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Visible Light Pulsed-Laser Polymerization at 532 nm Employing a Julolidine Dye Photosensitizer Initiation System

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ABSTRACT: The free-radical propagation rate coefficient of methyl methacrylate has been measured using a new version of pulsed-laser polymerization employing a visible light wavelength (532 nm) generated by a frequency-doubled Nd:YAG laser. The initiation system adopted was made up from 2,2′-bis(2-chlorophenyl)-4,4′,5,5′-tetraphenyl-1,2′-biimidazole), mercaptobenzoxazole, and 2,5-bis[(1*H*,5*H*-benzo-[*i,j*]quinolizin-1-yl)methylene]cyclopentanone. The propagation rate coefficients obtained were consistent with values recommended as benchmark values by an IUPAC working party. A series of consistency checks was performed to ensure the validity of the experimental approach. The experimental technique described in this paper extends the pulsed-laser polymerization method to a whole new range of UV-absorbing monomers that were previously inaccessible to study.

Introduction

The pulsed-laser polymerization (PLP) technique is now firmly established as the primary experimental method for evaluating propagation rate coefficients in free radical polymerization. The technique has been described in a number of papers[1,2] and has been recommended for use by an IUPAC Working Party.[3,4] The original PLP concepts were outlined by Alexandrov,[5] but the utility of the technique only became evident when Olaj and co-workers[6−8] proposed the use of size exclusion chromatography (SEC) to measure the molecular weight distributions generated in the PLP process.

Olaj *et al.*[6] formulated the extremely simple equation

$$\nu = k_p[M]t_f \qquad (1)$$

where [M] is the monomer concentration, k_p is the propagation rate coefficient, t_f is the time between laser flashes, and ν is the kinetic chain length of polymer formed between two consecutive laser pulses. Thus, by measuring the chain length of polymer formed between two successive laser pulses, it is possible to obtain a value for k_p independent of other kinetic events.

One other limitation to the technique lies in the use of a fixed UV wavelength generated by a pulsed laser. The wavelengths most commonly used are 355 nm as the third harmonic from a Nd:YAG laser, 351 nm (XeF) or 308 nm (XeCl) from an excimer laser, or 331 nm from a nitrogen laser. These wavelengths preclude a number of important monomers (e.g., *N*-vinyl carbazole and many substituted styrenes) from analysis, as the monomers themselves absorb strongly at these UV wavelengths, making the generation of primary radicals from photoinitiators inefficacious.

The two approaches that can be taken to solve this limitation are (a) the use of a photoinitiation system that operates at the second harmonic of the Nd:YAG laser, 532 nm, or (b) the use of a tunable pumped laser operating at higher wavelengths, e.g., 450 nm, together with an appropriate photoinitiator system. This paper details results obtained for the former option.

Photosensitized Initiation System

2,2′,4,4′,5,5′-Hexaarylbiimidazoles (or HABI's) have been used as photoinitiators in a number of free-radical initiated photoimaging systems.[9−11] They have reasonably strong absorption in the UV that can extend into the blue region. As 2,4,5-triphenylimidazole has the common name lophine, HABIs are sometimes called lophine dimers. HABIs are both thermochromic and photochromic and can be readily photocleaved to form a pair of lophyl radicals that can recombine within a solvent cage to form the dimer.

The lophyl radical (see Figure 1 for example) ($L^\bullet$) is known to be a poor initiator of free radical polymerization, because of both high stability and steric factors. However, the radical is an excellent hydrogen abstractor and this can be exploited in initiation by using a co-initiator compound such as a chain transfer agent to form secondary radicals ($R^\bullet$) that can initiate polymerization.

$$L_2 \xleftrightarrow{h\nu} 2L^\bullet + RH \rightarrow LH + R^\bullet$$

The design of HABI compounds for photoinitiation has been optimized to exploit this abstraction process with the synthesis of sterically hindered dimers that which yield radicals with long lifetimes. Thus dimers that are substituted in the ortho position make the most efficient photointiators.[12] The spectral response of HABIs can be extended well into the visible light region by photosensitization. Sensitisation is thought to occur[12] via a triplet−triplet energy transfer between sensitizer and initiator for certain sensitizer/HABI pairs. Suitable sensitizers[12] include xanthene or acridine dyes and normally extend the useful initiation range of HABIs to the 410−430 nm wavelength range.

In PLP the ideal situation would be to use a readily accessible pulsed-laser wavelength in the visible range, e.g., 532 nm, from a frequency-doubled Nd:YAG laser. Efficient photoinitiation at this wavelength is a considerable challenge and requires the use of a photosensitizer specifically designed to work at 532 nm for holography applications. Monroe[13] describes the use of 2,5-bis[(1*H*,5*H*-benzo[*i,j*]quinolizin-1-yl)methylene]cyclo-

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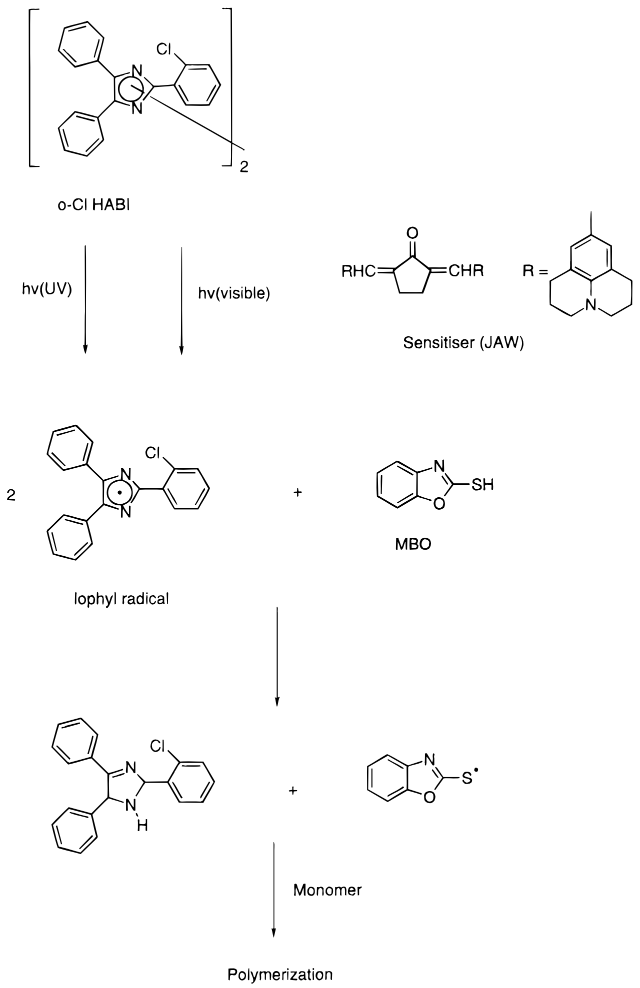

Figure 1. Reaction scheme for the initiation of polymerization by *o*-Cl-HABI and MBO. Also shown is the visible light sensitization of the reaction via JAW.

pentanone (given the abbreviation JAW as it is a julolidine derivative). Monroe clearly shows that the extinction coefficient of JAW at 532 nm is much higher than other ketone sensitisers. The proposed reaction mechanism[13] for JAW-sensitized HABI initiation is depicted in Figure 1. Upon irradiation with visible light, the ketone absorbs the laser energy and transfers this energy to the HABI. The abstraction reaction that follows between the HABI and a hydrogen donor, in this case mercaptobenzoxazole (MBO), results in a sulfur centered radical, which in turn acts as a polymerization initiator.

Experimental Section

Materials. Methyl methacrylate (Aldrich) was passed through a column of activated basic alumina, Brockmann 1 [60−150 μm] (Aldrich) and refrigerated until required. The reagents mercaptobenzoxazole (MBO) (Aldrich), 2,2′-bis(2-chlorophenyl)-4,4′,5,5′-tetraphenyl-1,2′-biimidazole (*o*-Cl-HABI) (TCI), phosphorus oxychloride (Aldrich), *N*,*N*-dimethylformamide (BDH), and julolidine (Aldrich) were used as received.

Synthesis of JAW. The dye 2,5-bis[(1*H*,5*H*-benzo[*i*,*j*]quinolizin-1-yl)methylene]cyclopentanone (JAW) was prepared according to the method described by Monroe.[13] The basic synthetic details are reproduced here for the convenience of the reader and the reaction sequence is illustrated in Figure 2.

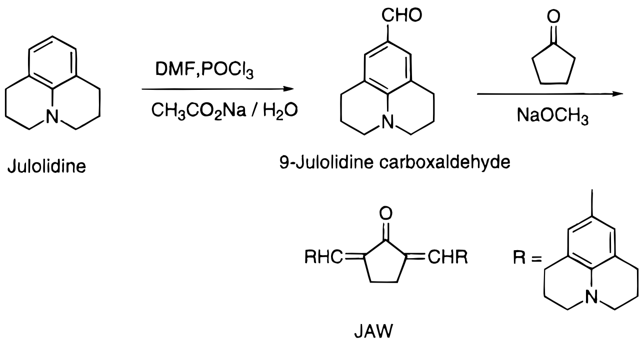

Figure 2. Synthetic scheme for the preparation of 2,5-bis[(1*H*,5*H*-benzo[*i*,*j*]quinolizin-1-yl)methylene]cyclopentanone.

Dry *N*,*N*-dimethylformamide (DMF) (23 mL, 0.28 mol) is charged to a round bottom flask fitted with a magnetic stirrer and pressure-equalizing dropping funnel. The flask is purged with dry nitrogen and cooled in a dry ice/2-propanol bath. Phosphorus oxychloride (8 mL, 0.086 mol) is then added slowly to the DMF. A solution of julolidine (9.9 g, 0.055 mol) in DMF (10 mL) is added dropwise with vigorous stirring to the mixture. Once the addition is complete, the reaction mixture is heated on a steam bath for 2 h and poured into a slurry of crushed ice and water (250 mL). The resulting solution is neutralized by the addition of a solution of sodium acetate (75 g, 0.91 mol in 125 mL of water). The precipitated aldehyde is collected by filtration and the filtrate kept at 0 °C overnight. The additional precipitate is collected and added to the first product. The combined precipitates are recrystallized from ethanol/water (with activated charcoal) to give 8.95 g (90% theoretical) of 9-julolidine carboxaldehyde as light yellow needles (mp 81−82 °C).

In the second step of the synthesis, cyclopentanone (2.85 g, 0.034 mol) and 9-julolidine carboxaldehyde (13.75 g, 0.076 mol) are added to 55 mL of methanol and stirred while sodium methoxide (0.7 g, 0.013 mol) is added over a 5 min interval. The solution is then quickly heated at reflux. Once a red solid begins to separate (usually after several minutes), the solution is allowed to stand and cool overnight. Subsequently, the reaction mixture is cooled in an ice bath and the resulting red precipitate is obtained via cold filtration. The resulting red powder is 2,5-bis[(1*H*,5*H*-benzo[*i*,*j*]quinolizin-1-yl)methylene]cyclopentanone, 27.2 g, (80% theoretical), red crystals (mp 268−278 °C).

Polymerizations. Purified monomer and initiator were charged to reaction cells (10 mm × 60 mm) and deareated by bubbling with nitrogen for 5 min, and the cells were sealed with rubber septa. All reactions were conducted at 21.8 °C with conversion of monomer to polymer maintained below 10%. Polymerization activity was terminated by precipitation of the polymer into methanol.

The experimental rig employed in these experiments was similar to the design of Davis *et al.*[14] A Spectra Physics Quanta-Ray DCR-11 pulsed Nd:YAG laser with a HG-2 harmonic generator was used to generate 355 and 532 nm laser radiation. Laser pulse energy was measured at 35 mJ/pulse with a Scientech digital power meter (model 36-5002) for both wavelengths and was directed vertically through the sensitized monomer solutions. The reaction cells were placed in a thermostated cell with a thermocouple attached to the outside wall of the cell to monitor the reaction temperature. The reaction mixtures were prepared under "dark-room" conditions and were protected from visible light with a covering of aluminum foil until just prior to exposure.

Analysis. Size Exclusion Chromatography (SEC). SEC analyses were performed on a modular system comprising a GBC Instruments LC1120 HPLC pump operating at room temperature, a SCL-10A Shimadzu autoinjector with a 99 position sample rack and variable injection loop facility, a column set, which consisted of a PL 5.0 μm bead-size guard column (50 × 7.5mm) followed by mixed bead Polymer Laboratories (PL) columns (300 × 7.5 mm, 10 μm mixed B, 2 × 5 μm mixed C and a 5 μm mixed D), and an in-line filter (0.2 μm). The data were collected using PL Data Capture Units (DCU) and analyzed using *PL Caliber* version 6.0 GPC/SEC software.[15] The eluent was THF at a flow rate of 1

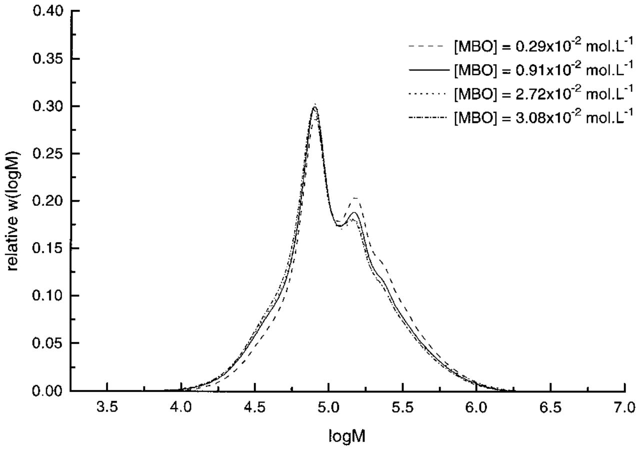

Figure 3. Effect of variation of the MBO concentration with constant *o*-Cl-HABI concentration. Laser repetition rate = 4 Hz.

mL·min^{-1}. The sample injection size was 200 μL in all cases, with data being collected at 2 points/s.

The differential refractive index detector was calibrated with a PMMA narrow polydispersity set consisting of 10 individual standards purchased from PL (1.14 × 10^3 to 1.577 × 10^6 MWT). The supplier-determined peak maxima molecular weight (M_p) was used in the generation of the calibration curves (fitted with third-order polynomials).

Data Analysis. The number molecular weight distribution was determined for each polymer via previously published transformations,[16] and the low molecular weight inflection point was identified by taking the maxima of the derivative of the distribution.

Results and Discussion

PLP Consistency Checks. A number of consistency checks have been recommended by an IUPAC working party to verify the accuracy of data generated from PLP experiments.[3,4] As this work deals with a modification to the conventional PLP experiment, it is appropriate to ensure that the novel photoinitiation systems presented here do not interfere with the k_p measurement, particularly as the initiation "mixture" includes a known chain transfer agent.

These consistency checks comprise the fulfillment of the following criteria; the propagation rate coefficient (k_p) must be invariant to laser repetition rate, initiator concentration, and laser power. The molecular weight distribution must also exhibit overtones corresponding to 2ν, 3ν, etc., and the inflection point molecular weight of these overtones are integer multiples of the primary peak inflection point molecular weight. Recently, Bergert[17] suggested a further criterion that should be added to the above, that there is no significant dark time initiation.

The experiments were conducted at 355 nm with the *o*-Cl-HABI/MBO system and then extended to 532 nm using JAW as the photosensitizer. The PLP consistency checks were made under both experimental conditions.

Homopolymerization of MMA at 355 nm. Effect of HABI and MBO. All PLP experiments in this work were conducted at 21.8 °C. The initial experiments confirmed that *o*-Cl-HABI or MBO alone do not initiate the photopolymerization of MMA at 355 nm. In contrast, various combinations of *o*-Cl-HABI and MBO were found to initiate MMA producing the characteristic PLP molecular weight distributions, as shown in Figures 3 and 4. The molecular weight distribution proved to be insensitive to low concentrations of MBO (3.0 × 10^{-3} to 3.08 × 10^{-2} mol·L^{-1}) at this laser repetition rate, indicating that chain transfer to MBO is not competitive with the propagation reaction under these reaction conditions. In addition k_p data for these and subsequent experiments suggest that the multistep initiation process *via* a stable radical species does not interfere with the PLP experiment to any reasonable extent. This may not be considered a surprising result, as Olaj *et al.*[18-20] have managed to obtain propagation rate coefficients from rotating sector-type experiments where the initiation process is also slowed compared with normal PLP. Clearly, very high concentrations of MBO may have a detrimental effect, however, this work shows that at concentrations less than 0.03 mol·L^{-1} it is possible to get chain initiation and successful PLP. The molecular weight distributions of PMMA produced at a fixed MBO level, varying the HABI concentration, are given in Figure 4. As expected, the HABI concentration does have an effect on the overall molecular weight distribution with the higher molecular weight overtones enhanced at low HABI concentrations. This is consistent with a low concentration of radicals leading to less termination at the laser flashes.

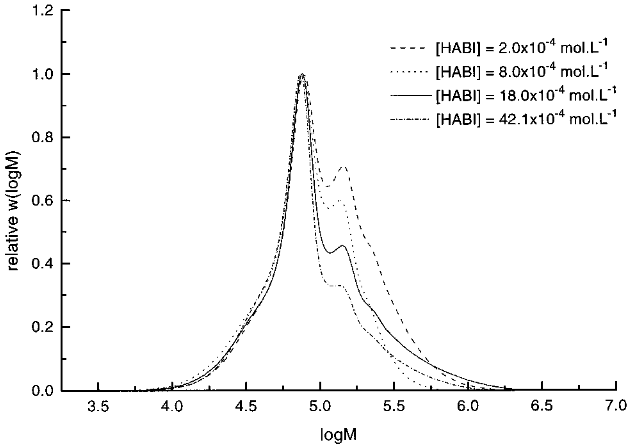

Figure 4. Variation of the *o*-Cl-HABI concentration with constant MBO concentration. Laser repetition rate = 4 Hz.

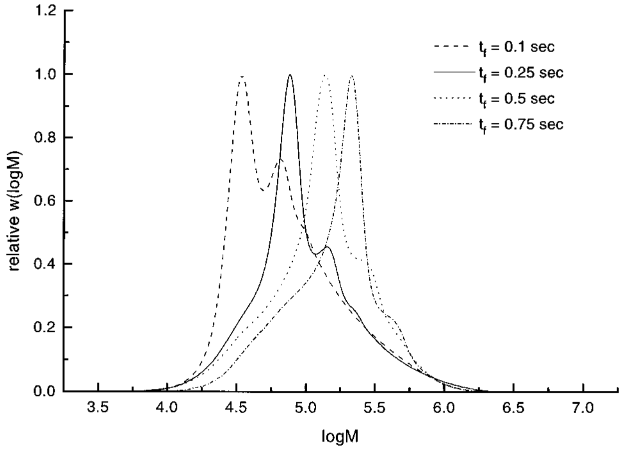

Figure 5. Variation of laser repetition rate with 1:1 *o*-Cl-HABI:MBO weight ratio.

Effect of Laser Repetition Rate. The effect of laser repetition rate was investigated using a fixed MBO:HABI ratio of 1:1. The molecular weight distributions are shown in Figure 5; from these it is clear that the pulsed laser controls the molecular weight distribution and dominates the primary chain starting and stopping processes. At the shorter pulsing times the higher molecular weight overtones become more pronounced and the secondary and tertiary peaks occur as expected.

Table 1. Propagation Rate Coefficients (k_p) of Reactions Employing *o*-Cl-HABI and MBO at 355 nm Laser Wavelength Irradiation (Molecular Weight Distribution Shown in Figures 3–5[a]

sample	10^{-4}[*o*-Cl-HABI] (mol·L^{-1})	10^{-3}[MBO] (mol·L^{-1})	t_f (s)	k_p (L·mol^{-1}·s^{-1})
1	2.44	2.88	0.25	282
2	3.66	9.09	0.25	282
3	3.68	27.27	0.25	283
4	3.83	30.84	0.25	278
5	2.00	4.35	0.25	271
6	8.00	4.76	0.25	270
7	18.69	3.91	0.25	279
8	42.66	6.74	0.25	279
9	9.25	4.03	0.1	283
10	11.67	4.21	0.5	295
11	9.98	3.11	0.75	277

[a] NOTE: all runs performed with UV laser power at 35 mJ/pulse.

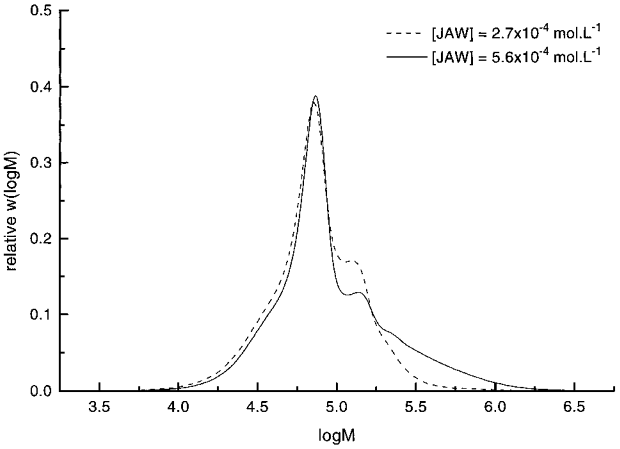

Figure 6. Visible light (532 nm) photosensitization of the polymerization of MMA with the additives *o*-Cl-HABI, MBO, and JAW with laser repetition rate at 4 Hz.

All of the propagation rate coefficients derived from the experiments at 355 nm are collated in Table 1, showing both internal consistency and concordance with IUPAC benchmark values.[3]

Homopolymerization of MMA at 532 nm. Effect of JAW. MBO and *o*-Cl-HABI do not absorb light at 532 nm and hence are incapable of undergoing a photochemical reaction at this wavelength. JAW absorbs at both 355 *and* 532 nm but does not initiate polymerization of MMA at either wavelength. The molecular weight distributions shown in Figure 6 were generated by using an initiator "mixture" of MBO, *o*-Cl-HABI, and JAW at 532 nm. There is a small influence of JAW concentration on the molecular weight distribution, which is characteristic for PLP. The propagation rate coefficients obtained from these reactions are once again consistent with accepted values,[3] as shown in Table 2.

Influence of Laser Power. The influence of laser power on the molecular weight distribution is shown in Figure 7. The results are consistent with the earlier work by Hoyle *et al.*,[21–23] and even at relatively low laser power the molecular weight distribution is characteristic of the PLP process.

Effect of Laser Repetition Rate. The influence of laser repetition rate at 532 nm is shown in Figure 8, where it is evident that the intermittent laser flash controls the shape of the molecular weight distribution. The k_p values obtained from these molecular weight distributions are given in Table 2.

Table 2. Propagation Rate Coefficients (k_p) of Reactions Employing *o*-Cl-HABI, MBO, and JAW at 532 nm Laser Wavelength Irradiation (Molecular Weight Distribution Shown in Figures 6–8[a]

sample	10^{-4}[*o*-Cl-HABI] (mol·L^{-1})	10^{-3}[MBO] (mol·L^{-1})	10^{-4}[JAW (mol·L^{-1})	t_f (s)	k_p (L·mol^{-1}·s^{-1})
12	7.91	3.61	2.75	0.25	280
13	6.58	3.04	5.65	0.25	263
14	5.20	6.81	3.79	0.25	281
15	4.91	4.11	3.58	0.25	268
16	7.66	4.92	3.52	0.25	284
17	8.43	7.03	6.41	0.1	275
18	10.55	5.28	3.99	0.5	277
19	8.58	5.98	3.01	0.75	284
20	5.42	3.62	3.69	1.0	275

[a] NOTE: all runs performed with laser power at 35mJ/pulse except runs 14–16 which were run at 25, 15, and 5 mJ/pulse, respectively.

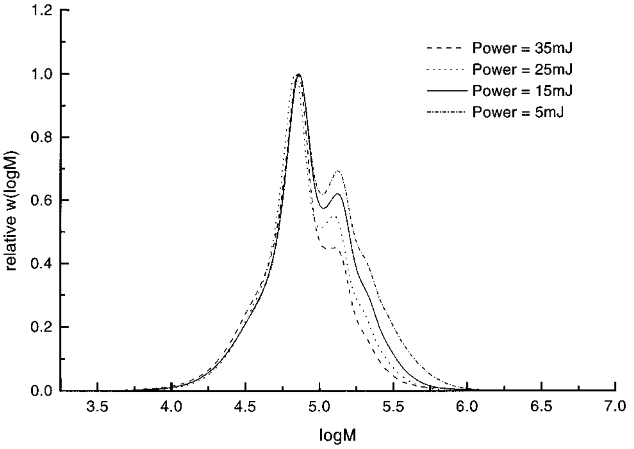

Figure 7. Variation of laser power at 532 nm on the visible light reaction of MMA at 532 nm. Laser repetition rate is 4 Hz. *o*-Cl-HABI:MBO:JAW weight ratios at 1:4:4.

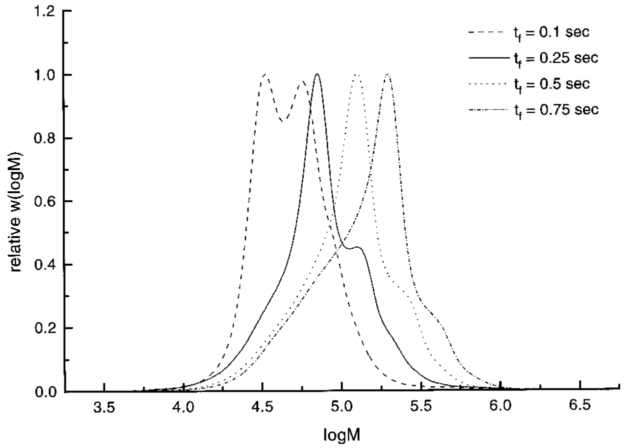

Figure 8. Variation of laser repetition rate on the reaction of MMA at 532 nm employing a *o*-Cl-HABI:MBO:JAW weight ratio of 1:4:4.

Overtones Consistency. The final criterion to be satisfied is that the inflection point molecular weight of the overtones of the molecular weight distribution are integer multiples of the primary overtone inflection point molecular weight. Displayed in Table 3 are the inflection point molecular weights for the molecular weight distributions generated in a 355 nm experiment (with the system *o*-Cl-HABI and MBO), and the photosensitized system at 532 nm (with the addition of JAW).

Conclusions

This work demonstrates the success of visible light PLP at 532 nm using a dye-sensitized system. This is

Table 3. Inflection Point Molecular Weight of Overtones for 355 and 532 nm PLP Experiments[a]

sample	laser wavelength (nm)	primary overtone MWT	first overtone MWT	first overtone multiple	second overtone MWT	second overtone multiple
6	355	68 391	142 889	2.08	217 771	3.18
18	532	62 517	122 744	1.96	195 884	3.13

[a] NOTE: MWT is molecular weight.

despite the presence of MBO, which might have been expected to interfere with the PLP process by acting as a chain transfer agent. The dye system *o*-Cl-HABI/MBO/JAW extends the utility of the PLP technique for measuring propagation rate coefficients.

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References and Notes

(1) Coote, M. L.; Zammit, M. D.; Davis, T. P. *Trends Polym. Sci.* **1996**, *6*, 189.
(2) Davis, T. P. *J. Photochem. Photobiol. A: Chem.* **1994**, *77*, 1.
(3) Beuermann, S.; Buback, M.; Davis, T. P.; Gilbert, R. G.; Hutchinson, R. A.; Olaj, O. F.; Russell, G. T.; Schweer, J.; van Herk, A. M. *Macromol. Chem. Phys.*, submitted for publication.
(4) Buback, M.; Gilbert, R. G.; Hutchinson, R. A.; Klumperman, B.; Kuchta, F.-D.; Manders, B. G.; O'Driscoll, K. F.; Schweer, J. *Macromol. Chem. Phys.* **1995**, *196*, 3267.
(5) Aleksanddrov, A. P.; Genkin, V. N.; Kitai, M. S.; Smirnova, I. M.; Sokolov, V. V. *Sov. J. Quantum Electron.* **1977**, *7*, 547.
(6) Olaj, O. F.; Bitai, I.; Hinkelmann, F. *Makromol. Chem.* **1987**, *188*, 1689.
(7) Olaj, O. F.; Bitai, I.; Gleixner, G. *Makromol. Chem.* **1985**, *186*, 2569.
(8) Olaj, O. F.; Bitai, I. *Die Angew. Makromol. Chem.* **1987**, *155*, 177.
(9) Dessauer, R.; Looney, C. *Photogr. Sci. Eng.* **1979**, *23*, 287.
(10) Tanaka, T.; Katoh, Y.; Imahashi, S.; Kajima, T.; Uhara, H. U.S. Patent 4 459 349, 1984; *Chem. Abstr.* **1983**, *98*, 90085g.
(11) Wada, M.; Fukuda, M. U.S. Patent 4 410 621, 1977; *Chem. Abstr.* **1984**, *100*, 43071z.
(12) Monroe, B. M.; Weed, G. C. *Chem. Rev.* **1993**, *93*, 435.
(13) Monroe, B. M. U.S. Patent 4 987 230, 1991; *Chem. Abstr.* **1991**, *115*, 123860f.
(14) Davis, T. P.; O'Driscoll, K. F.; Piton, M. C.; Winnik, M. A. *Macromolecules* **1989**, *22*, 2785.
(15) Polymer Laboratories, PL Caliber GPC/SEC software version 6.0, Polymer Laboratories Ltd., Essex Road, Church Stretton, Shorpshire SY6 6AX, UK.
(16) Hutchinson, R. A.; Aronson, M. T.; Richards, J. R. *Macromolecules* **1993**, *26*, 6410.
(17) Bergert, U.; Beuermann, S.; Buback, M.; Kurtz, C. H.; Russell, G. T.; Schmaltz, C. *Macromol. Rapid Commun.* **1995**, *16*, 425.
(18) Olaj, O. F.; Kremminger, P.; Schnoll-Bitai, I. *Makromol. Chem. Rapid Commun.* **1988**, *9*, 771.
(19) Olaj, O. F.; Schnoll-Bitai, I.; Kremminger, P. *Eur. Polym. J.* **1989**, *6*, 535.
(20) Zifferer, G.; Olaj, O. F. *Makromol. Chem.* **1990**, *191*, 1699.
(21) Hoyle, C. E.; Trapp, M. A.; Chang, C. H. *Polym. Mater. Sci. Eng.* **1987**, *57*, 579.
(22) Hoyle, C. E.; Trapp, M. A.; Chang, C. H. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 1609.
(23) Hoyle, C. E.; Trapp, M. A.; Chang, C. H.; Lantham, D. D.; McLaughlin, K. W. *Macromolecules* **1989**, *22*, 35.

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