Polymerisation of Vinyl Monomers with Benzyl Zirconium Compounds

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Summary The photo-induced polymerisation of styrene by tetrabenzylzirconium proceeds by two mechanisms depending on the wavelength of the radiation used.

WE have studied the polymerisation of styrene using $Zr(benzyl)_4$[1,2] as initiator in toluene as solvent at 30 °C. The polymerisation is photochemically activated and three distinct polymerisation processes occur depending on the wavelength (λ) of light employed. Our results are summarised in the Figure, where R is the initial rate of polymerisation measured dilatometrically in M s^{-1} and I is the intensity of radiation used. R_λ and R_d are the rates at wave-length (λ) and in the dark respectively. At $\lambda \geqslant 600$ nm the rate of polymerisation is close to that in the dark; when $450 < \lambda < 600$ the process is similar to the latter but photochemically activated; finally for $\lambda < 450$ nm the polymerisation rate is very much higher and increases progressively with wavelength reaching a maximum at 317 nm.

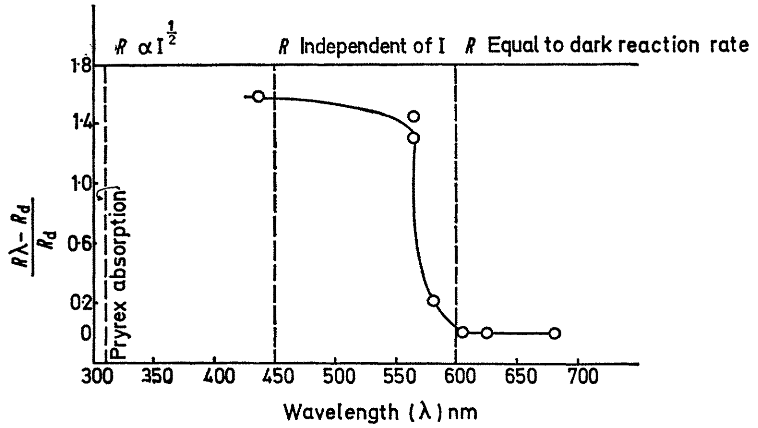


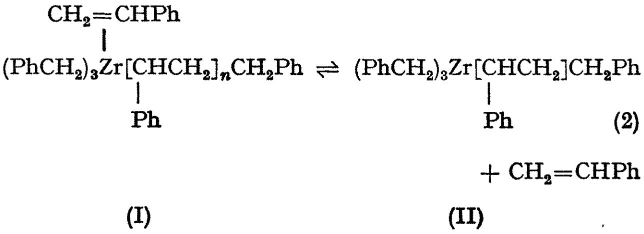
FIGURE. *Polymerisation of styrene at* 30 °C *in toluene at different wavelengths* $[M]_0 = 5M$, $[C]_0 = 0{\cdot}03M$, $R_d = 2{\cdot}6 \times 10^{-6}$ M s^{-1}

The kinetics of styrene polymerisation initiated by $Zr(benzyl)_4$ in the dark are closely represented by equation (1) where $[M]_0$ and $[C]_0$ are the initial concentrations of

$$R = A[M]_0^2[C]_0/(1 + B[M]_0) \qquad (1)$$

monomer and catalyst. The number average molecular weight is independent of the catalyst concentration and directly proportional to the monomer concentration, and the polydispersity is two. The energy of activation for the propagation reaction is approximately 10 kcal mol^{-1}. There are close kinetic similarities between this polymerisation process and the methyl methacrylate–$Cr(2\text{-}Me\text{-}allyl)_3$ system.[3] These catalysts polymerise ethylene at atmospheric pressure and at temperatures of −20 to 120 °C. Also the order of ease of polymerisation of a range of vinyl monomers is acrylonitrile $\gg$ methyl methacrylate = styrene $>$ *p*-bromostyrene. This evidence, together with additional data, which will be published elsewhere, indicates that the polymerisation proceeds by way of a co-ordinated-anionic type mechanism.

The photochemical polymerisation process occurring approximately in the range $450 < \lambda < 600$ is related to the dark reaction, *i.e.* the kinetics are similar to (1). An unusual feature is that although the polymerisation is photochemically activated the rate is independent of light intensity over most of the range. This is explained by the fact that the rate of chain termination is similarly increased at these wavelengths and values of $\overline{M}_n$ are half those obtained in the dark with identical catalyst and monomer concentrations. Propagation reactions for $\lambda > 450$ nm probably proceed through attack of the monomer on (I) which is present in low concentrations compared to (II).



$$\underset{\text{(I)}}{(PhCH_2)_3Zr\overset{CH_2=CHPh}{|}[\underset{|\atop Ph}{CH}CH_2]_nCH_2Ph} \rightleftharpoons \underset{\text{(II)}}{(PhCH_2)_3Zr[\underset{|\atop Ph}{CH}CH_2]CH_2Ph + CH_2{=}CHPh} \qquad (2)$$

Consistent with propagative species of type (I) is that substitution in the benzyl group directly affects the polymerisation rate. This is well illustrated for the polymerisation of ethylene in which it appears that substituents which give a more stable benzyl anion favour the polymerisation process. Thus $Zr(4\text{-}F\text{-}benzyl)_4$ was twice as active as $Zr(benzyl)_4$ whereas $Zr(3\text{-}Cl\text{-}benzyl)_4$ has only a tenth of the activity.

At wavelengths below *ca.* 450 nm the process is a free-radical polymerisation. This conclusion is derived from the fact $R \alpha I^{\frac{1}{2}}$ in this region, and, in the absence of monomer, $Zr(benzyl)_4$ is photolysed in toluene to give a range of products which are not formed at $\lambda > 450$, and are most probably obtained by attack of benzyl radicals on the solvent. These products include benzyltoluene, bibenzyl *etc.*

(Received, March 18*th,* 1971; *Com.* 342.*)*

[1] U.K. Patent Applications No. 26,923/69 and 26,924/69.

[2] U. Giannini, U. Zucchini and E. Albizzati, *Polymer Letters*, 1970, **8**, 405.

[3] D. G. H. Ballard and T. Medinger, *J. Chem. Soc. (B)*, 1968, 1176.