Emulsion Polymerization of Vinylidene Fluoride and Hexafluoropropylene: Average Number of Active Chains per Particle

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SUMMARY: The kinetic behavior of the emulsion polymerization of vinylidene fluoride and hexafluoropropylene is investigated. A set of polymerization reactions with largely different operating conditions was carried out. Reaction rates as a function of time and final numbers of polymer particles were measured for all reactions. The analysis of these data allowed us to estimate the evolution of the average number of active chains per particle, $\bar{n}$, with conditions ranging from a situation of complete compartmentalization up to pseudo-bulk conditions.

Introduction

When dealing with an emulsion polymerization, a key aspect is the degree of segregation of the active chains inside the growing particles, i.e. the so-called compartmentalization. The actual value of the average number of active chains per particle, $\bar{n}$, determines not only the reaction rate but also the evolution of the polymer molecular weight.

In this work, the dependence of $\bar{n}$ upon the reaction operating conditions for the emulsion polymerization of vinylidene fluoride (VDF) and hexafluoropropylene (HFP) is analyzed. From a data set of polymerization rate and final number of polymer particles, $\bar{n}$ was estimated using classical kinetic equations[1]. Widely different operating conditions were examined, with particle number and initiator concentration values covering about two orders of magnitude of variation. In particular, since all reactions were carried out in microemulsion[2], the number of particles was adjusted independently of reaction conditions by tuning the characteristics of the initial microemulsion. With respect to the standard approach to this kind of kinetic analysis (based on seeded reactions), this represents a significant advantage in terms of reduction of the experimental effort.

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By analyzing such a large range of operating conditions, it was possible to obtain values of $\bar{n}$ from about 60, a value corresponding to pseudo-bulk conditions, down to about 0.1, a situation usually defined as Smith-Ewart case I system. The modeling analysis of these data indicates the dominant role of the bimolecular termination at large $\bar{n}$ values, thus confirming the reliability of the kinetic parameter values adopted in a previous work limited to pseudo-bulk conditions[3]. Moreover, the relevance of a monomolecular termination mechanism (or desorption) at low $\bar{n}$ values is shown and the values of the corresponding kinetic parameters are reported.

Experimental

The polymerization reactions were carried out in the pilot plant reactor described by Apostolo et al.[3] in microemulsion. Accordingly, a thermodynamically stable aqueous dispersion of droplets of a fluorinated oil stabilized by a fluorinated surfactant is introduced in the reactor. Then the reactor is pressurized with the gaseous monomers and, during the reaction, a monomer mixture of suitable composition is continuously added in order to keep constant the reactor pressure while producing a copolymer with constant composition[4]. A constant reactor temperature of 80°C was used. Ammonium persulfate as free radical initiator was charged to the reactor in a single initial shot. The reactor is equipped with a monomer feed flowmeter through which an on-line measurement of reaction rate is obtained. Light scattering measurements provided by a Spectra Physics 2020 argon-ion laser operating at 514.5 nm were used to evaluate the final particle diameter.

Reaction rate: The following expression applies:

$$\Re_p = k_p C_m \frac{\bar{n} N_p}{N_A} \qquad (1)$$

where k_p is the propagation rate constant, C_m the monomer concentration inside the particle, $\bar{n}$ the average number of active chains per polymer particle, N_p the particle number per unit volume of water phase and N_A the Avogadro number. Through eq.(1), the average number of active chains is readily evaluated from the experimental data of reaction rate and particle number if k_p and C_m are available. Using the values of these quantities available from a previous work[3], the $\bar{n}$ values summarized in the table were estimated. Note that, even though the system under examination is a copolymer, following the pseudo-kinetic approach the

homopolymerization rate expression given by eq.(1) can be used. Accordingly, kp is a composition average propagation rate constant which, under conditions of constant copolymer composition[4] (as it is the case for all reactions in the table), has a constant value all along the reaction. As a consequence, C_m indicates the concentration of the monomer mixture in the particle, again a constant value at constant composition and pressure.

Table 1: Reaction recipe, particle size, polymerization rate, average number of active chains per particle, $\bar{n}$, and α' parameter (eq.4) for all experiments.

RUN	Initiator (g/l)	Pressure (bar)	$N_p \times 10^{-14}$ ($1/cm^3$)	d_p (nm)	$\Re_p \times 10^3$ (mol/l s)	$\bar{n}$ -	α' -
05	5	11	0.19	265	1.95	67	6758.7
02	5	11	1.10	149	2.03	12	207.5
06	5	11	1.40	137	2.08	10	126.7
03	5	11	4.32	94	2.01	3	13.3
31	0.5	21	2.31	116	1.51	2.2	4.41
92	0.5	21	3.86	97	1.73	1.5	1.54
97	0.5	21	6.22	84	2.16	1.2	0.60
94	0.5	21	15.4	61	2.57	0.6	0.09
96	0.5	21	16.8	59	2.64	0.5	0.08
87	0.05	21	4.35	93	0.51	0.4	0.051
89	0.05	21	5.88	85	0.54	0.31	0.029
86	0.05	21	11.8	66	0.57	0.16	0.007
90	0.05	21	17.0	60	0.53	0.11	0.004

Average number of active chains per particle. The $\bar{n}$ values in the table span from very high (67) to very low (0.11) values, thus covering the entire range of kinetic conditions or, following Smith and Ewart, from case III to case I. Therefore, it is interesting to compare these values with those given by the well-known Smith-Ewart equations[5]. Namely, following the classical analysis by Ugelstad and Hansen[6], the analytical solution of the balance describing the evolution of the average number of active chains per particle is:

$$\bar{n} = \frac{a}{4} \frac{I_m(a)}{I_{m-1}(a)} \qquad (2)$$

where $a = \sqrt{8\alpha}$ and $I_n(x)$ indicates the Bessel function of the first kind of order n. This equation has to be coupled with the material balance of the active chains in aqueous phase which, in dimensionless form, reduces to:

$$\alpha = \alpha' + m\bar{n} - Y\alpha^2 \tag{3}$$

where:

$$\alpha = \frac{k_e R^{\bullet} v N_A}{N_p\left(k_t^*/v\right)} \quad ; \quad \alpha' = \frac{\eta \Re_i N_A}{N_p\left(k_t^*/v\right)} \quad ; \quad m = \frac{k_d}{\left(k_t^*/v\right)} \quad ; \quad Y = 2\frac{k_t^* k_{tw}^* N_p}{v k_e^2} \tag{4}$$

The parameter α is the ratio between entry rate per particle ($\rho = k_e R^{\bullet} N_A / N_p$) and bimolecular termination (k_t^*/v, where the * indicates a molecular value), α' the ratio between the rate of radical production per particle ($\eta \Re_i N_A / N_p$, with $\Re_i$ decomposition rate of the initiator and η initiator efficiency) and k_t^*/v and m the ratio between monomolecular termination (or desorption, k_d) and k_t^*/v. The last quantity, Y, is related to the bimolecular termination in aqueous phase, whose rate constant on molecular basis is k_{tw}^*. Since values for initiator decomposition rate ($\eta \Re_i = k_I C_I \eta$, with $k_I \eta = 9 \cdot 10^{-5} 1/s$) and k_t^* ($= 9 \cdot 10^{-17}\ cm^3/mol\,s$) are available for the system under examination[3,7], α' can be considered an independent variable in eqs.(2) and (3) and the values corresponding to each $\bar{n}$ values are again reported in Table 1.

Let us analyze the case of high $\bar{n}$ values first. In the limit of pseudo-bulk conditions, the average number of active chains per particle, eq.(2), reduces to:

$$\bar{n} = \left(\frac{\alpha}{2}\right)^{1/2} \tag{5}$$

This equation can be combined with eq.(3) with m=0, since the role of chain desorption becomes negligible for systems at high $\bar{n}$ value[8]. In terms of α' and Y, the following two limiting expressions for $\bar{n}$ apply:

- Negligible termination in aqueous phase (Y~0):

$$\alpha \cong \alpha' \longrightarrow \bar{n} = \left(\frac{\alpha'}{2}\right)^{1/2} \tag{6}$$

- Dominant termination in aqueous phase:

$$\alpha = \left(\frac{\alpha'}{2}\right)^{1/2} \longrightarrow \bar{n} = \frac{1}{\sqrt{2}}\left(\frac{\alpha'}{Y}\right)^{1/4} \tag{7}$$

Therefore, the reaction rate (i.e. $\bar{n} N_p$) is independent of the particle number in both cases, while $\bar{n}$ is proportional to $\alpha'^{0.5}$ and $\alpha'^{0.25}$, respectively. By inspection of data in the first

four rows of Table 1 ($3 \leq \bar{n} \leq 67$), it is readily verified that the reaction rate is practically independent of the particle number and that $\bar{n}$ is proportional to $\alpha'^{0.496}$. This finding indicates that most of the radical produced in aqueous phase are captured by the particles, with a limited consumption by bimolecular terminations in aqueous phase.

Then, let us consider the data reported in the last four rows of the table, i.e. those corresponding to $\bar{n} < 0.5$. In these conditions, the role of the monomolecular terminations inside the particles is dominant and the following simplified equation for $\bar{n}$ applies:

$$\bar{n} = \frac{\alpha}{2\alpha + m} \cong \frac{\alpha}{m} \tag{8}$$

By substituting the expression in the material balance of active chains in aqueous phase, eq.(3), $\bar{n}$ is rewritten in terms of α' and Y as:

$$\alpha = \left(\frac{\alpha'}{Y}\right)^{1/2} \longrightarrow \bar{n} = \frac{1}{m}\left(\frac{\alpha'}{Y}\right)^{1/2} \tag{9}$$

Accordingly, the reaction rate is independent of the particle number and $\bar{n}$ is proportional to $\alpha'^{0.5}$. These predictions are confirmed by the data in Table 1 at low $\bar{n}$ which indicate the same behavior for the experimental reaction rate, and an estimated exponent value for α' of 0.482. Note that the limiting expression for α obtained when desorption is the dominant termination but at Y=0 predicts a dependence of the reaction rate by particle number ($\propto N_p^{0.5}$). This indicates that, at low initiator concentrations, a finite, even low value of terminations in aqueous phase has to be accounted for to properly simulate the system kinetics of the system.

The $\Re_p$ values at intermediate $\bar{n}$ values (0.5÷2.2) exhibit a moderate dependence upon the particle number. This behavior corresponds to the transition from the fully segregated to pseudo-bulk conditions, even though the classical plateau $\bar{n}$=0.5 for a range of α' values is not apparent, due to the relevance of the desorption mechanism.

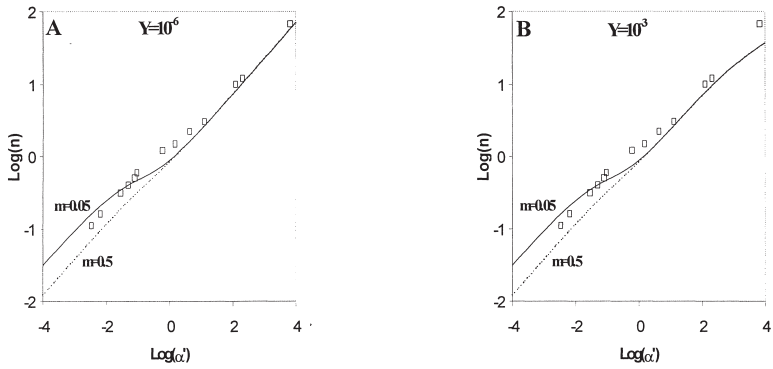

Figure 1. Log($\bar{n}$) vs Log(α'). Points: experimental data; lines: model calculations.

Let us compare the estimated $\bar{n}$ values with those predicted using eqs.(2) and (3). By assuming k_d inversely proportional to the square of the particle radius (=a/r_p^2), an average error of 21% is found when k_e = 100 1/s and a = $5 \cdot 10^{-13}$ cm^2/s. A comparison between prediction and experiment is shown in Figures 1a and 1b in terms of the classical $\bar{n}$ vs α' representation, at constant Y and m values (α is evaluated as a function of the remaining quantities through eq.(3)). Namely, two limiting values of both Y (10^{-6} and 10^{-3}) and m (0.05 and 0.5) were considered, roughly corresponding to minimum and maximum values found when using the estimated k_e and a values and the experimental data of particle size and number. It is apparent that a very limited termination in aqueous phase has to be considered to fit the data in the pseudo-bulk region (cf. Figure 1b) and, therefore, we will consider $Y=10^{-6}$ and m=0.1 as best fit values.

Finally, some comments about the estimated values for entry, k_e and desorption, k_d. The large k_e value indicates the strong tendency of all species in aqueous phase to quickly diffuse to the particles before reacting in aqueous phase at a significant extent. About desorption, starting from the general expression for k_d proposed by Asua et al[9] and assuming high probability for re-entry (β=0), the following equation is obtained:

$$k_d = \frac{k_{fm}}{k_p}\left(\frac{3D_w}{m + 2D_w/D_p}\right)\frac{1}{r_p^2} \qquad (10)$$

Where k_{fm} indicates the rate constant of transfer to monomer, D_w and D_p the monomer diffusivity in aqueous phase and particles, respectively, and m the partitioning coefficient of monomer between particles and aqueous phase. From the estimated value of a, using a value

of the ratio k_{fm} / k_p =6.5·10^{-4} (cf. ref [3]), and a diffusion coefficient in aqueous phase of 10^{-5} cm^2/s, the denominator ($m+2D_w/D_p$) in eq.(10) results around 4·10^4. This value, could be justified both by the very low solubility of the monomer in aqueous phase and by the reduced diffusivity in particle with respect to the aqueous phase.

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