Communications to the Editor

Organometallic Nonlinear Optical (NLO) Polymers. 1. Pendant Ferrocene NLO-phores in a Poly(methyl methacrylate) Copolymer. The First $\chi^{(2)}$ Organometallic NLO Polymer†

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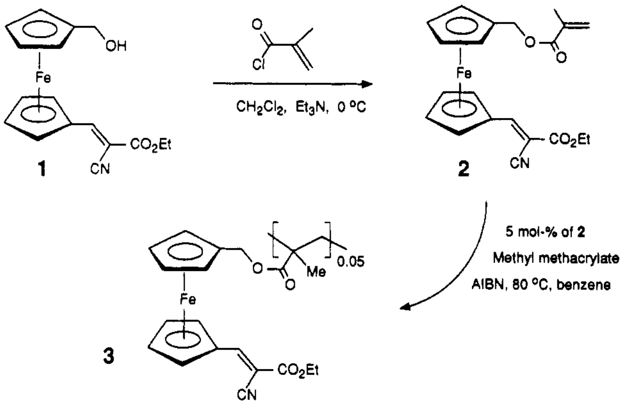
The development of materials for use in nonlinear optical (NLO) devices has become a vigorous area of research in the chemical community.[1] Several chemical compositions have been proven to be effective NLO materials. Polymeric materials are very attractive because of their processability which will lead to facile device fabrication.[2] Crystalline organometallic materials have been shown to exhibit efficient second-harmonic generation (SHG).[3] Of the organometallic systems studied thus far, ferrocene derivatives appear from theoretical[4] and experimental results to be the most attractive.[3] After 4 decades of organometallic chemistry no organometallic complex has out-performed ferrocene in synthetic versatility and overall stability (both thermal and photochemical).[5]

A key issue for $\chi^{(2)}$ materials has been achieving the required acentric ordering of molecules and then retaining this alignment. Marder and co-workers have shown that ferrocene systems which crystallize in noncentrosymmetric space groups have efficiencies orders of magnitude higher than urea.[6] For $\chi^{(3)}$ NLO materials, where a noncentrosymmetric macrostructure is *not required*, alkynyl-transition-metal coordination polymers have been used with good success.[7] In this paper we present the synthesis of the first organometallic polymer to undergo successful alignment by corona onset poling and then exhibit the $\chi^{(2)}$ NLO property of SHG.

The ferrocene monomer $\{\eta^5\text{-}C_5H_4CH_2O_2CC(CH_3){=}CH\}\{\eta^5\text{-}C_5H_4CH{=}C(CN)CO2Et\}Fe$ (**2**) was prepared from $\{\eta^5\text{-}C_5H_4CH_2OH\}\{\eta^5\text{-}C_5H_4CH{=}C(CN)CO_2Et\}Fe$ (**1**; Scheme I).[8] Copolymerization of **2** with methyl methacrylate under free-radical polymerization conditions produced copolymer **3**. Copolymer **3** was characterized by both spectroscopic and analytical methods.[9] The ethyl α-cyanoacrylate moiety on the ferrocene remained intact through the polymerization process. The thermal behavior of the polymer was nearly identical with that of poly(methyl methacrylate). We observed a T_g of 120 °C and a T_m of 225 °C for copolymer **3**.[10]

Scheme I



Polymer **3** was dissolved in chlorobenzene with some heating to make a 7% solution by weight. The films of **3** were made by doctor blading onto ordinary Pyrex microscope slides. The film thickness was in the range of 2–3 μm. After drying at reduced pressure at 174 °C for several hours, the films were corona onset poled at 126 °C for 30 min, cooled to 88 °C for 30 min, and then cooled ballistically to less than 40 °C with the field on at all times.[11]

Second-harmonic-generation measurements were performed using the 1064-nm fundamental output of a Nd:Yag laser. Detection of the second-harmonic generation generated in the polymer films was accomplished using a silicon photodiode in conjunction with optical filters. A digital oscilloscope was used to average approximately 100 signal pulses. A 1-mm-thick y-cut quartz crystal was used as a reference for the SHG measurements. An effective *d* value was estimated using the formula given by Knoesen et al.[12] The value of the organometallic copolymer was $d = 1.72$ pm/V compared to 0.45 pm/V for the quartz standard. Hence, the polymer displayed a SHG efficiency approximately 4 times that of the quartz standard.[13]

This work now demonstrates that indeed organometallic NLO-phores can be incorporated into polymer matrices, can be aligned through corona onset poling, and display SHG activity. Work continues in our group to further explore the design, synthesis, and evaluation of organometallic NLO polymeric materials.

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Supplementary Material Available: Listing of experimental procedures for compounds **2** and **3** (2 pages). Ordering information is given on any current masthead page.

References and Notes

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† Dedicated to the memory of Robert F. Kubin, who passed away during publication of this paper.

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(8) Selected spectroscopic data for **2**: ^{1}H NMR (CDCl$_3$) δ 8.14 (s, 1 H, $=CH$(CN)CO$_2$Et), 6.11 (s, 1 H, $=CH_2$), 5.58 (s, 1 H, $=CH_2$), 5.02 (t, *J* = 2 Hz, 2 H), 4.86 (s, 2 H, CH_2O), 4.70 (t, *J* = 2 Hz, 2 H), 4.36 (t, *J* = 2 Hz, 2 H), 4.32 (q, *J* = 7.2 Hz, CH_2CH$_3$), 4.27 (t, *J* = 2 Hz, 2 H), 1.94 (s, 3 H), 1.37 (t, *J* = 7.1, CH$_2$$CH_3$); UV-Vis (EtOH) λ = 518 nm (ϵ = 2.15 × 10^3 M^{-1} cm^{-1}). Anal. Calcd for $C_{21}H_{21}FeNO_4$: C, 61.94; H, 5.20; N, 3.44. Found: C, 61.72; H, 5.14; N, 3.38.

(9) Selected spectroscopic and analytical data for copolymer **3**: ^{1}H NMR (CDCl$_3$) δ 8.10 (s, 1 H, CH(CN)CO$_2$Et), 4.99 (br s, 2 H), 4.67 (br s, 2 H), 4.29 (q, *J* = 6.9 Hz, 2 H), 4.28 (br overlapping s, 2 H), 4.24 (br s, 2 H), 3.57 (s, CH_3), 1.83 (br s, CH_2), 1.76 (br s, CH_2), 1.35 (t, *J* = 6.9 Hz, CH$_2$$CH_3$), 0.99 (s, CH_3), 0.81 (s, CH_3); UV-Vis (EtOH) λ = 514 nm. Anal. Calcd for polymer **3**: N, 0.63. Found: N, 0.61.

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