Thermal and photochemical decomposition of a styrene-oxygen copolymer*

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RESUMEN: En este trabajo se estudia la ruptura térmica y fotoquímica de un poli-peróxido de estireno de peso molecular 2100. A partir de medidas de la velocidad de polimerización del estireno fotosensitizado por el poli-peróxido se puede concluir que la recombinación primaria es de 0.66. Los parámetros de Arrhenius obtenidos para la ruptura térmica son considerablemente menores que los obtenidos para la ruptura del di-tert-butil peróxido.

SUMMARY: The thermal and photochemical cleavage of a styrene-oxygen copolymer of molecular weight 2100 was studied by measuring its efficiency as initiator of styrene polymerization. The polymerization rates were compared to those obtained employing di-tert-butyl peroxide as initiator. The photopolymerization study indicates a quantum yield of cage recombination in the polyperoxide of 0.66. The Arrhenius parameters for the thermal cleavage are considerably smaller for the poly-peroxide than for the di-tert-butyl peroxide.

The presence of peroxide linkages in a macromolecule is a source of inestability. The thermal[1,2,3], photochemical[1] and ultrasonic[4] degradation of polymers is sensitive to the extend of peroxide linkages incorporated to the macromolecule. Furthermore, this peroxide linkages can also be responsable, at least partially, for the autopolymerization of vinyl monomers observed at relatively low temperatures[3]. The efficiency with which a poly-peroxide degradates and initiates the polymerization will depend upon the cleavage rate and the probability of avoiding cage recombination. This last effect, which will be strongly dependent upon the solvent and the macroradical lenght, has not so far been evaluated in this type of systems. In the present work we report these type of data for alcoxy radicals produced in the photocleavage of styrene-oxygen copolymers and evaluate the rate parameters for the thermal cleavage of peroxide links in the macromolecule.

EXPERIMENTAL

The polyperoxide (PP) was prepared according to the method described by Miller and Mayo employing AIBN (0.02 N) as initiator at 50°C under 1 atmosphere of oxygen. The reaction time employed was of 24 hours. The polymer obtained has a molecular weight of 2100 (determined by osmometry). The NMR spectra shows, besides the aromatic hydrogens, only a doublet and a triplet assigned to the group $-O-O-CH_2-CH-O-O$, indicating that the monomeric units are "isolated" by peroxide linkages. ϕ

Photolysis were carried out employing a medium pressure mercury lamp and a $NiSO_4$ filter solution to isolate the 3130 Å line. The extent of the polymerization was evaluated by precipitation of the polymer in methanol. A similar procedure was employed in the thermal reactions.

Di-tert-butyl peroxide (DTBP) was employed as a "model" peroxide both in the thermal and photochemical reactions.

RESULTS AND DISCUSSION

The polymerization of styrene (M) in the presence of an added initiator (either DTBP or PP) can be represented by the following simplified reaction scheme

$$M \quad\rightarrow\quad R\cdot \tag{1}$$

$$\text{Peroxide} \quad\xrightarrow{k_d}\quad [\,2\,RO\cdot\,] \tag{2}$$

$$\xrightarrow{h_\nu}\quad [\,2\,RO\cdot\,] \tag{2'}$$

$$[\,2\,RO\cdot\,] \quad\rightarrow\quad \text{cage products} \tag{3}$$

$$[\,2\,RO\cdot\,] \quad\rightarrow\quad 2\,RO\cdot \tag{4}$$

$$RO\cdot \ (\text{or } R\cdot) + M \rightarrow \quad M\cdot \tag{5}$$

$$M\cdot + M \quad\xrightarrow{k_p}\quad M\cdot \tag{6}$$

$$2\,M\cdot \quad\xrightarrow{k_t}\quad \text{polymer} \tag{7}$$

where reaction (1) takes into account the autoinitiation. This simplified mechanism leads to

$$V_P^2 - (V_P^2)_o = \frac{\alpha\, k_d}{k_t}\; k_P^2\; M^2\; \text{Peroxide} \tag{8}$$

and

$$V_P^2 - (V_P^2)_o = \alpha \frac{I_a}{k_t}\; k_p^2\; M^2 \tag{9}$$

for the thermal and photochemically initiated process. In this Eqns. V_P is the polymerization rate in presence of the peroxide, $(V_P)_o$ is the autopolymerization rate, and α measures the fraction of radical pairs which scape from the primary cage. Eqns (8) and (9) assume that there are no primary radical losses. This is supported by the low rate of initiation employed and the high reactivity of alcoxy radicals[5]. Furthermore, Eqn (9) assumes a unitary photocleavage quantum yield. This is in agreement with the repulsive character of the excited peroxide surfaces[6].

If the results obtained employing DTBP and PP under conditions of equal I_a are compared, Eqn (9) reduces to

$$\frac{(V_P^2 - (V_P^2)_o)\, \text{DTBP}}{(V_P^2 - (V_P^2)_o)\, \text{PP}} = \frac{\alpha\, \text{DTBP}}{\alpha\, \text{PP}} \tag{10}$$

which allows an evaluation of α PP since α DTBP can be consider to be one[7]. The values obtained by this method were 0.34, 0.31 and 0.37 at 41°C, 50°C and 60°C respectively. We can conclude them that α PP is nearly 0.34 and practically temperature independent. This value is intermediate between that of small radicals and that of large macroradicals for which it is usually assumed that a $\alpha \approx 0$ in modelling free radical polymerization kinetics. This difference can be attributed to the smaller size of the macroradicals produced in the present work. The mean average number of our polymers is less than 20 and hence, after cleavage, at least one of the units has at least 50% probability of being composed by less than 6 monomer units. The present result seems to contrast with results given by Decker and Mayo[8] that show that in n-hexane solution oxidation of poly-propylene nearly all the initiating radicals scape the cage. Nevertheless, it has to be consider that in their work macroradicals are produced single and that only small peroxide radicals are caged in pairs.

If a value of $\alpha = 0.34$ is coupled with a quantum yield of product formation of 5[1], we can conclude that the chain lenght is nearly 15, a value very close to the degree of polymerization. This result could indicate that in absence of inhibitors the Zip process has nearly an unitary efficiency.

Values of $(V_P^2 - (V_{P/o}^2))$ as a function of temperature for the thermal polymerization initiated by DTBP and PP are given in figure 1 as an Arrhenius type plot. The best-fit line have been drawn giving less weight to the low temperature data since, due to a large contribution of $(V_P)_o$, these results are subject to rather large errors. Since $^{\alpha}\text{DTBP} = 1$ and $^{\alpha}\text{PP}$ can be considered to be 0.34 as in the photochemical reaction[9], these data, together with the data reported for k_p and k_t by Mahabadi and O'Driscoll[10] allow an estimation of k_d. The values obtained are

$$\lg k_d\ (\text{sec}^{-1}) = 15 - 36.5\,/\,RT$$
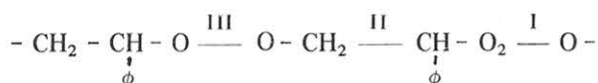
for DTBP and for the PP

$$\lg k_d\ (\text{sec-1}) = 10 - 30\,/\,RT$$

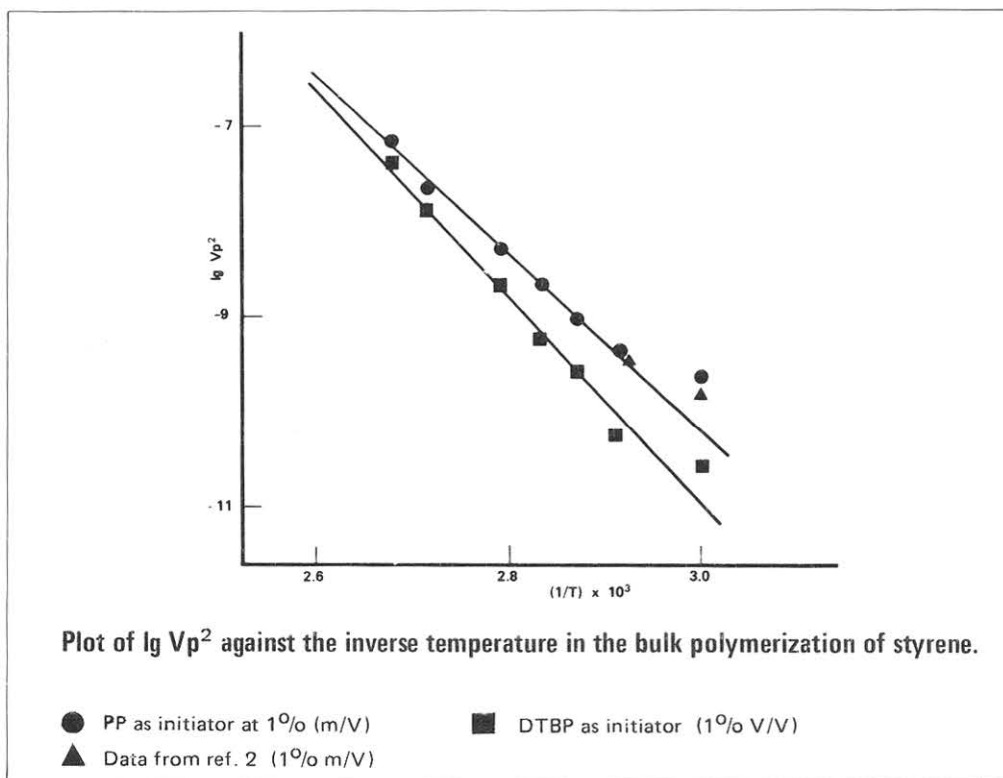where the activation energies are in kcal/mol.

The value of k_d for DTBP is similar to those reported in the literature[11]. The values obtained in the present work for $(k_d)_{PP}$ are in good agreement with those reported by Zikmund and show that both the activation energy and the pre-exponential A factors are considerably lower in the poly-peroxide. This result is similar to that observed for methyl methacrylate peroxides[3] but contrast with those reported for the decomposition of the peroxide of vinyl pirrolidone that decomposes considerably slower than di-tert-butyl peroxide[12].

The difference between E_{DTBP} and E_{PP} and A_{DTBP} and A_{PP} is outside our experimental error. In particular, the low E_{PP} and A_{PP} could be explained if the rupture is not taking place at a normal O-O linkage but at a particularly weak bond (i.e. the terminal O-O bond). Furthermore, it could be due to the monomer induced decomposition of small amounts of hydroperoxides produced in the polymerization under oxygen. This process that would be particularly important at low temperatures, could explain also the "curvature" observed in the Arrhenius plot.

It is interesting to compare the data obtained for k_d with the data reported by Zikmund for the polyperoxide consumption. For this process, the rate is nearly 100 times the rate of cleavage and the activation energy is only 17 kcal. The fact that the difference between both rates is larger than the average degree of polymerization show that the degradation has to be transferred between polymer chains. A simple degradation mechanism comprising O-O cleavage, Zip degradation, chain transfer and bimolecular chain termination can easily explain the fact that the activation energy in the decomposition is nearly half that of the initial cleavage. Furthermore, if the cleavage is partially "asisted" by the Zip degradation

$$- CH_2 - \underset{\phi}{CH} - O \overset{III}{\rule{1cm}{0.4pt}} O - CH_2 \overset{II}{\rule{1cm}{0.4pt}} \underset{\phi}{CH} - O_2 \overset{I}{\rule{1cm}{0.4pt}} O -$$

being the bond I and III weakened simultaneously with the cleavage of I, the low values found for the activation energies and preexponential A factor could be explained.

Plot of lg Vp² against the inverse temperature in the bulk polymerization of styrene.

● PP as initiator at 1%/o (m/V)   ■ DTBP as initiator (1%/o V/V)
▲ Data from ref. 2 (1%/o m/V)

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