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p,p'-Bis((triphenylphosphonio)methyl)benzophenone Salts as Photoinitiators of Free Radical and Cationic Polymerization

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ABSTRACT: We report herein the first known example of a wavelength-dependent photoinitiator exhibiting duality of behavior dependent upon irradiating wavelength. Our observations demonstrate certain arylphosphonium salts produce radicals at 366 nm and Lewis acids at 300 nm. Thus, appropriately designed examples of unimolecular free radical and cationic photoinitiators have been designed.

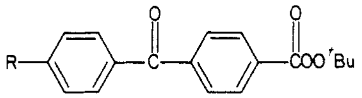
Introduction

During the past few years we have developed several classes of photoinitiators for the free radical polymerization of vinyl monomers.

$$\text{photoinitiator (PI)} \xrightarrow{h\nu} (\text{PI}^*)$$

$$(\text{PI}^*) \rightarrow \text{P}\cdot + \text{I}\cdot \text{ (free radical intermediates)}$$

Initiators based on certain benzophenone *tert*-butyl peresters[1-4]



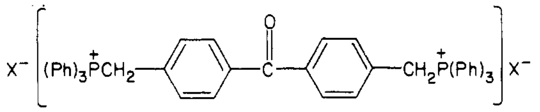
where R = CH_3, OCH_3, $BrCH_2$, ^{t}BuOOCO are especially attractive as radical sources because of their photosensitivity when irradiated at 366 nm. Recent efforts have centered on basically (π, π^*) absorbing systems (fluorenone, anthracene, and pyrene) because excited states of these systems are of lower energy than benzophenone and should, therefore, show less tendency to be quenched by aromatic monomers.

There are many reports in the literature regarding the photolysis of triphenylphosphonium salts and triphenylphosphine.[5-9] Tetraphenylphosphonium chloride as a solution in benzene and ethanol is reported to give biphenyl, triphenylphosphine, and chlorobenzene. These products have been explained by an electron-transfer mechanism which produces phenyl radicals by an elimination from tetraphenylphosphinyl.

$$Ph_4P^+,Cl^- \xrightarrow{h\nu} Ph_4P\cdot + Cl\cdot \rightarrow Ph_3P + Ph\cdot + Cl\cdot$$

Mao et al.[10] have reported the use of triphenylphosphines in photoinitiation in the polymerization of MMA and discussed various substituent effects.[11] Morgan and coworkers[12] have reported that triphenylphosphine strongly accelerates the rate of the thio/ene curing reaction and have also observed that addition of triphenylphosphine to a system already containing benzophenone or benzoin ether as a photoinitiator resulted in a marked acceleration in cure. In recent years Tsuda et al.[13,14] studied the free radical polymerization of MMA and styrene initiated by phosphonium salts having anions such as Br^-, Cl^-, and BF_4^-. Since phosphonium salts absorb mainly at wavelengths below 300 nm, these compounds are not useful photoinitiators when irradiated at wavelengths above 300 nm.

In this paper we report on the photoinitiated polymerization of methyl methacrylate and styrene in dichloromethane at 30 °C with 366-nm irradiation using phosphonium salt derivatives of benzophenone (1). These benzophenone phosphonium salts combine the properties of a long-lived triplet, benzophenone, with *p'*-positioned dissociable functionalities. As such, one extends the useful wavelength range at which the phosphonium salt may be used for photoinitiation much toward the visible (366 nm). We also describe the cationic polymerization of cyclohexene oxide at 300 nm with the same phosphonium salt photoinitiator. We believe this is the first report of a single compound which serves as a radical initiator when irradiated at one wavelength and a cationic photoinitiator when irradiated at a shorter wavelength.



1a, $X^- = BF_4^-$
b, $X^- = PF_6^-$
c, $X^- = Br^-$
d, $X^- = AsF_6^-$
e, $X^- = SbF_6^-$

Experimental Section

All solvents were dried over calcium hydride and purified by fractional distillation before they were used. Compounds used in the preparation of the phosphonium salts were reagent grade.

The monomers MMA and styrene (Aldrich) were freed of inhibitor by washing with a 5% NaOH solution followed by repeated washing with distilled water, dried, and distilled under reduced pressure just prior to use.

Cyclohexene oxide (Aldrich) was dried over calcium hydride, the middle fraction collected by distillation in a colored container out of direct light, and the pure material stored in the refrigerator.

All melting points are uncorrected. Ultraviolet spectra were obtained on a Varian Model 219 spectrometer. NMR spectra were taken on a Varian EM-360 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 337 spectrometer. The intensity of the radiation at 366 nm was continuously monitored by benzophenone/benzhydrol actinometry[15] at 30 °C and observed to be 9.15×10^{17} quanta/min. Elemental analyses were performed by Galbraith Microanalytical Laboratories and are within the satisfactory range.

In the cyclohexene oxide photopolymerization, a 12-mm-diameter Pyrex tube was degassed, sealed, and placed in a Rayonet reactor equipped with a merry-go-round sample holder and 300-nm lamps. The samples were rotated during irradiation.

The light intensity in this work was measured by a ferrioxalate actinometer and found to be 1.26×10^{18} quanta/min.

Preparation of *p,p'*-Bis((triphenylphosphonio)methyl)benzophenone Salts. These salts were made by ionic exchange from the bromide salt of *p,p'*-bis((triphenylphosphonio)methyl)benzophenone, which was synthesized by Thijs.[16] The bromide salt was purified by dissolving it in a small volume of CH_2Cl_2, followed by reprecipitation by adding excess hexane. The anion was replaced by reaction of the bromide salt with $KAsF_6$, KPF_6, $AgSbF_6$, or $NaBF_4$. Excess amounts of the latter salts were used to ensure complete formation of the required counterion. A representative method is as follows.

The corresponding AsF_6^- counterion was prepared by adding 3 g (12.8 mmol) of $KAsF_6$ to 4.5 g (5 mmol) of the bromide salt in 300 mL of water/methanol 50/50 by volume. After 3 h of stirring at room temperature, the salt was filtered off, washed with water several times, dissolved in dichloromethane, and dried over

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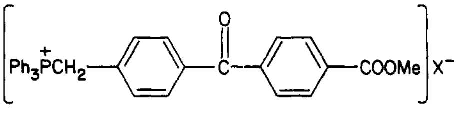
calcium chloride. After the solvent was removed, the salt was dried in vacuo at room temperature to give a 60% yield of colorless product. Further purification was achieved by dissolving the salts in small volumes of dichloromethane and reprecipitating them with excess hexane.

The corresponding PF_6^- and BF_4^- salts were prepared by replacing AsF_6^- with KPF_6 and $NaBF_4$, respectively. For SbF_6^- salt synthesis acetone/water 50/50 by volume was used instead of the methanol/water. The product was extracted with dichloromethane, dried over calcium chloride, and recovered as described above: **1a**, mp 146–148 °C (ϵ_{366} 154); **1b**, mp 131–133 °C (ϵ_{366} 222); **1c**, mp 174–176 °C (ϵ_{366} 180); **1d**, mp 139–141 °C (ϵ_{366} 141); **1e**, mp 118–120 °C (ϵ_{366} 184).

Monophosphonium salts such as **2** were also made according to the Thijs method.[16] The procedure previously reported for anion exchange was followed.



2a, $X^- = PF_6^-$ (mp 180-182 °C (ϵ_{366} 135))
b, $X^- = Br^-$ (mp 208-210 °C (ϵ_{366} 127))

NMR spectra for all phosphonium salts **1** and **2** were recorded in $CDCl_3$ with $(CH_3)_4Si$ as an internal standard. Infrared spectra were recorded in CH_2Cl_2. The NMR spectra of the monophosphonium salts **2** were all similar. Typical spectral data (**2**, $X^- = Br^-$) are as follows: NMR δ 3.9 (3 H, s), 5.7 (2 H, br d), 7.1–8.1 (23 H, m); IR 3050, 1740, 1660, 1450, 1270, 1110, 905 cm^{-1}.

The diphosphonium salts **1** also had generally similar NMR spectra. Spectral data for **1a**, **1b**, and **1d** are as follows. **1a**: NMR δ 5.3 (2 H, br d), 7.0–8.0 (19 H, m); IR 3050, 1660, 1610, 1440, 1270, 1110 cm^{-1}. **1b**: NMR δ 4.8 (2 H, br d), 6.8–7.8 (19 H, m); IR 3050, 1660, 1610, 1440, 1270, 1110, 840 cm^{-1}. **1d**: NMR δ 5.0 (2 H, br d), 7.0–8.0 (19 H, m); IR 3050, 1660, 1610, 1440, 1270, 1110 cm^{-1}.

Selected phosphonium salts gave elemental analyses within the expected ranges.

Photopolymerization. Required amounts of the monomer, initiator, and the solvent were placed in a 12-mm Pyrex tube, which was degassed under vacuum by conventional freeze–thaw techniques and sealed off under vacuum. Irradiation at 366 nm was carried out with a high-pressure mercury arc, as previously reported,[1] while irradiation at 300 nm for cyclohexene oxide photopolymerization was carried out by placing the tubes in a Rayonet reactor consisting of a merry-go-round holder which was rotated continuously by a motor and was surrounded by four medium-pressure mercury lamps of 300-nm wavelength.

After polymerization, the polymer was precipitated by the addition of excess methanol containing a few drops of dilute HCl, washed with methanol, and dried under vacuum. The polymer resulting was a white solid, which was purified by repeated reprecipitation from a CH_2Cl_2/methanol system.

Results and Discussion

Photopolymerization of MMA and Styrene. Polymerization of methyl methacrylate and styrene was carried out at 366 nm. The concentration of the salt was 1.7×10^{-3} mol/L for all solution polymerizations. All of the phosphonium salts **1** and **2** show typical benzophenone-like spectra though there is some longer wavelength absorption in most of them as well.

The photopolymerization of methyl methacrylate initiated by diphosphonium salts **1a–e** having each of the specific counterions is shown in Figure 1. The counterions affect the reactivity and this affects the polymer yield. We believe the effect of the counterion on reactivity derives from the mechanism of the radical process: electron transfer from the gegenion to the benzophenone triplet, followed by dissociation of the radical anion to phenyl radicals: $PF_6^- > AsF_6^- > SbF_6^- > BF_4^- > Br^-$.

The rate of initiation with initiators **1** is also compared with that of benzophenone bisperester[2] under the same experimental conditions (Figure 1). Phosphonium salt **1b** when heated with the monomer in the dark in the same solvent and in the same concentration gave no polymer.

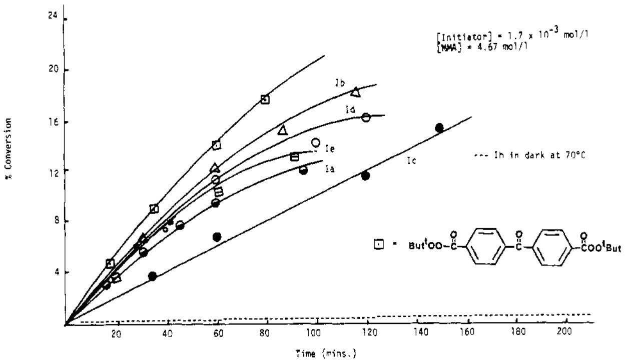


Figure 1. Photopolymerization of MMA in dichloromethane.

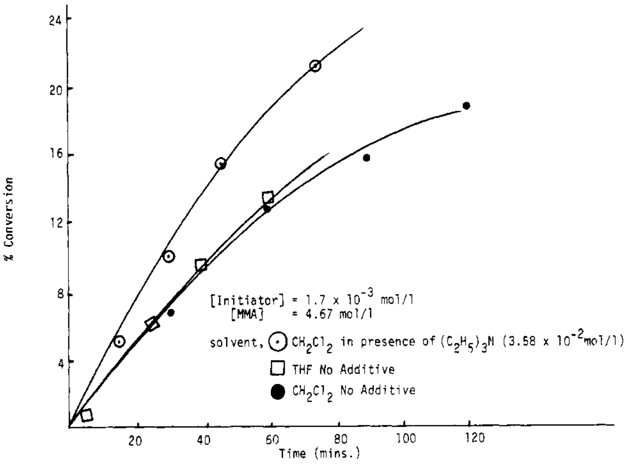


Figure 2. Photopolymerization of MMA initiated by **1b**.

The photopolymerization of MMA by **1b** is enhanced by the addition of small amounts of triethylamine prior to irradiation. Triethylamine is known to accelerate the rate of radical polymerization when used with benzophenone and MMA, and it behaves somewhat similarly with benzophenone phosphonium salt photoinitiators. However, immediately upon the addition of triethylamine to the phosphonium salt in MMA a slight, transient red color develops. A reasonable assumption is that the phosphonium ylide is produced,[14] a fact confirmed by the absorption spectrum of the solution, which shows a fully developed absorption maximum at 440 nm just a few minutes after the addition of 0.036 M triethylamine. The absorption spectrum is identical with that of similar phosphonium ylides.[22] Though the stability of the ylide is such that it cannot be isolated, it persists for at least 2 h at room temperature before the solution becomes again colorless.

Though the acceleration of polymerization by amines is characteristic of radical photoinitiated processes, formation of the ylide would clearly prevent homolytic dissociation of the phosphonium salt and mitigate against a radical process. The overall effect of triethylamine on the polymerization of MMA is, therefore, not first order in amine concentration as well as not being as large as one might normally expect for an amine-accelerated radical polymerization. Figure 2 shows the polymerization of MMA catalyzed by **1b** in the presence of triethylamine.

$$Ph_3P{=}C< \leftrightarrow Ph_3P^+{-}^-C<$$

Figure 3 compares the conversion of MMA to polymer initiated by the diphosphonium salt **1c** and a mono-

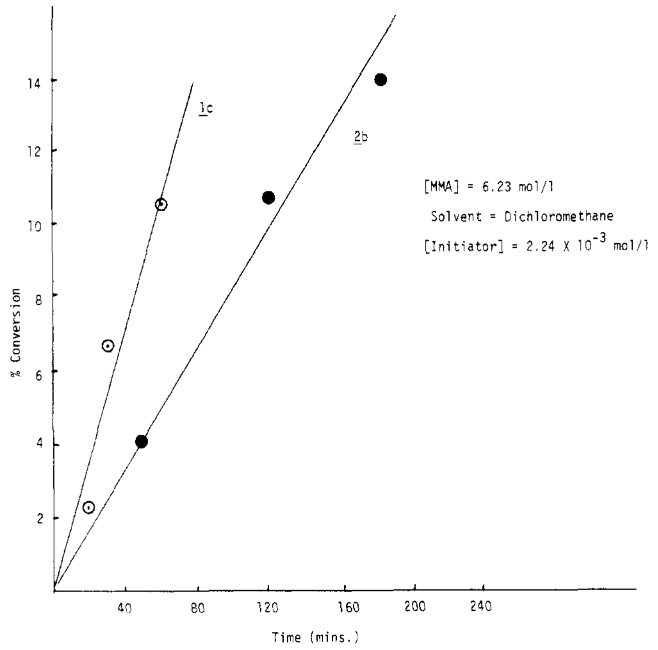


Figure 3. Photopolymerization of MMA initiated by **1c** and **2b**.

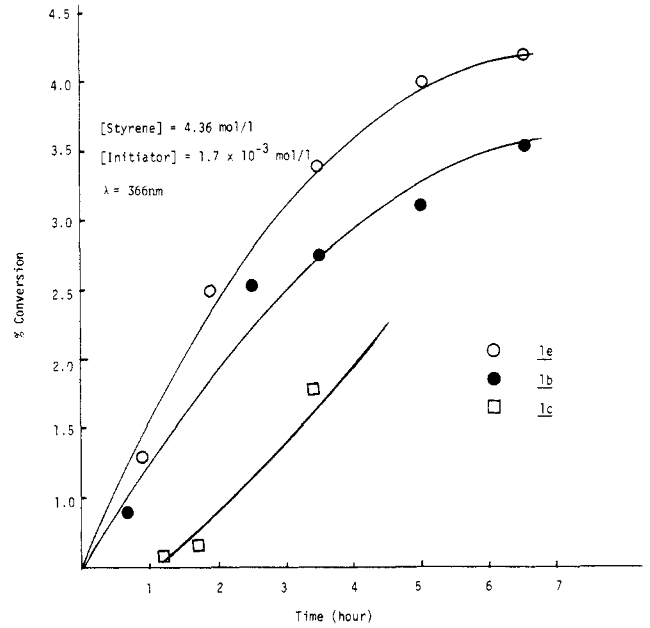
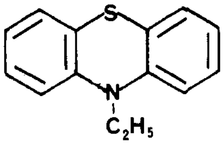
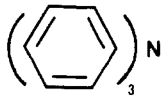
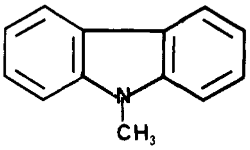


Figure 4. Photopolymerization of styrene in dichloromethane initiated by **1e**, **1b**, and **1c**.

phosphonium salt **2b**. The diphosphonium salt is more active than is the monophosphonium salt under the same conditions with the same counterion, Br$^-$. This is similar to the comparison of bis(benzophenone peresters) with monosubstituted analogues and means that the excited-state energy of the benzophenone triplet excited state can be shared by both of the two para-positioned dissociable functionalities. This rather simple observation is of most interest when one considers how the absorbed radiative energy gets from the chromophore doing the absorbing to the point in the molecule where dissociation takes place.

Figure 4 shows a conversion vs. time plot for styrene photopolymerization initiated by **1b,c,e** at 366 nm. The choice of the counterion affects polymer yield and the reactivity based on the counterion decreases in the following order: $SbF_6^- > PF_6^- > Br^-$. The photopolymerization of styrene is slower, as expected, than is that of MMA. An interesting observation is that phosphonium salt **1b** in styrene gave a nonquenchable fluorescence under the conditions of the experiment.

Table I
Effect of the Amine Structure on the Rate of Photopolymerization of MMA Initiated by 1b[a]

amine	R_p, L mol^{-1} s^{-1}	fluorescence obsrvn
	0	yes
	1.73 × 10^{-4}	no
	2.6 × 10^{-4}	no
Et_3N	3.85 × 10^{-4}	yes
no additive	2.3 × 10^{-4}	yes

[a] [MMA] = 4.67 mol/L, [initiator] = 1.7 × 10^{-3} mol/L, photopolymerization time = 2 h, and solvent = CH_2Cl_2.

Effect of Amine Additives on the Rate of Photopolymerization of MMA and Styrene. While the addition of small amounts of triethylamine enhances the rate of polymerization of MMA initiated by **1b**, other amines, when added to the polymerization mixture before irradiation, give quite different effects. Triphenylamine (E_t = 70.1 kcal/mol) and *N*-methylcarbazole (E_t = 70 kcal/mol) have little effect on the rate of photopolymerization of MMA at 0.02 M amine, while *N*-ethylphenothiazine (E_t = 65 kcal/mol) quenches the initiation reaction completely (Table I). These three amines are all typical accelerators in photoinitiated cationic phosphonium salt reactions and suggest, again, some of the differences between conjugated intramolecular photoinitiators such as **1** and **2** and the simple isolated chromophore unassisted by the absorbing benzophenone function. Thus one can explain the quenching effect of 0.02 M *N*-ethylphenothiazine in that this compound, with a low-energy triplet relative to benzophenone, accepts energy from the excited state of the initiator before that energy can be transferred through the molecule to the dissociable center. Triphenylamine and *N*-methylcarbazole, having triplet energies almost the same as benzophenone itself and likely somewhat greater than that of the phosphonium salts, do not quench the triplet before the energy finds its way to the dissociable phosphonium salt center. Triphenylamine is a known quencher for MMA polymerization initiated by benzophenone,[19] however, so the reaction initiated by the phosphonium salt occurs through a less rapidly quenched excited state than does the reaction of benzophenone itself. What this suggests is that the reactive state of the phosphonium salts has both (n, π*) and (π, π*) character, and, depending on the triplet energy of the quencher and the lifetime of the phosphonium salt triplet, this excited-state energy may impart to the molecule excited-state character either at the carbonyl group (n, π*) or at the phosphonium salt (π, π*). Thus, as observed with benzophenone perester initiators, effective low-energy triplet quenchers trap the (n, π*) triplet while borderline quenchers give the excited state

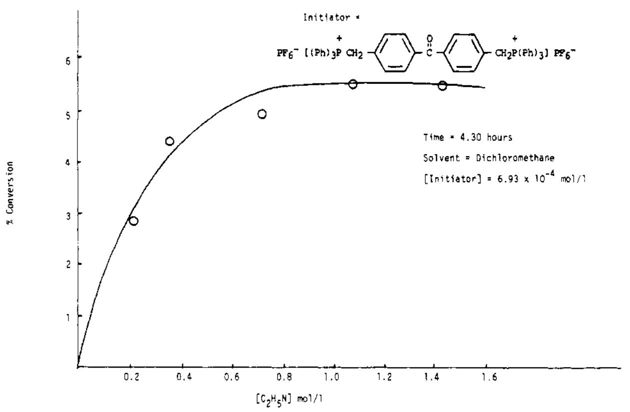


Figure 5. Dependence of photopolymerization of styrene on the triethylamine concentration.

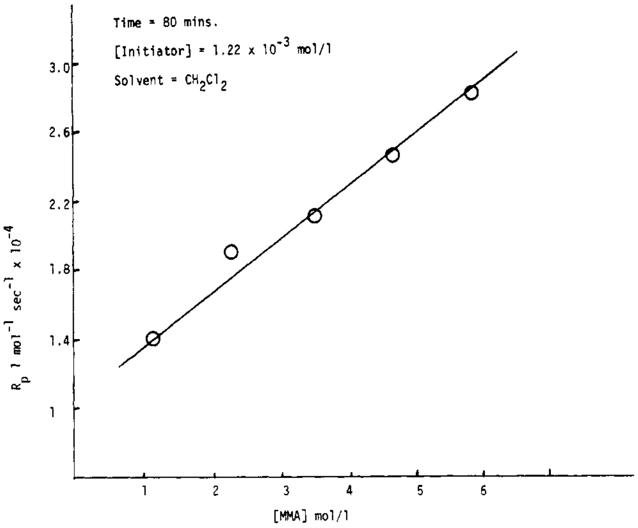


Figure 6. Photopolymerization of MMA initiated by **1b**.

more time to localize in the para-positioned functionality and to eventually lead to dissociation processes.

Figure 5 shows the effect of triethylamine concentration on the polymer yield for styrene photopolymerization with initiator **1b**. Polymer conversion increased initially as the concentration of the triethylamine was increased but then leveled off. We suspect this also is due to the formation of the ylide.

Effect of the Monomer and the Initiator Concentration and the Rate of Polymerization, R_p. The relationship between the rate of polymerization, R_p, using initiator **1b**, and MMA concentration in dichloromethane is linear over the range 1–6 M (Figure 6). With styrene and the same initiator the rate is decidedly nonlinear (Figure 7).

In the presence of a fixed concentration of triethylamine, the rate of photopolymerization of styrene first decreased with increasing styrene concentration and then increased again with increasing concentration of the monomer (Figure 8).

Taken together, not only do these data suggest that styrene does not quench the excited state of the benzophenone phosphonium salt equally over the entire range of styrene concentrations, as it quenches the excited state of various ketonic peresters,[1] but they also indicate that the photoinitiated reaction of styrene over the range of concentrations is likely proceeding by more than one mechanism. This is behavior not previously observed for any benzophenone-style photoinitiator.[1-4,15]

In the presence of triethylamine and at concentrations of styrene below 3 M, increasing concentrations of styrene retard the rate of the polymerization process by energy transfer to the styrene from the benzophenone triplet. This is the expected behavior for a benzophenone triplet whose excited-state energy lies below that of the styrene triplet. When the concentration of styrene exceeds 3 M, the rate of polymerization increases with concentration of the monomer until it reaches 5 M and then the rate levels off. This is unexpected behavior for benzophenone triplets in the presence of a lower energy triplet monomer. What this suggests is that the excited state of the photoinitiator involved in the initiation process is not the benzophenone triplet but more likely that of either the ylide or the phosphonium salt. In other words, at high concentrations of styrene and in the presence of triethylamine, another initiation process takes over from the excited states of **1a**, and that is not a process in which typical triplet quenchers interfere with typical benzophenone initiators.

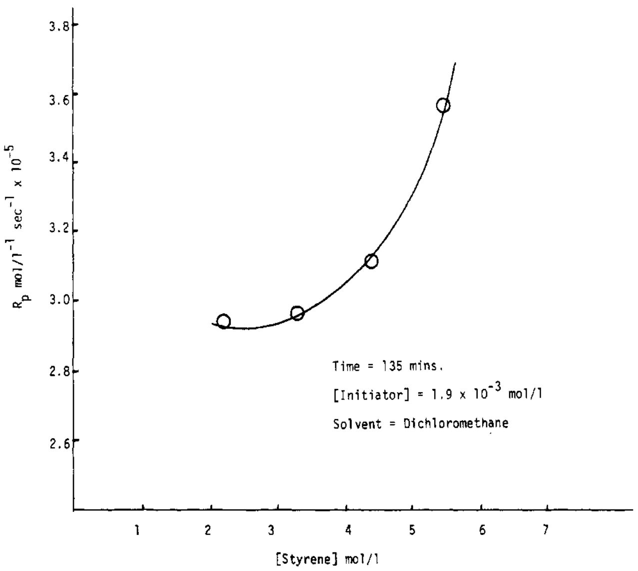


Figure 7. Photopolymerization of styrene initiated by **1b**.

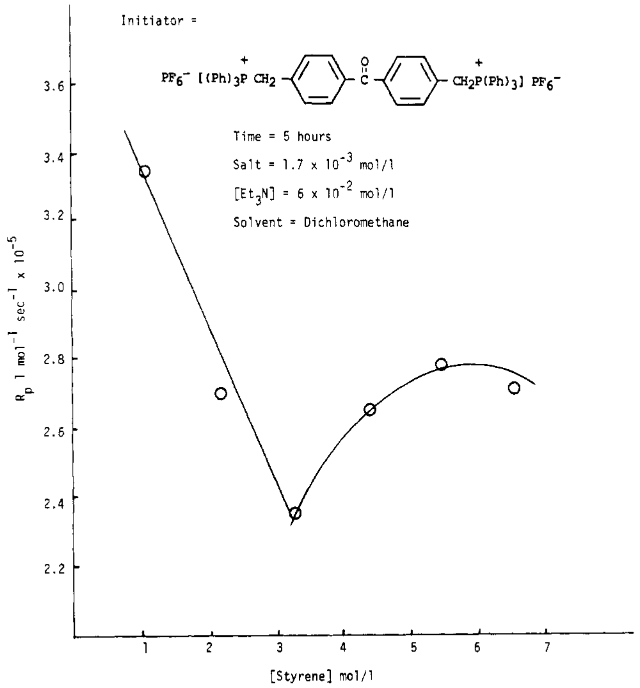


Figure 8. Photopolymerization of styrene in the presence of triethylamine.

There are two choices with regard to these differentiated initiation processes: (1) the excited state of the initiator

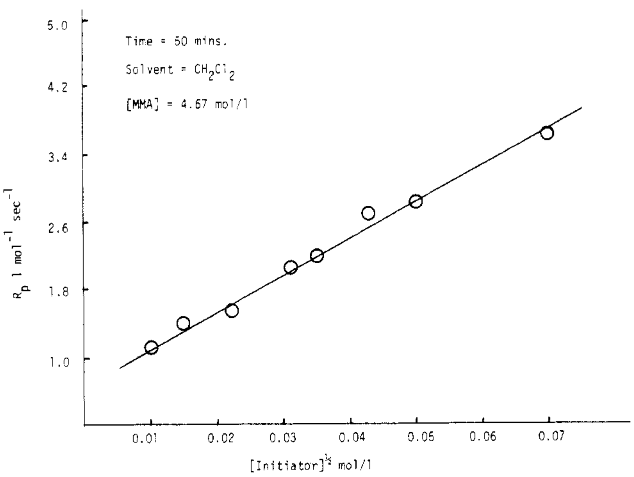


Figure 9. Photopolymerization of MMA initiated by **1b**.

at high concentrations of styrene is different from that at low concentrations or (2) the initiated chain at high concentrations of styrene is not the same as at low concentrations of styrene. At low concentrations of styrene in the presence of triethylamine, styrene quenches the excited state of the initiator which gives rise to the polymerization. This is a styrene concentration-dependent phenomenon and likely the radical chain passes through the benzophenone triplet. At high concentrations of styrene another process involving another excited state of the initiator takes over. This is a phosphonium salt initiated process and is likely a cationic reaction. In other words, at high concentrations of styrene and in the presence of triethylamine, initiator **1b** produces a cationic initiator and does not lead to a radical process!

Figure 9 shows the relationship between the rate of polymerization, R_p, of MMA and the initiator salt **1b** concentration. The rate of polymerization, as expected, is related to the initiator concentration by a square root dependence.

According to Figures 6 and 9, the equation for R_p in the polymerization of MMA by the indicated salt was formulated as

$$K_p = K[\text{MMA}][\text{phosphonium salt}]^{1/2}$$

This rate equation also indicates that initiation proceeds by a free radical mechanism and the effect of amine additive confirms that.

Photoinitiated Cationic Polymerization of Cyclohexene Oxide. Cyclohexene oxide did not photopolymerize in the absence of a catalyst under our experimental conditions even after 30 h of irradiation at either 300 or 366 nm. Though it is known that cyclohexene oxide with free radicals leads to cyclohexanone and cyclohexanol,[22,23] this did not occur when cyclohexene oxide was irradiated under photopolymerization conditions, rather obviously because cyclohexene oxide has virtually no absorption at either 366 or 300 nm.

We did find that cyclohexene oxide was polymerized photochemically in the presence of the phosphonium salt **1b**, but only when irradiation carried out at 300 nm. This is a wavelength where the triphenylphosphonium salt surely absorbs virtually independently of the aromatic carbonyl chromophore. No polymerization of cyclohexene oxide whatsoever took place when irradiation was carried out at 366 nm.

Polymer conversion increased with the time of polymerization and the initiator activity depended on the counterion. Figure 10 shows the effect of the counterion of the salt and its reactivity. According to the nature of the counterion, the polymerization rate fell in the following order: $AsF_6^- > Br^-$. The salt with BF_4^- is completely unreactive in cyclohexene oxide polymerization. No degassing is necessary. Thus the photoinitiated rate with **1e** was the same in both the presence and the absence of air. This observation indicates a nonradical process and that the (n, π*) triplet of the benzophenone chromophore is not very important in the photochemistry.

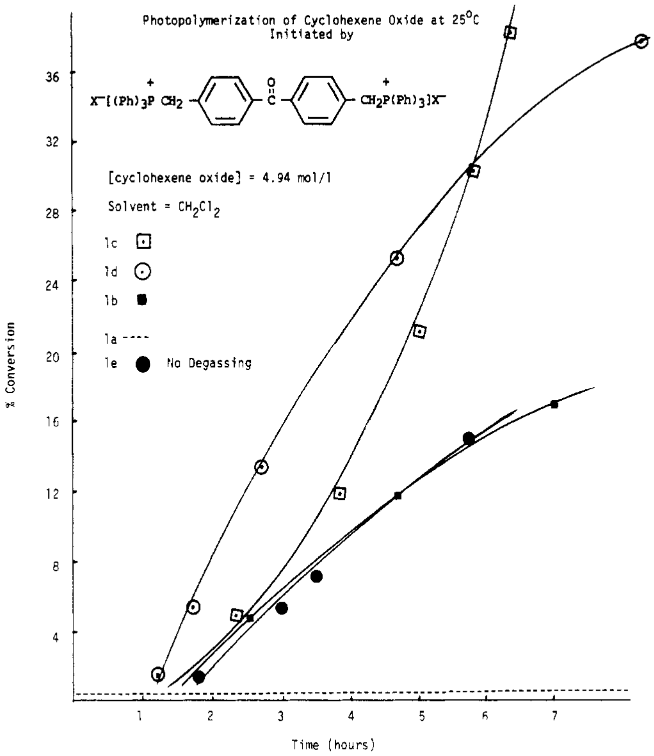


Figure 10. Photopolymerization of cyclohexene oxide at 25 °C.

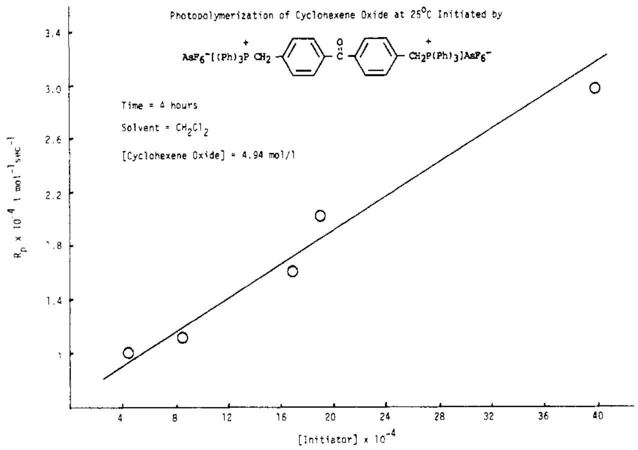


Figure 11. Photopolymerization of cyclohexene oxide at 25 °C initiated by **1d**.

Figure 11 shows the correlation between the rate of polymerization, R_p, and the initiator **1b** concentration. It is clear that R_p is directly proportional to the initiator concentration. Accordingly, the equation for R_p in the polymerization of cyclohexene oxide by the indicated salt was formulated as

$$R_p = K[\text{M}][\text{I}]$$

This rate equation indicates that initiation is proceeding by a cationic mechanism. The effect of air on the polymer conversion confirms that thought.

Figure 12 shows the effect of irradiation time on polymer conversion. These were degassed reaction tubes under the

Macromolecules **1984,** *17,* 2473–2479

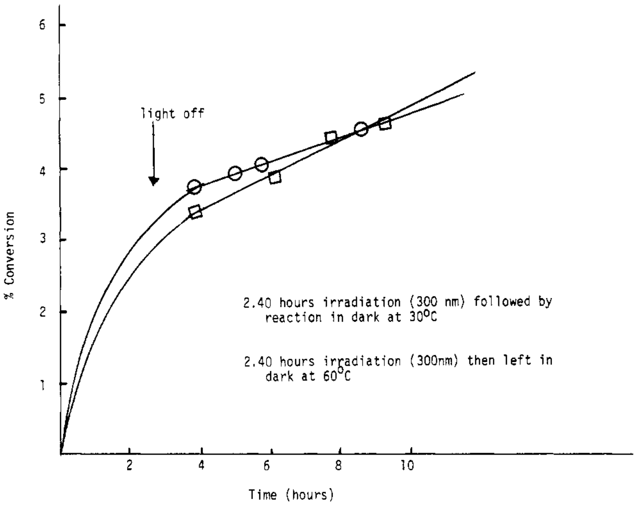


Figure 12. Photopolymerization of cyclohexene oxide initiated by **1b**.

same experimental conditions, irradiated for a specific time (2.40 h) and then transferred to a water bath at the indicated temperature for the time shown. The results show a slight increase in polymer conversion compared to that experiment where the reaction mixture is irradiated for the entire polymerization time.

A further distinction which can be made between phosphonium salts 1 in their abilities to photoinitiate free radical and/or cationic polymerization is the case where the anion is nonnucleophilic in character (e.g., SbF_6^- and PF_6^-). The salt is capable of photoinitiating both free radical and cationic polymerization when the monomer salt is irradiated at 300 nm but just free radical polymerization when the irradiation is carried out at 366 nm. At the same time, those analogous salts bearing nucleophilic anions such as $X = Br^-$ do not photoinitiate cationic polymerization due to the ability of these anions to form stable bonds and thus trap the growing cationic centers.

By selecting the proper anion and wavelength of irradiation, it is possible to carry out strictly free radical polymerization or a combination of free radical and cationic polymerization with the same photoinitiator.

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Free Radical Copolymerization Behavior of Methyl α-(Trifluoromethyl)acrylate and α-(Trifluoromethyl)acrylonitrile: Penultimate Monomer Unit Effect and Monomer Reactivity Parameters

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ABSTRACT: Radical copolymerizations of α-(trifluoromethyl)acrylonitrile (TFMAN) or methyl α-(trifluoromethyl)acrylate (MTFMA) were carried out by using styrene (St), *p*-chlorostyrene (pClSt), and methyl methacrylate (MMA) as comonomers. The copolymerizations of the St–TFMAN, pClSt–TFMAN, and St–MTFMA systems were found to follow the penultimate model equation of the copolymerization, and the monomer reactivity ratios were calculated to be $r_1 = 0.03$ and $r_1' = 0.24$, $r_1 = 0.07$ and $r_1' = 0.63$, and $r_1 = 0.05$ and $r_1' = 0.21$, respectively. On the other hand, the copolymerizations of the MMA–TFMAN, pClSt–MTFMA, and MMA–MTFMA systems follow the conventional copolymerization equation (the terminal model equation). The Q and e values of TFMAN and MTFMA obtained are $Q = 2.5$ and $e = 3.1$ and $Q = 0.8$ and $e = 2.9$, respectively. Substituent effects of the trifluoromethyl group on the ethylene double bond are discussed.

Methyl α-(trifluoromethyl)acrylate (MTFMA) and α-(trifluoromethyl)acrylonitrile (TFMAN) were prepared[1] in 1949, and subsequently they were found to be polymerizable with free radical,[1] anionic,[2-4] and γ irradiation[5] initiations and also to be copolymerizable with common monomers such as styrene.[2,3] Recently, Ito et al.[6] described polymerization behaviors of these fluoromonomers, but they did not study their copolymerization with comono-