Kinetic Study of the Reaction Between Atactic Polypropylene and Dicumyl Peroxide by Differential Thermal Analysis

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KINETIC STUDY OF THE REACTION BETWEEN ATACTIC POLYPROPYLENE AND DICUMYL PEROXIDE BY DIFFERENTIAL THERMAL ANALYSIS

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ABSTRACT

The reaction kinetics of atactic polypropylene (APP) in bulk with dicumyl peroxide (DCP) as a radical generator have been studied by means of thermal differential analysis. Hydrogen abstraction from APP by cumyl radicals gives (polypropylen)yl radicals which undergo transfer to DCP, chain scission, disproportionation, and crosslinking, as well as reaction with cumyl radicals. Chain scission is shown to be the faster and crosslinking the slower of these two processes, even at temperatures of 473 K and above. Activation parameters are determined, and an analysis of the different processes is made on their basis.

INTRODUCTION

The results obtained in our previous studies of the dehydrogenation of atactic polypropylene (APP) by sulfur [1, 2] seem to indicate that a useful reaction rate can be obtained by activation of the tertiary C–H groups rather than by promoting sulfur ring opening. A way to achieve this would be to

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form free radicals in the polymer chain by the action of an appropriate radical generator.

Polyolefins are often treated with free radicals, both to produce chain degradation and to promote crosslinking. The most relevant work about their use on polypropylene is that of Ido et al., [3], Rado [4], Pudov [5], Paushkin et al. [6], Kunert [7], and Capla [8], but all of these use either isotactic or mixed polypropylene. Only Rado [9] has studied the APP-radical reactive system, and then only to give an expression for maximum degradation, while Chodak [10] and Anderson [11] have studied crosslinking with added polyfunctional monomers.

Preliminary information about the relative rates of hydrogen abstraction, crosslinking, and degradation in APP is needed before a study of the dehydrogenation process can be carried out. The fact that APP autoxidation [12] shows a marked difference in behavior between the atactic and isotactic forms has led us to study the kinetics of the reaction between free radicals and APP in bulk in the temperature range 120-180°C with dicumyl peroxide as a free-radical generator.

EXPERIMENTAL

The APP used was TAQSA's "U" quality with $\bar{M}_n$ of 8000, purified by steam distillation, followed by washing and heating for 2 h at 180°C and 40 torr. The IR spectra of the resulting product were identical to that given in Ref. 13, except for a much lower level of residual oxidation. DCP was from Azco and was used as received.

Weighed samples of APP containing 0.01-1.0 mmol DCP/mol APP were placed in a Mettler 3000 differential scanning calorimeter and heated in a nitrogen atmosphere to the required temperature (in the 120-180°C range). The heat evolution and its rate were then plotted against time. Both isothermal and dynamic determinations were carried out, but no useful information could be obtained from the latter owing to the complex character of the process.

RESULTS AND DISCUSSION

The experimental curves (heat vs time) show the characteristic S-form of a successive process. The IR spectra of the reaction product (see Fig. 1) differ from those of the original APP by increased absorption in the ranges 3050-3200 and 1500-1700 nm (the latter in the form of a series of peaks), attribut-
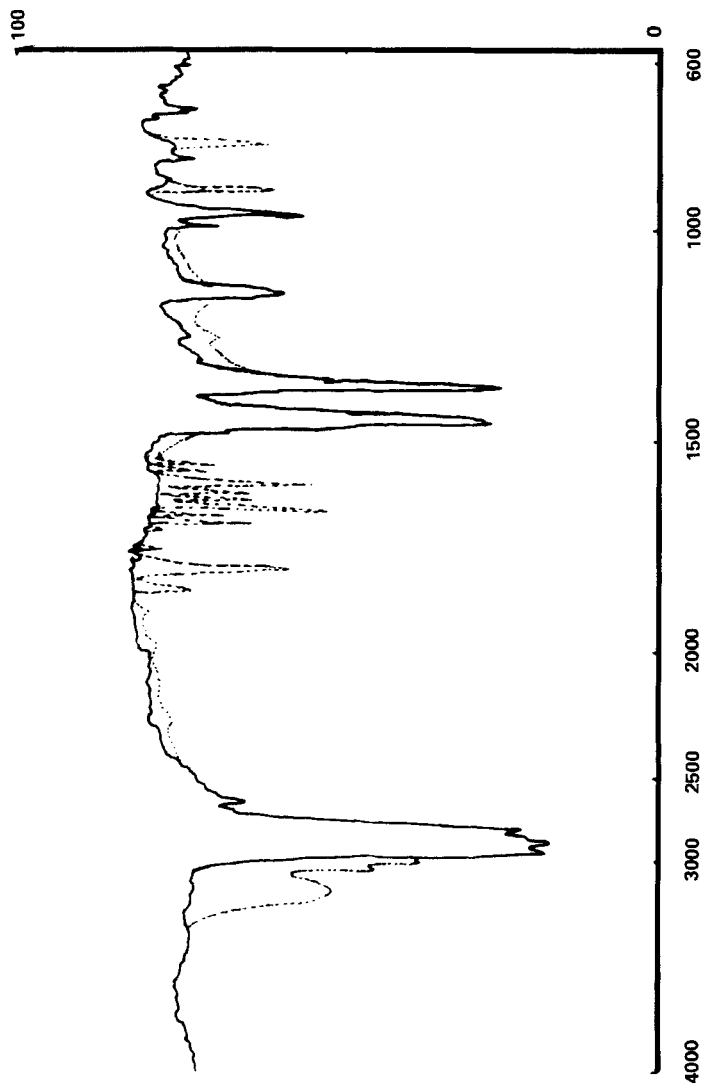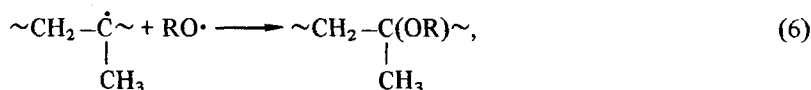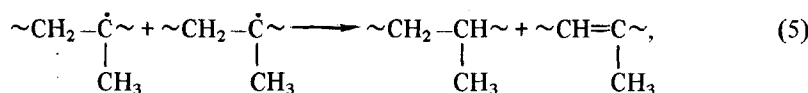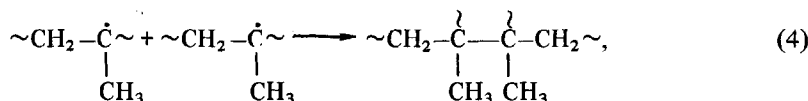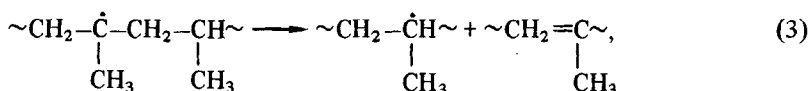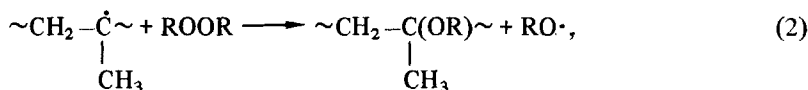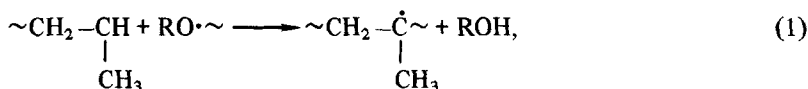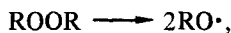
FIG. 1. IR spectra for purified atactic polypropylene (solid line) and for the APP-DCP reaction product (dotted line).

able to the presence of both hydroxyl and ether groups. There were two additional series of peaks—at 3000, 1670, and 800, and at 3020, 1810, and 905 nm—attributable to the presence of both trisubstituted and vinylic double bonds [14]. No other significant variations were observed.

In order to explain this behavior, given the data mentioned above, we consider all the reactions that can occur:

$$ROOR \longrightarrow 2RO\cdot,$$

$$\sim CH_2-\underset{\underset{CH_3}{|}}{CH} + RO\cdot\sim \longrightarrow \sim CH_2-\underset{\underset{CH_3}{|}}{\overset{\cdot}{C}}\sim + ROH, \tag{1}$$

$$\sim CH_2-\underset{\underset{CH_3}{|}}{\overset{\cdot}{C}}\sim + ROOR \longrightarrow \sim CH_2-\underset{\underset{CH_3}{|}}{C(OR)}\sim + RO\cdot, \tag{2}$$

$$\sim CH_2-\underset{\underset{CH_3}{|}}{\overset{\cdot}{C}}-CH_2-\underset{\underset{CH_3}{|}}{CH}\sim \longrightarrow \sim CH_2-\underset{\underset{CH_3}{|}}{\overset{\cdot}{C}H}\sim + \sim CH_2=\underset{\underset{CH_3}{|}}{C}\sim, \tag{3}$$

$$\sim CH_2-\underset{\underset{CH_3}{|}}{\overset{\cdot}{C}}\sim + \sim CH_2-\underset{\underset{CH_3}{|}}{\overset{\cdot}{C}}\sim \longrightarrow \sim CH_2-\underset{\underset{CH_3}{|}}{\overset{\wr}{C}}-\underset{\underset{CH_3}{|}}{\overset{\wr}{C}}-CH_2\sim, \tag{4}$$

$$\sim CH_2-\underset{\underset{CH_3}{|}}{\overset{\cdot}{C}}\sim + \sim CH_2-\underset{\underset{CH_3}{|}}{\overset{\cdot}{C}}\sim \longrightarrow \sim CH_2-\underset{\underset{CH_3}{|}}{CH}\sim + \sim CH=\underset{\underset{CH_3}{|}}{C}\sim, \tag{5}$$

$$\sim CH_2-\underset{\underset{CH_3}{|}}{\overset{\cdot}{C}}\sim + RO\cdot \longrightarrow \sim CH_2-\underset{\underset{CH_3}{|}}{C(OR)}\sim, \tag{6}$$

$$2RO\cdot \longrightarrow ROOR, \tag{7}$$

where R is the cumyl radical. For this system the heat evolution rate can be written to a first approximation as:

$$(\delta H/\delta t)_{P,T} = \Sigma(\delta H_i/\delta t)_{P,T} = \Sigma(\Delta H_i k_i A^p B^q \ldots), \tag{8}$$

where ΔH_i is the reaction enthalpy; k_i is the rate constant; A, B, . . . are the reactant concentrations; and p, q, . . . are the partial reaction orders for Step i.

Using Rado's treatment, which assumes all partial reaction orders to be 1, we arrive at the following expressions for the steady-state concentrations of the intermediate radicals:

$$[P\cdot] = \left\{(k_3 + k_4)/(k_r[ROOR]) + (k_6 + k_2(k_7[ROOR]/k_r)^{1/2})\right.$$
$$\left.(1/k_1[PH])\right\}^{-1}, \tag{9}$$

$$[RO\cdot] = [P\cdot](k_2[ROOR] + k_3 + (k_4 + k_5)[P\cdot])/(k_1[PH] - k_6[P\cdot]), \tag{10}$$

where k_r is the rate constant for DCP decomposition, k_i represent the rate constants of Reactions (1) to (7), $[P\cdot]$ is the (polypropylen)yl radical concentration, and $[PH]$ is that of polypropylene.

By using Eqs. (9) and (10), we arrive at the following expressions for reactant concentration:

$$[ROOR] = [ROOR]_i \exp(-t\cdot f(k_r k_1 k_2 k_3 k_4 k_5 k_6 k_7[P\cdot][RO\cdot]), \tag{11}$$

$$[PH] = [PH]_i \exp(-t\cdot f'(k_r k_1 k_2 k_3 k_4 k_5 k_6 k_7[P\cdot][RO\cdot]), \tag{12}$$

where $[ROOR]_i$ and $[PH]_i$ are the initial concentrations of DCP and APP, respectively.

By substituting Eqs. (9), (10), (11), and (12) in Eq. (8), we arrive at an expression for overall heat evolution of the form:

$$(\delta H/\delta t) = f(t, [PH]_i, [ROOR]_i). \tag{13}$$

In the temperature range studied, DCP decomposes very quickly, so that the contribution of its thermal decomposition and of Step (2) can be considered negligible at long reaction times. Under the same conditions, Steps (1) and (3) will become psuedo-first-order ones while, in Steps (4), (5), (6), and (7), the concentrations of all the species involved remain constant as long as the steady state is maintained, and their apparent reaction order will be zero. Thus, when all these conditions are satisfied, the apparent overall reaction order for the thermal evolution process will be unity. As may be seen in Fig. 2, the system fulfills this condition and the proposed reaction sequence can be considered to apply to the APP-DCP system.

Kinetic constants were determined from our data on reaction rate vs time by using Eq. (13) with reaction enthalpies calculated from data in Ref. 16 and values given in Ref. 17 for the DCP decomposition rate constant. An iterative treatment was carried out using the minimax nonlinear optimization routine
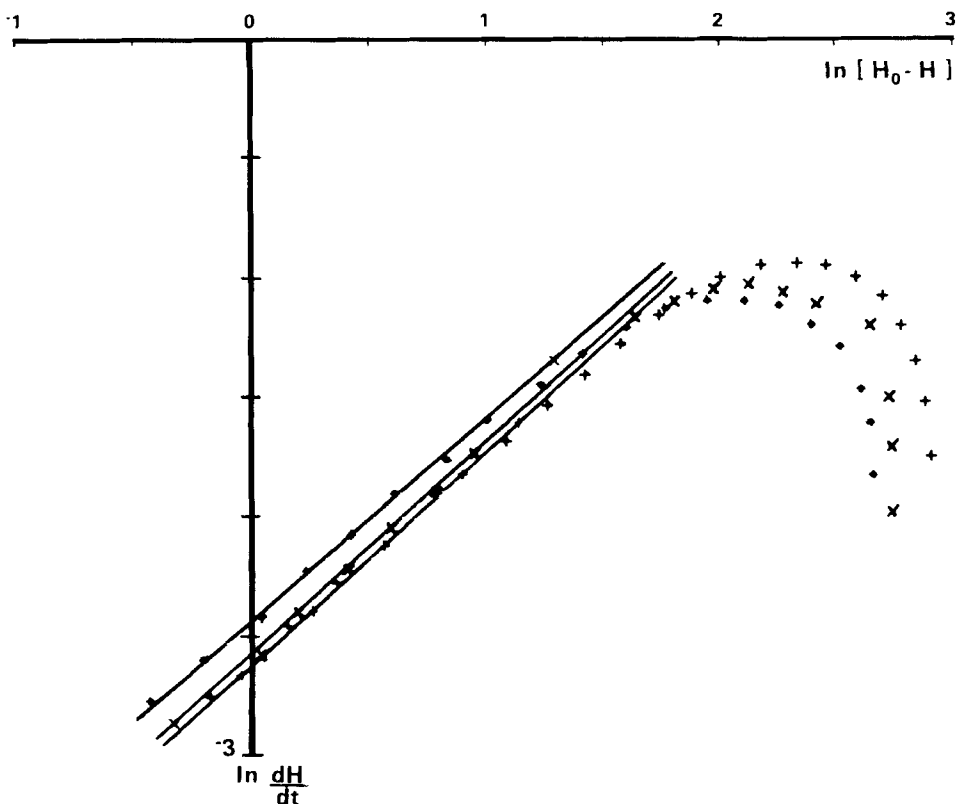
FIG. 2. Logarithmic plot of heat evolution rate vs heat evolved for the reaction between APP and DCP at 120 (+), 150 (X), and 180°C (*) and 27.9 mol DCP/mol APP.

developed by Madsen [18] and Schaër-Jacobsen [19], calculations being carried out on the IBM 3181 computer at the University of Barcelona. All optimizations did give correlation coefficients of 0.99 or better.

Results are given in Table 1. It can be concluded that the system follows such a reaction sequence, with the end radicals formed in Step (3) reacting in the same way as the tertiary ones.

Since the complex nature of the global process does not permit ready comparison between the reaction rates of the chain transfer (Reaction 2), chain scission (Reaction 3), crosslinking (Reaction 4), and disproportionation (Re-

TABLE 1. Rate Constants as a Function of Temperature for the System APP-DCP (in $m^3 \cdot mol \cdot s^{-1}$)

$t,\,°C$	k_1	k_2	k_3	k_4	k_5	k_6	k_7
120	0.30	10.08	3.56	4.94	14.44	11.41	9.23
130	—	—	—	5.15	14.10	11.62	—
140	—	10.53	3.76	5.30	13.86	—	9.04
150	0.31	10.81	3.76	5.59	13.53	12.00	9.18
160	0.34	—	3.96	—	13.40	12.65	8.79
170	—	11.12	4.06	5.74	13.20	12.97	8.67
180	0.37	11.27	4.16	5.80	13.08	13.48	8.46

action 5) processes, a simulation was made of their relative reaction rates (see Fig. 3). It can be readily appreciated that Process (3) is the fastest one and, thus, the polymer will degrade rapidly when treated with DCP in our temperature range, in marked contrast to the results found by Rado [15] for isotactic polypropylene. In order to ascertain whether a change in temperature could change this behavior, the ratio between the disproportionation and crosslinking rate constants, plotted vs temperature in Fig. 4, approaches a constant value at high temperatures, with an extrapolated value of 2.25, showing that no reversal of the degradation can be achieved by a temperature increase.

The temperature dependence of all the experimental rate constants satisfies both the Arrhenius and the transition state (TS) theory formulations, and the corresponding activation parameters are given in Table 2. For hydrogen abstraction (Reaction 1), the preexponential factor is rather higher than usual for bimolecular TS formation from two nonlinear molecules [20]. This could mean that APP is less sterically hindered than isotactic polypropylene (as found by Paushkin [21]), and that this attack takes place mainly in the syndiotactic zones in the chain. The reaction between polymer radicals and DCP molecules (Reaction 2), in contrast, seems to proceed via a "ring" TS. Chain scission (Reaction 3) seems to be a unimolecular process whose abnormally low preexponential factor may be due to the fact that there is a higher density of states in the TS than in the reactives, because the former has a looser structure than the latter, which is usual for unimolecular reactions with cyclic TS [22] such as the one that can be formed between a neighboring tertiary H-atom and the carbonium radical.
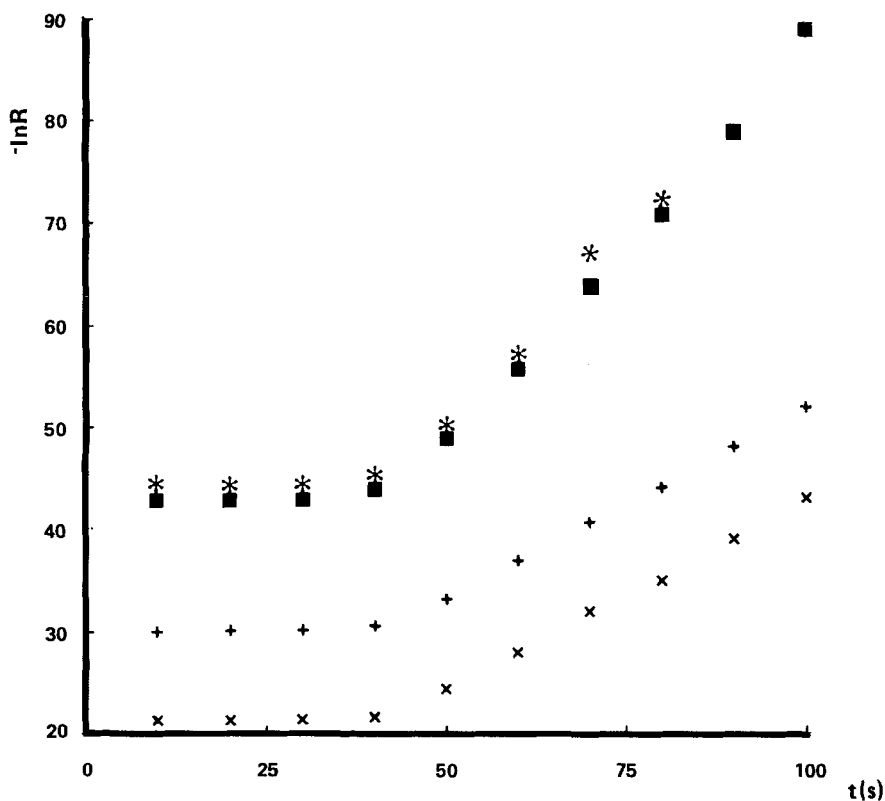
FIG. 3. Semilogarithmic representation of the calculated reaction rates (R)
vs time for the following processes: transference to DCP (Reaction 2) (+),
chain breaking (Reaction 3) (X), crosslinking (Reaction 4) (*), and chain dis-
proportionation (Reaction 5) (■).

The nearly identical and somewhat high activation energies found for cross-
linking (Reaction 4) and for the reaction of cumoxy radical with chain radical
(Reaction 6) may mean that both processes are diffusion controlled although
this seems unlikely in view of the very low viscosity of the system in the tem-
perature range studied. The preexponential factor of Eq. (13), on the other
hand, is of the same order of magnitude as that of Eq. (11), but nearly double
its value, showing that the former is hindered, probably from steric causes.
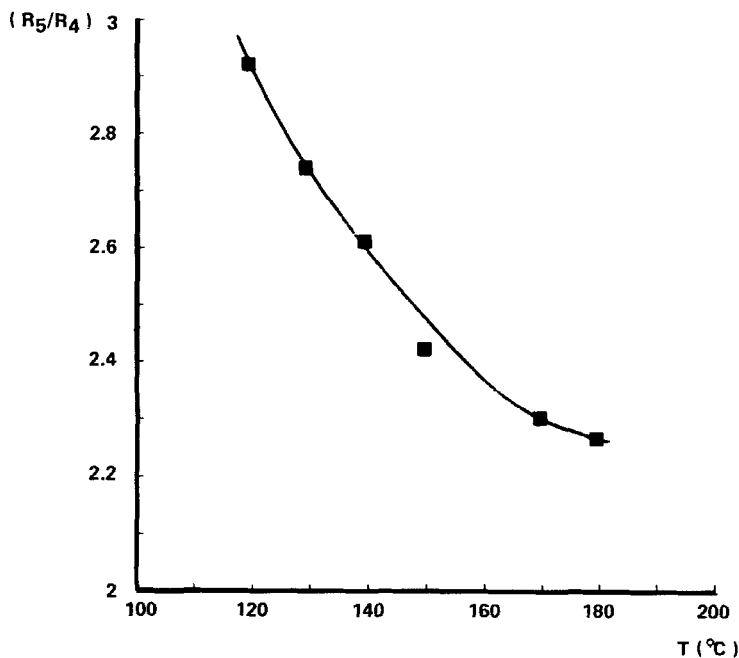Finally, while cumyl radical recombination (Reaction 7) is an elementary

FIG. 4. Plot of the ratio of rate constants for chain disproportionation and crosslinking vs temperature.

process and the negative activation energy is therefore justified, the negative activation energy found for radical disproportionation (Reaction 5) can be explained on the assumption that the process is not an elementary but a two-step one, the first step being the equilibrium transfer of an H-atom from one chain to the other (practically a homoenergetic process), and the second one being the recombination of the biradical thus formed:

$$\sim CH_2 - \overset{\bullet}{C} \sim + \sim CH - \overset{\bullet}{C} \sim \rightleftharpoons \sim CH_2 - CH \sim + \sim \overset{\bullet}{C}H - \overset{\bullet}{C}H \sim. \qquad (5a)$$
$$\qquad\quad |\qquad\qquad |\qquad\qquad\qquad\quad |\qquad\qquad |$$
$$\qquad\quad CH_3\qquad\quad CH_3\qquad\qquad\quad CH_3\qquad\quad CH_3$$

$$\sim \overset{\bullet}{C}H_2 - \overset{\bullet}{C} \sim \longrightarrow \sim CH_2 = CH \sim. \qquad (5b)$$
$$\qquad\quad |\qquad\qquad\qquad\quad |$$
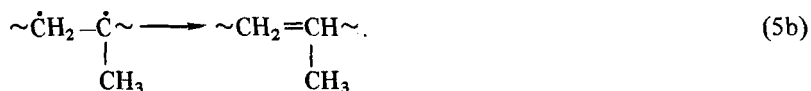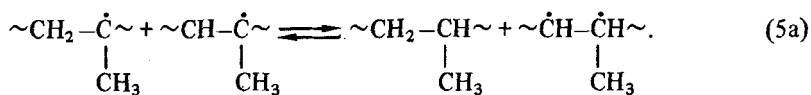$$\qquad\quad CH_3\qquad\qquad\qquad CH_3$$

TABLE 2. Thermodynamic Activation Parameters for the Reactions between APP and DCP[a]

Reaction	E_a, kJ/mol	A	$\Delta H^{\ddagger}$, kJ/mol	$\Delta S^{\ddagger}$, kJ·mol^{-1}·K^{-1}
1	5.09	5.96×10^4	8.59	-0.13
2	2.77	4.38×10^6	6.27	-0.11
3	3.84	8.26×10^9	7.34	-0.12
4	4.01	1.08×10^6	7.51	-0.11
5	-2.46	4.31×10^5	1.05	-0.12
6	4.07	2.31×10^6	7.57	-0.11
7	-2.10	8.94×10^5	1.40	-0.12

[a]Preexponential factors are given in $m^3 \cdot mol^{-1} \cdot s^{-1}$, except that for Reaction (3), which is given in s^{-1}.

The experimental activation value, then, would correspond to the sum of the reaction enthalpy of Reaction (5a) plus the activation energy of Reaction (5b), which is a radical recombination and can be negative.

That all the elementary processes in which (polypropylen)yl radicals participate (Reactions 2, 4, and 6) have the same and very small absolute value of the activation entropy could be because TS formation causes only a small variation in the polymer chain, while the fact that TS formation also entails a local restriction in chain rotational freedom justifies their negative values.

From the experimental results it can be concluded that, while treatment of APP with DCP produces readily formed carbonium radicals, these do react among themselves and with neighboring residues in the chain far too quickly to help sulfur activation. Similarly, the use of peroxides to open S rings cannot be considered likely unless this process is much more rapid than the APP attack.

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