

# The Effect of the Mixtures of Photoinitiators in Polymerization Efficiencies

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**ABSTRACT:** The photoinitiated polymerization of methyl methacrylate using the mixtures of camphorquinone (CQ) and acylphosphine oxides (monoacylphosphine oxide, MAPO, or bisacylphosphine oxide, BAPO) was studied to determine the possible synergistic effects. The addition of the acylphosphines to CQ resulted in an increase of the polymerization rate compared with CQ alone. On the other hand, a significant decrease of the polymerization quantum yield is observed for the mixtures compared with the pure acylphosphines. Therefore, the increase in the polymerization efficiency of the two mixtures studied, MAPO/CQ and BAPO/CQ (compared with CQ) can be traced to the larger light absorption

range, rather than to the onset of new mechanisms. The presence of the coinitiator ethyl 4-dimethylaminobenzoate, EDB, always present in CQ formulations, has no effect at all on the rates of polymerization photoinitiated by the acylphosphine oxides. From the point of view of photopolymerization quantum yields, an antagonistic effect is observed because of the energy transfer of the more efficient initiator (MAPO or BAPO) to the less efficient one (CQ). © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 129–134, 2009

**Key words:** photopolymerization; photoinitiators; mixed photoinitiators; photopolymerization synergy

## INTRODUCTION

Photoinduced polymerization is one of the most efficient processes for producing rapidly polymeric materials with well-defined properties.<sup>1</sup> During the last two decades, the fields of photopolymerization and photoimaging science and technology have grown from subjects of academic research into major industrial developments. They are now fields of central importance in polymer science and technology. Inherent to these technologies is the use of a photoactivator system, which is capable of absorbing the incident UV, and/or visible, radiation used for converting monomers or prepolymer systems into linear polymers or crosslinked networks.<sup>2</sup>

With the steady growth of the UV-radiation curing technology in manifold applications, a large variety of photoinitiators has been developed to meet efficiently the requirements inherent to these techni-

ques. Among the radical-type photoinitiators currently used in UV-curable systems, acylphosphine oxides were found to give superior overall performance.<sup>3</sup>

In recent years, many works have dealt with the simultaneous use of two or more photoinitiators in photopolymerizable formulations used in several applications, especially in dentistry. In many cases, an increase of the polymerization efficiency was observed, and this effect was defined as synergy, as the conversion rates were found to be larger than those observed when using the individual initiators separately.

Acylphosphine oxides are a class of photoinitiator, which include three basic compounds: monoacylphosphine oxides (MAPO), bisacylphosphine oxides (BAPO), and trisacylphosphine oxides (TAPO).<sup>4,5</sup> These compounds undergo fast  $\alpha$  cleavage of the benzoyl-phosphinoyl bond upon irradiation, producing a pair of radicals.<sup>6,7</sup> Because of this property, they have been reported as efficient photoinitiators for radical polymerization of vinyl compounds (acrylates, epoxy resins, unsaturated polyesters, etc). Beyond the wide variety of applications<sup>8,9</sup> of these photoinitiators, included in formulations for inks, coatings, and dental materials, they offer many advantages, including high radical producing efficiency, photobleaching, and stability, which make them especially useful in pigmented and thick-layered systems.<sup>10</sup>

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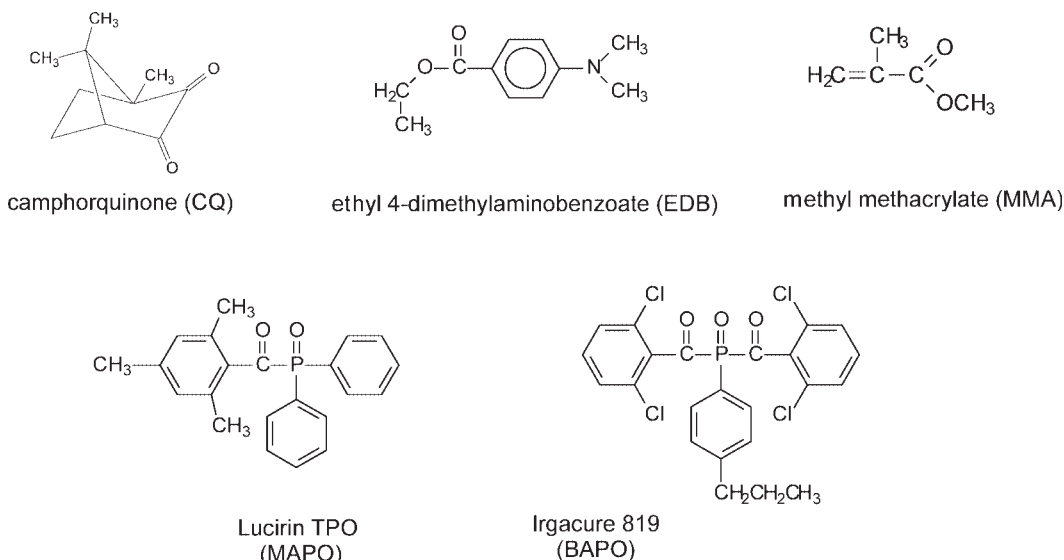
Camphorquinone (CQ) is the most widely used photosensitizer for visible light curing of dental resins,<sup>11</sup> although it presents some drawbacks like low polymerization efficiency, toxicity, and yellowing because of the need of an amine-derived coinitiator. The low polymerization efficiency of CQ results in low mechanical properties of resin composites as well as possible toxic effects to the human body from residual monomers.

In this work, we investigated the simultaneous use of CQ with acylphosphine oxides, to evaluate a possible increase in the polymerization efficiency as well as the eventual mechanisms that would lead to these effects.

## EXPERIMENTAL

### Materials

The monomer, methyl methacrylate (Aldrich) was distilled from ice bath at reduced pressure in the presence of hydroquinone, washed with 5% NaOH in water, and dried over CaCl<sub>2</sub>. The acylphosphine initiators, monoacylphosphine oxide (Lucirin TPO, MAPO) and biacylphosphine oxide (Irgacure 819, BAPO) were from BASF and CIBA-Geigy, respectively. Camphorquinone (CQ) and ethyl 4-dimethylaminobenzoate (EDB) were purchased from Aldrich. They all were used without further purification.



### Photopolymerization procedure

The kinetics of the light-induced polymerization of MMA (pure monomer, ~ 9M) in the presence of photoinitiators systems (CQ-EDB, MAPO, BAPO, and acylphosphine-CQ/EDB) was followed in a dilatometer.<sup>12,13</sup> The solutions were thoroughly deoxygenated by bubbling oxygen-free nitrogen for 40 min. The dilatometer consisted of two capillaries (internal diameter 0.18 cm) attached to a cylindrical reaction vessel (internal diameter 2.2 cm, volume 8.5 mL), which placed in a constant temperature bath (25°C) in front of the irradiation source. The reaction cell was placed in front of a 200 W Hg (Xe) lamp in an Oriel Universal Arc Lamp source. A 395 nm cutoff filter was placed between the lamp and the reaction cell to eliminate the UV-radiation.

Polymerization rates ( $R_p$ ) were calculated using eq. (1)<sup>14</sup>

$$R_p = \frac{\Delta V}{F \cdot f \cdot t} [\text{MMA}] \text{ (M/s)} \quad (1)$$

where  $\Delta V$  is the volume contraction in the capillary (measured with a cathetometer) at time  $t$ ,  $f$  the volume fraction of monomer MMA in the solution,  $F$  the volume contraction related to the densities of polymer and monomer solution,  $F = [(d_p - d_m)/d_p]$ , and  $d_p$  and  $d_m$  being the densities of the polymer and the monomer, respectively.

Actinometry was performed using the ferrioxalate/phenanthroline sensitizer. As the quantum efficiency of this actinometer ( $\phi$ ) depends on the irradiating wavelength, appropriate  $\phi$ -values were used for different wavelength ranges, i.e., 400–436 nm ( $\phi = 1.00$ ), 437–468 nm ( $\phi = 0.85$ ), 469–500 nm ( $\phi = 0.58$ ).<sup>15</sup>

Polymerization quantum yields ( $\Phi_p$ ) were calculated using

$$\Phi_p = \frac{R_p}{n_T} \quad (2)$$

where  $n_T$  is the photon flow in Einstein/s.

### Photochemical measurements

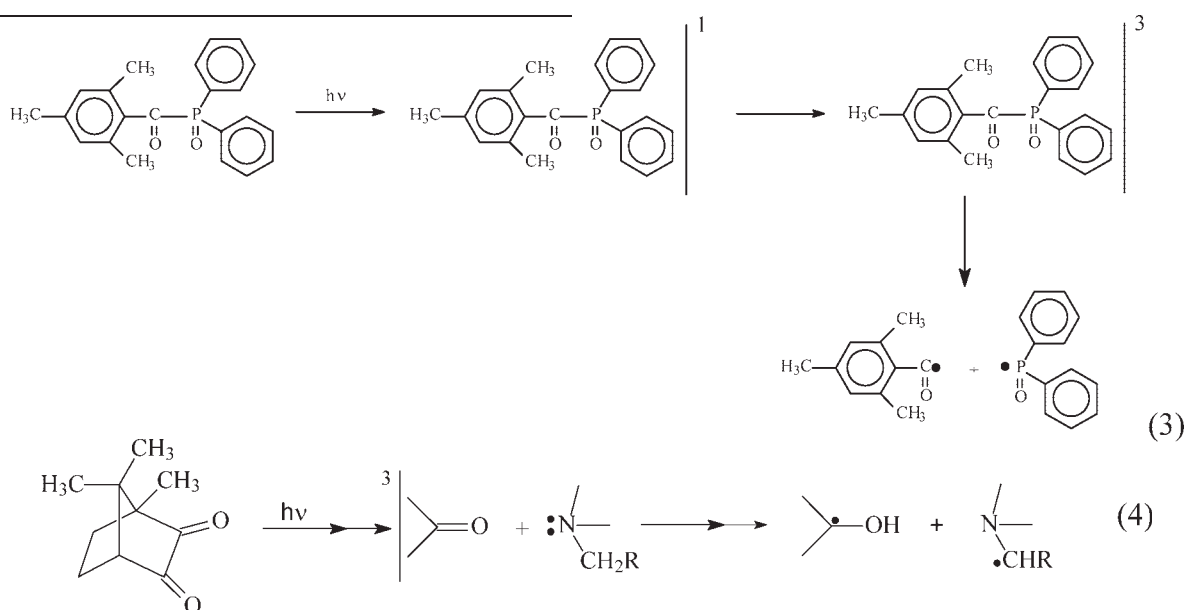
Static fluorescence quenching experiments were carried out at room temperature using a Hitachi F-4500 spectrofluorimeter on air-equilibrated solutions. MAPO and BAPO were excited at 380 and 370 nm, respectively, and their emission was determined at the maximum of the emission peaks, i.e., 430 and 465 nm. Absorption spectra were measured on a Hitachi U-2000 spectrophotometer.

The fluorescence lifetime of BAPO was measured using the single-photon timing technique on a CD-

9000 Edinburgh spectrometer, operating with a Ti:Sapphire laser, at room temperature ( $25^\circ\text{C} \pm 1^\circ\text{C}$ ). The excitation wavelength was 395 nm and the emission was monitored at 474 nm.

### RESULTS AND DISCUSSION

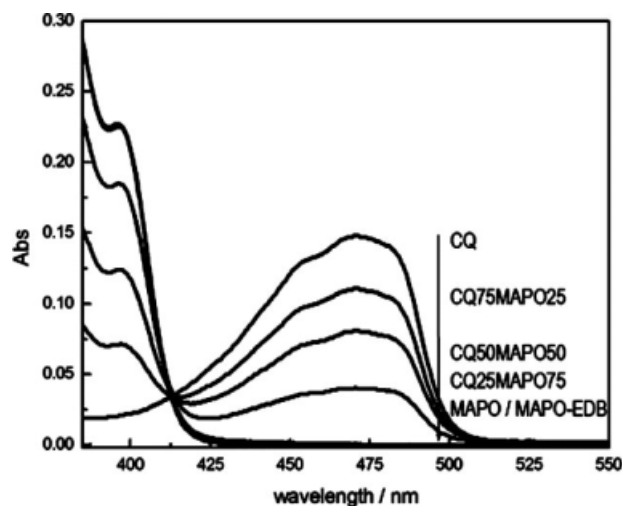
To evaluate the efficiency, and possible synergistic effects, in photopolymerization initiated by mixtures of two, or more, photoinitiators, it is necessary to know the  $R_p$  and the polymerization quantum yields of the systems.<sup>12</sup> It is well known that the radical producing mechanisms are different for both types of initiators. Although acylphosphines produce radicals via the photocleavage of a very short-lived triplet state [eq. (3)],<sup>9,16,17</sup> the mechanism for CQ involves the interaction of a longer lived triplet with a coinitiator, usually a substituted amine [eq. (4)].<sup>18,19</sup>



In the case of the simultaneous use of CQ and MAPO, the absorption spectra of the polymerization formulations used are shown in Figure 1. It can be seen easily that there is no effect on the absorption spectrum when the coinitiator EDB is added to MAPO. On the other hand, there is a gradual decrease of the CQ absorption around 470 nm when the acylphosphine initiator is added, simultaneous to the increase in the absorption in the blue region below 420 nm. An isosbestic point is observed at 415 nm.

The photopolymerization kinetics of MMA in the presence of the initiator systems was measured by

dilatometry, and the results are shown in Figure 2. The values for the rate constants are listed in Table I, together with the composition of the initiator systems and the polymerization quantum yields. It can be easily seen from the Figure that there is practically no change in the photopolymerization rate when the coinitiator EDB is added to the MAPO formulation. The presence of increasing concentrations of CQ lowers gradually the rate constant. On the other hand, the amount of absorbed photons varies with the proportion of CQ in the photoinitiator mixture because of the changes in the absorption spectra.



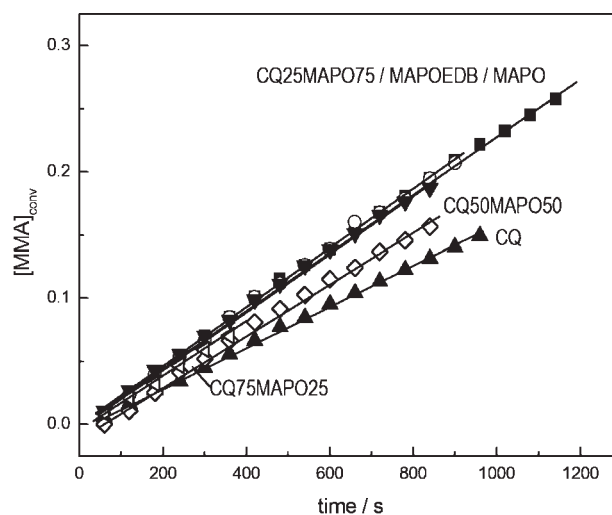
**Figure 1** Absorption spectra of MAPO and CQ alone and their mixtures.

The combination of both factors, i.e., the lowering of the rate and the increase in the flux of absorbed photons, results in different polymerization quantum yields, also shown in Table I.

Similar results were obtained for the BAPO/CQ system, which is shown in Figures 3 and 4, with the results listed in Table II.

It is interesting to notice that in both cases the quantum yields for the polymerization initiated by the mixture of the dyes are lower than that found for the systems in which the acylphosphines are used alone. At the same time they are higher than the quantum yields for CQ alone. The higher efficiency for the MAPO- or BAPO-initiated polymerization compared with CQ is expected from results of previous investigations.<sup>12</sup> The main point, which has to be determined, in terms of an eventual synergy, is if the efficiency of systems involving two initiators is higher than that found for the initiators used individually.

Assuming that both dyes initiate separately, and that the quantum yield of the mixture can be obtained from the individual contributions, the theoretical quantum yield obtained for the mixture should be



**Figure 2** Photopolymerization kinetics of MMA in the presence of MAPO and CQ alone and their mixtures.

$$\Phi_M = X_P \times \Phi_P + X_{CQ} \times \Phi_{CQ} \quad (5)$$

where  $\Phi_M$  is the ideal quantum yield for the photopolymerization initiated by the mixture, and  $\Phi_P$  and  $\Phi_{CQ}$  are the quantum yields for the photopolymerization initiated by the acylphosphine and CQ, respectively.  $X_P$  and  $X_{CQ}$  are the molar fractions of the acylphosphine initiators and CQ. The quantum yields calculated using eq. (1) are shown in Table III, and compared with the experimental ones. As can be seen, in all cases, the experimental quantum yield is lower than the calculated one, suggesting that instead of a cooperative synergic effect there may be an antagonistic effect.

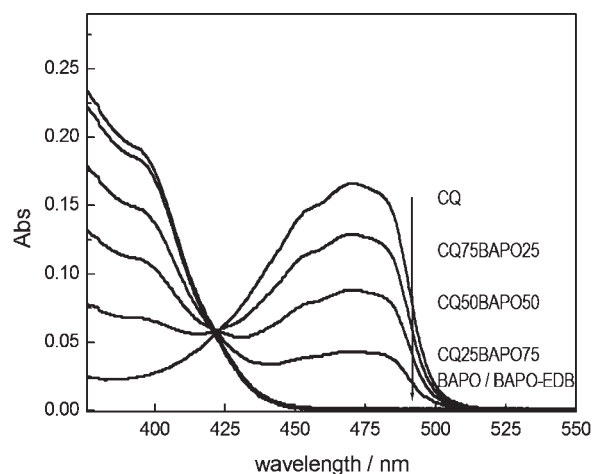
In this sense, an energy transfer from the more efficient dye to the less efficient one can be suggested



Toward this end, a study of the quenching of the excited states of both acylphosphines by CQ was undertaken. The corresponding Stern–Volmer plots are shown in Figure 5. As can be seen from the plots, CQ quenches efficiently the fluorescence of

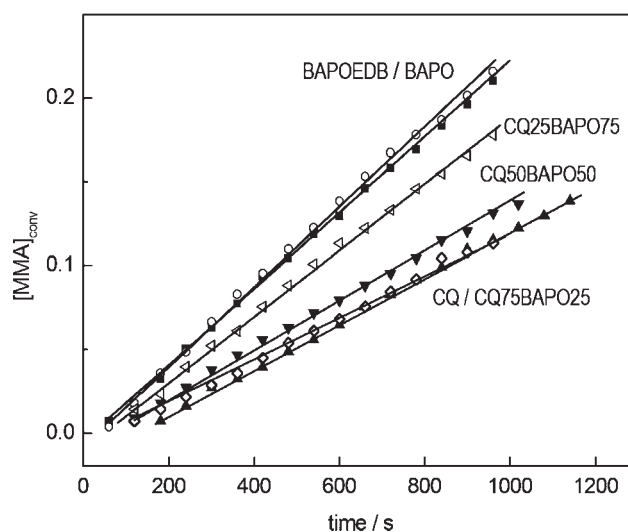
**TABLE I**  
Photopolymerization Rates, Photon Flux, and Polymerization Quantum Yields for the Polymerization of MMA Photoinitiated by CQ and MAPO Alone, and Their Mixtures

	[MAPO] 10 <sup>-4</sup> M	[CQ] 10 <sup>-3</sup> M	[EDB] 10 <sup>-2</sup> M	$R_p$ 10 <sup>-4</sup> M s <sup>-1</sup>	Photon flux 10 <sup>-7</sup> Einstein L <sup>-1</sup> s <sup>-1</sup>	$\Phi_{pol}$ M/ Einstein
MP	5.00	–	–	2.34	0.71	3,300
MP + EDB	5.00	–	3.00	2.36	0.72	3,300
CQ + EDB	–	5.00	3.00	1.60	3.30	480
CQ25MP75	3.75	1.25	3.00	2.27	1.50	1,500
CQ50MP50	2.50	2.50	3.00	2.03	2.20	940
CQ75MP25	1.25	3.75	3.00	2.07	2.65	780



**Figure 3** Absorption spectra of BAPO and CQ alone and their mixtures.

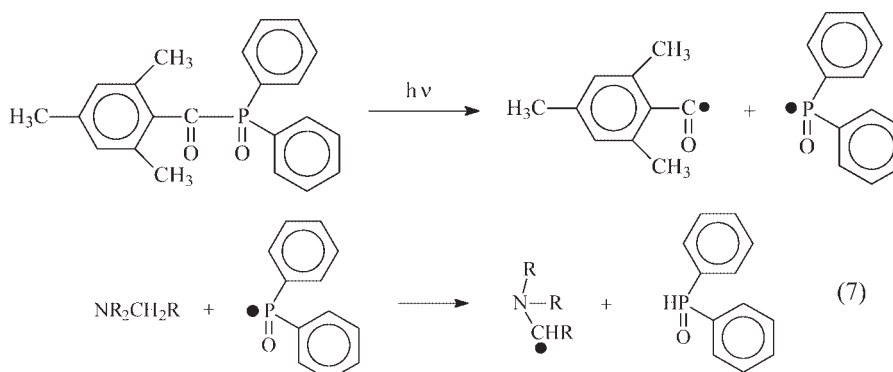
excited MAPO and BAPO, reducing the amount of the initiating process by those dyes. The Stern-Volmer constants are 65.5 and 70  $M^{-1}$ , respectively, for MAPO and BAPO. The singlet state lifetime of BAPO, determined by single photon counting, is 0.34 ns. Using this value together with the Stern-Volmer constant, the quenching rate constant is found to be  $2.1 \times 10^{11} M^{-1} s^{-1}$ . This high rate is above the diffusional limit and suggests Förster type energy transfer mechanism, compatible with the



**Figure 4** Photopolymerization kinetics of MMA in the presence of BAPO and CQ alone and their mixtures.

large overlap of the emission spectrum of the donor and the absorption spectrum of acceptor.<sup>20</sup>

On the other hand, experiments performed using the acylphosphines in the presence of EDB (which is a constant component in CQ formulations) show that there is no additional reaction between the excited acylphosphines and the amine nor between the phosphine radicals and the amine, as could be the case shown in eq. (7). These reactions would lead to the formation of more efficient amine-centered initiating radicals.



**TABLE II**  
Photopolymerization Rates, Photon Flux, and Polymerization Quantum Yields for the Polymerization of MMA Photoinitiated by CQ and BAPO Alone, and Their Mixtures

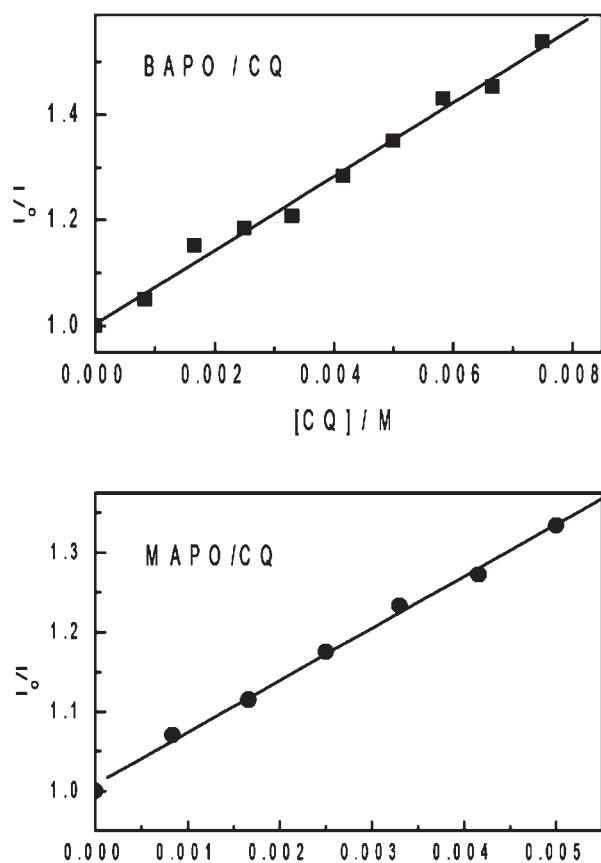
	[BAPO] $10^{-4} M$	[CQ] $10^{-3} M$	[EDB] $10^{-2} M$	$R_p$ $10^{-4} M s^{-1}$	Photon flux $10^{-7}$ Einstein $L^{-1} s^{-1}$	$\Phi_{pol} M/$ Einstein
BP	3.00	–	–	2.27	0.86	2,650
BPE + DB	3.00	–	3.00	2.35	0.91	2,600
CQ + EDB	–	5.00	3.00	1.40	2.77	500
CQ25BP75	2.25	1.25	3.00	1.95	1.92	1,010
CQ50BP50	1.50	2.50	3.00	1.42	1.40	1,020
CQ75BP25	0.75	3.75	3.00	1.32	2.40	550

**TABLE III**  
**Experimental and Calculated Polymerization Quantum Yields for the Polymerization of MMA Photoinitiated by CQ and MAPO and BAPO Alone, and Their Mixtures**

Initiator	$\Phi_{\text{pol}}$ (exptl) M/Einstein	$\Phi_{\text{pol}}$ (calc) M/Einstein
CQ	480	–
MP	3,300	–
CQ25MP75	1,500	2,600
CQ50MP50	940	1,900
CQ75MP25	780	1,200
BP	2,650	–
CQ25BP75	1,010	2,100
CQ50BP50	1,020	1,575
CQ75BP25	550	1,040

### CONCLUSIONS

The use of a mixture of photoinitiators (CQ with acylphosphine oxides (either MAPO or BAPO) was



**Figure 5** Quenching of MAPO and BAPO fluorescence by CQ.  $\lambda_{\text{exc}}$  380 and 370 nm, and  $\lambda_{\text{em}}$  430 and 465 nm, respectively.

evaluated to determine the possible synergistic effects. The observed increase in the polymerization efficiency when using a mixture of the dyes is due to the broadening of the absorption spectrum, so that more photons are absorbed.

On the other hand, there is no increase in the photopolymerization quantum yields, but rather a decrease when using the mixtures, indicating an antagonism instead of synergistic effect. This is due to energy transfer from the more efficient initiators (MAPO or BAPO) to the less efficient (CQ). Additionally, there were no indications that the presence of the coinitiator EDB does interact with the radicals originated from acylphosphine oxides.

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