

Kinetics of the Nonstationary Photopolymerization of Diacrylates

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Received 24 August 1999; accepted 13 March 2000

ABSTRACT: The kinetics of non-stationary photopolymerization (post-polymerization) of some diacrylates at the wide range of initial conversions was investigated. All kinetic curves has two regions: quick and short, slow and long. Experimental results were compared with the kinetic model of the photoinitial three-dimensional photopolymerization. It was determined that kinetic model allows us to describe the process of the post-polymerization in the whole range of conversions. The rate constants of the linear break of the primary and secondary chains in the interphase layer were estimated. The increasing rate constants in the interphase are the similar for investigated diacrylates and do not depend on the glycol chain. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1892–1895, 2002

Key words: post-polymerization; diacrylates; nonstationary photopolymerization; active and frozen radicals; microheterogeneous model

INTRODUCTION

The post-polymerization or nonstationary dark process of the photopolymerization is carried out after the completion of ultraviolet (UV) irradiation and gives important information about the mechanism of the process, particularly, the elementary break reactions.^{1,2} The kinetic curve of the post-polymerization process has two regions: quick and short and slow and long. These two regions indicate that two active radicals with the different life times carry out the process of post-polymerization.

Two basic concepts are used for the interpretation of the post-polymerization process: (1) diffusional controlled reactions (DCR) and (2) the microheterogeneous model. With regard to DCR, the basis for the analysis of experimental data is a famous kinetic equation of the initial stage of the stationary process. The parameters of this equation are the function of the mobility of macroradicals.^{3–7}

The second concept, the microheterogeneous model, is based in the following assumptions: (a) The rate of the three-dimensional polymerization is the sum of the rates of the homophase and heterophase process, where the homophase process operates in the volume of liquid oligomer and heterophase process operates in the interphase layer at the boundary of the solid polymer–liquid oligomer in the regime of the gel effect. The cut-off

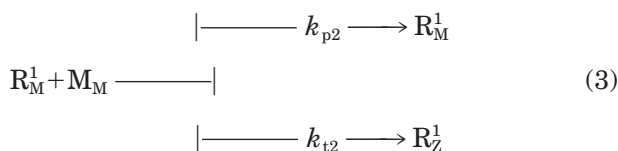
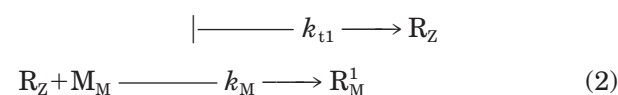
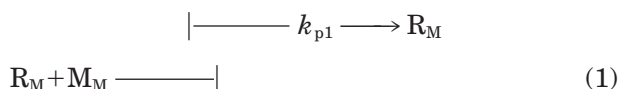
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Journal of Applied Polymer Science, Vol. 83, 1892–1895 (2002)
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DOI 10.1002/app.2317

rate is controlled by its growth rate; (b) The initiator is uniformly distributed between the phases and the interphase layer; and (c) Clusters of the solid polymer in the liquid oligomer phase and clusters of the liquid oligomer in the solid polymeric matrix have the fractal structure.^{8,9}

When analyzing post-polymerization, it is necessary to insure that the radicals (R_V) in the liquid monomeric phase have a small lifetime and can not deposit, thereby making an appreciable contribution to the post-polymerization process, the rate of which is completely instituted by the rate of homophase process in the interphase layer.

In view of the laws of the post-polymerization just presented, the kinetic scheme of the process flow diagram in the interphase layer is proposed as follows⁹:



According to the given schema (eqs. 1–3), the gel effect in the interphase layer is treated as a check for the rate of breaking the chain of the rate of its propagation, which acts as the progressing of a circuit [fundamental (eq. 1) and secondary (eq. 3)], and its breakway acts as two various outcomes of interplay of active radicals (R_m and R_{m1}) with the functional group of the monomer conducting, accordingly, to again obtain active radicals or freezing (nonlinear breaking of chain); that is, the formation of nonactive radicals R_Z and R_{Z1} .

The elementary reaction (eq. 2) depicts the reacting of the original secondary of active radicals R_{m1} from fundamentally frozen R_Z . This reaction (eq. 2) should be regarded as the act of “germination” of the frozen radical R_Z in an active zone of the interphase layer.

On the basis of eqs. 1–3, the equation for post-polymerization rate is:

$$\begin{aligned} dP/dt = W_{M0}[(1 - \alpha)\exp(-\beta t) + \alpha \exp(-\gamma t)] \\ \times [P(1 - P)/P_0(1 - P_0)] \end{aligned} \quad (4)$$

Therefore,

$$\begin{aligned} W_{M0} = (dP/dt)_{t=0} = k_2 P_0(1 - P_0)\gamma_v J_0(1 \\ - \exp(-y_0))/[1(1 + \exp(-y_0)(\exp(\tau_0) - 1))] \end{aligned} \quad (5)$$

$$\begin{aligned} k_2 = h(F_S/F_V)(f_M/f_V)(k_{p1}/k_{t1} \\ + k_M k_{p2}/k_{p1} k_{t2})/[M]_0 H_0 \end{aligned} \quad (6)$$

$$\alpha = (k_M k_{p2}/k_{p1} k_{t2})/(k_{p1}/k_{t1} + k_M k_{p2}/k_{p1} k_{t2}) \quad (7)$$

$$\beta = k_{t1}[M_M] \quad \gamma = k_{t2}[M_M] \quad (8)$$

$$y_0 = \varepsilon c_0 I_0 \quad \tau_0 = \gamma_v \varepsilon J_0 t_0^1 \quad (9)$$

where c_0 is the concentration of photoinitiator; ε is the molar coefficient of extinction; I_0 is the intensity of UV irradiation falling on the photopolymerization composition; l is the thickness of the polymeric layer; γ is the quantum yield; h is the thickness of the interphase layer; F_S/F_V is the proportion between the fractal characteristics of surface and and volume clusters of the solid polymer in the liquid monomeric phase and the liquid monomer in the solid polymeric matrix; f_M/f_V is the proportion between the initiation performances in the interphase layer and the bulk of the liquid monomer; t is the current time of post-polymerization from the beginning of the dark period; and t_0^1 is the duration of stationary light process prior to the beginning of dark period.

As evident from eqs. 5–7, k_2 is an effective constant of the rate of the stationary process of polymerization in the interphase layer, and α constitutes the relative contribution to it secondary chain. Parameters β and γ also are the kinetic constants of process determining the characteristic life time of the fundamental ($\tau_1 = \beta^{-1}$) and secondary ($\tau_2 = \gamma^{-1}$) radicals.

EXPERIMENTAL

The kinetics of post-polymerization of the following four diacrylates were investigated: 1,4-butanediol diacrylate (M—O—CH₂—CH₂—CH₂—CH₂—O—M), diethyleneglycol diacrylate (M—O—CH₂—CH₂—O—CH₂—CH₂—O—M), 1,6-hexanediol diacrylate (M—O—CH₂—CH₂—CH₂—CH₂—CH₂—CH₂—O—M), and dipropyleneglicol diacrylate (M—O—CH₂—CH₂—CH₂—O—CH₂—

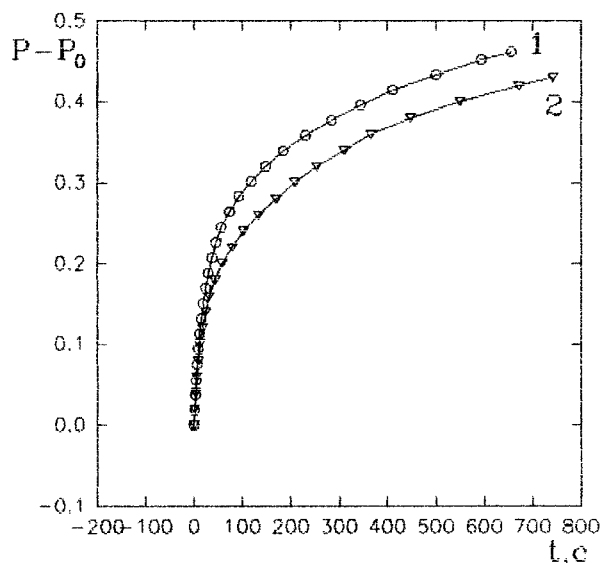


Figure 1 Experimental kinetic curves [$P - P_0 = f(t)$] for diethyleneglycol diacrylate (1: $P_0 = 0.2$; 2: $P_0 = 0.26$).

$\text{CH}_2\text{—CH}_2\text{—O—M}$), where M: $\text{CH}_2 = \text{CH—C(O)—}$. 2,2-Dimethoxy-2-phenylacetophenone (ketal) was used as the photoinitiator.

The experiments were carried out with an interferometric laser apparatus, with metering of the current H and the extreme achievable H_0 contraction of layer of photopolymerizing composition. Under their relation instituted relative integrated depth of polymerization $P = H/H_0$. Detailed methodology of the stationary kinetic measurements is described in ref. 21. In this study, at a determined stage of the light process, UV radiation was discontinued fixing the contraction of the layer of polymerization composition in a dark mode. Then radiation was continued until the end of polymerization, instituting a limiting contraction of layer, on which one instituted the thickness of its layer (l). The inflecting duration of the light period varied the original depth of polymerization P_0 for the dark period.

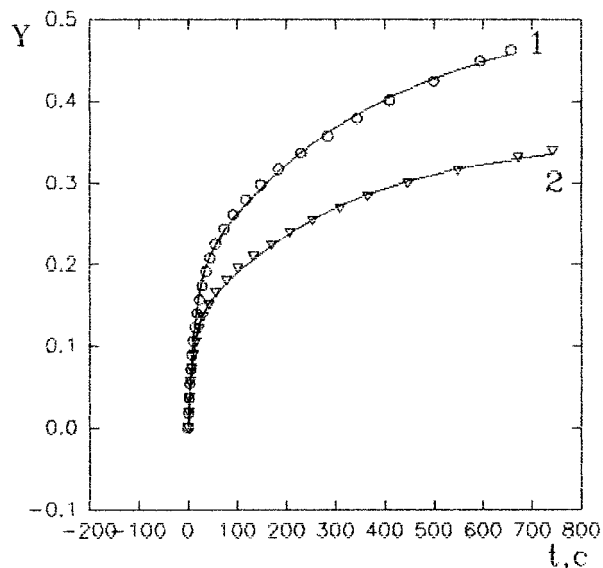


Figure 2 Interpretation of the experimental data in the form of kinetic curves ($Y = P_0(1 - P_0)\ln[P(1 - P_0)/P_0(1 - P)]$) from time t for 1,4-butanediol diacrylate (1: $P_0 = 0.2$; 2: $P_0 = 0.26$).

RESULTS AND DISCUSSION

The representative kinetic curves of post-polymerization in the form of dependence $P - P_0$ of time t are shown in a Figure 1. Two leases are clearly exhibited: quick and short with time of relaxation of ~ 10 s, and slow and long with time of relaxation of ~ 250 s.

For conformation of the experimental data, eq. 4 was converted to the following integrated form:

$$\ln[P(1 - P_0)/P_0(1 - P)] = W_{M0}[(1 - \alpha)(1 - e^{-\beta t})/\beta + \alpha(1 - e^{-\gamma t})/\gamma] \quad (10)$$

The value W_{M0} can be determined from the tangent of the angle of the kinetic curve at $t = 0$, or with the stationary eq. 5 for the end of the light period. However, both the maiden path and the second approach give significant inaccuracy in an

Table I Experimental Parameters α , β , and γ for Investigated Diacrylates

Monomer	Molecular Mass	$\alpha \pm \delta\alpha, 10^2$	$\beta \pm \delta\beta, 10 \text{ s}^{-1}$	$\gamma \pm \delta\gamma, 10^3 \text{ s}^{-1}$
1,4-Butanediol diacrylate	198	4.5 ± 0.6	10.2 ± 1.5	7.2 ± 0.8
Diethyleneglycol diacrylate	214	3.4 ± 1.0	7.2 ± 0.9	3.2 ± 0.8
1,6-Hexanediol diacrylate	226	1.7 ± 0.2	2.6 ± 0.6	1.9 ± 0.7
Dipropyleneglycol diacrylate	242	1.9 ± 0.8	4.5 ± 2.0	2.1 ± 0.7

Table II Rate Constants of Linear Breakway of Fundamental k_{t1} and Secondary k_{t2} Chain of Diacrylates

Monomer	$[M_0]$ mol/m ³	k_{t1} , 10 ⁴ m ³ /mol s	k_{t2} , 10 ⁷ m ³ /mol s
1,4-Butanediol diacrylate	4707	2.2	15.2
Diethyleneglicol diacrylate	4336	1.7	7.4
1,6-Hexanediol diacrylate	4146	0.6	4.6
Dipropyleneglicol diacrylate	3975	1.1	5.2

estimation of W_{M0} values. Therefore, eq. 10, a four-parameter equation, and the numerical values W_{M0} , α , β , and γ instituted under the experimental kinetic curves of post-polymerization, were determined by a method of optimization with the program PLOT-41.

Studies have shown that the method of optimization used here works well in a wide range of values of W_{M0} (that is, $\beta, \gamma > 0$ and $0 < \alpha < 1$) and adequately represents the physical sense of the polymerization. Good conformity was found between experimental dependence on time ($Y = P_0(1 - P_0)\ln[P(1 - P_0)/P_0(1 - P)]$) and the values calculated with eq. 10, as shown in Figure 2. In all cases (i.e., for each kinetic curve of polymerization), the connection between experimental and calculated dependence has a coefficient of correlation of ≥ 0.99 .

These results indicate that eq. 10 correctly describes the form of the kinetic curve of post-polymerization, with a small experimental error that is visible in the kinetic curves of Figures 1 and 2. At the same time, parameters α , β , and γ do not depend on the initial conversion P_0 of the dark period, and are presented in Table I. The relaxation time of the fundamental radicals ($\tau_1 = \beta^{-1}$) for the investigated diacrylates are similar and ~ 5 s (for dimethacrylates, 10 s). Relaxation times of the secondary radicals of diacrylates are ~ 200 – 400 s (for dimethacrylates, 100–200 s) and depend on the molecular mass of the monomer.

The rate constants of linear breakway of fundamental (k_{t1}) and secondary (k_{t2}) chain in the interphase layer were obtained with the parameters β and γ and the assumption that $[M_M] = [M_0]$ because the monomer concentration in the interphase layer $[M_M]$ is steady and unknown. Param-

eters k_{t1} and k_{t2} for the investigated diacrylates are presented in Table II.

CONCLUSIONS

The kinetics of nonstationary photopolymerization (post-polymerization) of some diacrylates in a wide range of initial conversions was investigated. Experimental data were compared with the kinetic model of the three-dimensional photopolymerization. The kinetic model describes the post-polymerization in the whole range of conversions. The rate constants of the linear break of primary and secondary chains in the interphase layer were estimated. The increasing rate constants in the interphase are similar for investigated diacrylates and do not depend on the glycol chain length.

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