensurate. Here we report the preparation of silver phenylacetylide and for the first time to observe the third-order optical nonlinearity of metal phenylacetylide compounds through heterodyned optical Kerr effect measurement.

Silver phenylacetylide was prepared from reaction of silver nitrate with excess ammonia in acetonitrile, followed by addition of slightly excess phenylacetylene. The precipitates were collected, washed thoroughly, then dried under vacuum.

The composition of the product was verified by FT-IR, where the typical monosubstituted benzene ring absorption peaks and the acetylene C≡C stretching absorption at 2064 cm^{-1} were evidently consistent with the formation of phenylacetylide, $(AgCCPh)_n$, which was further ascertained by elemental analysis, where the weight percent of C=45.67% and H=2.27% were very well coincident with the calculated values of C=45.96% and H=2.41% in $(AgCCPh)_n$.

The conjugated manner of such silver phenylacetylide may better be illustrated by its UV-vis absorption spectrum in comparison with that of the phenylacetylene as shown in **Figure 1**. The maximum absorption of phenylacetylene appears at 247 nm, without any absorption beyond 260 nm, while the maximum absorption of silver phenylacetylide appears at 260 nm and extends considerably into the visible region up to 600 nm. **Figure 2** shows the mass spectrum of silver phenylacetylide, where stable fragment at m/z of up to 1459 (heptamer) was observed. Since XPS analysis showed that the silver atoms were almost in the same state, the structure of silver phenylacetylide in the solid state could be described as a linear staircase polymer, while in solution, there were oligomeric species with n≤7.

The optical Kerr effect (OKE) measurement has been published elsewhere. For the

Figure 1. UV-vis spectra of phenylacetylene (a) and silver phenylacetylide (b)

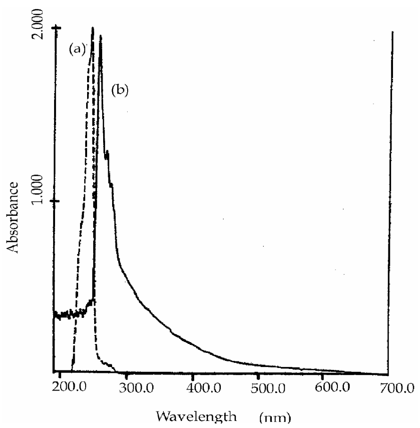
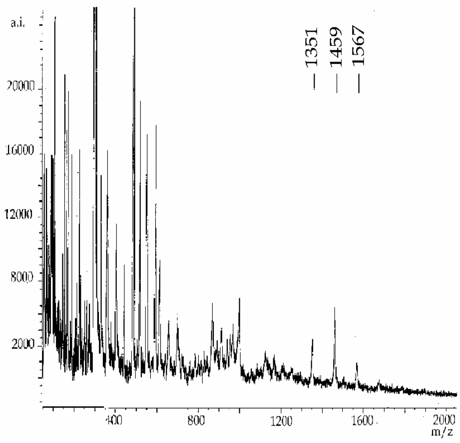


Figure 2. MS of silver phenylacetylide.



light was generated from the probe beam by slight rotation of the first polarizer which ensures the out-of-phase OHD in the OKE measurement[3]. We inserted a λ/4 waveplate between the input polarizer and the focusing lens to measure the real component of $\chi^{(3)}$.

Silver phenylacetylide in 1:1 dimethyl sulfoxide (DMSO) / $CHCl_3$ mixed solution (10^{-4} mol/L) was examined by OHD-OKE method with CS_2 as reference. Its time resolved OHD-OKE signals were comparatively strong. The effective third-order nonlinear susceptibility, $\chi^{(3)}$, and the second-order hyperpolarizability, γ, thus found were 2.4×10^{-14} esu and 5.18×10^{-32} esu respectively. Moreover, the relaxation time was clearly shorter than the laser pulse width, indicating the ultrafast optical response originated in the electron movement. We conclude that silver phenylacetylide itself is a promising material for the third-order nonlinear optical (NLO) applications.

References

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