Macromolecules **2001,** *34,* 7608−7612

Initiation of Cationic Polymerization by Using Allyl Anilinium Salts in the Presence of Free Radical Initiators

Ayşen Önen and Yusuf Yağcı*

Istanbul Technical University, Department of Chemistry, Maslak, Istanbul 80626, Turkey

Received April 20, 2001; Revised Manuscript Received July 27, 2001

ABSTRACT: Three novel addition−fragmentation agents (AFA), namely allyl-*N*,*N*-dimethylanilinium (ADA), methylallyl-*N*,*N*-dimethylanilinium (MADA), and ethoxycarbonylallyl-*N*,*N*-dimethylanilinium (EADA) salts with a hexafluoroantimonate counteranion were synthesized and characterized. Their capability to act as initiator and co-initiator for the cationic polymerization of cyclohexene oxide (CHO) was examined. Both the thermally latent effectiveness and the photochemically latent effectiveness of these salts, in promoting polymerization of CHO at 70 °C and $\lambda < 300$ nm, respectively, were investigated. The accelerating effect of thermal and photochemical radical sources were also demonstrated. The contribution of electron transfer and addition−fragmentation mechanisms were discussed. Photoinitiated polymerization of some other monomers such as *n*-butyl vinyl ether (BVE), isobutyl vinyl ether and *N*-vinylcarbazole (NVC) at $\lambda \geq 350$ nm using benzoin and an EADA initiating system was also performed.

Introduction

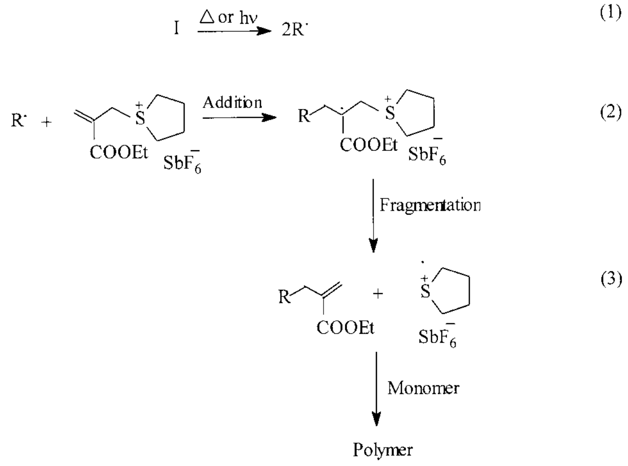
Photoinitiated cationic polymerizations appear to be very useful technology for UV-curable systems.[1] The discovery of onium salts as photoinitiators led to an extensive use of the rapid polymerization of a variety of multifunctional cationically polymerizable monomers to yield highly cross-linked films in numerous applications from printing inks to protective coatings.[2−4] To increase the utility of onium salt based photoinitiated cationic polymerizations in practical applications such as pigmented coatings, several indirect acting systems were proposed and extensively studied.[5] In such systems, radical photoinitiators, photosensitizers, and electron-donating compounds in conjunction with onium salts activated selectively at desired wavelengths required for practical applications.

Free radical addition fragmentation to specially designed allyl onium salts has been identified as an effective means of initiating cationic polymerization of cyclic ethers and vinyl ethers.[6−16] The intermediate radical cation, formed by the addition of the thermally or photochemically generated radical on the allylic salt, undergoes fragmentation, producing another radical cation which is capable of initiating cationic polymerization as illustrated on the example of allyl thiophenium salts (Scheme 1).

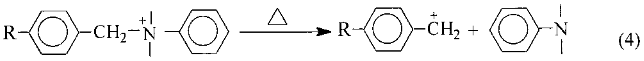
Compounds of these types include allylsulfonium salts,[6,7] allylpyridinium salts,[7,12] allyloxypyridinium salts,[9,10] allylphosphonium salts,[16] etc. The attractive features of this technique include the flexibility of the polymerization conditions which can be tuned not only to the desired wavelengths but also to temperature ranges by choosing appropriate radical initiators. Recently, Endo and co-workers investigated the thermal initiation by benzylammonium salts.[17,18] The thermolysis of these salts gives dimethylaniline and benzyl cations, the latter being very efficient in initiating cationic polymerizations.

It then occurred to us that free radical assisted addition−fragmentation reaction to allylic ammonium salts might also be extended, to indirectly generated reactive cations in addition−fragmentation type initiation. This article describes our development of cationic polymerization of various monomers initiated by novel addition fragmentation agents based on anilinium salts with various substituents at the allylic moiety.

Scheme 1



Scheme 2



Experimental Section

Materials. Ethyl-α-(bromomethyl) acrylate was synthesized as described previously.[19] *N*,*N*-Dimethylaniline (%98 Fluka) was distilled prior to use. 3-Bromo-1-propene (%98 Fluka), 3-bromo-2-methylpropene (Aldrich), benzyl bromide (%98 Fluka), and $NaSbF_6$ (Aldrich) were used as received. Cyclohexene oxide (CHO) (Fluka) was dried over CaH_2 and distilled. Reagent grade solvents were purified by conventional drying and distillation procedures. 2,2′-Azobis(isobutyronitrile) (AIBN) (Fluka) and benzoin (B) (Merck) were recrystallized from ethanol. Dibenzoylperoxide (DBP) (Fluka) was recrystallized from diethyl ether. 2,4,6-Trimethylbenzoyl diphenylphosphine oxide (TMDPO) (BASF) was recrystallized from ethanol/diethyl ether. Phenylazotriphenylmethane (PAT) was prepared as described previously.[20]

Synthesis of *N*-[2-(Ethoxycarbonyl)allyl]-*N,N*-dimethylanilinium Hexafluoroantimonate (EADA). A mixture of 0.529 g (4.37 mmol) *N*,*N*-dimethylaniline and 0.838 g (4.37 mmol) ethyl-α-(bromomethyl) acrylate in acetonitrile was stirred at room temperature for $^1/_2$ h. Acetonitrile was evaporated off, and the residue was dissolved in the minimum

10.1021/ma0106853 CCC: $20.00

amount of water and washed with ether. Finally 1.129 g (4.37 mmol) of $NaSbF_6$ was added to the aqueous phase in one portion and a white precipitate of EADA was collected, washed with water, and dried; mp 100 °C and yield 78%. ^1H NMR (δ in ppm): 7−8, **H**(arom); 5.9, C**H**$_2$=; 4.5, C**H**$_2$−N$^+$; 3.96−4.01, O−C**H**$_2$; 3.5, N$^+$−(C**H**$_3$)$_2$; 1.14−1.2, C**H**$_3$. Anal. Calcd for $C_{14}H_{20}NO_2SbF_6$ (469.93 g mol^{-1}): C, 38.3; H, 4.45; N, 2.97. Found: C, 37.2; H, 4.71; N, 2.6.

UV: $\lambda_{max} = 258$ nm, $\epsilon_{258\,nm} = 2.64 \times 10^3$ L mol^{-1} cm^{-1}.

Synthesis of *N*-[2-(Methyl)allyl]-*N*,*N*-dimethylanilinium Hexafluoroantimonate (MADA). A mixture of 0.483 g (3.99 mmol) of *N*,*N*-dimethylaniline and 0.538 g (3.99 mmol) of 3-bromo-2-methylpropene in acetonitrile was stirred at room temperature for 1 h. Acetonitrile was evaporated off, and the residue was dissolved in the minimum amount of water and washed with ether. Finally 1.032 g (3.99 mmol) of $NaSbF_6$ was added to the aqueous phase in one portion, and a white precipitate of MADA was collected, washed with water and dried; mp 82 °C and yield 50%. ^1H NMR (δ in ppm): 7−8, **H**(arom); 4.5, C**H**$_2$=; 3.96−4.05, C**H**$_2$−N$^+$; 3.5, N$^+$−(C**H**$_3$)$_2$; 1.15−1.2, C**H**$_3$. Anal. Calcd for $C_{12}H_{18}NSbF_6$ (413.93 g mol^{-1}): C, 34.87; H, 4.35; N, 3.39. Found: C, 34.4; H, 4.5; N, 2.61.

UV: $\lambda_{max} = 258$ nm, $\epsilon_{258\,nm} = 1.88 \times 10^3$ L mol^{-1} cm^{-1}.

Synthesis of *N*-[Allyl]-*N*,*N*-dimethylanilinium Hexafluoroantimonate (ADA). A mixture of 0.483 g (3.99 mmol) of *N*,*N*-dimethylaniline and 0.482 g (3.99 mmol) of 3-bromo-1-propene in acetonitrile was stirred at room temperature for 1 h. Acetonitrile was evaporated off, and the residue was dissolved in the minimum amount of water and washed with ether. Finally 1.032 g (3.99 mmol) of $NaSbF_6$ was added to the aqueous phase in one portion, and a white precipitate of ADA was collected, washed with water, and dried; mp 87 °C and yield 41%. ^1H NMR (δ in ppm): 7−8, **H**(arom); 5.4−5.65, C**H**$_2$=C**H**; 4.3, C**H**$_2$−N$^+$; 3.5, N$^+$-(C**H**$_3$)$_2$.

Anal. Calcd for $C_{11}H_{16}NSbF_6$ (397.93 g mol^{-1}): C, 33.17; H, 4.02; N, 3.51. Found: C, 32.58; H, 4.26; N, 3.46.

UV: $\lambda_{max} = 258$ nm, $\epsilon_{258\,nm} = 2.04 \times 10^3$ L mol^{-1} cm^{-1}.

Synthesis of *N*-[Benzyl]-*N*,*N*-dimethylanilinium Hexafluoroantimonate (BDA). A mixture of 0.285 g (2.36 mmol) of *N*,*N*-dimethylaniline and 0.403 g (2.36 mmol) of benzyl bromide in acetonitrile was stirred at room temperature for 3 h. Acetonitrile was evaporated and the residue was dissolved in minimum amount of water and washed with ether. Finally 0.610 g (2.36 mmol) of $NaSbF_6$ was added to the aqueous phase in one portion, and a white precipitate of BDA was collected, washed with water, and dried; mp 130 °C and yield 84%.

Anal. Calcd for $C_{15}H_{18}NSbF_6$ (447.75 g mol^{-1}): C, 40.1; H, 4.01; N, 3.12. Found: C, 39.13; H, 3.94; N, 2.9.

Polymerization. For thermal polymerizations, bulk monomer containing a known amount of allyl anilinium salt and a radical source was purged with nitrogen and placed in a constant-temperature bath at a given temperature. At the end of the given time, polymers were precipitated into methanol. In some cases after the precipitation of polymer in methanol the remaining solution was analyzed by gas chromatography (GC) in conjunction with mass spectroscopy (MS) (Varian 3700 GC equipped with a quartz capillary column, permaphase PVMS/54, length 25 m, and i.d. 0.3 mm connected to a Varian MAT-44 mass spectrometer). Quartz tubes and a low-pressure mercury lamp were employed for photopolymerizations below 300 nm. For the experiments with benzoin and TMDPO Pyrex tubes and merry go round type photoreactor with 16 Philips 8W/06 lamps emitting light at about 350 nm were used.

Characterization. UV−vis spectra were recorded on a Perkin-Elmer Lambda 2 spectrophotometer. Gel permeation chromatography (GPC) analyses were performed with a setup consisting of a Waters 600 pump, three Waters Styragel HR3, HR4, and HR4E columns with THF as the eluent at a flow rate of 0.3 mL/min, and a Waters differential refractometer (model 410). Molecular weights were calculated with the aid of polystyrene standards. ^1H NMR spectra were recorded in $CDCl_3$ on a Bruker 250 MHz instrument. Elemental analyses were performed on a CHNS-932 LECO instrument.

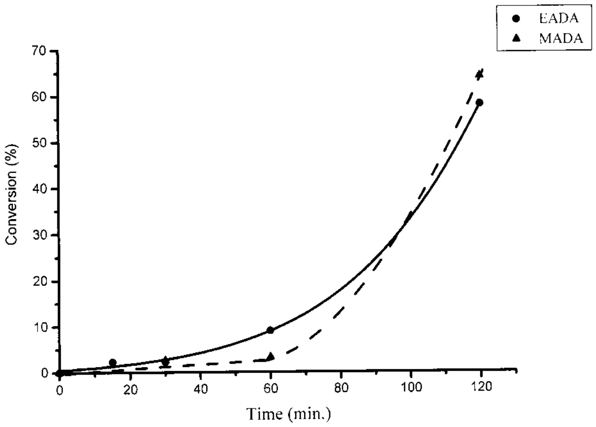
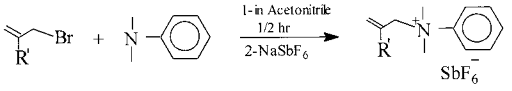


Figure 1. Thermal polymerization of CHO with allylanilinium salts. [salt] = 5×10^{-3} mol L^{-1} and [CHO] = 9.88 mol L^{-1} at 70 °C.

Scheme 3



(5)

R'=H, CH_3, $COOC_2H_5$

Results

The allylic anilinium salts were prepared by reacting the corresponding allylic bromide with *N*,*N*-dimethylaniline followed by an exchange reaction of Br with SbF_6. For the investigations described here, cyclohexene oxide (CHO) was chosen as a model monomer. CHO is not polymerizable by a radical mechanism and does not form oxidizable radicals in the course of polymerization.

Thermal Polymerization of CHO. Polymerization in the Absence of a Free Radical Source. Figure 1 shows time−conversion curves of the polymerizations of CHO with allylanilinium salts in the absence of additional radical sources at 70 °C. In this case, conversions lower than 10% were detected in 1 h, and in 2 h, the conversion went up to ≈60%.

As can be seen from Figure 1, long reaction times are required to reach satisfactory yields for the polymerization of CHO in the absence of additional radical sources at 70 °C.

Polymerization in the Presence of a Free Radical Initiator. The activity of allylanilinium salts in conjunction with different radical sources namely AIBN, BPO, and PAT, was evaluated in the bulk polymerization of cyclohexene oxide (CHO). Since the catalysts were soluble in the monomer, the polymerization system was homogeneous. The time conversion curves for CHO polymerization at 70 °C presented in Figures 2−4 clearly suggest that EADA and MADA polymerize CHO in the presence of radical sources whereas ADA-initiated polymerization of CHO only yield conversions up to 2.5% with all types of radical sources. For comparison with allylic type anilinium salts, benzylanilinium salt BDA (5×10^{-3} mol L^{-1}) was also polymerized in the presence of PAT (5×10^{-3} mol L^{-1}) at 70 °C for 30 and 60 min resulting in no polymer. Although all radical sources chosen initiate the polymerization, there are significant differences in polymerization rate increasing in the order AIBN < BPO < PAT, due to the differences in the decomposition rate constants and the reactivity of radicals toward the allylic double bond of the anilinium salts.[8] In the case of PAT as a radical initiator, very

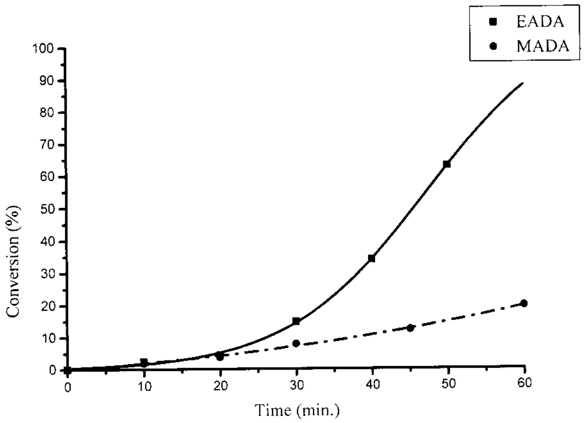


Figure 2. Thermal polymerization of CHO with allyl-*N*,*N*-dimethylanilinium salts in conjunction with AIBN as radical source: [salt] = [AIBN] = 5 × 10^{-3} mol L^{-1} and [CHO] = 9.88 mol L^{-1} at 70 °C.

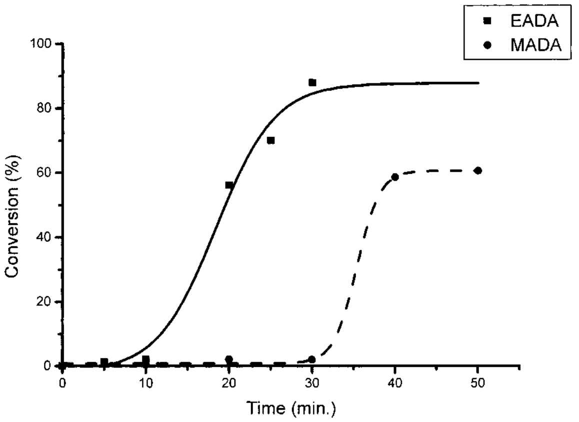


Figure 3. Thermal polymerization of CHO with allyl-*N*,*N*-dimethylanilinium salts in conjunction with BPO as radical source: [salt] = [BPO] = 5 × 10^{-3} mol L^{-1} and [CHO] = 9.88 mol L^{-1} at 70 °C.

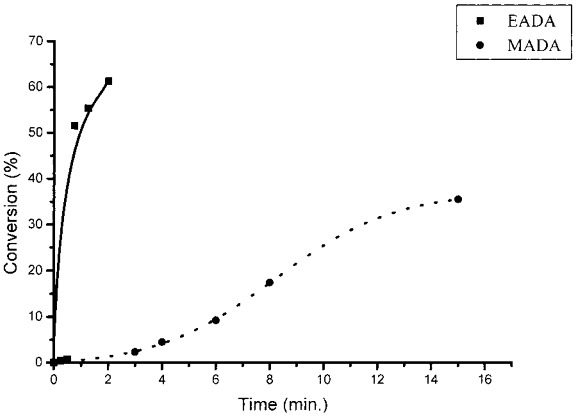


Figure 4. Thermal polymerization of CHO with allyl-*N*,*N*-dimethylanilinium salts in conjunction with PAT as radical source: [salt] = [PAT] = 5 × 10^{-3} mol L^{-1} and [CHO] = 9.88 mol L^{-1} at 70 °C.

fast polymerization rates were obtained for EADA whereas lower rates were detected for MADA. In all time–conversion curves, induction periods up to several minutes were observed due to the traces of impurities remaining in the system even after extensive purification of the initial compounds and purging the solutions with nitrogen.

All of the catalysts except for ADA served as polymerization initiators together with radical sources to afford a polymer of CHO.

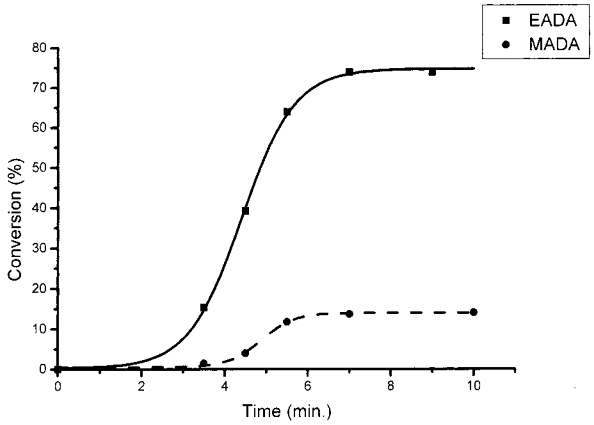


Figure 5. Photopolymerization of CHO: λ_{inc} = 258 nm, 20 °C, $OD_{258\ nm}$ = 0.95, [EADA] = 3.4 × 10^{-4} mol L^{-1}, [MADA] = 5.05 × 10^{-4} mol L^{-1}, and [CHO] = 9.88 mol L^{-1}.

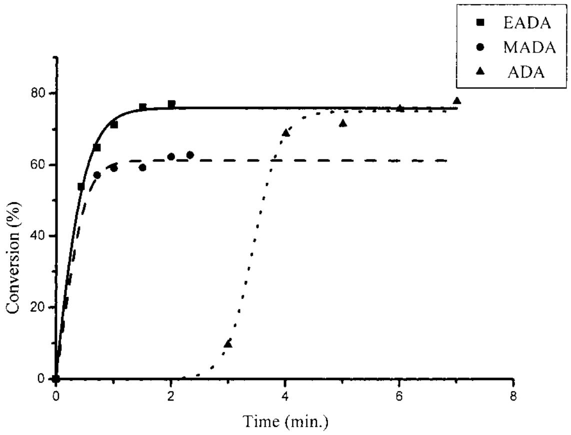


Figure 6. Photopolymerization of CHO with allyl-*N*,*N*-dimethylanilinium salts in the presence of benzoin: λ_{inc} = 367 nm, 20 °C, $OD_{367\ nm}$ (benzoin) = 0.1, $OD_{367\ nm}$ (anilinium salts) = 0 [salt] = 5 × 10^{-3} mol L^{-1}, [benzoin] = 2.4 × 10^{-2} mol L^{-1}, and CHO = 9.88 ^{2} mol L^{-1}.

Photopolymerization of CHO. Polymerization by Direct Photolysis of Allylanilinium Salts. Upon irradiation with UV light (λ < 300 nm), EADA initiates cationic polymerization with satisfactory yields; in contrast, low conversions are observed for MADA and no polymer was obtained in the case of ADA. In these experiments the salt concentrations were adjusted in order to obtain identical optical density values ($OD_{258\ nm}$ = 0.95). As indicated in the time–conversion curves of Figure 5, the order of salt activity was clearly EADA > MADA, as EADA-initiated polymerization reaches limiting conversion values of 75% in 10 min whereas limiting conversion of 14% is observed in the same time interval for MADA-initiated polymerization.

Polymerization in the Presence of Additional Radical Type Photoinitiators. No polymer was obtained when bulk CHO containing allylanilinium salt is irradiated at λ_{inc} > 350 nm, where all allylanilinium salts are transparent. However, the polymerization of CHO is induced upon the addition of a compound acting as a free radical source, i.e., decomposing into free radicals upon irradiation at λ_{inc}> 350 nm. For this purpose benzoin (B) and 2,4,6-trimethylbenzoyl diphenylphosphonyl oxide (TMDPO) were employed as light-absorbing chromophores, yielding oxidizable and nonoxidizable radicals, respectively. Figures 6 and 7 show that allylanilinium salts, when employed in conjunction with B or TMDPO, are very efficient initia-

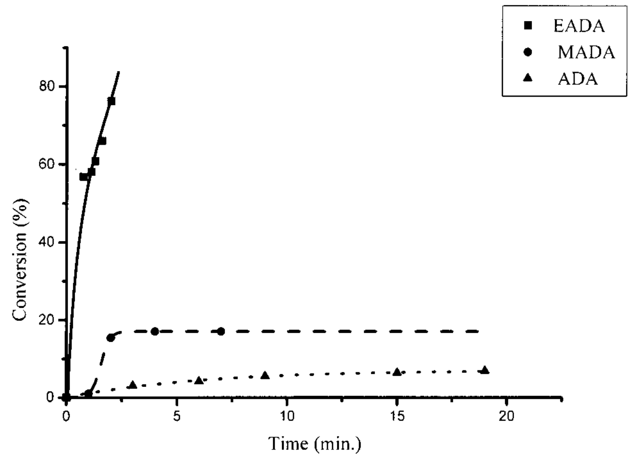


Figure 7. Photopolymerization of CHO with allyl-*N*,*N*-dimethylanilinium salts in the presence of TMDPO: $\lambda_{inc} = 380$ nm, 20 °C, $OD_{380\,nm}$ (TMDPO) = 0.95, $OD_{380\,nm}$(anilinium salts) = 0, [salt] = 5×10^{-3} mol L^{-1}, [TMDPO] = 1.7×10^{-3} mol L^{-1}, and CHO = 9.88 mol L^{-1}.

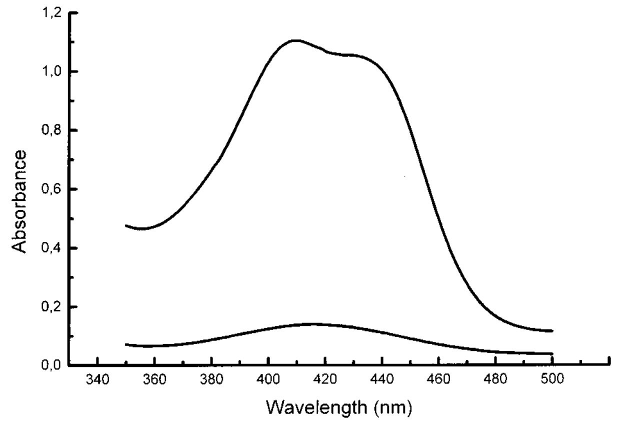
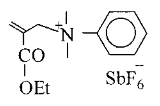


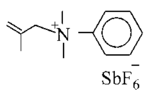
Figure 8. UV changes in the system MADA/PAT/CH_2Cl_2 at 70 °C. [MADA] = [PAT] = 5×10^{-3} mol L^{-1}.

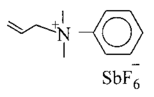
tors for the cationic polymerization of CHO. The polymerization rate is exceptionally high for EADA and the activity of allylanilinium salts decreases in the order EADA > MADA > ADA.

Discussion

Thermal Initiation. Recently various types of allylonium salts have been synthesized and employed together with free radical sources in the cationic polymerization.[6-16] The mechanism of the initiation consistent with previous studies, is explained in terms of radical addition fragmentation. In this study, allylanilinium salts having different substituents on the allylic double bond are employed in the presence of various radical sources in the polymerization of CHO.



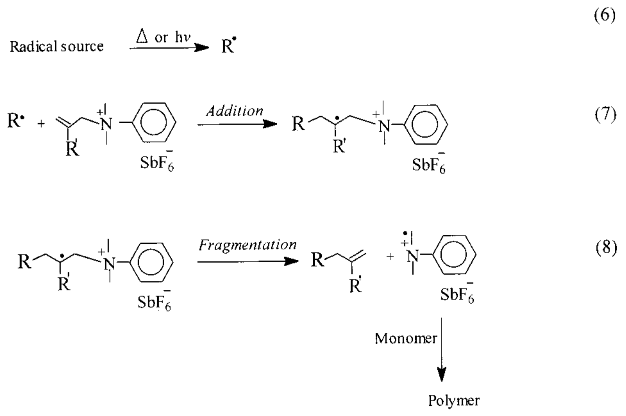




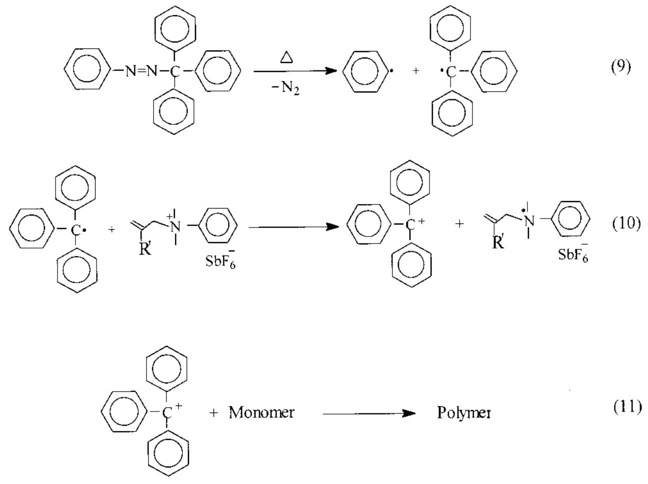
In the first step, radicals generated by heat add to the double bond of the allylanilinium salt, and subsequently, an anilinium radical cation is released by fragmentation as shown in Scheme 4.

Support for a polymerization according to reactions 6–8 may be derived from the fact that high polymerization rates are obtained only in the presence of free radicals, i.e., by thermally stimulating free radical initiators. For comparison, benzylanilinium salt was also employed in the same system and gave no polymer for longer periods of time.In contrast to AIBN and BPO, stable triphenyl methyl radicals are formed upon decomposition of PAT. These radicals can easily be oxidized to the corresponding carbocation by cationic salts with the appropriate reduction potentials according to the reactions indicated below.

Scheme 4



Scheme 5



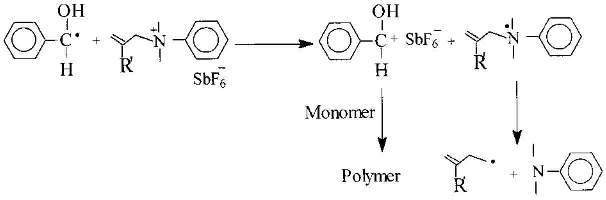
Apparently, the PAT/EADA system initiated an explosive polymerization reaction of CHO within 1 min (Figure 4). Formation of a stable triphenylmethyl cation (Figure 8) was detected by observing characteristic UV absorption bands of triphenylmethyl cation at 410 and 440 nm, upon heating solutions consisting of PAT and respective allylanilinium salt.[21] As Figure 1 suggests, cationic polymerization may also be initiated by allylanilinium salts without additional radical sources. In this case, radicals are formed by thermal decomposition of the allylic salt add to the double bonds of initiator units. This assumption is strongly supported by following the polymerization of CHO in the presence of benzylanilinium salt. In this case no polymer was obtained even in the presence of additional radical sources (Table 1).

Photoinitiation. Allylanilinium salts may also be used for direct photoinduced cationic polymerization. The absorption spectra of anilinium salts have a characteristic absorption with a maximum at around 258 nm. When absorbing light, the allylanilinium salts undergo decomposition, whereby initiating anilinium

Table 1. Thermal Polymerization of Bulk CHO Using Allylanilinium Salts (5×10^{-3} mol L^{-1}) and PAT (5×10^{-3} mol L^{-1}) at 70 °C

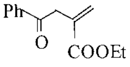
salt	radical source	time (min)	conversion (%)
benzylanilinium	PAT	60	
allylanilinium (EADA)	PAT	2	60

Scheme 6



(12)

type radical cations are formed. Regarding the photoinitiation at wavelengths where allylanilinium salts are transparent ($\lambda > 300$ nm), light-absorbing chromophores yielding oxidizable and nonoxidizable radicals like benzoin (B) and 2,4,6-trimethylbenzoyldiphenylphosphonyl oxide (TMDPO) can be employed in conjunction with allylanilinium salts. As can be seen from Figures 6 and 7 cyclohexene oxide (CHO) was polymerized quite effectively in the presence of allylanilinium salts and B or TMDPO as free radical sources. The efficiency of the allylanilinium salts in these systems is in the order EADA > MADA > ADA. In the absence of these compounds, the photolysis of a solution containing allylanilinium salts and CHO at $\lambda > 300$ nm failed to produce any precipitated polymer. The high efficiency in these cases can be explained in terms of an addition−fragmentation mechanism. Additional support for the initiation by addition−fragmentation processes in the polymerization was obtained by GC−MS analysis of the remaining methanol soluble products of the polymerization mixture where benzoin was used as a radical source. Notably, the peak for the unsaturated compound of the following structure (refer to eq 8) originating from the addition of benzoyl radicals, and subsequent fragmentation was detected besides benzaldehyde, methyl benzoate and *N*,*N*-dimethylaniline.



The formation of benzaldehyde and methyl benzoate from the photodecomposition of benzoin in the presence of onium salts has been previously reported.[22] Interestingly, the unsaturated compound originating from the addition of hydroxybenzyl radical could not be detected by GC−MS. This behavior may be due to participation of these radicals in electron-transfer reactions. This mechanism involves the oxidation of hydroxybenzyl radicals to corresponding carbocations by anilinium salts of appropriate reduction potentials. Identical redox reactions were observed with allylsulfonium salts and allyloxypyridinium salts.[6,9] In addition to CHO, butyl vinyl ether (BVE), isobutyl vinyl ether IBVE, and *N*-vinylcarbazole (NVC) were also examined. These monomers also polymerize readily in solutions containing EADA and benzoin. Typical results are presented in Table 2.

Table 2. Photoinitiated Polymerization of Various Monomers Using EADA (5×10^{-3} mol L^{-1}) and Benzoin (2.4×10^{-3} mol L^{-1}) in Methylene Chloride at Room Temperature, $\lambda_{inc} \cong 350$ nm

monomer	[M] (mol L^{-1})	time (s)	conversion (%)	$M_n \times 10^{-3}$ (g mol^{-1})
CHO	9.88	26	66	4.8
NVC	0.5	300	76	56.3
BVE	3.86	20	100	9.4
IBVE	3.83	20	100	10.1

In conclusion, the allylic anilinium salts were demonstrated to be co-initiators for cationic polymerization in conjunction with thermal and photochemical free radical sources. The mechanism involves the addition of radicals to the allylic double bond and subsequent fragmentation to yield reactive cations. In photopolymerizations, the initiating system enables one to adjust the sensitivity by selecting the free radical photoinitiator with the required absorption maxima. No polymerization occurs in the absence of any of the two components upon irradiation at wavelengths above 300 nm under the described experimental conditions, and both components are essential to this initiating system. In thermal polymerizations, the presence of free radicals results in an apparent acceleration of rate of polymerizations due to the free radical induced addition−fragmentation reactions. Depending on the nature of radicals produced photochemically or thermally, i.e, nucleophilic radicals, two of the salts, with ethoxycarbonyl (EADA) and methyl moieties (MADA) can also participate in electron-transfer reactions which contribute to the enhanced activity. These salts are also able to initiate cationic polymerization upon appropriate external stimulation, i.e., heating or irradiating at wavelengths below 300 nm, even in the absence of free radical initiators.

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MA0106853