Benzoin- and Benzoin Methyl Ether-Sensitized Photopolymerization of Styrene and Methyl Methacrylate: Quantum Yields and Mixing Effects

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Styrene and methyl methacrylate have been polymerized in a batch photoreactor using two sensitizers—benzoin ($C_6H_5COCHOHC_6H_5$) and benzoin methyl ether ($C_6H_5COCHOCH_3C_6H_5$)—and light with a peak intensity at 366 nm. Primary quantum yields have been calculated for each monomer-sensitizer combination. Effects of mixing on the rate of polymerization and product molecular weight distribution have been determined and correlated with a two-region reactor model.

SCOPE

Among impediments to the commercial development of photochemical processes have been a scarcity of reliable kinetic data, and the difficulty of accounting in reactor design for imperfect mixing and nonuniform absorption of the reaction-initiating light. The design of photopolymerization reactors is further complicated by the interactive effects of spatial nonuniformities and mixing on both the polymerization rate and the product molecular weight distribution. Theoretical models have been proposed to describe these effects, but few experimental results exist which might either confirm or invalidate the models.

The present study had as its objectives the determination of light absorbances and primary quantum yields for several sensitized photopolymerization reactions, and the experimental confirmation of theoretically predicted mixing effects in photoreactors. Styrene and methyl methacrylate were polymerized in a stirred batch photoreactor by using two sensitizers: benzoin ($C_6H_5COCHOHC_6H_5$) and benzoin methyl ether ($C_6H_5COCHOCH_3C_6H_5$). Light from a high pressure short-arc mercury lamp was filtered to pass only the wavelength band with its principal line at 366 nm. Rates were measured dilatometrically, and product molecular weights were determined by gel permeation chromatography. Quantum yields were calculated from measured polymerization rates at full illumination and perfect mixing, and confirmatory estimates of the quantum yields were obtained from the average molecular weights of the polymer products. Rates and product molecular weight distributions were then measured as functions of the fractional illumination of the reactor and the rotational speed of the stirrer, and the observed results were compared with theoretical predictions.

CONCLUSIONS AND SIGNIFICANCE

Primary quantum yields for light with a peak intensity at 366 nm are estimated to be 0.011 for styrene sensitized by benzoin, 0.072 for styrene sensitized by benzoin methyl ether, 0.029 for MMA sensitized by benzoin, and 0.32 for MMA sensitized by benzoin methyl ether.

The variation of the polymerization rate with the extent of illumination follows theoretical predictions when the reactor is perfectly mixed, but existing models are only partially successful in correlating the variation of the rate with the degree of mixing. Moreover, even in the absence of stirring, some diffusion of radicals or mixing by natural convection takes place, and so the use of a model consisting of light and dark regions with negligible interchange between them could lead to errors in design or scale-up when the reactor is not well mixed.

The molecular weight distribution of a polymer product is also sensitive to the interactive effects of partial illumination and mixing. If there is a sufficiently sharp demarcation between illuminated and nonilluminated regions and mixing is less than perfect, a bimodal molecular weight distribution may be obtained. Even if these conditions are not met, the product MWD in a real, nonuniformly illuminated and imperfectly mixed) reactor is shifted and broadened relative to that which would be obtained in a uniformly illuminated perfectly mixed reactor.

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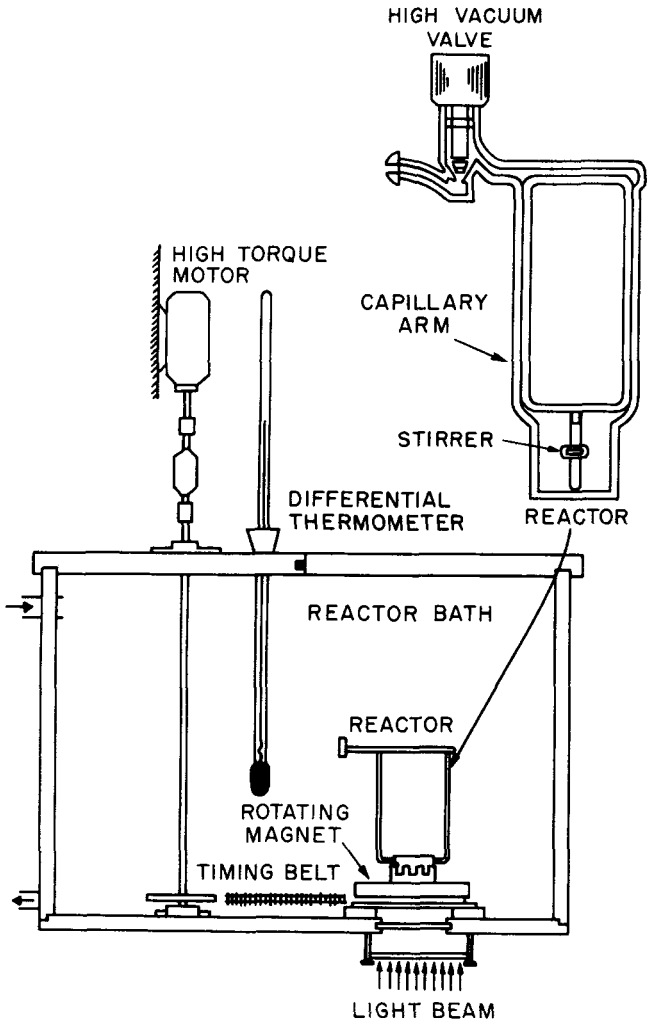

Fig. 1. Reactor bath assembly.

A number of studies of the design and analysis of photochemical reactors have appeared in the literature during the past ten years, with outstanding contributions in this area being made by J. M. Smith and J. S. Dranoff and their co-workers. Commercial applications of photochemistry have been somewhat slower to appear, but relatively recent papers such as those by Hutson and Logan (1972) and Klink et al. (1972) signal an increasing industrial interest in photochemical processing.

As many authors have noted, major impediments to the widespread utilization of photochemical processes have been the scarcity of kinetic data for photochemical reactions and the difficulty of accounting for spatial nonuniformities and imperfect mixing in designing photochemical reactors. The present study deals with photopolymerization reactions, an area in which the lack of reliable kinetic data and the difficulties associated with reactor design are particularly acute.

Primary quantum yields have been reported for several photosensitized polymerization reactions (for example, Oster and Yang, 1968), but most papers which deal with such reactions do not report quantum yields or provide sufficient data to calculate them. The positive effect of mixing on the rate of a nonuniformly initiated reaction has been shown theoretically in several studies (Hill and Felder, 1965; Hill and Reiss, 1968; Hill, Reiss, and Shendalman, 1968; Felder and Hill, 1969 and 1970; Chen and Hill, 1971; Shah and Felder, 1971; Shendalman and Hill, 1971) and experimentally by Yemin and Hill (1969), Kawakami and Isbin (1970), Muller, Eichacker, and Hill (1971), and Kawakami and Machi (1973). Theoretical studies of the effects of mixing on polymer product molecular weights have been carried out by Chen and Hill (1971) and Kawakami and Machi (1973), and an experimental study was carried out by Muller et al. (1971).

The present work had as its objectives the determination of kinetic parameters for several sensitized photopolymerization reactions and the experimental validation of existing theoretical models for mixing effects in photopolymerization reactors. Styrene and methyl methacrylate were each bulk polymerized in a batch photoreactor with benzoin and benzoin methyl ether used as photosensitizers, the degree of mixing and the fractional degree of illumination being varied in a controlled manner. This paper contains outlines of the experimental and calculational procedures used and summaries of the principal results. Additional details are given by Mendiratta (1975).

EXPERIMENTAL

Apparatus

The photopolymerization experiments were carried out by use of a reactor and constant temperature bath assembly similar to that described by Yemin and Hill (1969). The reactor was a stirred baffled pyrex glass vessel, with a 3.6 cm I.D., 3.5 cm inner height, and a stirrer blade 1.5 cm in diameter and 0.5 cm in width. The bottom of the reactor was flat, and the baffles were indented in the vessel walls. Brass masks with openings of different sizes could be inserted between the light source and the bottom of the reactor to provide nonuniform irradiation. Capillary arms were attached to the vessel to permit continuous dilatometric measurement of the extent of polymerization.

The reactor assembly is shown in Figure 1. A variable-speed, rotating ring magnet drove the reactor stirrer, which was a bar magnet enclosed in glass. Coupling between the two magnets could be maintained at stirring rates between 3 and 850 rev./min. The temperature bath surrounding the reactor was kept at $29.8 \pm 0.1°C$.

The optical system provided a parallel ultraviolet light beam. A 500 w. high-pressure short-arc mercury lamp (Osram HBO 500W/2) was housed in an air-cooled lamp housing and supplied with power by a regulated D.C. power supply. The lamp had a principal mercury line at 366 nm with a bandwidth of 12 nm at 10% of maximum intensity. The housing contained a spherical mirror which increased the effective intensity of the lamp. A compound quartz lens mounted in the housing collected the light over a large solid angle and produced a collimated beam, which passed through a 100 mm water filter and then a Corning 7-51 filter which transmitted light over a wavelength range of 310 to 420 nm. The filtered beam was reflected upwards by a 90 deg. tube and then passed through two convex lenses to improve its cross-sectional uniformity. The spectrum of the light transmitted to the reactor (determined from the manufacturers data on the lamp output spectrum and known transmission characteristics of the filters and the reactor glass) is shown in Figure 2. The intensity distribution in the light beam was mapped by using a selenium solar cell with a 1 mm^2 window, and the beam was found to be uniform within $\pm$ 2%.

Masks were prepared yielding optical thicknesses τ (total volume/illuminated volume) from 1 (with no mask) to 54. The characteristics of these masks have been described by Muller et al. (1971). The value of τ for each mask was obtained by light absorption measurements by using the potassium ferrioxalate actinometer (Hatchard and Parker, 1956) and by measurement of the light beam cross-sectional area. Values calculated both ways agreed to within 2%. Absorbances of pure monomer and monomer-sensitizer solutions were measured by using a Beckman ACTA-II spectrophotometer.

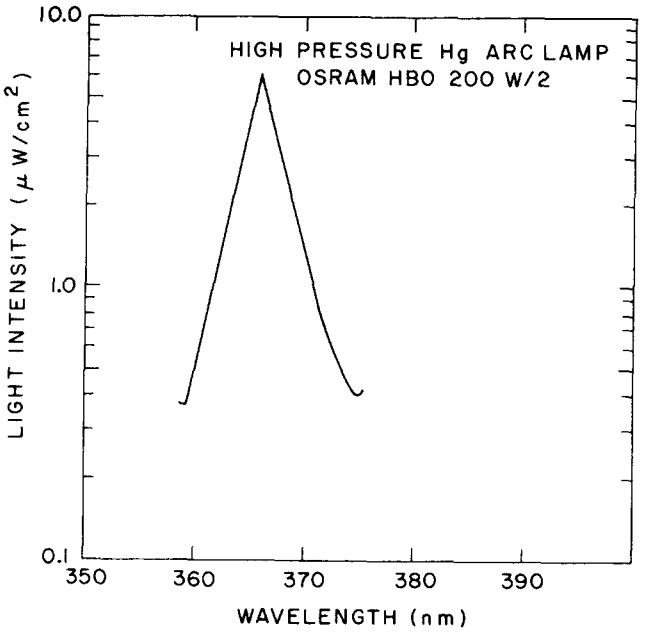

Fig. 2. Spectrum of incident light.

Reagent Preparation

Inhibitor was removed from 500 ml batches of Matheson, Coleman, and Bell reagent-grade styrene and Eastman Kodak reagent-grade methyl methacrylate by slow consecutive passage through two columns (4 cm diam × 20 cm long) packed with activated alumina. The monomers then were dried by slow passage through a column packed with silica gel particles and were stored in an amber glass bottle at −26°C. The purest grades of Eastman Kodak benzoin (2 hydroxy-1,2 diphenyl-ethanone) and Marubeni Co. (Japan) benzoin methyl ether (2 methoxy, 2-phenyl acetophenone) were used as sensitizers.

At the onset of a run, the sensitizer and monomer were transferred into a charging vessel which was linked to the reactor by a ball and socket joint. The monomer-sensitizer solution was degassed in three or four vacuum freeze-thaw cycles, after which the reactor and charging vessel were sealed and removed from the vacuum line. The degassed solution was transferred into the reactor vessel by tipping the assembly and allowing the solution to flow under the influence of gravity until the liquid level reached a point just below the top of the capillary tubes. A valve between the charging vessel and the reactor was closed, the two vessels were separated, and the absorbance of the solution left in the charging vessel was measured to determine the sensitizer concentration. The reactor was then lowered into the constant temperature bath.

Reaction Rate Measurement

After thermal equilibrium was achieved, the reactor was irradiated, and the meniscus height in one of the capillaries was measured at periodic intervals by using a cathetometer. The experiment was terminated when the meniscus reached the bottom of the capillary. Travel of the meniscus over the full length of the capillary corresponded to about 2% conversion of both monomers studied. Immediately after each run, the incident light intensity was measured by using the potassium ferrioxalate actinometer contained in a reactor identical to the one in which the polymerization had been carried out.

All experiments were conducted at a temperature 29.8 ± 0.1°C. Temperature measurements were made periodically throughout each polymerization run by using a differential thermometer. In most experiments, the maximum temperature variation was within ±0.002°C. The meniscus positions were corrected for the observed temperature variations, and a least-squares line was fit to the corrected data points. The measured rate of fall of the meniscus was proportional to the rate of polymerization; the proportionality constant was determined by using density data given by Boundy (1952) for styrene and by Mackay and Melville (1949) for methyl methacrylate.

Separate runs were carried out to determine the rates of thermal polymerization and monomer-initiated photopolymerization for all monomer-sensitizer combinations.

Product Molecular Weight Measurement

The molecular weight distribution of the polymer product was determined via gel permeation chromatography. After a run the reaction mixture was poured into methanol (Fisher Scientific—reagent grade) containing hydroquinone to quench the reaction and precipitate the polymer. The precipitate was collected in a sintered glass filter and thoroughly washed with methanol. The polymer product was dried under vacuum at room temperature for several days and was then dissolved in toluene (Fisher Scientific—reagent grade) at a concentration of 2 to 4 mg/ml prior to injection into the gel permeation chromatograph.

The chromatograph (Waters Model 300) was equipped with five columns with exclusion limits of 350 to 700, 700 to 2000, 2 000 to 5 000, 5 000 to 15 000, and 15 000 to 50 000. The columns were calibrated by using three standard polystyrene samples (supplied by Waters Associates) with molecular weights 110 000, 164 000, and 640 000 and three polymethyl methacrylate samples (supplied by Rohm and Haas) with molecular weights 19 400, 48 600 and 160 000. Number-average and weight-average molecular weights were determined from the GPC elution curves by numerical quadrature using Simpson's rule.

THEORETICAL

The mechanism of a bulk photosensitized free-radical polymerization may be written as follows:

$$\left.\begin{array}{l} S \xrightarrow{h\nu} 2R^{\cdot} \\ R^{\cdot} + M \longrightarrow M_1^{\cdot} \end{array}\right\} \quad r_i = \left(\frac{d[M_1^{\cdot}]}{dt}\right)_i = 2\phi I_{as} \qquad (1)$$

$$M_n^{\cdot} + M \rightarrow M_{n+1}^{\cdot} \quad r_p = k_p[M^{\cdot}][M] \qquad (2)$$

$$M_n^{\cdot} + M_m^{\cdot} \rightarrow P_{n+m} \quad r_{tc} = k_{tc}[M^{\cdot}]^2 \qquad (3)$$

$$M_n^{\cdot} + M_m^{\cdot} \rightarrow P_n + P_m \quad r_{td} = k_{td}[M^{\cdot}]^2 \qquad (4)$$

$$M_n^{\cdot} + M \rightarrow P_n + M_1'^{\cdot} \quad r_{trm} = k_{trm}[M^{\cdot}][M] \qquad (5)$$

$$M_n^{\cdot} + S \rightarrow P_n + R'^{\cdot} \quad r_{trs} = k_{trs}[M^{\cdot}][S] \qquad (6)$$

The net rate at which radicals disappear is $2k_t[M^{\cdot}]^2$, where $k_t = k_{tc} + k_{td}$.

Equations (1) to (6) are, respectively, initiation, propagation, termination by combination, termination by disproportionation, chain transfer to monomer, and chain transfer to sensitizer. Not shown are other possible steps such as initiation by thermal decomposition of the sensitizer or monomer and light-induced decomposition of the monomer, and unimolecular termination (for example, combination of radicals with the reactor wall or with impurities in the reaction mixture).

In the given expression for the initiation rate r_i, I_{as} is the rate of absorption of light by the sensitizer (einsteins per liter · s), and ϕ is the primary quantum yield, or the fraction of quanta absorbed which results in the initiation of chains.*

The quantum yield ϕ is normally a function of the wavelength of the initiating light, but it may be considered constant if the light is confined to a sufficiently narrow wavelength range by a monochromator or a set of glass or chemical band-pass filters. Glass filters were used

* ϕ is in fact the product of two terms: (1) the fraction of quanta absorbed which leads to decomposition of excited S molecules into primary radicals, rather than decomposition into stable fragments or deactivation by, for example, fluorescence or isomerization; (2) the fraction of primary radicals formed which combine with monomer to initiate chains rather than recombining with each other or combining with impurities.

in the present study, and the constancy of ϕ was accordingly assumed.

The initiation step is assumed to occur in a volume V_L, which may be less than or equal to the volume V_T. The rate of light absorption is taken to be constant throughout V_L and equals zero in the remainder of the reactor. The value of a parameter $\tau = V_T/V_L$ provides a measure of the degree of illumination. When $\tau = 1$ (full illumination), the rate of polymerization should be independent of the degree of mixing in the reactor, while for $\tau > 1$ (partial illumination), the rate should increase monotonically with the degree of mixing (Hill and Felder, 1965; Felder and Hill, 1969; Felder and Hill, 1970).

The rates of polymerization in the extreme states of no mixing and perfect mixing are as follows (Yemin and Hill, 1969):

$$r_{NM} = \frac{1}{\tau} k_p \left(\frac{\phi I_{as}}{k_t} \right)^{1/2} [M] \tag{7}$$

$$r_{PM} = \frac{1}{\tau^{1/2}} k_p \left(\frac{\phi I_{as}}{k_t} \right)^{1/2} [M] \tag{8}$$

where $k_t = k_{tc} + k_{td}$ is the combined rate constant for chain termination by either combination or disproportionation. It follows from Equations (7) and (8) that

$$\frac{r_{NM}}{r_{PM}} = \tau^{-1/2} \tag{9}$$

The different τ dependences of r_{NM} and r_{PM} result from the assumption that the chain termination steps [Equations (3) and (4)] are bimolecular, leading to a square-root dependence of the polymerization rate on the rate of light absorption I_{as}. If the reactor were fully illuminated ($\tau = 1$), the rate of polymerization would be $r = k_p(\phi I_{as}/k_t)^{1/2}[M]$. In an unmixed, partially illuminated reactor this expression is applicable in the illuminated region, but this region is only a fraction $1/\tau$ of the total reactor volume, so that the rate per unit volume of the reactor is given by Equation (7). In the perfect mixing extreme, the reactor behaves as though it were fully illuminated (that is, the radical concentration is uniform throughout the reaction volume), except that only a volume fraction $1/\tau$ contributes to the production of radicals. The effective light intensity is therefore I_{as}/τ, which when substituted into the given expression for r yields Equation (8).

Expressions for the number-average molecular weight $\overline{M}_n$ and the weight-average molecular weight $\overline{M}_w$ may be derived for the perfect mixing state from formulas given by Bamford et al. (1958), again by noting that when mixing is complete the reactor behaves as though it were irradiated with light with a uniform absorption rate I_{as}/τ:

$$(\overline{M}_n)_{PM} = \frac{k_p[M]MW}{k_{trs}[S] + k_{trm}[M] + \left(\frac{\phi I_{as}}{k_t \tau} \right)^{1/2} \left(\frac{k_{tc}}{2} + k_{td} \right)} \tag{10}$$

$$(\overline{M}_w)_{PM} = k_p[M]MW \frac{k_{trs}[S] + k_{trm}[M] + \left(\frac{3}{2} k_{tc} + k_{td} \right) \left(\frac{\phi I_{as}}{k_t \tau} \right)^{1/2}}{\left\{ k_{trs}[S] + k_{trm}[M] + \left(\frac{\phi I_{as} k_t}{\tau} \right)^{1/2} \right\}^2} \tag{11}$$

where MW is the molecular weight of the monomer. If chain transfer to monomer and sensitizer may be neglected, then both $(\overline{M}_n)_{PM}$ and $(\overline{M}_w)_{PM}$ are proportional to $\tau^{1/2}$.

Table 1. Molar Absorptivities

Substance	ϵ(liter/mole · cm)
Styrene	0.0155
Methyl methacrylate	0.00538
Benzoin	10.8
Benzoin methyl ether	88.5

The quantity I_{as} appearing in the preceding formulas is the rate of light absorption by the sensitizer. If I_o is the flux of radiation incident upon the reactor (as determined by actinometry), and the total rate of light absorption is averaged over the path length of the light, then

$$I_{as} = I_o \left\{ \frac{\epsilon_s[S]}{\epsilon_s[S] + \epsilon_m[M]} \right\} \frac{1 - \exp[-(\epsilon_m[M] + \epsilon_s[S])L]}{L} \tag{12}$$

where ϵ_m, ϵ_s are the molar absorptivities of monomer and sensitizer, respectively, and L is the total path length of the light in the reactor. Absorptivities measured at 366 nm for the four substances of interest in this study are listed in Table 1.

Averaging the rate of absorption of light over the axial path length in effect assumes that the effects on the reaction rate of axial nonuniformities due to light attenuation are negligible. Experimental results to be presented and numerical calculations based on the results of Hill and Felder (1965) both support the validity of this assumption for the systems studied.

A second assumption embodied in Equation (12) is that the monomer and sensitizer concentrations $[M]$ and $[S]$ are constant along the path length of the light. In the experiments performed in this study, the total monomer conversion never exceeded 2%, so that this assumption does not represent a significant source of error; if much higher conversions were achieved, local rates of reaction would have to be calculated and averaged, the axial variations in $[M]$ and possibly $[S]$ being taken into account.

QUANTUM YIELD DETERMINATIONS

Rate data obtained at full illumination ($\tau = 1$) and perfect mixing (stirrer speed = 850 rev./min.) were used to calculate the quantum yield ϕ for each monomer-sensitizer combination. From Equation (8) with $\tau = 1$

$$r_s = \frac{k_p}{k_t^{1/2}} \phi^{1/2} I_{as}^{1/2} [M] \tag{13}$$

The quantity I_{as} was determined for each run from Equation (12). The rate of sensitized polymerization r_s was calculated as

$$r_s = (r_t^2 - r_d^2 - r_u^2)^{1/2} \tag{14}$$

(George, 1967), where r_t is the measured rate, r_d is the rate of the thermal (dark) reaction, and r_u is the rate of the monomer-initiated photoreaction. The percentage correction for the thermal and monomer-initiated reactions was on the order of 1% for all monomer-sensitizer combinations except styrene-benzoin, for which the correction was as high as 12%.

TABLE 2. QUANTUM YIELDS*

Monomer	Sensitizer	$\phi^{1/2} k_p/k_t^{1/2}$	ϕ_{rate}	ϕ_{MW}
Styrene	Benzoin	1.605×10^{-3}	0.011 ± 0.003	0.02 — 0.07
Styrene	Benzoin methyl ether	4.042×10^{-3}	0.072 ± 0.01	0.05 — 0.15
Methyl methacrylate	Benzoin	1.269×10^{-2}	0.029 ± 0.006	0.02 — 0.06
Methyl methacrylate	Benzoin methyl ether	3.086×10^{-2}	0.32 ± 0.06	0.18 — 0.55

* For radiation with a peak intensity at 366 nm.

The value of I_{as} was varied from one run to another by changing the sensitizer concentration or by inserting a neutral density filter in the light beam to vary I_o, and the measured values of r_s were plotted against $(I_{as})^{1/2}$ for each monomer-sensitizer combination. Results for styrene are shown in Figure 3; the linearity of these plots verifies the assumption of bimolecular termination. Similar results were obtained for methyl methacrylate.

From Equation (13), the slope of the plot of r_s vs. $I_{as}^{1/2}$ for a particular system equals

$$\frac{k_p}{k_t^{1/2}} \phi^{1/2}[M]$$

The value of $[M]$ is 8.6 moles/liter for styrene and 9.5 moles/liter for methyl methacrylate. To estimate $k_p/k_t^{1/2}$ at 29.8°C, values of this ratio were calculated from tables of propagation and termination rate constants in the *Polymer Handbook* (Brandrup and Immergut, 1975), first halving the tabulated values of k_t to make them consistent with the termination rate laws of Equations (3) and (4). Least-squares lines were fit to Arrhenius plots of log $(k_p/k_t^{1/2})$ vs. $1/T$, with the following results:

Styrene:

$$k_p/k_t^{1/2} = 143 \exp(-2\,774/T) \qquad (15)$$

MMA:

$$k_p/k_t^{1/2} = 44.3 \exp(-1\,934/T) \qquad (16)$$

where T is in degrees Kelvin. For $T = 303.96$°K (29.8°C), these formulas yield $k_p/k_t^{1/2} = 0.0151$ for styrene and 0.0748 for methyl methacrylate.

Table 2 lists values of $\phi^{1/2} k_p/k_t^{1/2}$ determined for each monomer-sensitizer combination from the slopes of plots of r vs. $I_{as}^{1/2}$ (for example, the plots of Figure 3). These values were in turn used to estimate ϕ by using the values of $k_p/k_t^{1/2}$ at 29.8°C calculated from Equations (15) and (16). The results are given in Table 2 in the column labeled ϕ_{rate}; the uncertainty in the listed values is due principally to the uncertainty in the values of $k_p/k_t^{1/2}$ and is estimated to be ± 20%. Should more reliable estimates of k_p and k_t become available, the quantum yields may be recalculated from the figures in the first column of Table 2.*

It is in principle possible to obtain an independent determination of the quantum yield by measuring the variation of the number-average or weight-average molecular weight of the product with I_{as}, Equation (10) or (11) being used to determine ϕ. In practice this is usually not a satisfactory method: polymer molecular weights are more difficult to measure accurately than are polymerization rates; the values of the rate constants for chain

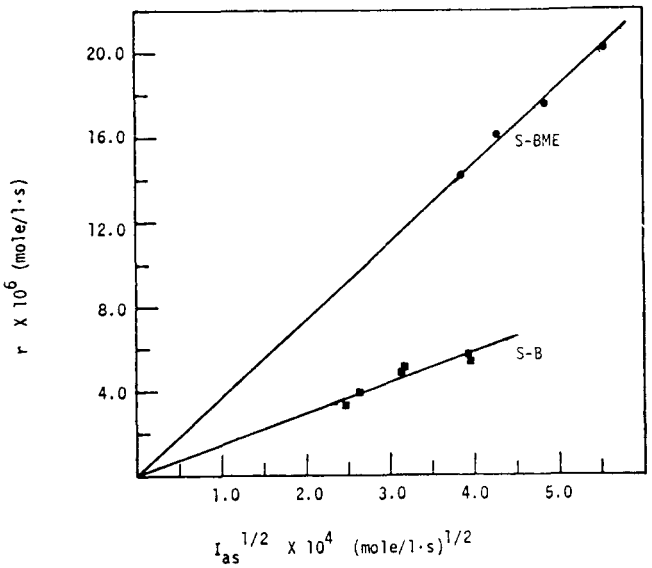

Fig. 3. Variation of polymerization rate with absorbed intensity for full illumination and perfect mixing: styrene-benzoin (S-B) and styrene-benzoin methyl ether (S-BME).

transfer, radical combination, and radical disproportionation are seldom known with a high degree of certainty, and there is no way to separate the products formed by the sensitized reaction from those formed by unsensitized and dark polymerization reactions.

Nevertheless, estimating ϕ by use of molecular weights should provide at least an order-of-magnitude check on the validity of the values calculated by use of rates. To obtain such estimates, we determined the average product molecular weights by viscometry and osmometry and by integration of gel permeation chromatograph elution curves. The results showed a considerable degree of scatter, and agreement between values obtained by different methods was poor. The GPC results displayed the greatest degree of consistency; these results were therefore judged to be the most reliable and were accordingly used in subsequent calculations.

For ease of calculation, chain transfer to both monomer and sensitizer was neglected. Neglecting chain transfer to monomer may be justified from data given by Flory (1953), but no data could be found for chain transfer to benzoin or benzoin methyl ether. It was assumed that $k_{td} << k_{tc}$ for styrene (Flory, 1953) and $k_{td}/k_{tc} = 3.1$ for methyl methacrylate (Bevington, 1961). Under these conditions, a plot of $\overline{M}_w$ or $\overline{M}_n$ vs. $I_{as}^{-1/2}$ should [from Equation (10) or (11)] yield a straight line whose slope is a multiplicative combination of $\phi^{-1/2}$ and known constants.

Plots of $\overline{M}_n$ (for styrene-benzoin, MMA-benzoin, and MMA-BME) and $\overline{M}_w$ (for styrene-BME) vs. $I_{as}^{-1/2}$ are shown in Figure 4. Least-squares lines through the origin were fit to the data, and the slopes were used to estimate values for the quantum yields. An error range of ±50%

* Quantum yields reported by Mendiratta (1975) and in a presented paper based on this work (Mendiratta et al., 1974) were calculated by using values of k_p and k_t given by Flory (1953) and differ from the values listed in Table 2. The latter values should be more accurate, being based on collections of data rather than on the results of a single experimental measurement.

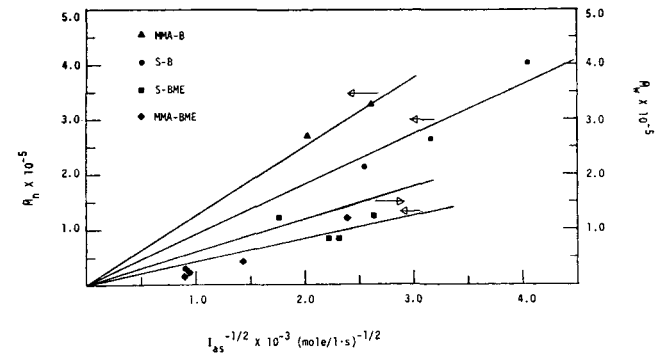

Fig. 4. Variation of product average molecular weight with absorbed intensity for full illumination and perfect mixing.

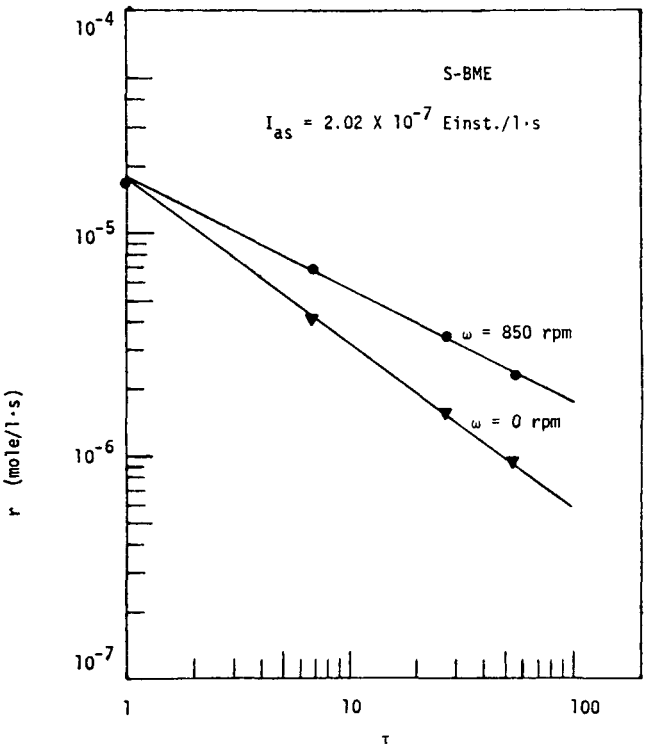

Fig. 5. Variation of benzoin methyl ether-sensitized styrene polymerization rate with optical thickness for a high stirring rate and no stirring.

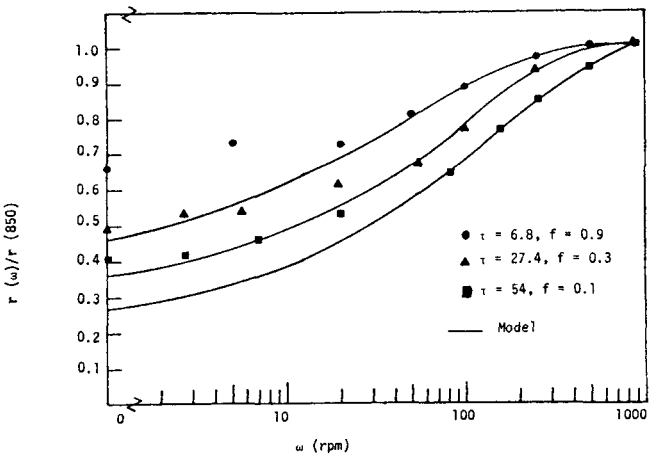

Fig. 6. Variation of benzoin methyl ether-sensitized styrene polymerization rate with stirrer speed for several optical thicknesses.

of the calculated values was assumed to account for scatter in the data and uncertainties in the values of the rate constants. The results, shown in the column headed ϕ_{MW} in Table 2, are reasonably consistent with the values calculated from measured polymerization rates.

MIXING EFFECTS ON POLYMERIZATION RATES

Polymerization runs were carried out using masks with values of τ ranging from 1 (no mask) to 54. Values of the rate r obtained for styrene-BME at a given intensity of absorbed radiation I_{as}, both with no stirring and at 850 rev./min., are plotted against τ on logarithmic coordinates in Figure 5. Similar plots were obtained for the MMA-benzoin and MMA-BME systems. Analogous measurements were not made for the styrene-benzoin system, for which the rate of the sensitized photoreaction was less than the rate of thermal reaction when τ exceeded 3.

According to Equations (7) and (8), the slope of a plot of log r vs. log τ at constant I_{as} should equal $-\frac{1}{2}$ for perfect mixing and -1 for no mixing. The slopes of the lines of these plots for a stirrer speed $\omega = 850$ rev./min. are -0.49, (styrene-BME), -0.47 (MMA-benzoin), and -0.49 (MMA-BME), showing that at this speed the reactor could indeed be considered perfectly mixed; however, the slopes for $\omega = 0$ rev./min. are -0.83 (styrene-BME), -0.67 (MMA-benzoin), and -0.87 (MMA-BME), so that even in the absence of stirring some diffusion of radicals or mixing by natural convection took place. A similar result was reported by Yemin and Hill (1969) and by Muller et al. (1971).

It is significant that the lines for $\omega = 0$ and $\omega = 850$ rev./min. intersect at a common ordinate value for $\tau = 1$ (full illumination). The implication of this result is that axial light attenuation did not have a measurable effect on the polymerization rate, and the averaging procedure used to derive Equation (12) for I_{as} is accordingly valid regardless of the degree of mixing in the reactor.

Kawakami and Isbin (1970) and Kawakami and Machi (1973) propose a model which correlates the overall reaction rate in a nonuniformly irradiated reactor with the rate of stirring. The model postulates distinct light and dark regions—in good correspondence with the conditions of the present system—with a circulation rate between them which depends on the stirrer speed in a manner prescribed by Rushton et al. (1946).

The BME-sensitized polymerization of styrene was carried out for a range of stirrer speeds at $\tau = 6.8$, 27.4, and 54.0. The ratio $r(\omega)/r_{PM}$ was calculated for each (ω, τ) pair, and curves for r/r_{PM} vs. ω were fit with Kawakami's model. (See Figure 6.) To obtain good fits it was necessary to use values of the coefficient of impeller discharge f (a model parameter) which differed considerably for different values of τ.

As Figure 6 shows, at $\omega = 850$ rev./min. the reactor could be considered perfectly mixed for $\tau = 6.8$ and 27.4 but probably not for $\tau = 54$, since the rate curve for this optical thickness does not appear to have leveled off at high stirrer speeds. On the other hand, for no τ does the measured value of r/r_{PM} approach the theoretical no-mixing limit of $\tau^{-1/2}$ [See Equation (9)] as the rate of stirring approaches zero, in agreement with the previous conclusion that the no-mixing state was never reached in the reactor.

Kawakami's model provides a fair qualitative representation of the variation of the rate with τ and ω when the reactor is close to perfect mixing, although the need to assume different impeller discharge coefficients for a fixed impeller-reactor geometry must be considered a deficiency in the model. However, the model as it is presently con-

stituted is incapable of representing the reactor behavior at low stirrer speeds, since it seems clear that mixing phenomena other than stirring become significant in this region.

The conclusion suggested by these results is that the effects of mixing on the reaction rate in a nonuniformly illuminated photoreactor can be taken into account reasonably well if the reactor is nearly perfectly mixed, but additional study is needed to model reactors far from this state. In particular, the use of a model of light and dark regions with negligible interchange between them may lead to significant errors in design or scale-up when the reactor is not well mixed.

MIXING EFFECTS ON PRODUCT MOLECULAR WEIGHTS

Gel permeation chromatography was used to analyze the products from several polymerization runs. The observed elution curves were generally quite broad, and the exclusion limits of the columns used did not permit accurate resolution of polymers with molecular weights above about 10^6; in consequence, the calculation of absolute values of average molecular weights was subject to considerable error. However, the observed variations in $\overline{M}_n$ and $\overline{M}_w$ with changes in stirring rate and optical thickness illustrate the effects of partial illumination and mixing on the product molecular weight distribution.

Three styrene-BME runs were carried out at perfect mixing (ω = 850 rev./min.) with τ = 1, 6.8, and 27.4. A typical GPC elution curve, that for τ = 6.8, is shown in Figure 7. The molecular weight distribution is seen to be essentially unimodal, although a peak (which may or may not be spurious) corresponding to a trace amount of a very low molecular weight species also appears in the elution curve. The value of the number-average molecular weight $\overline{M}_n$ calculated for the curve shown is 2.2×10^5.

An elution curve obtained for a low stirring rate and an optical thickness $\tau > 1$ is shown in Figure 8. The molecular weight distribution is clearly bimodal in this case.

To estimate the proportions of the two molecular weight fractions in each bimodal distribution, symmetry of the second (lower molecular weight) peak about its maximum was assumed, the full peak was drawn accordingly, and the first (high molecular weight) peak was obtained by subtracting the second one from the total measured signal.* The two peaks determined in this manner from the elution curve of Figure 12 are shown as dashed lines. The areas A_l and A_h under each peak were calculated by numerical integration, and the fractions x_l and x_h of the low and high molecular weight species were obtained as A_l/A_t and A_h/A_t, respectively, where $A_t = A_l + A_h$.

Results obtained in three groups of runs, each group at a constant light absorption rate I_{as}, are given in Table 3. The peak resolutions of the methyl methacrylate elution curves (runs 6 to 9) were extremely poor, and the individual peak values of $\overline{M}_n$ and $\overline{M}_w$ in Table 3 were accordingly estimated from the locations of the maxima of the peaks rather than by numerical integration.

Runs 1 and 2 illustrate the effect of mixing for a constant fractional illumination. When mixing is slight, two species are found, with (in this particular case) the lower molecular weight fraction being present in the greatest amount. As the extent of mixing increases, the peaks move toward each other ($\overline{M}_n$ increases for the low molecular weight fraction and decreases for the high molecular

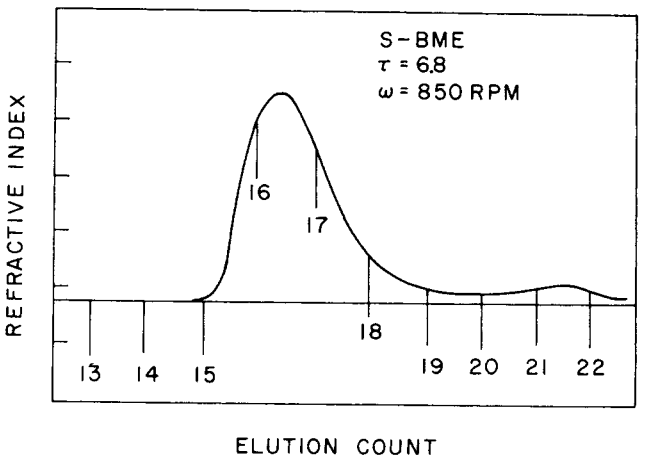

Fig. 7. Representative unimodal product molecular weight distribution.

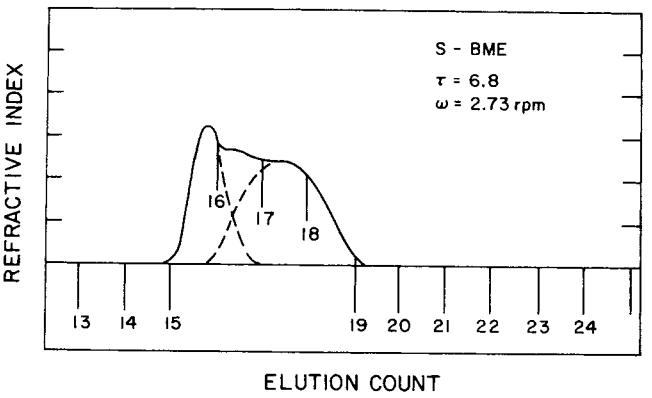

Fig. 8. Representative bimodal product molecular weight distribution.

weight fraction) until finally only one species is present. In addition, as mixing increases, the number-average molecular weight of the overall product decreases and the weight-average molecular weight increases, a result predicted theoretically by Chen and Hill (1971) and Kawakami and Machi (1973).

Runs 3 to 5 and 6 to 9 show the effect of the extent of illumination at a low mixing rate. If a small fraction of the reactor is illuminated, two species are found, with an order-of-magnitude difference between their average molecular weights. As a greater percentage of the reactor is illuminated (that is, as τ decreases), the average molecular weights of each species remain unchanged, but an increasingly large percentage of the total product appears in the low molecular weight fraction; eventually, when τ = 1 (full illumination), the low molecular weight species is the only one present. In consequence of this behavior, both the number-average molecular weight and the weight-average molecular weight of the total product increase as τ increases, that is, as less of the reactor volume is illuminated.

These results can be interpreted by postulating that all chains are initiated in the illuminated region, but some growing chains migrate into the dark region before they undergo termination. Polymer chains formed entirely in the light region would tend to have relatively low molecular weights, in view of the high radical concentration in this region. Such chains account for the bulk of the second peak when a bimodal distribution is obtained. On the other hand, when a radical finds its way into the dark region, where the concentration of radicals is low in

* An alternative procedure would be to fit a Gaussian function to one or another of the peaks and then to determine the second peak by difference, as was done by Muller et al. (1971).

Table 3. Product Molecular Weights

Run	System	τ	ω (rev./min.)	First Peak x_h	First Peak $\overline{M}_n$	Second Peak x_l	Second Peak $\overline{M}_n$	Total $\overline{M}_n$	Total $\overline{M}_w$
1	S-BME	6.8	850	—	—	1.00	2.2×10^5	2.2×10^5	3.8×10^5
2	S-BME	6.8	2.73	0.30	7.5×10^5	0.70	3.8×10^4	1.5×10^5	4.0×10^5
3	S-BME	3.0	0	0.13	7.8×10^4	0.87	1.0×10^3	1.2×10^4	5.9×10^4
4	S-BME	6.8	0	0.26	6.7×10^4	0.74	2.0×10^3	3.0×10^3	7.4×10^4
5	S-BME	13.6	0	0.35	8.2×10^4	0.65	1.2×10^3	1.9×10^3	1.0×10^5
6	MMA-BME	1.0	0	—	—	1.00	$*1.8 \times 10^4$	1.1×10^4	7.8×10^4
7	MMA-BME	3.0	0	0.07	$*7.2 \times 10^5$	0.93	$*1.5 \times 10^4$	1.6×10^4	1.5×10^5
8	MMA-BME	6.8	0	0.10	$*7.2 \times 10^5$	0.90	$*1.8 \times 10^4$	1.5×10^4	1.9×10^5
9	MMA-BME	27.4	0	0.38	$*7.2 \times 10^5$	0.62	$*1.8 \times 10^4$	4.7×10^4	3.1×10^5

* Molecular weight corresponding to peak elution count.

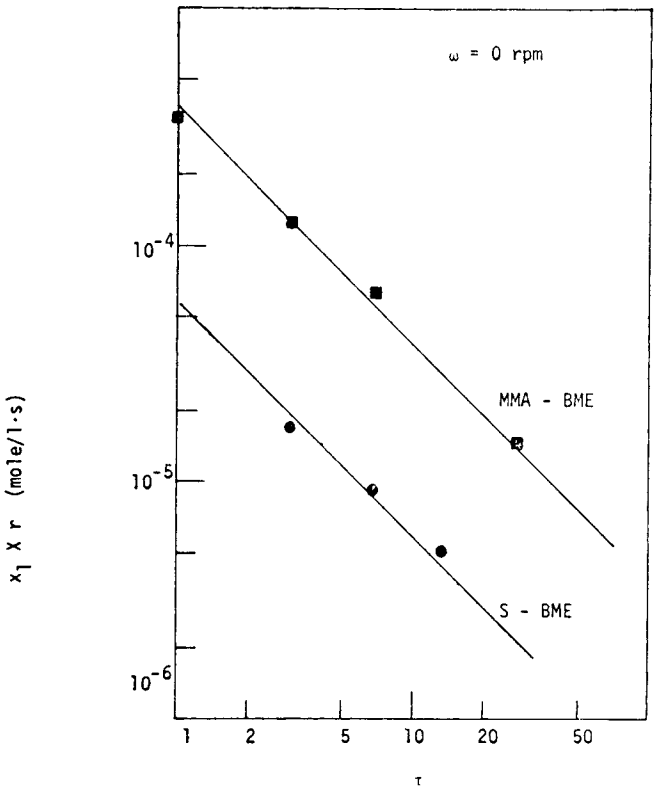

Fig. 9. Effect of optical thickness on rate of production of low molecular weight product for no stirring.

the absence of a high degree of mixing, it is likely to form a large chain before terminating. The first peaks of the observed bimodal distributions can be attributed to polymer formed in this manner.

Increasing the stirring speed for a constant τ tends to decrease the radical concentration in the light region and to increase it in the dark region, resulting in a movement of the two values of $\overline{M}_n$ toward each other. (See runs 1 and 2 in Table 3.) Lowering τ at a given (low) mixing rate should not alter the radical concentrations appreciably, so that the values of $\overline{M}_n$ and $\overline{M}_w$ should be unchanged, but by a surface/volume ratio effect it would decrease the likelihood that radicals would find their way into the dark region, thereby increasing the percentage of the product in the low molecular weight fraction. (See runs 3 to 5 and 6 to 9 in Table 3.)

An additional check on the validity of these hypotheses was obtained by calculating the rate of consumption of monomer to form the low molecular weight species as the fraction of this species formed (x_l) times the total polymerization rate and by plotting the logarithm of this quantity vs. log τ. (See Figure 9.) If the low molecular weight species can indeed be identified as the species formed entirely in the light region under conditions of negligible mixing, then from Equation (7) a line should be obtained with slope $= -1$. Such lines are in fact obtained for both styrene and methyl methacrylate, as Figure 9 shows.

Muller, Eichacker, and Hill (1971) obtained results for the benzoin-sensitized photopolymerization of methyl methacrylate which correspond quite closely to those reported in this paper. The same authors also report obtaining a high molecular weight species which they attribute to a reaction involving the illuminated reactor surface. Within the limits of the analytical equipment used, no evidence of such a species was found in the present study.

Kawakami and Machi (1973) present theoretical expressions for the molecular weight distribution of a polymer formed in a partially illuminated reactor, which predict the occurrence of bimodal distributions under the conditions of the present study. Attempts to fit the MWD data quantitatively by use of Kawakami's model have not been successful.

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NOTATION

A_l, A_h = areas under low and high molecular weight peaks in a bimodal gel permeation chromatograph elution curve

I_{as} = rate of absorption of light by the photosensitizer, einsteins/liter · s

I_o = radiation flux incident upon the reactor, einsteins/cm² · s

$k_p, k_{tc}, k_{td}, k_{trm}, k_{trs}$ = rate constants of propagation, termination by combination, termination by disproportionation, chain transfer to monomer and chain transfer to sensitizer, liter/mole · s

k_t = $k_{tc} + k_{td}$, liter/mole · s

L = path length of radiation in the reactor, cm

$[M]$ = monomer concentration, mole/liter
$[M\cdot]$ = total concentration of growing chains, mole/liter
$\overline{M}_n$ = number average molecular weight
$\overline{M}_w$ = weight average molecular weight
MW = molecular weight of monomer
r_{NM}, r_{PM} = polymerization rates for no mixing and perfect mixing, mole/liter · s
r_t, r_s, r_u, r_d = total polymerization rate, rate of sensitized photopolymerization, rate of unsensitized photopolymerization and rate of thermal polymerization, mole/liter · s
$[S]$ = photosensitizer concentration, mole/liter
x_l, x_h = fractions of low and high molecular weight species in polymer product
V_L, V_T = illuminated reactor volume and total reactor volume, liter

Greek Letters

ϵ_m, ϵ_s = molar absorptivities of monomer and sensitizer, liter/mole · cm
τ = optical thickness, V_T/V_L
ϕ = primary quantum yield, chains initiated/quantum absorbed
$\phi_{\text{rate}}, \phi_{mw}$ = ϕ as determined by polymerization rate measurement and average product molecular weight measurement
ω = stirrer speed, rev./min.

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Perturbed Hard-Chain Theory: An Equation of State for Fluids Containing Small or Large Molecules

Generalized van der Waals theory is used to establish a partition function that considers the effect of density on rotational and vibrational motions in addition to translational degrees of freedom. A three-parameter equation of state is derived from this partition function. The equation of state is applicable to small, spherical (argon-like) molecules and also to

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