European Polymer Journal, 1966, Vol. 2, pp. 9–14. Pergamon Press Ltd. Printed in England.

POLYMERIZATION OF METHYL METHACRYLATE BY ORGANO-METALLIC COMPOUNDS

THE MECHANISM OF INITIATION BY TRIETHYL-ALUMINIUM*

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(*Received* 18 *July* 1965)

Abstract—The polymerizations of methyl methacrylate and methyl acrylate in the presence of triethyl-aluminium are photochemical. The initiator is a yellow complex formed between monomer and triethyl-aluminium. Experimental evidence is weighted against a radical mechanism. An anionic insertion mechanism involving the photo-excited state of the yellow complex is proposed.

THE EARLIER parts of this series(1, 2) were mainly concerned with initiation by Grignard reagents. Some results on polymerizations initiated by triethyl-aluminium were also reported as this system reproduced the kinetic peculiarities of the Grignard-initiated polymerizations. Both systems show an optimum temperature for polymerization in the region 235–260° K. The initiation of methyl methacrylate polymerization by triethyl-aluminium had previously been reported only in patent literature.(3)

The kinetic similarities were cited as evidence that the mechanisms of initiation by Grignard reagents and triethyl-aluminium were very similar.(1) This opinion can no longer be sustained. Results presented here show that earlier workers failed to observe an important factor in the mechanism: the polymerization initiated by triethyl-aluminium is *photochemical.*

EXPERIMENTAL

Triethyl-aluminium, obtained from Ethyl Corporation, New York, was purified by distillation under high-vacuum and dispensed into graduated break-seal capsules. During this operation, and all subsequent manipulations, the pure samples were handled in sealed glass under high-vacuum, the only tap being a Springhams greaseless high-vacuum tap, with Viton A diaphragm, connecting the apparatus to the pumping manifold.

Monomers were prepared from commercial samples. After stabilizers had been removed by alkaline washes, the monomers were washed and dried by reflux over calcium hydride. Three high-vacuum distillations were carried out from fresh calcium hydride and the monomers were stored at −20° over calcium hydride in special phials under vacuum. Methyl acrylate polymerized slowly at room temperature in the presence of calcium hydride.

Toluene and other solvents were similarly treated.

Dilatometers were made by sealing a calibrated capillary tube on to the empty end of the break-seal capsules containing triethyl-aluminium. Monomer and diluent were distilled into the empty chamber and capillary and were mixed with the initiator by breaking the breakseal with a glass-sheathed magnet inserted previously. The dilatometers were placed in a Townson and Mercer Minus-Seventy thermostat bath, and the contraction followed.

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* Presented at the 2nd Australian Metal-organic and Co-ordination Chemistry Conference, University of New South Wales, 25 May, 1965.

Precautions should be observed in all sealed tube experiments of this type. Firstly the reaction on mixing is very exothermic, so the initial breaking of the seal should be done at reduced temperature (200–230°K), and also in the dark if the initial stages of polymerization are to be observed. Secondly in all sealed-tube experiments care must be taken to drive off adsorbed triethyl-aluminium from glass surfaces close to the seal before heating strongly. A sealed silica tube in this laboratory exploded on warming up to room temperature from liquid nitrogen temperature. The extensive aluminium mirror in the region of the seal and quantities of ethylene found in the vacuum line after sealing indicated that the tube burst under the pressure (v.p. 70 atm/25°) of ethylene formed by the pyrolysis and condensed in the tube during the sealing operation.

RESULTS

1. Toluene solutions containing triethyl-aluminium and methyl methacrylate have a broad absorption peak in the visible region with a maximum at ~400 mμ. In the presence of excess monomer the peak diminishes slowly in the presence of light at room temperature as polymerization occurs. The peak does not disappear entirely. In polymerization experiments the fully polymerized gels were always yellow and the colour persisted until destroyed by exposure to methanol, water or air.

2. Experiments with methyl acrylate showed that, when triethyl-aluminium was in five-fold molar excess (i.e. Al/MA ≥ 5), the colour did not fade when the tubes lay on the

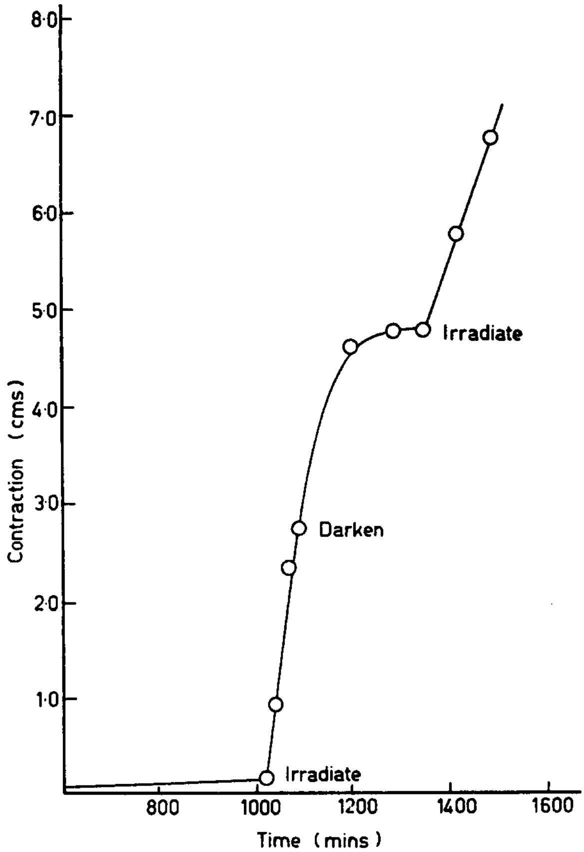


FIG. 1. Conversion curve (arbitrary units) for polymerization of methyl methacrylate in toluene solution in the presence of triethyl-aluminium at 256°K in darkness and illuminated with 100 W tungsten light.

bench at ambient temperature and illumination for many days. No polymerization occurred under these conditions.

3. N.m.r. spectra⁽⁴⁾ confirmed that under these conditions there is no loss of vinyl groups. The vinyl hydrogen region of the spectrum was completely transformed and the methoxyl hydrogen peak split, but the integrated trace showed that the ratio of vinyl to methoxyl hydrogens remained 1:1.

At triethyl-aluminium–monomer ratios less than 2:1, the vinyl–methoxyl hydrogen ratio, in methyl methacrylate, decreased from 2:3 when the tubes were illuminated at room temperature. The n.m.r. spectra were complicated by the presence of polymer and other saturated substances.

4. Figure 1 shows the course of a typical methyl methacrylate polymerization in toluene solution at 256°K. During the light period, the dilatometer was illuminated with a 100 W tungsten filament lamp.

Similar conversion curves were obtained for methyl acrylate polymerization at 258°K. At 273°K, the polymerization decayed more rapidly when the dilatometer was darkened. The lifetime was only a few minutes.

5. Temperature cycling experiments gave results very similar to those shown in Fig. 4 of Ref. 2, which were obtained from Grignard reagent initiated polymerization.

6. At constant illumination and reagent concentration, the intrinsic viscosity of chloroform solutions of the polymer produced, i.e. that part of the chloroform-soluble products insoluble in cold methanol, increased with conversion. The intrinsic viscosity of the total soluble products similarly increased with conversion.

7. A 1:1 molar mixture of methyl methacrylate and styrene polymerized to high conversion in toluene at 273°K by triethyl-aluminium gave copolymer, or polymer mixture, containing 60 per cent methyl methacrylate and 40 per cent styrene.

CONCLUSIONS

1. Results 1, 2, 4 and 6 contra-indicate a free-radical, stationary-state mechanism. Chains could be initiated by radicals derived from either direct photolysis or decomposition of an unstable photolysis product of the yellow complex. The energy of the light seems too small for the former and the temperature too low for the latter. Furthermore both are irreversible processes and would be inconsistent with the persistence of the colour at low monomer concentration under conditions that lead to fading and polymerization at higher monomer concentrations.

Figure 2 shows the decay of a typical methyl methacrylate polymerization at 256°K after light had been removed. Also shown are the theoretical decay curves for a methyl methacrylate radical polymerization at these temperatures, calculated using experimental values for the termination constant k_t at this temperature.⁽⁵⁾ Extrapolation of the higher temperature data⁽⁶⁾ to this temperature leads to higher values of k_t. The discrepancy with the observed decay would be greater in this case.

In a radical, stationary-state polymerization, the rate of approach to the stationary state, after illuminating, is approximately the same as the rate of decay from the stationary state, when illumination ceases. This is not the case (Fig. 1).

Increase in molecular weight with conversion is common with anionic and anionic insertion polymerizations, where initiation is often rapid and termination slow. In radical polymerization, where initiation is slower than termination, the molecular weight of the polymer is relatively insensitive to conversion over a wide range.

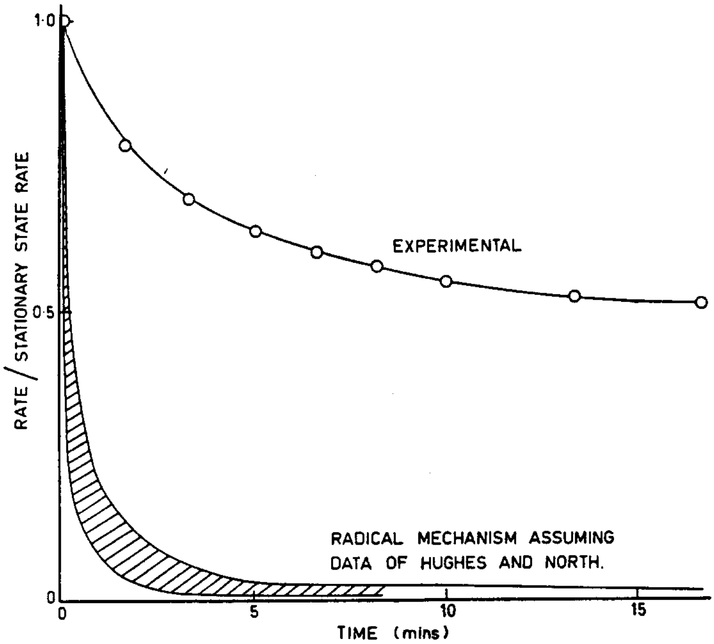
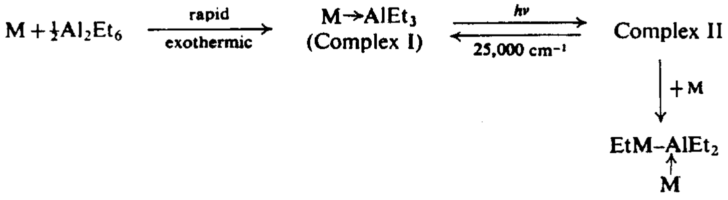


FIG. 2. The decay of polymerization at 256°K from the stationary state, after removing illumination, as observed and as predicted for a radical polymerization assuming the termination coefficients of Hughes and North.(5)

2. The copolymerization evidence is not inconsistent with a radical mechanism. At 333° K the polymer produced from this mixture by a radical mechanism would have the reversed composition. The reactivity ratios at 273° K are not known. On the other hand, it is becoming increasingly evident that it is unwise to generalize about reactivity ratios in anionic insertion polymerizations. These are not only a function of the monomers but of initiator and medium also. One would expect a preference for incorporation of methyl methacrylate, but stryene compositions as high as 30 per cent have been reported for the polymerization of 1 : 1 styrene–methyl methacrylate mixtures by Grignard reagents at room temperature.(7)

3. The optimum temperature effect, *at constant illumination*, is still very similar to that observed in Grignard reagent systems. The mechanism proposed to explain this effect:(2) rapid initiation, propagation requiring energy of activation, and a termination or deactivation reaction requiring a higher energy of activation is supported by new evidence. Result 4 confirms that the deactivation process has a high energy of activation.

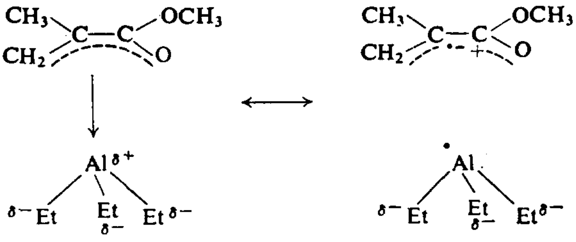
4. The experimental evidence is consistent with an initiation mechanism:



$$\begin{tikzcd} M + \tfrac{1}{2}Al_2Et_6 \arrow[r, "\text{rapid}", "\text{exothermic}"'] & \begin{matrix} M\rightarrow AlEt_3 \\ (\text{Complex I}) \end{matrix} \arrow[r, shift left, "h\nu"] & \text{Complex II} \arrow[l, shift left, "25{,}000\ cm^{-1}"] \arrow[d, "+M"] \\ & & \begin{matrix} EtM\text{–}AlEt_2 \\ \uparrow \\ M \end{matrix} \end{tikzcd}$$

The reversibility of the second step and the necessity of a second monomer in the insertion reaction are required by the observation that the colour does not fade in the presence of excess triethyl-aluminium.

5. This last observation, and the breadth of the absorption band, suggest that Complex I and II may possibly represent the lower and upper states of a charge-transfer complex:



The increased positive charge on the monomer in the upper state, due to a higher proportionate contribution from the structure on the right, would enhance the possibility of the insertion of monomer into the aluminium–ethyl bond. If a charge-transfer complex is present, it is easy to see how an insertion polymerization may be photochemical.

6. The detailed mechanism is still untested, but the evidence to hand shows that the true initiator is not the organo-metallic compound but a compex between this and the monomer. It has been suspected for many years that these anionic insertion polymerizations were co-ordination polymerizations. The present system is the first case where co-ordination of the monomer has been shown to play an essential part in the initiation mechanism.

Acknowledgements—Thanks are due to Dr. T. Kurucsev, of this department, and Dr. T. Mole, of C.S.I.R.O., for helpful advice and discussion, and to C.S.I.R.O. for the award of a post-graduate scholarship to B.A.C.

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Résumé—Les polymérisations de méthyl-méthylacrylate et de méthyle-acrylate, en présence d'aluminium-triéthyle sont photochimiques. L'agent initiateur est un complexe jaune formé entre un aluminium-triéthyle et monomère. L'évidence expérimentale est évaluée par rapport à un mécanisme radical. Un mécanisme à insertion anionique, exigeant un état photo-excité du complexe jaune y est proposé.

Sommario—Le polimerizzazioni di metil-metilacrilate e di metil-acrilate, in presenza d'alluminio-trietile sono fotochimiche. Il catalizatore è un complesso giallo formato fra un alluminio-trietile e monomero. Le prove sperimentali sono valutate in rapporto ad un mecanismo radicale. Un mecanismo a inserzione anionica, richiedendo uno stato foto-eccitato del complesso giallo vi è proposto.

Zusammenfassung—Die Polymerisationen von Methyl Akrylsäuremethylester und Akrylsäuremethylester in Gegenwart von Triäthylaluminium sind lichtchemisch. Der Initiator ist ein gelber Komplex welcher zwischen dem Monomer und dem Triäthylaluminium gebildet wird. Ein Versuchsbeweis wird gegen einen radikalen Mechanismus erwogen. Ein anionischer Zwischenschaltungsmechanismus welcher den photo-erregten Zustand eines gelben Komplexes einschliesst, wird vorgeschlagen.