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POLIMERY

MIESIĘCZNIK POŚWIĘCONY CHEMII, TECHNOLOGII I PRZETWÓRSTWU POLIMERÓW

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Kinetics modeling of linear and crosslinking photopolymerizations

Part II. OVERALL RATE OF POLYMERIZATION (INCLUDING INITIATION, PROPAGATION AND TERMINATION STEPS)***)

Summary — A review with 36 references covering a comparison of modeling of linear and crosslinking photopolymerizations. The overall rates of polymerization are discussed, including initiation, propagation and termination steps. The kinetics of free-radical polymerization is described and ways are presented to evaluate individual rate constants.

Key words: photopolymerization, photoinitiators, kinetics of initiation, propagation and termination steps.

When a free radical polymerization is first started the number of propagating radicals in the system increases from zero. In the early stage of polymerization the frequency of termination reactions will also increase from zero, because the termination rates (k_{tc} and k_{td}), are proportional to the square of the total concentrations of all radicals in the system. The rate at which radicals are generated will be balanced by the rate at which radicals recombine, and the concentration of radicals in the system will reach a steady value. This steady state is reached very early in the linear polymerization reaction. The assumption that the rate of initiation (R_i) equals the rate of termination (R_t) is known as the steady-state assumption [2, 3]:

$$R_i = 2fk_d[\mathrm{I}] \tag{1}$$

$$R_t = 2k_t[P^\bullet]^2 \tag{2}$$

$$R_i = R_t \text{ under steady-state conditions} \tag{3}$$

where (*cf.* Part I, eqns. 13 and 70): *f is the photoinitiator efficiency, k_d and k_t are the rate constants of photoinitiator decomposition and termination, respectively, [I] and $[P^\bullet]$ are the concentrations of photoinitiator and propagating radicals, respectively.*

Under the steady-state condition

$$\frac{\mathrm{d}[P^\bullet]}{\mathrm{d}t} = 0 \tag{4}$$

Substitution of eqns. (1) and (2) into eqn. (3) gives:

$$2fk_d[\mathrm{I}] = 2k_t[P^\bullet]^2 \tag{5}$$

Hence, the total concentration of propagating radicals (experimentally accessible quantities) is

$$[P^\bullet] = \left(\frac{fk_d[\mathrm{I}]}{k_t}\right)^{1/2} \tag{6}$$

The rate of polymerization is defined as the rate of disappearance of the monomer, which is d[M]/dt (the concentration of monomer [M] decreases with time, so d[M]/dt is negative). The monomer is consumed by two reactions, initiation and propagation, therefore

$$\frac{-\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = R_i + R_{pr} \tag{7}$$

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***) Part I see [1].

The initiation process accounts for a negligible amount of monomer if a high-molecular-weight crosslinked polymer is produced. Then the rate of polymerization (R_p) can be taken as equal to the rate of propagation (R_{pr})

$$R_p = R_{pr} \tag{8}$$

and the polymerization rate constant (k_p) is equal to the propagation rate constant (k_{pr})

$$k_p = k_{pr} \tag{9}$$

and R_p is given by

$$R_p = \frac{-\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = k_p[\mathrm{M}][P^\bullet] \tag{10}$$

Substitution of eqn. (6) into eqn. (10) gives

$$R_p = \frac{-\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = \frac{k_p}{k_t^{1/2}}[\mathrm{M}](fk_d[\mathrm{I}])^{1/2} \tag{11}$$

The rate of polymerization (R_p) is given in mol · liter^{-1} ·s^{-1}. The photoinitiator concentration [I] given by equation (12) (*cf.* Part I, eqn. 7)

$$[\mathrm{I}] = [\mathrm{I}]_0 \exp(-k_d t) \tag{12}$$

can be inserted into eqn. (11) to give

$$\frac{-\mathrm{d}[\mathrm{M}]}{[\mathrm{M}]} = k_p\left(f\frac{k_d}{k_t}[\mathrm{I}]_0\right)^{1/2} \exp(-k_d t)\mathrm{d}t \tag{13}$$

Integration of eqn. (13) between [M] = $[\mathrm{M}]_0$ at $t = 0$ and [M] at t gives

$$-\ln\frac{[\mathrm{M}]}{[\mathrm{M}]_0} = k_p\left(f\frac{k_d}{k_t}[\mathrm{I}]_0\right)^{1/2}\left(1-\exp(k_d t)\right) \tag{14}$$

The above equation gives the amount of polymer in terms of the mols of monomer converted which was produced in time t.

Dead-end linear polymerization is a useful technique to evaluate k_d. Equation (14) can be written [2] as

$$-\ln\frac{[\mathrm{M}]}{[\mathrm{M}]_0} = \frac{2V_0}{k_d}\cdot\left(1-\exp(k_d t)\right) \tag{15}$$

where parameter V_0 is defined as

$$V_0 = k_p\left(f\frac{k_d}{k_t}\right)^{1/2}[\mathrm{I}]_0^{1/2} \tag{16}$$

The useful feature of eqn. (15) is that k_d is separated from the other rate constants because it is the only kinetic parameter in the experimental function. If the starting initiator concentration $[\mathrm{I}]_0$ is insufficient to make all the monomer polymerize, the reaction will reach a dead end after a long time (t → ∞). The corresponding limiting value of [M] can be used to assess k_d, provided this concentration can be determined accurately and the polymerization does not exhibit autoacceleration effects at high conversions [4]. It is convenient to expand the exponential function in eqn. (15) into a power series and to simplify the resulting expression to

$$\frac{-\ln\frac{[\mathrm{M}]}{[\mathrm{M}]_0}}{t} = V_0\left(1-\frac{1}{2!}\left(\frac{k_d}{2}\right)t+\frac{1}{3!}\left(\frac{k_d}{2}\right)^2 t^2+\ldots\right) \tag{17}$$

If the t term is much larger than the t^2, eqn. (17) can be reduced to

$$\frac{-\ln\frac{[\mathrm{M}]}{[\mathrm{M}]_0}}{t} = V_0 - V_0\left(\frac{k_d}{4}\right)t \tag{18}$$

A plot of the left-hand side of eqn. (18) *vs.* time produces a straight line with intercept (at $t = 0$) equal to V_0 and slope useful to calculate k_d [5].

For linear photopolymerization, R_p is given [3] by the equation

$$R_p = \frac{k_p}{k_t^{1/2}}\cdot(\Phi_d I_a)^{1/2}\cdot[\mathrm{M}] \tag{19}$$

where

$$I_a = I_0\,\varepsilon[\mathrm{I}]_0 l \tag{20}$$

where: *I_a is the intensity of light absorbed, I_0 is the intensity of incident light, Φ_d is the quantum yield of the photoinitiator decomposition into free radicals, ε is the molar extinction coefficient of the photoinitiator, l is the path length of a sample* (*cf.* Part I, eqn. 16).

According to eqns. (19) and (20), R_p should vary initially with the square-root of initiator concentration ([I]). Assuming the Beer-Lambert law to hold true, R_p becomes

$$R_p = \frac{k_p}{k_t^{1/2}}\cdot\left(\Phi_d \mathrm{I}_0 \varepsilon[\mathrm{I}]_0 l\right)^{1/2}[M] \tag{21}$$

For the photoinitiator endowed with a high molecular absorptivity (ε), R_p will not exhibit the half-order dependence on initial initiator concentration [6]. The values of ε vary on passing from one initiator to another and so varies the concentration at which deviations from the square-root dependence are observed.

It is difficult to measure k_t directly [7—10]. However, photopolymerizations offer the unique advantage of controlling the propagating radical concentration [$P^\bullet$] by exposing or shielding the polymerizing sample from the light source [11—13]. Assuming termination to be exclusively a bimolecular process and k_t to be approximately constant over a small time interval, the termination rate constant (k_t) can be calculated from eqns. (22) and (23) [13] as follows

$$\frac{\frac{2(t_t - t_0)}{k_p}}{k_t^{1/2}} = \frac{1}{k_t^{1/2}}\left(\frac{[\mathrm{M}]_t}{(R_p)_t} - \frac{[\mathrm{M}]_0}{(R_p)_0}\right) \tag{22}$$

$$\frac{k_p}{k_t^{1/2}} = \frac{R_p}{[\mathrm{M}]I_a^{1/2}\Phi_d} \tag{23}$$

where *$[M]_0$ and $[M]_t$ are the monomer concentrations and $(R_p)_0$ and $(R_p)_t$ are the rates of polymerization at the beginning of polymerization (t_0) and after a time of irradiation (t_t), respectively.*

The rate of polymerization (R_p) can be measured directly by the photo-DSC (*cf.* Part III). The ratio k_t/k_p can be calculated from the dependence of k_t and k_p on the monomer conversion (*i.e.*, monomer conversion = degree of double bonds conversion, only for monofunctional monomers) (p) [14—17]. The monomer conversion can be measured directly by the photo-DSC (*cf.* Part III).

In the photocrosslinking polymerization, the rate of polymerization (R_p) is dependent on the monomer diffusivity in the polymerized matrix and on the distance from the illuminated surface of the polymerized film (x) (depth of curing) (Fig. 1.) [18, 19]. A sample at the surface is exposed to the highest intensity of light and double bond conversions are greatest. Depending on the thickness of the sample, the differences between conversions at the surface and in the bulk of the sample can be appreciably different. The variations in the conversion with depth are dependent on the molar absorptivity and concentration of the photoinitiator (Fig. 2).

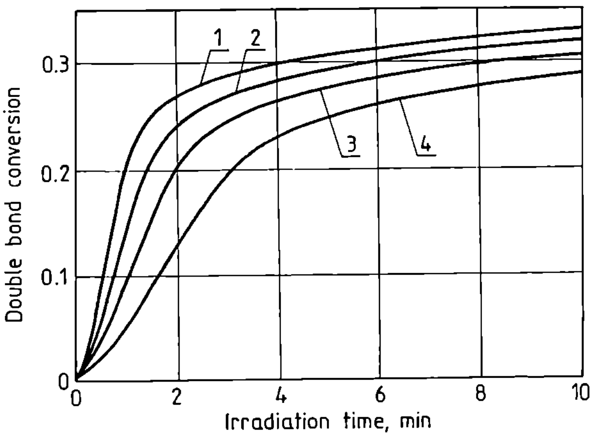

Fig. 1. Simulated profile of conversion of double bonds in a multifunctional monomer vs. polymerization time at different depths in the polymer: 1 — surface, 2 — 1.4 mm, 3 — 2.8 mm, and 4 — 4.6 mm [16]

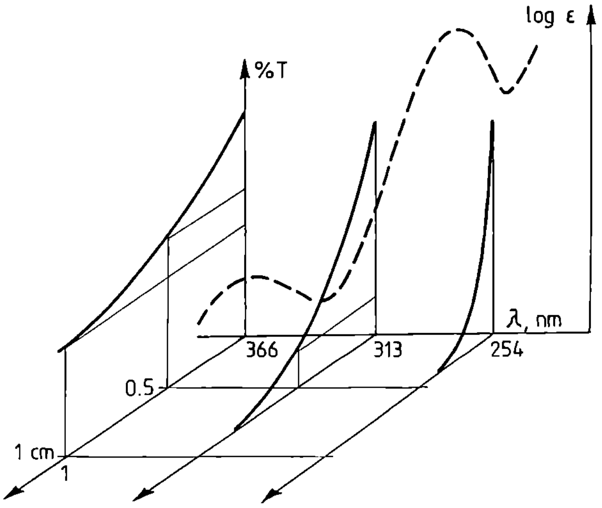

Fig. 2. Absorption spectrum of a photoinitiator, log ε = f(λ); fraction of light transmitted (% T) at different wavelengths as a function of the optical path length (x); in this example, one-half of the incident light is absorbed within 1 cm, 1 mm and 10 μm at 366, 313 and 254 nm, respectively [18]

The rate of polymerization is expressed as

$$R_p = \frac{-\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = k_{DM}\left(\frac{\partial^2[\mathrm{M}]}{\partial x^2}\right) - k_p[\mathrm{M}][\mathrm{P}^\bullet] \tag{24}$$

where k_{DM} *(cm^2 · s^{-1}) is the monomer diffusion rate constant.*

In the initiation by photolysis of an initiator (I), the rate of initiation (R_i) depends directly on the intensity of the incident light (I_0), as well as on [I], and the rate of linear polymerization is ideally proportional to $(I_0[\mathrm{I}])^{1/2}$. Deviations from the predicted dependence of R_p on [M], $[\mathrm{I}]^{1/2}$, and x are common in crosslinking photopolymerization. The initiation rate and the initiation efficiency f may depend on [M] if primary radicals escape from their monomer cage by reaction with the nearest monomer molecules. At high initiation rates, some of the primary radicals formed by photodecomposition of the initiator can terminate kinetic chains. This primary termination causes that the observed R_p depends on [M] raised to a power greater than unity and reduces the dependence of R_p on [I] to less than the power 0.5. The intensity of incident light (I_0) dependence (Fig. 3) and depth (z) dependence (Fig. 4) of the photocuring level (gel content) have been modeled with computer programes [19, 21, 22].

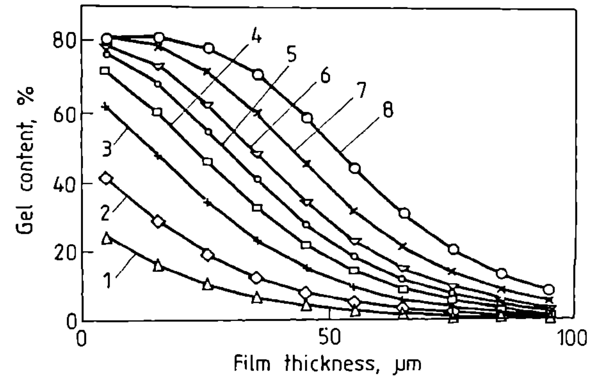

Fig. 3. Calculated plots of the photocuring profiles at different UV-irradiation energies [19] (mJ/cm^2): 1 — 5, 2 — 10, 3 — 20, 4 — 30, 5 — 40, 6 — 50, 7 — 50, 8 — 100

Then n-th order polymerization model assumes the rate of polymerization (R_p) to obey the following equation

$$R_p = k_p(1-p)^n \tag{25}$$

where k_p *is the polymerization rate constant, p is the fractional conversion of double bonds after time (t)* [23—25].

The autocatalytic model considers the effect of autocatalysis by the reactant as an independent reaction of order m [26, 27]:

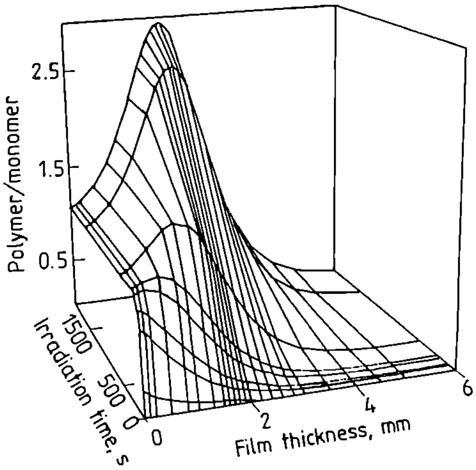

Fig. 4. Calculated plots of the photocuring profiles at different distances from the irradiated surface [17]

$$R_p = k_p p^m (1-p)^n \tag{26}$$

where *n is the reaction order exponent and m is the autocatalytic exponent.*

However, the autocatalytic model does not explicitly include the effects of initiator and inhibitor concentrations on the rate of polymerization.

The average life time of the kinetic chain (τ) is given by the ratio of the steady-state radical concentration to the steady-state rate of radical disappearance [2]:

$$\tau = \frac{[P^\bullet]}{2(k_{tc} + k_{td})[P^\bullet]^2} = \frac{1}{2(k_{tc} + k_{td})[P^\bullet]} \tag{27}$$

where *k_{tc} and k_{td} are the rate constants of termination by combination and disproportionation.*

Substitution for [P$^\bullet$] from eqn. (10)

$$[P^\bullet] = \frac{R_p}{k_p[\mathrm{M}]} \tag{28}$$

gives

$$\tau = \frac{k_p[\mathrm{M}]}{2(k_{tc} + k_{td})R_p} \tag{29}$$

where:

$$k_t = k_{tc} + k_{td} \tag{30}$$

is obtained as the average life time of the kinetic chain (τ):

$$\tau = \tfrac{1}{2}\,(fk_d[\mathrm{I}])^{1/2} k_t^{1/2} \tag{31}$$

Generally crosslinking polymerization has three regimes in the reaction kinetics mechanism (Fig. 5) [18, 28—33]:

— inhibition zone: radicals generated by photoinitiator decomposition are consumed by oxygen and/or inhibitor present in the monomer;

— propagation zone: after inhibitor has been consumed, the radical concentration increases with time to accelerate curing;

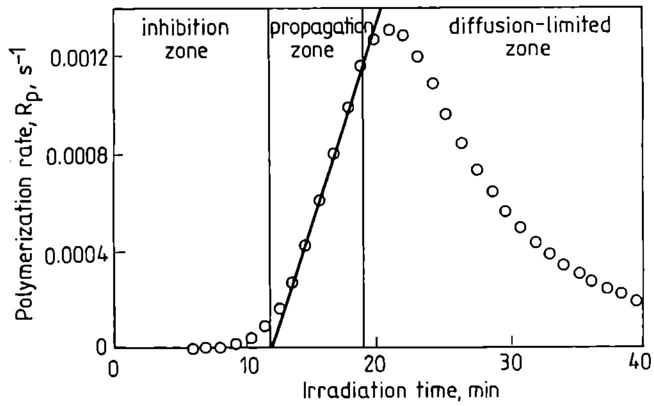

Fig. 5. Rate of polymerization vs. time, defining the inhibition zone, propagation zone and the diffusion-limited zone [30]

— diffusion-limited zone: polymerization rate slows on account of diffusion limitations of radicals and the monomer.

The influence of temperature of individual rate constant k_d, k_p and k_t can be expressed by the Arrhenius equation [35]

$$k = A \exp\left(\frac{-E_a}{RT}\right) \tag{32}$$

where *A is the preexponential factor, E_a is the Arrhenius activation energy, R is the gas constant (1.987 cal · deg^{-1} · mol^{-1}), and T is the absolute temperature.*

Taking the natural logarithms on both sides gives:

$$\ln k = \ln A - \frac{E_a}{RT} \tag{33}$$

and the differential form is:

$$\frac{d \ln k}{d\left(\frac{1}{T}\right)} = \frac{-E_a}{R} \tag{34}$$

A plot of ln *k* *vs.* 1/*T* yields a straight line; *A* and E_a can be determined from the intercept and the slope ($-E_a/R$), respectively. Because of experimental uncertainities, a plot covering a larger temperature range will produce a grater precision in the value of E_a [36]. The intercept of the plot corresponds to a value of 1/*T* of 0, and is equal to ln *A*. However, a long extrapolation of a plot of experimental data may produce an inaccurate value of *A* [37]. An alternative approach is to calculate ln *A* from the E_a value and the data for the reaction rate constant at some temperature in the middle of the range of temperature-rate data. Each 10°C increase in reaction temperature will result in a two- to three-fold increase in the rate of polymerization. Chain transfer to polymer increases as the reaction temperature is increased.

The values of *A* and E_a can provide a full description of the thermodynamic data polymerization: enthalpy of activation (ΔG°) and entropy of activation (ΔS°) [38]:

$$\Delta S^{\circ} = R\left(\ln A - \ln\left(\frac{kT}{h}\right) - 1\right) \qquad (36)$$

where: *k is the Boltzmann constant, h is Planck's constant.*

The three separate k_d, k_p and k_t Arrhenius expressions can be combined in a straightforward manner to obtain the temperature dependence of the $k_p(k_d/k_t)^{1/2}$ ratio in the expression for R_p in eqn. (11) [2]

$$\ln\left(k_p\left(\frac{k_d}{k_t}\right)^{1/2}\right) = \ln\left(A_p\left(\frac{A_d}{A_t}\right)^{1/2}\right) - \left(\frac{E_p + \frac{1}{2}E_d - \frac{1}{2}E_t}{RT}\right) \qquad (37)$$

The overall activation energy for the rate of polymerization (E_{R_p}) *is*

$$E_{R_p} = E_p + \tfrac{1}{2}E_d - \tfrac{1}{2}E_t \qquad (38)$$

and can be measured by plotting R_p against $1/T$. The units of the activation energies are:

E_{R_p} = kJ · mol^{-1} of polymerizing monomer
E_t = kJ · mol^{-1} of propagating radicals
E_d = kJ · mol^{-1} of initiator

For photochemically initiated polymerization, E_d is practically zero.

Note: *This article has been written by Dr. Julita Jakubiak Head of the Joint Project "Mechanisms, kinetics and applications of photopolymerization initiated by visible light photoinitiators", supervised by Prof. J. F. Rabek and Prof. J. P. Fouassier. Dr. J. Jakubiak spent one year (1998/1999) as post-doc researcher with the Polymer Research Group, Department of Dental Biomaterial Science, Karolinska Institute, The Royal Academy of Medicine, Stockholm, Sweden (directed by Prof. J. F. Rabek) and one year (1999/2000) as post-doc researcher at the Laboratoire de Photochimie Generale, CNRS, University of Mulhouse, France (directed by Prof. J. P. Fouassier).*

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