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Free radical promoted cationic polymerization by using bisacylphosphine oxide photoinitiators: substituent effect on the reactivity of phosphinoyl radicals

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Abstract

The cationic polymerization of cyclohexene oxide (CHO) was achieved upon UV irradiation ($\lambda = 380$ nm) of methylene chloride solutions containing a series of bisacylphosphine oxides and onium salts, such as diphenyliodonium hexafluorophosphate ($Ph_2I^+PF_6^-$) or *N*-ethoxy-2-methylpyridinium hexafluorophosphate ($EMP^+PF_6^-$). A feasible initiation mechanism involves the photogeneration of phosphinoyl radicals and benzoyl radicals in the first step. Subsequent oxidation of phosphinoyl radicals by onium salts yields phosphonium ions capable of initiating the polymerization of CHO. In agreement with the proposed mechanism, the polymerization efficiency was directly related to the reduction potential of the onium salts, i.e. $Ph_2I^+PF_6^-$ ($E_{red}^{1/2} = -0.2$ V) was found to be more efficient than $EMP^+PF_6^-$ ($E_{red}^{1/2} = -0.7$ V). The variation in reactivity of the different phosphorous radicals was correlated with p-character of the phosphinoyl radical as reflected by the ^{31}P hyperfine coupling constant. The results were compared to a monoacylphosphine oxide, (2,4,6-trimethylbenzoyl) diphenylphosphine oxide, which showed only a low efficiency in promoting cationic polymerization. In addition to CHO monomer, butyl vinyl ether and *N*-vinyl carbazole were polymerized in the presence of bisacylphosphine oxides and onium salts with high efficiency.

Keywords: Free radical photoinitiator; Bisacylphosphine oxides; Free radical promoted cationic polymerization

1. Introduction

Photoinitiated cationic polymerization of monomers, such as epoxides and vinylethers, plays a crucial role in many commercial applications, such as coatings, inks, adhesives, and in the preparation of advanced technical substrates [1–3]. Because of the additives used in different applications, when targeting a specific spectral sensitivity, the wavelength flexibility of photoinitiation becomes a fundamental factor in determining the curing performance of specific formulations. Therefore, photoinitiating systems for cationic polymerization that are sensitive particularly to longer wavelengths are increasingly important for specific applications [4]. Most of the existing photoinitiating systems for cationic polymerization are based on the use of certain onium salts [5,6], such as diphenyliodonium [7], triphenylsulfonium [8], and alkoxypyridinium [9–11] salts. However, these salts do not absorb significantly above 300 nm unless additional chromophores are incorporated into the salt structure. This requires multi-step synthetic and purification procedures. Therefore, for practical reasons the sensitivity range of easily available onium salts was extended to wavelengths $\lambda > 350$ nm with the aid of sensitizers, such as free radical photoinitiators [12–16], charge transfer complexes [17], singlet and triplet photosensitizers [18–20]. In all cases, onium salts act as electron acceptors in redox reactions with free radicals, electron donor compounds in charge transfer complexes, and long-living electronically excited states of sensitizers, respectively. Among these approaches, so-called free radical promoted cationic polymerization is an elegant and fairly flexible way to generate cationic species capable of initiating polymerization of monomers. The overall mechanism involves oxidation of photochemically formed radicals by onium salts (On^+) with suitable reduction

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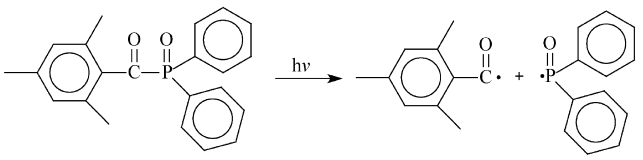
potentials:

$$R\cdot \xrightarrow{On^+} R^+ \quad (1)$$

There is considerable literature on the use of many photoinitiators in free radical promoted cationic polymerization. Benzoin and its derivatives [21], acylphosphine oxides [22], *o*-phataldehyde [23], vinyl halides [24], and polysilanes [25,26] have been successfully used as radical sources in free radical promoted cationic polymerization. More recently, several visible light absorbing systems to generate oxidable radicals were also reported. For instance, radicals formed by the irradiation of systems containing a xanthene dye and an aromatic amine, were oxidized by a diphenyliodonium salt [15]. Similarly, the dimanganese decacarbonyl-organic halide combination is an efficient co-initiator for visible light cationic polymerization when used in conjunction with onium salts [27]. In another study, a commercial titanocene type photoinitiator, Irgacure 784, was used as the free radical source generated by irradiation with visible light. An initiation mechanism involving electron transfer between the photoproducts of titanocene and the onium salt was proposed [28]. Acylphosphine oxides and acylphosphanates with different structures have been used [29] as photoinitiators for free radical polymerization. The long-wavelength absorption characteristics make these compounds particularly useful for the polymerization of TiO_2 pigmented formulations containing acrylate or styrene type monomers and of glass fiber reinforced polyester laminates with reduced transparency [30]. Extensive investigations [31–34] on the photochemistry of acylphosphine oxides revealed that they undergo α-cleavage with fairly high quantum yields as shown below (Eq. (2)) for the example of trimethylbenzoyl diphenylphosphine oxide (**1a**) ($\Phi_\alpha = 0.56$) [34].



1a **1b** **1c** (2)

The capability of acylphosphine oxides to promote the cationic polymerization of appropriate monomers was also examined [22]. Although polymerizations of tetrahydrofuran and butyl vinyl ether were readily initiated upon irradiation in the presence of **1a** and diphenyliodonium salt at 379 nm, where only **1a** absorbs light, it could not be definitely concluded whether and how both radicals that were generated (**1b**, **1c**) can act as free radical promoters according to reaction (1). However, polymerization, ESR spin-trapping and laser flash photolysis studies revealed that benzoyl [35,36] and phosphinoyl radicals [22] do not react with significant rate constants with Ph_2I^+ ions ($k < 10^6 \times M^{-1}\ s^{-1}$) but abstract hydrogen from appropriate donors (e.g. solvent or monomer) [37]. However, the resulting carbon centered radicals are converted to carbocations by reaction with Ph_2I^+ ions, which initiate the cationic polymerization.

In this article, we report the use of bisacylphosphine oxides as photoinitiators in free radical promoted cationic polymerization, and discuss the reactivity on the basis phosphinoyl radical structure. Three onium salts with different redox properties were selected as co-initiators. The structures of the bisacylphosphine oxides and onium salts are shown in Chart 1.

2. Experimental

2.1. Materials

2,4,6-Trimethylbenzoyldiphenylphosphine oxide (**1a**), bis-(2,6-dimethoxybenzoyl)-2,4,4-trimethylpenthylphosphine oxide (**2a**), bis-(2,4,6-trimethylbenzoyl)-2,4,4-trimethyl penthylphosphine oxide (**3a**) and bis-(2,4,6-trimethylbenzoyl)-phenylphosphine oxide (**4a**) were obtained from Ciba, and used as received. Diphenyliodonium hexafluorophosphate [7] ($Ph_2I^+PF_6^-$), triphenylsulfonium hexafluoro phosphate [8] ($Ph_3S^+PF_6^-$) and *N*-ethoxy-2-methylpyridinium hexafluorophosphate [38] ($EMP^+PF_6^-$), were prepared as described previously. Cyclohexene oxide (CHO, 98 %, Aldrich) and butylvinyl ether (BVE, 98% Aldrich,) were washed with aqueous NaOH solution, dried over CaH_2, and distilled under reduced pressure. *N*-Vinyl carbazole (NVC, 98 %, Aldrich) was recrystallized from ethanol.

2.2. Photopolymerization

Photopolymerizations were carried out under a nitrogen atmosphere. Prior to irradiation, the appropriate solutions of monomers containing predetermined amounts of acylphosphine oxides, onium salts, and dichloromethane (solvent) were placed in pyrex tubes, which were previously heated with a heat gun and flushed with dry nitrogen to remove traces of water, and irradiated at $\lambda = 380$ nm in an AMKO Ltd photoreactor equipped with a HBO 100 W xenon lamp and a monochromator. The viscous polymer solutions formed during the irradiation were poured into methanol. The precipitated polymers were then filtered and dried in vacuo. The conversion % was determinated for all samples gravimetrically.

2.3. Analysis

Number average molecular weights (M_n) of the polymers were determined by gel permeation chromatography (GPC) on a Waters instrument equipped with a R410 differential refractometer and a 600E pump using monodisperse polystyrene standards. THF was used as the eluent at a flow rate of 1.0 ml/min. ^{1}H-NMR measurements were performed in $CDCl_3$ solution using a Bruker 250 MHz

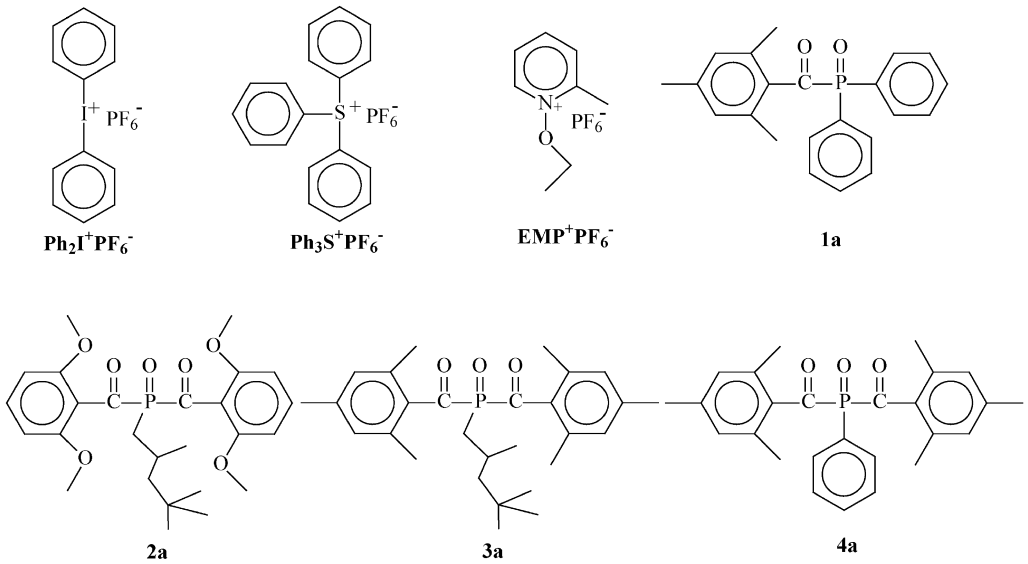
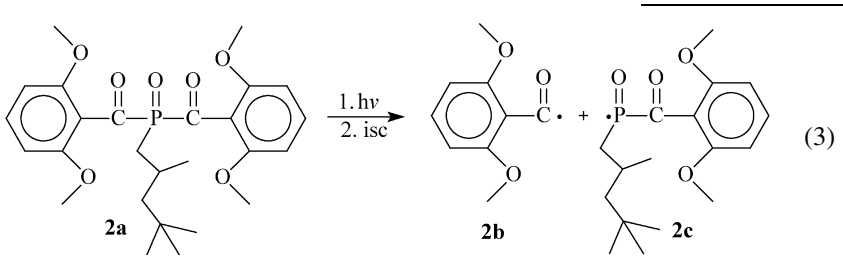


Chart 1. Chemical formulas of onium salts and acylphosphine oxides used in this study.

instrument. UV spectra were recorded on a Perkin–Elmer Lambda 2 spectrophotometer. Laser flash photolysis experiments employed the pulses from a Spectra Physics GCR-150-30 Nd: YAG laser (355 nm, ca. 5 mJ/pulse, 5 ns) and a computer-controlled system that has been described elsewhere [39]. Solutions of the photoinitiators were prepared at concentrations such that the absorbance was ~0.3 at the excitation wavelength employed. Quenching rate constants were measured by using argon-saturated static samples contained in a 1×1 cm^2 Suprasil quartz cell. Fresh solutions were prepared at each quencher concentration.

3. Results and discussion

Bisacylphosphine oxides undergo initial α-cleavage from the triplet excited state to afford radicals [34] as shown in reaction (3) for the example of bis(2,6-dimethoxy)-2,4,4-trimethylpentylphosphine oxide (**2a**).



(3)

Polymerization studies of cyclohexene oxide (CHO) were performed in the presence of acylphosphine oxides (**1a**–**4a**) and onium salts. The polymerizations were performed under irradiation at $\lambda = 380$ nm where all onium salts, $Ph_2I^+PF_6^-$, $EMP^+PF_6^-$, and $Ph_3S^+PF_6^-$, are transparent and the light is absorbed exclusively by the acylphosphine oxide photoinitiators **1a**–**4a** (Fig. 1). CHO was chosen as the cationically polymerizable model monomer, because it is not prone to undergo hydrogen abstraction nor can it be polymerized by a radical mechanism. As shown in Table 1, CHO was polymerized effectively with all the investigated acylphosphine oxide photoinitiators (**1a**–**4a**) as promoters in the presence of diphenyl iodonium salt. In the case of pyridinium salt, however, only bisacylphosphine oxides (**2a**–**4a**) are effective in inducing cationic polymerization with a lower rate. Notably, the triphenyl sulfonium salt is not capable of initiating free radical promoted cationic polymerization. The difference in the reactivity of the onium salts is in agreement with their reduction potentials (Table 2).

Since benzoyl radicals (**1b**–**4b**), produced by α-cleavage (Eq. (3)) from the acylphosphine oxides (**1a**–**4a**), do not undergo significant redox reactions with even strong oxidants such as iodonium salts [35], the phosphinoyl radicals (**1c**–**4c**) formed as partners of the geminate pair must be responsible for the formation of reactive cationic species. We propose that this process involves a redox reaction in which the onium salt is reduced by the phosphinoyl radical (**2c**) to form a phosphinum cation (**2d**) as shown in the photoreaction of **2a** with iodonium salt

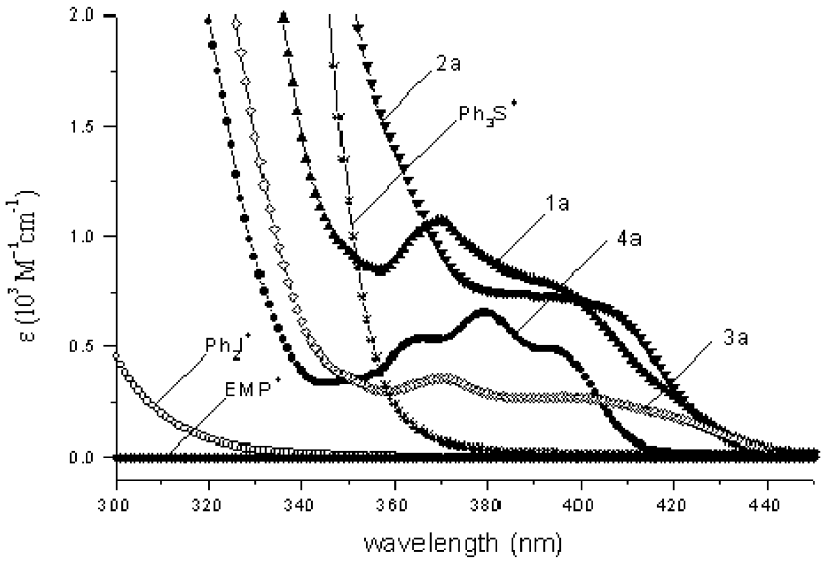
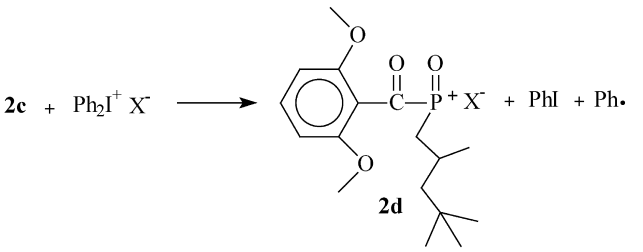


Fig. 1. Optical absorption spectra of onium salts and acylphosphine oxides in CH_2Cl_2. (**1a**, ▲; **2a**, ▼; **3a**, ◇; **4a**, ●; Ph_2I^+, ○; EMP, ◆; Ph_3S^+, ×).

(Eq. (4)):



(4)

The absolute rate constants for the reaction of phosphinoyl radicals with Ph_2I^+ and EMP^+ were determined by laser flash photolysis. Laser flash photolysis (355 nm excitation) of **4a** affords a readily detectable transient absorption corresponding to the phosphinoyl radical **4c** with maxima at 330 and 450 nm [42]. The transient decayed with mixed kinetics. The benzoyl radical **4b** does not interfere with the kinetics since it possesses only a weak absorption in the spectral area, where the phosphinoyl radical absorbs [43]. Therefore, the decay kinetics could be utilized to determine absolute rate constants for the reaction of the phosphinoyl radical with onium salts. Laser flash photolysis experiments were performed at different concentrations of onium salts. The pseudo-first-order treatment of the decay of the absorption of **4b** according to Eq. (5) yields the second-order rate constants k_{onium}, were k_{obs} represents the observed pseudo-first order rate constant at various concentrations of Ph_2I^+ or EMP^+, and k_0 represents the first-order (estimated) rate constant for the decay of the radical in the absence of added quencher (see Fig. 2).

$$k_{obs} = k_0 + k_{onium}[onium] \quad (5)$$

A rate constant for the reaction of **4b** with Ph_2I^+ ($k_{Ph_2I} = (1.6 \pm 0.2) \times 10^7\ M^{-1}\ s^{-1}$) larger than for EMP^+ ($k_{EMP} = (0.6 \pm 0.1) \times 10^7\ M^{-1}\ s^{-1}$) was observed, which is consistent with the larger reduction potential of Ph_2I^+ compared to EMP^+ (Table 2). For comparison the rate constants for the reaction of various radicals with Ph_2I^+ are collected in Table 3. Notably, these values are all of the same order of magnitude.

Table 1
Free radical promoted cationic polymerization of CHO (9.88 mol l^{-1}) by using acylphosphine oxides in the presence of onium salts in CH_2Cl_2 at $\lambda = 380$ nm for 100 min

Acylphospihine oxide[a]	Onium salt[b]	Conversion (%)	M_n[c] (g mol^{-1})	M_w/M_n[c]
1a	Ph_2I^+	5.6	3400	1.4
	EMP^+	0	–	
	Ph_3S^+	0	–	
2a	Ph_2I^+	8.9	3000	1.4
	EMP^+	1.9	2800	1.3
	Ph_3S^+	0	–	
3a	Ph_2I^+	31	4500	1.4
	EMP^+	9.6	4300	1.5
	Ph_3S^+	0	–	
4a	Ph_2I^+	35	3500	2.9
	EMP^+	14	3400	1.4
	Ph_3S^+	0	–	

[a] (Acylphosphine Oxide) = 5×10^{-3} mol l^{-1}.
[b] (Onium Salt) = 5×10^{-3} mol l^{-1}.
[c] Determined by GPC.

Table 2
Redox potentials of the cationic salts

Cationic salt	$E_{red}^{1/2}$ V(SCE)	Reference
Ph_2I^+	−0.2	[40]
EMP^+	−0.7	[14]
Ph_3S^+	−1.2	[41]

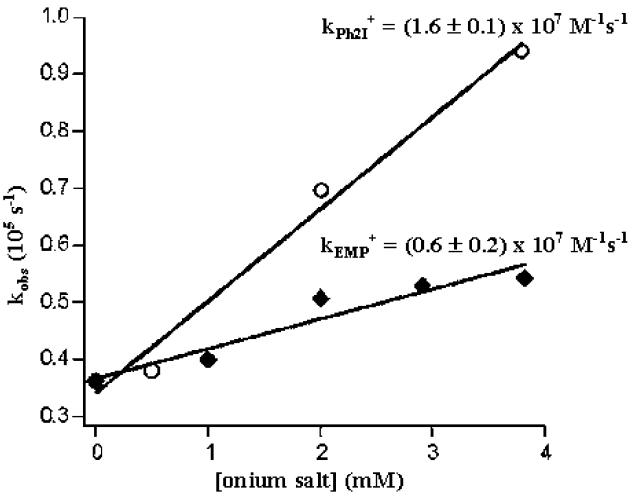
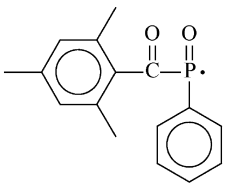
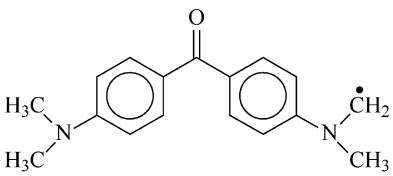
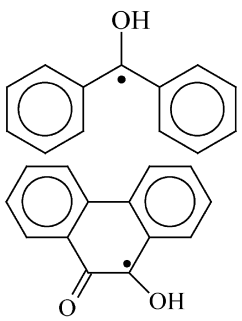
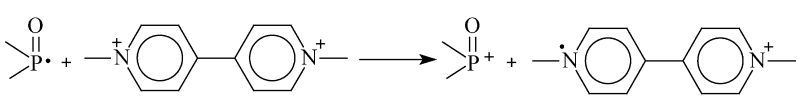


Fig. 2. Pseudo-first-order decay rate constants (k_{obs}) of the phosphinoyl radical **4c** versus onium salt concentration (Ph_2I^+, ○ or EMP^+, ◆), measured following laser flash photolysis (355 nm, 8 ns) of argon-saturated acetonitrile solutions of **4a** at different onium salt concenrations.

The radical precursors (**1a**–**4a**) show significant differences in promoting the cationic polymerization of CHO in the presence of onium salts (Table 1). In general, the bisacylphosphine oxides (**2a**–**4a**) are more reactive than the monoacylphosphine oxide (**1a**). Among the bisacylphosphine oxides (**2a**–**4a**), the most reactive initiator is **4a**. The differences can be discussed in terms of differences in the reactivity of the phosphinoyl radicals (**1c**–**4c**), because the quantum yields of radical formation from **1a**–**4a** (α-cleavage) are similar (0.5 – 0.6) [34]. It is expected that the electron donating/withdrawing effect of the substituents plays an important role in the reactivity of the radicals in the oxidation process by onium salts (Eq. (4)). Radicals with electron donating groups undergo oxidation with higher rate constants. It should be pointed out that phosphinoyl radicals formed from bisacylphosphine oxides, **2c**–**4c**, possess electron withdrawing benzoyl substituents and their reactivity should be lower than those formed from **1a**. However, contradictory to the expectation based on redox properties, the bisacylphosphine oxides perform significantly better than the monoaclyphosphine oxide. Therefore, other factors are dominating. Radical reactivity towards olefins is often correlated with radical stability [42,45,46], which is, in turn, related to localization of the radical center or s-character of a localized orbital. On the other hand, electron delocalization and enhanced p-character should improve the reactivity of the radicals in the redox process. The ^{31}P hyperfine coupling, an experimental parameter determined by EPR, is indicative of the degree of localization of the lone electron on the phosphorus. For the phosphinoyl radicals (**1c**–**4c**) it has been established previously [42] that the ^{31}P hyperfine coupling constant correlates well with the radical reactivity. It was shown that for typical radical reactions (addition to olefinic monomers and oxygen, and atom abstractions) localization of the lone electron in the σ-orbital on the phosphorus (high ^{31}P hyperfine coupling constant, s-character) enhances reactivity for these reactions, whereas delocalization of the electron (low ^{31}P hyperfine coupling constant, p-character) promotes electron-transfer reactions [42]. Table 4 reports the ^{31}P hyperfine coupling constants of radicals **1c**–**4c** together with the relative efficiencies in cationic polymerization of CHO in the presence of onium salts. For comparison, the rate constant for a standard reaction [42] (Eq. (6)), the reduction of methyl viologen by the radicals **1c**–**4c**, is reported in Table 4.

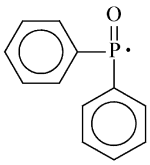
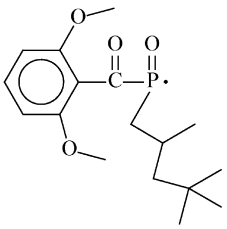
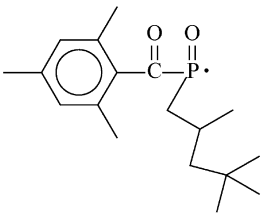
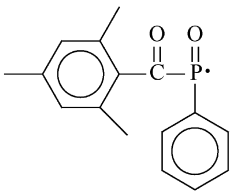
Table 3
Rate constants for the reaction of various radicals with diphenyliodonium salt

Radical	$k \times 10^{-7}$ (M^{-1} s^{-1})	Reference
	1.6	This work
	1.6	[44]
	3.0	[44]
	0.5	[44]



(6)

Table 4
^{31}P Hyperfine coupling and rate constants for oxidation of phosphinoyl radicals and relative initiation efficiencies of the precursor acylphosphineoxides

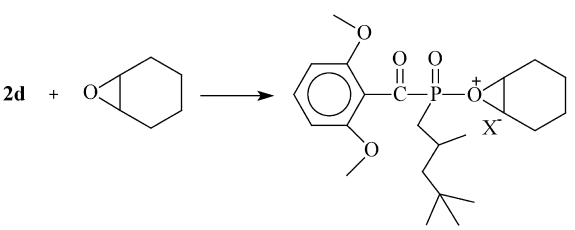
Radical	Onium salt	Relative efficiency[a]	$k^{+}_{R\cdot\rightarrow R}$ ($M^{-1}\,s^{-1}$)[b]	^{31}P hyperfine coupling[b]
	Ph_2I^+	1	$< 10^6$	369G
	EMP^+	0		
	Ph_2I^+	1.6	1.5×10^9	286G
	EMP^+	0.34		
	Ph_2I^+	5.5	2.6×10^9	255G
	EMP^+	1.7		
	Ph_2I^+	6.2	2.8×10^9	270G
	EMP^+	2.5		

[a] Estimated on the basis of conversion for **1a**/$Ph_2I^+PF_6^-$ initiating system under the same experimental conditions. For details see Table 1.
[b] Data taken from Ref. [42].

As can be seen from Table 4, the relative efficiencies of polymer formation from CHO in the presence of onium salts correlate well with the rate constants of the oxidation reaction of the different phosphinoyl radicals by methyl viologen, and correlate inversely with the ^{31}P hyperfine coupling constant.

Under our experimental conditions, no polymerization of CHO with the **1a**/EMP^+ system was observed, suggesting that the carbonyl moiety in the phosphorous radicals produced from **2a**–**4a** is essential for successful polymerization. The phosphinoyl radical **1c** which does not possess the carbonyl moiety promotes the polymerization of CHO only with strong oxidants such as Ph_2I^+ and then at a lower rate. As mentioned above, it was reported that the phosphinoyl radical **1c** does not react with Ph_2I^+ ions ($k < 10^6\ M^{-1}\ s^{-1}$) but abstract hydrogen from an appropriate donor (solvent or monomer) [22,37]. The resulting carbon centered radicals are converted to carbocations by reaction with Ph_2I^+ ions, which then initiate the cationic polymerization.

It is noteworthy that neither diphenyl iodonium nor pyridinium salts initiates the polymerization in the absence of acylphosphine oxides upon irradiation at 380 nm. Therefore, the phosphonium ions **2d**–**4d** that are formed according to reaction (4) must be capable of initiating the cationic polymerization of CHO as described in reactions (7) and (8). If the proposed mechanism (Eqs. (3), (4), (7), (8)) is correct, then poly(cyclohexene oxide) chains with attached benzoylphosphinoyl end groups should be formed. Indeed, ^{1}H-NMR measurements revealed, apart from aliphatic protons, the presence of aromatic protons from the phosphinoyl moiety in the polymer (Fig. 3).



(7)

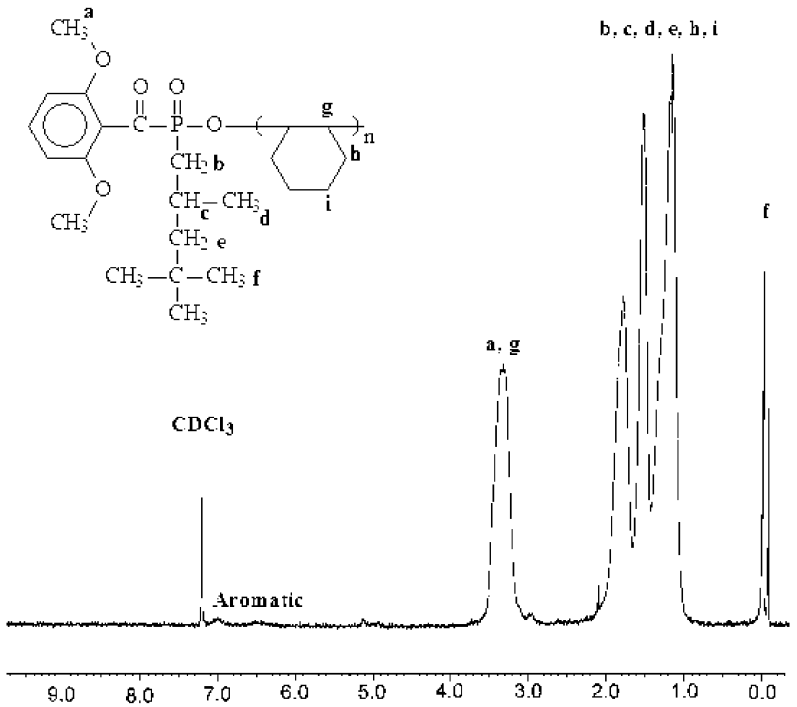
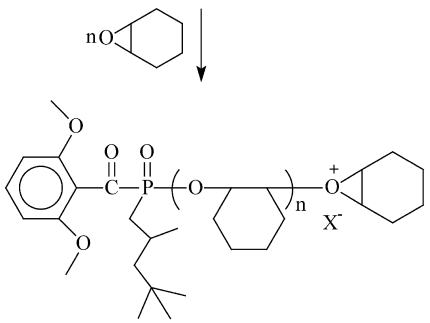


Fig. 3. ^{1}H-NMR spectrum of poly(cyclohexene oxide) obtained from **2a**.



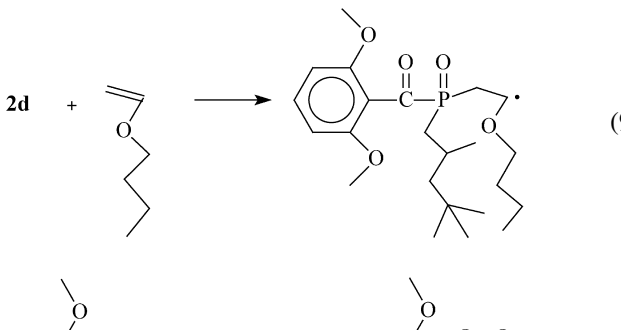
(8)

In addition to the monomer CHO, butyl vinyl ether (BVE) and *N*-vinyl carbazole (NVC) were also studied in the photopolymerization reactions. Methylene chloride solutions of **4a** in the presence of Ph_2I^+ and the monomers CHO, BVE, or NVC were readily polymerized upon irradiation at 380 nm (Table 5). The highest conversion was observed for NVC, followed by BVE (Table 5). Molecular weights of the resulting polymers followed the same trend. In the case of the BVE monomer, in addition to oxidation by Ph_2I^+, phosphinoyl radicals react with the monomer molecules producing electron donor radicals (Eq. (9)). These photochemically formed radicals can easily be oxidized by Ph_2I^+ to the corresponding carbocations, the initiating species (Eq. (10)).

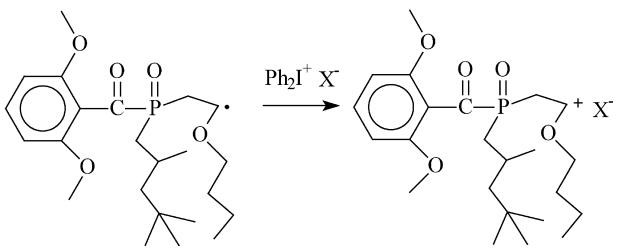
Table 5
Photoinitiated polymerization of some monomers in the presence of **4a** (5×10^{-3} mol l^{-1}) and $Ph_2I^+PF_6$ (5×10^{-3} mol l^{-1}) in CH_2Cl_2 at 380 nm for 60 min

Monomer (mol l^{-1})	Conversion (%)	M_n[a] $\times 10^{-3}$ (g mol^{-1})	M_w/M_n[a]
CHO (9.88)	35	3.5	2.9
BE (7.72)	78	8.5	2.9
NVC (2.07)	86	10.8	2.8
NVC[b] (2.07)	21	16.6	5.2

[a] Determined by GPC.
[b] In absence of $Ph_2I^+PF_6^-$.



(9)



(10)

In the case of NVC, a more powerful electron donating monomer, very efficient polymerization occurred. However, it should be pointed out that NVC is also polymerizable via a free radical mechanism [47]. For comparison, free radical polymerization of NVC initiated by **4a**, in the absence of diphenyl iodonium salt, was also performed. The photopolymerization efficiency in the presence of Ph_2I^+ (cationic + radical system) was much higher than in the

absence of Ph_2I^+ (radical system) under the same experimental conditions (Table 5).

4. Conclusions

Acylphosphine oxides in combination with suitable onium salts, such as iodonium and pyridinium salts, are efficient photoinitiators for cationic polymerization. The proposed initiation mechanism involves the photogeneration of phosphinoyl radicals and benzoyl radicals in the first step (Eq. (3)). Subsequent oxidation of phosphinoyl radicals by onium salts yield phosphonium ions (Eq. (4)) capable of initiating the polymerization of monomers (Eq. (7)). The efficiency of the latter step (Eq. (4)) is controlled by the redox potential of the onium salt and electron delocalization (p-character) of the phosphinoyl radical.

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