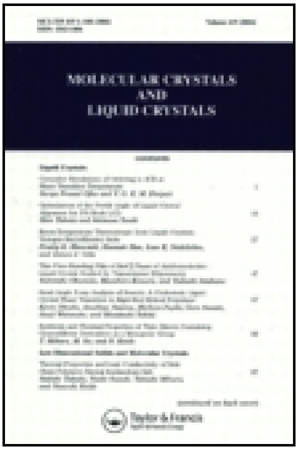

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006.

To cite this article: Soo Young Park , Tatsuo Wada & Hiroyuki Sasabe (1993): Third-Harmonic Generation of Polymeric Charge-Transfer Complex Film, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 227:1, 151-158

To link to this article: http://dx.doi.org/10.1080/10587259308030968

Mol. Cryst. Liq. Cryst. 1993, Vol. 227, pp. 151–158
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Printed in the United States of America

THIRD-HARMONIC GENERATION OF POLYMERIC CHARGE-TRANSFER COMPLEX FILM

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Abstract Nonlinear optical property of polymeric charge transfer complex was investigated in terms of the complex composition. The third-order nonlinear optical susceptibility $\chi^{(3)}{}_{1111}(-3\omega;\omega,\omega,\omega)$ of poly-n-vinylcarbazole complexed with 2,4,7-trinitrofluorenone or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone was evaluated by means of the rotational Maker fringe of third-harmonic generation at the fundamental wavelength (ω) of 1.906 μm. The magnitude of $\chi^{(3)}$ was 10^{-12} esu order and was increased linearly with the content of charge-transfer complex in the film.

INTRODUCTION

Extensive research efforts are focused on the search of the effective third-order nonlinear optical material for applications in electro-optical and photonic devices in mind. In particular organic polymers are receiving much attention due to their quite good processability with moderate to large nonlinear optical susceptibility and rapid response time.[1] Until now, π-electron conjugated polymers have been investigated most intensively due to their large third-order nonlinearity as high as 10^{-9} esu and response time of femto-second range that may meet the practical device requirements potentially.[1] However, the fabrication of good quality film for the practical device structure is greatly limited due to their insolubility in organic solvents, instability in air, and the strong absorption at visible wavelength region.

To realize the polymeric nonlinear optical devices, we are more interested in the processable polymers with reasonable third-order nonlinearity. Recently it has been reported by Gotoh et. al [2] and also by Gong et. al.[3] that the third-order nonlinearity of organic charge-transfer (CT) complex was as high as 10^{-9} esu order comparable to that of the best-known π-electron conjugated polymer poly(2,4-hexadiyn-1,6-diol-bis(p-toluenesulfonate)). Therefore we think that the polymeric CT complex is a good candidate for our approach since we expect the efficient nonlinearity of CT complex could be combined with the good processability related to the polymer property.

Furthermore, the absorption wavelength and coefficient of CT excitation is adjusted by the proper selection of donor and/or acceptor material and their stoichiometry, which may lead to the possible control of nonlinear optical response.

Until now there has been few work on the third-order nonlinearity of polymeric CT complexes. Ghoshal et. al. [4] measured the $\chi^{(3)}(-\omega;\omega,\omega,-\omega)$ of poly-n-vinylcarbazole (PVK)-based CT complex film by the degenerate four-wave mixing technique and Harelstad et. al.[5] measured $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ of poly-1-vinylpyrene-based CT complex film by the third-harmonic generation.

In this work we investigated the effect of CT complex density on the third-harmonic generation $\chi^{(3)}_{1111}(-3\omega;\omega,\omega,\omega)$ of PVK-based polymeric CT complex film with an aim to understand the fundamental nonlinear optical properties of polymeric CT film. 2,4,7-trinitrofluorenone (TNF) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) were used as the electron acceptors at various stoichiometric ratio to the carbazole donor unit.

EXPERIMENTAL

Materials

PVK (product of Tokyo Kasei) was reprecipitated from dichloroethane solution into methanol and dried in vacuo at 40^{o} C. TNF (Tokyo Kasei) and DDQ (Tokyo Kasei) were recrystallized from acetic acid and dichloromethane solution respectively and dried in vacuo. Spectroscopic-grade tetrahydrofuran and chlorobenzene were used without further purification. Fused silica plate was washed with detergent, deionized water and dried in vacuo.

Preparation of films

Polymeric CT complexes of PVK/TNF were prepared in solution by dissolving both components in tetrahydrofuran according to the stoichiometric ratio up to 1:1. PVK/DDQ CT complexes were prepared similarly in chlorobenzene solution. Homogeneous CT complex solutions were spin-coated on the fused silica substrates and dried completely in vacuo. The concentration of solution was properly adjusted to yield an optical quality sub-micron films on fused silica substrate. Thickness of the polymeric CT complex film was measured using the Sloan Dektek IIA stylus instrument and the absorption spectrum was taken on the Shimadzu UV3100 spectrophotometer using the transmission geometry.

THG measurement

The standard Maker fringe technique was used for the third-harmonic generation (THG) measurement. [6] The 1.064 μm output beam from the Q-switched Quanta-Ray DCR IIA, Nd:YAG laser operated at 10 Hz was focused into a high pressure H_2 filled Raman shifter. The 1.906 μm first Stokes line was separated by the dispersion prism and was used as the fundamental beam of THG measurement. The incident beam was splitted into two by a beam splitter, one for a sample and the other for a reference. As a reference, fused silica plate of 1 mm thickness was used. The sample was mounted on a goniometer in the vacuum chamber to eliminate the effect of air on THG. Through the monochromator, only the generated third-harmonic beams (636 nm) were detected by the photomultiplier tubes of the sample and reference respectively and were accumulated in the boxcar integrator. The polarizations for both input (ω) and output (3ω) beam were along the axis of goniometer rotation. The signal ratio of sample to reference was taken as a function of the goniometer rotation to compensate the drift of laser power. The $\chi^{(3)}{}_{1111}$ $(-3\omega;\omega,\omega,\omega)$ value of CT complex film was evaluated from the Maker fringe patterns according to the equation of Kajzar et. al.[6]

RESULT AND DISCUSSION

Extremely uniform, optically-clear, polymeric CT complex films were prepared on the fused silica substrate by adjusting the concentration of CT complex solution and also the spinning speed. According to the formation of $\pi-\pi$ CT complex there appeared new optical absorption (CT band) at longer wavelength corresponding to the transition from the highest (also from the second highest for PVK) occupied molecular orbital of donor to the lowest unoccupied molecular orbital of acceptor.[7] Figure 1 shows the absorption spectra of polymeric CT complex films of PVK. It is shown that the CT absorption of PVK/TNF is tail-like extending up to 650 nm (red-orange in color) and that of PVK/DDQ is very broad centered at around 800 nm (green), although the PVK was completely transparent at the visible region and the TNF or DDQ alone absorbed light only at a wavelength less than 440 nm (yellow).

The absorption coefficient of CT excitation shown in Figure 2 was calculated from the film thickness and the absorbance at the wavelength of 440 nm for PVK/TNF and 800 nm for PVK/DDQ respectively. It seems that the coefficients saturate above the acceptor content of around 40 % both for the PVK/TNF and PVK/DDQ, which means that the polymeric CT complex film is composed of the CT complexes with the fair amount of uncomplexed donor and acceptor. Then it seems reasonable to suppose that the number density of CT complex in film is directly related to the magnitude of

CT absorption coefficient of Figure 2 although it is difficult to figure out the absolute density without knowing the accurate value of molar absorption coefficient.

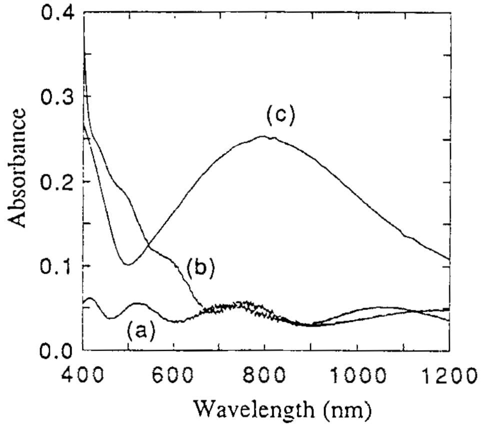

FIGURE 1 Absorption spectra of (a) 0.52 μm thick PVK, (b) 0.78 μm thick PVK/TNF of 30 mole % acceptor, and (c) 0.54 μm thick PVK/DDQ of 30 mole % acceptor

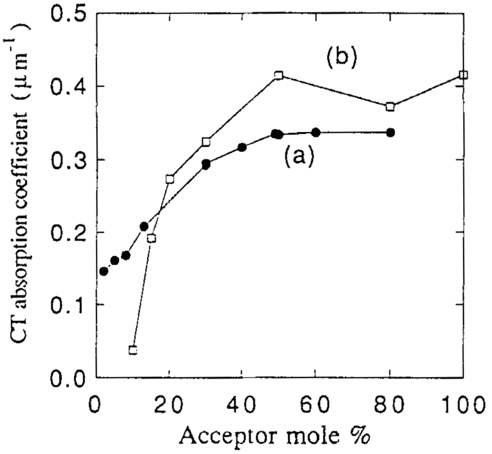

FIGURE 2 CT absorption coefficient of (a) PVK/TNF film measured at 440 nm and of (b) PVK/DDQ film measured at 800 nm as a function of acceptor content

All the polymeric CT complex films were very uniform in thickness and optically clear without scattering. The optical quality is well-demonstrated in Figure 3 as the transmission interference fringe. The refractive indices of PVK/TNF films at the non-absorbing region could be calculated from the transmission interference fringes by

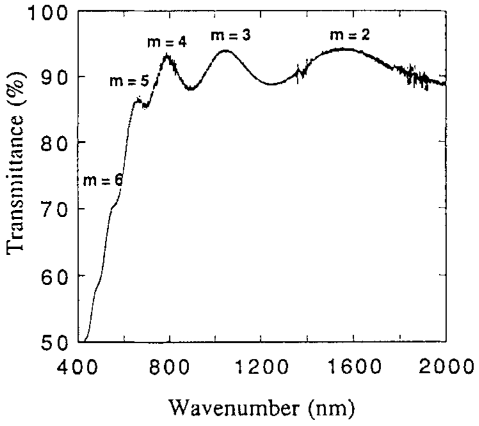

FIGURE 3 Transmission interference fringe of PVK/TNF film of 50 mole % acceptor , 0.90 μm thick

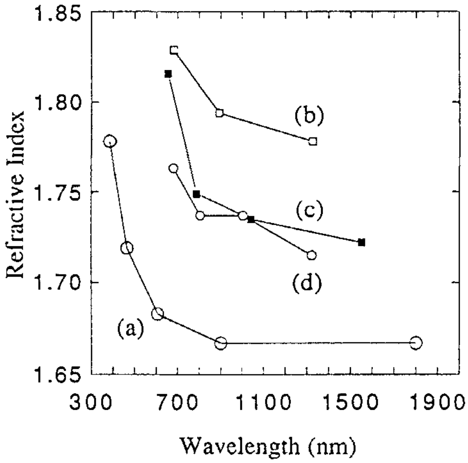

FIGURE 4 Refractive index dispersion of PVK/TNF film calculated from the transmission interference; (a) PVK, (b) 30 %, (c) 50 %, and (d) 80 % acceptor respectively.

using the basic formula $2n(\lambda)d = m\lambda$ for maximum transmission; $n(\lambda)$ is a refractive index at the wavelength λ, d is a thickness of the film, and m is a mode number. Figure 4 shows the calculated refractive indices of PVK/TNF. It is seen that the refractive index value of polymeric CT complex is slightly higher than that of PVK and shows maximum at certain composition of acceptor.

Clear Maker fringe patterns of the polymeric CT complex films were obtained reproducibly since these films were very uniform and strong enough not to be damaged by the tightly focused 0.5 MW pulsed beams of 1.906 μm. An example of Maker fringe measured is shown in Figure 5 with the solid line depicting the fitting result to the Kajzar's equations.[6] A good agreement was usually seen between the calculated and measured THG intensities.

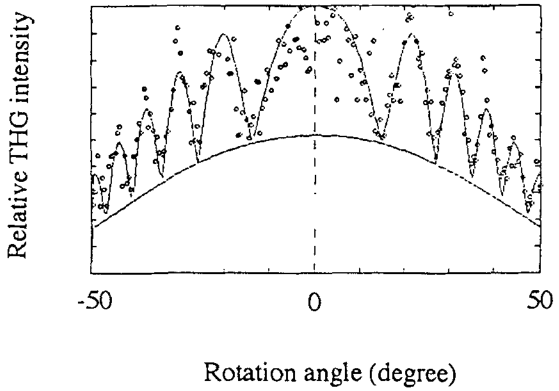

FIGURE 5 Rotational Maker fringe of third-harmonic intensity from 1.13 μm thick PVK/TNF film of 80 mole % acceptor

The $\chi^{(3)}_{1111}$ $(-3\omega;\omega,\omega,\omega)$ values obtained by fitting the third-harmonic Maker fringe into Kajzar's equation[6] are shown in Figure 6 as a function of the acceptor content in the film. It is seen that the $\chi^{(3)}$ saturates above certain level of acceptor content much like the CT absorption coefficient shown in Figure 2. The saturated value of $\chi^{(3)}_{1111}$ $(-3\omega;\omega,\omega,\omega)$ was around 1.0×10^{-12} esu and 2.25×10^{-12} esu for PVK/TNF and PVK/DDQ respectively. We speculate that the lower CT excitation energy of PVK/DDQ compared to that of PVK/TNF is responsible for the higher value of third-order nonlinearity.

In Figure 7 the $\chi^{(3)}_{1111}$ $(-3\omega;\omega,\omega,\omega)$ value of polymeric CT complex film was reploted as the function of the CT absorption coefficient. Since the CT absorption coefficient is supposed to be proportional to the number density of CT complex in film, the linear relationship shown in Figure 7 proves that the third-order nonlinearity of polymeric CT complex film truly comes from the CT complex formation.

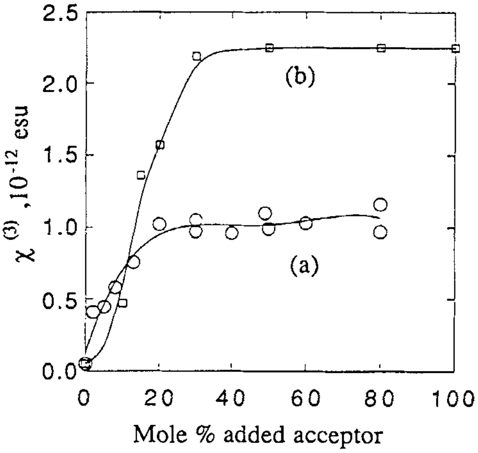

FIGURE 6 Third-order nonlinear optical coefficient $\chi^{(3)}_{1111}(-3\omega;\omega,\omega,\omega)$ of (a) PVK/TNF and (b) PVK/DDQ as a function of acceptor content

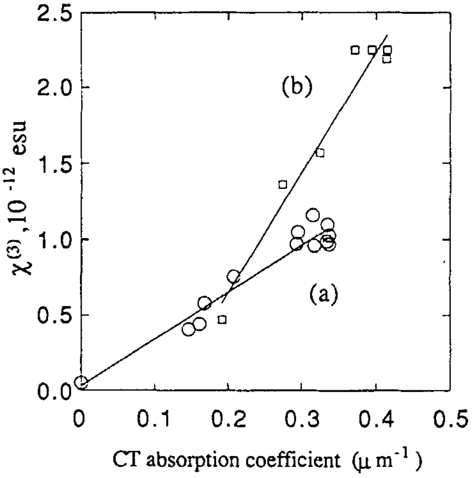

FIGURE 7 Third-order nonlinear optical coefficient $\chi^{(3)}_{1111}(-3\omega;\omega,\omega,\omega)$ of (a) PVK/TNF and (b) PVK/DDQ as a function of CT absorption coefficient

CONCLUSIONS

The present work shows that polymeric CT complex is an interesting class of material for NLO application with its excellent processability into thin films, control of linear and nonlinear optical properties by the selection of donor and/or acceptor material and also by the adjustment of their stoichiometry.

The $\chi^{(3)}_{1111}$ $(-3\omega;\omega,\omega,\omega)$ of polymeric CT complex increased linearly with the content of CT complex formed. The maximum value of $\chi^{(3)}_{1111}$ $(-3\omega;\omega,\omega,\omega)$ measured was 1.0×10^{-12} and 2.25×10^{-12} esu for PVK/TNF and PVK/DDQ respectively.

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