Solid state polymerization of *N*-substituted acrylamides: 1.

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Based on the assumption that the radiation-induced solid state polymerization process is non-stationary, non-isochoric and that chain termination reactions do not occur, a general equation has been derived describing the dependence of conversion on the time of irradiation. The change of the average molecular weight as well as the change of the factor characterizing the structure *versus* time of irradiation have been also taken into consideration.

Theoretical considerations of radiation-induced solid state polymerization have been carried out by several investigators[1–20] who gave different interpretations of the mechanism and kinetics of this process.

The kinetic scheme presented below is based on some observations made during the study of the solid state polymerization of a series of *N*-substituted acrylamides and some *N*-substituted methacrylamides performed in our laboratory.

Taking into account that for all these monomers the polymerization rate increases with temperature rise and existence of free radicals after the termination of polymerization was stated, the following free radical mechanism is postulated.

Starting from the well known equation

$$\frac{-\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = K_p\,[\mathrm{M}]\,[\mathrm{R}^{\cdot}] \tag{1}$$

where [M] denotes monomer concentration and $[\mathrm{R}^{\cdot}]$ is the free radical concentration. The assumption is made that solid state polymerization proceeds without the termination reaction, i.e. the cessation of chain propagation in the crystalline phase is not bound with deactivation of free radicals. Therefore the weight of macroradicals is assumed to be approximately equal to the polymer weight P.

If the average molecular weight is $\bar{M}_p$, then, at any moment, the number of moles of the polymer equivalent to the number of moles of macroradicals will be $P/\bar{M}_p$ and the radical concentration mol/l will be:

$$[\mathrm{R}^{\cdot}] = \left[\frac{P}{\bar{M}_p}\right] \tag{1a}$$

However not all radicals present in the system participate in the polymerization to the end of the process.

Changes in the crystalline structure during polymerization or the presence of other macromolecules can stop the propagation of any particular macroradical.

The effective concentration of radicals is therefore different from the real concentration, and an additional parameter must be introduced:

$$\left[\frac{p}{\bar{M}_p}\right]^n$$

On the other hand in some cases the polymerization can stop at a given degree of conversion which may be caused by the geometrical arrangement of the monomer molecules in the crystalline state.

In this case a part of the monomer A does not take part in the reaction so that consequently equation (1) can be altered in the following way:

$$\frac{-\mathrm{d}[M/m]}{\mathrm{d}t} = K_p\left(\frac{M-A}{m}\right)\left(\frac{P}{\bar{M}_p}\right)^n \tag{2}$$

where A is the part weight of monomer which does not polymerize in the solid state; m is the molecular weight of the monomer; $\bar{M}$ is the average molecular weight of the polymer; $[M/m]$ is the concentration of the monomer in mol/l; $[P/M_p]$ is the concentration of macromolecules in mol/l, corresponding to the concentration of macroradicals and n is a parameter characterizing the reactivity of radicals in the solid state.

However for conversion above 10% the change of the system volume cannot be omitted:

$$V = V_{\mathrm{mon}} + V_{\mathrm{pol}}$$

$$V_{\mathrm{mon}} = \frac{M-A}{d_{\mathrm{mon}}} + \frac{A}{d_{\mathrm{mon}}}$$

where d_{mon} is the monomer density

$$V_{\mathrm{pol}} = \frac{M_0 - M}{d_{\mathrm{pol}}}$$

where d_{pol} is the polymer density; M_0 is the initial weight of monomer and M is the actual weight of monomer.

$$V = \frac{M-A}{d_{\mathrm{mon}}} + \frac{M_0-M}{d_{\mathrm{pol}}} + \frac{A}{d_{\mathrm{mon}}}$$

Denoting

$$\frac{1}{d_{\mathrm{mon}}} = \alpha$$

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$$\frac{1}{d_{\mathrm{pol}}} = \beta$$

and

$$\gamma = \alpha - \beta$$

gives

$$V = \gamma M + \beta M_0$$

Substituting this relationship into equation (2) and taking into account that $P = M_0 - M$:

$$\left[\frac{M-A}{m}\right] = \frac{M-A}{mV} = \frac{M-A}{m(\beta M_0 + \gamma M)}$$

and

$$\mathrm{d}\left[\frac{M}{m}\right] = \mathrm{d}\frac{M}{m(\beta M_0 + \gamma M)} = \frac{1}{m}\,\frac{\beta M_0}{(\beta M_0 + \gamma M)^2}\,\mathrm{d}M$$

After rearrangement the following equation results:

$$-\frac{\beta M_0(\beta M_0 + \gamma M)^{n-1}}{(M-A)\,(M_0 - M)^n}\,\mathrm{d}M = K_p\,\frac{\mathrm{d}t}{(\bar{M}_p)^n} \qquad (3)$$

$\bar{M}_p$ is a function of time and can be determined only experimentally.

The simpler case when $A = 0$ and $n = 1$ has been presented at the Second Symposium on Radiation Chemistry[22].

More detailed analysis of the solid state polymerization shows that the exponent n usually is not constant, but varies with time owing to changes is the structure of the monomer–polymer system occurring during the polymerization process.

The value n can be then presented in the form:

$$n = n_0 + g(t)$$

where n_0 denotes the constant component and $g(t)$ is the variable component function of time. After substitution equation (3) will take the following form:

$$-\frac{\beta M_0}{(M-A)(M_0 - M)}\left(\frac{\beta M_0 + \gamma M}{M_0 - M}\right)^{n_0 - 1}\mathrm{d}M$$

$$= K_p\left(\frac{M_0 - M}{\beta M_0 + \gamma M}\right)^{g(t)}(\bar{M}_p)^{-[n_0 + g(t)]}\,\mathrm{d}t \qquad (4)$$

Usually $A = 0$ means that the polymerization proceeds to the total conversion into polymer. In that case equation (4) is transformed into the following relationship:

$$-\frac{\beta M_0}{M(M_0 - M)}\left(\frac{\beta M_0 + \gamma M}{M_0 - M}\right)^{n_0 - 1}\mathrm{d}M$$

$$= K_p\left(\frac{M_0 - M}{\beta M_0 + \gamma M}\right)^{g(t)}(\bar{M}_p)^{-[n_0 + g(t)]}\,\mathrm{d}t \qquad (5)$$

The left-hand side of equation (5) is a function of the variable M, while the right-hand side is the product of the factor

$$\bar{M}_p^{-[n_0 + g(t)]}$$

being only a function of time and the factor:

$$\left(\frac{M_0 - M}{\beta M_0 + \gamma M}\right)^{g(t)}$$

being the function of two variables t and M.

The average molecular weight, $\bar{M}_p$, is a function of time. According to our experimental data confirmed also by other investigators for different monomers[4] the average molecular weight *versus* time of irradiation increases with time reaching a maximum and then decreases slowly.

It is evident that the function $\bar{M}_p(t)$ reaches its lowest value when $t = 0$, then $\bar{M}_p(0) = m$ and consequently:

$$\frac{\mathrm{d}\bar{M}_p(t)}{\mathrm{d}t} = 0$$

This last statement is based on the observation of the shape of the curve presenting the dependence of $\bar{M}_p$ *versus* t in the proximity of $t = 0$.

It is difficult to characterize the function $g(t)$. Of course, $g(t) = 0$ when $t = 0$, and in this case, $n = n_0$. Besides, the assumption that:

$$\frac{\mathrm{d}g(t)}{\mathrm{d}t} = 0 \quad \text{when } t = 0$$

seems to be wholly justified from the point of view of the mechanism of the process, the function $g(t)$ shows a minimum when $t = 0$.

This assumption leads to some simplification of the equation (5).

Denoting:

$$\left(\frac{M_0 - M}{M_0 + M}\right)^{g(t)} \equiv \phi(M,t)$$

and

$$[\bar{M}_p(t)]^{-[n_0 + g(t)]} \equiv \psi(t)$$

Expanding the function $\psi(t)$ in a series about $t = 0$ and omitting the terms with exponent of t higher than 2 and taking into account the properties of functions $\bar{M}_p(t)$ and $g(t)$ mentioned above, a simple relation is obtained:

$$\psi(t) = m^{-n_0}\left\{1 + \frac{1}{2}\left[g''(t)_{t=0}\ln m - \frac{n_0}{m}\bar{M}_p{}''(t)_{t=0}\right]t^2\right\} \qquad (6)$$

where $g''(t)_{t=0}$ is the value of the second derivative of function $g(t)$ for $t = 0$ and $\bar{M}_p{}''(t)_{t=0}$ is the value of the second derivative of function $\bar{M}_p(t)$ for $t = 0$.

In a similar way expanding the function $\phi(M,t)$ and omitting terms with exponents higher than 2 the following relationship is obtained:

$$\phi(M,t) = 1 + [\tfrac{1}{2}g''(t)_{t=0}\ln d_{\mathrm{pol}}]\,t^2 \qquad (7)$$

Finally after substitution of equations (6) and (7) into equation (5) and again neglecting terms containing variables *m* and *t* with exponents greater than 2 the equation can be presented in the following form:

$$-\frac{\beta M_0}{M(M_0-M)}\left(\frac{\beta M_0+M}{M_0-M}\right)^{n_0-1}\mathrm{d}M$$

$$=K_p m^{-n_0}\left\{1+\frac{1}{2}\left[g''(t)_{t=0}\ln m\, d_{\mathrm{pol}}-\frac{n_0}{m}\bar{M}_p''(t)_{t=0}\right]t^2\right\}\mathrm{d}t \tag{8}$$

Substituting M by conversion:

$$S=\frac{M_0-M}{M_0}$$

the equation becomes:

$$\frac{\beta M_0}{M_0(1-S)M_0S}\left(\frac{\beta M_0+\gamma M_0(1-S)}{M_0S}\right)^{n_0-1}-M_0\mathrm{d}S$$

$$=\frac{\beta}{SM_0(1-S)}\left(\frac{\beta M_0-\gamma M_0-\gamma M_0S}{M_0S}\right)^{n_0-1}M_0\mathrm{d}S$$

$$=\frac{\beta}{S(1-S)}\left(\frac{\alpha M_0-M_p\gamma S}{M_0S}\right)^{n_0-1}\mathrm{d}S$$

$$=\frac{\beta}{S(1-S)}\left(\frac{\alpha-\gamma S}{S}\right)^{n_0-1}\mathrm{d}S$$

Finally the following equation is obtained:

$$\frac{\beta}{S(1-S)}\left(\frac{\alpha-\gamma S}{S}\right)^{n_0-1}\mathrm{d}S$$

$$=K_p m^{-n_0}\left\{1+\frac{1}{2}\left[g''(t)_{t=0}\ln md_{\mathrm{pol}}-\frac{n_0}{m}\bar{M}_p''(t)_{t=0}\right]t^2\right\}\mathrm{d}t \tag{9}$$

CONCLUSIONS

Based on the following assumptions that the radiation-induced solid state polymerization is: (a) non-stationary; (b) the termination reaction does not occur; (c) the process is non-isochoric and (d) the factor characterizing the structure is changing during the reaction of polymerization, one general equation has been derived describing the dependence of conversion on the time of irradiation.

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