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Synthesis and Polymerization of 6-(Alkyloxyphenyl)carbonyl Substituted Spirobenzopyran

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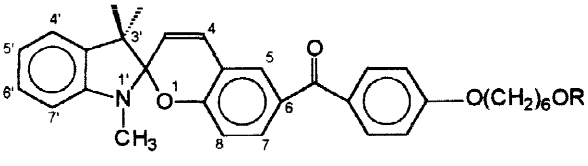
Abstract: 6-(Alkyloxyphenyl)carbonyl substituted spirobenzopyran (COSP) was synthesized from 6-(hydroxyphenylcarbonyl)substituted salicylaldehyde and indoline, followed by alkylhydroxylation with 6-chloro-1-hexanol. Resulting COSP was modified to a methacryloyl substituted COSP derivative, which was polymerized with styrene (ST) and butylmethacrylate (BMA) to give a terpolymer of COSP-ST-BMA (PCOSP). COSP monomers and PCOSP were thermally more stable than 6-nitrospirobenzopyran. Fast photochromic coloration was observed from a COSP doped polymer or PCOSP film upon irradiation with a light of 340 nm.

Photochromic spirobenzopyrans (SP) and their polymers have collected much interests for their high photosensitivity and fast response in a rigid medium.[1] The photochromic properties of SP arise from the photo-induced reversible ring opening/closure process, which are highly affected by the substituents on the SP molecules[4]. In particular, 6-nitrospiropyran (6NSP), which has a strong electron withdrawing nitro group at the conjugation terminal, has been intensively investigated.[2]

However, the nitro derivatives have critical problem of low thermal decomposition temperature[3]. Such a low decomposition temperature has limited the application of 6NSP in the processing requiring high temperature condition. In this respect, investigation of new SP derivatives with increased thermal stability is crucial for derivatization and application of SP.

In order to design a thermally stable SP with fast photochromic response, we introduce (alkoxyphenyl)carbonyl substituted spirobenzopyran since cleavage of C-C(=O)(aryl) is likely to occur at much higher temperature compared to that of C-(NO_2). Furthermore the alkoxyphenyl group provide polymerizable functional group with appropriated spacing group. Herein we report synthesis of 6-(p-alkyloxyphenyl)carbonylspirobenzopyran (COSP, **1**) and its derivatives.



1, R = H; 2, R = COC(CH_3)=CH_2

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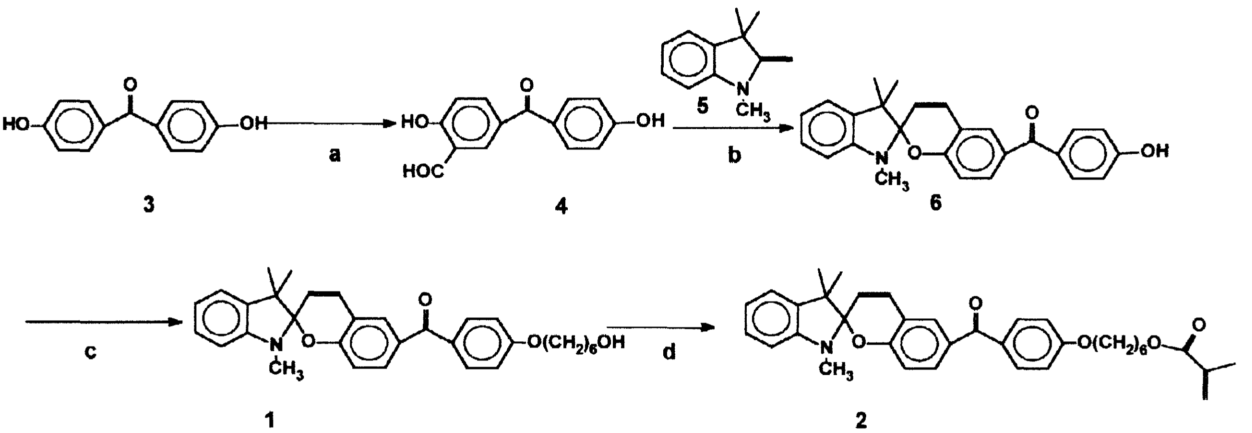
Compound **1** was prepared starting from 4,4-dihydrobenzophenone (**3**) over 3 steps as summarized in Scheme 1. To a stirred solution of **3** and NaOH in water, chloroform was added slowly at 65 °C. The mixture was stirred for 1 hr then refluxed for 16 hrs. Removal of excess chloroform and purification of the product by flash chromatography on silica gel gave colorless crystals of **4**.[4] 6-(Hydroxyphenylcarbonyl)spirobenzopyran, **6**, was prepared from **4** and indoline (**5**) using methanol as a solvent.[5]



Scheme 1. Synthesis of 6-(Alkyloxy)phenylcarbonyl substituted spiropyran (**COSP**). Conditions employed: a) $CHCl_3$ (2equiv.), NaOH(10 equiv.)/H_2O, 28 %.; b) **4** (3.3 equiv.), **5** (1 equiv.) in MeOH at 50 °C, 96 %.; c) $Cl(CH_2)_6OH$ (1.2 equiv.), K_2CO_3 (1.3 equiv), reflux, 80 %.; d) Methacrylchloride (1.3 equiv.), $N(CH_2CH_3)_3$ (6.8 equiv.)/THF, r.t., 98 %.

To a stirred suspension of **6** and K_2CO_3 in acetonitrile was added 1-chlorohexanol at room temperature and the mixture was refluxed overnight. After cooling to r.t., removal of precipitates and solvent, followed by chromatography on silica gel afforded **1**.[6] Thermogravimetric analysis on **1** carried out under nitrogen atmosphere at a heating rate of 10 °C/min indicated that **1** is stable up to 230 °C. On the other hands the nitro derivative (6NSP) showed weight loss beginning from ~ 150 °C.

Since **1** is thermally more stable than the nitro derivatives, it possesses much wider application than the nitro derivatives. Furthermore the hydroxyl end group allows us to synthesize new photochromic monomers. Hydroxyl group was modified by acylation using methacryloyl chloride. Thus methacryloyl chloride was added dropwise to a stirred solution of **1** and triethylamine in THF at room temperature. After 3 hrs of stirring, removal of insoluble solids and solvent, followed by purification afforded **2**.[7] Starting decomposition temperature of **2** was observed at ~ 250 °C by TGA as shown in Figure 1. Compound **2** was polymerized under radical polymerization condition using a mixture of styrene (ST) and butyl methacrylate (BMA). Thus a mixture of 20.3 wt % of **2**, 50 wt % of

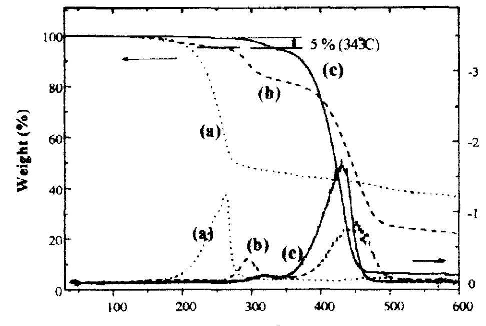


Figure 1. TGA profiles of (a) 6NSP (·······), (b) **1** (———), and (c) terpolymer of COSP-styrene-butylmethacrylate (**7**, - - - - -).

styrene, 29 wt % of butylmethacrylate, and 0.7 wt % of AIBN in THF was refluxed under a nitrogen atmosphere for 72 hrs. After cooling to room temperature, the solution was treated by a mixture of diethyl ether and hexane to yield precipitates, which were reprecipitated and dried under vacuum to give a terpolymer of COSP-styrene-butylmethacrylate, 7.[8] Average molecular weight (Mw) of 7 was 16,800 (Mw/Mn = 1.58) and starting decomposition temperature was observed at 250 °C (Figure 1).

Transparent film of 7 was prepared by solution coating method using xylene as a solvent. Figure 2 shows UV spectral change of a glass covered with 7 by a light of 340 nm. Within a few minute of irradiation, the film changed its color to blue, which bleached to original colorless state after switching off the light. Optical density of the film accompanied by the formation of merocyanine form was increased sharply when exposed to the light source and decreased when the film was protected from a light. Importantly, the thermal bleaching was much faster in the film of 7 than that of PMMA film containing 20 wt % of 6NSP. Thus the film of 7 showed complete decay to original absorbance (Figure 3), while the film of 6NSP showed base line increase after irradiation indicating photo-decomposition.

In conclusion, new 6-(alkyloxyphenyl)carbonyl spirobenxzopyran graft polymers showed increased thermal and light stability, providing much challenges to photochromic application.

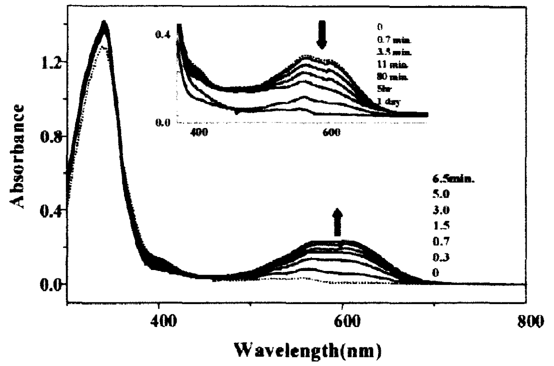


Figure 2. Spectral changes of polymer film of 7 upon irradiation of a light of 340 nm. Inset shows bleaching of the irradiated film for 1 day under dark condition. Time intervals are given.

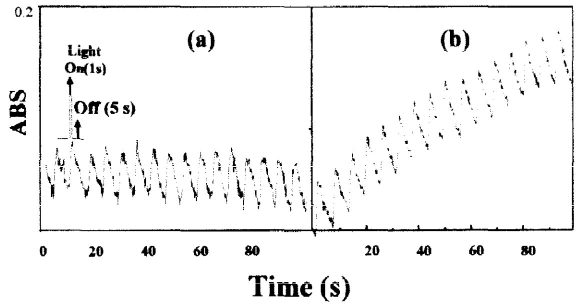


Figure 3. Photochromic switching of spirobenzopyran: (a) film of 7, (b) PMMA film doped with 20 wt % of 6NSP. Absorbance changes were monitored at 560 nm.

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Referenes and notes

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4. Mp; 176 °C. IR (KBr, cm^{-1}); 1653(-CHO group). ^{1}H-NMR (300MHz, acetone-d_6): δ 11.25 (s, 1H), 10.01 (s, 1H), 9.20 (s, 1H), 8.08(s, 1H), 7.88 (d, 1H, J=8.6Hz), 7.60 (d, 2H, J=8.7Hz), 6.99 (s, 1H, J=8.6Hz), 6.84 (d, 2H, J=8.7Hz). MS (m/z); 242 (M$^+$, 75), 213 (18), 149 (51), 121 (100), 93 (23), 65 (27).
5. Mp; 85 °C. IR (KBr, cm^{-1}); 952 (C_{spiro}-O). ^{1}H-NMR (300MHz, $CDCl_3$) δ 9.86 (s, 1H), 7.74 (d, 2H, J=8.6Hz), 7.61(s, 1H), 7.59 (d, 1H), 7.21 (t, 1H), 7.09 (d, 1H), 7.01~6.82 (m, 4H), 6.76(d, 1H, J=7.8Hz), 6.55 (d, 1H, J=7.6Hz), 5.76 (d, 1H, J=10.3Hz), 2.77 (s, 3H), 1.33 (s, 3H), 1.19 (s, 3H). ^{13}C-NMR δ 20.4, 26.3, 29.3, 52.4, 105.8, 107.3, 115.2, 115.7, 116.6, 118.8, 119.8, 120.7, 121.9, 128.1, 129.8, 130.2, 130.4, 132.9, 133.1, 136.8, 148.4, 158.7, 161.1, 195.7. MS (m/z); 397(M$^+$, 63), 382 (34), 368 (7), 262 (12), 159 (100), 121 (23). High-resolution MS; Calculated for $C_{26}H_{23}O_3N$: 397.1678, Found: 397.1675.
6. Mp; 48 °C. IR(KBr, cm^{-1}); 953(C_{spiro}-O), ^{1}H-NMR (300MHz, $CDCl_3$) δ 9.87(s, 1H), 7.79(d, 2H, J=8.7Hz), 7.60(s, 1H),7.58(d, 1H, J=8.0Hz), 7.19 (t, 1H), 7.08 (d, 1H, J=6.6Hz), 7.02~6.81 (m, 4H), 6.74 (d, 1H, J=8.0Hz), 6.52 (d, 1H, J=7.7Hz), 5.75 (d, 1H, J=10.3Hz), 4.05 (t, 2H, J=6.4Hz), 3.67 (t, 2H, J=6.0Hz), 2.75 (s, 3H), 1.83 (m, 2H), 1.67~1.38 (m, 6H), 1.31 (s, 3H), 1.19 (s, 3H). ^{13}C-NMR δ 20.4, 25.9, 26.2, 29.3, 29.5, 33.0, 52.4, 63.2, 68.5, 105.7, 107.3, 114.3, 115.0, 118.8, 119.8, 120.6, 121.9, 128.1, 129.5, 129.6, 130.7, 130.8, 132.4, 132.6, 132.9, 136.9, 148.4, 158.4, 162.8, 194.7. MS (m/z); 497 (M+, 36), 482 (8), 368 (7), 173 (43), 158 (100), 143 (12), 121 (11). High-resolution MS; Calculated for $C_{32}H_{35}NO_4$: 497.2566, Found: 497.2568.
7. Mp; 70 °C. IR (KBr, cm^{-1}); 1718 (-COO-), 953 (C_{spiro}-O); ^{1}H-NMR (300MHz, $CDCl_3$) δ 7.79 (d, 2H, J=8.7Hz), 7.60 (s, 1H), 7.57 (d, 1H, J=8.1Hz), 7.19 (t, 1H, J=7.6Hz), 7.10 (d, 1H, J=7.1Hz), 6.96~6.83 (m, 4H), 6.76 (d, 1H, J=8.1Hz), 6.56 (d, 1H, J=7.7Hz), 6.11 (s, 1H), 5.76 (d, 1H, J=10.3Hz), 5.54 (s, 1H), 4.18 (t, 2H, J=6.6Hz), 4.05 (t, 2H, J=6.3Hz), 2.74 (s, 3H), 1.83 (m, 2H), 1.73 (m, 2H), 1.57~1.38 (m, 4H), 1.32 (s, 3H), 1.17 (s, 3H). ^{13}C-NMR δ 10.7, 20.4, 26.1, 26.2, 26.3, 28.9, 29.3, 29.4, 32.4, 65.0, 68.4, 105.7, 107.3, 114.3, 115.0, 118.8, 119.8, 120.6, 121.9, 125.7, 128.1, 129.5, 130.7, 130.9, 132.6, 132.9, 136.9, 148.4, 158.4, 162.8, 194.7. MS (m/z); 565 (M$^+$, 75), 550 (17), 368 (8), 159 (100), 121 (13). High-resolution MS; Calculated for $C_{36}H_{39}NO_5$: 565.2828, Found: 565.2832.
8. IR (KBr, cm^{-1}); 1724 (-COO-), 955 (C_{spiro}-O); ^{1}H-NMR (300MHz, $CDCl_3$) δ 7.79 (d, J=8.7Hz), 7.60 (s), 7.3 ~ 6.5 (m, broad) 5.76 (d, J=10.3Hz), 4.0 ~ 3.0 (m, br), 2.74 (s), 2.3 (br), 2.0 ~ 1.0 (m, br), 0.9 ~ 0.5 (m, br).