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Diffusion-Controlled Reactions in Vinyl Chloride Suspension Polymerization

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Summary: The vinyl chloride suspension polymerization is kinetically modeled with a general approach for the independent calculation of diffusion effects on polymerization reactions. For the initiator decomposition, propagation and termination an apparent rate coefficient is determined, built up from two contributions: the intrinsic rate coefficient and a diffusional contribution. The diffusional contribution is calculated with the Smoluchowski model, the diffusion coefficients being determined from the free volume theory. When applying the free volume theory no adjustable parameters are used. The intrinsic rate coefficients are taken from the literature. Hence, a model without any adjustable parameters is obtained. Calculations show that the glass effect appears only at (very) high conversions. Due to the cage effect the initiator efficiency decreases strongly as soon as the monomer phase has disappeared. The gel effect always occurs in the polymer-rich phase and results in a decrease of the termination rate coefficient at the start of the third stage in the polymerization process. There is a good agreement with experimental results.

Keywords: diffusion-controlled reactions; free volume theory; glass effect; kinetics (polym.); poly(vinyl chloride) (PVC)

Introduction

The suspension polymerization of vinyl chloride has been modeled extensively[1-5]. In general, a good simulation of the monomer conversion and the moments of the molecular mass distribution is obtained. However, an evaluation of the applied models[6,7] shows that an adjustment of parameters to calculate the effect of diffusional limitations on the polymerization reactions is required. As a result, extrapolation to other operating conditions becomes difficult. This paper reports on a modeling effort to avoid the need for adjustable parameters by the independent calculation of the diffusional effects. The considered diffusion-controlled processes are the cage effect, the glass effect and the gel effect, corresponding to initiation, propagation and termination respectively. For the description of the polymerization process in three stages, reference is made to literature[1-3].

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Polymerization reactions

The reactions taken into account in the free radical suspension polymerization of vinyl chloride include initiation, propagation, termination and chain transfer to monomer[1] (Table 1).

Table 1. Reactions in the suspension polymerization of vinyl chloride

Type of reaction		
Decomposition of the initiator	$I_k \xrightarrow{f_k k_{d,k}} 2R_{0,k}$	(1)
Chain initiation	$R_{0,k} + M_k \xrightarrow{k_{inI,k}} R_{1,k}$	(2)
Propagation	$R_{i,k} + M_k \xrightarrow{k_{p,k}} R_{i+1,k}$	(3)
Chain transfer to monomer	$R_{i,k} + M_k \xrightarrow{k_{tr,k}} P_{i+1,k} + Cl_k$	(4)
	$Cl_k + M_k \xrightarrow{k_{inCl,k}} R_{1,k}$	(5)
Termination by combination	$R_{i,k} + R_{j,k} \xrightarrow{k_{tc,k}^{ij}} P_{i+j,k}$	(6)
Termination by disproportionation	$R_{i,k} + R_{j,k} \xrightarrow{k_{td,k}^{ij}} P_{i,k} + P_{j,k}$	(7)
Termination with *Cl* radical	$R_{i,k} + Cl_k \xrightarrow{k_{tCl,k}} P_{i,k}$	(8)

The reaction scheme is valid in both the monomer-rich phase ($k = 1$) and the polymer-rich phase ($k = 2$). The reactions in the polymer-rich phase are considered to become diffusion-controlled, while the reactions in the monomer-rich phase are reaction-controlled. Hence, the rate coefficients in the monomer-rich phase are equal to the intrinsic rate coefficients, marked with subscript 0. The initiator is a peroxide and the partitioning of the initiator between the monomer-rich phase and the polymer-rich phase is fixed to 0.77[1]. The phase equilibria calculations and the calculation of the Flory-Huggins interaction parameter are taken from literature[3], with the solubility parameters calculated as discussed further.

As a first approximation, the apparent rate coefficients $k_{inI,k}$ and $k_{inCl,k}$, respectively for the chain initiation with an initiator primary radical $R_{0,k}$ (step (2)) and a Cl_k radical (step (5)), are taken equal to the apparent propagation rate coefficient $k_{p,k}$ (step (3)).

The chain transfer to monomer reaction (steps (4) and (5)) is different from the classic transfer of the radical function to a monomer molecule[1,8]. It starts with a head-to-head propagation step (included in step (4)), followed by a *Cl* shift and a β scission, resulting in a dead polymer molecule $P_{i+1,k}$ and a Cl_k radical. The reaction of the Cl_k radical with a monomer molecule (step

(5)) starts a new macroradical $R_{1,k}$, completing the chain transfer to monomer reaction. If it is not required to calculate the branching content of the polymer molecules, these elementary reactions are combined into steps (4) and (5), and an overall apparent rate coefficient $k_{tr,k}$ is applied for step (4). Termination of macroradicals with Cl_k radicals (step (8)) is also included in the model. The apparent rate coefficients of the above reactions are considered to be chain length independent.

As for the termination mechanism, there is still discussion in literature whether the combination (step (6)) or the disproportionation (step (7)) is dominant[2]. Here, they are both considered. The apparent termination rate coefficients are considered to be chain length dependent.

Mass balances

The reaction scheme results in the following mass balances for the involved components.

Initiator:
$$\frac{1}{V_k}\frac{d(V_k I_k)}{dt} = -f_k k_{d,k} I_k \tag{9}$$

Macroradicals R_i ($i = 1,...,\infty$):

(the IUPAC preferred factor 2[9] is introduced in the termination reaction contributions)

$$\begin{aligned}\frac{1}{V_k}\frac{d(V_k R_{1,k})}{dt} = {} & 2 f_k k_{d,k} I_k - k_{p,k} R_{1,k} M_k - k_{tr,j} R_{1,j} M_j + k_{p,k} Cl_k M_k \\ & - 2R_{1,k}\sum_{j=1}^{\infty}\left(k_{td,k}^{1j} + k_{tc,k}^{1j}\right)R_{j,k} - 2k_{tCl,k} R_{1,k} Cl_k\end{aligned} \tag{10}$$

$$\frac{1}{V_k}\frac{d(V_k R_{i,k})}{dt} = k_{p,k}\left(R_{i-1,k} - R_{i,k}\right)M_k - k_{tr,k} R_{i,k} M_k - 2R_{i,k}\sum_{j=1}^{\infty}\left(k_{td,k}^{ij} + k_{tc,k}^{ij}\right)R_{j,k} - 2k_{tCl,k} R_{i,k} Cl_k \tag{11}$$

Polymer molecules P_i ($i = 1,...,\infty$):

$$\frac{1}{V_k}\frac{d(V_k P_{1,k})}{dt} = 2R_{1,k}\sum_{j=1}^{\infty} k_{td,k}^{1j} R_{j,k} + 2k_{tCl,k} R_{1,k} Cl_k \tag{12}$$

$$\frac{1}{V_k}\frac{d(V_k P_{i,k})}{dt} = 2R_{i,k}\sum_{j=1}^{\infty} k_{td,k}^{ij} R_{j,k} + 2k_{tCl,k} R_{i,k} Cl_k + k_{tr,k} R_{i-1,k} M_k + \sum_{j=1}^{i-1} k_{tc,k}^{j,i-j} R_{j,k} R_{i-j,k} \tag{13}$$

For the primary radicals $R_{0,k}$ and for the Cl_k radicals the steady state approximation is applied, resulting in:

$$R_{0,k} = \frac{2 f_k k_{d,k} I_k}{k_{p,k} M_k}; \quad Cl_k = \frac{k_{tr,k} M_k \sum_{i=1}^{\infty} R_{i,k}}{k_{p,k} M_k + k_{tCl,k}\sum_{i=1}^{\infty} R_{i,k}} \tag{14}$$

Moment balances

The method of moments is used to calculate the average properties of the molecular mass distribution (MMD). The s-th moment of the number molecular mass distribution for the macroradicals $\lambda_{s,k}$ (s=0,1,2,3) and for the polymer molecules $\mu_{s,k}$ (s=0,1,2,3) is calculated (eqs. not shown here) to obtain the moments of the molecular mass distribution ($\overline{M}_{n,k}, \overline{M}_{m,k}, \overline{M}_{z,k}$) in each phase k (k=1,2). The MMD moments are calculated with $\mu_{s+1,k}/\mu_{s,k}$ (s=0,1,2) and are combined[2] to calculate the total moments ($\overline{M}_n, \overline{M}_m, \overline{M}_z$) of the molecular mass distribution.

In deriving the moment balances use is made of the overall termination rate coefficient $\langle k_{t,2} \rangle$ (eq. 15), which is a function of the apparent termination rate coefficients $k_{t,2}^{ij}$ ($= k_{tc,2}^{ij} + k_{td,2}^{ij}$) for steps (6) and (7) and the macroradical concentrations R_i:

$$\langle k_{t,2} \rangle = \frac{\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} k_{t,2}^{ij} R_i R_j}{\left(\sum_{i=1}^{\infty} R_i\right)^2} \tag{15}$$

The R_i are found by solving the algebraic equations (10) – (11) resulting from the application of the pseudo steady state approximation to the macroradicals[10]. The fraction of termination by disproportionation ($\langle k_{td,2} \rangle / \langle k_{t,2} \rangle$) and combination ($\langle k_{tc,2} \rangle / \langle k_{t,2} \rangle$) is taken equally important.

Combination of reaction and diffusion

In general, the apparent rate coefficient k_{obs} of a reaction is influenced by two contributions (eq. 16): the intrinsic rate coefficient k_{chem} and a diffusion contribution k_{diff}[9,11].

$$\frac{1}{k_{obs}} = \frac{1}{k_{chem}} + \frac{1}{k_{diff}} \tag{16}$$

The apparent termination rate coefficient in the polymer-rich phase, $k_{t,2}^{ij}$, is then calculated from:

$$\frac{1}{k_{t,2}^{ij}} = \frac{1}{k_{t0}} + \frac{1}{k_{diff,2}^{ij}} \tag{17}$$

Likewise, expressions for the apparent propagation rate coefficient $k_{p,2}$, for the apparent chain transfer to monomer rate coefficient $k_{tr,2}$, and for the apparent termination rate coefficient between a macroradical and a *Cl* radical $k_{tCl,2}$ are used (eq. 18).

$$\frac{1}{k_{p,2}}=\frac{1}{k_{p0}}+\frac{1}{k_{diff,2}};\quad \frac{1}{k_{tr,2}}=\frac{1}{k_{tr0}}+\frac{1}{k_{diff,2}};\quad \frac{1}{k_{tCl,2}}=\frac{1}{k_{t0}}+\frac{1}{k_{diff,2}} \tag{18}$$

The decomposition of the initiator is modeled according to[14]:

$$I_2 \underset{k_{-d,2}}{\overset{k_{d,2}}{\rightleftarrows}} (R_0 \ldots R_0)_2 \xrightarrow{k_{diff,2}} R_{0,2} + R_{0,2} \tag{19}$$

$k_{d,2}$ is the decomposition rate coefficient of the initiator, $k_{-d,2}$ the recombination rate coefficient for the primary radicals $R_{0,2}$ and $k_{diff,2}$ is the diffusion contribution for the rate of the decomposition of the initiator. Reaction (19) corresponds to reaction (1) with overall rate coefficient $f_2k_{d,2}$. The mass balance for the initiator, making use of the steady state assumption for the primary radicals in their cage $(R_0 \ldots R_0)_2$ results in:

$$\frac{1}{V_2}\frac{d(V_2I_2)}{dt}=-k_{d,2}I_2+k_{-d,2}(R_0 \ldots R_0)_2=-\frac{k_{diff,2}}{k_{diff,2}+k_{-d,2}}k_{d,2}I_2=-f_2k_{d,2}I_2 \tag{20}$$

in which f_2 is the fraction of primary radicals that effectively turns into growing macroradicals. This leads to the following equation for f_2 :

$$\frac{1}{f_2}=1+\frac{k_{-d,2}}{k_{diff,2}} \tag{21}$$

However, reaction scheme (19) does not account for side reactions, such as recombination after decarboxylation, which lead to a more reduced efficiency[15]. This is accounted for by introducing a chemical efficiency f_0:

$$\frac{1}{f_2}=\frac{1}{f_0}+\frac{k_{-d,2}}{k_{diff,2}} \tag{22}$$

The initiator efficiency in the monomer-rich phase f_1 is equal to f_0 and is fixed for all simulations. Furthermore, as $k_{-d,2}$ is unknown, its value is put equal to 1 $m^3mol^{-1}s^{-1}$, which leads to:

$$\frac{1}{f_2}=\frac{1}{f_0}+\frac{1}{k_{diff,2}} \tag{23}$$

Eq. (23) is derived from a simple kinetic scheme. In reality more reactions occur during the decomposition of the initiator. However, for a more fundamental approach to model diffusional limitations more data concerning the kinetic rate coefficients of these reactions are needed. Furthermore, it is found that eq. (23) gives a good description of the initiator efficiency as a function of concentration and temperature. Moreover, the same modeling approach for diffusional effects is used as for the diffusional effects in propagation and termination reactions (eqs. (17) and (18)). There are no adjustable parameters with this approach. Finally, if more data on initiator decomposition become available, eq. (23) is easily extended to complex kinetic reaction schemes.

The diffusion contribution k_{diff}

A general expression for the diffusion contribution $k_{diff,2}$ of the apparent rate coefficient for two species y and z is determined using the Smoluchowski model[16-18]:

$$k_{diff,2} = 4\pi(r_y + r_z)(D_y + D_z)N_A \tag{24}$$

(r_y+r_z) is the distance between the two species when reaction occurs. The latter is taken as the Lennard-Jones diameter of a monomer molecule σ_m[13](=4.69 10^{-10} m). N_A is the Avogadro constant. (D_y+D_z) is the mutual diffusion coefficient consisting of two contributions of the reacting species y and z[16,17]. For the initiator primary radical, the monomer and for the *Cl* radical these contributions are the center-of-mass diffusion coefficients D_x(cent) ($x=y$ *or* z). It is reasonable to calculate D_x(cent) as the self-diffusion coefficient[17], as described with the free volume theory (see next paragraph). For a macroradical with chain length i, the contribution called D_p^i, consists of two terms: $D_p^i(\text{cent})$, and the reaction diffusion coefficient D_p(rd). The latter corresponding to the movement of the radical chain end during a propagation step. $D_p^i(\text{cent})$ is also calculated as the self-diffusion coefficient. $D_p(\text{rd})$ follows from[13,16,17]:

$$D_p(\text{rd}) = \frac{1}{6}k_{p,2}M_2a^2 \tag{25}$$

a is the root-mean-square end-to-end distance per square root of the number of monomer units in a polymer chain (=6.09 10^{-10} m). Applying the above, the diffusion contributions $k_{diff,2}$ to the apparent rate coefficients for initiator decomposition, propagation, chain transfer to monomer and termination are obtained from the following expressions:

decomposition $$k_{diff,2} = 4\pi\sigma_m(2D_i)N_A \tag{26}$$

propagation, chain transfer $$k_{diff,2} = 4\pi\sigma_m D_m N_A \tag{27}$$

termination $$k_{diff,2}^{ij} = 2\pi\sigma_m(D_p^i + D_p^j)N_A \tag{28}$$

Cl termination $$k_{diff,2} = 2\pi\sigma_m D_c N_A \tag{29}$$

The factor 2 instead of 4 arises from the application of the Smoluchowski model to the termination reaction. The diffusion coefficients remain to be determined.

Self-diffusion coefficients : General equations

The self-diffusion coefficients for the monomer (D_m(cent)), the macroradicals with chain length i ($D_p^i(\text{cent})$), the initiator primary radicals (D_i(cent)) and the Cl radical (D_c(cent)) are calculated with the free volume theory[19-21] (the notation 'cent' is omitted in order not to overload the eqs.):

$$D_x = D_{x,0} \exp\left(-\frac{E^*}{RT}\right) \exp\left(-\frac{\tilde{V}_{xj}^*}{\tilde{V}_{FH}/\gamma}\right) \qquad x = c, i, m \tag{30}$$

$$D_p^i = \overline{D}_{p,0} \exp\left(-\frac{\tilde{V}_{pj}^*}{\tilde{V}_{FH}/\gamma}\right) \tag{31}$$

The diffusion coefficients are determined by three parameters : (1) a pre-exponential factor, (2) an activation energy E^* representing the energy needed to make a diffusional jump and (3) a free volume contribution representing the availability of free volume and thus accounting for the concentration and most of the temperature dependency. The macroradical diffusion coefficient pre-exponential factor $\overline{D}_{p,0}$ accounts for the molecular mass dependency (see further). $\tilde{V}_{xj}^*$ ($x = c, i, m, p$) is the (molar) volume a molecule needs to make a diffusional jump. $\tilde{V}_{FH}$ is the hole free volume of the polymer-monomer mixture of the polymer-rich phase available for diffusion and γ is the mixture overlap factor ($0.5 \leq \gamma \leq 1$ [19,21,22]). This factor is needed to take into account the overlap between free volume elements. $\tilde{V}_{FH}$ and γ can be calculated from[22]:

$$\tilde{V}_{FH}/\gamma = \frac{\hat{V}_{FH}/\gamma}{\dfrac{\omega_m}{M_{mj}} + \dfrac{\omega_p}{M_{pj}}} \tag{32}$$

M_{mj} and M_{pj} are the molecular mass of the monomer and macroradical jumping unit and ω_m and ω_p are the monomer and polymer mass fraction in the polymer-rich phase. $\tilde{V}_{xj}^*$ can also be expressed as $\hat{V}_x^* M_{xj}$, with $\hat{V}_x^*$ the specific volume a molecule needs to make a diffusional jump. $\hat{V}_{FH}$ is the specific hole free volume and is calculated from the physical properties of the mixture ($T_{g,m-p} \leq T < T_{g,p}$)[21]:

$$\frac{\hat{V}_{FH}}{\gamma} = \omega_m \frac{\hat{V}_m^0(T_{g,m})}{\gamma_m}(f_{H,m}^G + \int_{T_{g,m}}^{T} \alpha_{l,m} dT') + \omega_p \frac{\hat{V}_p^0(T_{g,p})}{\gamma_p}(f_{H,p}^G - (\alpha_{l,p} - \alpha_{c,p})(T_{g,p} - T)) \qquad (33)$$

The temperature dependency of the monomer thermal expansion coefficient $\alpha_{l,m}$ is taken into account, while for the polymer the liquid thermal expansion $\alpha_{l,p}$ can be considered constant over the considered temperature range. $T_{g,x}$ ($x=m,p$) and $T_{g,m\text{-}p}$ are the glass transition temperatures of the pure monomer, the pure polymer and the monomer–polymer mixture. For $T_{g,p} \leq T$, $(\alpha_{l,p} - \alpha_{c,p})$ is replaced with $\alpha_{l,p}$[21]. $f_{H,x}^G$ and $\hat{V}_x^0(T_{g,x})$ are the fractional hole free volume and the specific volume of the pure component ($x=m,p$) at $T_{g,x}$. γ_x is the hole free volume overlap factor. The close-packed crystalline state expansion coefficient $\alpha_{c,p}$ is calculated from eq. (34)[21]

$$\alpha_{c,p} = \frac{1}{T_{g,p}} \ln\left(\frac{\hat{V}_p^0(T_{g,p})(1 - f_{H,p}^G)}{\hat{V}_p^0(0)}\right) \qquad (34)$$

Self-diffusion coefficients : Calculation of parameters

Pre-exponential factors $D_{m,0}$ is calculated from the Dullien equation[20,21,23]:

$$D_{m,0} = \frac{0.124\,10^{-16}\,\tilde{V}_{c,m}^{2/3} RT}{M_m \eta \hat{V}_m^0} \exp\left(\frac{\gamma_m \hat{V}_m^* / K_{11}}{K_{21} - T_{g,m} + T}\right) = 1.14\,10^{-7}\,\mathrm{m^2 s^{-1}} \qquad (35)$$

in which K_{11}/γ_m and K_{21} are the monomer free volume parameters, equal to $\hat{V}_m^0(T_{g,m})\alpha_{l,m}/\gamma_m$ and $f_{H,m}^G/\alpha_{l,m}$ respectively and calculated as such (Table 2). $\tilde{V}_{c,m}$ (=179 10^{-6} $\mathrm{m^3 mol^{-1}}$[3]) and M_m are the monomer molar critical volume and molecular mass; η and $\hat{V}_m^0$ are the pure monomer viscosity and volume. Despite the presence of temperature in the equation, the value of $D_{m,0}$ does not strongly depend on temperature and can be considered constant.

The pre-exponential factors $D_{c,0}$ and $D_{i,0}$ are taken equal to $D_{m,0}$. This assumption is made because no better means are available for the direct calculation of these pre-exponential factors.

The pre-exponential factor of the polymer diffusion coefficient $\overline{D}_{p,0}$ is determined by calculating the polymer diffusion coefficient at ω_p=1, and setting this coefficient equal to the diffusion coefficient derived from the reptation theory[29]. Because the polymer-rich phase is a concentrated solution over the entire conversion range, it is expected[16] that $D_p^i \sim M^{-2}$. As the free volume theory can best be applied in concentrated or highly concentrated solutions[30], it should equal the melt diffusion coefficient as described by the reptation theory.

Table 2. Physical properties and free volume properties of the monomer and the polymer

Property	Units	$x=m$ (monomer)	$x=p$ (polymer)
$\rho_x = 1/\hat{V}_x^{0}$ [24,3]	[kgm^{-3}]	$94.469/0.2707^{1+(1-T(K)/432)^{0.2716}}$	$10^3 \exp(0.4296-(3.274\,10^{-4}\,T(K)))$
η[25]	[Nm^{-2}s]	$6.4\,10^{-9}T^2-5.27\,10^{-6}T+1.18\,10^{-3}$	-
$\hat{V}_x^* = \hat{V}_x^0(0)$ [26]	[m^{3}kg^{-1}]	$7.94\,10^{-4}$	$6.66\,10^{-4}$
$\widetilde{V}_{xj}^* = \widetilde{V}_x^0(0)$ [26],eq.(40)	[m^{3}mol^{-1}]	$49.6\,10^{-6}$	$132.85\,10^{-6}$
$f_{H,x}^{G}$ [27]	[-]	0.025	0.025
$\alpha_{l,x}$[24,28]	[K^{-1}]	$1.42\,10^{-3}$	$5.85\,10^{-4}$
$T_{g,x}$	[K]	70	353.15
γ_x	[-]	1.0	1.0
E^*	[kJmol^{-1}]	16.4	-
δ_x[26]	[(Jm^{-3})$^{1/2}$]	$16.19\,10^3$ (1)	$19.73\,10^3$
M_m	[kgmol^{-1}]	0.0625	-

(1) From : $\delta_m=(E_{coh}/\widetilde{V}_m^0)^{1/2}$; $E_{coh}=\Delta H_{vap}-RT$ with $\Delta H_{vap}=20.4$ kJmol^{-1}(20°C)

The reptation diffusion coefficient $D^i_{reptation}$ is calculated from[31]:

$$D^i_{reptation} = \frac{G_N^0}{135}\left(\frac{\rho_p RT}{G_N^0}\right)^2 \frac{\langle R^2\rangle}{M}\frac{M_{cr}}{M^2\eta_{cr}} \tag{36}$$

in which G_N^0 is the shear modulus of the rubbery plateau. $<R^2>$ is the mean-square end-to-end distance of the polymer chain with molecular mass M ($=iM_m$) and density ρ_p. η_{cr} is the zero shear melt viscosity at the critical molecular mass of the polymer M_{cr}. In Table 3, the values and expressions for the physical properties used in the calculation of $D^i_{reptation}$ in eq. (36) are given.

The two expressions (eq. (31) at ω_p=1 and eq. (36)) are set equal (eq. 37) at $1.2T_{g,p}$ and solved for $\overline{D}_{p,0}$. At this temperature both theories are valid and the physical properties required for the diffusion coefficients calculations are known. At $T_{g,p}$ itself a lot of physical properties change drastically implying a higher degree of uncertainty.

$$D^i_{reptation}\Big|_{\omega_p=1;T=1.2T_{g,p}} = D^i_p\Big|_{\omega_p=1;T=1.2T_{g,p}} \tag{37}$$

From eq. (37) one obtains [m^{2}s^{-1}]:

$$\overline{D}_{p,0} = \frac{6.53\,10^{-10}}{M^{1.892}} = \frac{1.24\,10^{-7}}{i^{1.892}} \tag{38}$$

Table 3. Values and expressions for physical properties used in $D^{i}_{reptation}$ (eq. 36)

Property	Units	Value/expression
G_N^0 (=$2\rho_p RT/M_{cr}$)[31]	[Nm^{-2}]	$1.5\ 10^6$
M_{cr}[26]	[$kgmol^{-1}$]	6.25
$<R^2>^{1/2}$ (this study)	[m]	$2.833\ 10^{-9}M^{0.554}$
$\log\eta_{cr}(1.2T_{g,p})$[26]	[$Nm^{-2}s$]	3.89

Activation energy E^* is estimated from a plot[21] as a function of the solubility parameters δ_m and δ_p and the molar volume of the pure solvent $\tilde{V}_m^0$ [m^3mol^{-1}] at a reference temperature (20°C). A fit of this plot[32] (eq. 39), is used to calculate E^* [$Jmol^{-1}$]. The same E^* is used in all D_x (eq. (30)).

$$\log(E^*) = 0.8988\ln\left(\log\left(\left(\delta_m - \delta_p\right)^2 \tilde{V}_m^0 / 4.1868\right)\right) + 3.4575 \qquad (39)$$

Free volume parameters Calculating diffusion coefficients based on the free volume theory requires the knowledge of detailed volumetric and physical properties of the monomer and the polymer. Their temperature relationships are obtained from correlations (Table 2), while the jump volumes $\tilde{V}_{xj}^*$ ($x=c,i,m,p$) are calculated as the size of the jump unit at 0K obtained from group contribution methods[19-21]. The monomer jump volume $\tilde{V}_{mj}^*$ is the volume of the molecule itself while the polymer jump segment can be calculated from eq. (40)[21].

$$\tilde{V}_{pj}^* = 0.6224\,10^{-6}T_{g,p} - 86.95\,10^{-6} \qquad (40)$$

The primary radical jump unit is calculated as half of the initiator (Bis(2-ethylhexyl) peroxydicarbonate or Trigonox EHP) volume at 0K (=149.5 10^{-6} m^3mol^{-1}). For the *Cl* radical a value of 19.3 10^{-6} cm^3mol^{-1} is used. The fractional hole free volume at the glass transition temperature $f_{H,x}^G$ ($x=m,p$) is derived from the Williams-Landel-Ferry (WLF) equation[27].

Other important free volume parameters are the pure component overlap factors γ_m and γ_p. For γ_m it is suggested to regress viscosity-temperature (η) and density-temperature ($\hat{V}_m^0$) data of the pure monomer with eq. (35) to obtain values for the parameters K_{11}/γ_m, K_{21}-$T_{g,m}$ and $D_{m,0}$. However, no statistically significant results could be obtained from this regression due to the strong correlation between these parameters, even after reparametrization of the exponential term. Furthermore, as several good fits of the experimental data could be obtained with sets of significantly different parameter values, these regression results are not used as such. The main conclusion that could be drawn from the regression was that γ_m is close to one or should be even higher. As the theoretically maximum value is 1, γ_m is taken equal to 1. γ_p can be calculated from[21]

$$\gamma_p = \frac{\hat{V}_p^0(T_{g,p})\alpha_{l,p}}{K_{12}/\gamma_p} \quad \text{in which} \quad \frac{K_{12}}{\gamma_p} = \frac{\hat{V}_p^*}{2.303 C_1 C_2} \tag{41}$$

C_1=19.84 and C_2=43.89 are the WLF constants for the polymer[33]. The resulting value for γ_p is also higher than 1. Therefore, the maximum value of 1 is used in all calculations.

Effect of conversion on diffusion

This effect follows from the dependence of the self-diffusion coefficients on the polymer mass fraction ω_p in the polymer-rich phase. The calculated self-diffusion coefficients at a polymerization temperature of 55°C are presented in Figure 1 as a function of ω_p. The initiator is the peroxide Bis(2-ethylhexyl) peroxydicarbonate or Trigonox EHP (f_0=1). Only one macroradical diffusion coefficient is presented corresponding to a molecular mass of 10^5 g mol^{-1}. D_p^i and D_i have a stronger concentration dependency than D_m, as expected. For D_c, this dependency is even smaller. It is less obvious that the initiator primary radical diffusion coefficient D_i has an even stronger concentration dependency than D_p^i, but this follows from the free volume theory. The jump unit molar volume of the initiator primary radical $\tilde{V}_{ij}^*$ is higher than that of a polymer segment $\tilde{V}_{pj}^*$ (see Table 2). The absolute value of D_i is higher than D_p^i because the pre-exponential factor of the polymer diffusion coefficient is lower than that of the initiator. D_p^i and D_i roughly have the same value for high values of ω_p. These diffusion coefficients can now be used to calculate the apparent rate coefficients, the conversion and the moments as a function of polymerization time.

Simulation of conversion and molecular mass distribution

With the values for intrinsic kinetic rate coefficients from literature (Table 4) and the calculated diffusion coefficients, the variation of the apparent rate coefficients as a function of conversion is shown in Figure 2. The calculated conversion and the moments of the MMD as a function of polymerization time are also shown in Figure 2.

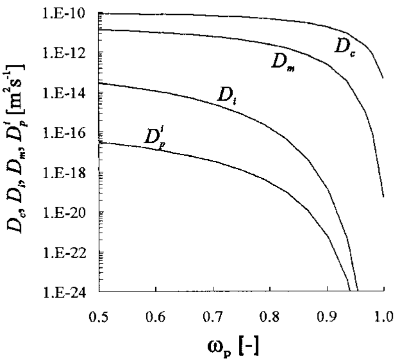

Figure 1. Self-diffusion coefficients for the *Cl* radical (D_c), the primary radical of initiator (D_i) for Trigonox EHP, the monomer (D_m) and one polymer chain length (D_p^i, 10^5 g mol^{-1}) as a function of the polymer mass fraction ω_p in the polymer-rich phase.

It can be seen in Figure 2 that the gel effect (expressed by $<k_{t,2}>$) and the cage effect (expressed by f_2) become very pronounced from the start of the third stage. As the monomer is consumed, the viscosity in the polymer-rich phase increases and the diffusion coefficients decrease significantly. However, the apparent propagation rate coefficient $k_{p,2}$ does not decrease. This is in agreement with literature[37] where experimental evidence for the absence of diffusion-control of the propagation rate coefficient was reported. For the simulation in Figure 2, a final conversion of 86% is reached and a negligible glass effect is calculated. The minimum conversion levels at which the glass effect is not yet pronounced were estimated[37] between 83% to 91%.

Table 4. Intrinsic rate coefficients data

Rate coefficient $k_0 = A\exp(-E/RT)$	A [m^{3}mol^{-1}s^{-1}]	E [kJ mol^{-1}]
k_{p0}[3,34,35]	5.0 10^4	27.63
$2k_{t0}$[1,34,35]	1.3 10^9	17.59
$C_M = k_{tr0}/k_{p0}$[3,36]	5.78 [-]	23.01

This can be further elaborated when considering experimental data for the T_g of the monomer-polymer mixture[1] ($=T_{g,m\text{-}p}$). Agreement with the reported results is obtained. At the considered reaction temperature the composition of the polymer-rich phase to undergo a transition to the glassy state of the mixture is about 90wt% to 95wt% of polymer. As the monomer conversion to obtain such a high composition is never reached in the simulation shown in Figure 2, the drop in $k_{p,2}$ is not seen here. However, a separate calculation of the apparent propagation rate coefficient (dotted line in Figure 2) for higher mass fractions of polymer in the polymer-rich phase results in a drop of $k_{p,2}$ starting at 90wt% to 95wt%, corresponding with the experimental data for $T_{g,m\text{-}p}$[1]. The drop in the polymerization rate can completely by explained by the gel effect and the cage effect. The glass effect does not play a role until higher conversions[6,7].

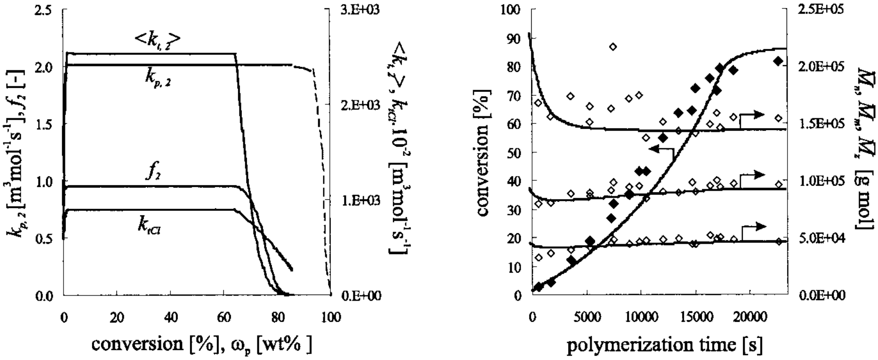

Figure 2. (left) (full lines) Apparent rate coefficients in the polymer-rich phase as a function of conversion and (dotted line) predicted apparent propagation rate coefficient $k_{p,2}$ as a function of the polymer mass fraction ω_p in the polymer-rich phase; (right) Conversion (◆) and molecular mass moments (◇) as a function of polymerization time; (full lines) simulation (integration of eqs. (9)-(13) with method of moments with parameters of Tables 2-4; reactor volume = 0.002 m^3, vinyl chloride = 0.3 kg, water = 0.7 kg, initiator 0.061 wt% based on the monomer).

Conclusions

The effect of diffusional limitations on the polymerization reactions has been calculated from first principles. An elementary reaction scheme is considered for this calculation. Both the combination of reaction and diffusion and the calculation of the diffusion contributions to the apparent rate coefficients for the polymerization reactions that can become diffusion-controlled are performed in a consistent way for all reactions. It is found that the decrease in polymerization rate is entirely accounted for by the gel effect and the cage effect. The glass effect only slightly appears at higher conversions. This is in agreement with experimental results. Also the predicted conversion at which the glass effect becomes pronounced, agrees with experimental data for the glass transition temperature of the monomer-polymer mixture. As the effect of diffusion can now be calculated independently, the estimation of the intrinsic rate parameters of the vinyl chloride suspension polymerization from experimental data is within reach.

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[1] T.Y. Xie, A.E. Hamielec, P.E. Wood, D.R. Woods *Polymer*, **1991**, 32(6), 537-557
[2] T.Y. Xie, A.E. Hamielec, P.E. Wood, D.R. Woods *Polymer*, **1991**, 32(6), 1098-1111
[3] C. Kiparissides, G. Daskalakis, D.S. Achilias, E. Sidiropoulou *Ind. Eng. Chem. Res.*, **1997**, 36, 1253-1267
[4] G. Talamini, A. Visentini, J. Kerr *Polymer*, **1998**, 39(10), 1879-1891
[5] G. Talamini, A. Visentini, J. Kerr *Polymer*, **1998**, 39(18), 4379-4384
[6] N. Tefera, G. Weickert, K.R. Westerterp *J. Appl. Polym. Sc.*, **1997**, 63(12), 1649-1661
[7] N. Tefera, G. Weickert, K.R. Westerterp *J. Appl. Polym. Sc.*, **1997**, 63(12), 1663-1680
[8] W.H. Jr. Starnes, F.C. Schilling, I.M. Plitz, R.E. Cais, D.J. Freed, R.L. Hartless, F.A. Bovey *Macromolecules*, **1983**, 16(5), 790-807
[9] R.G. Gilbert *Pure & Applied Chemistry* **1992**, 64(10), 1563-1567
[10] M.J. Monteiro, N. Subramaniam, J.R. Taylor, B.T.T. Pham, M.T. Tonge, R.G. Gilbert *Polymer*, **2001**, 42, 2403
[11] J.B.L. de Kock, A.M. Van Herk, A.L. German *J. Macromol. Sci. - Polymer Reviews*, **2001**, C41(3), 199-252
[12] B.S. Casey, M.F. Mills, D.F. Sangster, R.G. Gilbert, D.H. Napper *Macromolecules*, **1992**, 25, 7063-7065
[13] P.A. Clay, R.G. Gilbert *Macromolecules*, **1995**, 28, 552-569
[14] W.A. Pryor, K. Smith *J. Am. Chem. Soc.*, **1970**, 92(18), 5403-5412
[15] G. Odian *Principles of polymerization*, **1981**, 2nd ed., Wiley, New York
[16] G.T. Russell, R.G. Gilbert, D.H. Napper *Macromolecules*, **1992**, 25, 2459-2469
[17] G.T. Russell, R.G. Gilbert, D.H. Napper *Macromolecules*, **1993**, 26, 3538-3552
[18] G.T. Russell *Aust. J. Chem.*, **2002**, 35, 399-414
[19] J.M. Zielinski, J.L. Duda *AIChE J.*, **1992**, Vol. 38, No. 3, 405-415
[20] J.M. Zielinski *Macromolecules*, **1996**, 29, 6044-6047
[21] J.S. Vrentas, C.M. Vrentas *Eur. Pol. J.*, **1998**, Vol. 34, No. 5/6, 797-803
[22] P. Neogi *Diffusion in Polymers*, **1996**, Marcel Dekker
[23] F.A.L. Dullien *AIChE J.*, **1972**, Vol. 18, No. 1, 62-70
[24] R.H. Perry, D.W. Green, *Perry's Chemical Engineers' Handbook*, **1998**, 7th edition, McGraw-Hill, New York
[25] Aspen Plus
[26] D.W. Van Krevelen, *Properties of Polymers*, **1997**, 3rd ed., Elsevier
[27] J.D. Ferry, *Viscoelastic Properties of Polymer*, **1970**, 2nd ed., Wiley, New York
[28] J. Bandrup, E.H. Immergut, *Handbook of Polymers*, **1989**, 3rd. ed., New York, Wiley
[29] M. Doi, S.F. Edwards *The Theory of Polymer Dynamics*, **1986**, Oxford University Press, New York
[30] L. Masaro, X.X. Zhu *Progr. Polym. Sci.*, **1999**, 24, 731-775
[31] W.W. Graessley, *J. Polym. Sci., Polym. Phys. Ed.*, **1980**, 18, 27-34
[32] M.P. Tonge, R.G. Gilbert *Polymer*, **2001**, 42, 1393-1405
[33] J.E. Mark *Physical Properties of Polymers Handbook*, **1996**, AIP Press, New York
[34] G.M. Burnett, W.W. Wright *Proc. R. Soc. Lond.*, **1954**, A221, 41-53
[35] S.I. Kuchanov, D.N. Bort *Polym. Sci. USSR*, **1973**, 15, 2712-2736
[36] A.H. Abdel-Alim, A.E. Hamielec *J. Appl. Polym. Sci*, **1986**, 16, 783-799
[37] W.H. Jr. Starnes, B.J. Wojciechowski, H. Chung, G.M. Benedikt, G.S. Park, A.H. Saremi *Macromolecules*, **1995**, 28, 945-949