Nanocomposite Photonic Polymers. 1. Third-Order Nonlinear Optical Properties of Capped Cadmium Sulfide Nanocrystals in an Ordered Polydiacetylene Host

Robert E. Schwerzel*
Georgia Tech Research Institute, EOEML, 925 Dalney Street, Atlanta, Georgia 30332-0825

Kevin B. Spahr, John P. Kurmer, and Van E. Wood
Battelle, 505 King Avenue, Columbus, Ohio 43201-2693

Jerry A. Jenkins
Department of Chemistry, Otterbein College, Westerville, Ohio 43081

Received: November 26, 1997; In Final Form: March 27, 1998

The third-order nonlinear optical (NLO) response of colloidal "quantum-dot" cadmium sulfide (CdS) nanocrystals has been measured both in solution and in Langmuir−Blodgett (L−B) multilayers of a polydiacetylene (PDA) "alloy" NLO polymer. The PDA "alloy" was composed of a tailored mixture of diacetylene monomers having carboxylic acid "head" groups and benzamide "head" groups, in each case separated from the diacetylene moiety by an eight-carbon spacer group, so as to disrupt the strong aggregation, leading to excessive light scattering, that normally occurs with L−B films of carboxyl-terminated PDAs. It is shown that at 530 nm the nonlinear refractive index (n_2) of a nanocomposite PDA film containing thiophenol-capped CdS nanocrystals, as measured by both Z-scan and degenerate four-wave mixing (DFWM) techniques, is 11×10^{-8} cm^2/MW, while that of an undoped PDA film is only 3×10^{-8} cm^2/MW. This demonstrates the concept of a "nonlinear−nonlinear" optical material, in which the NLO response of an embedded quantum-dot semiconductor can add constructively to that of a NLO polymer having complementary wavelength characteristics.

I. Introduction

In recent years, interest in the synthesis, characterization, and application of colloidal "quantum dot" (QD) semiconductor materials has grown markedly.[1] This increased attention reflects both the strong size dependence of the optical and electronic properties of these materials[2,3] and the fact that the materials are relatively easy to make with well-controlled particle sizes.[1,4] The size dependence arises because the physical size of the particles—which are typically about 20−80 Å in diameter—is smaller than the electron wave function, leading to "quantum confinement" effects that result from the "squeezing" of the electronic structure by the physical boundaries of the particles. Thus, one can synthesize a given semiconductor, such as cadmium sulfide (CdS), in colors ranging from water white to deep orange simply by increasing the particle diameter from approximately 20 Å to 60 Å, with no change in chemical composition. Other optical properties of the particles, such as refractive index and NLO response, exhibit similar changes with particle size.

Our interest in these materials stems from the ease with which the size and composition of the core semiconductor particle can be varied, while independently controlling the chemical properties of the particle by "capping" the surface with functionalized thiol reagents which form a monolayer or partial monolayer of organic groups.[4,5] This independent control of the optical properties and the chemical behavior of these particles provides an unprecedented opportunity to design new materials in which quantum-dot semiconductors having specific optical and electronic properties are combined with other components to create tailored nanocomposite materials for specific device applications.

We have previously described measurements of the third-order NLO response of CdS QDs capped with a variety of organic thiol and amine reagents in organic solvents[5] and the fabrication and characterization of polydiacetylene "alloys" which form stable, high-quality L−B multilayer films having exceedingly high optical clarity.[6] In this paper, we describe the third-order nonlinear optical response of a prototypical nanocomposite "nonlinear−nonlinear" optical polymer,[7] consisting of thiophenol-capped CdS quantum dots embedded in a L−B multilayer film of polydiacetylene alloy.[8]

II. Results and Discussion

The "Nonlinear−Nonlinear" Optical Polymer Concept. The material system that we refer to as a "nonlinear−nonlinear" optical polymer is a nanocrystalline QD semiconductor having a large value of the nonlinear refractive index (n_2) and an absorption band edge at a relatively short wavelength, dispersed in a host NLO polymer material also having a large value of n_2 *and having the same sign of n_2 as the semiconductor QD particles*, but with a longer wavelength absorption band and a transmission window in the vicinity of the semiconductor QD band edge. These relationships are shown schematically in Figure 1 (adapted from ref 7). Because the value of n_2 (like that of the linear refractive index, n) falls off more slowly with wavelength than does the absorbance, there can be substantial overlap between the n_2 dispersion curves for the QD semiconductor and the NLO polymer within the transmission window

S1089-5639(98)00344-2 CCC: $15.00

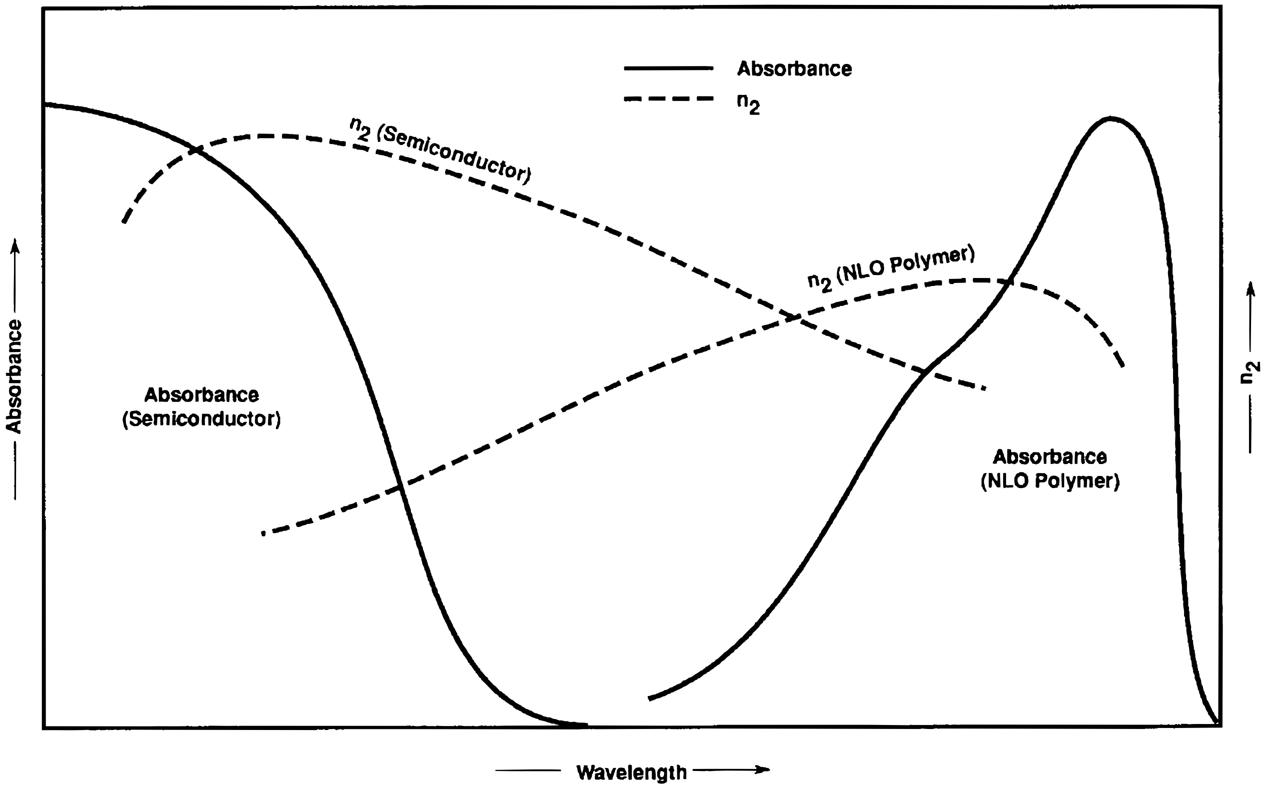


Figure 1. Schematic representation of the “nonlinear–nonlinear” optical material concept (adapted from ref 7).

of the combined material, as indicated in Figure 1. Provided that the sign of n_2 is the same for the two components within this wavelength region, the two values should add constructively, leading to a large and relatively constant overall value of n_2 across the transmission window of the material. This in turn should make possible the rational design of “device-friendly” materials by a proper choice of NLO polymers and QD semiconductors, so as to place the transmission window in a suitable wavelength region as dictated by overall system constraints (such as the characteristics of light sources, detectors, etc.).

CdS Quantum Dots. CdS QD particles having a mean diameter of 33 ± 9 Å were prepared by the reverse micelle method of Steigerwald and Brus[4] and capped with thiophenol, which has been shown to give the particles good solubility in organic solvents such as pyridine and chloroform.[4,5] A representative 400 keV transmission electron micrograph (TEM) of these particles (deposited on a carbon support from pyridine solution) is shown in Figure 2. Cadmium lattice planes are visible in some of the particles; the size distribution was estimated by measuring a number of the particles in the TEM image. The linear absorption spectrum of a highly concentrated (20% w/v) solution of these particles in spectroscopic grade pyridine is shown in Figure 3. The key feature is the broad onset of absorbance at around 520 nm; as noted above, the onset wavelength decreases with decreasing particle size, while for a given particle size, the magnitude of absorbance varies with concentration according to Beer’s law. Thus, while the shape of the curve is essentially concentration-independent, the absolute absorbance at a given wavelength varies linearly with concentration. In Figure 3, the onset of absorbance appears shifted to a longer wavelength than would be expected for particles in the 30–35 Å size range because the high concentration of the solution has significantly increased the intensity of the long-wavelength “tail” of the absorption band. This concentration was chosen to gain an understanding of how the absorption properties of high concentrations of the particles would compare with the absorption spectrum of the polydiacetylene film, since we intended to incorporate high concentrations of the particles into the films if possible.

The sign and magnitude of the nonlinear refractive index (n_2) of the particles were measured by pulsed Z-scan[8] and by pulsed degenerate four-wave mixing (DFWM) techniques, respectively, in pyridine solution at several concentrations ranging from 5% (w/v) to 20% (w/v) and at several wavelengths from 528 to 490 nm, as reported previously;[5] a nitrogen-pumped dye laser having a pulse energy of 20 μJ and a pulse duration of 5 ns was used. In those studies, we found that the observed (negative) values of n_2 increased smoothly as the wavelength was decreased (that is, as the pulse wavelength moved more and more into the absorption band), indicating resonant enhancement of the NLO response, and ranged from around -4×10^{-8} cm^2/MW for a 5% (w/v) solution at 528 nm to around -14×10^{-8} cm^2/MW for a 20% (w/v) solution at 490 nm.[5] A typical Z-scan curve for these solutions is shown in Figure 4, demonstrating the characteristic shape for a negative nonlinearity.[9]

Polydiacetylene “Alloys”. When amphiphilic diacetylene monomers (having a hydrophilic “head” group and a fatty, hydrophobic “tail” group) are dispersed on a clean water surface in preparation for the deposition of L–B multilayer films on a substrate, it is often observed that the resulting films are opaque because of the extensive light scattering caused by the formation of two-dimensional crystallites of the diacetylene headgroups at the air–water interface. This is clearly unacceptable for materials that are ultimately intended for use in nonlinear optical waveguides, diffraction gratings, and other active optical components.

To alleviate this problem, we have devised an approach to disrupting the crystallinity of the polar headgroups by incorporating smaller amounts of modified diacetylene monomers having less polar headgroups that act as plasticizers for the polar

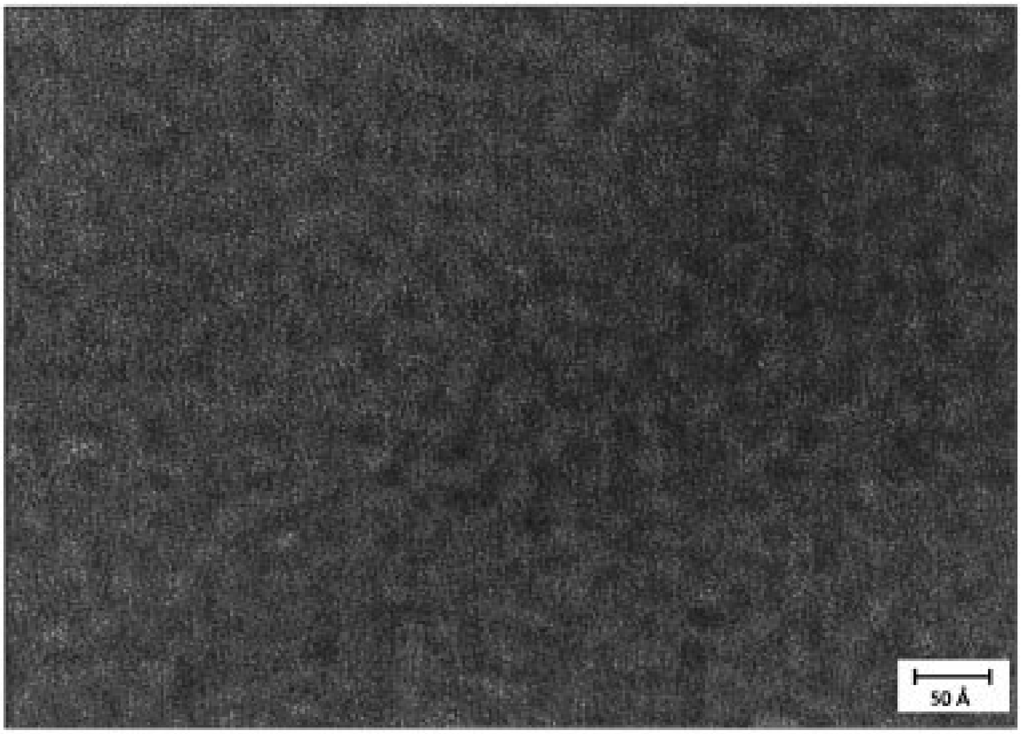


Figure 2. A 400 keV transmission electron micrograph of thiophenol-capped CdS nanoparticles, deposited from pyridine solution (magnification = 2 000 000×).

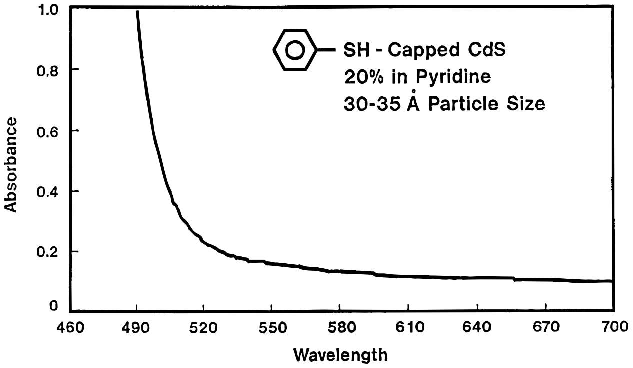


Figure 3. Visible absorption spectrum of thiophenol-capped CdS nanoparticles in pyridine (33 Å diameter, 20% w/v).

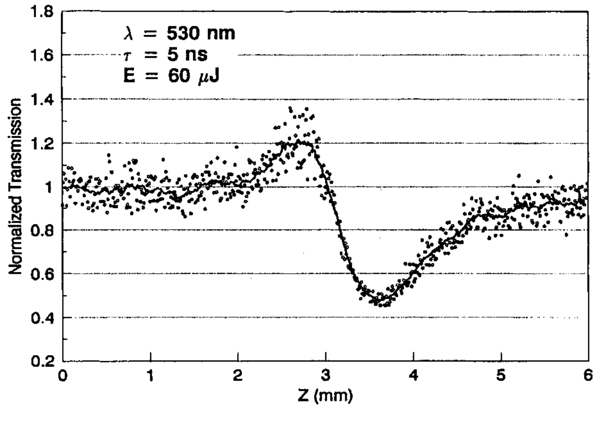
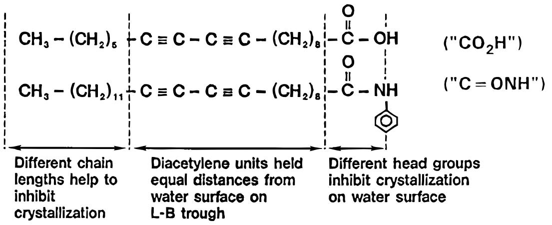


Figure 4. Z-scan of thiophenol-capped CdS particles in pyridine (negative n_2, 530 nm, 5 ns pulse, 60 μJ pulse energy).

moieties; we refer to the resulting mixed diacetylene systems as diacetylene "alloys", since their compression behavior on the L−B trough differs systematically from that of either pure component.[6] In the specific case of the polydiacetylene alloy used for this work, two components were used as shown in Scheme 1, in a 3:1 molar ratio. The major component, having a carboxylic acid headgroup, provided strong interaction with the water surface and served as the primary building block for the multilayer assemblies. The minor component, having the amide headgroup, was codissolved with the major component prior to spreading the solution on the water surface and served to disrupt the two-dimensional crystallinity of the carboxylic acid groups *without affecting the placement of the diacetylene moiety with respect to the water surface.* Because both components had the same eight-carbon spacer group between the headgroup and the diacetylene group, all of the diacetylene units were held at approximately the same distance from the water surface. Thus, the solid-state photopolymerization of the diacetylenes, achieved by exposure to a small "black light" after all the desired layers of monomer had been transferred to the substrate, occurred as smoothly as would have been the case with only a single headgroup. Finally, the two monomer components also had different fatty hydrocarbon chain lengths, to help minimize any tendency for crystallization between adjacent layers (which could also introduce light scattering and reduce the optical clarity of the multilayer films).

This alloy could be used to fabricate L−B films having over 100 layers with very high optical transparency, with no observable deterioration of quality either upon polymerizing the monomers by UV irradiation of the multilayer film with a hand-held "black light" or by storage at room temperature for periods

SCHEME 1: Monomer Composition of the Polydiacetylene "Alloy" Used in This Work



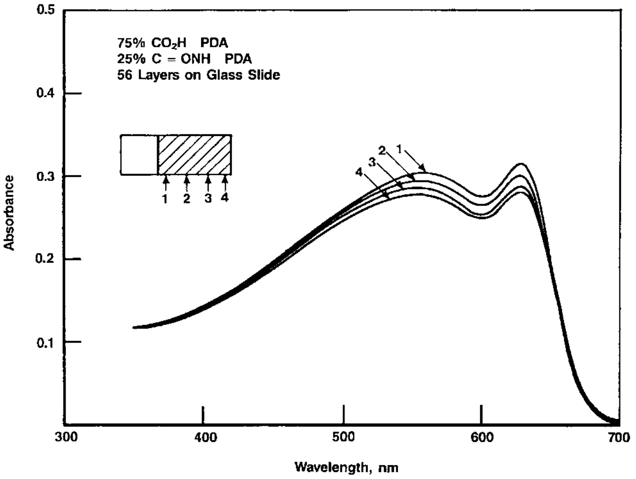


Figure 5. Visible absorption spectrum of polydiacetylene alloy L−B multilayer film on glass slide (56 layers), measured at several locations along the slide.

of over 8 months at room temperature. It is important to note that standard Class 100 clean-room procedures were followed in the fabrication of these films, including the microfiltration of all solvents and of the deionized water used in the L−B trough through an 0.2 μm membrane filter and the UV irradiation of the trough water immediately upon its placement in the trough to kill any bacteria that could compromise the mechanical integrity of the multilayer films.

The absorption spectrum of a representative multilayer film of this polydiacetylene alloy on a clean glass slide, measured at several locations along its length, is shown in Figure 5. This spectrum shows both the high optical quality of the film, as evidenced by a lack of scatter-induced divergence of the curves at the short wavelength side of the spectrum,[6] and the presence of both the blue form of the PDA (with an absorbance peak at 620 nm) and the red form (with a broader absorbance peak at around 560 nm). This sometimes occurs in these systems; while the films appear visually to be optrically clear and deep blue in color, there is occasionally a component of the red form present in the films, presumably because of thermal and solvent-induced relaxation of the side chains around the polydiacetylene polymer backbone.

Z-scan and DWFM measurements of n_2 for pure multilayer PDA films of this type, using 5 ns, 20 μJ pulses at 530 nm, showed n_2 to be negative, as for the CdS particles, and to have a value of approximately -3×10^{-8} cm^2/MW. By comparison, a sample of pure CS_2 gave a value of n_2 of $+5 \times 10^{-8}$ cm^2/MW, and a sample of pure pyridine gave a value of $+1 \times 10^{-8}$ cm^2/MW. A typical Z-scan curve for a pure PDA multilayer film is shown in Figure 6, again illustrating the characteristic shape for a material with negative nonlinear index.

Nanocomposite CdS/PDA Polymer. The absorption spectra shown in Figures 3 and 5, together with the negative sign of n_2 observed for both the CdS nanoparticles and the PDA films as shown in Figures 4 and 6, suggest that the CdS/PDA system would be an ideal model system to demonstrate the principles of a nanocomposite "nonlinear−nonlinear" optical material. As noted before and illustrated schematically in Figure 1,[7] a nanocomposite photonic polymer of this type should have the desirable property of providing a nearly constant value of n_2 across the transmission window between the QD absorbance band edge and the NLO polymer long-wave absorbance peak. This obtains because the magnitude of n_2 falls off more gradually with wavelength than does the absorbance coefficient and because the contributions to n_2 from the two components (QD semiconductor and NLO polymer) should add constructively by virtue of their sign identity. Thus, as the wavelength increases above the QD band edge and that component of n_2 begins to drop off, the contribution to n_2 from the NLO polymer will begin to increase, offsetting the decline in the QD component. The result is a "device-friendly" NLO material having a relatively constant nonlinear index across the window of low optical absorbance loss. In principle, such materials could be designed to position the transmission window at any desired wavelength in the visible or near-IR by an appropriate choice of the NLO polymer and the QD semiconductor composition and particle size.

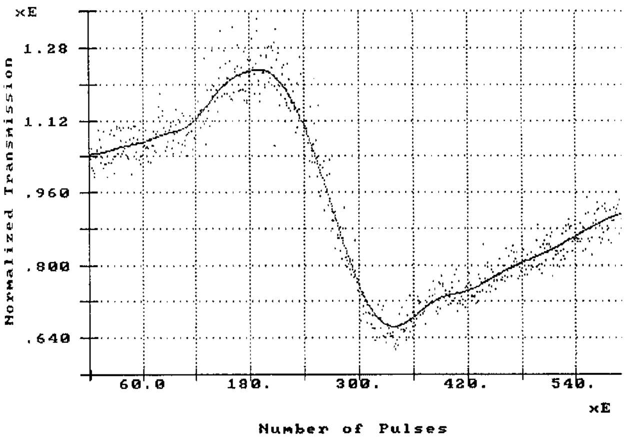


Figure 6. Z-scan of pure polydiacetylene alloy L−B multilayer film on fused silica slide (48 layers, negative n_2, 530 nm, 5 ns pulse, 20 μJ pulse energy).

The nanocomposite films reported here were prepared by dispersing a microfiltered chloroform solution containing a 1:1 weight ratio of the thiophenol-capped CdS particles and the diacetylene alloy monomers onto the L−B trough. Following evaporation of the solvent and compression of the resulting CdS/diacetylene monolayer, multilayer films ranging from 48 to 126 layers were prepared by dipping freshly cleaned fused silica slides and UV-polymerizing the monomers as before. The films were visually dark blue and optically clear, as were the undoped films. The presence of the QD CdS nanoparticles in the multilayer film was confirmed by energy-dispersive X-ray analysis, which indicated that the particles occupied about 10% of the volume of the film. Z-scan (Figure 7) and DFWM analysis confirmed that the nanocomposite films retain the negative sign for n_2 of the individual components and gave a magnitude of n_2 of approximately 11×10^{-8} cm^2/MW at 530 nm. This corresponds to an increase in the value of n_2 by a factor of nearly 4 as compared to the value observed for pure PDA multilayer films, with no particles added. While this is nowhere near the orders-of-magnitude gain that will likely be required to enable the development of practical devices that utilize n_2 for optical switching or modulation, it is nonetheless a significant demonstration of the potential for improving the NLO response of tailored optical materials by rational combinations of QD semiconductor particles and NLO polymers.

III. Summary and Conclusion

As a preliminary demonstration of the concept of a "nonlinear−nonlinear" optical material,[7] we have fabricated multilayer L−B films of a polydiacetylene alloy containing a 1:1 weight ratio of thiophenol-capped CdS quantum dot nanoparticles having core diameters of approximately 33 Å. The resulting films are

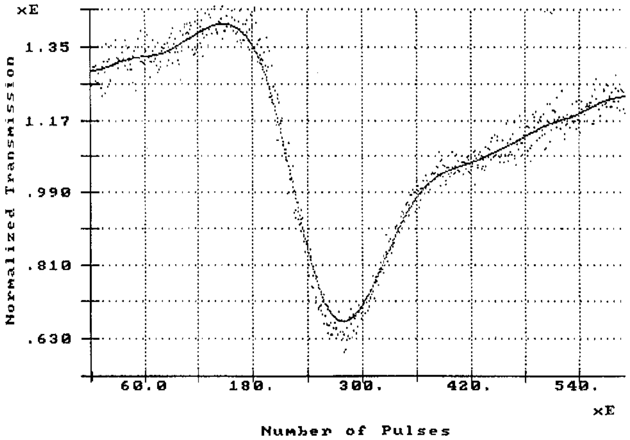


Figure 7. Z-scan of polydiacetylene alloy L−B multilayer film containing 1:1 weight ratio of thiophenol-capped CdS particles, on fused silica slide (126 layers, negative n_2, 530 nm, 5 ns pulse, 20 μJ pulse energy).

optically clear and deep blue in color and have been stored at room temperature for periods of over 8 months with no indication of mechanical deterioration (such as cracking or becoming cloudy). Measurements of the near-resonance third-order nonlinear refractive index (n_2) at 530 nm by means of Z-scan and degenerate four-wave mixing showed the value of n_2 to be 11×10^{-8} cm^2/MW, nearly a factor of 4 increase over the value for undoped PDA films. This wavelength was chosen because it is well within the transmission window between the absorbance band edge of the CdS particles and the long-wavelength absorbance bands of the PDA. The factor of 4 increase, while not sufficient to enable device applications, is noteworthy because the PDA backbone and the CdS core particle are separated by at least 4 or 5 Å by the thiophenol-capping groups on the CdS particles and by the side groups that surround the PDA backbone. We anticipate that closer coupling between the particles and the polymer backbone in future implementations of this concept should lead to significantly larger enhancements in third-order NLO response.

IV. Experimental Section

Materials. The capped CdS QD particles and the diacetylene monomers were prepared by standard procedures, as reported before.[5,6] Freshly obtained spectroscopic grade pyridine, $CHCl_3$, and CS_2 (all from Aldrich) were used as received for all experiments. Deionized water was prepared in a Class 100 clean room using a Milli-Q apparatus (Millipore Corp.) and was further microfiltered through 0.2 μm filters immediately prior to each use. ACS reagent grade $Cd(ClO_4)_2$ (Aldrich, 99+%) was used in the subphase water of the L−B trough.

Procedures. UV−vis−NIR spectra were obtained using a Cary 17 spectrophotometer. L−B multilayer films were prepared using a computer-controlled KSV L−B trough, located in the Class 100 clean room. All solutions were filtered through 0.2 μm filters immediately prior to use. The PDA films were polymerized by irradiation with a small "black light" for 15−20 min after L−B deposition of the full multilayer stack, under Class 100 conditions.

NLO Measurements. A commercial nitrogen-pumped tunable dye laser (10 Hz repetition rate, pulse duration 5 ns, pulse energy typically 20−60 μJ) was used for both the Z-scan and degenerate four-wave mixing measurements. The films were studied on clean fused silica substrates, and liquid solutions were studied in 1.0 mm path length fused quartz cuvettes (Hellma, "Spectrosil"); in all cases, any NLO response from the substrate or cell was subtracted out before data analysis. In the DFWM studies, both pump beams and the probe beam were all obtained from the same pulse, using suitable beam splitters and delay lines.

Acknowledgment. We wish to thank the Office of Naval Research (Solid State and Surface Chemistry Program), the Senior Research Faculty Leader Program of Georgia Tech Research Institute, and the Corporate Technical Development Program of Battelle Memorial Institute for financial support of this work. Additional financial support was provided by the Strategic Defense Initiative Organization (SDIO), through a Phase I SBIR subcontract from Materials Technologies Corporation (Milford, CT). We are particularly grateful to Prof. David Whitten (University of Rochester and Los Alamos National Laboratory) for his considerable assistance in enabling us to learn the L−B technique. We also wish to thank Mr. Robert Wyant (Battelle) for assistance with the preparation of the diacetylene monomers, Mr. Evan Werkema, Ms. Asali Odom, and Ms. Princess Simpson (all of Georgia Tech Research Institute) for assistance in the preparation of the CdS nanoparticles, Mr. James Busch (Battelle) for assistance with the NLO measurements, and Dr. Daniel Campbell, Mr. James Suggs, and Mr. Jeffrey Moore (Georgia Tech Research Institute) for many helpful discussions.

References and Notes

(1) See, for example: (a) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Science* **1995**, *270*, 1335. (b) Alivisatos, A. P. *Science* **1996**, *271*, 933. (c) Alivisatos, A. P. *J. Phys. Chem.* **1996**, *100*, 13226.

(2) (a) Rossetti, R.; et al. *J. Chem. Phys.* **1985**, *82*, 552. (b) Brus, L. E. *IEEE J. Quantum Electron.* **1986**, *QE-22*, 1909. (c) Brus, L. E. *Nouv. J. Chim.* **1987**, *11*, 123.

(3) Tolbert, S. H.; Herhold, A. B.; Johnson, C. S.; Alivisatos, A. P. *Phys. Rev. Lett.* **1994**, *73*, 3266.

(4) Steigerwald, M. L.; Brus, L. E.; et al. *J. Am. Chem. Soc.* **1988**, *110*, 3046.

(5) Schwerzel, R. E.; Kurmer, J. P.; Wood, V. E.; Jenkins, J. A. In *Nonlinear Optical Properties of Organic Materials III*; Khanarian, G., Ed.; SPIE Proceedings Volume 1337; SPIE: Bellingham, WA, 1990; p 132.

(6) Schwerzel, R. E.; Spahr, K. B.; Kurmer, J. P.; Ramsey, K. A. In *Nonlinear Optical Properties of Organic Materials II*; Khanarian, G., Ed.; SPIE Proceedings Volume 1147; SPIE: Bellingham, WA, 1989; p 157.

(7) Schwerzel, R. E.; Spahr, K. B. *ACS Polym. Prepr.* **1994**, *35* (2), 116.

(8) See also: Olsen, A. W.; Kafafi, Z. H. *J. Am. Chem. Soc.* **1991**, *113*, 7758.

(9) Shiek-Bahae, M.; et al. *IEEE J. Quantum Electron.* **1990**, *26*, 760.