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Diphenyldiselenide As Novel Non–salt Photoinitiator for Photosensitized Cationic Polymerization of N-Vinyl Carbazole

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Summary: Photoinitiated cationic polymerization of N-vinyl carbazole (NVC) with diphenyldiselenide (DPDS) as an initiator and aromatic nitriles such as dicyanonaphthalene (DCN) and dicyanoanthracene (DCA) as sensitizer was studied at $\lambda > 290$ nm in CH_2Cl_2 solvent using single electron transfer (SET) reactions in this investigation. Aromatic nitriles were found to be effective photosensitizer in initiating polymerization at wavelength $\lambda > 290$ nm where DPDS ($\lambda_{max} = 246$ nm) do not absorb. However, the DPDS works well as an initiator with both DCN and DCA. An initiation mechanism is also proposed that involves the formation of selenium radical cation as actual initiating species. Upon photoirradiation, these radical cations are formed by single electron transfer between the excited singlet state sensitizer and the ground state of DPDS.

Keywords: cationic polymerization; diphenyldiselenide; N-vinyl carbazole; photoelectron transfer reaction; photopolymerization

Introduction

Enhanced research activity for cationic polymerization has been centered towards the design and synthesis of novel photo polymerization system due to increasing commercial and technical applications[1–3]. Onium salt initiated cationic polymerization is performed below 300 nm that limits its practical applications[4–7], therefore it is required to extend the spectral sensitivity to high wavelength (>300 nm) region where medium and high-pressure mercury lamp emits most spectrum of their radiation. This problem can be solved either by chemical attachment of chromophoric group to the initiator or by using photosensitization process. The latter process is convenient and more applicable as compare to incorporation of chromophore. A photosensitization includes photoelectron transfer (PET) either with photo-excited sensitizer[8–11], free radical[12,13] or with electron donor compounds in the excited charge transfers complexes[14]. Single electron transfer (SET) induced generation of radical ions and their synthetic potential is an emerging concept in organic synthesis [15]. Diselenides with aromatic nitriles are well-known photosensitization system for *in situ* generation of electrophilic selenium species in selenenylation reactions[16]. However, the same methodology was used to study the photo polymerization of N-vinyl carbazole (NVC). The present article describes the use of diphenyldiselenide (DPDS) as non-salt initiator for photosensitized cationic polymerization of NVC. To the best of our knowledge with existing literature, the present system is a novel photosensitization system for cationic polymerization.

Experimental

Materials

N-vinylcarbazole (NVC) (Aldrich) was recrystallized twice from ethanol, thor-

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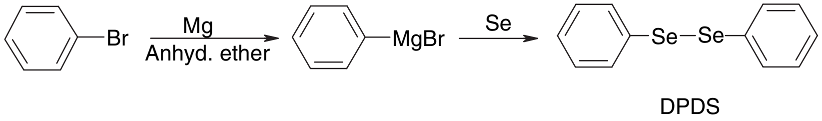


Scheme 1.
Synthesis of DPDS.

oughly dried under vacuum and used freshly. Dichloromethane (CH_2Cl_2) purified by usual methods [17] and doubly distilled over CaH_2 before use. Anthracene, naphthalene, bromine, cuprous cyanide (CuCN), N, N-dimethyl formamide (DMF), copper sulphate ($CuSO_4$), dioxane, acetonitrile, and diethyl ether were purchased from Merck (India), purified by usual methods and used.

Synthesis of Diphenyl Diselenide (DPDS)

It was synthesized according to literature method [18] as shown in Scheme 1: Yield: 75%, bright yellow crystals Mp: 62–64 °C. Elemental analysis: calcd. for $C_{12}H_{10}Se_2$: C, 46.13; H, 3.2. Found: C, 46.12; H, 3.2. IR (Nujol) 3020 (Ar C–H Str.), 1600, 1500, 1461,1400 (Ar C–H bending), 823, 757 cm^{-1}. ^{I}H NMR (200 MHz, $CDCl_3$): δ: 7.57 (m, 2H, Ph), 7.22 (m, 3H, Ph) ppm.

Synthesis of 1,4-Dicyanonaphthalene (DCN)

It was synthesized in two steps as shown in Scheme 2.

a. Synthesis of 1,4-Dibromonaphthalene (DBN)

It was synthesized according to literature method [19].Yield: 67% 19.05 g, slight orange needle crystals, Mp: 82–83 °C (observed). Elemental analysis: calcd for $C_{10}H_6Br_2$: C, 41.95; H, 2.1; Br, 55.94. Found: C, 41.82; H, 2.2; Br, 55.89. IR (Nujol) 3030 (Ar C–H Str.), 1600, 1500, 1463 (Ar C–H bending), 850 cm^{-1}. ^{I}H NMR (200 MHz, $CDCl_3$): δ: 8.16 (m, 2H, Ph), 7.56 (m, 4H, Ph) ppm.

b. Synthesis of 1,4-Dicyanonaphthalene (DCN)

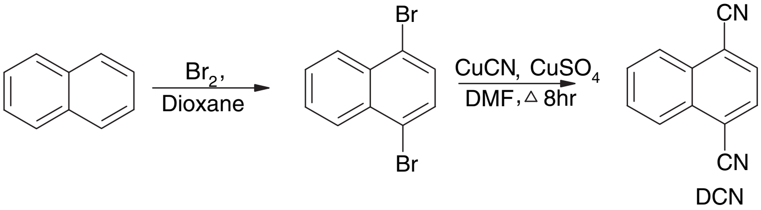
It was synthesized according to literature method [20] by using the above precursor molecule (DBN). Yield: 32%, White crystalline needles, Mp: 208–210 °C. Elemental analysis: calcd for $C_{12}H_6N_2$: C, 80.89; H, 3.1; N, 15.73. Found: C, 80.93; H, 3.2; N, 15.73. IR (Nujol) 3030 (Ar C–H Str.), 2225 (C≡N Str.), 1600, 1500, 1463 (Ar C–H bending), 850 cm^{-1}. ^{I}H NMR (200 MHz, $CDCl_3$): δ: 8.32 (m, 2H, Ph), 7.98 (m, 4H, Ph) ppm.

Synthesis of Dicyanoanthracene (DCA)

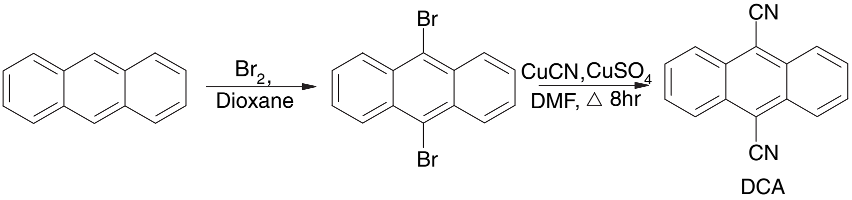
It was synthesized in two steps as shown in Scheme 3.

c. Synthesis of 9,10-Dibromoanthracene (DBA)

The method was exactly same as that employed for DCN in Scheme 2. Yield: 69%, Mp: 222–223 °C (observed). Elemental analysis: calcd for $C_{14}H_8Br_2$: C, 50.00; H, 2.3; Br, 7.61. Found: C, 49.53; H, 2.4; Br,



Scheme 2.
Synthesis of DCN.



Scheme 3.
Synthesis of DCA.

47.57. IR (Nujol) 3030 (Ar C–H Str.), 1600, 1580 1461 (Ar C–H bending), 840 cm^{-1}. ^{I}H NMR (200 MHz, $CDCl_3$): δ: 8.57 (s, 4H, Ph), 7.63 (s, 4H, Ph) ppm.

d. Synthesis of 9,10-Dicyanoanthracene (DCA)

It was synthesized by using the above precursor molecule (DBA). It was synthesized similar manner to DCN. Yield: 37% Mp: 338 °C. Elemental analysis: calcd for $C_{16}H_8N_2$: C, 84.30; H, 3.5; N, 12.20. Found: C, 84.20; H, 3.6; N, 12.23. IR (Nujol) 3030 (Ar C–H Str.), 2362, 2212 (C≡N Str.), 1622, 1500, 1463 (Ar C–H bending), 763 cm^{-1}. ^{I}H NMR (200 MHz, $CDCl_3$): δ: 8.51 (m, 4H, Ph), 7.88 (m, 4H, Ph) ppm.

General Procedure for Photo Polymerization of NVC

A mixture of monomer (NVC, 390 mg, 2 mM), initiator (DPDS, 6 mg, 0.02 mM) and 0.02 mM of sensitizer (DCN/DCA: 3.6/4.6 mg) was placed in Pyrex ampoule containing small magnetic stirrer, degassed for 30 minutes followed by the addition of freshly dried dichloromethane. Three freeze-pump-thaw cycles were performed in order to make the reaction contents free of dissolved gases. Finally, the reaction mixture was irradiated in a Pyrex vessel at a distance of 8 cm from the 450 W Hanovia (medium pressure) lamp using quartz–jacketed immersion well in combination with a Pyrex filter at RT. After running the reaction certain period of time the polymer was precipitated with 10-fold excess of methanol, washed, and dried at room temperature under vacuum. It was then characterized for molecular weight analysis by size exclusion chromatography (SEC) and ^{1}H NMR respectively.

Characterization

Molecular weight was measured by GPC in chloroform as eluent (flow rate: 1 ml/min) on a setup consisting of a pump and six Ultra Styragel column (50 to 10^5 Å porosities) and detection was carried out with the aid of UV-100 and RI-150 detector. Molecular weight (M_n) and polydispersities (M_w/M_n) were determined using a calibration curve obtained by polystyrene standards from PSS Germany. ^{1}H NMR spectra were recorded on a Brüker 200 MHz instrument with $CDCl_3$ as the solvent and tetramethylsilane as internal standard. IR spectra were recorded on a Perkin–Elmer model 683 grating IR spectrometer. UV/Vis spectra were taken on a Shimadzu UV - 2550 spectrophot-

Table 1.
Free energy estimation of photosensitization process

Sensitizer	$E_{0,0}$$^{a)}$ (eV)	$E_{1/2}$$^{redb)}$ (eV)	$\Delta G_{ET}$$^{c)}$ (Kcal. /mol)	Photosensitization possible
DCN	3.45	−1.28	−18.90	Yes
DCA	2.88	−0.89	−14.75	Yes

a) singlet state energy of sensitizers.
b) half wave reduction potential (vs standard calomel electrode).
c) Free energy change of sensitizers.

ometer in solid state. Elemental analysis was performed on a Carlo Erba CHNS - O analyzer instrument.

Results and Discussion

The sensitizer and initiator were well synthesized and characterized as mentioned in experimental section. Their structures were determined by NMR & IR spectroscopy beside elemental analysis; both initiator and sensitizers are stable in presence of air and moisture. Polymers were characterized by GPC and ^{1}H NMR spectra. Fig. 1 depicts UV absorption spectra of DCN, DCA and NVC. Fluorescence quenching of sensitizer, i.e., DCN ($\lambda_{max} = 320$ nm, $\lambda_{em} = 391$ nm) and DCA ($\lambda_{max} = 430$ nm, $\lambda_{em} = 461$ nm) by initiator, DPDS, follows the Stern-Volmer relation.

Fluorescence quenching in these cases occurs *via* the single electron transfer (SET) mechanism involving the charge transfer (CT) stabilized exciplex. The Weller equation [21] that describes the thermodynamics of the interaction (i.e., free energy change (ΔG_{ET})) between the photosensitizer and the initiator during single electron transfer photosensitization is given by equation 1 as,

$$\Delta G_{ET} = E^{ox}_{1/2}[D] - E^{red}_{1/2}[A] - E_{o,o} \qquad (1)$$

Here $E^{ox}_{1/2}[D]$ is the oxidation potential of the DPDS (donor), $E^{red}_{1/2}[A]$ is the reduction potential of the acceptor (DCN & DCA) and $E_{o,o}$ is the singlet excited state energy of sensitizer species. Putting the literature values of oxidation potential of DPDS, [22] reduction potential, and excitation energy [23] of DCN and DCA involved in equation 1 gives the free energy value of the photosensitization system utilized in the study. The negative value of free energy was obtained in both cases, which suggest that photosensitization is possible with the DPDS/DCA and DPDS/DCN system respectively.

Polymerization

The objective of the present study was to develop a novel photosensitization system based on non-salt initiator for cationic polymerization in the near UV and Visible region of light. It is well known fact that both DCN and DCA absorb at longer wavelength region (>290 nm) and initiates DPDS to generate selenium cation radi-

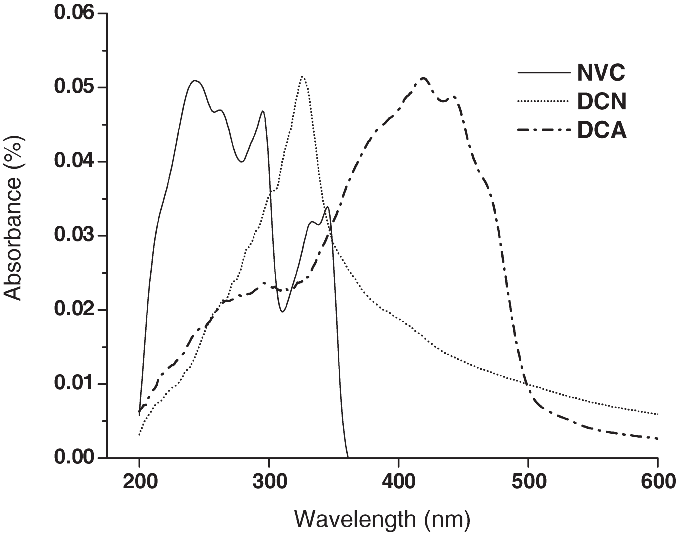
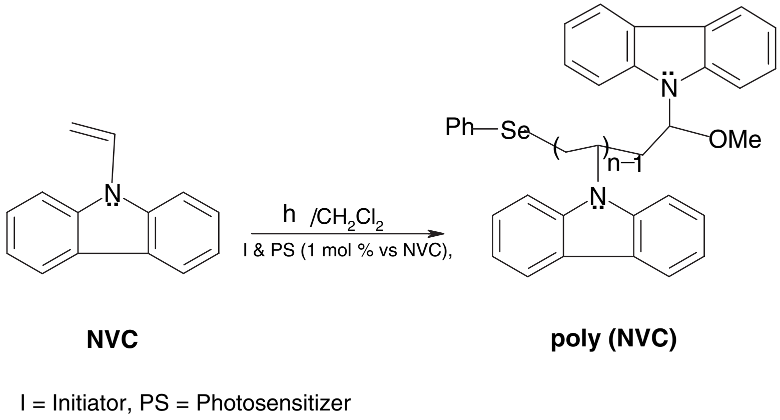


Figure 1.
Electronic absorption spectrum of sensitizer (DCN, DCA) and monomer (NVC).



Scheme 4.
Photopolymerization of NVC.

cal.[16] Moreover, desired reactions products resulted when the various α-olefins add to this formed selenium radical cation.[16,24] We have employed this concept of photochemical generation of selenium radical cation in photopolymerization of NVC at RT in CH_2Cl_2 as shown by Scheme 4. The mole ratios of various components involved is given as [NVC]: [DPDS]: [Sensitizer] = 100: 1: 1.

In both cases, the reaction was quenched at regular time intervals (3, 6, 10, and 15 h) in 10-fold excess of methanol as precipitating solvent. Table 2 shows the results of the photopolymerization of NVC at different intervals of time. It seems the rate of polymerization is very fast as seen by 50 % conversion reached in just 3 h. The molecular weight reached after running the reaction for 15 h with DCN/DPDS and DCA/DPDS was 21,200 and 11,800. However, the monomer conversion (run number 4) was higher in case of DCN/DPDS as compared to DCA/DPDS with relatively lower polydispersity (2.1).

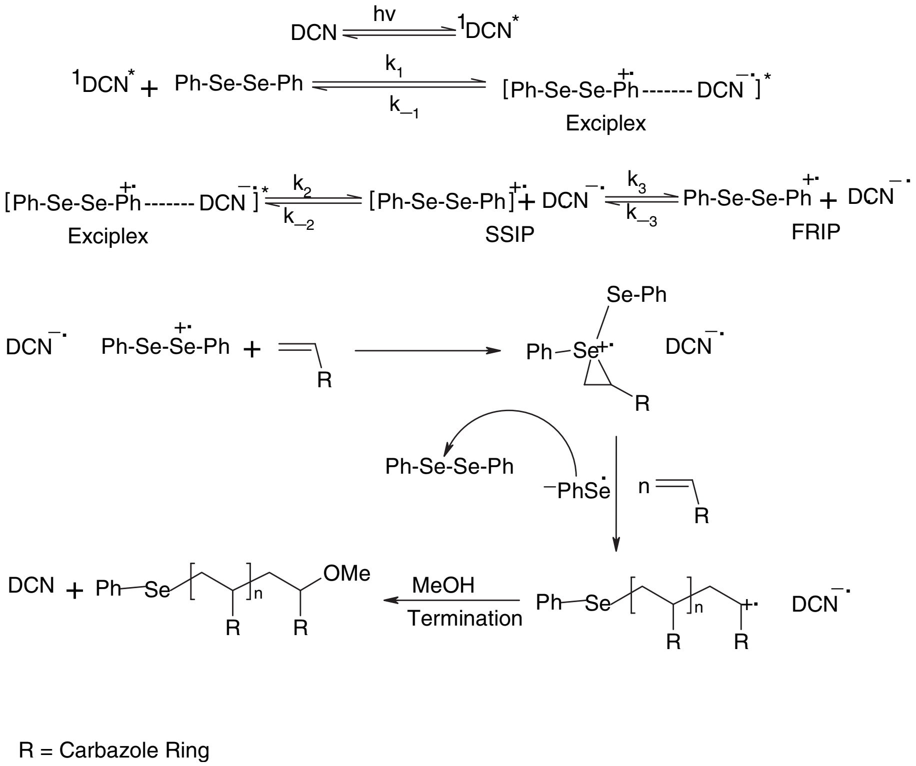
The higher activity of DCN/DPDS system as compared to DCA/DPDS system could be ascribed to the formation of free radical ion pair (FRIP), which in turn is attributed to better exciplex formation between initiator and sensitizer upon photoirradiation (Scheme 5).

Fig. 2 and 3 show GPC eluograms of 3 hr and 15 hr for DCN/DPDS and DCA/DPDS system respectively. The GPC eluograms show that there is a low molecular weight hump, which is observed after 15 h in DCA/DPDS system. However, a low molecular weight hump that was present in DCN/DPDS system at 3 h has got disappeared at 15 h of reaction. The hump during the reaction could be due to the two different active species prevailing at the time of initiation out of which one got dead and other continued to grow with time, whereas initial hump might be because of an impurity within the system. The nature and type of such reaction is a speculation to

Table 2.
Photosensensitized cationic polymerization of NVC[a] with DPDS

Run	Sensitizer	Time (h)	Conv[b] (%)	$M_{n,SEC}$[c] ($\times 10^{-3}$)	PDI[d]
1	**DCN**	3	55	8.4	1.6
2		6	62	15.0	1.8
3		10	68	17	1.9
4		15	80	21.2	2.1
5	**DCA**	3	47	3.6	1.7
6		6	51	7.6	2.2
7		10	59	11.5	2.6
8		15	62	11.8	2.7

[a] [NVC] = 2 M in CH_2Cl_2.
[b] gravimetric.
[c] obtained from SEC.
[d] Calibrated using PS standards with $CHCl_3$ as eluent.



Scheme 5.
Mechanism of photocationic polymerization of NVC.

the observation seen from our experimental results.

However, few controlled experiments were performed for 3 hr in order to examine the activity by DPDS/DCN system, viz., (a) The polymerization of NVC in dichloromethane at RT was performed with DPDS but without sensitizer (DCN), (b) the polymerization of NVC in dichloromethane and (c) the polymerization of

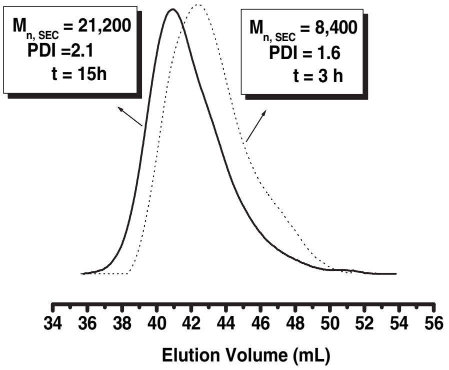


Figure 2.
GPC eluograms of pNVC where, [NVC] = 2M in CH_2Cl_2. [NVC]: [DPDS]: [**DCN**] = 100:1:1.

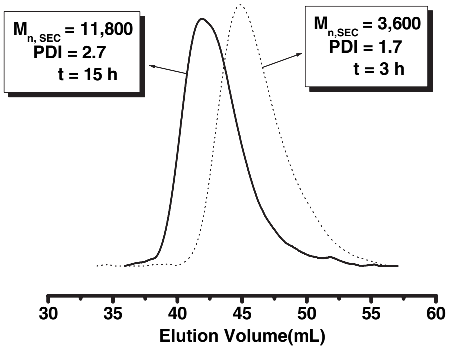


Figure 3.
GPC eluograms of pNVC where, [NVC] = 2M in CH_2Cl_2. [NVC]: [DPDS]: [**DCA**] = 100:1:1.

NVC in dichloromethane with sensitizer and without DPDS. White turbidity appeared in first two cases whereas clear solution was seen in case 'c' during precipitation of reaction mixture in cold methanol. The mother liquor consisting the white turbidity was evacuated and sample submitted for ^{1}H NMR analysis. The ^{1}H NMR spectrum resembles the peaks due to monomer (NVC) and not the polymer. In addition, no polymer peak was seen in RI detector during GPC analysis therefore, no polymer in controlled experiments. Thus, the aforementioned observation with obtained experimental data plus favorable free energy of photosensitization supports our strategy for cationic polymerization of NVC at RT.

Mechanism of Photoreaction

A plausible mechanism for the photosensitized cationic polymerization of NVC with DPDS and DCN as a representative example is illustrated in Scheme 5. The mechanism of photosensitization using DCN or DCA with DPDS system was reported by G Pandey *et al*.[24] It was shown that the reactivity of PhSe. radical towards π bond is low because of faster rate of radical recombination reactions [25] that is reversible in nature. [26] This clearly indicates that electrophilic selenium radical cation acts as true species in initiating the cationic polymerization of NVC. The mechanism involves selenium radical cation [16] which is the actual initiating species that is formed by single electron transfer from ground state initiator to excited state sensitizer upon photo-irradiation and reacts with NVC to give corresponding radical cation, which further propagates the chain, by reacting subsequent NVC molecules with DCN$^-$. (less nucleophilic counter anion).

Conclusion

The present study proposed a combination of novel non-salt initiator (DPDS) along with different (DCN or DCA) sensitizer for the photocationic polymerization of NVC. The sensitizers and initiators were synthesized and well characterized. The polymer, pNVC, was formed with both sensitization systems but with relatively broader molecular weight distribution. However, it was found that molecular weight increases with time in both cases. Finally, a mechanism of photopolymerization occurring with selenium radical cation was proposed and found to fit our experimental results. Thus, our study proves that the present photosensitization system effectively initiates the cationic polymerization of NVC at RT.

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