Polymer 42 (2001) 6681–6685

polymer

www.elsevier.nl/locate/polymer

Synthesis of a novel addition-fragmentation agent based on Michler's ketone and its use as photo-initiator for cationic polymerization

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Received 20 December 2000; received in revised form 10 February 2001; accepted 23 February 2001

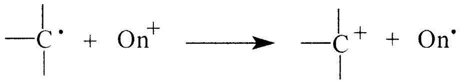
Abstract

A novel addition-fragmentation agent (AFA), 4,4′-bis{N,N,dimethyl, N (2-ethoxy carbonyl-1-propenyl) ammonium hexafluoro antimonate}benzophenone (MKEA) as a photo-initiator for cationic polymerization was synthesized from the precursor Michler's ketone (MK) and characterized. MKEA initiates cationic photo-polymerization of cyclic ethers like cyclohexene oxide (CHO) via conventional addition fragmentation mechanism. Unlike the previously reported AFAs, this initiator does not require supplementary free radical sources. Polymerizations and spectroscopic investigations were performed to help understand the mechanism, with results suggesting that radicals steming from the photo-induced hydrogen abstraction participate addition fragmentation reactions to yield reactive species capable of initiating cationic polymerization. Photo-induced polymerizations of vinyl monomers such as butyl vinylether, isobutyl vinylether and N-vinylcarbazole and a bisepoxide such as 3′,4′-epoxycyclohexyl-3′,4′-epoxycyclohexene carboxylate by using MKEA were also achieved. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Photo-initiated cationic polymerization; Addition-fragmentation agent; Michler's ketone

1. Introduction

UV curable systems based on the photo-polymerization of appropriate monomer mixtures find numerous applications in various industrial areas [1,2]. The design of new reactive monomers and oligomers, formulations and improved initiators will be more vitalized in the new millennium because of the increasing force for the use environmentally friendly technologies such as UV curing. In addition to the application well advanced free radical photo-polymerization in UV curing of acrylate based systems, the corresponding cationic polymerization with a variety of photo-latent initiators consisting of onium salt structures have hitherto been carried out [3,4]. It was shown that iodonium [5], sulphonium [6,7] and alkoxy pyridinium [8,9] salts serve as effective photo-initiators for curing of epoxy and vinyl monomers. The search for new initiating systems for cationic polymerization has focused on the development of initiator or initiator and co-initiator combinations having wavelength flexibility for various formulations containing additives. This often requires absorption of the initiating system at wavelengths where additives are transparent or their absorption is not high to reduce the overall curing efficiency. Previously, such flexibility for photo-initiated cationic polymerization using onium salts has been achieved by several ways. Photo-sensitizers [10], free radical photo-initiators [11] and charge transfer complexes [12] have been successfully employed in order to broaden their spectral response. Among these, the use of free radical photo-initiators together with onium salts is an elegant and fairly flexible way to generate reactive species capable of initiating cationic polymerization [13]. This process is based on the oxidation of photo-chemically generated radicals by the ground state onium salt according to the following reaction [14].



$$-\overset{|}{\underset{|}{C}}{\cdot} + On^{+} \longrightarrow -\overset{|}{\underset{|}{C}}{}^{+} + On^{\cdot} \tag{1}$$

However, the success of the process depends on the redox potentials of both onium salt and free radical formed. Thus, only photo-initiators that produce electron donor radicals can participate in the cation generating redox reaction. In order to overcome such limitations we have developed addition-fragmentation type initiation by using allylic salts of the following structure [15–21].

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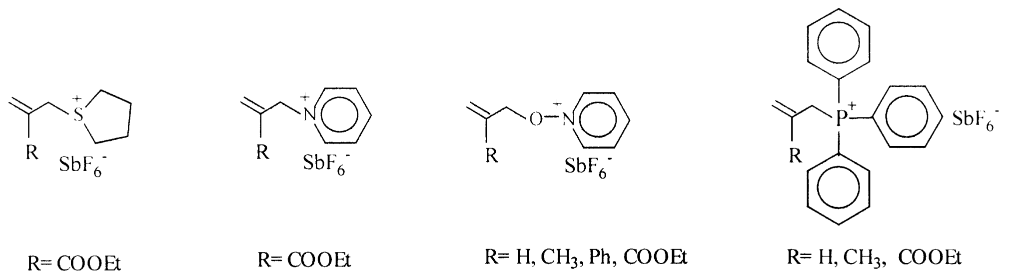
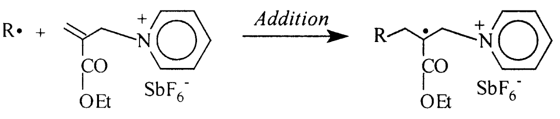
PII: S0032-3861(01)00162-8



Our goal was to devise again a free radical approach to generation of reactive cations, which does not suffer from the thermodynamical limitations. The radicals generated by either heat or light add to the double bond of the addition fragmentation agent (AFA) and subsequently an onium radical cation is released, which initiates the polymerization. In reactions (2) and (3), this mechanism is illustrated on the example of allyl pyridinium salt [16].

$$\text{Radical source} \xrightarrow{\Delta \text{ or } h\nu} R\cdot \tag{2}$$



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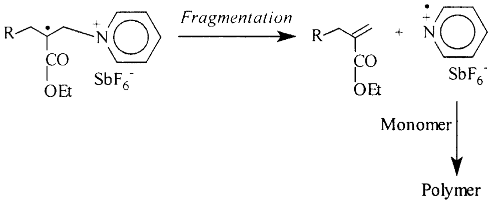


(4)

(5)

The obvious advantage of using AFAs for cationic polymerization is that, depending on the nature of the radical source used, initiation can be triggered either by heat or light. Moreover, as far as photo-polymerization is concerned, it is extremely easy to synchronize to a desired wavelengths' range by chosing appropriate radical initiators. In the present work, we report the synthesis of a new ammonium type AFA possessing 4,4′-bis(dimethylamino) benzophenone (Michler's ketone) structure. It was expected and will be shown below that due to the fact that Michler's ketone is a complete initiating system alone [22], the new AFA formed therefrom does not require additional radical source.

2. Experimental

2.1. Materials

Michler's ketone 4,4′-bis(dimethyl, amino)benzophenone (Aldrich) was recrystalized from ethanol. Ethyl α-(bromomethyl)acrylate was prepared according to the literature procedure. Cyclohexene oxide (CHO), butylvinyl ether (BVE), isobutylvinyl ether (IBVE) and solvents were purified by conventional drying and distillation procedures. N-Vinyl carbazole was crystallized from ethanol. Bisepoxide, 3′,4′-epoxycyclohexyl-3′,4′-epoxycyclohexene carboxylate (EEC), commercial product of Ciba Specialty Chemicals, CY-179, was used as received.

2.2. *Synthesis of Michlers ketone-ethyl-acrylate Salt (MKEA) (4,4′-bis{N,N, dimethyl, N (2-ethoxy carbonyl-1-propenyl) ammonium hexafluoro antimonate} benzophenone)*

4,4′-bis{N,N, dimethyl, N (2-ethoxy carbonyl-1-propenyl) ammonium hexafluoro antimonate} benzophenone (MKEA) was synthesized by reacting a mixture of 0.235 g (1.22×10^{-3} mol) of ethyl α-(bromomethyl) acrylate and 0.1643 g (6.12×10^{-4} mol) of Michler's ketone in 20 ml acetonitrile for 6 days at room temperature. Acetonitrile was evaporated and the residue was extracted with ether/water (20 ml/4 ml). An equimolar amount of $NaSbF_6$ 0.3167 g (1.22×10^{-3} mol), was then added to the aqueous layer and light yellow precipitate obtained with a yield of 5%, Elemental Analysis: Calc.C, 36.04%; H, 3.93%; N, 2.9%. Found: C, 37.1%; H, 4.01%; N, 3.22%. ^{1}H-NMR (δ in ppm) in CD_3CN: 6.67–6.93, 7.6–7.9, $\mathbf{H}_{arom}$; 3.58, $(\mathbf{CH}_3)_2\text{—}N^+\text{—}$; 4.6, $\text{—}\mathbf{CH}_2\text{—}N^+$; 5.9, $\mathbf{CH}_2\text{=}C\text{—}$; 4.0, $\text{—}\mathbf{CH}_2\text{—}O\text{—}$; 1.19, $\mathbf{CH}_3\text{—}CH_2\text{—}$. UV($CH_2Cl_2$): $\lambda_{max} = 361$ nm, $\epsilon_{361\ nm} = 43076\ l\ mol^{-1}\ cm^{-1.}$

2.3. *Polymerization*

Appropriate solutions of monomer and MKEA were degassed with nitrogen prior to irradiation. After a given time polymers were precipitated into methanol, filtered and dried in vacuo. Merry-go-round type photo-reactor with 16 Philips 8W/06 lamps, emitting $\lambda > 300$ nm was employed as a light source.

2.4. *Analysis*

U.V.-visible spectra were recorded on a Perkin Elmer Lambda 2 spectrometer. Gel permeation chromatography (G.P.C.) analyses were performed with a set up consisting of a Waters pump and a four Ultrastyragel columns with porosities 10^5, 10^4, 10^3, 500 Å. THF was used as the eluent, at a flow rate of 1 ml min^{-1} and detection was carried out with differential refractometer. Molecular weights were

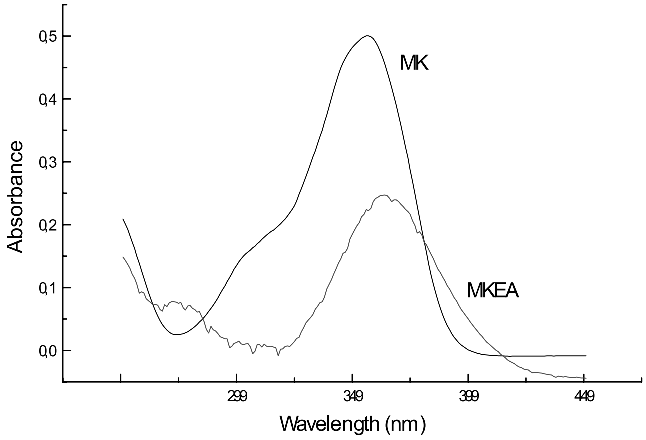


Fig. 1. UV spectra of 1.35×10^{-5} mol l^{-1} CH_2Cl_2 solutions of Michler's Ketone (MK) and its corresponding allylic salt (MKEA).

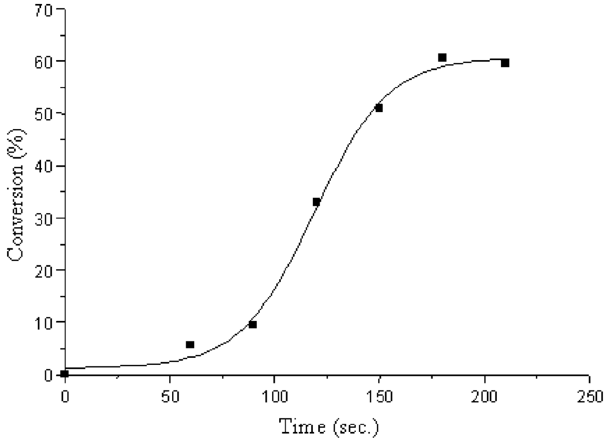
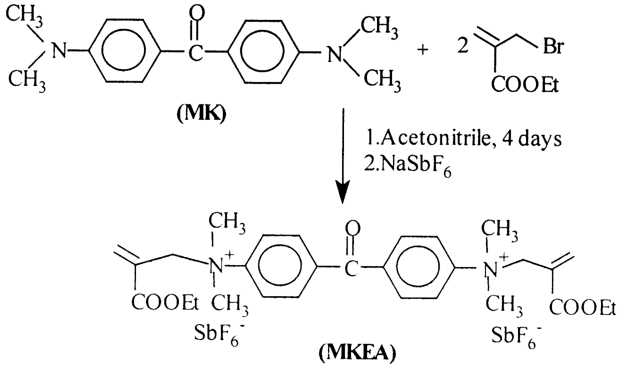


Fig. 2. Photo-polymerization of CHO in the presence of MKEA, [CHO] = 9.88 mol l^{-1}, [MKEA] = 2.2×10^{-5} mol l^{-1}, $\lambda_{inc} = 350$ nm.

calculated with the aid of polystyrene standards. ^1H-NMR were taken on a Bruker-250 MHz spectrometer.

3. Results and discussion

The allyl ammonium salt was prepared by the reaction of corresponding ally bromide with Michler's ketone followed by exchange reaction of bromide with SbF_6^-.

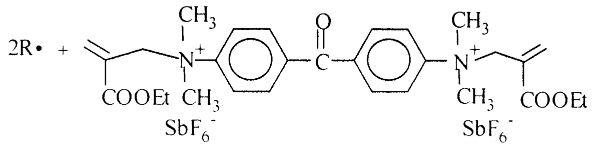


(6)

The structure of the ammonium salt was confirmed by elemental analysis as well as spectroscopic investigations. The ^1H-NMR spectrum, recorded in CD_3CN evidenced resonance signals of $-CH_3$, $-OCH_2$, $-CH_2$, $-CH_2{=}C-$, $-N^+-CH_3$ and aromatic protons of relative intensities corresponding to the number and type of protons. Compared to the UV spectrum of precursor Michler's ketone, the main absorption band of the salt is red-shifted (Fig. 1). Usually, the introduction of electron donating substituents such as amino groups in the para position shifts the main absorption band towards to longer wavelengths (see Ref. [2], p. 153). In this case, however, the amino group is quarternized and electron donating nature arising from the non-bonding electrons of nitrogen has been overturned. The observed slight red-shift of the main absorption band may be due to the strong charge transfer characteristic of the excited state induced by ammonium salt structure and the effect of acrylic moiety. This interesting effect was also found with the AFA synthesized by the alkylation of the amino group bearing visible light free radical initiator.

The photo-initiated cationic polymerization of cyclohexene oxide was carried out with MKEA (Fig. 2). The polymerization did not take place up to 1 min irradiation probably owing to the trace impurities present in the system, but the reaction reached 60% conversion immediately thereafter. The strong electron donating monomers such as N-vinyl carbazole, isobutyl vinylether and n-butyl vinyl ether undergo explosive polymerization upon illumination of light (Table 1).

On the basis of photo-chemistry of MK and the preceding reports on polymerization with AFAs, the initiating species generated from MKEA in this cationic polymerization could be considered to be ammonium radical cations. To facilitate the understanding of the initiating species, the spectral investigation of the polymers obtained with MKEA was performed. From the UV spectrum of the polymer isolated by reprecipitation with MeOH (Fig. 3), the absorption maxima at 360 nm attributable to the end MK moiety was observed. Because the corresponding peak was present in the polymer, MK moiety should be at the centre of the polymer chain. Accordingly, radicals formed by hydrogen abstraction mechanism adds to the double bond, and subsequently ammonium radical cation is released which initiates the polymerization.

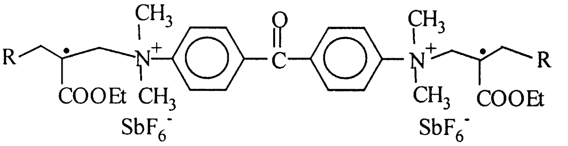


(7)

Table 1
Photo-initiated polymerization of various monomers using MKEA (2.2×10^{-5} mol l^{-1}) in methylene chloride at room temperature, $\lambda_{inc} = 350$ nm

Monomer	[M] (mol l^{-1})	Time (s)	Conversion (%)	$Mn^a \times 10^{-3}$ (g mol^{-1})
CHO	7.9	300	76	14
NVC	1.23	1	97	26
BVE	6.21	120	78	8
IBVE	6.13	1	38	13

[a] Determined by GPC according to polystyrene standards.



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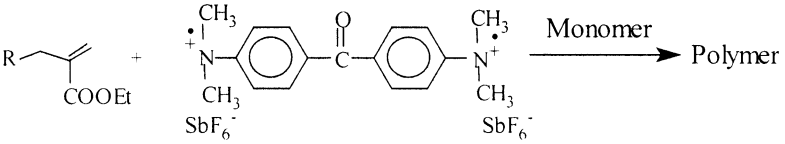
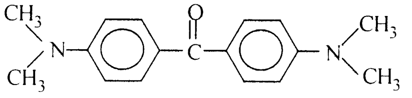
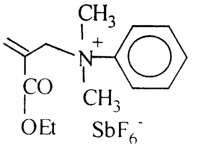


(9)

Further support for the initiation mechanism was obtained by polymerizing cyclohexene oxide with an initiating system consisting of radical generating and addition fragmentation components independently. Using combination of MK and N,N dimethyl anilinium ethyl acrylate salt (DMEA) of the following structure at a concentration providing the same absorbance at the irradiation wavelength produced polymers with similar yields (Table 2).



(MK)



(DMEA)

Notably, higher molecular weight values observed with the polymers with MKEA indicates the bifunctional nature of the initiating system, i.e., growth occurs from both ends. In this connection it should be pointed out that the hydrogen donating efficiency of MKEA is expected to be reduced by the quarternization. However, allylic structure of the initiator provides additional potential hydrogen donating sites. It has been previously shown [23] that benzophenone triplets undergoes efficient hydrogen abstraction from the allylic salts of similar structure.

Table 2
Photo-initiated polymerization[a] of CHO in the presence of allyl ammonium salts at room temperature for 3 min, $\lambda_{inc} = 350$ nm ([DMEA] = 5×10^{-3} mol l^{-1}, [MKEA] = 2.2×10^{-5} mol l^{-1}, [MK] = 2.49×10^{-5} mol l^{-1} [CHO] = 9.88 mol l^{-1})

Salt	Radical source	Conversion (%)	$Mn^a \times 10^{-3}$ (g mol^{-1})
DMEA	MK	71	6.8
MKEA	–	69.34	10.9

[a] Determined by GPC according to polystyrene standards.

Photo-crosslinking activity of the initiator was tested and compared with those of other reported AFAs by using a bifunctional epoxy monomer, EEC (Table 3). Upon irradiation, gelation with MKEA took place more efficiently than those with ammonium, alkoxy pyridinum and pyridinium type allylic salts. Moreover, these salts require additional radical sources such as benzoin for the first step of the process.

To illustrate also the free radical initiation activity of MKEA, photo-initiated polymerization of methyl methacrylate was carried out. As can be seen from Table 4, MKEA is efficient initiator as the precursor MK indicating potential practical application of the salt in hybrid curing formulations containing both acrylate and epoxy structures.

In conclusion the allylic salt synthesized from the free

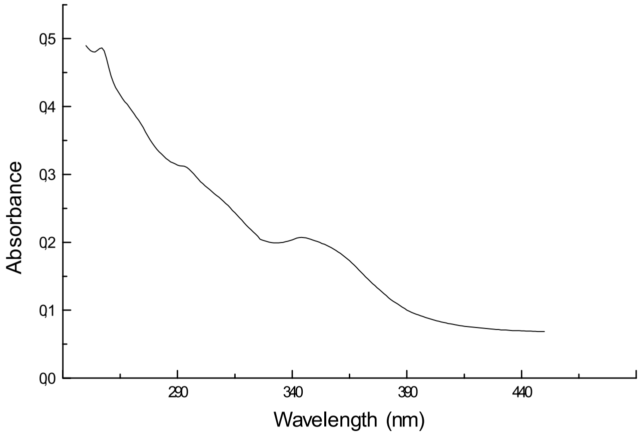


Fig. 3. UV absorption spectra of poly(cyclohexene oxide) initiated by the allylic salt MKEA in CH_2Cl_2.

Table 3
Photo-chemical gelation of 3′,4′-epoxycyclohexyl-3′,4′-epoxycyclohexene carboxylate (EEC) by AFAs: $[\mathrm{AFA}] = 5 \times 10^{-3}$ mol/L, $[\mathrm{Benzoin}] = 2.4 \times 10^{-2}$ mol/L, $\lambda_{inc} = 370$ nm, OD_{370} nm (Benzoin) = 0.10. (R = COOEt)

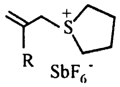
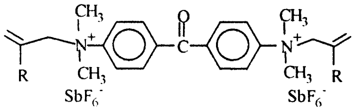
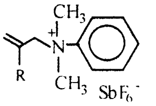
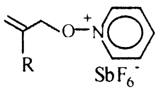
AFA	Benzoin	Gelation time (min)
	+	17
	− +	23 42
	+	110
	+	120

Table 4
Photo-initiated bulk polymerization of MMA for 45 min at room temperature, $\lambda_{inc} = 350$ nm

Photo-initiator (mol l^{-1})	Conversion (%)	$Mn^{a} \times 10^{-3}$ (g mol^{-1})
MK (2.49×10^{-5})	4.73	225
MKEA (2.2×10^{-5})	4.74	132

[a] Determined by GPC according to polystyrene standards.

radical initiator MK was demonstrated to be photo-latent initiator in the cationic polymerization of cyclic ethers and vinyl monomers. The photo-latency was explained in terms of addition-fragmentation reaction of the free radicals generated by hydrogen abstraction of aromatic carbonyl moiety.

Acknowledgements

The authors would like to thank Ciba Specialty Chemicals and Istanbul Technical University, Research Fund for the financial support.

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