Synthesis and Nonlinear Optics of Soluble Poly(phenyleneethynylene)

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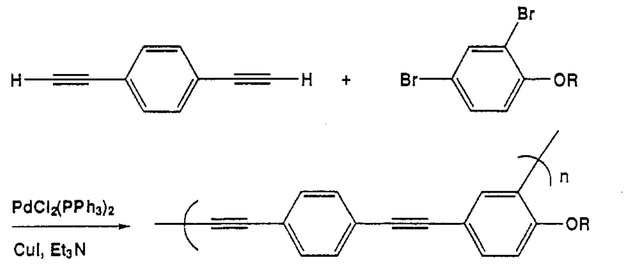
Nonlinear π-conjugated polymers which include poly(diacetylene),[1] polyacetylene,[2] and poly(phenylenevinylene)[3] in relation to a potential use in the optoelectronic field have attracted much attention. Among them, polydiacetylenes exhibit the highest nonlinear susceptibility (χ^3) of the order of 10^{-6} esu in the resonant region for poly-PTS[4] [poly(2,4-hexadiyne-1,6-diol bis(*p*-toluenesulfonate))] and poly-DCH[5] [poly[1,6-bis(*N*-carbazolyl)-2,4-hexadiyne]] single crystals. However, polymers such as poly(phenyleneethynylene) containing triple bonds in the main chain still remain undeveloped due to the lower solubility[6] despite the unique π-conjugation system. Soluble poly(aryleneethynylene) type polymers have recently been prepared by the incorporation of pyridine and a long alkyl-substituted thiophene moiety into the main chain.[7,8] On the other hand, the introduction of the *m*-phenylene structure into the main chain in the poly(phenyleneethynylene) may provide high processability and the maximum absorption shift to a shorter wavelength due to the suppression of the insoluble rigid linear structure.

This paper describes the synthesis and the nonresonant third-order nonlinearity of a new type of poly(phenyleneethynylene) which is soluble in common organic solvents and does not include heterocyclic components.

The Pd-catalyzed coupling reaction of ethynyl compounds with aryl bromide or iodide is widely used for the preparation of ethynylarenes.[9] A similar reaction of 1,4-diethynylbenzene with 1-alkoxy-2,4-dibromobenzene (*n* = 15, 17, and 21)[10] in triethylamine led to the desired soluble polymers (**I**)[11] with conversions of 60, 80, 89%, respectively (Scheme I). Particularly, **I** (*n* = 21) was found to be superior to the shorter alkyl-substituted polymers in processability. The film cast from a chloroform solution has a maximum absorption at 335 nm, quite different from other third-order poly(diacetylenes) which have strong absorptions around 600 nm. The $\chi^3(\omega)$ of **I** (*n* = 21), which was determined by the nanosecond time-resolved DFWM (degenerate four wave mixing) method in a benzene solution at 532 nm, is 1.8×10^{-9} esu. This value is comparable to the largest nonresonant $\chi^3(\omega)$ (3×10^{-9} esu) of poly-PTS.[1]

Scheme I



(I) : R = $CH_3(CH_2)_n$, n= 15, 17, 21

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References and Notes

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(10) 1-Alkoxy-2,4-dibromobenzene was obtained by the reaction of 2,4-dibromophenol with sodium hydride in DMF followed by alkyl bromide (*n* = 15, 17, and 21) treatment at 55 °C.

(11) In a general procedure, 1,4-diethynylbenzene (4.8 mmol) and 1-(docosyloxy)-2,4-dibromobenzene (4.8 mmol) were refluxed for 6 h in triethylamine (70 mL) in the presence of $PdCl_2(PPh_3)_2$/CuI (0.014/0.026 mmol). After removal of insoluble material and the solvent, the residue was dissolved in chloroform to be precipitated into methanol to give the pale yellow polymer powder which is soluble in chloroform, benzene, THF, DMF, and carbon disulfide. The molecular weight for **I** (*n* = 21) determined by GPC in DMF was 4×10^4. IR (film): 2200 cm^{-1} ($\nu_{C\equiv C}$). ^1H NMR (400 MHz, $CDCl_3$): δ 7.469 (m, 5H), 6.831 (m, 2H), 4.022 (t, 2H), 1.849 (m, 2H), 1.535 (m, 2H), 1.240 (m, 36H), 0.877 (t, 3H).