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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Abu-Abdoun, I. I. and Ledwith, A. (1998) 'Polymerization Induced by N,N,N',N''Tetraphenyl-p-phenylenediamine Cation Radical Salts', *Journal of Macromolecular Science, Part A*, 35: 4, 673 – 690

To link to this Article: DOI: 10.1080/10601329808002005

URL: <http://dx.doi.org/10.1080/10601329808002005>

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POLYMERIZATION INDUCED BY N,N,N',N'TETRAPHENYL-p-PHENYLENEDIAMINE CATION RADICAL SALTS

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ABSTRACT

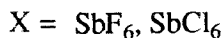
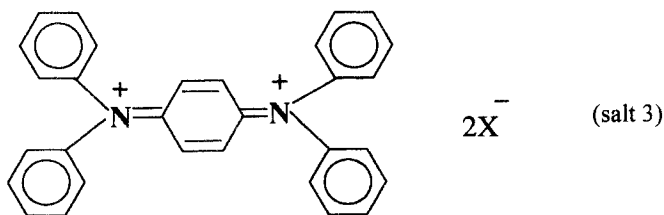
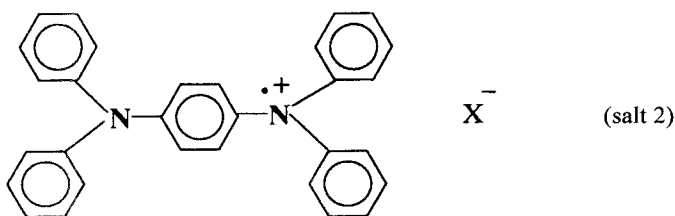
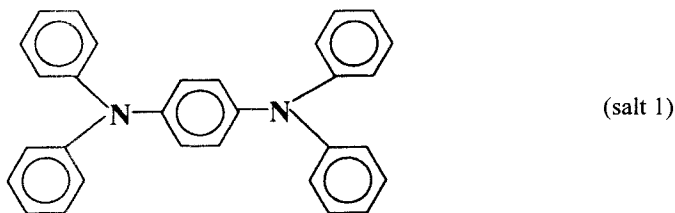
Cation radical and dication of N,N,N',N'tetraphenyl-p-phenylenediamine (TPDA) having SbF_6^- or SbCl_6^- counterion were synthesized by chemical oxidation and characterized. These salts were shown to be useful initiators for the cationic polymerization of cyclohexene oxide, tetrahydrofuran and N-vinylcarbazole. The dication salt is more reactive than the cation radical salt. The calculated propagation rate constant (K_p) for polymerization of cyclohexene oxide by the cation radical and dication salts ($X^- = \text{SbF}_6^-$) of TPDA where, 2.71×10^2 and $5.51 \times 10^2 \text{ M sec}^{-1}$, respectively.

INTRODUCTION

Thermally stable onium salts, such as diaryliodonium ($\text{Ar}_2\text{I}^+\text{X}^-$) and triarylsulfonium salts ($\text{Ar}_3\text{S}^+\text{X}^-$) with low nucleophilic complex metal halide anions such as, SbF_6^- are well established photoinitiators for the cationic polymerization of epoxide and vinyl monomers [1, 2].

Previously, we reported on the synthesis and applications of phosphonium and arsonium salts for the photoinitiated cationic polymerization of cyclohexene oxide, p-methyl styrene and styrene [3, 4]. Recently, we [5] reported that N-substituted phenothiazine cation radical salts can initiate the cationic polymerization of cyclohexene oxide (CHO), tetrahydrofuran (THF) and n-vinyl carbazole (NVC) photochemically and thermally, depending on the salt chemical structure.

Photoinduced electron-transfer reactions between benzyl alcohol and the electrochemically generated cation radical of TPDA (1), causes the oxidation of alcohol into benzaldehyde and reduction of the cation radical to neutral diamine [6]. We have prepared salts (2) and (3), by chemical oxidation in a good yield. As far as we know, there is no previous report on the use of these salts as polymerization initiators, this paper describes the use of salt 2 and 3 for the polymerization of N-Vinyl carbazole, cyclohexene oxide and tetrahydrofuran.



EXPERIMENTAL

Materials

Monomers cyclohexene oxide, tetrahydrofuran and N-vinyl carbazole were obtained commercially (Aldrich) and purified conventionally. Solvents dichloromethane, carbon tetrachloride, diethylether (Aldrich) were dried over calcium hydride and distilled before use. p-Diiodobenzene, diphenylamine, potassium carbonate, copper powder, n-dodecane (Aldrich) were used without further purification. Melting points are uncorrected.

Spectroscopic Measurements

Ultraviolet spectra were obtained on a Unicam SP1800 Ultraviolet spectrophotometer. Infrared spectra were recorded using potassium bromide (KBr discs) with a Perkin-Elmer grating infrared spectrophotometer (Model 577). NMR spectra were taken in CDCl_3 , on a Perkin-Elmer 60 MHz Spectrometer (Model R12B) using deuterated solvents with tetramethylsilane as the internal standard.

Polymerization Procedure

The selected amounts of the monomer and initiator in dichloromethane were placed in a 15 mm diameter Pyrex tube, the solution degassed under vacuum by conventional freeze thaw techniques and sealed off under vacuum. Photopolymerization was carried out using a Rayonet merry-go-round photoreactor with 350 nm lamps, or a 250 Watt medium pressure mercury lamp with interference filter fixed at 25 cm distance from the lamp. After the irradiated time the reaction mixtures were transferred to a water bath at 50°C in case of THF polymerization. Cyclohexene oxide polymerization reaction tubes were placed in a holder and irradiated for the required period while immersed in a water bath at 25°C. The polymer was precipitated in methanol, filtered, dried and weighed. The polymer yield and the rate of polymerization were determined gravimetrically [3]. The number averaged molecular weight, (M_n) of the polymer was measured in toluene on a Hewlett Packard, Model 501 High Speed Membrane Osmometer. The gel permeation chromatograms were obtained with styragel columns (Waters), using a Waters Associates Model 200 GPC at 25°C, using toluene as eluent, flowing at the rate of 1 ml/min and a polymer concentration of 1 mg/ml. Molecular weights were calculated with reference to polystyrene standards.

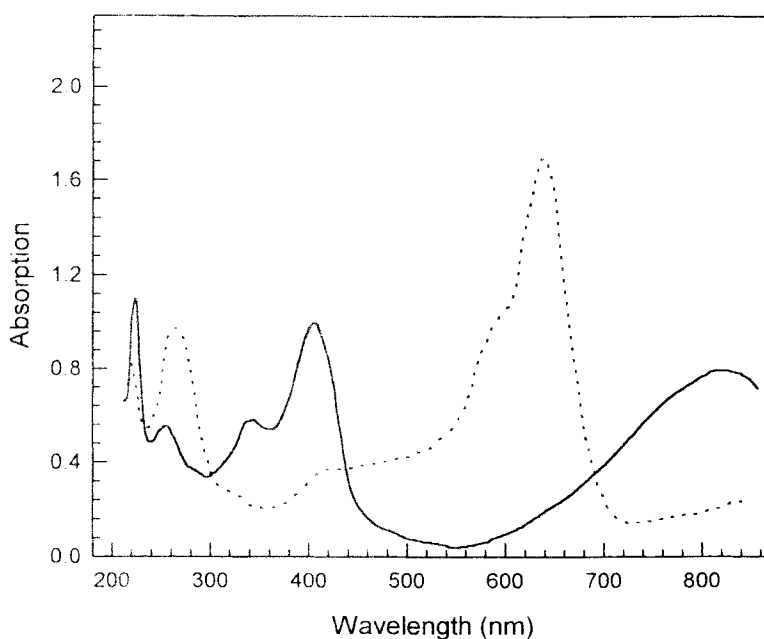


Figure 1. Absorption spectrum of salts 2 and 3 in CH_2Cl_2 , $\text{X} = \text{SbF}_6$
 ——— 2 - - - - 3

RESULTS AND DISCUSSION

Synthesis

*N,N,N',N'*Tetraphenyl-*p*-phenylenediamine (1) was synthesized in good yield by the procedure of Fox [7], with some modifications. Cation radical dication salts were obtained by chemical oxidation and characterized. U.V. visible spectra of the cation radical (2) and dication (3) in dichloromethane are shown in Figure 1.

*N,N,N',N'*Tetraphenyl-*p*-phenylenediamine (1)

A mixture consisting of 6.6 g (0.02 mol) of *p*-di-iodobenzene, 16.9 g (0.1 mol) of diphenylamine, 4.0 g of potassium carbonate 0.1 g of copper powder and 20 ml of *n*-dodecane was heated in a three-necked flask equipped with a mechanical stirrer, nitrogen inlet and a condenser. The reaction mixture was flushed with nitrogen for approximately 30 minutes initially, after that time, the temperature rose slowly to reflux for 12 hours while stirring. The resulting mixture was cooled, filtered and the residue dissolved in toluene, dried over magnesium sulfate, and the

solvent removed. Crystallization of the residue from isopropyl alcohol-water resulted in two fractions which were isolated. Ethanol was added to the insoluble fraction and heated to reflux for one hour. The hot solution was then filtered, and the collected fraction was dried under vacuum to give a white crystalline material. Yield was about 60%, melting point was 187-188°C (literature [7] (187-188°C) correspond to the following $C_{30}H_{24}N_2$.

Elemental analysis: Calcd. for $C_{30}H_{24}N_2$, C = 87.35% ; H = 5.86 % .

Found C = 86.83 % ; H = 5.84%.

Bis(N,N,N',N'Tetraphenyl-p-phenylenediamine) (Salt 2), X = SbF₆

0.416 gram from a dry powdered silver hexafluoroantimonate ($AgSbF_6$), was dissolved in 10 ml dry dichloromethane by stirring magnetically for 10 minutes in a three-necked flask equipped with magnetic stirrer and nitrogen inlet. When all the silver salt dissolved, 0.5 g of the diamine compound (1) dissolved in 10 ml of dry dichloromethane was added dropwise over a few minutes. The reaction turned a deep green color and was stirred for a further 15 minutes. This was then cooled in a dry ice-acetone bath; 0.225 g of resublimed iodine in 10 ml sodium dried ether was added over a 5 minute period, then the mixture was stirred for a further 20 minutes and left to cool to room temperature. The resulting solution was precipitated into 100 ml cooled dry diethyl ether, washed several times with ether and dried at room temperature in a vacuum oven, yield 70%. The salt consisted of fine green needle-shaped crystals, melting point was 256-258°C. The salt produced is soluble in dichloromethane, acetonitrile, acetone and alcohol, but insoluble in diethyl ether, carbon tetrachloride and hexane. Its stability was surprising in the dark and in laboratory conditions, even in very dilute solution. U.V/visible spectrum in dichloromethane (Figure 1) shows λ_{max} 405 was $4.4 \times 10^4 \text{ cm}^{-1}\text{M}^{-1}$, $\log \epsilon = 4.64$

Elemental analysis: Calcd. for $C_{30}H_{24}N_2SbF_6$, C = 55.58% ; H = 3.73% ; N = 4.93.

Found C = 54.64% ; H = 3.75% ; N = 4.16.

Bis (N,N,N',N' Tetraphenyl-p-phenylenediamine) Dication (Salt 3), X = SbF₆

In a three-necked round bottomed flask equipped as described earlier, was added 0.835 gm of silver hexafluoroantimonate, dissolved in 15 ml CH_2Cl_2 by stirring magnetically for about 10 minutes. 0.5 g of the neutral diamine (1) in 5 ml dichloromethane was added slowly. Reaction was instantaneous and the deep blue colored reaction mixture was left stirring for about 10 minutes, then cooled in a dry ice-acetone bath and 0.45 gm resublimed iodine in 20 ml sodium dried ether was

added dropwise over about 5 minutes. When the addition was complete, the reaction mixture was left to warm to room temperature. The salt was isolated as described before; the deep blue fine crystalline salt was isolated after drying. Yield about 50%, m.p. = 246-248°C decomposed. Figure 1 shows the U.V/visible spectrum in CH_2Cl_2 λ_{max} 900 nm, 645 nm; shoulders 595, 405 nm. $\epsilon_{635 \text{ nm}} = 3.66 \times 10^4 \text{ cm}^{-1}\text{M}^{-1}$; $\log \epsilon = 4.56$.

Elemental analysis: Calcd. for $\text{C}_{30}\text{H}_{24}\text{F}_{12}\text{N}_2\text{Sb}_2$, C = 40.85% H = 2.74%.
Found C = 40.65% ; H = 2.83%.

Bis(Tetraphenyl-p-phenylenediamine) Dication (Salt 4), X = SbCl₆

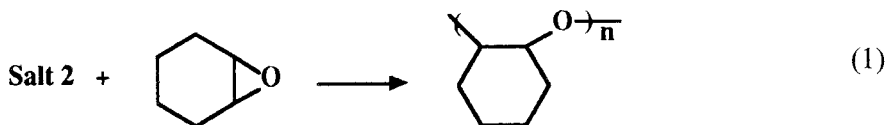
Tetraphenyl-p-phenylenediamine, 1.0 g, was dissolved in dry dichloromethane 10.0 ml and a solution of antimony pentachloride 3.6 ml 50/50 by volume $\text{CH}_2\text{Cl}_2/\text{SbCl}_5$ in 5.0 ml CH_2Cl_2 was added slowly. The color of the reaction mixture changed from deep green to deep blue after the addition was complete. After stirring magnetically for about 10 minutes, the reaction mixture was poured into a four-fold excess of dry diethyl ether, filtered and washed several times with ether and dried under vacuum, at room temperature. The fine dark blue crystals were stored under vacuum in the dark. Yield about 70%, melting point was 135-137°C, λ_{max} in CH_2Cl_2 at 645 nm, ϵ_{max} was $3.7 \times 10^4 \text{ cm}^{-1}\text{M}^{-1}$, $\log \epsilon_{645} = 4.56$; shoulder at 595, 405 nm.

Elemental analysis: Calcd. for $\text{C}_{30}\text{H}_{24}\text{Cl}_{12}\text{N}_2\text{Sb}_2$, C = 33.30%; H = 2.23%.
Found C = 33.70% ; H = 2.32%.

Polymerization

Polymerization of Cyclohexene Oxide

To examine the photo stability of these salts, polymerization was carried out under normal laboratory light, in the dark and photochemically by irradiation from mercury lamp at 25°C, under the following conditions: monomer concentration was 0.988 M, initiator concentration was $2.15 \times 10^{-4}\text{M/l}$, in CH_2Cl_2 , polymerization was carried out at 25°C.



The results of polymerization under laboratory conditions are compared with polymerization in the dark and the results are shown in Figure 2. This shows the rate of polymerization is faster at laboratory light compared to the dark reactions.

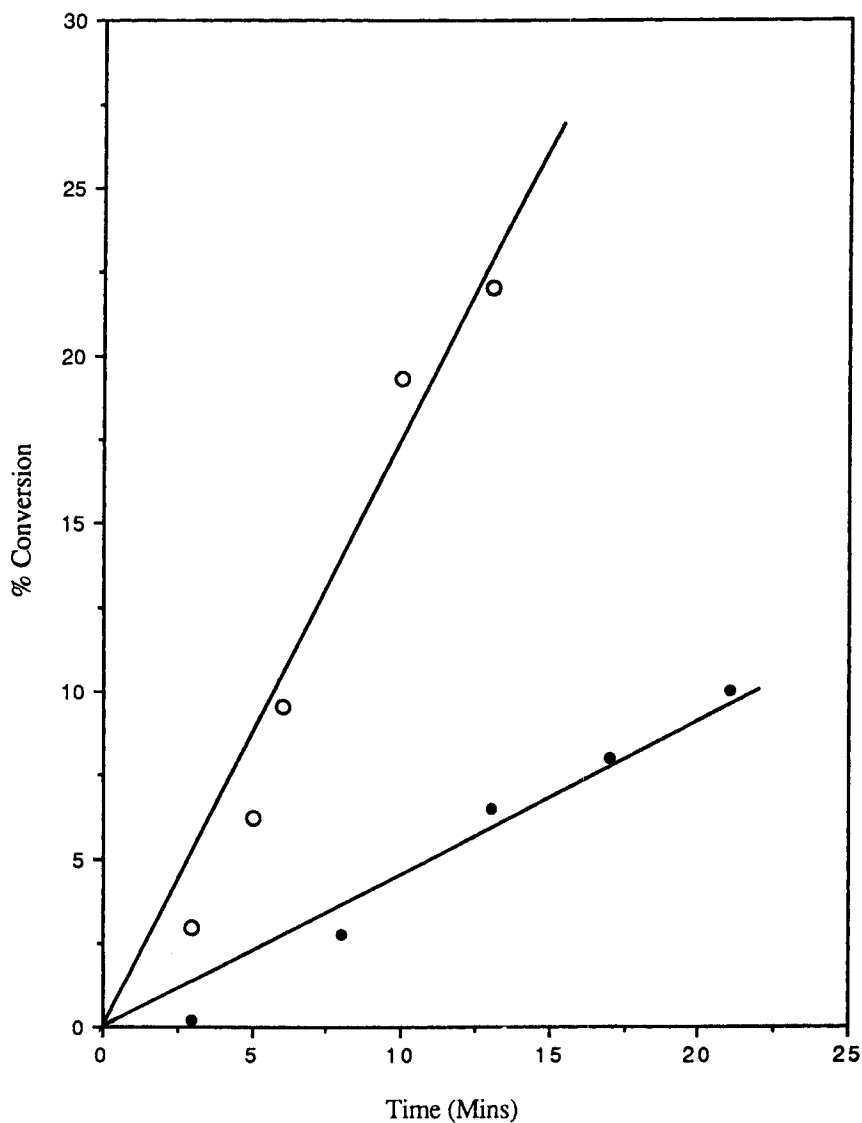


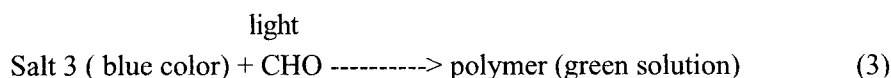
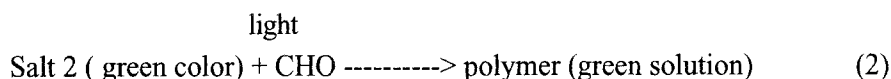
Figure 2. Polymerization of cyclohexene oxide by salt (2)
[M] = 0.988 M, [I] = 2.15×10^{-4} M

○ In lab. light ● In the dark

The color of the reaction mixture was green and did not change during the reaction period.

Photochemical induced polymerizations by irradiation from mercury lamp were carried out at 25°C. The reaction mixtures were irradiated by means of a 250 Watt medium pressure mercury lamp at 25 cm distance.

Thermal Polymerization of cyclohexene oxide initiated by salts and 2 and 3 was carried out under the same conditions, and the results are shown in Figure 3. It is clear that the polymerization rate is enhanced by exposure to light. Polymerization initiated by the dication (salt 3), $X = \text{SbF}_6^-$, showed a faster rate of initiation compared to initiation by cation radical (salt 2), having the same counterion. The color of the reaction mixture changed from blue to green as the initiator was injected into the monomer.



The effect of the counter ions (SbF_6^- and SbCl_6^-) on the polymerization of cyclohexene oxide was examined in a series of experiments using salt ($X = \text{SbCl}_6^-$). No polymer formation observed after 70 minutes, salt concentration of 2.15×10^{-4} M. However; the color of the reaction mixture was changed from blue to a green color within two minutes from injection of the salt solution into the monomer.

To examine the effect of salt concentration on the polymerization reaction initiated by salt 2, polymerization was initiated by low salt concentration, so that difficulties arising from slow initiation equilibria and side reactions were virtually eliminated.

We have examined the change in concentration of the cation radical (green color) resulting from salt 3 (blue color) during the polymerization of cyclohexene oxide using UV absorption spectroscopy. In one experiment the UV absorption of the reaction mixture [cyclohexene oxide and dication] in CH_2Cl_2 at 405 nm was measured at 100% conversion to polymer. The salt absorption at λ_{405} was 2.3. For the cation radical ϵ_{405} was $4.4 \times 10^4 \text{ cm}^{-1} \text{ mol}^{-1}$, substituting these values in Beer's law, we have; $2.3 = 4.4 \times 10^4 \times C \times L$, the concentration of the green color (C) was found to be 5.5×10^{-5} M. The initial concentration of salt 3 ($X = \text{SbF}_6^-$) in the reaction mixture was 9.0×10^{-5} M, the % concentration of the green colored species is $5.5 \times 10^{-5} / 9.0 \times 10^{-5} \times 100 = 61\%$, which correspond to dication salt consumption.

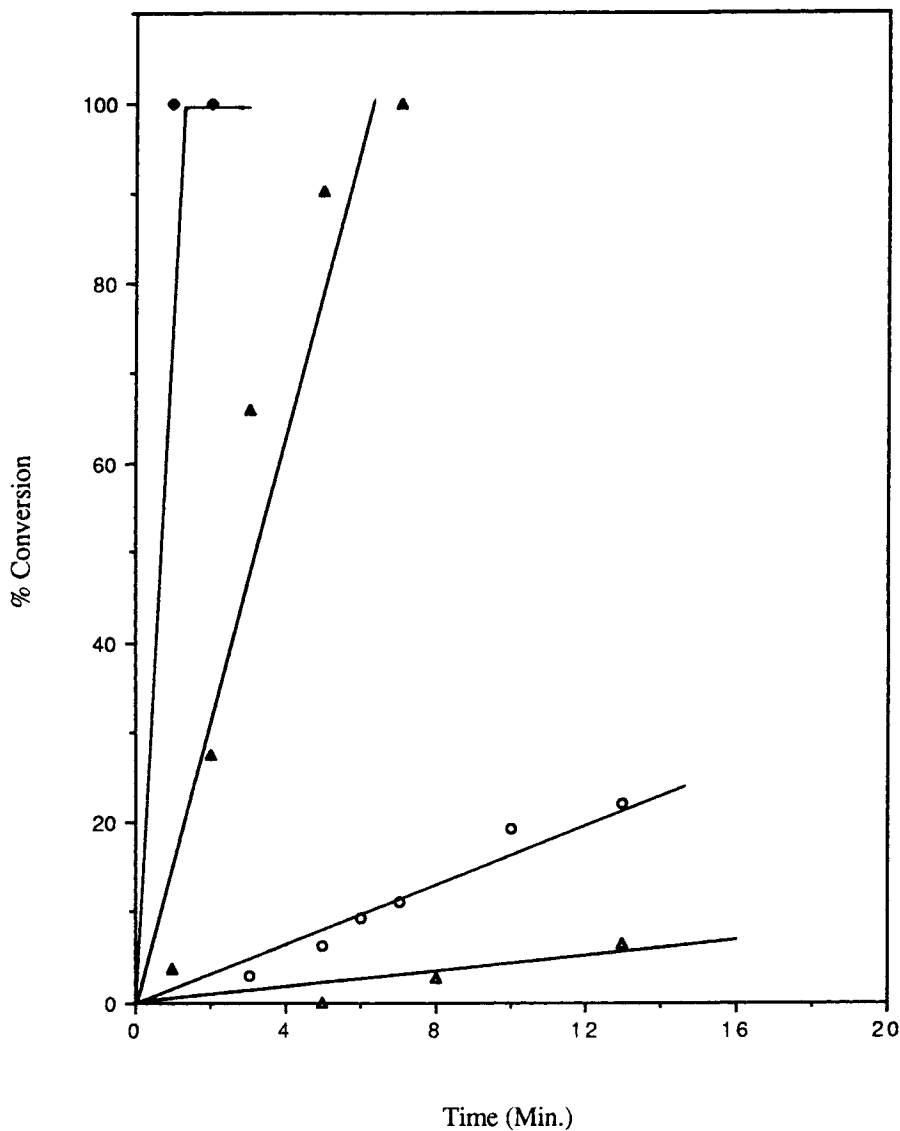


Figure 3. Polymerization of cyclohexene oxide initiated by salts 2 and 3
 $[M] = 0.988 \text{ M}$, $[I] = 9.0 \times 10^{-5} \text{ M}$, ($X = \text{SbF}_6$).

Salt 2 \blacktriangle Hg Lamp \circ Lab. light \triangle Dark, \blacksquare Salt 3

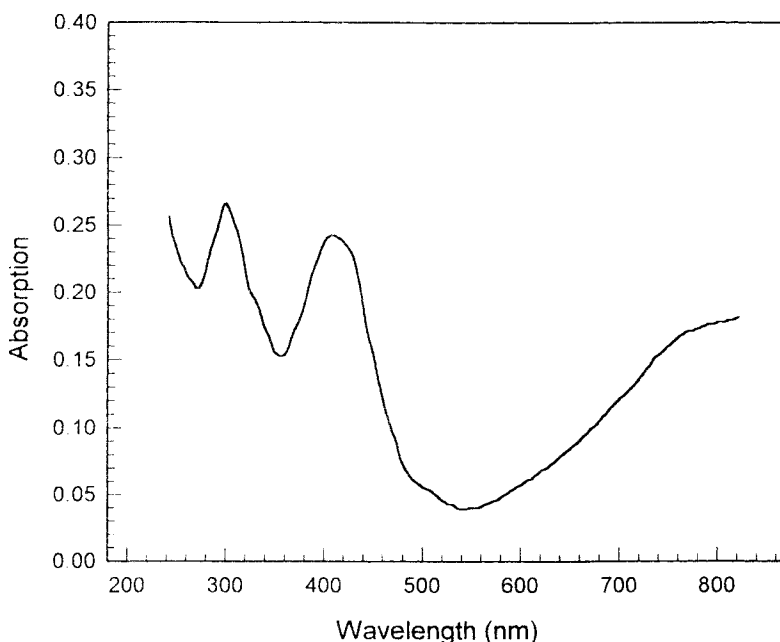


Figure 4. Atypical absorption spectra of the reaction mixture of salt 3 and cyclohexene oxide, $[M] = 0.988 \text{ M}$, $[I] = 9.0 \times 10^{-5} \text{ M}$, in CH_2Cl_2

The absorption spectra of the reaction mixture is shown in Figure 4, and of the polymer obtained after several reprecipitations from acetone is shown in Figure 5. The number average molecular weight (M_n Osmometry) in this experiment was found to be $2.84 \times 10^4 \text{ g per mole}$.

Effect of Salt 3 Concentration on the Rate of Polymerization

The effect of variation in the concentration of salt 3 ($X = \text{SbF}_6^-$) on the polymerization of cyclohexene oxide at a fixed time of 2 minutes was studied. Monomer concentration was 0.988 M , in dichloromethane at 25°C . The polymerization was carried out under normal laboratory light. The relationship between the concentration of the initiator and the % conversion to polymer is shown in Figure 6. It is clear that the rate of polymerization (R_p) is a direct function of the concentration of the initiator.

The conversion to polymer increases with the salt concentration and with irradiation time, while the molecular weight of the isolated polymer decreases with increase in the salt concentration, as shown in Table 1. A green colored reaction mixture was obtained as the salt was injected into the monomer.

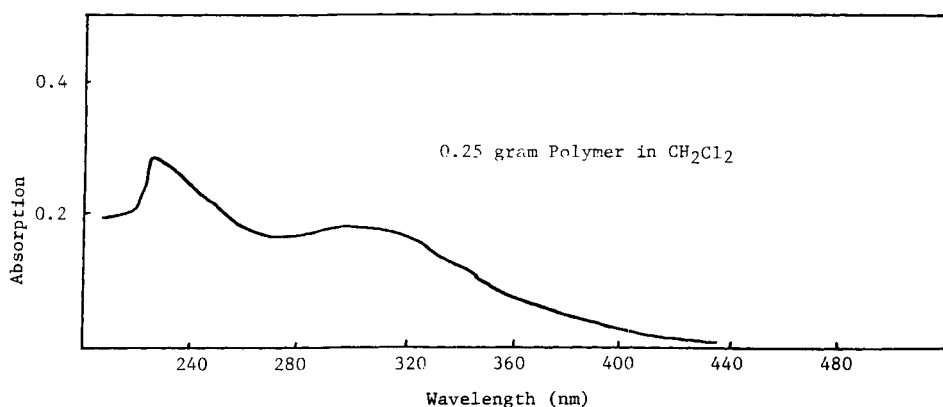
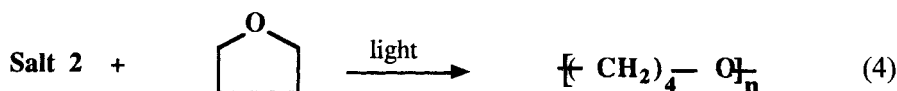


Figure 5. Absorption spectra of poly(cyclohexene oxide) in CH_2Cl_2 polymerized by salt 3 after 5 times reprecipitation in acetone, (conc. = 0.25 g polymer in 5 ml CH_2Cl_2).

Polymerization of THF (Bulk) Initiated by Salt 2

The reaction mixtures were irradiated by a 250 Watt medium pressure mercury lamp for 20 minutes, then transferred to a water bath at 50°C in the dark for the time indicated. Salt 2 was used at concentration was 6.17×10^{-4} M, The results are shown in Figure 7.



Thermal polymerization was carried out for the comparison with photopolymerization reactions by salt 2. These reaction mixtures were transferred to a water bath at 50°C and left in the dark for 11.0 hours. The % conversion of the recovered polymer was 4.5 %, while in the case of photopolymerization 5.2 % conversion obtained after two hours. In both experiments, the color of the reaction mixtures did not change in either the photo or the thermal polymerization reactions.

Polymerization of THF by salt 3 ($\text{X}^- = \text{SbF}_6^-$) was carried out in the dark and, the salt concentration was 2.26×10^{-4} M. The reaction mixture was left for 150 minutes in water bath at 50°C , 4.0% conversion was obtained, the number average molecular weight (M_n) of the recovered polymer was 6.8×10^{-4} . Figure 8 shows the absorption spectrum of the irradiated reaction mixture of salt 2 and THF

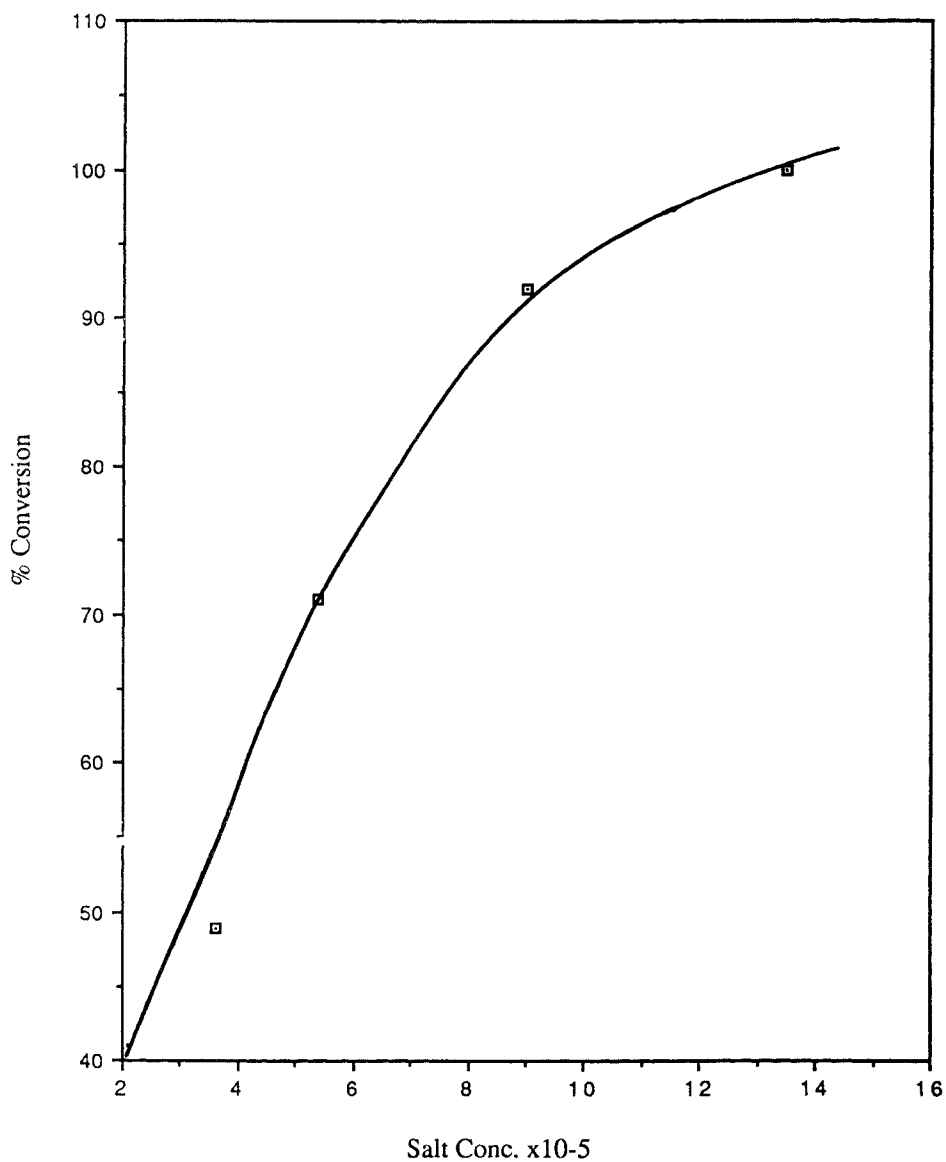


Figure 6. Thermal polymerization of cyclohexene oxide initiated by salt (3), ($X = \text{SbF}_6$). Initiator concentration effect, Time = 2 minutes, $[M] = 0.988 \text{ M}$.

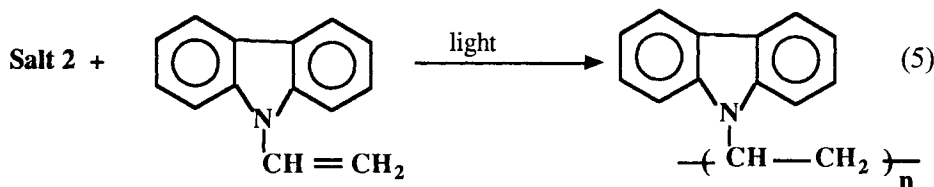
TABLE 1. Effect of Salt 3 ($X^- = \text{SbF}_6^-$) Concentration on Polymer Molecular Weight Polymerization Reaction Time = 2 Minutes

[Initiator]x10 ⁵ M	M _n x 10 ⁻⁴ g/mol
3.60	4.72
5.50	3.00
9.00	2.73
13.50	2.27

before precipitation in methanol. The color of the reaction mixture changed to green within a few minutes from mixing.

Photo Polymerization of N-vinylcarbazole Initiated by Salt 2

The results of photocopolymerizations of N-vinylcarbazole by salt 2 are shown in Figure 9, The reaction mixtures were irradiated by a 250 Watt medium pressure mercury lamp as described before.



Molecular weights of the polymer obtained were determined by gel permeation chromatography (GPC) and the results are shown in Table 2. It is clear that M_n of the polymer recovered increases with increasing the reaction time. No change in the reaction mixture color was observed.

The polymerization of N-vinyl-carbazole initiated by salt 2 was studied using different sources of light and reaction conditions. The concentration of the monomer and initiator were as described in Figure 9. Polymerization time was fixed at 10 minutes, the results obtained are given in Table 3.

The absorption spectrum of the reaction mixture (5) irradiated by the Hg lamp unfiltered is shown in Figure 10. An increase in the absorption of the reaction mixture at λ_{max} 825 nm was observed, which could be due to the formation of the cation radical of N-vinylcarbazole.

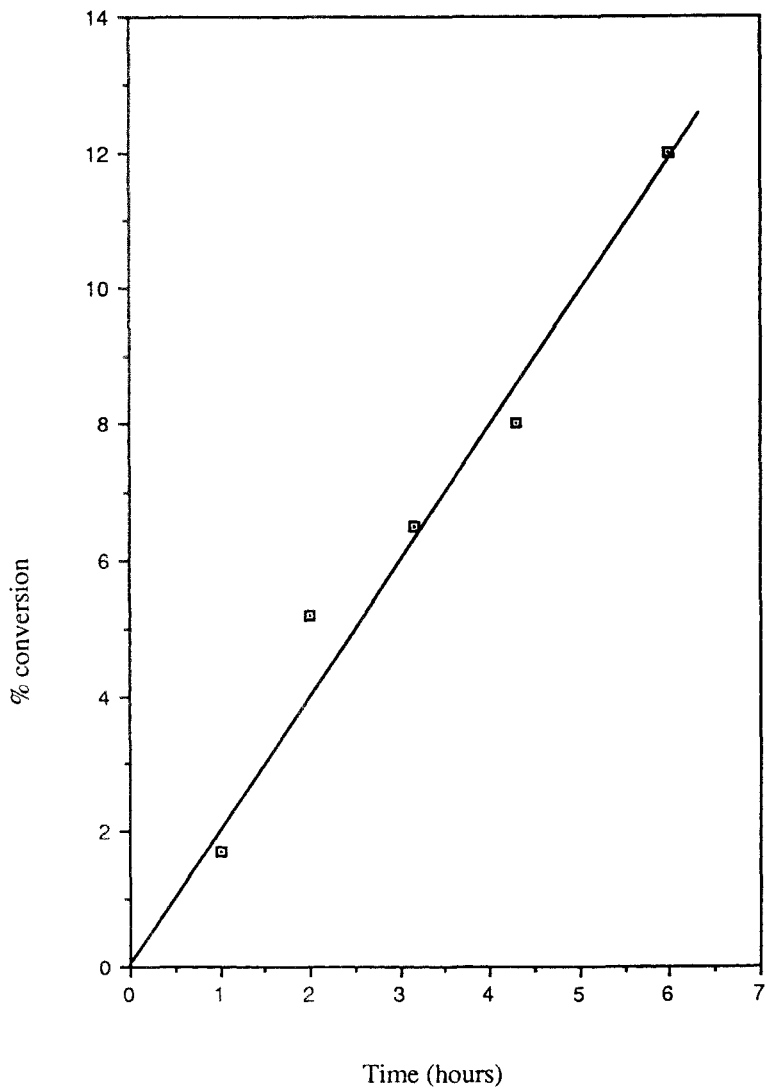


Figure 7. Photoinduced polymerization of THF (Bulk), initiated by salt 2 $[I] = 6.17 \times 10^{-4}$ M at 25°C. Irradiation time = 20 minutes.

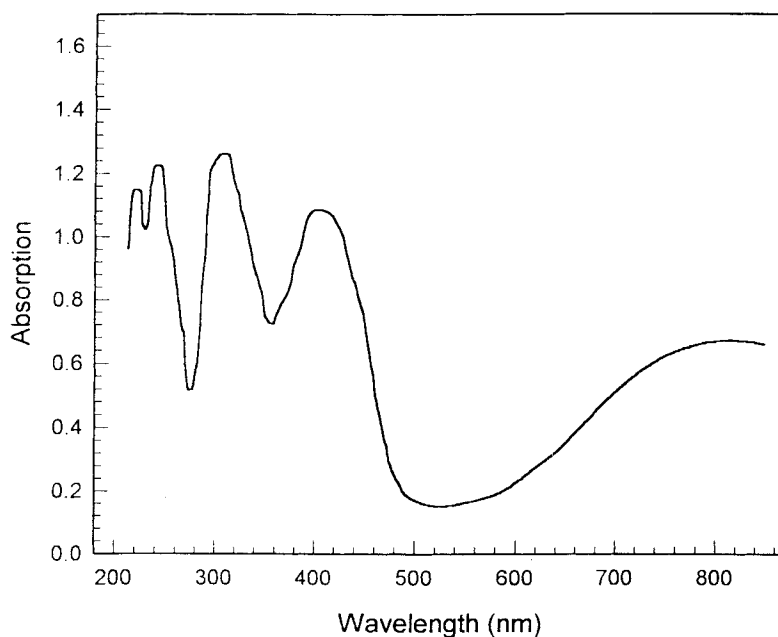


Figure 8. Absorption spectrum of the photochemical reaction mixture THF + salt 2.

In the case of photoinitiation by these salts ($X = \text{SbF}_6^-$), where very fast initiation and no termination is assumed, this enables the kinetics of polymerization to be simplified and the propagation rate constant (K_p) to be determined, using the following equation: $R_p = K_p [m_o][C_o]$, where; R_p is the rate of polymerization, $[m_o]$ and $[C_o]$ are the initial monomer and initiator concentrations, respectively.

Calculated (K_p) for polymerization of cyclohexene oxide initiated by cation radical (salt 2) is $2.71 \times 10^2 \text{ M sec}^{-1}$, and by the dication (salt 3) is $5.51 \times 10^2 \text{ M sec}^{-1}$, these values are in a reasonable agreement with expectations considering the relative reactivities of cyclohexene oxide and the initiator functionality.

CONCLUSIONS

Cation radical and dication salts of tetraphenyl-p-phenylenediamine can be used as cationic initiators for the polymerization of epoxide and vinyl monomers. Polymerization initiated by the dication salt salts showed rate twice as fast compared

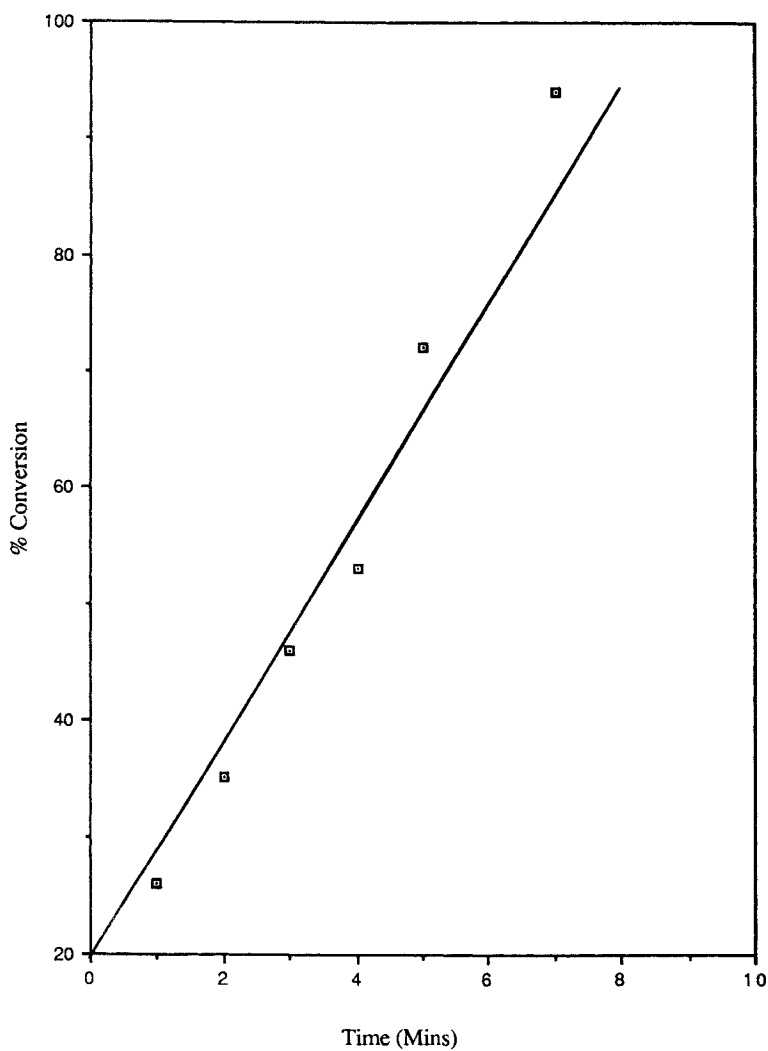


Figure 9. Photopolymerization of N-Vinylcarbazole initiated by salt 2 $[M] = 0.262 \text{ M}$, $[I] = 2.86 \times 10^{-5} \text{ M}$, in CH_2Cl_2 at 25°C . Using Hg Lamp (unfiltered) at 25 cm distance from reaction.

TABLE 2. Effect of Polymerization Time on Polymer Number Average Molecular Weight (M_n)

% Conversion	$M_n \times 10^{-5} \text{ g/mol}$
35.0	1.35
46.0	1.52
72.0	1.74

TABLE 3. Polymerization of N-vinyl Carbazole by Salt 2, Time = 10 Minutes, [M] = 0.262 M, [I] = 2.86×10^{-5} M, at 25°C, Solvent was Dichloromethane

Light Source	% Conversion	Remarks
Hg Lamp 440 nm filter	zero	only salt absorbed
dark	zero	-
Hg lamp 365 nm filter	46	only monomer absorbed
Hg lamp unfiltered	100	monomer and salt absorbed

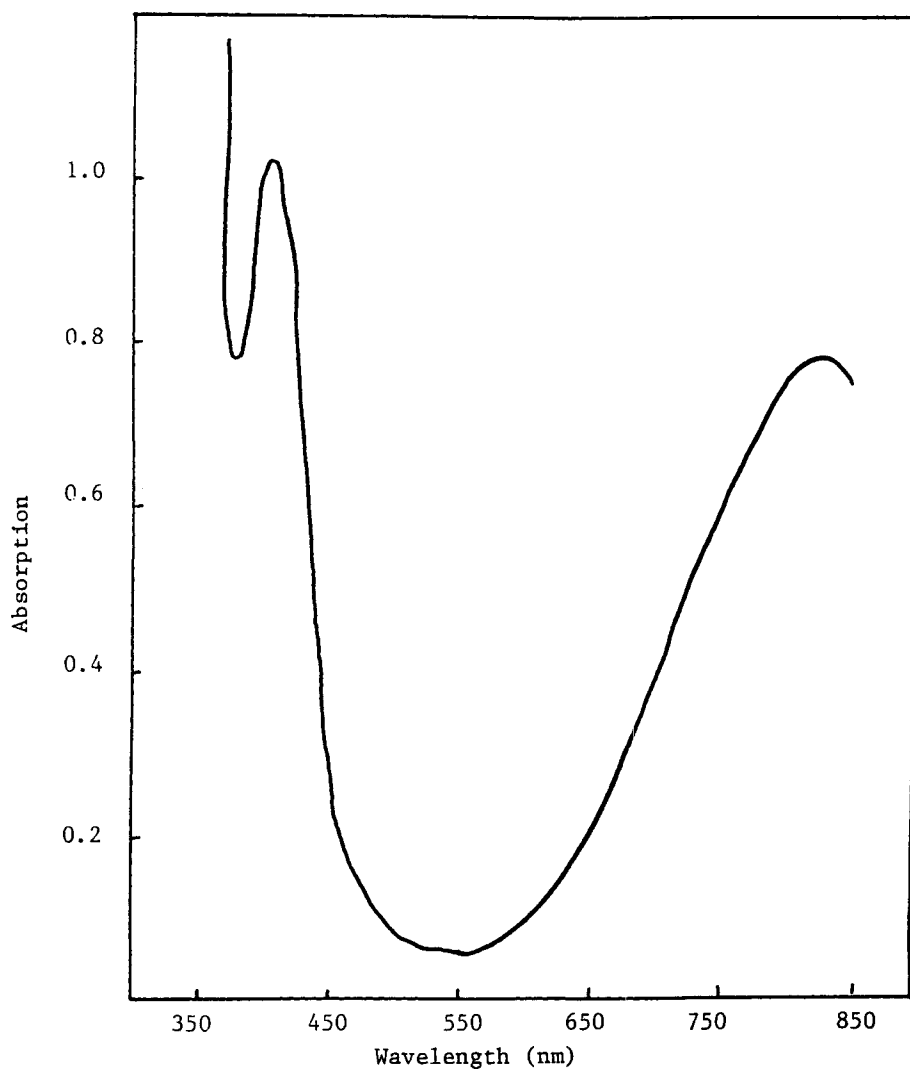


Figure 10. Absorption spectrum of the photochemical reaction mixture NVC + salt 2.

to that initiated by the monocation radical having the counterion (SbF_6^-). Photolysis of the reaction mixture enhanced the rate of polymerization.

ACKNOWLEDGEMENTS

This work was completed in the Department of Chemistry, University of Liverpool, whose support is gratefully acknowledged. I. Abu-Abdoun is also grateful for support from KFUPM.

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Received June 5, 1997

Revision received December 1, 1997