Photopolymerization of Acrylates in the Presence of Phenolic Derivatives: Role of the Photoinitiating System

M. Dossot,[1,*] H. Obeid,[1] X. Allonas,[1] P. Jacques,[1] J.P. Fouassier,[1] A. Merlin[2]

[1]*Département de Photochimie Générale, UMR CNRS 7525, Ecole Nationale Supérieure de Chimie de Mulhouse, 3, rue A. Werner, 68093 Mulhouse Cedex, France*
[2]*Laboratoire d'Étude et de Recherche sur le Matériau Bois, Faculté des Sciences–UFRSTMP, Université Henri Poincaré, Nancy 1, UMR INRA 1093, BP 239, 54506 Vandoeuvre, France*

ABSTRACT: The effects of wood phenolic compounds on the photopolymerization of an acrylate resin were evaluated under model conditions, in the presence of different photoinitiating systems, based on a bisacylphosphineoxide derivative, an amine, and isopropylthioxanthone. The steady-state photolysis of these systems and their excited-state processes were also characterized. The kinetic scheme, derived from these experiments, promoted discussion of the performances attained in photopolymerization experiments. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 1154–1164, 2004

Key words: photopolymerization; photochemistry; coatings; photolysis; kinetics (polym.)

INTRODUCTION

Acrylate coatings are widely used in the field of wood furniture protection and UV-curing of such resins represents an important industrial process.[1–3] However, some inhibition and retardation effects are observed and are attributed to the release of phenolic derivatives (POHs) present at the wood interface and migrating into the resin.[4,5] These POHs can lead to three effects: (1) a reaction with the initiating or polymeric radicals as in thermal polymerization of coatings, (2) an interaction with the photoinitiator PI excited states, and (3) a decrease of the amount of absorbed light attributed to the usual inner-filter effect. If the presence of POHs affects the initiation step—because of the mechanism involved in the production of the initiating radicals—the nature of PI can play a decisive role. For instance, it has been shown that cleavable photoinitiators (type I PI) are less sensitive to the presence of POHs than other usual systems based on the photoreduction of aromatic ketones by amines (type II PI).[5] In the benzophenone/*N*-methyldiethanolamine system (BP/MDEA), the POHs efficiently photoreduce the benzophenone triplet state: this photoreduction process, which competes with the MDEA interaction (thereby decreasing the production of the initiating amino-alkyl radicals), leads to phenoxy radicals, which are partly responsible for the inhibition and retardation effects.[5] In addition, by use of laser spectroscopy, it was also shown that no interaction occurs between the phenols and the ketyl radical (which are known to be scavengers for polymeric radicals[1]). In a cleavable photoinitiator such as dimethoxy-phenylacetophenone (DMPA),[5] the homolytic bond cleavage occurs from a very short-lived triplet excited state that prevents any competitive reaction with POHs. Moreover, the generated benzoyl radical does not react with POHs.[5]
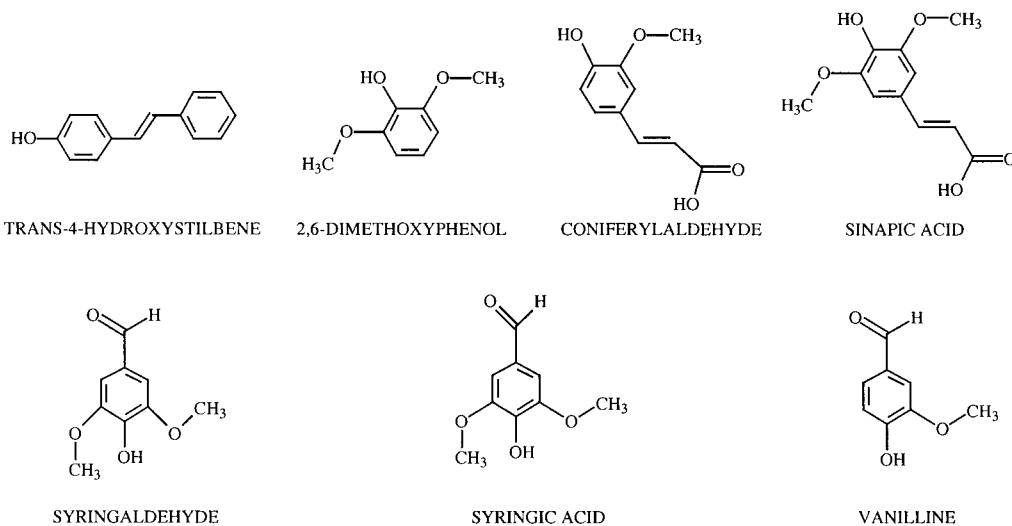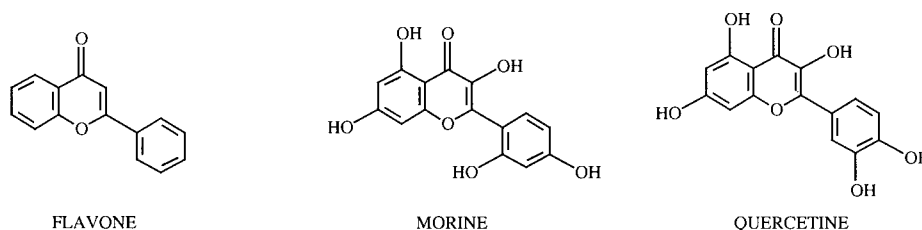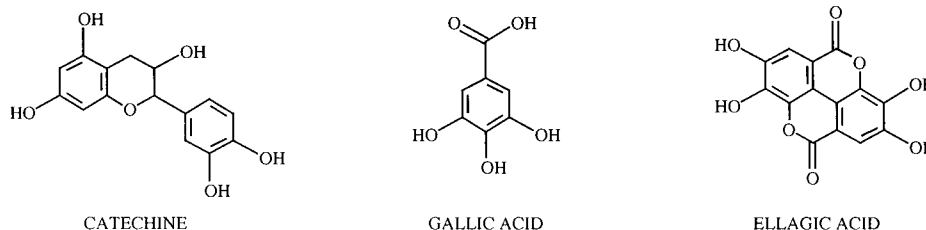
Among type II PIs, ITX (2-isopropyl-thioxanthone)/amine is also widely used. Mono- and bisacylphosphineoxide derivatives (APODs) [among them bis(2,4,6-trimethyl-benzoyl)-phenylphosphineoxide, hereafter designated BAPO] belong to a new class of type I PI that becomes increasingly important in various industrial applications, especially for pigmented varnishes or thick film coatings.[6,7] The APODs triplet lifetimes are lower than 1 ns[7] so that POHs should interact only with the initiating phosphinoyl radical formed after light absorption (photolysis quantum yields are high: about 0.5–0.7[6,7]).

The aims of this article were to (1) evaluate the effects of the phenolic compounds on the photopolymerization of an acrylate resin, in model conditions, in the presence of different photoinitiating systems, based on BP/MDEA, ITX/MDEA, BAPO, and BAPO/MDEA; (2) show some synergistic effects in the combination of two photoinitiators (BAPO and ITX with or without MDEA) toward influencing the POHs; (3) investigate the excited

Monophenols

TRANS-4-HYDROXYSTILBENE	2,6-DIMETHOXYPHENOL	CONIFERYLALDEHYDE	SINAPIC ACID

SYRINGALDEHYDE	SYRINGIC ACID	VANILLINE

Polyphenols

Tannin models

FLAVONE	MORINE	QUERCETINE

Flavonoïds

CATECHINE	GALLIC ACID	ELLAGIC ACID

Chart 1

state processes; and (4) propose a kinetic scheme to account for the possible interactions between POHs and the excited states.

EXPERIMENTAL

Compounds used

BP, MDEA, ITX were obtained from Fluka (Buchs, Switzerland) and BAPO (trade name Irgacure 819) from Ciba Specialties. The set of POHs (Fluka, Al-

drich) was selected to mimic the compounds extracted from wood materials (Chart 1): it contains monophenols either bearing carboxyl functions or not, polyphenols belonging to flavonoids (including flavone itself as a parent compound), and models of wood tannins. Some POHs have a strong absorption band at 366 nm (for instance, coniferylaldehyde, quercetine, or syringaldehyde) and are then responsible for an important inner-filter effect. Because the tannins directly extracted from wood samples have no well-defined mo-

TABLE I
Different Photoinitiating Systems Used in This Study

Photoinitiating systems	Weight percentages used in the formulation			
	BP	ITX	BAPO	MDEA
BP/MDEA	2	—	—	5
ITX/MDEA	—	2	—	5
BAPO	—	—	2	—
BAPO/MDEA	—	—	2	5
BAPO/ITX	—	2	2	—
BAPO/ITX/MDEA	—	2	2	5

lecular weight, all the POHs were thus introduced at the same weight percentage: the corresponding concentrations for 1% w/w ranged from 3.9 to 7.6 × 10^{-2} *M* according to the POHs. Photoinitiating combinations are indicated in Table I.

Extinction coefficients ε (in M^{-1} cm^{-1}) at 366 nm of the different phenols in THF are[8]: about 0 (2,6 dimethoxyphenol, vanilline, gallic acid, catechine), 24 (syringaldehyde, syringic acid, synapic acid, flavone), 32 (*trans*-4-hydroxystilbene), 3500 (coniferaldehyde), 8100 (ellagic acid), 19,150 (morine), 27,090 (quercetine), and about 1000 for tannins.

According to the concentrations used, it can be easily seen that POHs having ε values > 100 lead to an optical absorption at 366 nm higher than 0.025 in a 50 μm thick film: this applies to coniferaldehyde, ellagic acid, morine, and quercetine, which will exhibit a very strong inner-filter effect. Under the same experimental conditions, the optical density of BP ($\varepsilon \sim 100M^{-1}$ cm^{-1}), BAPO ($\varepsilon \sim 400M^{-1}$ cm^{-1}), and ITX ($\varepsilon \sim 5000M^{-1}$ cm^{-1}) were about 0.05, 0.1, and 0.5 respectively. As a consequence, it is expected that the importance of the contribution of the inner-filter effect will be dependent of the PI/POH combination used: for example, the amounts of light absorbed by ITX and coniferaldehyde are almost similar whereas, in the case of BP and BAPO, the light is mainly absorbed by this phenol.

Real-time photopolymerization of the coating

The photopolymerization kinetics were recorded with a FTIR spectrometer (Nicolet, Nexus 870), running in the rapid-scan mode with a time resolution of 0.2 s and a spectral bandwidth of 4 cm^{-1}. The sample was irradiated with the light emitted by a xenon lamp; the UV light was passed through a band-pass filter centered at 366 nm and having a bandwidth of 20 nm; the intensity after the filter was varied from 2.5 to 11 mW cm^{-2}. The geometry of the apparatus allowed the recording of FTIR spectra during the UV irradiation, which provided real-time kinetics.

The acrylate resin (Ebecryl 605 from UCB Chemicals) was chosen for its good mechanical properties, adhesion (on polypropylene film, glass, or wood surfaces), and final % conversion (even at rather low irradiation intensity).

The resin was inserted between two polypropylene films separated by a Teflon spacer of 50 μm, and the whole system was squeezed between two round BaF_2 windows that were fixed onto an aluminum cell (the residual oxygen in the resin was thus rapidly consumed and the kinetics obtained by RT-FTIR were representative of the effect of the POHs). The cell was horizontal to prevent any drift of the sample. The monomer conversions as a function of time were obtained by following the decrease of the absorption band of the monomer C=C stretching modes at 1620 and 1645 cm^{-1}. The initial rate of polymerization R_p and the final % conversion Φ_c^f were thus deduced. It is possible to define two useful normalized parameters to quantify the effects of the POHs in the formulation. Using the rates of polymerization of the system $R_p(0)$ and $R_p(P)$ in the absence and in the presence of a phenol, one can define ΔR_p by

$$\Delta R_p = \frac{R_p(0) - R_p(P)}{R_p(0)}$$

and $\Delta\Phi_c^f$ from the final % conversion with and without phenol by

$$\Delta\Phi_c^f = \frac{\Phi_c^f(0) - \Phi_c^f(P)}{\Phi_c^f(0)}$$

These two normalized parameters do not allow focused attention on the evolution of R_p and ϕ_c^f on the addition of POHs but offer the possibility of visualizing the effect of the POHs: the effect is even less pronounced when ΔR_p and $\Delta\phi_c^f$ are low.

Steady-state photolysis

The setup was composed of an HPK lamp (125 W, Philips, The Netherlands) cooled by air; an interferential filter to select the 366-nm radiation; a quartz cell (width, 1 cm); and a device to bubble-dry argon in the solution. UV spectra of the solution were taken, on a Beckman DU 640 spectrophotometer, at selected times during the irradiation.

Nanosecond transient absorption spectroscopy

The 355-nm 3rd harmonic output of a Nd : YAG pulsed laser (Powerlite from Continuum) was used as the excitation beam (pulse width, 6 ns; intensity reduced to 6 mJ). The excitation light could also be tuned to 410 nm

by using an OPO system. The light of a pulsed xenon lamp (450 W) was used as the probe beam. The transmitted light was analyzed with a monochromator and a photomultiplier; the resulting signal was stored in a digital oscilloscope. The whole system was under computer control. Bubbling argon for at least 15 min ensured the removal of oxygen from the solution.
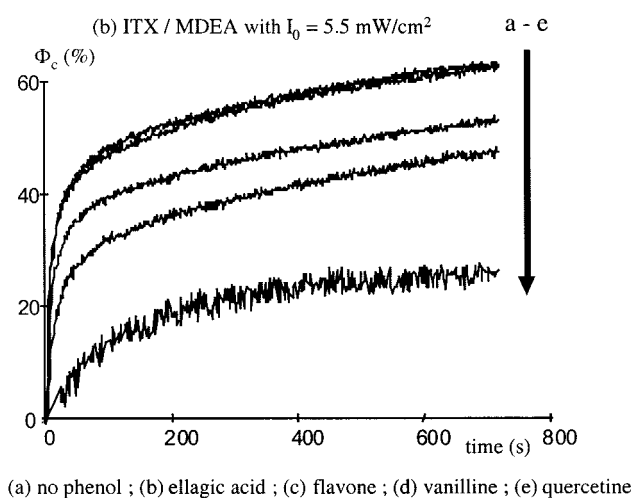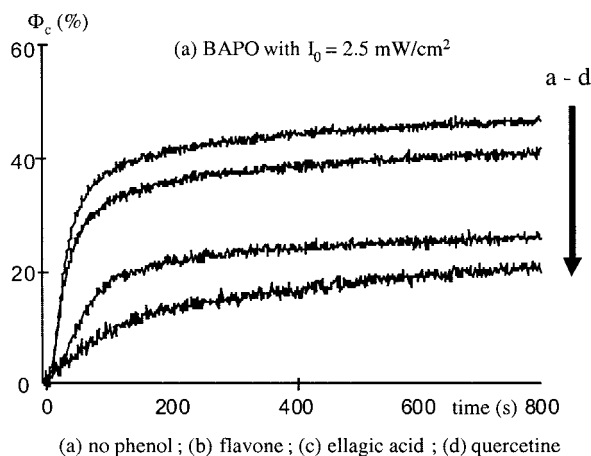
RESULTS AND DISCUSSION

Film photopolymerization experiments

In this section, the overall effect of the POHs on the polymerization reaction will be investigated. Discriminating the role of the POHs requires a low light intensity (<10 mW cm^{-2}).

Effect of POHs in three photoinitiating systems: BP/MDEA, ITX/MDEA, and BAPO

Figure 1 gives some examples of the kinetics recorded in the presence of several POHs with BAPO and ITX/MDEA as photoinitiators. The polymerization of the acrylate resin levels off at relatively low conversions. This could be likely attributable to the gradual consumption of the PIs, which causes the detrimental role of the inner-filter effect of the POHs to increase as a function of the irradiation time, thereby decreasing the rate of initiation. In addition, the film rapidly becomes increasingly viscous and the mobility of the radicals is reduced.

From all the recorded kinetics, ΔR_p and $\Delta \Phi_c^f$ values were obtained and are graphically displayed in Figure 2. The three PIs behave differently depending on the nature of the POHs. BP/MDEA leads to the highest inhibition toward nearly all the POHs. In the presence of the ITX/MDEA and BAPO systems, the POHs generally have little effect. However, two phenols (quercetine and coniferylaldehyde) remain very strong retardation agents (high ΔR_p values) because of a strong inner-filter effect. Another interesting feature is the strong reduction of both ΔR_p and $\Delta \Phi_c^f$ parameters for morine, compared to those of quercetine, in the presence of BAPO. The fact that these two flavonoids do not exhibit the same behavior indicates that this class of POHs induces a chemical effect inherent to their structure in addition to the inner-filter effect. Because different woods release different flavonoids, the nature of such a chemical effect should be strongly dependent on the wood substrate. The ITX/MDEA system is more efficient than BP/MDEA in the presence of catechine, ellagic acid, and gallic acid. Concerning ellagic acid, the fact that ITX absorbs more strongly than BP reduces the inner-filter effect of this POH. In the BAPO-based system, it is worth noting that there is a significant decrease of the magnitude of the effects for POHs bearing a carboxyl group, such as vanilline, syringic acid, sinapic acid, and syringaldehyde. Co-

(a) no phenol ; (b) flavone ; (c) ellagic acid ; (d) quercetine

(a) no phenol ; (b) ellagic acid ; (c) flavone ; (d) vanilline ; (e) quercetine

Figure 1 Photopolymerization kinetics in the presence of BAPO and ITX/MDEA as photoinitiating systems and several phenolic compounds as inhibitors.

niferylaldehyde remains an exception, certainly because of its pronounced inner-filter effect (but a chemical reason cannot be ruled out). Very interestingly, the use of ITX/MDEA and BAPO-based systems promotes some improvements of the photopolymerization efficiency in a complementary manner: this is indicated by the striped bars in the histograms of Figure 2 for the parameter ΔR_p; thus it may be interesting to combine these two systems into a three-component system, BAPO/ITX/MDEA.

BAPO and ITX/MDEA–based multicomponent systems

Four systems were studied: BAPO as the reference, BAPO/ITX, BAPO/MDEA, and BAPO/ITX/MDEA, in the presence of vanilline, quercetine, ellagic acid, and two tannins, European oak (*Quercus Robur*) and eastern white pine (*Pinus Strobus*) tannins. Rates of
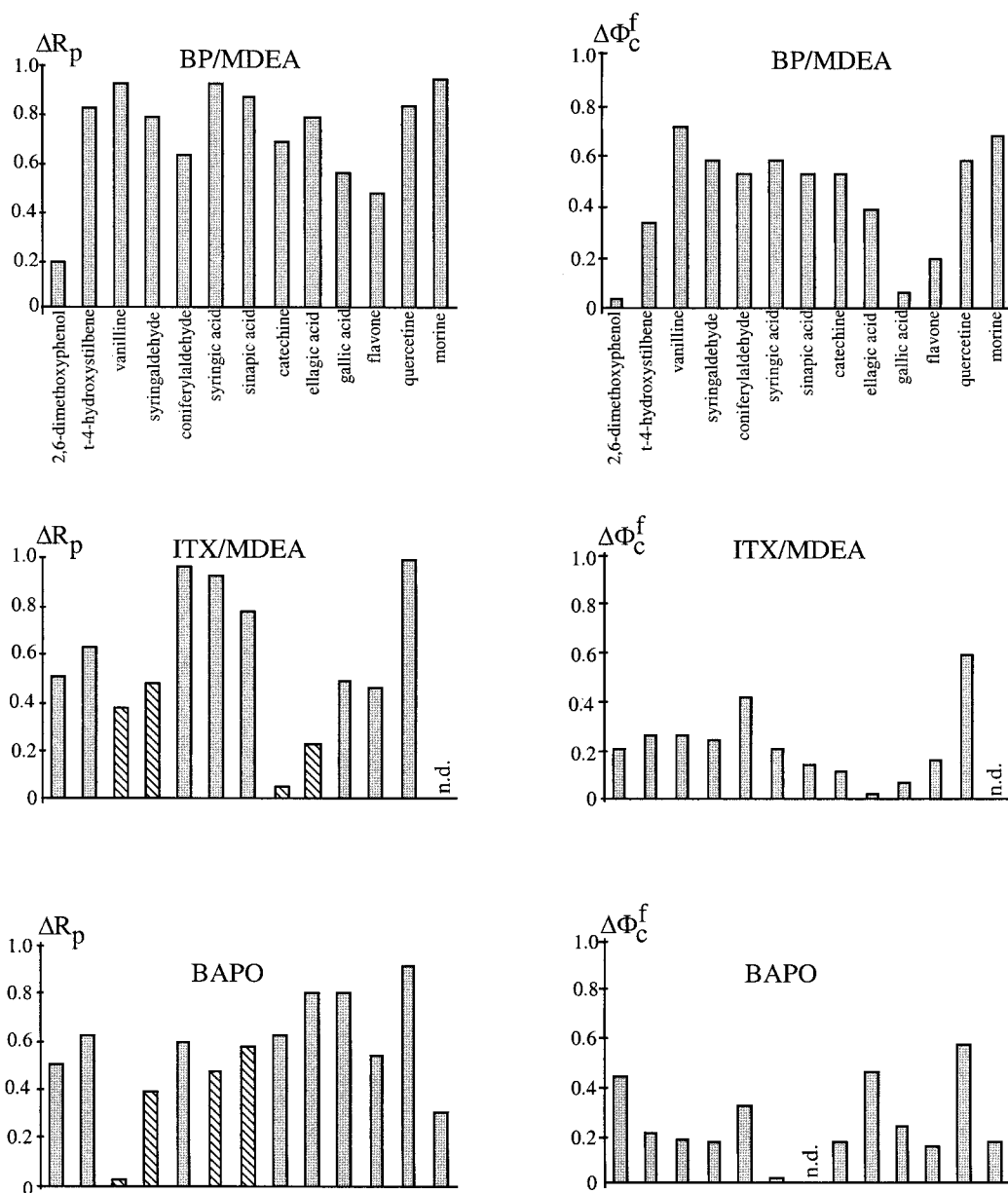
Figure 2 Comparison of ΔR_p and $\Delta \Phi_c^f$ (see text) for BP/MDEA ($I_0 = 2.5$ mW cm^{-2}), ITX/MDEA ($I_0 = 5.5$ mW cm^{-2}), and BAPO ($I_0 = 2.5$ mW cm^{-2}), in the presence of phenolic derivatives (n.d., not determined). The effect of the POHs on the rate of polymerization and the final % conversion are even less pronounced when ΔR_p and $\Delta \Phi_c^f$ are low.

polymerization R_p and final % conversion Φ_c^f are displayed in Figure 3 for vanilline and quercetine. When no phenol is introduced, these photoinitiating systems lead to different R_p values (in the BAPO and BAPO/MDEA systems, the latter is almost twice as fast as the former) but the differences in Φ_c^f are smoothed. The same conclusion can be drawn for BAPO/ITX and BAPO/ITX/MDEA (striped bars in Fig. 3 help make the comparison). Consequently, MDEA in the presence of BAPO certainly generates initiating radicals. When POHs are added, the behavior difference between vanilline and quercetine is mostly attributed to the inner-filter effect, as supported by the considerations developed in the experimental section.

Figure 4 compares the role of ellagic acid and model tannins. For ellagic acid, BAPO/ITX/MDEA proved again to be the most efficient system (R_p values). This is less the case with wood tannins: the data for the oak tannin are similar to those obtained with vanilline, whereas for the pine tannin, BAPO/MDEA appears almost as efficient as BAPO/ITX/MDEA.

These data clearly show that the effect of the POHs is different when the photoinitiating system is changed, which means that, in addition to the inner-filter effect and the possible chemical effect usually observed in thermal polymerization reactions (which mostly affects the propagation step), strong interactions between the excited states and the
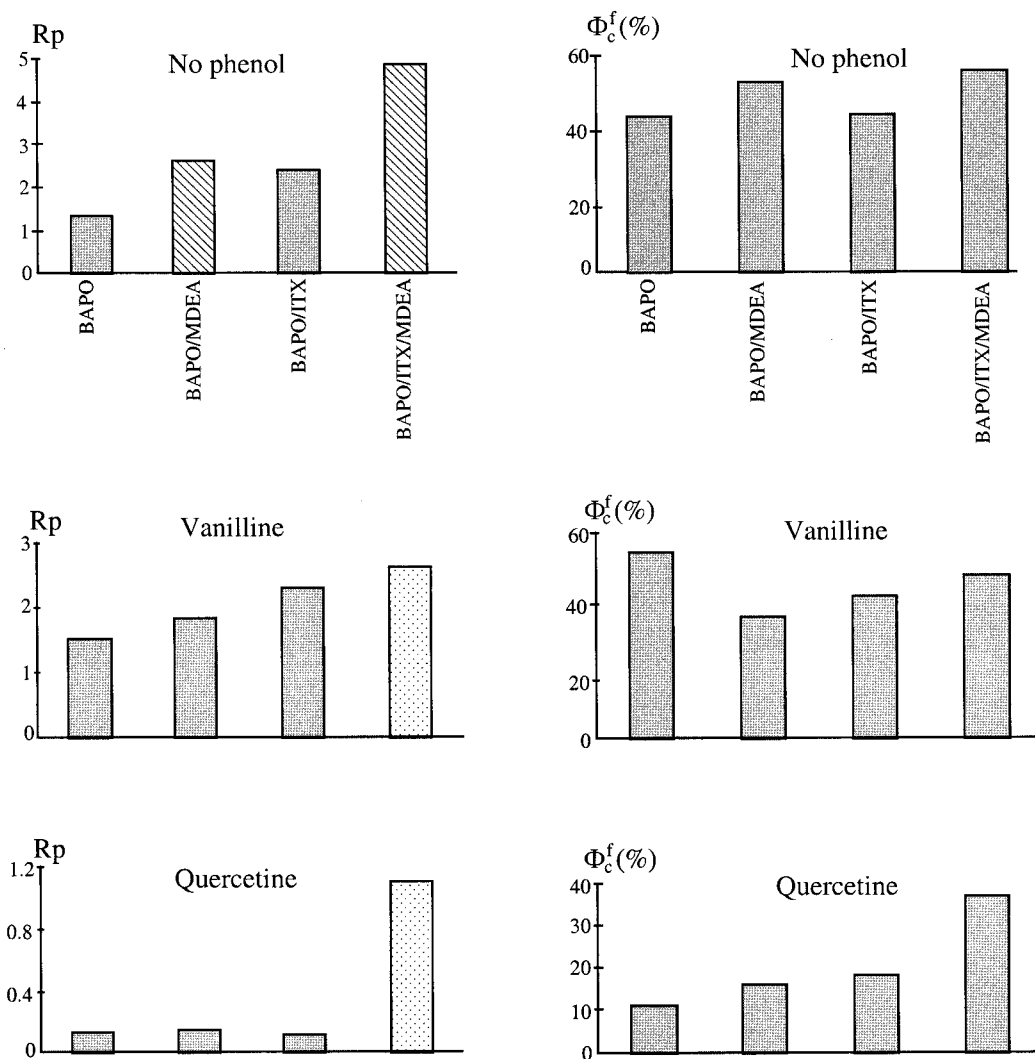
Figure 3 Effects of selected phenols on R_p and Φ_c^f in the case of various photoinitiating systems (R_p values are expressed in $M\,s^{-1}$). Note that the R_p scales are not the same for the three POHs.

POHs must be expected to have an influence in the studied systems.

Photochemical and photophysical study of BAPO-based systems

Steady-state UV-photolysis of BAPO in the presence of POHs and amine in acetonitrile

Photolysis of BAPO is known[7] to occur according to Scheme 1 and a strong bleaching in the BAPO absorption band is observed,[7] as expected upon light irradiation. In the presence of MDEA, the same bleaching occurs, but a growing absorption appears around 350 nm, attributed to the formation of a photoproduct that should not exert any detrimental effect on the coloration of the final coating.

The photolysis of BAPO was also studied in the presence of several POHs in deoxygenated solutions (Fig. 5): coniferylaldehyde exhibits the same behavior as that of vanilline, whereas with 2,6-dimethoxyphenol, the photolysis is faster (the latter has two *ortho* substituents, in contrast to the other POHs presented in Fig. 5, which might contribute to form some specific intramolecular hydrogen bonds that could reduce the bond dissociation energy of the phenolic bond and improve the photolysis). In the UV spectra of the solutions recorded at the end of the photolysis, there was almost no further contribution of BAPO because it completely disappeared in the time window used in our experimental conditions (the light intensity was ~ 1 mW cm^{-2}). As stated above, the inner-filter effect of the POHs becomes increasingly important as the PIs are being consumed.

Excited-state interactions

Quenching by phenolic compounds. Because of the absorption of most of the POHs at the laser excitation wavelength, only usual uncolored phenols can be
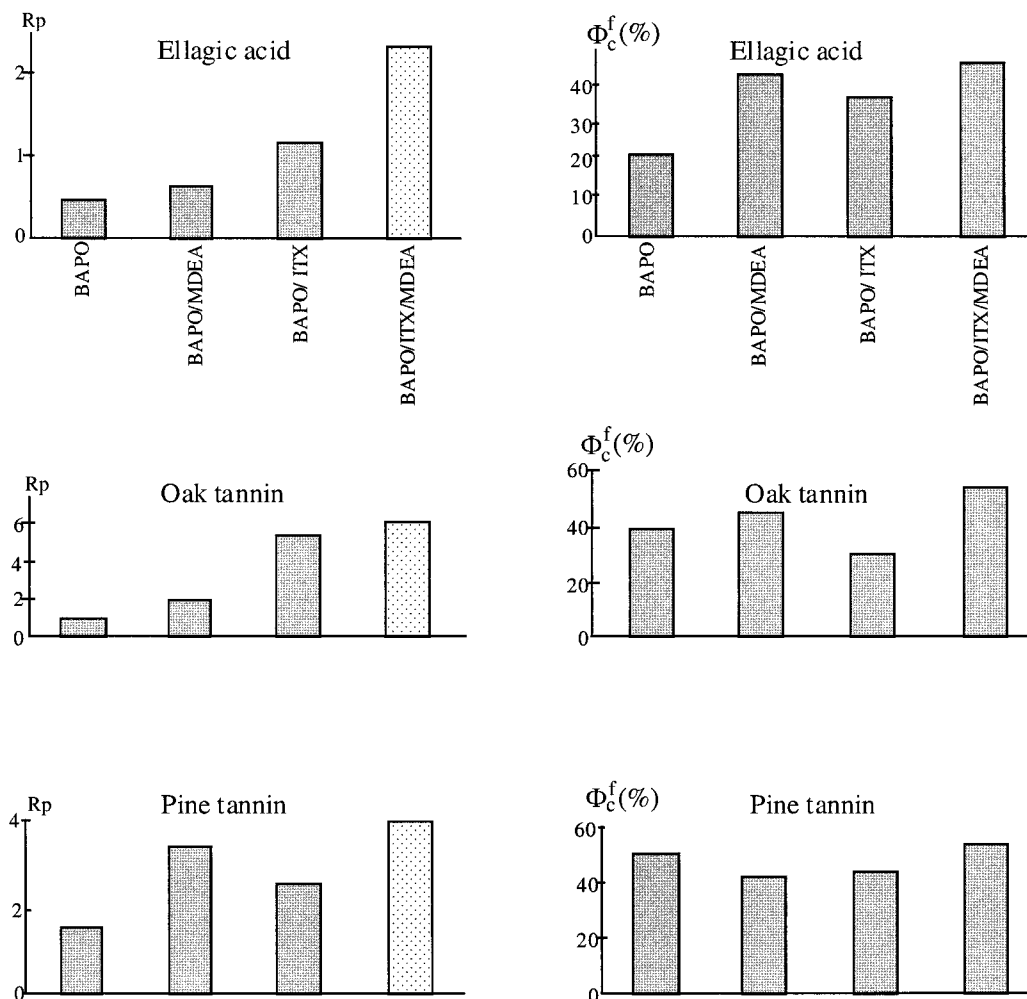
Figure 4 Effects of tannins on R_p and Φ_c^f in the case of various photoinitiating systems (R_p values are expressed in M s^{-1}). Note that the R_p scales are not the same for the three POHs.

used in this section. Figure 6(a) shows the transient absorption kinetics at 340 nm after laser excitation of BAPO in the presence of 2,6-dimethoxyphenol. No

quenching is observed: a limit value for the quenching rate constant is estimated to log $k_Q < 4.5$ (the quenching rate constant between a phosphinoyl radical and a
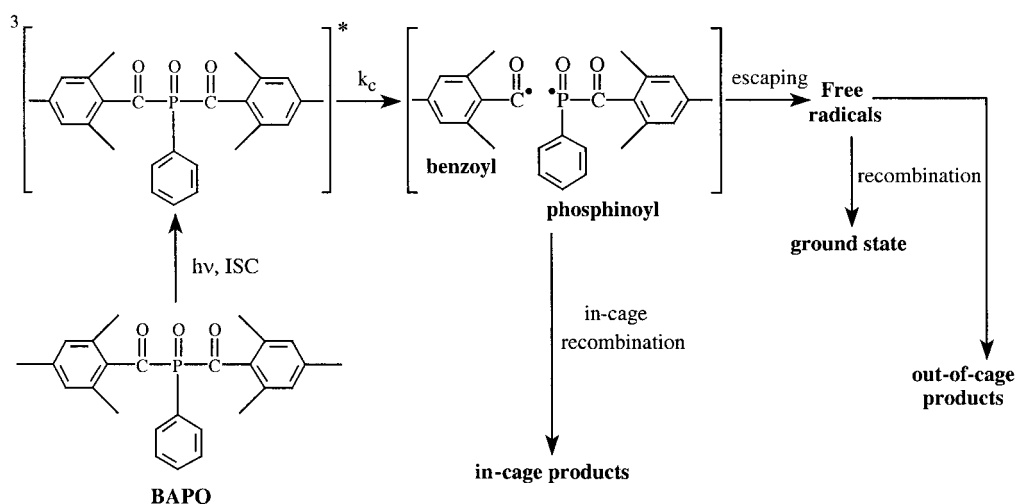

Scheme 1
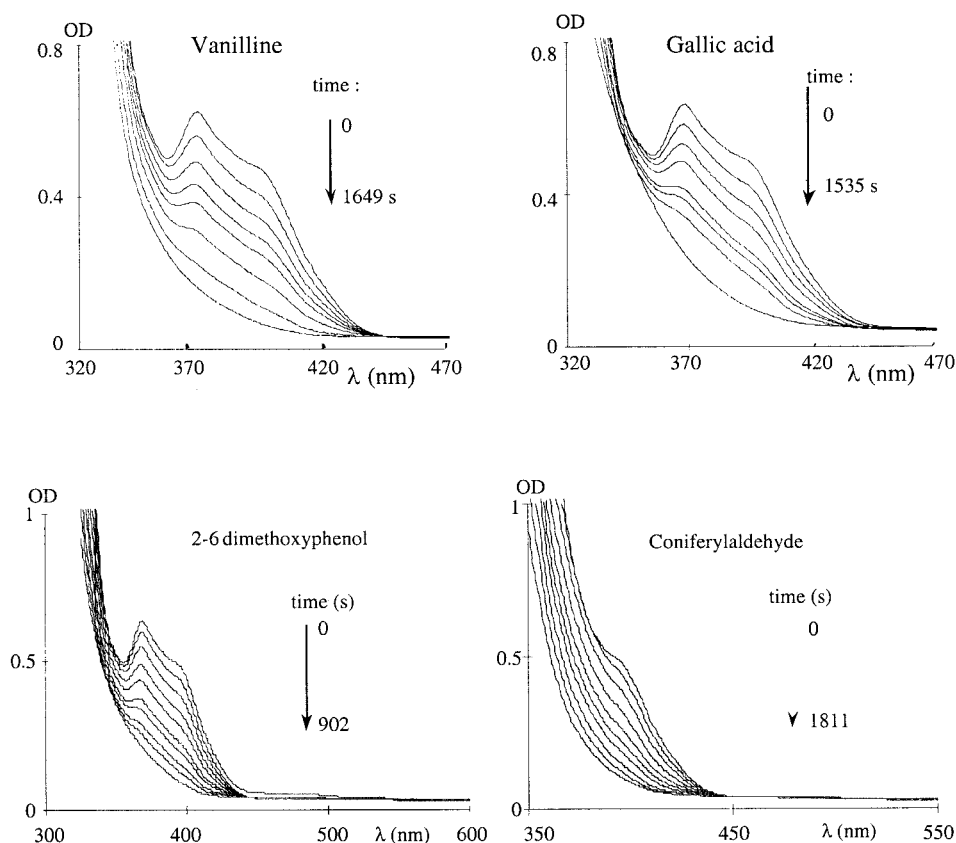
Figure 5 Photolysis of BAPO at 366 nm, in the presence of four phenolic derivatives in deoxygenated acetonitrile solutions.

thiophenol was measured[9] as $k_{PhSH} = 2.3 \times 10^5 \, M^{-1}$ s^{-1}); if it occurs, a reasonable reaction might be a hydrogen abstraction; however, wood phenolic extractives also contain compounds such as flavonoids and ellagitannins, which have well-known antioxidant properties. These properties strongly depend on the surrounding medium, and more specifically on the ability of the solvent to make hydrogen bonds with the

solute.[10] If BAPO is used in a formulation containing monomers that are able to form such hydrogen bonds with POHs, the quenching of the phosphinoyl radical might be more efficient.

Interaction with MDEA. Figure 6(b) shows the quenching of the phosphinoyl radical by MDEA (log k_q = 7.2; this value shows that the amine quenching is competitive with the monomer quenching (almost similar rate
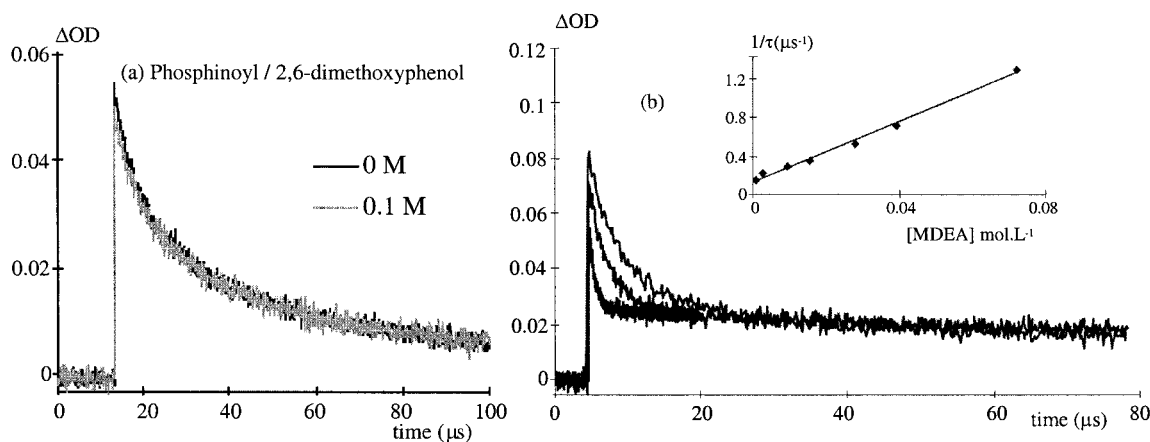
Figure 6 (a) Interaction between the phosphinoyl radical of BAPO and 2,6-dimethoxyphenol (kinetics are recorded at 340 nm). (b) Quenching of the phosphinoyl radical of BAPO by MDEA in acetonitrile (kinetics are recorded at 340 nm).
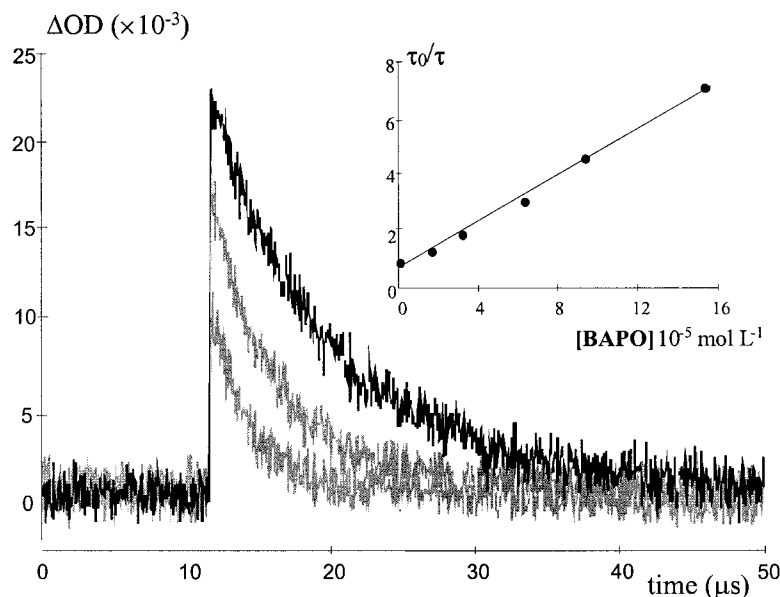
Figure 7 Quenching of the triplet state of ITX by BAPO in acetonitrile.

constants for both processes). A residual absorption in a very long time scale (above the ms time range) appears, which could be attributed to a compound resulting from the H-abstraction on the αC—H bond of the amine. An amino-alkyl radical is concomitantly generated that leads to an efficient initiation of the polymerization reaction.

Energy transfer between the ITX triplet state and BAPO in acetonitrile. The sensitization of APODs by ITX was already evidenced by CIDEP experiments chemically induced dynamic electron spin polymerization).[11] Figure 7 shows the decrease of the ITX triplet absorption, after laser excitation at 410 nm, upon addition of increasing amounts of BAPO (because BAPO also absorbs at 410 nm, an inner-filter effect is observed on the kinetics; i.e., the transient absorption intensity of ^{3}ITX decreases at time zero). It was not possible to record the transient absorption of the phosphinoyl radical attributed to an important absorption of BAPO at the corresponding wavelengths. A high quenching rate constant was deduced from the Stern–Volmer plot: $k_q = 4.5 \times 10^9\ M^{-1}\ s^{-1}$. The reaction cannot be a direct hydrogen atom transfer because the ketyl radical of ITX was not observed. Using thermodynamic experimental data for ITX and BAPO reported in Table II, the free energy change can be calculated when the ITX triplet state acts as an electron acceptor or an electron donor. For ^{3}ITX as an acceptor, $\Delta G_{et} > +0.88$ eV, and for ^{3}ITX as a donor, ΔG_{et} is around 0.3 eV; photoinduced electron transfer is thus not favorable (moreover, the ketyl anion of ITX was not detected). By contrast, the energy transfer should be exergonic by 0.2/0.3 eV (values calculated from data[12] collected in Table II).

Kinetic scheme for the excited-state interactions

A mechanistic scheme for the excited state processes involved in the photoinitiation step is proposed in Scheme 2 (where AH and ϕOH stand for MDEA and the phenolic compounds, respectively). The following discussion will be essentially focused on the behavior of the excited states of the different photoinitiating systems (BAPO, ITX/BAPO, BAPO/MDEA, ITX/MDEA, BAPO/ITX, and BAPO/ITX/MDEA) and the POHs are thus considered as quenchers or radical scavengers. It is clear that this discussion by itself offers an explanation of the efficiency of the photopolymerization reaction in the presence of POHs for which no inner-filter effect is operative: this holds true for 2,6-dimethoxyphenol, vanilline, gallic acid, catechine, syringaldehyde, syringic acid, synapic acid, flavone, and *trans*-4-hydroxystilbene.

In the case of coniferaldehyde, ellagic acid, morine, and quercetine, the practical efficiency observed in photocuring experiments is obviously dependent on the excited state processes (same discussion as mentioned above) but also considerably affected by the

TABLE II
Thermodynamic Properties of BAPO and ITX in Acetonitrile

	$E_{p/2}^{ox}$ (V/sce)	$E_{p/2}^{red}$ (V/sce)	E_T (eV)
BAPO	> 2	−1.57	2.46[a]
ITX	1.54	−1.63	2.64[b]/2.75[c]

[a] From Dietliker.[7]
[b] From Schnabel.[12]
[c] This work.

$$ITX \xrightarrow{h\nu} {}^1ITX^*$$

$$Polymer \xleftarrow[M]{k_{M2}} A^\bullet + ITXH^\bullet \xleftarrow[k_5]{AH} {}^3ITX^* \xrightarrow[k_6]{\phi OH} \phi O^\bullet + ITXH^\bullet$$

$$\downarrow k_{en} \quad BAPO$$

$$BAPO \xrightarrow{h\nu} {}^1BAPO^* \xrightarrow{k_{isc}} {}^3BAPO^* \xrightarrow[k_2]{\phi OH} products$$

with $\phi OH \xrightarrow{k_2} \phi O^\bullet + products$ and $AH \xrightarrow{k_1} A^\bullet + products$

$$\downarrow k_c$$

$$A^\bullet + Ar_2POH \xleftarrow[k_3]{AH} Ar_2PO^\bullet \xrightarrow[k_4]{\phi OH} \phi O^\bullet + Ar_2POH$$

and

$$products \xleftarrow[k_3]{AH} ArCO^\bullet \xrightarrow[k_4]{\phi OH} products$$

$$A^\bullet + Ar_2POH \xrightarrow[M]{k_{M2}} Polymer$$

$$Ar_2PO^\bullet \text{ and } \xrightarrow{M} Polymer$$

$$ArCO^\bullet \xrightarrow[M]{k_{M1}} Polymer$$
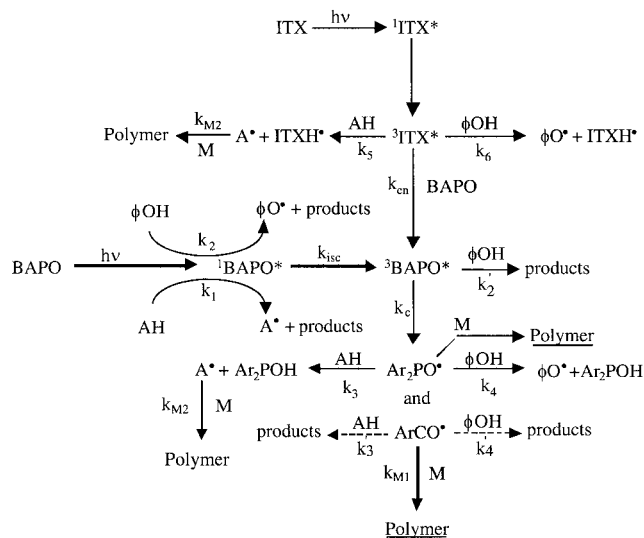
Scheme 2

trivial inner-filter effect, which reduces the amount of light absorbed. In our opinion, it is difficult to completely quantify the role of this effect associated with each POH/PI combination. As mentioned earlier, it is clear that the negative role of the four above-listed POHs (1) increases with their extinction coefficients, (2) is even more important when the PIs have a low ε value (e.g., with BP or BAPO compared to ITX), and (3) is minimized when using ITX-based photoinitiating systems. These statements can presumably explain in large (if not a major) part the role of these four POHs.

When BAPO is used alone, the excited singlet state of BAPO is formed by light absorption. Then, as already observed in other APODs, a very fast intersystem crossing process to the triplet state occurs (on the picosecond time scale) and is followed by a fast cleavage process (within <1 ns) and the production of the phosphinoyl Ar_2PO and benzoyl $ArCO$ radicals.[7,13–15] Upon addition of POHs, reactions can occur either with ${}^1BAPO^*/{}^3BAPO^*$ (rate constant k_2 or k_2') or with the phosphinoyl or the benzoyl radicals (rate constants are k_4 and k_4', respectively). Because of the short lifetimes of ${}^1BAPO^*$ and ${}^3BAPO^*$, however, this quenching process should not affect the radical production. Although nothing can be experimentally observed, a detrimental scavenging of the initiating phosphinoyl radical by POHs cannot be ruled out.

In the ITX/BAPO system, the light can also be absorbed by ITX, although ITX alone does not initiate the polymerization of Ebecryl 605. The efficiency increases when going from BAPO to ITX/BAPO and likely originates from two effects: the superimposition of BAPO and the ITX absorptions at 366 nm, so that a higher quantity of photons is absorbed by the formulation and the energy-transfer process between ${}^3ITX$ and

BAPO (rate constant k_{en}), which generates the BAPO triplet state and then the benzoyl and phosphinoyl radicals. Such a sensitization of APODs by ITX in the polymerization of an acrylate monomer was also previously reported.[11] When phenols are present, this pathway will be in competition with the photoreduction of ${}^3ITX$ by POHs (the rate constants values k_6 depend on the structure of the phenols but typically they range from 10^9 to 10^{10} M^{-1} s^{-1}).

When adding MDEA to the formulations, other possibilities of interaction can exist. In the case of BAPO/MDEA, MDEA can quench the excited states of BAPO and scavenge the benzoyl (rate constant k_3') and the phosphinoyl (rate constant k_3) radicals. Significantly competitive interactions with the excited singlet and triplet states are ruled out because of the other very fast processes involved in these excited states. An efficient reaction is the hydrogen transfer between the phosphinoyl radical of BAPO and MDEA (rate constant k_3), which leads to an amino-alkyl radical, less sensitive to fragmentation and recombination processes (as those evidenced for the phosphinoyl radical itself[16,17]): this contributes to opening a new route for the initiation step.

In the BAPO/ITX/MDEA photoinitiating system, the usual photoreduction reaction of ${}^3ITX$ by MDEA (rate constant k_5)—which still produces the same initiating amino-alkyl radical—must be added to all the others. This reaction can efficiently compete (according to the concentrations used and the relative values of the rate constants) with the BAPO/ITX energy-transfer process and the POHs/ITX interaction.

CONCLUSIONS

This study provides evidence for the inhibition/retardation effects of phenolic compounds on a radical polymerization reaction and allows us to understand how a photoinitiating system works in the presence of these POHs. The better performance, observed in the presence of the three-component system (when no POH is added) in photopolymerization experiments—compared to any other two-component systems—results from the presence of two photoinitiating systems (BAPO/MDEA and ITX/MDEA/BAPO) that work in parallel. More incident photons are thus absorbed; in addition to the classical initiation routes observed with BAPO and ITX/MDEA, two additional initiation pathways occur through BAPO/MDEA and BAPO/ITX interactions. The particular behavior for each of them toward the inhibiting effect of the phenols is obviously dependent on the chemical formula and the physicochemical properties of the POHs (bond dissociation energy of the phenolic O—H bond, oxidation potential, etc.) and explains the results obtained in the model working conditions defined in this study (monochromatic 366-nm light, low light intensity, and

inert atmosphere). It would be helpful now to investigate the role of the polymerizable matrix (and to use a mixture of monomers and oligomers) in practical UV-curing conditions (polychromatic UV and visible light, high light intensity, under air), which was not considered here. The effect of the chemical structure of the amine deserves to be studied in further detail. The design of other efficient visible photosensitive systems is obviously of interest. Further investigations are now in progress in these directions.

References

1. Fouassier, J.-P. Photoinitiation, Photopolymerization and Photocuring; Hanser Publishers: Munich, 1995.
2. Kostelnik, R. Radiat Technol Rep 1994, 8, 16.
3. Dufour P. In Radiation Curing in Polymer Science and Technology, Vol. I; Fouassier, J.-P., Rabek J. F., Eds.; Elsevier Science: New York, 1993; p 1.
4. Stoye, D.; Freitag W. In Resins for Coatings; Stoye, D., Freitag, W., Eds.; Hanser Publishers: Munich, 1996.
5. Dossot, M.; Sylla, M.; Allonas, X.; Merlin, A.; Jacques, P.; Fouassier, J.-P. J Appl Polym Sci 2000, 78, 2061.
6. Rutsch, W.; Dietliker, K.; Leppard, D.; Köhler, M.; Misev, L.; Kolczak, U.; Rist, G. Prog React Coatings 1996, 27, 227.
7. Dietliker K. A Compilation of Photoinitiators Commercially Available for UV Today; Sita Technology: London, 2002; pp 63–128.
8. Godard, V. Ph.D. Thesis, University Henri Poincaré, Nancy, France, 1998.
9. Jockusch, S.; Turro, N. J. J Am Chem Soc 1998, 120, 11773.
10. Foti, M.; Ruberto, G. J Agric Food Chem 2001, 49, 342.
11. Williams, R. M.; Khudyakov, I. V.; Purvis, M. B.; Overton, B. J.; Turro, N. J. J Phys Chem B 2000, 104, 10437.
12. Schnabel W. In Lasers in Polymer Science and Technology, Vol. II; Fouassier, J.-P., Rabek, J. F., Eds.; CRC Press: Boca Raton, FL, 1990.
13. Jockusch, S.; Koptyug, I. V.; McGarry, P. F.; Sluggett, G. W.; Turro, N. J.; Watkins, D. M. J Am Chem Soc 1997, 119, 11495.
14. Sluggett, G. W.; Turro, C.; George, M. W.; Koptyug, I. V.; Turro, N. J. J Am Chem Soc 1995, 117, 5148.
15. Sluggett, G. W.; McGarry, P. F.; Koptyug, I. V.; Turro, N. J. J Am Chem Soc 1996, 118, 7367.
16. Gatlik, I.; Rzadek, P.; Gescheidt, G.; Rist, G.; Hellrung, B.; Wirz, J.; Dietliker, K.; Hug, G.; Kunz, M.; Wolf, J.-P. J Am Chem Soc 1999, 121, 8332.
17. Kolczak, U.; Rist, G.; Dietliker, K.; Wirz, J. J Am Chem Soc 1996, 118, 6477.