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Organic NLO Polymers. Linear and Accordion Main-Chain NLO Polymers
Prepared by a Knoevenagel Polycondensation

by

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A new main-chain NLO polymer was prepared by transesterification and the Knoevenagel polycondensation. The latter polymer product was obtained as a higher molecular weight polymer with good solubility in organic solvents. New <i>bis</i>(arylcarboxaldehyde) monomers were prepared and copolymerized with <i>bis</i>(cyanoacetate) monomers to afford accordion main-chain NLO polymers. The polymers were characterized by spectroscopic and analytical data, thermal analysis, and GPC.						
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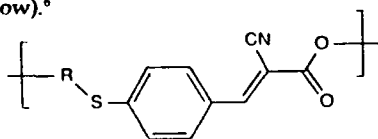
ORGANIC NLO POLYMERS. LINEAR AND ACCORDION MAIN-CHAIN NLO POLYMERS PREPARED BY A KNOEVENAGEL POLYCONDENSATION

Michael E. Wright* and Sanjoy Mullick

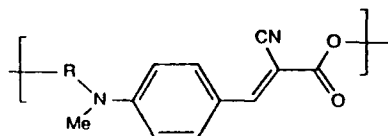
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Introduction

The design and synthesis of new NLO materials for SHG applications can be accomplished through a variety of strategies.¹ Polymeric NLO materials have said by many workers in the field to have several design advantages.² The area of polymeric NLO materials within itself has several design strategies. The NLO-phore can be incorporated as side-chain³ or incorporated into a heavily cross-linked polymer matrix.⁴ A very attractive approach to polymeric NLO materials is the incorporation of the NLO-phore directly in the polymer backbone. Hall and coworkers⁵ prepared the first NLO polymer of this type and shortly thereafter Lindsay and coworkers prepared related NLO main chain polymers (see below).⁶



University of Arizona, Hall & coworkers



NWC Chemistry Division, Lindsay & coworkers

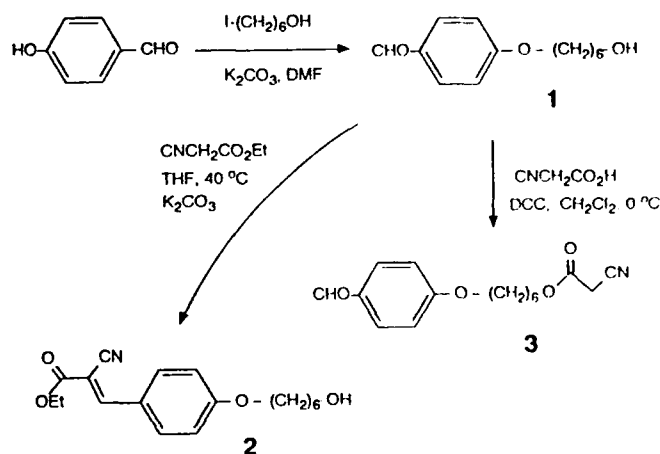
A variation to the main chain NLO-phore approach was recently reported by Lindsay and coworkers.⁶ In this strategy the polymer backbone is folded into an accordion shape with the donor and acceptor groups fixed at alternating apex of the accordion. In the design of polymeric NLO materials the key to success lies in obtaining materials with a high degree of alignment and the ability to retain that oriented state over long periods of time at elevated temperatures.

In our efforts to synthesize organometallic NLO polymers we discovered that we could prepare linear and accordion main-chain organometallic NLO polymers by employing the very mild and efficient Knoevenagel reaction as a polycondensation technique. In this paper we present our results on the use of the Knoevenagel polycondensation technique for the synthesis of polymers containing organic NLO-phores. The approach is useful for the preparation of both linear and accordion main-chain NLO polymers.

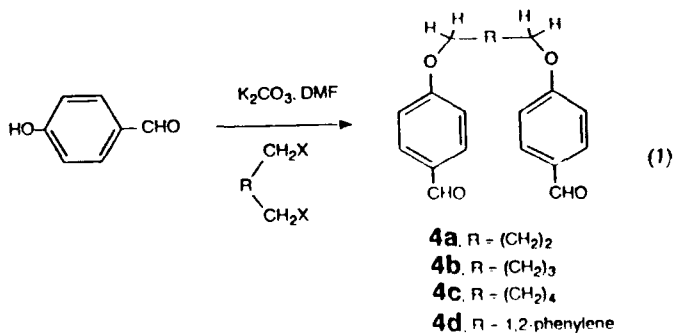
Results & Discussion

Monomer Synthesis. Treatment of *p*-hydroxybenzaldehyde with 6-iodohexanol in the presence of potassium carbonate afforded compound 1 in excellent yield. The condensation of 1 with ethyl cyanoacetate was carried out employing K_2CO_3 in THF solution. Compound 1 was reacted with cyanoacetic acid and the coupling reagent, DCC, to afford in very high yield monomer 3 (Scheme 1). The dicyclohexylurea produced in the synthesis of 3 is removed by filtration and then flash column chromatography on silica gel. Compound 3 is recrystallized from chloroform and hexanes to afford analytical pure monomer. In the pure state monomer 3 is found to be stable indefinitely when stored at $-25^\circ C$.

Scheme 1

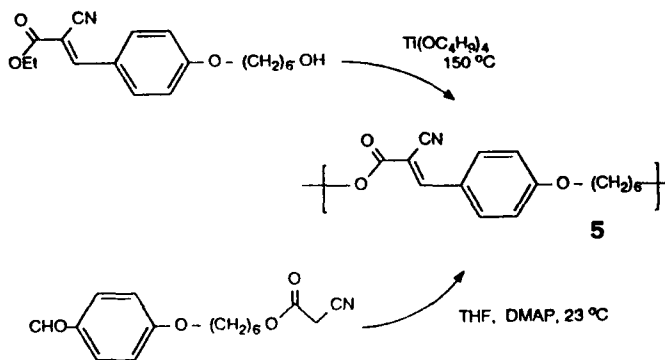


The *bis*(carboxaldehyde) comonomers, 4a-d, were prepared treatment of the α,ω -diiodoalkanes and 1,2-*bis*(chloromethyl)benzene with *p*-hydroxybenzaldehyde and potassium carbonate in DMF (eq 1). In each case the comonomers were isolated as light yellow or pink microcrystalline solids. Although some of these *bis*(carboxaldehyde) comonomers have been prepared previously, we find the use of potassium carbonate in DMF a safe alternative to sodium hydride, sodium metal, or alcoholic potassium hydroxide. Dalton and coworkers⁷ have recently reported the synthesis of 4b using K_2CO_3 /THF/KI and 1,5-dibromopentane with comparable success.



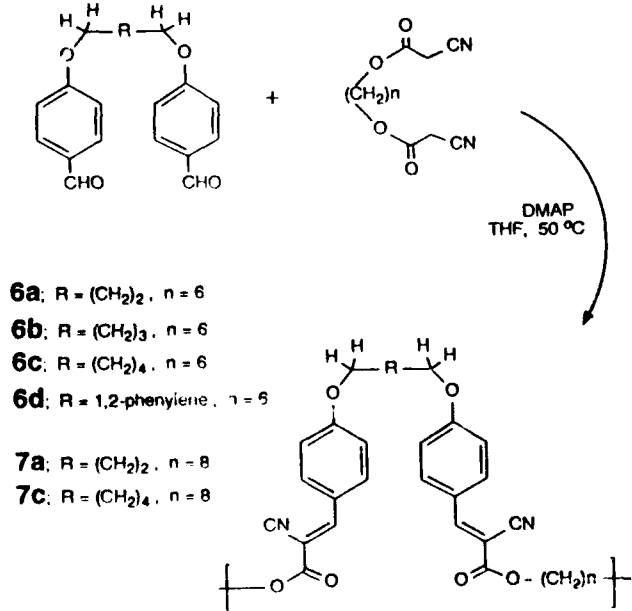
Polymer Synthesis and Characterization. Polymerization of monomers 2 and 3 were carried out employing standard transesterification and Knoevenagel reaction conditions, respectively (Scheme 2). Since both polymerization reactions yield the same polymer, 5, it is viewed as an opportunity to contrast the two techniques. The transesterification polycondensation of monomer 2 afforded somewhat lower molecular weight polymer than the Knoevenagel polycondensation. Similar results are obtained when using $(\text{Bu})_2\text{Sn}(\text{laurate})_2$ as the Lewis acid catalyst. Our results illustrate that fairly high molecular weight homopolymer can be obtained and exhibit good solubility in common organic solvents.

Scheme 2



The polymerization of 3 using DMAP proceeds smoothly at ambient temperature to afford a polymer with an average molecular weight of 32,000. The remarkably mild reaction conditions for the Knoevenagel polycondensation technique are the most outstanding feature when contrasting the two polymerization techniques. The excellent solubility of 5 in most organic solvents (up to ~10% by weight) appears to be a consequence of the mild reaction conditions.

Scheme 3



The Knoevenagel polycondensation technique has been applied to the copolymerization of monomers 4 with bis(cyanoacetate) monomers (Scheme 3). The accordion copolymers are prepared in high yield and obtained in analytical pure form after precipitation from hexanes. The polymers are soluble in organic solvents.

Concluding Remarks

The Knoevenagel polymerization technique should prove quite versatile because of the very mild reaction conditions and the availability of suitable monomers. We have presented the synthesis of both linear and accordion main-chain NLO polymers using the Knoevenagel polycondensation technique. Future work in our laboratory will focus on extending the scope of this reaction to include more functional elaborate organic and organometallic monomers.

Experimental Section

Preparation of $[\text{=CHC}(\text{H}_2\text{O}(\text{CH}_2)_6\text{O}_2\text{C}(\text{CN})\text{C=}]_n$ (5). A Schlenk flask was charged with 3 (0.50 g, 1.7 mmol), DMAP (0.42 g, 3.5 mmol), THF (10 mL) and then allowed to react with stirring at ambient temperature for 4 h. The solvents were evaporated under reduced pressure and the crude product was recrystallized from CHCl_3 /pentane (1/5, v/v) to afford 5 as a yellow solid (0.47 g, 77%). ^1H NMR (CDCl_3) δ 8.15 (s, 1 H, $=\text{CH}$), 7.98 (d, $J = 9.0$, 2 H, Ar), 6.98 (d, $J = 9.0$, 2 H, Ar), 4.32 (t, $J = 6.5$, 2 H, CH_2OAr), 4.06 (t, $J = 6.4$, 2 H, $\text{CH}_2\text{O}_2\text{C}$), 1.86-1.53 (m, 8 H, CH_2 's); ^{13}C NMR (CDCl_3) δ 163.4 (CO_2), 154.4 (Ar C), 134.4 (Ar CH), 124.2 ($=\text{C}(\text{CN})\text{CO}_2$), 117.0 ($=\text{CHAr}$), 115.9 (Ar CH), 114 (CN), 68.2 (CH_2O), 66.2 ($\text{CH}_2\text{O}_2\text{C}$), 28.9, 28.4, 26.2 (CH_2 's). Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{O}_3\text{N}$: C, 70.83; H, 6.32%. Found: C, 70.68; H, 6.34%.

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- Full experimental details will be published elsewhere.