Second-Order Nonlinear Optical Property of Heterocyclic Pyridinium Betaine Dispersed in Poly(methyl methacrylate)

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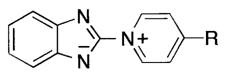
A new class of second-order nonlinear optical material: 2-[1-(4-butylpyridinio)]benzimidazolate dispersed in poly(methyl methacrylate) was investigated by the Maker fringe method using a Q-switched Nd:YAG laser (1064 nm), indicating that the poled film exhibited the second-order nonlinear optical coefficient, d_{33}, of 1.8 ± 0.2 pm V^{-1}.

Heterocyclic betaines have received much attention because of their unusually high dipole moments ascribed to their zwitterionic character and exhibiting negative solvatochromism.[1] Recently, pyridinium heterocyclic betaines consisting of a negatively charged aromatic donor and a positively charged aromatic acceptor groups were found to be applicable as a second-order nonlinear optically active molecule from theoretical investigations.[2] Pyridinium heterocyclic betaines have also been reported to exhibit the large negative first-order hyperpolarizability, β, because $\Delta\mu$ in equation 1,[3] which is described within the dipolar approximation on the basis of the two-state model, is negative.[4]

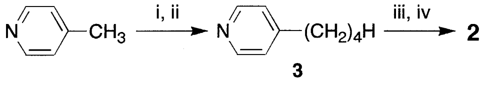
$$\beta_\mu(0) = \{3(M_{ge})^2\Delta\mu\}/\{2(\hbar\omega_{ge})^2\} \qquad (1)$$

where $\beta_\mu(0)$ is the static β value, $\Delta\mu = \mu_e - \mu_g$ is the difference between the dipole moments in the excited and the ground states, $\hbar\omega_{ge}$ is the transition energy, and M_{ge} is the transition dipole moment between the ground and the excited states. Additionally, it has been revealed that the β value of 2-(1-pyridinio)benzimidazolate (**1**) is estimated for (110 ± 25) X 10^{-30} esu in chloroform, which is 5-fold larger than that of 4-nitroaniline in chloroform,[5] by the hyper-Rayleigh scattering measurement.[6]


1: R = H
2: R = $(CH_2)_4H$

Here, we report for the first time a new class of second-order nonlinear optical (NLO) material consisting of 2-[1-(4-butylpyridinio)]benzimidazolate (**2**) as a guest molecule dispersed in poly(methyl methacrylate) (PMMA). Second-order NLO organic molecules on which have usually been studied are aromatic compounds with a pair of electron-donating- and electron-withdrawing-groups at the π-conjugating sites.[3,7] Second-order NLO activities of these types of molecules are owing to charge transfer between electron-donating- and electron-withdrawing-groups through π-conjugation. In the meantime, the NLO activity of the present pyridinium heterocyclic betaine is attributed to the short-range charge transfer through the bond bearing the character of σ-bonding from the charged aromatic donor group to the charged aromatic acceptor group linked with directly.[3,8]

Betaine **2** was obtained by modifying the method reported by Alcalde et al.[8] as shown in Scheme 1.



Scheme 1. *Reagents and conditions*: i, LDA, THF, 0 °C, 2 h; ii, $CH_3(CH_2)_2Br$, THF, r.t., 2 h; iii, 2-chlorobenzimidazole, 140 °C, 1 h; iv, aqueous NH_3, r.t., 30 min.

Namely, betaine **2**[9] was prepared by a quaternization reaction of 4-butylpyridine (**3**) with 2-chlorobenzimidazole[10] followed by the deprotonation of *N*-(2-benzimidazolyl)pyridinium chloride by aqueous ammonia. Betaine **2** is very soluble in common polar organic solvents such as chloroform, methanol, ethanol, acetone, THF and so on, although betaine **1** exhibits poor solubility in common organic solvents. Thus, an optical-quality thin film of PMMA (M_n: 4.3 X 10^5, determined by gel permeation chromatography; T_g: 101 °C determined by differential scanning calorimetry) containing 20 wt% of betaine **2** could be obtained by a spin coating method from their THF solution on an ordinary glass substrate.[11] Figure 1 shows the UV-vis spectrum of betaine **2** dispersed in a PMMA thin film, λ_{max} of which is 378 nm. The absorbance around λ_{max} decreased by being poled at 110 °C for 20 min with a corona poling method as shown in Figure 1, indicating the promotion of chromophore orientation by electric poling.

The second harmonic generation (SHG) of the thin film was measured in transmission by means of the Maker fringe

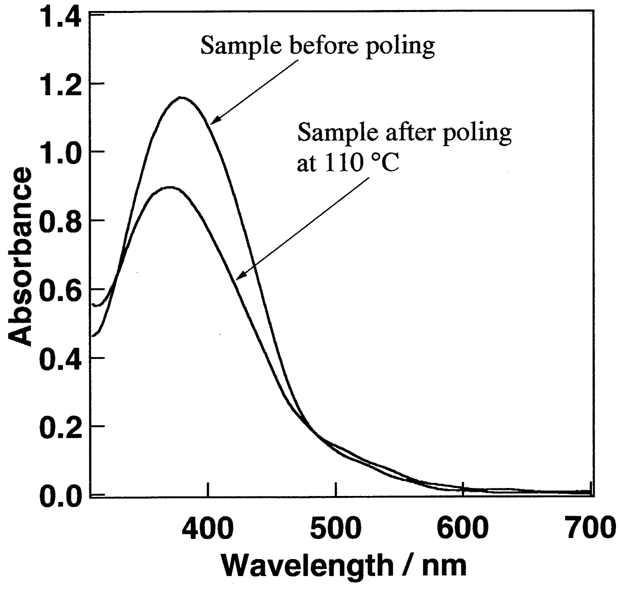


Figure 1. UV-vis absorption spectra of betaine **2** dispersed in a PMMA thin film before and after corona poling.

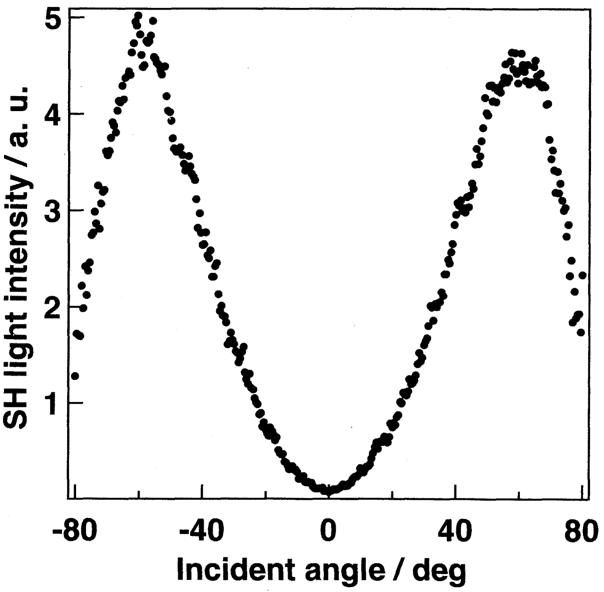


Figure 2. Relationship between SH light intensity and the incident angle of an exciting beam for betaine **2** dispersed in a PMMA thin film after corona poling.

method.[12] A Q-switched Nd:YAG laser (Spectron SL404G, λ = 1064 nm, 10-Hz repetition rate, 6-ns pulse duration) was used for the exciting light source. The p-polarized laser beam was chosen using a $\lambda/4$ wave plate and a linear polarizer. Figure 2 describes the relationship between SH light intensity and the incident angle of an exciting beam for the spin-coated film obtained after corona poling. The second-order NLO coefficient, d_{33}, of the spin-coated film was determined by the mean square methods using the relationship of SH light intensity and an incident angle of an exciting beam between –80° and 80° proposed by Jerphagnon et al.[12] A 1 mm-thick y-cut quartz (d_{11} = 0.46 pm V^{-1}) was used as a reference sample. From the calculation, 1.8 ± 0.2 pm V^{-1} of d_{33} was obtained. An application of pyridinium heterocyclic betaines in nonlinear optics is worthy of notice and can lead to the development of a new class of second-order NLO material.

References and Notes

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9 Equimolar 2-Chlorobenzimidazole with **3** was stirred at 140 °C for 1 h and cooled. The residual solid by being washed with diethyl ether was dissolved in the mixed solvent of ethanol and diluted hydrochloric acid. The solution was treated with activated charcoal and the filtrate was concentrated followed by deprotonation with aqueous ammonia. The precipitate was purified by silica gel column chromatography with chloroform–methanol (40:1) as eluent. Recrystallization from acetone afforded **2**. Selected data for **2**: ^{1}H NMR (90 MHz, CDCl$_3$) δ 1.00 (t, 3H, J = 6.4 Hz), 1.3–2.1 (m, 4H), 2.89 (t, 2H, J = 8.1 Hz), 7.13 (dd, 2H, J = 3.3, 6.2 Hz), 7.7–7.9 (m, 4H), 9.88 (d, 2H, J = 7.0 Hz); IR (KBr pellet) 3125, 3045, 2955, 2930, 2895, 2870, 1705, 1636, 1610, 1555, 1500, 1465, 1415, 1410, 1395, 1340, 1305, 1295, 1265, 1190, 1120, 1095, 1000, 955, 930, 900, 840, 800, 745, 620, 565, 505 cm^{-1}; MS (*m/z*) 251 (M$^+$, 11%), 222 [M$^+$ – (C$_2$H$_5$), 100%]; Anal. Found: C, 76.7; H, 6.95; N, 16.9%. Calc for C$_{16}$H$_{17}$N$_3$: C, 76.46; H, 6.82; N, 16.72%). R_f (SiO$_2$, chloroform–methanol, 40:1) 0.15. For **3**: bp, 69 °C (8 Torr); ^{1}H NMR (90 MHz, CDCl$_3$) δ 0.93 (t, 3H, J = 6.4 Hz), 1.1–1.9 (m, 4H), 2.61 (t, 2H, J = 7.7 Hz), 7.10 (d, 2H, J = 5.9 Hz), 8.48 (d, 2H, J = 5.9 Hz); MS (*m/z*) 135 (M$^+$, 41%), 93 (100%).

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