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Excited State Enhancement of the Third Order Optical Nonlinearity of Polyalkylthiophene Pumped by Low Repetition Rate Femtosecond Ti:S Amplifier

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EXCITED STATE ENHANCEMENT OF THE THIRD ORDER OPTICAL NONLINEARITY OF POLYALKYLTHIOPHENE PUMPED BY LOW REPETITION RATE FEMTOSECOND TI:S AMPLIFIER

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Abstract Optical pumping effect on the third order optical nonlinearity of poly(3-dodecylthiophene) was investigated by 2 beam degenerate four wave mixing technique using low repetition rate femtosecond Ti:S amplifier. Four wave mixing signal from the sample was significantly enhanced by optical pumping at 400 nm. Femtosecond time resolved studies on four wave mixing and excited state dynamics of the entitled compound were carried out to elucidate the mehcanism of enhancement. Exciton formed by optical pumping in one dimensional polymer backbone might presumably play an important rule on the enhancement of four wave mixing amplitude.

INTRODUCTION

Organic compounds with large optical nonlinearity are the promising materials available for the future photonic applications on data processing and communication.[1] Besause the organic materials provide the larger nonlinear optical susceptibility as well as the faster temporal response based on the electronic polarization of the π electrons in the molecule rather than inorganic materials. Regardless of number of advantages for the organic materials compared with the inorganics, nonlinear optical susceptibility of organics reported so far has been a couple of orders smaller than the criterion for a practical use. Garito and colleagues have reported that the picosecond optical pumping on the solution of diphenylhexatriene enhanced the third order nonlinear susceptibility by a couple of orders of magnitude compared with the ground state.[2-3] They concluded the enhancement of third order optical nonlinearity with optical pumping came from the excited state. In this case, enhanced third order susceptibility of small conjugated molecules by optical pumping is the order of 10^{-32} esu which is much smaller than the criterion for the practical use. Conjugated polymers in which the electrons are one-dimensionally confined to the polymer chain backbone have been

well known to exhibit a high electric conductivity as well as a high third order optical nonlinearity.[4] Therefore the conjugated polymers are of great interest to investigate the third order nonlinear optical properties in the excited states. Our preliminary results exhibited that the third order optical nonlinearity from a conjugated polymer, poly(3-dodecylthiophene) (C12PT) in chloroform solution was enhanced by femtosecond optical pumping at 400 nm.[5] In the present paper, femtosecond pump-probe technique is available to investigate the temporal aspect on $\chi^{(3)}$ enhancement of conjugated polymer by optical pumping.

EXPERIMENTAL

C12PT was synthesized by polymerization of 3-dodecylthiophene monomer with $FeCl_3$ in chloroform solution under a nitrogen flushing atmosphere.[6] The sample is a chloroform solution at a concentration of 6.2 mg / ml in a 0.5 mm length glass cell. Solution was circulated in a glass cell to avoid the thermal effect on pump-probe measurement. Absorption spectrum of C12PT in a chloroform solution has a maximum at 440 nm and transparent at the wavelength longer than 550 nm.

Third order optical nonlinearity was measured by two beam degenerate four wave mixing (DFWM) technique[7] using femtosecond Ti:S amplifier system operatiing at 10 Hz. Two fundamental pulses at 800 nm with 200 fs temporal duration and 40 μJ energy were served as the probe pulses for DFWM measurement. Two probe pulses were crossed into the sample with an angle of 5 degree as to be spatially and temporally overlapped each other. Delay time between two probe pulses was controlled by a translation stage with a resolution of 0.5 μm. Two probe pulses make an orthogonal polarization geometry to avoid the thermal grating. Self diffracted DFWM signal was detected by a photomultiplier tube at a specific direction.

RESULTS AND DISCUSSION

Femtosecond Ti:S amplifier system allows us to investigate an optical pumping effect on the third order optical nonlinearity of C12PT with the ultrafast temporal resolution. Optical pumping effect on DFWM was performed by introduction of pumping pulse at 400 nm with 40 μJ energy generated by second harmonics of fundamental pulse. Delay time between pump and two probe pulses was regulated by the translation stage with a 2 μm resolution. DFWM amplitude variation with pump pulse was monitored as a function of delay time between pump and two probe pulses as shown in Figure 1.

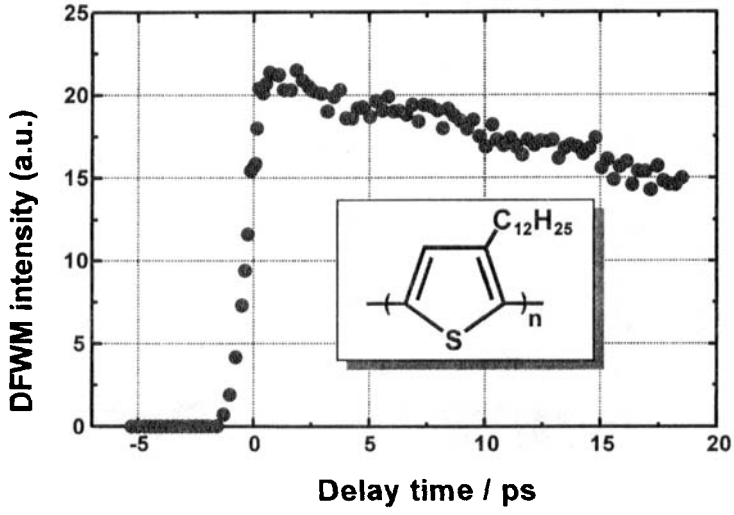

FIGURE 1 Optical pumping effect on DFWM intensity as a function of delay time between the pump at 400 nm and two probe pulses at 800 nm. Positive delay time means that pump pulse proceeds the two probe pulses, viceversa for negative delay time. Inset of the figure shows the chemical structure of the polymer.

When no pumping pulse is applied, the 10 times higher concentration of C12PT provides the same intensity compared with the present case. This means that the DFWM amplitude without pumping originates from the chloroform solvent, as well as the DFWM signal from C12PT without pumping at the present concentration is extremely low to be detected by our system. DFWM signal at a negative delay time in which the two probe pulses proceed the pump pulse, gives the same intensity as that without pumping, while it grows and decays at positive delay time in which the pump pulse proceeds the two probe pulses. DFWM amplitude with optical pumping at 400 nm increased by three orders of magnitude compared with that without pumping at a delay time of 133 fs, and is also proportional to the square of concentration for C12PT. Enhancement of DFWM amplitude with optical pumping presumably originates from the photoexcitation in a conjugated polymer from these results. The time evolution of DFWM as shown in Figure 1 might indicate the decay process of excitation in a conjugated polymer. Although pumping intensity dependence at 400 nm on DFWM is now under investigation to estimate the absolute excitation, it is apparent that $\chi^{(3)}$ with optical pumping could be achieved by several orders magnitude larger than that in ground state. Photoexcitation in a conjugated polymer in which the electrons could be confined in a one dimensional polymer backbone is well known to be the exciton.[8] Two mechanisms could be evaluated at the present stage. One might be a resonance

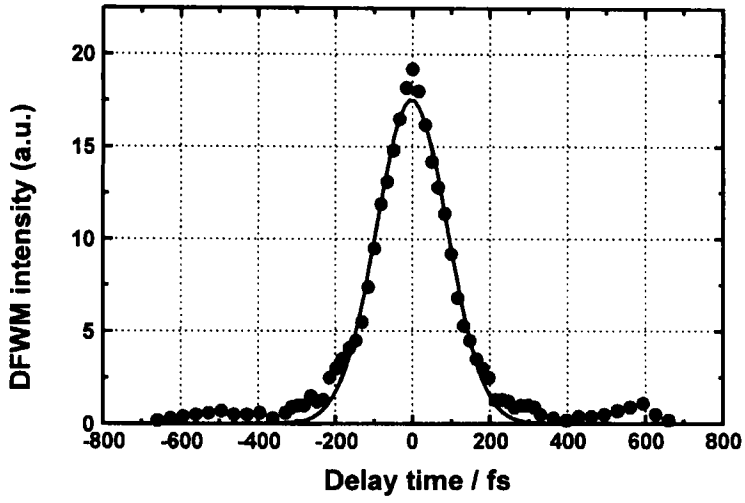

FIGURE 2 Temporal profile of degenerate four wave mixing intensity with pumping pulse at 400 nm as a function of delay time between two probe pulses at 800 nm. The pump pulse is fixed 133 fs prior to the two probe pulses.

effect in which the wavelength of probe pulses overlaps the absorption band of exciton transition from a lowest state to one of the higher states. The second one might be an enhancement of the transition dipole of the optically pumped exciton transition and a difference of the dipole moment between the electronic states involving the optical nonlinearity. Further works are in progress to assign the real mechanism. Temporal profile of DFWM amplitude by varying the delay time between the two probe pulses with an optical pumping is in good agreement with that of probe pulses at 800 nm as shown in Figure 2. This might correspond to the electronic dephasing in exciton state which is demonstrated to response within an ultra short time scale.

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