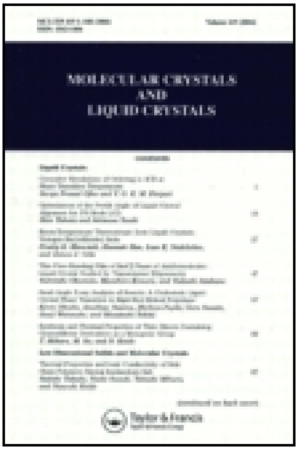

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Third-Order Optical Nonlinearity of Poly(1,6-Heptadiyne) Derivatives Containing Mesogenic Moiety

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THIRD-ORDER OPTICAL NONLINEARITY OF POLY(1,6-HEPTADIYNE) DERIVATIVES CONTAINING MESOGENIC MOIETY

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Abstract Poly (1,6-heptadiyne) derivatives with side group liquid crystalline mesogens were prepared by the metathesis polymerization with transition metal catalyst. It was found that the $MoCl_5$-based catalyst systems were very effective for the polymerization of 1,6-heptadiyne monomers with various mesogenic groups. Polymerization of these monomers gave to the conjugated polyenes that contain cyclic recurring unit in the polymer backbone. Resulting polymers with electron donating mesogenic groups exhibited good solubility in common organic solvents and were easily spin coatable on fused silica substrate. Copolymerization of the mesogen-containing monomers with diethyl dipropargyl malonate (DEDPM) was also attempted to improve their physical properties. The third-order nonlinear optical susceptibility, $\chi^{(3)}$, was evaluated by the optical third-harmonic generation measurement. The near-resonant $\chi^{(3)}$ value was found to be in the range of $1.75 \sim 8.22 \times 10^{-11}$ esu at the fundamental wavelength of 1.907 μm.

INTRODUCTION

There has been an increasing interest in the third-order optical nonlinearity of conjugated polymers for potential application in the ultrafast optical devices.[1,2] In particular, polyacetylene, polydiacetylene, polythiophene, etc.[3,4] have been found to possess very large third-order optical nonlinearity according to the extended π-electron delocalization along the main chain. However, the fabrication of practical device has been limited since these conjugated polymers are generally insoluble in organic solvents and infusible as well. Therefore, as a trade-off, we have been interested in the synthesis of new processable π-electron conjugated polymers with minimum pay-off of nonlinearity.

Recently, we have developed a series of substituted polyacetylenes, by the metathesis polymerization of 1,6-heptadiyne derivatives [5-9]. Generally, these polymers were highly soluble in common organic solvents enough to be spin-cast into quality film of controlled thickness. It was found that the substituted polacetylenes were highly conducting when doped with acceptors owing to the extensive π-electron conjugation along the main chain.

In the present work, we report the synthesis of a novel class of conjugated homo- and copolymers of 1,6-heptadiyne derivatives containing alkoxy biphenyl and alkoxy azobenzene side groups, and the measurement of their linear and third-order nonlinear optical properties.

EXPERIMENTAL

Monomers

Scheme I outlines the synthesis of a series of the monomers. Diethyl dipropargyl malonate (DEDPM) was prepared as described in the literature.[7,10] The monomers, M-I and M-II, were synthesized by the reaction of dipropargyl acetyl chloride (DPAC) with the corresponding alcohols R_1 or R_2 in the presence of triethylamine(TEA) using tetrahydrofuran solvent. Details of the synthesis and characterization of the monomers have already been reported.[11]

Polymers

The homo- and copolymerization of the monomers (DEDPM, M-I, and M-II) were carried out by $MoCl_5$ as the metathesis catalyst. Polymerization procedure was the same as reported elsewhere.[7,12]

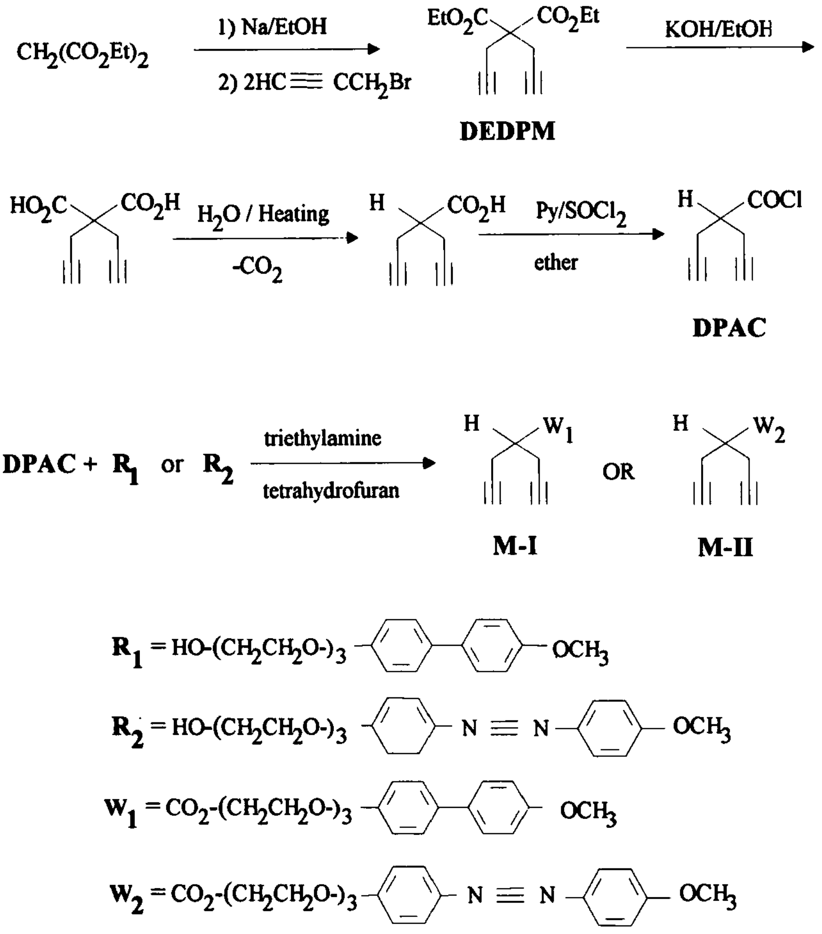
Film preparation

Polymers were completely dissolved in tetrahydrofuran at the concentration of 4% by weight. Homogeneous polymer solution was spin-coated on the fused silica substrate and dried completely in vacuum. Thickness of the polymer film was measured using the Sloan Dektek IIA stylus instrument and the electronic and near-IR spectra were taken on the Shimadzu UV3100 spectrophotometer.

Nonlinear optical property

The standard Maker fringe technique was used for the third-harmonic generation (THG) measurement. The 1.064 μm output beam from the Q-switched Quanta-Ray DCR IIA, Nd:YAG laser was focused into a high pressure H_2-filled Raman

SCHEME I



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 divided into two by a beam splitter, one for 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, the intensity of generated third-harmonic beam (635 nm) was detected by the photomultiplier tube of the sample and reference respectively and were accumulated in the boxcar integrator. The signal ratio of sample to reference was taken as a function of goniometer rotation to compensate the drift of laser power. The polarizations for both the fundamental and harmonic beam were along the axis of goniometer rotation. The $\chi^{(3)}$ (-3ω; ω,ω,ω) value was calculated by comparing the compensated signal intensity with that from the standard fused silica plate ($\chi^{(3)} = 2.4 \times 10^{-14}$ esu at the fundamental wavelength of 1.907 μm).

RESULTS AND DISCUSSION

Scheme II outlines the homo- and copolymerization of DEDPM, M-I, and M-II by $MoCl_5$ and the TABLE I summarizes the polymerization results. The number average molecular weight (Mn) and polydispersity (Mw/Mn) of the poly(1,6-heptadiyne) derivatives were found to be in the range of 2.5 ~ 4.7 x 10^4 and 2.25 ~ 3.55, respectively. PDEDPM and P-I homopolymers exhibited good solubility in common organic solvents such as chloroform, THF, DMF, etc., and were easily spin coatable on fused silica substrate to give uniform thin films, whereas P-II homopolymer had poor film quality due to the limited solubility in the above solvents. However, all the copolymers of M-I and M-II with DEDPM gave good quality films by the spin-coating of homogeneous solution. Thin films of around 100 nm thickness were successfully fabricated on the fused silica substrate from the 4 weight % tetrahydrofuran solution.

The obtained films were extremely uniform in thickness over the whole area of substrate and were optically clear without any scattering of light. The surface roughness after the polymer coating was about 20 Å which ensures the fine quality of spin-cast polymer films.

FIGURE 1 and 2 show the electronic spectra of poly(1,6-heptadiyne) films with biphenyl and azobenzene substituents respectively in comparison with PDEDPM. There is seen a common and distinct π–π* transition of conjugated polymer backbone at around 540 nm for all the homo- and copolymers synthesized, which is absent in the electronic spectra of monomers. There is no other electronic transition peak except this 540 nm one for PDEDPM, since it contains only the aliphatic substituent besides the polyacetylenic main chain. On the other hand, the homo- and copolymers of M-I with DEDPM show the additional π–π* transition of biphenyl group at 270 nm (FIGURE 1) and the copolymers of M-II show the additional π–π* transition of azobenzene group at 360 nm (FIGURE 2).

All the poly(1,6-heptadiyne) films were optically clear and transparent in the near IR range (1000 - 2300 nm). It was also noted that these films were quite stable in air, since we did not find any change of electronic spectra during the several weeks' monitoring period after the film fabrication.

SCHEME II

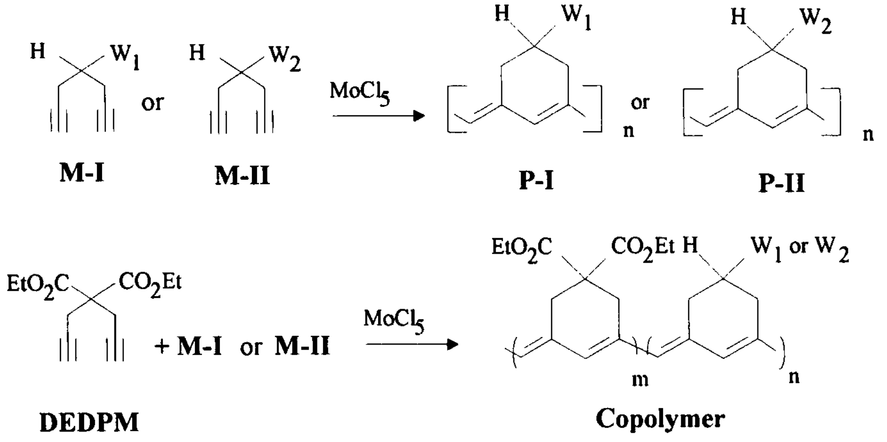


TABLE I Polymerization of DEDPM, M-I and M-II by $MoCl_5$[a].

Polymer Designation	Monomer System	M/C[b]	$[M]_0$[c]	Yield[d] (%)	GPC[e] Mn/10^4	GPC[e] Mw/Mn
PDEDPM	DEDPM	50	0.25	91	4.7	3.15
P-I	M-I	50	0.25	85	4.5	2.73
P-II	M-II	50	0.25	80	-	-
PDEDPM/P-I (3:1)	DEDPM / M-I (3:1)	50	0.25	89	3.6	2.25
PDEDPM/P-I (1:9)	DEDPM / M-I (1:9)	50	0.25	85	2.5	3.55
PDEDPM/P-II (4:1)	DEDPM / M-II (4:1)	50	0.25	87	3.2	2.96
PDEDPM/P-II (3:1)	DEDPM / M-II (3:1)	50	0.25	86	2.9	2.94
PDEDPM/P-II (1:1)	DEDPM / M-I (1:1)	50	0.25	80	2.7	2.49

[a] Polymerization was carried out at 60°C for 24h in dioxane. [b] Monomer to catalyst mole ratio. [c] Initial monomer concentration. [d] Methanol insoluble copolymer. [e] Values were obtained by GPC analysis with polystyrene standards.

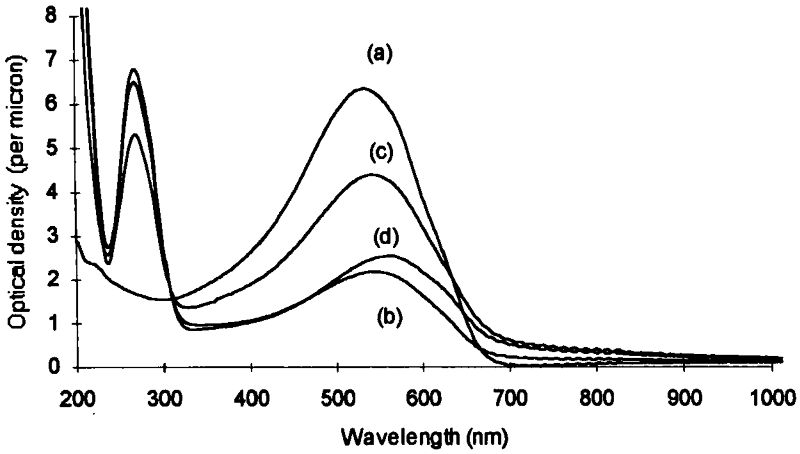


FIGURE 1 Electronic spectra of (a) PDEDPM, (b) P-I, (c) PDEDPM/P-I (3:1), and (d) PDEDPM/P-I (1:9).

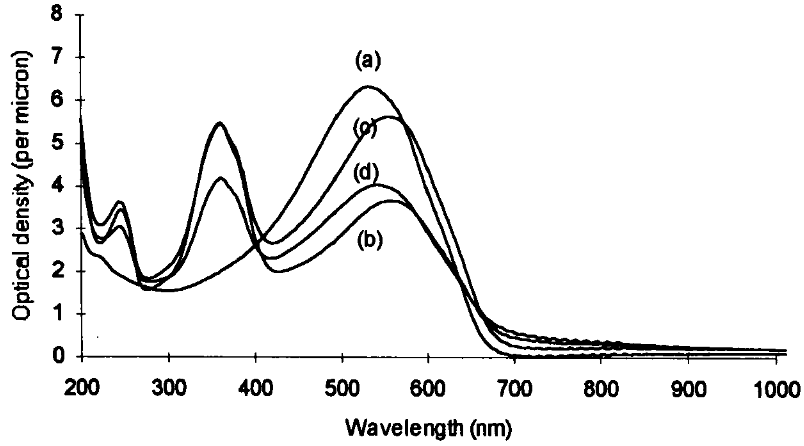


FIGURE 2 Electronic spectra of (a) PDEDPM, (b) PDEDPM/P-II (1:1), (c) PDEDPM/P-II (3:1), and (d) PDEDPM/P-II (4:1).

The nearly same wavelength of the main-chain π–π* transition and the shape of the peak suggest that the degree of π-electron conjugation along the polymer backbone is almost the same in spite of the different chemical groups attached to the 4,4-position of 1,6-heptadiyne. In other words, the nature of the polyacetylenic oscillator (chromophore) is assumed to be the same for all the homo- or copolymers. However, it should be noted that the substitution strongly affects the optical density (OD) of this transition.

Comparing the OD of PDEDPM with that of P-I and copolymers in FIGURE 1, we find that the value of OD decreases as the bulkiness of the substituent chemical group increases. The OD of diethyl group substituted PDEDPM is 6.3 x 10^4 cm^{-1} and that of bulky biphenyl substituted P-I is only 2.1 x 10^4 cm^{-1}. It is also seen that the OD of copolymer decreases with the content of bulky P-I component increases. Such an observation can be rationalized by the fact that number density of oscillator (conjugated π-electronic main chain) should decrease with increasing volume of the substituents, namely the substituents may simply act as the diluent of main-chain π-electron oscillator.

The copolymer of P-II with PDEDPM also showed the reduced OD of main chain $\pi-\pi^*$ transition compared to that of PDEDPM homopolymer in accordance with the diluent effect of bulky azobenzene group. However, it is seen from FIGURE 2 that the magnitude of OD does not follow the order of copolymer composition. In particular, the PDEDPM/P-II (3:1) copolymer shows the highest OD with the significant red-shift of the absorption peak. We suppose that the specific interaction of the main chain with the azobenzene chromophore may have resulted in the complicated linear optical property.

FIGURE 3 demonstrates the THG Maker fringe from the very thin film of PDEDPM/P-II (3:1) copolymer where the intensity of the THG beam is normalized to that of the 1 mm thick standard fused silica. It is seen that the 120 nm-thick PDEDPM/P-II (3:1) film generated around 1000 times the signal from 1 mm fused silica.

The $\chi^{(3)}$ (-3ω; ω,ω,ω) of the polymer sample was calculated from the THG Maker fringe according to the simple Eq. (1) which is applicable when the sample thickness (l) is much smaller than its coherence length (l_c),[13]

$$\chi^{(3)} = \frac{2}{\pi}\chi_s^{(3)} \frac{\sqrt{I_{3\omega}}}{\sqrt{I_{3\omega,s}}} \frac{l_{c,s}}{l} \tag{1}$$

where, $\chi^{(3)}$ is the third-order nonlinear optical coefficient and $l_{c,s}$ is the coherence length of the standard sample (fused silica),

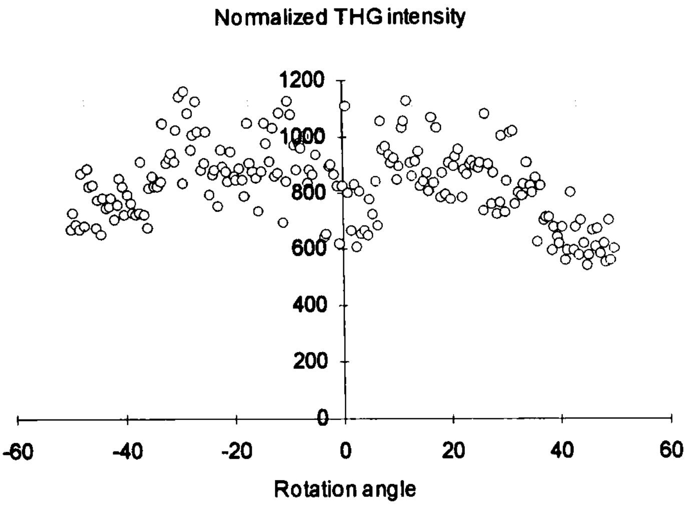


FIGURE 3 Normalized THG intensity from 120 nm thick PDEDPM/P-II (3:1) copolymer coated on the fused silica substrate.

TABLE II Linear and nonlinear optical properties of polymer films.

Polymer	Film thickness (nm)	Absorption peak (nm)	$\chi^{(3)}$ 10^{-11} esu
PDEDPM	151	541	6.45
P-I	131	540	3.14
P-II[a]	-	-	–
PDEDPM / P-I (3:1)	84	540	5.75
PDEDPM / P-I (1:9)	87	560	3.98
PDEDPM / P-II (4:1)	95	550	3.59
PDEDPM / P-II (3:1)	120	560	8.22
PDEDPM / P-II (1:1)	120	560	5.58

[a] Not measured due to poor solubility

$I_{3\omega}$ and $I_{3\omega,s}$ are the peak intensities of THG from the sample and standard respectively. The calculated $\chi^{(3)}$ values of poly(1,6-heptadiyne) derivatives are summarized in Table II. We find that the $\chi^{(3)}$ $(-3\omega; \omega,\omega,\omega)$ value of these soluble conjugated polymers is quite high approaching 10^{-10} esu. In particular the PDEDPM/P-II (3:1) film showed the highest $\chi^{(3)}$ value. Since the third-harmonic wave (3ω= 635 nm) in our experiment locates at the near-absorbing region (see FIGURE 1 and 2) of the electronic spectra, the $\chi^{(3)}$ value shown in TABLE II might be somewhat enhanced from the non-resonant $\chi^{(3)}$ value. However, it should be mentioned that the $\chi^{(3)}$ values of these polymers as a class are much higher than that of other processble conjugated polymers such as the polyalkylthiophenes reported earlier.[14] It was reported that the non-resonant $\chi^{(3)}$ of polyalkylthiophene was around 1×10^{-11} esu, and even the fully- resonant one was $3.5\text{x}10^{-11}$ esu at best.

In conclusion, the substituted poly(1,6-heptadiyne)s as a class were found to be a very promising materials for the third-order optical nonlinearity with their quite high $\chi^{(3)}$ values, easy processing by spin-coating, stability and the good linear optical qualities.

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