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NONLINEAR OPTICAL PROPERTIES OF BLUE AND RED PHASE POLYDIACETYLENE FILMS

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ABSTRACT Third-order nonlinear optical susceptibilities $|\chi^{(3)}|$ of the blue and red phase polydiacetylene (poly-5,7-dodecadiyne-1,12-di-n-butyl urethane) films have been evaluated by third harmonic generation measurements in the fundamental wavelength region from 1.5 to 2.1 μm. Some details of fabrication of blue and red thin oriented films are also reported.

INTRODUCTION

Conjugated polymers have been extensively investigated for their remarkable nonlinear optical properties owing to their delocalized π-electrons. Polydiacetylenes (PDAs) are a group of conjugated polymers which have the general formula $\frac{1}{4}RC-C\equiv C-CR'\frac{1}{4}$, where R and R' are substitutional side groups. One special feature of PDAs is a variety in sample forms: By choosing side groups, PDAs can be prepared in the forms of single crystals and solutions in organic solvents, as well as in the form of thin films by usual vacuum deposition technique. Another feature of PDAs is their chromic behavior. In spite of the variety of side groups, most PDAs are obtained in the color form either of the blue or red-phase. In this paper, we report how to fabricate blue and red phase oriented PDA films suitable for studies of the third-order nonlinear optical properties. A specific polydiacetylene poly-5,7-dodecadiyne-1,12-di-n-butyl urethane (R and R'=$C_4H_8OCONHC_4H_9$), denoted hereafter C_4UC_4, was used to prepare blue and red-phase films in the present study.

Fabrication of thin oriented films

Since poly-C_4UC_4 cannot be dissolved in usual organic solvents, one has to make use of polymerization procedure from a monomer film to obtain a polymer film. Vacuum deposition method is useful for fabrication of

thin monomer films, because thermal polymerization activity of some diacetylene monomer is not so high. The monomer films are easily converted to the blue polymer films by irradiation of UV light. For the measurement of nonlinear optical properties, it is desirable to make polymer chains to align along a specific direction. We could recently develop a unique method to fabricate oriented films of some PDAs on top of an isotropic substrate by vacuum deposition.[1] The method is constituted of preliminary deposition process, rubbing process and final deposition process. Details of which are written in reference 1.

The blue PDA-C_4UC_4 has the absorption peak at about 1.9 eV after polymerization. The blue films can be also converted into the red films by heating up to about 400 K without causing much disorder. This thermo-chromism is, however, reversible, i.e., the red phase film obtained in this way is unstable at room temperature and returns gradually back to the blue film. From a recent study of thermo-chromic behaviors of a series of PDAs, having the side-groups represented by C_4UC_n(n is the number of carbon atoms), the thermo-chromism of these materials is essentially reversible, but becomes irreversible when the yield of polymerization is not so high.[2]

In Fig. 1, we show the influence of the yield of polymerization on the thermo-chromic behavior of C_4UC_4 blue films. In the plot, only the

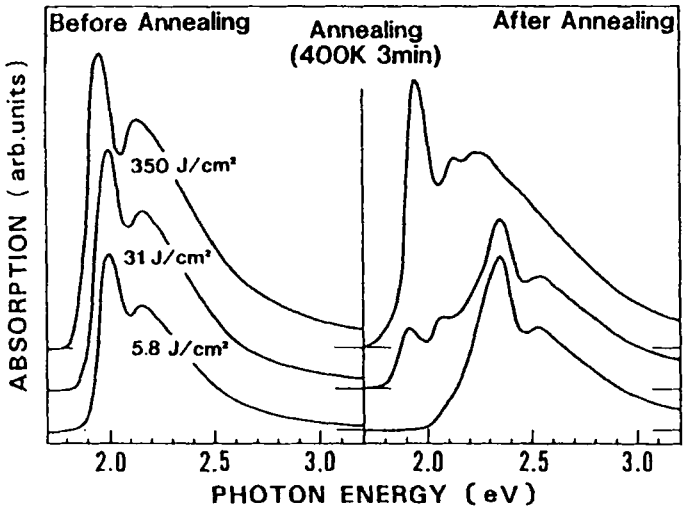

FIGURE 1 The thermo-chromic behavior of PDA films. The yield of photo-polymerization changes as irradiation dosage of UV light change.

relative values of polymerization yield are shown. It is readily seen that the red phase structure is stabilized when the polymerization yield is low. But as the polymerization yield increases, a large part of film returns to the blue form by cooling to room temperature. The quality of the red films seems to be somewhat poor compared with that of the blue film, due to the disorder induced in the monomer regions through the heat-treatment. As a matter of fact, the surface of the red film was found to become more coarse than that of the blue film from the measurement of stylus-type thickness meter.

THG Measurement

Measurements of third harmonic generation (THG) have been done to evaluate the third-order nonlinear susceptibility $|\chi^{(3)}(-3\omega;\omega,\omega,\omega)|$ of blue and red-phase PDA-C_4UC_4 films. The pump-light was generated through wave-mixing using a Nd:YAG laser and a tunable dye laser pumped by the second harmonic light of the Nd:YAG laser. The typical peak power density of the pump light was 80 MW/cm^2. The wavelength of pump light was tunable in a range from 1.5 to 2.1 μm by changing the wavelength of dye laser. The $|\chi^{(3)}|$ values of the PDA films were determined by Maker fringe method using an expression given by Kubodera et al..[3] Correction for the effect of internal absorption of the third harmonic light in films and for the reflection loss at sample surface were made following the equation by Kanetake et al..[4] A 1 mm-thick silica glass plate was used as the standard for the $|\chi^{(3)}|$ value. All measurements were done in the air. The effect of air for the THG measurement of the silica glass plate could be avoided by using a focusing lens having a short focal length(f≈5cm).

The $|\chi^{(3)}|$ values for blue and red-phase PDA-C_4UC_4 films are shown in Fig. 2, as a function of the pumping photon energy. Absorption spectra of the same films are also shown in this figure. The $|\chi^{(3)}|$ spectra show a clear three-photon resonance effect to the ^1B_u excitons in both phase films. In the blue phase, the $|\chi^{(3)}|$ spectra show a secondary peak at about 2.3 eV, where the exciton of red-phase films is located. However, this peak cannot be attributed to the resonance effect to the red-phase exciton created in the original blue phase film by the laser irradiation, since the $|\chi^{(3)}|$ values of the red phase in this

region are considerably smaller than those of the blue phase and cannot account for the observed intensities of THG at the second peak. It is also unlikely that the second peak is due to the two-photon resonance to an optically forbidden(^1A_g) state. If there is an ^1A_g state responsible for such a two-photon resonance, its energy will be about 1.6 eV, which is considerably lower than the ^1B_u exciton at 1.9 eV. Electro-absorption measurements have been carefully made, but there was no detectable electro-absorption signal in these region. The origin of the second peak is tentatively attributed to the three-photon resonance to the band edge.

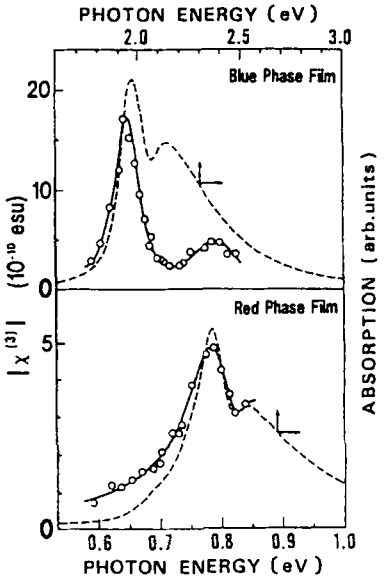

FIGURE 2 The third-order nonlinear susceptibility and absorption spectra of the blue and red-phase PDA films.

The $|\chi^{(3)}|$ values for red phase film are smaller than those of blue film nearly by a factor of four. This difference in the nonlinear optical response of the blue and red phase films should by related to difference in the electronic structures of the backbone chains in the both phases. A three level model, including the ground state, allowed(^1B_u) and forbidden(^1A_g) π-π^* excitons can provide a semi-quantitative account for the observed $|\chi^{(3)}|$ values in the blue and red-phase films. Details of analysis will be reported elsewhere.

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