

Polymerization of *N*-Vinylcarbazole by Multiwalled Carbon Nanotube

Arjun Maity, Mukul Biswas

Department of Chemistry, Presidency College, Kolkata, India

Received 15 August 2006; accepted 3 December 2006

DOI 10.1002/app.25958

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: *N*-vinylcarbazole (NVC) was polymerized in bulk or in toluene in presence of multiwalled carbon nanotube (MWCNT) without any extraneous catalyst. The formation of poly*N*-vinylcarbazole (PNVC) was endorsed by striking agreement of FTIR, fluorescence and UV-visible spectroscopic, thermogravimetric stability, differential scanning calorimetry, and dielectric characteristics of this polymer with the corresponding literature data for authentic PNVC samples prepared by free radical or carbocationic initiation. The polymerization was supposed to be initiated by a single electron

transfer between N lone pair of NVC and the electron deficient MWCNT moieties. While PNVC homopolymer is non-conducting (10^{-12} to 10^{-16} S/cm), a composite of PNVC with MWCNT isolated from the polymerization system showed high dc conductivity varying from 1.3 to 33 S/cm depending upon the extent of MWCNT loading in the composite. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 4121–4126, 2007

Key words: poly*N*-vinylcarbazole; multiwalled carbon nanotube; polymerization; spectroscopy; conductivity

INTRODUCTION

N-vinylcarbazole (NVC) is an interesting and potential monomer which is readily polymerized by free radicals from conventional initiator *N,N'*-azobis(isobutyronitrile) (AIBN). Carbocationic polymerization of this monomer was reported by numerous researchers.¹ A variety of Lewis acids such as FeCl₃, BF₃, AsF₃, POCl₃, AsCl₃, VOCl₃ metal salts, and oxides particularly those of 3d transition metal oxides, were explored to initiate NVC polymerization by carbocationic pathway means.¹

Electron transfer polymerization of this monomer with halogens² was studied extensively and formation of dark Würst cation radicals and of PNVC was suggested for chloranils³ and other charge transfer agents.² Several informative reviews are available on such polymerization processes.^{1,2}

More recently, various carbon allotropes such as carbon black (CB),⁴ acetylene black (AB)⁵ and buckminsterfullerene (BMF)^{6,7} were used to polymerize NVC monomer. Grafting of vinyl polymers with CB was reported by Tsubokawa et al. during free radical initiated polymerization of monomers in presence of

CB.^{8–10} Biswas et al. also reported initiation of NVC polymerization by CB, AB, and fullerene without any external oxidant vis-à-vis formation of PNVC-CB/AB composites with improved physical properties.^{4,5,7}

During recent times single and multiwalled carbon nanotubes (SWCNT and MWCNT) have attracted considerable research attention in the preparation of nanocomposites with various speciality and conventional polymers. These materials exhibit outstanding physicochemical and optoelectronic properties, typical of both CNT and the polymer moieties.^{11–20}

In this background, we have lately observed that MWCNT can also initiate the polymerization of NVC monomer and that it is possible to prepare a highly conducting composite of PNVC with MWCNT via this *in situ* polymerization. This article presents our results on the initiation of polymerization of NVC by MWCNT and relevant experimental investigations carried out in support of the formation of PNVC in the system. Some data will also be provided highlighting the improved conductivity values of the PNVC-MWCNT composite recovered from this polymerization system.

Correspondence to: M. Biswas (mukul_biswas@vsnl.net).

Contract grant sponsor: Department of Science and Technology (DST); contract grant number: SR/S5/NM-14.

Contract grant sponsor: Council of Scientific and Industrial Research (CSIR-UGC-NET); contract grant number: 8/155(18)/2003-EMR-I.

EXPERIMENTAL

Materials

MWCNT was purchased from Aldrich (Milwaukee, WI) and preheated at 120°C for 2 h in vacuum and then used to polymerize NVC. NVC (BASF, Germany) was recrystallized from *n*-hexane and stored in the dark

Journal of Applied Polymer Science, Vol. 104, 4121–4126 (2007)
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TABLE I
FTIR Bands of "C" and Standard PNVC Sample along with their Assignments

Systems	Observed peaks (cm ⁻¹)	Assignments	Reference
"C" obtained from MWCNT polymerization system	721	Ring deformation of substituted aromatic structure	This study
	745	>CH ₂ rocking vibration	
	1157	Out of plane deformation of vinylidene gr	
	1328	>CH ₂ deformation of vinylidene gr	
	1452	Ring deformation of NVC moieties	
	1624	C=C stretching vibration of vinylidene gr	
	2924	Aromatic C—H stretching vibration	
PNVC homopolymer	722	Ring deformation of substituted aromatic structure	[22]
	748	>CH ₂ rocking vibration	
	1220	Out of plane deformation of vinylidene gr	
	1329	>CH ₂ deformation of vinylidene gr	
	1447	Ring deformation of NVC moieties	
	1640	C=C stretching vibration of vinylidene gr	
	2968	Aromatic C—H stretching vibration	

before use. All other solvents and reagents were of AR grade and purified by standard method prior to use.

Polymerization of NVC by MWCNT and preparation of PNVC-MWCNT composite

A homogeneous mixture of 0.5 g of NVC and 0.5–0.75 g of MWCNT was taken in a conical flask and heated at 65°C for 1 h. THF was added to the reaction mixture and whole mass was added to an excess of MeOH. The separated blackish mass "A" was filtered and washed with boiling MeOH²¹ to remove any unreacted monomer and thereafter, again washed with acetone. The blackish mass "A" was dried at 70°C in vacuum for 3 h to constant weight and contained PNVC along with CNT.

In another procedure, 0.5 g of NVC was dissolved in 5 mL toluene in a 25 mL conical flask and 0.5–0.75 g of MWCNT was suspended in the medium. The reaction mixture was refluxed at 110°C for 5 h and thereafter, it was added to an excess of MeOH. The precipitated blackish mass "B" was processed as before.

The products "A" and "B" were refluxed finally in toluene and the solution yielded a white product "C" upon precipitation by MeOH which was subsequently characterized as PNVC.

It is relevant to point out that by repeated extraction with benzene it was possible to recover MWCNT quantitatively after the polymerization. This feature is significant considering the cost of the MWCNT.

Characterization and property evaluation

The FTIR spectrum of the white mass "C" obtained as above was taken on a JASCO-410 instrument in

pressed KBr pellet. The intrinsic viscosity [η] of the white product "C" was determined with an Ostwald viscometer in a benzene solution at 25°C. UV-visible and emission spectra for "C" were determined with a Hitachi U 3210 model spectrophotometer. Dielectric properties of PNVC homopolymers were recorded on LCR Hi-tester by using pellets at 5 ton pressure at 25°C. The pellet was silver coated and cured for 24 h before being used for measurement. Thermal stability was determined on a Shimadzu DT 40 instrument at a heating rate of 10°C per minute, sample mass = 4 mg in aerial atmosphere. Differential scanning calorimetric analyses of "C" were performed on a Stanton Redcroft STA 625 model instrument in N₂ atmosphere. Direct current (dc) resistivity measurements were conducted on pressed pellets of "A", "B", and of "C" (13 mm diameter, 0.1 mm breadth) with silver coating, using four-probe technique. The unit manufactured by Scientific Equipment and Services, Roorke, India, comprised a low constant current source (Model LCS-02), a digital microvoltmeter (Model DMV-001), and a PID controlled oven (Model PID-200).

RESULTS AND DISCUSSION

Characterization of the product

The products "A" and "B" were actually composites of MWCNT with "C". However, "C" was subsequently characterized to be PNVC by the following studies.

Spectroscopic characteristics

FTIR studies

Table I summarizes the major FTIR peaks [Fig. 1(a)] observed with "C" obtained in the polymerization

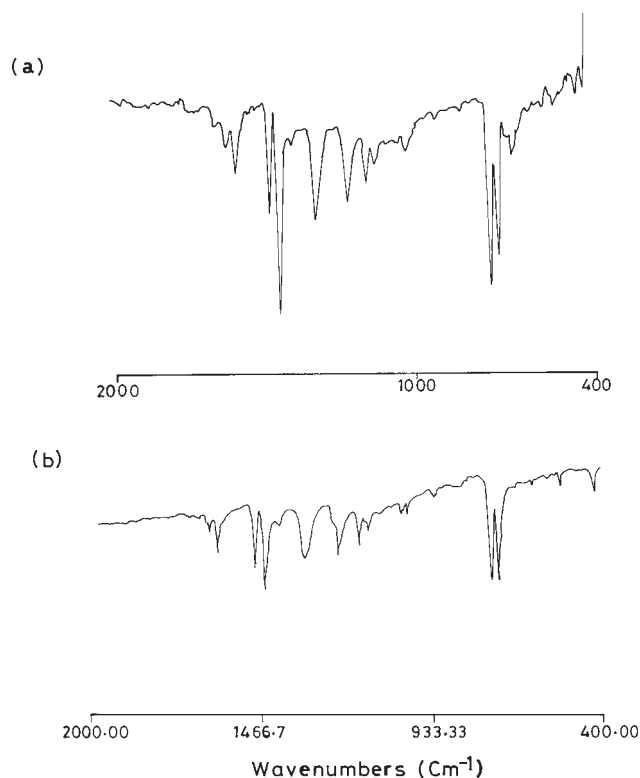


Figure 1 FTIR Spectrum of (a) "C" prepared by the present polymerization system; (b) standard PNVC sample.

system along with their probable assignments and the literature data for FTIR of PNVC homopolymers.^{22,23} That the chemical identity of "C" was actually PNVC, was endorsed by the appearance of FTIR peaks (cm^{-1}) at 721, 745, 1157, 1328, 1452, 1624, and 3048 cm^{-1} in the region 600–4000 cm^{-1} . These peaks matched with the reported FTIR peaks for PNVC reported by Chen et al. [Fig. 1(b)]²³ and by us.^{4,7}

UV-visible absorption and emission characteristics

UV-visible absorption spectra of "C" (Fig. 2) revealed two prominent peaks at 270 and 293 nm due to optical transitions in pendant carbazole moieties. In support, Cao and coworkers²⁴ also reported two peaks at 260 and 320 nm for polycarbazole thin film.

The fluorescence spectrophotometric pattern of PNVC is reportedly composed of two structure-less bands centered around 370 and 420 nm assigned to excimer state.²⁵ These bands are formed between adjacent carbazole units only when the carbazole is attached directly to the chain backbone at the N position. The emission spectrum of "C" (Fig. 3) obtained from the present polymerization system revealed a shoulder at 370 and a peak at 410 nm respectively. The agreement between the literature

and observed values unfortunately was not decisively close but certainly hinted at the formation of PNVC in the system.

Dielectric characteristics

Permittivity (ϵ') and dielectric loss parameter ($\tan \delta$) values for "C" prepared by MWCNT were measured at different frequencies and at two different temperatures (Table II) and compared with the corresponding literature data for PNVC homopolymers.²⁵ The fair agreement between these values endorsed the formation of PNVC in the present polymerization system.

Thermogravimetric studies

The initial decomposition temperature of "C" recovered from the present polymerization system was around 400°C and complete weight loss occurred at around 700°C [Fig. 4(a)]. The small mass losses observed in Figure 4(a) around 100–200°C were due to impurities (as the DTA curve revealed no thermal

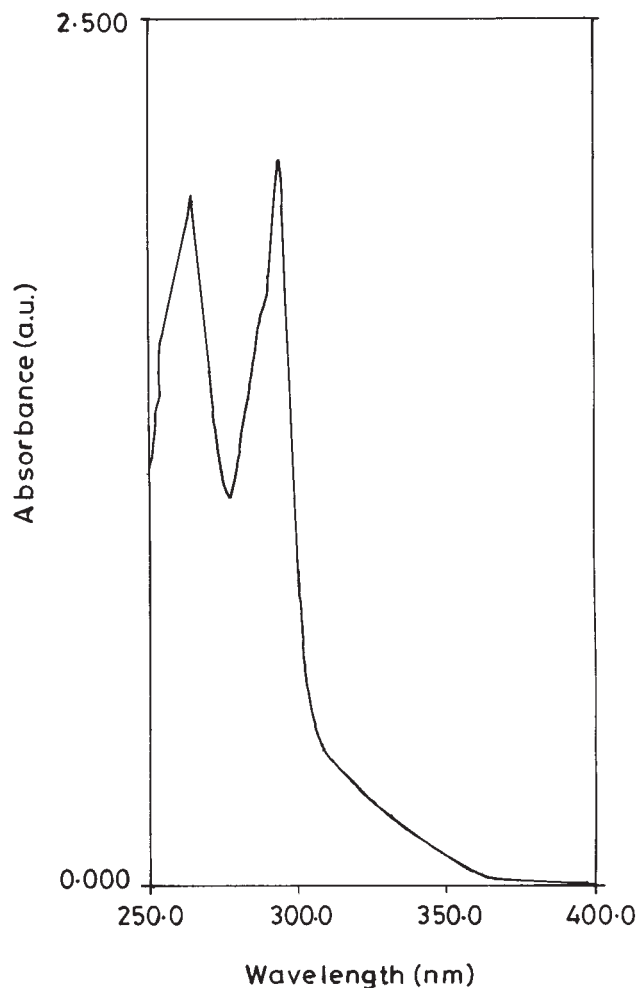


Figure 2 UV-visible absorption spectrum of "C".

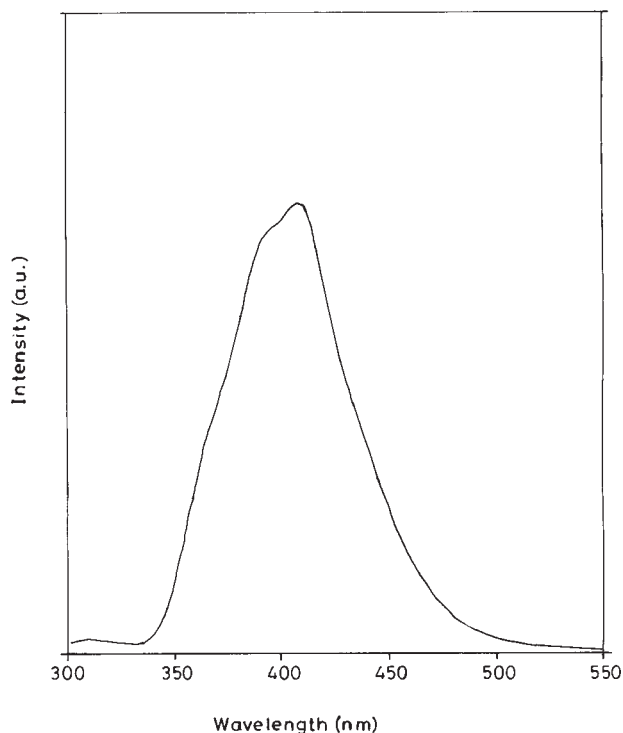


Figure 3 Room temperature fluorescence spectrum of "C".

process). The TG curve [Fig. 4(b)] for PNVC sample obtained by Chen et al.²³ matched with the corresponding curve for "C." DTA studies of "C" revealed manifestation of two exothermic peaks at 420 and 528°C corresponding to the region of maximum weight loss (Fig. 5). These exotherms manifest from oxidative degradation of PNVC-backbone containing the pendant carbazole moieties. This feature was fully consistent with the reported thermogravimetric behavior of PNVC homopolymers prepared by conventional methods.²⁶

Figure 6 presents the heat flow versus temperature (150–300°C) plot (DSC) for "C" which revealed the onset of a transition in the temperature range 215–240°C. Relevantly, the literature value for the T_g of PNVC homopolymer is 227°C.²⁵

TABLE II
Dielectric Properties of "C" from NVC-MWCNT Polymerization System

Sample	Frequency (Hz)	Temperature (°C)	ϵ	$\tan \delta$
"C" prepared in this system	10×10^3	30	4.89	0.0027
	100×10^3	30	4.96	0.0027
	100×10^3	130	3.73	0.0039
PNVC homopolymer [25]	10^4	—	—	$(2-6) \times 10^{-4}$
	50–1 MHz	20	3	—

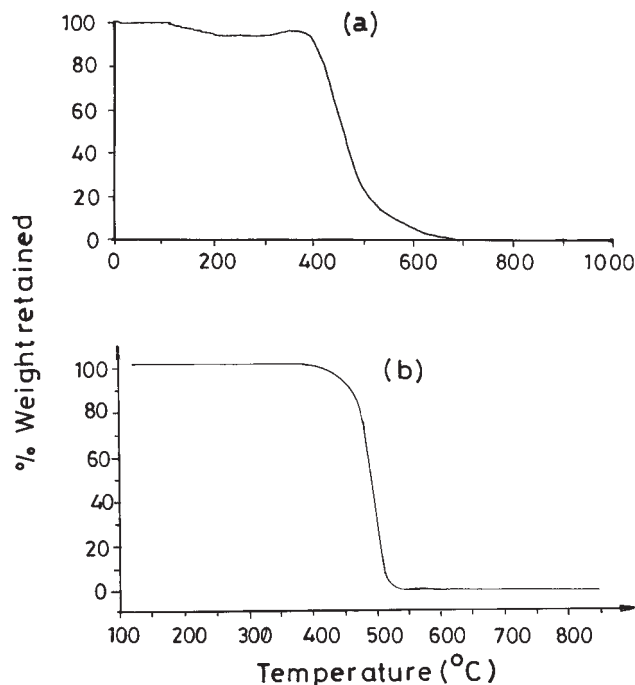


Figure 4 TGA of (a) "C" prepared by the present polymerization system; (b) standard PNVC sample.

General features of polymerization and mechanistic aspects

The various experimental observations discussed earlier convincingly endorsed the identity of C as PNVC homopolymer in the present polymerization system. Table III presents some typical data on the polymerization of NVC by MWCNT and composite formation between PNVC and MWCNT. Entries 1 and 2 indicate that the % conversion to PNVC increased with increasing time of interaction at a fixed amount of NVC and MWCNT in the initial feed. Entries 2–3 and 4–5 suggest that % conversion to PNVC increased with increasing MWCNT amount

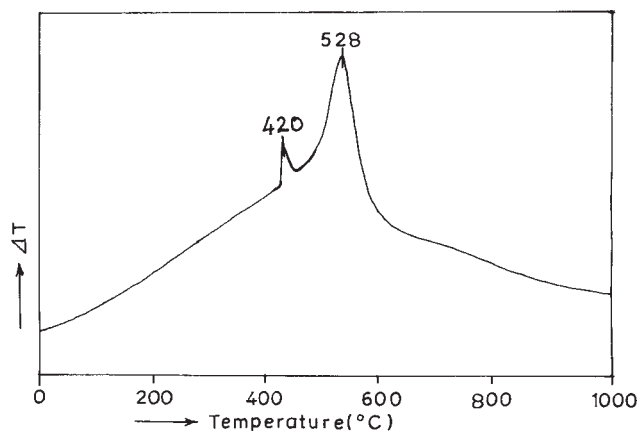


Figure 5 DTA scan of "C".

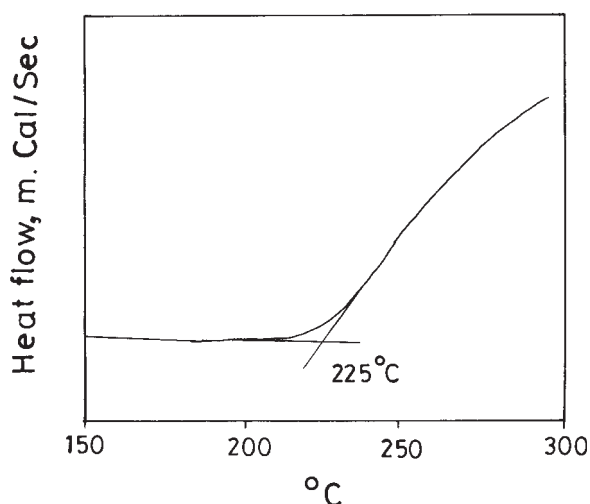
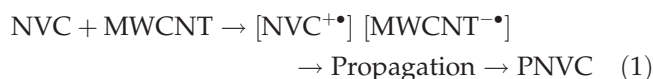


Figure 6 DSC curve of "C".

in the initial feed in both NVC (solid)-MWCNT and NVC (toluene)-MWCNT polymerization systems. As in typical heterogeneous reactions, the lower yield of PNVC in the latter system resulted from decreased availability of NVC monomer at the interaction site on MWCNT due to competitive adsorption of toluene.

It is important to note in this context that in the absence of MWCNT in the systems, there was practically very little PNVC formed in toluene medium under similar conditions as in Table III and some low conversion (less than 10%) was realized in the case of bulk polymerization. Thus the polymerization of NVC occurred in reasonably high yield only when both NVC and MWCNT were mixed together under conditions indicated in Table III. It should be pointed out here that a remarkable feature of this system was the initiation of NVC polymerization directly by MWCNT without any extraneous oxidant. This observation was similar to that reported

for NVC-Buckminsterfullerene,^{6,7} NVC-CB⁴ and NVC-AB⁵ polymerization systems. Accordingly, it appears that the polymerization of NVC was initiated via a single electron transfer reaction⁴⁻⁷ between the lone pair of N of NVC (electron donor) and MWCNT moieties acting as electron acceptor. In this context, it may be relevant to recall that ESR spectrum of pristine SWCNT reportedly shows a very strong ferromagnetic resonance signal implying presence of odd electrons in SWCNT.²⁷ Hence, the observed polymerization of NVC by MWCNT could proceed following the pathway:



The PNVC-MWCNT composite was isolated from the system as described in the experimental section. This scenario was similar to what was observed by Armes and coworkers^{28,29} and also by Biswas and Maity³⁰⁻³² for polymer-metal oxide, polymer-carbon black (CB)⁴/acetylene black (AB)^{5,33-36} and polymer-Buckminsterfullerene⁷ nanocomposite systems.

Conductivity characteristics

It is well-known that PNVC is essentially a nonconducting polymer (10^{-12} to 10^{-16} S/cm).³⁷ Interestingly, the PNVC-MWCNT composites exhibited (Table IV) remarkably improved conductivity values (1.3–33 S/cm) depending upon the extent of MWCNT loading in the composite. Another feature of interest was that the conductivities realized with other allotropes of carbon such as CB,⁴ AB⁵ or BMF⁷ (entries 2–4, Table IV) were much lower.

This feature should be regarded as a very useful and distinctive aspect of the PNVC-MWCNT composite system when compared with PANI-CNT^{13,14}

TABLE III
Some Typical Data on the Polymerization^a of NVC by MWCNT alone

Entry no (a)	Initial feed		Time of interaction (min) (d)	Product	
	Weight (g), NVC (b)	Weight (g), MWCNT (c)		Total weight (g) (e)	% of "C" ^b formed ^c (f)
1	0.50	0.50	15	0.68	36
2	0.50	0.50	60	0.80	60
3	0.50	0.75	60	1.10	70
4	0.50	0.50	360	0.60	20
5	0.50	0.75	360	0.87	25

^a Polymerization conditions: Entries 1–3, both NVC and MWCNT in solid phase; temperature 65°C. Entries 4 and 5, NVC in toluene (5 mL) and MWCNT in solid phase; temperature 110°C.

^b Molecular weight of the fractionated "C" (as determined by viscometry in benzene solution at 25°C) was about 4200.

^c % "C" formed in the present polymerization system = $\{(e - c) \times 100\}/b$.

TABLE IV
Conductivity Data of some PNVC-based Nanocomposite Systems

Entry no	Materials	Conductivity (S/cm)	Reference
1	PNVC homopolymer	10^{-12} to 10^{-16}	[37]
2	PNVC-MWCNT composite a. (entry 1, Table III) b. (entry 2, Table III) c. (entry 3, Table III)	1.33 13 33	This study
3	PNVC-CB composite	10^{-1}	[4]
4	PNVC-AB composite	10^{-2}	[5]
5	PNVC-BMF composite	10^{-2}	[7]

or PPY-CNT³⁸ systems in envisaging materials development programs based on PNVC and MWCNT.

CONCLUSIONS

Multiwalled carbon nanotube was able to polymerize NVC monomer in bulk (at 65°C) or in toluene solvent (at 110°C) and a highly conducting PNVC-MWCNT composite could be isolated via this polymerization system. The formation of poly*N*-vinylcarbazole was endorsed by various physiochemical analyses. In a typical set of experiments the dc conductivity values of the composites were found to vary between 1.33 and 33 S/cm depending upon the extent of MWCNT loading in the composite.

Thanks are also due to the authorities of Presidency College, Kolkata, for facilities.

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