

Fractionation of Low Molecular Weight Polyethylene by High-Pressure Soxhlet Extraction

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SYNOPSIS

The use of quantitative, high-pressure Soxhlet extraction for the fractionation of low molecular weight polyethylene samples is described. Liquid carbon dioxide was found to be a suitable solvent for the lowest molecular weight hydrocarbons but failed to solubilize hydrocarbons with molecular weights greater than C-40–C-50. Liquid pentane was found to be an effective solvent for hydrocarbons that were insoluble in liquid CO₂. Careful, stepwise adjustment of the extraction solvent temperature produced polymer fractions with molecular weight distributions substantially narrower than those of the parent materials. Polymer fractions with molecular weights up to C-90 were analyzed by high-temperature gas chromatography. These analyses demonstrated the effectiveness of the technique in fractionating polymers according to molecular weight. Further evidence was provided by thermal analysis of the fractions that indicated melting-point transitions that were much sharper than those of the parent materials. High-pressure Soxhlet extraction offers considerable potential as a general method for purification and fractionation of synthetic and natural polymers.

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INTRODUCTION

In recent years, there has been considerable interest in the purification and fractionation of synthetic oligomers and polymers using supercritical fluids (SCFs) as solvents. These fluids have been used to produce polymer samples of narrow molecular weight distribution by utilizing the readily adjustable solubility parameters of solvents in the supercritical state.^{1,2} However, polymer fractionation using SCFs is frequently performed at very high pressures, which necessitates the use of expensive and elaborate equipment.

An interesting alternative for polymer purification and fractionation involves the use of subcritical fluid solvents in a high-pressure Soxhlet extractor. A schematic diagram of such a device can be seen in Figure 1. It operates in a manner analogous to conventional Soxhlet extraction except that the ex-

traction unit is housed inside a pressure vessel capable of maintaining pressures up to 1500 psi. Thus, extractions can be performed using solvents at temperatures above their normal boiling points. Examples of suitable solvents include carbon dioxide, propane, fluorotrichloromethane, and pentane. Jennings³ used this device for extraction of polyaromatic hydrocarbons from coal fly ash and volatiles from fruit.

Effective fractionations are performed by using solvents that exhibit limited solubility for the solute of interest. The solvent solubility parameter of the liquified gas is adjusted by varying the temperature inside the vessel, allowing for the stepwise extraction of polymers according to molecular weight. Since the unit is totally self-contained, it requires minimal supervision after reaching thermal equilibrium. Fresh solvent is continually produced by evaporation and is recycled through the sample chamber, thereby minimizing solvent usage. This paper will discuss the use of high-pressure Soxhlet extraction for the fractionation of low molecular weight polyethylene samples and the properties of the resulting materials.

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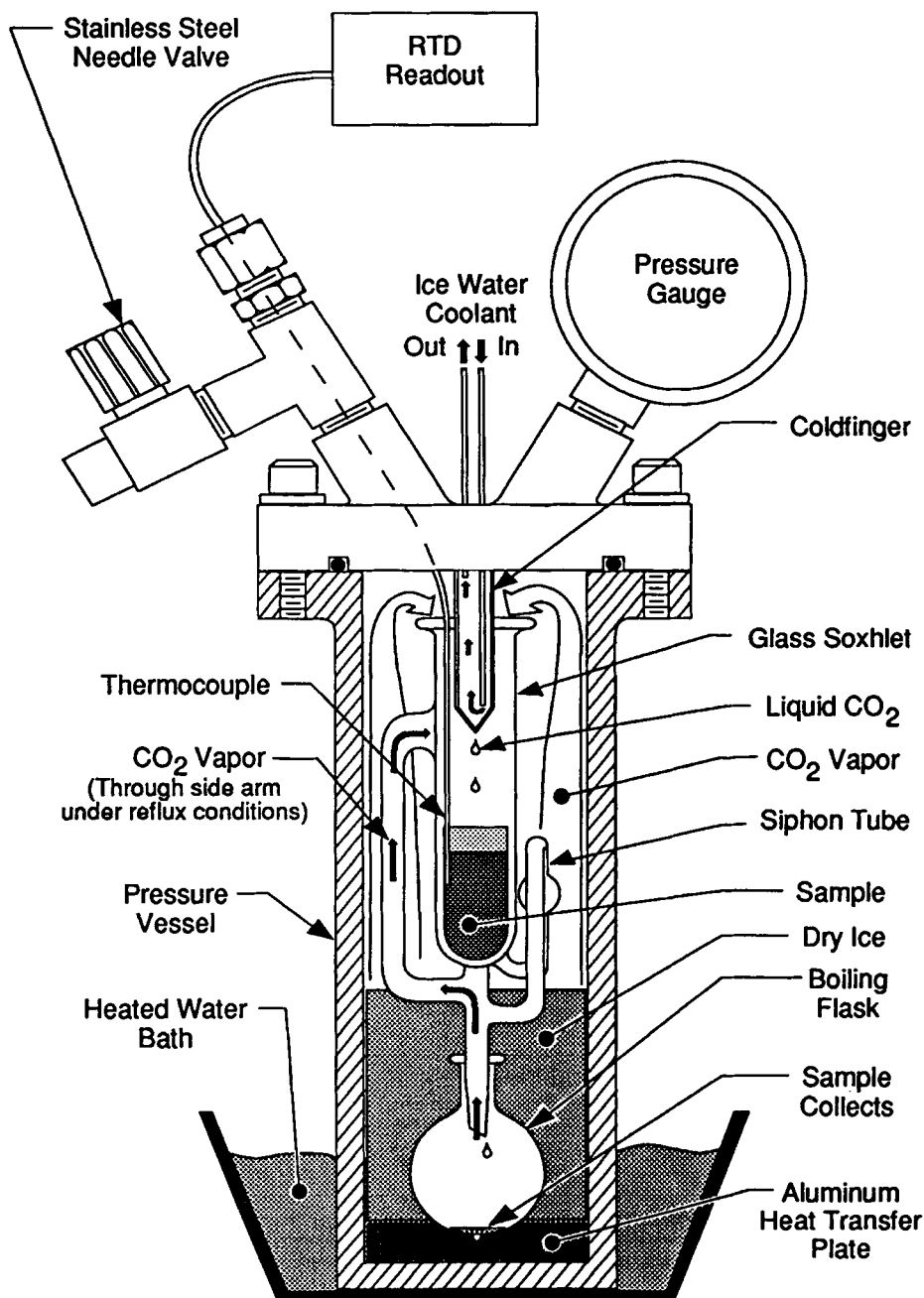


Figure 1 Schematic diagram of high-pressure Soxhlet extractor.

EXPERIMENTAL

Extractions were performed using a J & W Scientific High Pressure Soxhlet Extractor (Part No. 300-1000) modified to accept a hanging-type Soxhlet thimble (KIMAX Extraction Siphon, VWR Cat. No. 27710-007) and a temperature probe (Omega RTD Cat. No. PR-11-2-100-1/8-12-E) attached to an LED thermocouple readout (Omega Model CN-310-

PN-C). The thimble body was suspended beneath the cooling finger using two pieces of wire, as seen in Figure 2. The tip of the temperature probe was positioned outside the cellulosic thimble and ca. 1–2 cm above the bottom of the glass thimble body. The extractor housing was immersed in an Equatherm water bath (Lab Line Instruments). Auxiliary cooling of the extractor coldfinger, when used, was provided by a circulating temperature bath (Lauda Instruments, Model RM 6).

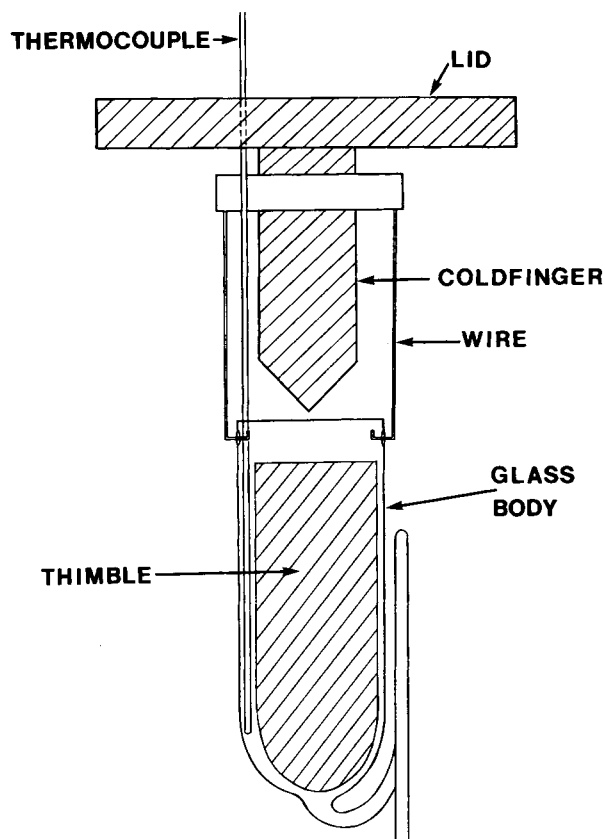


Figure 2 Schematic diagram of hanging Soxhlet extractor body.

Polywax-655 and Polywax-1100 were obtained from Petrolite Corp. (St. Louis, MO) and used as received. HPLC-grade pentane obtained from Baxter Travenol and commercial-grade CO₂ obtained from Moore Bros. (Sacramento, CA) were used as received. Polywax samples were ground in a mortar and pestle prior to introduction to the Soxhlet thimble.

Single-thickness extraction thimbles, 19 × 90 mm (VWR cat. no. 2800 199) were cut down to 65 mm to fit into the siphon body. They were filled with polymer and a plug of cotton was placed into the thimble to hold the material in place. The thimble was then placed into the siphon body that was suspended below the coldfinger of the extractor top, as described previously. The solvent of interest and the suspended polymer were placed in the extractor body and the lid was bolted shut. The extractor was then immersed in the water bath and the temperature of the bath and auxiliary cooling were adjusted to produce the desired temperature within the extractor thimble.

CO₂ extractions were performed by charging the extractor with 250 g of dry ice. Extractions with

pentane were performed using 200 g charges of liquid. After completion of each CO₂ extraction, the vessel was degassed and the polymer was removed as a neat sample. When pentane was used as a solvent, the polymer solution or slurry was poured out of the extractor and the solvent was boiled away on a warm hotplate. Neat polymer extracts were diluted 20 : 1 with toluene prior to GC injection. The extractor was then recharged with fresh solvent and the extraction was repeated at the next set of conditions.

High-temperature GC analysis was performed using an HP 5890A gas chromatograph with an FID detector (400°C) attached to an HP 3392A integrator. Typical gas flows were the following—carrier: hydrogen, 20 mL/min; FID: hydrogen, 30 mL/min; air, 300 mL/min; and nitrogen makeup, 30 mL/min. Injections were made cool-on-column using an on-column injector (J & W Scientific, part no. 200-1020-03) and a 30 m, high-temperature DB-5 column (0.25 mm i.d., 0.1 micron film thickness, J & W Scientific). The following column conditions were employed during the runs: Initial $T = 120^{\circ}\text{C}$; initial hold = 0 min; ramp = $10^{\circ}\text{C}/\text{min}$, final $T = 400^{\circ}\text{C}$; and final hold = 90 min. Hydrocarbon peak assignments were made by comparison to retention data obtained for a mixture of C-18, C-28, C-40, and C-60 hydrocarbon standards.

Thermal analyses were performed on a DuPont DSC-10 differential scanning calorimeter. Data were acquired and analyzed using a DuPont Thermal Analyst 2000 System.

RESULTS AND DISCUSSION

Table I shows the results of a series of extractions performed on Polywax-655 utilizing both CO₂ and pentane as extraction solvents. Extractions 1–6 were performed using CO₂, and extractions 7–13 were performed using pentane. In extractions 1–6 of Polywax 655, the solvent temperature varied between 12 and 43°C and was controlled by adjusting the coldfinger and/or heating bath temperatures. The temperature within the extraction thimble varied within a 1–2°C range as the liquid level within the thimble rose and fell. As would be expected, the pressure inside the vessel increased with increasing solvent temperature and varied between 650 and 790 psig. Extraction times ranged between 24 and 61 h.

The solubility of Polywax-655 in liquid CO₂ is not very appreciable. Less than 0.1 g was solubilized in extractions 1–5 and none was solubilized in extraction 6. This may indicate decreased solubility of

Table I Fractionation of Polywax-655 Using Liquid CO₂ and Liquid Pentane^a

Extraction No.	Solvent	Extraction Time (h)	Cooling Bath Temp (°C)	Extraction Temp (°C)	Pressure (psig)	No. Grams Extracted
1	CO ₂	24	0	12-13	650	0.1
2	CO ₂	24	0	14-15	675	< 0.1
3	CO ₂	24	0	17-18	700	< 0.1
4	CO ₂	40	0	21-23	720	< 0.1
5	CO ₂	59	10	32-33	750	< 0.1
6	CO ₂	61	20	42-43	790	0
7	Pentane	18	None	39-41	< 50	1.2
8	Pentane	43	None	41-43	< 50	0.6
9	Pentane	27	None	44-45	< 50	0.1
10	Pentane	26	None	57-58	< 50	0.3
11	Pentane	25	None	61-62	< 50	0.7
12	Pentane	22	None	71-72	< 50	1.6
13	Pentane	21	None	84-85	< 50	0.5

^a 4.5 g of polymer were charged to the extractor.

the polymer at increased temperatures or complete extraction of all CO₂ soluble components by the conclusion of extract 5. Extracts 7-13 were performed with liquid pentane as the solvent. Auxillary cooling was not used. Apparently, heat transfer through the vessel lid is sufficiently high to allow condensation of gas on the coldfinger and subsequent cycling. Extraction temperatures ranged between 39 and 85°C. The extraction times ranged between 18 and 43 h. The vessel pressure was less than 50 psig in all cases. As seen, the solubility of polymer in liquid pentane is much greater than in liquid CO₂.

Figures 3 and 4 show a series of high-temperature GC analyses performed on the Polywax-655 extracts 1-13 along with the parent polymer. Extract 1 is composed primarily of hydrocarbons with molecular weights less than C-30. Extracts 2-5 indicate some enrichment in the C-40-C-50 range, although the

primary components are C-20-C-40 hydrocarbons. Upon switching to liquid pentane in extraction 7, enrichment in the C-30-C-50 hydrocarbons can be seen. Increased concentration of higher molecular weight components was observed as the extraction proceeded, and fractions 12 and 13 were found to be highly enriched in C-50-C-80 hydrocarbons.

Table II shows the conditions used to fractionate Polywax-1100 using liquid pentane. The extraction times ranged between 24 and 70 h within a temperature range of 40-92°C. Vessel pressures did not exceed 60 psig. As seen, the quantity of polymer extracted increases steadily from 0.1 g for extract 1 to 1.6 g for extract 7. The remaining 0.5 g of polymer was removed in the eighth extraction.

Figure 5 shows a series of high-temperature GC analyses performed on the Polywax-1100 fractions. A chromatogram of the parent material is shown for comparison. Also shown is a gas chromatograph of

Table II Fractionation of Polywax-1100 Using Liquid Pentane^a

Extraction No.	Solvent	Extraction Time (h)	Cooling Bath Temp (°C)	Extraction Temp (°C)	Pressure (psig)	No. Grams Extracted
1	Pentane	24	None	40-41	10	0.1
2	Pentane	36	None	43-46	10	0.2
3	Pentane	30	None	51-56	18	0.3
4	Pentane	51	None	57-65	24	0.4
5	Pentane	40	None	65-72	32	0.8
6	Pentane	43	None	75-80	34-40	1.1
7	Pentane	70	None	79-84	40-48	1.6
8	Pentane	52	None	87-92	52-60	0.5

^a 5.0 g of polymer were charged to the extractor.

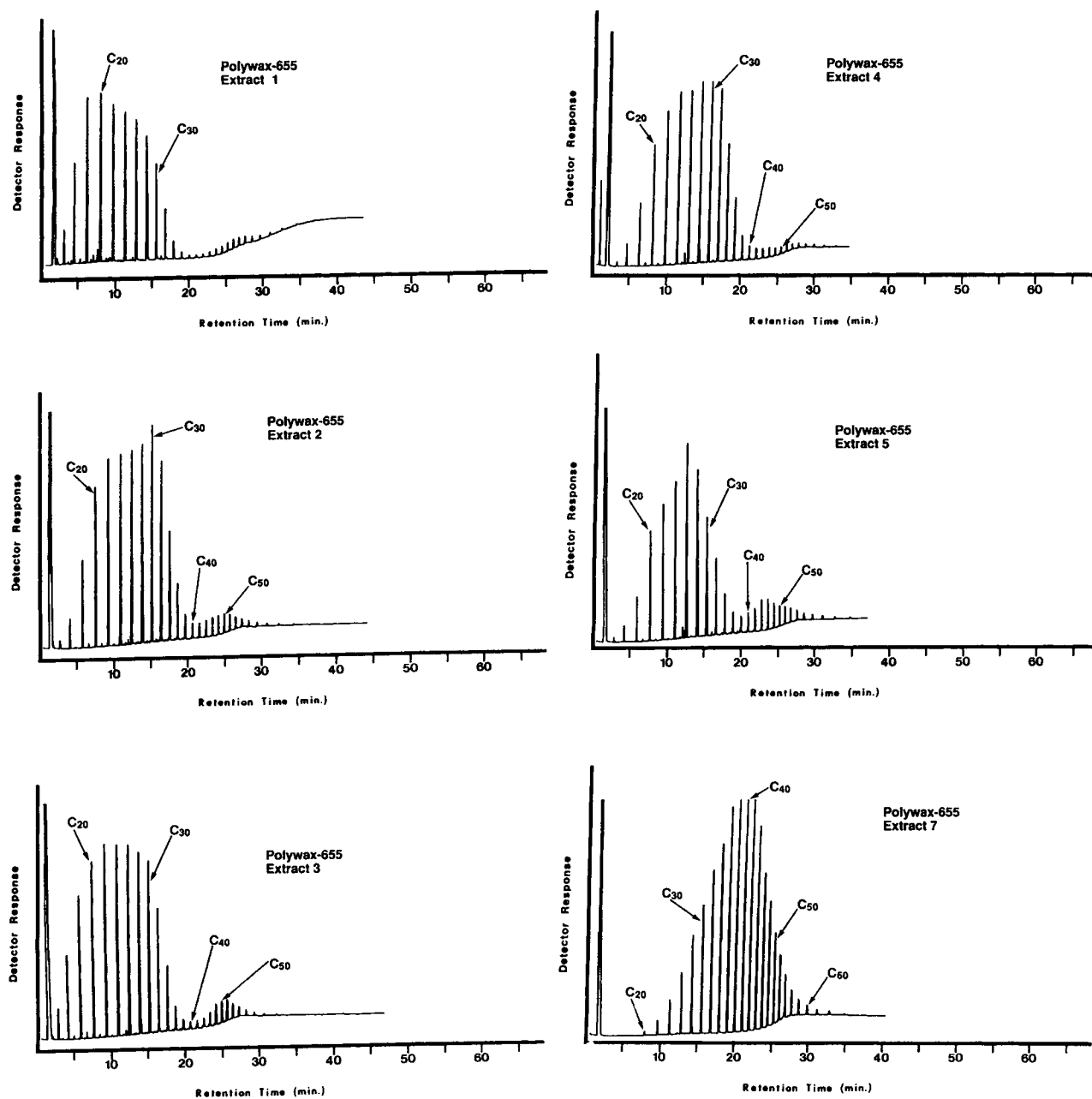


Figure 3 High-temperature GC analysis of Polywax-655 extracts 1-6.

the four hydrocarbon standards used to assign molecular weights to the components of each fraction. Extracts 1 and 2 are composed primarily of hydrocarbons with molecular weights less than C-60. However, fraction 1 is seen to contain a greater quantity of C-20-C-40 hydrocarbons. Fractions 3 and 4 are composed primarily of C-50 to C-70 hydrocarbons, whereas fractions 5 and 6 are composed largely of C-60 to C-90 hydrocarbons. Apparently, C-90 hydrocarbons, with a molecular weight of 1262,

represent the highest molecular weight capable of being volatilized for GC analysis. In fact, hydrocarbons of ca. C-76 and greater begin to exhibit peak fronting, which is attributed to thermal degradation of the analytes after extended residence times in the column at 400°C. Analysis of C-90+ fractions will require use of other chromatographic techniques such as SFE or HPLC.

Tables III and IV show the T_m and T_m onset slopes for Polywax-1100 and Polywax-655, respectively.

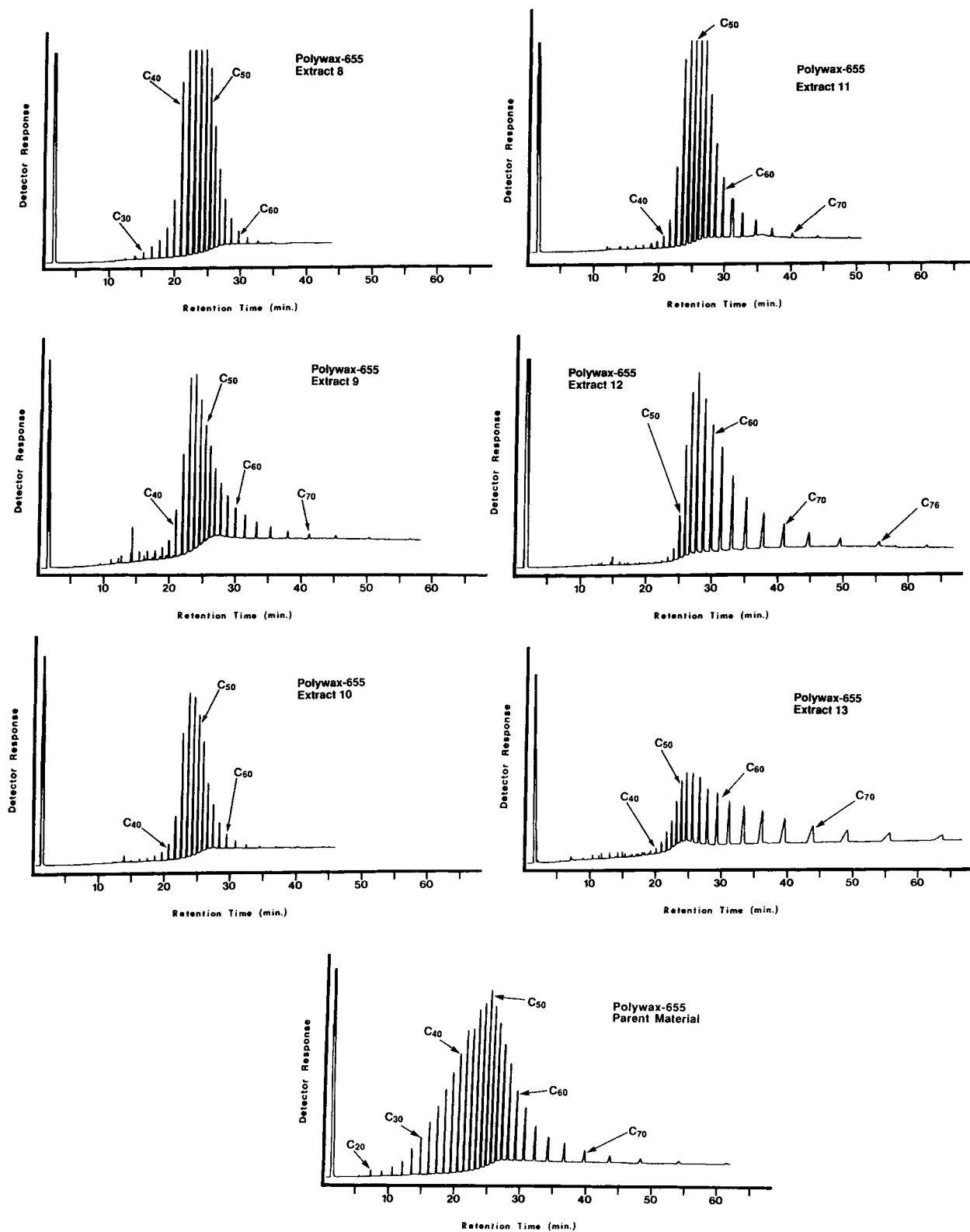


Figure 4 High-temperature GC analysis of Polywax-655 extracts 8-13 along with chromatogram of parent polymer.

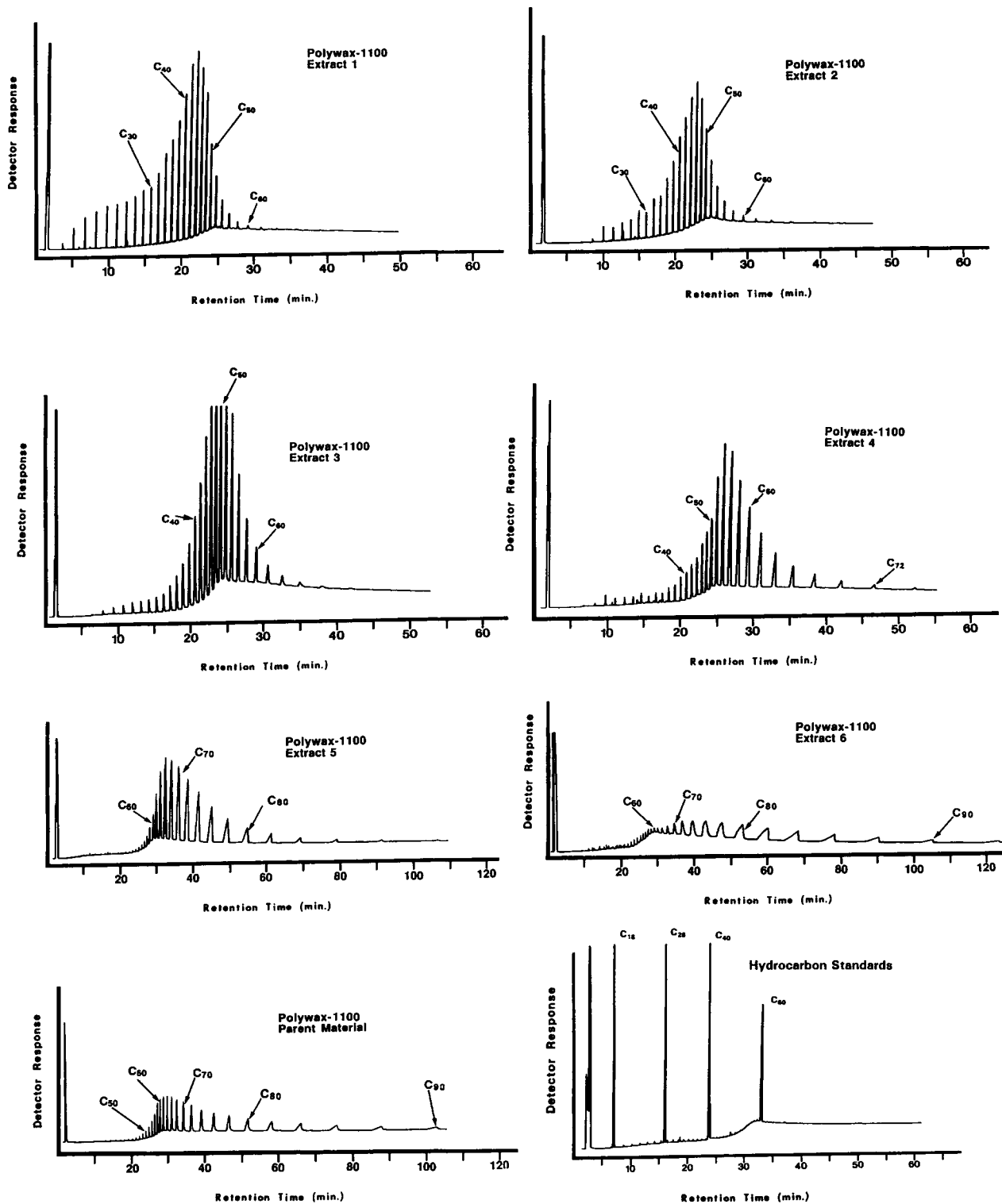


Figure 5 High-temperature GC analysis of Polywax-1100 extracts 1-6 along with chromatogram of parent polymer.

Both tables indicate a gradual increase in the melting point for each fraction. The Polywax-655 fractions exhibited melting points between 50.0 and

107.2°C. These compare to the parent material that had a broad T_m with a peak at 94.0°C. Insufficient quantities of Polywax-655 extracts 1, 2, 4, and 5 were

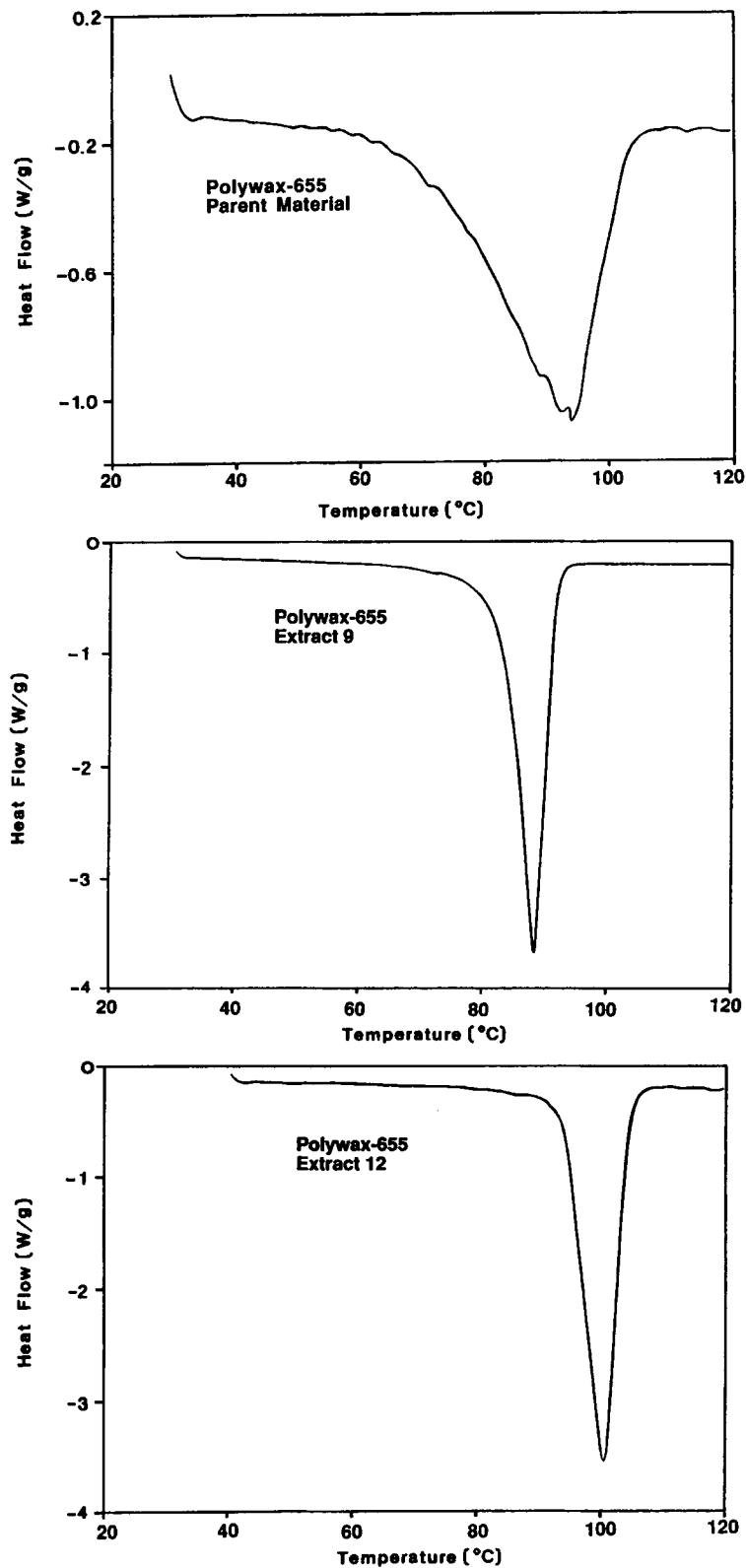


Figure 6 DSC traces of Polywax-655 extracts 9 and 11 along with thermogram of parent polymer.

available for thermal analysis. The Polywax-1100 fractions exhibited T_m values ranging between 85.7 and 120.0, which compare to the parent polymer T_m of 111.4.

Representative examples of Polywax-655 thermograms along with the parent polymer thermogram are illustrated in Figure 6. As seen, extracts 9 and 12 have much sharper melt-point transitions than that of the parent material; however, some overlap of the melt points does occur. Virtually all of the Polywax-655 and Polywax-1100 fractions were found to have significantly sharper transitions than those of the parent polymers. This becomes more evident after examination of the T_m onset slopes in Tables III and IV, where larger, negative values indicate sharper thermal transition. By comparison, indium has a T_m onset of -13.71 .

The sharpness of these transitions in conjunction with the GC data indicates the effectiveness of high-

Table III T_m and T_m Onset Slopes for Polywax-1100

Extract No.	T_m	Onset Slope (mW/°C)
1	85.7	-0.34
2	88.3	-0.26
3	95.5	-1.93
4	102.6	-2.94
5	106.3	-4.23
6	111.4	-9.17
7	115.4	-9.17
8	120.0	-4.05
Parent	111.4	-0.86

Table IV T_m and T_m Onset Slopes for Polywax-655

Extract No.	T_m	Onset Slope (mW/°C)
3	50.0	—
7	80.5	-0.84
8	87.7	-4.57
9	88.7	-3.91
10	92.5	-4.33
11	94.0	-4.86
12	100.5	-5.36
13	107.2	-1.68
Parent	94.0 (broad)	-0.35

pressure Soxhlet extraction for analytical-scale polymer fractionation. In our laboratory, we are currently developing a prep-scale version of this device that will be capable of processing up several hundred grams of polymer per charge. The operational features of this device and applications will be the subject of a future manuscript.

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