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Bulk and suspension polymerization of vinyl chloride: the two-phase model*

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An in-depth investigation into the validity of the two-phase model in describing the bulk and suspension polymerization of vinyl chloride monomer is carried out, in the light of the latest theoretical and experimental works that have appeared in the literature. Particular attention is paid to the influence upon the reaction of the transfer of free radicals and of the distribution of the chemical initiators between the two phases. Equations giving, respectively, the kinetic chain length and the degree of polymerization of the polymer, as a function of conversion, are calculated. A good agreement between these theoretical models and the experimental data is observed. Methods for the detemination of the kinetic parameters, and numerical values of some of them are also given. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Many kinetic models have appeared in the literature to describe the bulk and suspension polymerization† of vinyl chloride (VC). Among them the most generally accepted one is. at present, the so-called 'two-phase model', as first proposed by one of the current authors[1,2] about 30 years ago. Since then, many papers have been published, some of which suggesting modifications of the model that should make it more consistent with the polymerization behaviour. Moreover, inasmuch as the model describes the reaction only in the range from its onset up to the conversion at which one of the phases disappears (at about 73% conversion at 50°C), much modelling work has been done with the aim of describing the reaction in its second part, up to the limiting conversion. We have thought that a critical review of this wide and complex matter would be very useful

In the present paper, a deep investigation of the two-phase model is carried out, taking into account, particularly, the comprehensive and rather recent works by Xie *et al.*[3], and by Weickert and coworkers[4,5]. Values of the kinetic constants and parameters as well as simple methods for their determination are also provided. The second part of the polymerization process, i.e. the part of the reaction extending from the disappearance of one of the phases as far as the limiting conversion, will be analysed in a further paper.

THE TWO-PHASE MODEL

According to this model, owing to the poor solvent capacity of VC with respect to its own polymer (PVC), during bulk and suspension polymerizations of VC, the system splits into two phases‡ shortly after the onset of reaction (conversion $< 0.1\%$ at 50°C).

One of these two phases is a very dilute liquid monomer phase (polymer volume fraction $V_2 < 0.001$), whereas the other one is a very concentrated quasi solid or gel-like phase ($V_2 = 0.6$ at 50°C). Then, both bulk and suspension polymerization of VC occurs simultaneously in two phases. The polymerization rate in the concentrated gel phase will be higher than that in the dilute monomeric phase as a result of the significantly higher viscosity of the medium and consequently the much lower termination rate. If R_m is the specific polymerization rate in the monomeric phase, and R_c that in the concentrated phase, then, assuming that the ratio between the two rates is constant, one can write

$$R_c = QR_m \text{ (where } Q > 1)$$

If X denotes the degree of conversion of the reaction and A the weight ratio of monomer to polymer in the concentrated phase, the overall polymerization rate: dX/dt is given by the following equation:

$$\frac{dX}{dt} = R_m(1 - X - AX) + QR_mAX = R_m(1 + qX) \quad (1)$$

where $q = (QA - A - 1)$

One can observe that if $Q = 1$ (i.e. $R_m = R_c$), $q = -1$ and equation (1) becomes, as expected, equal to the kinetic equation that is valid for the homogeneous free radical polymerizations. It is worthwhile to note that:

- when $Q < (A + 1)/A$, q has a negative value, then the polymerization rate linearly decreases with increasing X;

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† It has been demonstrated that bulk and suspension polymerization of VC are kinetically equivalent

‡ In suspension polymerization, the splitting into two phases occurs inside each drop of monomer

- when $Q = (A + 1)/A$, $q = 0$ and the polymerization rate is independent of X, and always equal to R_m;
- when $Q > (A + 1)/A$, q has a positive value, hence the polymerization rate linearly increases with increasing X.

The composition of the gel phase (and therefore also the value of A) changes with temperature. So, the critical value of Q, at which $q = 0$, also changes with temperature. As we shall see later, under the polymerization conditions normally adopted, Q is always higher than this critical value, so the polymerization shows an autocatalytic behaviour.

In equation (1), R_m is given by:

$$R_m = \frac{k_p}{(2k_{tm})^{0.5}} \times (R_i)^{0.5}$$

where k_p is the rate constant of the propagation stage, k_{tm} is the rate constant of the termination stage in the dilute phase, and R_i is the initiation rate.

If R_i can be considered constant, as it is for example in the case of initiation by gamma rays or by chemical initiators having a very small decomposition rate constant (k_d), through integration of equation (1) one obtains

$$\frac{\ln(1 + qX)}{q} = \kappa(R_i)^{0.5}t \tag{2a}$$

or

$$X = \frac{1}{q}\left[\exp(q\kappa R_i^{0.5}t) - 1\right] \tag{2b}$$

where

$$\kappa = \frac{k_p}{(2k_{tm})^{0.5}}$$

and t is time. If R_i is not constant, for the integration of equation (1) one needs to know how R_i varies with t (or X).

For the chemical initiators it is generally assumed that

$$R_i = R_{i0}e^{-k_dt}$$

where

$$R_{i0} = 2fk_dI_0$$

in which f denotes the initiator efficiency, I_0 the concentration of initiator at $t = 0$ and k_d the decomposition rate constant of the initiator. Hence, equation (1) becomes

$$\frac{dX}{dt} = \kappa(R_{i0})^{0.5}\left[\exp(-\frac{k_dt}{2})\right](1 + qX) \tag{3}$$

By integrating equation (3) between 0 and X and between 0 and t, one obtains:

$$X = \frac{1}{q}\left\{\exp\left[\left(\frac{2q}{k_d}\right)\kappa R_{i0}^{0.5}\left(1 - \exp\left(-\frac{k_dt}{2}\right)\right)\right] - 1\right\} \tag{4a}$$

or, in the logarithmic form:

$$\frac{\ln(1 + qX)}{q} = \left(\frac{2}{k_d}\right)\kappa R_{i0}^{0.5}\left[1 - \exp\left(-\frac{k_dt}{2}\right)\right] \tag{4b}$$

It is worth pointing out that, as results from equations (2a) and (2b), when chemical initiators with a small k_d at the temperature of polymerization are employed (R_i = constant), the conversion curves should completely overlap when they

are plotted as X versus $t(R_i^{0.5})$ instead of X versus t. This has been found experimentally by many authors[1,2,6-13].

On the contrary, this is not valid in the case of polymerizations carried out with initiators having a high k_d, as equations (4a) and (4b) demonstrate. Later on, we shall return to this subject,

CONFIRMATIONS AND LIMITATIONS OF THE TWO-PHASE MODEL

The above reported mathematical treatment substantially corresponds to that developed by Talamini[1,2]. The following assumptions are contained in the treatment:

(1) The two phases are in thermodynamic equilibrium, thus the composition of each phase remains constant throughout the reaction.
(2) The ratio between the steady-state concentrations of free radicals in the two phases is constant.
(3) When a chemical initiator is used, the partition law of the initiator between the two phases does not vary throughout the reaction, i.e. the ratio between the initiator concentrations in the two phases I_m/I_c, is constant.

Some authors[3,14-18] have been very critical of these assumptions, particularly of the second one, which is valid only if the transfer of free radicals between the phases is absent. In the following, we shall examine thoroughly each of these assumptions in the light of the various and more recently published works, and, in particular, of the above-cited works by Weickert et al.[4,5] and by Xie et al.[3].

Equilibrium between phases

During the polymerization, the amount of the concentrated phase increases, whereas that of the dilute phase decreases. At a given conversion degree, X_f, the monomeric phase disappears, and the system consists of only the concentrated phase. From this point onwards, the reaction proceeds under homogeneous conditions. Xie et al.[19] showed that the two phase are in thermodynamic equilibrium throughout the conversion range in which they co-exist. Consequently, X_f is a function only of the temperature and, moreover, its value is equal to the weight fraction of polymer in the concentrated phase. Then, the quantity A of equation (1) is equal to

$$A = \frac{(1 - X_f)}{X_f}$$

and consequently:

$$q = \frac{Q(1 - X_f)}{X_f} - \frac{(1 - X_f)}{X_f} - 1 = \frac{Q(1 - X_f) - 1}{X_f} \tag{5}$$

This relationship among q, Q and X_f was first proposed by Abdel-Alim and Hamielec[12]. Another way to obtain this relationship is by the following procedure.

X_f is the conversion degree at which heterogeneous conditions end and homogenous conditions begin. Hence, at X_f both sets of kinetic equations, i.e. those of heterogeneous and homogeneous polymerization, must hold. Then, bearing in mind that $R_c = QR_m$, one has

$$\left(\frac{dX}{dt}\right)_{X = X_f} = R_m(1 + qX_f) = QR_m(1 - X_f)$$

from which

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

which corresponds to equation (5).

Xie *et al.* also determined the values of X_f at various polymerization temperatures and the relationship between the Flory–Huggins parameter χ and the temperature, This last relationship transpires as

$$\chi = \frac{1286.4}{T} - 3.02 \qquad (6)$$

where T is in Kelvin.

By using the data of Xie *et al.*, one can calculate, albeit approximately, the temperature at which the polymerization occurs with the polymerizing VC/PVC system at its critical temperature, T_c, i.e. in homogeneous conditions in the whole range of conversion from 0 to final conversion. In fact, for a binary polymer–solvent mixture, the value of χ at T_c is given by

$$\chi_c = \frac{1}{2} + \frac{1}{P^{0.5}} \qquad (7)$$

where P is the degree of polymerization of the polymer.

In the VC polymerization, the chain transfer reaction to monomer plays the main role in determining the length of the polymeric chain. Therefore, in the case of PVC, the number average polymerization degree, P_n is roughly given by

$$P_n \approx \frac{1}{C_M} \qquad (8)$$

where C_M is the monomer transfer constant and P_n the number average polymerization degree. C_M depends on the temperature, according to the following equation[3,10]:

$$C_M = 5.78 \times \exp\left(\frac{-2768.1}{T}\right) \qquad (9)$$

By simultaneously using equations (6)–(9)§, the polymerization temperature, T_{pc} coinciding with the critical temperature of the system, can be determined. The resulting temperature is

$$T_{pc} \approx 361K \; (88°C) \qquad (10)$$

The following conclusions can be drawn:

- the two phases, throughout the conversion range where they coexist, are in thermodynamic equilibrium;
- when the temperature is higher than about 90°C, the polymerization should occur in a unique homogeneous phase up to the final conversion.

Regarding the second point, it is worthwhile noting that in a work by Tavan *et al.*[20] on the bulk polymerization of VC initiated by gamma rays, kinetic data for reactions run at 90°C are reported. Actually, at this temperature the autocatalysis is much less pronounced than at 50 and 70°C. In fact, at the latter temperatures an autocatalytic behaviour up to reaction completion is noticed, while at 90°C the reaction rate increases only to a degree of conversion of 0.1–0.15, after which it remains practically constant. Moreover, in a successive work, Palma *et al.*[21] found that

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§ equation (7) holds rigorously only if the polymer has a very narrow molecular weight distribution. Then, the substitution of P with P_n in equation (7) is a rather large approximation

at 110°C the bulk polymerization of VC proceeds up to high conversion in a unique, transparent, homogeneous phase.

Free radicals steady-state concentrations in the two phases

In a recent work, Xie *et al.*[3] have developed a comprehensive kinetic scheme for VC bulk/suspension polymerization, based on the two-phase model. In the scheme, all the reaction processes that one can think of occurring in the VC polymerization are taken into account. Among them the processes of migration of free radicals between the two phases are included.

According to Xie *et al.* the transfer of free radicals from the dilute to the concentrated phase is due to the precipitation of the chain radicals, growing in the dilute phase, when they achieve a critical length, r_c, whereas the transfer of free radicals from the concentrated to the dilute phase occurs through desorption of radicals from the particles of the gel phase. From the kinetic scheme, the authors derive a complex kinetic equation that they show coincides with that of Talamini [equation (1)], when transfer of radicals between the two phases is absent. In the kinetic equation, the transfer of radicals from the dilute to the gel phase is given by the precipitation constant of polymeric radicals K^*, which is linked to the transfer constant to monomer, C_M, and the radical critical length, r_c through the following relationship:

$$K^* = (1 - C_M)^{r_c - 2} \qquad (11)$$

Xie *et al.* have experimentally found that K^* depends on temperature according to the following equation:

$$K^* = [0.25T(C) - 7.89] \times 10^{-4}$$

The transfer of radicals in the other direction, i.e. from the gel to the dilute phase, is quantified by the parameter K'_{de}, and being due to the desorption of radicals from the particles of the gel phase, depends on the size of these last particles according to the following equation:

$$K'_{de} = \frac{K^*_{de}}{d_p^2} \qquad (12)$$

where K^*_{de}, is a function of temperature and d_p is the diameter of the gel phase particles.

The temperature dependence of K^*_{de}, can be expressed by the following expression:

$$K^*_{de} = 5.08 \times 10^{-8} \exp\left(\frac{-392.8}{RT}\right) \; (dm^2) \qquad (13)$$

where T is in Kelvin and R is in atm l mol^{-1} K^{-1}.

By using the theoretical and experimental data of Xie *et al.*, it is then possible to quantify the processes of migration of radicals between the two phases.

For example, at 50°C, $K^* \cong 4.7 \times 10^{-4}$. Then, as Xie *et al.* pointed out, at this temperature *ca.* $4.7 \times 10^{-2}\%$ of the radicals produced from initiator and transfer to monomer will precipitate out from the dilute phase before termination. This magnitude of K^* indicates that the precipitation may not affect the radical concentration in the dilute phase significantly. It is interesting to examine, on the other hand, how much this precipitation influences the radical concentration in the gel phase. By assuming that the ratio between the concentrations of initiator in the two phases is equal to 1, and that fk_d is the same in both the phases, the ratio between the number of free radicals produced in each of the two phases, per unit of time, is equal to the ratio between the volumes of the two phases.

T (°c)	K_{de}^* (dm^2)	d_p^2 (dm^2)	$K'_{de} = K_{de}^*/d_p^2$
40	1.15×10^{-14}	6.25×10^{-12}	1.84×10^{-3}
50	1.84×10^{-14}	6.25×10^{-12}	2.94×10^{-3}
60	2.87×10^{-14}	6.25×10^{-12}	4.59×10^{-3}
70	4.37×10^{-14}	6.25×10^{-12}	6.99×10^{-3}

At 50°C, the weight fraction, m_c, of the concentrated phase is equal to 1 at a conversion of about 73%. Then at a conversion of 1%, $m_c \approx 0.0137$. The ratio between the volumes of the two phases at 1% of conversion is then given by

$$\frac{V_c}{V_m} = \frac{\left(\dfrac{0.0137}{\rho_c}\right)}{\left[\dfrac{(1 - 0.0137)}{\rho_m}\right]}$$

where ρ_c and ρ_m are the densities of the concentrated and of the monomeric phases, respectively. At 50°C, $\rho_c = 1.2$ and $\rho_m = 0.85$, thus

$$\frac{V_c}{V_m} = 9.8 \times 10^{-3} \approx 10^{-2}$$

Therefore, for every 100 radicals produced in the dilute phase, one radical is produced in the gel phase. As we have seen above, only *ca.* 0.05 radicals for every 100 produced in the dilute phase precipitate. Therefore, at this stage, i.e. at *ca.* 1% conversion, the contribution of the radicals coming from the dilute phase to the total production of radicals in the gel phase is about 5%. This percentage will decrease, of course, with increasing conversion, It becomes approximately equal to 1 at 5% conversion, and equals 0.05 at 44% conversion, i.e. when the ratio $V_c/V_m = 1$.

It is possible that this percentage could be higher, because the ratio I_c/I_m can be lower than 1 and the efficiency coefficient in the gel phase, f_c, can be smaller than that in the monomeric phase, f_m. However, it is reasonable to think that at 1% conversion, the amount of radicals produced in the dilute phase, entering the gel phase, will rarely be higher than 10% of the total radicals produced in the gel phase. An estimation of the magnitude of the radical migration in the other direction, i.e. from gel to dilute phase, is possible using equations (12) and (13). What is needed for this calculation is an accurate estimate of the diameter, d_p of the gel-phase particles as a function of conversion. There are many works in the literature dealing with the morphogenesis of the particles of the concentrated phase during the bulk polymerization of VC. In some of these papers[17,22–28], values of d_p at different conversions are reported. It can be seen from these works that at a degree of conversion in the range 0.001–0.01, d_p is of the order of 0.2–0.3 μm. These values are independent of the temperature of polymerization. It has also been experimentally observed that in the same conversion range the particles can agglomerate, forming new and much larger particles (with diameters more than twice those quoted above). In *Table 1*, the values of K'_{de} calculated at four temperatures, putting $d_p = 0.25$ μm are reported. It can be seen that K'_{de} is very small over the whole range of temperatures. Therefore, the migration of radicals from the gel to the dilute phase can also be considered negligible shortly after the beginning of the polymerization, i.e. at a conversion rate lower than 1%.

This value of conversion is an order of magnitude lower than that reported in the work by Xie *et al.* In our opinion these authors underestimate, in their calculations, the size of the gel-phase particles. After the above discussion, one can confirm that the ratio between the steady-state concentrations of free radicals in the two phases remains constant during the polymerization, except possibly for a range of a few units per cent of conversion, immediately after the reaction onset.

Initiator partition law

As we have seen above, the two phases are in thermodynamic equilibrium throughout the conversion range in which they co-exist. Consequently, in the same conversion range, the composition of each of the phases remains constant. Under these conditions, there is no reason why the partition law of the initiator between the two phases has to change during the polymerization. Then, one can write

$$\frac{I_c}{I_m} = K_I$$

where K_I is the initiator partition coefficient.

In their work, Xie *et al.* find that this ratio I_c/I_m is constant, with a value of 0.77. Furthermore, they find that this value is independent of temperature and initiator type.

Conclusions

On the grounds of the above-developed considerations, one can conclude that the assumptions contained in Talamini's original treatment are valid in the whole range of coexistence of the two phases, with the exception of a small range of conversion at the beginning of the polymerization, in which, because of the very small ratio V_c/V_m and the small size of the gel phase particles, the transfer of radicals between the two phases might be rather significant. Hence, the kinetic equations (1), (2a), (2b)–(4a) and (4b) obtained by assuming Q, q and X_f constant, can be considered to be rather effective at describing the bulk and suspension polymerization of VC up to the conversion degree X_f. This conclusion is in agreement with the observations of Weickert *et al.*[4,5]. These authors have completed a deep examination of various kinetic equations reported in the literature and finish by proposing their own equation, that in the range $0 < X \leq X_f$, coincides exactly with the above-reported equation (4). This equation, as has already been demonstrated, derives directly from equation (1), with only the introduction of the correction that accounts for initiator consumption during the polymerization. Weickert *et al.* demonstrate that their equation is in excellent agreement with the experimental data.

KINETIC PARAMETERS AND CONSTANTS

Q and q parameters

The simplest way to obtain the values of these two parameters is to use the kinetic data from polymerizations carried out at constant initiation rate. In fact, in this case, the conversion as a function of time is given by equation (2). As we have pointed out above, R_i is exactly constant throughout the reaction, if for instance, gamma radiation is used as the initiation method, but R_i can also be considered constant, to a very good approximation, when chemical initiators with a very low k_d at the polymerization temperature are used (e.g. BPO, LPO or AIBN at 40–60°C). In all these cases, for the determination of q, it is sufficient

to know the times t_1 and t_2 which are necessary with a given R_i, to reach the conversion degrees X_1 and X_2, respectively. In fact, from equation (2) we obtain

$$\frac{\ln(1+qX_2)}{\ln(1+qX_1)} = \frac{t_2}{t_1}$$

Similarly, if the relationship between X and $R_i^{0.5} \times t$ is known, the value of q can be obtained by

$$\frac{\ln(1+qX_2)}{\ln(1+qX_1)} = \frac{\left[(R_i)^{0.5}t\right]_2}{\left[(R_i)^{0.5}t\right]_1}$$

In any case, for a rapid determination of q, it is useful to draw the theoretical curve $\ln(1+qX_2)/\ln(1+qX_1)$ against q, as is reported in *Figure 1*, for $X_2 = 0.6$ and $X_1 = 0.2$. The experimental value of t_2/t_1 (or $\left[(R_i)^{0.5} \times t\right]_2/\left[(R_i)^{0.5} \times t\right]_1$) corresponds with the value of the curve on the ordinate axis;
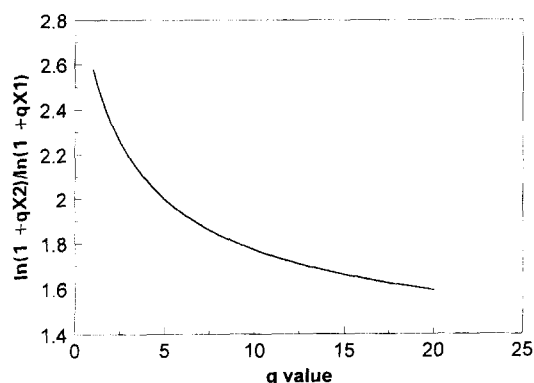

Figure 1 Theoretical curve for $\ln(1+qX_2)/\ln(1+qX_1)$ versus q parameter ($X_1 = 0.2$, $X_2 = 0.6$)

hence the value of q can be read immediately on the abscissa axis.

We have found two papers in the literature dealing with the bulk polymerization of VC, initiated by gamma radiation. In the first one, by Tavan et al.[20], a series of curves of X versus $(R_i)^{0.5} \times t$, each of them corresponding to a given polymerization temperature is reported; in the other one, by Russo and Stannett[31], the polymerization has been carried out at different temperatures, and for each temperature some curves of X versus t each of them corresponding to a different dose rate, are reported. Moreover, many papers exist in the literature in which curves of X versus t or X versus $I^{0.5} \times t$ obtained by using LPO, BPO or AIBN as initiator are reported. In *Table 2*, the values of q calculated by employing the experimental results of various authors are collected. The data of *Table 2* show that

- q is not very sensitive to the type of initiation and to the nature of the chemical initiators;
- in the case of the radiation initiated polymerization (RIP), a good agreement is observed between the values of q determined through the kinetic data reported in the two different papers;
- for the chemically initiated polymerizations (CIP) the values of q are rather widely scattered (they lie in the range 3.3–6.4);
- even with this rather large scatter in the values of q, one can observe that the values of q from CIP experiments are mostly higher than those derived from RIP works; in fact the general average value of q for CIP at 50°C, calculated using the data relative to all three initiators, results equal to 5 against the slightly lower value of 4.2 found in the case of RIP.

Table 2 Values of q from literature data

| Initiation	T (°C)	Polymerization type	q^{a}	q^{b}	Reference
Gamma rays	25	Bulk	3.8		31
	30	Bulk		3.5	20
	40	Bulk	4.3		31
	50	Bulk		4.2	20
	70	Bulk		5.1	20
	90	Bulk		4.0	20
BPO	50	Bulk	4.1–4.3 (4.2)	3.5	2
	50	Suspension	4.4–6.4 (5.7)		2
	50	Bulk + Suspension (*)		3.9	2,32
AIBN	50	Bulk	4.3–5.0 (4.8)		2
	50	Suspension	3.3–6.2 (5.3)		2
	50	Bulk + Suspension (*)		6.4	2,32
	30	Bulk		4.3	12
	50	Bulk		5.2	12
	70	Bulk		5.0	12
	65	Suspension	5.0–5.3 (5.2)		33
LPO	50	Bulk	3.4–5.0 (4.8)		2
	50	Suspension	4.0–6.0 (5.2)		2
	50	Bulk + Suspension (*)		4.4	2,32
	60	Suspension	6.4		34

[a] Values of q determined from the curves X vs t, for each case the extreme values of q and its average value (the number in brackets) are reported
[b] Values of q determined from the curves X vs $R_i^{0.5}t$ (gamma rays) or X vs $I^{0.5}t$ (chemical initiators); the q values must be considered mean values
(*) The curve X vs $I^{0.5}t$ has been drawn using all the data from Ref. 2 (bulk + suspension polymerization) and Ref. 32 (suspension polymerization)

Table 3 Values of Q at different temperatures

T (°C)	q	X_f	Q	Q_0
25	3.8	0.84	26.2	6.2
30	3.5	0.82	21.5	5.5
40	4.3	0.77	18.7	4.3
50	4.2	0.73	15.0	3.7
70	5.1	0.55	8.4	2.2
90	4.0	0.17	2.0	1.2
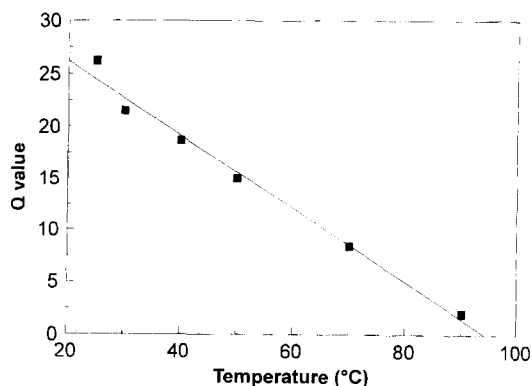
Figure 2 Q parameter *versus* temperature (°C). Data from *Table 3*

Weickert *et al.*[5] through a statistical elaboration of their own kinetic data and of those of various other authors, obtained a mean value of q at 50°C for chemically initiated polymerization, equal to 4.2. Faraday[29], using the values of the reaction times necessary to reach 35 and 70% conversion, respectively, and relative to a total of 48 polymerizations and three different initiators, calculated a mean value of q equal to 5 ± 2. This author highlights the great uncertainty in the values of q due to the rather poor reproducibility of the batch heat-up period, at the beginning of the polymerization, and/or to an imperfect control of the isothermicity of the reaction. This uncertainty is surely much lower in the case of the values of q obtained from the kinetic data of gamma-ray initiated polymerizations, because of:

- the certain constancy of the initiation rate;
- the activation energy of the initiation stage being practically equal to zero, so that the polymerization rate is almost insensitive to possible variations of temperature during the reaction;
- the absence of the non-isothermal heat up period at the beginning of the polymerization; in fact the irradiation starts when the system has already reached the polymerization temperature.

Therefore, among all the values of q collected in *Table 2*, the most reliable ones have to be considered those calculated using the kinetic curves of the gamma-ray initiated polymerizations.

Then, from the values of q obtained from RIP we have calculated the values of Q at different temperatures through equation (5) and the values of X_f reported in the paper by Xie *et al.*[19]. The results of these calculations are collected in *Table 3*.

In *Table 3*, the values of Q_0 are also reported. Q_0 gives the value of Q at which q would be equal to zero and, consequently, the polymerization rate would be constant and equal to R_m in the whole range of conversion $0-X_f$. By plotting the values of Q from *Table 3* against T, the

straight line of *Figure 2* is obtained. The temperature at which $Q = 1$, corresponds with T_{pc}. From *Figure 2*, this temperature results to be equal to about 91°C, in fairly good agreement with the above-determined value of about 88°C, in spite of the great approximations introduced for their calculation. So, the temperature at which the polymerization of VC passes from a heterogeneous to a homogeneous reaction, and vice versa, should be around 90°C. Later on we shall deal again with the parameters q and Q.

The initiator partition coefficient, K_I

When a chemical initiator is employed, the specific polymerization rate in the two phases is given, respectively, by

$$R_m = k_p \left(\frac{f_m k_d I_m}{k_{tm}} \right)^{0.5}, \quad R_c = k_p \left(\frac{f_c k_d I_c}{k_{tc}} \right)^{0.5}$$

In fact, it is reasonable to assume that k_p and k_d have the same value in the two phases, and that the difference between the specific rates is due to the different values of the termination rate constant and to a possible difference in the efficiency and in the concentration of initiator. Therefore

$$Q = \frac{R_c}{R_m} = \left(\frac{k_{tm}}{k_{tc}} \times \frac{f_c}{f_m} \times \frac{I_c}{I_m} \right)^{0.5} \quad (14a)$$

$$Q = \left(\frac{k_{tm}}{k_{tc}} \times \frac{f_c}{f_m} \right)^{0.5} \times K_I^{0.5} \quad (14b)$$

Let us now see the influence of K_I on the polymerization feature. If we indicate with:

- W_i, the weight of initiator per unit weight of VC/PVC system;
- m_m, the weight fraction of the monomeric phase;
- m_c, the weight fraction of the concentrated phase;

and assume $W_i =$ constant (very small k_d), then in each instant of the polymerization, it must hold

$$\left(\frac{m_m}{\rho_m} \right) \times I_m + \left(\frac{m_c}{\rho_c} \right) \times I_c = W_i$$

where the concentrations of initiator are expressed as weight per unit volume¶.

However, $m_c = 1 - m_m$, and $I_c = K_I I$. Moreover, at $t = 0$, $I_m = I_{m_0} = \rho_m \times W_i$. Now, it is possible to write

$$\rho_c m_m I_m + K_I \rho_m I_m - K_I \rho_m m_m I_m = \rho_c I_{m_0}$$

or

$$\frac{I_m}{I_{m0}} = \frac{1}{\left(m_m + K_I \left(\frac{\rho_m}{\rho_c} \right) - K_I \left(\frac{\rho_m}{\rho_c} \right) m_m \right)} \quad (15)$$

The ratio I_m/I_{m_0} can be expressed as a function of X, instead of m_m. In fact,

$$m_m = 1 - \left(\frac{X}{X_f} \right)$$

¶ If the consumption of the initiator is not negligible, W_i is given by: $W_i = W_{i0} \exp(-k_d t)$, where W_{i0} is the initiator charge at the beginning of the polymerization ($t = 0$)
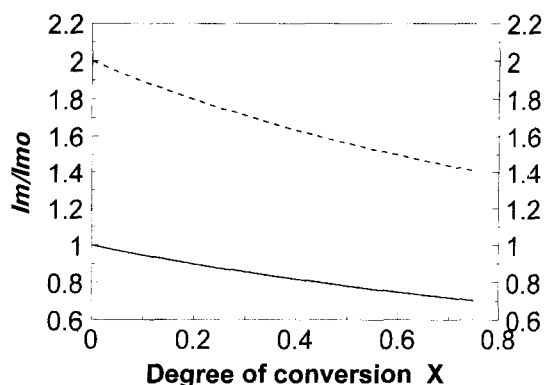
Figure 3 Initiator concentration versus degree of conversion X for $K_1 = 2$. $T = 50°C$. ——, I_m/I_{m0}; - - -, I_c/I_{m0}
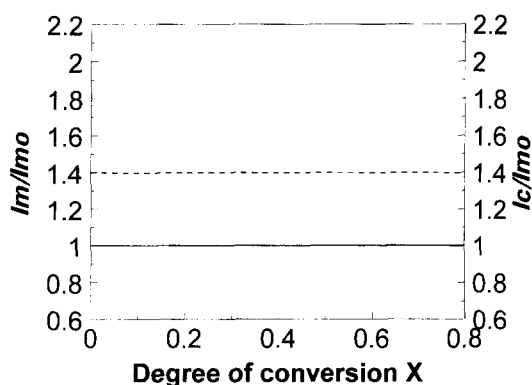

Figure 4 Initiator concentration versus degree of conversion X for $K_1 = 1.4$. $T = 50°C$. ——, I_m/I_{m0}; - - -, I_c/I_{m0}
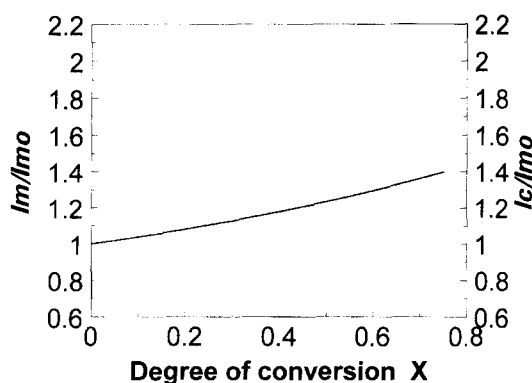

Figure 5 Initiator concentration *versus* degree of conversion X for $K_1 = 1$. $T = 50°C$. ——, I_m/I_{m0}; - - -, I_c/I_{m0} (the two curves overlap)
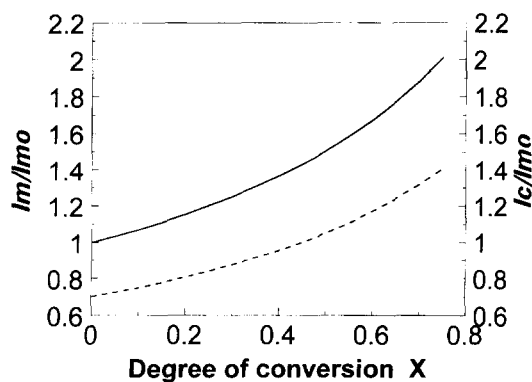

Figure 6 Initiator concentration *versus* degree of conversion X for $K_1 = 0.7$. $T = 50°C$. ——, I_m/I_{m0}; - - -, I_c/I_{m0}

Thus from equation (15), one obtains

$$\frac{I_m}{I_{m0}} = \frac{1}{(1 - \alpha X)} \qquad (16)$$

where

$$\alpha = \frac{1}{X_f}\left(1 - \frac{\rho_m}{\rho_c} \times K_1\right)$$

One can observe that:

- when $K_1 = \rho_c/\rho_m$, $\alpha = 0$, $I_m = I_{m0} = $ constant, and $I_c = K_1 I_{m0}$ in the whole range of conversion $0 < X < X_f$;
- at $X = X_f$, $I_m/I_{m0} = 1/K_1 \times \rho_c/\rho_m$ and $I_c = (\rho_c/\rho_m) \times I_{m0}$.

Furthermore, since ρ_c is linked to the density of the monomer, ρ_M, and to the density of the polymer ρ_p, through the following relationship:

$$\frac{1}{\rho_c} = \frac{(1 - X_f)}{\rho_M} + \frac{X_f}{\rho_p}$$

it results that when $K_1 = 1$ (as $\rho_M \cong \rho_m$),

$$\alpha = \frac{(\rho_p - \rho_M)}{\rho_p}$$

Note that in this case α coincides with the coefficient B that Abdel-Alim and Hamielec[12] introduced in their kinetic equation to take into account the volume contraction that occurs during the polymerization. Then, on the grounds of the equations stated above, the simple Talamini expression [equation (1)] must be re-written in the following manner:

$$\frac{dX}{dt} = \frac{R_{m0}(1 + qX)}{(1 - \alpha X)^{0.5}} \qquad (17)$$

where $R_{m0} = \kappa(2f_m k_d I_{m0})^{1/2}$.

Equation (17) coincides, respectively, with equation (1) when $K_1 = \rho_c/\rho_m$ ($\alpha = 0$) and with the equation of Abdel Alim and Hamielec when $K_1 = 1$ $\left(\alpha = (\rho_p - \rho_m)/\rho_p\right)$.

It is worth noting that a value of K_1 equal to 1 means that the initiator distributes itself between the two phases in proportion to their volume fraction, whereas a value of K_1 equal to ρ_c/ρ_m means that the initiator distributes itself between the two phases in proportion to their weight fraction. It is also interesting to note that if K_1 is higher than ρ_c/ρ_m, I_m and I_c decrease during the polymerization, whereas if K_1 is lower than ρ_c/ρ_m, I_c and I_m increase during the polymerization.

Plots of the two ratios I_m/I_{m0} and I_c/I_{m0} *versus* X, for different values of K_1 are shown in *Figures 3–6*.

It is possible to simplify the integration of equation (17) by introducing the following approximation:

$$(1 - \alpha X)^{0.5} \cong 1 - 0.5\alpha X$$

With this substitution, the integration of equation (17) between 0 and X and 0 and t gives

$$\frac{(2q + \alpha)}{2q^2}\ln(1 + qX) - \frac{\alpha X}{2q} = R_{m0}t \qquad (18)$$

One can note that, when $\alpha = 0$, equation (18) coincides, as one would expect, with equation (2), which has been obtained by the integration of equation (1).

It has to be pointed out that in changing K_1, it follows that the three parameters α, Q and q also change. More precisely, when K_1 decreases, α increases, whereas both Q and q decrease [see equations (5) and (14b)]. One can see from equation (18) that in the case of the chemically initiated polymerization, the parameter q determined with the

Table 4 Values of the ratio q/q_e ($T = 50°C$)

K_1	0.5	0.70	0.77	1.00	1.40*	2.00	2.50
q/q_e	0.62	0.73	0.80	0.90	1.00	1.20	1.39
α	0.88	0.68	0.62	0.39	0.00	−0.58	−1.07

* Value of ρ_c/ρ_m
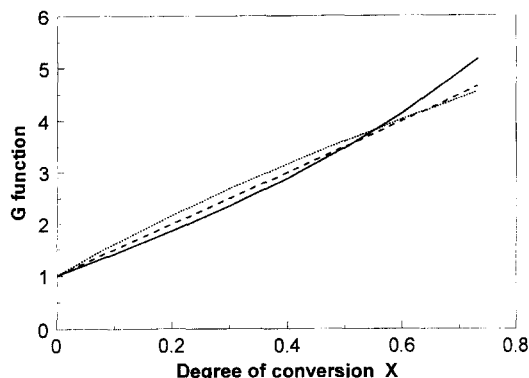
Figure 7 G function *versus* degree of conversion X at $T = 50°C$. ——,
$K_1 = 0.7$; - - -, $K_1 = 1.4$; · · ·, $K_1 = 2.5$
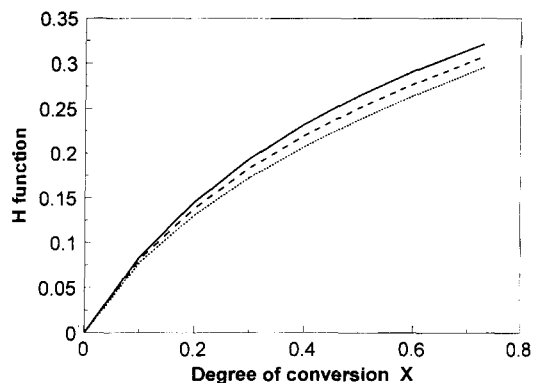
Figure 8 H function *versus* degree of conversion X at $T = 50°C$. ——,
$K_1 = 0.7$; - - -, $K_1 = 1.4$; · · ·, $K_1 = 2.5$

above-described method (*Figure 1*), represents the 'true' value of q only when $\alpha = 0$ (i.e. $K_1 = \rho_c/\rho_m$). In all the other cases, it has to be considered an empirical parameter (q_e) featuring the autocatalytic behaviour of the reaction. The relationship between q and q_e can be found through calculations, using equation (18), of t_2/t_1, i.e. the ratio between the times spent to reach the degrees of conversion 0.6 and 0.2, respectively, and then determining q_e through the curve of *Figure 1*. The result of this is that the ratio q/q_e is almost independent of the absolute value of q and, respectively, lower or higher than 1 depending on whether K_1 is smaller or greater than ρ_c/ρ_m.

In *Table 4*, values of the ratio q/q_e corresponding to different values of K_1 are collected.

Averaging all the data from *Table 2*, we have found that for the chemically initiated polymerization at 50°C, $q_e = 5$. Then the 'true' q appearing in equations (17) and (18) will be equal to $0.62 \times 5 = 3.1$ for $K_1 = 0.5$; $0.73 \times 5 = 3.65$ for $K_1 = 0.7$, and so on.

By using these detemined values of q and the values of α collected in *Table 4*, one can calculate the values of the quantity $(1 + qX)/(1 - \alpha X)^{0.5}$ [see equation (17)] and of the quantity on the left of equation (18), at different values of X and in correspondence to various values of K_1.

Henceforth, these two quantities will be indicated by the letters G and H, respectively. They are both functions of X and give:

- G, the ratio between the polymerization rate at the degree of conversion X and R_{m0};
- H, the product between the time spent to reach the degree of conversion X and R_{m0}.

The curves of G and H as a function of X drawn in *Figures 7 and 8* represent the following three different cases:

(1) $K_1 = 0.7$, $\alpha = 0.68$, $q = q_e \times 0.73 = 3.65$;
(2) $K_1 = 1.4$, $\alpha = 0$, $q = q_e = 5$ [in this case, equations (17) and (18) coincide with equations (1) and (2a), respectively];
(3) $K_1 = 2.5$, $\alpha = -1.07$, $q = q_e \times 1.39 = 6.95$.

The curves of *Figures 7 and 8* show that K_1 affects the kinetic behaviour of polymerization very slightly. One can note, in fact, that in correspondence with a great variation of K_1 (from 2.5 to 0.7), the maximum change of G and H is only 12–15%.

Evidently, the variations of α and q occurring, in opposite directions with changing K_1 are almost entirely mutually compensating. In other words, the increase or decrease of the initiator concentration that occurs during the reaction when K_1 is different from ρ_c/ρ_m (see *Figures 3–6*) is almost completely balanced by the decrements or increments of the q value.

Another interesting observation is that G deviates from the 'ideal' linear dependence X, observed when $K_1 = \rho_c/\rho_m$, in a 'positive' or in a 'negative' sense , according to whether $K_1 > \rho_c/\rho_m$ or $K_1 < \rho_c/\rho_m$ (see *Figure 7*). The deviations are, in any case, quite small.

Then, the reaction, as a consequence of its low sensitivity to K_1, can be described, whatever the value of K_1 may be, by the simple equations (1) and (2), instead of the more complex equations (17) and (18). Therefore, for practical purposes, it is convenient to adopt for G and H the following two simple expressions:

$$G = (1 + qX) \qquad (19)$$

$$H = \frac{[\ln(1 + qX)]}{q} \qquad (20)$$

where $q = q_e$.

The low sensitivity of the reaction to the partition coefficient of the initiator makes it very difficult, if not impossible, to prove the existence of differences among the K_1 values of different initiators, on the basis of kinetic tests. This is probably the reason for which Xie *et al.*, in their kinetic study, found the same value of K_1 (0.77) for all the initiators employed, in spite of their different nature. As Kelsall and Maitland[17] have pointed out, the polymerization feature is also influenced by the value of the ratio f_c/f_m. From equations (5), and (14b), one can calculate that a lowering of this ratio from 1 to 0.5 causes, at 50°C, a more than 40% decrease in q, resulting in a less pronounced autocatalysis of the reaction. As distinct from the previous case, these variations in the value of q, induced by f_c/f_m, are not compensated for by simultaneous variations of other parameters. As one can note, the q data given in *Table 2* do not indicate significant differences in the ratios f_c/f_m among the three initiators BPO, AIBN and LPO.

If the consumption of initiator is not negligible, the relationship between H and t can be described by the

following:

$$H = \frac{2}{k_d} Rm_0 \left[1 - \exp\left(-\frac{k_d}{2}t \right) \right]$$

from which one obtains

$$t = -\frac{2}{k_d} \ln\left(1 - \frac{k_d}{2} \frac{H}{Rm_0} \right)$$

A series expansion of the natural logarithm gives the following equation:

$$t = \frac{2}{k_d} \left(\frac{k_d}{2} \frac{H}{Rm_0} + \frac{1}{2} \left(\frac{k_d}{2} \right)^2 \left(\frac{H}{Rm_0} \right)^2 \right. \\ \left. + \frac{1}{3} \left(\frac{k_d}{2} \right)^3 \left(\frac{H}{Rm_0} \right)^3 + ... \right)$$ (21)

It is possible to see that, if k_d is very small, one obtains:

$$R_{m0}t = H$$

corresponding to equations (2a), and (18).

In the case of radiation initiated polymerizations, it holds that

$$R_{ic} = \Phi_m I_r (1 - X_f + \Phi_{rel} X_f) \rho_c$$

$$R_{im} = \Phi_m I_r \rho_m$$

where I_r is the dose rate, and $\Phi_{rel} = \Phi_p/\Phi_m$ is the ratio between the rate constants for radical formation from polymer (Φ_p) and monomer (Φ_M), respectively.

Therefore, one has:

$$\frac{R_{ic}}{R_{im}} = F \times \frac{\rho_c}{\rho_m}$$

with

$$F = (1 - X_f + \Phi_{rel} X_f)$$

One can see that in addition to the ratio R_{ic}/R_{im}, R_{ic} and R_{im} also remain constant during the reaction, so that the q parameters evaluated for radiation polymerization and collected in *Table 2* are 'true' q.

Moreover, one can note that the radiation-initiated polymerizations correspond to chemically initiated polymerizations with $f_c/f_m = F$ and $K_I = \rho_c/\rho_m$.

Xie et al.[3] for the initiators AIBN and Perkadox 16-W40 have found $K_I = 0.77$ and $f_c/f_m = 1$. Assuming the same value of f_c/f_m and K_I for BPO, LPO and generally for all the chemical initiators, since we have found that, at 50°C, $q_e = 5$, one obtains $q_{(true)} = 5 \times 0.8 = 4$ (see *Table 4*). This value is very close to the value (4.2) of q found in the case of the radiation polymerization at the same temperature. Therefore, one has

$$F \times \frac{\rho_c}{\rho_m} \cong 0.77$$

from which one obtains

$$\Phi_{rel} \cong 0.38$$

Then, bearing in mind that the value of q determined for the radiation polymerization is, owing to the above-mentioned reasons, very reliable, knowing the value of Φ_{rel} obtained by other methods, one could verify the accuracy of the values of the various parameters found in the case of the chemically initiated polymerizations. Moreover, from the value of Q from *Table 3*, one could calculate the value

of ratio k_{tm}/k_{tc} at different temperatures. Unfortunately, we have not found in the literature any experimental or theoretical datum concerning Φ_{rel}.

KINETIC CHAIN LENGTH AND POLYMERIZATION DEGREE

In the case of the free radical homogeneous polymerization the kinetic chain length, ν, is given by the equation

$$\nu = \frac{k_p}{2(k_t f k_d)^{0.5}} \times \frac{M}{I^{0.5}}$$ (22)

where M is the concentration of monomer.

From the previously reported equations one obtains

$$k_{tc} = \frac{k_{tm} f_c K_I}{Q^2 \, f_m}$$

$$M_c = (1 - X_f) M_m \frac{\rho_c}{\rho_m}$$

$$I_c = K_I I_m$$

where M_c and M_m are the concentrations of VC in the gel and in the dilute phase, respectively. Hence, using equation (22) the kinetic chain length in the two phases is:

$$\nu_c = \frac{Q k_p (1 - X_f) M_m \rho_c (f_m)^{0.5}}{2 K_I (k_{tm} f_c k_d)^{0.5} I_m^{0.5} \rho_m (f_c)^{0.5}}$$ (23)

$$\nu_m = \frac{k_p M_m}{2(k_{tm} f_m k_d)^{0.5} I_m^{0.5}}$$ (24)

Then, one obtains:

$$\nu_c = Q(1 - X_f) \frac{\rho_c}{\rho_m} \frac{f_m}{f_c} \frac{1}{K_I} \nu_m$$ (25)

which gives the relationship between the instantaneous kinetic chain lengths of the two phases. If p_m and p_c are the weight fractions of polymeric chains formed at a certain instant in the concentrated and dilute phase, respectively, the instantaneous kinetic chain length, ν, of the whole polymerizing system is given by

$$\nu = \left[\frac{p_m}{\nu_m} + \frac{p_c}{\nu_c} \right]^{-1}$$ (26)

If dX, dX_m and dX_c are the infinitesimal increments of the conversion degree related, respectively, to the overall system, the dilute phase and the concentrated phase, one has

$$p_m = \frac{dX_m}{dX}$$ (27a)

and

$$p_c = \frac{dX_c}{dX}$$ (27b)

On the other hand, from the previous kinetics treatment, one obtains:

$$dX_m = R_m (1 - X - AX) \, dt$$ (28a)

$$dX_c = Q R_m AX \, dt$$ (28b)

$$dX = R_m (1 + qX) \, dt$$ (28c)

with

$$A = \frac{(1 - X_f)}{X_f}$$

Combining equations (25)–(28c) one obtains:

$$\nu = \frac{1 + qX}{1 - \beta X} \nu_m \qquad (29a)$$

where β is given by

$$\beta = \frac{1}{X_f}\left(1 - \frac{f_c}{f_m}\frac{\rho_m}{\rho_c}K_I\right)$$

At $X = X_f$, ν must be equal to ν_c. Actually, it can be shown that putting $X = X_f$ in equation (29a), one obtains equation (25). Moreover, it is possible to see that if $f_c/f_m = 1$, β coincides with the coefficient α of equation (16). Then, since $f_c \leq f_m$, β will be either equal to or higher than α.

As one can deduce from equation (24),

$$\nu_m = \nu_{m0}(1 - \alpha X)^{1/2}$$

where ν_{m0} is the kinetic chain length at $X = 0$.
Then:

$$\nu = \nu_{m0}\frac{(1 + qX)(1 - \alpha X)^{0.5}}{(1 - \beta X)} \qquad (29b)$$

If dM is the infinitesimal number of moles of reacted monomer and $d\dot{M}$ is the infinitesimal number of moles of radicals formed by the initiator and reacting in propagation, then ν, according to its definition is given by

$$\nu = \frac{dM}{d\dot{M}}$$

If $M_{\nu c}$ is the monomer molecular weight, one has

$$dM = \frac{dX}{M_{\nu c}} \text{ and thus } \nu = \frac{dX}{M_{\nu c}\, d\dot{M}}$$

Similarly, the average value $\bar{\nu}$ of the kinetic chain length corresponding to a finite increment of the conversion degree, will be

$$\bar{\nu} = \frac{\Delta X}{M_{\nu c}\Delta \dot{M}}$$

For the range of conversion $0-X$ one has that $\Delta X = X$; therefore combining the above equations,

$$\frac{1}{\bar{\nu}} = \frac{1}{X}\int_0^x \frac{dX}{\nu} \qquad (30)$$

Introducing equation (29) and the approximation $(1 - \alpha X)^{0.5} \cong (1 - (\alpha/2)X)$, one obtains

$$\frac{1}{\bar{\nu}} = \frac{1}{\nu_{m0}X}\int_0^x \frac{(1 - \beta X)}{(1 + qX)\left(1 - \frac{\alpha}{2}X\right)}\, dX \qquad (31)$$

from which, by integration:

$$\frac{\nu_{m0}}{\bar{\nu}} = \frac{2(\beta + q)}{(\alpha + 2q)}\frac{\ln(1 + qX)}{qX} + \frac{(\alpha - 2\beta)}{(\alpha + 2q)}\frac{\ln\left(1 - \frac{\alpha}{2}X\right)}{-\frac{\alpha}{2}X} \qquad (32a)$$

It is possible to see that, as one expected:

$$\lim_{x \to 0} \frac{\nu_{m0}}{\bar{\nu}} = 1$$

equation (32a) can be written also in the following form:

$$\frac{\nu_{m0}}{\bar{\nu}} = \frac{2(\beta + q)}{(\alpha + 2q)}\frac{\ln(1 + qX)}{qX}$$
$$+ \frac{(\alpha - 2\beta)}{(\alpha + 2q)}\left(1 + \frac{\alpha}{4}X + \frac{\alpha^2}{6}X^2 + \ldots\right) \qquad (32b)$$

The relationship between $\bar{\nu}$ and P_n is given by the Mayo equation:

$$\frac{1}{P_n} = \left(1 - \frac{C}{2}\right)\frac{1}{\bar{\nu}} + C_m \qquad (33)$$

where C is the fraction of bimolecular termination occurring by combination. Inserting equation (32b) in equation (33) and limiting the series expansion to the first two terms, one obtains

$$\frac{1}{P_n} = \frac{1}{\nu_{m0}}\left(1 - \frac{C}{2}\right)$$
$$\left[\frac{2(\beta + q)}{(\alpha + 2q)}\frac{\ln(1 + qX)}{qX} + \frac{(\alpha - 2\beta)}{(\alpha + 2q)}\left(1 + \frac{\alpha}{4}X\right)\right] + C_m \qquad (34a)$$

From equation (34a) one has

$$\lim_{x \to 0}\frac{1}{P_n} = \frac{1}{\nu_{m0}}\left(1 - \frac{C}{2}\right) + C_m \qquad (34b)$$

Then, the value of ν_{m0} can be determined by extrapolation to $X = 0$ of the data either of $\bar{\nu}$ [equation (32a)] or of P_n [equation (34a)], corresponding to various conversions. Of course, in the second case one needs to know the value of C and of C_M.

According to Xie *et al.*[35] the monomer transfer constant has a different value in the two phases because of the different monomer concentrations. Such being the case, one can easily show that the equation giving P_n as a function of X becomes the following one:

$$\frac{1}{P_n} = \frac{1}{\bar{\nu}}\left(1 - \frac{C}{2}\right) + C_{Mc}$$
$$+ (C_{Mm} - C_{Mc})\frac{1}{X_f}\left[\frac{(qX_f + 1)}{q^2X}\ln(1 + qX) - \frac{1}{q}\right] \qquad (35)$$

where $\bar{\nu}$ is given from equations (32a) and (32b), and C_{Mm} and C_{Mc} are the transfer constants to monomer in the dilute and concentrated phases, respectively.

From the paper of Xie *et al.*, one has that, at 50°C, $C_{Mm} = 0.477 \times 10^{-3}$ and $C_{Mc} = 0.791 \times 10^{-3}$. Both of these values are significantly lower than the value of C_M experimentally determined by many other authors[12,30,36–39] at the same temperature. Moreover, the assumption of a different value of C_M in the two phases is questioned by the remark that the same value of C_M has been experimentally found for both the heterogeneous (bulk) and homogeneous (solution) polymerization[30,37]. Later, we return to this subject. Danusso *et al.*[36] have determined the value of $\bar{\nu}$ at different conversions in the bulk polymerization of VC at 50°C, using AIBN as an initiator, labelled with ^{14}C, at a concentration of about 3.58×10^{-2} mol l^{-1}. On the samples used for the measurement of $\bar{\nu}$ the authors have also determined P_n. Moreover, they have obtained $C = 0.5$, $C_m = 10.35 \times 10^{-4}$, k_d (AIBN) $= 1.08 \times 10^{-4}$ min^{-1}, $f_m = 1$. The data of $\bar{\nu}$ and P_n are collected, for convenience of the reader, in *Table 5*.

The extrapolation to $X = 0$ either of $\bar{\nu}$ or of P_n gives a value of ν_{m0} of about 2100. Both the extrapolations have been carried out neglecting the datum (of $\bar{\nu}$ and P_n)

Table 5 Data of $\bar{\nu}$ and P_n by Danusso *et al.*[36]. Initiator: AIBN, $I_{mo} = 3.58 \times 10^{-2}$ mol/l, $T = 50°C$

X	0.02	0.05	0.07	0.11	0.17	0.22	0.39	0.66
$\bar{\nu}$	1525	2325	2420	31130	3400	3200	3660	3960
P_n	637	736	757	772	779	775	842	808
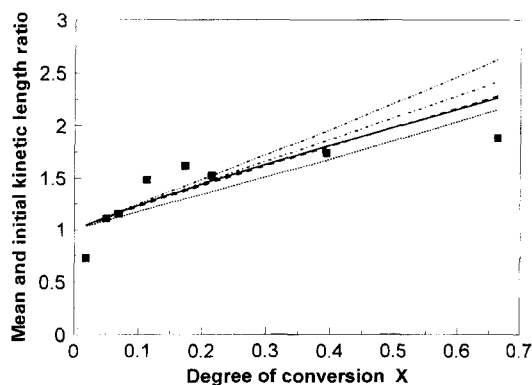
Figure 9 Plot of $\bar{\nu}/\nu_{m0}$ versus degree of conversion X at $T = 50°C$. ——, $K_I = 1.4, f_c/f_m = 1$; - - -, $K_1 = 1, f_c/f_m = 1$; · · ·, $K_1 = 0.5, f_c/f_m = 0.8$; – · –, $K_1 = 1, f_c/f_m = 0.8$; – ·· –, $K_1 = 1, f_c/f_m = 0.55$; ● experimental points
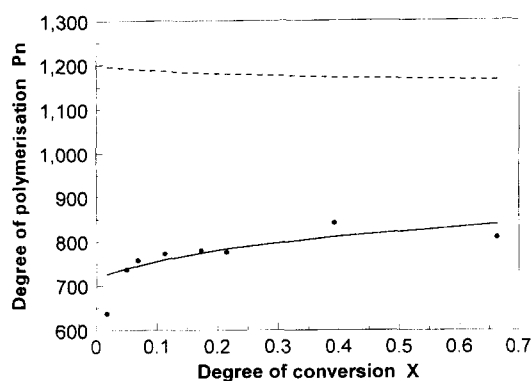
Figure 10 Degree of polymerisation P_n *versus* degree of conversion X. Comparison of theoretical curve with experimental data at $T = 50°C$. ●, experimental data from Ref. 36; ——, curve from equation 34a - - -, curve from equation 35

at $X = 0.02$, because of its anomalously small value due, probably, to the influence of the polymer formed in the early stages of the reaction when the presence of small quantities of oxygen and/or of impurities of the monomer, cuts down the kinetic chain length. The correctness of this assumption and thus of the extrapolations, can be verified by comparison of the above-determined values of ν_{m0} with that calculated using equation (24). From the literature one sees that, at $50°C$, $k_p/(k_m)^{0.5} = 0.6$ (1 mol^{-1} min^{-1})$^{1/2}$ [2,29,36,37,40]. Then, under the experimental conditions adopted by Danusso *et al.*, one has:

$$\nu_{m0} = \frac{0.6 \times 13.6}{2(1.08 \times 10^{-4} \times 3.58 \times 10^{-2})^{1/2}} = 2075$$

As one can note, this value of ν_{m0} is in very good agreement with the foregoing one, determined by extrapolation of $\bar{\nu}$ and P_n. In *Figure 9*, some curves $\bar{\nu}/\nu_{m0}$ versus X drawn using equation (32a) are reported. Each of these curves corresponds to a different set of values of the parameters $K_1, f_c/f_m$ and q. In the same figure, the experimental points

obtained from the data of $\bar{\nu}$ of *Table 5*, putting $\nu_{m0} = 2100$, are also collected.

The following considerations can be developed:

(1) The ratio f_c/f_m is equal or very close to 1; in fact, values of this ratio lower than 1 shift the theoretical curves away from the experimental points, particularly at the higher percentage conversions.

(2) The influence of K_1 on $\bar{\nu}$ is very small; one can observe that the two curves corresponding to $K_1 = 1$ and $K_1 = 1.4$ are practically coincidental, whereas the curve corresponding to $K_1 = 0.5$ is shifted downwards slightly (*ca.* 5%) to lower values of $\bar{\nu}$; evidently the changes in α somewhat different to those in β are almost completely compensated for by the variations in Q and q.

(3) In consideration of this small sensitivity of $\bar{\nu}$ on K_1 and fixing $f_c/f_m = 1$, one can adopt, for practical purposes, as an equation giving the dependence of $\bar{\nu}$ on X, the simple equation deriving from equation (32a), putting $\alpha = \beta = 0$, and $q = q_e = 5$. It is conceded, however, that comparison between the theoretical curves and experimental points indicates a value of K_1 lying between 0.5 and 1 (in agreement with Xie *et al.*).

Then, using values of $\nu_{m0} = 2100$, $C = 0.5$, $C_M = 10.35 \times 10^{-4}$, $\alpha = \beta = 0$, and $q = 5$ we have calculated the curve P_n versus X with equation (34a).

In *Figure 10*, this curve is compared with the experimental data of P_n collected in *Table 5*. One can see that the theoretical curve fits quite well the experimental points with the exception of that at $X = 0.02$. In the same figure, the theoretical curve obtained from equation (35) using the values of C_{Mm} and C_{Mc}, suggested by Xie *et al.*[55], is reported. One can note that the curve is in total disagreement with the points. In fact, owing to the rather low values of both C_{Mm} and C_{Mc} and to the higher value of C_{Mc} with respect to C_{Mm}, the curve traces values of P_n which are too great, and exhibits a negative slope. Xie *et al.*, on the contrary, found good agreement between their theoretical curves and the experimental data of P_n obtained through polymerization carried out in suspension using Perkadox 16-W40 as the initiator.

The reason for these two widely differing results is unclear to us. Values of P_n of PVC corresponding to different conversions are reported also in a work by Abdel-Alim and Hamielec[12] and in a work by Vidotto *et al.*[37]. In both the works the polymerization has been carried out at $50°C$, using as an initiator:

● in the first work, AIBN at a concentration of 4.4×10^{-2} mol l^{-1};

● in the second work, LPO at a concentration of 4.2×10^{-2} mol l^{-1}.

Unfortunately, the experimental data that are reported in the first work are few and scattered so that an extrapolation of P_n to $X = 0$ is quite problematic. However, a comparison between our theoretical curve of *Figure 10* and that reported in the paper by Aldel-Alim and Hamielec, shows that these last authors, because of the slightly higher concentration of AIBN that they used, have found values of P_n slightly lower than those of Danusso *et al.* On the contrary, a fairly good extrapolation can be carried out using the similarly scattered but numerous data of P_n of the work by Vidotto *et al.* The limiting value of P_n at $X = 0$ is
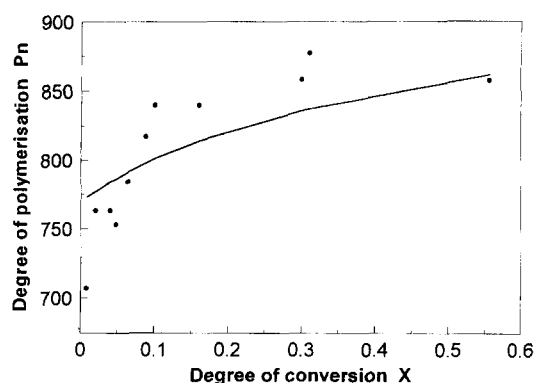
Figure 11 Degree of polymerisation P_n *versus* degree of conversion X. Comparison of theoretical curve with experimental data at $T = 50°C$. ●, experimental data from Ref. 37; ——, curve from equation 34a

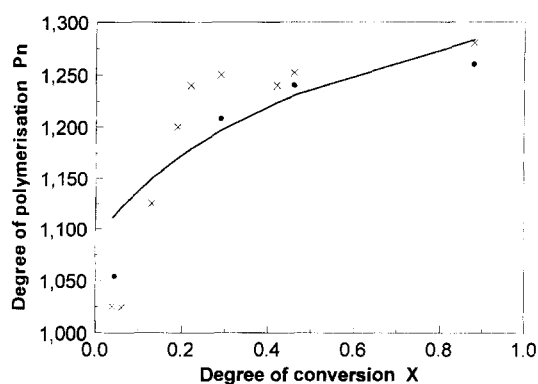**Figure 12** Degree of polymerisation P_n *versus* degree of conversion X. Comparison of theoretical curve with experimental data at $T = 40°C$. ●, experimental data from Ref. 30, osmometric data; ×, experimental data from Ref. 30, viscometric data; ——, curve from equation 34a

about 770 from which a value of ν_{m0} of about 2840 can be calculated, using equation (34a). Adopting for k_d of LPO, at 50°C, the value $6.9 \times 10^{-5}\,min^{-1}$ (determined in carbontetrachloride)[41] and assuming $f_m = 1$, from equation (24) one obtains, in this case,

$$\nu_{m0} = \frac{0.6 \times 13.6}{(6.9 \times 10^{-5} \times 4.2 \times 10^{-2})^{0.5}} = 2400$$

Since this value of ν_{m0} results to be significantly lower than that obtained through extrapolation of P_n, one of the two following hypothesis, or both of them together, ought to be valid:

- f_m in the case of LPO is lower than 1 (~0.7);
- k_d of LPO in VC is lower than that in carbontetrachloride.

As one can see in *Figure 11*, setting ν_{m0} as 2840 and using the same values of the parameters of the previous case, the theoretical curve drawn using equation (34a) fits reasonably well with the experimental data of $\bar{P}_n$, again with the exception of the point at the lowest value of X.

The dependence of the molecular weight of the polymer on conversion has also been studied by Russo and Stannett[30] in a work dealing with the bulk polymerization of VC at 40°C, initiated by gamma radiation at a dose rate of 0.175 Mrad. The authors have determined the number average molecular weight $(\bar{M}_n)$ by viscometry and, for some samples of polymer, by osmometry. By extrapolation of the $(\bar{M}_n)$ data to $X = 0$, and putting

$C = 0.5^*$ one obtains $\nu_{m0} \cong 3600$. In the case of radiation-initiated polymerization at 40°C, $q = 4.3$ (see *Table 2*) and fixing $F \cong 0.55$ (see the previous paragraph), one can put $\beta = 0.58$. Moreover, Russo and Stannett have found $C_M = 7.1 \times 10^{-4}$. In *Figure 12*, the curve obtained from equation (34a) using the above-mentioned various parameters is compared with experimental data. One can see that the theoretical curve fits the experimental points fairly well, particularly those ones corresponding to osmometric measurements. It should be pointed out that the equations (32a), and (34a) are strictly valid only when the initiation rate remains constant during the reaction, otherwise one must take into account, in his calculation, the changes of them due to the variation in the initiation rate.

CONCLUSIONS

(1) The theoretical kinetic equations obtained on the basis of the two-phase model, considering the phases as two independent loci of reaction, illustrate quite well the particular autocatalytic feature of the bulk and suspension polymerization of VC in the whole conversion range in which the two phases co-exist. Deviations from the model may occur in a small conversion range at the beginning of the reaction (conversion < 1%), because of a non-negligible transfer of free radicals between the phases.

(2) The theoretical equations giving, respectively, the average kinetic chain length, and the number average degree of polymerization of the polymer, as a function of conversion, calculated assuming the polymer formed at each instant of the reaction as a mixture of the polymers formed independently in the two phases, agree quite well with the experimental data.

(3) In the case of chemically initiated polymerizations, possible differences in the partition coefficient between the phases for different initiators have a rather small influence on the kinetic behaviour of the reaction and on the polymerization degree of the polymer because of the mutually compensating variations of other kinetic parameters.

(4) By using both kinetic and thermodynamic experimental data, a critical polymerization temperature (i.e. the temperature above which the polymerizing system consists of a unique homogeneous phase) of around 90°C is obtained.

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*At 40°C, this parameter is probably a little higher than 0.5, since the greater activation energy of the disproportionation with respect to the combination-termination

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