Use of Diaryliodonium/Phosphine Radical-Chain Chemistry for Visible Photoinitiation of Cationic Polymerizations. Trimethyl Phosphite as a Co-initiator of the Ring-Opening Polymerization of Cyclohexene Oxide[1]

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Received May 4, 1998
Revised Manuscript Received August 10, 1998

Introduction

Diaryliodonium salts have attracted considerable attention in recent years because of their ability to function as photoinitiators of cationic polymerizations.[2] However, the use of iodonium salt photoinitiators in industrial applications such as UV curing of epoxy resins is limited by the weak absorption of these salts in the near UV region (300−350 nm). Therefore, the development of methods to extend the usefulness of iodonium salt photoinitiators by allowing the use of near UV or visible light has been pursued by several groups.[3]

Iodonium salts react with phosphines (PZ_3) to give arylphosphonium salts (ArP^+Z_3) and iodoarenes (ArI) (eq 4).[4] The mechanism is a radical chain that involves phosphoranyl radicals ($ArP^\bullet Z_3$) as one-electron reductants for the iodonium salts (eq 1).[4] The diaryliodine intermediate ($Ar_2I^\bullet$) generated in the redox step (eq 1) rapidly fragments to give an iodoarene and an aryl radical ($Ar^\bullet$) (eq 2). The aryl radical completes the chain by adding to the phosphine to give the arylphosphoranyl radical (eq 3).[4b]

$$Ar_2I^+ + ArP^\bullet Z_3 \rightarrow Ar_2I^\bullet + ArP^+Z_3 \qquad \text{(prop)} \qquad (1)$$

$$Ar_2I^\bullet \rightarrow Ar^\bullet + ArI \qquad \text{(prop)} \qquad (2)$$

$$Ar^\bullet + PZ_3 \rightarrow ArP^\bullet Z_3 \qquad \text{(prop)} \qquad (3)$$

$$Ar_2I^+ + PZ_3 \rightarrow ArI + ArP^+Z_3 \qquad \text{(net)} \qquad (4)$$

The iodonium-phosphine radical chain is extremely efficient; the reaction of 4,4′-di-*p*-tolyliodonium hexafluorophosphate with triphenylphosphine, for example, has been estimated to have an average chain length of ≥100.[4b] This efficiency is due to the extreme rapidity of all three propagation steps,[5] which makes them able to compete strongly with bimolecular termination steps.

This chemistry can be used to start cationic polymerization if the phosphine used gives an arylphosphonium product (ArP^+Z_3) that can react with monomer by the transfer of a proton or other cationic group. Accordingly, an attractive possibility for starting ring-opening polymerizations of cyclic ethers is using Z = OMe and forming a trimethoxyphosphonium cation, which can methylate monomer (R_2O) by an S_N2 reaction (eq 5) and lead to polymerization (eq 6).

$$ArP^+(OMe)_3 + R_2O \rightarrow ArP(O)(OMe)_2 + R_2O^+\text{-}Me \qquad (5)$$

$$R_2O^+Me + nR_2O \rightarrow \text{polymer} \qquad (6)$$

Hence, we proposed (and presented preliminary evidence for) the use of trimethyl phosphite (TMP) as a co-initiator for iodonium-induced photopolymerizations of tetrahydrofuran.[7] This paper reports further evidence for this thesis in the form of experiments on the visible-light polymerization of the representative monomer,[3a] cyclohexene oxide (**2**), using 4,4′-di-*tert*-butyldiphenyliodonium hexafluorophosphate (**1**), TMP, and the visible-light-sensitive phenyl radical source, phenylazoisobutyronitrile (PAIBN ≡ Ph−N=N−CMe_2CN).[8]

Results and Discussion

Cyclohexene oxide solutions of iodonium salt (**1**), TMP, and PAIBN were illuminated with three 500-W halogen lamps to give poly(cyclohexene oxide) (Table 1). Conversions to polymer varied depending on the reactant concentrations (experiments 3a−d, 4a−c) and time of photolysis (experiments 3c,e−g). Control experiments that omitted one of the reactants (experiment 1c, TMP; experiment 1d, PAIBN) or the light (experiment 1b) gave negligible conversions (<1%). We also established that iodonium salt (**1**), a known efficient UV initiator of cationic polymerization, is incapable of starting polymerization by itself under the visible photolysis conditions used in this work (experiment 1e).[9] Finally, we note that GC analysis of a solution containing solely the azo photoinitiator showed that 70% of the PAIBN remained unchanged after the usual 5-h photolysis period (experiment 2).[10]

All of these observations are consistent with the mechanism outlined in the Introduction. The radical-chain reaction is initiated by the photolysis of PAIBN to form phenyl radicals, which subsequently add to the phosphite (analogous to eq 3) to give phenyltrimethoxyphosphoranyl radicals ($PhP^\bullet(OMe)_3$). This phosphoranyl radical then completes the initiation process by reducing the iodonium salt analogously to eq 1.

The free-radical propagation cycle (eqs 1−3) then begins with eq 2 and results in the conversion of iodonium salt (**1**) to the *p*-*tert*-butylphenyltrimethoxyphosphonium salt ($ArP^+(OMe)_3$). The phosphonium salt methylates the cyclohexene oxide monomer, beginning the cationic polymerization, as shown in Scheme 1.

Conversion to poly(cyclohexene oxide) increased predictably with increasing irradiation time (experiments 3c,e−g). The conversion to polymer decreased significantly when the iodonium salt concentration was decreased from 0.01 to 0.005 M (compare experiments 4a and 4b); a simple consequence of the accompanying reduction in theoretical yield of the key phosphonium salt product of the radical chain. However, doubling the iodonium concentration to 0.02 M had little effect on polymer yield (experiment 4c), probably because of incomplete consumption of the iodonium salt at both of the higher concentrations. The conversion to polymer was insensitive to PAIBN concentration (experiments 3e,h,i), as expected from the fact that at the lowest concentration ([PAIBN] = 0.022 M), the photoinitiator already absorbed nearly all of the light in the 400−450 nm range.[11]

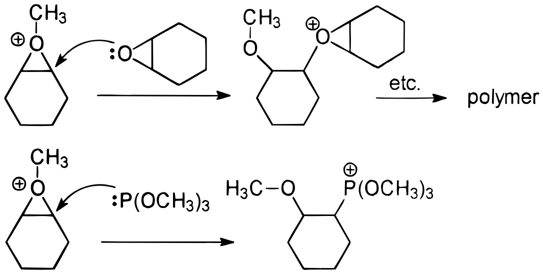
10.1021/ma980703p CCC: $15.00

Table 1. Polymerization of Cyclohexene Oxide by Visible Irradiation of Diaryliodonium Salt/Trimethyl Phosphite/Phenylazoisobutyronitrile Solutions

expt[a]	$[Ar_2I^+]$[b], M	[TMP][c], M	[PAIBN][d], M	time, h	% conv[e]	M_w[f]	X_n[g]
1a	0.010	0.166	0.022	5.0	30	–[h]	–
1b	0.010	0.166	0.022	5.0 dark[i]	0.4	–	–
1c	0.010	none	0.022	5.0	0.2	–	–
1d	0.010	0.166	none	5.0	0.6	–	–
1e	0.010	none	none	5.0	0.2	–	–
2	none	none	0.016[j]	5.0	0.0[j]	–	–
3a	0.010	0.042	0.022	5.0	36	5100	30.1
3b	0.010	0.084	0.022	5.0	24	4400	26.0
3c	0.010	0.166	0.022	5.0	17	3500	20.7
3d	0.010	0.325	0.022	5.0	8.4	–[k]	–[k]
3e	0.010	0.166	0.022	1.0	0.7	–	–
3f	0.010	0.166	0.022	2.0	5.2	–	–
3g	0.010	0.166	0.022	3.0	6.6	–	–
3h	0.010	0.165	0.045	5.0	22	–	–
3i	0.010	0.165	0.090	5.0	22	–	–
4a	0.005	0.166	0.022	5.0	12	–	–
4b	0.010	0.166	0.022	5.0	30	–	–
4c	0.020	0.166	0.022	5.0	25	–	–

[a] Like-numbered experiments used common stock solutions and were irradiated simultaneously. [b] 4,4′-Di-*tert*-butyldiphenyliodonium hexafluorophosphate. [c] TMP, trimethyl phosphite. [d] PAIBN, phenylazoisobutyronitrile. [e] Percent conversion to poly(cyclohexene oxide). [f] Polydispersities (M_w/M_n) were 1.8 ± 0.1. [g] Number-average degree of polymerization calculated from M_w and M_w/M_n. [h] –, not analyzed. [i] Reaction tube was kept in the dark for 5.0 h. [j] GC analysis showed 70% of the azo compound remained unchanged. [k] Filtration of the reprecipitated polymer was unsuccessful.

Scheme 1



Increasing the trimethyl phosphite concentration led to a dramatic decrease in the conversion to polymer (experiments 3a–d). Thus, TMP is a polymerization inhibitor in this system. In addition, the molecular weight and number-average degree of polymerization (X_n) of the isolated poly(cyclohexene oxide) decreased with increasing [TMP] (experiments 3a–c). The linear relationship between $1/X_n$ and the ratio of phosphite concentration to monomer concentration ([TMP]/[**2**]) shown in Figure 1 demonstrates that TMP is a chain-transfer agent for the polymerization.[12] The best fit slope of Figure 1 corresponds to a chain transfer constant for TMP ($C_{TMP} = k_{TMP}/k_{monomer}$) of $C_{TMP} = 1.2$.

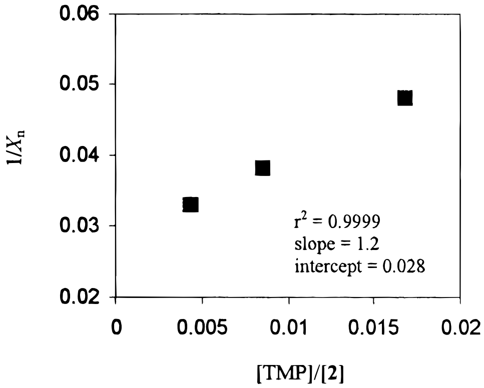
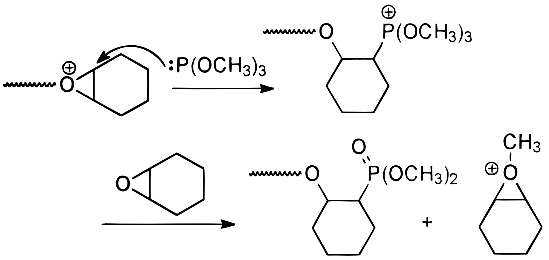


Figure 1. Reciprocal of number-average degree of polymerization ($1/X_n$) versus phosphite/monomer concentration ratio ([TMP]/[**2**]).

Scheme 2



The phosphite inhibits polymerization by virtue of its nucleophilicity. It competes with monomer molecules for both reaction at the cationic center of the methylated monomer (or of small growing oligomer chains) (Scheme 1) and for reaction with the aryltrimethoxyphosphonium salt formed by the radical chain (eq 7, R = Ar). The methylphosphonium cation formed by eq 7 can start polymerization or react similarly with the phosphite (eq 7, R = Me). This reaction (eq 7, R = Me) represents a cationic-chain Arbuzov rearrangement of TMP to methyl dimethylphosphonate and reduces the amount of TMP available to participate in the radical-chain process that forms the polymerization-starting phosphonium cations.

$$R{-}P^+(OMe)_3 + P(OMe)_3 \rightarrow R{-}P(O)(OMe)_2 + MeP^+(OMe)_3 \quad (7)$$

Chain transfer by phosphite comes about through its successful competition with monomer molecules for reaction with the cationic center of the growing polymer (Scheme 2). The chain transfer constant we report in this paper, $C_{TMP} = 1.2$, means that this phosphite's reactivity toward S_N2 reaction with the oxonium ion centers of the growing polymers is very similar to that of the ether monomer.

Because TMP both inhibits the polymerization and limits polymer molecular weight, its concentration must be carefully balanced so that sufficient phosphite is present to efficiently capture the aryl radicals that propagate the radical-chain process, yet not be so great as to lead to unacceptable levels of inhibition and chain-transfer (as in experiment 3d, for example).[14] Literature rate constants can be employed to calculate that at the lowest [TMP] employed in this work (0.042 M) approximately 15% of the aryl radicals were captured by the chain-propagation reaction with TMP.[15]

We finally note that chain transfer (Scheme 2) and polymerization inhibition (Scheme 1) by phosphite are very similar processes, the only difference being whether a polymer-chain-initiating species or a polymer-chain-propagating species is intercepted. Because both of these unproductive processes are promoted by the nucleophilicity of the phosphine, it may be possible to minimize their negative impact on the usefulness of this chemistry by using a less nucleophilic trialkoxyphosphine.

Conclusion

The radical-chain reaction of trimethyl phosphite with a diaryliodonium salt results in the formation of trimethoxyphosphonium cations, which bring about the cationic polymerization of cyclohexene oxide. Furthermore, when a visible-sensitive radical source such as PAIBN is used, polymerization can be accomplished using readily available, inexpensive light sources. Finally, because it is phosphoranyl radicals that are responsible for reducing the iodonium salt, the redox characteristics of monomer-derived radicals are unimportant and, in principle, any cationically polymerizable monomer should be polymerizable using this chemistry.

Experimental Section

Cyclohexene oxide was filtered through alumina, distilled from CaH_2, and then refrigerated until use. 4,4′-Di-*tert*-butyldiphenyliodonium hexafluorophosphate[17] and phenylazoisobutyronitrile[8a] were prepared according to literature methods. All other reagents were used as received from commercial suppliers. GPC analysis employed THF as eluant (flow = 1 mL/min) and Waters Styragel columns with molecular weights reported relative to polystyrene standards. GC analysis used a 30-m × 0.53-mm HP-1 column, helium carrier gas, split injection mode, and flame ionization detection. Octadecane was used as an internal standard.

Solutions of the iodonium salt in cyclohexene oxide were prepared under nitrogen. Aliquots (2 mL) of the stock solution were transferred to Pyrex test tubes (i.d. = 1.0 cm) capped with rubber septa, and TMP and PAIBN were added by syringe. The tubes were placed in a merry-go-round apparatus contained in a transparent polycarbonate jar (3 mm wall thickness). The jar was equipped for cooling by circulating tap water (20 ± 5 °C) and surrounded by three halogen work lights purchased from a local hardware store. The work light housing includes an 8-mm thickness of tempered glass as a heat and UV shield. The distance between the path of the sample tubes and the 110−130 V, 500-W, 118-mm tungsten−halogen bulbs (color temperature ≈ 3000 K)[18] was approximately 25 cm. At the end of the reaction period solutions were poured into 10 mL of 5% NH_4OH in methanol. The precipitated poly(cyclohexene oxide) was vacuum filtered, air-dried, and weighed to give the percent conversions given in Table 1. For GPC and NMR, the polymer was dissolved in CH_2Cl_2 and reprecipitated with methanol followed by drying under vacuum. ^{1}H NMR (δ, $CDCl_3$, 60 MHz): 3.5 (2H, br), 1.5 (8H, br).

Acknowledgment. We thank Dr. Eric A. Fossum for assisting with the GPC analyses and for helpful discussions. We also thank Mr. Lee Stanek for carrying out experiment 2. This work was supported by a WSU Foundation Special Projects Grant.

References and Notes

(1) Presented at the 30th Great Lakes Regional Meeting of the American Chemical Society, Chicago, IL, May 1997; Paper 236.

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(5) The rate constant (k_{set}) for the single-electron transfer (eq 1) has been estimated, $k_{set} \approx 4 \times 10^9$ M^{-1} s^{-1}.[4b] The lifetime of diphenyliodine (eq 2) formed by the anthracene-sensitized photolysis of a diphenyliodonium salt in acetonitrile solution was estimated to be at most 0.2 ns.[6] The addition of phenyl radicals to phosphines (eq 3) is also very fast. For example, the rate constant for addition of the *p*-tolyl radical to triphenylphosphine has been found to be approximately 3×10^8 M^{-1} s^{-1}.[4b]

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(9) This cannot be due solely to a failure to photolyze the iodonium salt at the employed long wavelengths because the iodonium/PAIBN system also fails to give polymer (experiment 1c). The failure of the iodonium/PAIBN system must reflect the inability of cyclohexene oxide, unlike other cyclic ethers such as THF and 1,3-dioxolane, to carry a chain for reduction of the onium salt (see ref 7). This inability may be due to a poor reducing ability of the α-cyclohexene oxide radical or due to a relatively low reactivity of the α-hydrogens of the epoxide toward abstraction by phenyl radicals or due to both of these factors.

(10) The quantum yield (ϕ) for decomposition of PAIBN at 430 nm has been reported in the literature, $\phi = 0.07$ mol/einstein.[8b] Taking this value of ϕ as representative over the range of wavelengths that were absorbed by PAIBN in these experiments[11] and using the data from experiment 2 allow an estimate of the light intensity (I_0) felt by the reaction solutions in our experiments, $I_0 \approx 4 \times 10^{-6}$ einstein L^{-1} s^{-1} (photon flux at exposed surface ≈ $2{-}3 \times 10^{-9}$ einstein cm^{-2} s^{-1}).

(11) Absorbances and percent absorptions of the reaction solutions with [PAIBN] = 0.022 M as calculated from the visible spectrum of PAIBN in methanol are: 400 nm, 3.41, 99.96%; 410 nm, 2.82, 99.85%; 420 nm, 2.10, 99.21%; 430 nm, 1.38, 96.0%; 440 nm, 0.82, 85%; 450 nm, 0.46, 65%.

(12) As proposed in ref 7. To our knowledge, other literature does not mention trialkyl phosphites as chain-transfer agents for cationic polymerizations. However, acyclic ethers have been used as chain-transfer agents for ring-opening cationic polymerizations and function in an analogous manner (i.e., nucleophilic attack on growing polymer followed by transfer of an alkyl group to monomer) to that proposed for TMP in this paper.[13a] Other nucleophiles that have been used or identified as chain-transfer agents in ring-opening cationic polymerizations include water,[13b] ammonia,[13b] acetic anhydride,[13c] and butylene glycol.[13d.]

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(14) In fact, these polymerizations are clearly not optimized. It is clear that a TMP concentration of less than 0.042 M (experiment 3a) is best for achieving efficient polymerization.

(15) Literature values for the rate constant for phenyl radical addition to TMP are $k_{TMP} \approx 2 \times 10^8$ M^{-1} s^{-1} at room temperature (*p*-tolyl radical)[4b] and $k_{TMP} \approx 3.5 \times 10^8$ M^{-1} s^{-1} at 45 °C.[16a] We take the rate constant for hydrogen abstraction by phenyl radical from cyclohexene oxide (all positions) as approximately equal to that for hydrogen abstraction from THF, $k_H \approx 5 \times 10^6$ M^{-1} s^{-1} at 25 °C.[16b] The concentration of neat cyclohexene oxide is 9.9 M. We also assume here that the rate constants for reactions of the *p*-*tert*-butylphenyl and *p*-tolyl radicals are essentially the same as those for the reaction of unsubstituted phenyl radicals, see: Pryor, W. A.; Echols, J. T., Jr.; Smith, K. *J. Am. Chem. Soc.* **1966**, *88*, 1189−1199.

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MA980703P