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Synthesis of Nonlinear Optical Polymers with Large Photoconductive Sensitivity and Transparency

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SUMMARY: Novel nonlinear optical (NLO) chromophore, 2-{3-[2-(4-methylsulfonylphenyl)vinyl]carbazol-9-yl}ethanol was synthesized and subsequently reacted with methacryloyl chloride to give a photoconducting NLO monomer **(M1)**. 2-Methylacrylic acid 2-[3-(diphenylhydrazonomethyl)carbazol-9-yl]ethyl ester **(M2)** was also synthesized as a comonomer to enhance the carrier mobility of the NLO polymer. Photoconducting NLO polymers, **P1** and **P2** were obtained by the copolymerization of **M1** with methyl methacrylate and **M2**, respectively. These polymers were well soluble in organic solvents and showed glass transition at 177 ℃ and 196 ℃, respectively. Polymer films of **P1** and **P2** were optically clear, and were transparent at wavelengths longer than 420 nm. The electro-optic coefficient (r_{33}) of poled **P1** films was measured to be ~5 pm/V at 632.8 nm. The photoconductive sensitivities of **P1** and **P2** were 6.2×10^{-14} $S\cdot cm^{-1}/mW\cdot cm^{-2}$ and 5.6×10^{-11} $S\cdot cm^{-1}/mW\cdot cm^{-2}$.

Introduction

Photorefractive materials are potentially useful in the high-density optical data storage, optical image processing, dynamic holography and optical computing.[1,2] Photoconducting nonlinear optical (NLO) polymers are the most promising candidates for these photorefractive applications.[3,4] Photoconductivity and second-order NLO activity, necessary to implement the photorefraction, are normally provided by the respective chromophores, which are chemically attached to polymer backbone or simply dispersed as a guest. Fully functionalized polymers with chemically attached chromophores are very stable and reliable for the photorefractive applications.[5,6] However, they suffer from the difficulties in the synthesis, the control of copolymer composition, and consequently the optimization of photorefractivity. Therefore, we are rather interested in the use of a single monolithic chromophore, namely photoconducting NLO chromophore, for the preparation of corresponding side-chain polymer.

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We have demonstrated that the heteroaromatic compounds like carbazole,[7,8] indole,[9] or indoline[10] with 2-(4-nitrophenyl)vinyl substituent at 3 or 5-position are examples of monolithic chromophore. It was shown that the polymers containing these monolithic chromophores as side chain exhibited excellent NLO activity and moderate photoconductivity.[7-10] Two main problems were realized when we try to utilize these polymers as photorefractive media. First, the absorption maxima (λ_{max}'s) of these chromophores were located at the wavelength longer that 420 nm with their apparent cut-off usually extended into 550 nm. Such an insufficient transparency in visible region is a real problem, since even a small tailing absorption at the wavelength of laser source (for example, 532 nm or 633 nm) is sufficient to prevent the polymer from getting photorefractive net gain. Second, the photoconductive sensitivity of monolithic chromophore was not high enough to assure fast response.

In this work, we report the appropriate molecular design and synthesis to solve these problems. To afford better transparency in the visible region, we synthesized monolithic chromophore, 2-{3-[2-(4-methylsulfonylphenyl)vinyl]carbazol-9-yl}ethanol, with apparent cut-off at 420 nm. To improve the photoconductive sensitivity, we synthesized 2-methylacrylic acid 2-[3-(diphenylhydrazonomethyl)carbazol-9-yl]ethyl ester as a comonomer of photoconductive NLO polymer.

Experimental

Instruments

^{1}H-NMR spectra were recorded with the use of Bruker AMX 300 spectrometer. IR spectra were measured with KBr pellet or KBr windows on Midac FT-IR spectrophotometer. Mass spectrometer data were obtained from JMS AX505WA using electron impact (EI) mode. Shimadzu UV 2101PC double beam spectrophotometer was used for the UV-Vis absorption spectra. Gel permeation chromatography (GPC) was performed at the flow rate of 1.0 mL/min in THF at 30 ℃ with Waters HPLC component system equipped with five Ultra-μ-styragel® columns (2×10^5, 10^5, 10^4, 10^3, 500 Å), which was calibrated with polystyrene standards. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out under nitrogen atmosphere at the heating rate of 10 ℃/min on Perkin Elmer DSC7 and Du Pont 2950, respectively.

Synthesis of Monomers

Synthetic pathway to the photoconducting nonlinear optical monomer, 2-methylacrylic acid 2-

{3-[2-(4-methylsulfonylphenyl)vinyl]carbazol-9-yl}ethyl ester (**M1**), and the comonomer for enhanced carrier mobility, 2-methylacrylic acid 2-[3-(diphenylhydrazonomethyl)-carbazol-9-yl]ethyl ester (**M2**) is outlined in Schemes 1.

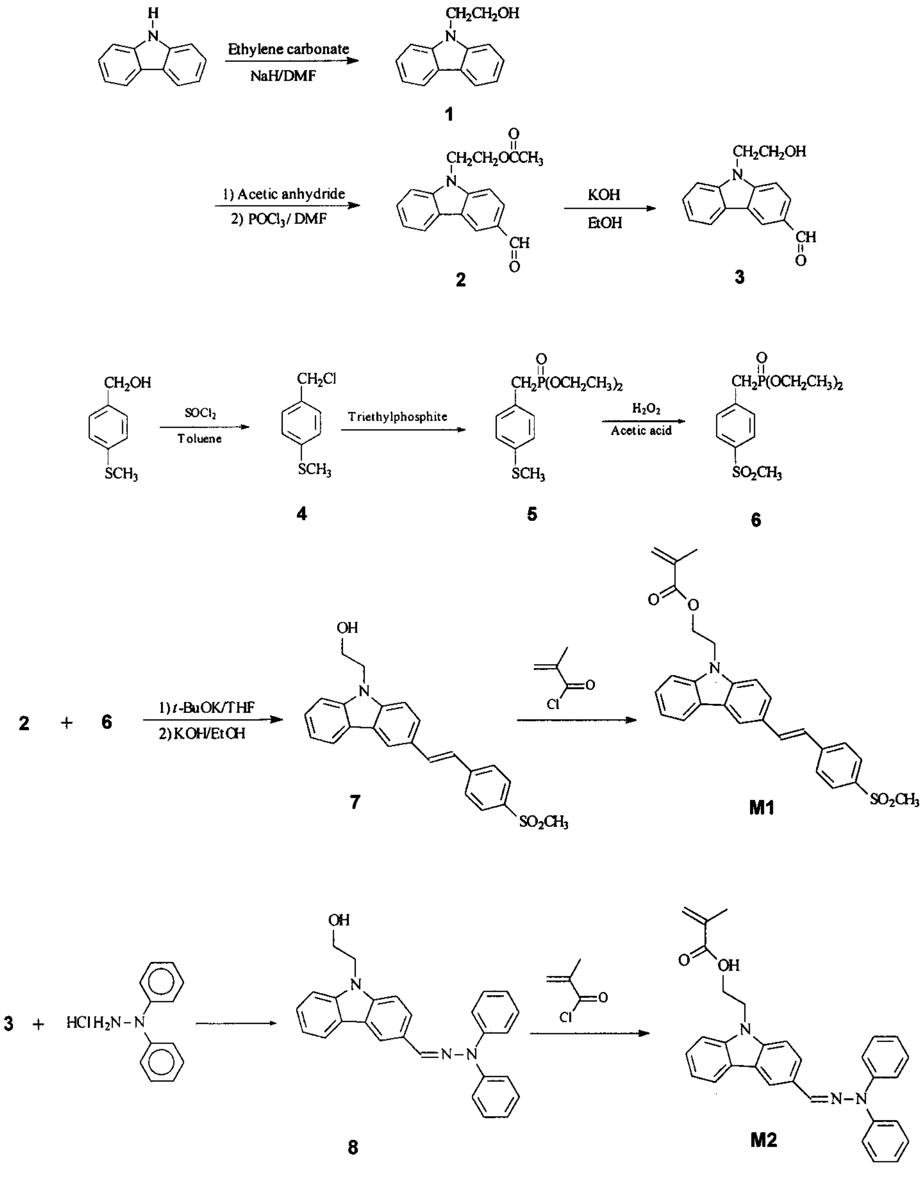
2-(Carbazole-9-yl)ethanol (**1**), acetic acid 2-(3-formylcarbazol-9-yl)ethyl ester (**2**) and 9-(2-hydroxyethyl)-9H-carbazole-3-carbaldehyde (**3**) were prepared as reported earlier.[7]

4-(Methylthio)benzyl chloride (4). 4-(Methylthio)benzyl alcohol (2.00 g, 13.0 mmol) was dissolved in 10 mL of dry toluene and thionyl chloride (1.42 mL, 19.5 mmol) was added dropwise at room temperature. The reaction mixture was stirred at 80 ℃ for 2 h, and then cooled to room temperature. Toluene and excess thionyl chloride were removed under reduced pressure. The crude product was distilled in vacuum to yield 1.48 g of faint yellow liquid (66%). ^{1}H-NMR ($CDCl_3$) 2.37 (s, 3H, SCH_3), 4.44 (s, 2H, $ClCH_2$), 7.12 (d, 2H, aromatic protons), 7.18 (d, 2H, aromatic protons).

Diethyl 4-(methylthio)benzyl phosphonate (5). To the 10 mL of triethylphosphite heated to reflux, **4** (3.00 g, 17.4 mmol) was added dropwise and refluxed for additional 2 h. After cooling, the excess triethylphosphite was removed under reduced pressure. The product was purified by silica gel column chromatography (ethylacetate/n-hexane = 2/1) to yield 4.31 g of water clear liquid (90%). ^{1}H-NMR ($CDCl_3$) 1.23 (t, 6H, CH_2CH_3) 2.47 (s, 3H, SCH_3), 3.07 (d, 2H, PCH_2), 3.97 (q, 4H, CH_2CH_3), 7.18 (t, 4H, aromatic protons).

Diethyl 4-(methylsulfonyl)benzyl phosphonate (6). To a magnetically stirred solution of **5** (10.0 g, 36.5 mmol) in 30 mL of glacial acetic acid was added hydrogenperoxide (30% in water, 10.4 mL, 91.3 mmol) at room temperature. After refluxing for 2 h, the solvent was removed under reduced pressure. The product was purified by silica gel column chromatography (methanol/ethylacetate = 1/6) to yield 6.56 g of white solid (59%). ^{1}H-NMR ($CDCl_3$) 1.27 (t, 6H, CH_2CH_3), 3.06 (s, 3H, SO_2CH_3), 3.21 (d, 2H, PCH_2), 4.02 (q, 4H, CH_2CH_3), 7.50 (d, 2H, aromatic protons), 7.88 (d, 2H, aromatic protons).

2-{3-[2-(4-Methylsulfonylphenyl)vinyl]carbazole-9-yl}ethanol (7). A magnetically stirred solution of **6** (3.37 g, 11.0 mmol) in 40 mL of tetrahydrofuran (THF) was treated with potassium *t*-butoxide (1.85 g, 16.5 mmol) at room temperature. A solution of **2** (3.00 g, 11.0 mmol) in 10 mL of THF was added and then the reaction mixture was heated at reflux for 30 min. After cooling, potassium hydroxide (2.46 g, 44.0 mmol) and 40 mL of ethanol were added and the solution was heated again at reflux for 30 min. The solution was cooled and the solvent was removed under reduced pressure. The residue was poured onto ice-cold water and neutralized with 1 N HCl solution. The precipitate was collected by suction-filtration and the resulting yellow solid was recrystallized from chloroform/ethanol (1/2) to yield 2.19 g of greenish yellow crystal (51%). mp 164 ~ 166 ℃; ^{1}H-NMR ($CDCl_3$) 1.64 (br, 1H, alcohol proton), 3.07 (s, 3H, SO_2CH_3), 4.10 (t, 2H, NCH_2), 4.51 (t, 2H, OCH_2), 7.14 (d, 1H, J = 16.3, stilbene proton), 7.49 (d, 1H, stilbene proton); IR (KBr, cm^{-1}) 3515 (-OH), 1587 (-CH=CH),1290, 1151 ($-SO_2-$).



Scheme 1. Synthesis of monomers (**M1** and **M2**).

1-[3-(Diphenylhydrazonomethyl)carbazol-9-yl]ethanol (8). To a magnetically stirred solution of 1,1-diphenylhydrazine hydrochloride (2.77 g, 12.5 mmol) in 100 mL of ethanol was added sodium acetate trihydrate (2.56 g, 18.8 mmol) at room temperature. And then a solution of **3** (2.50 g, 10.4 mmol) in 100 mL ethanol was added dropwise for 30 min. After stirring for 3 h, ethanol was removed under reduced pressure and the residue was poured onto water. The product was extracted with chloroform, washed with plenty of brine and distilled water, and dried over $MgSO_4$. The solvent, chloroform was removed under reduced pressure. The dark brown crude product was purified by silica gel column chromatography (ethyl acetate/n-hexane = 1/1) to yield 4.02 g of dark yellow solid (94%). mp 81 ~ 83 ℃; ^{1}H-NMR ($CDCl_3$) 3.94 (t, 2H, CH_2N), 4.36 (t, 2H, CH_2O), 7.09 ~ 7.16 (m, 7H, aromatic protons), 7.26 ~ 7.36 (m, 8H, aromatic protons), 7.75 (d, 1H, aromatic proton), 7.96 (d, 1H, aromatic proton), 8.10 (s, 1H, aromatic proton); IR (KBr, cm^{-1}) 3388 (-OH), 1597 (C=N).

2-Methylacrylic acid 2-{3-[2-(4-methylsulfonylphenyl)vinyl]carbazol-9-yl}ethyl ester (M1). To a magnetically stirred solution of **7** (2.00 g, 5.12 mmol) in 100 mL dry methylene chloride was added triethylamine (1.73 mL, 15.4 mmol) and methacryloyl chloride (1.00 mL, 10.2 mmol) at 0 ℃. The reaction mixture was allowed to warm up to room temperature and was stirred for 30 min. The solution was washed with saturated sodium bicarbonate solution, and dried over $MgSO_4$. The solvent was removed under reduced pressure. The yellow residue was purified by silica gel column chromatography (ethyl acetate/chloroform = 1/15) to give 1.67 g of yellow solid (71%). mp 181 ~ 183 ℃; ^{1}H-NMR ($CDCl_3$) 1.74 (s, 3H, $C{=}CCH_3$), 3.01 (s, 3H, SO_2CH_3), 4.48 (t, 2H, NCH_2), 4.55 (t, 2H, OCH_2), 5.42 (s, 1H, vinyl proton), 5.87 (s, 1H, vinyl proton), 7.08 (d, 1H, J = 16.3, stilbene proton), 7.36 (d, 1H, stilbene proton); IR (KBr, cm^{-1}) 1716 (ester C=O), 1630 (vinyl group), 1587 (-CH=CH-), 1290, 1151 ($-SO_2-$); m/z (EI, high resolution) calc'd for $C_{27}H_{25}O_4N_1S_1$, 459.15, found 459.15.

2-Methylacrylic acid 2-[3-(diphenylhydrazonomethyl)carbazol-9-yl]ethyl ester (M2). This monomer was prepared from **8** (5.00 g, 12.3 mmol), triethylamine (5.20 mL, 37.0 mmol), and methacryloyl chloride (2.40 mL, 24.6 mmol) in 50 mL dry of methylene chloride by the same procedure as described for **M1** (4.70 g of yellow solid, 81%). mp 121 ~ 123 ℃; ^{1}H-NMR ($CDCl_3$) 1.80 (s, 3H, $C{=}CCH_3$), 4.52 (t, 2H, CH_2N), 4.57 (t, 2H, CH_2O), 5.47 (s, 1H, vinyl proton), 5.92 (s, 1H, vinyl proton), 7.17 ~ 7.27 (m, 7H, aromatic protons), 7.38 ~ 7.47 (m, 8H, aromatic protons), 7.86 (d, 1H, aromatic proton), 8.07 (d, 1H, aromatic proton), 8.20 (s, 1H, aromatic proton); IR (KBr, cm^{-1}) 1712 (ester C=O), 1631 (vinyl group), 1597 (-C=N-); m/z (EI, high resolution) calc'd for $C_{31}H_{27}N_3O_2$, 473.21, found 473.21.

Polymerization

Photoconducting NLO polymers, **P1** and **P2** were obtained by the copolymerization of **M1** with methyl methacrylate and **M2**, respectively. A mixture of **M1** (1.2 g, 2.6 mmol), methyl methacrylate (MMA, 0.85 g, 8.0 mmol.), 2,2-azobisisobutyronitrile (AIBN, 12 mg, 0.7 mol%) and 15 mL of dried N-methyl pyrrolidinone (NMP) was degassed by standard freeze-pump-thaw method. After sealing the ampoule, the reaction mixture was heated at 65 ℃ for 24 h. After cooling, the resulting solution was cooled to room temperature, diluted to twice original volume with chloroform and then poured into methanol to precipitate the polymer **P1**, which was purified by repeated reprecipitation from chloroform to methanol. 1.7 g of **P1** was obtained (83%).

P2 was similarly copolymerized. The molar ratio of **M1** (1.30 g, 2.80 mmol) to **M2** (1.34 g, 2.80 mmol) was 1:1. NMP (15 mL) and AIBN (0.7 mol%) were used as solvent and initiator respectively (2.0 g, 76%).

Fabrication of Polymer Film

The prepared polymers (**P1** and **P2**) were dissolved in tetrachloroethane (10 wt%) and the solution was filtered with a Teflon membrane filter (Millipore, 0.22 μm). Thin polymer films were spin-coated at 1500 rpm onto indium-tin-oxide (ITO) coated glass. Residual solvent was removed by heating the films in vacuum oven for several days. Film thickness was measured to be about 1.2 μm with TENCOR P-10 profilometer.

Electro-Optic Coefficient

For the measurement of electro-optic coefficient (r_{33}), contact poling was carried out. A gold electrode was sputter-coated in 10^{-6} Torr vacuo on the polymer film backed with ITO glass. To align the chromophores, the sample was heated and then appropriate poling voltage was applied to the gold electrode. After 15 min, the film was cooled down to about 30 ℃ and the poling voltage was removed. The electro-optic coefficient of the poled polymer was measured at the wavelength of 632.8 nm (He-Ne laser) using a simple reflection method.[11]

Photoconductivity

The dark- and the photo- conductivities of polymer films were evaluated by measuring a current through the polymer film sandwiched between gold and ITO using Keithley 617 electrometer. ORIEL 300 W Xe lamp was used as a light source. Positive voltage was applied to ITO electrode and the light was shed through ITO electrode. Photoconductive sensitivity was calculated as the ratio of photoconductivity to the light intensity.

Results & Discussions

Synthesis of Monomers

Photoconducting NLO chromophore, 2-{3-[2-(4-methylsulfonylphenyl)vinyl]carbazol-9-yl}-ethanol (**7**) was obtain by Wadsworth and Emmons reaction between acetic acid 2-(3-formyl-carbazol-9-yl)ethyl ester (**2**) and diethyl 4-(methylsulfonyl)benzyl phosphonate (**6**) in 51% yield. Compound **2** was synthesized from carbazole in three steps, i.e. hydroxyethylation, protection of hydroxy group, and Vilsmeier formylation in 57% overall yield. Compound **6**, was prepared according to the reported method,[12] which consists of three sequential steps starting from 4-(methylthio)benzyl alcohol, namely, chlorination, phosphonation and oxidation in 35% overall yield. Photoconducting NLO monomer (**M1**) was prepared in 71% yield by the reaction of 7 with methacryloyl chloride.

2-Methylacrylic acid 2-[3-(diphenylhydrazonomethyl)carbazol-9-yl]ethyl ester (**M2**), was synthesized from **3** and 1,1-diphenylhydrazine hydrochloride, and subsequent reaction with methacryloyl chloride in 76% overall yield.

Physical Properties of Polymers

Photoconducting NLO polymers, **P1** and **P2**, were prepared by free radical polymerization. Tab. 1 summarizes the molecular weights and glass transition temperatures of them. Polymers are highly soluble in common solvents such as chloroform, dichloroethane, DMF and NMP. However, they were partially soluble in THF. Due to this good solubility and moderate molecular weight as listed in Tab. 1, optical quality thin films could be easily obtained by spin coating. Thermal properties of the polymers were examined by DSC and TGA measurements. From the DSC thermograms, glass transition temperatures (T_g's) of **P1** and **P2** were found to be 177 ℃ and 196 ℃, respectively. Compared to the T_g of PMMA (120 ℃), those of **P1** and **P2** are quite high presumably due to the bulkiness of the carbazole-based chromophore which severely restrict main-chain and side-group motions in these polymers. TGA thermograms showed that the polymers were relatively stable up to 220 ℃ (the temperature of 2% weight loss, under nitrogen).

As expected from the weaker electron-withdrawing ability of sulfone group than that of nitro group, π - π^* absorption bands of **P1** and **P2** in UV-Vis spectrum (Fig. 1) were significantly blue-shifted relative to the nitro-containing photoconducting NLO polymers reported earlier by us.[7-10] The amount of blue-shift was larger than 80 nm, which provided the polymers (**P1** and **P2**) with a broad transparency window in the visible region.

Tab. 1. Properties of polymers

Polymer	m_{feed} [a]	conversion (%)	M_n [b]	M_w/M_n	T_g (℃) [c]
P1	1 : 3 (**M1**: MMA)	83	42700	3.03	177
P2	1 : 1 (**M1** : **M2**)	76	28400	4.29	196

[a] Mole ratio of monomers in the feed.
[b] Measured by GPC in THF using polystyrene standards.
[c] Determined by DSC at a heating rate of 10 ℃/min under N_2.

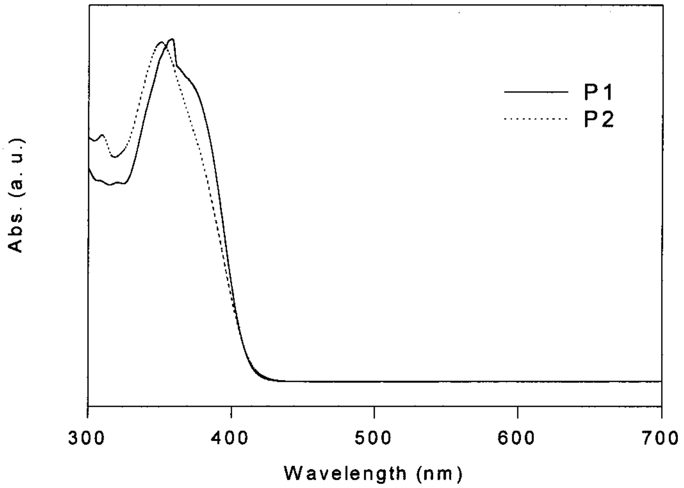


Fig. 1: UV-VIS spectra of **P1** and **P2**

NLO and Photoconducting Properties

First hyperpolarizability (β) of chromophores was calculated by MOPAC 6 using PM3 Hamiltonian. The β value of photoconducting NLO chromophore (7) was 18.0×10^{-30} esu, which was about half of that of well-known 4′-(dimethylamino)-4-nitrostilbene (**DANS**). To investigate the dependence of electro-optic coefficient (r_{33}) on the poling field, we poled polymer film of **P1** at 120 ℃ under the electric field of 0.2, 0.4 and 0.6 MV/cm, respectively. As shown in Figure 2, r_{33} increased linearly with the poling field and 5 pm/V was achieved at the electric field of 0.6 MV/cm. The r_{33} value is expected to increase further by the optimization of poling temperature and field.

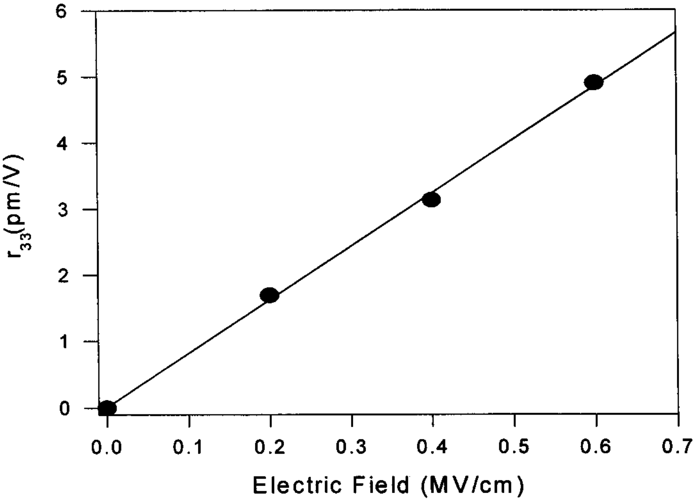


Fig. 2: Dependence of electro-optic coefficient (r_{33}) of **P1** on poling field.

When 3.38 mW/cm^2 light of Xe lamp was irradiated on the polymer films of **P1** and **P2**, orders of magnitude increase in the current density was observed. Photoconductivity values of polymer films were calculated from these photocurrent densities as a function of electric field as shown in Figure 3. Estimated photoconductivity values were 2.1×10^{-13} S·cm^{-1} and 1.9×10^{-10} S·cm^{-1} at the electric field of about 0.6 MV/cm for **P1** and **P2**, respectively. It should be noted that **P2** has 1000 times higher photoconductivity than **P1**, though their absorption spectra are virtually same (Fig. 1), which strongly suggests that **P2** possesses more efficient charge transporting property than **P1**. This higher photoconductivity of **P2** is, no doubt, due to **M2**, which contains carbazole-hydrazone moiety with enhanced carrier transporting property. The calculated photoconductive sensitivities are 6.2×10^{-14} S·cm^{-1}/mW·cm^{-2} for **P1** and 5.6×10^{-11} S·cm^{-1}/mW·cm^{-2} for **P2**, under the 3.38 mW/cm^2 irradiation from Xe lamp.

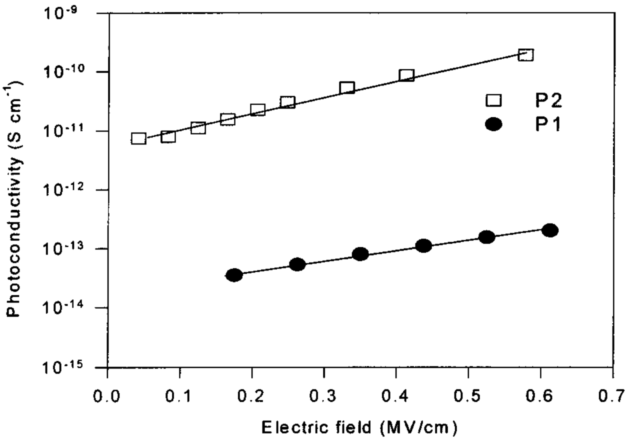


Fig. 3: Photoconductivities of **P1** and **P2**.

Conclusion

We synthesized photoconducting NLO side-chain polymers with large photoconductive sensitivity and broad transparency in visible region. 2-{3-[2-(4-Methylsulfonylphenyl)vinyl]-carbazole derivative was synthesized as photoconducting NLO chromophore with absorption maximum at 350 nm and apparent cut-off at 420 nm. 2-Methylacrylic acid 2-[3-(diphenylhydrazonomethyl)carbazol-9-yl]ethyl ester was also utilized as a comonomer to increase photoconductive sensitivity of photoconducting NLO polymer by thousand times.

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