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Substituted vinyl bromides as photoinitiators for cationic polymerizations

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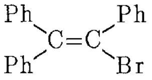
Summary:

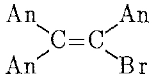
The cationic polymerization of typical monomers, e.g. of oxiranes such as cyclohexene oxide and 1,4–butanedioldiglycidyl ether or of vinyl ethers such as n–butylvinyl ether, is induced by UV irradiation of monomer formulations containing a substituted vinyl bromide as light absorbing agent and an appropriate non–absorbing onium salt. Experiments performed with 1,2,2–triphenyl vinyl bromide or 1,2,2–tri(4–methoxyphenyl) vinyl bromide and N–ethoxy–2–methyl–pyridinium or triphenyl sulfonium hexafluoro–phosphate are described in the paper.

INTRODUCTION

Recently, we have succeeded in initiating the cationic photopolymerization of appropriate monomers with initiator systems containing substituted vinyl bromides of the structures



(PPPVB)



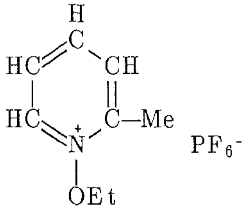
(AAAVB)

Ph: phenyl; An: anisyl ≡ 4–methoxyphenyl

Reactive initiator systems contained, in addition to a vinyl bromide, an onium salt: triphenyl–sulfonium hexafluorophosphate (TPSP) or N–ethoxy–2–methyl pyridinium hexafluorophosphate (EMP).

$Ph_3S^+ PF_6^-$

(TPSP)



(EMP)

The polymerizations were initiated by UV radiation at wavelengths corresponding to the absorption bands of the vinyl bromides where the onium salts absorb light only very weakly or not at all. Typical absorption spectra of

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the initiator components are shown in Fig.1. Both bulk and solution polymerizations were performed. Details are described below.

EXPERIMENTAL PART

(a) Materials

Dichloromethane (E.Merck) was washed with sulfuric acid, aqueous Na_2CO_3 solution and water. After drying with $CaCl_2$ it was distilled from CaH_2. *Triphenyl sulfonium hexafluorophosphate* (TPSP) was synthesized from triphenylsulfonium bromide, $Ph_3S^+Br^-$, and sodium hexafluorophosphate according to a prescription of Dektar and Hacker [1]. The salt was recrystallized from ethanol. $Ph_3S^+Br^-$ was prepared by a Grignard reaction from bromobenzene and diphenylsulfoxide. *N–Ethoxy–2–methyl pyridinium hexafluorophosphate* was synthesized from 2–methylpyridine–N–oxide (Jansen) and triethoxyoxonium hexafluorophosphate (Aldrich) as described by Reichardt [2]. *1,2,2–tri–phenylvinyl bromide and 1,2,2–tri(4–methoxyphenyl) vinyl bromide* were prepared as described in the literature [3-5].
Cyclohexene oxide [CHO, 7–oxabicyclo(4.1.0)heptane], *1,4–butanedioldiglycidyl ether* [BGE] and *glycidylphenyl ether* [GPE] were refluxed over CaH_2 for some hours and were afterwards fractionally distilled. BGE was obtained from Ciba–Geigy, and CHO and GPE were purchased from Aldrich. *1,2–Epoxycyclohexylmethyl–1,2–epoxycyclohexane carboxylate* [EEC] was used as obtained from Ciba–Geigy. n–Butylvinyl ether [nBVE] (Aldrich) was washed with water, dried with $CaCl_2$ and distilled from CaH_2. Subsequently, it was refluxed over sodium wire and then fractionally distilled.

(b) Polymerizations.

Ampoules containing 3 ml of the neat monomer or the monomer solution were exposed to the UV radiation of a Rayonet photoreactor equipped with 16 lamps (type RPR 3500 A). Subsequently, dichloromethane was added to the reaction system and the polymer was precipitated with methanol. The monomer conversion was obtained by weighing the dried polymer.

RESULTS

(a) Optical Absorption Spectra.

Fig.1. shows the absorption spectra of the substituted vinyl bromides PPPVB and AAAVB and of TSTP and EMP. One can see that the vinyl bromides absorb light of $\lambda > 300$ nm much more strongly than the two onium salts.

(b) Bulk Polymerizations.

As can be seen from Table 1 PPPVB acts as an efficient initiator for the polymerization of CHO and BGE in conjunction with TPSP. At the vinyl bromide concentrations applied in these experiments the photolyzing light was mainly absorbed by PPPVB. However, it becomes obvious from Table 1 that CHO also polymerized in the absence of PPPVB to some extent. This is due to the fact that the emission spectrum of the lamps of the photoreactor covers a rather broad range. Therefore, some of the light was absorbed by TPSP, which is known to act as an initiator for cationic polymerizations if excited directly. Notably, the purified BGE polymerized much more readily than the unpurified technical product. This demonstrates the deteriorating influence of impurities on the initiation of cationic polymerizations.
CHO also was polymerized when AAAVB instead of PPPVB, or EMP instead

Table 1. Bulk Polymerization of CHO and BGE at T = 35°C [a].

Monomer	[PPPVB] (mol/l)	[TPSP] (mol/l)	Conversion (%)	Irrad.Time (hrs)
CHO	$8.8x10^{-4}$	$4.8x10^{-3}$	11.6	0.25
CHO	0	$4.8x10^{-3}$	2.0	0.25
BGE[b]	$1x10^{-3}$	$4.9x10^{-3}$	Gel	0.5
BGE[b]	0	$4.9x10^{-3}$	0	0.5
BGE[c]	$6.7x10^{-4}$	$4.9x10^{-3}$	Gel	5.0
BGE[c]	0	$4.9x10^{-3}$	0	5.0

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[a] The samples were irradiated in the photoreactor at the nominal wavelength $\lambda = 350$ nm without a cut–off filter; $I = 9.5x10^{-5}$ Einstein/cm^2 s.

[b] purified product [c] unpurified product

of TPSP was used. A typical result obtained with the initiator system AAAVB/EMP is shown in Table 2. In this case a cut–off filter was used which prevented light absorption by the onium salt. Consequently, CHO did not polymerize in the absence of AAAVB.

Table 2. Bulk Polymerizatization of CHO at T = 35°C [a].

Monomer	[AAAVB] (mol/l)	[EMP] (mol/l)	Conversion (%)	Irrad.Time (hrs)
CHO	$9.8x10^{-4}$	$4.6x10^{-3}$	27	0.9
CHO	0	$4.6x10^{-3}$	0	0.9

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[a] The samples were irradiated in the photoreactor at the nominal wavelength $\lambda = 350$ nm through a 4 mm cut–off filter WG 335 (Schott).

c) Polymerizations in CH_2Cl_2 solutions.

Polymers also were formed upon irradiation of solutions of monomers in dichloromethane. Typical results are shown in Table 3 and Fig.2.

Notably, the bifunctional monomer EEC formed an insoluble gel. Gel formation after 50 min. also was observed upon irradiation of a 2 molar solution of unpurified BGE under the conditions given in Table 3.

Table 3. Polymerization of various monomers in dichloromethane solution at T = 35°C [a]. [PPPVB] = $8.8x10^{-4}$ mol/l; [TPSP] = $4x10^{-3}$ mol/l.

Monomer	[Monomer] (mol/l)	polymerization rate (%/min) [b]		M_w [c]
nBVE	3.9	21.4	(0.7)	$2–6x10^4$
CHO	7.1	2.0	(0.13)	$2–20x10^3$
EEC	2.0	0.7	(0.0)	
GPE	5.0	0.5	(0.0)	$2x10^3$

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[a] The samples were irradiated in the photoreactor at the nominal wavelength $\lambda = 350$ nm without a cut–off filter; $I = 9.5x10^{-5}$ Einstein/cm^2 s.

[b] Numbers in brackets indicate the rate of monomer conversion measured in the absence of PPPVB.

[c] Weight average molar mass obtained by GPC on the basis of calibration with polystyrene standards

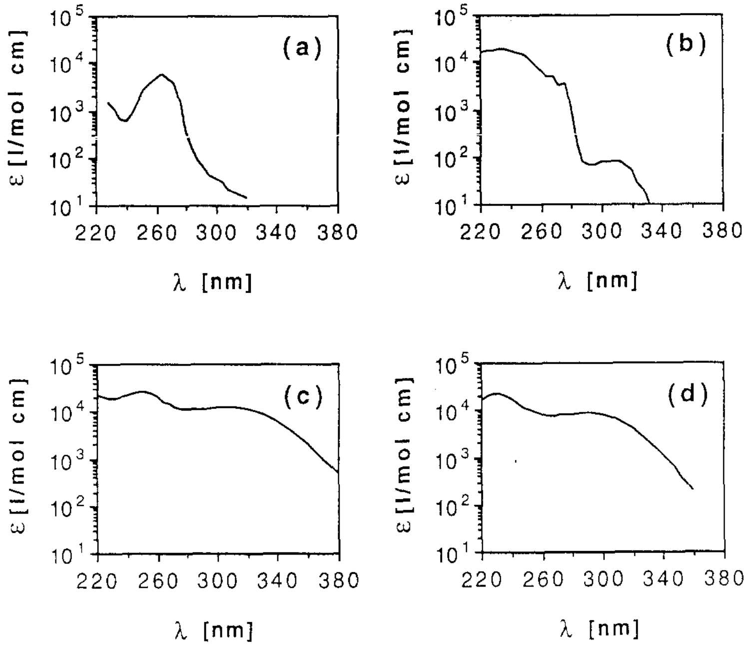


Fig.1. Optical absorption spectra of EMP (a), TPSP (b), AAAVP (c) and PPPVB (d). The spectra were recorded at room temperature with CH_2Cl_2 solutions.

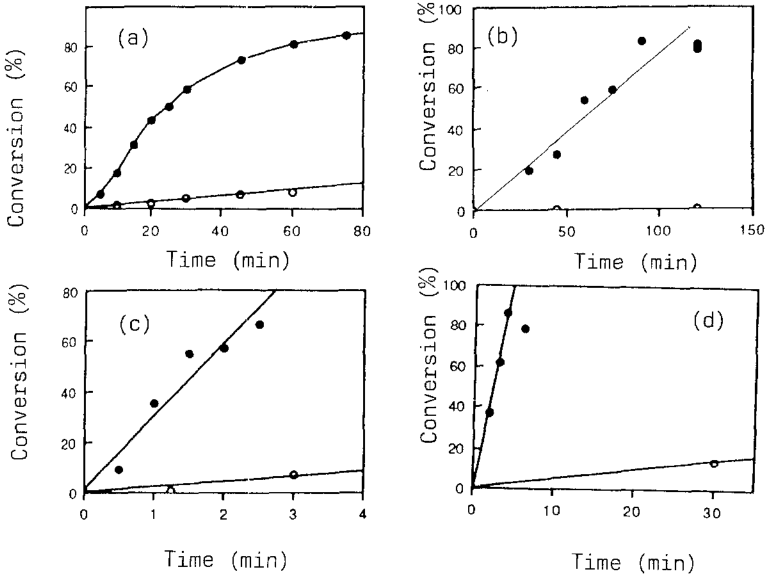
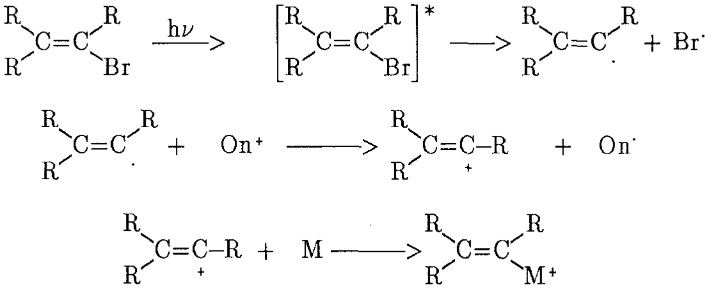


Fig.2. Polymerization of CHO (a), EEC (b), GPE (c) and nBVE (d) in CH_2Cl_2 solution at 35°C. Initiator system PPPVB (8.8×10^{-4} mol/l)/TPSP (4×10^{-3} mol/l). Experimental points denoted by open circles were obtained in the absence of PPPVB.

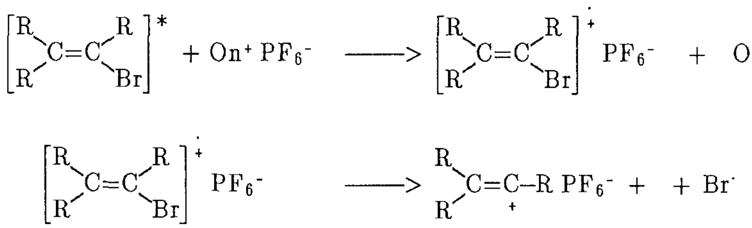
DISCUSSION

From the results of this work it is concluded that the photolysis of PPPVB or AAAVB yields an intermediate which rapidly reacts with TPSP or EMP thus forming a species capable of initiating the cationic polymerization of oxirane compounds and vinyl ethers. According to Kitamura et al. [6] the photolysis of vinyl bromides involves in the primary step the homolysis of carbon–bromine bonds which leads to the formation of vinyl/bromine radical pairs. While part of the radicals undergo electron transfer forming vinyl cations and bromide ions others escape the solvent cage. Vinyl cations formed in this way are incapable of initiating the cationic polymerization. This becomes obvious from the fact that monomer formulations only containing vinyl bromide are not polymerized. This is probably due to the high nucleophilicity of bromide ions. The latter readily react with vinyl cations or terminate cationic chain reactions at a very early stage. Therefore, at present, a mechanism explaining the role of onium salts should consider reactions of vinyl radicals with onium ions. This is illustrated by reactions (1) – (3). Vinyl radicals are oxidized by onium ions and vinyl cations formed in this way initiate the cationic polymerization of monomer M:


(1)
(2)
(3)

Since PF_6^- ions, the counter ions employed in the present case, are not nucleophilic they should not exert any significant influence on these reactions.

An alternative mechanism might be based on the reaction of electronically excited vinyl bromide molecules with onium ions via electron transfer:


(4)
(5)

Vinyl cations formed by reaction (5) would be capable of initiating cationic polymerizations and, because of the non–nucleophilicity of PF_6^- ions, cationic chain propagation would not be prevented by reaction of the growing chains with counter ions.

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