

Supporting Information

Advanced liquid chromatography of polyolefins using simultaneous solvent and temperature gradients.

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1. Experimental Information

Size exclusion chromatography. Polystyrene equivalent molar masses and dispersities of the samples were determined on a PL-GPC 220 high-temperature chromatograph (Polymer Laboratories, Church Stretton, UK, now Agilent Technologies) equipped with a differential refractive index (RI) detector. The samples (4 mg) were dissolved in 2 mL of 1,2,4-trichlorobenzene for 2 hr together with 0.025 % BHT which acted as a stabiliser to prevent sample decomposition/degradation. 1,2,4-trichlorobenzene with 0.0125 % BHT was used as the mobile phase at a flow rate of 1 mLmin⁻¹. Three 300 × 7.5 mm² PLgel Olexis columns (Agilent Technologies, UK) were used together with a 50 × 7.5 mm² PLgel Olexis guard column. 200 µL of each sample solution was injected. All experiments in HT-SEC were carried out at 150 °C. The instrument was calibrated using narrowly distributed polystyrene standards (Agilent Technologies, UK).

Interaction chromatography. Interaction chromatography experiments were done on a Polymer Char HT-2D-LC instrument (Valencia, Spain), comprising of an autosampler, two separate ovens, switching valves and a high-pressure binary pump equipped with a vacuum degasser (Agilent, Waldbronn, Germany). The main oven (Oven 1) was used to accommodate the porous graphitic carbon (PGC) column. The injector and switching valves are located in the second oven (Oven 2) kept at 160 °C. The autosampler is a separate unit connected to the injector through a heated transfer line.

An evaporative light scattering detector (ELSD, model PL-ELS 1000, Polymer Laboratories, Church Stretton, England) was used with the following parameters: A gas flow rate of 1.5 Lmin⁻¹, a nebuliser temperature of 160 °C, and an evaporator temperature of 270 °C. The evaporator temperature was only changed to 230 °C when a decane/1,2-dichlorobenzene solvent system was used. A PGC column (Hypercarb[®], Thermo Scientific, Dreieich, Germany) with the following parameters: 10 – 300 mm length and 4.6 mm i.d., packed with porous graphite particles with a particle diameter of 5 µm, and a pore size of

250 Å. The flow rate of the mobile phase was 0.5 mLmin⁻¹ in all experiments except during the cooling stage of TGIC experiments. 200 µL of each sample was injected at a concentration of 1.2 mg mL⁻¹ for all experiments carried out in the present work.

Solvent gradient interaction mode. The column was placed in the column oven maintained at 160 °C. The SGIC separations were accomplished by applying a linear gradient from the adsorption promoting solvent (listed in Materials and solvents Section) to TCB. The volume fraction of TCB was linearly increased to 100% within 30 min (15 mL) after the sample injection. The initial chromatographic conditions were re-established with 100% adsorption promoting solvent.

Temperature gradient interaction mode. Temperature gradient interaction chromatography (TGIC) separations were achieved by using either ODCB or TCB as the mobile phase. The temperature and mobile phase flow profile used are illustrated in Fig. S1. Detailed modifications of the temperature gradient are specified in the following sections. For the purpose of this work, all TGIC elution volumes are corrected to start at 0 mL from when the flow was increased from 0.02 to 0.5 mL/min. This means that the injection of the sample and column cooling for all experiments was done in 0.6 mL i.e. at a flow of 0.02 mL/min for 30 min.

Two solvent gradient cycles at different column temperatures. In the first instance (Method 1 in Fig. S2), the first solvent gradient cycle was applied from 100% decane to 100% ODCB in 20 mins (10 mL) at 120 °C. The conditions were re-established within 2 min (1 mL). The temperature of the column was simultaneously increased from 120 °C to 170 °C. These conditions were maintained for a further 8 mins (4 mL, >3 column volumes) to allow the column temperature to stabilize and the adsorption conditions to be re-established. Thereafter, a second solvent gradient cycle was applied in 20 mins (10 mL) at 170 °C. In a second variation of the first experiment (Method 2), a shallower gradient was used. The gradient was applied from 100% decane to 60% ODCB in 20 mins (10 mL) before re-establishing adsorption conditions.

The rest of the conditions were not changed in the second method. The ELS detection conditions were as follows: nebuliser temperature 160 °C; evaporator temperature 230 °C; gas flow 1.5 L/min.

Solvent gradient at low temperature then applying a temperature gradient. A solvent gradient cycle was applied from 100% decane to 100% 1,2-dichlorobenzene in 20 mins (10 mL) at 120 °C. Thereafter, a temperature gradient was applied at 4 °C/min from 120 °C to 170 °C. The flow under the solvent and temperature gradients was kept at a constant flow rate of 0.5 mL/min.

Simultaneous solvent and temperature gradients. In these experiments, the sample was injected in TGIC mode at 160 °C in an adsorption promoting solvent. The solvent gradient was set to start 40 min after the start of the experiment requiring 30 min (15 mL) for solvent change from the adsorption promoting solvent to TCB. The temperature of the column was manipulated to start at -4, 0, +4 and +8 min after the start of the gradient. The heating rate during the elution step was set to 4 °C/min requiring 30 min (15 mL) to complete from 40 – 160 °C. The solvent and temperature gradients are shown in Fig. S4. Due to the system delay, the gradient reaches the head of the Hypercarb column after a delay of ~ 1.7 mL while the temperature gradient has an immediate effect.

Solvent gradient mode with two temperature zones. A two-column set up illustrated in Fig. S5 was setup in two ovens connected by a capillary tube with minimal volume delay. Two 100 mm and 10 mm Hypercarb columns were placed in oven 1 and 2, respectively. The temperatures of the ovens were programmed as indicated in Table S1. A 1-decanol→TCB_{30 min} solvent gradient was used for the elution.

2. Supporting figures

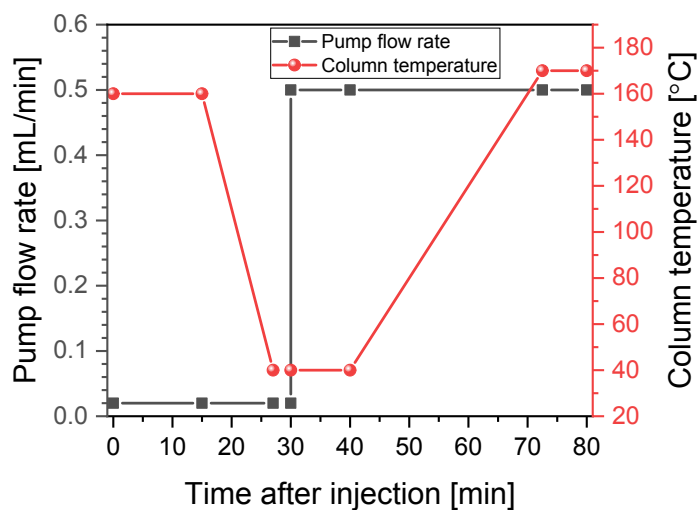


Figure S1. TGIC temperature and mobile phase flow profiles. The temperature profile is shown by the red line and the flow profile by the black line.

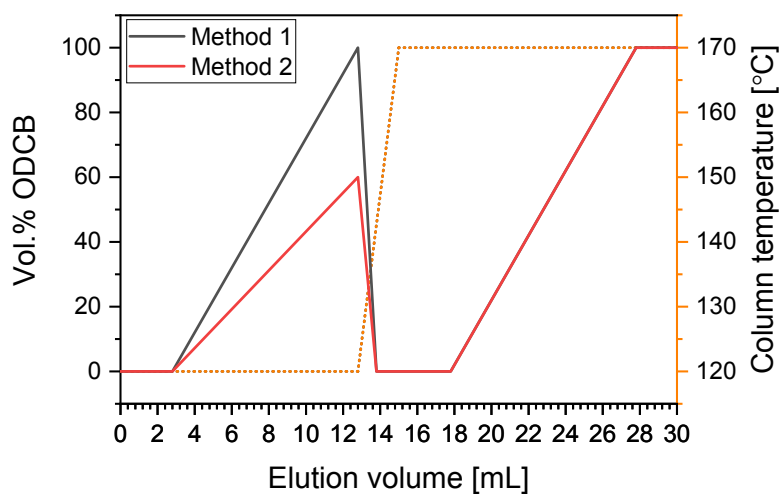


Figure S2. Solvent gradient and temperature profiles used for the separation of low molar mass HDPE and high molar mass copolymer blends.

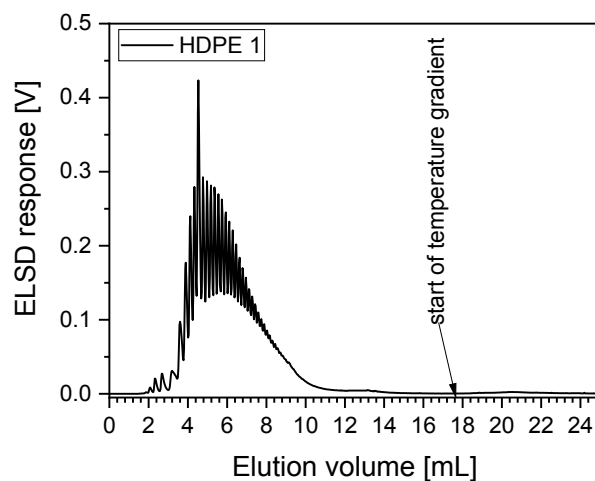


Figure S3. Analysis of HDPE 1 at 120 °C using a solvent gradient followed by a temperature gradient.

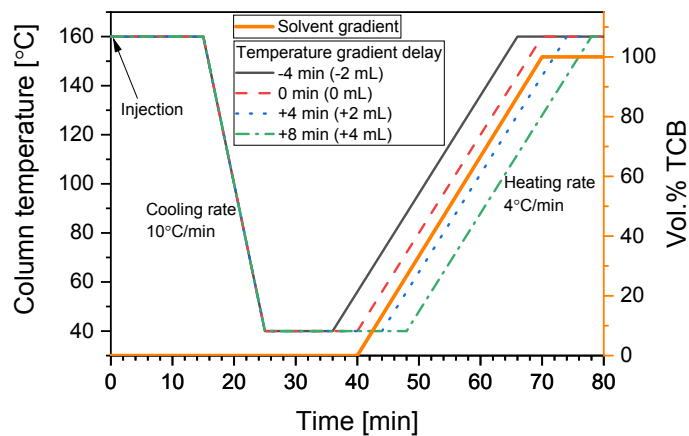


Figure S4. Temperature and solvent gradient profiles used simultaneously for the elution of 1:1 blends of LLDPE 1 and 2 as well as LLDPE 4 and 7.

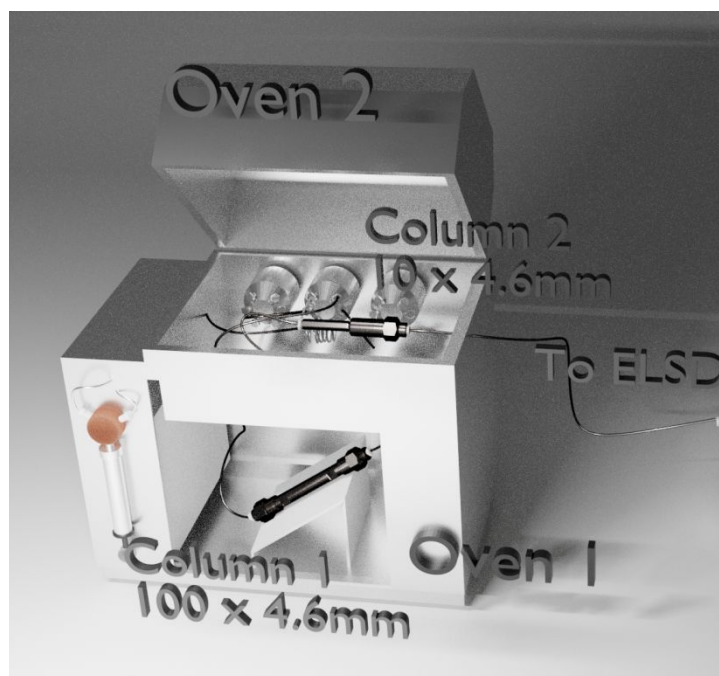


Figure S5. Diagram showing the column setup used for the separation of LLDPE blends with two columns in different temperature zones.

3. Supporting tables

Table S1. Peak elution volumes (V_e), full width at half maximum (w) and the calculated resolution (R) obtained from the simultaneous application of a solvent and temperature gradient for the sample blend LLDPE 1 + 2. The experimental error of elution volumes is also given.

	Peak V_e [mL]		$V_{e(y)} - V_{e(x)}$	w		$w_{(y)} + w_{(x)}$	R
	LLDPE 1	LLDPE 2		LLDPE 1	LLDPE 2		
SGIC	10.40±0.01	10.81±0.01	0.41	0.22	0.19	0.40	1.22
TGIC	15.44±0.01	16.91±0.01	1.47	0.95	0.68	1.63	1.06
-4min	16.48±0.01	17.54±0.01	1.06	0.77	0.52	1.29	0.97
0min	18.97±0.01	20.09±0.01	1.12	0.62	0.67	1.29	1.02
+4min	20.09±0.01	21.09±0.01	1.00	0.49	0.44	0.93	1.26
+8min	21.58±0.01	22.02±0.01	0.44	0.24	0.24	0.48	1.08

Table S2. Peak elution volumes (V_e), full width at half maximum (w) and the calculated resolution (R) obtained from the simultaneous application of the of a solvent and temperature gradient for the sample blend LLDPE 4 + 7. The experimental error of elution volumes is also given.

	Peak V_e [mL]		$V_{e(y)} - V_{e(x)}$	w		$w_{(y)} + w_{(x)}$	R
	LLDPE 4	LLDPE 7		LLDPE 4	LLDPE 7		
SGIC	9.19±0.01	9.55±0.01	0.36	0.29	0.21	0.50	0.84
TGIC	11.07±0.01	12.48±0.01	1.41	1.35	1.14	2.49	0.67
-4min	13.69±0.01	14.51±0.01	0.82	0.49	0.70	1.19	0.81
0min	15.21±0.01	15.51±0.01	0.30	0.23	0.27	0.50	0.72
+4min	16.80±0.01	17.20±0.01	0.40	0.33	0.18	0.51	0.93
+8min	18.33±0.01	18.83±0.01	0.50	0.28	0.25	0.53	1.13

Table S3. Column temperature for the respective 100- and 10-mm columns used for the solvent gradient elution of ethylene-co-1-octene copolymers.

Experiment	Zone temperature [°C]	
	Column 1 (100 mm)	Column 2 (10 mm)
1	160	160
2	150	160
3	160	150