

Dependence of Initial Rate on Initial Initiator Concentration in Photoinitiated Polymerizations

The rate of radical production in a stirred photoinitiated polymerization is often approximated by^{1,2}

$$R_i = I_0 \phi \epsilon [S] l \quad (1)$$

where I_0 = intensity of incident light, ϕ = quantum yield for production of radicals, ϵ = molar extinction coefficient of initiator at the wavelength employed, $[S]$ = initiator concentration, and l = path length. Assuming the usual radical termination processes and the steady state, the initial rate of polymerization is then given by

$$R_{p0} = \frac{k_p}{k_t^{1/2}} [(I_0 \phi \epsilon [S]_0 l)^{1/2} [M]_0] \quad (2)$$

where k_p = the rate constant for propagation reaction, k_t = the rate constant for termination reaction, $[M]$ = monomer concentration and for concentrations subscript 0 indicates initial values. According to eq. (2), the initial rate of polymerization should vary linearly with the square-root of initial initiator concentration, keeping everything else constant. However, the limitations of eq. (1) as an approximation, especially at high initiator concentrations, have not always been clearly stated. Deviations from the postulated square-root dependence have sometimes been deemed anomalous.³⁻⁵ The derivation presented below will show that these deviations are not anomalous and can, at least partially, be explained. It will also point out the basic difference between thermal and photoinitiation.

The rate of photochemical initiation is given by

$$R_i = \phi I_a \quad (3)$$

where I_a is the moles (einsteins) of light absorbed. For most initiators, the light absorption is not small and I_a will vary within the reaction vessel even though the concentration of initiator is kept uniform by efficient stirring. This is quite different from thermal initiation, where the rate of radical production is uniform throughout the reaction vessel. Assuming the validity of Beer's law

$$R_i = \phi I_0 (1 - e^{-\epsilon [S] l}) \quad (4)$$

where l is the path length in the reaction system. The initial rate of polymerization is then given by

$$R_{p0} = \frac{k_p}{k_t^{1/2}} [\phi I_0 (1 - e^{-\epsilon [S]_0 l})]^{1/2} [M]_0 \quad (5)$$

According to eq. (5), as the initiator concentration is increased, the initial rate of polymerization will first increase and then asymptotically approach a constant value. In fact, after a certain threshold initiator concentration is exceeded, the rate of polymerization will be essentially independent of initiator concentration. This threshold initiator concentration will depend on the values of ϵ and l . For low values of the exponent, eq. (5) reduces to eq. (1). Thus for low initiator concentrations we will get the square-root dependence of initial rate on the initial initiator concentration. In the literature, investigators have reported deviations from the half-order dependence at high initiator concentrations. Instead of considering them to be expected behavior, they are considered anomalous and unnecessary explanations have been offered. In all cases levelling of the initial rate at higher initiator concentrations is observed which is quite consistent with eq. (5) given above. Table I summarizes the λ_{\max} , wavelength of maximum absorbance and ϵ for various commonly used photoinitiators. The values of ϵ vary quite a bit from one initiator to another. Hence the concentration at which the deviation from the simple square-root dependence is observed will vary from one initiator to another. Table I also lists the values of concentrations at which the real rate will differ from that calculated according to eq. (2) by 10% for various photoinitiators.

It is clear that, for photoinitiators with high molar absorptivity, the initial rate of polymerization will not exhibit half order dependence on initial initiator concentration. The exact relationship involving the exponential function should be used for interpreting the rate data.

TABLE I
Light Absorption Characteristics of Various Photoinitiators

Initiator	λ_{\max} (nm)	ϵ ($M^{-1}cm^{-1}$)	Concn (mM) ^a
Azobisisobutyronitrile	360	11.9	18.03
2,2'-Azobis(4-cyanovaleric acid)	345	20.2	10.62
Benzoin methyl ether	341	215	0.998
Benzoin isopropyl ether	325	280	0.766
2,2'-Diethoxyacetophenone	335	72	2.98

^a Path length is assumed to be 1 cm.

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