

# Fractionation of partially stereoregular poly(propylene oxide)

K. Alyürük

Department of Chemistry, Faculty of Arts and Sciences, Middle East Technical University, Ankara, Turkey

and T. Özden and N. Colak

Department of Chemistry, Faculty of Arts and Sciences, University of Dicle, Diyarbakir, Turkey

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Partially stereoregular poly(propylene oxide) samples were synthesized via reactions catalysed by a preformed analytically defined trimethylaluminium hydrolysate. These samples were fractionated into two contrastingly different fractions.

(i) D-polymers: This fraction constituted the major part (up to 90%). It mainly contained cyclic low molecular weight oligomers ( $MW < 1000$ ). The linear chains found in D-polymers had hydroxyl end groups. No double bonds could be detected spectroscopically.

(ii) K-polymers: This fraction was high molecular weight stereoregular polymer. Stepwise thermal precipitation from dilute isooctane solution of K-polymers yielded a succession of fractions which differed in melting point. It appears that the phase equilibria during the thermal precipitations were not controlled by the molecular weights of species.

(Keywords: trimethylaluminium hydrolysate; stereoregular; poly(propylene oxide); fractionation; end-group analysis; cyclic oligomers)

## INTRODUCTION

Partial hydrolysates of some metal alkyls act as catalysts for stereoregular polymerization of propylene oxide. It has been shown that these catalysts produce high molecular weight isotactic polymer, but this is also accompanied by the production of low molecular weight oily polymers. The degree of tacticity of the product depends on the type of catalyst used, but can also show marked variations in different fractions of the same product. These observations have been tentatively interpreted as follows:

(i) The catalyst systems are essentially mixtures of different catalytic species with differing powers of stereoregulation<sup>1</sup>.

(ii) Active sites vary their mode of operation, viz. stereoregulating ability is lost and regained from time to time, with the net effect of producing a stereoblock copolymer, composed of isotactic and atactic blocks<sup>2</sup>.

Following the work of Price *et al.*<sup>3</sup> it would appear that the main irregularities in the otherwise isotactic chains are due to the presence of units bonded head to head or tail to tail. Information about the distribution of such structural irregularities in the polymer chain would be of value in understanding the mechanism of stereoregulation. Booth *et al.*<sup>4</sup> carried out an extensive fractionation of poly(propylene oxide) produced by a catalyst based on diethylzinc, but results are open to question because of the uncertain nature of the catalyst used. (The diethylzinc was hydrolysed in the presence of monomer, and since the hydrolysis reaction extended over a period comparable with that of the polymerization, the latter may have been initiated by intermediates as well as products of the hydrolysis.)

In this communication we present the results of fractionating partially isotactic poly(propylene oxide) formed in a reaction catalysed by a preformed analytically defined trimethylaluminium hydrolysate.

## EXPERIMENTAL

### Materials

All reagents were purified by standard procedures prior to fractionation on a column with an efficiency of approximately 25 theoretical plates. Isooctane (Merck 'pro analysi' grade) was fractionated on this column and the fraction boiling at 95–96°C (690 torr) collected.

### Preparation of poly(propylene oxide) samples

The polymerization reaction was carried out under high vacuum conditions by mixing propylene oxide with freeze-dried bis-dimethylaluminium oxide-dioxane complex<sup>5</sup> ( $\text{Me}_2\text{AlOAlMe}_2 \cdot \frac{1}{2}\text{O}_2\text{C}_4\text{H}_8$ ). Polymerization was terminated by adding a mixture of benzene and methanol, and the polymers were isolated by freeze-drying from the filtered solution. The products were dissolved in isooctane ( $1 \text{ g l}^{-1}$ ) and chilled to 0°C for 48 h, at which temperature the supernatant solution was separated from the precipitated polymer-rich phase by decantation. Both the polymers which were insoluble (K-polymer) and soluble (D-polymer) in isooctane at 0°C were isolated by freeze-drying. Further details of reaction conditions and the relative proportions of K- and D-polymers are given in Table 1.

**Table 1** Preparation of poly(propylene oxide) samples

Polymerization number	$[C] \times 10^3$ <sup>a</sup>	Polymerization time	Polymerization temp. (°C)	% P <sup>b</sup>	% D <sup>c</sup>	$\bar{M}_n$ <sup>d</sup>	$\bar{M}_v \times 10^{-4}$ <sup>e</sup>
P1	15.0	3 min	40	7.0	97.1	494	—
P2	11.0	5 day	40	19.0	94.7	688	—
P3	5.1	34 day	40	14.0	91.3	940	5.0
P4	5.0	22 day	80	21.0	91.3	668	6.0
P5	9.0	6 day	80	22.0	90.9	786	—
P6	30.0	270 min	80	24.0	94.2	781	—
P7	5.0	12 day	100	27.4	94.2	943	3.8

<sup>a</sup> Molarity of Al atoms in reaction mixture

<sup>b</sup> Percentage yield of polymer

<sup>c</sup> Per cent D-polymer in the whole polymer

<sup>d,e</sup> Molecular weight averages of <sup>d</sup>D- and <sup>e</sup>K-polymers, respectively

### Fractionation of D-polymers

The isooctane solution of D-polymers (2 g dl<sup>-1</sup>) was successively extracted with water and the water-soluble fraction (D<sub>w</sub>) isolated by freeze-drying. The supernatant isooctane solution was evaporated and the residue treated with azeotropic ethanol to give ethanol-soluble (D<sub>e</sub>) and ethanol-insoluble (D<sub>k</sub>) fractions. In Figure 1 the g.p.c. chromatograms of a D-polymer and of its D<sub>w</sub>, D<sub>e</sub> and D<sub>k</sub> fractions are compared.

### Fractionation of K-polymers

The procedure of Booth *et al.*<sup>4</sup> was used to fractionate the K-polymers, viz. solid polymer was precipitated from an isooctane solution of the sample (1 g l<sup>-1</sup>) initially at 60°C by lowering the temperature in 3°C decrements to 0°C. At each precipitation step the temperature of the system (*t<sub>p</sub>*) was kept constant for 24 h prior to isolation of the polymer-rich phase.

### Characterization of polymers

Number-average molecular weights were measured cryoscopically in recrystallized benzene. Viscosity-average molecular weights were calculated from the intrinsic viscosities measured in toluene at 25°C using the following relation<sup>6</sup>:

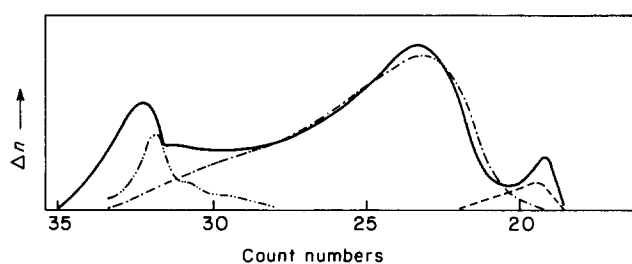
$$[\eta] = 1.29 \times 10^{-4} \bar{M}_v^{0.75} \quad (1)$$

Melting points were determined on a hot-stage polarizing microscope. G.p.c. chromatograms were obtained using a Waters Associates GPC-200 instrument at 40°C. The flow rate was 1 cm<sup>3</sup> min<sup>-1</sup>, and eluted volumes were measured by a 5 cm<sup>3</sup> siphon counter. The sample column bank consisted of Styragel columns with the following pore sizes: 10<sup>7</sup>, 10<sup>6</sup>, 10<sup>5</sup>, 10<sup>4</sup> and 5 × 10<sup>2</sup> nm (for K-polymers) and 10<sup>4</sup>, 5 × 10<sup>3</sup>, and 6 × 10<sup>2</sup> nm (for D-polymers). The g.p.c. chromatograms were normalized, so that in the figures the area under each chromatogram is proportional to the weight per cent of the fraction concerned.

## RESULTS AND DISCUSSION

### The nature of the D-polymers

In addition to the several fractions of D-polymers, which were defined in the experimental section, we have also detected (by v.p.c.) but were unable to isolate another volatile fraction (D<sub>v</sub>) in the collected condensates of freeze-dried solutions. However, a comparison of the dilatometric and gravimetric results showed that this



**Figure 1** G.p.c. chromatograms of D, D<sub>w</sub>, D<sub>e</sub> and D<sub>k</sub> fractions of sample P6: — D-polymer of P6; - - - D<sub>w</sub> of P6; - · - · D<sub>e</sub> of P6; · · · · D<sub>k</sub> of P6

gives a negligible error in the per cent conversions and weight percentages given in the tables.

In contrast to the non-crystallizable and oily D<sub>w</sub> and D<sub>e</sub> fractions, the D<sub>k</sub> fraction, which shows spherulite structure under a polarizing microscope, is solid at room temperature. However, its presence in the D-polymers appears to be merely a consequence of imperfect separation of K-polymer, and it is absent in many samples (Table 2). It would seem that in the fractionation procedure 0°C is a critical temperature for the separation of K- and D-polymers.

The D<sub>w</sub> and D<sub>e</sub> fractions were examined spectroscopically to establish the nature of the end groups. The i.r. spectra of the D<sub>w</sub> fractions showed an extremely low -OH stretching absorption. The alternative possibility of unsaturated end groups should be easily detectable by n.m.r., since in a hypothetical pentamer ( $M_n = 290$ ), for example, a double bond at each end would give a ratio of approximately 1/3 for double bond protons/methyl protons. No such unsaturation was detected in the n.m.r. spectra of the D<sub>w</sub> polymers, and we therefore conclude that they are mainly cyclic oligomers. The average mole fraction ( $\bar{X}_c$ ) of cyclic polyethers in D<sub>w</sub> fractions was estimated by comparing their i.r. spectra with that of Waters Associates Poly(propylene glycol) standard no. 41993 using the following equation:

$$\bar{X}_c = 1 - (\bar{M}_n/825)(\ln h_{wMc}/\ln h_{Mc})(\ln h_{OH}/\ln h_{wOH}) \quad (2)$$

where  $\bar{M}_n$  and 825 are cryoscopically measured molecular weights,  $h_{Mc}$  and  $h_{wMc}$  are per cent transmissions at 2985 cm<sup>-1</sup>,  $h_{OH}$  and  $h_{wOH}$  are per cent transmissions at 3475 cm<sup>-1</sup> for sample and standard respectively (see Table 2).

In the D<sub>e</sub> fractions the number of -OH groups per chain estimated from the i.r. spectra was in some cases as high as 2. If D<sub>w</sub> and D<sub>e</sub> fractions were formed during the

polymerization reaction by a transfer process (Table 3 shows that more than one polymer molecule is formed per Al atom), the formation of –OH end groups would require the simultaneous formation of double bonds, which are not found. We therefore ascribe the presence of –OH end groups to oxidative degradation of originally cyclic polyethers. This is supported by the presence of considerable carbonyl and peroxy carbonyl absorption in the i.r. spectra of some D<sub>e</sub> polymers, which increased in intensity with ageing of the samples. On the other hand the i.r. spectrum of the D<sub>e</sub> fraction of P<sub>3</sub> measured about a fortnight after the preparation of the sample to avoid excessive ageing showed no indication of carbonyl or peroxy carbonyl groups, and contained 72 mol % of cyclic polyethers.

#### Fractionation of the K-polymers

The fractionation results are given in Table 4. From the dilute isooctane solution, the polymer precipitates as a solid phase over the whole range of temperatures from 46 to 0°C. This contrasts with Booth *et al.*<sup>4</sup> who found that poly(propylene oxide) of molecular weight about 10<sup>6</sup> showed a critical temperature of 40°C below which liquid–liquid phase separation occurred predominantly on the basis of molecular weight. In the present work the average molecular weights were approximately 10<sup>4</sup>–10<sup>5</sup> and our results show that for this range of molecular weights the critical temperature for liquid–liquid phase separation must be less than 0°C.

The melting points (*t<sub>m</sub>*) of the K fractions (at which the last traces of crystallinity disappear) show a steady

**Table 2** Fractionation of D-polymers

Sample	D <sub>w</sub>			D <sub>e</sub>			D <sub>k</sub>	
	Wt % <sup>a</sup>	$\bar{M}_n$	$\bar{X}_c$ <sup>b</sup>	Wt %	$\bar{M}_n$	$\bar{X}_c$	Wt %	$\bar{M}_v$
P1	17.6	269	0.95	79.8	1194	0.43	2.6	26000
P2	13.0	266	0.79	86.0	1264	–	1.0	23000
P3	13.0	272	0.95	87.0	1630	0.72	nil	–
P4	9.1	393	0.70	90.9	1369	–	nil	–
P5	14.1	277	0.82	84.0	1312	–	1.9	26000
P6	12.8	272	–	83.3	1014	–	3.9	29000
P7	20.5	476	0.47	79.5	1524	–	nil	–

<sup>a</sup> Weight fraction in the whole D-polymer

<sup>b</sup> Mole fraction of cyclic oligomers

**Table 3** The number of D<sub>w</sub> and D<sub>e</sub> chains formed per Al atom used

Sample	<i>E<sub>w</sub></i> <sup>a</sup>	<i>E<sub>e</sub></i> <sup>b</sup>
P1	2.5	2.5
P2	6.5	9.3
P3	10.0	11.0
P4	7.6	21.6
P5	9.3	12.0
P6	3.0	5.0
P7	19.0	22.4

<sup>a</sup> Number of D<sub>w</sub> chains per Al atom

<sup>b</sup> Number of D<sub>e</sub> chains per Al atom

**Table 4** Fractionation of K-polymers

<i>t<sub>p</sub></i> (°C)	P3			P4			P7		
	<i>t<sub>m</sub></i> <sup>a</sup> (°C)	% W <sub>i</sub> <sup>b</sup>	<i>M<sub>v</sub></i> × 10 <sup>-4</sup>	<i>t<sub>m</sub></i> (°C)	% W <sub>i</sub>	<i>M<sub>v</sub></i> × 10 <sup>-4</sup>	<i>r<sub>m</sub></i> (°C)	% W <sub>i</sub>	<i>M<sub>v</sub></i> × 10 <sup>-4</sup>
46	68	0.6	3.0	61	0.6	2.5	–	–	–
43	66	0.7	10.5	65	0.8	10.5	65	0.5	9.0
40	65	0.4	2.5	–	0.1	2.5	64	0.1	8.5
37	63	0.3	7.5	62	0.1	7.0	64	0.1	6.5
34	62	0.4	14.5	61	0.3	6.5	63	0.1	6.0
30	–	0.4	3.5	60	0.3	10.5	63	0.3	5.9
27	59	0.2	10.5	58	0.6	12.5	62	1.1	5.7
24	58	0.5	7.0	–	0.7	8.5	–	nil	–
21	56	0.8	4.0	56	0.8	7.0	61	0.1	5.2
18	–	0.8	2.0	55	0.6	5.0	58	0.2	4.9
15	–	1.0	3.0	–	1.2	4.0	54	0.4	4.5
12	–	0.9	2.7	52	0.8	3.5	–	0.6	3.5
9	–	0.9	3.2	51	0.8	2.8	48	0.1	3.5
5	–	0.7	3.0	49	0.6	2.9	46	0.4	3.0
0	46	0.1	3.3	–	0.4	2.0	–	1.8	2.5

<sup>a</sup> *t<sub>m</sub>* = melting point of crystals

<sup>b</sup> % W<sub>i</sub> = per cent of the precipitated fraction in the whole polymer

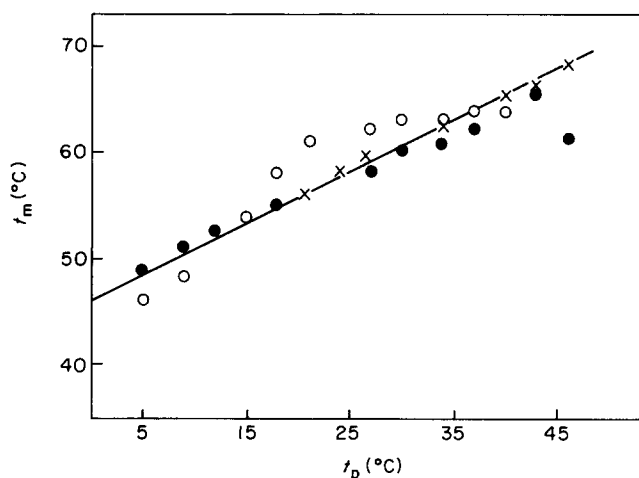


Figure 2 Relation between the melting points of crystals and the precipitation temperature: ○ P7; ● P4; × P3

decrease as the precipitation temperature ( $t_p$ ) is lowered (Figure 2). The results of  $^{13}\text{C}$  n.m.r. spectroscopy<sup>7</sup> show a correlation between structural regularity and  $t_m$ , and we conclude that isotactic sequence length determines crystallite size and hence  $t_m$ .

The chromatograms of the various K fractions (Figure 3) show that the average molecular weight decreases with  $t_p$  (and  $t_m$ ) and for the lowest melting fractions the effect of end groups is likely to be a contributory factor in lowering  $t_m$ . However, even the highest melting fraction shows a very broad molecular weight distribution, and we conclude that in general there is no selective effect of molecular weight during precipitation at a given  $t_p$ .

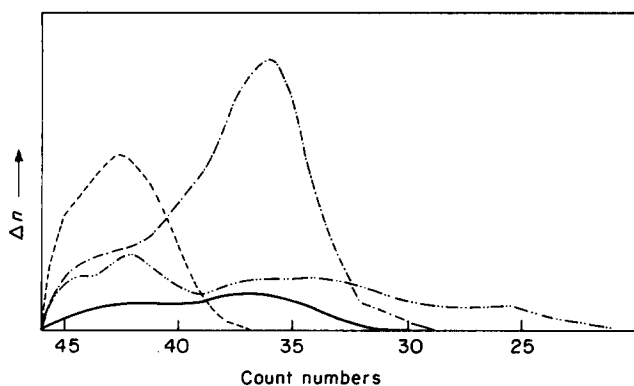


Figure 3 G.p.c. chromatograms of several fractions of P7: ······  $t_p=43^\circ\text{C}$ ; -·-·-·  $t_p=30^\circ\text{C}$ ; ———  $t_p=27^\circ\text{C}$ ; - - - -  $t_p=12^\circ\text{C}$

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