Electrochemical Formation of Initiators for Polymerization of Ethylene

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Summary Coupling of aluminium and transition-metal anodes in an anhydrous electrolytic solution saturated with ethylene initiates polymerization to oils or to high molecular weight polyethylene.

A NEW electrochemical method for preparing metal-containing catalysts for olefin polymerization has been studied. It involves the anodic dissolution of aluminium with a transition metal in an electrolytic solution such as 1,2-dichloroethane containing a tetra-alkylammonium salt. The electrolytic solution is contained in a pressure-resistant cell,[1] stirred by rotation around an inclined axis, and dipped in a thermostatic bath, usually at 0°. The system is electrolysed with aluminium as anode; when about 1000 C have passed, current flow is reversed and 10—60 C are fed with a transition metal (usually chromium, titanium, or vanadium) as anode. The anodic current efficiency in the oxidation of aluminium corresponds to a mean oxidation state of 1·5—1·7. The cathodic reaction involves 1,2-dichloroethane, as hydrolysis and aqueous extraction of the effluent show formation of chloride ion with current efficiency corresponding approximately to $1Cl^-: 1e^-$.

Polymerization of ethylene with electrochemical initiation

Expt.	Electrical charge (C) Al anode	 Cr anode	Reaction time (h)	$P(C_2H_4)$ (atm) Initial	 Final	Polymer obtained (g) Oils	 Polyethylene
1	530	9	31	33·0	7·8	0·25	12·10
2	1008	18	8	28·4	1·8	0·30	16·40
3	1045	19	269	36·3	15·7	7·77	3·82
4	1160		108	31·8	15·8	5·45	8·35
5	5800		162	28·1	15·9	35·90[a]	2·30

Solvent: 1,2-dichloroethane 36 g; electrolyte Bu_4NCl 0·5 g.
Expts. 1—3: Al 99·99% (60 cm^2 wetted surface); electrodeposited Cr (5 cm^2); currents 5—20 mA.
Expts. 4—5: technical grade Al (60 cm^2 in expt. 4; 5 cm^2 in expt. 5); current 10—2 mA (expt. 4) or 10 mA (expt. 5), during all reaction time.
Constant current maintained in each expt. Voltages in the range 30—5 V.
Temperature: expts. 1, 2, 4, and 5: 0°; expt. 3: 25°.
[a] Cell refilled with C_2H_4 during reaction.

The best polymerization results have been obtained by coupling aluminium and chromium anodes and using tetrabutylammonium chloride as electrolyte, at 0°. In general, aluminium is dissolved first, while the chromium electrode acts as the cathode. Under conditions of low current, absence of water, and high purity of the aluminium anode only a small amount of ethylene, if present, is converted into low molecular weight polymers at this stage. After this the chromium electrode is anodized and high molecular weight polyethylene (m.p. initial 132°, final 135°, by thermal differential analysis; crystallinity 85—90%) is vigorously produced. If ethylene is already present during electrolysis polymerization starts as soon as the chromium is anodized and continues after the current is stopped.

As the rate of polymerization and the overall conversion depend on the quantity of chromium anodically dissolved, it is possible to convert limited quantities of ethylene into polyethylene in high yield by means of a short current pulse. As a tough film of polymer forms on the surface of the chromium in a few minutes, further electrolysis requires high voltages (100—300 V for 1—3 mA), and only limited improvements in rate and conversion can be obtained by successive short pulses in electrical feed. After electrolysis, polymer forms as a spongy mass of increasing thickness around the first compact layer adhering to the chromium electrode.

The best rates of conversion are obtained (i) if the chromium is anodized at a relatively high current density, with vigorous stirring, so that a quantity of chromium is dissolved before the anode is completely polarized by the polymer layer (expt. 1), or (ii) by adding ethylene when aluminium and chromium are both present in solution (expt. 2). Comparable results have been obtained with sublimed chromium or electrodeposited chromium anodes.

If the temperature is increased above 0°, lower rates of conversion are found, and significant amounts of liquid, branched chain, partly unsaturated polymers are formed, by a reaction which progressively competes with the formation of polyethylene as temperature increases (expt. 3).

Composite anodes, which allow simultaneous dissolution of aluminium and chromium, can be used, as well as alloys of aluminium with low chromium content.

Technical grade aluminium, which contains small amounts of transition metals, also allows formation of the same kind of polyethylene[2] (expt. 4). The relative proportions of oils and polyethylene also depend on anodic current density; higher current densities lead to lower yields in polyethylene, so that liquid polymers are obtained as the main product (expt. 5). Liquid fractions of polymerized products are separated from polyethylene by extraction with n-pentane or n-heptane; both products are hydrolysed with $HCl-H_2O-MeOH$ mixtures, and volatile components are then removed *in vacuo*.

At room temperature, or above, anodic dissolution of pure aluminium alone causes the formation of liquid polymers; however, at 0°, polymerization of ethylene to branched chain polymers also takes place in the absence of transition metal if the concentration of aluminium in solution is great enough. Stirring the solution during electrolysis and low anodic current densities are therefore important in avoiding local over-concentration of anodic products.

The polymerization is initiated by various transition metals, which are present in the system as metallic electrodes. This method, therefore, allows an "absolute" comparison among the efficiencies of different transition metals as polymerization catalysts. Kinetic studies on electrochemically initiated polymerizations of vinyl compounds such as styrene and methyl methacrylate,[3,4] and diolefins such as butadiene,[4,5] have been reported recently.

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