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Structure and Reactivity of Addition Fragmentation Agents in Photochemically and Thermally Induced Cationic Polymerization

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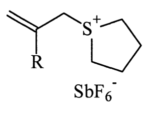
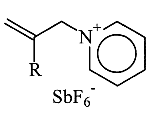
SUMMARY: Specially designed allylic onium salts with different hetero-atoms and various substituent patterns at the allylic double bond have been shown to be very efficient initiators for cationic polymerization. They can be used alone or in conjunction with radical initiators. The mechanism of initiation involves radical formation, radical addition and fragmentation. In some cases, oxidation reactions were found to contribute to the formation of initiating species. In this work, the role of structural parameters onto reactivity is discussed.

Introduction

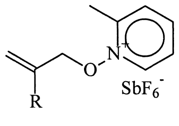
Photo-initiated cationic polymerization is a very interesting method to cure formulations containing epoxy monomers. Bi-functional epoxy monomers can be converted to insoluble networks by acids and cationic species formed upon photolysis of onium salts such as iodonium and sulphonium salts [1]. In order to increase the utility of photo-initiated cationic polymerization in practical applications such as pigmented coatings several indirect acting systems were proposed and extensively studied. In such systems, radical photo-initiators, photo-sensitizers and electron donating compounds in conjunction with onium salts activated selectively at desired wavelengths required for the particular applications [2]. We have recently developed an alternative initiating system based on specially designed allylic salts of the following structure.



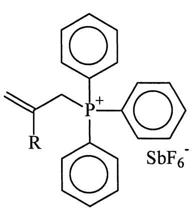
R = COOEt
Allyl-thiophenium salts, AT [3,4]



R = COOEt
Allyl-pyridinium salts, AP [5]



R = H, CH_3, Ph, COOEt
Allyl-oxypyridinium salts, AOP [6,7]



R = H, CH_3, COOEt
Allyl-triphenyl phosphyl salts, APP [8]

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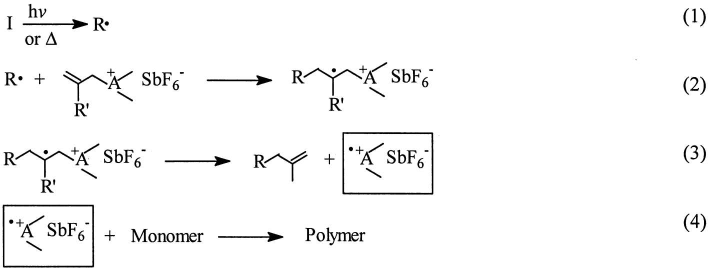
The presented salts in conjunction with conventional radical initiators were shown to very efficiently initiate cationic polymerizations [9-12]. Depending upon the type of radical initiator selected, initiation could be triggered by either light or heat. For photo-polymerization due to the large variety of radical initiators chosen, one can easily adjust the system to any desired wavelength. Furthermore, this system is not limited to oxidizable radicals. In fact, there is virtually no additional requirement to the radical initiator rather than produce radicals with a high yield. In this study it will be shown that the very initiation mechanism might slightly change with the type of radical initiator, and different efficiencies are found for various substitution patterns or hetero-atoms at the onium moiety.

The Mechanism of Addition-Fragmentation Type of Initiation

The main idea about addition-fragmentation initiation of cationic polymerization is that primarily radicals are formed. Many types of radical initiators, such as the thermally excitable AIBN and benzoyl peroxide or the photo-active benzoin have been tested useful in this respect. Radicals formed during the exposure of heat or light add to the allylic double bond of the allyl onium addition-fragmentation agent (AFA). The highly reactive intermediate produced thereby deactivates by releasing an onium radical cation, which in its turn reacts with monomer starting the cationic chain growth. In other words, fragmentation brings about the elimination of substituents that formerly prevented the cationic centre from reacting with the monomer, the onium agent becomes activated.

This type of initiation has been used for a couple of model monomers: cyclohexene oxide (CHO), butylvinyl ether, p-methoxystyrene, N-vinylcarbazol and the bi-functional, network forming (3,4-epoxycyclohexylmethyl)-3',4'-cyclohexane carboxylate. The mostly applied model monomer CHO combines the advantages that it is polymerized in an exclusively cationic mode, does not polymerize with any of the AFAs in the dark and does not produce oxidizable radicals in the course of initiation. Cationically polymerizable monomers, such as vinyl ethers and tetrahydrofuran were found to produce easily oxidizable free radicals, which may interact with radicals stemming from external radical sources.



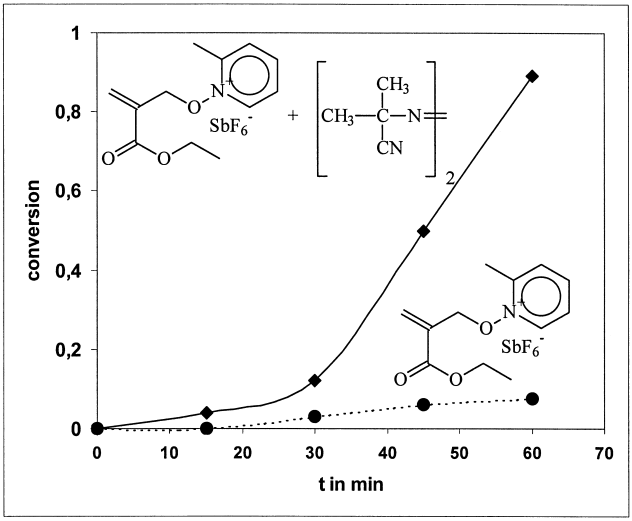


Fig. 1. Thermal polymerization of CHO using and an AOP type AFA (c = 5 x 10^{-3} mol l^{-1}) and azobisiso butyronitrile (AIBN, c = 5 x 10^{-3} mol l^{-1}) at 70°C. Conversion = $(M_0\text{-}M)/M_0$

Proof for the addition fragmentation mechanism was derived from the following three observations:

- **In the presence of radical initiators far higher initiation rates are monitored.** In Fig. 1, this is demonstrated on the example of an allyl-pyridinium salt and benzoin as radical initiator. An identical behaviour is found for all AFAs investigated, and with both thermally or photosensitized radical initiators alike.

- **Respective onium salt homologues, non-equipped with the allyl group do show far lower efficiencies in polymerization.** If there was no contribution of the allylic moity but only a thermal or photo-chemically initiated rupture of the respective onium salt – alkyl / alkoxy bonds to the release of reactive onium radical-cations, initiation should occur to a similar extent.

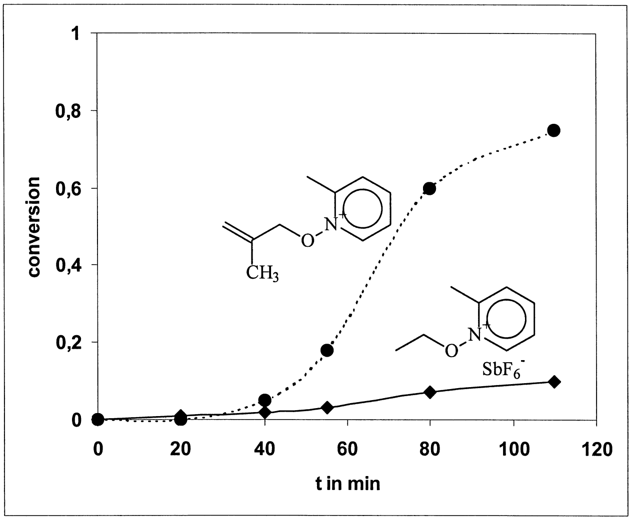
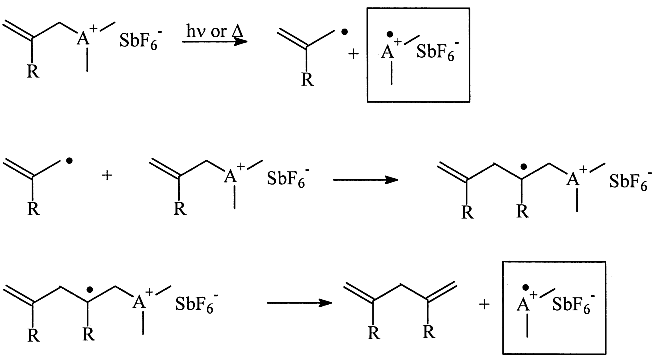


Fig. 2. Photo-polymerization of CHO, λ_{inc} = 280 nm, 20°C, OD_{280nm} = 0.95. c (AFA) = 1 x 10^{-3} mol l^{-1}, c (EMP) = 1.3 x 10^{-3} mol l^{-1}

In fact, the initiation mechanism demonstrated in Fig. 2 is somewhat more complex than displayed in equations (1-4). The onium salt itself can also undergo thermal or photochemical decomposition, a process by which radicals and initiating radical cations are formed. The radicals are supposed to react with intact AFA molecules, thus generating an additional initiating cation.



- **Low molecular weight products consisting of radical initiator fragments and of particles derived from the allylic moiety** were analytically detected. In Fig. 3, compounds that have been clearly detected in one example are given. An insight into the mechanism of fragment formation is given in equations (8-13). As equation (13) demonstrates, there are also some side reactions, which not directly lead to the formation of initiating cations. However, as for (13), also the formation of radicals can be a starting point for a new initiation event: radicals may add to intact AFAs thus repeating the addition-fragmentation cycle.

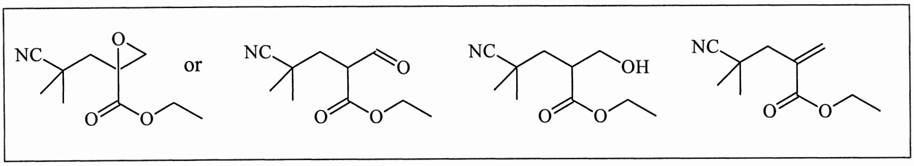
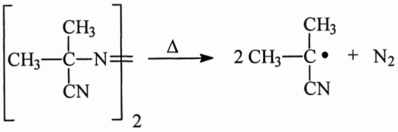
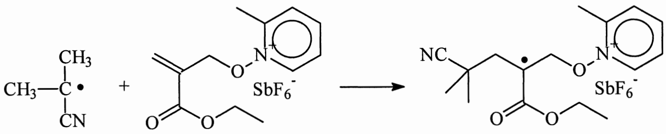


Fig. 3. Compounds clearly detected in gas chromatogram of methanol-soluble products formed during the bulk polymerizaton of CHO initiated by ethoxycarbonyl AOP



$$\left[CH_3-\overset{CH_3}{\underset{CN}{C}}-N=\right]_2 \xrightarrow{\Delta} 2\,CH_3-\overset{CH_3}{\underset{CN}{C}}\bullet + N_2$$

(8)



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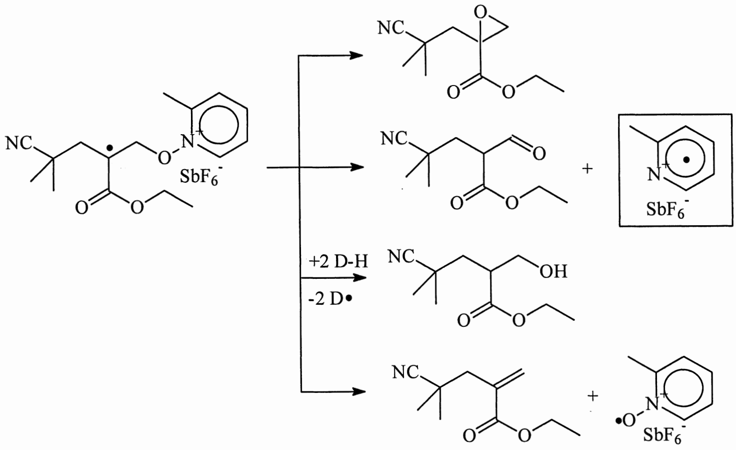


(10)

(11)

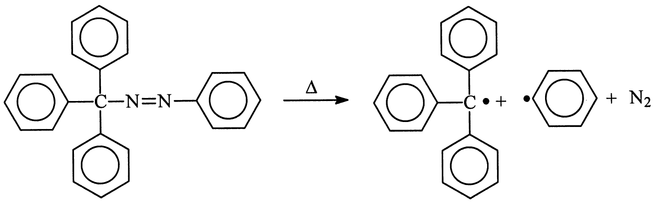
(12)

(13)

Notably, not in all cases fragmentation products could be detected as clearly and plausible as depicted in Fig. 3. It is suggested that the epoxy-structures shown in (10), or respective allylic compounds formed in similar reactions with other AFAs are to a large extent incorporated into the polymerization chain and are thus not susceptible to the analysis method used.

Apart from addition-fragmentation, there is another initiation mechanism which accounts for the formation of initiating cationic species: easily oxidizable radicals, such as the triphenylmethyl radical derived from phenylazo triphentylmethane (PAT), may be oxidized by the AFA forming a cationic centre on the initially radical initiator molecule. In this oxidation type initiation scheme polymerization rates are generally high as compared with the addition-fragmentation scheme. Furthermore, in the case of PAT, an UV-absorption ascribed to the triphenylmethyl carbocation could be detected in monomer-free test solutions.

However, reaction (14) does not occur with all AFAs. Naturally, only AFAs with a suitable reduction potential can oxidize the primarily formed radicals. These phenomena will be discussed in the next chapter.



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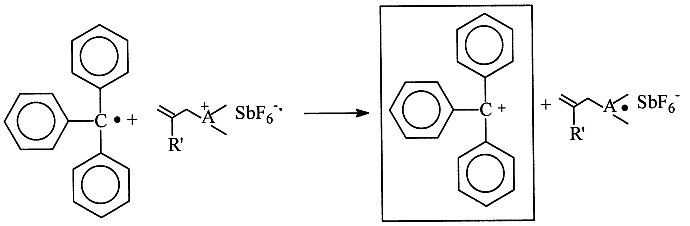


(16)

The Effect of Hetero Atom

In the addition fragmentation scheme the reaction leading to the very realease of initiating species is a bond-rupture between allylic and onium moity. Naturally, there has to be an effect of the type of hetero-atom of the onium cation. Bond dissociation energies rise in the order N-O (8.24 x 10^5 J mol^{-1}) < C-S (1.07 x 10^6 J mol^{-1}) < C-P (1.09 x 10^6 J mol^{-1}) < C-N (1.19 x 10^6 J mol^{-1}). As seen in Fig. 4 however, there is some different order if various AFAs are used for a direct, thermal polymerization. In this case, the initiation efficiency drops in the order of AT>AP≈AOP>> APP.

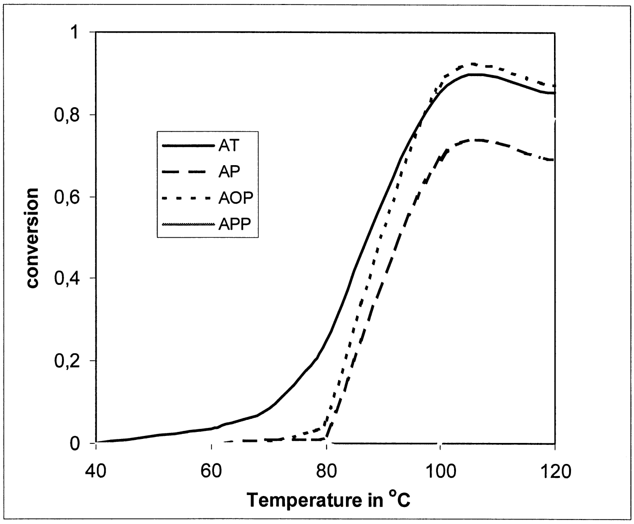


Fig. 4. Thermal bulk- polymerization of CHO initiated by various AFAs (all ethoxycarbonyl AFA). c(AFA) = 5 x 10^{-3} mol l^{-1} . Polymerization for 1 h

It was explained earlier already that in the polymerization using AFAs without any added radical source, there is two separate cycles of bond rupture between hetero-atom and allylic moity giving rise to two initiating onium cations (see equations (5) and (7)). The influence of bond-dissociation energy should be very strong in this case. However, the reactivity of the onium cations towards the monomer is most probably very different for different types of onium cations. From point of view of steric hindrance the triphenylphosphyl cation is expected to have a relatively limited reacting efficiency with monomer. The phosphorus centred cationic centre is in this case almost entirely shielded by the large phenyl groups. The other AFAs, and especially the least bulky allyl-thiophenium cation should be much less limited in this respect.

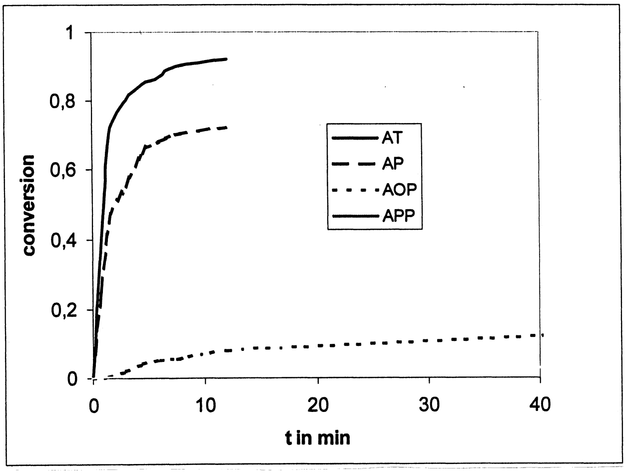


Fig. 5. Photoinitiated bulk polymerization of CHO with AFAs (all ethoxycarbonyl AFA) in the presence of 2,4,6-trimethylbenzotyl diphenylphopshonyloxide (DPO). c(DPO) = 1.7x 10^{-3} mol l^{-1}, c(AFA) = 5 x 10^{-3} mol l^{-1}. λ_{inc} = 380 nm. OD_{380nm} (DPO) = 0.95, $OD_{380\,nm}$ (AFA) = 0

If polymerization is carried out with additional radical sources (see Fig. 5), a dependency resembling the one depicted in Fig. 4 is found. In this case the initiating efficiency falls in the order of AT > AOP >> AP > APP. The large difference in efficiency between AOP and AP in this case shows clearly an effect of bond-dissociation energy. Notably, there can be no difference in steric behaviour between the initiating cations formed with AOP and AP, since it is the same species. To summarise this, besides bond dissociation energy it is especially also the reactivity of the initiating cations towards monomer that determine the overall initiation rate. It is believed that this reactivity is to a large extent to do with steric factors.

As had been mentioned earlier (see reactions (14) and (15)), with oxidizable radicals, there are in some cases electron transfer reactions which also account for initiation acts. However, not with all types of AFA this mechanism was observed.

Table 1. Electron transfer reaction with ethoxycarbonyl AFAs followed by UV absorption bands at 420 nm upon reaction with PAT, c (PAT) = c (AFA) = 5 x 10^{-3} mol l^{-1} . Absorption band bands at 420 nm are ascribed to triphenylmethyl carbocation.

AFA	Electron Transfer
AT	Yes
AP	No
AOP	Yes
APP	No

Obviously, only onium salts with a suitable redox potential are able to initiate an electron transfer according to equation (14). In the absence of electron transfer reaction, as for AP and APP, initiation is likely to follow a pure addition-fragmentation path.

The Effect of Allylic Moiety

When differently substituted allyloxy-pyridinium salts were, together with cationically polymerizable monomer subjected to UV-irradiation, only very little difference in initiation efficiency was found (see Fig. 6). The mechanism is in this case explained in terms of direct photolysis of the N-O bond, giving radicals which according to reactions (5) to (7) give rise to a surplus of initiating pyridinium radical cations. In photo-sensitization, where the very energy-absorbing site is the pyridinum ring, bond ruptures (5) occur most probably only at the adjacent N-O position, and are also not influenced by the relatively far substituent at the allylic moity.

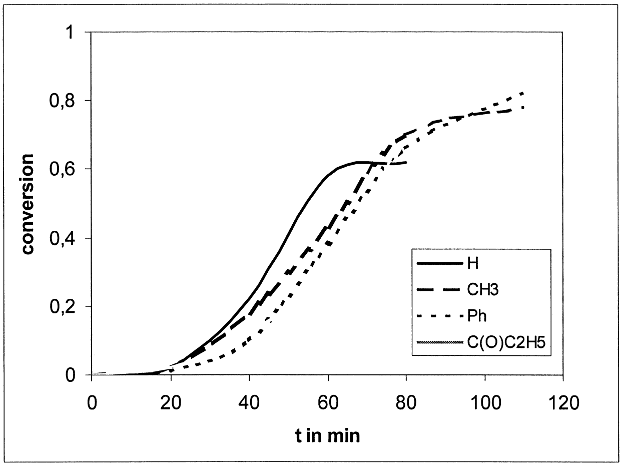
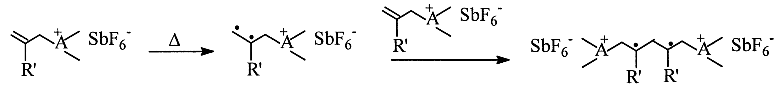


Fig. 6. Photo-polymerization of CHO with various AOP type AFAs: λinc = 280 nm, 20°C; OD_{280nm} = 0.95. c(AOP-H) = 5.6 x 10^{-4} mol l^{-1}; c(AOP-CH_3) = 1 x 10^{-3} mol l^{-1}; c(AOP-Ph) = 3.4 x 10^{-4} mol l^{-1}; c(AOP-C(O)C_2H_5) = 1.3 x 10^{-3} mol l^{-1})

On the other hand, for thermal polymerization with various allyloxy-pyridinium salt quite a strong influence of the substitution pattern was monitored (Fig. 7). In contrast to photolysis, in thermal sensitization all bonds of the molecule absorb energy to the same extent and the probability of bond-ruptures does in this case depend on the bond-dissociation energy of all bonds involved. However, on the example of the allyloxy-pyridinium salts it is difficult to decide which radicals are actually formed and how therefore the differences in initiation behaviour can be explained. Respective GC-MS investigations gave also no conclusive results. An alternative explanation could be in this case that upon heating the double bonds of the allyloxy initiators open, as is known for a variety of monomers, which would give rise to the formation of bi-radicals. These species might also be active in adding to allylic double bonds. As illustrated in equations (16) and (17), in the course of such a modified addition-fragmentation cycle there would again be two initiating species formed per one initial bond rupture.



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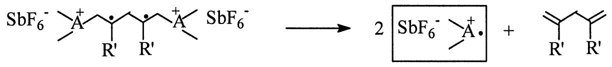

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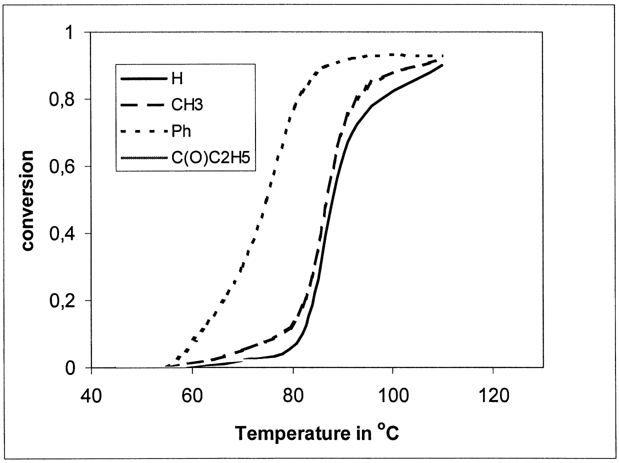


Fig. 7. Thermal polymerization of CHO with various AOP type AFAs: c(AOP) = 5×10^{-3} mol l^{-1}.

The investigation of the influence of different substitutes in conjunction with radical initiators gave some interesting, additional insight into the reaction mechanism. In Fig. 8, an example of CHO polymerization by AOPs with different allylic substituents in the presence of benzoyl peroxide (BPO) is given.

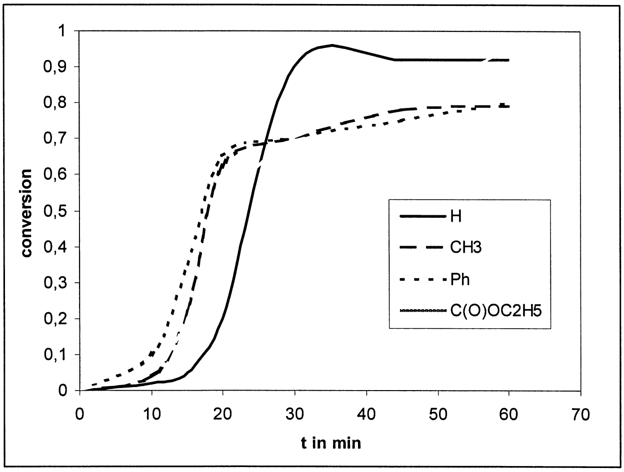


Fig. 8. Thermal polymerization at 70°C of CHO with AOP type AFAs and BPO as radical source. C (AFA) = c(BPO) = 5 x 10^{-3} mol l^{-1}

Interestingly, there is virtually no difference in initiation efficiency in this case. It is a well-known fact that rate constants for the addition of radicals to olefinic double bonds depend strongly on the substitution pattern. For example, for the addition of cyclohexyl radicals to substituted olefines (CH_2=CH-R), relative rate constants of 1, 84 and 3.000 were determined for n-butyl, phenyl and carboxymethyl, respectively [13]. If the addition reaction (2) was the rate-determining step, initiation efficiencies would vary dramatically for the four different AFAs depicted. This investigation showed, that in the cycle of addition-fragmentation, it is the fragmentation step that is rate-determining. Naturally, if the entire initiation scheme is looked upon, there are other factors which also might be rate-determining, such as the reaction with monomer (especially for phosphonium salts), or also the rate of electron transfer, in the cases were the mechanism involves this type of reaction. An example for the latter is illustrated in Fig. 9.

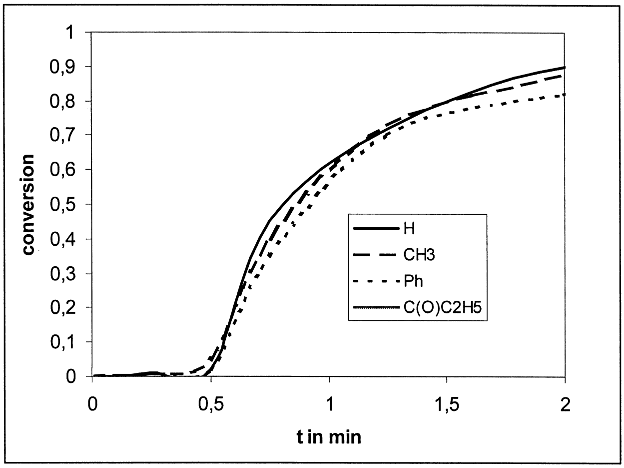
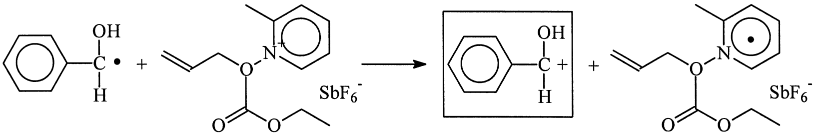


Fig. 9. Photo-polymerizaton of CHO with AOP in presence of benzoin. λ_{inc}=367 nm, OD_{367nm} = 0.10, c(AFA) = 5 x 10^{-3} mol l^{-1}, c(benzoin) = 2.4 x 10^{-2} mol l^{-1}

As shown in Fig. 9, upon polymerization of CHO with benzoin and various AOPs, the ethoxycarbonyl derivative show a much higher initiation rate than the other AOP derivatives. In investigations with PAT, radicals of which are susceptible to electron donation, it had been shown that in fact the ethoxycarbonyl is the most favourable to undergo electron transfer reactions according to (15). In other words, it is assumed that also for hydroxyphenyl radicals stemming from benzoin there might be electron transfer reactions with suitable AFAs (18). Whether or not the AFA is prone to electron transfer with radicals present does therefore not only depend on the hetero-atom, but also on the substituents at the allylic bond.



(18)

Conclusions

It has been shown that the initiation efficiency of various AFAs depends on the following factors:

- Reactivity of the onium cation towards the monomer. Possibly for sterical reasons, the reactivity of pyridinium and especially of thiophenium is higher than the one of the bulky phosphonyl radical.
- Ease of bond rupture between the onium and allylic moieties. The differences brought about by different bond dissociation energies are however small as compared with the possible steric influence on reactivity. Therefore, although fragmentation was shown to be rate-determining in the addition-fragmentation cycle, the overall initiation efficiency is dominated by the very reactivity of the onium cation towards monomer molecules
- Electron transfer reactions from radicals to the onium cations play a role especially for AT and AOP, not for AP and APP agents. For AOP it was shown that especially the ethoxycarbonyl, and to lower extent the unsubstituted derivative are prone to electron transfer processes. Notably, only for relatively nucleophilic radicals initiation involves electron transfer. For all other radicals, an predominantly addition-fragmentation path of initiation is assumed.

Acknowledgments

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