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Photoinitiated Cationic Polymerization of Vinyl Ethers Using Substituted Vinyl Halides

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ABSTRACT: The photoinitiated cationic polymerization of typical vinyl ether monomers, such as isobutyl vinyl ether, di(ethylene glycol) divinyl ether, tri(ethylene glycol) divinyl ether, 1,4-butanediol divinyl ether, and 1,6-hexanediol divinyl ether, by use of aryl-substituted vinyl halides was studied. The cationic polymerization of these monomers was initiated at 0 °C or room temperature upon irradiation at λ = 350 nm in CH_2Cl_2 solutions with one of the following compounds: 1-bromo-1,2,2-tris(*p*-methoxyphenyl) ethene, 1-bromo-1-(*p*-methoxyphenyl)-2,2-diphenylethene, 1-bromo-1,2,2-triphenylethene, and 1-chloro-2,2-bis(*p*-methoxyphenyl)ethene in the presence of zinc iodide (ZnI_2). A mechanism involving formation of an adduct between the monomer and the products yielded from the photoinduced homolysis of the vinyl halide followed by electron transfer is proposed. In the subsequent step, the terminal carbon−halide bond in this adduct is activated by the coordinating effect of ZnI_2. This polymerization exhibited some characteristics of pseudoliving cationic polymerization.

Introduction

Initiators that generate reactive species capable of initiating cationic polymerization by external stimuli—photolysis or heating—are extremely important in the control of the initiation step.[1] Much attention has focused on the photochemical mode since it can be performed at low temperatures and adapted to different irradiation wavelengths. Many cationic photoinitiators are known, and their photochemistry has been studied in detail. Among them, the onium-type photoinitiators such as iodonium,[2] sulfonium,[3] and alkoxypyridinium[4] salts are important due to their thermal stability, solubility in most of the cationically polymerizable monomers, and efficiency in generating reactive species upon photolysis. A common strategy employed for improving the performance of these photoinitiators, particularly at long wavelengths, is to combine them with radical sources or with photosensitizers or via the formation of charge transfer complexes with strong electron donors.[4−9] Epoxides are commonly cured cationically, but vinyl ethers (VEs) comprise another important class of monomers for UV-curable coatings and offer environmentally friendly formulations which cationically polymerize more rapidly than epoxides.[10] Conventionally, UV-radiation curing or cross-linking of VE monomers and oligomers is achieved by the photochemical generation of Brønsted acids from onium salts with non-nucleophilic counteranions.[2,10] Recently, Endo and co-workers reported phosphonates as nonionic (Endo et al. uses the term "non-salt") type thermally latent initiators for VE polymerization.[11] Although these initiators eliminate the contamination of the polymer by the inorganic residues arising from the counteranion of the onium salt, the high temperatures required for the activation limit their practical application. Recently, a new photoinitiating system eliminating the use of toxic AsF_6^- and SbF_6^- anions for the controlled polymerization and cross-linking of vinyl ethers has been reported.[12] The system presented in Scheme 1 is essentially based on the concept of living cationic polymerization of vinyl ethers[13] developed by Higashimura and Sawamoto[14] and utilizes diphenyliodonium halides in the presence of zinc halide as a Lewis acid.[12,15] Quite recently, it was also demonstrated that the polymerization can be performed even in aqueous medium when the Lewis acid is changed to water-tolerant ytterbium triflate ($Yb(OTf)_3$) in the initiating system.[16]

Another approach to generating cations photochemically is the use of aryl-substituted vinyl halides such as 1-bromo-1,2,2-triphenylethene (PPPVB), which leads to the formation of vinyl cations in a two-step process.[17−20] In the primary step, the photoinduced homolysis of the carbon−bromine bond leads to the formation of vinyl/bromine radical pairs (Scheme 2). Some of the radicals undergo electron transfer forming vinyl cations and bromide ions, while others escape the solvent cage. It appears that the vinyl cations formed in this way are incapable of initiating the cationic polymerization as is shown by the fact that monomer formulations containing only vinyl bromide are not polymerized.[21] This is due to the high nucleophilicity of bromide ions which readily react with vinyl cations inside the solvent cage or due to termination of the cationic polymerization at a very early stage. However, the addition of onium salts with non-nucleophilic counterions to the formulations containing the vinyl halide provides an alternative mechanism of initiating cationic polymerization of various cyclic and vinylic monomers.[22] In this case, the vinyl radicals undergo an electron transfer reaction with the onium cation to form vinyl cations (Scheme 3). Naturally, the subsequent propagation reaction requires a non-nucleophilic counterion to avoid termination of the polymerization.

The photoinitiating system described above has limitations in that the most active anions tend to be toxic, and it does not provide an advantage over the use of a radical source to decompose the iodonium salt to form the initiating cations. The present paper

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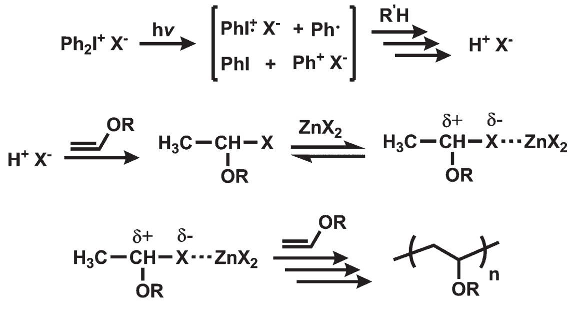
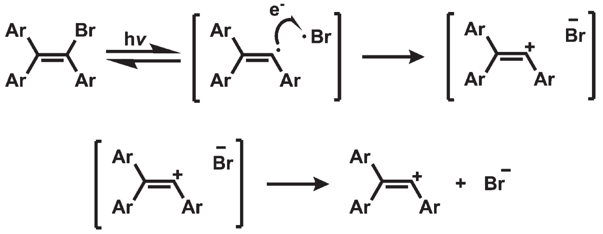
Scheme 1. Photoinitiated Living Cationic Polymerization of Vinyl Ethers[15]

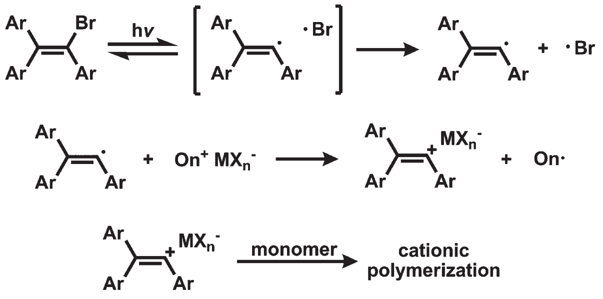


R'H: monomer or solvent
X: Cl, Br or I

Scheme 2. Photoinduced Vinyl Cation Formation[17−20]



Scheme 3. Free Radical Promoted Cationic Polymerization by Using Vinyl Halides in the Presence of Onium Salts



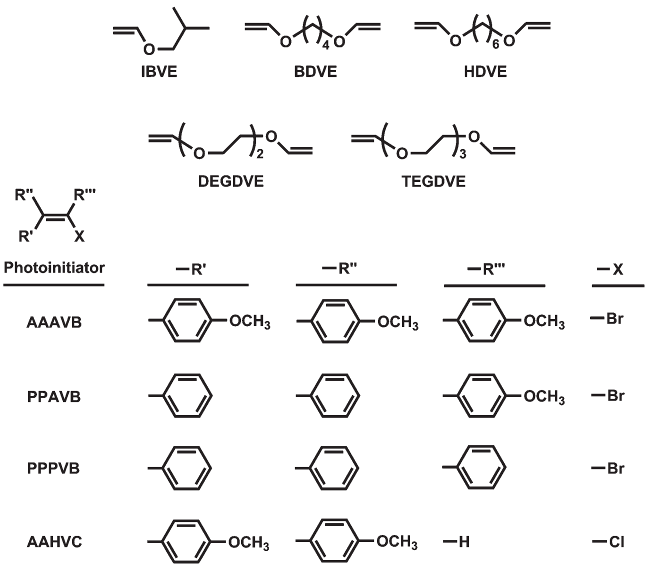
On$^+$ MX$_n^-$: onium salt with non-nucleophilic counterion
MX$_n^-$: AsF$_6^-$, PF$_6^-$ or SbF$_6^-$

describes the activity of substituted vinyl halides in conjunction with zinc iodide as a photochemically initiating system for the cationic polymerization of vinyl ethers. This initiating system provides several advantages. Substituted vinyl halides are highly soluble in organic medium, in particular bulk monomer, and have absorption at longer wavelengths (up to 380 nm). Moreover, the environmental drawback caused by toxic counteranions is overcome as the initiating system does not require onium salts of any kind.

Experimental Section

Materials. Isobutyl vinyl ether (IBVE, 99%, Aldrich) was distilled from CaH$_2$ in vacuo. Difunctional monomers, di(ethylene glycol) divinyl ether (DEGDVE, 99%, Aldrich), tri(ethylene glycol) divinyl ether (TEGDVE, 98%, Aldrich), 1,4-butanediol divinyl ether (BDVE, 98%, Aldrich), and 1,6-hexanediol divinyl ether (HDVE, 97%, Aldrich) were used as received. Dichloromethane (CH$_2$Cl$_2$, Carlo Erba) was distilled from CaH$_2$ with a fractionation column. Diphenyliodonium iodide (DPII, 98%, Alfa Aesar), zinc iodide (ZnI$_2$, anhydrous, Merck), poly(ethylene glycol) (PEG, M_n = 1500 g/mol, Fluka), and deuterated chloroform (CDCl$_3$, Roth) were used as received. Substituted vinyl halides, namely 1-bromo-1,2,2-tris(*p*-methoxyphenyl)ethene (AAAVB), 1-bromo-1-(*p*-methoxyphenyl)-2,2-phenylethene (PPAVB), and 1-bromo-1,2,2-triphenylethene (PPPVB), were prepared as described in the literature.[23−25] The chloro analogue of AAAVB was not readily prepared and so 1-chloro-2,2-bis(*p*-methoxyphenyl)ethene (AAHVC) was prepared in its place using the method used for the other photoinitiators.[23−25] The melting points are as follows. AAAVB: 122−124 °C (lit.[26] 118−119 °C); PPAVB: 130−132 °C (lit.[25] 130−131 °C); PPPVB: 116−118 °C; AAHVC: 81−82 °C.

Chart 1. Substituted Vinyl Halide Type Photoinitiators and Monomers



The ^{1}H NMR (250 MHz, Si(CH$_3$)$_4$) spectra are as follows. AAAVB: δ (CDCl$_3$) 7.25 (dd, J = 7.9 and 7.9 Hz, 4H, ArH), 6.86 (dd, J = 8.6 and 8.6 Hz, 4H, ArH), 6.64 (dd, J = 26.2 and 8.6 Hz, 4H, ArH), 3.82 (s, 3H, Ar′−OCHH_3) 3.76 (s, 3H, Ar″−OCHH_3), 3.70 (s, 3H, Ar‴−OCHH_3). PPAVB: δ (CDCl$_3$) 7.35 (br, 5H, ArH), 7.22 (br, 2H, ArH), 7.07 (br, 3H, ArH), 6.97 (br, 2H, ArH), 6.69 (d, J = 8.5 Hz, 2H, ArH), 3.75 (s, 3H Ar−OCHH_3). PPPVB: δ (CDCl$_3$) 7.36 (br, 5H, ArH), 7.30 (br, 2H, ArH), 7.16 (br, 3H, ArH), 7.05 (br, 3H, ArH), 6.94 (br, 3H, ArH). AAHVC: δ (CDCl$_3$) 7.26 (d, J = 6.3 Hz, 2H, ArH), 7.13 (d, J = 8.6 Hz, 2H, ArH), 6.91 (d, J = 8.6 Hz, 2H, ArH), 6.81 (d, J = 8.6 Hz, 2H, ArH), 6.43 (s, 1H, C=C−H) 3.83 (s, 3H, Ar′−OCHH_3), 3.80(s, 3H, Ar″−OCHH_3).

The structures of the monomers and vinyl halide photoinitiators are presented in Chart 1.

Photopolymerization. A typical photopolymerization procedure of IBVE was as follows. A Pyrex tube was heated in vacuo with a heat gun and flushed with dry nitrogen. AAAVB (1.3 mg, 3.1×10^{-6} mol) was dissolved in IBVE (1.0 mL, 7.7×10^{-3} mol) in the Pyrex tube followed by addition of 1.0 mL of a stock solution containing 4.0 mg of zinc iodide (1.3×10^{-5} mol) and 10.0 mg of PEG (6.7×10^{-6} mol) in CH$_2$Cl$_2$. PEG was used in polymerization mixture to improve solubility of ZnI$_2$ by the coordination effect.[27] The tube was sealed off under a nitrogen atmosphere and exposed to light continuously at 0 °C for 240 min in a Rayonet merry-go-round photoreactor in which the sample was surrounded by a circle of 16 lamps emitting light nominally at 350 nm (run 1 in Table 1). The light intensity at the location of the sample was measured by a Delta Ohm model HD-9021 radiometer (I = 3.0 mW cm^{-2}). The irradiation time of 240 min for these experiments was selected so that a significant amount of polymerization had been achieved. At the end of the photoirradiation experiments all systems were still in a liquid state.

A typical photocuring procedure for BDVE was as follows. AAAVB (1.3 mg, 3.1×10^{-6} mol) was dissolved in BDVE

(0.5 mL, 3.2×10^{-3} mol) in a Pyrex tube followed by addition of 1.0 mL of a stock solution containing 4.0 mg of zinc iodide (1.3×10^{-5} mol) and 10.0 mg of PEG (6.7×10^{-6} mol) in CH_2Cl_2. The tube was sealed off and irradiated around 350 nm at room temperature (~22 °C) in the Rayonet photoreactor (run 5 in Table 2). The gelation time was determined by periodically inverting the tube and noting any viscosity increase, and the system was considered to have gelled when no flow of the solution was observed. At the end of the photoirradiation experiments, all systems containing AAAVB photoinitiator had vitrified, thus terminating the polymerization.

For both monofunctional and difunctional monomers, the polymerization was quenched by addition of a small amount of methanol. Since only the monomer is soluble in methanol, additional methanol was used to quantitatively transfer the polymer solution or gel into another container and to precipitate the polymer (linear polymer and/or gel) so that the conversion of monomer to polymer could be determined gravimetrically. For difunctional monomers, the gel content was determined by measuring the weight loss after 24 h extraction of the cross-linked polymer at room temperature with dichloromethane (a good solvent for the linear polymer).

Analysis. A Cary 3000-Bio (Varian) spectrometer was used to measure the UV−vis absorption spectra of the compounds and the photobleaching behavior of the formulation. For the photobleaching experiment, very thin quartz cells (with 0.5 mm path length) consisting of two quartz slides and silicone rubber were employed. Empty cells were used to zero the instrument baseline, and a cell with monomer was used as reference for the formulated monomer systems. Samples were irradiated for certain periods (up to 2400 s) with 350 nm radiation (with a bandwidth of ca. ±20 nm) using a Rofin Polilight PL400, and the photobleaching behavior was observed by monitoring changes in the absorbance with irradiation time. The incident light intensity ($I = 11.5$ mW cm^{-2}) was measured by a USB2000 fiber-optic spectroradiometer (Ocean Optics, Inc.).

Table 1. Photopolymerization of Isobutyl Vinyl Ether (1.0 mL, 7.7×10^{-3} mol) Induced by Irradiation of Various Photoinitiators (1.5×10^{-3} mol L^{-1}) at 350 nm ($I = 3.0$ mW cm^{-2}) at 0 °C in the Presence of ZnI_2 (6.3×10^{-3} mol L^{-1}) Dissolved in CH_2Cl_2 (1.0 mL) by the Aid of Poly(ethylene glycol) (3.3×10^{-3} mol L^{-1}); Time of Irradiation Was 240 min

run	photoiniator	conversion (%)[c]	M_n[d]	PDI[d]
1	AAAVB[a]	53.7	28 660	1.77
2	PPAVB[a]	29.9	22 800	1.67
3	PPPVB[a]	23.8	30 900	1.47
4	AAHVC	0		
5	DPII[b]	5.2	9950	1.43

[a] See Chart 1 for full names of the photoininitiators. [b] DPII: diphenyliodonium iodide. [c] Monomer conversions were determined gravimetrically. [d] Number-average molecular weights (M_n) and polydispersities (PDIs) were determined using gel permeation chromatography.

Molecular weights and polydispersities of the linear polymers were determined at 30 °C by gel permeation chromatography (GPC) using a Viscotek GPCmax Autosampler system consisting of a pump, three ViscoGEL GPC columns (G2000H_{HR}, G3000H_{HR}, and G4000H_{HR}) (7.8 mm internal diameter, 300 mm length), a Viscotek UV detector, and a Viscotek differential refractive index (RI) detector with tetrahydrofuran as eluent with a flow rate of 1.0 mL min^{-1}. The effective molecular weight separation of the columns ranged over 456−42 800 g mol^{-1} for G2000H_{HR}, 1050−107 000 g mol^{-1} for G3000H_{HR}, and 10 200−2 890 000 g mol^{-1} for G4000H_H. Both detectors were calibrated with polystyrene standards having narrow molecular weight distribution, and so the quoted molecular weights of the polymers therefore are expressed in terms of polystyrene equivalents. Data were analyzed using Viscotek OmniSEC Omni-01 software.

For further analysis of the mechanism of the initiation process, the photochemical formation of the adduct from vinyl halide and IBVE in the absence of zinc iodide was investigated by ^{1}H NMR spectroscopy. For this purpose, AAAVB (5.0 mg, 1.2×10^{-5} mol) was dissolved in 0.4 mL of $CDCl_3$ in a NMR tube (Aldrich, Tube L diameter 7 in. 5 mm, Thift, grade Series 300), and IBVE (0.10 mL, 7.7×10^{-4} mol) was added to this solution. ^{1}H NMR spectra of the solution were recorded with $Si(CH_3)_4$ as an internal standard using a Bruker AC250 (250.133 MHz) instrument before and after 150 min irradiation.

Photodifferential Scanning Calorimetry. The photocuring of TEGDVE with varying concentrations of zinc iodide was studied by photodifferential scanning calorimetry (photo-DSC) studies at 40 °C. The polymerizations were carried out under a N_2 atmosphere in a modified Perkin-Elmer DSC-7 to allow for irradiation of the sample and reference pans by use of a bifurcated fiber-optic guide leading to minimization of the thermal heating effect of the light source.[28] Heat flow and temperature calibrations of the DSC instrument were performed with zinc and indium standards. The Rofin Polilight PL400 was employed as an UV source in the photo-DSC studies using wavelengths of 350 ± 20 nm. The irradiation time was controlled by a shutter between the radiation source and the light guide.

The polymerization mixture (2−5 mg) was weighed into a DSC pan, and the pan immediately placed into the pan holder of the DSC set at a predetermined temperature. Two 0.05 mm thick PET covers (6 mm diameter) with two vent holes were used to minimize sample evaporation and to provide a stable baseline by covering the DSC pan holders. After placement of the sample, the equipment was stabilized for a period of 3−10 min and to allow purging of air from the cell. Once stabilized, the DSC run was begun, but for the first 60 s, a shutter prevented irradiation of the sample to stabilize the light source and to establish the heat flow baseline. When the shutter was quickly removed, a short induction period was observed before the polymerization commenced, and an exotherm was observed. Irradiation was continued after the exotherm peak until no change was observed

Table 2. Photoinduced Cross-Linking of Various Divinyl Ethers (0.5 mL) Initiated by Irradiation of 1-Bromo-1,2,2-tris(*p*-methoxyphenyl)ethane (AAAVB) or Diphenyliodonium Iodide (DPII) (2.0×10^{-3} mol L^{-1}) at 350 nm ($I = 3.0$ mW cm^{-2}) at Room Temperature in the Presence of ZnI_2 (8.4×10^{-3} mol L^{-1}) Dissolved in CH_2Cl_2 (1.0 mL) by the Aid of Poly(ethylene glycol) (4.4×10^{-3} mol L^{-1})

run	monomer	initiator	irradiation wavelength (nm)	gelation time (min)[c]	monomer conversion (%)[d]	gel content (%)[e]
5	BDVE[a]	AAAVB	350	9	60.7[f]	100
6	HDVE[a]	AAAVB	350	8	52.3[f]	95.1
7	DEDVE[a]	AAAVB	350	8	50.4[f]	95.6
8	BDVE[a]	DPII	350		0	0
9	BDVE[a,b]	DPII	300	2	50.2[f]	95.8

[a] See Chart 1 for monomers. [b] Irradiation intensity was 1.0 mW cm^{-2}. [c] Gelation was followed qualitatively by simply inverting the tube, and the system was considered to have gelled when there was no flow of solution on inverting the tube. [d] Conversion of monomer to polymer was determined from weight of the precipitated cross-linked polymer in proportion to weight of the monomer. Note that for divinyl monomers this is not the same as the conversion of vinyl groups. [e] Gel content was determined by measuring the weight loss after 24 h extraction with methylene chloride at room temperature. [f] For these systems, the cross-linking systems vitrified prior to the end of irradiation.

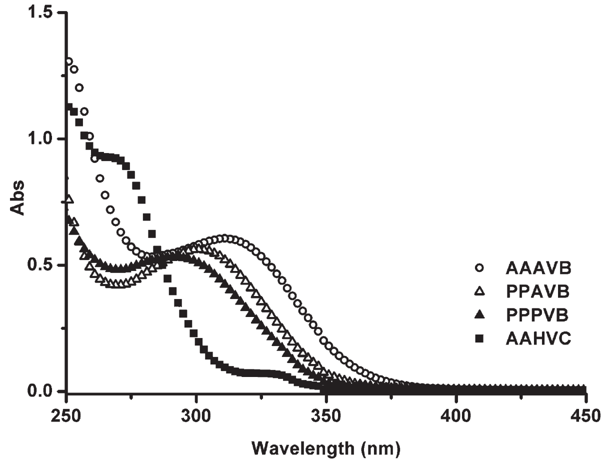


Figure 1. UV−vis spectra of 1-bromo-1,2,2-tris(*p*-methoxyphenyl)ethene (AAAVB), 1-bromo-1-(*p*-methoxyphenyl)-2,2-phenylethene (PPAVB), 1-bromo-1,2,2-triphenylethene (PPPVB), and 1-chloro-2,2-bis(pmethoxyphenyl) ethene (AAHVC) in CH_2Cl_2 ($C = 3.3 \times 10^{-5}$ mol L^{-1}).

in the heat flow. To remove the slight imbalance of the thermal heating effect on the sample and reference pans, the cured sample was again irradiated with the same conditions to produce a background which was subtracted from the data of the first run. The rate of conversion ($d\alpha/dt$) can be defined as given in eq 1 since the measured heat flow in DSC is proportional to the conversion rate. The heat flow curves were integrated to obtain the polymerization heat (H) as a function of time and this was transformed into the fraction of vinyl conversion (α) (eq 2) by use of the value for the heat of polymerization (ΔH_{tot}) of 60 J/mol.[29,30]

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H_{\text{tot}}}\left(\frac{dH}{dt}\right)_T \tag{1}$$

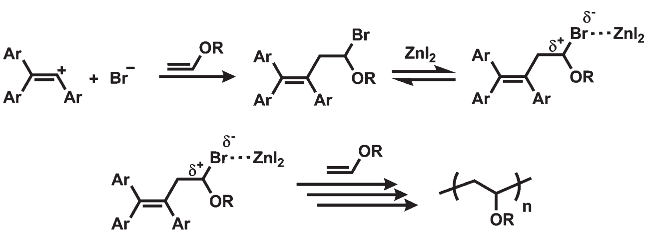
$$\alpha = \frac{1}{\Delta H_{\text{tot}}}\int_0^t \left(\frac{dH}{dt}\right)_T dt \tag{2}$$

Results and Discussion

Figure 1 shows the absorption spectra of the substituted vinyl halides. The vinyl halides, AAAVB, PPAVB, and PPPVB, absorb strongly above 300 nm presumably due to the conjugation of their three phenyl groups through the vinyl bond, but 1-chloro-2,2-bis(*p*-methoxyphenyl)ethene (AAHVC) has much weaker absorption in this region because it only contains two phenyl units. In addition, vinyl halides substituted with phenyl rings containing electron donating group (such as $-OCH_3$) absorb light at longer wavelengths. For example, vinyl bromide substituted with three anisole moieties (AAAVB) has a broad spectral absorption which extends to the near-UV region (up to 380 nm) that makes AAAVB particularly useful for long-wavelength applications (see Figure 1).

The photoinitiated polymerization of IBVE with each of the substituted vinyl halides (listed in Chart 1) was studied in the presence of zinc iodide. As can be seen from Table 1, IBVE was polymerized quite effectively with all of the vinyl halides except AAHVC. The extent of polymerization and thus the photoinitiator efficiency increased in the order AAAVB > PPAVB > PPPVB > AAHVC, which correlates well with the absorbance of these photoinitiators at around 350 nm. An additional reason for the poor performance of AAHVC relative to the other three photoinitiators is that it is a vinyl chloride rather than a bromide which may lessen the likelihood of the formation of the carbocation and chloride during photolysis.[12] For comparison with the photoinitiation efficiency of the vinyl halides, the photopolymerization of IBVE with DPII was also performed (see Table 1). The observed low activity of DPII may be due to its weak absorption at the wavelengths of the radiation source (350 nm), whereas all vinyl halides show fairly strong absorptions at wavelengths above 350 nm and therefore better photoinitiator activity. The electron-donating substitutents of the vinyl halides also favor the redox reaction leading to the formation of vinyl cations.

Scheme 4. Photoinitiated Cationic Polymerization Vinyl Ethers by Vinyl Cations in the Presence of Zinc Iodide



To further investigate the polymerization process, experiments were performed where either the vinyl halide or the zinc halide was omitted. This omission of either of the two components failed to produce polymer, which is consistent with the proposed mechanism shown in Scheme 4. In this mechanism, vinyl cations, photochemically generated from the rupture of the carbon−halide bond followed by electron transfer, can directly react with the monomer. The direct evidence for the reaction of vinyl cations generated this way with vinyl ethers was previously obtained by laser flash photolysis experiments, and the bimolecular rate contant for the formation of a new carbocation from the vinyl cation and monomer was found to be in the range of $k = 10^5$ L s mol^{-1}.[31] The rapid reaction of bromide ion with this new cation leads to the formation of the monomer adduct with a structure resembling those used in conventional living cationic polymerization initiated by the HI/ZnI_2 system.[32] Further activation by the coordinating effect of ZnI_2 affords the desired chain growth.

In order to gain more insight into the initiation mechanism, the change in the optical absorption spectrum of the polymerization solution was recorded as a function of irradiation time. As can be seen from Figure 2, with increasing irradiation time, the absorption spectra maximum at 253 nm and the shoulder at 315 nm decrease while a concomitant new maximum at 266 nm grows as indicated by the isosbestic points at 260 and 291 nm. The new band at 266 nm is attributed to the formation of the adduct from the photoinitiator and the monomer. Therefore, it is concluded that vinyl halides very effectively photolyze and take part in the initiation process.

Additional support for the crucial role of vinyl halides in the initiation process was obtained by ^1H NMR analysis of the polymerization mixture in $CDCl_3$ in the absence of ZnI_2 where IBVE and AAAVB were used as monomer and photoinitiator, respectively. In this case, while the adduct is expected to form, the subsequent chain growth does not occur because the adduct can not be activated when no Lewis acid is present in the system. Figure 3 shows ^1H NMR spectra of the solutions before and after photolysis. The spectrum of the solution before irradiation (Figure 3A) consists of only proton resonances due to IBVE and AAAVB. However, in the NMR spectrum of the irradiated sample (Figure 3B), new signals corresponding to the terminal CH−Br protons[33] at 5.58 ppm and CH_2 protons between 2.4 and 3.1 ppm were detected, in addition to protons of a series of side products occurring from different combination and coupling of active species. These results substantiate the suggested photoinitiation mechanism, according to which adduct formation is the initial step.

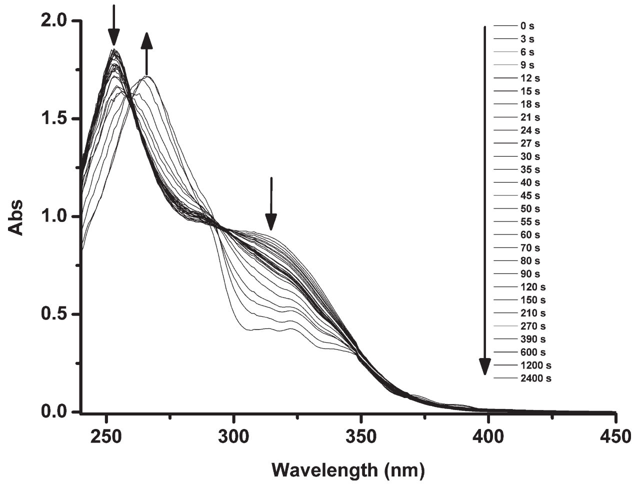


Figure 2. Photobleaching behavior of the photoinitiating system in a formulation consisting of 1-bromo-1,2,2-tris(*p*-methoxyphenyl)ethene (1.2×10^{-3} mol L^{-1})/ZnI_2 (1.6×10^{-3} mol L^{-1}) in tri(ethylene glycol) divinyl ether during irradiation at 350 nm in a quartz cell with 0.5 mm thickness at room temperature (I = 11.5 mW cm^{-2}).

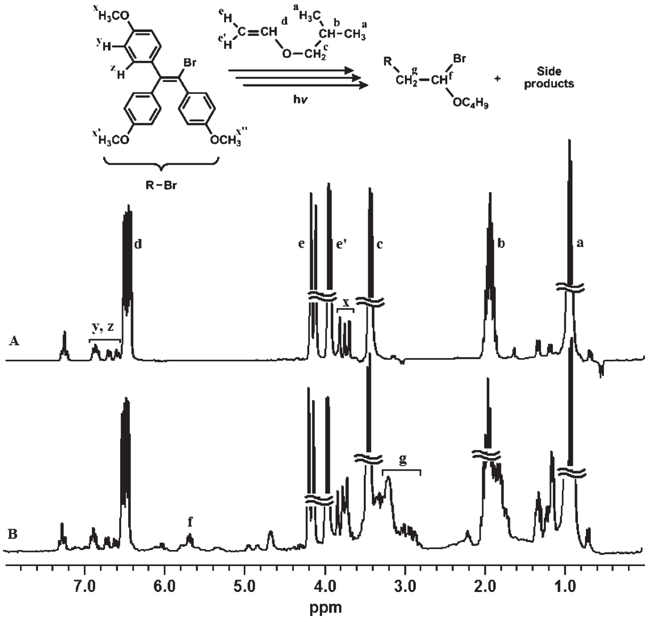


Figure 3. ^1H NMR traces of solution consisting of isobutyl vinyl ether and 1-bromo-1,2,2-tris(*p*-methoxyphenyl)ethene in $CDCl_3$ but in the absence of ZnI_2 before (A) and after (B) irradiation for150 min.

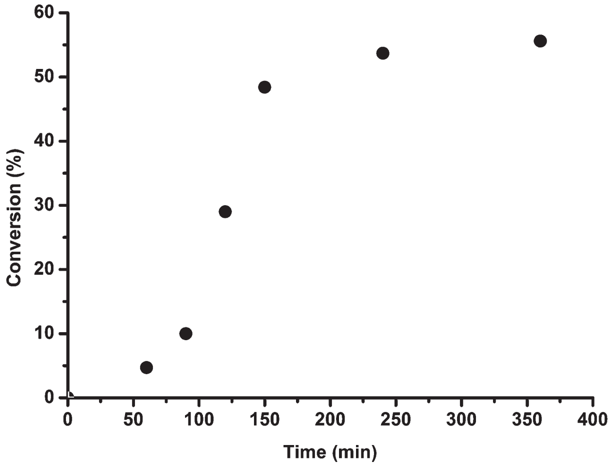


Figure 4. Time–conversion profile in photopolymerization of isobutyl vinyl ether (1.0 mL) induced by irradiation of 1-bromo-1,2,2-tris-(*p*-methoxyphenyl)ethene (1.6×10^{-3} mol L^{-1}) at 350 nm (I = 3.0 mW cm^{-2}) at 0 °C in the presence of ZnI_2 (6.3×10^{-3} mol L^{-1}) dissolved in CH_2Cl_2 (1.0 mL) by the aid of poly(ethylene glycol) (3.3×10^{-3} mol L^{-1}).

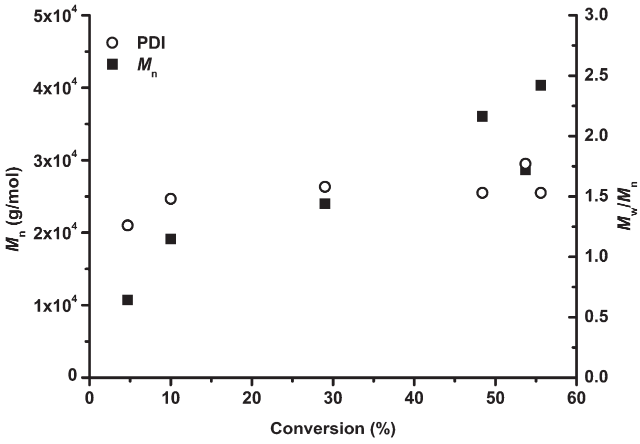


Figure 5. Conversion–M_n and conversion–molecular weight distribution (M_w/M_n) profiles in photopolymerization of isobutyl vinyl ether induced by irradiation of 1-bromo-1,2,2-tris(*p*-methoxyphenyl)ethene (see caption of Figure 4 for details).

In the initiation of this type of polymerization,[15] the reaction of the halide adduct with ZnI_2 leads to the formation of suitable nucleophilic counteranion which stabilizes the growing carbocation and thus prevents the chain termination and chain transfer processes. In order to examine the possible living nature of the described photoinitiated cationic polymerization of IBVE, studies of the time dependence of decrease in monomer concentration, number-average molecular weight (M_n), and polydispersity index (PDI) were carried out (see Figures 4 and 5). Three stages in the polymerization are observed. After a period of retarded polymerization which presumably corresponds to the consumption of the reactive species by the impurities, accumulation of the adduct, and the initial stages of chain growth, the monomer consumption increased rapidly with polymerization time and then slows down (Figure 4). This rapid rise in monomer consumption is due to the continuing generation of active cations by the irradiation, which accelerates the polymerization rate. The last stage of reduced polymerization rate may occur when all of the vinyl bromide is consumed and where the concentration of propagating species stops rising and the monomer concentration begins to be depleted. This interpretation is supported by the photolysis data in Figure 2. This data shows that for an irradiation intensity of 11.5 mW cm^{-2} the photoinitiator has been largely consumed after 40 min of irradiation. Assuming equivalence of irradiation time and irradiation intensity, this implies that at an irradiation intensity of 3 mW cm^{-2} the photoinitiator has been largely consumed after 160 min of irradiation, and this irradiation period corresponds to the stage where the rate of conversion begins to slow due to loss on monomer.

The relationship between M_n and conversion shown in Figure 5 is rather scattered but appears to be approximately linear, which suggests that the polymerization behavior is pseudoliving, by which is meant that the polymerization is a chain growth system where the propagating species is relatively stable against termination. Figure 5 also shows that the polydispersity is relatively constant and close to 1.5. These results indicate that although "true controlled/living polymerization" was not completely achieved, a reasonable control over the molecular weight was attained. The fact that the polydispersity is significantly different

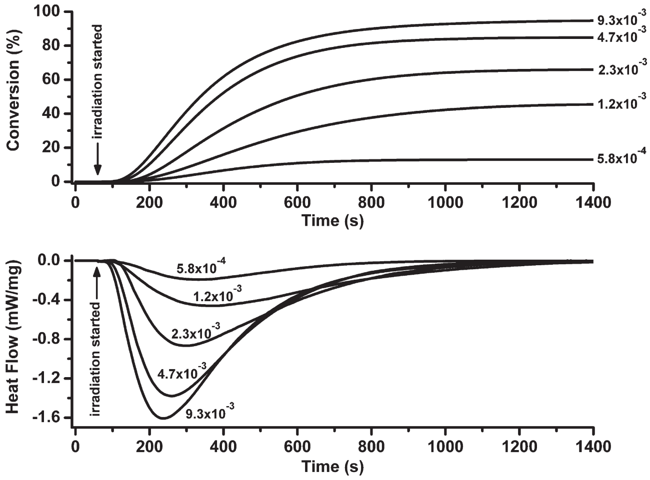


Figure 6. Photopolymerization at 40 °C of tri(ethylene glycol) divinyl ether initiated by irradiation of various amounts (varying from 5.8×10^{-4} to 9.3×10^{-3} mol L^{-1}) of 1-bromo-1,2,2-tris(*p*-methoxyphenyl) ethene (AAAVB) in the presence of ZnI_2 (1.6×10^{-3} mol L^{-1}) around 350 nm (I = 8.0 mW cm^{-2}).

from unity is expected since the initiating species, the vinyl bromide−monomer adduct in this case, is generated continuously during the irradiation period so that growing chains with large differences in chain lengths are present at the same time.

To further investigate this photoinitiating system, the efficiency of the AAAVB/ZnI_2 system with varying concentrations of zinc halide was studied by isothermal photo-DSC. Figure 6 shows the photo-DSC polymerization of the TEGDVE with 350 nm radiation. As is shown in the lower part of Figure 6, the heat flow (related to the polymerization rate) exhibited an induction period (as observed previously in the time−conversion profile in Figure 4). The induction period is followed by an exotherm peak which occurred at a shorter time and with a larger heat flux maximum as the concentration of AAAVB was raised. This behavior is consistent with the effect of raised AAAVB concentration on the rate of initiation and thus the rate of polymerization, as can be seen from the upper part of Figure 6. In addition, the final conversion of vinyl groups increased as the photoinitiator concentration was raised. This suggests that there exists a slow termination process in this system or that the propagation step in Scheme 4 is an equilibrium reaction with some reversible characteristics.

Apart from TEGDVE, several other difunctional vinyl ether monomers were also examined. All monomers polymerized readily in solutions containing AAAVB and ZnI_2. Typical results are shown in Table 2. As can be seen by comparison of the data runs 8 and 9 (Table 2), DPII is an not an efficient photoinitiator when irradiated at 350 nm because it only absorbs strongly at shorter wavelengths,[15] and as a result, very small monomer conversion is found and no gelation is observed even after after prolonged irradiation times.

Conclusions

The combination of substituted vinyl halides with ZnI_2 results in efficient photoinitiators for the cationic polymerization of vinyl ethers. The initiation mechanism involves photoinduced free radical generation by the homolysis of the carbon−halide bond and subsequent electron transfer to yield reactive cations capable of forming an adduct with the monomer. The efficiency of the vinyl cation formation is controlled by the nature of the vinyl halide substituent. Apparently, an electron-donating substituent provides more favorable thermodynamic conditions for the redox process and causes a shift of the absorption maximum to longer wavelengths, i.e., closer to the emission maximum of the radiation source. Once the adduct between vinyl halide and monomer is generated, complexation with ZnI_2 causes the formation of polymer of low polydispersity, which implies pseudoliving polymerization.

The major advantage of these combined initiating systems is their sensitivity to photoinitiaton at longer wavelengths than usually found. Moreover, these systems do not require radical initiating sources, hazardous protonic acids, or onium salts of any kind to form the intermediate adduct. Further studies to develop related photoinitiating systems which do not require metal salts are now in progress.

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