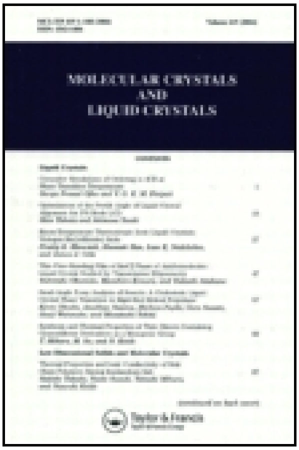

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FEMTOSECOND RELAXATION DYNAMICS IN THIOPHENE-BASED POLYMERS

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Abstract We report on ultrafast absorption measurements on newly synthetized low band gap thiophene-based polymers in film and solution, using femtosecond pump and probe technique. The results show very fast excited state kinetics, which occur on a femtosecond and picosecond time scale. The ultrafast relaxation of the photoexcitation is related to exciton dynamics.

INTRODUCTION

Conjugated polymers are attracting considerable interest and seem to be promising candidates for applications in all optical and high speed optoelectronics, because of their large and fast optical non-linearities. Among conjugated polymers, poly(alkyl-thiophene)s are at present the center of active investigation because they present a very fast time response and are soluble, chemically stable and easily processable. In these polymers, which possess a non-degenerated ground state, the photogenerated intra-chain electron-hole pair is confined by the preferred sense of bond alternation and forms neutral intra-chain self-trapped exciton, whose evolution can be followed by measurements with femtosecond time resolution.

In this study we report on femtosecond photoinduced absorption measurements of thiophene-based polymers with low band gap. Femtosecond pump and probe experiments have been performed on newly synthetized polymers, namely: poly(3-decyl-2,5-thiophene-vinylene) (PTV3C_{10}), poly(3,4-dibutyl-thiophene-2,5-diyl-vinylene) (PTV3,4C_4), poly(3,3'-dibutyl-2,2'-dithiophene-5,5'-diyl-vinylene) (PDTV3C_4), poly(3-pentoxy-2,5-thiophene) (PPT) and poly(3-pentoxy-2,5-thiophene-vinylene) (PPTV). The low energy gap in PTVs is due to the presence of the vinyl group, which increases both the conjugation length and the backbone rigidity with respect to poly(alkyl-thiophene)s. In the case of PPT the absorption spectrum is red shifted by the presence of the electron releasing pentoxy group.

In this work we also describe the excitation source, represented by a hybridly mode-locked cavity dumped dye laser, that generates femtosecond pulses with high stability in amplitude and duration. This source is characterized by a new resonator design which minimizes the effects of external perturbations on cavity alignment.

EXPERIMENTAL

Femtosecond pump and probe experimental system

The source of the femtosecond pump and probe beams was a cavity dumped hybridly mode-locked Rhodamine 6G dye laser with DODCI as saturable absorber. The laser layout is shown in Figure 1. The use of a cavity dumper provides a reduction of the repetition rate of the pulses with consequent increase of their peak power (up to 350 kW); this is particularly usefull for pump and probe measurements.[1] The main advantages are no need of complex amplification systems for single wavelength measurements and reduction of thermal effects in the samples. The dye laser was synchronously pumped by a frequency-doubled 76 MHz cw mode-locked Nd:YLF laser. The linear resonator of the dye laser contains two focussing stages for the gain medium and the saturable absorber and four Brewster-angled fused silica prisms for dispersion compensation. The double pass cavity dumper operated at a repetition rate of 1.9 MHz.

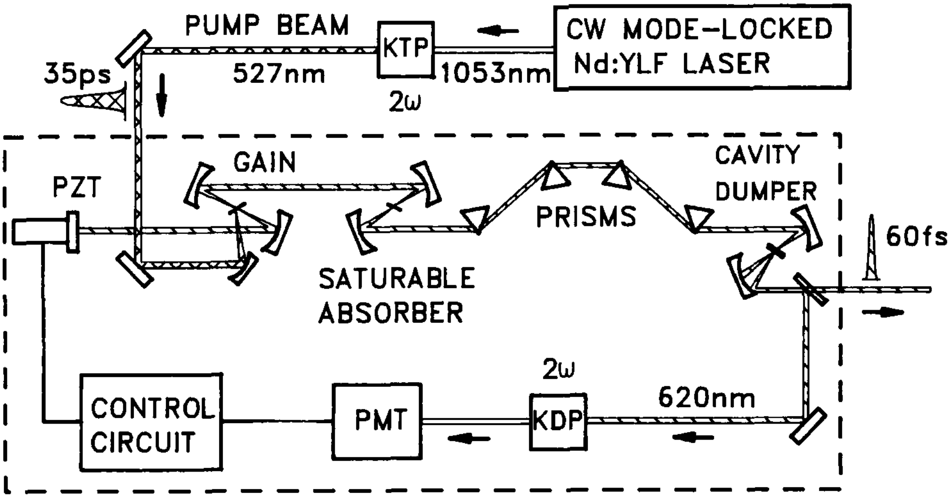

FIGURE 1 Femtosecond dye laser layout.

The flat high reflecting end mirror was mounted on a piezoelectric translational stage for active cavity length control. The dye laser cavity was directly mounted on the optical table. This system produces light pulses of 60 fs duration, centred at a wavelength of 627 nm, with 350 kW peak power, characterized by an excellent amplitude and duration stability. These performances were obtained by the use of a new resonator configuration, different from the usual confocal one, that minimizes the misalignment sensitivity and allows a more efficient stabilization of the output power by a feedback loop on cavity length.[2-3] The residual fluctuations of the output power were of the order of one percent.

For the pump and probe measurements the pump beam was mechanically chopped at 1 kHz and the difference between the transmitted and incident probe power was detected with a lock-in amplifier, thus reducing the residual signal fluctuations at the chopping frequency. The measurements were carried out at room temperature with parallel and perpendicular polarizations of the pump and probe beams.

Polymer samples

The polymer PTV3C_{10} and PTV3,4C_4 were synthetized according to the procedure described in Ref.4. The PDTV3C_4 was prepared oxidizing poly(3,3'-dybutyl-2,2'-dithienyl ethylen) with $FeCl_3$ in chloroform. The polymers PPT and PPTV were prepared oxidizing pentoxy-thiophene with $FeCl_3$ in chloroform.

The measurements in solution were performed using chloroform as solvent; unoriented films of PTV3,4C_4 were prepared by spin coating from a chloroform solution onto polished glass substrates . The films were kept under a vacuum of 10^{-3} torr to minimize photo-oxidation.

RESULTS AND DISCUSSION

Poly(alkyl-thiophene-vinylene)s

The absorption spectra of PTV3C_{10} and PTV3,4C_4 are similar with the maximum around 560 nm, that of PDTV3C_4 is more blue shifted with the maximum around 540 nm. This fact suggests that the conjugation length of the last polymer is somewhat shorter than the others two. The transient transmission change for PTV3C_{10} and PDTV3C_4 as a function of probe delay, with perpendicular polarizations of the pump and probe beams, are shown respectively in Figure 2a and b. After subtraction of the coherent coupling term the data for PTV3C_{10} can be fitted by a biexponential function with time constants τ_1=40±20 fs and τ_2=880±60 fs. The large uncertainty in the fast time constant is due to the time resolution limits of the experimental system. The pump and probe data for PDTV3C_4 can be fitted with a two exponential function with time constants τ_1=80±10 fs and τ_2=1010±90 fs. The decay curve of PTV3,4C_4, that presents a behavior similar to that of PTV3C_{10}, can be fitted by a two exponential function with time constants τ_1=40±20 fs and τ_2=1000±90 fs.

The relaxation kinetics of these polymers can be interpreted in terms of exciton dynamics.[5] Due to the non degeneracy of the ground state,the electron-hole pair photogenerated in the same chain remains bound and forms a neutral self-trapped exciton (STE).[6]

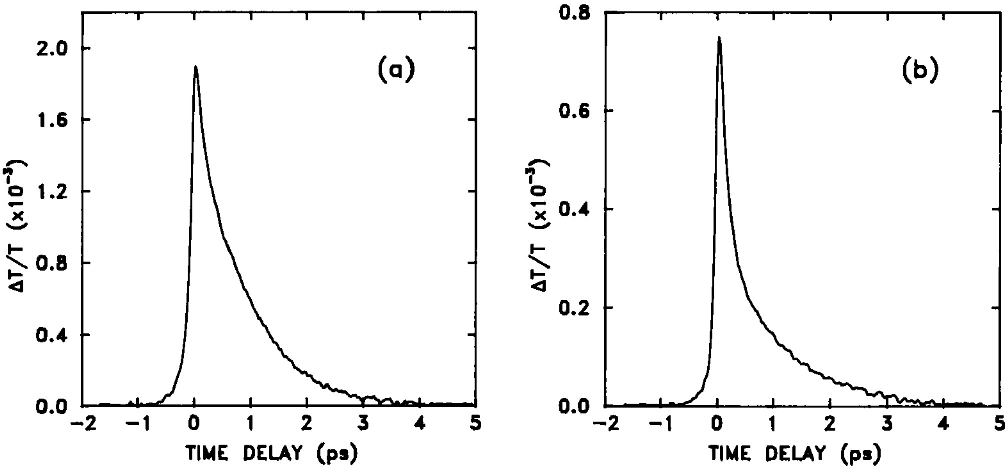

FIGURE 2 Change ΔT in the probe transmission T measured as a function of probe delay for PTV3C_{10} (a) and PDTV3C_4 (b) with perpendicular pump and probe polarizations.

We believe that the fast time constant τ_1 of the transient transmission change of the measured PTVs can be attributed to the combination of two relaxation mechanisms: thermalization and direct recombination of hot self-trapped excitons (HSTE). The fact that the time constant τ_1 of PTV3C$_{10}$ and PTV3,4C$_4$ are very similar is an indication that the first exciton relaxation stage is almost independent of the size and location of the side groups. PDTV3C$_4$ presents a longer time constant τ_1: the relaxation process of HSTE is less efficient than in the other two polymers.

We attribute the second time constant to the ground state recovery of the thermalized STE. This slower component probably corresponds to a combination of two relaxation mechanisms, namely an intrinsic recombination by tunneling through the barrier between the STE and ground state potentials and a diffusion along the chain to reach recombination centers such as defects in the polymer structure or ends of the chain segments.[7]

We have also measured the transient transmission change for PTV3,4C$_4$ in film. The initial part of the decay is nearly biexponential, with time constants similar to those measured in solution. Moreover, in the film a long lived bleaching is observed. This slower component may correspond to direct interchain photoexcitation or to intrachain polaron photoproduction[8] or to the existence of a fraction of crystalline phase possessing an extensive delocalization.

Poly(3-pentoxy-2,5-thiophene), poly(3-pentoxy-2,5-thiophene-vinylene)

The presence of the electron releasing pentoxy group determines the decrease of the energy gap of these polymers, so the excitation wavelength of the laser falls within the absorption band. The wavelength of the absorption peak is 540 nm for PPT and 550 nm for PPTV. The comparison of the pump and probe data of these two polymers shows the effects of the vinyl group on the relaxation processes. The photoinduced bleaching data for PPT and PPTV as a function of probe delay are shown in Figure 3a and b respectively.

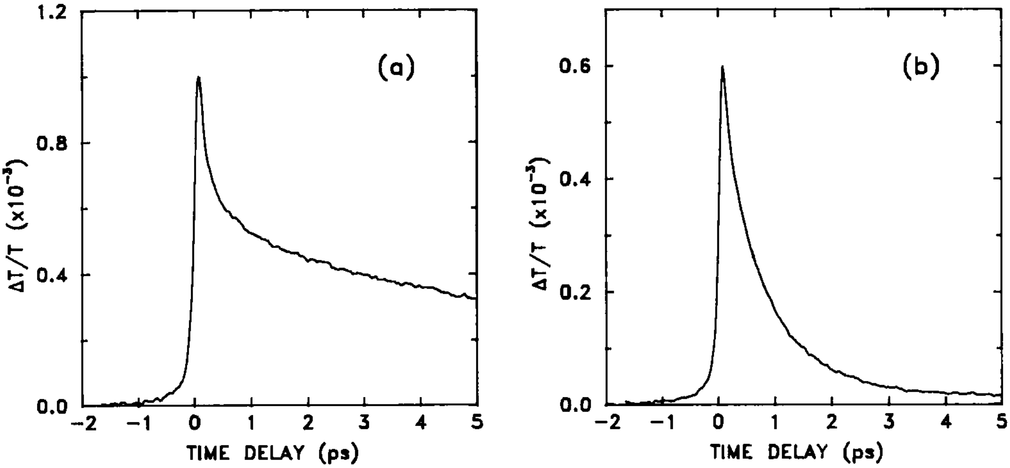

FIGURE 3 Change ΔT in the probe transmission T measured as a function of probe delay for PPT (a) and PPTV (b) with perpendicular pump and probe polarizations.

Particular care has been taken to eliminate any dopant impurity from the polymer solution. The two polymers present a very different relaxation dynamics. In particular, the PPTV's data are very similar to those of PTVs shown in the previous section. The decay curve of PPT is multi-exponential and reaches a plateau after about 100 ps. The similarity between the decay curve of PPTV and those of PTVs is an indication that the relaxation mechanisms are the same. The decay kinetics of PPT is rather complex and slower. We believe that this is a further indication of the fact that the vinyl group increases the backbone rigidity and probably the confinement of the photogenerated species. The long lived bleaching observed in PPT may result from recombination of free polaron pairs executing a random walk on the polymer chain.

CONCLUSIONS

The relaxation dynamics of photoexcitations in newly synthetized low energy gap thiophene-based polymers in film and solution have been studied, using femtosecond pump and probe. The kinetics of the absorbance changes is explained in terms of exciton dynamics. We have studied the influence of the vinyl group on the backbone rigidity and spatial confinement of the photogenerated electron-hole pairs.

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