A new class of second-order non-linear optical material: stilbazolium benzimidazolate covalently bound to polymer backbone

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This paper describes the first example of the preparation of stilbazolium benzimidazolate covalently bound to polymer backbone using a novel methacrylate monomer, 2-{4-[2-(4-methacryloyloxyphenyl)ethenyl]pyridinio}benzimidazolate. A free radical copolymerization of 2-{4-[2-(4-methacryloyloxyphenyl)ethenyl]pyridinio}benzimidazolate (1 equiv.) with butyl methacrylate (6 equiv.) provided a methacrylate polymer containing 1.7 mol% of betaine units. The resulting polymer exhibited a glass transition temperature of 30 °C. The number-average (M_n) and weight-average (M_w) molecular masses were 36 900 and 79 300, respectively, estimated by GPC measurement. The second-order non-linear optical property of the obtained polymer was investigated by second-harmonic generation (SHG) measurements applying the Maker fringe method using a Q-switched Nd : YAG laser (1064 nm) as an exciting beam after corona-poling, indicating that the d_{33} value of the resulting copolymer was 5.1 pm V^{-1}.

Organic second-order non-linear optical (NLO) materials have been the subject of intense studies because their high NLO activity, chemical resistance, and easy processibility are available for NLO applications such as fast waveguides and electro-optic modulation.[1] Second-order NLO organic molecules which have usually been studied are aromatic compounds with a pair of electron-donor and electron-acceptor groups at the π-conjugating sites, so-called D–π–A system molecules.[2] Recently, various types of NLO molecules classified as non-classical D–π–A system molecules have been developed[3] for the improvement of physical properties of NLO molecules and for solving the problem of the trade-off between optical non-linearity and cutoff wavelength. On the other hand, heterocyclic betaines have received much attention because of their unusually large dipole moments ascribed to their zwitterionic character and exhibiting negative solvatochromism.[4] Rutkis *et al.* have reported[5] the NLO properties of the Langmuir–Blodgett film consisting of indane-1,3-dionepyridinium betaine.

Our research group has revealed that pyridinium or stilbazolium benzimidazolates consisting of a negatively charged aromatic donor and a positively charged aromatic acceptor group, which are not classified as classical D–π–A system molecules, are applicable as second-order non-linear optically active molecules from theoretical investigations[6] and hyper-Rayleigh scattering measurement.[7] One distinct characteristic of pyridinium betaine compounds is that the dipole moment of the ground state often changes its sign with excitation.[6] The value of the first hyperpolarizability, β, is proportional to the difference between the dipole moment of the ground state and that of the excited state within the framework of the two-state model;[2] therefore, β can be enlarged by decreasing the dipole moment of the ground state.[8] In many cases, the increase in β of classical D–π–A system molecules is accompanied by an increase in the dipole moment of the ground state.[2] Large dipole moments often lead to temporal or thermal relaxation of the noncentrosymmetric alignment of NLO-phores due to dipole–dipole interactions, which results in the temporal or thermal relaxation of second-order NLO activities. It may be possible to use pyridinium betaine compounds to solve this problem owing to the characteristics mentioned above.

Recently, our research group has investigated the second-order NLO properties of thin films of some pyridinium betaines dispersed in poly(methyl methacrylate) (PMMA) by the Maker fringe measurements.[9] However, the limited solubility and centrosymmetric aggregation of pyridinium betaines seemed to inhibit the increase in the second-order NLO susceptibility. To solve these problems, we have tried to prepare pyridinium benzimidazolate covalently attached to a polymer backbone. Here, we report the first example of the preparation of stilbazolium benzimidazolate covalently bound to a polymer backbone as well as the preliminary results of the NLO investigations.

Experimental

Materials

1-Methyl-2-pyrrolidinone (NMP) was distilled over CaH_2 under reduced pressure. Tetrahydrofuran (THF) was distilled twice (over CaH_2 and sodium) for the removal of traces of water. Butan-1-ol, propan-2-ol, triethylamine (Wako Pure Chemical Industries, Ltd.) and 4-picoline (Tokyo Kasei Kogyo Co., Inc.) were used after distillation over CaH_2. 4-Hydroxybenzaldehyde, methacryloyl chloride (Tokyo Kasei Kogyo Co., Inc.), 2,2′-azoisobutyronitrile (AIBN, Wako Pure Chemical Industries, Ltd.), acetic anhydride and acetic acid (Kanto Chemical Co., Inc.) were commercially available and used as received. Butyl methacrylate was distilled just before use. 2-Chlorobenzimidazole was prepared by modifying the method reported by Harrison *et al.*[10] 4-[2-(4-Hydroxyphenyl)ethenyl]pyridine **1** was prepared by the method in the literature[11] using 4-hydroxybenzaldehyde and 4-picoline as the starting materials. Yield, 45% as pale yellow crystals. δ_H [$(CD_3)_2SO$; 90 MHz] 6.7–7.0 (m, 3H, phenyl and ethenyl protons), 7.3–7.8 (m, 6H, phenyl, pyridyl, and ethenyl protons), 8.56 (d, *J* 6.0, 2H, pyridyl protons); *m*/*z* 197 (M^+), 180, 168, 139, 115, 89, 63, 51. (Found: C, 79.3; H, 5.65; N, 7.0. Calc. for $C_{13}H_{11}NO$: C, 79.17; H, 5.62; N, 7.10%.)

Instrumentation

UV–VIS absorption spectra were measured in the transmission mode on a Shimadzu Model U-2100 spectrophotometer. ^1H NMR spectra were recorded with a Hitachi R-90H FT NMR (90 MHz) spectrometer or a Bruker AM-400 FT NMR (400 MHz) spectrometer. *J* Values are given in Hz. IR spectra were measured in the transmission mode on a Jasco A-202 IR spectrometer. Mass spectrometry was conducted on a Hitachi

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Mass Spectrometer M-80B by electron ionization method. Differential scanning calorimetry (DSC) measurements were carried out on a Shimadzu Model DSC-50 with a helium flow rate of 20 ml min^{-1} and a heating rate of 10 °C min^{-1}. Gel permeation chromatography (GPC) was performed on a Tosoh HLC-802A instrument equipped with TSK gels G5000H$_6$, G4000H$_6$, G3000H$_6$ and G2000H$_6$ using polystyrene standards in THF eluent.

2-{4-[2-(4-Hydroxyphenyl)ethenyl]pyridinio}benzimidazolate 2

Under an argon atmosphere, a mixture of 2-chlorobenzimidazole (1.42 g, 9.28 mmol), **1** (1.44 g, 9.28 mmol) and dry butan-1-ol (18 ml) was stirred at 100 °C for 12 h and cooled. This reaction mixture was poured into diethyl ether (1000 ml), and the resulting precipitate was collected by filtration. The residual solid was washed with diethyl ether and dissolved in methanol (300 ml) at 60 °C. The solution was treated with 10 ml of aqueous ammonia at 60 °C. To this mixture was added water (400 ml). The resulting precipitate was collected by filtration. The crude product was purified by recrystallization from acetone–methanol which afforded the title compound **2** (2.84 g, 88%) as orange crystals. Elemental analysis indicated the crystals of **2** included two molecules of water per molecule. δ_H (CD_3OD, 400 MHz) 6.89 (d, *J* 8.7, 2H, phenylene protons), 7.11 (dt, *J* 3.2, 9.3, 2H, benzimidazolate protons), 7.29 (d, *J* 16.2, 1H, =*CH*–phenylene), 7.58 (dt, *J* 3.2, 9.3, 2H, benzimidazolate protons), 7.67 (d, *J* 8.7, 2H, phenylene protons), 7.96 (d, *J* 16.2, 1H, =*CH*–pyridyl), 8.17 (d, *J* 7.2, 2H, pyridyl protons), 9.43 (d, *J* 7.2, 2H, pyridyl protons); ν_{max}/cm^{-1} 3125, 3080, 3040, 2940, 2900, 2855, 1635, 1615, 1590, 1510, 1475, 1450, 1425, 1395, 1325, 1310, 1280, 1190, 1170, 1115, 1055, 1000, 965, 940, 920, 880, 845, 845, 750, 670, 630, 540, 515; *m/z* 313 (M^+), 284, 222, 209, 197 [M^+ −(benzimidazolate)], 180, 168, 152, 144, 133, 117, 115, 105, 90, 77, 63, 51, 39, 28 (Found: C, 68.5; H, 5.6; N, 12.1. Calc. for $C_{20}H_{15}N_3O + 2H_2O$: C, 68.75; H, 5.48; N, 12.03%).

4-[2-(4-Methacryloyloxyphenyl)ethenyl]pyridine 3

Under an argon atmosphere, methacryloyl chloride (2.87 g, 25.0 mmol) was added to **1** (4.93 g, 25.0 mmol) in dry THF (100 ml) in the presence of hydroquinone (0.028 g, 0.25 mmol) and triethylamine (5.05 g, 50.0 mmol). The reaction mixture was stirred at ambient temperature for 2 h, and poured into saturated aqueous sodium hydrogen carbonate (500 ml). The crude product was extracted with chloroform (5 × 100 ml), and the solvent was evaporated. The crude product was purified by recrystallization from acetone–diethyl ether, affording the title compound **3** (6.63 g, 94%) as white crystals. δ_H ($CDCl_3$, 400 MHz) 2.07 (dd, *J* 1.0, 1.5, 3H, $-CH_3$), 5.78 (m, 1H, $=CH_2$), 6.37 (m, 1H, $=CH_2$), 6.98 (d, *J* 16.3, 1H, =*CH*–phenylene), 7.16 (dt, *J* 2.0, 8.6, 2H, phenylene protons), 7.29 (d, *J* 16.3, 1H, =*CH*–pyridyl), 7.36 (dd, *J* 1.5, 4.6, 2H, pyridyl protons), 7.57 (dt, *J* 2.0, 8.6, 2H, phenylene protons), 8.58 (dd, *J* 1.5, 4.6, 2H, pyridyl protons); ν_{max}/cm^{-1} 3030, 3005, 2930, 1725 (–C=O), 1685, 1635, 1595, 1550, 1510, 1450, 1415, 1375, 1320, 1290, 1240, 1215, 1200, 1170, 1135, 1105, 1015, 990, 975, 955, 885, 875, 865, 820, 640, 600, 545; *m/z* 265 (M^+), 197, 167, 139, 115, 69 [$H_2C{=}C(CH_3)CO^+$], 41 [$H_2C{=}C(CH_3)^+$], 28 (Found: C, 76.9; H, 5.8; N, 5.1. Calc. for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28%).

2-{4-[2-(4-Methacryloyloxyphenyl)ethenyl]pyridinio}benzimidazolate 4

Path A. Under an argon atmosphere, methacryloyl chloride (2.61 g, 25.0 mmol) was added to **2** (2.91 g, 8.33 mmol) in dry NMP (30 ml) in the presence of hydroquinone (0.0092 g, 0.083 mmol) and triethylamine (4.23 g, 41.8 mmol). The reaction mixture was stirred at 60 °C for 2 h, and poured into saturated aqueous sodium hydrogen carbonate (500 ml). The crude product was extracted with chloroform (5 × 50 ml), and the solvent was evaporated. Recrystallization from acetone–methanol afforded the title compound **4** (1.51 g, 48%) as orange crystals; δ_H ($CDCl_3$, 400 MHz) 2.09 (dd, *J* 1.0, 1.5, 3H, $-CH_3$), 5.82 (m, 1H, $=CH_2$), 6.39 (m, 1H, $=CH_2$), 7.12 (d, *J* 16.2, 1H, =*CH*–phenylene), 7.15 (dt, *J* 3.2, 6.2, 2H, benzimidazolate protons), 7.26 (dt, *J* 2.3, 8.5, 2H, phenylene protons), 7.62 (d, *J* 16.2, 1H, =*CH*–pyridyl), 7.65–7.72 (m, 4H, phenylene and benzimidazolate protons), 7.78 (d, *J* 7.2, 2H, pyridyl protons), 9.87 (d, *J* 7.2, 2H, pyridyl protons); ν_{max}/cm^{-1} 3115, 3075, 3040, 2925, 1735 (esteric –C=O), 1685, 1635, 1615, 1595, 1550, 1505, 1465, 1450, 1415, 1395, 1375, 1320, 1295, 1265, 1230, 1205, 1165, 1130, 1050, 1010, 950, 875, 835, 805, 750, 710, 675, 655, 635, 620, 585, 560, 540, 515, 500; *m/z* 381 (M^+), 352, 314, 312, [$M^+ - (H_2C{=}C(CH_3)CO)$], 283, 265, 201, 183, 167, 152, 133, 118, 102, 90, 69 [$H_2C{=}C(CH_3)CO^+$], 58, 43, 41 [$H_2C{=}C(CH_3)^+$], 28 (Found: C, 75.1; H, 5.0; N, 11.0. Calc. for $C_{24}H_{19}N_3O_2$: C, 75.57; H, 5.02; N, 11.02%).

Path B. The procedures were similar to those for the preparation of **2**. The purification was carried out by column chromatography on Florisil in chloroform–methanol (volume ratio 10 : 1) as eluent. Recrystallization from acetone–methanol afforded **4** in a yield of 18%.

Polymerization

Butyl methacrylate (0.427 g, 3.00 mmol), **4** (0.191 g, 0.500 mmol) and AIBN (0.0058 g, 0.035 mmol) were dissolved in propan-2-ol (7.0 ml), and the solution was degassed. The sealed tube was heated at 60 °C for 24 h. Then, the reaction mixture was poured into 300 ml of methanol, affording a red–brown precipitate. The polymer obtained was reprecipitated twice from its THF solution into excess methanol and dried *in vacuo*. The yield of the polymer was 0.060 g (9.7%); δ_H ($CDCl_3$, 400 MHz) 0.8–2.1 (m, 0.983 × 3H), 1.2–2.2 (m, 0.983 × 3H + 0.017 × 5H), 3.7–4.1 (m, 0.983 × 2H), 7.0–7.3 (m, 0.017 × 5H), 7.6–7.8 (m, 0.017 × 7H), 9.8–9.9 (m, 0.017 × 2H); ν_{max}/cm^{-1} 2960, 2935, 2875, 1730 (ester –C=O), 1620, 1600, 1555, 1540, 1505, 1470, 1390, 1265, 1240, 1175, 1155, 1065, 1020, 1000, 965, 945, 880, 845, 805, 745, 540, 515.

SHG Measurement

P(BMA-4) was deposited on an ordinary cover glass by spin-coating at a rate of 2000 rpm from a 10 mass% THF solution. The poling procedure of a spin-coated film was achieved by poling normal to the surface by corona discharge. The distance of the tungsten needle from the surface was 25 mm. The needle side was set to 10 kV negative to an aluminium heating plate. After 20 min of poling at the set temperatures, the spin-coated film was cooled to ambient temperature with continuous corona poling. The second harmonic generation (SHG) at 532 nm was measured in transmission by means of the Maker fringe method.[12] An experimental apparatus for the Maker fringe measurement was shown in our previous report.[13] An outline is as follows. A Q-switched Nd : YAG laser (Spectron SL404G, $\lambda = 1064$ nm, 10 Hz repetition rate, 6 ns pulse duration) was used for the exciting light source after its pulse energy had been decreased to <1 mJ through neutral density filters. The polymer sample was placed on a rotating stage, and rotated around a horizontal axis from an incident angle of −80 to +80°. SHG signals were detected by a photomultiplier tube. The signal from the photomultiplier tube was integrated with a boxcar integrator (Stanford Research SR-250). The p-polarized laser beam was chosen using a $\lambda/4$ wave plate and a linear polarizer.

The second-order NLO coefficient, d_{33}, was evaluated by applying a mean-square method[14] to the relationship between the SH light intensity and the incident angle of the exciting beam measured by the Maker fringe method using eqn. (1) proposed by Jerphagnon *et al.*[12]

$$I_{2\omega}=[512\pi^2/(cw^2)]I_\omega{}^2 d_{33}{}^2 t_\omega{}^4 T_{2\omega} R(\theta) p^2(\theta) B(\theta) \times I_\omega{}^2 \sin^2\Psi(\theta)/(n_\omega{}^2-n_{2\omega}{}^2)^2 \quad (1)$$

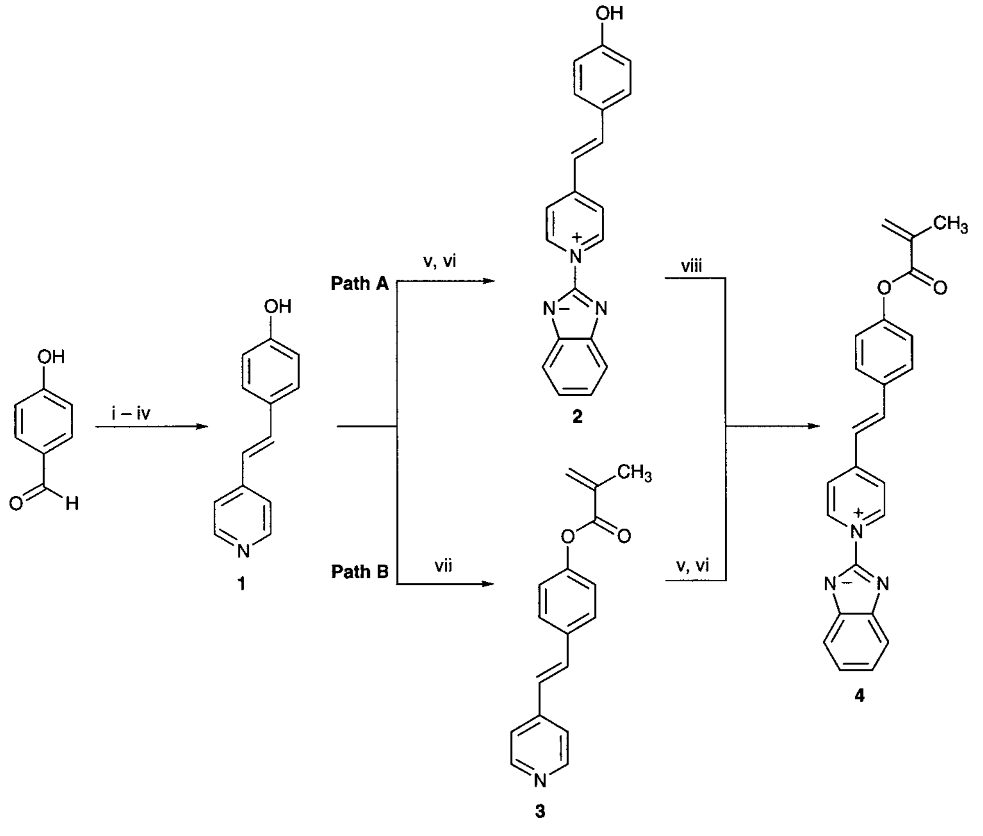
where $I_{2\omega}$ is the intensity of SH wave in a uniaxial poled material generated by p-polarized exciting wave, the intensity of which is represented by I_ω, c is the velocity of light, w is the spot radius of the Gaussian beam, θ is the incident angle of the exciting wave, t_ω and $T_{2\omega}$ are Fresnel-like transmission factors, n_ω and $n_{2\omega}$ are the refractive indices, $R(\theta)$ is the multiple reflection correction, $p(\theta)$ is a projection factor, $B(\theta)$ is the beam size correction, and $\Psi(\theta)$ is the angular dependence of the second harmonic power. 1 mm thick y-cut quartz ($d_{11}=0.46$ pm V^{-1}) was used as a reference sample.

Results and Discussion

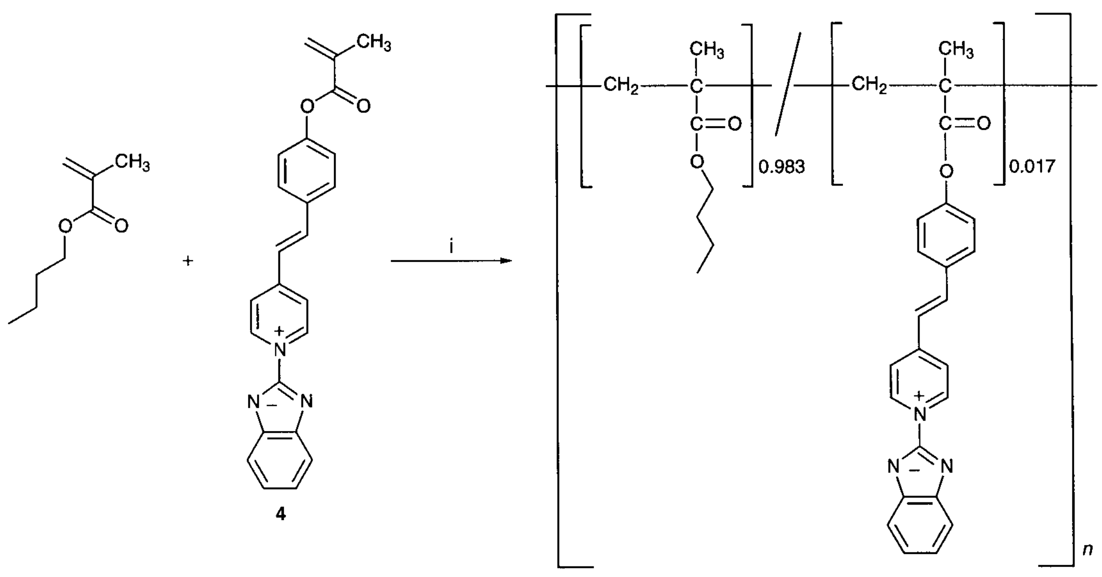
A novel monomer for radical polymerization, *i.e.* 2-{4-[2-(4-methacryloyloxyphenyl)ethenyl]pyridinio}benzimidazolate **4**, was prepared by use of 4-[2-(4-hydroxyphenyl)ethenyl]pyridine as a starting material (Scheme 1). Path A is the synthetic pathway *via* formation of the betaine structure, followed by introduction of the methacryloyl moiety, and Path B is that *via* introduction of the methacryloyl moiety, followed by a formation of the betaine structure. Both pathways gave monomer **4**; however, the overall yield from **1** to **4** *via* Path A (42%) was higher than that *via* Path B (17%), due to the good yield for formation of the betaine structure using **2**.

The radical homopolymerization of **4** did not proceed due to the poor solubility of **4** in common organic solvents. The radical copolymerization of **4** with butyl methacrylate was carried out in propan-2-ol at 60 °C for 24 h using AIBN as the initiator, affording the random copolymer as shown in Scheme 2. The molar ratio of **4** to BMA in the feed was determined to 1 : 6 so that the betaine moiety in the resulting polymer could avoid aggregation.[9] This polymerization reaction proceeded favourably in alcoholic media, and did not proceed in the other organic polar solvent such as THF, DMF, DMSO and NMP.

We chose butyl methacrylate as the comonomer to make the resulting copolymer very soluble in organic solvents and to investigate the second-order NLO property of the resulting polymer, in spite of the low glass transition temperature, *i.e.* 30 °C. The composition of the resulting copolymer **P(BMA-4)** was determined from a comparison of the signal areas of the ^{1}H NMR spectrum, indicating the introduction ratio of **4** was 1.7 mol%. This introduction ratio for the betaine moiety is rather small considering the molar ratio of **4** to BMA in the feed. This is considered to be due to the low reactivity and the poor solubility of **4**, which would result from the large dipole moment of **4** in the ground state. The problem of solubility could be solved by introducing an electron-withdrawing group to the 4′ position of the stilbazole moiety, which decreases the dipole moment of stilbazolium betaine in the ground state.[8,15] Gel permeation chromatography (GPC) indicated that the number-average (M_n) and weight-average (M_w) molecular masses of **P(BMA-4)** were 36 900 and 79 300, respectively, and no monomers were detected. **P(BMA-4)** is very soluble in common polar organic solvents such as chloroform, acetone, THF and so on. Thus, an optical-quality thin film of **P(BMA-4)** could be obtained by spin-coating a 10 mass% THF solution of **P(BMA-4)** on an ordinary cover glass. Fig. 1 shows the UV–VIS spectra of a spin-coated film of **P(BMA-4)**, the thickness of which was < 1 µm, before and after corona poling. The absorbance *ca.* λ_{max} decreased by being corona poled at 70 °C for 20 min applying a voltage of 4 kV cm^{-1} as shown in Fig. 1. Taking into account that the UV–VIS spectra were measured by a transmission method, this result indicates the promotion of chromophore orientation by electric poling.



Scheme 1 *Reagents and conditions*: i, Ac$_2$O, room temp., 1 h; ii, Ac$_2$O, 4-picoline, 120 °C, 72 h; iii, NaOH, MeOH, H$_2$O, reflux, 2 h; iv, aq. HCl; v, 2-chlorobenzimidazole, butan-1-ol, 100 °C, 12 h; vi, aq. NH$_3$; vii, methacryloyl chloride, THF, Et$_3$N, room temp., 2 h; viii, methacryloyl chloride, NMP, Et$_3$N, room temp., 2 h



4

P(BMA-4)

Scheme 2 *Reagents and conditions*: i, Pr^{i}OH, AIBN, 60 °C, 24 h

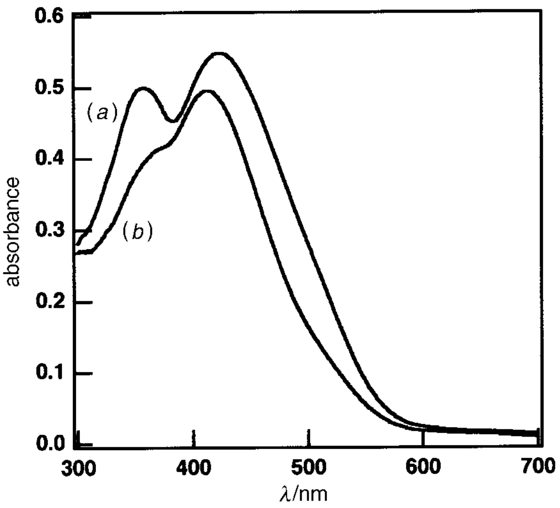


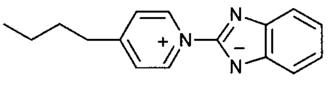
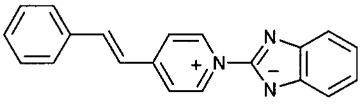
Fig. 1 UV–VIS absorption spectra of a spin-coated film of **P(BMA-4)**; (*a*) before corona poling, (*b*) after corona poling at 70°C

Additionally, a blue-shift of the maximum absorption band was observed. This result may be ascribed to a negative solvatochromic behaviour of betaine compounds, because the environment around the chromophores became polar due to the noncentrosymmetric alignment of betaine moieties which have large dipole moments.

The second harmonic generation (SHG) of the thin film was measured in transmission by means of the Maker fringe method. Fig. 2 shows the relationship between SH light intensity and the incident angle of the exciting beam for the spin-coated film obtained after corona poling. The poling treatment was effective above 30 °C; however, the optimum poling temperature was 70 °C.

The second-order NLO coefficient, d_{33}, of the spin-coated film was determined by the mean-square methods[12] using the relationship between SH light intensity and the incident angle of the exciting beam [eqn. (1)]. A value of 5.1 pm V^{-1} for d_{33} was calculated. Table 1 summarizes the optical properties of **P(BMA-4)** as well as those of the similar pyridinium betaines dispersed in PMMA from the literature.[9] The content of 20 mass% of 2-(4-butylpyridinio)benzimidazolate or 10 mass% of 2-[4-(2-phenylethenyl)pyridinio]benzimidazolate is equivalent to 8.0 or 3.4 mol% respectively for the pyridinium betaines

Table 1 Optical properties of **P(BMA-4)**

sample	mol content of betaine/mol%	λ_{max}/nm	λ_{cutoff}/nm	d_{33}/pm V^{-1}
P(BMA-4)	1.7	420	600	5.1
 20 wt% in PMMA	8.0	378[a]	590[a]	1.8[a]
 10 wt% in PMMA	3.4	420[b]	600[b]	1.6[b]

[a]The values from ref. 8(*a*). [b]The values from ref. 8(*b*).

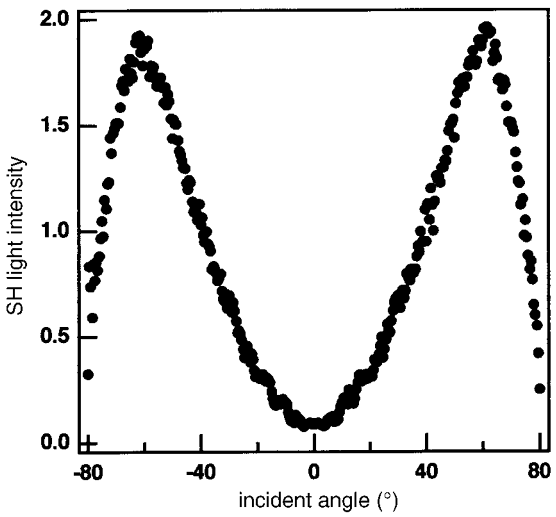


Fig. 2 Relationship between SH light intensity and the incident angle of an exciting beam for a spin-coated film of **P(BMA-4)** after corona poling at 70 °C

with respect to the monomeric unit of PMMA. The present **P(BMA-4)** contained a rather low proportion of betaine component, *i.e.* 1.7 mol%; however, it exhibited a d_{33} value of 5.1 pm V^{-1} which is large compared to those of the similar pyridinium betaines dispersed in PMMA. It may be because stilbazolium betaines dispersed in PMMA tend to aggregate centrosymmetrically because of their large dipole moments that the rather small value of d_{33} was obtained.[9] The rather large d_{33} value of the present **P(BMA-4)** is considered to be due to polymeric effects, such as uniform dispersion of the betaine species and promotion of dissociation of the aggregated betaines. The increase in the content of the betaine unit would lead to an increase in the NLO susceptibility. Additionally, the d_{33} values could be enlarged by a modification of the stilbazole moiety, *i.e.* the introduction of an electron-withdrawing group in the 4′ position which would also lead to an increase in the solubility in organic solvents.[15] The preparation of polymeric materials containing a higher content of modified pyridinium betaine units and the introduction of pyridinium betaine units into high T_g polymeric matrixes will be the subject of future investigations.

Conclusions

We achieved the preparation of stilbazolium benzimidazolate covalently bound to a polymer backbone by a copolymerization of a novel methacrylate monomer, 2-{4-[2-(4-methacryloyloxyphenyl)ethenyl]pyridinio}benzimidazolate, with butyl methacrylate. The content of betaine units was 1.7 mol%. The second-order NLO property of the copolymer obtained was investigated by SHG measurement, indicating that the d_{33} value of the resulting copolymer was 5.1 pm V^{-1} after corona poling at 70 °C. The application of pyridinium heterocyclic betaines in non-linear optics is worthy of note and may lead to a new class of second-order NLO material.

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