Ring Opening Polymerization of Ethylene Oxide by the $Y(P_{204})_3$–$Al(i\text{-}Bu)_3$–H_2O Catalyst

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Abstract

Ring opening polymerization of ethylene oxide was carried out for the first time in toluene using the rare earth coordination catalyst: $Y(P_{204})_3$–$Al(i\text{-}Bu)_3$–H_2O. The polymerization activity is strongly dependent upon the molar ratio of these three components and polymerization conditions. This new catalyst gives high molecular weight poly(ethylene oxide) with a high reaction rate and a high yield. Poly(ethylene oxide) so prepared was characterized by infrared spectrophotometry, differential scanning calorimetry and X-ray diffraction.
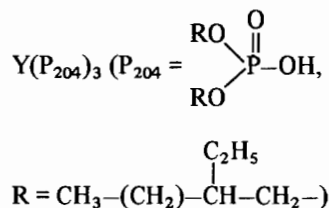
Introduction

High molecular weight poly(ethylene oxide) is one of the commonly used water soluble polymers, widely used as adhesive, surfactant, plasticizer, dispersant, lubricant and sizing etc. A variety of catalysts have been developed for the polymerization of epoxides [1–3]. But only a few catalysts give high molecular weight poly(ethylene oxide) with a high reaction rate. For instance, the $Al(i\text{-}Bu)_3$–H_2O system gives a high reaction rate and high conversion, but a polymer of low molecular weight.

It has been shown for the first time that the rare earth coordination catalyst $Y(P_{204})_3$–$Al(i\text{-}Bu)_3$–H_2O can polymerize ethylene oxide into high molecular weight polymers with a high reaction rate. In this paper, we report some characteristics of the polymerization, with emphasis on the effect of the molar ratio of these three components and polymerization conditions on catalytic activity, as well as the properties of the rare earth poly(ethylene oxide) so obtained.

Experimental

Ethylene oxide was thoroughly dried with calcium hydride before use. Toluene was refluxed over a molecular sieve (4 Å).

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$$Y(P_{204})_3 \quad (P_{204} = \begin{array}{c} RO \\ \diagdown \\ RO \end{array} \underset{}{\overset{\displaystyle O \atop \|}{P}}-OH,$$

$$R = CH_3-(CH_2)-\underset{\underset{C_2H_5}{|}}{CH}-CH_2-)$$

was prepared according to ref. 4. Its purity was confirmed by differential thermal analysis.

Polymerization of ethylene oxide was carried out in toluene under nitrogen. The resulting polymer was precipitated and washed several times by hydrogenated benzine, and then dried *in vacuo*.

The intrinsic viscosity of the polymers prepared was determined by Ubbelohde viscometer in water (0.025 g PEO/50 ml) at 30 °C. The viscosity-average molecular weight was calculated according to the following equation [5]

$$[\eta] = 12.5 \times 10^{-5} \, \bar{M}_\eta^{0.78} \, (30 \, °C)$$

The infrared spectra of poly(ethylene oxide) were recorded on a Nicolet-5D-FTIR spectrophotometer. Thermal analysis was performed on a CDR-1 calorimeter. X-ray diffraction was taken on a Geigerflex D/Max-rA diffractometer.

Results and Discussion

Features of Polymerization

The effect of the Al/Y molar ratio on polymerization is illustrated in Table 1. It is seen from the data that with an increasing molar ratio of Al/Y, the conversion of the polymerization increased markedly to attain the maximum value. The molecular weight of the resulting polymer was also significantly influenced by the Al/Y molar ratio. A molecular weight as high as 2.85×10^6 poly(ethylene oxide) was obtained at Al/Y = 6 under the polymerization conditions tested.

In order to check the effect of the H_2O/Al molar ratio on the polymerization, the polymerization was

TABLE 1. Effect of the Al/Y Molar Ratio[a]

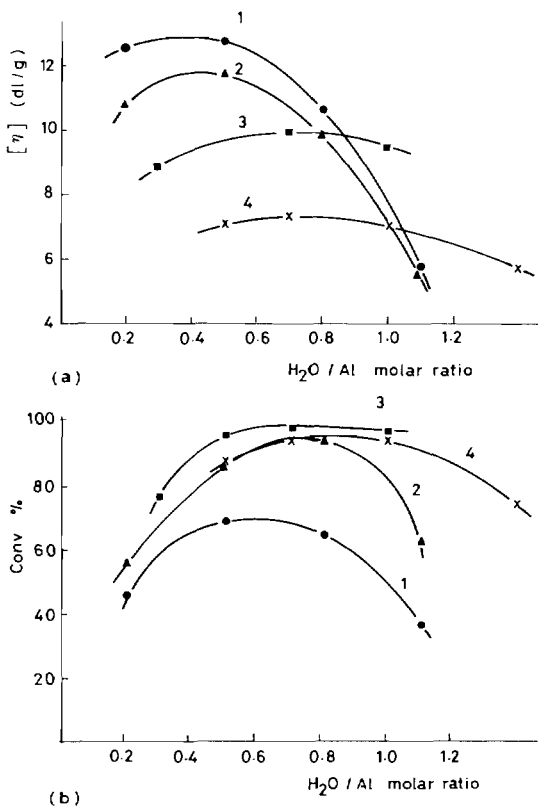| Al/Y	4		5		6		7	
[Y] (mmol/l)	conversion (%)	$\bar{M}_\eta$ 10^{-4}	conversion (%)	$\bar{M}_\eta$ 10^{-4}	conversion (%)	$\bar{M}_\eta$ 10^{-4}	conversion (%)	$\bar{M}_\eta$ 10^{-4}
6.72	10.1	43.9	29.7	125.8	38.8	260.3	56.2	182.6
10.5	21.9	73.1	52.1	161.3	66.7	220.3	79.4	158.5
14.7	38.6	130.1	73.5	169.2	78.1	202.4	95.2	149.3
18.9	49.5	157.3	69.1	157.1	86.2	284.9	100.0	109.0

[a][EO] = 2.5 mol/l, H_2O/Al = 0.5, 70 °C, 7 h.

Fig. 1. Effect of H_2O/Al molar ratio on [η] (a) and conversion (b). Al/Y = 6 (1), 8 (2), 12 (3), 16 (4); [Y] = 9.75 × 10^{-3} mol/l; [EO] = 2.5 mol/l; 70 °C; 7 h; toluene.
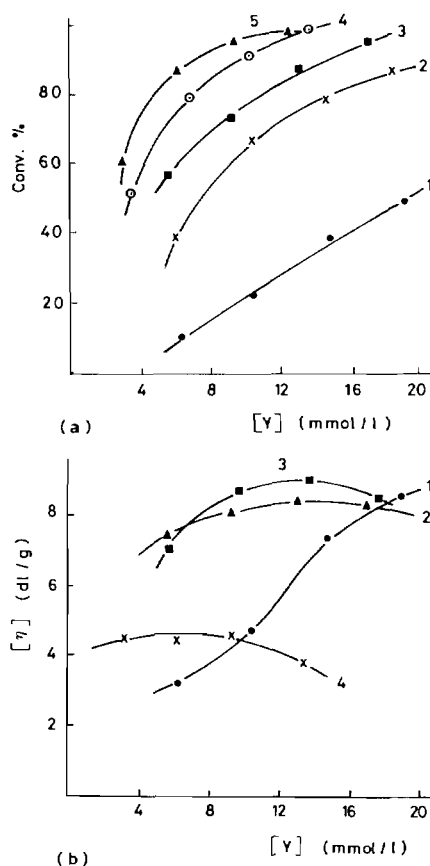

Fig. 2. Effect of [Y] on polymerization with H_2O/Al = 0.5, [EO] = 2.5 mol/l, 70 °C, 7 h, toluene. (a): Al/Y = 4 (1), 6 (2), 8.37 (3), 12 (4), 17.64 (5); (b): Al/Y = 4 (1), 5 (2), 8.37 (3), 17.64 (4).

performed with different H_2O/Al molar ratios under several given Al/Y molar ratios. Figure 1 indicates that the influence of the H_2O/Al molar ratio is far less critical than that of Al/Y. The favourable H_2O/Al molar ratio is in the range of 0.3 to 0.8.

Figure 2 illustrates the effect of the catalyst concentration on the polymerization of ethylene oxide under the conditions [EO] = 2.5 mol/l, 70 °C, 7 h. The yield of poly(ethylene oxide) increased as the catalyst concentration increased. The most favourable catalyst concentration is in the range of 9 × 10^{-3} to 15 × 10^{-3} mol/l. Maximum intrinsic viscosity of

poly(ethylene oxide) can be reached at a higher Al/Y molar ratio with lower catalyst concentration.

The effect of temperature on polymerization is summarized in Table 2. The data show that both the conversion of the monomer and the intrinsic viscosity of poly(ethylene oxide) increase with an increase of temperature between 40 and 80 °C.

The effect of reaction duration on polymerization is shown in Fig. 3. The yield of poly(ethylene oxide)

TABLE 2. Effect of Temperature on Polymerization[a]

T (°C)	40	50	60	70	80
Conversion (%)	20.4	30.0	37.6	38.6	62.8
$[\eta]$ (dl/g)	5.27	7.42	8.22	9.48	13.24

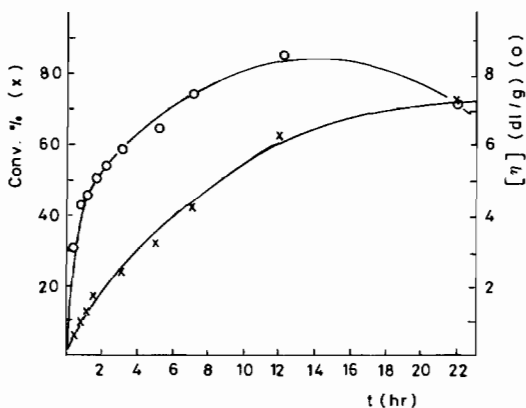[a]Al/Y = 6, H_2O/Al = 0.5, [Y] = 7.3 × 10^{-3} mol/l, [EO] = 2.5 mol/l, 7 h, toluene as solvent.

Fig. 3. Effect of reaction duration. Al/Y = 6, H_2O/Al = 0.5, [Y] = 7.4 × 10^{-3} mol/l, [EO] = 2.5 mol/l, 71.5 °C, toluene.

increased linearly within 2 h and deviation occurred afterwards which may be caused by the viscose reaction medium. The intrinsic viscosity of the resultant poly(ethylene oxide) increased with the duration of polymerization within 12 h. The decrease of the molecular weight of the resulting polymer at more than 12 h may be due to the degradation of poly(ethylene oxide).

The above results indicate that the $Y(P_{204})_3$–Al(i-Bu)$_3$–H_2O catalytic system is an effective catalyst for preparing high molecular weight poly(ethylene oxide).

Characterization of Poly(ethylene oxide)

The poly(ethylene oxide) so prepared has a high molecular weight, as high as 2.85 × 10^6.

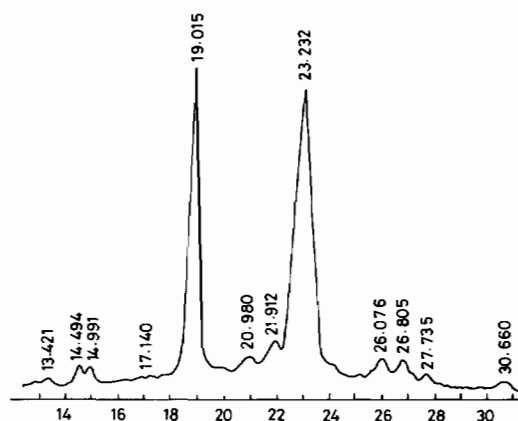The infrared spectra of poly(ethylene oxide) characterized by a strong absorption peak at 960

Fig. 4. Exemplary X-ray pattern taken from the poly-(ethylene oxide).

cm^{-1} reveal that the specimens are crystalline polymers.

Indeed, the X-ray diffraction spectra of poly(ethylene oxide), as shown in Fig. 4, shows that there are two intense and sharp reflections at Bragg angles of 2θ = 19.015° and 23.232° with several very weak reflections. It has been found that rare earth poly(ethylene oxide) so prepared has a crystallinity of 60–70% according to the method reported in ref. 5.

The differential scanning calorimetric diagram of the polymer shows the existence of two peaks at 64–71 and 415 °C, which are attributed to crystallization and thermal decomposition respectively.

References

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