

'Immortal' Polymerization. Polymerization of Epoxide catalysed by an Aluminium Porphyrin-Alcohol System

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Ring-opening polymerization of epoxide catalysed by a (tetraphenylporphinato)aluminium chloride-alcohol system affords a polyether having a controlled molecular weight of narrow distribution with the number of the polymer molecules exceeding the number of aluminium porphyrin molecules; this is due to exchange between the alcohol and the (porphinato)aluminium alkoxide, which is the active species, resulting in the 'immortal' nature of the polymerization.

Living polymerization¹ is of interest with respect to the synthesis of polymers with a controlled molecular weight of narrow distribution. Typically, the initiation and propagation reactions proceed uniformly with respect to all polymerizing molecules, neither termination nor chain transfer taking place, forming a polymer with a uniform molecular weight, the number of the polymer molecules being equal to the number of initiator molecules.

A representative example is the polymerization of styrene initiated by an alkali metal species.² However, the living nature of this polymerization does not mean immortality, and the anionic growing species is 'killed' by reaction with protic species such as water to give a 'dead' polymer molecule.

This communication describes the first example of 'immortal' polymerization with anionic or nucleophilic growing species, where the growing polymer is not 'killed' even in the presence of a protic compound that reacts with the growing species. The ring-opening polymerization of epoxide to form polyether by the (tetraphenylporphinato)aluminium chloride (TPPAI₂Cl)-alcohol system gives a polymer with a controlled molecular weight of narrow distribution where the number of the polymer molecules exceeds the number of aluminium porphyrin molecules. Although the name 'immortal' polymer was previously used for poly(ethylene sulphide) formed using a diethylzinc-water catalyst,³ the results reported only show some of the characteristics of a 'living' polymer but no accurate determination of the molecular weight was reported.

Polymerization of 1,2-epoxypropane by TPPAI₂Cl⁴ proceeded readily at room temperature in the absence or presence of methanol (Table 1). The molecular weight of the product was found to decrease with increasing quantity of added MeOH, as determined by gel permeation chromatography (g.p.c.). Quite unexpectedly, the molecular weight distribution of the product was very narrow even when the reaction was performed in the presence of MeOH, the ratio of

the weight average and the number average molecular weights (\bar{M}_w/\bar{M}_n) ranging from 1.07 to 1.17. Because of the narrow molecular weight distribution, the number of the polymer molecules (N_p) may be calculated on the basis of the number average molecular weight. In the absence of MeOH, the number of the polymer molecules was equal to that of TPPAI₂Cl (N_{Al}). In the presence of MeOH, the number of the polymer molecules was found to increase, indicating the fact that MeOH participates in the reaction as a chain transfer agent. At any ratio of epoxide to TPPAI₂Cl, the number of the polymer molecules formed per one TPPAI₂Cl molecule was found to correspond to the ratio $\{[MeOH] + [TPPAI_2Cl]\} / [TPPAI_2Cl]$. Thus, the polymer molecules grow from TPPAI₂Cl as well as from all the molecules of MeOH present.

Since the active propagating species of the polymerization of epoxide by TPPAI₂Cl is a porphinatoaluminium alkoxide (TPPAIOR),⁴ these findings indicate that rapid exchange between the aluminium alkoxide and alcohol takes place, resulting in growth of a polymer molecule on the newly formed aluminium alkoxide. In fact, the presence of chlorine from TPPAI₂Cl and an alkoxy group from the alcohol at the

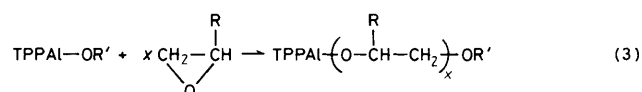
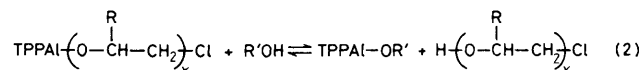
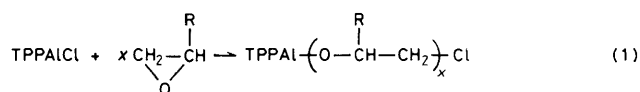


Table 1. Polymerization of 1,2-epoxypropane (propylene oxide, PO) by the TPPAI₂Cl-MeOH system.^a

[MeOH] ₀ /[TPPAI ₂ Cl] ₀	[PO] ₀ /[TPPAI ₂ Cl] ₀	Time (h)	Conversion (%)	\bar{M}_n^b	\bar{M}_w/\bar{M}_n^b	N_p/N_{Al}^c
0	200	48	100	10000	1.17	1.2
1	200	48	100	6500	1.13	1.8
3	200	48	100	3100	1.07	3.7
7	200	48	100	1500	1.07	7.7
9	200	0.5	70	780	1.10	10.4
9	200	48	100	1300	1.08	8.9
24	500	48	100	1200	1.08	24.2
49	1000	600	75	900	1.09	48.3

^a At room temperature, without solvent. ^b Estimated by g.p.c. using poly(1,2-epoxyethane) and poly(propylene glycol) as standard. ^c Ratio of the number of polymer molecules (N_p) to TPPAI₂Cl (N_{Al}).

end of the polymer molecule was confirmed by the ^{13}C n.m.r. spectrum of the product.

The formation of a polymer with a narrow molecular weight distribution even in the presence of alcohol indicates that exchange between TPPAlOR and alcohol takes place much faster than propagation, *i.e.*, insertion of the epoxide into TPPAlOR (equations 1–3). In fact, the rapid exchange between TPPAlOR and alcohol was observed in the ^1H n.m.r. spectrum of the mixture. For example, when a CDCl_3 solution of (tetraphenylporphinato)aluminium ethoxide (TPPAIOEt) was added to an equimolar amount of 2,2-dimethylpropanol at room temperature, the signals due to TPPAIOEt decreased in intensity while new signals assigned to TPPAlOCH₂CMe₃ appeared within 7 min, and no further change was observed, attaining an equilibrium ratio of TPPAIOEt to TPPAlOCH₂CMe₃ of 63 to 37.

In the forward reaction of equation (2), the alcohol may be regarded as the chain transfer agent for the growing porphinatoaluminium alkoxide. In contrast to the usual chain

transfer reaction, however, the polymer molecule liberated is also an alcohol, therefore it may again act as a chain transfer agent and again become an active species (the reverse reaction). As a result, the polymer molecules are not 'killed' but become temporarily 'dormant' by the reaction with alcohol, therefore the overall polymerization reaction can be considered 'immortal'. Preliminary studies have shown that the polymerization of epoxide by aluminium porphyrin is 'immortal' even in the presence of acetic acid or hydrogen chloride.

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