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## Addition-fragmentation type reactions in photoinitiated cationic polymerization

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### Abstract

*This chapter outlines the use of addition-fragmentation reactions in cationic polymerization, and the requirements that addition fragmentation agents (AFAs) have to meet. Specially designed allyl-onium salts with various substituents on the allylic moiety are efficient coinitiators in radical promoted cationic polymerization. Depending upon the radical initiator chosen, cationic polymerizations may be initiated either thermally or photochemically. The mechanism involves the addition of free radicals formed by the radical initiator and a subsequent fragmentation of the energy-rich intermediate yielding reactive radical cations. In some cases, oxidation of*

*the primarily formed free radicals contributes to the formation of initiating species. To various extents, some of the AFAs are also able to initiate cationic polymerization upon external stimulation (heating or UV irradiation) without added radical initiators. Initiation mechanism of bifunctional AFAs possessing, in addition to the allylic structure, radical generating sites such as Michler's ketone, benzophenone or morpholino ketone are also discussed. Regarding variety in applications and various advantages, addition-fragmentation reactions appear to be of interest in photoinduced cationic polymerizations.*

## 1. Introduction

Addition- fragmentation reactions are a versatile and exceptionally interesting tool for polymer synthesis. There are two important synthetic areas where addition-fragmentation processes occur: in radical chain transfer (Addition-fragmentation agents, AFAs, are used as chain transfer agents) and in cationic photo or thermal polymerization.

*In chain transfer*; these reactions aim at gaining control over molecular weight and make it possible to synthesize end-functionalized polymers, often macromonomers, which may further be employed in block or graft copolymerization<sup>1,2</sup>.

*In cationic polymerization*; it is possible to very efficiently initiate the polymerization with the help of specially designed AFAs (Allyl-onium salts) in conjunction with conventional radical initiators. The mechanism involves the formation of radicals by heating or irradiating the radical initiator, the addition of these radicals to an AFA molecule and the fragmentation of the AFA. In order to show good performances in initiation reactions AFAs have to be equipped with functional groups or substituents which either promote radical addition or facilitate the fragmentation of reaction intermediates.

In recent years, a reversible addition-fragmentation chain transfer reaction (RAFT) is also used as a controlled polymerization method<sup>3</sup>. As this is beyond of our scope, in this chapter we will focus only on the use of addition-fragmentation reactions in photoinduced cationic polymerization.

## 2. Addition-fragmentation agents for cationic polymerization

Polymerizations which are induced by external stimulation, such as heating or photo-irradiation are of great practical interest due to their applicability for the curing of coatings and printing inks and for resist technology. Many technologically important monomers (vinyl ethers, oxiranes) are only polymerizable in a cationic mode, which was the reason for the development of cationic photo and thermal initiators<sup>4</sup>.

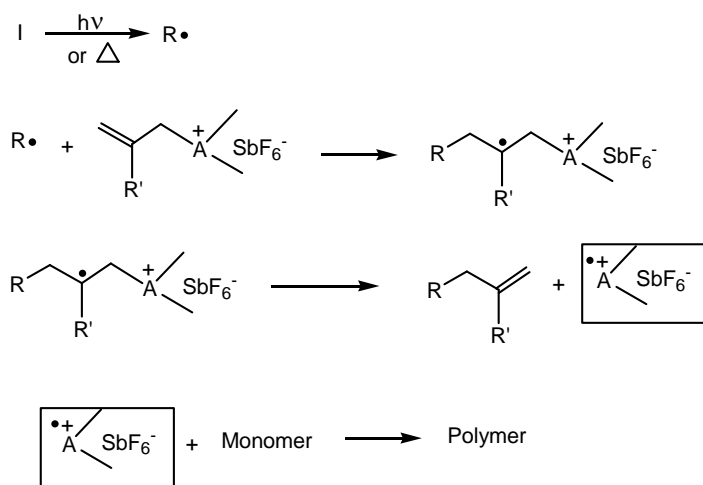
Photoinitiated polymerization is based on the photogeneration of acids and reactive cations. Diaryliodonium<sup>5</sup>, triarylsulphonium<sup>6,7</sup>, *N*-alkoxy pyridinium salts<sup>8</sup> and mixed ligand arene cyclopentadienyl metal salts<sup>9</sup> are widely used as powerful photoinitiators for cationic polymerization. The major concern for their practical uses was related to the overlap of their absorbances with the emission spectra of the commercial medium and low pressure mercury lamps. Since this requirement is not fulfilled for certain easily available cationic photoinitiators it was tried to extend their photosensitivity to higher

wavelengths, e.g.,  $\lambda > 350$  nm with the aid of appropriate compounds. Free radical photoinitiators<sup>10</sup>, photosensitizers<sup>11</sup>, or charge transfer complexes<sup>12</sup> have been successfully employed to extend their spectral response to longer wavelengths. In this case electron transfer from the excited photosensitizer or photogenerated electron donor radicals to the onium salts results in the formation of reactive species which are capable of initiating the cationic polymerization of related monomers. The details of such indirect activations have been discussed in another chapter.

Another method to overcome this problem is to develop 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.

For cationic polymerization via addition-fragmentation reactions, thermal radical initiators, like 2,2'-azobisisobutyronitrile (AIBN), benzoyl peroxide (BPO), or radical photo initiators, such as benzoin or acylphosphine oxides, are used to produce free radicals. These radicals add to the double bond of the allyl onium salt and subsequently an onium radical cation is released, which initiates the polymerization (see Scheme 1). Thus, fragmentation brings about the elimination of substituents that formerly prevented the cationic center from reacting with the monomer, 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. The substitution of the allylic double bond towards addition facilitates the addition step. Furthermore, the bond to be ruptured should be one of the weakest bonds in the molecule. It is  $S^+ - C$ ,  $N^+ - O$ , and  $N^+ - C$  bonds that are cleaved.

The obvious advantage of using AFAs for cationic polymerization is that, depending on the nature of the radical source used, an initiation can be triggered by either heat (e.g., with AIBN or benzoyl peroxide) or light (with, e.g., benzoin)<sup>13</sup>. As far as photo polymerization is concerned, it is extremely easy to tune to a desired wavelength range (the emission maximum of the irradiation source used) by choosing appropriate radical



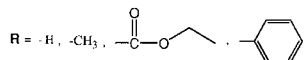
**Scheme 1.** Initiation of Cationic Polymerization by Addition-Fragmentation Reactions.

initiators. Notably, the development of radical polymerization leads to numerous radical initiators with excellent radical yields and good storage stability. Moreover, this type of initiation does not depend on the electronic structure of the radicals produced providing that any radicals capable of adding double bonds may be employed. This possibility is not offered by any other existing salts, including iodonium salts which initiate cationic polymerization via redox reactions with radicals (See Chapter 3). Allylic salts with various substituents in the allylic moiety were shown to be very efficient AFAs for the initiation of a cationic polymerization<sup>14</sup>.

The most common used AFAs in cationic polymerization and their activation mode are summarized in Table 1.

**Table 1.** AFAs for cationic polymerization and their activation mode

Type of AFA	A <sup>+</sup> (Heteroatom) <sup>a</sup>	Ionic Species <sup>a</sup>	Type of Activation			
			Direct		Indirect <sup>b</sup>	
			Thermal	Photo	Thermal	Photo
<i>N</i> -Allyloxy pyridinium			+	+	+	+
<i>N</i> -Allyl pyridinium			+	+	+	+
Allyl sulphonium			+	-	+	+
Allyl phosphonium			+	-	+	+
Dienic			nd	nd	+	+
Allyl Ammonium			+	+	+	+



<sup>a</sup>Counter ion is omitted. <sup>b</sup>In the presence of radical initiators.

As N<sup>+</sup>-O and S<sup>+</sup>-C bonds are relatively weak, the reactivity of allyloxy pyridinium derivatives and tetrahydrothiophenium based are higher when compared to the allyl pyridinium salts. Although the addition reactions are very much affected by the substituents at the allylic double bond, in the case of allyloxypyridinium derivatives, there is no remarkable influence of the substituent. It is clear that the addition is not rate determining. Most probably, the fragmentation is rate determining. The initiation by the reaction of pyridinium radical cations to the monomer is a relatively fast process, therefore the search for more efficient AFAs should be directed towards the introduction of more labile bonds in proximity to the allylic group. So, energetically favorable living groups are formed by fragmentation.

## 2.1. Type of activation

### 2.1.1. Direct activation

In the case of a direct activation, a specially designed allyl onium salt, itself, can undergo a decomposition to form radical cations and radicals. Therefore, the addition-fragmentation agent should have a relatively weak bond like N<sup>+</sup>-O, which can be ruptured directly by thermal or photolytic methods. So, allyloxy pyridinium salts may also be used as direct photoinitiators. When being exposed to UV light (absorption reaches up to  $\lambda \leq 290$  nm) allyloxy pyridinium salts initiate cationic polymerizations with better rates that compare favorably with ethoxy pyridinium. From this high reactivity, the conclusion is drawn that, also in the direct photolysis, addition-fragmentation reactions take place. Formed primarily after the photolytic N-O bond rupture, the allyloxy radicals add to intact salts species thus triggering the formation of initiating pyridinium radical cations. Thus, apart from the primarily formed pyridinium radical cation (N-O bond dissociation), another portion of initiating species is formed by addition-fragmentation. This interesting addition fragmentation is outlined in Scheme 2. There is no significant influence of the substituent on the initiation efficiency supporting the assumption (stated earlier) that fragmentation rather than addition is rate determining. The photolytical N-O bond rupture is probably not much affected by the substituent at the allylic bond.

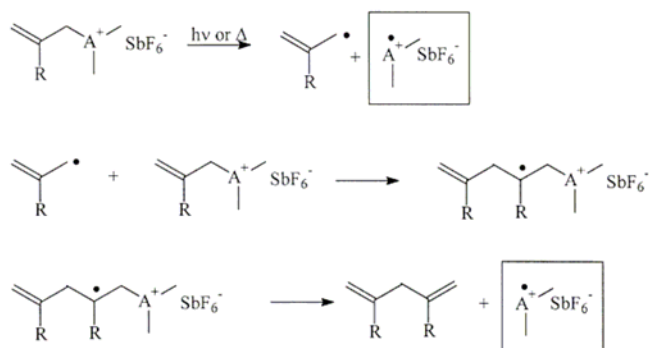
The order of the activity depends on the bond dissociation energies of the bonds next to the allylic moiety. The strength of related bonds are in the order of N-O (200 kcal/mol) < C-S (260 kcal/mol) < C-P (265 kcal/mol) < C-N (290 kcal/mol). Although the order is like that the other parameters, such as reactivity of the radical cations with monomers also influence the initiation efficiency<sup>15</sup>. The factors affecting the polymerization efficiency were theoretically discussed using semi-empirical quantum mechanical techniques<sup>16</sup>.

In the absence of the additional radical sources, radicals can also be formed by thermal decomposition of the salt. However, it is difficult to decide which radicals are formed and how differences in initiation between the various allyloxy salts can be explained. An alternative explanation would be that upon heating, the double bonds of the allyloxy initiators open which would give rise to the formation of biradicals. These species might also be active when adding to allylic double bonds.

### 2.1.2. Indirect activation

#### 2.1.2.1. Via addition-fragmentation reactions in the presence of radical sources

The principle of this class of reactions consists in the reaction of a thermally or photolytically formed radical with an allyl-onium salt generating a radical onium



**Scheme 2.** Addition-Fragmentation Mechanism for Direct Initiation.

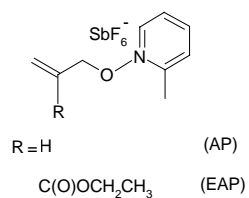
intermediate. These reactive species undergo a fragmentation giving rise to the formation of initiating cations (see Scheme1). The advantage of using this method is that, upon choosing appropriate radical initiators, one can easily tune polymerization conditions to a desired wavelength or temperature range for cationic photo- and thermal polymerization, respectively. AIBN, BPO, phenylazotriphenylmethane (PAT), etc. are some of the radical sources that can be used as radical initiators. They are listed in Table 2. Although all radical sources chosen, initiate the polymerization, there may be significant differences in polymerization rate, due to the differences in the decomposition rate constants and the reactivity of the radicals toward the allylic double bond of the AFAs.

#### 2.1.2.2. Via oxidation of radicals

Interestingly, with some AFA/radical initiator pairs apart from addition-fragmentation there are also oxidation reactions that account for the initiation. In contrast to BPO and AIBN, benzoin and PAT, have a significantly higher initiation activity. These compounds decompose upon photolysis and thermolysis yielding nucleophilic hydroxybenzyl and triphenylmethyl radicals, respectively. Whilst the other radicals (benzoyl and phenyl radicals) are expected to participate in the addition-fragmentation type initiation, nucleophilic radicals are oxidized by the salt giving rise to the respective cations which may react with a monomer and thus initiate the chain growth. The effectiveness of such electron transfer reactions is related to the redox potentials of both radicals and salts used in the system.

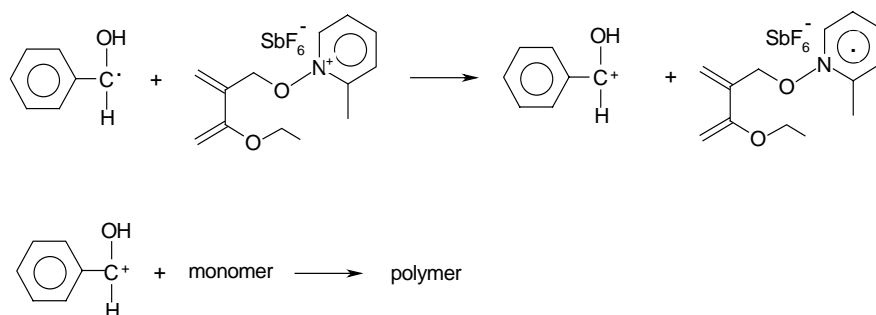
The oxidation step also depends on the type and the substituents of the AFAs. Especially allyloxy pyridinium salts are efficient co-initiators for cationic polymerization inconjunction with suitable radical initiators. The mechanism follows either the addition-fragmentation-polymerization route, or involves the oxidation of free radicals, depending on the free radical source used and the salt. *N*-[2-(ethoxycabonyl)allyloxy]- $\alpha$ -picolinium hexafluoroantimonate (EAP), and *N*-[2-allyloxy]- $\alpha$ -picolinium hexafluoroantimonate (AP) of the following structures, are the two representatives with the highest susceptibility to oxidation reactions. EAP is the most suitable for oxidizing free radicals. In other words, the mechanism shown in Scheme 3, involving the oxidation of

hydroxyphenyl radicals stemming from benzoin by EAP probably accounts for the fastest initiation<sup>17</sup>.



**Table 2.** Radical Sources Used in Addition-Fragmentation Type Initiation.

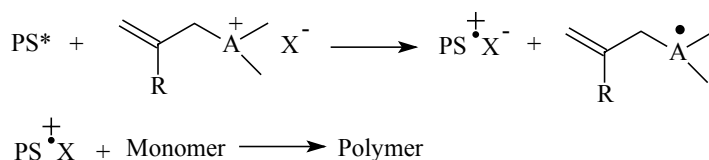
Radical Source	Structure	Radicals participating in Electron Transfer	Radicals participating in Addition-Fragmentation
4,4'-Azobisisobutyronitrile (AIBN)		--	
Dibenzoylperoxide (BPO)		--	
Phenylazotriphenylmethane (PAT)			
Benzoin (B)			



**Scheme 3.** Oxidation of Hydroxybenzyl Radicals from Benzoin by EAP.

### 2.1.3. Via photosensitization

Photosensitization is a very attractive way to initiate cationic polymerization since the triggering of the initiation may be extended to much longer wavelengths where the photoinitiator is transparent and the photosensitizers such as heterocyclic and polynuclear aromatic compounds absorb the incident light. Photosensitization of onium salts and their mechanistic considerations have been discussed in another chapter. Cationic photopolymerization via allyl onium salts in the presence of additional photosensitizers such as anthracene, perylene, benzophenone or phenothiazine were also reported<sup>18</sup>. In principle, the photosensitization mechanism for allylic salts is very much similar to that proposed for onium salts. Thus, the electron transfer between photoexcited sensitizer and ground state allylic salt induces the decomposition of the salt yielding a photosensitizer radical cation. These radical cations initiate the polymerization via various pathways as indicated elsewhere.

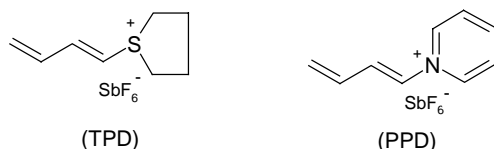


The redox potential of the allylic salt is very important for the photosensitization process and it appears that only alkoxy pyridinium type allylic salts were found suitable for this kind of activation. Photosensitization has also some restrictions due to the mobility of the sensitizer molecules in the system<sup>19</sup>. As the viscosity of the system increases, the diffusion of the photosensitizer towards the initiator molecules becomes difficult and the efficiency of the electron transfer from the photosensitizer to the initiator molecule decreases. To overcome these restrictions new allyl onium salts which also include photoactive group in the same molecule were synthesized (*vide infra*)<sup>20,21</sup>.

## 3. Other types of addition-fragmentation agents

### 3.1. Diene type

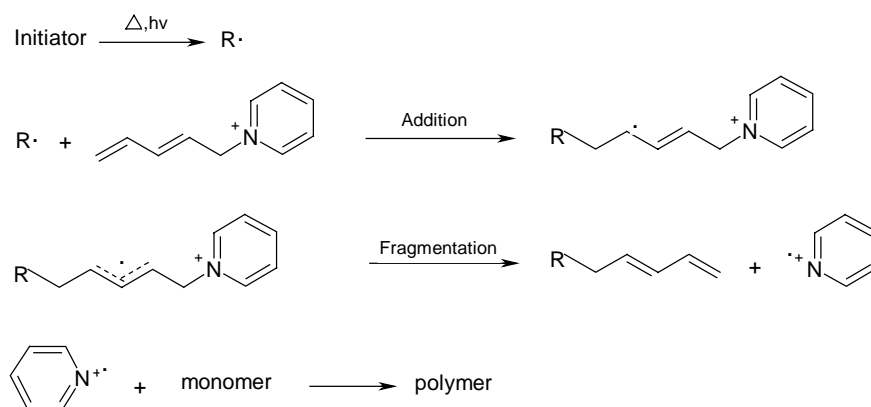
Diene type AFAs were also found to exhibit chain transfer properties and to be used for diene functional macromonomers<sup>22, 23</sup>. Some diene type AFAs that initiate systems for the cationic polymerization thermally and photochemically in conjunction with radical sources were also described. AIBN, BPO, PAT, and benzoin can be used as radical initiators.



Initiating species are produced by a radical addition-fragmentation mechanism in a manner similar to that described for dienic free radical AFAs<sup>22, 23</sup>. Together with the



addition-fragmentation products, pyridinium (or thiophenium) radical cations are formed. These species are potentially able to initiate cationic polymerization. The formation of these radical cations via addition-fragmentation mechanism is illustrated in Scheme 4. Depending on the nature of the free radicals, both addition-fragmentation and electron transfer mechanisms may be operative<sup>24</sup>.



**Scheme 4.** Addition-Fragmentation Type Initiation for Dienic Salts.

### 3.2. Bifunctional AFAs

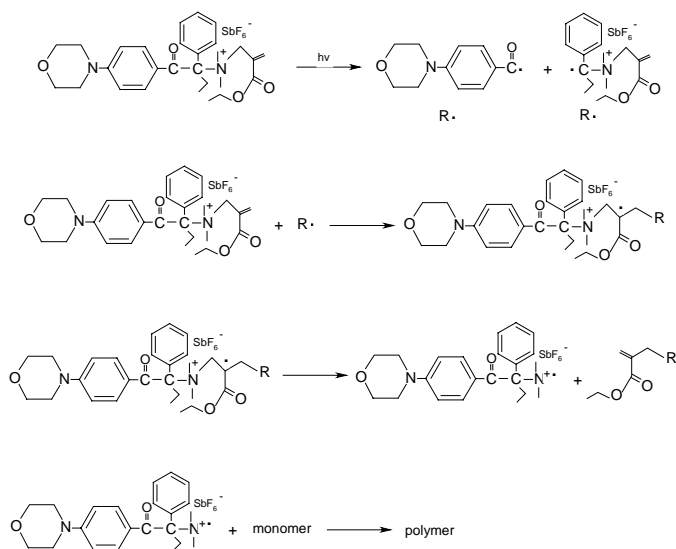
These types of initiators include an intrinsic chromophoric group for radical generation and an allylic salt structure for the addition fragmentation in the same structure<sup>25, 26, 27</sup>. The advantage of the system is to generate free radicals without additional radical sources by irradiating the initiator itself. Bifunctional AFAs can be classified in two classes according to their type of radical generation:

1. Intramolecular Bond Cleavage (Morpholino derivatives)
2. Intermolecular Hydrogen Abstraction (Benzophenone and Michler's Ketone derivatives)

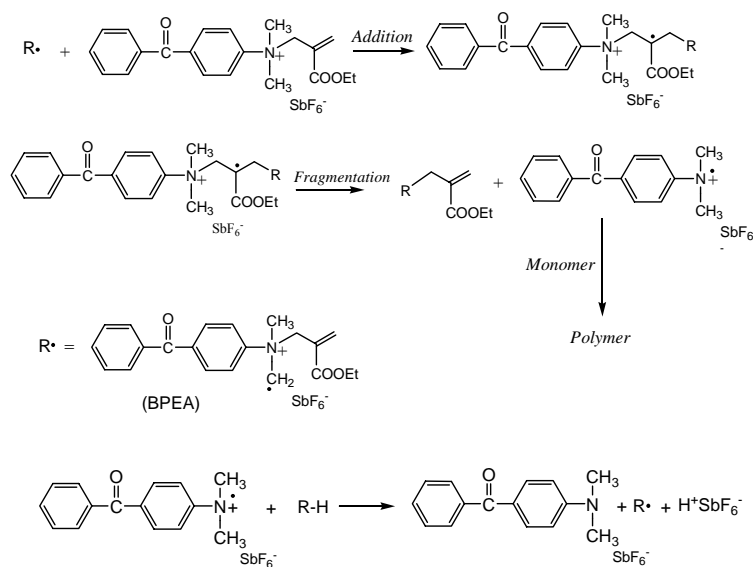
Morpholino ketone ethyl acrylate salt, BDMEA, is a good example for intramolecular type of AFA. Upon absorption of light it undergoes  $\alpha$ -cleavage analogous to the precursor morpholino photoinitiator and forms radicals which may be then added to another molecule (Scheme 5)<sup>25</sup>

Upon irradiation of the benzophenone-allyl salt, BPEA, benzophenone moiety produces radical species by hydrogen abstraction from ground state BPEA in a mechanism similar to that of benzophenone. These radicals add to the allylic double bond and an ammonium radical cation is released and initiates the polymerization<sup>27</sup>.

Radical cations may abstract a H atom from the medium (solvent, monomer or ground state allylic salt) and this intermediate dissociates to give a strong acid. Besides the direct initiation by radical cations, a Brønsted acid can also initiate the polymerization (Scheme 6).

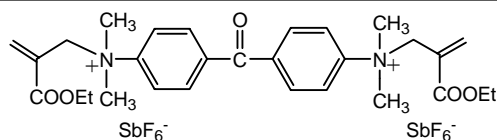


**Scheme 5.** Initiation of Cationic Polymerization by Morpholino allyl salt (BDMEA).



**Scheme 6.** The Initiation Mechanism when using the Benzophenone-allyl Salt (BPEA).

Structurally similar Michler's ketone ethyl acrylate salt, MKEA, also generates radicals by H abstraction, and the initiation mechanism is similar to BPEA<sup>26</sup>.



(MKEA)

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