Column fractionation of partially stereoregular poly(propylene oxide)

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A column packed with glass beads has been used to fractionate partially stereoregular poly(propylene oxide) (PPO). PPO was first crystallized onto the glass beads from isooctane solution by stepwise lowering the column temperature. Each layer of PPO, which was deposited at different temperature ranges, was extracted by washing the beads with several columns full of isooctane. Thus several fractions differing in both stereoregularity and molecular weight were obtained by progressively increasing the extraction temperature and the solvent residence time in the column. It is concluded that in the procedure described above PPO can be fractionated on the basis of structural and steric regularity. The observed steady increase in the molecular weight of fractions with extraction temperature was interpreted as being due to the fact that the stereoregularity of chains increases with their molecular weight.

(Keywords: poly(propylene oxide); stereoregular; Pruitt–Baggett catalyst; column fractionation; fractional crystallization)

INTRODUCTION

Partially stereoregular poly(propylene oxide) (PPO) can be fractionally crystallized from dilute isooctane solution into stereoregularly uniform fractions[1,2]. It has also been found that, in the isothermal crystallization of stereoregularly uniform PPO samples from dilute isooctane solutions, the higher-molecular-weight components precipitate faster, thus allowing a fractionation on the basis of molecular weight[3].

Polymer samples with narrow molecular-weight distributions and uniform stereoregularities might find interesting applications in the field of polymer science. However, owing to the necessity of using dilute solutions, the fractions obtained with the above procedure[3] were too small in amount to be used in other work.

The purpose of this communication is to describe a column fractionation technique that separates partially stereoregular PPO into stereoregularly uniform fractions which differ both in structural regularity and in molecular weight.

EXPERIMENTAL

Materials

All reagents were purified by standard procedures prior to fractionation by distillation on a column with an efficiency of approximately 25 theoretical plates. Isooctane (Merck 'Proanalysis Grade') was fractionated on this column and the fraction boiling at 368–369 K (690 torr) collected. In the following, the 0.2% solution of diphenylamine (antioxidant) in isooctane was simply termed isooctane.

Preparation of PPO samples

PPO was synthesized by using a Pruitt–Baggett type of catalyst[4]. Crystallizable polymers were separated from non-crystallizable oligomers by precipitating from an isooctane solution at 273 K[1]. In order to prevent any degradation, the PPO samples and the fractions obtained from these samples were stored in sealed ampoules, under vacuum and in the dark.

Characterization of polymers

Viscosity-average molecular weights were calculated from the intrinsic viscosities measured in toluene at 298 K using the following relation[5]:

$$[\eta]\,(\mathrm{dl\,g^{-1}}) = 1.29 \times 10^{-4} \bar{M}_v^{0.75} \qquad (1)$$

Melting points were measured on a hot-stage polarizing microscope: PPO solutions in benzene were put one drop at a time on a glass plate. The benzene was evaporated by blowing air. The deposited film of polymer on the glass plate was melted in an oven at about 363–373 K. The temperature of the oven was decreased gradually to room temperature over 12–15 h. Such treated samples crystallized in the form of spherulites. On the hot stage of the polarizing microscope the films were heated at a rate of 0.2 K min^{-1}. The temperature at which the spherulites completely disappeared was noted as the melting point T_m^*.

G.p.c. chromatograms were obtained by using a Millipore–Waters g.p.c. instrument with 10^4, 10^3 and 10^2 nm Microstyragel columns at 293 K. Sample concentrations were 2.5 g dl^{-1} (in dimethylformamide). The g.p.c. instrument was calibrated by using polyether-based polyurethane standards.

Apparatus

An all-glass fractionation column with a Teflon-plug valve was constructed (*Figure 1*). The packing material for the column was obtained by crushing glass bottles in a hammer-mill and collecting the beads between two sieves of sizes 1.0 and 0.5 mm. In order to prevent escape of the glass beads from the column during the discharging of liquids, a number of lead balls, of 4 mm diameter, were placed between the beads and the Teflon plug of the

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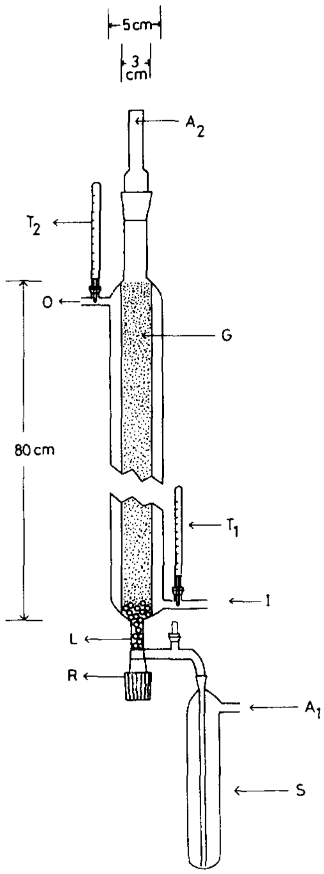

Figure 1 The fractionation column; I and O, inlet and outlet of constant-temperature water; T_1 and T_2, thermometers; G, glass beads; L, lead balls; R, Teflon-plug valve; A_1 and A_2, inlet of compressed air; and S, siphon flask

valve. The glass beads allowed about 270 cm^3 of free volume in the column. The temperature along the column can be controlled to within 0.5 K by circulating a water supply from a constant-temperature bath through the column jacket at a flux of 10 litre min^{-1}. The column and water circulating tubes were all thermally insulated. Isooctane (or PPO solution in isooctane) occupying the free volume of the column placed in a siphon flask can be charged into the column in a few seconds by blowing compressed air (through A_1, *Figure 1*). The liquid content of the column can also be quickly discharged by application of pressurized air (through A_2, *Figure 1*).

Procedure

PPO samples were fractionated on this column according to either one of the following two methods.

Method I. PPO solution in isooctane (17 g l^{-1}) at 343 K was charged into the column. PPO was crystallized onto the glass beads by decreasing the column temperature in 5 or 10 K decrements (viz. 323, 313, 308, 303, 293, 283 and 273 K). At each step of the crystallization the temperature of the column was kept constant for 48 h. Thus each one of the polymer layers, which formed at different stages of crystallization, with the exception of the one that crystallized at the highest temperature (viz. 323 K), might be characterized by its upper (T_i) and lower (T_p) freezing temperatures from the solution, where the T_i and T_p values of two successive layers coincide. Finally, the residual solution at $T_p = 273$ K was discharged off the column, and the column was washed with isooctane at this temperature. In spite of the fact that no filtering device was used in the column, owing to the excellent adhesion of the PPO crystals onto the glass beads, the discharged solutions were always homogeneous. Starting from the final layer, with smallest T_p (i.e. the layer that crystallized within the temperature range $T_i = 283$ K to $T_p = 273$ K), each one of these layers was separated into several fractions by extracting with isooctane. For this purpose the column was heated up to the T_i of the particular fraction, prior to filling the column with isooctane at the same temperature. After a residence time (t_r) of 5 min, the solution was discharged. The PPO in the collected solution was recovered by evaporation of the solvent, redissolved in benzene, filtered and freeze-dried. The same procedure of extraction was repeated by progressively increasing the solvent residence time until the rate of solution of PPO becomes vanishingly small at the particular extraction temperature, T_{ex} (in method I, apart from $T_{ex} = 298$ K, T_{ex} was always equal to the T_i of the layer under question).

Method II. PPO (which was synthesized from another batch of polymerization) solution in isooctane (13 g l^{-1}) at 348 K was charged into the column and the temperature was regulated at $T_p = 313$ K. At the end of 36 h of precipitation time, the solution was discharged off and kept for future use. The precipitate on the glass bead support, with unknown T_i, was washed off with hot isooctane and discarded. The stored solution (with $T_i = 313$ K) was heated up until it became clear and recharged into the column, and PPO was crystallized onto the glass beads at $T_p = 303$ K for 36 h. The residual solution was discharged off, and kept again for future use. The column was washed off with isooctane at temperature T_p, prior to heating it to T_{ex} (where $T_{ex} = (T_i + 5)$ K) and at this temperature the polymer deposit on the glass beads was fractionated, as already described in method I. The same procedure was repeated with the stored solution by decreasing T_p by 10 K decrements.

RESULTS AND DISCUSSION

The different fractions that were extracted at the same T_{ex}, according to a particular method, were found to have equal T_m^* values, and the T_m^* values increase with increasing T_{ex} (*Tables 1* and *2*). ^{13}C n.m.r. studies have shown that the T_m^* value of a sufficiently high-molecular-weight PPO is related to the concentration of the sterically and structurally irregular repeat-unit isomers[2]. It appears that during stepwise cooling of the isooctane solution of PPO in the column, chains with uniform stereoregularities (i.e. chains with similar concentrations of sterically and structurally irregular repeat-unit isomers) fractionally crystallized together. In the subsequent extraction process, only the chains incorporated into the crystals (or into the layers of crystals) which were soluble (fusible) at T_{ex} or at lower temperatures (in the presence of solvent) were extractable. Therefore we conclude that both methods (I and II) fractionate partially stereoregular PPO on the basis of structural and steric regularity.

Before discussing the variation of $\bar{M}_v$ among the isolated fractions, it is worth comparing the intrinsic

Table 1 Column fractionation of PPO by method I

Fraction	T_{ex} (K)	t (min)	T_m^* (K)	$\bar{M}_v \times 10^{-5}$ (g mol^{-1})	w_i (%)^a
F_1	283.0	5	309.5	0.50	4.74
F_2		17	309.5	0.54	2.61
F_3		47	309.0	1.14	2.38
F_4		105	308.0	1.68	2.79
F_5		180	308.0	0.54	1.81
F_6		900	308.0	0.31	3.38
F_7		1800	308.5	0.54	2.33
F_8	293.0	5	312.0	1.43	3.60
F_9		15	311.6	1.70	3.16
F_{10}		30	312.5	1.20	2.30
F_{11}		90	312.8	1.81	2.88
F_{12}		180	313.5	1.37	2.50
F_{13}		240	314.0	1.30	1.58
F_{14}		1440	314.0	1.39	2.07
F_{15}		2280	314.0	4.50	2.43
F_{16}		5160	313.0	0.88	2.81
F_{17}		8040	314.0	1.51	3.55
F_{18}	298.0	20	312.0	3.02	3.32
F_{19}		75	313.0	3.26	1.71
F_{20}		300	312.5	3.53	2.94
F_{21}		3180	312.0	2.49	2.52
F_{22}		6060	311.0	2.26	2.17
F_{23}	303.0	10	319.5	3.81	2.86
F_{24}		105	318.0	4.15	2.50
F_{25}		1440	317.0	4.13	2.18
F_{26}		4740	317.0	3.13	2.35
F_{27}	308.0	5	325.5	3.84	1.70
F_{28}		60	324.5	4.77	1.51
F_{29}		2880	324.0	4.00	0.71
F_{30}		6300	324.0	1.33	3.28
F_{31}	313.0	5	329.5	3.28	1.47
F_{32}		120	330.0	3.09	1.76
F_{33}		6780	327.0	3.09	1.73
F_{34}	323.0	5	341.0	5.20	4.87
F_{35}		35	341.0	4.96	1.55
F_{36}		1380	339.0	4.26	1.66
F_{37}		2880	340.0	4.39	0.98
F_{38}	333.0	5	341.0	6.93	4.13
F_{39}		10	341.0	6.93	1.40
F_{40}		30	341.5	7.23	1.45
F_{41}		2880	341.0	7.08	2.46

^{a} The percentage (mass) yield of the extraction; total weight of extracted polymer = 4.6532 g

Table 2 Column fractionation of PPO by method II

Fraction	T_{ex} (K)	t (min)	T_m^* (K)	$\bar{M}_v \times 10^{-5}$ (g mol^{-1})	w_i (%)^a
S_1	288.0	5	315.5	0.52	4.18
S_2		15	315.5	1.23	2.29
S_3		60	315.5	1.90	6.76
S_4		840	315.5	9.00	5.37
S_5		900	315.5	9.29	7.19
S_6	298.0	5	319.0	6.99	3.43
S_7		10	319.0	6.93	2.35
S_8		20	319.0	7.57	2.88
S_9		90	319.0	6.88	4.11
S_{10}		540	319.0	9.35	17.14
S_{11}		720	319.0	8.00	2.35
S_{12}	308.0	5	330.0	11.73	2.14
S_{13}		10	330.0	12.28	2.23
S_{14}		25	330.0	11.60	1.70
S_{15}		120	330.0	9.26	2.23
S_{16}		1440	330.0	12.50	9.48
S_{17}	318.0	5	343.0	6.87	0.94
S_{18}		150	343.0	4.84	0.71
S_{19}		300	343.0	9.58	2.23

^{a} Total weight of extracted polymer = 3.4667 g

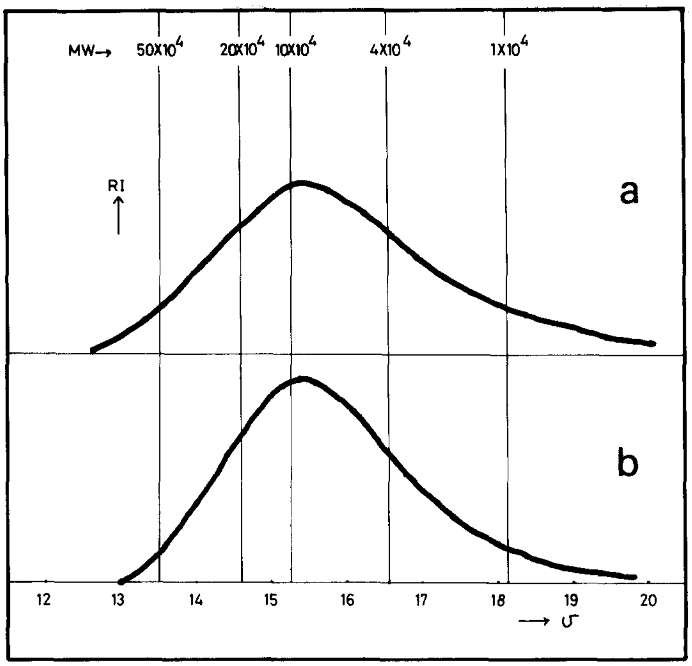

Figure 2 G.p.c. chromatograms of (a) F_{24} and (b) F_{26} (cf. *Table 1*); RI, refractive index difference; v, elution volume (cm^3)

viscosity of the whole polymer used in method I (viz. $1.41 \, dl \, g^{-1}$) with the weight-average intrinsic viscosities of the collected fractions (viz. $1.50 \, dl \, g^{-1}$), which indicates that the polymer samples were satisfactorily protected against degradation. The $\bar{M}_v$ of the fractions increases steadily with increasing T_{ex} (*Tables 1* and *2*). This observation is consistent with a previous conclusion that, in the synthesis of PPO by using either partial hydrolysates of trimethylaluminium or Pruitt–Baggett type catalysts, the steric and structural regularity of chains increases with increasing chain length[2].

The estimated heterogeneity indices of the fractions were around 3.0–5.0 (g.p.c. data, *Figure 2*), indicating rather broad molecular-weight distributions. The attempted fractionation on the basis of molecular weight by progressively increasing solvent residence time at the particular T_{ex} failed except for the extractions of stereoregularly poorest polymer deposits (viz. S_1–S_5 in *Table 2*). It was found that in both methods the $\bar{M}_v$ of the fractions were almost constant for a given T_{ex} irrespective of the solvent residence time. Thus it appears that the rate of extraction is not controlled by the molecular weight of the species. On the other hand, a preliminary study of the kinetics of the extraction process indicated that the rate of solution of the crystals was mainly controlled by the effective surface area (A) of the crystals. In fact, when the reciprocal of the square root of the instantaneous mass (m) of PPO deposit, which is extractable at T_{ex}, was plotted against the extraction time (t) (where t is the time elapsed from the first contact of the solvent at T_{ex} until the completion of the extraction under question (i.e. $t = \sum_i t_r$)), straight lines with high linear regression coefficients (0.920–0.997) were obtained. This relation is expected provided that A and m are related (or approximated) to each other as:

$$A = km^{3/2} \tag{2}$$

where k is a constant, which is proportional to the specific volume of the crystals.

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