Impregnation and Polymerization of Vinylic Monomers in Porous Media.   II. Polymerization in Situ

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Synopsis

In this work, we have studied the kinetics of polymerization of styrene and of methyl methacrylate in a porous asbestos cement medium initiated by the thermal decomposition of a radical initiator. Our results show that the presence of the porous medium appreciably modifies the rate of polymerization. Two factors have been proposed to explain this effect: a variation of the constant of decomposition of the initiator resulting from the alkalinity of the surface, and a modification of the rate constant of chain propagation related to the electron-releasing or attracting capacity of the double bond of the monomer. Nevertheless, the polymerization remains solely initiated by radicals resulting of the thermal decomposition of the initiator as the rate varies according to the square root of the initiator concentration and tends toward zero for polymerization containing no peroxide.

INTRODUCTION

One possesses relatively little information on the mechanism and on the kinetics of polymerization of vinylic monomers on minerals with high specific area. Some authors have observed that the presence of minerals greatly alters the rate of polymerization. Thus, Friedlander[1] noted that styrene is rapidly polymerized in the presence of sodium montmorillonite by a radical mechanism.

According to Solomon,[2] the kinetics of polymerization depends on the electron-releasing or attracting capacity of the double bond of the monomer. Thus, in the case of styrene, which has a double bond rich in electrons, an electron transfer would take place from the monomer toward the mineral. In this way, free radicals (radical cations) would be formed, capable of initiating the polymeric chain. On the other hand, in the case of a monomer such as methyl methacrylate, whose double bond is poor in electrons, Solomon observed a considerable slowing down in the kinetics, which he explained by an electron transfer from the growing polymeric chain toward the mineral which would thus oxidize the free radicals and inhibit polymerization.

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A modification in the kinetics of polymerization could equally well result from a variation in the activity of the initiator. The influence of this factor on the kinetics of polymerization has not yet been taken into account. Wagenaar[3] showed recently that the rate of decomposition of benzoyl peroxide is doubled when the pH of the medium is changed from 8 to 10. With other peroxides, an opposite phenomenon occurs. Thus, with dicumyl peroxide, the rate of decomposition is divided by two when the pH goes from 8 to 10. Inasmuch as asbestos cements are minerals with a basic surface, we can expect this factor to play a certain effect in the polymerization of vinyl monomers in these porous media.

This work is devoted to the study of the kinetics of polymerization of styrene and of methyl methacrylate initiated by the thermal decomposition of benzoyl peroxide (Merck 1641) and of bis(4-*tert*-butylcyclohexyl) peroxydicarbonate (Nourylande Perkadox 16). The half-times of decomposition of these initiators at 80°C are respectively 5 hr and 4 min. Benzoyl peroxide is an initiator which is well adapted to the study of polymerization at temperatures between 80° and 120°C. Bis(4-*tert*-butyl-cyclohexyl) peroxydicarbonate is only appropriate for polymerization carried out at temperatures below 70°C.

Benzoyl peroxide is well suited for the polymerization of styrene and methyl methacrylate; bis(4-*tert*-butylcyclohexyl) peroxydicarbonate is especially suitable for the polymerization of methyl methacrylate and not adapted to the polymerization of styrene because of the low value of the overall rate constant of the polymerization of this monomer.[7]

EXPERIMENTAL

The quantitative study of polymerization in porous media presents rather delicate experimental problems since the two main techniques for measuring the kinetics of polymerization, dilatometry and gravimetry, cannot be utilized. In this work, we have used differential scanning calorimetry (DSC).

The apparatus used was a du Pont differential scanning calorimeter (Model 900.600) coupled with the basic console of the du Pont 900 Thermal Analyzer. This apparatus, which can work isothermically or at a constant heating rate, was calibrated with a series of metals with low melting point.

The monomer was previously distilled twice under nitrogen. The asbestos cement support used in this work was an Eflex plate (trade name of the Eternit Co.) industrially produced.   It was an autoclaved asbestos cement with a pore radius in the region of 150 Å and total pore volume equal to 0.10 cm^3/g.

A piece of asbestos cement of the same dimension as the calorimeter capsule, after being dried at 120°C under vacuum for 15 hr, was immersed in the mixture of the monomer and the initiator through which nitrogen had previously been passed to eliminate all traces of oxygen. The time of impregnation of the tablet was limited to 30 min. This is sufficiently

long to achieve total impregnation. The impregnated tablet was then placed in a capsule of the calorimeter which was hermetically sealed. The loss of monomer during polymerization was less than 2%. After polymerization, no trace of polymer was noticeable on the inner walls of the capsule, therefore there is no drainage of monomer from the sample after hermetic sealing.

RESULTS

Test of Calorimetric Method and Calculation of Heat of Polymerization

Polymerization heat was determined from a nonisothermal polymerization carried out at a heating rate of 2°C/min. The heat of polymerization is equal to 16.1 kcal/mole for styrene and 13.8 kcal/mole for methyl methacrylate. These values are in excellent agreement with the values of 16.1 to 16.7 determined for styrene by Tong and Kenyon[4] and Roberts, Walton, and Jessup,[5] and with 13 to 13.9 kcal/mole found by other authors[6] for methyl methacrylate.

With a view to determine the accuracy of the calorimetric method, we studied the kinetics of polymerization of styrene in bulk, initiated by 0.10 mole/l. (2.6% by weight) of benzoyl peroxide at several temperatures. Figure 1 shows the kinetics. From the tangents of the origin, we calculated the initial rates of polymerization R_{pi}. Knowing these, we calcu-
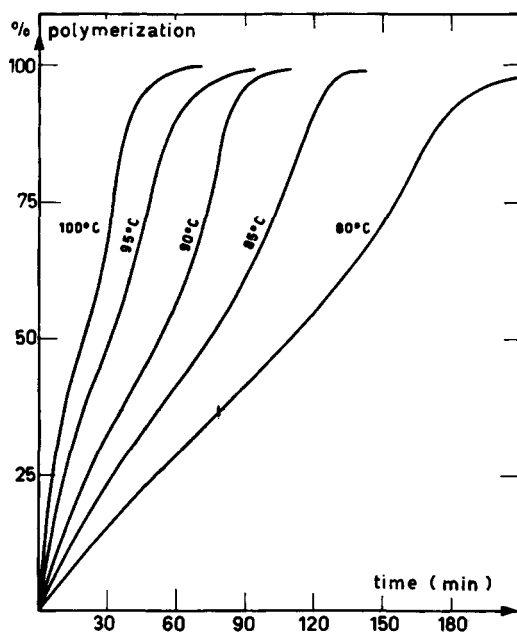

Fig. 1. Kinetics of polymerization of styrene in bulk. Inflence of temperature (initator benzoyl peroxide, 0.10 mole/l).

TABLE I

Rate Constants of Polymerization of Styrene Initiated by Benzoyl Peroxide—Influence of Temperature

T, °C	[M], moles/l.	[I], moles/l.	R_{pi},[a] moles/l. sec	$R_{pi}/I^{1/2}M$, l.$^{1/2}$ mole$^{-1/2}$ sec^{-1}	$R_{pi}/I^{1/2}M$, l.$^{1/2}$ mole$^{-1/2}$ sec^{-1} (refs. 8 and 9)	Degree of conversion,[b] %
80	8.19	0.10	7.8×10^{-4}	3.0×10^{-4}	3.3×10^{-4}	97.8
85	8.14	0.10	12.6×10^{-4}	4.9×10^{-4}	5.0×10^{-4}	98.9
90	8.10	0.10	20.0×10^{-4}	7.8×10^{-4}	7.8×10^{-4}	99.4
95	8.06	0.10	30.6×10^{-4}	12.0×10^{-4}	11.8×10^{-4}	99.1
100	8.01	0.10	47.1×10^{-4}	18.6×10^{-4}	17.9×10^{-4}	99.7

[a] R_{pi}: Initial rate.

[b] Determined from the heat of polymerization.

lated the overall rate constant on the basis of the formula for the overall rate constant for radical polymerization:[7]

$$A = \left[f \frac{K_d}{K_t} \right]^{1/2} K_p = \frac{R_{pi}}{I^{1/2}M}$$

where K_p and K_t are, respectively, the rate constants of chain propagation and termination; and f and K_d are, respectively, the efficiency factor and the constant of decomposition of the initiator.

We observe that the agreement between the rate constant determined by calorimetry and that given by Bevington[8] and Bawn and Mellish[9] (Table I) is excellent. It appears, therefore, that differential microcalorimetry is an experimental technique which is extremely valid, not only for determining the kinetics at a high degree of conversion, but also to determine the initial kinetics.

Comparison Study of Polymerization in Bulk and in the Asbestos Cement Substratum

In a first series of experiments, we studied the polymerization of styrene in bulk and in asbestos cement. These polymerizations were initiated by 0.021, 0.041, and 0.083 mole/l. of benzoyl peroxide (0.5%, 1.1%, and 2.2% by weight) at 100° and 120°C, and by 0.101 mole/l. (4.2% by weight) of bis(4-*tert*-butylcyclohexyl) peroxydicarbonate at 60°C. The results for these experiments are given in Figures 2, 3, 4, and 5 and in Table II.

The results for the polymerization of methyl methacrylate are given in Figures 6, 7, 8, and 9 and in Table III. In this series of experiments, the concentration of the initiator varied from 0.013 to 0.050 mole/l. (0.5% to 2.1% by weight) for the polymerization initiated by bis(4-*tert*-butylcyclohexyl) peroxydicarbonate at 50° and 70°C, and was equal to 0.083 mole/l. (2.1% by weight) for the polymerization initiated by benzoyl peroxide at 70°C.
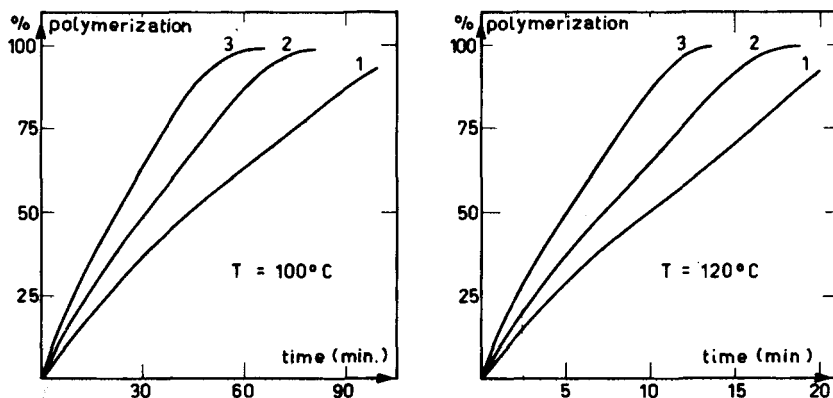

Fig. 2. Polymerization of styrene in bulk. Influence of concentration of benzoyl peroxide: (1) 0.021 mole/l.; (2) 0.041 mole/l.; (3) 0.083 mole/l.

TABLE II

Polymerization of Styrene in Bulk and in Asbestos Cement

T, °C	[I], mole/l.	In bulk			In asbestos cement			Refs. 10-12
		R_{pi}, mole/l. sec	$R_{pi}/I^{1/2}M$, $l.^{1/2}$mole$^{-1/2}$sec^{-1}	Degree of conversion, %	R_{pi}, mole/l. sec	$R_{pi}/I^{1/2}M$, $l.^{1/2}$mole$^{-1/2}$sec^{-1}	Degree of conversion, %	$R_{pi}/I^{1/2}M$, $l.^{1/2}$mole$^{-1/2}$sec^{-1}
Initiator Benzoyl Peroxide								
100	0.021	19.4×10^{-4}	16.9×10^{-4}	98.2	28.7×10^{-4}	25.0×10^{-4}	98.9	
	0.041	28.0×10^{-4}	17.2×10^{-4}	99.2	42.1×10^{-4}	25.9×10^{-4}	98.9	
	0.083	38.7×10^{-4}	16.8×10^{-4}	98.7	58.1×10^{-4}	25.2×10^{-4}	98.9	
			mean value 17.0×10^{-4}			mean value 25.4×10^{-4}		17.9×10^{-4}
120	0.021	85.0×10^{-4}	75.5×10^{-4}	99.5	116.3×10^{-4}	103.4×10^{-4}	99.4	
	0.041	120.2×10^{-4}	75.4×10^{-4}	99.0	163.8×10^{-4}	102.8×10^{-4}	99.4	
	0.083	172.5×10^{-4}	76.6×10^{-4}	99.6	226.1×10^{-4}	100.3×10^{-4}	99.4	
			mean value 75.8×10^{-4}			mean value 102.2×10^{-4}		81.5×10^{-4}
Initiator Bis(4-tert-butylcyclohexyl) Peroxydicarbonate								
60	0.101	9.6×10^{-4}	3.6×10^{-4}	96.3	10.0×10^{-4}	3.8×10^{-4}	96.3	3.3×10^{-4}

TABLE III
Polymerization of Methyl Methacrylate in Bulk and in Asbestos Cement

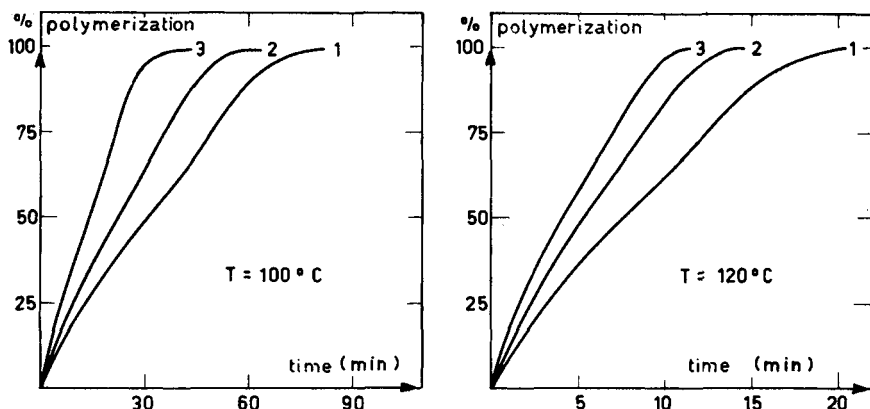| T, °C	[I], mole/l.	In bulk			In asbestos-cement			Refs. 11 and 12
		R_{pi}, mole/l. sec	$R_{pi}/I^{1/2}M$, l.$^{1/2}$ mole$^{-1/2}$ sec^{-1}	Degree of conversion, %	R_{pi}, mole/l. sec	$R_{pi}/I^{1/2}M$, l.$^{1/2}$ mole$^{-1/2}$ sec^{-1}	Degree of conversion, %	$R_{pi}/I^{1/2}M$, l.$^{1/2}$ mole$^{-1/2}$ sec^{-1}
Initiator Bis(4-tert-butylcyclohexyl) Peroxydicarbonate								
50	0.013	7.08×10^{-4}	6.68×10^{-4}	95.2	4.72×10^{-4}	4.45×10^{-4}	95.8	
	0.025	11.01×10^{-4}	7.36×10^{-4}	96.0	6.29×10^{-4}	4.21×10^{-4}	95.8	
	0.050	14.95×10^{-4}	7.06×10^{-4}	95.8	9.44×10^{-4}	4.46×10^{-4}	95.8	
			Mean value 7.03×10^{-4}			mean value 4.37×10^{-4}		7.23×10^{-4}
70	0.013	39.6×10^{-4}	38.6×10^{-4}	96.1	28.9×10^{-4}	28.2×10^{-4}	96.4	
	0.025	56.4×10^{-4}	38.9×10^{-4}	96.4	42.7×10^{-4}	29.5×10^{-4}	96.4	
	0.050	83.8×10^{-4}	40.9×10^{-4}	96.7	54.8×10^{-4}	26.7×10^{-4}	96.4	
			mean value 39.5×10^{-4}			mean value 28.1×10^{-4}		43.9×10^{-4}
Initiator Benzoyl Peroxide								
70	0.083	15.2×10^{-4}	5.8×10^{-4}	96.4	18.3×10^{-4}	7.0×10^{-4}	96.4	5.5×10^{-4}

Fig. 3. Polymerization of styrene in the pores of asbestos cement. Influence of concentration of benzoyl peroxide: (1) 0.021 mole/l.; (2) 0.041 mole/l.; (3) 0.083 mole/l.
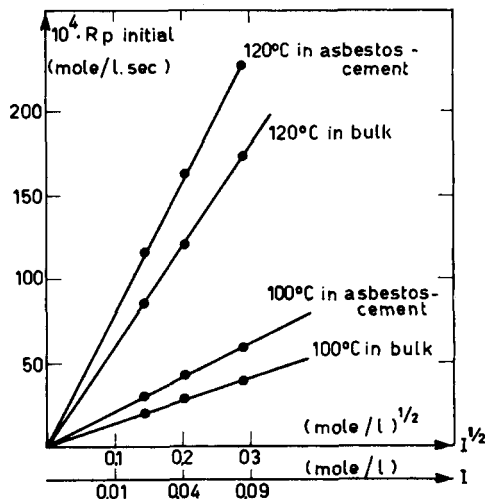

Fig. 4. Initial polymerization rate of styrene as a function of the square root of the benzoyl peroxide concentration.

DISCUSSION OF RESULTS

When one examines attentively the results obtained in this study, one observes (Tables II and III) that the kinetics of polymerization undergoes modifications in various ways following the absorption of the monomer on the porous mineral substratum.

Thus, the polymerization of styrene by benzoyl peroxide is considerably speeded up by the mineral, while the polymerization of methyl methacrylate initiated by the bis(4-tert-butylcyclohexyl) peroxydicarbonate is greatly slowed down. On the other hand, the polymerization of methyl methacrylate initiated by the benzoyl peroxide is accelerated and the ki-
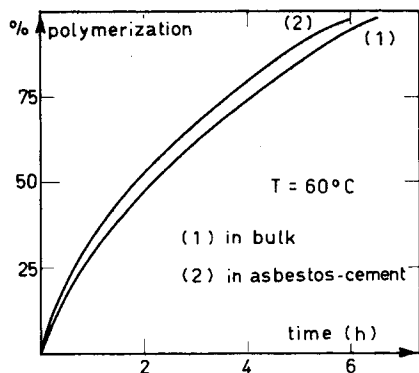
Fig. 5. Polymerization of styrene initiated by 0.101 mole/l. bis(4-*tert*-butylcyclohexyl) peroxydicarbonate.
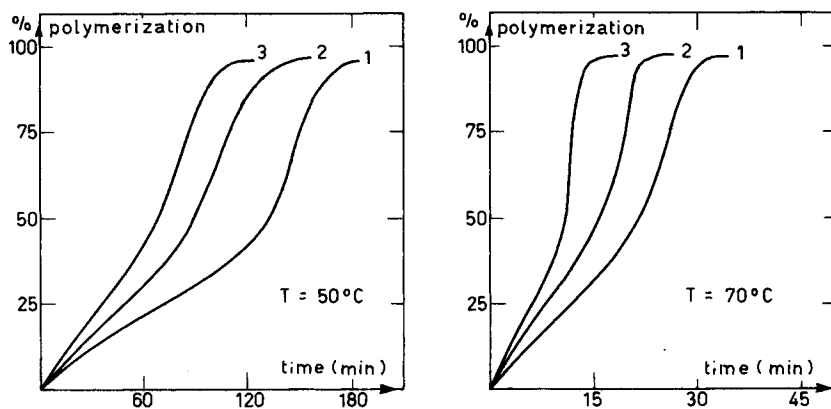

Fig. 6. Polymerization of methyl methacrylate in bulk. Influence of concentration of bis(4-*tert*-butylcyclohexyl) peroxydicarbonate: (1) 0.013 mole/l.; (2) 0.025 mole/l.; (3) 0.050 mole/l.
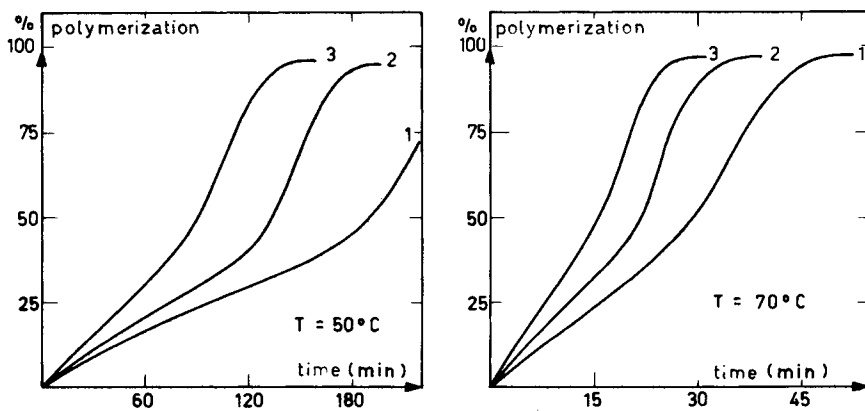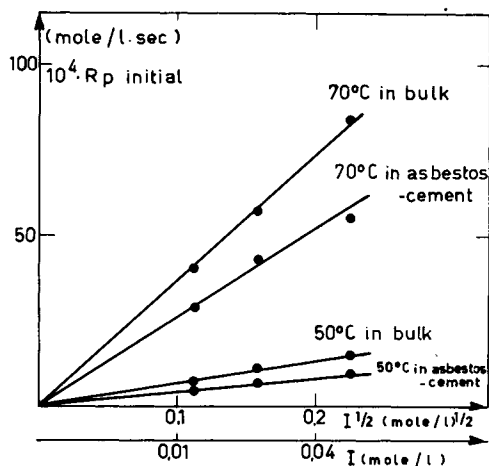

Fig. 7. Polymerization of methyl methacrylate in the pores of asbestos cement. Influence of concentration of bis(4-*tert*-butylcyclohexyl) peroxydicarbonate: (1) 0.013 mole/l.; (2) 0.025 mole/l.; (3) 0.050 mole/1.

Fig. 8. Initial polymerization rate of methyl methacrylate as a function of the square root of bis(4-*tert*-butylcyclohexyl) peroxydicarbonate concentration.
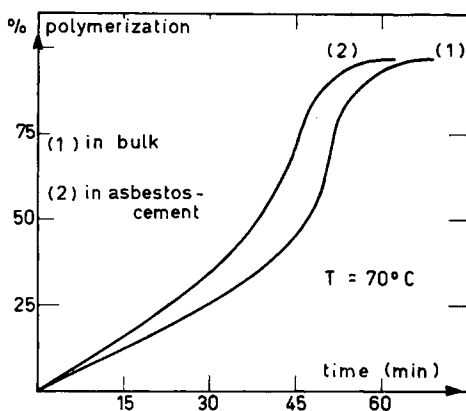

Fig. 9. Polymerization of methyl methacrylate initiated by 0.083 mole/l. benzoyl peroxide.

netics of polymerization of styrene initiated by the bis(4-*tert*-butylcy-clohexyl) peroxydicarbonate is practically unaltered.

We determined the dependence of the rate with regard to the concentration of the initiator in the case of the polymerization of styrene initiated by benzoyl peroxide (Fig. 4) and in methyl methacrylate initiated by bis-(4-*tert*-butylcyclohexyl) peroxydicarbonate (Fig. 8). It can be seen that the initial rate varies in proportion to the square root of the initiator. It can be noted equally that it tends toward zero for zero concentration in peroxide. This result is important because it shows that within the limits of experimental accuracy, polymerization is solely initiated by the thermal decomposition of the initiator.

The porous substratum, therefore, does not enter directly into the chain initiation and chain termination steps via an oxidoreduction mechanism as Solomon had proposed for certain high specific surface minerals.

In our opinion, we must put forward the influence of several factors in order to explain the substantial variations induced by the substratum. The first element that can exert an effect is modification of the constant of decomposition of the initiator K_d as a consequence of the alkalinity of the support. Equally, there might be changes in the constant of chain propagation K_p. This would be observed as a speeding up of propagation in the case of a double bond rich in electrons as in styrene, and as a slowing down in the case of a double bond poor in electrons (methyl methacrylate). The latter proposition is in keeping with the observations of Solomon[2] concerning the polymerization of styrene and methyl methacrylate on substrata of high specific surface without, however, introducing an oxidoreduction mechanism which modifies the initiation or the termination steps.

Examination of Tables II and III shows us that in the case of initiation by benzoyl peroxide, there is a marked acceleration in the rate of polymerization. It seems logical to attribute this result to an increase in the constant of decomposition of the initiator as a consequence of the basic character of the substratum. The fact that the increase in speed is more substantial in the case of styrene than in that of methyl methacrylate could result from some effect of the support on the constant of chain propagation.

In the case of polymerization of styrene initiated by benzoyl peroxide, there would be a cumulation of two accelerative effects, one arising from an increase in the rate of initiation, and the other resulting from the increase in the speed of chain propagation.

With regard to the polymerization of methyl methacrylate initiated by benzoyl peroxide, the accelerative effect due to the increase in the initiation speed would be partially counteracted by a depressive effect of the substratum on the constant by chain propagation.

As regards the initiation by bis(4-*tert*-butylcyclohexyl) peroxydicarbonate, we observe, in the case of the polymerization of methyl methacrylate, a substantial slowing down of the reaction, whereas in the case of styrene the kinetics are practically unchanged. Here again, we must propose two distinct effects in order to justify these variations in kinetics. In the polymerization of methyl methacrylate, there is a kinetic slowing down which would appear to result from a reduction of the constant of decomposition of the initiator potentiated by a diminution of the rate constant of chain propagation. In the polymerization of styrene, two antagonistic effects come into play: a diminution of the constant of decomposition of the initiator and an increase in the constant of chain propagation. So far we do not have a coherent explanation as to why the substrate increases the rate of decomposition of benzoyle peroxide and retards the rate for the peroxydicarbonate. It would be nice, before making speculation, to have

decomposition experiments run on the initiators themselves in the cement substrate for the decomposition rate measurements.

CONCLUSIONS

The limited number of results obtained in this study does not permit us to draw definite conclusions concerning the mechanism and the kinetics of polymerization in porous asbestos cement media. Nevertheless, we have been able to show that the substratum can intervene at several levels. The substratum would appear to come into play first of all indirectly at the initiation level; to be more precise, there would be an increase in the constant of decomposition of benzoyl peroxide and a decrease in the constant of decomposition of bis(4-*tert*-butylcyclohexyl) peroxydicarbonate. There would also appear to be an intervention on chain propagation, i.e., an acceleration of propagation in the case of styrene and a reduction of speed in the case of methyl methacrylate. We must also emphasize the fact that the polymerization is initiated solely by free radicals resulting from the thermal decomposition of the initiator.

We can also conclude from this study that initiation by thermal decomposition of an initiator is well adapted to polymerization in porous media since it enables us to obtain a high rate of polymerization at relatively moderate temperatures.

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