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Following Polymerization Kinetics of Multifunctional Acrylates in Real Time by Fluorescence Probe Methodology

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ABSTRACT: We report a new method which uses fluorescence probe methodology to follow the kinetics of polymerization and postirradiation processes of multifunctional acrylates in real time.

Background

In the search for systems which undergo a faster and more controllable photopolymerization, the use of visible lasers to initiate and transform, rapidly, a liquid monomer into solid polymer is an obvious goal. In view of the recent development of initiating systems active at 488, 514, and 632 nm, both Ar ion and He/Ne lasers have been used for such purposes.[3] Pulsed lasers are often employed in polymer science to obtain kinetic constants for free-radical polymerization.[4-8] Continuous-output lasers provide high rates of initiation. With the spatial coherence of the laser beam, by using multifunctional monomers, one can directly create complex spatial images[9-11] or directly write a complex electronic circuit at micronic resolution.[12] However, the use of the powerful, shaped-laser irradiation and multifunctional monomers to form a solid photopolymer creates many critical unsolved problems. The most critical of these is that there is no adequate method to study, in real time, the kinetics of polymerization or the kinetics of the relaxation processes of systems which gel rapidly.

Several new methods have been reported recently which purport to follow the kinetics of polymerization of monomers that transform rapidly from a liquid resin into a solid material.[13] The most recent is a technique based on IR spectroscopy [real-time infrared (RTIR) spectroscopy] that has been developed with the possibility of observation of photopolymerization processes in a fraction of a second.[14-17] Compared with other techniques, RTIR shows a distinct advantage in that it provides accurate evaluation of the important kinetic parameters and the dark polymerization that developed after the irradiation. However this method is limited to thin films. Therefore it does not answer many important questions, e.g. the kinetics of the rheological changes,[18] the effect of volume relaxation,[19,20] and the photo-cross-link density changes which occur as the depth of cross-linked resin is increasing. Almost more important, it provides no way for spatial resolution, i.e., following the kinetics of the process as a function of dimension. The purpose of this paper is to describe a new and promising method of observation, in real time, of the processes occurring during a photopolymerization initiated by a pulsed or continuous-output laser. The method uses changes in the fluorescence intensity and spectral characteristics observed for a probe molecule during a rapidly photo-cross-linking process. The technique can use either the changes of the ratio of excimer to monomer emission in a polyaromatic probe such as pyrene[21] or the changes of the fluorescence of molecules evidencing the intramolecular charge-transfer (ICT) properties.[22,23] The fluorescence intensity and the shape of the spectra of the latter type fluorescing molecule is exceedingly sensitive to changes of the microenvironment and we have chosen it on which to base the real-time kinetic measures reported.[20,21,24-26]

Results and Discussion

(1) Characteristics of the Probe. Our method employs dansylamide (DA) as a fluorescing probe. DA has been commonly used as a probe to study of polymer properties.[26-28] Its molar absorption coefficient in ethyl acetate[29] is about 4.5×10^3 L/mol. Under the experimental conditions used in our experiments ([DA] = 5.24×10^{-4} mol/L), the monitoring light (λ_{ex} = 345 nm) penetrates about 1 mm into the probed, polymerizing sample. By changing either the DA concentration or the excitation wavelength one can change the depth to which the probe beam penetrates the sample and thus probe the kinetics as a function of dimension. The absorption spectrum of DA overlaps, in part, with the UV absorption spectrum of the photoinitiator used to initiate polymerization. This initiator, RBAX,[30] is a solvent-soluble derivative of Rose Bengal[31] which also strongly quenches the fluorescence of the emitting excited state of DA. Since the photoinitiator absorbs light in the excitation region used for DA and it also quenches its fluorescence, it is not possible to establish, exactly, the quenching constant data from the Stern–Volmer equation. However it is important to emphasize that (1) the shape of the fluorescence spectra of DA is not RBAX concentration dependent, and (2) during the irradiation the initiator is bleached at the point at which polymerization occurs.[32] The latter may cause a significant increase in the fluorescence intensity. The bleaching process, however, occurs only during the irradiation time, so all spectral changes observed after the irradiation are the result of postirradiation processes, e.g., by the relaxation of cross-linked polymer, by changes in temperature, or by dark polymerization. It is well-known that molecules evidencing ICT may initiate free-radical polymerization; nevertheless, in a control experiment, the intensity of the monitoring light (λ = 345 nm) causes no observable changes in the polymerizing system. This eliminates DA-initiated polymerization in the system under observation.

(2) Measurements of Polymerization Efficiency. The fluorescence changes observed for DA during the thermally initiated polymerization of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA) are shown in Figure 1. The data clearly demonstrate that the fluorescence spectra undergo a large hypsochromic shift accompanied by an increase in the fluorescence quantum yield as the degree of monomer converted into polymer increases. This behavior is typical for flexible molecules which show ICT.[25,33] The ratio of the fluorescence intensities monitored at 460 and 500 nm appears to be a linear function of monomer conversion into polymer. The

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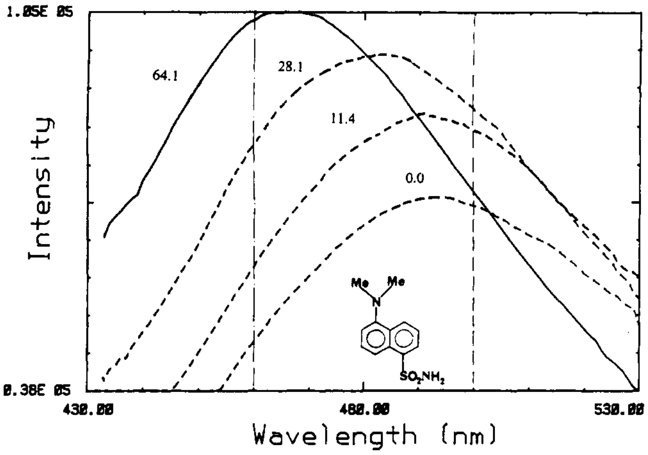

Figure 1. The changes of the fluorescence emission spectra of dansylamide (λ_{ex} = 345 nm) caused by the progress of thermally initiated polymerization of a TMPTA–VP (9:1) mixture. The numbers on the fluorescence curves indicate the percent of monomer conversion into a polymer (measured using FTIR spectroscopy).

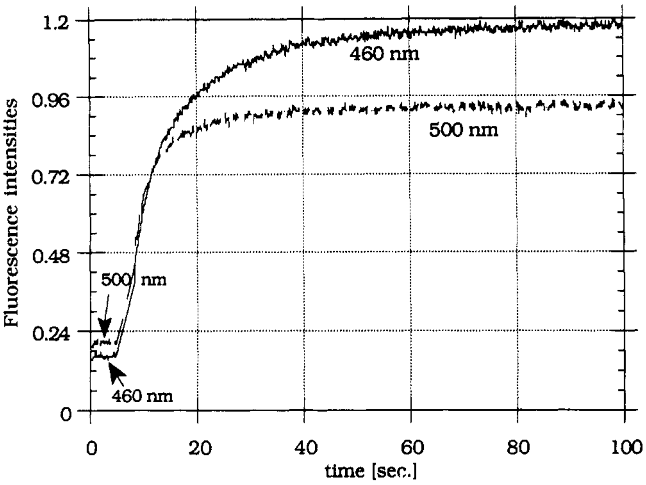

Figure 2. The real-time changes of fluorescence intensities of the probe, recorded at 460 (1) and 500 (2) nm. (For the calculation of polymerization efficiency, the normalization considering the apparatus characteristics is required.)

following empirical equation illustrates this relationship:

$$\% \text{ of monomer conversion} = (R/0.0125) - 31.2 \quad (1)$$

The real-time changes of fluorescence intensities recorded at 460 and 500 nm observed after a 3-s laser pulse (600 mW/514 nm) are presented in Figure 2. From the ratio (R) reached after the temperature of the sample is equilibrated to ambient temperature, one can using eq 1 to calculate the percent of monomer conversion. The rate (R_p) of polymerization can be represented by the equation

$$R_p = -d[\text{TMPTA}]/dt = k_p[\text{RBAX}]^{0.5}[\text{TMPTA}] \quad (2)$$

For a given time of irradiation, the yield (percent of monomer converted into a solid polymer) of polymerization should be proportional to $[\text{RBAX}]^{-0.5}$. Figure 3 clearly shows that the relation is as predicted by the eq 2.

(3) Analysis of Postirradiation Processes. Since the ratio of fluorescence intensities monitors the degree of polymerization (after equilibration to room temperature), changes in fluorescence intensity at 460 nm can be used for the study of the processes occurring directly after irradiation. As can be seen in Figure 2, the fluorescence at 460 nm is more sensitive to the overall changes taking place in polymerizing sample.

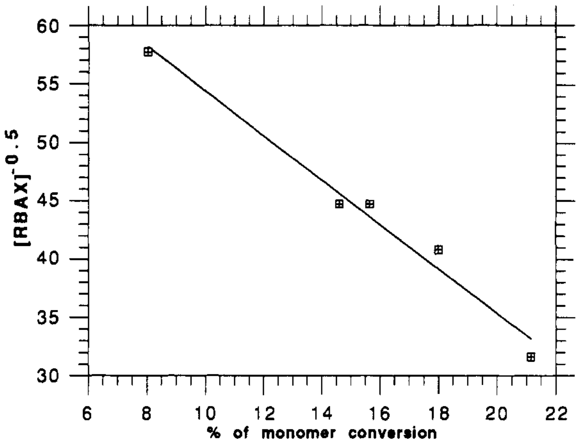

Figure 3. The relationship between initiator (RBAX) concentration and the final yield of photoinitiated (3-s laser flash) polymerization of a TMPTA–VP (9:1) mixture.

To describe the fluorescence intensity changes directly after irradiation, free-volume relaxation kinetics are used. The single relaxation time model[34] states that the rate of change of free volume, V_f, is proportional to the deviation from the equilibrium free volume. In our model we assume that free volume is produced during irradiation faster than the rate of free-volume relaxation. Thus directly after irradiation, the polymerized system contains a certain excess of free volume:

$$-dV_f/dt = kV_f \quad (3)$$

assuming V_f^0 = the initial value of free volume, V_f = the free volume after time, t, and $V_f^a = V_f^0 - V_f$, one can write the following equation:

$$V_f^a = V_f^0(1 - e^{-kt}) \quad (4)$$

where k is a rate constant for the free-volume relaxation.

For a probe in which a rotation-dependent nonradiative decay (k_{nr}) links the excited-state conformation to the media free volume (ϑ_f), one can express k_{nr} in terms of solvent free volume as

$$k_{nr} = k_{nr}^0 \exp(-\beta V_0/\vartheta_f) \quad (5)$$

where k_{nr}^0 is the intrinsic rate of molecular relaxation of the excited molecule, V_0 is the van der Waals volume of the probe, and β is a constant characteristic for particular probe. The nonradiative decay rate, k_{nr}, is related to the fluorescence yield according to

$$k_{nr} = k_r\{(1/\Phi_f) - 1\} \quad (6)$$

where k_r is the radiative decay rate constant of the probe. Equations 5 and 6 give the fluorescence-dependent free volume:

$$\ln\{(1/\Phi_f) - 1\} = \ln(k_r/k_{nr}^0) + \beta V_0/\vartheta_f \quad (7)$$

and finally

$$\vartheta_f = \beta V_0/\{\ln[\Phi_f/(1 - \Phi_f)] - \ln(k_r/k_{nr}^0)\} \quad (8)$$

Combining eqs 4 and 8, the relationship between the increase of fluorescence intensity of the probe and decrease of free volume can be derived as

$$\ln\{\Phi_f/(1 - \Phi_f)\} = \{B/(1 - e^{-kt})\} + A \quad (9)$$

where $A = \ln(k_r/k_{nr}^0)$, and $B = \beta V_0/V_f^0$.

The above relationship indicates that $\ln\{\Phi_f/(1 - \Phi_f)\}$ will increase when the excess of free volume is decreasing.

The fluorescence intensity increases, as recorded at 460 nm and shown in Figure 2, do not rise single exponentially,

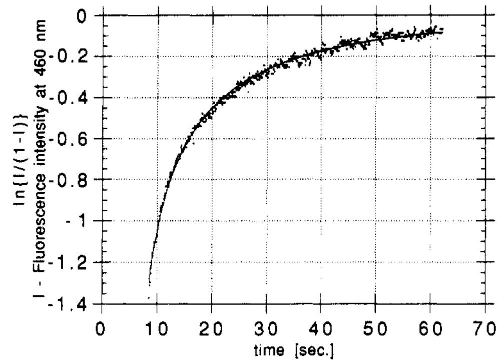

Figure 4. The experimental data of fluorescence intensity recorded at 460 nm (points) and fitted curve (using eq 9) for postpolymerization processes observed after laser (3-s flash) initiated polymerization of a TMPTA–VP (9:1) mixture; [RBAX] = 13 × 10^{-4} mol/L.

but fit, within acceptable error, a double-exponential form. This rising profile of fluorescence intensity and a fitted curve (using eq 9) is shown in Figure 4. The deconvoluted forms of fluorescence intensity rising profile are

$$\ln\{I_{460}/(1 - I_{460})\} = -9.22/\{1 - \exp(-0.496\ \mathrm{s}^{-1}\ t)\} - 0.315/\{1 - \exp(-0.067\ \mathrm{s}^{-1}\ t)\} + 10.3 \quad (10)$$

The first component has a high amplitude which, according to eq 9, may vary because it contains the V_f^0 value, and this is RBAX concentration dependent. (We emphasize that the fluorescence emission is recorded after a 3-s laser exposure, so our analysis does not start at $t = 0$ s but after a certain time of continuous change in the tested sample.) The nature of the value describing the amplitude of the second component (−0.067), based on the above experiment, is unclear. The physical meaning of the third constant (10.3) is also not clear because only one exponential fluorescence rise which has meaning is described by eq 9.

To explain the two exponential rise profile of the fluorescence intensity, we have considered other physical changes occurring during laser photoinitiated polymerization of vinyl monomers. It is well-known that the polymerization of vinyl monomers is highly exothermic and that the rate of heat evolution can also be used for the kinetic study of polymerization, especially polymerization initialized by laser emission.[35–38] Since, under our experimental conditions, about 75–150 mg of solid polymer is formed, the amount of heat accompanying the polymerization is considerable. The solid, hot polymeric bar (about 2-mm diameter) which is formed is surrounded by cold nonpolymerized monomer. During polymerization the rate of heat evolution is greater than the rate of heat transport into cold environment, and the temperature of the polymerizing system increases. When the light of the laser is off, the polymerization we are observing is limited to dark polymerization (if it occurs after 3 s of irradiation) and the temperature of the sample decreases rapidly because of heat transport into cold environment. This temperature decrease causes an increase in viscosity. Temperature decrease, according to Doolittle,[39] also leads to a decrease of the free volume and this results in an increase of fluorescence intensity. In order to understand this effect of temperature, the changes in fluorescence intensity at 460 nm and the temperature of the polymerized sample were recorded simultaneously. The result is shown in Figure 5.

The phenomenon observed is as one expects. During laser-initiated polymerization the temperature of the polymerizing system increases substantially. The temperature increase is caused, as the control experiment demonstrates (see Figure 6), mostly by the heat of polymerization. The thermocouple response indicates an exponential temperature decay. The monoexponential fitting of the temperature decrease can be described as follows:

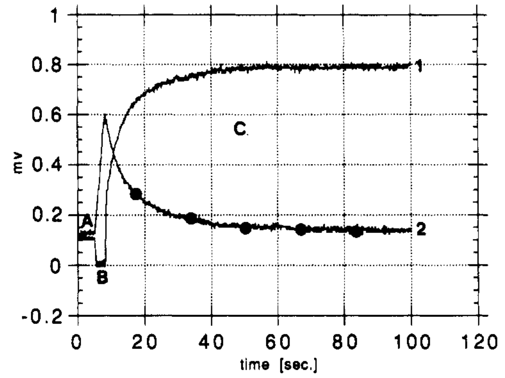

Figure 5. The changes of fluorescence intensities at 460 nm (1) and response of the thermocouple (2) caused by a 3-s laser flash. The stages of the recorded curves are (A) before irradiation (5 s); the shutter for the photomultiplier tube at 460 nm is opened; (B) irradiation time (3 s); the shutter at 460 nm is closed; (C) the postirradiation time; the shutter at 460 nm is opened. The thermocouple response is recorded continuously.

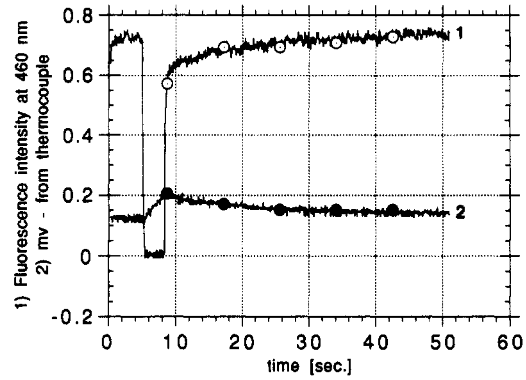

Figure 6. The fluorescence changes (1) and thermocouple response (2) after 3-s exposure of the polymerized sample to the laser beam (sample from the experiment recorded in Figure 5). The stages of recording are as in Figure 5.

$$\text{temp} = 0.120 \exp(1/0.0716\ \mathrm{s}^{-1}\ t) \quad (11)$$

Comparing the results from eqs 10 and 11, one can see a high correlation between two rate constants, one from the second component of eq 10 and the second from eq 11 (0.0670 and 0.0716 s^{-1}, respectively). This suggests that the fluorescence intensity rise, in part, is controlled by the temperature decrease of the sample. It is important to emphasize that on the basis of thermocouple characteristics one can estimate the maximum temperature to be as high as 160 °C. To confirm, experimentally, that the fluorescence intensity rise profile has a component controlled by the rate of temperature decrease, an identical laser-initiated polymerization was carried out in a rectangular brass block (instead of a quartz cell) with a small (1.5 mm) aperture by means of which to cause, and observe, the polymerizing of the monomer. A thermocouple was also inserted at the spot of polymerization. The polymerization was initiated using exactly the same exposure as for polymerization carried out in the quartz cell. The fluorescence intensity rise and temperature-change profiles are shown in Figure 7.

The deconvoluted fluorescence intensity rise profile contains two components with $k = 0.50\ \mathrm{s}^{-1}$ and $k = 0.147$

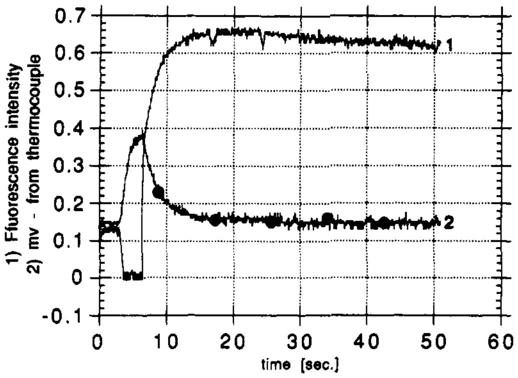

Figure 7. The fluorescence intensity changes (1) and thermocouple response (2) recorded after 3 s laser initiated photopolymerization carried out in a brass block. The stages of recording are as in Figure 5.

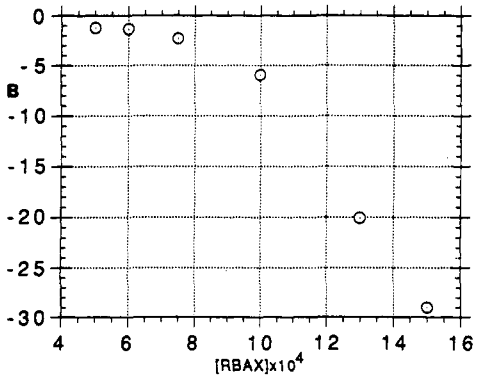

Figure 8. The relationship between constant D (from eqs 9 and 12) and RBAX concentration.

s^{-1}. The first rate constant is almost identical to that presented in eq 10 ($k = 0.496\ s^{-1}$) as measured in a quartz cell. The second rate constant, which corresponds to the temperature decreasing, is double that obtained from eq 10. The observed differences are easy to explain if one considers the brass and the liquid monomer heat capacities. One additional important conclusion can be derived from these two experiments. Only one parameter causes the fast ($k = 0.5\ s^{-1}$) rise of fluorescence intensity. From the data presented above, the following general equation describing the fluorescence intensity changes can be derived:

$$\ln\{\Phi_f/(1-\Phi_f)\} = B/(1-e^{-k_1t}) + C/(1-e^{-k_2t}) + D \qquad (12)$$

From eq 9 it is known that $B = \beta V_0/V_f^0$. This suggests that the value of B may vary as the degree of monomer conversion varies, e.g. the B value should be lower for high photoinitiator concentration and higher for low photoinitiator concentration. This relationship, namely that predicted by eq 12, is shown in Figure 8.

The constant C, as the experiments with the brass block and the quartz cell have shown, likely characterizes the heat capacity and conductivity of the environment in which the photopolymerization occurs. The constant D contains at least two parameters. The first is the constant A, from eq 9, and second from the relationship linking the temperature effect to the free volume.[33] Thus D may vary substantially for different degrees of monomer conversion (variation of k_{nr}^0 and k_r) and it can be dominated by the physical properties of the environment.

The k_1 and k_2 values obtained for different RBAX concentrations are presented in Table I. It is clear that k_1 and k_2 are the constants of two different processes. The character of the slower process has already been discussed.

Table I
Rate Constants k_1 and k_2 Obtained for Postirradiation Processes of the Photoinitiated Polymerization of a TMPTA–VP (9:1) Mixture

[RBAX], mol/L	k_1, s^{-1}	k_2, s^{-1}	[RBAX], mol/L	k_1, s^{-1}	k_2, s^{-1}
15×10^{-4}	0.552	0.037	7.5×10^{-4}	0.700	0.042
13×10^{-4}	0.495	0.067	7.0×10^{-4}	0.419	0.045
10×10^{-4}	0.406	0.040			

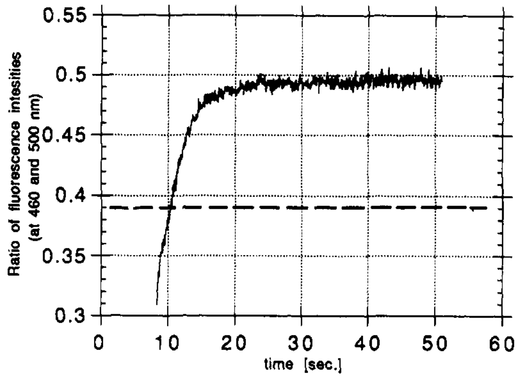

Figure 9. The changes of the ratio (R) value recorded after laser initiated (3 s) polymerization of a TMPTA-VP (9:1) mixture; [RBAX] = 13×10^{-4} mol/L; photopolymerization was carried out in a brass block.

The nature of the faster process is unclear. According to Decker,[12,15,16] after irradiation, the polymerization appears to continue for about 1 s and this posteffect is less pronounced when using acrylates forming a highly cross-linked polymer network with less chain mobility. The half-life time of the process described by k_1 is about 1.4 s. This is very close to Decker's results. However certain of our experimental data, in part, are in contradiction with an explanation which considers only dark polymerization. Figure 9 shows the changes of the ratios of the fluorescence intensities at 460 and 500 nm recorded directly after laser exposure. The dashed line indicates the R value observed for the starting monomer mixture ($R = 0.39$). Directly after the laser flash (3 s) R is much lower than is R for the starting material. On the basis of Decker's[12-14] results we can state that after a long laser irradiation (which our system uses), the highest possible degree of polymerization is nearly reached. In our experiments triacrylate was used as a monomer for which dark polymerizations are less distinct than they are for monoacrylates. If one considers the response to the probe, Figure 9 thus shows how the ratio changes for a partially (see Figure 3) polymerized semirigid material which appears to behave as a hot liquid system. From an Arrhenius plot (Figure 10) measured for the irradiated sample with about 20% of the monomer converted into polymer, it is easy to calculate that in order to obtain a ratio of the fluorescences as low as that observed directly after polymerization the temperature of the sample would have to be nearly 650 °C! From the data presented in Figure 5 it is known that the highest temperature recorded inside the sample is about 160 °C. Since the polymerized sample contains about 80% of liquid monomer, the sample most likely behaves more like a very viscous solution than like a highly polymerized gel immediately after the polymerization has occurred. Considering all the observations, we propose that directly after irradiation the system is polymerized but contains as much free volume as would an identical mixture of liquids.[40] Since such a liquidous system is sterically and thermodynamically forbidden, the polymer starts to collapse in order to approach equilibrium. This collapse is controlled by the thermodynamics of the process. Though one cannot exclude the possibility of a dark po-

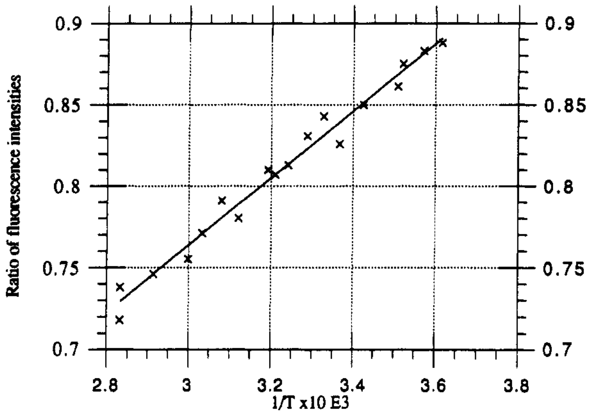

Figure 10. The Arrhenius plot of the polymerized TMPTA–VP (9:1) mixture. Degree of double bond conversion about 20%.

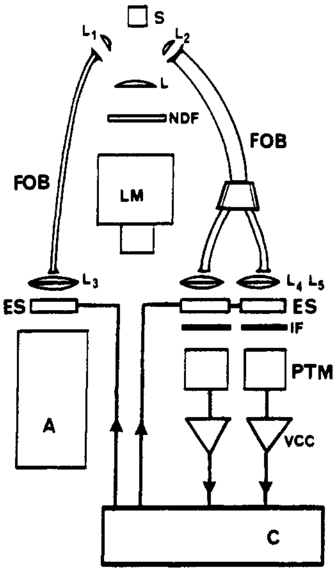

Figure 11. Optical and electronic arrangement for laser-flash experiments. C, computer; A, argon ion laser; ES, electronic shutter; VCC, voltage-to-current converter; PMT, photomultiplier tube; IF, interference filter; L1, L2, L3, focusing lens; L4, L5, collimating lens; LM, lamp and excitation monochromator; NDF, neutral density filter; FOB, fiber optic bundle; S, sample.

lymerization reaction process, on the basis of our results it is not the major process occurring after laser irradiation is ceased.

Experimental Section

General. Acetylated decarboxlated Rose Bengal (RBAX) was prepared using procedures described earlier.[30,38] 2-Ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA) was purchased from Saratomer. 1-Vinyl-2-pyrrolidinone (VP), *N*-phenylglycine, and dansylamide (DA) were purchased from Aldrich. All compounds were used without further purification.

The kinetics of the postirradiation processes were studied using a polymerizing solution composed of 1 mL of VP, 9 mL of TMPTA, RBAX (concentration was varied from 5×10^{-4} to 20×10^{-4} mol/L), *N*-phenylglycine ($c = 0.05$ mol/L), and dansylamide ($c = 5.24 \times 10^{-4}$ mol/L).

Fluorescence measurements were performed using a Spex-Fluorolog 1680 spectrofluorimeter. The conversion of monomer into a polymer was measured by IR spectroscopy using a Nicolet 20 DX FTIR spectrometer.

Apparatus (Figure 11). Fluorescence data in the form of output voltage from a locally assembled, current-to-voltage converter were digitized and stored by a commercially available computer program (Unkel Software, Cambridge, MA). In each experiment a concurrent subroutine controlled the opening and closing of electronic shutters (Vincent Associates L23 and VS25) in complementary fashion in laser and fluorescence light paths, respectively. Two legs of a trifurcated fiber optic bundle (Oriel 77536) transmitted fluorescence emission to a pair of photomultiplier tubes (S-5 response), each guarded by an appropriate, narrow-band, interference filter. A slightly modified spectrofluorimeter (Perkin-Elmer MPF-44A) provided fluorescence excitation probe light, attenuated sufficiently by neutral density filters to eliminate any detectable fluorescence changes incurred by the beam itself. A 514-nm, argon ion laser beam (Spectra-Physics Model 2016) was directed via a large core, quartz fiber optic (Oriel 77531) to the front face of a quartz sample cuvette (or to the aperture of the brass block) where the focused image just overfilled the image of the probe beam (about 1.5-mm diameter). Laser output was measured by a Scientech Model 365 power meter. On the basis of the nominal dimensions of the focused laser beam determined photographically, the intensity of the 0.60-W beam at the sample face was 1.3×10^{-4} einsteins s^{-1} cm^2; in practice the extent of photopolymerization exceeded this nominal beam diameter by about 50%. In some experiments the output of a calibrated copper–constantan thermocouple, positioned inside the sample cuvette where the probe and laser beams entered, was recorded along with the emission signal.

Preliminary manipulation of data was performed by Lotus 123 and detailed analysis by "KaleidaGraph". An optional facility in the Unkel software allowed for digital filtering of stored data to remove high-frequency noise if desired.

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