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ADDITION - FRAGMENTATION TYPE INITIATORS FOR CATIONIC POLYMERIZATION

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Abstract: Addition - fragmentation reactions are a versatile and exceptionally interesting tool in preparative polymer chemistry. With the aid of specially designed allyl-onium salts (addition - fragmentation agent, AFA) in conjunction with conventional radical initiators it is possible to very efficiently initiate cationic polymerizations. The mechanism involves (a) the formation of radicals by heating or irradiating the radical initiator, (b) the addition of these radicals to an AFA molecule and (c) the fragmentation of the AFA. In step (c) radical cations are produced, which with high rates initiate the polymerization of cationically polymerizable monomers (e.g., cyclohexene oxide, CHO). In order to show good performance 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.

INTRODUCTION

Polymerizations which are induced by external stimulation, such as heating or photo-irradiation are of great practical interest due to their utilization for curing of coatings and printing inks and for resist technology [1]. Many technologically important monomers (vinyl ethers, oxiranes) are only polymerizable in a cationic mode, what was the reason for the development of cationic photo- and thermal initiators. Among these, specially designed allyl-onium salts which initiate via the radical addition - fragmentation scheme are a promising novelty [2]. Onium salts (pyridinium, sulfonium, thiophenium salts, etc.) contain

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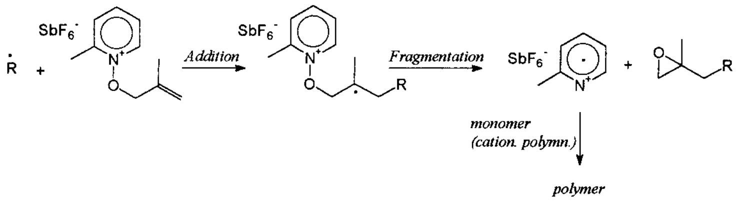
organic cations which by themselves (without external stimulation like, e.g., heat or light) because of steric reasons only scarcely initiate cationic polymerizations [3]. In order to make the presented allyl-onium salts able to initiate cationic polymerizations, they have to be reacted with free radicals. In other words, although the polymerization is eventually of a cationic mode, free radicals have to be produced in the first instance. Cationic polymerizations were succeeded using thermal radical initiators, like 2,2'-azobisisobutyronitrile (**AIBN**), benzoyl peroxide (**BPO**), or radical photo-initiators, such as benzoin or acylphosphine oxides, as free radical source. The radicals generated by either heat or light add to the double bond of the allyl onium salt and subsequently an onium radical cation is released, which initiates the polymerization. In reactions (1) and (2), this mechanism is illustrated on the example of a methyl-allyl pyridinium salt [4].

$$\text{Radical Source} \xrightarrow{\Delta \text{ or } h\nu} \overset{\bullet}{\text{R}} \qquad (1)$$



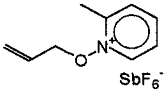
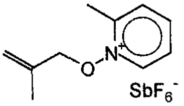
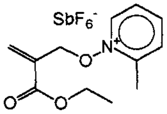
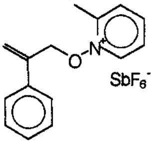
(2)

Fragmentation brings about the elimination of substituents that formerly prevented the cationic center from reacting with 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. Naturally, the bond to be ruptured should be one of the weakest bonds in the molecule.

The obvious advantage of using AFAs for cationic polymerization is that, depending on the nature of the radical source used, initiation can be triggered by either heat (e.g., with **AIBN** or **BPO**) or light (with, e.g., benzoin). Moreover, as far as photo-polymerization is concerned, it is extremely easy to tune to a desired wavelengths' range (the emission maximum of the irradiation source used) by choosing appropriate radical initiators. Notably, the development of radical polymerization lead to numerous radical initiators with excellent radical yields and good storage stability.

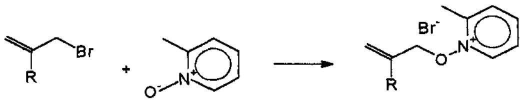
ALLYLOXY-PYRIDINIUM BASED AFAs

Allyloxy-Pyridinium salts with various substituents at the allylic moiety were shown to be very efficient coinitiators in radical promoted cationic polymerization of monomers such as cyclohexene oxide (CHO) [5] (see Tab. 1).

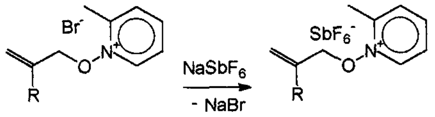
	**AFA 1** [5]		**AFA 2** [4, 5]
	**AFA 3** [5, 6]		**AFA 4** [5, 7]

Tab. 1. Allyloxy-Pyridinium based AFAs for Cationic Polymerization

Their synthesis involves the reaction of the respective bromoallylic compound with picolinium N - oxide (3). In this reaction the target cation is directly obtained. The counter anion, bromide, however is too nucleophilic. It would make a cationic polymerization rather difficult since bromide easily recombines with the growing cationic chain ends thus terminating polymerizations at a very early stage. Therefore, bromide has to be exchanged for an anion with a lower nucleophilicity, such as hexafluoroantimonate, SbF_6^-. The anion exchange can often be carried out in aqueous solution by directly adding $NaSbF_6$ (for **AFAs 1, 2 and 4**). In the case of **AFA 3**, where a direct anion exchange gives very low yields, the exchange was achieved via a nitrate intermediate.

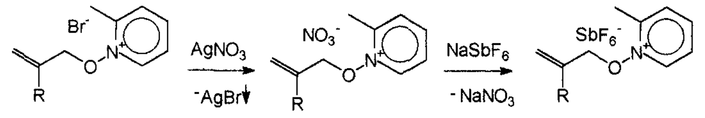


(3)



(4)

for R = H, CH_3, Ph



(5)

for R = $C(O)OCH_2CH_3$

In the presence and by activation of free radicals sources, allyloxy-pyridinium based AFAs are able to initiate cationic polymerization. In Fig. 1, time conversion curves for the polymerization of CHO at 70°C are presented. For this experiment, **BPO** was used as radical donor.

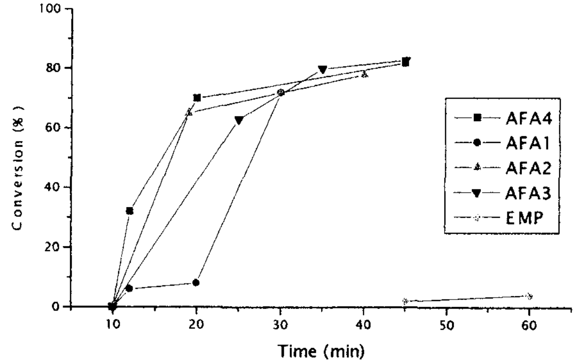
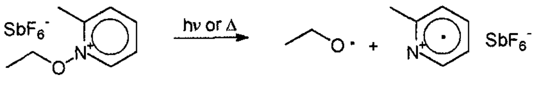


Fig. 1. Thermal Polymerization of CHO with BPO as radical source. [Pyrid. Salt] =[BPO]=$5x10^{-3}$ mol l^{-1}, at 70 °C

Interestingly, all investigated AFAs have about the same initiation efficiency. This is taken as a sign that radical addition to the AFA is not the rate determining step. From radical chemistry it is well known that the addition of free radicals to double bonds depends strongly on the substitution pattern. For example, for the addition of cyclohexyl radicals to substituted ethylene (CH_2=CH-R) relative rate constants are 1, 84 and 3000 for n-butane, phenyl and carboxymethyl, respectively [8]. It is therefore very likely that in the case of allyloxy-pyridinium based AFAs the fragmentation step is rate determining.

In Fig. 1, the polymerization by the system AFA / **BPO** is compared with the polymerization initiated by a system N-ethoxypicolinium hexafluoroantimonate (**EMP**) / **BPO**. **EMP** is a cationic initiator, which, upon photolysis or excessive heating releases pyridinium radical cations, i.e., the same reactive species that account for the initiation in the cases of allyloxy-pyridinium based AFAs.



EMP

(6)

Thus, **EMP** is a suitable model compound to rule out a polymerization that might be initiated by a direct thermal or photochemical activation of the allyloxy-pyridinium based AFAs. The negligibly low activity of **EMP** in comparison with **AFAs 1-4** is a proof for the fact that indeed radical addition fragmentation accounts for the high efficiency in cationic initiation.

The mechanism of initiation involves, as briefly mentioned above (see reactions (1) and (2)) the addition of radicals to the allylic double bond and the subsequent rupture of the N^+-O bond. Apart from the initiating pyridinium radical cation there are also some other side products which are split off from the AFA in the course of fragmentation. By GC-MS analysis of methanol soluble fractions after the polymerization it was found that epoxides, hydroxyl and aldehyde compounds may be formed.

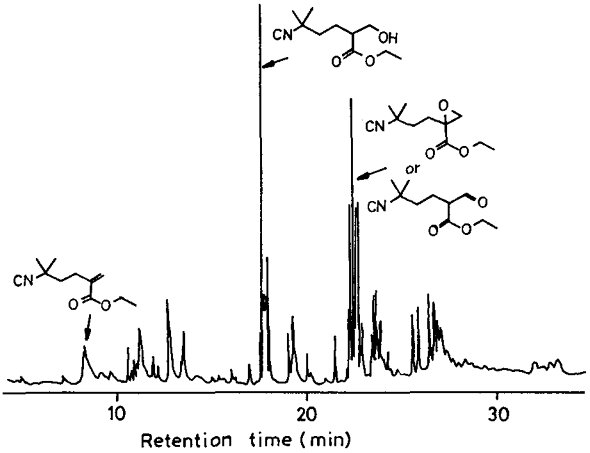


Fig. 2. Gas chromatogram of the methanol soluble products formed during CHO bulk polymerization initiated by **AFA 3** and **AIBN** (**[AFA 3]=[AIBN]**= $5x10^{-3}$ mol l^{-1} Polymerization at 70°C for 1 h.

In Fig. 2, a GC-MS for the system **AIBN** / **AFA 3** with peaks of the respective low molecular weight side products is presented. The analytical detection of these compounds is taken as another proof that the initiation mechanism indeed involves addition-fragmentation.

With phenylazotriphenyl methane (**PAT**) as a radical source, a slightly different initiation behavior is observed. As depicted in Fig. 3, the initiation rate is high for **AFAs 1** and **3**, and relatively low for **AFA 2** and **4**. This phenomenon, which seems to contradict with the findings with **BPO** (see Fig. 1) is explained on the bases of a slightly different initiation mechanism. It was found that with the **AFAs 1** and **3** there are also redox reactions accounting for the initiation. These AFAs are able to oxidize the triphenyl methyl radical formed while heating **PAT**. The triphenyl methyl cation thus generated acts as an additional initiating species.

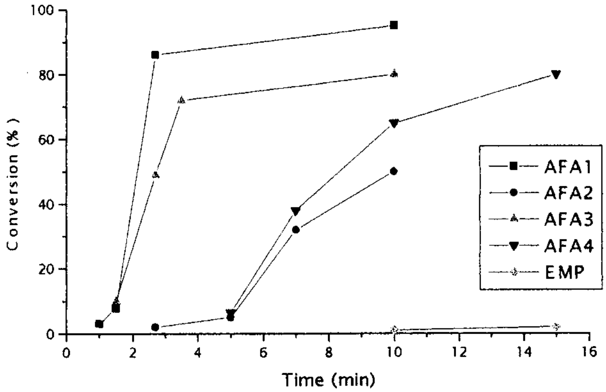
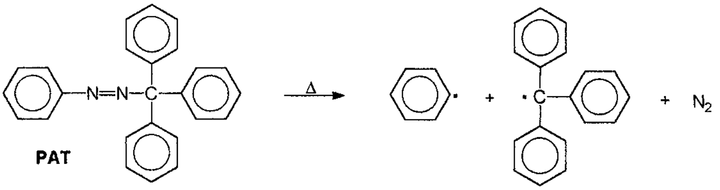


Fig. 3. Thermal Polymerization of CHO with **PAT** as radical source. [Pyrid. Salt]=[PAT]=5 x 10^{-3} mol l^{-1}, at 70 °C

(7)



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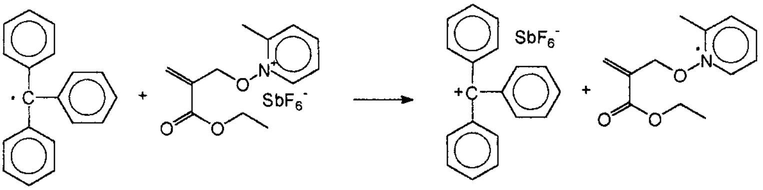


For the **AFAs 1** and **3** characteristic UV absorption bands between 410 and 440 nm owing to triphenylmethyl carbocations were found by heating solutions containing **PAT** and the respective AFA (see Fig. 4). For all other allyloxy-pyridinium initiators including **EMP**, this absorption did not occur under similar experimental conditions.

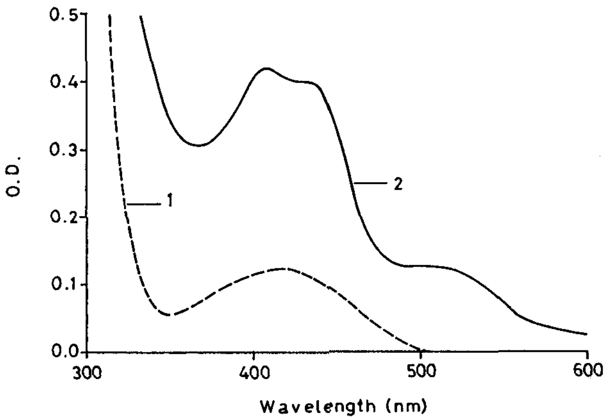


Fig. 4. UV-vis spectrum of a solution containing **AFA 3** and **PAT**. (**[AFA 3]**=**[PAT]** = $6x10^{-4}$ mol l^{-1}) before heating (1) and after 3 h heating at 70°C (2).

Interestingly, all AFAs presented in Tab. 1 do also initiate cationic polymerization upon heating without additional radical sources. The efficiency in this mode of polymerization rises in the order **EMP** < **AFA 3** < **AFA 1** < **AFA 2** < **AFA 4** (Fig. 5). With **EMP**, there is only traces of polymer formed after one hour reaction at 125°C.

It is assumed that also in this case radicals are formed by thermal decomposition of the salt. These subsequently add to double bonds of intact initiator units. This assumption is strongly supported by the finding that with **EMP** there is a significantly lower proneness to cationic initiation as compared with allyloxy-pyridinium initiator salts. If the direct initiation via thermally induced rupture of the N^+-O bond would account for the polymerization, initiation should occur to a similar extent with **EMP** also. However, it is difficult to decide which radicals are formed and how differences in initiation between the various allyloxy salts can be explained, since respective GC-MS investigations did not yield conclusive results.

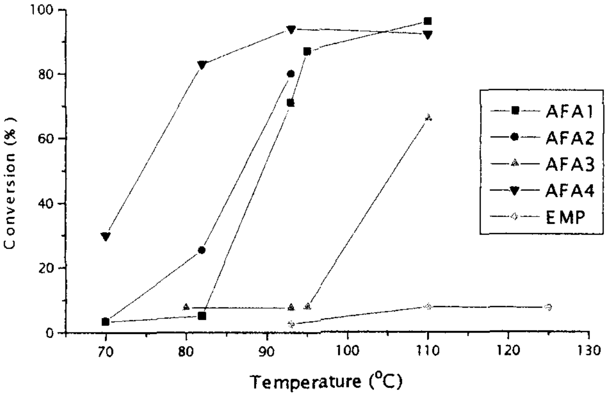


Fig. 5. Thermal Polymerization of CHO. [Pyrid. Salt] = 5×10^{-3} mol l^{-1}. Reaction time 1 h.

Allyloxy pyridinium initiators may also be used for photoinduced cationic polymerization. The absorption spectra of pyridinium salts have a characteristic π–π^* absorption with a maximum at ca. 265 nm and an absorption tail reaching up to 290 nm. When absorbing light, the allyloxy pyridinium salts undergo a decomposition (see reaction (6)), whereby initiating pyridinium type radical cations are formed. This phenomenon is well-known from EMP and other N-oxy pyridinium type initiators and has been utilized for numerous cationic polymerizations. As Fig. 6 shows, there is however a significantly higher initiation efficiency for allyloxy pyridinium salts than for **EMP** giving rise to the conclusion that with the AFAs there is another process accounting for the formation of initiating species.

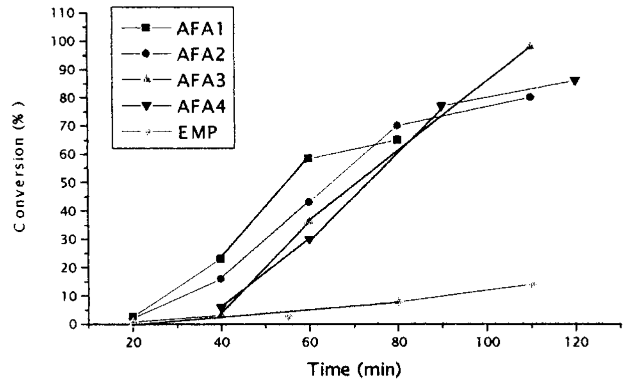
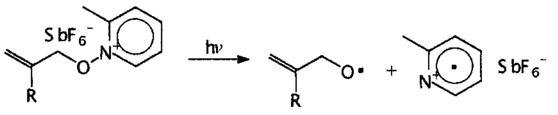
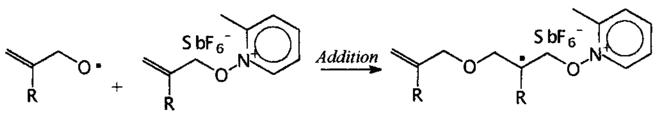


Fig. 6. Photo-polymerizations of CHO.
λ_{inc} = 280 nm,
$O.D._{280\,nm}$ =0.95.
20° C.

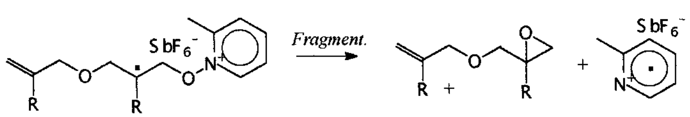
It is highly likely that the oxygen centered radicals formed upon N^+-O bond dissociation add to allylic double bonds of intact salt units thus triggering fragmentation and the production of another pyridinium radial cation. Thus, upon absorption of one photon up to two initiating species could be produced, provided the quantum yield of N^+-O bond rupture was unity and the yield in addition and fragmentation 100 %. Again, there is no significant influence of the substituent onto the initiation efficiency supporting the earlier stated assumption that fragmentation rather than addition is rate determining. The photolytic N^+-O bond rupture is probably not much effected by the substituent at the allylic double bond.



(9)



(10)

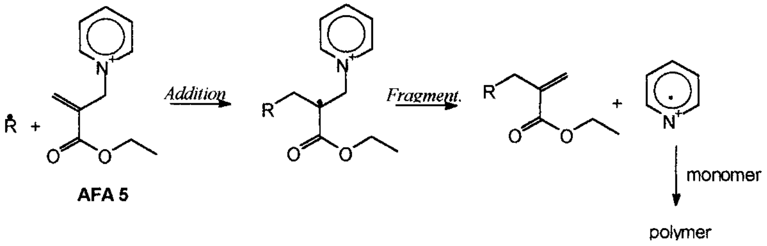


(11)

Regarding photo-polymerization, initiation with near UV light or even with visible light seems to be desirable. The presented AFAs are very useful tools in this context. By choosing the appropriate radical photo initiators, the wavelength of light suitable for the initiation can be easily tuned to the emission wavelength of the lamp used. Thus, benzoin was tried as a potential radical initiator. With irradiation wavelengths as high as 370 nm, exceptionally fast polymerizations were encountered giving rise to the conclusion that radicals formed upon benzoin photolysis readily add to the AFAs thus leading to the generation of initiating pyridinium radical cations.

ALLYL-PYRIDINIUM BASED AFA

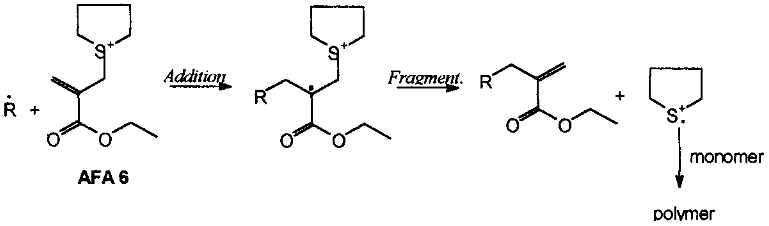
Apart from allyloxy-pyridinium compounds, allyl-pyridinium salts were developed as coinitiators for cationic polymerization [9]. Their synthesis consists in the reaction of pyridinium with the respective bromo-allyl compound and a subsequent anion exchange for hexafluoro antimonate. The initiation mechanism resembles very much the one described for the **AFAs 1-4** with the difference that allyl-pyridinium salts are somewhat less reactive. This circumstance is explained by the relatively high bond dissociation energy of the N^+-C bond in comparison with the N^+-O bond.



(12)

ALLYL-SULFONIUM BASED AFA

Besides pyridinium salts, sulfonium salts are also used for cationic polymerization. By the reaction of tetrahydrothiophen with the respective bromo allyl compound, the bromine derivative of **AFA 6** is obtained [10, 11]. In order to transform it to a coinitiator suitable for cationic polymerization, the anion has to be exchanged, e.g., for hexafluoroantimonate. In the course of addition-fragmentation apart from initiating thiophenium radical cations also various other side products mainly of acrylic nature are formed, which were detected by GC-MS. In Fig. 7, a gas chromatogram displaying the respective peaks is given for the pair **AFA 6 / AIBN**.



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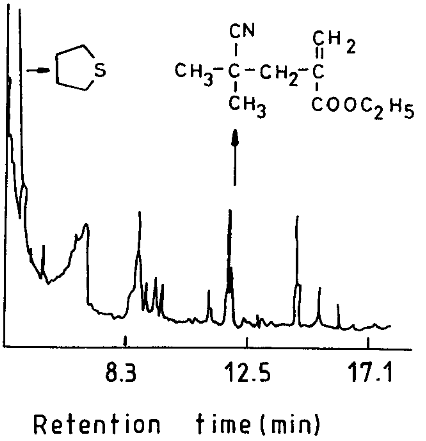

Fig. 7. Gas chromatogram of the methanol-soluble product formed during thermal polymerization of CHO initiated by **AFA 6 / AIBN** at 60°C.

When **PAT** was used as a thermal radical initiator, the initiation was exceptionally rapid. Since in this case the above mentioned characteristic absorption of triphenylmethyl carbocations was formed (410 and 440 nm), the oxidation of triphenyl methyl radicals by AFA 6 has to be taken into account. Hence, cations from both the AFA and from **PAT** result in a high overall initiation rate.

As far as photoinitiation is concerned it has to be pointed out that the **AFA 6** does not possess suitable chromophoric groups. An initiation by direct absorption of light can therefore be disregarded. However, with radical photo-initiators, such as benzoin and phosphine oxides, very fast cationic polymerizations were found. With these radical initiators polymerizations were carried out at 340 and 380 nm.

CONCLUDING REMARKS

It has been shown that certain allyl-onium salts are very useful in cationic polymerization when used in conjunction with free radical initiators. The mechanism of initiation is explained in terms of radical addition-fragmentation. Depending on the type of radical initiator used the polymerization may be triggered by either heat or light. If the onium salt possesses intrinsic chromophoric groups, photoinitiation may be efficiently initiated also in the absence of additional radical initiators. Other, possibly even more reactive onium salts that initiate cationic polymerization via the radical addition-fragmentation scheme are currently under investigation.

REFERENCES

[1] Y. Yağci, I. Reetz, *Progr. Polym. Sci.*, in print

[2] Y. Yagci, I. Reetz, *Trends Polym. Sci.*, in print

[3] Q.Q. Zhu, W. Schnabel, *Polymer*, in print (1997)

[4] I. Reetz, V. Bacak, Y. Yağci, *Polym. Int.*, in print (1997)

[5] V. Bacak, I. Reetz, Y. Yağci, W. Schnabel, *Polym. Int.*, submitted (1997)

[6] I. Reetz, V. Bacak, Y. Yağci, *Macromol. Chem. Phys.* **198**, 19 (1997)

[7] P. Monecke, Y. Yağci, W. Schnabel, *Polymer*, in print (1997)

[8] J. Fossey, D. Lefort, J. Sorba, *"Free Radicals in Organic Chemistry"*, John Wiley, Chichester (1995) p. 141

[9] Y. Yağci, A. Önen, *J. Polym. Sci., Part A; Polym. Chem.* **34**, 3622 (1996)

[10] S. Denizligil, Y. Yağci, C. McArdle, *Polymer* **36**, 3093 (1995)

[11] S. Denizligil, R. Resul, Y. Yağci, C. McArdle, J.-P. Fouassier, *Macromol. Chem. Phys.* **197**, 1233 (1996)