Polymer Bulletin 32, 713–718 (1994)

Polymer Bulletin

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Monomer conversion kinetics in the radical initiated reactive processing

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Abstract

Modification of polymers by radical initiated addition of reactive monomers has two limiting cases: grafting of long chains accompanied by homopolymer formation and isolated substitution by the monomer units, respectively. In both cases (which in simplified form can be treated similarly) the efficiency, i.e. the monomer conversion after decomposition of a given amount of the initiator is a practically important characteristic of the process. Knowing the temperature dependent rates of the reactions, this conversion is calculable.

Introduction

Radical initiated reactive processing has growing importance in production of speciality polymers. Especially important is the modification of chemically inert and physically weekly interacting polyolefins with highly polar or reactive monomers (e.g. with maleic anhydride or trialkoxy-vinyl silanes). The maleic anhydride functionalization of apolar polymers has a long history [1-4] and the continuous process has growing importance reflected by the recent publications [5,6]. The grafting of polyethylene with vinylsilane monomers in extruders is an established industrial procedure [7].

With coarse simplification the extruder is approximated by a tubular reactor with a steady temperature profile and a constant flow rate of material. In a previous publication [8] it was shown, that the decomposition kinetics of the radical initiator can be given in a relatively simple form for this case if the temperature profile is hyperbolic (i.e. the reciprocal absolute temperature varies linearly with respect to the residence time). As the temperature corresponding to the maximal decomposition rate is calculable from the Arrhenius parameters of initiator decomposition and the rate of temperature change, these results give good orientation for the optimal working temperature profile and the suitable initiator, respectively.

Another important aspect of the reactive processing is the optimal efficiency of monomer and initiator. If the initiator is practically totally decomposed (as it is desirable) remaining monomer corresponds to a loss. On the other hand, if the monomer is totally consumed and considerable amount of initiator remains in the melt, other reactions (e.g. crosslinking) can take place. Thus, the consumption of monomer during the decomposition of initiator is a practically important characteristic of the radically initiated reactive processing.

Kinetics of monomer consumption

In the age of the classical radical polymerization kinetics an important result was the discovery made by Tobolsky [9] known generally as "dead end" polymerization saying that the total decomposition of initiator results not in complete monomer conversion and the limiting conversion is function of the kinetic parameters. For the isothermal reaction he assumed

$$-\frac{d[M]}{dt} = k_p[R^\cdot][M] \tag{1}$$

and the steady-state radical concentration was expressed by the time-dependent initiator concentration, giving for the monomer consumption rate Eq. (2):

$$-\frac{d[M]}{dt} = k_p\sqrt{\frac{2fk_d}{k_b}}\sqrt{[I]_0}\exp\left(-\frac{k_d}{2}t\right)[M] \tag{2}$$

This differential equation is easy to solve and it gives for the unreacted monomer concentration in function of the time the following expression:

$$-\log\frac{[M]}{[M]_0} = 2k_p\sqrt{\frac{2f}{k_dk_b}}\sqrt{[I]_0}\left(1-\exp\left(-\frac{k_d}{2}t\right)\right) \tag{3}$$

In the expressions (1-3) k_d is the initiator decomposition rate constant, 2f is the number of radicals formed from one initiator molecule, k_b is the rate constant of bimolecular termination and k_p is the propagation rate constant.

Under conditions of the reactive processing the radical initiated reactions of an unsaturated monomer with the polymer can be characterized by two limiting cases. In the first case the monomer homopolymerizes and the chain transfer reactions are negligible. If the initiator radicals are of sufficient reactivity graft copolymers together with homopolymers are formed and the ratio of grafted polymer depends on the rates of radical formation on the polymer relative to the radical formation by the direct addition of the initiator radical, $I^\bullet$ to the monomer:

$$\begin{gathered} I^\cdot + PH \xrightarrow{k_{ip}} IH + P^\cdot \xrightarrow[M]{k_p} P-M^\cdot \\ I^\cdot + M \xrightarrow{k_{im}} I-M^\cdot \end{gathered} \tag{4a-b}$$

As the further growth process characterized by the rate constant k_p is the same for grafted and homoradicals, the grafted fraction φ_g of the total polymerized monomer is as follows:

$$\varphi_g = \frac{k_{ip}[PH]}{k_{ip}[PH] + k_{im}[M]} \tag{5}$$

where [PH] stands for the concentration of active sites of the polymer. Generally, this can be taken as constant and thus the grafted fraction depends hyperbolically on the monomer concentration. For the total monomer consumption rate, however, the expression (1) is clearly valid.

In the second case the monomer (e.g. maleic anhydride) is practically unable to homopolymerize, but there is a rapid chain transfer to the polymer resulting in the following chain process (k_t and k_a are the rate constants of radical transfer and monomer addition, respectively):

$$\begin{aligned} P-M^{\cdot} + PH &\xrightarrow{k_t} P-MH + P^{\cdot} \\ P^{\cdot} + M &\xrightarrow{k_a} P-M^{\cdot} \end{aligned} \qquad \textbf{(6a-b)}$$

If the kinetic chains are long, the effects of initiation and termination are negligible and the monomer consumption rate is given by (7):

$$-\frac{d[M]}{dt} = [R^{\cdot}]\frac{k_a k_t [PH][M]}{k_a[M] + k_t[PH]} \qquad (7)$$

where $[R^{\cdot}] = [P^{\cdot}] + [M^{\cdot}]$ is the sum of the radical concentrations. Clearly, if the radical transfer to the polymer is rapid enough (k_t [PH] > > k_a[M]) the monomer consumption rate corresponds again to (1) with $k_p = k_a$. Thus, this practically important case can be treated like the previous one. Consequently, the following simplified treatment of the nonisothermal reaction is equally applicable for radical initiated grafting and modification, respectively.

To approximate the nonisothermal reaction conditions during the reactive processing, we assume again the hyperbolic time dependence of temperature as in [8]:

$$1/T = 1/T^{*} - Ct \qquad \textbf{(8)}$$

The T^{*} reference temperature corresponding to the maximum rate of initiator decomposition is given by the expression (9):

$$T^{*} = B/(\log A - \log B - \log C) \qquad \textbf{(9)}$$

where $B = E_d/R$ contains the energy of activation of initiator decomposition, A is the preexponential factor of this reaction and C is the rate of change of reciprocal temperature. On the time scale T^{*} corresponds to the t = 0 point.

The temperature/time dependence of the rate constans can be given as follows:

$$\begin{aligned} k_d &= k_d^{*}\exp(BCt) \\ k_p &= k_p^{*}\exp(B'Ct) \\ k_b &= k_b^{*}\exp(B''Ct) \end{aligned} \qquad \textbf{(10a-c)}$$

where k_d^{*} etc, are the values of rate constants at $T = T^{*}$ and the B values are the corresponding activation energies divided by R.

Now, the time (and temperature) dependent initiator concentration, according to our earlier results [8] is:

$$[I] = [I]^* \exp(1 - \exp[BCt]) \qquad (11)$$

and the rate constants (6a-c) make possible to obtain - using the steady state assumption for the radical concentration $[R^\bullet]$ - the following differential equation of monomer consumption:

$$-\frac{d[M]}{dt} = k_p^* \sqrt{\frac{2fk_d^*}{k_b^*}} \sqrt{[I]^*} \exp\left\{\frac{1 + (B + 2B' - B'')Ct - \exp[BCt]}{2}\right\} [M] \qquad (12)$$

Principially, one can solve the D.E. analytically, but this is not very profitable. It is better to integrate numerically the following form:

$$\log\frac{[M]}{[M]^*} = -K\sqrt{[I]_0} \int_0^t \exp\left\{\frac{1 + (B + 2B' - B'')Ct - \exp[BCt]}{2}\right\} dt \qquad (13)$$

The constant K is equal to $K = k_p^*(2fk_d^*/k_b^*/e)^{1/2}$. Here we used the result $[I]^* = [I]_0/e$ obtained earlier.

Discussion

It is easy to see that the integrand of Eq. (13) has the limiting values of zero for great positive and negative values of the time t (i.e. for very low and very high temperatures). This function F is shown on Fig. 1.

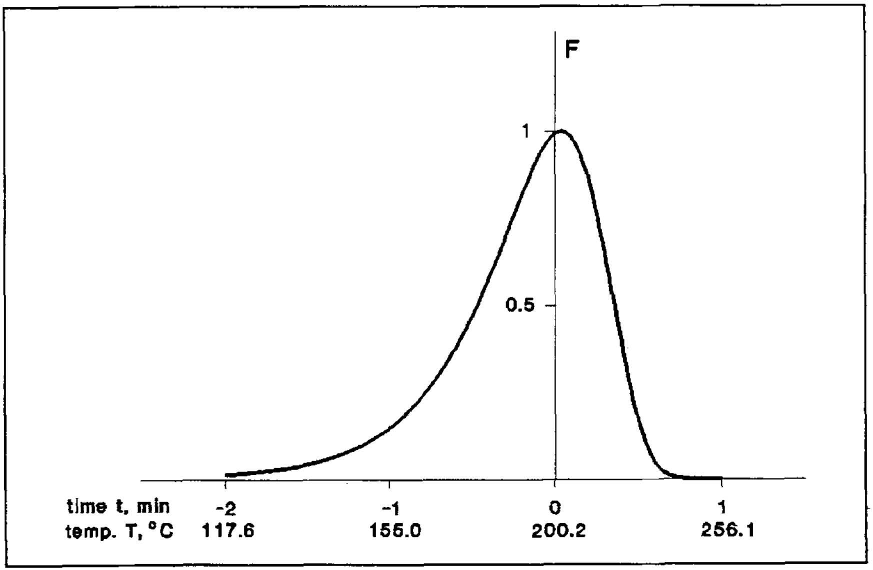

Fig. 1 *The integrand of Expression (13) (the function F) for the DCP/EMA system. Heating rate 50 K min^{-1}*

The parameters of the depicted function are the rate of temperature increase $C=2.2312\ 10^{-4}K^{-1}min^{-1}$, corresponding to 50 K min^{-1} and B = 17680 K from the temperature dependence of dicumyl peroxide decomposition. Unfortunately, for the high temperatures of reactive processing it is nearly impossible to find propagation and termination rate constants for the monomers used. For illustration, we used calculated values of the high reactivity monomer ethyl methacrylate. The Arrhenius parameters were those of Cardenas [10] and Davis et al. [11]. Table 1 contains the values of the initiator decomposition, monomer propagation and bimolecular termination at the reference temperatures T^* (maximum rate of initiator decomposition) for 35, 50 and 70 K min^{-1} temperature increase rate.

Table I Rate constants of the dicumyl peroxide - ethyl methacrylate system

Rate of temperature increase		T^* °C	k_d min^{-1}	$10^{-6}k_p$ L $mol^{-1}min^{-1}$	$10^{-8}k_b$ L $mol^{-1}min^{-1}$
rate K min^{-1}	10^4C $K^{-1}min^{-1}$				
35	1.5903	195.9	2.803	0.476	13.61
50	2.2312	200.2	3.948	0.500	13.88
70	3.0705	204.3	5.440	0.522	14.14
B = 17680, B' = 2461, B'' = 1022 K					

With the above rate constants were calculated the values of the constant K of the expression (13). For the sake of simplicity, 2f = 1 was assumed. The values of the integral in (13) were calculated numerically from t = 0 (where the value of the function F is equal to 1) in the negative direction (lower part) and from t = 0 to increasing t values (upper part above the reference temperature). These integrals, together with the product of the integral and the constant K are listed in Table II.

Table II Values of the integral and the constant K of Eq. (13)

Rate of temp. K min^{-1}	$\int_{-\infty}^{0} Fdt$	$\int_{-\infty}^{\infty} Fdt$	K $L^{½}mol^{-½}min^{-1}$	$K\int_{-\infty}^{\infty} Fdt$
35	0.80376	1.31235	13.102	17.194
50	0.57288	0.93539	16.174	15.129
70	0.41629	0.67961	19.638	13.346

Peroxide initiators are used in reactive processing typically in 0.1-1 % amounts. Knowing that the density of polyethyene melt at 190 °C is 0.761 g cm^{-3} [12], 1 % dicumyl peroxide initiator corresponds to 28.15 mmol L^{-1} concentration. Taking this and the appropriate value from the Table II for 50 K min^{-1}, Eq. (13) gives M/M_0 = exp (-2.5382)=

= 0.0790 i.e. approximately 8 % of the initial amount of monomer remains unreacted after the complete decomposition of the initiator. If the amount of initiator was 0.1 %, the final conversion has the value of 55 %.

Summary

Under conditions of reactive processing at low concentrations of initiator low final conversion of the reactive monomer can manifest itself, similarly to the "dead end" polymerization under isothermal conditions. In our calculations we used independent literature data for rates of dicumyl peroxide decomposition and ethyl methacrylate (taken as model compound) propagation and bimolecular termination, respectively. It is remarkable that the calculated monomer conversions assume very realistic values at initiator concentrations used in practice.

Acknowledgement

The financial support of the Hungarian Scientific Research Fund OTKA T 4454 is gratefully acknowleged.

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Accepted March 2, 1994 C