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Liquid crystal polymers containing macroheterocyclic ligands

8. Synthesis and characterization of poly{1-(2-methyl-4-(4′-carboxybenzo-15-crown-5)phenyl)ethynyl-4-(11-vinyloxyundecan-1-yloxy)benzene}

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SUMMARY

The synthesis and cationic polymerization of 1-[2-methyl-4-(4'-carboxybenzo-15-crown-5)phenyl]ethynyl-4-(11-vinyloxyundecan-1-yloxy)benzene (8) are described. Both 8 and poly(8) were characterized by a combination of thermal optical microscopy and differential scanning calorimetry. Both 8 and poly(8) display an enantiotropic nematic mesophase and side chain crystallization. The isotropization temperature of poly(8) is 19°C higher than that of 8.

INTRODUCTION

Liquid crystalline host-guest complexes of low molar mass[1-6] and polymer[7-14] systems containing macroheterocyclic ligands are of interest since they provide an approach to self assembled systems which combine selective recognition with external regulation.[2,14,15] We are investigating the molecular design of main chain[7] and side chain[8-13] liquid crystalline polymers containing macroheterocyclic ligands. Two polymer architectures were considered for the case of side chain liquid crystalline polymers. The first one contains the macroheterocyclic ligand within the structure of the mesogenic side group.[7-9,11,13] The second one contains the macroheterocyclic ligand within the structure of the polymer backbone.[10,12]

We are interested in the design of liquid crystalline polymer structures containing macroheterocyclic ligands which are hydrolytically stable and can be synthesized by a polymerization technique which can lead to well defined polymers. Previous research from our laboratory has demonstrated that various mesogenic vinyl ethers can be polymerized by living cationic polymerization.[9,10,12,17-19] The first goal of this paper is to describe the synthesis of a mesogenic vinyl ether which contains both a crown ether and a C≡C triple bond. The second goal of this paper is to provide preliminary results on its cationic polymerizability and on the mesomorphic behavior of the resulting polymer.

EXPERIMENTAL

Materials.

4-Bromophenol (99%), 2-methyl-3-butyn-2-ol (98%), boron tribromide in CH_2Cl_2 (1M), 3-methylanisole (99%), trifluoracetic anhydride (99%), $PdCl_2(PPh_3)_2$, 11-bromoundecan-1-ol (98%), butyl vinyl ether (98%) (all from Aldrich) were used as received. Diacetato(1,10-phenanthroline)palladium(II) was prepared as previously described.[10]

Synthesis of Monomer and Polymer.

Scheme 1 describes the synthesis of 1-(2-methyl-4-(4'-carboxybenzo-15-crown-5)phenyl)ethynyl-4-(11-vinyloxyundecan-1-yloxy)benzene (8).

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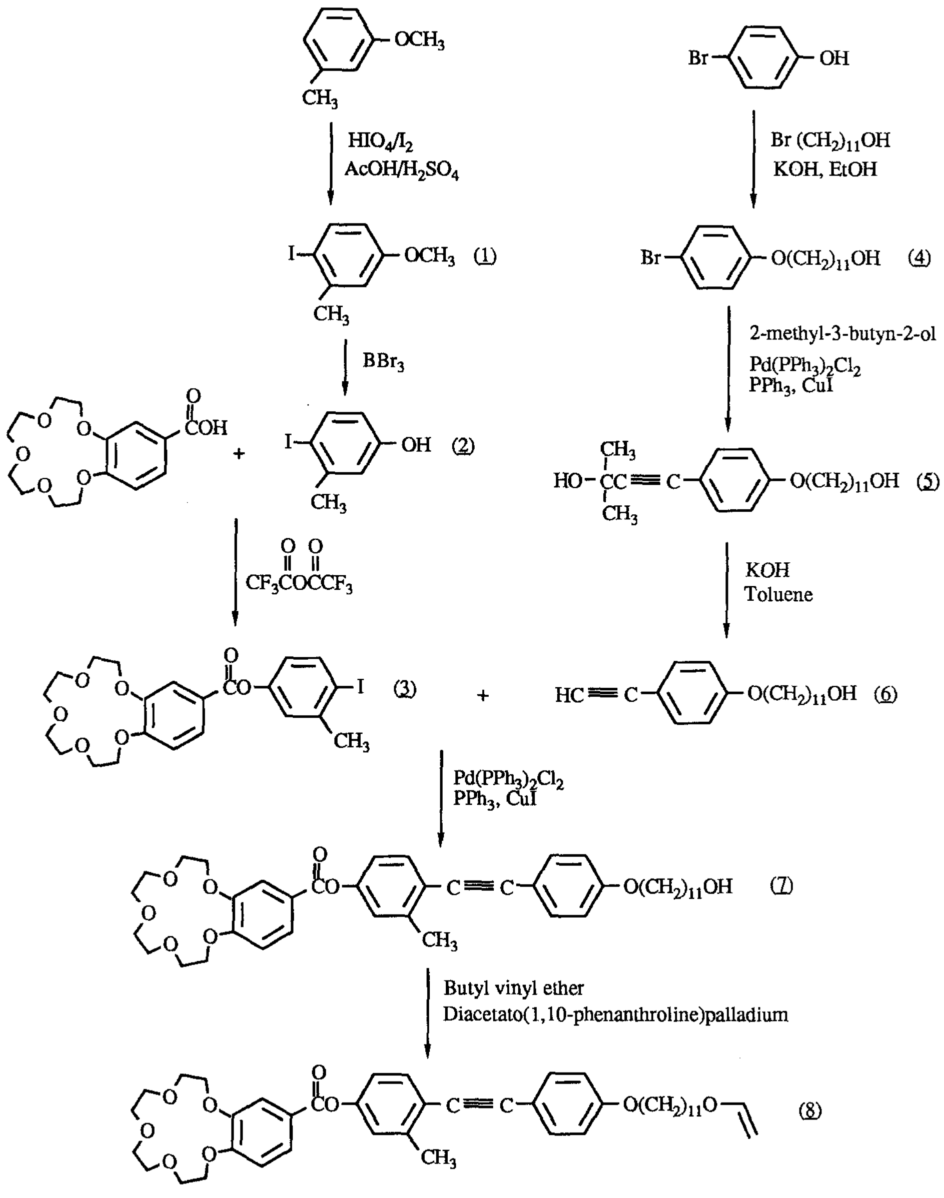


Scheme 1. Synthesis of monomer 8.

4-Iodo-3-methylanisole (1).

3-Methylanisole (33.8 g, 277 mmol) was dissolved in a mixture of acetic acid (300 mL), sulfuric acid (7.2 mL), and H_2O (60 ml) followed by addition of periodic acid (12.7 g, 55.5 mmol) and iodine (28.2 g, 111 mmol).[20] The solution was heated to 65°C for 16 h. After cooling to room temperature diethyl ether and water were added. The diethyl ether layer was washed with aqueous $NaHCO_3$ and then water. The diethyl ether was rotovapped to a light yellow oil which was vacuum distilled to yield 62.5 g (91%) of a clear crystalline solid: mp 42-44°C; ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm) 2.39 (3 protons, CH_3, s), 3.76 (3 protons, OCH_3, s), 6.45 (1 proton, aromatic, d of d), 6.82 (1 proton, aromatic, d of s), 7.62 (1 proton, aromatic, d).

4-Iodo-3-methylphenol (2).

1 (20.8 g, 84 mmol) dissolved in dry CH_2Cl_2 was added to 1M BBr_3 in CH_2Cl_2 (101 mL) cooled in a dry ice/acetone bath. The reaction mixture was then allowed to warm to room temperature and stirred at room temperature overnight. The excess BBr_3 was destroyed by the slow addition of water at 0°C during which time a precipitate formed. Upon addition of diethyl ether the precipitate dissolved and the organic layer was washed with aqueous $NaHCO_3$ and then water. The solvent was removed under vacuum and the resulting solid was recrystallized from hexane:benzene (3:1) to afford 14.7 g (75%) of a light yellow solid: mp 89-90°C; ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm) 2.37 (3 protons, CH_3, s), 4.81 (1 proton, OH, s), 6.42 (1 proton, aromatic d of d), 6.77 (1 proton, aromatic ,d of s), 7.60 (1 proton, aromatic, d).

4-Iodo-3-methyl-1-(carboxybenzo-15-crown-5)benzene (3).

To a heterogeneous solution of 4'-carboxybenzo-15-crown-5[8] (7.78 g, 24.9 mmol) in CH_2Cl_2 (60 mL) was added trifluoroacetic anhydride (3.8 mL, 27 mmol) at which time the solution became homogeneous. 4-Iodo-3-methylphenol (2) (3.52 g, 16 mmol) was then added and the reaction mixture was stirred at room temperature for 4 h. The CH_2Cl_2 layer was washed with water, dilute aqueous NaOH and then water again. The organic layer was separated and removed under vacuum. The resulting white solid was washed with methanol and recrystallized from ethanol to yield 8.8 g (67%) of a white solid: mp 88-90°C; IR (KBr) 1716 cm^{-1}; ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm) 2.44 (3 protons, CH_3, s),3.78 (8 protons, $O\underline{H_2}C\underline{H_2}O$ in crown ring, s), 3.94 (4 protons, $OC\underline{H_2}CH_2OPh$ in crown ring, br s), 4.22 (4 protons, $OCH_2C\underline{H_2}OPh$ in crown ring, br s), 6.76 (1 proton, aromatic crown , d of s), 6.90 (1 proton, aromatic crown, d), 7.09 (1 proton, aromatic benzene, d of s), 7.63 (1 proton, aromatic crown, d of s), 7.72 (2 protons, aromatic benzene, d), 7.81 (2 proton, aromatic crown and benzene, m).

4-Bromo-1-(11-hydroxyundecan-1-yloxy)benzene (4).

Into a solution of 4-bromophenol (3) (4.10 g, 23.7 mmol) in ethanol (50 mL) was dissolved KOH (1.38 g, 24.6 mmol). 11-Bromoundecan-1-ol (5.95 g, 23.7 mmol) was then added and the solution heated to reflux for 24 h. At this time, the solution was filtered and the filtrate concentrated to a clear oil. The oil was dissolved in $CHCl_3$ and washed with 10% aqueous KOH, two times with water, and dried over anhydrous $MgSO_4$. The $CHCl_3$ was removed under vacuum producing a clear oil which crystallized upon cooling. Recrystallization from hexanes yielded 5.69 g (70%) of white flakes: mp 42-44°C; ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm) 1.15-1.83 (18 protons, $(CH_2)_9$, m), 3.64 (2 protons, CH_2OH, t), 3.91 (2 protons, OCH_2, t), 6.79 (2 protons, aromatic, d), 7.33 (2 protons, aromatic, d).

4-Ethynyl-1-(11-hydroxyundecan-1-yloxy)benzene (6).

To a homogeneous solution of 4-bromo-1-(11-hydroxyundecan-1-yloxy) benzene (4) (2.50 g, 7.29 mmol) and 2-methyl-3-butyn-2-ol (0.62 g, 7.38 mmol) in triethylamine (20 mL) were added bis(triphenylphosphine)palladium chloride (102 mg, 0.15 mmol), copper (I) iodide (110 mg, 0.58 mmol) and triphenylphosphine (190 mg, 0.73 mmol).[21] The reaction mixture was heated to 90°C (bath temperature) until the aryl halide conversion was complete (about 7 h which was monitored by ^{1}H-NMR) and then cooled to room temperature. Benzene and aqueous ammonium chloride were then added and the mixture was stirred for 0.5 h. The aqueous layer was separated and the organic layer washed two times with water and dried over anhydrous $MgSO_4$. The solvent was removed under vacuum yielding the alkynol as a tan solid (5) which was triturated with hexanes:benzene (1:1) before deprotection. In order to remove most of the palladium catalyst, the compound was dissolved in $CHCl_3$ containing activated carbon, filtered, and the solvent was removed under vacuum. (Passing through a short column of neutral alumina is also sufficient).

The deprotection of the alkynol (5) was performed by dissolving the solid in toluene (45 mL) adding KOH (0.42 g, approximately one equivalent based on the aryl bromide) and heating to reflux until the removal of the protecting group is complete (1 h, monitored by ^{1}H-NMR). Decantation, evaporation under vacuum, and recrystallization from hexanes yielded 1.26 g [60% overall yield from (4)] of a light yellow solid: mp 50-52°C; IR (KBr) 3270 cm^{-1} (triple bond CH stretch); 2110 cm^{-1} (triple bond C-C stretch); ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm) 1.16-1.87 (18 protons, $(CH_2)_9$, m), 3.00 (1 proton, -CH, s), 3.65 (2 protons, $C\underline{H}_2OH$, t), 3.95 (2 protons, OCH_2, t), 6.83 (2 protons, aromatic, d), 7.41 (2 protons, aromatic, d).

1-(2-Methyl-4-(4'-carboxybenzo-15-crown-5)phenyl)ethynyl-4-(11-hydroxyundecan-1-yloxy)benzene (7).

6 (1.39 g, 4.8 mmol) and 3 (2.56g, 4.8 mmol) were dissolved in Et_3N (50 mL) and to this homogeneous solution was added bis(triphenylphosphine)palladium chloride (67 mg, 0.096 mmol), CuI (73 mg, 0.38 mmol), triphenylphosphine (126 mg, 0.48 mmol) and heated to reflux for 2 h. Once cooled to room temperature additional benzene was added followed by aqueous ammonium chloride. After stirring for 1 h, the organic layer was separated and washed twice with water and dried over anhydrous $MgSO_4$. The solvent was removed to afford a yellow solid which was recrystallized from hexane:benzene (3:1) to yield 2.02 g (61%) of a off white solid: mp (DSC) 123°C (74°C); ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm) 1.02-1.86 (18 protons, $(CH_2)_9$, m), 2.52 (3 protons, CH_3, s), 3.65 (2 protons, $C\underline{H}_2OH$, t), 3.78 (8 protons, $OC\underline{H}_2C\underline{H}_2O$ in crown ring, s), 3.85-4.04 (6 protons, $OC\underline{H}_2CH_2OPh$ in crown ring and OCH_2, m), 4.22 (4 protons, $OCH_2C\underline{H}_2OPh$ in crown ring, m), 6.82-7.17 (5 protons, 1 aromatic crown and 1 aromatic benzene, m), 7.40-7.57 (3 protons, aromatic benzene, m), 7.66 (1 proton, aromatic crown, d of s), 7.83 (1 proton, aromatic crown, d of d).

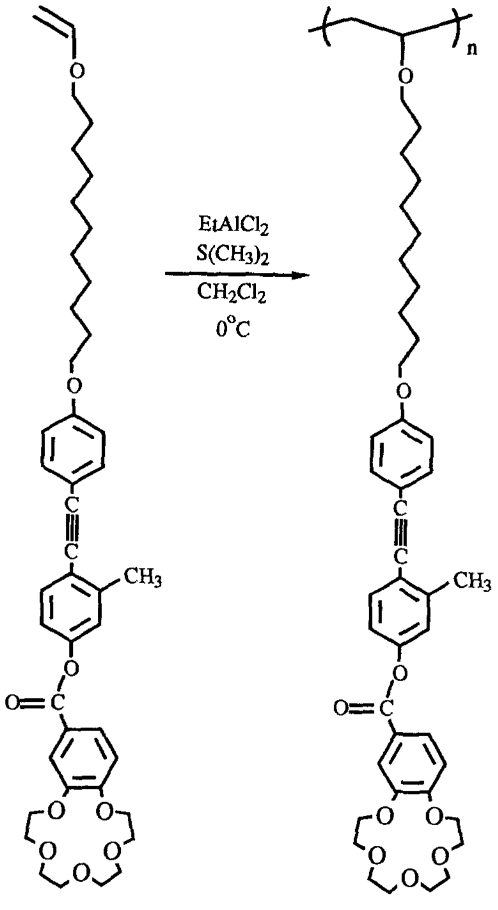
1-(2-Methyl-4-(4'-carboxybenzo-15-crown-5)phenyl)ethynyl-4-(11-vinyloxyundecan-1-yloxy)benzene (8).

7 (0.745 g, 1.08 mmol) was dissolved in dry $CHCl_3$ (2.7 mL) and added to a mixture of the diacetato(1,10-phenanthroline)palladium (II)[22] (48 mg, 0.12 mmol), butyl vinyl ether (6 mL) and $CHCl_3$ (1.6 mL). The mixture was heated to 62°C for 24 h. After cooling, the mixture was filtered to remove the catalyst. To the resulting yellow filtrate was added activated carbon and the mixture again filtered. The filtrate was then concentrated under vacuum yielding a light yellow solid. Purification by column chromatography using neutral alumina and CH_2Cl_2 as eluent afforded 0.50 g (65%) of a white solid: ^{1}H-NMR

($CDCl_3$, TMS, δ, ppm) 1.01-1.87 (18 protons, $(CH_2)_9$, m), 2.52 (3 protons, CH_3, s), 3.67 (2 protons, CH_2O-vinyl, t), 3.78 (8 protons, $OC\underline{H}_2C\underline{H}_2O$ in crown ring, s), 3.85-4.07 (7 protons, $OC\underline{H}_2CH_2OPh$ in crown ring, $OCH{=}C\underline{H}_2$ and OCH_2, m), 4.09-4.31 (5 protons, $OCH_2C\underline{H}_2OPh$ in crown ring and $OCH{=}C\underline{H}_2$, m), 6.47 (1 proton, $OC\underline{H}{=}CH_2$, q), 6.78-7.13 (5 protons, 1 aromatic crown and 4 aromatic benzene, m), 7.39-7.56 (3 protons, aromatic benzene, m), 7.64 (1 proton, aromatic crown, d of s), 7.82 (1 proton, aromatic crown, d of d).

Synthesis of Poly(8).

Scheme 2 describes the synthesis of poly(8). The polymerization of 8 was carried out at 0°C in dry CH_2Cl_2 under dry nitrogen. The reaction was initiated by addition of an $EtAlCl_2$ solution in n-hexane (0.07 mL) into a mixture of 8 (0.504 g, 0.705 mmol) dissolved in dry CH_2Cl_2 (4 mL) containing dimethyl sulfide (0.090 mL) at 0°C.[23] After 3 hours the reaction was quenched with $CH_3OH{:}NH_4OH$ (3:1) and precipitated into methanol. Reprecipitation into methanol from CH_2Cl_2 (twice) yielded a light brown precipitate of high molecular weight polymer. Mn = 43,900, Mw/Mn = 3.32.



Scheme 2. Synthesis of poly(8)

TECHNIQUES

Both monomers and polymers were characterized by a combination of techniques consisting of 200 MHz ^{1}H-NMR spectroscopy, high pressure liquid chromatography (HPLC), gel permeation chromatography (GPC with polystyrene standards), differential scanning calorimetry (DSC using 20°C/min), and optical polarized microscopy. Details of these experimental techniques are available elsewhere.[7,8]

RESULTS AND DISCUSSION

The previous examples of side chain liquid crystalline polymers containing crown ethers in the mesogenic groups were synthesized with polymethacrylate and polysiloxane backbones.[8,9,11,13] At the same time the polymers containing crown ether units in the polymer backbone were prepared by the cationic cyclopolymerization of 1,2-bis(2-ethenyloxyethoxy)benzene derivatives.[10,12] Additional publications from our laboratory have demonstrated that vinyl ethers containing mesogenic groups with functionalities like aromatic esters, cyano, nitro, double bonds etc. can be polymerized by a cationic mechanism leading to polymers with narrow molecular weight distribution.[17-20] It was therefore of interest to see whether a vinyl ether containing a diaryl C≡C triple bond can be polymerized by cationic polymerization.

The synthesis of 8 is outlined in Scheme 1. Its cationic polymerization is presented in Scheme 2. Cationic polymerization initiated by $H_2O/AlEtCl_2/S(CH_3)_2$ was performed in CH_2Cl_2 at 0°C. A high molecular weight polymer with broad polydispersity was obtained. Although only preliminary, this experiment demonstrates that vinyl ethers containing C≡C triple bonds are tolerated by this initiating system. Figure 1 presents representative DSC traces of 8 and poly(8). 8 exhibits an enantiotropic nematic mesophase. Poly(8) presents side chain crystallization and a enantiotropic nematic mesophase. Regardless of the thermal history of the sample, on the heating scan poly(8) exhibits two melting transitions. In the first heating scan the second melting overlaps the isotropization transition. On the subsequent heating scans the second melting appears at a lower temperature and therefore poly(8) exhibits a well separated enantiotropic nematic mesophase. Table I summarizes the characterization of both 8 and poly(8). Investigations on the synthesis of poly(8) with narrow molecular weight distribution are in progress.

Table I. Characterization of 8 and poly(8)

Compound	Phase transitions (°C) and corresponding enthalpy changes (kcal/mru)	
	Heating[a]	Cooling[a]
8[b]	k 93 (11.58) n 103 (0.23) i	i 101 (0.19) n 37 (4.05) k
Poly(8)[c]	g 43 k 93 (1.84) n 129 (0.51) i	i 118 (0.23) n 45 (1.79) k 33 g
	g 29 k 80 (2.74) k 104 (0.25) n 122 (0.20) i	i 117 (0.22) n 43 (1.49) k 28 g

a) g = glassy, k = crystalline, n = nematic
b) Data collected from first heating and cooling scans
c) Data collected from first and second heating and cooling scans.

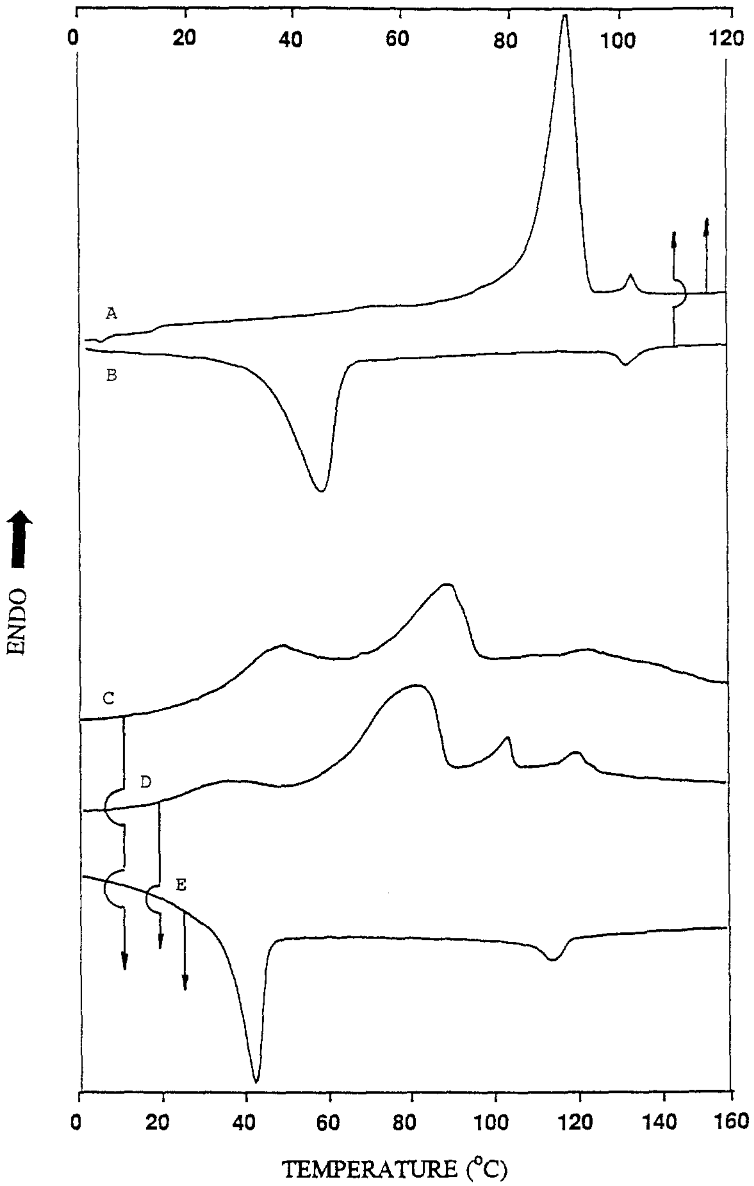


Figure 1. Normalized DSC traces (20°C/min) of A) 8, first heating scan B) 8, first cooling scan C) poly(8), first heating scan D) poly(8), second heating scan E) poly(8), first and second cooling scan.

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