ELSEVIER

Polymer 43 (2002) 2575–2579

polymer

www.elsevier.com/locate/polymer

Polymer Communication

Photoinitiated cationic polymerization using a novel phenacyl anilinium salt

Fatmanur Kasapoglu, Aysen Onen, Niyazi Bicak, Yusuf Yagci*

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

Received 5 November 2001; received in revised form 2 January 2002; accepted 2 January 2002

Abstract

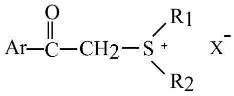
A novel phenacyl anilinium salt, *N*-phenacyl, *N*,*N*-dimethylanilinium hexafluoroantimonate, (PDA), has been synthesized and used as photoinitiator for cationic polymerization of cyclohexene oxide (CHO), butyl vinyl ether (BVE) and *N*-vinyl carbazol (NVC). Plausible mechanism of the photoinitiation involves the decay of the excited PDA with both heterolytic and homolytic cleavages of carbon–nitrogen bond. Thus, phenacylium cations formed directly or subsequent intermolecular electron transfer, respectively, initiate the polymerization.

Keywords: Photoinitiated cationic polymerization; Phenacyl anilinium salt

1. Introduction

In recent years, photoinitiated cationic polymerization received more interest than the corresponding photoinitiated free radical polymerization [1]. The vast majority of photo induced polymerization and crosslinking reactions, used in industrial applications for various techniques, e.g. those concerning surface coating and micro lithography, involve a free radical mechanism [2]. A wide range of free radical photoinitiating systems, fulfilling requirements for industrial applications, e.g. wavelength selectivity, solubility, etc. are now available and their chemistry is well established [3]. The free radical photopolymerization has, therefore, reached an advanced level. On the contrary, the corresponding cationic polymerization, by which commercially important monomers such as epoxides and vinyl ethers are polymerized, has gained importance after the pioneering work of Crivello et al. who introduced sulphonium and iodonium salts as efficient photoinitiators for cationic polymerization [4–6]. Later on, a number of other photoinitiating systems based on ionic and non-ionic compounds were described [6–17].

A large portion of today's relevant research concerns photoinitiators, i.e. introduction of new initiators or improving solubility, particularly in commercially important monomers, or modifying the spectral sensitivity of existing ones. In this respect, the recent work of Crivello is noticeable [18]. These authors described the facile synthesis of a novel series of second generation of dialkylphenacylsulphonium salts (DPS) of the following structure



$\mathrm{Ar{-}\overset{\overset{O}{\|}}{C}{-}CH_2{-}S^{+}R_1R_2\quad X^{-}}$

Significant features of the DPSs involve the possibility to design the compatibility with commercially important monomers and spectral sensitivity [19].

It was shown by Nakano and Endo that certain anilinium salts act as latent thermal initiators for cationic polymerization [20]. On the other hand, these compounds do not undergo light induced reactions and cannot be used as cationic photoinitiators. However, specially designed allyl anilinium salts were shown to be highly appropriate for the thermal and photochemical initiation of cationic polymerization [21]. In this case, photoinitiation is achieved by the added free radical photoinitiators via addition–fragmentation reactions (Scheme 1). Obviously, the allyl anilinium salts are not photoinitiators but participate in the addition–fragmentation reaction with the initial free radicals being provided by a conventional photochemical photoinitiator.

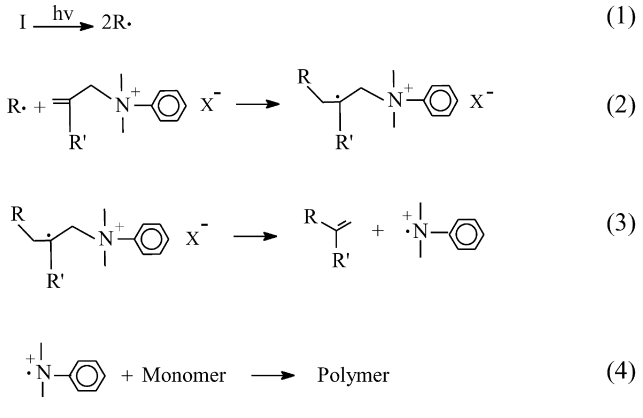
Phenacyl anilinium salts with non-nucleophilic counter

---

* Corresponding author. Tel.: +90-212-285-3241; fax: +90-212-285-6386.

E-mail address: yusuf@itu.edu.tr (Y. Yagci).

PII: S0032-3861(02)00029-0



Scheme 1.

anions are expected to act as latent photoinitiators, because the phenacyl moiety can be photochemically excited and *N*,*N*-dimethylaniline would behave as a good leaving group due to its weak basicity.

In this article, we describe the activity of *N*-phenacyl, *N*,*N*-dimethylanilinium hexafluoroantimonate (PDA), as a photoinitiator for cationic polymerization. As it will be shown later PDA initiates cationic polymerization efficiently upon irradiation at wavelengths where the commercial photoinitiators, such as triarylsulphonium and diaryliodonium salts have either no absorption or tail absorption, respectively.

2. Experimental

2.1. Materials

N,*N*-dimethylaniline (98%, Fluka) was distilled prior to use. Bromoacetophenone (Fluka) and sodium hexafluoroantimonate (Aldrich) were used as received. Diphenyliodonium hexafluorophosphate (Fluka) and triphenylsulphonium hexafluorophosphate (Alfa Products) were recrystallized from ethanol. Benzyl anilinium hexafluoroantimonate was prepared as described previously [21]. Cyclohexene oxide (CHO) (Fluka), was dried over CaH_2 and distilled. Acetone and methanol (Merck) were used as received. Butyl vinyl ether (BVE) (Aldrich), was extracted with water, dried with sodium and distilled. *N*-vinyl carbazol (NVC) (Fluka) was recrystallized from ethanol. Methylene chloride was first extracted with sulphuric acid, washed with water, then extracted with 5% NaOH solution, and again washed with water. It was then dried over calcium chloride and fractionally distilled.

2.2. Synthesis of N-phenacyl, N,N-dimethylanilinium hexafluoroantimonate

Into a 100 ml round bottom flask equipped with a magnetic stirrer and a reflux condenser were placed 1.5 g (7.54×10^{-3} mol) of bromoacetophenone, 0.914 g (7.54×10^{-3} mol) *N*,*N*-dimethylaniline and 1.951 g (7.54×10^{-3} mol) $NaSbF_6$ and 50 ml of acetone. The reaction mixture was brought to reflux and held at this temperature for 15 min. The dark pink solution was filtered to remove NaBr, which was formed during the reaction. Then the solvent was removed on a rotary evaporator, leaving *N*-phenacyl, *N*,*N*-dimethylanilinium hexafluoro antimonate (PDA) as a tan solid. The product was recrystallized twice from ethanol solution. The salt washed with water and dried at vacuum, mp. 122 °C, yield 54%. ^{1}H-NMR (δ in ppm): 7.5–8, C_6H_5; 6.12, $N^+{-}CH_2$; 3.77, $N^+{-}(CH_3)_2$. Elemental analysis: $C_{16}H_{18}ON^+SbF_6^-$ (475.69 g mol^{-1}) Calcd. C, 40.36 %; H, 3.78 %; N, 2.94 %. Found C, 40.14 %; H, 3.98 %; N, 2.27 %. UV: $\lambda_{max} = 255$ nm, $\epsilon_{255\ nm} = 21{,}615\ l\ mol^{-1}\ cm^{-1}$.

2.3. Polymerization

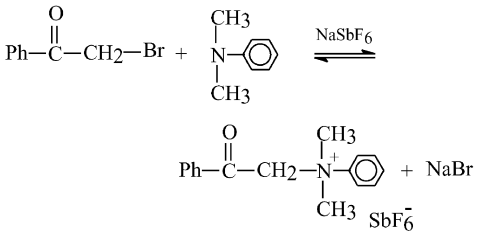
Appropriate solutions of monomer and PDA were mixed in pyrex tubes and degassed with nitrogen prior to irradiation by a merry-go-round type reactor equipped with 16 Philips 8 W/06 lamps emitting light at $\lambda > 300$ nm and a cooling system. At the end of a given time, polymers were precipitated into methanol, filtered, dried and weighed. Conversions were determined gravimetrically.

2.4. Characterization

UV–Vis spectra were recorded on a Perkin–Elmer Lambda 2 spectrophotometer. ^{1}H-NMR spectra were recorded on a Bruker 250 MHz instrument. Elemental analysis was performed on a CHNS-932 LECO instrument. GC–MS analysis was performed with Varian 3700 GC equipped with quartz capillary column, permaphase PVMS/54, length 25 m, i.d. 0.3 mm connected to a Varian MAT-44 mass spectrometer. GPC analyses were performed via set-up consisting of a Waters pump and three styragel HR3, HR4, HR4E columns with THF as the eluent, at a flow rate of 1 ml min^{-1} and detection was carried out with a differential refractometer. Molecular weights were calculated with the aid of polystyrene standards.

3. Results and discussion

A simple one-pot reaction, described for the preparation of DPS, was used for the synthesis of the phenacyl anilinium salt, PDA [18]. Accordingly, phenacylbromide was reacted with *N*,*N*-dimethylaniline in the presence of sodium hexafluoroantimonate



(5)

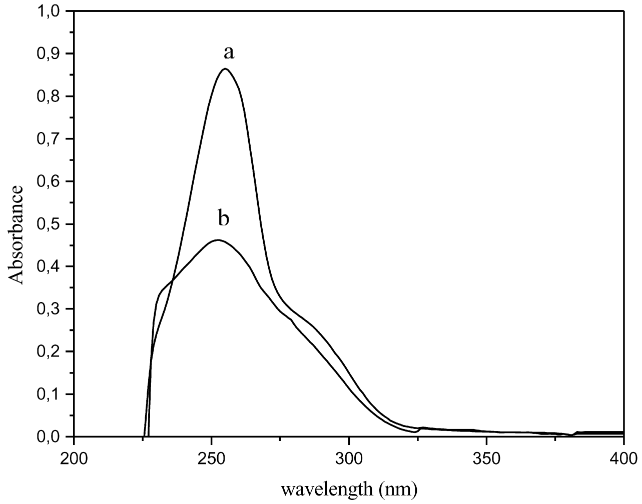


Fig. 1. Absorption spectra of PDA (4×10^{-5} mol l^{-1}) in CH_2Cl_2 before (a) and after 15 min irradiation (b).

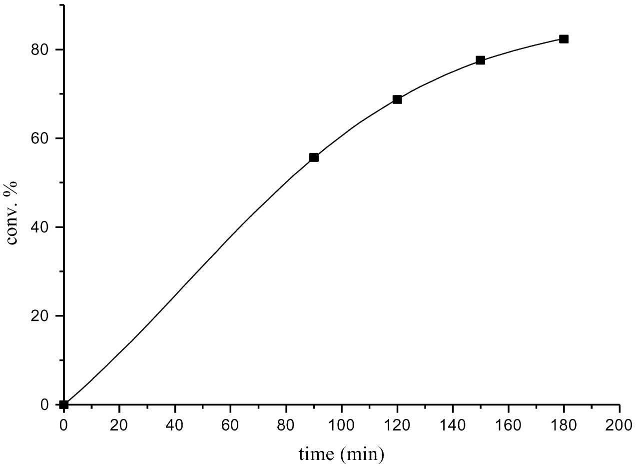


Fig. 2. Photopolymerization of CHO (9.88 mol l^{-1}) by using PDA (5×10^{-3} mol l^{-1}) at $\lambda > 300$ nm.

The precipitation of insoluble NaBr strongly shifts the two simultaneous equilibrium reactions towards the desired final product. The structure of the salt was confirmed by means of ^{1}H-NMR spectroscopy and elemental analysis. Simple anilinium salts are photochemically stable. Therefore, on using these compounds no polymerization takes place upon photolysis. However, incorporation of a chromophoric phenacyl moiety introduces photochemical activity to the salt. As can be seen from Fig. 1a, the absorption spectrum of PDA, exhibits an n–π^* absorption with a maximum at about 300 nm, characteristic of acetophenone derivatives.

The utilization of phenacyl anilinium salt as photoinitiator for cationic polymerization of several monomers was tested. As can be seen from Table 1, CHO readily polymerized upon irradiation of the monomer solution containing PDA at $\lambda > 300$ nm. As can be seen from Fig. 2, conversion to poly(cyclohexene oxide) increases linearly as the irradiation time increases and reaches to a limiting conversion after about 3 h irradiation. It should also be pointed out that PDA is thermally stable. A control experiment under identical conditions did not produce any precipitable polymer after heating monomer solution containing PDA at 70 °C for 3 h. Apart from CHO, BVE and NVC were also polymerized. Notably, strong electron donating monomer, NVC, polymerizes more efficiently.

Table 1
Photopolymerization of various monomers in the presence of PDA (5×10^{-3} mol l^{-1}) at room temperature. $\lambda > 300$ nm

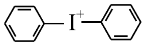
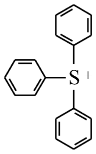
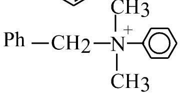
Run	Monomer (mol l^{-1})	Time (min)	Conversion (%)	$M_n{}^a \times 10^{-3}$
1	CHO (9.88)	180	82.4	3.7
2	CHO^b (9.88)	180	75.4	5.0
3	NVC^c (2.07)	30	87.9	47.9
4	BVE (7.72)	150	30.0	11.7

[a] Determined by GPC.
[b] In the presence of 2,6-di-*t*-butyl-4-methyl pyridine.
[c] In CH_2Cl_2.

For the sake of comparison, results obtained with triphenylsulphonium salt, diphenyliodonium salt and structurally related benzyl anilinium salt are shown in Table 2. Notably, diphenyliodonium salt also initiated the polymerization of CHO, but at a much lower rate due to the weak absorption at $\lambda > 300$ nm. On the other hand, triphenylsulphonium salt is inefficient since it is completely transparent at the irradiation wavelength. It is also interesting to note the inefficiency of benzyl anilinium salt indicating the importance of chromophoric phenacyl moiety for successful polymerization. These results indicate that PDA is manifestly superior to the commercially available onium type photoiniators as far as initiation efficiency at wavelengths above 300 nm where commercial lamp emits light is concerned.

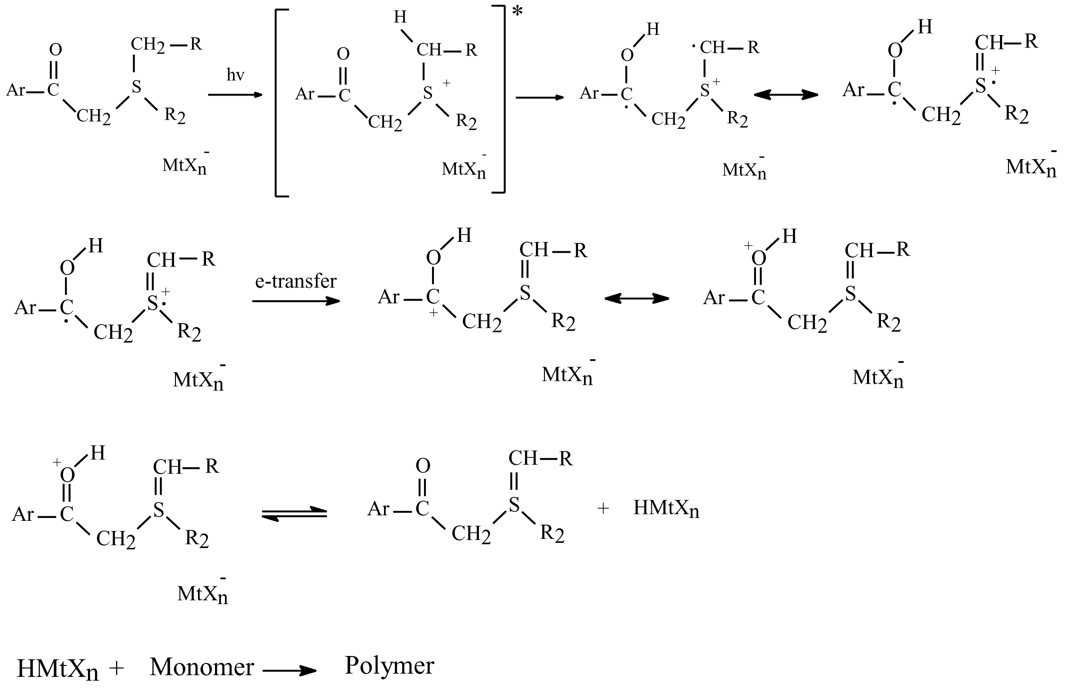
The photoinitiation of cationic polymerization by the corresponding phenacylsulphonium salts was proposed to proceed

Table 2
Photopolymerization of CHO (9.88 mol l^{-1}) by using various salts at room temperature. $\lambda > 300$ nm, [Salt] = 5×10^{-3} mol l^{-1}, time = 180 min

Salt	Conversion (%)	$M_n{}^a \times 10^{-3}$
PDA	82.4	3.7
 PF_6^-	46.6	11.4
 PF_6^-	0	–
 SbF_6^-	0	–

[a] Determined by GPC.

via a reversible process [19]. The intramolecular hydrogen abstraction of photo excited salt from the carbon atoms neighbouring sulphur atom is followed by internal electron transfer. Subsequent deprotonation gives a sulphur ylide and a protonic acid, which initiates the polymerization (Scheme (2)).



(6)

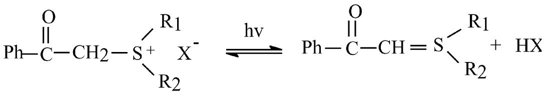
(7)

(8)

(9)

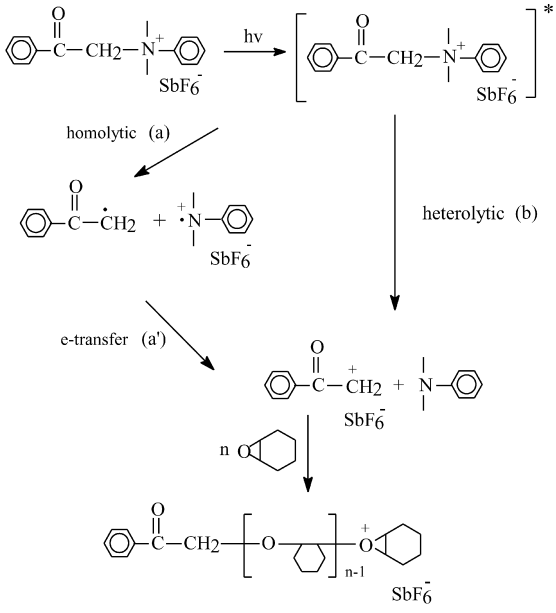
Scheme 2.

First, we considered that the same mechanism also implies for the initiation by the anilinium salt, since it is structurally similar and there are hydrogen atoms adjacent to positively charged nitrogen atom available for the hydrogen abstraction by the excited carbonyl. In our case, when the irradiation was carried out in the presence of 2,6-di-*t*-butyl-4-methyl pyridine, which is known to act as a proton scavenger, the polymerization was not affected (Table 1, runs 1 and 2). As mentioned before the overall mechanism described for the sulphonium salts is essentially reversible and in the absence of monomers, the ylides rapidly react with the protonic acid to afford the starting salt (reaction (10))



$$\mathrm{Ph{-}C(=O){-}CH_2{-}S^+(R_1)(R_2)\ X^-} \overset{h\nu}{\rightleftharpoons} \mathrm{Ph{-}C(=O){-}CH{=}S(R_1)(R_2)} + \mathrm{HX} \qquad (10)$$

Whereas the phenacyl anilinium salts undergo an irreversible photolysis leading to fragmentation of the photoinitiator (Scheme 3, Fig. 1b). Based on these results, the following mechanism for the initiation of the polymerization by the phenacyl anilinium salts is suggested. Electronically excited PDA may undergo heterolytic cleavage (reaction (12b)) resulting in the formation of phenacylium cations capable of initiating cationic polymerization. Similar photodecomposition mechanism was proposed by Tsunooka and coworkers [22–25] who used phenacyl ammonium salts having dimethyldithiocarbamates as photobase generators. It is also feasible that homolytic cleavage (reaction (12a)) followed by the intermolecular electron transfer (reaction (12a′)) essentially yields the same species. It should be also noted that termination can occur by the reaction of the growing chain with dimethyl aniline.



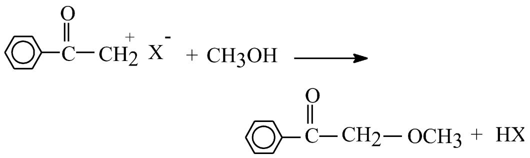
(11)

(12)

(13)

Scheme 3.

Further support for the initiation by phenacylium cations was obtained by analyzing photolysis products in methanol in the absence of a monomer. Notably, GC–MS detection of *N*,*N*-dimethyl aniline ($m/z = 121$) and phenacylmethyl ether ($m/z = 150$) formed according to reaction (14) and its deprotonated products ($m/z = 149$) confirms the proposed mechanism



(14)

In conclusion, the preliminary results show that, upon irradiation, phenacyl anilinium salt is capable of initiating cationic polymerization of appropriate monomers such as CHO, BVE and NVC. Although the present state of knowledge does not permit any conclusions on the exact nature of the initiation mechanism, it is clear that UV irradiation of PDA yields reactive phenacylium cations. Further studies concerning the effect of substituents at the anilinium moiety on the initiator activity together with the use of various photosensitizers in conjunction with the anilinium salt for the initiation of cationic polymerization are now in progress.

Acknowledgements

The authors would like to thank Istanbul Technical University, Research Fund and Turkish State Planning Association (DPT) for financial support.

References

[1] Pappas SP. In: Allen NS, editor. Photopolymerization and photo imaging science and technology. London: Elsevier, 1991.
[2] Davidson S. Exploring the science, technology and applications of U.V and E.B. curing. London: SITA Technology Ltd, 1999.
[3] Dietliker K. Chemistry and technology of UV and EB formulation for coating, inks and paints, vol. III. London: SITA Technology Ltd, 1991.
[4] Crivello JV, Lam JHW. J Polym Sci, Polym Chem Ed 1980;18:2677.
[5] Crivello JV, Lam JHW. J Polym Sci, Polym Chem Ed 1980;18:2967.
[6] Crivello JV, Lam JHW. Macromolecules 1979;10:1307.
[7] Yagci Y, Yildirim S, Onen A. Macromol Chem Phys 2001;202:527.
[8] Onen A, Yagci Y. Polymer 2001;16:6681.
[9] Yagci Y, Kornowski A, Schnabel W. J Polym Sci, Polym Chem Ed 1992;30:1987.
[10] Reetz I, Bacak V, Yagci Y. Polym Int 1997;43:27.
[11] Denizligil S, Yagci Y, McArdle C. Polymer 1995;36:3093.
[12] Denizligil S, Resul R, Yagci Y, McArdle C, Fouassier JP. Macromol Chem Phys 1996;197:1233.
[13] Yagci Y, Reetz I. Prog Polym Sci 1998;23:1485.
[14] Schumann H. Chem Zeitung 1984;108:209.
[15] Meier K, Zweifel H. J Imag Sci 1986;30:174.
[16] Meier K, Zweifel H. J Radiat Curing 1986;13:28.
[17] Schnabel W. Macromol Rapid Commun 2000;21:628.
[18] Crivello JV, Kong S. Macromolecules 2000;33:825.
[19] Crivello JV, Kong S. Macromolecules 2000;33:833.
[20] Nakano S, Endo T. J Polym Sci, Polym Chem Ed 1995;33:505.
[21] Onen A, Yagci Y. Macromolecules 2001;34:7608.
[22] Tachi H, Tsunooka M. J Photopolym Sci Technol 1999;12:313.
[23] Tachi H, Shirai M, Tsunooka M. J Photopolym Sci Technol 2000;13:153.
[24] Tachi H, Yamamoto T, Shirai M, Tsunooka M. J Polym Sci Polym Chem 2001;39:1329.
[25] Tsunooka M, Tachi H, Yamamoto T, Shirai M. Polym Preprints 2001;42:720.