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ARTICLE

Electro-initiated cationic polymerization in the presence of potassium hexafluoroantimonate

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This work presents the electrochemically-induced polymerization of vinyl ether monomers by using potassium hexafluoroantimonate ($KSbF_6$) as the initiating species. Static characterization of the resulting polymers was investigated by ATR-FT-IR. Real-time FT-NIR was used to study the kinetics of the electro-initiated polymerizations. Under certain conditions, rapid cationic polymerization kinetic profiles and high final conversion of monomer to polymer could be obtained. The reaction rate could be readily adjusted based on the applied voltage or by the introduction of an alkaline additive, which along with the observation of extended post curing clearly demonstrated the cationic nature of the electrochemical process. The thermo-stability of the polymerized product was investigated by TGA.

Introduction

In recent years, iodonium salts and sulfonium salts have been used widely as photoinitiators for cationic photopolymerizations.[1-4] Upon absorption of UV light to induce direct photolysis or through the oxidation of an appropriate photosensitizer activated at longer wavelengths, iodonium and other onium salts can generate strong Bronsted acids,capable of effective initiation of cationic polymerizations involving monomers such as vinyl ethers and epoxides.[5,6] These iodonium or sulfonium salts undergo a photo-induced reduction to form a +1 state iodobenzene or a +2 state diphenyl sulfide products. Crivello and Mowers found that sulfonium and iodonium salts also could be electrochemically reduced to these same initiating species to promote cationic polymerization. The mechanism involving reduction of the diaryliodonium and triarylsulfonium salts by free radical species, which formed by electrolysis of trace amounts of water present in the reaction mixture was postulated. These investigators believed that the complex cationic structures played an important role in the electro-initiated cationic polymerization.[7,8] Sezer and coworkers reported the electrochemical initiation involving cationic polymerization of heterocyclic and vinyl monomers at low potentials

in the presence of allylic hexafluoroantimonate salts. The mechanism postulated was an addition-fragmentation decomposition of allylic salts by free radical species, which formed by electrolysis of trace amounts of water present in the system. They also believed the complex cationic structures were essential for the polymerization reaction.[9] However, we noticed that vinyl ethers and epoxy monomers were initiated by strong Bronsted acids that were composed of an anionic component and the hydrons (H+). What's more, Akbulut and coworkers reported the electro-initiated cationic polymerizatiom of epoxides by using tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as an electrolyte.[10] Cyclohexene oxide and 1,2-epoxy-4-(epoxyethyl)cyclohexane were electro-initiated by using tetrabutylammonium fluoroborate (TBAFB) and terabutylammonium hexafluorophosphate (TBAHP) as electrolytes.[11,12] Electropolymerization of p-chloro-α-methylstyrene was investigated by using aluminum and mercury as metallic cationic initiators generated electrochemically and ClO^-, PF_6^-, SbF_6^- as the supporting electrolyte anions.[13] Yousef et al. reported electro-initiated cationic polymerization of p-chloromethyl styrene by using different sacrificial materials in the presence of SbF_6^- and ClO_4^- as supporting anion electrolytes.[14] Electro-initiated cationic polymerization of epoxy Novolac resin was investigated by using

diaryliodonium hexafluoroantimonate as initiator.[15] The preparation and polymerization of a bifunctional imidazolium-based ionic liquid monomer that incorporated both a vinyl group and a thiophene moiety was reported using Bu_4NPF_6 as electrolyte by Lee and coworkers.[16] Electropolymerization of N-alkyl-3,4-ethylenedioxypyrroles with different alkyl chain lengths was reported by Darmanin and Guittard using tetrabutylammonium hexafluorophosphate as electrolyte. $Bu_4N^+PF6^-$ and $Bu_4N^+ClO4^-$ were used as the electrolyte to investigate the electropolymerization of 3,4-ethylenedioxypyrrole (EDOP) derivative containing a perfluorobutyl chain (F-butyl).[17,18]

It's worth noting that all the electro-initiated cationic polymerization metioned above involed MX_n^- anions. Then we propose that the MX_n^- anions determine the polymerization instead of the cations，so in this work, $KSbF_6$ was used to substitute the iodonium salts and onium salts to investigate the polymerization of vinyl ether monomers. What's more, $KSbF_6$ is a raw material to synthesise sulfonium salts. In this way, we can save the cost by using $KSbF_6$ to substitute the sulfonium salts.

Real-time FT-IR has been proven to be a versatile and effective technique to investigate the kinetics of photo-initiated polymerizations.[19-21] However, there are almost no reports on investigating the kinetics of electro-initiated polymerization by this approach. In this work, we choose ITO conductive glasses, which allow transmission of the near-infrared spectrum, as the electrode for the kinetic study of electro-initiated polymerization of vinyl ether monomers.

Experimental part

Materials

Ethylene glycol monovinyl ether was purchased from J & K Technology Co., LTD. Di(ethylene glycol)vinyl ether were purchased from TCI Japan. 1,4-Butanediol vinyl ether was purchased from Acros Organics. Hydroxyethyl acrylate (HEA) and hexamethylene diacrylate (HDDA) were donated by Sartomer. $KSbF_6$ were purchased from Changzhou Runtec Chemical LTD. KPF_6 and KBF_4 were purchased from Beijing Universal Century Technology Co., LTD. Ethanol was purchased from Beijing Chemical Works. All other chemical reagents were obtained from Sinopharm Group Chemical Reagent Co., LTD and used as received without further purification.
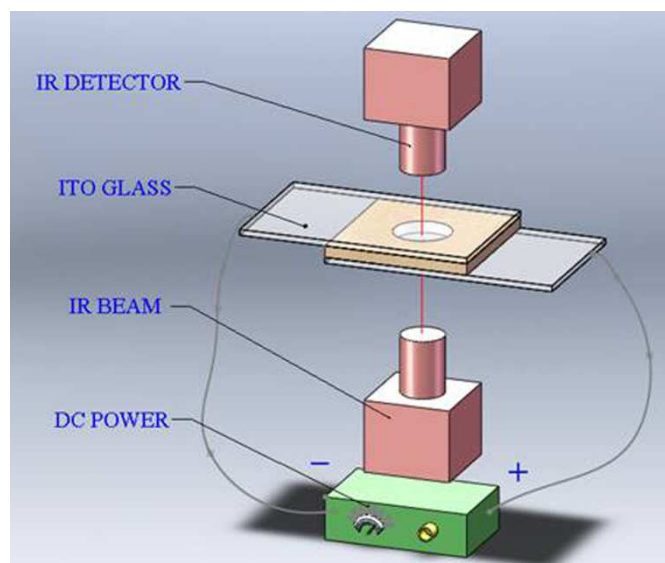
ATR-FT-IR

All electrolyses were conducted in a two-electrode undivided cell with inert graphite as working and counter electrode. The distance between the anode and cathode electrode was 6 mm. A solution of ethylene glycol monovinyl ether containing 0.5 wt% $KSbF_6$ was put into the cell for electro-initiated polymerization. Electropolymerizations were conducted for 15 min under a constant potential voltage (36 V), supplied by DC-stabilized electrical source (Dahua, Beijing, China) with the controllable voltage from 0.0 to 100.0 V. The graphite anode was then immersed in ethanol with

ultrasonic agitation applied for 5 min to remove any unreacted monomer. After evaporation of residual solvent under vacuum, the polymeric product was analyzed by ATR-FT-IR (Thermo Electro Corporation, Waltham, MA).

Kinetics of electro-initiated polymerization

The samples prepared with the various monomers and initiator were placed in a sealed mold made from ITO conductive glasses and insulated spacers with a 10 mm diameter and 2 mm in thickness were, then initiated by constant potential voltage over the range of approximately 1 V to 36 V. The double bond conversion of vinyl ether monomers was monitored by real-time near-FT-IR spectroscopy (Thermo Electro Corporation, Waltham, MA) according to the absorbance change of peak area from 6100 to 6250 cm^{-1}. The diagram of experimental apparatus is shown in Scheme 1.

Scheme 1 Diagram of experimental apparatus for real-time FT-NIR

TGA

The Thermal Gravimetric Analysis of the polymeric product which was analyzed by ATR-FT-IR was then investigated by TGA(TA instruments, Q500) with the heating rate of 5℃/min in a flow of N_2.

Results and Discussion

ATR-FT-IR

When the electrolysis of a solution of ethylene glycol monovinyl ether containing 0.5 wt% $KSbF_6$ was carried out, rapid polymerization took place solely at the graphite anode with no polymerization noted at the cathode. No polymerization was observed without $KSbF_6$. Figure 1(a) is the FT-IR spectrum of

ethylene glycol monovinyl ether, while Figure 1(b) is the ATR-FT-IR spectrum of the product after electropolymerization. The disappearance of the characteristic mid-IR peaks associated with the vinyl ether double bond (1620.17 cm^{-1}) indicated the polymerization of the monomer.
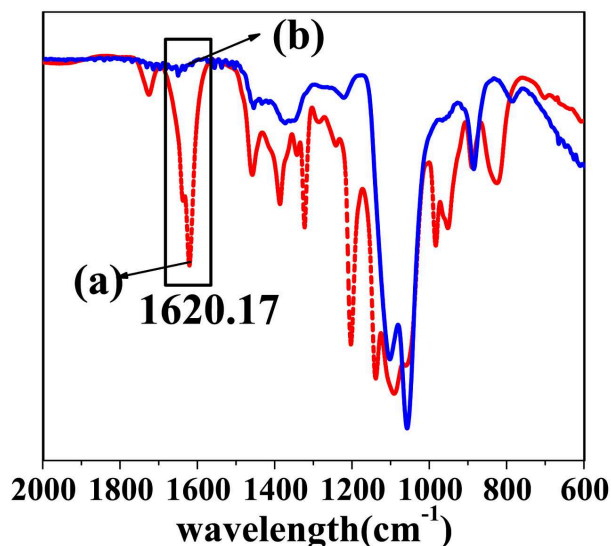

Fig.1 Static IR spectra of ethylene glycol monovinyl ether (a) before and (b) after electropolymerization.

Kinetics of electro-initiated polymerization

As shown in Figure 2(a), ethylene glycol monovinyl ether, di(ethylene glycol)vinyl ether and 1,4-butanediol vinyl ether could be efficiently initiated by KSbF$_6$ when the applied voltage was 36 V, while under the same conditions, hydroxyethyl acrylate (HEA) and hexanediol diacrylate (HDDA) could not be polymerized, which indicates a cationic polymerization mechanism is involved. It was clear that rapid polymerization and high double bond conversion were achieved under the electric field strength of 36 V and 2 mm separation for ethylene glycol monovinyl ether. Thus, ethylene glycol monovinyl ether was chosen as the monomer for further investigations. The kinetics of electro-initiated polymeriztion of ethylene glycol monovinyl ether using 0.5 wt% KSbF$_6$ as initiator under different voltages (36 V, 6 V, 4.5 V, 3.75 V, 3.0 V, 2.25 V and 1.5 V) were also investigated. As shown in Figure 2(b), low double bond conversion was achieved under low voltage, while the double bond conversion could reach up to 70 % at 3.0 V in 15 min. By increasing the voltage to 4.5 V, the double bond conversion was almost 100 %. By continuing to increase the voltage, the final double bond conversion was essentially complete (nearly 100 %), while the polymerization rate progressively increased with each increase in the voltage, as shown in Figure 2(c). It was noted that intermediate values of double bond conversion (approximately 70 %) and polymerization rate were achieved with the application of 3.0 V for 15 min. Therefore, these conditions were adopted for further studies.
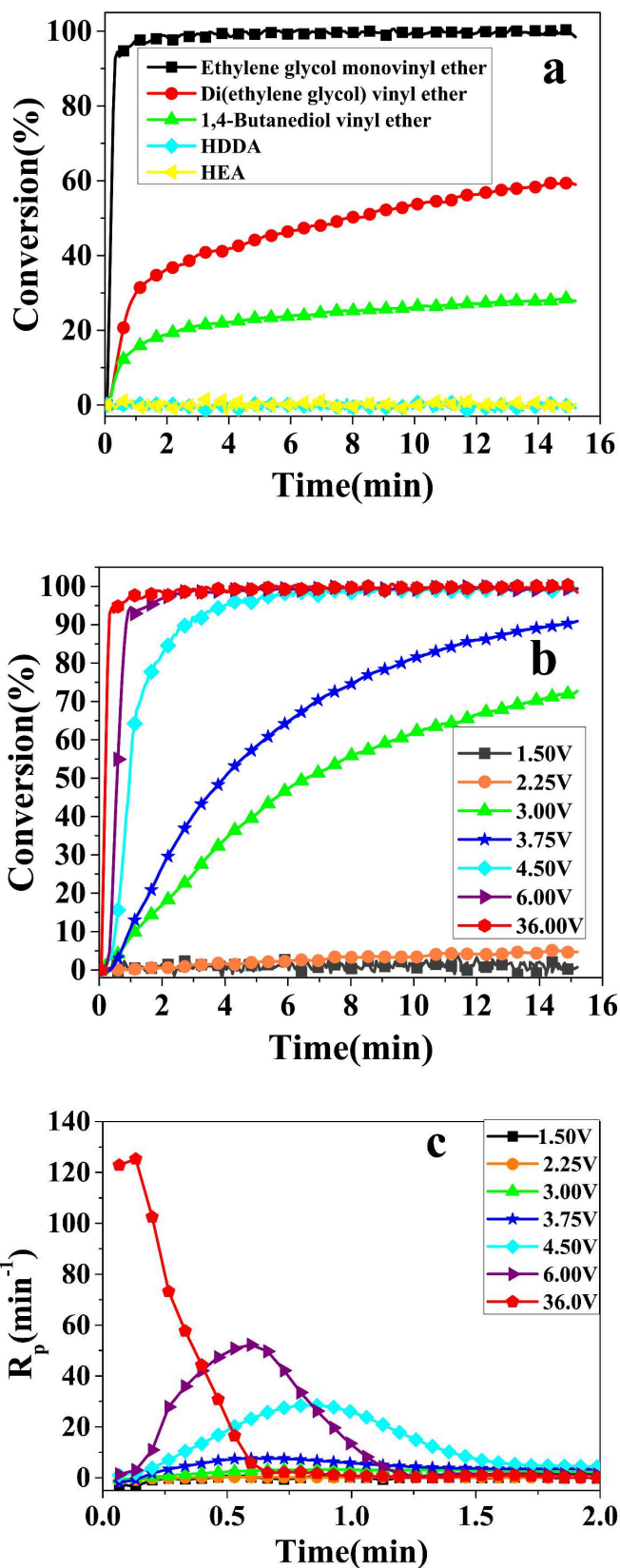

Fig.2 (a) Electro-initiated polymerization kinetics of ethylene glycol monovinyl ether, di(ethylene glycol)vinyl ether, 1,4-butanediol vinyl ether,

HDDA and HEA using 0.5 wt% $KSbF_6$ as the initiator at a voltage of 36 V; (b) and (c) Electro-initiated polymerization kinetics of ethylene glycol monovinyl ether using 0.5 wt% $KSbF_6$ as the initiator at different voltages.

Various alkaline compounds were used as the termination agent for the cationic polymerizations. Different mass ratios of KOH ($KOH:KSbF_6$=0:1, 1:20, 1:15, 1:10, 1:0) were added to the system. As shown in Figure 3, the reaction rate and the double bond conversion dropped dramatically with the progressive addition of KOH with almost no polymerization observed when the weight ratios was $KOH: KSbF_6$=1:10, which provides further evidence that the electro-initiated polymerization involved a cationic process.
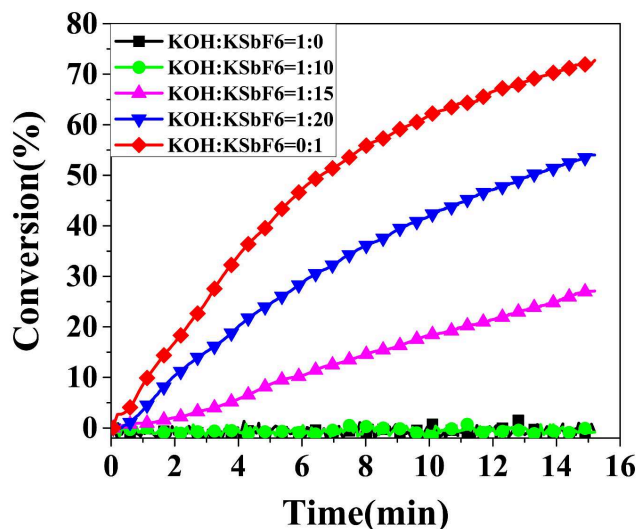

Fig.3 Inhibition of polymerization based on different amounts of KOH ($KOH:KSbF_6$ mass ratio=1:0, 1:10, 1:15, 1:20, 0:1) in the polymerization of ethylene glycol monovinyl ether using 0.5 wt% $KSbF_6$ as the initiator at voltages of 3 V.

It is well known that the active centers in cationic polymerizations can survive for extended time periods, which is evident from the post curing that occurs in cationic polymerization.[22-24] A solution of ethylene glycol monovinyl ether containing 0.5 wt% $KSbF_6$ was exposed to a voltage of 3 V for either 1 min or 3 min to begin the electrochemical polymerization process with conversion monitoring continued after the electric field was removed to investigate the post curing process. As shown in Figure 4(a), the double bond conversions were only 9.1 % and 33.5 %, respectively, when the electric field was turned off; however, conversion reached 24.2 % and 43.5 %, respectively, within 15 min. For further study the post curing, repeated cycles (10) of 1 min with the electric power on followed by 5 min with the field off were applied while monitoring conversion. As shown in Figure 4(b), double bond conversion increased continuously with post cure being obvious over the entire range of the cationic polymerization reaction. In fact, after the initial cycle that produced the highest actively initiated reaction rate, the subsequent rates associated with the periodic reactivation demonstrated that the electrochemical reaction remained efficient considering the decreasing monomer concentrations as shown in Figure 4(c).
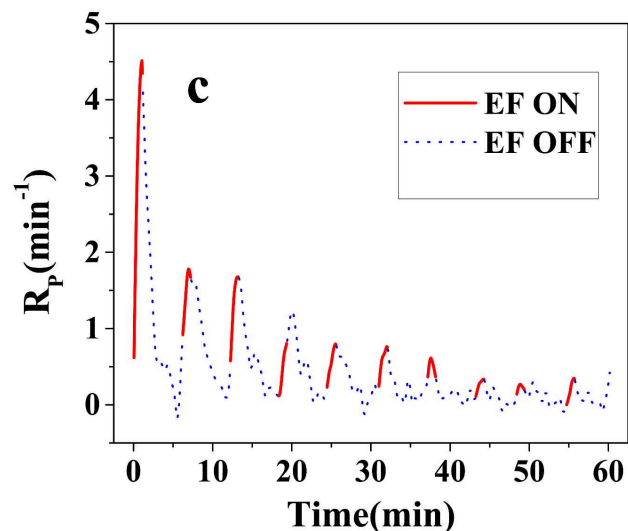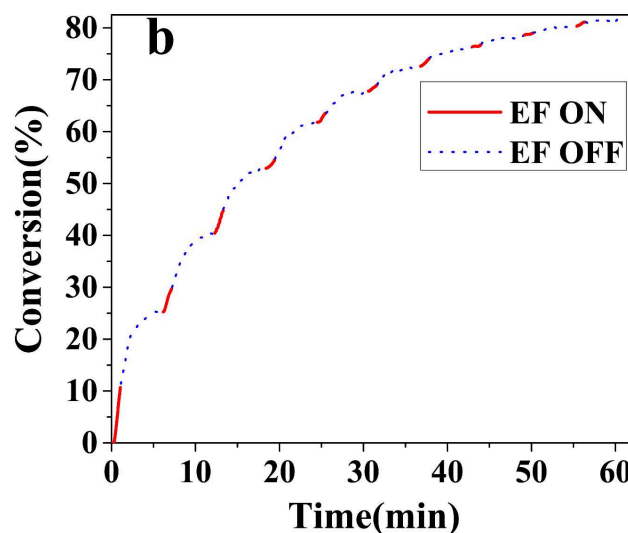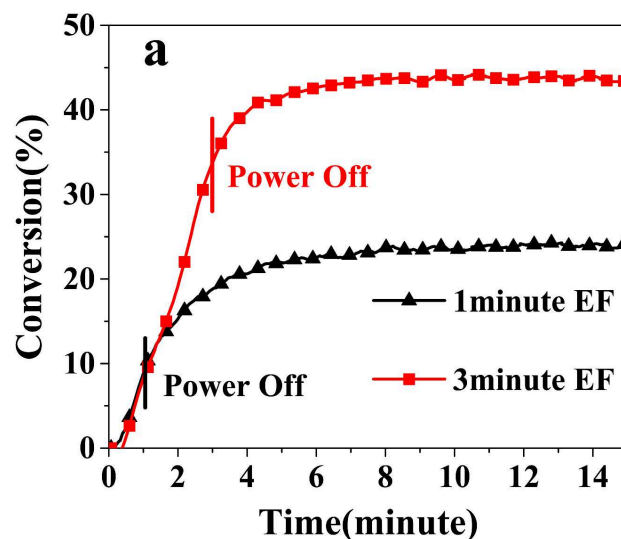
Fig.4 (a) Post curing of ethylene glycol monovinyl ether using 0.5 wt% $KSbF_6$ as the initiator when turning off the electrical power (3 V) at 1min or, 3 min; (b) and (c) Electro-initiated polymerization kinetics of ethylene glycol monovinyl ether using 0.5 %wt $KSbF_6$ as the initiator at voltages of 3 V. The solid lines represents the 1 min intervals during which the electrical power was on with the dashed lines indicating the intervening 5 min periods with the power off.

TGA

As shown in figure 5, TGA results indicated that the products achieved by electropolymerization had two main weight loss process , while the temperatures of the maximum weight loss rate were 335.61°C and 417.35°C.
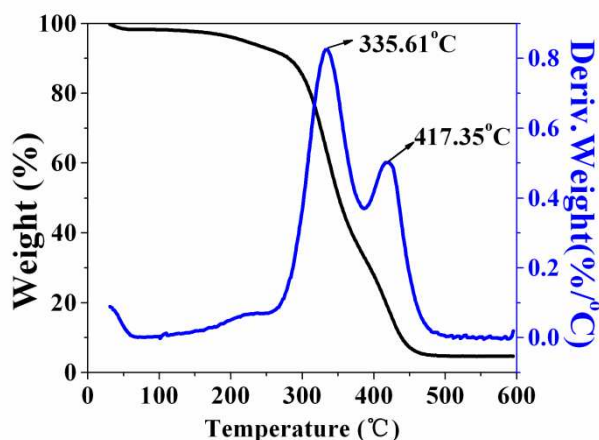

Fig. 5 TGA of poly （ethylene glycol monovinyl ether） with a heating rate of 5°C/min in a flow of N_2.

Mechanism of the electro-initiated polymerization

The monomers like vinyl ethers which undergo a cationic polymerization were polymerized through electro-initiated polymerization in the presence of $KSbF_6$. But the monomers like HEA and HDDA which undergo a free radical polymerization, no polymerization occurred by electric field in the presence of $KSbF_6$. What's more, the obvious post-curing of electro-initiated polymerization of ethylene glycol monovinyl ether indicated the long-lived active center, which followed the profile of cationic polymerization.

So what's the active center? Was it the free-radical cationic generated by direct oxidation of the monomer at the anode or the Lewis acid generated by $KSbF_6$ after capturing a proton? To answer this question, we investigated the kinetics of the electro-initiated polymerization of ethylene glycol monovinyl ether with or without different kinds of potassium salts by RT-FT-IR. As shown in Fig 6(a), no polymerization occurred without potassium salts, in this way, the mechanism of free-radical cationic generated by direct oxidation of the monomer at the anode could be excluded. And as shown in Fig6(b), the rate of the electro-initiated polymerization of ethylene glycol monovinyl ether with different kinds of potassium salts is $Rp(KBF_4) < Rp(KPF_6) < Rp(KSbF_6)$, which was in accordance

with the iodonium salts with different anions for photopolymerization.[25] This indicated the existence of Lewis acid. In further confirmation, the PH near the anode electrode after electrolysis was measured and found to be very low indicating the formation of an acid. What's more, the obvious inhibition effect of KOH indicated the polymerization was initiated by a Lewis acid.
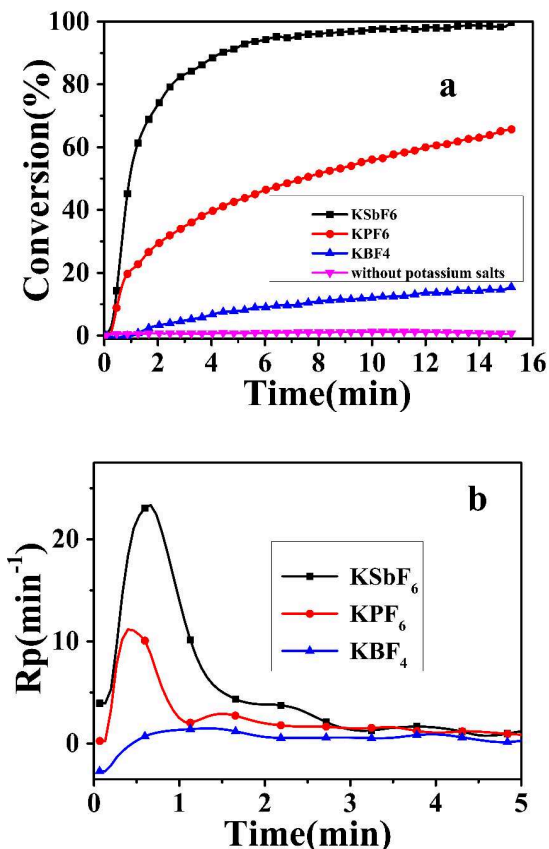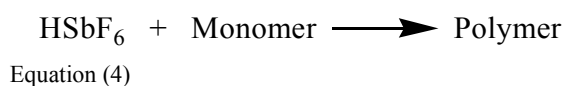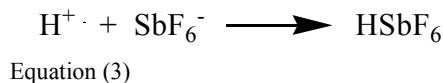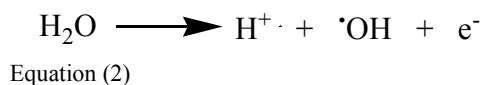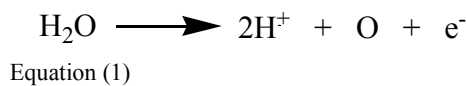

Fig.6 Kinetics of electro-initiated polymerization of ethylene glycol monovinyl ether using 0.5 wt% different kinds of potassium salts($KSbF_6$, KPF_6, KBM_4)as the initiator at voltages of 4.5 V.

Then, how did the Lewis acid form? A mechanism involving reduction of diaryliodonium salts by free radical species formed by electrolysis of trace amount of water present in the reaction mixture is postulated by James V.Crivello and Willam A.Mower in electro-initiated cationic polymerization of typical vinyl and heterocyclic monomers.[7] And Yusuf Yagci and co-workers postulated a mechanism involving addition-fragmentation decomposition of allylic salts by free radical species formed by electrolysis of trace amounts of water.[9] So in this paper, we agreed with the first part of the mechanism what James V.Crivello and Yusuf Yagci postulated, which was the electrolysis of trace amounts of water. So in this way, the Lewis acid was formed by combining $KSbF_6$ with protons which was generated by electrolysis of trace amounts of water at the anode electrode. The mechanism of electro-initiated cationic polymerization of vinyl ethers in the presence of $KSbF_6$ was shown in equation 1 to equation 4.

$$H_2O \longrightarrow 2H^+ + O + e^-$$

Equation (1)

$$H_2O \longrightarrow H^{+\cdot} + {}^{\cdot}OH + e^-$$

Equation (2)

$$H^{+\cdot} + SbF_6^- \longrightarrow HSbF_6$$

Equation (3)

$$HSbF_6 + Monomer \longrightarrow Polymer$$

Equation (4)

Conclusions

In this paper, the electrochemical cationic polymerization of vinyl ether monomers initiated by $KSbF_6$ is presented. Real-time FT-NIR was demonstrated to be a highly effective tool with which to investigate the kinetics of electro-initiated polymerization by using ITO conductive glass substrates which allowed the transmission of the near-infrared spectrum in sample thicknesses appropriate for electrochemical processing. Rapid polymerization rates and high double bond conversion indicated that $KSbF_6$ is an effective electro-initiator for these polymerizations. The obvious post curing process involving the electron-rich vinyl ether monomers as well as the inhibitory effects of KOH clearly indicates a cationic polymerization mechanism.

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Notes and references

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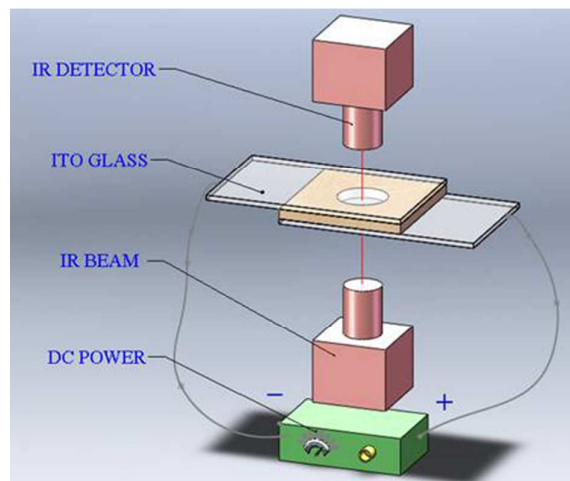21 F. Xu, J.-L. Yang, Y.-S. Gong, G.-P. Ma, J. Nie, *Macromolecules* **2012**, *45*, 1158.

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Graphical abstract

    The kinetics of electro-initiated polymerization of vinyl ethers in the presence of potassium hexafluoroantimonate are investigated by RT-FT-NIR. The apparatus for real time monitoring the kinetics of the reaction is set up by using ITO conductive glasses, which allows the transmission of NIR. In this article, potassium hexafluoroantimonate, just like sulfonium salts, has been proved to be an efficient initiator for electro-initiated polymerization of vinyl ethers. The results show that the electro-initiated polymerization in the presence of potassium hexafluoroantimonate follows a cationic nature , which is proved by obvious post-curing and the inhibition effects of potassium hydroxide.