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Photoinitiated Cationic Polymerization of Vinyl Ethers Using Substituted Vinyl Halides in the Presence of Metallic Zinc

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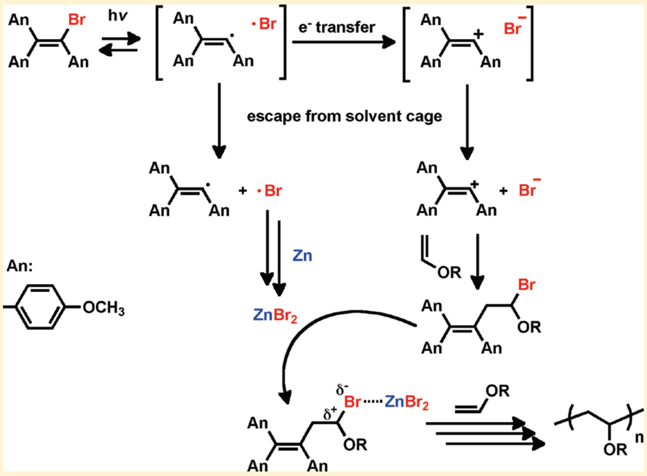
S Supporting Information

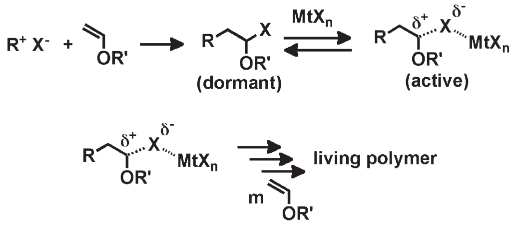
ABSTRACT: A novel photoinitiation approach for Lewis acid-catalyzed cationic polymerization of vinyl ethers, based on in situ formation of zinc halide, has been developed. The proposed mechanism of photoinitiation involves photoinduced generation of vinyl cations from subtituted vinyl halide, 1-bromo-1,2,2-tris(*p*-methoxyphenyl)ethene, by electron transfer and subsequent reaction with the monomer to form an adduct. In the process, zinc bromide, which plays central role in propagation step, was generated simultaneously by the reaction of metallic zinc with the photochemically produced bromine radicals. The living nature of the polymerization was studied by the investigation of time dependence of logarithmic conversion and molecular weights. The capability of the photoinitating system to induce cross-linking was also demonstrated using various difunctional monomers.



Because of the enormous interest in tailor-made materials for specific application in various fields such as bioengineering, medicine, biochemistry and material science, synthesis of such engineered macromolecular structures has become the main subject of the polymer science. However, these common polymerization techniques have still some drawbacks that need the attention of the polymer community. For instance, radical polymerization has important problems such as molecular oxygen inhibition, toxicity of monomers, requirement of high temperature and inability in polymerization of certain monomers (i.e., vinyl ethers). As an alternative method, various approaches of living cationic polymerization[1] have been reported for the synthesis of polymers of industrially important monomers to overcome the disadvantages related to free radical polymerization.

For decades, living cationic polymerization has been principally achieved by tuning nucleophilicity of counteranion generated in the presence of a metal halide, an externally added weak Lewis base, or an added salt.[1b,2] Among the living cationic polymerizations, the Lewis acid-catalyzed approach has been perfectly adapted to light-induced living cationic polymerization.[3] In this methodology, photochemically generated cationic species (either carbocation or Brønsted acid) from photoinitiators containing halogen react with monomer (i.e., vinyl ether) and form a halide-monomer adduct required in the first stage of the propagation. Addition of new monomers to the adduct is catalyzed by Lewis acid, namely metal halides, by coordination of metal ion with the halogen of the adduct (Scheme 1).

Scheme 1. Living Cationic Polymerization of Vinyl Ethers



R⁺: H⁺ or carbocation; X: Cl, Br or I

Although onium salts are the most widely employed photoinitiators in cationic photopolymerization, new photoinitiation modes[4] such as vinyl halides[5] in conjunction with co-initiators have recently been proposed as alternative photoinitiators with improved solubility and spectral response. Principally, photolysis of vinyl halides generates vinyl/halogen radicals and subsequently vinyl cations[5,6] that initiate cationic polymerization in the presence of metal halides such as zinc halides (Scheme 2).[7]

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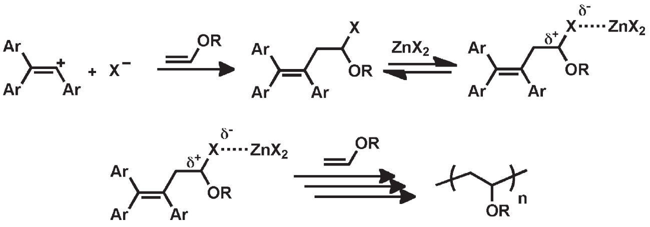
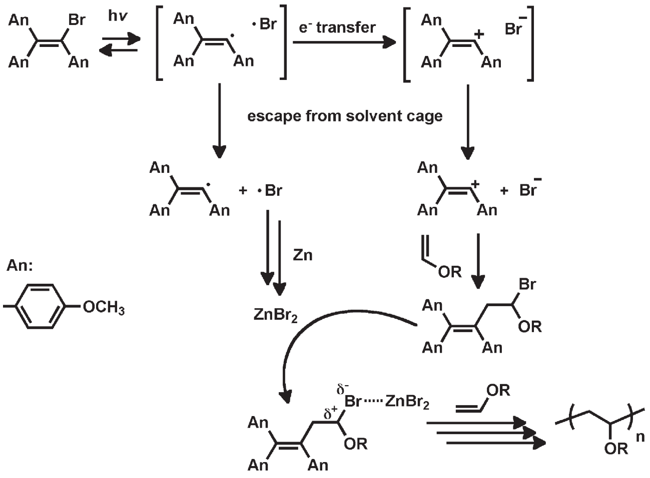
Lewis acid or metal halide plays the central role in the activation of propagating chains in this type of living polymerization. The common metal halides including ZnX_2, TiX_4, SnX_4, WX_6 and MoX_5 employed in such polymerizations are extremely sensitive to water and can be deactivated or transformed to less active Lewis acids in the presence of even small amount of air moisture and become useless in the activation process.[2,8] Thus, such polymerizations must be carried out under strictly dry conditions. One possible way to overcome this drawback is to use of water-tolerant Lewis acids such as ytterbium triflate [$Yb(OTf)_3$].[3d] Alternatively, the Lewis acid (e.g., zinc halide) can be produced in the polymerization medium. As reported previously, metallic zinc is readily converted to $Zn(OH)_2$ by peroxide radicals when it is treated with H_2O_2 aqueous solution and consequently oxidized to ZnO.[9] Essentially, zinc can be utilized as a reducing agent for free radicals leading to the formation of zinc salts. This redox process is also valid for halogen radicals; for instance, when vinyl halides are exposed to light at appropriate wavelengths,[5] they produce both vinyl, which then can be transformed to vinyl cation by spontaneous electron transfer, and halogen radicals capable of oxidizing metallic zinc. Therefore, photolysis of vinyl halides affords not only formation of vinyl cations required in the initiation step but also concomitant generation of zinc halides required in the propagation step (Scheme 3).

Scheme 2. Photoinitiated Cationic Polymerization Vinyl Ethers by Vinyl Cations in the Presence of Zinc Halide

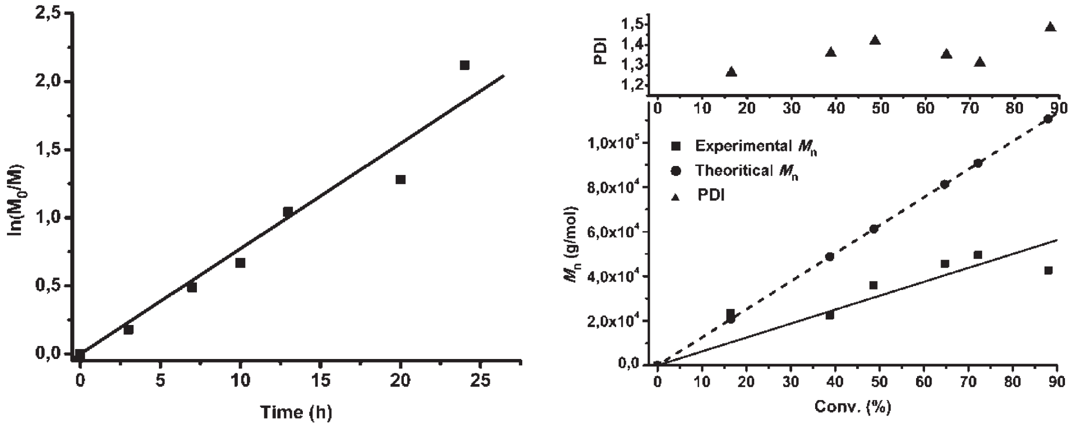


Scheme 3. Photo-Induced Cationic Polymerization of Vinyl Ethers in the Presence of Metallic Zinc



The current paper reports the cationic living polymerization of isobutyl vinyl ether (IBVE) initiated by the photolysis of a substituted vinyl halide, 1-bromo-1,2,2-tris(*p*-methoxyphenyl)ethene (AAAVB) in the presence of metallic zinc. The capability of this novel photoinitating system to induce cross-linking was also evaluated utilizing several difunctional monomers.

As proposed previously, photolysis of a vinyl halide in the presence of vinyl ether monomer yields an adduct through a reaction between the photochemically generated vinyl cation and the monomer.[7] In the subsequent step, a zinc halide coordinates with the halogen atom leading to insertions of the monomers to the adduct and, in turn, triggers chain propagation (Scheme 2). In this approach as presented in Scheme 3, Lewis acid (i.e., zinc bromide) was produced *in situ* during the photoinduced decomposition of vinyl halide, AAAVB. In addition to their participation in zinc bromide formation, some portion of the photochemically generated vinyl radicals undergo spontaneous electron transfer reaction yielding vinyl cations that essentially form monomer adducts. Subsequently, chain propagation proceeds after the activation of the adduct thus formed by the coordination with zinc bromide. The polymerization then continues in the usual manner as described for conventional living cationic polymerization mechanism.[2,3,10] Because of its limited solubility in organic medium,



(a) (b)

Figure 1. Kinetic plots of cationic living photopolymerization of isobutyl vinyl ether (7.68 $mol \cdot L^{-1}$) initiated by photolysis of 1-bromo-1,2,2-tris(*p*-methoxyphenyl)ethene (6.12×10^{-3} $mol \cdot L^{-1}$) in the presence of metallic zinc (6.12×10^{-2} $mol \cdot L^{-1}$); and polydispersity index (PDI) values of resulting polymers. $T = 0$ °C; $\lambda = 350$ nm; $I = 3.0$ $mW \cdot cm^{-2}$.

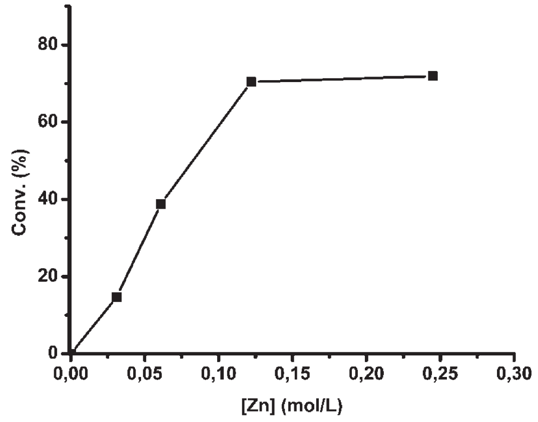


Figure 2. Effect of metallic zinc concentration on cationic living photopolymerization of isobutyl vinyl ether (7.68 mol·L^{-1}) initiated by 1-bromo-1,2,2-tris(*p*-methoxyphenyl)ethene (6.12 × 10^{-3} mol·L^{-1}). T = 0 °C; t = 7 h; λ = 350 nm; I = 3.0 mW·cm^{-2}.

Table 1. Photoinitiated Cationic Polymerization of Isobutyl Vinyl Ether (7.68 mol·L^{-1}) Initiated by 1-Bromo-1,2,2-tris-(*p*-methoxyphenyl)ethene (6.12 × 10^{-3} mol·L^{-1})[a]

entry	catalyst (mol·L^{-1})	convn (%)	M_n (g·mol^{-1})	PDI
1	Zn (0.031)	14.7	12 800	1.64
2	Zn (0.061)	38.8	22 500	1.36
3	Zn (0.122)	70.4	67 900	1.34
4	Zn (0.245)	71.9	59 100	1.35
5[b]	ZnI_2 (0.061)	85.2	48 500	2.03

[a] T = 0 °C; t = 7 h; λ = 350 nm; I = 3.0 mW·cm^{-2}. [b] Irradiation was ceased after 6 h since the solution became extremely viscous.

Table 2. Photo-Induced Cross-Linking of Various Difunctional Vinyl Ethers Using 1-Bromo-1,2,2-tris(*p*-methoxyphenyl)ethene (1.22 × 10^{-2} mol·L^{-1}) and Zinc (6.12 × 10^{-2} mol·L^{-1})[a]

entry	monomer (mol·L^{-1})[b]	gelation time (min)[c]	convn (%)[d]	gel content (%)[e]
6	TEGDVE (4.90)	45	46.9	86.1
7	BDVE (6.32)	30	76.6	95.4
8	DEGDVE (6.12)	90	29.3	72.4

[a] T = room temperature; λ = 350 nm; I = 3.0 mW·cm^{-2}. [b] TEGDVE: tri(ethylene glycol) divinyl ether. BDVE: 1,4-butanediol divinyl ether. DEGDVE: di(ethylene glycol) divinyl ether. [c] Gelation was followed qualitatively by simply observing motion of the magnetic bar in the tube, and the system was considered to have gelled when there was no flow of solution. Irradiation was ceased at this moment. [d] Conversion of monomer to polymer was determined from weight of the precipitated polymer in proportion to weight of the monomer. [e] Gel content was determined by measuring the weight loss after 24 h extraction with methylene chloride at room temperature.

10-fold excess of metallic Zn with respect to photoinitiator concentration was used throughout the polymerizations.

Possible living nature of the polymerization of IBVE initiated by photolysis of AAAVB in the presence of excess metallic zinc at 0 °C was examined by the investigation of reaction kinetics (Figure 1). As can be seen, the polymerization proceeded with first-order kinetic with respect to monomer concentration. Moreover, reasonably low polydispersity index (PDI) values were attained. However, the experimental molecular weights are lower than the calculated values. Although the propagation of the polymerization proceeds in a controlled manner, the new initiating species are produced photochemically at the any stage of the process and relatively low molecular weight polymers are also formed. Thus, the polymerization exhibits a quasi-living character.

Figure 2 and Table 1 summarize the effect of metallic zinc amount on the polymerization. As seen in Figure 2, the final conversion increases with increasing metallic zinc concentration up to 0.122 mol·L^{-1}, and levels off thereafter. The behavior is probably due to the limited light absorption. At sufficiently high Zn concentrations, the solution becomes almost opaque and the penetration of the light into solution is prevented. Furthermore, at this Zn concentration, the amount of vinyl halide may not be sufficient as it was utilized for the generation of both vinyl cation and $ZnBr_2$.

Notably, polymerizations under identical experimental conditions utilizing ZnI_2 directly resulted in the formation of polymers with high conversions but lower molecular weight and higher polydispersity (Table 1, entry 5). This clearly indicates that metallic zinc assisted polymerizations proceed in a more controlled manner.

The described approach can also be employed in UV curing applications of alkylvinyl ethers. Thus, potential activity of the photoinitiating system was examined in cross-linking of several difunctional monomers, namely tri(ethylene glycol) divinyl ether (TEGDVE), 1,4-butanediol divinyl ether (BDVE) and di(ethylene glycol) divinyl ether (DEGDVE). The formulations containing AAAVB, metallic zinc, and cross-linkable monomer were exposed to light. As presented in Table 2, all the monomers employed underwent cross-linking upon irradiation confirming possible value in practical applications involving UV curing of vinyl ether based formulations.

In conclusion, a new photoinitiating system based on *in situ* formation of zinc halide has been described for living cationic photopolymerization of vinyl ethers. Polymerization formulation consists of a vinyl ether monomer, a vinyl halide type photoinitiator and a metallic precursor, zinc. The polymerization shows usual characteristics of living mode when polymerization kinetics and PDIs of the resulted polymers are evaluated. The photoinitiating system is also useful in photoinduced cross-linking of difunctional monomers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental procedures and ^{1}H NMR spectra of AAAVB and resulting poly(isobutyl vinyl ether). This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

(1) (a) Crivello, J. V. *J. Polym. Sci., Polym. Chem.* **1999**, *37*, 4241–4254. (b) Kanazawa, A.; Kanaoka, S.; Aoshima, S. *Macromolecules* **2010**, *43*, 2739–2747. (c) Banerjee, S.; Paira, T. K.; Kotal, A.; Mandal, T. K. *Polymer* **2010**, *51*, 1258–1269. (d) Ida, S.; Ouchi, M.; Sawamoto, M. *J. Polym. Sci., Polym. Chem.* **2010**, *48*, 1449–1455. (e) Kanazawa, A.; Kanaoka, S.; Aoshima, S. *J. Polym. Sci., Polym. Chem.* **2010**, *48*, 916–926. (f) Aoshima, S.; Kanaoka, S. *Chem. Rev.* **2009**, *109*, 5245–5287.

(2) Sawamoto, M. *Prog. Polym. Sci.* **1991**, *16*, 111–172.

(3) (a) Kwon, S.; Chun, H.; Mah, S. *Fiber. Polym.* **2004**, *5*, 253–258. (b) Kwon, S.; Lee, Y.; Jeon, H.; Han, K.; Mah, S. *J. Appl. Polym. Sci.* **2006**, *101*, 3581–3586. (c) Kahveci, M. U.; Tasdelen, M. A.; Yagci, Y. *Polymer* **2007**, *48*, 2199–2202. (d) Kahveci, M. U.; Tasdelen, M. A.; Cook, W. D.; Yagci, Y. *Macromol. Chem. Phys.* **2008**, *209*, 1881–1886. (e) Kahveci, M. U.; Tasdelen, M. A.; Yagci, Y. *Macromol. Rapid Commun.* **2008**, *29*, 202–206.

(4) (a) Yagci, Y.; Jockusch, S.; Turro, N. J. *Macromolecules* **2010**, *43*, 6245–6260. (b) Yagci, Y.; Reetz, I. *Prog. Polym. Sci.* **1998**, *23*, 1485–1538.

(5) (a) Johnen, N.; Schnabel, W.; Kobayashi, S.; Fouassier, J. P. *J. Chem. Soc. Faraday T* **1992**, *88*, 1385–1389. (b) McNeely, S. A.; Kropp, P. J. *J. Am. Chem. Soc.* **1976**, *98*, 4319–4320. (c) Kitamura, T.; Kobayashi, S.; Taniguchi, H. *J. Am. Chem. Soc.* **1986**, *108*, 2641–2645. (d) Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. *Vinyl Cations*; Academic Press, Inc: New York, 1979.

(6) Galli, C.; Gentili, P.; Guarnieri, A.; Kobayashi, S.; Rappoport, Z. *J. Org. Chem.* **1998**, *63*, 9292–9299.

(7) Kahveci, M. U.; Uygun, M.; Tasdelen, M. A.; Schnabel, W.; Cook, W. D.; Yagci, Y. *Macromolecules* **2009**, *42*, 4443–4448.

(8) (a) Kennedy, J. P.; Iván, B. *Designed polymers by carbocationic macromolecular engineering: theory and practice*; Hanser: Munich, Germany, and New York, 1992. (b) Satoh, K.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2000**, *33*, 4660–4666. (c) Satoh, K.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1999**, *32*, 3827–3832. (d) Satoh, K.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2000**, *33*, 5836–5840.

(9) Ji, Z. G.; Zhao, S. C.; Wang, C.; Liu, K. *Mater. Sci. Eng. B-Solid* **2005**, *117*, 63–66.

(10) (a) Kojima, K.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1989**, *22*, 1552–1557. (b) Kamigaito, M.; Sawamoto, M.; Higashimura, T. *J. Polym. Sci., Polym. Chem.* **1991**, *29*, 1909–1915. (c) Sawamoto, M.; Okamoto, C.; Higashimura, T. *Macromolecules* **1987**, *20*, 2693–2697.