A Kinetic Study of Benzoyl Peroxide Decomposition in Graft Copolymerization Bath

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Synopsis

The rates of decomposition of benzoyl peroxide have been studied in water alone and in the presence of the components of graft copolymerization bath, viz. diphenyl and acrylic acid, in the temperature range of 363–403 K. Kinetic parameters such as reaction order for the peroxide, preexponential factor, and activation energy were evaluated from experimental data. The implication of these results to the initiation of graft copolymerization of acrylic acid onto polyester fabrics is discussed.

INTRODUCTION

The results of kinetic investigation of chemically induced graft copolymerization of acrylic acid onto polyester fabrics[1] have indicated that energy of activation for the decomposition of the initiator cannot be neglected in the total activation energy and that the initiation step plays an important role in the rate of the overall process. A kinetic study of the decomposition of benzoyl peroxide, being the initiator in the graft copolymerization, in water alone and in the grafting bath is a subject of this paper.

The decomposition of benzoyl peroxide was studied in some detail in a number of organic solvents such as ethers, alcohols, aromatics, chlorinated solvents, etc.[2] These kinetic studies showed that the rate of decomposition may be given by the following empirical equation:

$$-\frac{dx}{dt} = k_1 x + k_2 x^n \tag{1}$$

where x = concentration of the peroxide, t = time, k_1 = rate constant of spontaneous decomposition (homolysis of peroxide bond), and k_2 = rate constant of induced decomposition. For most of the solvents studies the order of induced decomposition, n, equals about 3/2. The same form of the kinetic expression (1) can be derived assuming a simple kinetic scheme as was done by Nozaki and Bartlett.[3] The authors evaluated the activation energies for the homolysis and induced decomposition of benzoyl and peroxide in benzene solvent in the range of ~140 and ~100 kJ/mol, respectively.

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The decomposition of benzoyl peroxide has not been studied in the same detail in other solvents, and no data have been found for decomposition of the peroxide in water systems. The nonavailability of data is mostly due to the fact that the solubility of benzoyl peroxide in water is negligible and systems of that type are ill-defined. Most of the peroxide is in solid state, the minority is in solution, and as a consequence of the decay one part of the solid might dissolve.

EXPERIMENTAL

The experiments were carried out in the laboratory dyeing apparatus Longclose, at the temperatures 363, 373, 383, and 403 K. Glycerol was employed as a heat transfer agent in the apparatus. Six reaction vessels, each containing 50 cm^3 of reaction solution, were placed in a constant-temperature bath after the desired temperature had been reached. After a given time the reaction vessel was removed from the constant temperature bath and immediately frozen to terminate the decomposition reaction. Sampling time was small compared to reaction time. The decomposition of benzoyl peroxide was studied in the following systems:

1. benzoyl peroxide–water;
2. benzoyl peroxide–water–acrylic acid;
3. benzoyl peroxide–water–diphenyl;
4. benzoyl peroxide–water–acrylic acid–diphenyl.

The initial concentrations of the reaction components were as follows: benzoyl peroxide 2 g/dm^3, acrylic acid 40 g/dm^3, and diphenyl 3 g/dm^3. The concentration of benzoyl peroxide was determined by an iodometric method using an acidic potassium iodide in excess and backtitrating of the liberated free iodine with sodium thiosulfate.

IDENTIFICATION OF KINETIC PARAMETERS

As was already mentioned, a rather complicated kinetics of benzoyl peroxide decomposition can be expressed by the simple equation (1). It should be borne in mind, however, that this equation is valid for a homogeneous liquid system only. As the benzoyl peroxide is only slightly soluble in water, or water solutions, one may expect a possible contribution of diffusion to the overall rate of the decomposition process. Therefore, the first attempt to evaluate kinetic data was to employ models well known in chemical reaction engineering,[4] e.g., the model of the unreacted core or the model of shrinking spherical particles with different rate controlling steps, however, unsuccessfully.

Owing to complexity of the process, we decided to employ an empirical approach to the decomposition kinetics. The following conventional (Arrhenius type) kinetic expression is proposed:

$$-\frac{dx}{dt} = kx^n = k_0 \exp\left(-\frac{E}{RT}\right)x^n \tag{2}$$

where k_0 = preexponential factor, E = apparent activation energy, R =

universal gas constant, t = time, and T = temperature. Although the simplified kinetic model does not reflect the real mechanism of benzoyl peroxide decomposition, it should, however, be pointed out that in the case of the chain reaction power law model there is usually an asymptotic solution of true kinetics.[5] It is evident that increasing the complexity of the model involves an increase in the number of kinetic parameters which are necessary for the mathematical description of the process and, consequently, have to be identified. This relatively simple form of kinetic expression (2) enables analytical solution of this differential equation with the use of the following initial condition:

$$t = 0; \qquad x = 1.$$

The integrated form of eq. (2) is

$$x^{1-n} = 1 + (n - 1)tk_0 \exp(-E/RT) \qquad (3)$$

As is seen, eq. (3) presents the concentration profile of benzoyl peroxide vs. decomposition time. By taking logarithms and subtracting both sides of eq. (3), we obtain

$$\ln \frac{x^{1-n} - 1}{(n - 1)t} = \ln k_0 - \frac{E}{RT} \qquad (4)$$

Introducing the following transformations of variables,

$$Y = \ln \frac{x^{1-n} - 1}{(n - 1)t} \quad \text{and} \quad X = \frac{1}{T}, \qquad (5)$$

and of parameters,

$$K_1 = lnk_0 \quad \text{and} \quad K_2 = -E/R, \qquad (6)$$

one obtains a linear expression,

$$Y = K_1 + K_2 X. \qquad (7)$$

Employing a linear regression one can easily determine kinetic parameters K_1 and K_2 if only the reaction order n is known or assumed. In order to identify the parameter n, a simple optimization method—the Fibonacci search technique[6]—was utilized. The objective function J (performance index) defined as the sum of the squares of the deviations of experimental concentrations from the calculated ones,

$$J = \frac{\Sigma(x_{\text{exptl}} - x_{\text{calcd}})^2}{N - 3} \qquad (8)$$

where N is the number of experimental points, was minimized.

TABLE I
Identified Kinetic Parameters of Benzoyl Peroxide Decomposition
in Various Systems

Parameters \ Systems	BP–H$_2$O	BP–H$_2$O–AA	BP–H$_2$O–DPh	BP–H$_2$O–AA–DPh
Preexponential factor k_0, (min^{-1})	5.0×10^{11}	1.8×10^{2}	2.6×10^{10}	2.4×10^{21}
Activation energy E (kJ/mol)	88.55	21.83	82.92	161.45
Reaction order n	1.70	1.21	1.27	1.37
Performance index J	3.1×10^{-4}	5.1×10^{-3}	7.6×10^{-3}	2.5×10^{-3}

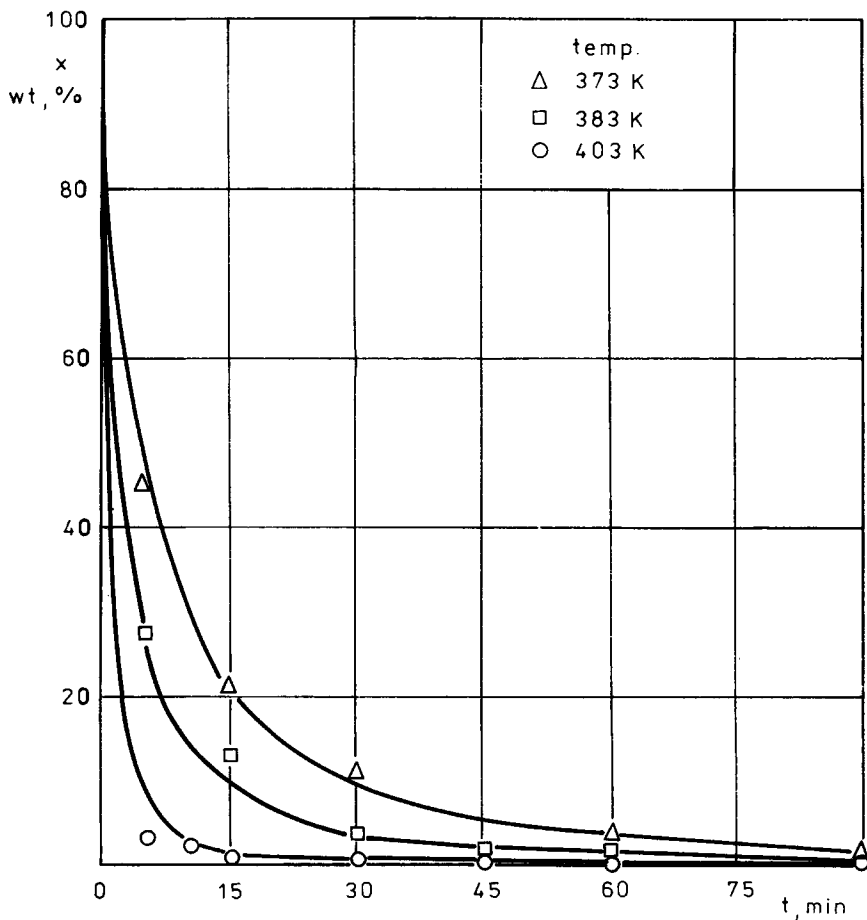[a] BP = benzoyl peroxide; AA = acrylic acid; DPh = diphenyl.

Fig. 1.   Concentration of benzoyl peroxide in water vs. time. Temperature (K): ($\triangle$) 373; ($\square$) 383; ($\bigcirc$) 403.

RESULTS AND DISCUSSION

Numerical identification of the kinetic parameters of benzoyl peroxide decomposition, by applying the Fibonacci search technique, resulted in the values listed in Table I. These "most probable" values are strictly valid under experimental conditions. The calculated values of the reaction order are, in all cases, above unity, i.e., ranging from 1.2 to 1.7. The values of apparent activation energy range from 21 to 161 kJ/mol, depending on the system explored. The unexpected low value of activation energy for the system benzoyl peroxide–water–acrylic acid may be explained by the possible contribution of induced decomposition by acrylic acid radicals to the rate of disappearance of benzoyl peroxide. It is well known that the induced decomposition has lower activation energy than the homolysis of the peroxide bond and that low temperatures favor induced decomposition.[2] There is no reference in the literature to activation energy for the thermal decomposition of benzoyl peroxide in water systems, although the values found for the pyrolysis of a compound of type RCOR (133–156 kJ/mol) seem to indicate that the
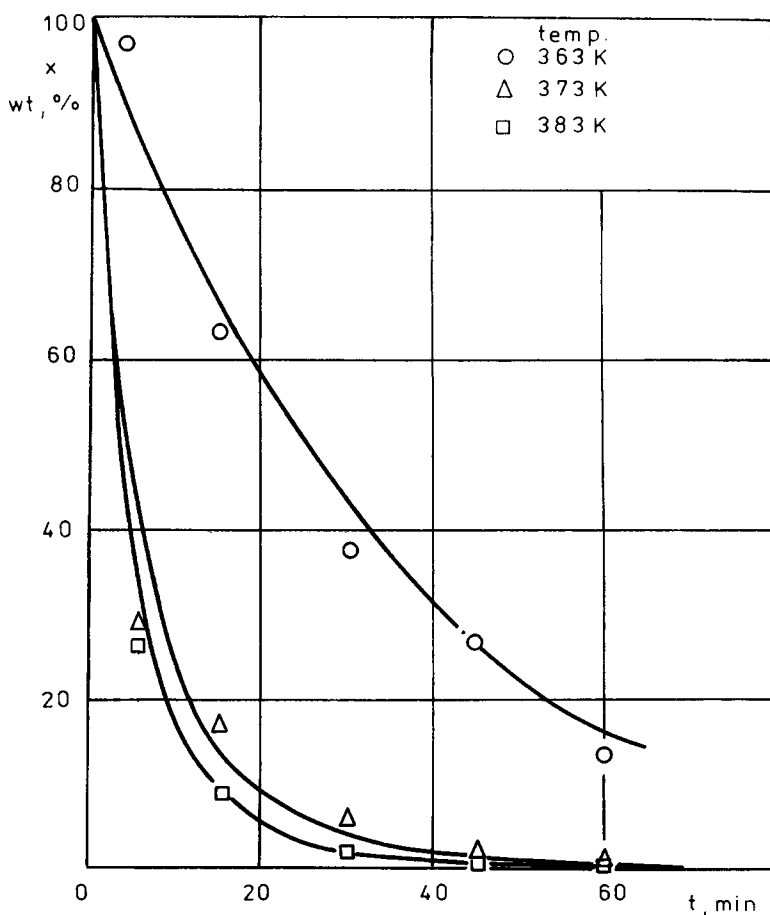

Fig. 2. Concentration of benzoyl peroxide in water solution of acrylic acid vs. time. Temperature (K): (○) 363; (△) 373; (□) 383.

value 161 kJ/mol for the grafting bath could be in the correct order of magnitude.[7] It is worth remembering that according to the following equation,

$$E = E_p + \frac{E_d}{2} + \frac{E_g}{2} - \frac{E_t}{2} \tag{9}$$

derived in our previous paper,[1] half of the activation energy for the decomposition of the initiator contributes to the activation energy of the overall grafting process. Comparing the value of $E_d/2$, equal to about 80 kJ/mol, with the apparent activation energy for the graft copolymerization of acrylic acid onto PET fabrics, 90 kJ/mol, one can conclude that the initiation step plays an important role in the rate of the overall process.

A comparison between the calculated (solid line) and experimental values of benzoyl peroxide concentration is presented in Figures 1, 2, 3, and 4 for the systems investigated. It is evident that the calculated profiles are in good agreement with the experimental data.
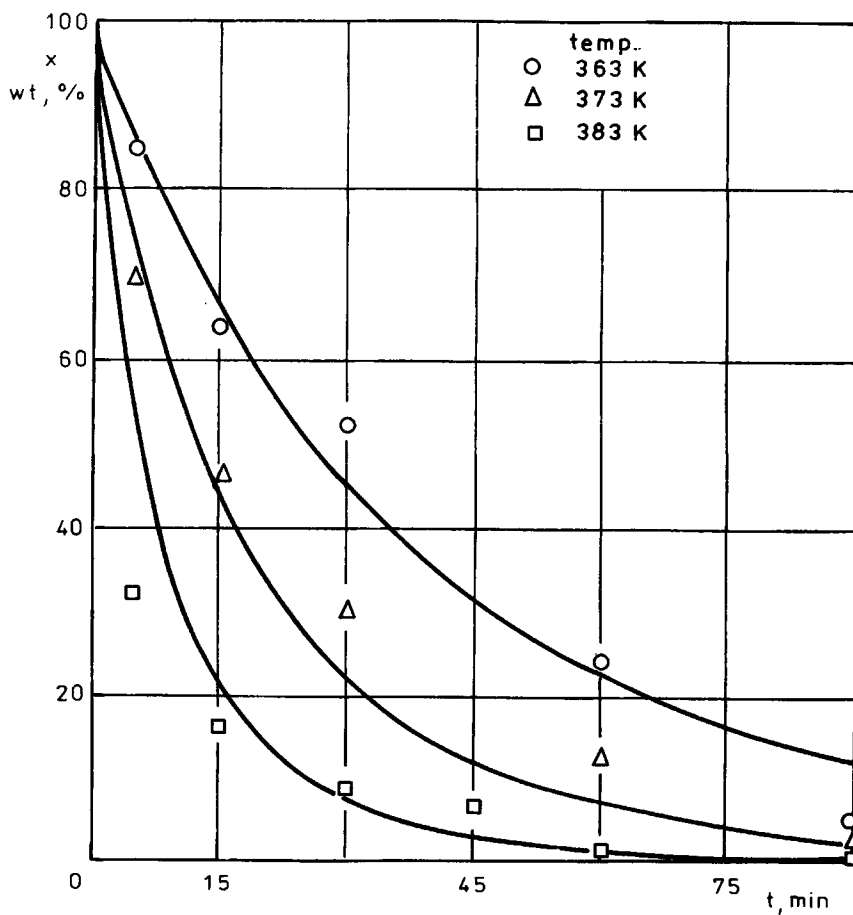

Fig. 3. Concentration of benzoyl peroxide in the diphenyl–water system vs. time. Temperature (K): (○) 363; (△) 373; (□) 383.
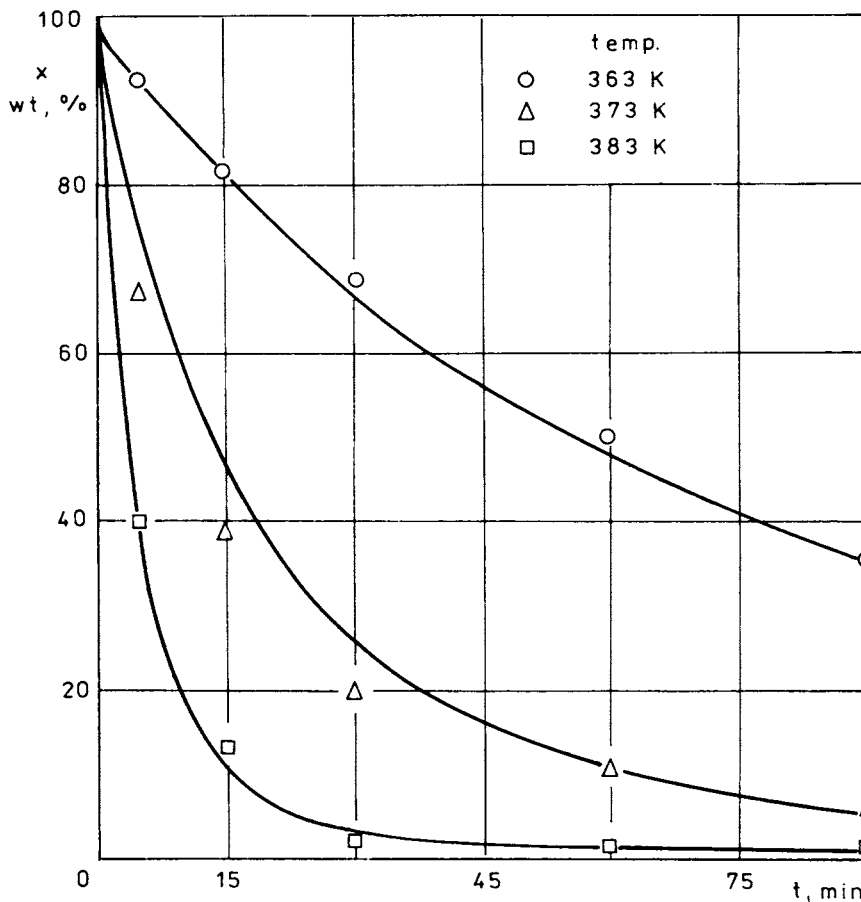
Fig. 4.   Concentration of benzoyl peroxide in grafting bath (water–acrylic acid–diphenyl) vs. time. Temperature (K): (○) 363; (△) 373; (□) 383.

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