UV and Fluorescence Characterization of Styrene and Methyl Methacrylate Polymerization

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SYNOPSIS

Polymerization of styrene and methyl methacrylate (MMA) were studied by UV and fluorescence spectroscopic techniques. Using a sharp decrease in the extinction coefficient at 250 nm and the fluorescence quantum yield at 308 nm of styrene following polymerization, styrene conversion in solution polymerization by UV and fluorescence measurements were found to correlate well with IR results monitoring the disappearance of vinyl groups, at three different temperatures (65, 70, and 75°C). The activation energy of about 6 kcal/mol was obtained. Using the decrease in UV absorbance of MMA during polymerization, solution polymerization of MMA was studied and compared with IR results. Due to the solvent absorbance, the UV method underestimates the conversion to a certain extent. When a small amount of styrene is added in MMA polymerization as a reactive extrinsic comonomer, the conversion of styrene measured by fluorescence is found to be faster than MMA, due to the characteristic reactivity ratios of MMA and styrene. The correlation curve could be used to estimate MMA conversion from styrene fluorescence, providing a method more sensitive than the viscosity-dependent fluorescence probe technique. Bulk polymerization of styrene was studied by bifurcated fiber-optic fluorescence. Due to self-quenching, little fluorescence of styrene is observed up to 75% conversion, but increases sharply from 75 to 85% conversion, followed by a drastic decrease during the last 15% conversion. In comparison to other methods of following vinyl polymerization such as refractive index, density, and gel permeation chromatography, these spectroscopic techniques provide real-time in situ capability as well as better sensitivity, especially in the later stages of polymerization. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

During the last 10 years, our laboratory has been involved in the development and the applications of sensitive optical techniques for in situ characterization of cure and water uptake in high temperature, high performance polymers and composites such as epoxy,[1] polyimide,[2] polyamide,[3] and polyurethane.[4] The approach we have taken is careful analysis of the spectral changes in UV and fluorescence manifested either by an extrinsic reactive probe, which mimics the curing agent or by the curing agent itself as the cure progresses. These spectral changes occur as a consequence of the reactions of the func-

tional groups attached to the aromatic molecules during cure. For example, an aromatic diamine as the curing agent in epoxy cure is converted from the primary amine to the tertiary amine. During polyimide syntheses, the amine groups in the aromatic diamine are changed to the amide first and eventually to the imide groups. Different substituents on aromatic rings produce different spectral characteristics. Based on these spectral changes that can be correlated to the extent of cure, fiber-optic fluorescence[5] and UV external reflection[6] have been developed to characterize cure in a high-temperature cure environment.

The polymers we studied so far were condensation type polymers that contain at least one component with changing functional groups as polymerization proceeds as described in the above examples. In trying to extend our approach to the vinyl poly-

merization, we are faced with different situations. Only a few vinyl monomers exhibit UV absorption and/or fluorescence in the convenient spectral range above 200 nm. Therefore, viscosity-sensitive, non-reactive extrinsic probes have been used to follow some vinyl polymerization.[7] These probes are not sensitive to conversion until it reaches more than 50%, even though Paczkowski and Necker's group recently reported on several new probes that may be more sensitive.[8] In a few monomers that exhibit favorable UV absorption and/or fluorescence characteristics, there is enough spectral change following polymerization. For example, in styrene and methyl methacrylate (MMA), the double bond is in conjugation with the side group. Upon polymerization, the conjugated double bond disappears, causing changes in UV absorption[9] and/or fluorescence spectra.[10] In fact, UV[9c] and fluorescence[10] techniques have been used to estimate residual monomer content in polystyrene. Therefore, it is expected that the UV absorption and/or fluorescence response of these monomers are more sensitive to the conversion than the nonreactive, viscosity-sensitive probes. In cases where a monomer is not absorbing or fluorescent, we can use a small amount of absorbing or fluorescent comonomer with a similar reactivity as an extrinsic sensor.

In this study, we explore these approaches in the polymerization of styrene and MMA in bulk as well as in solution using UV and fluorescence techniques. For polymerization of styrene, UV absorption and fluorescence of styrene are monitored. For MMA polymerization, UV absorption of MMA and fluorescence of a small amount of styrene as an extrinsic sensor are monitored. In addition, fiber-optic fluorescence was explored for monitoring bulk polymerization of styrene, as a potential on-line monitoring technique.

EXPERIMENTAL

Purification of Monomers and Polymers

After removing inhibitors by washing several times with 10% NaOH aqueous solution and distilled water, followed by drying over calcium chloride, styrene or MMA monomer was vacuum distilled and stored in the refrigerator until use. Any residual monomer from monodisperse polystyrene (MW of 35,000) from Polyscience Co. was removed by repeated precipitation of 10% chloroform solution in methanol, followed by drying under vacuum at 60°C for 3 days. Poly(MMA) (PMMA) from Scientific Polymer

Products (MW 93,300 with polydispersity of 2.0) was purified also by repeated precipitation of the toluene solution in methanol, followed by the same drying condition as for polystyrene.

Study of Solution Polymerization

Solution polymerizations (10% by weight in 1,2-dichloroethane) of MMA or styrene were carried out with 2% benzoyl peroxide as an initiator under dry argon, unless otherwise specified. Styrene was added to the preheated solvent containing the initiator. MMA in the solvent was heated for 15 min to the reaction temperature of 75°C, before 5 mL of the solvent with the initiator was added.

For fluorescence measurements, an aliquot of 50 μL was taken at certain time intervals and diluted to make absorbance below 0.05 for fluorescence in order to stay in a linear range of fluorescence intensity vs. concentration. For solution polymerization of styrene, the excitation wavelength was 280 nm. For solution polymerization of MMA, unlaced MMA, or MMA laced with 0.1% by weight of styrene, was studied. The excitation wavelength for the laced MMA was at 250 nm. For UV measurements, an aliquot of 50 μL was diluted to make absorbance around one.

FTIR was also used to monitor polymerization by injecting an aliquot of 50 μL from the polymerization solution into the liquid IR cell which had a fixed path length. Contribution from the solvent was subtracted from the sample spectra. For styrene, the decrease at 993 and 914 cm^{-1}, due to out of plane bending of the C=CH group, was monitored with the aromatic C=C stretching at 1495 cm^{-1} as the internal reference. For MMA, the conjugated C=C stretching at 1638 cm^{-1} was monitored, using an aliphatic CH stretching at 2845 cm^{-1} as the internal reference.

Study of Bulk Polymerization

In situ monitoring of bulk polymerization of styrene was carried out by using a fiber-optic fluorescence cable from Perkin–Elmer attached to a Perkin–Elmer LS 50 fluorescence spectrometer. Degassed styrene with 2% benzoyl peroxide was injected into the preheated sample holder with quartz windows and allowed to polymerize at 130°C for 6 h, followed by 33 h of heating at 180°C in a box to minimize background fluorescence to the optical cable. The distance between the end of the optical cable to the quartz window was 5 mm.
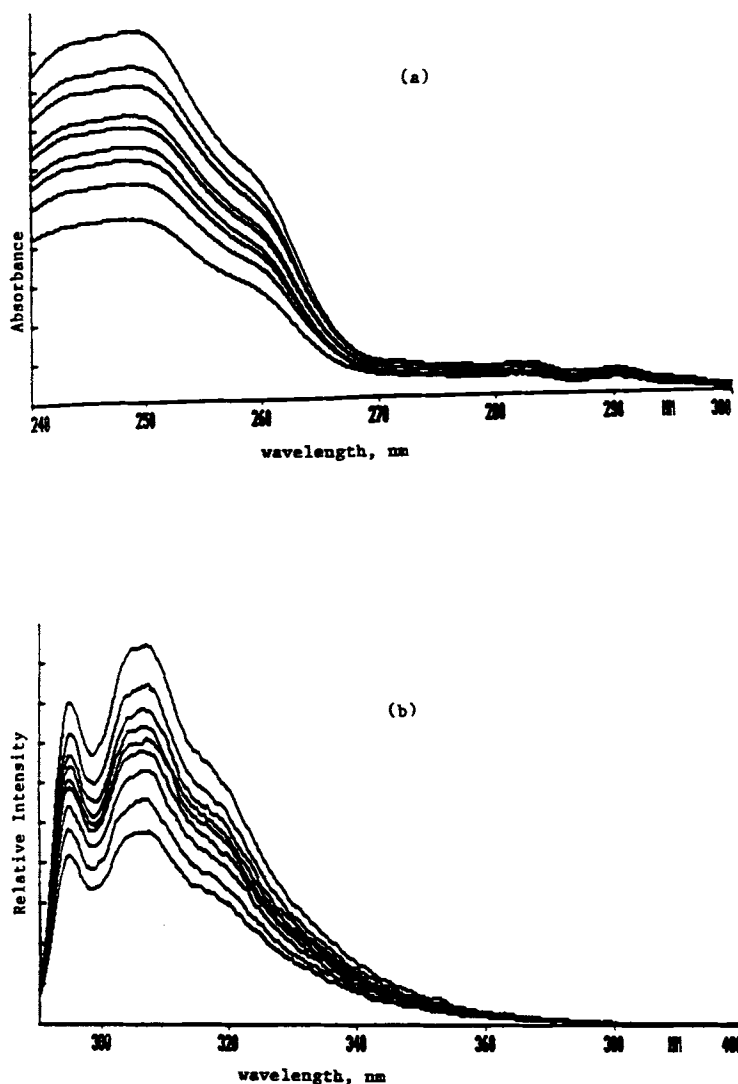
Figure 1   Changes of (a) UV and (b) emission spectra of styrene as a function of polymerization time in 1,2-dichloroethane at 75°C. Polymerization times from top to bottom, 0, 1, 2, 3, 4, 6, 8, 12, and 22 h (excitation wavelength for emission spectra was 280 nm).

RESULTS AND DISCUSSION

Solution Polymerization of Styrene

From the study of the characteristic UV and fluorescence spectra of styrene and polystyrene in 1,2-dichloroethane, the extinction coefficient of styrene at 250 nm is found to be about 100 times greater than that of polystyrene. This result is in agreement with the reported values.[9a] The fluorescence emission spectra of styrene in 1,2-dichloroethane shows double peaks at 295 and 308 nm in agreement with Basile's result,[10a] while polystyrene shows a monomeric peak at 285 nm and the excimer peak at 335 nm, as observed by others.[10b] Even though the fluorescence intensities of polystyrene peaks are a

function of the concentration and the molecular weight, they are a few hundred times weaker than that of the styrene at 308 nm. Using the spectra of styrene and polystyrene, UV and fluorescence of the mixtures of styrene and polystyrene were simulated. Because of the much larger extinction coefficient and the fluorescence quantum yield of styrene in comparison to polystyrene, the simulated spectra were dominated by the styrene spectra until the conversion reached 99.9%. Experimental results support the predictions of the simulation as shown in Figure 1(a,b) for the changes in UV spectra and fluorescence emission spectra, respectively, when styrene is polymerized in 1,2-dichloroethane at 75°C. The absorption peak at 250 nm and the emission

peak at 308 nm decreased with reaction time. The monomer conversions, obtained in proportion to the intensity due to negligible polymer contributions to the spectra, are shown in Figure 2 as a function of polymerization time, where UV and fluorescence data as well as IR based conversions are plotted at three polymerization temperatures. There is a good agreement among the results obtained by three different techniques. The initial rate obtained from the initial slope of the conversion vs. time is summarized in Table I. The activation energy of about 6 kcal/ mol was obtained, which compares favorably to about 5 kcal/mol for the case of styrene polymerization in toluene with the same amount of benzoyl peroxide.[11]

In terms of the kinetic plots for this reaction, the second-order plot seems to fit the experimental data better than the first-order plots, in accordance with the prevailing trend obtained in the case of styrene polymerization in solution.[12]

Solution Polymerization of MMA

MMA Polymerization Without an Extrinsic Sensor

MMA shows a UV peak near 220 nm in 1,2-dichlorethane with an intensity at least 20 times stronger than PMMA. Due to the absorption of 1,2-dichloroethane as the solvent at 220 nm, the extinction coefficient is difficult to quantify accurately. Nevertheless, because MMA absorbs far more strongly than PMMA, solution polymerization of MMA without any extrinsic sensor was monitored by UV and IR. Figure 3 shows the changes in UV spectra as a function of polymerization time in 10% solution polymerization of MMA in 1,2-dichloro-
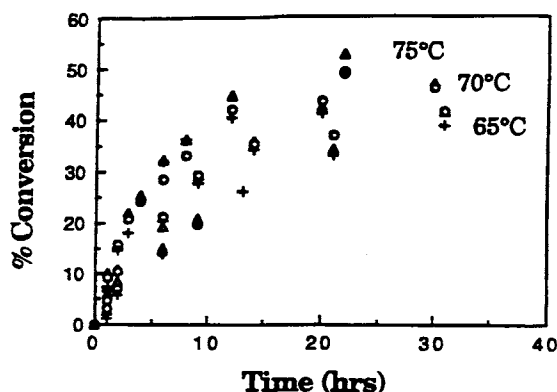
Figure 2 Percent monomer conversion of styrene polymerization in 1,2-dichloroethane at three different temperatures by (△) UV, (○) fluorescence, and (+) IR spectroscopies.

**Table I** Initial Rate of Polymerization for Solution Polymerization of Styrene in 1,2-Dichloroethane

	Temperature (°C)		
	65	70	75
Initial rate (%/h)	2.2	3.2	6.2
ΔE (kcal/mol)		5.9	

The experimental errors are < 5%.

ethane, after subtraction of the UV absorption of the solvent. The absorption peak at 220 nm decreases with time due to the much weaker absorption by PMMA. Figure 4 shows the corresponding changes in IR spectra after subtraction of solvent IR absorption. It is noted that the internal reference peak due to an aliphatic CH stretching is fairly constant at 2845 cm^{-1}, but the peak at 1638 cm^{-1} due to the vinyl group decreases sharply over polymerization time. The percent conversion of the monomer (MMA) is plotted in Figure 5 to compare the results of the IR and UV techniques. The data points represent the average of a few runs and has a maximum error of about 5%. In Figure 5, the conversion by IR is consistently greater than by UV, probably due to the errors involved in subtraction of UV absorption of the solvent.

MMA Polymerization with an Extrinsic Sensor

Because MMA does not have fluorescence, a small amount of styrene, 0.1% by weight of MMA, was added as a reactive comonomer into the polymerization mixture. Therefore, the polymerization of this system containing 0.1% benzoyl peroxide could be followed not only by UV for MMA disappearance, but also by fluorescence for styrene disappearance. The aliquots (50 μL) were diluted in 1,2-dichloroethane to obtain UV absorbance of the solution lower than 0.05 at 250 nm so that the same solution could be used for the fluorescence study. UV spectra of the solution is dominated by MMA, due to the very small concentration of styrene. They are very similar to Figure 3 corresponding to the unlaced MMA. The fluorescence emission spectra are similar to Figure 1(b) for pure styrene solution polymerization. When the percent conversion is compared by UV, fluorescence, and IR as illustrated in Figure 6, styrene conversion as tracked by fluorescence is found to be much faster than that tracked by IR and UV, which are dominated by MMA. As in unlaced MMA, we observe the underestimation of the
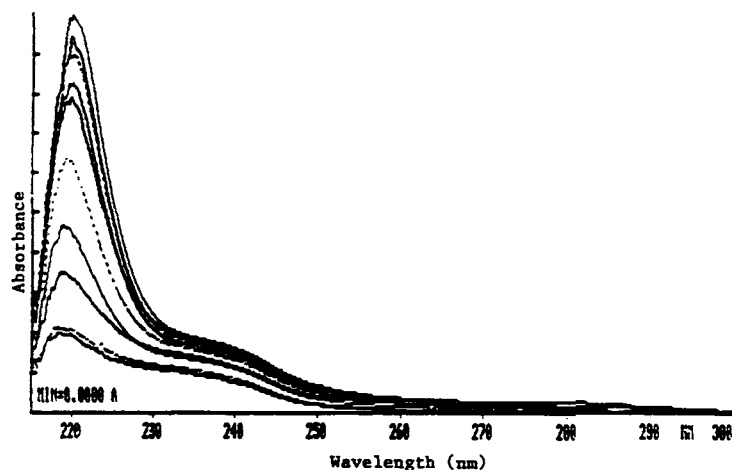
Figure 3   Change of UV spectra of MMA with polymerization at 75°C. Polymerization times from top to bottom, 0, 0.5, 1, 2, 3, 5, 8, 12, 18, and 23 h.

conversion by UV as compared to IR-based conversion. Because MMA conversion by IR seems more accurate, we can plot styrene conversion by fluorescence as a function of MMA conversion by IR. The experimental points in Figure 7 is such a plot, illustrating a higher conversion of styrene than MMA. This type of a correlation curve can be used to convert the signal from the extrinsic sensor to that of the monomer under study. The trend of faster styrene consumption, as observed experimentally in Figure 7, can be explained when one considers eq. (1) that relates the degree of overall conversion based on both monomers to changes in the feed composition during copolymerization.[13]
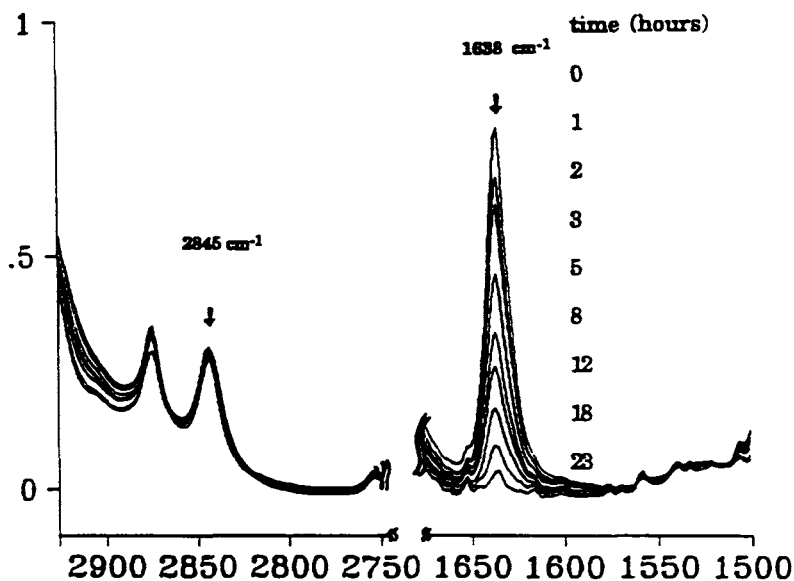
$$1 - \frac{M}{M_O} = 1 - \left[\frac{f_1}{(f_1)_O}\right]^\alpha \left[\frac{f_2}{(f_2)_O}\right]^\beta \left[\frac{(f_1)_O - \delta}{f_1 - \delta}\right]^\gamma \quad (1)$$

where

$$\alpha = \frac{r_2}{1 - r_2}, \quad \beta = \frac{r_1}{1 - r_1},$$

$$\gamma = \frac{1 - r_1 r_2}{(1 - r_1)(1 - r_2)}, \quad \delta = \frac{1 - r_2}{2 - r_1 - r_2}$$

M and M_O are the combined concentrations of two monomers at time t and the initial time. Therefore

Figure 4   Change of IR spectra of MMA with polymerization at 75°C.
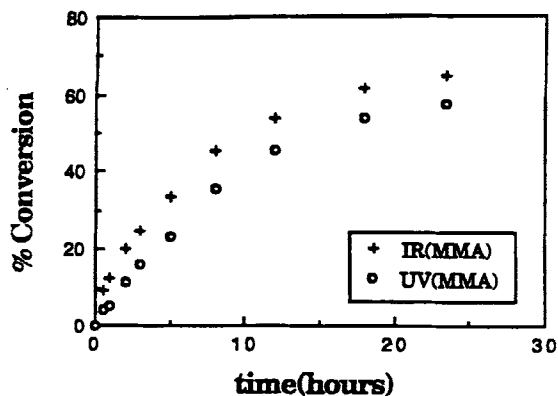
Figure 5 Percent monomer conversion of MMA polymerization at 75°C by UV and IR spectroscopies.

Figure 6 Correlation among the measurements of UV (MMA), fluorescence (styrene), and IR (MMA).

$(1 - M/M_o)$ is the overall conversion based on both monomers. The feed composition f_1 and f_2 correspond to that of MMA and styrene, respectively. The value of r_i is the ratio of the rate constant for a reactive propagating species adding to its own monomer to the rate constant adding to the comonomer. According to the literature values, r_1 for MMA is 0.46, and r_2 for styrene is 0.52.[14] From the definition, we can derive the separate expression for the conversion of MMA or styrene as eqs. (2) and (3).

$$\text{Conversion of MMA} = 1 - \frac{[M_1]_t}{[M_1]_o}$$

$$= \frac{(f_1)_o - f_1\left[1 - \left(1 - \frac{M}{M_o}\right)\right]}{(f_1)_o} \quad (2)$$

because

$$[M_1]_t = f_1\{[M_1]_t + [M_2]_t\} = f_1 M$$

$$\text{Conversion of styrene} = 1 - \frac{[M_2]_t}{[M_2]_o}$$

$$= \frac{(f_2)_o - f_1\left[1 - \left(1 - \frac{M}{M_o}\right)\right]}{(f_2)_o} . \quad (3)$$

Because styrene consumption is experimentally faster than MMA consumption, we can infer that f_1 increases with conversion. As f_1 varies from 0.9990 to 0.9999, we can calculate the overall conversion $(1 - M/M_o)$ according to eq. (1). Based on eqs. (2) and (3), we can calculate the MMA and styrene conversion as a function of overall conversion. The results
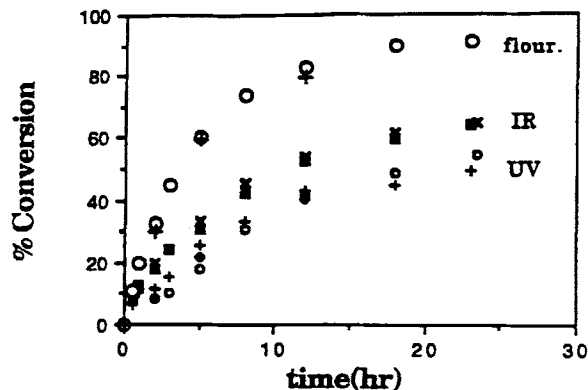
are summarized in Table II. As noted in Table II, the overall conversion goes up sharply with an increase in f_1. The values are very similar to MMA conversion, as expected. However, the styrene conversion is much faster than the other due to the particular values of r_1 and r_2. When the calculated MMA and styrene conversion are plotted in Figure 7, there is an excellent agreement with the experimental results.

Bulk Polymerization of Styrene Studied by *In Situ* Fiber-Optic Fluorescence

Bulk polymerization of styrene was studied by *in situ* monitoring of the fluorescence intensity of styrene, which is placed near the front window between two quartz plates in a heated metal block. Figure 8 shows the schematic diagram of this setup where a bifurcated fiber (diameter 0.4 cm) was used. The
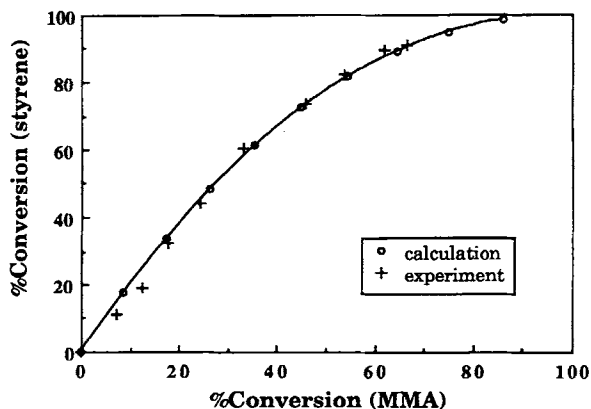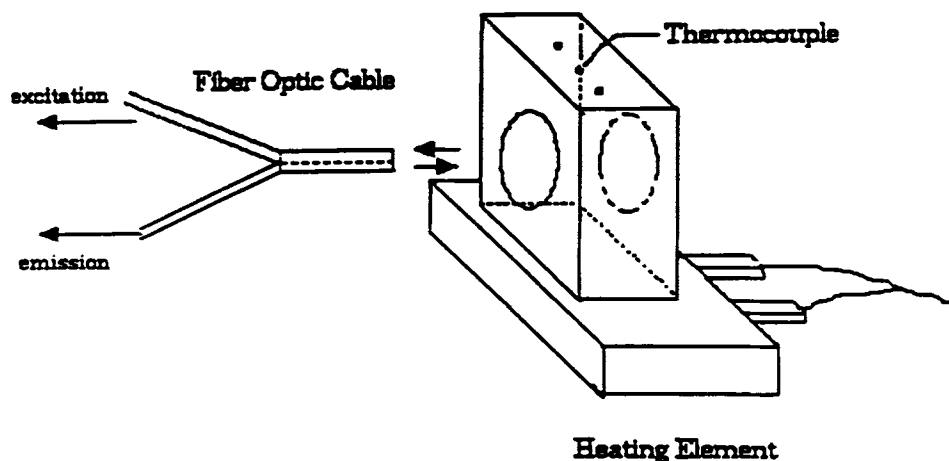

Figure 7 Comparison of experimental data and calculated data of percent conversion of styrene sensor as a function of percent conversion of MMA in styrene laced (0.1% by weight) MMA solution polymerization.

Figure 8 Schematic diagram of in situ monitoring of bulk styrene polymerization using a fluorescence fiber-optic cable.

end of the fiber has a circular cross section where one-half of the circle is connected for excitation and the other half is for the emission collection, as shown in Figure 8. The end was placed 5 mm from the quartz window.

First, the control experiment was carried out with the quartz windows subjected to the polymerization temperature without any styrene. No change in the fluorescence spectra was observed other than con-stant background intensity near 380 nm due to quartz when excited at 250 nm. The intensity near 308 nm where styrene emits was quite weak. When styrene is added, the spectra was the same as the background, because of the self-quenching of neat styrene. However, as polymerization proceeds first

at 130°C, we can observe the emission at 308 nm due to the styrene decrease. In these cases, the con-centration of styrene is small enough to show fluo-rescence. When the temperature was raised to 180°C to push the reaction to completion, the peak at 308 nm decreased partly due to the high measurement temperature and partly to the reduction in unreacted styrene monomer. The percent conversion under these polymerization conditions was determined by IR, in order to correlate with the fluorescence in-tensity due to styrene at 308 nm. Figure 9 is such a plot. Up to about 75% of reaction, little fluorescence intensity is observed due to high concentration of styrene, but it increases sharply from 75 to 85% conversion, followed by a drastic decrease during the last 15% conversion.

Table II Calculated Values of Conversions in Styrene Laced (0.1% by Wt) MMA Polymerization

f_1[a]	Conversions		
	Overall $(1 - M/M_o)$	MMA	Styrene
0.9990	0	0	0
0.9991	0.086	0.086	0.177
0.9992	0.174	0.174	0.339
0.9993	0.263	0.262	0.484
0.9994	0.354	0.354	0.612
0.9995	0.447	0.447	0.724
0.9996	0.543	0.543	0.817
0.9997	0.643	0.642	0.893
0.9998	0.747	0.747	0.949
0.9999	0.860	0.860	0.986

[a] The feed composition of MMA.
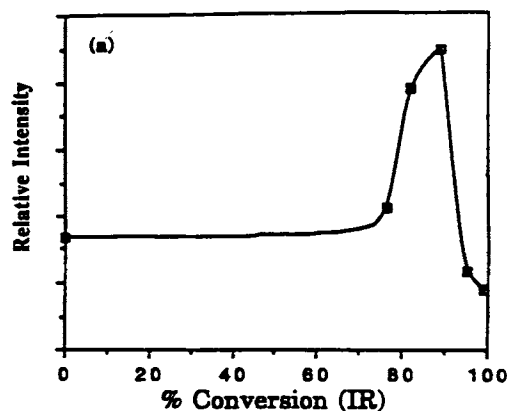
Figure 9 Correlation curve between relative emission intensity at 308 nm and percent conversion (IR) (exci-tation was at 250 nm).

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