

# 1-heptene, 3-heptenes and cumene as model compounds of SBS block copolymers. Study of their photoreactions in the presence of photoinitiators of polymerization

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## Abstract

The photoreactions of 1-heptene, 3-heptene and cumene in the presence of unimolecular and bimolecular reaction photoinitiators (1,1-dimethoxy-1-phenyl-acetophenone, DMPA, and benzophenone, BP) has been investigated. Quantum yields of the reactions and identification of the photoreaction products has permitted to elucidate the steps and the mechanism of the mentioned photoreactions. This helps to know the reactions which take place in more complicated systems, such is the case of the photopolymerization of acrylic monomers in SBS block copolymer matrices, of which these compounds could serve as models.

For heptene derivatives, the photoreaction in the presence of BP takes place through direct abstraction of an allylic hydrogen atom, and in minor extension, of other hydrogen atoms of the heptene aliphatic chain. As the main form of termination, the heptenyl and the ketyl radicals formed coupled inside the solvent cage. Photoreaction in the presence of DMPA occurs by direct attack of the radicals formed from the initiator ( $\text{PhCO}^\bullet$ ,  $\text{Ph}(\text{MeO})_2\text{C}^\bullet$ , and  $\text{CH}_3^\bullet$ ) to the heptene double bond. When this double bond is terminal oligomerization occurs.

For cumene, the photoreaction takes place through direct abstraction of the benzylic hydrogen atom in both cases. © 1997 Elsevier Science S.A. All rights reserved.

*Keywords:* Photoinitiators; Photoreduction; Photofragmentation; Binder model compounds; SBS matrices; Radical addition

## 1. Introduction

The photopolymerization reaction of acrylic monomers in a polymer medium have been successfully employed for industrial applications since the mid 1950s, especially in circuit boards and printing plates, given the advantages it has over conventional techniques (speed, economy, ecological care, etc). In both fields, a photoinitiator, a monomer and an oligomer or prepolymer are formulated together other ingredients (binder and additives) to form the film or plate which will be irradiated. Those elements not strictly polymerizable have the purpose of improving the final properties of the material [1].

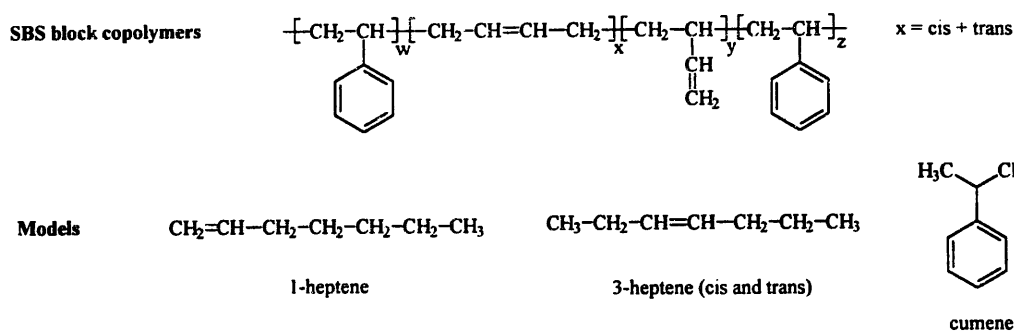
Some authors have recently investigated the polymerization of acrylic monomers in polymer matrices [2], but little work has been devoted to clarify the exact role of the binder in the polymerization process when employed in commercial formulations. The term "binder" is currently used as oppo-

site to "reactive diluents", which usually designs monomers and oligomers, i.e. functional groups which undergo reaction (polymerization) when the formulation is irradiated. Nevertheless, and given that the final product is a whole crosslinked material, the photopolymerization should affect the binder to some extent, being grafted to the crosslinked acrylic polymer or forming a semi-interpenetrated crosslinked polymer system.

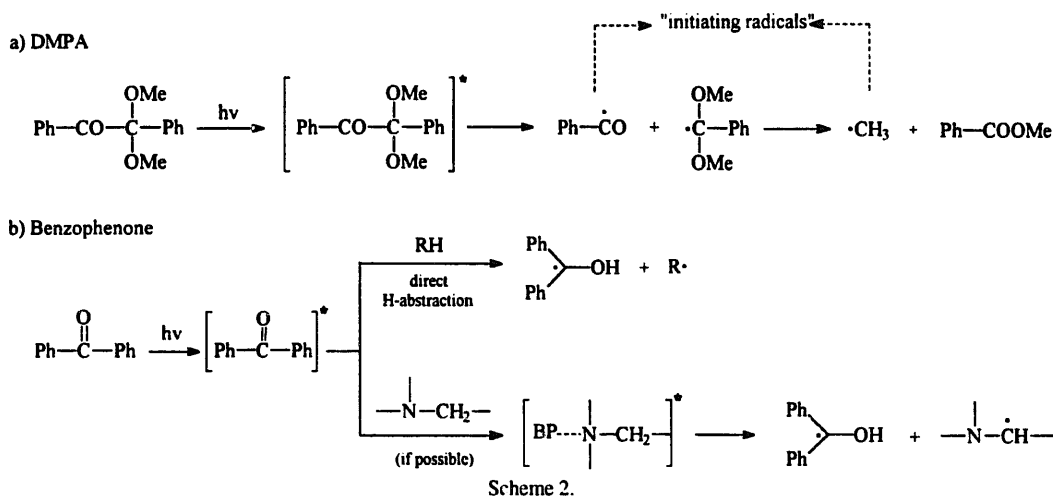
In the well-developed industry of printing plates, the binders are polymers which basically give dimensional stability to the plates before and after irradiation, and provide them with the appropriate properties of stiffness, abrasion resistance, hardness, etc., when employed in their final application. Many of these binders are rubber-like polymers, with structures of styrene-butadiene-styrene (SBS) sequences (blocks). The remaining double bond of the butadiene moiety is generally a mixture of *cis*-, *trans*- and vinyl structures (Scheme 1).

An essential component of photocurable compositions is the photoinitiating system, whose function is to absorb the light and to generate free radicals which then initiate the

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Scheme 1.



Scheme 2.

polymerization. The most used photoinitiators for commercial applications are those belonging to the family of aromatic ketones. Within this group, two main sub-families can be distinguished: photofragmenting and bimolecular-reaction photoinitiators. Benzoin derivatives (especially DMPA), and benzophenone are, respectively, the most representative of each sub-group, and their photochemical behaviour has been extensively studied, both in the absence [3] and in the presence [4] of monomers.

The primary photochemical reaction of both photoinitiators is shown in Scheme 2.

In this paper, we present a study of the photochemical reaction in the presence of two commercial photoinitiators (benzophenone and 1,1-dimethoxy-1-phenyl acetophenone) of some *n*-heptenes and cumene, which have been taken as models of the chemical structure of the most used binders in the industry of printing plates (Scheme 1). The analysis of the products obtained and, consequently, the elucidation of the photoreaction mechanism constitutes the principal objective of this work and will give a better insight of the role played by the elastomeric binder in printing plate formulations. This will help the design of systems in which polymerization takes place in solid matrices.

## 2. Experimental

### 2.1. Materials

Benzophenone (BP, from Aldrich) was recrystallized twice from *n*-hexane. 1,1-dimethoxy-1-phenyl acetophenone (DMPA, from Ciba-Geigy), cumene, 1-, 3-*cis*- and 3-*trans*-heptene (all from Aldrich) and cyclohexane (CHX, spectroscopic grade from Fluka) were used as received.

### 2.2. Quantum yield determination

Solutions of  $\approx 10^{-2}$  M of BP or DMPA in neat models were irradiated with a 500 W Hg medium-pressure lamp at 334 nm and the photoreaction followed by UV-VIS spectroscopy (Shimadzu UV-265FS) as described previously [5]. BP solutions were always degassed by bubbling  $\text{N}_2$ ; DMPA irradiations were done in air.

### 2.3. Semipreparative irradiations

Solutions of BP (under nitrogen) and DMPA (in air) in the corresponding model compound were irradiated with a

900 W Xe lamp filtering wavelengths below 320 nm, and directly injected in the gas chromatography–mass spectrometry (GC–MS) system. Identification of products was made by their mass fragmentation and, in the case of pinacol, by comparison with an authentic sample.

#### 2.4. GC–MS experiments

GC–MS experiments were carried out using an HP-5890 gas chromatograph coupled to an HP-5971A mass detector (Hewlett Packard, Palo Alto, CA, USA). A laboratory-made fused-silica capillary column (column SE-54; 25 m × 0.25 mm × 0.3 μm) with OV-1 as stationary phase, was kept at 70 °C for 6 min and then programmed from 70 to 240 °C at 6 °C min<sup>-1</sup>. Helium was used as the carrier gas. Slightly differences in retention times for photoproducts are due to a change in columns during experimental work.

Aberchrome 540 was used as actinometer and employed as usual.

### 3. Results and discussion

#### 3.1. Quantum yields of photoreaction in the model systems

##### 3.1.1. Benzophenone

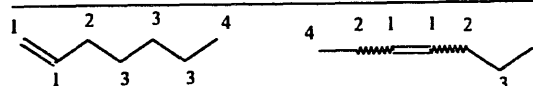
The photoreaction of *n*-heptenes and cumene in the presence of BP took place in similar manner to that of cyclohexane, which was used as reference for the process of direct benzophenone triplet photoreduction [6] (Scheme 2(b)). This indicates that BP photoreduces efficiently in these media

Table 1  
Quantum yields of BP photoreduction and DMPA photofragmentation

Solvent	$\phi_{\text{red}}(\text{BP})$	$\phi_{\text{frag}}(\text{DMPA})$
cyclohexane	0.47	0.76
1-heptene	0.29	0.77
c-3-heptene	0.24	0.51
t-3-heptene	0.26	0.47
cumene	0.44	0.89

Table 2  
Calculated relative rates of hydrogen abstraction from *n*-heptenes and cyclohexane by benzophenone triplet

Position	Character of C–H equiv	$K_r(\text{rel})$	$\nu_{\text{rel}}(1\text{-heptene})$	$\nu_{\text{rel}}(3\text{-heptene})$	$\nu_{\text{rel}}(\text{C}_6\text{H}_{12})$
1	Aromatic	0.016	0.048 (3H)	0.032 (2H)	–
2	Allylic	74	148 (2H)	296 (4H)	–
3	Secondary	40	240 (6H)	80 (2H)	480 (12H)
4	Primary	1	3 (3H)	6 (6H)	–
$\nu_{\text{tot}} = \nu \sum \nu_{\text{rel}}$			391	382	480



and the photoproducts seem to be similar to those in CHX. Quantum yields of BP photoreduction are listed in Table 1.

As can be seen, quantum yields are almost identical in the three *n*-heptenes investigated, and are some lower than the value found in CHX. These differences are those expected and follow the same order as the theoretical relative rates of photoreduction, which have been calculated using the values of the relative kinetic constants for hydrogen abstraction by a BP triplet published by Giering et al. [7] (Table 2).

Although the results of this calculation are in agreement with the experimental values, some assumptions have been made:  $k_{\text{red}}$  of allylic C–H has been taken as the value given for a benzylic C–H, as it has been assumed they have a similar reactivity towards a BP triplet, and  $k_{\text{red}}$  for the different secondary positions have been taken as the same, whereas Winik et al. have shown that the *n*-alkyl positions are not exactly equivalent towards photoreduction of BP, the C<sub>*n*-2</sub> site being the preferred position for reaction [8].

From Table 2 can be seen that the overall rate of photoreduction of 1-, 3-*cis*- and 3-*trans*-heptene should be the same, but 3-heptenes will probably react mainly through allylic positions, whereas 1-heptene could have more dispersion in the positions of the hydrogen abstracted. Hydrogens from the double bond (assuming for them the value of  $k_{\text{red}}$  for aromatic C–H) should not react.

The photoreactor quantum yield in cumene is high as expected, and the value is of the same order of magnitude as that in CHX, indicating a good character as hydrogen donor.

##### 3.1.2. DMPA

Photofragmenting quantum yields of DMPA in the model compounds are shown in Table 1. The values are high, that in 1-heptene being equal than in CHX. The values in the 3-heptenes are slightly lower, and, given that the reaction produced is unimolecular (fragmentation), the differences should be related to in-cage recombination of the radicals formed. This will be explained in the next section.

#### 3.2. Photoreaction analysis and mechanism

##### 3.2.1. Benzophenone

Solutions of the models in the presence of BP were irradiated for 2 h in a 900 W Xe lamp and injected directly in the GC–MS system. The crude product of reaction showed some

Table 3  
Results of the photoreaction of the model compounds in the presence of BP

Substrate	Products	$t_{ret}$	Yield <sup>a</sup> (%)	$m/e$ <sup>b</sup>
1-heptene	heptene dimers <b>1</b>	17.3	10.9	152 ( $M^{++} - C_3H_7$ ), 137 ( $M^{++} - C_4H_9$ ), 97 ( $M^{++} - C_7H_{13}$ )
		17.4	4.2	194 ( $M^{++}$ ), 137, 97
		19.7	12.5	194 ( $M^{++}$ ), 137, 97
	pinacol <b>2</b>	38.3	– <sup>a</sup>	183 ( $M^{++} - C_{13}H_{11}O$ ), 105, 77
		heptene-ketyl <b>3a–c</b>	36.7	4.7
	39.1		5.9	280 ( $M^{++}$ ), 182, 105, 77
	39.6		21.6	280 ( $M^{++}$ ), 250 ( $M^{++} - C_2H_5$ ), 182, 105, 77
	heptene-ketyl (allylic) <b>4a,b</b>	40.6	21.7	262 ( $M^{++} - H_2O$ ), 183, 105, 77
		40.9	8.4	262 ( $M^{++} - H_2O$ ), 183, 105, 77
		c-3-heptene	heptene derivatives <b>5</b>	7–7.3
pinacol <b>2</b>	38.5		– <sup>a</sup>	183 ( $M^{++} - C_{13}H_{11}O$ ), 105, 77
heptene-ketyl (allylic) and	37.0		25.2	222, 183, 105, 77
	37.3		28.3	208, 183, 105, 77
heptene-ketyl <b>6a–d</b>	38.2		8.6	222, 183, 105, 77
38.7	7.9	208, 183, 105, 77		
t-3-heptene	heptene derivatives <b>5</b>	14–17	28.8	
	pinacol <b>2</b>	38.3	– <sup>a</sup>	183 ( $M^{++} - C_{13}H_{11}O$ ), 105, 77
	heptene-ketyl and (allylic)	36.3	15.5	222, 183, 105, 77
		36.7	15.1	237, 208, 183, 105, 77
	heptene-ketyl <b>6a–d</b>	37.5	6	222, 183, 105, 77
		37.8	6.6	208, 183, 105, 77
cumene	methyl styrene <b>7</b>	11.4	5	118 ( $M^{++}$ ), 117 ( $M^{++} - 1$ ), 103 ( $M^{++} - CH_3$ ), 78
	Ph-CO-CH <sub>3</sub> <b>8</b>	13.2	5	120 ( $M^{++}$ ), 105, 77, 51
	Ph-C(CH <sub>3</sub> ) <sub>2</sub> -OH <b>9</b>	13.9	5	136 ( $M^{++}$ ), 121 ( $M^{++} - CH_3$ ), 77, 43
	Ph-C(CH <sub>3</sub> ) <sub>2</sub> -C(CH <sub>3</sub> ) <sub>2</sub> -Ph <b>10</b>	27.7	79.3	238 ( $M^{++}$ ), 119 ( $M^{++} - C_9H_{11}$ ), 77
	pinacol <b>2</b>	38.4	– <sup>a</sup>	183 ( $M^{++} - C_{13}H_{11}O$ ), 105, 77

<sup>a</sup> Pinacol precipitated in the reaction vessel, and was not considered for yield calculations.

<sup>b</sup> Characteristic peaks and principal fragmentations of the mass spectra.

intense peaks (which indicated more than 80% yield) as well as some minor signals which could not be identified. After irradiation solid crystals always appeared in the reaction vessel, and these were separated and identified as pinacol. The principal products are listed in Table 3.

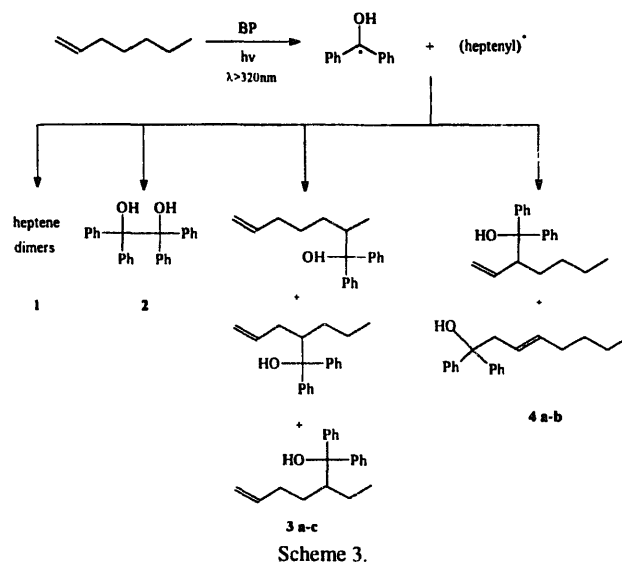
The products formed are shown in Scheme 3 and can be explained by means of the well-known mechanism of direct photoreduction of BP triplet by aliphatic compounds.

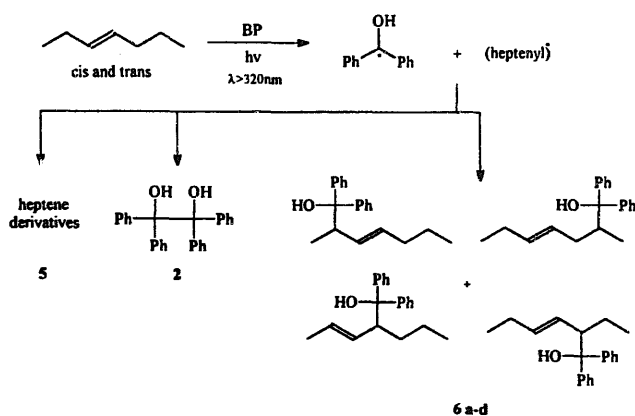
In irradiations of BP/heptenes two well differentiated groups of peaks have been found in the GC chromatogram, together with the peaks corresponding to BP ( $t_r = 27.2$  min) and pinacol ( $t_r = 38.3$  min).

In 1-heptene, the first group of peaks ( $t_r = 17–20$  min) corresponds to heptene derivatives, with all-aliphatic structures which maintained fragmentation characteristics of the presence of a double bond. Two of the products have been identified as heptene dimers given they present molecular peak of  $M^{++} = 194$ . They do not present any fragmentation indicative of aromatics.

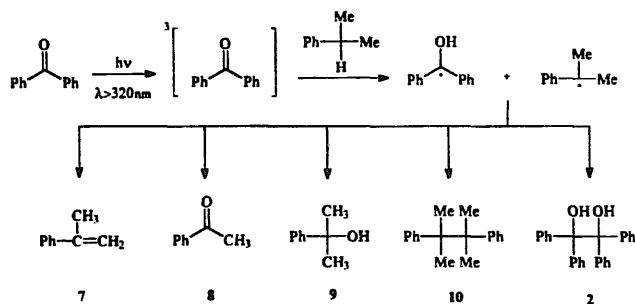
The second, and more intense, group of peaks ( $t_r = 36–41$  min), have been found to correspond to structures coming from the coupling of heptenyl and ketyl radicals, given their mass spectra: peaks characteristic of ketyl radical and its fragments ( $PhCO^{++}$  and  $Ph^{++}$ ), together with those coming from heptene. Several peaks were found in irradiations of all

models, corresponding to the different possible position isomers. Assignations of these peaks in Table 3 have been made taking in account slight differences between spectra, which support one particular structure or exclude other. In 1-heptene as substrate, the mass peak at 262 ( $M^{++} - H_2O$ ) has been taken as characteristic of an allylic structure (products **4a** and **4b**), given this dehydration will be preferentially present





Scheme 4.



Scheme 5.

when it leads to a conjugated skeleton. The peak at 39.6 min (product 3c) has been assigned by means of its fragment of  $m/e = 250$  which corresponds to  $M^{+} - \text{Et}$ . From the six possible isomers obtainable (five H-abstractable positions plus one allylic isomerization), we only observe five products, which is in accordance with the studies of Winnik and Giering and precludes that the direct photoreduction takes place with methylic hydrogens.

Photoreaction of BP in 3-c- and 3-t-heptenes led to, basically, the same results than that in 1-heptene, i.e. a first group of peaks consistent with heptene derivatives and a second one which corresponds to heptene-ketyl structures (Table 3). The most intense peaks have been assigned to the three possible allylic structures (Scheme 4). Two other smaller peaks, presenting the same fragmentations, appeared in this group which correspond to the structures 6a-d.

These findings reveal that photoreduction of BP takes place through direct hydrogen abstraction, mainly but not only, allylic hydrogen atoms, leaving the heptene double bonds unreacted. It also seems that no reaction takes place through the final methyl group of the alkene. The radicals formed mainly couple inside the solvent cage, but structures of heptene dimers and ketyl dimer (pinacol) are also found.

Photoreaction of cumene in the presence of BP took place, as expected, through direct abstraction of the benzylic hydrogen atom in a very clean reaction (Scheme 5). The products obtained are listed in Table 3. No evidence of coupling

between ketyl and cumyl radicals have been obtained, probably due to a higher steric hindrance.

### 3.2.2. DMPA

Irradiation of the models investigated in the presence of DMPA were performed in the same way, but they were not degassed. In general, photoreactions gave a higher proportion of secondary products. The principal products obtained are listed in Table 4. The peak corresponding to the principal product of all the irradiations has been identified as methyl benzoate.

In the photoreaction of DMPA/1-heptene, some minor peaks were found corresponding to octane, methyl-heptanes (all presenting  $M^{+} = 114$ ) and other aliphatic structures. These products come from attack of the methyl radical produced in the primary photoreaction (Scheme 2(b)). The remaining peaks come from the direct attack of the benzoyl radical or the  $\text{PhCO-C}^-(\text{OMe})_2$  radical at one extreme of the double bond. Considerations of steric hindrance and relative reactivity of the two carbons lead us to suppose this attack occurs at  $C_1$ . The three most intense peaks correspond respectively to the structures: benzoyl- $C_7H_{15}$ ; benzoyl- $C_{14}H_{29}$  and benzoyl- $C_{21}H_{43}$ , i.e. Ph-CO-heptane, Ph-CO-dimer and Ph-CO-trimer. The product at  $t_r = 41.6$  min corresponds to the structure Ph-CO-heptane- $C(\text{OMe})_2$ -Ph (Scheme 6).

This result means that a relatively important polymerization reaction (oligomerization) takes place when 1-alkenes are irradiated in the presence of DMPA.

With 3-c- and 3-t-heptenes the products obtained correspond exclusively to attack of the radicals at both positions of the double bond (Table 4 and Scheme 7), as well as two peaks which correspond to the structure Ph-CO-heptane- $C(\text{OMe})_2$ -Ph. No evidence has been found of dimers or trimers of heptane, which is a consequence of the higher steric hindrance of the double bond. The relative intensities of the photoproducts were also approximately the same in 3-c- and 3-t-heptene.

No evidence of hydrogen abstraction has been found, as only traces of Ph-CHO and Ph-COOH have been detected.

The fact that the radicals coming from DMPA fragmentation directly attack the heptene double bond explains the difference in photofragmenting quantum yield found for the initiator when it is irradiated in 1-heptene or 3-heptenes. The different reactivity of an electrophilic radical towards a terminal or a disubstituted double bond explains that in the latter case the reaction proceeds more slowly, then favouring the in-cage recombination reaction of the primary radicals formed.

The products resulting from the irradiation DMPA/cumene are listed in Table 4, those corresponding to methyl benzoate and, in this case, benzaldehyde being the most intense. The photoreaction in this medium is the expected: direct fragmentation of DMPA and subsequent reactions of the radicals formed (H-abstraction, disproportionation and coupling) (Scheme 8).

Table 4  
Results of the photoreaction of the model compounds in the presence of DMPA

Substrate	Products	$t_{ret}$	Yield <sup>a</sup> (%)	$m/e$ <sup>b</sup>
1-heptene	aliphatic photoproducts (methyl heptanes and others) <b>18</b>	2–4	10.2	
	octane <b>11</b>	5	2	114 (M <sup>+</sup> ), 85 (M <sup>+</sup> – C <sub>2</sub> H <sub>5</sub> ), 71 (M <sup>+</sup> – C <sub>3</sub> H <sub>7</sub> )
	methylbenzoate <b>12</b>	8.1	18.3	136 (M <sup>+</sup> ), 105 (M <sup>+</sup> – OCH <sub>3</sub> ), 77, 51
	Ph–C(OCH <sub>3</sub> ) <sub>2</sub> –heptane	24.1	3.2	217, 151 (M <sup>+</sup> – C <sub>7</sub> H <sub>15</sub> ), 105, 77
	<b>13a,b</b>	24.8	5.4	
	Ph–CO–heptane <b>14</b>	25.2	15.4	204 (M <sup>+</sup> ), 133 (ML + 13), 120 (ML), 105, 77
	Ph–CO–dimer <b>15</b>	34.9	13.0	302 (M <sup>+</sup> ), 231 (M <sup>+</sup> – C <sub>5</sub> H <sub>11</sub> ), 203 (M <sup>+</sup> – C <sub>7</sub> H <sub>15</sub> )
	Ph–CO–heptane–C(OCH <sub>3</sub> ) <sub>2</sub> –Ph <b>16</b>	41.6	5.4	323 (M <sup>+</sup> – OCH <sub>3</sub> ), 151
Ph–CO–trimer <b>17</b>	56.2	8.8	400 (M <sup>+</sup> ), 329 (M <sup>+</sup> – C <sub>5</sub> H <sub>11</sub> ), 280 (M <sup>+</sup> – C <sub>8</sub> H <sub>7</sub> O)	
c-3-heptene	aliphatic photoproducts (methyl heptanes and others) <b>18</b>	2–4	28.1	
	methylbenzoate <b>12</b>	8.9	13.3	136 (M <sup>+</sup> )
	Ph–CO–C <sub>3</sub> H <sub>7</sub> <b>19</b>	15.0	5.5	148 (M <sup>+</sup> ), 133 (ML + 13), 120 (ML)
	Ph–CO–C <sub>4</sub> H <sub>9</sub> <b>20</b>	18.8	5	162 (M <sup>+</sup> ), 133, 120
	Ph–CO–heptane <b>21a</b>	25.1	5	204 (M <sup>+</sup> ), 162 (M <sup>+</sup> – C <sub>3</sub> H <sub>7</sub> )
	<b>21b</b>	25.4	8.3	204 (M <sup>+</sup> ), 148 (M <sup>+</sup> – C <sub>4</sub> H <sub>9</sub> )
	Ph–C(OCH <sub>3</sub> ) <sub>2</sub> –heptane	26.9	5.8	217, 151
	<b>22a,b</b>	28	2.3	
Ph–CO–heptane–C(OCH <sub>3</sub> ) <sub>2</sub> –Ph	45.6	2.1	354 (M <sup>+</sup> ), 323 (M <sup>+</sup> – OCH <sub>3</sub> ), 221, 151, 105	
<b>23a,b</b>	45.7	1		
t-3-heptene	aliphatic photoproducts (methyl heptanes and others) <b>18</b>	2–4	16.1	
	methylbenzoate <b>12</b>	8.2	14	136 (M <sup>+</sup> )
	Ph–CO–C <sub>3</sub> H <sub>7</sub> <b>19</b>	14.2	4	148 (M <sup>+</sup> )
	Ph–CO–C <sub>4</sub> H <sub>9</sub> <b>20</b>	18.1	2.9	162 (M <sup>+</sup> )
	Ph–CO–heptane <b>21a</b>	24.4	5.6	204 (M <sup>+</sup> ), 162 (M <sup>+</sup> – C <sub>3</sub> H <sub>7</sub> )
	<b>21b</b>	24.7	7.1	204 (M <sup>+</sup> ), 148 (M <sup>+</sup> – C <sub>4</sub> H <sub>9</sub> )
	Ph–C(OCH <sub>3</sub> ) <sub>2</sub> –heptane	26.2	7.6	217, 151
	<b>22a,b</b>	27	8.1	
Ph–CO–heptane–C(OCH <sub>3</sub> ) <sub>2</sub> –Ph	44.7	4	323 (M <sup>+</sup> – OCH <sub>3</sub> ), 151, 105	
<b>23a,b</b>	44.8	1		
cumene	Ph–CHO <b>24</b>	6.1	– <sup>a</sup>	106 (M <sup>+</sup> ), 105, 77
	Ph–CO–CH <sub>3</sub> <b>8</b>	9.9	18.3	120 (M <sup>+</sup> ), 105 (M <sup>+</sup> – CH <sub>3</sub> ), 77, 51
	Ph–C(CH <sub>3</sub> ) <sub>2</sub> –OH <b>9</b>	10.9	14.1	136 (M <sup>+</sup> ), 121 (M <sup>+</sup> – CH <sub>3</sub> ), 91, 77, 43
	Methylbenzoate <b>12</b>	11.2	29.6	136 (M <sup>+</sup> ), 105 (M <sup>+</sup> – OCH <sub>3</sub> ), 77
	Ph–COOH <b>25</b>	15.2	– <sup>a</sup>	122 (M <sup>+</sup> ), 105 (M <sup>+</sup> – OH), 77
	Ph–CO–C(CH <sub>3</sub> ) <sub>2</sub> –Ph <b>26</b>	33.6	7.9	224 (M <sup>+</sup> ), 209 (M <sup>+</sup> – CH <sub>3</sub> ), 119 (M <sup>+</sup> – C <sub>7</sub> H <sub>5</sub> O)
	Ph–C(CH <sub>3</sub> ) <sub>2</sub> –C(CH <sub>3</sub> ) <sub>2</sub> –Ph <b>10</b>	35.5	13.9	238 (M <sup>+</sup> ), 119 (M <sup>+</sup> – C <sub>9</sub> H <sub>11</sub> )
	cumyl–C(OCH <sub>3</sub> ) <sub>2</sub> –Ph <b>27</b>	36.7	11.3	270 (M <sup>+</sup> ), 239 (M <sup>+</sup> – OCH <sub>3</sub> ), 151, 119

<sup>a</sup> Saturated peaks in the mass spectra.

<sup>b</sup> Characteristic peaks and principal fragmentations of the mass spectra.

#### 4. Conclusions

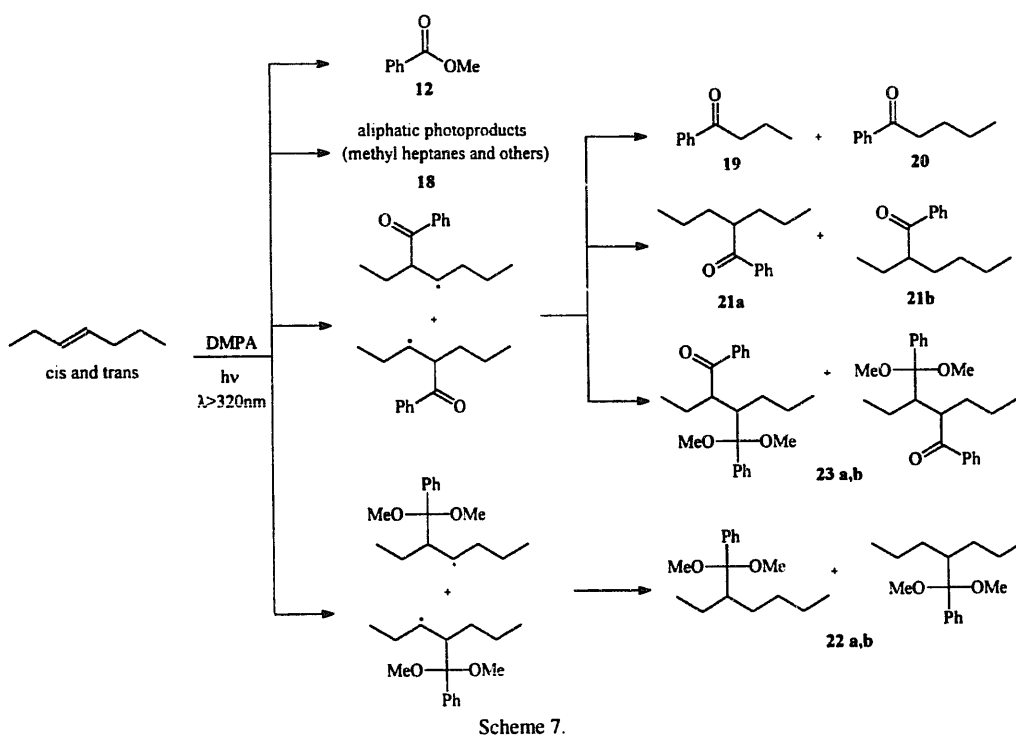
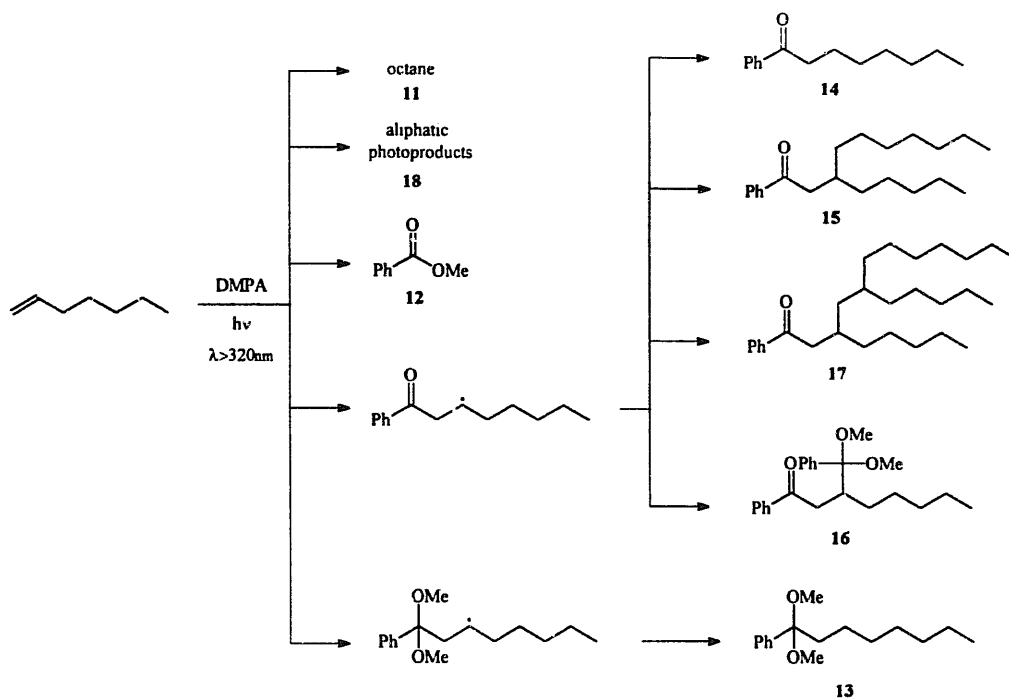
Quantum yields of photoreaction of the hydrocarbons tested in the presence of both photoinitiators are high. The analysis of the products confirms that the primary photoreaction is a hydrogen abstraction, in the case of BP, and the addition to the double bond of the radicals coming from  $\alpha$ -scission of DMPA. These radicals have been identified as: Ph–CO<sup>•</sup>, Ph–(MeO)<sub>2</sub>C<sup>•</sup> and CH<sub>3</sub><sup>•</sup>.

Benzophenone reacts by abstracting mainly the allylic and secondary hydrogens, leaving the double bond of *n*-alkenes

unreacted. As the heptenyl radicals formed cannot add to nonpolarized double bonds, the main mode of termination is coupling with the stable and long-lived ketyl radicals. Small amount of heptene dimers were also found.

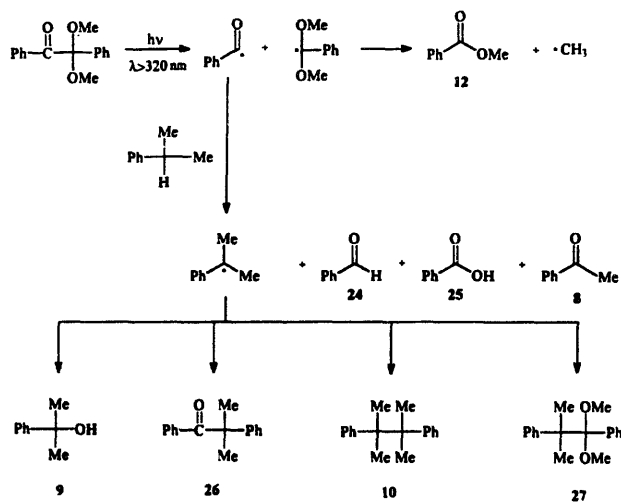
DMPA reacts by direct attack of the radicals produced at the double bond of the *n*-alkene. No evidence has been found of reaction through abstraction of hydrogen atoms by the formed radicals. For 1-heptene (terminal double bond), dimer and trimer structures of heptene are also found.

This leads to a certainly higher reactivity of the models in the presence of DMPA, given that: (a) it has higher quantum yield of photoreaction; (b) two active radicals are formed



per photon absorbed, and both are able to react with the double bond of the alkenes; and (c) when the unsaturation is terminal the photoreaction could continue until giving oligomers of  $n = 2$  and 3.

Photoreaction of both initiators with cumene takes place with high efficiency through direct abstraction of the benzylic hydrogen atom. In the case of benzophenone this occurs via the triplet state of BP, and in the case of DMPA the abstracting



species is the benzoyl radical obtained from fragmentation.

From these results it can be proposed that the overall efficiency of the photochemical reaction induced in an SBS binder will be higher when DMPA is used as photoinitiator than when a bimolecular mechanism of photoinitiation takes place. Investigations currently under way with commercial SBS block copolymers confirm these findings and will be the subject of further publications.

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