



## Polymer communication

## Influence of type of zinc salts on photoinitiated living cationic polymerization of vinyl ethers

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## ABSTRACT

Activities of a series of zinc salts in Lewis-acid-mediated cationic photopolymerization of vinyl ethers have been studied. Readily soluble zinc salts including zinc stearate, zinc acetate and zinc oxide; zinc iodide; and metallic zinc were employed as a Lewis acid in propagation stage of the cationic polymerization initiated by photolysis of a substituted vinyl halide, 1-bromo-1,2,2-tris(*p*-methoxyphenyl)ethene (AAAVB). As a model monomer isobutyl vinyl ether (IBVE) was polymerized by the described system in the presence of the zinc salts or metallic zinc for investigation of efficiencies of the Lewis acids. Novel system containing organo-zinc compounds yielded polymers in more controlled manner. For further evaluation of potential living character of the system, polymerization of IBVE catalyzed by zinc stearate was monitored, and as a result, the polymerization showed quasi-living nature. Activity of the catalyst system in photo-induced crosslinking of difunctional vinyl ether was evaluated as well.

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## 1. Introduction

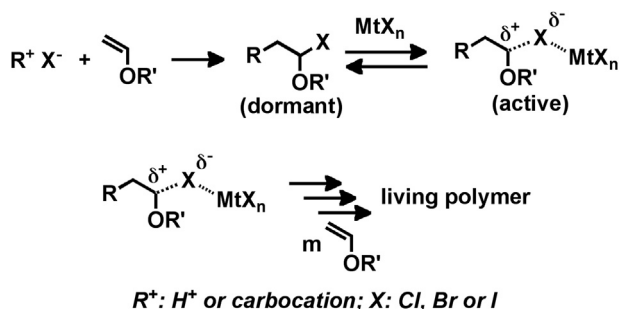
Tailor-made macromolecular materials have been commonly used in numerous fields including biomedical and pharmaceutical applications, tissue engineering, biochemistry, electronics and catalyst systems. In recent years, interest in such engineered macromolecular structures has been significantly increased after the development of controlled/living polymerization and coupling techniques or improvement of existing approaches. Lewis-acid-assisted living cationic polymerization offers several advantages for the preparation of well-defined polymers of cationically polymerizable monomers [1] including vinyl ethers [2], styrene derivatives [3], isobutylene [4] and indene [5]. Typical reactions for this type of initiation are presented in Scheme 1 on the example of the cationic polymerization of vinyl ethers. We and others recently adapted this approach to light-induced living cationic polymerization in which photochemically generated cationic species react with the monomer to form a halide-monomer adduct [6].

Although control over molecular weight and polydispersity can not be achieved, photoinitiated mode of cationic polymerization is extensively used on an industrial scale for a number of various applications including surface coatings, inks, adhesives, varnishes, microelectronics, microlithography, and dyes due to their many advantages [7]. Like all photopolymerization processes, photo-initiated cationic polymerization minimizes energy consumption and eliminates the need for solvents as diluents [7b,7c]. In this polymerization method, onium salts are the most commonly used cationic photoinitiators [8]. Regarding initiation by these prominent photoinitiators, both direct and indirect systems can be applied [9]. In direct initiating systems, the light is absorbed by the onium salt leading to its decomposition. In contrast to this, in indirect systems the energy is absorbed by additional components. Upon photolysis, either the additives themselves or species formed from the additives react with the onium salts thus producing initiating species. Free radical photoinitiators [10], polynuclear aromatic compounds [11], electron donor charge transfer components [12], and C60 [13] have been successfully used as additives to initiate cationic polymerization at selective wavelengths.

Substituted vinyl halides were also shown to be excellent long wavelength free radical promoters for cationic polymerization in conjunction with onium salts [14]. In a related study from this laboratory, we demonstrated that these compounds also have the ability to

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Scheme 1. Living cationic photopolymerization of vinyl ethers.

initiate cationic polymerization of vinyl ethers in the presence of Lewis acids such as zinc halides without requirement of onium salts [2a].

In general, Lewis acid ( $\text{MtX}_n$ ) plays the most important role in the photoinitiated living cationic polymerization. In the propagation step, the carbon–halogen bond of photochemically formed adduct is activated by coordination effect of the Lewis acid. However, utilization of metal halides as Lewis acid suffers from some drawbacks associated with solubility and irreproducibility problems. Furthermore, Lewis acids such as zinc halides are highly hygroscopic and therefore, the polymerization solution should be prepared under strictly dry conditions. One possible way to overcome these limitations is *in situ* formation of zinc halide in the polymerization media [15]. A recent study from our group concerning *in situ* formation of zinc halide to overcome such shortcomings that limit the potential applications of photoinitiated cationic polymerization.

On the basis of this knowledge, it seemed appropriate to investigate efficiency of soluble or readily dispersible zinc salts such as zinc stearate, zinc acetate and zinc oxide in Lewis acid catalyzed cationic photopolymerization of various vinyl ethers. As will be shown below, their activities in the polymerization were also compared with that of zinc iodide and zinc in which zinc bromide was formed an *in situ* manner. Living nature of the system was evaluated by the analysis of polymerization kinetics as demonstrated on the example of zinc stearate. In addition, initiating ability of the system in crosslinking of difunctional vinyl ethers was also studied.

## 2. Experimental

### 2.1. Materials

Isobutyl vinyl ether (IBVE, 99%, Aldrich) was distilled from  $\text{CaH}_2$  *in vacuo*. Difunctional monomer, tri(ethylene glycol) divinyl ether (TEGDVE, 98%, Aldrich), was used as received. Metallic zinc powder (particle size <45  $\mu\text{m}$ ,  $\geq 95\%$ , Merck), zinc iodide ( $\text{ZnI}_2$ , anhydrous, Merck), zinc stearate ( $\text{ZnSt}_2$ , Aldrich), zinc acetate ( $\text{ZnAc}_2$ , Aldrich), zinc oxide ( $\text{ZnO}$ ,  $\geq 99.0\%$ , Aldrich) and other chemicals were used as received. 1-bromo-1,2,2-tris(*p*-methoxyphenyl)ethene (AAAVB) was prepared as described in the literature [16].

### 2.2. Photopolymerization

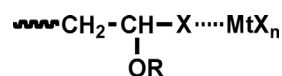
In a typical photopolymerization procedure of IBVE, a Pyrex tube equipped with magnetic bar was heated *in vacuo* with a heat gun, and flushed with dry nitrogen. Zinc stearate ( $6.12 \times 10^{-3} \text{ mol L}^{-1}$ ) and AAAVB ( $6.12 \times 10^{-3} \text{ mol L}^{-1}$ ) was dissolved in IBVE (1.00 mL,  $7.68 \text{ mol L}^{-1}$ ) in the Pyrex tube under vigorous stirring and then the tube was sealed off under nitrogen atmosphere. The formulation was stirred and exposed to light continuously at  $0^\circ\text{C}$  for 30 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. The light intensity at the location of the sample was measured by a Delta Ohm model HD-9021 radiometer ( $I = 3.0 \text{ mW cm}^{-2}$ ). At the end of the photoirradiation, the resulted polymer was dissolved with a little amount of dichloromethane and precipitated in excess amount of methanol (For Zinc stearate Conv.: 35.5%;  $M_n$ : 40,209 g/mol; PDI: 1.46).

A typical photocuring procedure for difunctional vinyl ether was as follows. Lewis acid ( $\text{ZnSt}_2$ ,  $\text{ZnAc}_2$  or  $\text{ZnI}_2$ ,  $3.92 \times 10^{-3} \text{ mol L}^{-1}$ ) and photoinitiator, AAAVB ( $3.92 \times 10^{-3} \text{ mol L}^{-1}$ ), was added into TEGDVE (0.60 mL,  $4.90 \text{ mol L}^{-1}$ ) in a Pyrex tube, which was previously heated with a heat gun under vacuum and flushed with dry nitrogen. The mixture was bubbled with nitrogen for 2–3 min and sealed off. The tube was exposed to light ( $\lambda \sim 350 \text{ nm}$ ) at room temperature ( $\sim 22^\circ\text{C}$ ) in the Rayonet photoreactor. The gelation time was determined when stirring was completely stopped since viscosity of the solution increased and flow of the solution was ceased. 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. The gel content was determined by measuring the weight loss after 24 h extraction of the crosslinked polymer at room temperature with dichloromethane (a good solvent for the linear polymer).

## 3. Results and discussion

As stated in the introduction section, living cationic polymerization of vinyl ether and related vinyl compounds have been used to obtain well-defined polymers with controlled molecular weight and a low polydispersity index. The living nature is achieved by incorporation of a suitable Lewis acid ( $\text{MtX}_n$ ) with a propagating chain which is represented below.



Obviously, Lewis acid such as  $\text{ZnX}_2$ ,  $\text{TiX}_4$ ,  $\text{SnX}_4$  and  $\text{BX}_3$  electrophilically activates the carbon–halogen bond of the propagating chain. Employment of such metal halides usually results in heterogeneous system that can deeply affect polymerization pathway and, in turn, polymer structure. To achieve polymerization through a completely homogeneous system, a novel formulation containing soluble photoinitiator, vinyl halide and soluble Lewis acid, organo-zinc compounds has been developed. In this context, activities of various Lewis acids were examined in photopolymerization of isobutyl vinyl ether (IBVE) using vinyl halide as a photoinitiator at  $0^\circ\text{C}$  (Table 1). Although activities of organo-zinc compounds in the

Table 1

Polymerization of isobutyl vinyl ether ( $7.68 \text{ mol L}^{-1}$ ) initiated by photolysis of 1-bromo-1,2,2-tris(*p*-methoxyphenyl)ethene ( $6.12 \times 10^{-3} \text{ mol L}^{-1}$ ) in the presence of various zinc-based catalysts ( $6.12 \times 10^{-3} \text{ mol L}^{-1}$ ).  $T = 0^\circ\text{C}$ ;  $t = 30 \text{ min}$ ;  $\lambda = 350 \text{ nm}$ ;  $I = 3.0 \text{ mW cm}^{-2}$ .

Entry	Lewis acid	Conversion (%)	$M_n$ (g mol <sup>-1</sup> )	PDI
1	$\text{Zn}(\text{St})_2$	35.5	40,209	1.455
5	$\text{Zn}(\text{Ac})_2$	35	23,775	1.808
2	$\text{ZnO}$	38.4	34,460	1.405
3	$\text{Zn}^a$	20	32,171	1.278
4	$\text{ZnI}_2$	65.8	53,222	2.016

<sup>a</sup> Irradiation time = 130 min.

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