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Cationic polymerization of cyclohexene oxide initiated by a ternary system consisting of free radical photoinitiator, diphenyl acetylene and triphenylsulphonium salt

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Summary

Vinyl cation-based initiating system for cationic polymerization of cyclohexene oxide (CHO) has been developed by using photochemical free radical sources in conjuction with diphenyl acetylene (DPA) and triphenyl sulphonium hexafluorophosphate. An initiation mechanism involving the formation of substituted vinyl radical and subsequent oxidation to the corresponding cations is proposed.

Introduction

Onium salts such as diphenyliodonium [1,2] and triphenyl sulphonium [3] salts are the most widely applied cationic photoinitiators. Their role in the initiation has been studied in detail [4]. In general, the photopolymerization by onium salts is initiated by three ways; (i) direct photolysis [4], (ii) photosensitization [5] and (iii) and free radical promoted initiation [6-9]. The latter two modes are particularly important in extending the spectral sensitivity of the onium salts to longer wavelengths where commercial lamps emmit light. Free radical promoted initiation mechanism involves electron transfer from photochemically generated radicals to onium salts [8]. Depending upon the redox potentials of the free radicals and onium salts involved, carbon centered radicals may be oxidized to the corresponding cations capable of initiating cationic polymerization of appropriate monomers.

$$R^{\bullet} + On^{+} \longrightarrow R^{+} + On^{\bullet} \qquad (1)$$

While diphenyl iodonium [6,7] and *N*-alkoxy pyridium [9] salts are readily used in free radical promoted cationic polymerizations, triarylsulphonium salts are relatively weak oxidizing agents due to their low reduction potential ($E_{1/2}^{red}$). In this connection it should be pointed out that several sulphonium salts with more favourable redox potentials, i.e. complex sulphonium salts, were found [10] to participate in cation forming redox reactions. More recently, Johnen et al. [11] succeeded in initiating cationic photopolymerization of cyclohexene oxide (CHO) and 1,4-butanedioldiglycidyl ether by using triphenylsulphonium salt in conjuction with vinyl bromides. Although the possibility of electron transfer mechanism between excited vinyl halide and the cationic salt is not precluded, the initiating vinyl cations were postulated to be formed by oxidation of vinyl radicals by the salt according to the following reactions.

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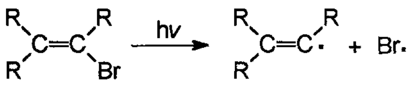


(2)

(3)

$R = CH_3OC_6H_5$, C_6H_5

It then occured to us that the above described sulphonium salt assisted reaction might also be extended, by analogy, to indirectly generated vinyl radicals.
This article describes our development of cationic polymerization of cyclohexene oxide (CHO) based on the oxidation of vinyl radicals formed by photolysis.

Experimental

Materials

Triphenylsulphonium hexaflurophosphate ($Ph_3S^+PF_6^-$) was prepared according to the previously described procedure [3]. 2,2-Dimethoxy-2-phenyl acetophenone (DMPA) benzoin (B), benzoin methylether (BME) (Fluka), trimethylbenzoyldiphenylphosphin oxide (TMDPO) (BASF) and diphenyl acetylene (DPA) (Aldrich) were used without further purification. Cyclohexene oxide (CHO) (Aldrich) and methylene chloride were purified by conventionel drying and distillation procedures.

Photopolymerization

Appropriate solutions of CHO containing selected combinations of DMPA, sulphonium salt and DPA in methylene chloride in pyrex tubes were bubbled through dry nitrogen before irradiation by an AMKO Ltd. photoreactor equipped with a HBO 100 W xenon lamp and monochromator. At the end of irradiation, polymers were obtained from the reaction mixture by precipitation with ten-fold excess methanol containing a little base.

Analysis

U.V. spectra were recorded on a Perkin-Elmer Lambda 2 spectrophotometer. Gel permeation chromatography analyses were performed with a set-up consisting a Waters pump and four Ultrastyragel columns with porosities 10^5, 10^4, 10^3 and 500 A°. THF was used as the eluent, at a flow rate of 1 ml min^{-1} and detection was carried out with a differential refractometer. Molecular weights were determined with the aid of polysytrene standards.

Results and Discussion

Following the above-mentioned strategy, CHO was polymerized with combination of a free radical source, diphenyl acetylene and triphenylsulphonium salt in methylene chloride. It is well known [12] that radicals add to acetylenic compounds to form more reactive vinyl radicals.

(4

For the radical generation process, we have employed photochemical sources of free radicals, such as benzoin alkyl ethers and alkoxyacetophenones which find commercial application in u.v. curable coatings [13]. Polymerizations were performed at λ=350nm where DPA and $Ph_3S^+PF_6^-$ are transparent and all the light emitted is absorbed by DMPA (Figure 1). CHO was deliberately chosen as cationically polymerizable monomer since it is not prone to undergo hydrogen abstraction nor can be polymerized by a radical mechanism.

As can be seen from Table 1, CHO was polymerized effectively with all benzoin derivatives employed in the presence of DPA and sulphonium ions. In Figure 2 , the conversion of CHO into polycyclohexene oxide is plotted vs irradiation time. The plateau value reached after 5h irradiation may correspond to the situation when all or either of the three components are consumed. Notably, the three components of the initiating systems are indispensable for the polymerization to occur; either no polymer or negligible amount of polymer is formed in the absence of one or more compounds under our reaction conditions. Simple triarylsulphonium salts do not undergo radical induced decomposition. Successful polymerization in this case may be attributed to the better electron donating property of the vinyl radicals. Electron donating substituents such as methoxy and hydroxy groups and electrons of the double bond increase the electron density on the radical site. Photochemically generated hydroxy benzyl or alkoxy benzyl radicals must be expected to undergo immediate addition to DPA and subsequent oxidation to vinyl cations as described for vinyl bromide initiating system (vide ante). We propose that the vinyl cation is the initiating species in this system. H-NMR analysis of the produced polycylohexene oxide showed the presence of the aromatic moieties as a chain end group.

Table 1. Photoinitiated Polymerization[a] of Cyclohexene oxide (7.9 mol l^{-1}) in CH_2Cl_2

Photoinitiator (mol l^{-1})	DPA (mol l^{-1})	Ph_3S^+ (mol l^{-1})	Time (min)	Conversion (%)	$M_n \times 10^{-3}$ (g mol^{-1})
DMPA (5 x 10^{-3})	10^{-2}	10^{-2}	90	6.8	7.4
DMPA (5 x 10^{-3})	—	10^{-2}	90	0.6	—
B (5 x 10^{-3})	10^{-2}	10^{-2}	90	16.5	6.7
BME (5 x 10^{-3})	10^{-2}	10^{-2}	90	10.1	6.4
TMPDO[b] (5 x 10^{-3})	10^{-2}	10^{-2}	90	0.5	—

[a] λ = 350 nm, room temp.

[b] λ = 380 nm

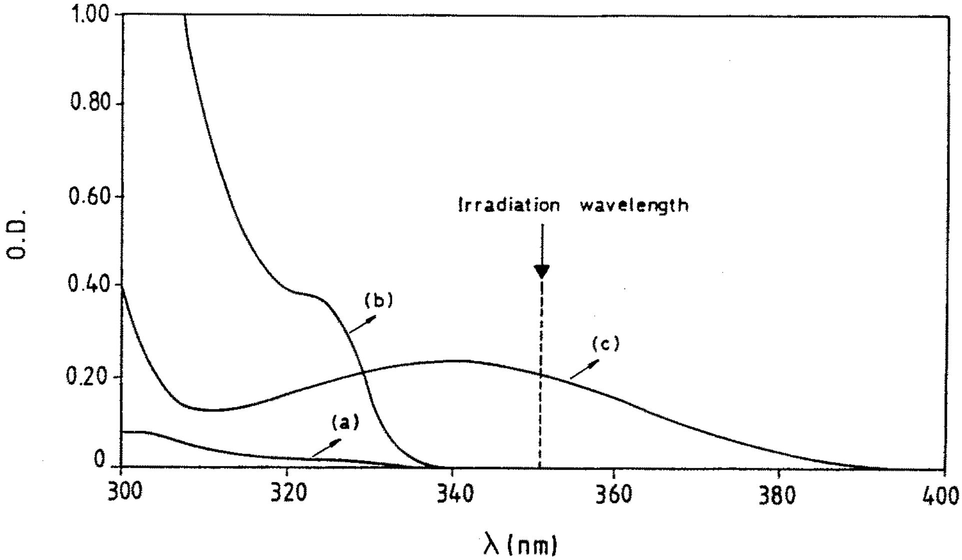


Figure 1. Absorption spectra of dichloromethane solutions containing (a) $Ph_3S^+PF_6^-$ (10^{-3} mol l^{-1}), (b) DPA (10^{-3} mol l^{-1}) and (c) DMPA (10^{-3} mol l^{-1}).

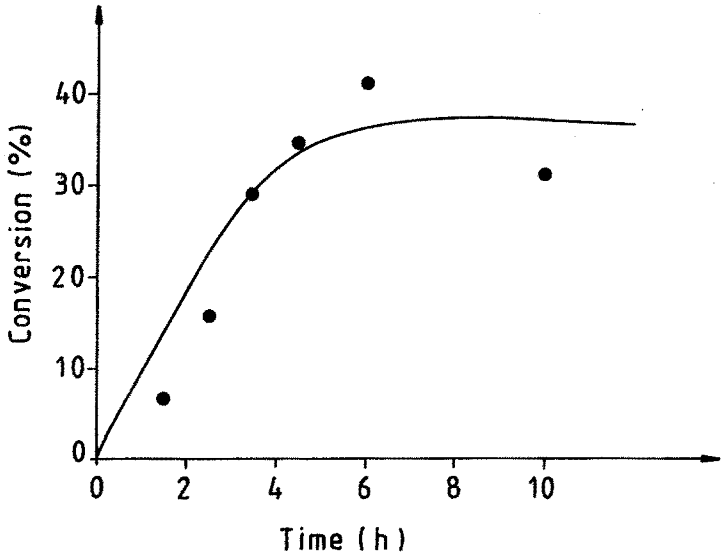
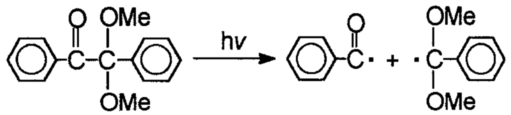


Figure 2. Photopolymerization of cyclohexene oxide at room temperatue. The conversion of cyclohexene oxide to poly(cyclohexene oxide) vs. the irradiation time. $\lambda_{inc.}$=350 nm. [DMPA] = 5 x 10^{-3} mol l^{-1}, [DPA]= 10^{-2} mol l^{-1} and [$Ph_3S^+PF_6^-$]= 10^{-2} mol l^{-1}.



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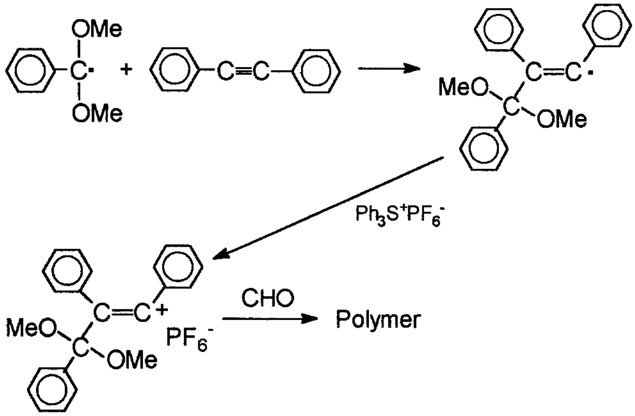
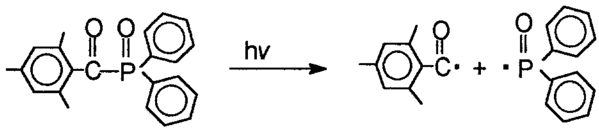


(6)

(7)

(8

The effectiveness of benzoin derivatives strongly supports the proposed reaction pathway in which vinyl radical is required in the initiation step, since neither benzoyl nor alkoxy benzyl radicals participate in redox reaction with sulphonium salts. Interestingly, another free radical photoinitiator, trimethylbenzoyldiphenylphosphine oxide which undergoes α-clevage [14] according to the following reaction, does not promote the cationic polymerization of CHO.



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Both benzoyl and phosphonyl radicals possess electron withdrawing groups and resultant vinyl radicals are not nucleophilic enough for the subsequent oxidation step. The enhached activity of benzoin (B) and benzoin methylether (BME) in the polymerization (see Table 1) may be attributed to the less sterically hindered structure of the corresponding alkoxy and hydroxy benzyl radicals.

Conclusion

The experimental results fully support the idea that, in principle at least, electron donating free radicals in the presence of substituted acetylenes such as DPA would yield vinyl radicals which may then lead to the formation of reactive cations in the presence of sulphonium salts.

Acknowledgement

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