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Bulk and suspension polymerisation of vinyl chloride at high conversion

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A previous paper (Talamini, G., Visentini, A. and Kerr, J., *Polymer* 1998, **38**(10), 1879) has dealt with the first stage of the bulk and suspension polymerisation of vinylchloride where the reaction occurs contemporaneously in two phases, one of them very dilute and the other one very concentrated in polymer. The present paper deals with the second stage of polymerisation extending from the conversion at which the dilute phase disappears up to the limiting conversion. In this stage the reaction occurs in an homogeneous and more and more viscous environment. From an analysis of the curves, polymerisation rate *versus* conversion degree, it results that the chemically initiated polymerisations are submitted to the combined action of the gel effect and the lowering of the initiator efficiency. A kinetic equation, obtained through small modifications of the 'Gelfunction' of Weickert and Thiele (*Plaste Kautsch.*, 1983, **30**, 432), is suggested. The suggested equation expounds quite well the kinetic feature of reactions initiated by different initiators. A comparison between chemically and gamma radiation-initiated polymerisations, is also carried out. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: vinylchloride; polymerisation; kinetics)

INTRODUCTION

Bulk and suspension polymerisation of vinyl chloride (VC) develops through two consecutive kinetically different stages.

In the first stage, the reaction occurs under heterogeneous conditions; in fact, owing to the scarce solubility of the polymer (PVC) in its own monomer (VC) the polymerising system splits off into two phases at the onset of polymerisation (conversion lower than 0.1%). One of the phases is a very dilute liquid monomeric phase (volume fraction of PVC < 0.001), whereas the other one is a very concentrated quasi-solid or gel-like phase (volume fraction of PVC *ca.* 0.6 at 50°C). During the reaction, the weight fraction of the gel phase increases, whereas that of the monomeric phase decreases until, at a given conversion degree, X_f, this last phase disappears. At this point the second stage begins and the reaction goes on in a unique homogeneous phase up to the limiting degree of conversion X_l. Hence, the first stage lasts during the range of conversion 0–X_f, whereas the second stage extends in the range X_f–X_l.

In a previous study[1] we have examined the first stage of the polymerisation, where the reaction owing to the higher specific rate in the concentrated phase (due to the gel effect), with respect to that in the dilute phase, shows an autocatalytic behaviour.

The kinetic equations that we have found to describe the reaction quite well in this first stage are collected, for the convenience of the reader, in the next paragraph.

In the present paper, we complete the analysis of the polymerisation, dealing with its second stage, i.e. the stage extending between the degrees of conversion X_f and X_l.

A slight modification of the 'Gelfunction' of Weickert and Thiele[2] is suggested in order to fit it to expound the different kinetic features shown by reactions initiated using different initiators. A comparison between chemically and radiation-initiated polymerisations is also carried out.

KINETIC EQUATIONS IN THE FIRST STAGE

According to the two-phase model[1], the chemically initiated bulk and suspension polymerisation of VC are both well expounded by the following equations:

$$\frac{dX}{dt} = R_{m0}(1 + qX)\left[\exp\left(-\frac{k_d t}{2}\right)\right] \tag{1a}$$

where t is time; q is the autocatalysis factor, k_d is the decomposition rate constant of the initiator; R_{m0} is the specific polymerisation rate in the dilute phase at $t = 0$. R_{m0} is given by:

$$R_{m0} = \kappa R_{i0}^{0.5}$$

where

$$\kappa = \frac{1}{\sqrt{2}}\frac{k_p}{\sqrt{k_{tm}}}$$

(with k_p the propagation rate constant and k_{tm} the termination rate constant in the dilute phase) and,

$$R_{i0}^{0.5} = (2f_m k_d I_{m0})^{0.5}$$

with f_m the initiator efficiency in the dilute phase and I_{m0} the initiator concentration at $t = 0$.

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If the initiation rate can be assumed constant and equal to R_{i0} in the whole conversion interval, as for example in the case of a small value of k_d (at the polymerisation temperature) or with reactions initiated by gamma radiation, equation (1a) becomes:

$$\frac{dX}{dt} = R_{m0}(1 + qX) \tag{2a}$$

Through integration of the equation (1a) and equation (2a), one obtains, respectively,

$$X = \frac{1}{q}\left\{\exp\left[\left(\frac{2q}{k_d}\right)R_{m0}\left(1 - \exp\left(-\frac{k_d t}{2}\right)\right)\right] - 1\right\} \tag{1b}$$

or, in the logarithmic form

$$\frac{\ln(1 + qX)}{q} = \left(\frac{2}{k_d}\right)R_{m0}\left[1 - \exp\left(-\frac{k_d t}{2}\right)\right] \tag{1c}$$

and:

$$X = \frac{1}{q}[\exp(qR_{m0}t) - 1] \tag{2b}$$

or, in logarithmic form:

$$\frac{\ln(1 + qX)}{q} = R_{m0}t \tag{2c}$$

Other peculiar kinetic aspects of the heterogeneous first stage of the reaction are the following ones:

(1) the specific polymerisation rate in the concentrated phase, where the weight fraction of PVC is equal to X_f, is Q times higher than that in the dilute phase;

(2) the relationship among q, Q and X_f is:

$$q = \frac{Q(1 - X_f) - 1}{X_f};$$

(3) the specific polymerisation rate in the dilute phase, where the concentration of polymer is very small, can be considered coincident with the specific rate at $X = 0$ (R_{m0} of equation (1a) and equation (2a));

(4) as also Xie *et al.*[3] have found, the ratio between the initiator efficiency in the two phases, f_c/f_m, is equal to 1 in the whole conversion range 0 to X_f.

THE SECOND STAGE OF REACTION

The limiting conversion

The bulk and suspension polymerisation of VC does not reach, as that of many other monomers, the total conversion, but stops at a limiting degree of conversion, X_l, lower than unity. X_l increases with increasing polymerisation temperature. The most accepted explanation of this fact is that, at X_l, the polymer/monomer mixture has such a composition that its glass transition temperature, T_g, is equal to the polymerisation temperature. In other words, the polymerising system, when it reaches X_l, becomes a glass-like solid in which the polymerisation cannot occur any more. According to the free volume theory[4] the polymer volume fraction, V_p, at the glassy transition state, is given by the following equation:

$$V_p = \left(\frac{\alpha_m(T - T_{gm})}{\alpha_p(T_{gp} - T) + \alpha_m(T - T_{gm})}\right) \tag{3}$$

where T_{gm} and T_{gp} are the glass transition temperature of the monomer and polymer, T the glass transition temperature of the mixture, α_m and α_p are the volume expansion coefficient of monomer and polymer, respectively. In the case of VC and PVC, Xie *et al.*[3] furnish the following values for the different parameters:

$$T_{gm} = 70 \text{ K}$$

$$T_{gp} = 87.1 - 0.132T_p \ (^\circ\text{C})$$

where T_p is the polymerisation temperature (°C)

$$\alpha_m = 9.98 \times 10^{-4}$$

$$\alpha_p = 5.47 \times 10^{-4}$$

The relationship between X_l and V_p is:

$$X_l = \frac{V_p}{1 + \varepsilon(1 - V_p)} \tag{4}$$

where:

$$\varepsilon = \frac{\rho_m - \rho_p}{\rho_p}$$

with ρ_m and ρ_p monomer and polymer densities at the polymerisation temperature. Xie *et al.*[3] give:

$$\rho_m = 947.1 - 1.746T - 3.24 \times 10^{-3}T^2 \ (\text{g l}^{-1})$$

with T in °C

$$\rho_p = 10^3 \exp(0.4296 - 3.274 \times 10^{-4}T) \ (\text{g l}^{-1})$$

with T in K.

Then, using equations (3) and (4), and the above reported values and relationship for the different parameters, one can calculate X_l at various temperatures. According to Weickert and co-workers[5,6], X_l can be determined through the following equations:

$$X_l = \frac{1}{0.66208 + \dfrac{79.26}{T_p - 113.45}} \tag{5}$$

where T_p is the polymerisation temperature in K.

In *Table 1* we have collected the values of X_l corresponding to five different polymerisation temperatures

Table 1 Values of X_l at different polymerisation temperatures

	Polymerisation temperature (°C)					Polymerisation type
	50	55	60	65	70	
From Eq. (3) and Eq. (4)	0.960	0.968	0.976	0.983	0.990	Bulk
From Eq. (5)	0.961	0.969	0.977	0.985	0.992	Bulk
Ref. 3 (calculated)	0.942	0.953	0.964	0.974	0.985	Suspension
Ref. 3 (experimental)	0.930	0.942	0.950	0.954	0.967	Suspension

Table 2 X_l for bulk polymerisation initiated by gamma radiation

	Temperature (°C)				
	25	30	40	50	70
Experimental, Ref. 7	0.960	—	> 0.970	—	—
Experimental, Ref. 8	—	> 0.920	—	> 0.960	> 0.980
Theoretical, from Eq. (5)	0.916	0.925	0.944	0.961	0.992

in the range 50–70°C, and calculated using equations (3), (4) and (5). In the same table the values of X_l both calculated and experimentally determined by Xie *et al.*[3] are also reported. One can note the excellent agreement between the values of X_l calculated through equations (3) and (4) and those obtained using equation (5). The convenience of employing this last simple equation for the calculation of X_l appears clearly evident. Another observation is that the theoretical values of X_l obtained by Xie *et al.* are smaller than those calculated by us. The difference is due to the unconverted monomer that, in the case of the suspension polymerisation, is dissolved in the water phase (Xie *et al.* operated in suspension with a water/monomer ratio equal to 2). One can observe that the difference between the values of X_l of the two types of polymerisation (bulk and suspension) decreases with increasing temperature: in fact the solubility of VC in water decreases with increasing the temperature. Moreover, it is worthwhile noting that the experimental values of X_l found by Xie *et al.*[3] are lower than the theoretical ones. This can probably be ascribed to the efficiency of the chemical initiator that becomes practically equal to zero before the polymerising system reaches the glassy-state conditions. This hypothesis could be confirmed by the observation that, in the case of bulk gamma-radiation-initiated polymerisation[7,8], the experimental values of X_l are about equal or even higher that those obtained from equation (5), as one can see in *Table 2*. Then, a still active propagation reaction, also under the glassy-state conditions, cannot be excluded.

Kinetic behaviour of the reaction

According to Weickert and co-workers[2,5] the kinetic feature of the homogeneous bulk polymerisation of monomers such as, for example, styrene or methylmethacrylate, in which the gel (or Trommsdorff) effect is present, is well expressed by an equation that they call 'Gelfunction' consisting of the product of two quantities, both of them a function of the degree of conversion X.

If the consumption of the initiator can be neglected, the Gelfunction, GF, gives the ratio between the specific polymerisation rate at $X(R_p)$ and that at $X = 0(R_{p0})$ and can be expressed by the following equation:

$$\frac{R_p}{R_{p0}} = \mathrm{GF} = M(X) \cdot N(X) \tag{6a}$$

where

$$M(X) = \frac{\exp(gX^2)}{1 + gX^2} \tag{6b}$$

$$N(X) = \left[1 - \left(\frac{X}{X_l}\right)^3\right]^b \tag{6c}$$

If the consumption of the initiator is not negligible (high k_d) the ratio R_p/R_{p0} is given by:

$$\frac{R_p}{R_{p0}} = \mathrm{GF} \cdot \left[\exp\left(-\frac{k_d}{2}t\right)\right] \tag{6d}$$

$M(X)$ and $N(X)$ take into account the decrease, respectively, of the termination rate constant and of the efficiency of initiator occurring during the polymerisation because of the increase in the viscosity of the reaction medium. Weickert and Thiele[2] have found that the value of the parameters g and b depends on the type of monomer, whereas the ratio b/g is quite independent of the monomer nature and can be put equal to 0.294. Therefore, GF varies only with the nature of the monomer, whereas it is independent of the kind of chemical initiator employed. In other words, GF of a given monomer is always the same for all the chemically initiated polymerisations. What can vary by changing the initiator is only the initial value of the efficiency, f_0, besides, of course, the decomposition rate. Moreover, one can note that, according to GF, the initiator efficiency, f, begins to decrease immediately at the onset of polymerisation, becoming equal to zero at X_l.

Weickert and Thiele[2] have found that a function such as GF describes quite well the bulk and suspension polymerisation of both styrene and methylmethacrylate. These authors[5] have applied GF also for describing the second homogeneous stage of VC bulk and suspension polymerisation. They assumed that, in the range of conversion X_f–X_l, if the consumption of initiator is negligible, GF gives the ratio R_p/R_{m0} between the specific polymerisation rate at X and $X = 0$. Therefore, on the basis of the above given definition, GF at X_f is equal to the parameter Q of the first heterogeneous stage. Then, knowing Q and X_f one can calculate, through equations (6a)–(6c) the value of the parameter g of GF. From the works dealing with the first heterogeneous stage, one has that, at 50–55°C, $Q \cong 15$ and $X_f \cong 0.7$. Then, putting $X_l = 0.96$, one obtains:

$$g = 14$$

With this value of g, from equation (6c) one has that $f_c/f_m = 0.13$, i.e. a value in clear disagreement with the value of 1 experimentally found for this ratio (see above).

In subsequent works, Weickert *et al.*[5,6] have suggested the following equation for expounding the second stage of VC polymerisation:

$$\frac{R_p}{R_{m0}} = Q\,\frac{X_l - X}{X_l - X_f} \tag{7}$$

Previously, Abdel-Alim and Hamielec[10] had proposed the following analogous equation:

$$\frac{R_p}{R_{m0}} = Q\,\frac{1 - X}{1 - X_f} \tag{8}$$

One can see that equation (8) corresponds to equation (7) with $X_l = 1$.

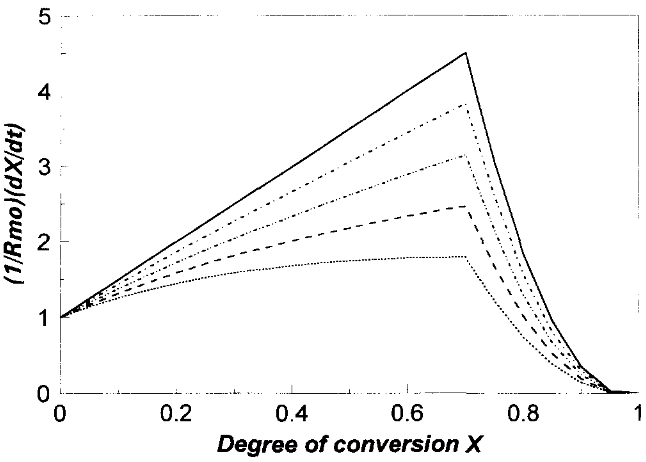

Figure 1 Curves of $(1/R_{m0})(dX/dt)$ *versus* X. (————) $\delta = 0$; (—·—·—) $\delta = 0.5$; (—··—··—) $\delta = 1$; (— — —) $\delta = 1.5$; (···) $\delta = 2$

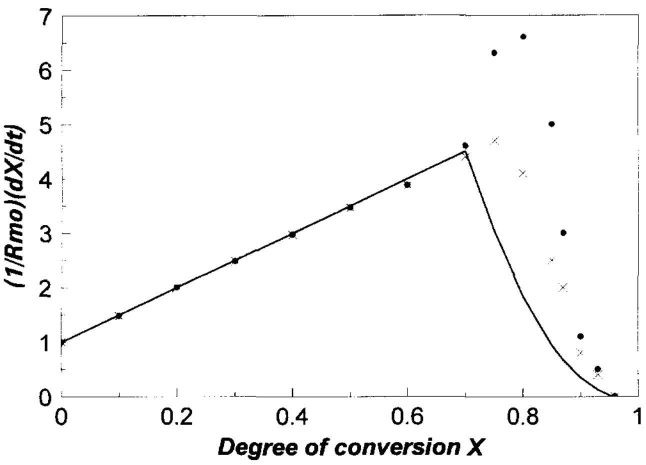

Figure 2 Curves of $(1/R_{m0})(dX/dt)$ *versus* X. Comparison of theoretical curve with experimental data. (————) $\delta = 0$; Experimental data from Ref. 11: (●) LPO; (×) AIBN

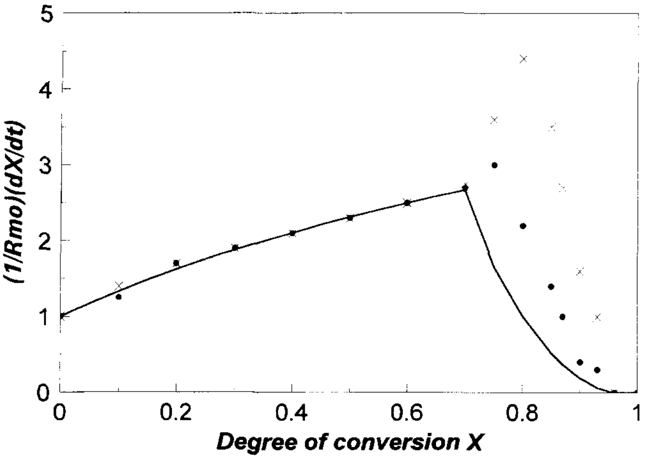

Figure 3 Curves of $(1/R_{m0})(dX/dt)$ *versus* X. Comparison of theoretical curve with experimental data. (————) $\delta = 1.35$. Experimental data (our lab): (●) TBHP; (×) EP

According to both equation (7) and equation (8) the specific polymerisation rate decreases continuously after X_f reaching the value zero, respectively, at $X = X_l$ and at $X = 1$. Also, in this case, the kinetic equation is the same for all the chemically initiated reactions independently from the initiator nature. Then, according to Weickert *et al.* the polymerisation rate in the second stage of reaction is well expressed by the following equation, in which the exponential term takes into account the change of the rate due to the consumption of the initiator:

$$\frac{1}{R_{m0}}\frac{dX}{dt} = Q\,\frac{(X_l - X)}{(X_l - X_f)}(1 - X)\exp\left(-\frac{k_d}{2}t\right) \qquad (9)$$

Equation (9) neglects the change of the rate due to the decrease of the volume (about 12%) occurring in the range of conversion X_f–X_l.

As we have seen above, in the first stage the reaction is well described by equation (1a). This equation can be rewritten in a form containing the variable X only, instead of the two independent variables X and t. In fact from equation (1c) one has:

$$\exp\left(-\frac{k_d}{2}t\right) = [1 - \delta H(X)] \qquad (10)$$

where:

$$\delta = \frac{k_d}{2R_{m0}}$$

and

$$H(X) = \frac{\ln(1 + qX)}{q}$$

Then equation (1a) becomes:

$$\frac{1}{R_{m0}}\frac{dX}{dt} = (1 + qX)(1 - \delta H(X)) \qquad (1d)$$

It is worthwhile noting that:

(1) when k_d is small, δ is also small and the reaction, in the first stage, is well expounded by equation (2);

(2) δ decreases with increasing R_{m0} (in fact, the higher the polymerisation rate the shorter the time spent to reach a given conversion and, consequently, the smaller the consumption of initiator).

Through equation (10), equation (9) becomes:

$$\frac{1}{R_{m0}}\frac{dX}{dt} = Q[1 - \delta H(X_f)]\frac{(X_l - X)}{(X_l - X_f)}(1 - X)\exp\left[\frac{k_d}{2}(t_f - t)\right] \qquad (9a)$$

where t_f is the time spent to reach the conversion degree X_f.

In *Figure 1* some curves $(l/R_{m0})(dX/dt)$ *versus* X, each of them corresponding to a different value of δ, are collected. The curves have been drawn using equation (1a) for the first stage of the reaction and equation (9) for the second stage of the reaction, and assuming that the consumption of the initiator after X_f can be neglected. Moreover, the following parameter values have been assigned:

$$X_l = 0.96 \quad q = 5 \quad X_f = 0.7 \quad Q = 15$$

In *Figures 2* and *3* the theoretical curves corresponding to $\delta = 0$ and $\delta = 1.35$ are compared with the experimental data relative to polymerisation initiated by AIBN and LPO at 50°C (data taken from Ref. 11) and bis(4-*t*-butylcyclohexyl)peroxydicarbonate (TBHP) and bis(ethylperoxy)dicarbonate (EP) at 55°C (data obtained in our lab). One can see that, whereas in the first stage of reaction the agreement between theoretical curves and experimental data is quite good ($\delta = 0$ for LPO and AIBN; $\delta = 1.35$ for TBHP and EP), in the second stage of the reaction deviations are present in all cases, particularly in the polymerisations initiated

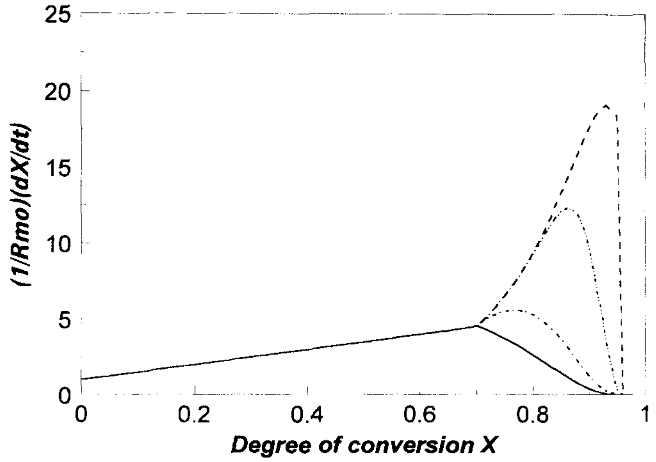

Figure 4 Curves of $(1/R_{m0})(dX/dt)$ *versus* X. Theoretical curves drawn using equation (1d) (range 0–X_f) with $\delta = 0$ and equation (9b) (range X_f–X_l) with: (————) $a = 0$; (-·-·-) $a = 1.7$; (-··-··-) $a = 6$; (— — —) $a = 200$

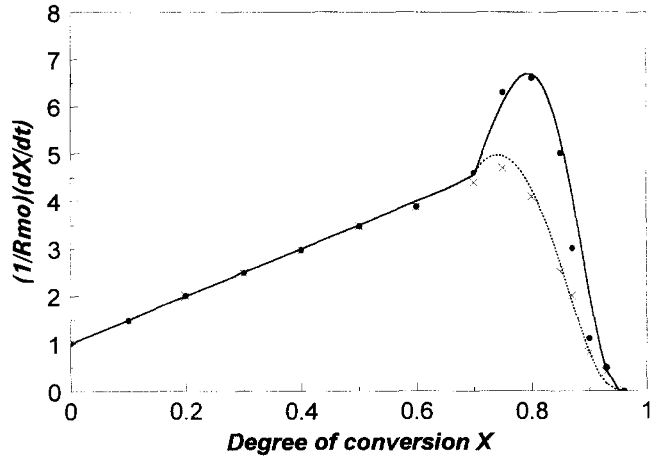

Figure 5 Curves of $(1/R_{m0})(dX/dt)$ *versus* X. Comparison of theoretical curve with experimental data. (————) $\delta = 0$, $a = 2.1$; (···), $\delta = 0$, $a = 1.4$. Experimental data from Ref. 11: (●) LPO; (×) AIBN

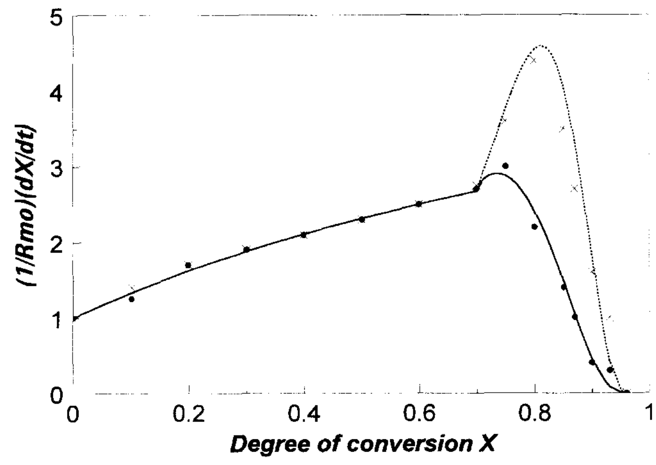

Figure 6 Curves of $(1/R_{m0})(dX/dt)$ *versus* X. Comparison of theoretical curve with experimental data. (————) $\delta = 1.35$, $a = 1.35$; (···) $\delta = 1.35$, $a = 2.7$. Experimental data from our lab: (●) TBHP; (×) EP

by LPO and EP. Differently from what equation (9) and equation (9a) foresee, the polymerisation rate continues to increase also after X_f, passes through a maximum and then decreases, reaching the value 0 at X_l. The maximum is more or less pronounced according to the nature of the initiator.

This behaviour can be explained if one assumes that, after X_f, the gel effect increases, whereas the initiator efficiency, f, decreases. If this assumption is valid, the kinetics, after X_f, should be described by a function deriving from the 'Gel-function', GF, of Weickert and Thiele, introducing in it suitable modifications, in order to take into account the two following experimental results:

(1) the ratio between the initiator efficiency in the concentrated phase and that in the dilute phase is equal to 1 (i.e. f at X_f is equal to f_0);

(2) the influence of the reaction medium on f (after X_f) depends on the nature of the initiator.

Hence, we have modified GF, replacing in it the $N(X)$ function (see equations (6a)–(6c)) with the following function, $N^*(X)$:

$$N^*(X)=\left[1-\left(\frac{X-X_f}{X_l-X_f}\right)^a\right]^b \qquad (11)$$

The exponent a in equation (11) is an adjustable parameter, and its value depends on the nature of the initiator. The exponent b is the same as that in equation (6c).

Therefore, the kinetic equation describing the polymerisation, in the range X_f–X_l, neglecting the initiator consumption after X_f, becomes the following one:

$$\frac{1}{R_{m0}}\frac{dX}{dt}=M(X)N^*(X)\left[1-\delta H(X_f)\right](1-X) \qquad (9b)$$

At X_f the function $N^*(X)$ is equal to 1, then one has:

$$M(X_f)=Q$$

Knowing the value of Q one can then calculate the value of the parameter g of the $M(X)$ function (see equation (6b)). As we have seen above, at 50–55°C, $Q = 15$; therefore $g = 9$ and $b = 0.294 \times 9 = 2.6$.

In *Figure 4* the curves obtained using equation (1d) and equation (9b) putting $\delta = 0$ and changing the value of a, are collected. One can see that the greater the exponent a, the higher the maximum, i.e. the lower the influence of the reaction medium on f. In fact, when $a = \infty$, $N^*(X) = 1$ (i.e. $f/f_0 = 1$) in the whole range of conversion X_f–X_l. This last condition should occur quite well in the case of gamma ray-initiated polymerisations.

Actually, examining the curves X/t reported in Refs. 7 and 8 and corresponding to polymerisations carried out in the temperature range of 40–90°C, one can note that the reaction shows an autocatalytic behaviour up to $X = 0.9$.

In *Figures 5* and *6* the theoretical curves corresponding to different values of δ and a are compared with the experimental data of the polymerisations initiated by AIBN, LPO, TBHP and EP. The values of δ and a resulting from this comparison for each of the four initiators, are collected in *Table 3*.

It would be interesting to know if the parameter a is in some way correlated to any of the physical–chemical properties (size, polarity, etc.) of the initiator or of the free radicals produced from it. Of course, in order to reach this aim, one needs to know the value of the parameter a for a high number of initiators.

Before concluding, it is worthwhile noting that, knowing the value of δ and R_{m0}, one can calculate the value of k_d of the initiator at the polymerisation temperature. In the case of the initiator TBHP we have found $\delta = 1.35$ at 55°C.

Table 3 Values of δ and a

Initiator	T (°C)	δ	a
AIBN	50	0	1.4
LPO	50	0	2.3
TBHP	55	1.35	1.35
EP	55	1.35	2.7

Moreover, at the adopted experimental conditions we had $R_{m0} = 2.3 \times 10^{-3}\ \text{min}^{-1}$. Then:

$$k_d = 4.6 \times 10^{-3} \times 1.35 = 6.2 \times 10^{-3}\ \text{min}^{-1}$$

Xie *et al.*[3] give the following relationship between k_d and T for the initiator TBHP:

$$k_d = 2.31 \times 10^{15} \exp(-29.1\ \text{kcal}/RT)$$

Using this equation one obtains, at 55°C, $k_d = 7.5 \times 10^{-3}\ \text{min}^{-1}$, a value in quite good agreement with that above obtained through δ.

CONCLUSIONS

The following conclusions can be drawn:

(1) in the second stage of the VC bulk and suspension polymerisation (conversion range X_f–X_l), an increase of the polymerisation rate with X, due to the gel effect, is occurring;

(2) in the radiation-initiated polymerisations, where the initiation step is only weakly influenced by the viscosity of the reaction medium, the polymerisation rate increases up to $X \cong 0.9$;

(3) the increase of the rate due to the gel effect is well expounded by the function proposed by Weickert and Thiele;

(4) in the case of the chemically initiated polymerisations, a decrease of the reaction rate caused by a lowering of the initiator efficiency, f, occurs contemporaneously with the increase of the rate due to the gel effect;

(5) as a result of the two above combined effects, the rate of the chemically initiated polymerisations reaches a maximum value at a given conversion degree X (lower than 0.9), and then decreases down to the value zero at X_l;

(6) the position (value of X) and height of the maximum depend on the nature of the initiator;

(7) the lowering of f with X is well described by an equation obtained through a small modification of the equation suggested by Weickert and Thiele.

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