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Organic Main-Chain NLO Polymers. 1. Copolymerization of *Bis*(arylcarboxaldehyde) and *Bis*(cyanoacetate) Monomers Via the Knoevenagel Condensation.

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13. ABSTRACT (Maximum 200 words)

Two monomers, 4-[$CO_2Et(CN)C{=}CH]C_6H_4O(CH_2)_6OH$ (**2**) and 4-$(CHO)C_6H_4O$-$(CH_2)_6O_2CCH_2CN$ (**3**), both containing NLO-phores, were prepared and polymerized by different methods. The Knoevenagel polycondensation technique provided polymers of good molecular weight and tractable in organic solvents. A series of *bis*(carboxaldehyde) comonomers were prepared in the study, $[4\text{-}(CHO)C_6H_4]_2R$ {**4a**, R= $(CH_2)_4$; **4b**, R= $(CH_2)_5$; **4c**, R= $(CH_2)_6$; **4d**, R= 1,2-$(CH_2)_2C_6H_4$}, and copolymerized with $CNCH_2CO_2(CH_2)_6O_2CCH_2CN$ to afford new series of accordion polymers (**6**) which contain NLO-phores. The copolymers were obtained with molecular weights (M_n) in the range of 3100 to 30,100 and λ_{max} of ~346 nm. We did not observe T_g's for the copolymers above 10 °C, only T_m's in the range of 123 to 200 °C.

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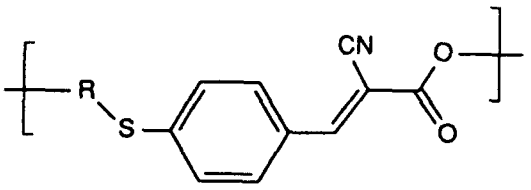
Abstract. Two monomers, 4-[$CO_2Et(CN)C{=}CH]C_6H_4O(CH_2)_6OH$ (**2**) and 4-$(CHO)C_6H_4O(CH_2)_6O_2CCH_2CN$ (**3**), both containing NLO-phores, were prepared and polymerized by different methods. Monomer **2** was polymerized under transesterification conditions [$Ti(OC_4H_9)_4$, 150 °C] and **3** through a Knoevenagel polycondensation [4-(dimethylamino)pyridine (DMAP), THF, ~23 °C]. The Knoevenagel polycondensation technique provided polymers of good molecular weight and tractable in organic solvents. A series of *bis*(carboxaldehyde) comonomers were prepared in the study, $[4\text{-}(CHO)C_6H_4]_2R$ {**4a**, R= $(CH_2)_4$; **4b**, R= $(CH_2)_5$; **4c**, R= $(CH_2)_6$; **4d**, R= 1,2-$(CH_2)_2C_6H_4$}, and copolymerized with $CNCH_2CO_2(CH_2)_6O_2CCH_2CN$ to afford new series of accordion polymers (**6**) which contain NLO-phores. In the case of polymers **6a** and **6c** we found insolubility limited our ability to characterize the materials. Copolymerization of **4a** and **4c** with $CNCH_2CO_2(CH_2)_8O_2CCH_2CN$ afforded copolymers **7a** and **7c**, respectively, which did exhibit good solubility (~10 % by weight) in most organic solvents. The copolymers were obtained with molecular weights (M_n) in the range of 3100 to 30,100 and λ_{max} of ~346 nm. We did not observe T_g's for the copolymers using DSC analysis, only T_m's in the range of 123 to 200 °C.

[End of Abstract]

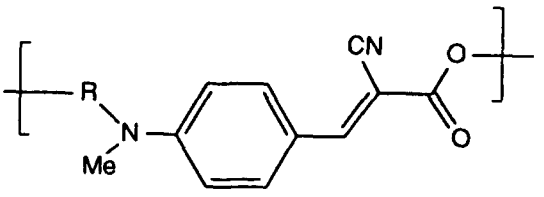
Introduction

The design and synthesis of new NLO materials for SHG applications can be accomplished through a variety of strategies.[1] Polymeric NLO materials are said by many workers in the field to have several design advantages.[2] The area of polymeric NLO materials within itself possesses numerous design strategies. The NLO-phore can be incorporated as side-chain[3] 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 coworkers[5] prepared the first NLO polymer of this type and shortly thereafter Lindsay and coworkers prepared related NLO main chain polymers (see below).[6] Although the second harmonic generation (SHG) measurements for the materials prepared by Lindsay and coworkers were not spectacular, they showed a great deal of promise for the main chain NLO-phore in that the materials retained alignment and activity for long periods of time. Theory indicates that if alignment of polymer chains containing a series of repeating units can be acheived there will be a significant enhancement in the NLO properties.

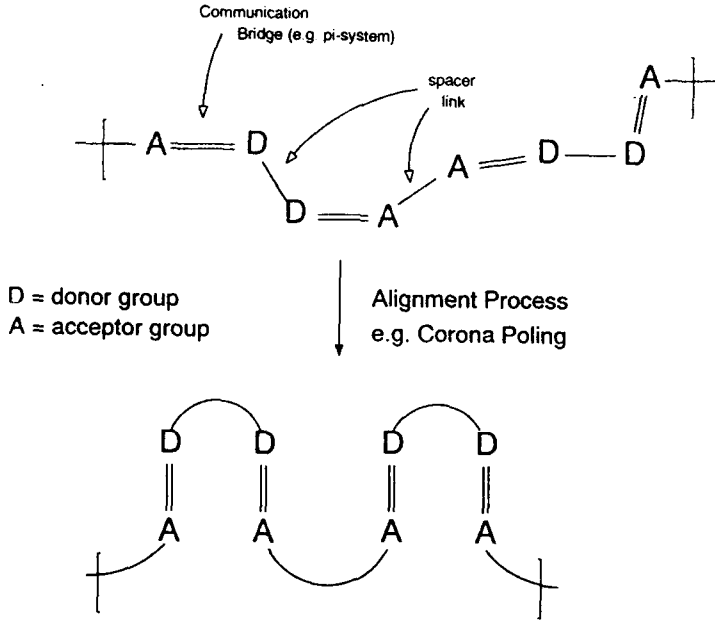


University of Arizona, Hall & coworkers



NWC Chemistry Division, Lindsay & coworkers

A variation to the main chain NLO-phore approach was recently reported by Lindsay and coworkers.[6b] 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 (see below). In the alignment process (*i.e.* corona poling) the need for complete reorientation of a polymer chain is eliminated. 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.

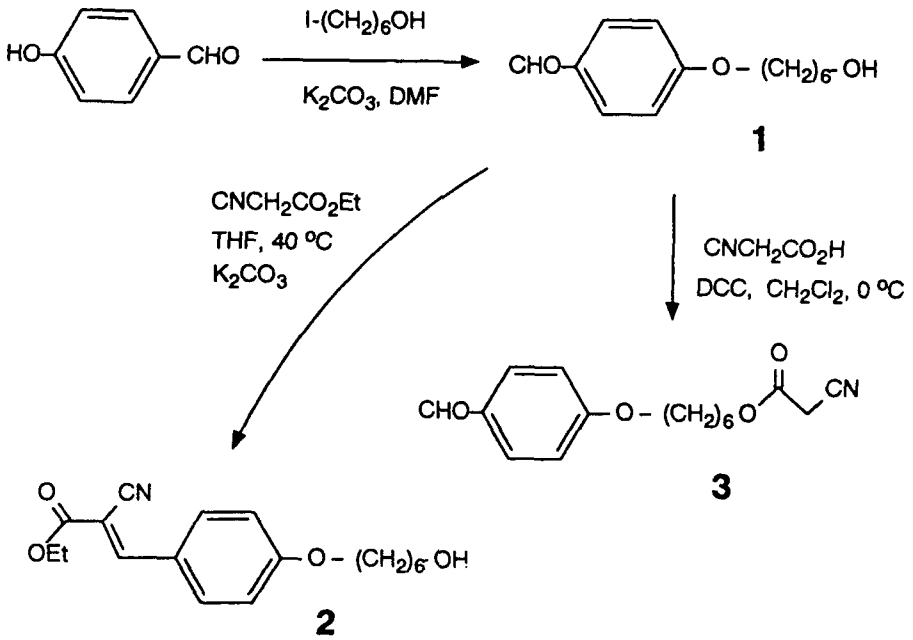


In our efforts to synthesize organometallic NLO polymers we discovered that we could prepare linear and accordion main-chain organometallic NLO polymers[7] by employing the very mild and efficient Knoevenagel reaction[8] as a polycondensation technique. In this paper we present our results on the use 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.

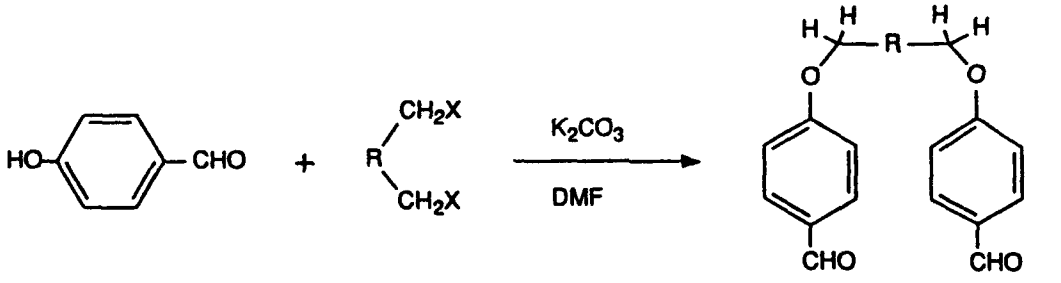
Results & Discussion

Monomer Synthesis. Treatment of *p*-hydroxybenzaldehyde with 6-iodohexanol in the presence of potassium carbonate afforded compound **1** in excellent yield.[9] The condensation of **1** with ethyl cyanoacetate was carried out employing K_2CO_3 in THF solution. Using a procedure related to that reported by Hall and coworkers[5d] monomer **2** is prepared using 4-(dimethylamino)pyridine (DMAP) as the base in the Knoevenagel condensation (Scheme 1). Compound **1** was reacted with cyanoacetic acid and the coupling reagent, dicyclohexylcarbodiimide (DCC), to afford in very high yield monomer **3** (Scheme 1).[10] The dicylohexylurea 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 °C.

Scheme 1



The *bis*(carboxaldehyde) comonomers, **4a-d**, were prepared treatment of the α,*omega*-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,[11] we find the use of potassium carbonate in DMF a safe alternative to sodium hydride, sodium metal, or alcoholic potassium hydroxide. Dalton and coworkers have recently reported the synthesis of **4b** using K_2CO_3/THF/KI and 1,5-dibromopentane with comparable success.[12]



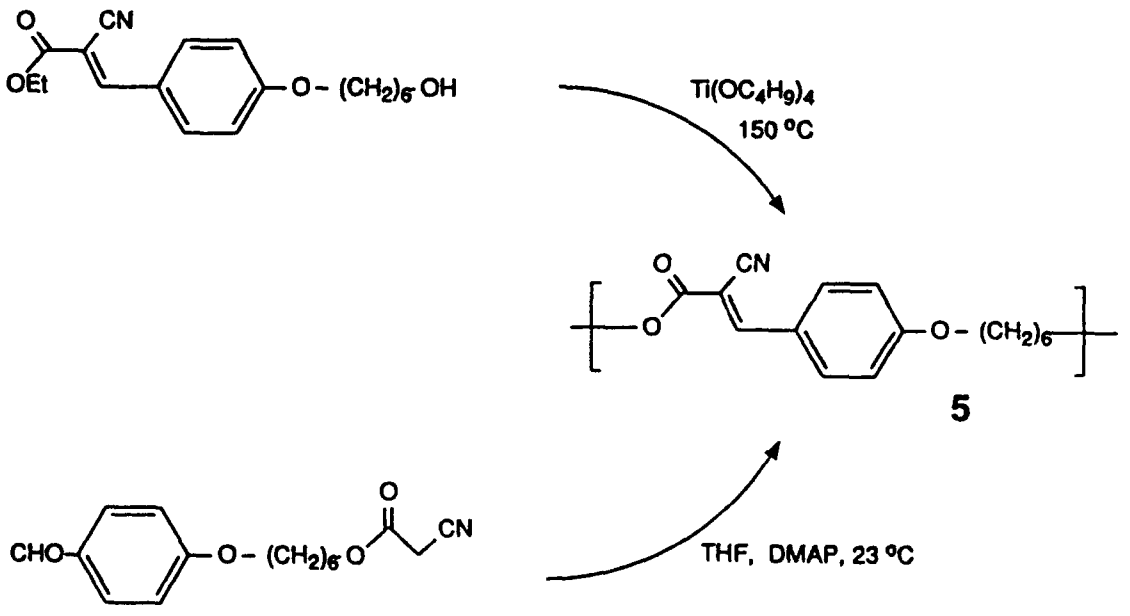
(1)

4a, R = $(CH_2)_2$
4b, R = $(CH_2)_3$
4c, R = $(CH_2)_4$
4d, R = 1,2-phenylene

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 (Table 1). Similar results are obtained when using $(Bu)_2Sn(luarate)_2$ as the Lewis acid catalyst. However, we did not exhaustively try and optimize the transesterification polymerization conditions so it may be possible to obtain higher molecular weight polymer. The conditions we employed were very similar to those used by both the groups of Hall and Lindsay. The highest average molecular weights (M_n = ~60,000) are obtained by Hall and coworkers when a comonomer (*e.g.* methyl 12-hydroxydodecanoate) is utilized.[5d] Our results illustrate that farily high molecular weight homopolymer can be obtained and exhibit good solubility in common organic solvents.

Scheme 2



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Insert Table 1 here

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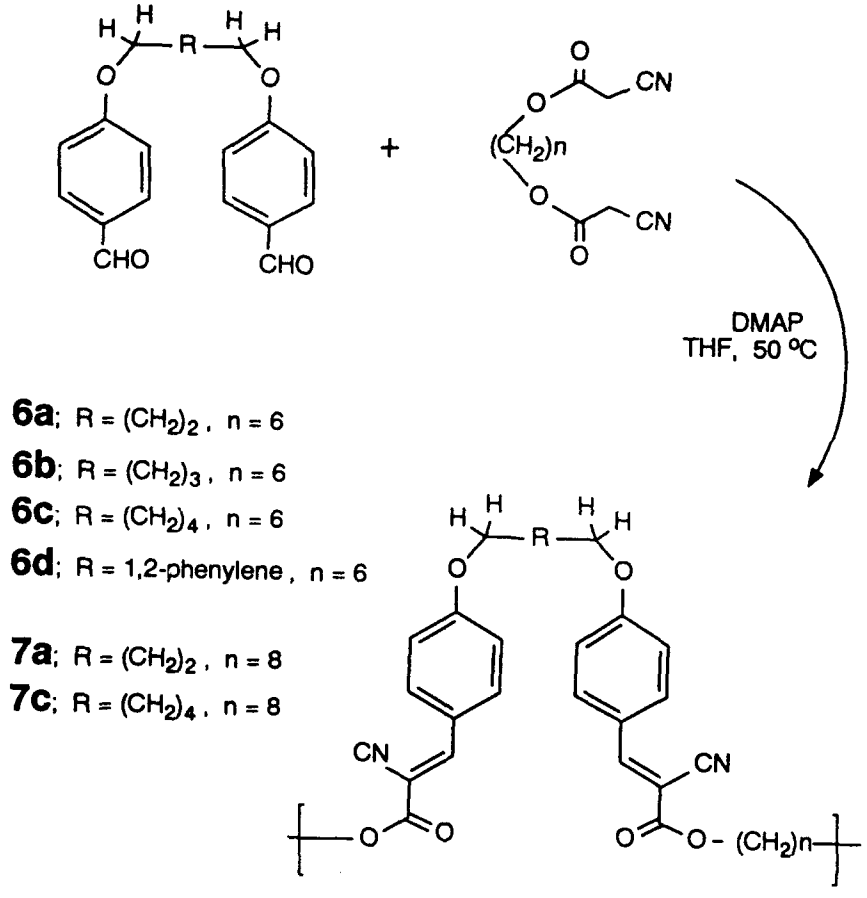
The polymerization of **3** using DMAP proceeds smoothly at ambient temperature and in a relatively short time frame. The stereochemistry about the alkene is assigned the *E*-geometry based on comparison of the NMR chemical shift of the vinyl proton to related systems.[5] Other mild bases such as potassium carbonate can be utilized with similar success. The remarkably mild reaction conditions for the Knoevenagel polycondensation technique are the most outstanding feature when contrasting the two polymerization techniques. Mild reaction conditions are harmonious with excellent functional group tolerance and thus eliminated the problem of depolymerization due to excessive temperatures. The excellent solubility of **5** in most organic solvents (~10% by weight) is most likely a consequence of the mild reaction conditions.

The Knoevenagel polycondensation technique has been applied to the copolymerization of monomers **4** with *bis*(cyanoacetate) monomers (Scheme 3). The latter monomers are easily prepared from treatment of the appropriate diol with excess ethyl cyanoacetate and a transesterification catalyst.[13] The accordion copolymers are prepared in high yield and obtained in analytical pure form after precipitation from hexanes. In the case of **6a** and **6c** the polymeric products are insoluble and precipitate as the polymerization reactions proceed. Utilization of the *bis*(cyanoacetate) obtained from 1,8-octandiol afforded copolymers **7a** and **7c**. These latter polymers are soluble in organic

solvents, but of modest molecular weight (see Table 1). We observe a single gemometric isomer for the copolymers, and as above, is assigned the *E*-isomer.

Scheme 3



Thermal analysis of the polymers is carried out under a nitrogen atmosphere. Differential scanning calorimetry (DSC) analysis of the polymers displays only T_m's with no sign of glass transitions (Figure 1). The scanning rate was 10.0 °C and the results

were obtained from heating scans. After finishing a DSC scan the rapid cooling of the sample would diminish crystallinity in the sample. No apparent glass transitions are observed concomitant with the loss of crystallinity. However, if slow cooling of the sample was carried out (5 °C/min), recrystallization occurred.

Thermal gravimetric analysis (TGA) of the polymers showed good thermal stability to 300+ °C under an atmosphere of nitrogen. The break points for thermal decomposition occurred in the vicinity of 370 °C for for both the linear and accordion type polymers (see Table 1).

****

Insert Figure 1 here

****

Conluding Remarks

This work demonstrates that polymers containing NLO-phores are readily available through a Knoevenagel polycondensation technique. The polymerization technique should prove quite versatile because of the very mild reaction conditions and the availibility 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

Methods. All manipulations of compounds and solvents were carried out by using standard Schlenk techniques. Solvents were degassed and purified by distillation under nitrogen from standard drying agents. Spectroscopic measurements utilized the following instrumentation: ^{1}H NMR, Varian XL 300; ^{13}C NMR, Varian XL 300 (at 75.4 MHz). NMR chemical shifts are reported in δ versus Me_4Si in ^{1}H NMR and assigning the $CDCl_3$ resonance at 77.00 ppm in ^{13}C spectra. Infrared, Perkin Elmer 1750 FT-IR; UV-Vis, hp-8452A. The DCC, ethyl cyanoacetate (98% purity), cyanoacetic acid, $Ti(OC_4H_9)_4$, p-hydroxybenzaldehyde, 6-chlorohexanol, 1,4-diiodobutane, 1,5-diiodopentane, 1,6-diiodohexane, 1,8-octanediol, and 1,6-hexanediol were purchased from Aldrich Chemical Co. and used as received. The K_2CO_3 (granular, AR grade, Mallinckrodt) was purchased from Baxter. The *bis*(cyanoacetates), $CNCH_2CO_2(CH_2)_6O_2CCH_2CN$ and $CNCH_2CO_2(CH_2)_8O_2CCH_2CN$, were prepared in similar manner as reported.[12] Thermal analysis of the polymers was performed using a Perkin Elmer TGA7 and DSC7 station. GPC data was collected on a Varian 5000 HPLC employing a PL size-exclusion column (300 x 7.5 mm, 5μ particle size) using the mixed-pore size. Molecular weight data is referenced relative to polystyrene standards. Elemental analyses were performed at Atlantic Microlab Inc, Norcross, Geogria.

Preparation of {4-[$CO_2Et(CN)C=CH$]$C_6H_4O(CH_2)_6OH$} (2). A Schlenk flask was charged with 4-$CHOC_6H_4O(CH_2)_6OH$ (0.5 g, 2.3 mmol), $CNCH_2CO_2Et$ (0.28 g, 2.5 mmol), K_2CO_3 (0.93 g, 6.8 mmol), THF (15 mL), and then heated to reflux for 4 h. The mixture was allowed to cool and then diluted with water. The mixture was extracted with diethyl

ether (2 x 150 mL), the organic layers were then combined, washed with brine, and finally dried over K_2CO_3. The solvents were removed under reduced pressure and the crude product was crystallized from EtOAc/hexanes (1/2, v/v) to afford pure **2** as a yellow crystalline solid (0.71 g, 84% mp 94-95°C). ^{1}H NMR ($CDCl_3$) δ 8.15 (s, 1 H, C<u>H</u>O), 7.97 (d, *J* = 8.6 Hz, 2 H, Ar), 6.94 (d, *J* = 8.6 Hz, 2 H, Ar), 4.33 (q, *J* = 7.3 Hz, 2 H, C<u>H</u>$_2$O$_2$C), 4.01 (t, *J* = 6.3 Hz, 2 H, C<u>H</u>$_2$OAr), 3.65 (t, *J* = 6.6 Hz, 2 H, C<u>H</u>$_2$OH), 1.82-1.34 (m, 8 H, C<u>H</u>$_2$'s); ^{13}C NMR ($CDCl_3$) δ 163.4 (CO_2), 154.4 (=<u>C</u>(CN)), 133.7 (Ar CH), 124.2 (=<u>C</u>HAr), 116.0 9 (<u>C</u>N), 115.2 (Ar CH), 68.3 (<u>C</u>H$_2$OAr), 66.0 (<u>C</u>H$_2$O$_2$C), 62.8 (<u>C</u>H$_2$OH), 32.6, 29.0, 25.8, 25.5 (CH_2's), 14.2 (<u>C</u>H$_3$); IR (CH_2Cl_2) $\nu_{C=O}$ 1719.0 cm^{-1}. Anal. Calcd for $C_{18}H_{23}O_4N$: C, 68.12; H, 7.30%. Found C, 68.20; H, 7.29%.

Preparation of {4-(CHO)C$_6$H$_4$O(CH$_2$)$_6$O$_2$CCH$_2$CN} (3). A Schlenk flask was charged with 4-$CHOC_6H_4O(CH_2)_6OH$ (5.00 g, 22.5 mmol), $CNCH_2CO_2H$ (1.92 g, 22.5 mmol), DCC (4.65 g, 22.5 mmol), CH_2Cl_2 (20 mL), and then allowed to react at 0 °C with stirring for 2 h. The mixture was filtered through a pad (4 x 7 cm) of deactivated silica gel and the pad washed with chloroform/methanol (200 mL, 50/1, v/v). The solvents were removed under reduced pressure and the crude product recrystallized from $CHCl_3$/hexanes (1/5, v/v) to afford pure **3** as a yellow crystalline solid (6.65 g, 72%, mp 56-57 °C). ^{1}H NMR ($CDCl_3$) δ 9.86 (s, 1 H, C<u>H</u>O), 7.81 (d, *J* = 7.2, 2 H, Ar), 6.97 (d, *J* = 7.2, 2 H, Ar), 4.21 (t, *J* = 6.6, 2 H, C<u>H</u>$_2$OAr), 4.03 (t, *J* = 6.4, 2 H, C<u>H</u>$_2$CO$_2$) 3.45 (s, 2 H, CH_2CN), 1.84-1.44 (m, 8 H, CH_2's); ^{13}C NMR ($CDCl_3$) δ 190.8 (<u>C</u>HO), 164.1 (CO_2), 162.9 (Ar C), 131.9 (Ar CH), 129.8 (Ar C), 114.7 (Ar CH), 113.0 (<u>C</u>N), 68.1 (<u>C</u>H$_2$O), 66.8 (<u>C</u>H$_2$CN), 28.8, 28.2, 25.5, 24.7 (CH_2's); IR (CH_2Cl_2) $\nu_{C=O}$ 1751 cm^{-1}. Anal. Calcd for

$C_{16}H_{19}NO_4$: C, 66.43; H, 6.62%. Found: C, 66.30; H, 6.65%.

Preparation of {4-CHOC$_6$H$_4$OCH$_2$CH$_2$}$_2$ (4a). A Schlenk flask was charged with *p*-hydroxybenzaldehyde (4.98 g, 40.3 mmol), diiodobutane (5.00 g, 16.0 mmol), K_2CO_3 (5.00 g, 36.2 mmol), DMF (20 mL), and then heated at reflux for 12 h. The mixture was allowed to cool and then diluted with water. The mixture was extracted with chloroform (2 x 150 mL), the organic layers combined, washed with brine, and then dried over K_2CO_3. The solvents were removed under reduced pressure and the crude product was purified by recrystallization from $CHCl_3$/hexanes (1/5, v/v) to afford pure **4a** as a light-purple crystalline solid suggesting the presence of traces of iodine (4.79 g, 72%, mp 99-100 °C, lit.[11] mp 103-104 °C). ^{13}C NMR ($CDCl_3$) δ 190.8 (<u>C</u>HO), 163.9 (Ar C), 132.1 (Ar CH), 130.0 (Ar C), 114.8 (Ar CH), 67.7 (<u>C</u>H$_2$O), 25.8 (CH$_2$); IR (CH_2Cl_2) $\nu_{C=O}$ 1689 cm^{-1}.

Preparation of {4-CHOC$_6$H$_4$OCH$_2$CH$_2$}$_2$CH$_2$ (4b). A Schlenk flask was charged with *p*-hydroxybenzaldehyde (2.83 g, 23.2 mmol), diiodopentane (3.00 g, 9.3 mmol), K_2CO_3 (3.00 g, 21.7 mmol), DMF (15 mL), and then heated at reflux for 12 h. The mixture was allowed to cool and then diluted with water. The mixture was extracted with chloroform (2 x 150 mL), the organic layers were then combined, washed with brine, and finally dried over K_2CO_3. The solvents were removed under reduced pressure and the crude product was purified by recrystallization from $CHCl_3$/ hexanes (1/5, v/v) to afford pure **4b** as a light-pink crystalline solid suggesting the presence of traces of iodine (1.67 g, 58%, mp 81-82 °C). ^{1}H NMR ($CDCl_3$) δ 9.88 (s, 2 H, C<u>H</u>O), 7.83 (d, *J* = 8.8 Hz, 4 H, Ar), 6.99 (d, *J* = 8.8 Hz, 4 H, Ar), 4.06 (t, *J* = 6.4 Hz, 4 H, CH$_2$O), 1.57-1.87 (m, 6 H,

CH_2's); ^{13}C NMR ($CDCl_3$) δ 190.8 (CHO), 163.5 (Ar C), 132.0 (Ar CH), 129.9 (Ar C), 114.7 (Ar CH), 68.1 (CH_2O), 28.8, 22.7 (CH_2's); IR (CH_2Cl_2) $\nu_{C=O}$ 1688 cm^{-1}. Anal. Calcd for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45%. Found: C, 72.89; H, 6.46%.

Preparation of {4-$CHOC_6H_4OCH_2CH_2CH_2$}$_2$ (4c). A Schlenk flask was charged with *p*-hydroxybenzaldehyde (2.71 g, 22.2 mmol), diiodohexane (3.00 g, 8.9 mmol), K_2CO_3 (3.00 g, 21.7 mmol), DMF (15 mL), and then heated at reflux for 12 h. The mixture was allowed to cool and then diluted with water (100 mL). The mixture was extracted with chloroform (2 x 150 mL) and the organic layers were combined, washed with brine (50 mL), and then dried over K_2CO_3. The solvents were removed under reduced pressure and the crude product crystallized from $CHCl_3$/ hexanes (1/5, v/v) to afford pure **4c** as an off-white crystalline solid (1.94 g, 67%, mp 105-106 °C, lit.[11] mp 106-10 °C). ^1H NMR ($CDCl_3$) δ 9.89 (s, 2 H, CHO), 7.83 (d, *J* = 8.6 Hz, 4 H, Ar), 6.99 (d, *J* = 8.6 Hz, 4 H, Ar) 4.09 (t, *J* = 6.3 Hz, 4 H, CH_2O), 1.91 (m, 4 H, CH_2's), 1.68 (m, 4 H, CH_2's); ^{13}C NMR ($CDCl_3$) δ 190.8 (CHO), 164.0 (Ar C), 132.0 (Ar CH), 130.0 (Ar C) 114.7 (Ar CH), 68.2 (CH_2O), 28.9, 25.8 (CH_2's); IR (CH_2Cl_2) $\nu_{C=O}$ 1688 cm^{-1}.

Preparation of {1,2-(4-$CHOC_6H_4OCH_2$)$_2$$C_6H_4$} (4d). A Schlenk flask was charged with *p*-hydroxybenzaldehyde (15.40 g, 125.8 mmol), 1,2-*bis*(chloromethyl)benzene (10.0 g, 57.2 mmol), K_2CO_3 (15.00 g, 108.5 mmol), DMF (30 mL), and then heated at reflux for 24 h. The mixture was allowed to cool, diluted with water, and then extracted with chloroform (2 x 150 mL). The organic layers were combined, washed with water (2 x 100

mL), brine (100 mL), and then dried over K_2CO_3. The solvents were removed under reduced pressure and the crude product was purified by passing it through a column of alumina (4 x 30 cm) and eluting with a mixture of EtOAc/Hexanes (300 mL, 80/20, v/v). Evaporation of the solvents under reduced pressure afforded pure **4d** as a white microcrystalline solid (15.7 g, 80%, mp 140-141 °C). ^{1}H NMR ($CDCl_3$) δ 9.87 (s, 2 H, CHO), 7.82 (d, *J* = 4.8 Hz, 4 H, Ar), 7.40-7.50 (m, 4 H, Ar), 7.03 (d, *J* = 4.8 Hz, 4 H, Ar), 5.25 (s, 4 H, CH_2O); ^{13}C NMR ($CDCl_3$) δ 190.6 (CHO), 163.5 (Ar C), 134.3 (Ar C), 132.0 (Ar CH), 130.0 (Ar C), 129.3, 129.0 (Ar CH's), 115.0 (Ar C), 68.3 (CH_2O); IR (CH_2Cl_2) $\nu_{C=O}$ 1695 cm^{-1} Anal. Calcd for $C_{22}H_{18}O_4$: C, 76.29; H, 5.24%. Found: C, 75.65; H, 5.27%.

Preparation of [=CHC$_6$H$_4$O(CH$_2$)$_6$O$_2$C(CN)C=]$_n$ (5). A Schlenk flask was charged with **3** (0.50 g, 1.7 mmol), DMAP (0.42 g, 3.5 mmol), THF (10mL) and the contents 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%). ^{1}H NMR ($CDCl_3$) δ 8.15 (s, 1 H, =C<u>H</u>), 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, C<u>H</u>$_2$OAr), 4.06 (t, *J* = 6.4, 2 H, C<u>H</u>$_2$O$_2$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 (=<u>C</u>(CN)CO_2), 117.0 (=CHAr), 115.9 (Ar CH), 114 (<u>C</u>N), 68.2 (<u>C</u>H$_2$O), 66.2 (<u>C</u>H$_2$O$_2$C), 28.9, 28.4, 26.2 (CH_2's). Anal. Calcd for $C_{16}H_{17}O_3N$: C, 70.83; H, 6.32%. Found: C, 70.68; H, 6.34%.

Preparation of [=CHC$_6$H$_4$O(CH2)$_5$OC$_6$H$_4$[CH=C(CN)CO$_2$(CH$_2$)$_6$O$_2$C(CN)C=]]$_n$ (6b)

A Schlenk tube was charged with **4b** (0.2 g, 0.6 mmol), $CNCH_2CO_2(CH_2)_6O_2CCH_2CN$

(0.16 g, 0.6 mmol), DMAP (0.24 g, 1.92 mmol), THF (10 mL) and the contents allowed to react at room temp. with stirring for 4 h. The reaction was stopped and the solvent was evaporated under reduced pressure and the crude product was purified by recrystallization from $CHCl_3$/pentane (1/5, v/v) to afford pure **6b** as a yellow solid (0.28 g, 85%). ^1H NMR ($CDCl_3$) δ 8.16 (s, 2 H, =CH), 7.98 (d, J = 8.6 Hz, 2 H, Ar), 6.97 (d, J = 8.6 Hz, 2 H, Ar), 4.32 (t, J = 6.2 Hz, 4 H, CH_2OAr), 4.08 (t, J = 7.8 Hz, 4 H, CH_2O_2C), 1.93-1.49 (m, 14 H, CH_2's); ^{13}C NMR ($CDCl_3$) δ 163.2 (Ar C), 161.9 (CO_2), 154.4 (=C(CN)CO_2), 133.7 (Ar CH), 124.4 (=CHAr), 115.2 (Ar CH), 68.1 (CH_2O_2C), 66.3 (CH_2OAr), 28.8, 28.4, 25.5, (CH_2's). Anal. Calcd for $[C_{31}H_{32}N_2O_6]_{53}$: C, 70.40; H, 6.06%. Found: C, 69.77; H, 6.20%.

Preparation of [1-{=CHC$_6$H$_4$OCH$_2$}-2-{CH=C(CN)CO$_2$(CH$_2$)$_6$O$_2$C(CN)C=}-C$_6$H$_4$OCH$_2$}C$_6$H$_4$]$_n$ (6d). A Schlenk tube was charged with **4d** (0.20 g, 0.6 mmol), $CNCH_2CO_2(CH_2)_6O_2CCH_2CN$ (0.15 g, 0.6 mmol), DMAP (0.21 g, 0.70 mmol), THF (10 mL) and the contents allowed to react at 50 °C with stirring for 4 h. The reaction was stopped and the solvent was evaporated under reduced pressure. The crude product was recrystallized from $CHCl_3$/pentane (1/5, v/v) to afford pure **6d** as a light yellow solid (0.26 g, 81%). ^1H NMR ($CDCl_3$) δ 8.17 (s, 2 H, =CH), 8.0 (d, J = 8.4 Hz, 2 H, Ar), 7.52 (m, 2 H, Ar), 7.44 (m, 2 H, Ar), 5.27 (s, 4 H, CH_2OAr), 4.32 (t, J = 6.0 Hz, 4 H, CH_2O_2C), 1.81-1.52 (m, 8 H, CH_2's); ^{13}C NMR ($CDCl_3$) δ 163.0 (Ar C), 162.5 (CO_2), 154.2 (=CCNCO_2), 134.2 (Ar C), 133.7 (Ar CH), 129.4 (Ar C), 129.0 (Ar CH), 124.8 (=CHPh), 115.4 (Ar CH), 68.4 (CH_2OAr), 66.2 (CH_2O_2C), 28.4, 25.5 (CH_2's). Anal. Calcd for $[C_{34}H_{30}N_2O_6]_{25}$: C, 72.34; H, 5.33%. Found: C, 71.95; H, 5.60%.

Preparation of [=CHC$_6$H$_4$O(CH$_2$)$_6$OC$_6$H$_4$CH=C(CN)CO$_2$(CH$_2$)$_8$O$_2$C(CN)C=]$_n$ (7c) A Schlenk tube was charged with **4c** (0.20 g, 0.60 mmol), $CNCH_2CO_2(CH_2)_8O_2CCH_2CN$ (0.17 g, 0.6 mmol), DMAP (0.15 g, 1.2 mmol), THF (10 mL), and the contents allowed to react at ambient temperature for 8 h. The reaction was stopped and the solvent was evaporated under reduced pressure. The crude product was purified by recrystallization from $CHCl_3$/pentane (1/2, v/v) to afford **6c** as a white solid (0.27 g, 77%). ^{1}H NMR ($CDCl_3$) δ 8.16 (s, 2 H, =C<u>H</u>), 8.01 (d, *J* = 9.0 Hz, 2 H, Ar), 6.97 (d, *J* = 9.0 Hz, 2 H, Ar), 4.30 (t, *J* = 6.5 Hz, 4 H, C<u>H</u>$_2$OAr), 4.06 (t, *J* = 6.4 Hz, 4 H, C<u>H</u>$_2$O$_2$C), 1.86-1.40 (m, 20 H, CH_2's); ^{13}C NMR ($CDCl_3$), δ 163.2 (Ar C), 163.0 (CO_2), 154.2 (=<u>C</u>CNCO$_2$), 133.7 (Ar CH), 124.2 (=<u>C</u>HAr), 116.1 (CN), 115.2 (Ar CH), 68.1 (<u>C</u>H$_2$OPh), 66.3 (<u>C</u>H$_2$O$_2$C), 29.03, 28.9, 28.5, 25.8, 25.7 (<u>C</u>H$_2$'s). Anal. Calcd for $[C_{34}H_{38}N_2O_6]_{12}$: C, 71.09; H, 6.63%. Found: C, 70.92; H, 6.78%.

[=CHC$_6$H$_4$O(CH$_2$)$_4$OC$_6$H$_4$CH=C(CN)CO$_2$(CH$_2$)$_8$O$_2$C(CN)C=]$_n$ (7d) Polymer **7d** was prepared in 54% isolated yield using a procedure outlined for polymer **6b**. Spectroscopic and analytical data: ^{1}H NMR ($CDCl_3$) δ 8.19 (s, 2 H, =C<u>H</u>), 8.02 (d, *J* = 9.0 Hz, 4 H, Ar), 6.99 (d, *J* = 9.0 Hz, 4 H, Ar), 4.32 (t, *J* = 6.7 Hz, 4 H, C<u>H</u>$_2$OAr), 4.16 (br s, 4 H, C<u>H</u>$_2$CO$_2$), 2.06-1.39 (m, 16 H, C<u>H</u>$_2$'s); ^{13}C NMR ($CDCl_3$), δ 163.2 (Ar C), 163.1 (CO_2), 154.1 (=<u>C</u>(CN)), 133.7 (Ar CH), 124.1 (=<u>C</u>HAr), 116.0 (CN), 115.2 (Ar CH), 68.1 (<u>C</u>H$_2$OAr), 66.3 (<u>C</u>H$_2$O$_2$C), 29.0 28.9, 28.5, 25.8, 25.7 (<u>C</u>H$_2$'s).

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Table 1. Selected physical and spectroscopic data for polymers **4, 6b, 6d, 7a,** and **7c.**

Polymer	M_n	M_w	*UV-Vis* (CH_2Cl_2)	T_m (°C)	*TGA* (N_2, *break point*°C)
$[=CHC_6H_4O(CH_2)_6O_2C(CN)C=]_N$ (transesterification)	6800	14,100	λ_{max}= 346 nm ($\varepsilon = 3.1 \times 10^4$)	93, 104[b]	383[a]
$[=CHC_6H_4O(CH_2)_6O_2C(CN)C=]_N$ (Knoevenagel)	30,100	57,700	λ_{max}= 346 nm ($\varepsilon = 2.91 \times 10^4$)	123	376
Polymer 6b	26,200	47,600	λ_{max}= 346 nm ($\varepsilon = 5.44 \times 10^4$)	148	359
Polymer 6d	21,600	35,500	λ_{max}= 340 nm ($\varepsilon = 5.48 \times 10^4$)	73	
Polymer 7a	3100	6100	λ_{max}= 346 nm ($\varepsilon = 5.38 \times 10^3$)	192, 205[b]	
Polymer 7c	9800	16,600	λ_{max}= 346 nm ($\varepsilon = 2.48 \times 10^4$)	159, 182[b], 188[b]	

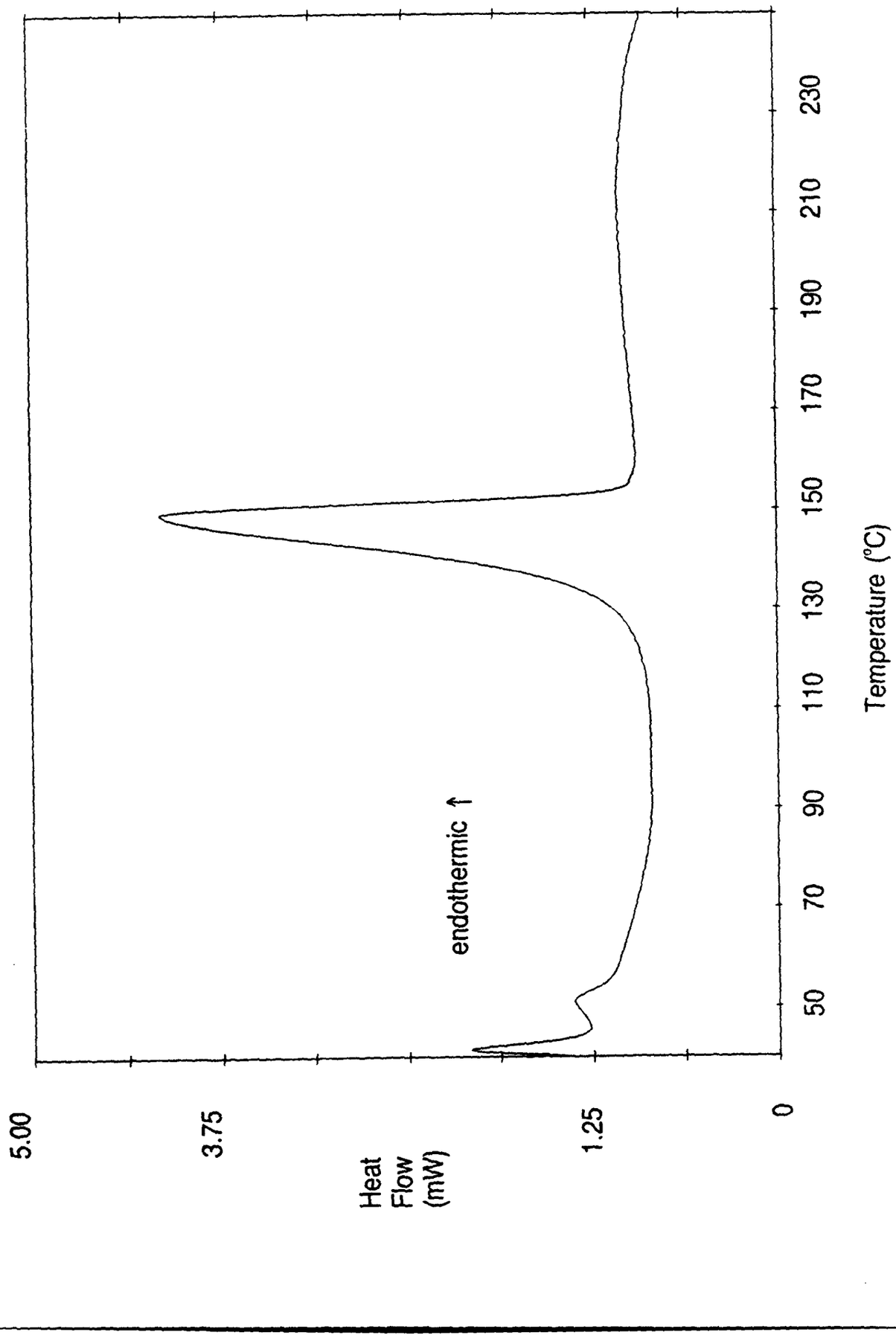
[a] under a nitrogen atmosphere, ramp rate of 10 °C/min. Break point is the temperature where a continuous and rapid weight loss began to occur.

[b] a minor endotherm possibly due to Liquid crystal behavior.

Captions for Figures

Figure 1. Differential scanning calorimeter plot for polymer **6b**. The analysis was carried out under an atmosphere of nitrogen and at a ramp rate of 10°C/min. This is the initial DSC scan of the material.

Figure 1


5.00
3.75
1.25
0
Heat Flow (mW)
endothermic ↑
50
70
90
110
130
150
170
190
210
230
Temperature (°C)