Polymerization of Methacrylonitrile with Triethylaluminium

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The rate of polymerization of methacrylonitrile in the presence of triethylaluminium in benzene varies linearly with [monomer] and square of [catalyst] and proceeds by an anionic mechanism.
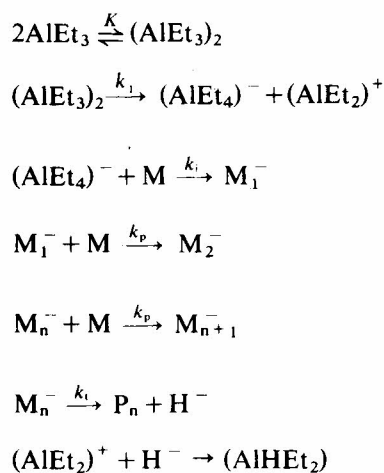
The polymerization of vinyl monomers in the presence of $Al(C_2H_5)_2Br$-$Co(acac)_3$ catalyst system was reported[1] to proceed by an anionic coordination mechanism. However, this catalyst system failed to initiate the polymerization of methacrylonitrile. Triethylaluminium was found to initiate the polymerization of this monomer in the absence of any other transition metal compound. Hence a kinetic study was made on triethylaluminium-methacrylonitrile system in benzene at 50°C. This monomer has been chosen for two reasons: (i) it contains a highly electronegative cyano group which should facilitate a nucleophilic attack and (ii) absence of α-hydrogen atom may sustain chain termination by hydrogen abstraction from a polymer molecule by a growing chain, leading to subsequent branching from the newly formed active center.

Thiophene-free benzene, dried over anhydrous calcium chloride was distilled and stored over sodium wire. Methacrylonitrile, free from inhibitors, was distilled under reduced pressure and stored under nitrogen atmosphere. Triethylaluminium was prepared as reported in the literature[2].

Polymerization was carried out in a dry box which was continuously flushed with pure nitrogen. In each run, benzene, triethylaluminium and methacrylonitrile were mixed, thermostated and after a definite time interval poured into ethanol, the precipitated polymer filtered, dried *in vacuo* (40 mm Hg/40 C) and weighed.

At constant [triethylaluminium], the rate of polymerization varied linearly with the first power of [monomer], whereas at constant [monomer] the rate was dependent on the square of [catalyst]. The activation energy was calculated to be 34.3 kJ mol^{-1},

the magnitude of which was similar to that expected for an ionic mechanism[3]. The rates of polymerization in the absence (1.42×10^{-6} mol dm^{-3}) and presence of 0.025 mol dm^{-3} hydroquinone (1.4×10^{-6} mol dm^{-3}) were found to be the same, thus providing further support to the ionic mechanism. Similar observations were reported by Beaman[4] for an anionic mechanism for the polymerization of methacrylonitrile by butylmagnesium bromide and triphenylmethylsodium. The polymerization of a number of monomers in the presence of butylmagnesium, benzylmagnesium, phenylmagnesium and ethylmagnesium bromides was earlier shown to proceed by an anionic mechanism[5]. Hence, an anionic mechanism, as depicted in Scheme 1, may be assumed in the present system also.

$$2AlEt_3 \overset{K}{\rightleftharpoons} (AlEt_3)_2$$

$$(AlEt_3)_2 \overset{k_1}{\longrightarrow} (AlEt_4)^- + (AlEt_2)^+$$

$$(AlEt_4)^- + M \overset{k_i}{\longrightarrow} M_1^-$$

$$M_1^- + M \overset{k_p}{\longrightarrow} M_2^-$$

$$M_n^- + M \overset{k_p}{\longrightarrow} M_{n+1}^-$$

$$M_n^- \overset{k_t}{\longrightarrow} P_n + H^-$$

$$(AlEt_2)^+ + H^- \rightarrow (AlHEt_2)$$

Scheme 1

Assuming steady state kinetics the rate expression has been derived to be

$$R_p = \frac{k_p k_1 K [AlEt_3]^2 [M]}{k_t}$$

References

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