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Electroiniated cationic polymerization in the presence of addition-fragmentation agents

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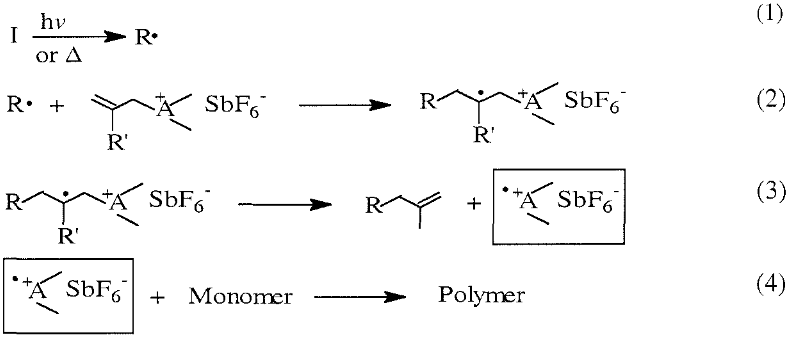
Summary

Electrochemical initiation of cationic polymerization of heterocyclic and vinyl monomers such as cyclohexene oxide (CHO) and butyl vinylether (BVE), respectively at low potentials in the presence of allylic salts namely, allyl-thiophenium (AT), allyl-triphenyl phosphonium (APP), allyl-isoquinolinium (AIQ), allyl-pyridinium (AP) and allyl-dimethyl anilinium salts, was investigated. The mechanism of this polymerization was studied using cyclic voltammetry and by electropolymerization experiments performed in undivided and H-type cells. A mechanism involving addition-fragmentation decomposition of allylic salts by free radical species formed by electrolysis of trace amounts of water present in the system is postulated.

Introduction

Onium salts [1] of iodonium [2], sulphonium [3,4] and alkoxypyridinium [5-8] type with non-nucleophilic counter ions can be employed successfully for the photoinitiation of cationic polymerization of epoxides and vinyl ethers. Simple onium salts absorb the ligh at c.a. 300 nm and can be activated directly upon irradiation at these wavelengths. In order to have wider flexiblity in various practical applications several indirect acting initiating systems were proposed. For instance, photoiniated cationic polymerization [9] can be realized at the wavelength range of 350-600 nm by using appropriate free radical photoiniators [5, 8], photosensitizer[10, 11] and forming charge transfer complexes[12]. Thermal activation in conjunction with free radical initiators is also possible [9]. Recently, Crivello [13] reported rapid and efficient electrochemical initiation of cationic polymerization using iodonium salts at low potentials. In this case, iodonium salts were reduced by the radicalic species formed by electrolysis.

We have recently developed [14-36] an elegant and flexible way of initiating cationic polymerization by the use of specially designed allylic addition-fragmentation agents (AFA) in conjunction with free radical sources. The obvious advantage of using AFAs is that initiation can be triggered by either heat or light. Moreover, as far as photopolymerization is concerned, it is extremely easy to tune a desired wavelengths' range (the emission band of the light source used) by choosing appropriate radical initiators. The system takes the advantage of the availability of the numerous radical initiators with excellent yields and good storage stability. Moreover, it is not limited to electron donor radicals, i.e. any radicals which are capable of adding double bonds may be employed. This possibility is not offered by any other existing salts, including iodonium salts which are known to be the strongest oxidants. Allylic salts with various substituents in the allylic moiety were shown to be very efficient AFAs for the initiation of cationic polymerization. Schematically, the proposed mechanism based on product analysis and polymerization studies is shown in Scheme 1 where I and A represent thermal or photochemical free radical initiator and hetero atom in the allylic salt, respectively.



Scheme 1

The aim of this work was to investigate the effect of electrolysis on the decomposition of the AFAs in order to evaluate the interaction between electrochemically generated radical species with the allylic salt. The results obtained were correlated with the mechanism of cationic polymerization using thermal and photochemical free radical initiators in addition-fragmentation type initiation.

Experimental

Materials

All salts, namely, allyl-thiophenium [14] (AT), allyl-triphenyl phosphonium [25] (APP), allyl-isoquinolinium [24] (AIQ), allyl-pyridinium [16] (AP) and allyl-dimethyl anilinium [31] (ADA) salts with hexafluoroantimonate counter anion, were prepared as previously described. Monomers, cyclohexene oxide (CHO) and butyl vinylether (Aldrich), were vacuum distilled from calcium hydride (CaH_2) before use. Dichloromethane (CH_2Cl_2) (Lab-scan) was washed with conc. H_2SO_4 until the acid layer remained colorless, then washed with water, aq. %5 NaOH and then water again. It was then pre-dried with $CaCl_2$ and distilled from CaH_2.

Electropolymerization

All electrolyses were conducted in a standart three electrode cell under constant potential using a Wenking POS 73 model potentiastat. The reference electrode was Ag wire (The redox potential of ferrocene/ferrocenium couple was found to be 220 mV against this reference electrode). Electrochemical cell was charged with a 50/50 mixture of solvent and 0.1 mol l^{-1} salt as supporting electrolytes. An electrochemical H-cell with cathode and anode compartment separated by a glass frit was used for analysis of anode and cathode products. Solution was poured into methanol after electrolysis and the precipitates were dried under vacuum. Cyclic voltammetry experiments were carried out in the same three electrode cell at a scan rate 100 mV/s and in the range of 0.0-(-1.5) V vs Ag.

Analyses

Gel permeation chromatography (g.p.c) analyses were performed with a set up consisting of an Agilent 1100 RI apparatus equipped with three Waters ultrastyragel columns (HR series 4, 3, 2 narrow bore), with THF as the eluent at a flow rate of 0.3 mL/min and a refractive index detector. Molecular weights were calculated with the aid of polystyrene standards.

Results and Discussions

The structure of the allylic salts used in this study and their onset and peak potentials, obtained from their cyclic voltammogram in cathodic direction (Figure 1), are represented in Table 1. The SbF_6^- anion was deliberately chosen due to its reported electrochemical stability [37]. Thus, electroactivity of the salts should be solely due to the cationic moiety of the salt. According to the peak potentials presented in Table 1, ADA is the most susceptible to reduction. In addition to cathodic direction, electroactivity of the allylic salts were also tested both in anodic direction. In anodic direction there is no significant peak in the range of 0.0 V to 1.80 V vs Ag wire for all salts investigated except ADA which has an anodic peak at 1.13 V and corresponding reverse peak at 1.05 V and 0.53 V in reverse direction (Figure 2). These results indicate that direct oxidation of the salts at the anode can be disregarded. Moreover, it is known [38, 39] that onium ions are already in a highly oxidized state and are stable electrolytically under oxidizing conditions.

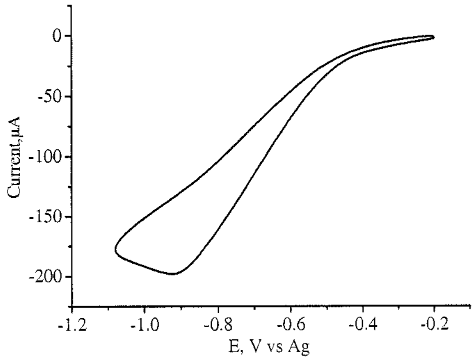


Figure 1. Cyclic voltamoggram of ADA (0.1 mol l^{-1}) in dichloromethane in the cathodic direction scan rate: 100 mv s^{-1}.

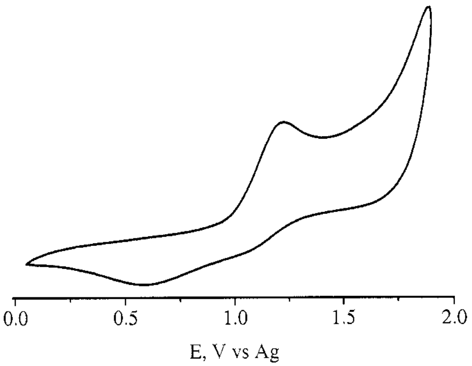
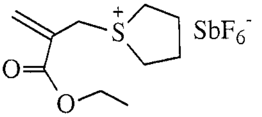
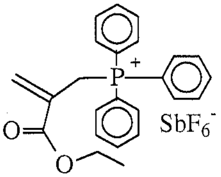
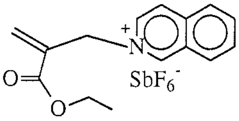
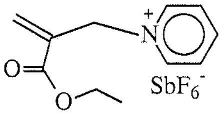
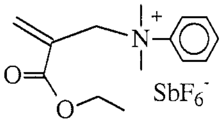


Figure 2. Cyclic voltamoggram of ADA (0.1 mol l^{-1}) in dichloromethane in the anodic direction scan rate: 100 mv s^{-1}

Table 1. Structure and redox potentials of allylic salts

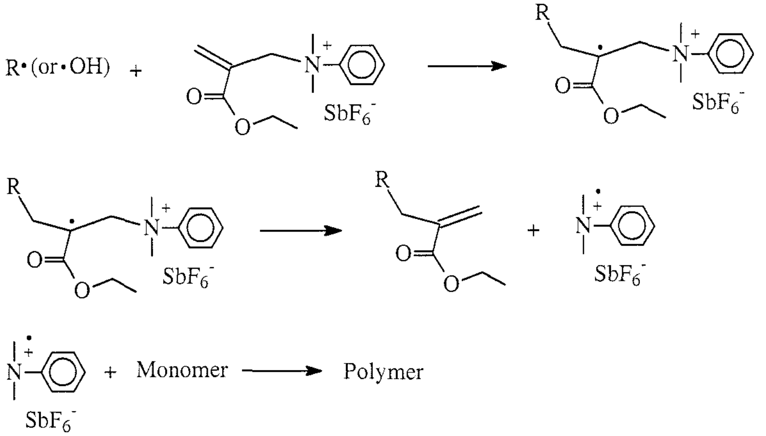
Salt	Structure	Onset potential(V)	Peak Potential, Ep (V)
Allyl-thiophenium salt, **AT**		-0.7	-1.1
Allyl-triphenyl phosphonium salt, **APP**		-0.8	-0.95
Allyl-isoquinolinium salt, **AIO**		-0.8	-0.98
Allyl-pyridinium salt, **AP**		-0.9	-1.23
Allyl-dimethyl anilinium salt, **ADA**		-0.53	-0.95

A series of experiments were performed using cyclohexene oxide (CHO) and butyl vinylether (BVE), as representative monomers of commercially important epoxides and vinyl monomers, respectively, to demonstrate addition-fragmentation character of the allylic salts in electroinitiated cationic polymerization. The results are shown in Table 2. The electrolyses were conducted at 1.8 V for the times indicated. It is interesting to note that all salts are effective in initiating cationic polymerization electrochemically. Notably, APP seems to be the least efficient salt to induce electroinitiated polymerization. In this connection, it should be pointed out the similar initiating efficiency of the triphenylphosphonium salt was found in the polymerizations using thermal and photochemical radical sources. In this case, from point of steric hindrance the triphenylphosphinium cation is expected to have a relatively limited reacting efficiency with monomer [25]. The phosphorous centered

Table 2. Electroinitiated cationic polymerization[a] of cyclohexene oxide (CHO) and butyl vinyl ether (BVE) in the presence of allylic salts in dichloromethane.

Monomer(mol l^{-1})	Alylic Salt	Time(sec)	Conversion(%)	M_n[b]($g\ mol^{-1}$)
CHO (Bulk)	AT	60	3	2200
CHO (4.89)	AT	60	5	2100
CHO (4.89)	APP	600	1	1800
CHO (4.89)	AP	10	15	2900
CHO (4.89)	AIQ	60	2	2400
CHO (4.89)	ADA	5	50	5300
BVE (3.88)	AT	120	50	nd[c]
BVE (3.88)	ADA	3	20	nd[c]

[a][Allylic Salt] = 0.1 mol l^{-1}, applied potential = 1.8 V vs Ag wire, W.E = Pt (area = 0.4 cm^2)
[b]Determined by GPC according to polystyrene standards
[c]Not determined



(7)

(8)

(9)

Scheme 2

cationic centre is expected is almost entirely shielded by the large phenyl groups.

In order to gain a better insight to polymerization mechanism, we have conducted experiments in a divided H-cell under identical experimental conditions. While no polymerization took place in cathode compartment, polymerization appears to occur at the surface of the anode. According to these results, direct reduction of the salts is not responsible for the initiation and cationic species generated indirectly in the anode are involved in the initiation of the polymerization. In analogous to the electroinitiated cationic polymerization using iodonium salts [13], we propose that the mechanism for the decomposition of allylic salts and initiation of cationic polymerization proceeds through a complex series of steps involving the electrolysis of trace amounts of water present in the system. At potentials above 1.0 V, besides oxidation process water produces hydroxyl radicals at the anode according to the following reaction.

$$H_2O \longrightarrow H^+ + \bullet OH + e^- \qquad (5)$$

These can further react with monomer or solvent to produce secondary alkyl radical species.

$$RH + \bullet OH \longrightarrow R\bullet + H_2O \qquad (6)$$

The radicals generated by either direct electrolysis and by secondary reactions add to the double bond of the allylic salt and subsequently an onium radical cation is released, which initiate the polymerization. In scheme 2, this mechanism is illustrated on the example of anilinium salt, DMAMA. Fragmentation brings about the elimination of substituent that formerly prevented the cationic center from reacting monomer, i.e., the onium salt becomes unblocked. The allylic moiety represents the reactive site for the addition step whereas the charged onium cation is a latent initiating species which is released only by fragmentation.

In conclusion, electroinitiated polymerization employing allylonium salts represents a novel, rapid and efficient means of addition fragmentation type initiation. In this work we have demonstrated that polymerizations proceed in solution or in bulk at very low electric potentials only at the anode. Polymerization mechanism involves a electrochemical generation of radicals followed by the usual addition-fragmentation scheme as described for thermally and photochemical radical generation processes.

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