

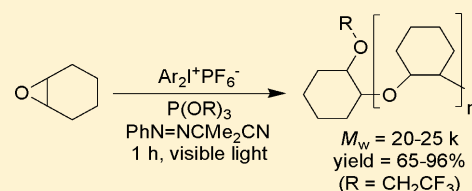
Trialkyl Phosphites and Diaryliodonium Salts as Co-initiators in a System for Radical-Promoted Visible-Light-Induced Cationic Polymerization¹

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S Supporting Information

ABSTRACT: Trialkyl phosphites ((RO)₃P) can act as co-initiators for the diaryliodonium-induced cationic polymerization of cyclohexene oxide (CHO) or THF. A radical initiation step is also required, consistent with the essential role of a radical chain reaction of the phosphite with the iodonium salt to form polymerization-starting aryltrialkoxyposphonium salts (ArP⁺(OR)₃). We used the visible photolysis of phenylazoisobutyronitrile (PAIBN) as the radical initiation step. The presence of multiple fluorine substituents on the phosphite, as in tris(2,2,2-trifluoroethyl) phosphite (TFP), allows polymerization to proceed with a minimal amount of chain transfer from nucleophilic attack by the phosphite. In a typical experiment, a CHO solution of bis(4-*tert*-butylphenyl)iodonium hexafluorophosphate (0.05 M), TFP (0.1 M), and PAIBN (0.02 M) was illuminated with a 65-W compact fluorescent bulb for 1 h, resulting in a 78% conversion to poly(cyclohexene oxide) with an average molecular weight (*M*_w) of 25000. We also used competition experiments to determine approximate rate constants for reactions of phenyl radicals with CHO (*k* = 2 × 10⁶ M⁻¹ s⁻¹) and with TFP (*k* = 2 × 10⁸ M⁻¹ s⁻¹).



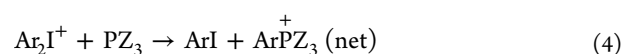
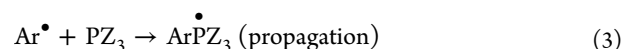
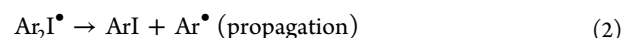
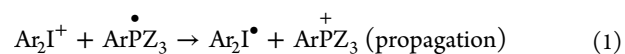
INTRODUCTION

Diaryliodonium salts (Ar₂I⁺Y⁻) with non-nucleophilic anions (e.g., PF₆⁻, BF₄⁻) have long been known to function as photoinitiators of cationic polymerizations.² The mechanism involves photolysis of the iodonium salt to form an aryl radical and an iodoarene radical cation leading to the formation of Brønsted acids, which start the polymerization.^{2–6} With certain monomers, such as THF and 1,3-dioxolane, radical-chain chemistry of the aryl radicals with the monomer can lead to monomer-derived cations that are also capable of starting polymerization.^{7–9}

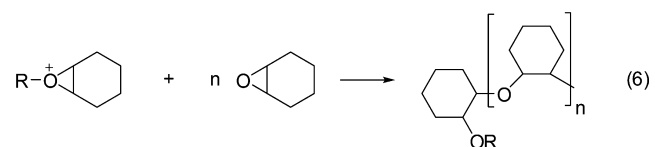
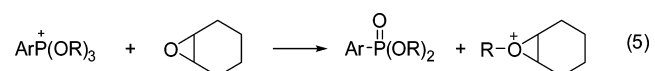
However, the use of iodonium salts in applications such as photocurable coatings and composites, printing inks, and stereolithography is limited by the weak absorption of these salts in the visible region.^{3–6} Therefore, there has been considerable interest in developing iodonium-based systems for visible-light-induced cationic polymerization (VLICP).^{10–23} A number of approaches have been employed including the modification of iodonium structure to extend the λ_{max} and the use of photosensitizers that can do photoinduced electron transfer to the iodonium salt. Another approach involves using light to initiate a reductive radical chain reaction of the iodonium salt with an additive (co-initiator) to form reactive cations.^{20–23}

We reported previously that trimethyl phosphite (TMP) functions as a co-initiator for the iodonium-induced polymerization of cyclohexene oxide (CHO).²³ The mechanism involves a radical-chain reaction^{24,25} (eqs 1–4, Z = OMe) to

give an arylphosphonium ion (ArP⁺(OMe)₃) that can methylate the monomer (eq 5, R = Me), leading to polymerization (eq 6). A key step in the radical chain is the single-electron transfer (SET) from the arylphosphoranyl radical (ArP[•](OMe)₃) to the iodonium salt (eq 1).



(Z = OR or Ph)

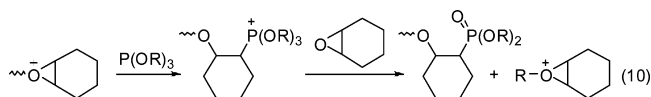
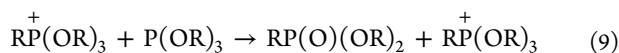
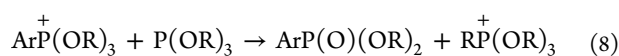
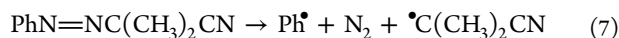


Initiation of the radical chain can be accomplished by visible photolysis of phenylazoisobutyronitrile (PAIBN, λ_{max} = 395

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nm)²⁶ to form phenyl radicals (eq 7). Thus, a diaryliodonium salt, TMP, and PAIBN comprise one system for visible-light-induced cationic polymerization (VLICP).²³ However, prolonged irradiation times were required, and relatively small polymers were obtained. This was attributed to the nucleophilic phosphite both consuming itself by an Arbuzov reaction (eqs 8 and 9) and bringing about polymerization chain transfer by competing with the monomer for electrophilic sites on the growing polymer (eq 10).



For this work, we decided to explore the use of other alkoxyphosphines (phosphites) as co-initiators in otherwise identical systems for VLICP. We reasoned that halogen-substituted alkoxy groups would reduce the nucleophilicity of the phosphite, thus allowing polymerization to proceed without undue competition from the nonproductive Arbuzov and chain-transfer reactions (eqs 8–10). Accordingly, we tested tris(2,2,2-trifluoroethyl) phosphite (P(OTfe)₃) (TFP) and found it to be a superior co-initiator for iodonium-induced VLICP. In this paper, we report the results of experiments comparing polymer yields and molecular weights afforded by various phosphite co-initiators including TMP and TFP. Also reported are the results of mechanistic experiments aimed at providing greater understanding of the TFP/iodonium polymerization system.

RESULTS AND DISCUSSION

Isolated yields and absolute molecular weights of poly(cyclohexene oxide) (polyCHO) were determined in some

initial experiments that compared TMP, TFP, and dimethyl phenylphosphinite (DMPP) (Table 1). Bis(4-*tert*-butylphenyl)-iodonium hexafluorophosphate **1a** (0.01 M) and PAIBN (0.02 M) were included in the reaction solutions. Illumination was provided by a 500-W halogen lamp. TMP and TFP both gave a modest 36% yield of polyCHO ([phosphite] = 0.04–0.05 M, 5 h, entries 1a and 3a). In contrast, DMPP gave only 3% conversion (entry 2a). Control experiments that left out the phosphite, the iodonium salt, or light did not polymerize. With TFP, higher phosphite concentrations gave higher polymer yields (65–78%, entry 5), but with TMP the opposite effect was observed (17–24%, entry 1). Polymers with significantly higher *M_w* (20000–30000) were obtained in the reactions that used TFP compared to those that used TMP (11000–18000, entry 1). The use of a UV-filtering material slowed the TFP-induced polymerization, but a significant yield of polymer was still obtained (21%, entry 6b). Thus, visible light is sufficient for bringing about polymerization in the TFP/iodonium/PAIBN system.

All three phosphites (TFP, TMP, DMPP) react rapidly with phenyl radicals (eq 3)²⁷ to form arylphosphoranyl radicals (ArP[•]Z₃) that do not possess fast unimolecular decomposition pathways.²⁸ Thus, chain-propagating single-electron-transfer to the iodonium salt (eq 1) is not precluded, and the observed large differences in co-initiation ability are not due to different propensities to undergo the required radical-chain chemistry (eqs 1–3). In contrast, a clear difference exists in these phosphites' relative nucleophilicities. Literature reports on phosphine reactivity²⁹ and indirect measurements of the electron availability on phosphorus,³⁰ as well as DFT calculations done as part of this study (see later discussion) all point to a nucleophilic reactivity series of DMPP > TMP > TFP. Of course, in valence-bond terms, TFP's non-nucleophilic nature is simply due to the electron withdrawing effect of the fluorines. Thus, TFP is a superior polymerization co-initiator because its counterproductive reactions as a nucleophile (eqs 8–10) are slow. This interpretation also explains why higher [TFP] resulted in faster photopolymerizations to form

Table 1. Photopolymerization of CHO Using **1a**, PAIBN, and TMP, DMPP, or TFP^a

entry	PZ ₃	expt	[PZ ₃] (M)	time ^b (h)	yield ^c (%)	<i>M_w</i> ^d	<i>M_w</i> / <i>M_n</i> ^d	<i>X_n</i> ^d
1	TMP	a	0.04	5 + 0	36	18000	1.54	119
		b	0.08	5 + 0	24	16900	1.61	107
		c	0.17	5 + 0	17	11100	1.45	78
2	DMPP	a	0.04	5 + 0	3	na ^e		
		b	0.04	5 + 20	8	na ^e		
3	TFP	a	0.05	5 + 0	36	21700	1.56	142
		b	0.05	5 + 20	38	22700	1.52	152
4	TFP	a	0.04	2 + 20	9	20800	1.49	142
		b	0.04	3 + 20	20	22600	1.56	148
		c	0.04	4 + 20	51	28600	1.51	193
		d	0.04	5 + 20	43	26800	1.52	180
5	TFP	a	0.01	5 + 20	38	29800	1.49	205
		b	0.10	5 + 20	65	32200	1.44	228
		c	0.15	5 + 20	69	32000	1.57	208
		d	0.19	5 + 20	78	na ^e		
6	TFP	a	0.04	5 + 20	40	na ^e		
		b ^f	0.04	5 + 20	21	na ^e		

^aIrradiation with 500-W halogen bulbs at ca. 18 °C. [1a] = 0.01 M. [PAIBN] = 0.02 M. The experiments grouped in each entry used common stock solutions and were irradiated simultaneously. Entry 1 results were reported previously.²³ ^bTime of irradiation + postirradiation dark time. ^cIsolated percent yield of polyCHO. ^dAbsolute molecular weights determined by GPC-MALLS. ^eNot analyzed. ^fIrradiation with UV filter film in place.

polymers with undiminished molecular weights (entry 5), whereas higher [TMP] gave lower yields and smaller polymers (entry 1). On one hand, high [TMP] leads to more of the detrimental side reactions (eqs 8–10), but TFP is not nucleophilic enough to undergo these reactions even when its concentration is high. On the other hand, high [TFP] promotes more efficient phenyl radical scavenging (eq 3) with less termination due to reaction of the phenyl radicals with the monomer.

Upon further experimentation we found it possible to use NMR to simultaneously observe both the iodonium/phosphite radical chemistry and the cationic polymerization. Conversion to polymer was determined by integrating the α -proton resonances of CHO (3.0 ppm) and polyCHO (3.4 ppm), and reactions of the phosphite and iodonium salt were observed by both ^{31}P and ^1H NMR. Unless otherwise noted, all NMR experiments used a 65-W compact fluorescent lamp (CFL) as the visible light source.

TFP was compared to five other commercially available phosphites in a series of experiments that were run under identical conditions (Table 2). Two of these, tris(isopropyl)

Table 2. Photopolymerization of CHO Using 1a, PAIBN, and Various Co-initiators^a

entry	co-initiator	% polym ^b	% ArI ^c	M_w	M_w/M_n	X_n	
7a	P(OCH ₂ CF ₃) ₃	45	59	nd ^d	19000	1.49	130
7b	P(O- <i>i</i> -Pr) ₃	43	65	20	15600	1.40	113
7c	P(OC ₂ H ₄ Cl) ₃	29	66	30	15500	1.48	107
7d	P(O- <i>n</i> -C ₁₃ H ₂₇) ₃	9	61	10	13500	1.34	103
7e	P(OSiMe ₃) ₃	9	24	10	na ^e		
7f	BnOP(OEt) ₂	16	59	10	9700	1.34	74
7g	PhNMe ₂	42	47	60	13800	1.43	99

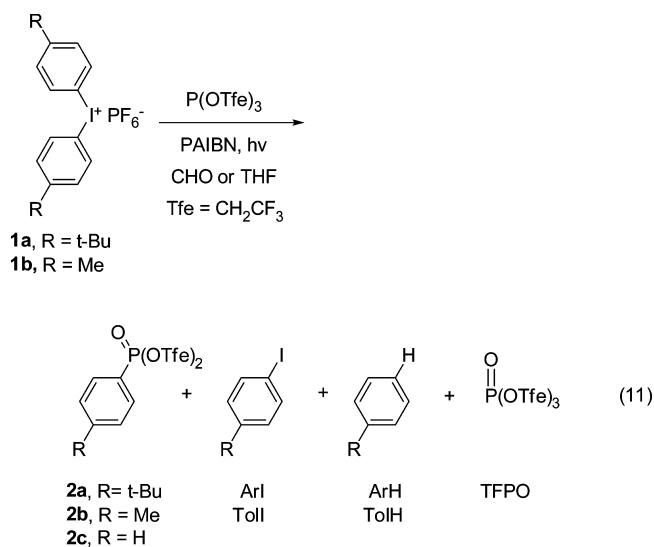
^a[1a] = 0.01 M, [PAIBN] = 0.7 mM, [co-initiator] = 0.10 M. Illumination with a 65-W CFL at ca. 34 °C for 2.0 h. Absolute molecular weights determined by GPC-MALLS. ^bPercent conversion to polyCHO by ^1H NMR initially after the illumination period and after standing for an additional 5 days dark period. ^cPercent conversion of 1a to 4-*tert*-butyliodobenzene. ^dNot detected. Limit of detection estimated at 5%. ^eNot analyzed.

phosphite (43%, entry 7b) and tris(2-chloroethyl) phosphite (29%, entry 7c), gave comparable polymer yields to that afforded by TFP (45%, entry 7a). However, the others gave sharply reduced yields (entries 7d–f), and all five gave polymers of diminished M_w indicating more chain transfer due to greater phosphite nucleophilicity. It is also interesting to note that all of the tested phosphites reacted with iodonium salt 1a to produce significant NMR yields of 4-*tert*-butyliodobenzene (10–30% ArI, entry 7b–f) except for TFP (<5% ArI, entry 7a).

N,N-Dimethylaniline (DMA) was reported to function as a co-initiator for iodonium-initiated VLICP of CHO when various organic dyes were used as photoinitiators.²⁰ The mechanism was proposed to involve a radical-chain leading to the formation of an iminium ion ($\text{CH}_2=\text{N}^+(\text{CH}_3)_2$), which starts the polymerization. Therefore, we included DMA in our comparison of alternative co-initiators (Table 2, entry 7g). The fact that DMA gave a 42% polymer yield when using PAIBN as a radical initiator substantiates the previously proposed radical chain mechanism.²⁰

Having established that TFP is the most effective co-initiator among commercially available phosphites, we focused further

experimentation on optimizing reaction conditions and using product studies to establish the mechanism of the TFP/iodonium/PAIBN photopolymerization system. These experiments and the nonpolymer products that were formed are summarized by eq 11.



In attempting to optimize the TFP system, we found that relatively high concentrations of both the phosphite (0.20 M) and the iodonium salt 1a (0.05 M) were advantageous (Table 3, entry 8i). However, higher concentrations of the azo initiator

Table 3. TFP-Co-initiated CHO Polymerization: Effect of Reactant Concentrations^a

entry	[1a]	[TFP]	[PAIBN]	% polym ^b	M_w	M_w/M_n	X_n
8a	0.01	0.10	0.02	65	25400	1.60	162
8b	0.02	0.10	0.02	84	na ^c		
8c	0.05	0.10	0.02	78	25000	1.62	158
8d	0.01	0.10	0.10	65	25400	1.62	160
8e	0.02	0.10	0.10	67	na ^c		
8f	0.05	0.10	0.10	69	22900	1.50	156
8g	0.01	0.20	0.02	80	24700	1.55	162
8h	0.02	0.20	0.02	84	na ^c		
8i ^d	0.05	0.20	0.02	96	24300	1.54	161
8j	0.01	0.20	0.10	72	25400	1.47	176
8k	0.02	0.20	0.10	81	na ^c		
8l	0.05	0.20	0.10	80	20300	1.65	126

^aConcentrations are in mol/L. Solutions were illuminated with a 65-W CFL at ca. 34 °C for 1.0 h. Absolute molecular weights were determined by GPC-MALLS. ^bPercent conversion to polymer by ^1H NMR. ^cNot analyzed. ^d2a (~6%) and TFPO (~10%) were detected by ^{31}P NMR.

generally gave lower polymer yields (entries 8d,e,f,j,k,l). Moreover, under the optimum conditions of entry 8i, conversion to polymer with $M_w = 24300$ was excellent at 96% after only 1 h photolysis with the 65-W CFL. We also note here that the completely polymerized solutions afforded by these experiments are transparent and nearly colorless unlike that afforded by VLICP systems that use a dye as the light-absorbing component.²⁰

Small product peaks at 22.4 and 21.8 ppm were observed in the ^{31}P NMR of the optimized run (entry 8i) as well as in several of the experiments reported in subsequent tables. The

peak at 22.4 ppm was identified as bis(2,2,2-trifluoroethyl) *tert*-butylphenylphosphonate ($\text{ArP}(\text{O})(\text{OTfe})_2$) **2a**. This assignment was verified by adding a synthetic sample of **2a** to the NMR tube and reacquiring the spectrum. The resonance at 21.8 ppm was due to the unsubstituted phenyl phosphonate, $\text{PhP}(\text{O})(\text{OTfe})_2$ **2c** (lit.³¹ shift = 21.3 ppm). The formation of the phosphonates **2a** and **2c** is consistent with the idea that intermediate phosphonium salts ($\text{ArP}^+(\text{OTfe})_3$ and $\text{PhP}^+(\text{OTfe})_3$) start polymerization by transferring a trifluoroethyl group to the monomer (eq 5, $R = \text{Tfe}$). Thus, unlike most other photoinduced cationic polymerization systems involving iodonium salts, this system does not rely on the generation of Brønsted acids.

A multiplet observed at -75 ppm in the ^{19}F NMR spectra of highly purified polyCHO from entries 5a, 8a, and 8i revealed the presence of 2,2,2-trifluoroethoxy end groups (Figure 1).³²

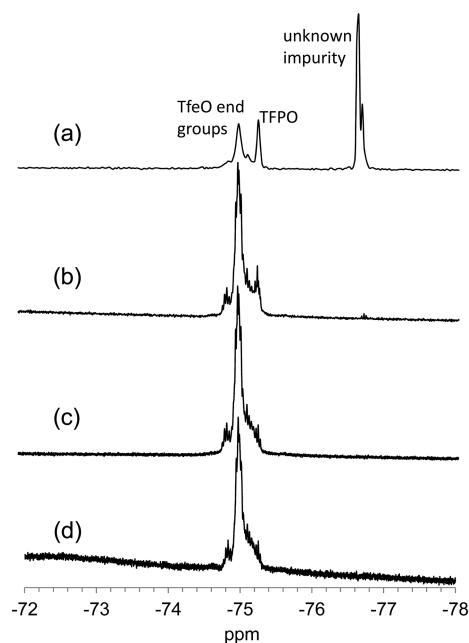


Figure 1. ^{19}F NMR of polyCHO after successive reprecipitations from $\text{CHCl}_3/\text{MeOH}$: (a) crude; (b) after one precipitation; (c) after two precipitations; (d) after three precipitations.

This observation provides further evidence for the alkylation step (eq 5) as the key to starting the cationic polymerization. In contrast, the ^{31}P NMR of the purified polymers did not show resonances attributable to phosphorus-containing end groups, consistent with our proposal that TFP does not react with active centers on the growing polymer. Using *p*-bromofluorobenzene as an internal standard, integration of the ^{19}F spectrum of polyCHO from entry 8a showed a 1:8 ratio of TfeO end groups to polymer chains. Most likely, chain transfer to monomer due to traces of water³³ causes the number of polymer molecules to be greater than the number of initiating end groups. The somewhat elevated molecular weight distributions observed ($M_w/M_n = 1.3\text{--}1.6$) are higher than the ideal for a living polymerization most likely due to this same factor.³⁴ Using the 1:8 end group to polymer ratio in conjunction with the degree of polymerization in entry 8a ($X_n = 162$) leads to a value for the chain transfer constant ($C = k_{tr}/k_p$) of $C = 20$. Corroboration of this conclusion comes from the 20:1 mol ratio of polyCHO (from $X_n = 161$ and polymer yield = 65%) to **2a** (6% yield based on 0.05 M iodonium salt) observed in entry 8i.

The TFP/iodonium/PAIBN combination can also bring about the cationic polymerization of THF (entry 10a, Table 4), although as expected,³⁵ THF polymerization was slower than CHO polymerization under these conditions (entry 9a). Control experiments that omitted the light (entry 10e) or PAIBN (entries 9b and 10b) did not polymerize. Omission of the TFP (entries 9c and 10c) gave much lower conversions to polymer, thus demonstrating TFP's essential role as a co-initiator.

Air oxidation of TFP to tris(2,2,2-trifluoroethyl) phosphate (TFPO) was a side reaction in the polymerizing solutions. Integration of the ^{31}P NMR spectra revealed yields of TFPO of approximately 20% based on the starting TFP concentration (entries 9a and 10a, Table 4). This product (ca. 10%) was also detected in entry 8i (Table 3). This oxidation reaction must be a photoinitiated radical process because in the experiments which omitted light or the azo initiator, significantly less oxidized product was observed (entries 9b, 9e, and 10b). Because this reaction did not appear to adversely affect the ability of the iodonium/TFP/azo combination to bring about photopolymerization we did not concern ourselves further with it and our experiments used nondegassed solutions unless otherwise noted.

Table 4. Photopolymerization of CHO and THF Using **1a**, PAIBN, and TFP^a

entry	expt	[TFP]	[PAIBN]	% yields ^b					
				polymer ^c		TFPO ^d	2a ^e	ArI ^c	ArH ^c
9, CHO	a	0.10	0.02	47	52	20	2	5	na
	b	0.10	none	nd	nd	7	na	nd	na
	c	none	0.02	2	5	nd	na	nd	na
	d	none	none	nd	nd	nd	na	nd	na
	e ^f	0.10	0.02	nd	nd	4	nd	nd	na
10, THF	a	0.10	0.02	6	22	30	5	18	12
	b	0.10	none	nd	nv ^g	9	nd	nd	na
	c	none	0.02	0.2	nv ^g	nd	nd	20	21
	d	none	none	nd	nv ^g	nd	nd	nd	na

^a[**1a**] = 0.05 M. 65-W CFL with UV filter at ca. 30 °C for 1.0 h. Reactant concentrations are given in mol/L. ^bNMR yields. "na" = not analyzed. "nd" = not detected. ^cConversion of monomer to poly(CHO) or poly(THF). The second column is after an additional 18–20 h in the dark. ^dYield of tris(2,2,2-trifluoroethyl) phosphate based on TFP from ^{31}P NMR integrals. ^eYields of $\text{ArP}(\text{O})(\text{OTfe})_2$ **2a**, 4-*tert*-butyliodobenzene (ArI), and *tert*-butylbenzene (ArH) based on **1a**. ^fKept in the dark for 24 h. ^gNo increase in viscosity was observed so not analyzed.

Table 5. Product Studies and Thermal Initiation^a

entry	solvent	[1a] (M)	init ^b	time (min)	% yields ^c					
					poly(CHO) ^d	TFPO ^e	2a ^f	2c ^f	ArI ^f	2a/2c ^g
11a	none	0.01	PAIBN	60	32	25	4	nd	na	0.69
				250	53	15	10	14	20	
11b	none	0.01	none	60	0	6	nd	nd	na	
				250	20	16	nd	nd	na	
11c	none	none	none	60	0	6	nd	nd	nd	
				250	0	21	nd	nd	nd	
12a	CD ₃ CN ^h	0.02	PAIBN	60	1	15	27	14	33	2.0
				270	3	32	62	44	85	1.4
12b ⁱ	CD ₃ CN ^h	0.02	PAIBN	60	1	8	20	13	28	1.5
				270	4	11	59	33	77	1.8
12c	CD ₃ CN ^h	0.02	none	270	1	16	16	nd	26	
13a ^j	none	0.02	BPO, Δ ^j	120	34	90	7	10	na	0.72
13b ^j	none	0.02	none, Δ ^j	120	2	8	na	na	na	

^a[TFP] = 0.10 M. Illumination with a 65-W CFL at ca. 34 °C unless otherwise noted. ^bRadical initiator included at 0.02 M. "BPO" = benzoyl peroxide. ^cNMR yields. ^dPercent conversion of CHO to polymer. ^eYield of TFP oxide based on TFP. ^fYields of ArP(O)(OTfe)₂ 2a, PhP(O)(OTfe)₂ 2c, and 4-*tert*-butyliodobenzene based on the iodonium salt. ^gRatio of arylphosphonate 2a to phenyl phosphonate 2c as determined by ³¹P NMR. ^hCD₃CN cosolvent, [CHO] = 3.7 M. Reactions run in NMR tubes. ⁱSolution was degassed by N₂ purge. ^jThermal initiation; reactions run at 92 °C in dark.

In the THF experiments (entry 10, Table 4), we were able to determine the yields of all aryl-containing products by ¹H NMR because the *tert*-butyl protons' resonances were not obscured by the spectrum of the monomer (as with CHO). The results provide further evidence for the key role of the arylphosphonium salt (ArP⁺(OTfe)₃) in starting polymerization. The diaryliodonium salt was consumed at the same rate in the absence of TFP (18% ArI, entry 10a) as it was when TFP was present (20% ArI, entry 10c), but polymerization only occurred to a significant extent in the TFP-containing solution.³⁶ Clearly, the THF polymerization is facilitated greatly when aryl radicals from the iodonium salt are diverted to reaction with the phosphite (5% yield 2a, entry 10a). Thus, alkylation of the monomer by the arylphosphonium salt to form phosphonate 2a (eq 5) is implicated as the main polymerization-starting step.

The role of the azo compound PAIBN is made clear by the experiments reported in Table 5. With solutions containing PAIBN (0.02 M, entry 11a), polymerization was relatively fast (32%, 60 min), and phenylphosphonate 2c was formed (14%, 250 min). In the absence of PAIBN (entry 11b), polymerization was much slower (0%, 60 min) and no 2c was detected.³⁷ Hence, phenyl radicals from PAIBN photolysis (eq 7) have the same fate as chain-propagating aryl radicals, meaning that PAIBN initiation of the radical chain comes about through the reaction of phenyl radicals with TFP to form phosphoranyl radicals (eq 3), which do SET with the iodonium salt (eq 1) and ultimately end up as phosphonate 2c. Polymerization can also be brought about by thermal radical initiation using benzoyl peroxide (entry 13a), and the observed 10% yield of 2c reveals the mode of initiation as being the same as with PAIBN photolysis. Hence, it is not a photolytic reaction of the iodonium salt that brings about polymerization, but rather it is a free-radical chain reaction (eqs 1–3) that can be initiated by any source of phenyl radicals.

The yields of aryl phosphonate 2a and phenyl phosphonate 2c are nearly equal under these conditions (2a/2c = 0.7, entries 11a and 13a), indicating that the radical chain reaction of iodonium 1a with TFP is not a true chain reaction (average kinetic chain length = approximately 1.0) under these conditions. (Still, because the initiation sequence also produces

a phosphonium salt, two polymerization-starting cations are produced per initiation event.) When acetonitrile-*d*₃ was used as a cosolvent with CHO (entry 12, [CHO] = 3.7 M) the radical chain reaction to form ArI and 2a was faster than in neat CHO ([CHO] = 9.9 M). Furthermore, the 2a/2c ratio increased by the same factor of about 2.5 that the CHO concentration had been decreased by (2a/2c = 1.5–2.0, entries 12a,b). Thus, reactions of propagating radicals with the monomer (CHO) represent a significant set of termination reactions. Most likely, H-abstraction from CHO by aryl radicals is followed by radical coupling of monomer-derived radicals.³⁸

Yet, even when these termination reactions are removed by omitting CHO and using nonreactive CD₃CN as the solvent³⁹ the TFP/iodonium reaction is surprisingly slow (Table 6). For example, the reaction of iodonium salt 1a with TFP (entry 14) is ca. 10 times slower than the reaction of 1a with Ph₃P (entry 15). Therefore, the kinetic chain length of the TFP/iodonium reaction must be much shorter than that of the very efficient Ph₃P/iodonium radical chain (eqs 1–4, Z = Ph).²⁴ However, TFP reacts rapidly when Ph₃P is present (20–50% yield of 2a, entry 16–22).⁴⁰ Moreover, the yield ratio of aryl phosphonate to aryl phosphonium salt (2a/ArP⁺Ph₃) is proportional to the starting ratio of [TFP] to [Ph₃P] (Figure 2). Thus, TFP and Ph₃P compete nearly equally for reaction with aryl radicals (while Ph₃P continues to propagate a chain reaction for their formation).

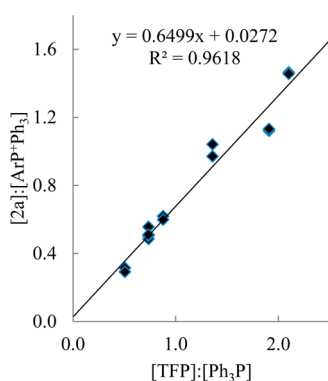
The slope of Figure 2 corresponds to the relative rate constants of TFP and Ph₃P in their respective reactions with phenyl radicals (slope = $k_{\text{TFP}}/k_{\text{Ph}_3\text{P}} = 0.65$). The triphenylphosphine rate constant has been estimated previously, $k_{\text{Ph}_3\text{P}} = 3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.²⁴ Thus, we can estimate a rate constant of $k_{\text{TFP}} = 2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for the reaction of TFP with phenyl radicals (eq 3, Z = OTfe). More importantly, we conclude that the inefficiency of the TFP/iodonium chain is not due to this reaction being slow.

Similar experiments in which CHO was allowed to compete with triphenylphosphine for 4-methylphenyl radicals generated from the radical chain reaction of Ph₃P with bis(4-methylphenyl)iodonium hexafluorophosphate 1b are reported in Table 7. The results are graphed in Figure 3, the slope of

Table 6. Competition Experiments: Reactivity of TFP vs Ph₃P toward Aryl Radicals^a

entry	reactant molarities			time (min)	% yield ^b		
	[1a]	[TFP]	[Ph ₃ P]		ArI	2a	ArP ⁺ Ph ₃
14 ^c	0.02	0.15	none	3	3	2	na
				10	12	8	na
15 ^c	0.02	none	0.16	3	44	na	35
				10	88	na	86
16	0.02	0.15	0.3	3	72	18	57
				10	89	19	64
17	0.01	0.15	0.15	15	70	39	33
				45	89	45	42
18	0.01	0.2	0.25	3	67	23	48
				10	86	31	55
19	0.001	0.3	0.15	3	66	39	24
				10	87	49	32
20	0.01	0.3	0.15	3	59	30	31
				10	81	41	39
21	0.02	0.15	0.15	3	50	18	29
				10	81	32	53
22	0.01	0.15	0.15	3	63	21	42
				10	85	30	59

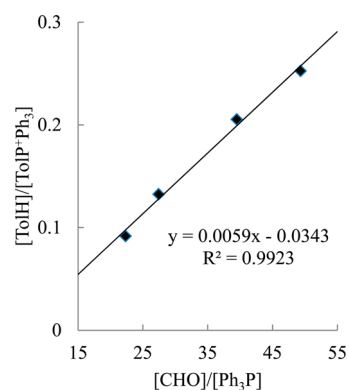
^aCD₃CN solutions were irradiated with a 500-W halogen lamp at ca. 15 °C. ^bNMR yields based on 1a. ^cPAIBN was also included at 0.02 M.

**Figure 2.** Yield ratio vs [reactant] ratio for TFP vs Ph₃P competition experiments.**Table 7. Competition Experiments: Reactivity of CHO vs Ph₃P with Aryl Radicals^a**

entry	[CHO]	[Ph ₃ P]	TolI ^b	TolH ^b	TolP ⁺ Ph ₃ ^b
23	5.0	0.10	76	16	64
24	4.0	0.10	100	17	83
25	2.8	0.10	99	12	89
26	2.5	0.11	99	9	93

^aCD₃CN solutions of bis(4-methylphenyl)iodonium hexafluorophosphate 1b (0.01 M) were irradiated with a 65-W CFL for 60 min at ca. 30 °C. Reactant concentrations are in mol/L. ^bNMR yields based on the iodonium salt.

which (slope = $k_{\text{CHO}}/k_{\text{Ph}_3\text{P}} = 0.0059$) allows the rate constant for reaction of phenyl radicals with cyclohexene oxide to be estimated as $k_{\text{CHO}} = 2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. Using these data along with our value for k_{TFP} , one calculates that only about 50% of the aryl radicals were captured by the phosphite in polymerization experiments that used $[\text{TFP}] = 0.1 \text{ M}$. Thus, the efficiency of phenyl radical scavenging is probably the main

**Figure 3.** Yield ratio vs [reactant] ratio for CHO vs Ph₃P competition experiments.

reason for the observed positive correlation of polymer yield with starting TFP concentration (Table 3).

We also carried out DFT calculations as part of this study (Table 8). As expected, the phosphite HOMO energies show that TFP ($E_{\text{HOMO}} = -7.4 \text{ eV}$) is inherently much less nucleophilic than the nonfluorinated phosphites TMP and DMPP ($E_{\text{HOMO}} = -6.2$ and $E_{\text{HOMO}} = -5.6 \text{ eV}$). More importantly, the calculations allow an estimate of the corresponding phenylphosphonium salts' reduction potentials, which in turn allow us to gauge ΔG for the crucial single electron transfer step (eq 1). The validity of the obtained reduction potentials is bolstered by the excellent agreement of the value obtained for tetraphenylphosphonium with a literature value for its half-wave reduction potential (av calcd $E_{\text{red}} = -2.0 \text{ V}$ vs SCE, lit.⁴¹ $E_{1/2} = -1.87 \text{ V}$ vs SCE). Using the computed phosphonium reduction potentials and the (in our opinion) best literature value available for $E_{1/2}$ for diphenyliodonium salts ($E_{1/2} = -0.7 \text{ V}$ vs SCE)⁴² leads to estimates of ΔG_{SET} for the various phosphines that are instructive. The result calculated for TFP ($\Delta G_{\text{SET}} = -1.5 \pm 4.5 \text{ kcal/mol}$, entry 30) points to the most probable reason for the inefficiency of the TFP/iodonium chain reaction, this being a nearly thermoneutral (nonexergonic) and, therefore, slow SET step (eq 1). In contrast, trimethyl phosphite ($\Delta G_{\text{SET}} = -27 \pm 3 \text{ kcal/mol}$, entry 28) and triphenylphosphine ($\Delta G_{\text{SET}} = -31 \pm 3 \text{ kcal/mol}$, entry 27), both of which react rapidly in radical-chain fashion with iodonium salts, form phosphoranyl radicals that can transfer an electron to the iodonium salt in a very exergonic process. Of course, the phosphoranyl radical from TFP ($\text{PhP}^{\bullet}(\text{OTf})_3$) is a relatively poor reductant due to the same fluorine inductive effect that makes TFP a weak nucleophile. Thus, in the further refinement of this system for VLICP, it might be feasible to design a relatively non-nucleophilic phosphite co-initiator that can also form a phosphoranyl radical capable of an exergonic electron transfer to the iodonium salt.

CONCLUSION

The combination of a trialkyl phosphite, PAIBN, and an iodonium salt can be an effective system for visible-light induced cationic polymerization of cyclic ethers such as CHO and THF. When TFP is used as the phosphite, the resulting polymers have high molecular weights and low polydispersities and are nearly colorless, unlike other systems that make use of dyes as photosensitizers. Other trialkyl phosphites also serve as co-initiators but result in lower M_w polymers. TFP's non-

Table 8. Energies Determined by DFT Calculations^a on Phosphines (PZ₃), Phosphoniums (PhP⁺Z₃), and Phosphoranyl Radicals (PhP[•]Z₃)

entry	PZ ₃	PZ ₃ HOMO (eV)		PhP ⁺ Z ₃ – PhP [•] Z ₃ (kcal/mol)		E _{red} vs SCE ^b (V)		ΔG _{SET} ^c (kcal/mol)	
		6-31G	DZVP	6-31G	DZVP	6-31G	DZVP	6-31G	DZVP
27	PPh ₃	-5.30	-5.54	57.8	63.8	-2.17 ^d	-1.91 ^d	-34	-28
28	P(OMe) ₃	-6.05	-6.34	62.0	67.2	-1.99	-1.76	-30	-24
29	PhP(OMe) ₂	-5.63	-5.89	69.2	76.3	-1.68	-1.36	-22	-15
30	P(OTf) ₃ ^e	-7.21	-7.62	85.8	94.2	-0.96	-0.58	-6	+3
31	P(OC ₂ H ₄ Cl) ₃	-6.75	-7.01	73.2	77.9	-1.51	-1.29	-19	-14
32	BnOP(OEt) ₂	-5.98	-6.24	54.2	59.3	-2.33	-2.10	-38	-32
33	P(OSiMe ₃) ₃	-5.49	-5.74	46.2	52.5	-2.68	-2.40	-69	-62

^aGeometries were optimized using MNDO/d.⁵⁰ DFT/B3LYP calculations used either the 6-31G(d,p)⁵¹ or the DZVP⁵² basis set. ^bE_{red} vs SCE calculated from E(PhP⁺Z₃) – E(PhP[•]Z₃) by multiplying by 23.06 kcal mol⁻¹ V⁻¹ and subtracting the absolute voltage of the standard calomel electrode (4.68 V).⁵³ ^cΔG for single-electron transfer to diaryliodonium salt calculated from the DFT-derived phosphonium E_{red} and the literature E_{1/2} for diphenyliodonium, E_{1/2} = -0.7 V vs SCE.⁴² ^dLiterature E_{1/2} for Ph₄P⁺ Cl⁻ is -1.87 V vs SCE.⁴¹ ^eTf = 2,2,2-trifluoroethyl.

nucleophilic nature allows polymer chains to grow without excessive chain transfer. The mechanism is as shown in eqs 1–7. However, the reaction of TFP with iodonium salt (eq 4) is slow because the radical chain reaction (eqs 1–3) is impaired by a nearly thermoneutral SET propagation step (eq 1). Alkylation of the monomer by the arylphosphonium salt ArP⁺(OTf)₃ (eq 5) is responsible for starting the cationic polymerization as evidenced by both the formation of aryl phosphonate **2a** and the ¹⁹F NMR detection of CF₃CH₂O end groups on the polymer.

EXPERIMENTAL SECTION

General Methods. NMR spectra were obtained on a 300 MHz instrument with chemical shifts referenced to solvent deuterium signals. ¹⁹F NMR spectra were processed using backward linear interpolation (BLIP) to remove the broad resonance due to poly(tetrafluoroethylene) in the probe. Cyclohexene oxide was filtered through alumina and vacuum distilled from CaH₂. THF was distilled from Na/benzophenone. The iodonium salts² and PAIBN²⁶ were prepared using literature methods. Iodonium salt **1b** required four recrystallizations from H₂O to reduce the amount of *o,p* impurity to <2%: mp 175.7–177.2 °C; lit.² mp 169–173 °C. All other compounds were commercial products used as received.

GPC used THF as eluant with absolute molecular weight determination by a multiangle light scattering (MALLS) detector. We found dn/dc = 0.114 mL/g for polyCHO. Polydispersities (M_w/M_n) ranged from 1.3 to 1.6 according to no apparent pattern. Prior to GPC analysis, polyCHO was purified by dissolution in CHCl₃ followed by precipitation with MeOH. Semiempirical MO and DFT calculations were carried out using Hyperchem software and a personal computer with full details given in the Supporting Information.

Integration of the ¹H and/or ³¹P NMR was employed to determine relative product yields. Key ¹H NMR resonances (ppm) used for yield determination were as follows: CHO, 3.05; polyCHO, 3.4; THF, 3.65, 1.75; polyTHF, 3.3, 1.5; TFP, 4.3; **2a/2c**/TFPO (overlap), 4.6; **2a**, 1.36; **1a**, 8.0, 1.25; ArI, 7.1–7.2, 7.5–7.6, 1.23; ArH, 1.26, **1b**, 2.37; TolI, 2.25; TolH, 2.30; ToIP⁺Ph₃ PF₆⁻, 2.48. Key ³¹P NMR resonances (ppm) used for yield determination were: TFP, +139; TFPO, -2; **2a**, +22; **2c**, +21. When possible, yield results from ³¹P NMR were checked using ¹H NMR, and the results generally agreed within ±2%.

2a. Bis(4-*tert*-butylphenyl)iodonium chloride (429 mg, 1.0 mmol) was reacted with TFP (83 μL, 1.5 mmol) under UV irradiation in DMSO-*d*₆. Ether/H₂O extraction and flash chromatography (alumina/hexanes/EtOAc) gave 162 mg (43%) **2a** as a viscous liquid: ¹H NMR (CDCl₃) δ 1.35 (s, 9H), 4.35 (m, 2H), 4.45 (m, 2H), 7.54 (dd, *J* = 8.5, 4.4 Hz, 2H), 7.76 (dd, *J* = 14, 8.3 Hz, 2H). ¹³C NMR δ 31.1, 35.4 (d, *J* = 1.4 Hz), 62.3 (dq, *J* = 5.1, 38 Hz), 121.4 (d, *J* = 198 Hz), 122.7 (dq, *J* = 9.4, 277 Hz), 126.1 (d, *J* = 17 Hz), 131.9 (d, *J* = 12 Hz), 157.8 (d, *J* = 3.6 Hz); ³¹P NMR δ 22.6; ¹⁹F NMR δ -75.01 (t, *J* = 8.5 Hz); MS

m/z 378 (M⁺), 363, 335; HRMS (ESI) *m/z* calcd for [C₁₄H₁₇F₆O₃P + Na]⁺ 401.0717, obsd 401.0725.

Photochemical Conditions. The light source was either a 500-W, 118-mm tungsten–halogen bulb (also known as a “work lamp”) or a 65-W (200-W equivalent) compact fluorescent lamp (CFL). Some experiments used a UV-filtering sheet from Edmund Scientific placed between the light source and the reaction tubes. This material had a transmission <4% at wavelengths <400 nm. The experiments grouped in each entry used common stock solutions and were irradiated simultaneously on a merry-go-round apparatus.

Photopolymerization Experiments. Reaction solutions (2.0 mL) were prepared under N₂ in dry 1.0-cm borosilicate test tubes capped with rubber septa. In early experiments (Table 1), the merry-go-round apparatus was placed in a plastic container containing a water bath held at 18 ± 2 °C, and illumination was from three work lamps arranged around the outside of the plastic container as described previously.²³ After irradiation, the solutions were poured into 10 mL of 5% NH₄OH in methanol. The precipitated poly(cyclohexene oxide) was vacuum filtered, air-dried, and weighed to give the conversions reported in Table 1.

The experiments reported in Tables 2–5 used the 65-W CFL placed in the middle of the merry-go-round apparatus. This light source stays relatively cool so no cooling other than air circulation provided by the merry-go-round motor was provided. A thermometer placed on the merry-go-round with the tubes invariably registered 30–35 °C at the end of the irradiation period. After irradiation, the reaction solutions were immediately diluted in CDCl₃ and the NMR spectra were obtained.

Competition Experiments. Reactions were run in NMR tubes. The NMR tube was either placed in a Pyrex cooling water jacket (ca. 15 °C) at a distance of 2.5 cm from the work lamp bulb (Table 6) or rotated around the 65-W CFL on the merry-go-round apparatus (Table 7).

ASSOCIATED CONTENT

Supporting Information

NMR spectra and GC–MS results for compound **2a**. Computational method and detailed results. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interest.

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- (36) The products and slight polymerization observed in entry 10c come about through a radical-chain reaction of the iodonium salt with THF to form α -THF cations capable of starting cationic polymerization.⁷
- (37) The 20% conversion to polymer observed upon 250 min of irradiation when the azo compound was not included (entry 11b) was due to unintended UV photolysis of the iodonium salt. When a UV filter was used between the light source and the tubes, control experiments like this one did not polymerize (see entries 9b and 10b, Table 4).
- (38) A reviewer suggested that monomer-derived radicals may lead to polymerization through their reaction with the phosphine, with subsequent electron transfer leading to a reactive phosphonium ion, which could start polymerization either by alkylating the monomer or by expelling TFP to form a monomer-derived oxonium ion. We obtained no specific evidence for the formation of CHO radical dimers and we cannot rule out the possibility that some CHO radicals propagated by reacting with TFP, but we think that the observed effects of lowering the monomer concentration (entry 12) and increasing the TFP concentration (entries 5 and 8) argue strongly for radical termination as the primary mode of reactivity for the CHO-derived radical.
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