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Solubility characteristics of poly(N-vinylcarbazole) prepared by Co(II) loaded 13X molecular sieve

Madhusudan Banerjee[1], **Mukul Biswas**[1*], **and Mrinal M. Maiti**[2]

[1]Department of Chemistry, Indian Institute of Technology, Kharagpur 721302, India
[2]Materials Science Centre, Indian Institute of Technology, Kharagpur 721302, India

ABSTRACT

During the polymerization of N-vinylcarbazole (NVC) by Co(II)-13X the resultant polymer ($\bar{M}_n$ = 6000) is soluble in benzene or toluene but partly soluble in methylethyl ketone (MEK). To ascertain whether the MEK insolubility is due to polymer tacticity, the polymer has been further characterized by ^{13}C NMR analysis. The atactic structure of polyN-vinylcarbazole (PNVC) initiated by Co(II) has been established from a comparison of methine carbon ($-\underset{|}{C}H$) peaks with the same for a cationic PNVC(BF_3/Et_2O, isotactic) and radical PNVC (AIBN, atactic).

INTRODUCTION

Recent studies[1,2] from this laboratory on the polymerization of NVC by 13X molecular sieve exchanged with various 3d-metal ions, such as Mn(II), Co(II), Ni(II), Cu(II) and Zn(II), have established some novel kinetic and mechanistic features of these systems. It has been consistently observed during this research that PNVC thus obtained shows partial solubility in MEK, although it is soluble in benzene. Since partial solubility in MEK is usually regarded as a first hand criterion|3| for stereoregularity - it was felt significant to investigate the polymer structure by ^{13}C NMR in regard to possible tacticity. Salient results highlighted in this communication establish that the observed MEK-insolubility of PNVC is not due to stereoregular PNVC. The NVC-Co(II)-exchanged 13X polymerization system has been characterized and the polymer prepared by this catalyst has been chosen for microstructure analysis.

EXPERIMENTAL

Materials : N-vinylcarbazole (BASF Co.) was purified and dried by standard methods[4]. 3d-Metal(II) exchanged 13X molecular sieves were prepared by stirring the 13X zeolite in 0.2M solutions of metal(II) salt at 35°C under select conditions[4,5].

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[*] To whom all correspondence should be addressed

Polymerization : Polymerizations were conducted in Pyrex vessels (50 ml) in nitrogen atmosphere under constant stirring with recipe as in Table 1. All experimental manipulations, including charging reaction vessels with solvents, monomer and catalysts were performed in a glove box under N_2. The catalyst, after activation at 500°C for 2h and subsequent cooling to room temperature (35°C), was transferred to the monomer solution under nitrogen atmosphere. The progress of the polymerization was followed gravimetrically.

Gel Permeation Chromatography : The molecular weight and molecular weight distribution of PNVC were measured on a Toyo Soda GPC instrument using THF as solvent with a flow rate of 1 ml min^{-1} at room temperature.

^{13}C NMR Spectrum : The ^{13}C NMR spectrum of the polymer was recorded on a Hitachi Perkin Elmer Spectrometer using $CDCl_3$ solvent. The peaks were analyzed in respect of intensity and area.

RESULTS AND DISCUSSION

PNVC was recovered as a powdery white mass in all cases of polymerization by 13X exchanged with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II). In all instances, PNVC shows partial solubility in MEK, while it is soluble in benzene. Table 1 presents some quantitative solubility data for PNVC prepared with Co(II)-13X system. A similar observation has been reported by Biswas et al.[6,7,8] for the polymerization of this monomer by other catalysts, such as $CoCl_2$-Py/$ZnEt_2$ or carbon black.

The molecular weight characteristics of the PNVC obtained with Co(II)-13X-NVC are as follows :

$$\bar{M}_w = 23{,}000,\ \bar{M}_n = 6{,}000 \text{ and } \bar{M}_w / \bar{M}_n = 3.83$$

It is unusual that PNVC of such low $\bar{M}_n$ would show partial solubility in MEK in as much as a commercial thermally polymerized PNVC ($\overline{DP}$ = 5600) is soluble in this solvent as well as in benzene.

Figure 1 represents the ^{13}C NMR spectrum of the backbone carbons of PNVC produced by Co(II)-13X catalyst along with AIBN[9] and $BF_3.Et_2O$[10] initiated PNVC.

The $-\overset{|}{C}H-$ carbon peaks for AIBN initiated PNVC appear at 50.95, 50.04 and 49.50 ppm while the corresponding peaks for Co(II)-13X initiated PNVC appear at 50.04, 48.96 and 48.42 ppm and those for a cationic PNVC initiated by $BF_3.Et_2O$ occur at 50.70, 50.01 and 49.55 ppm, respectively.

The $-CH_2-$ peaks for the Co(II)-13X and AIBN initiated PNVC are distinct from those of $BF_3.Et_2O$ initiated PNVC, which reveal only two peaks at 35.82 and 34.25 ppm respectively. Table 2 shows the percentage of the relative peak areas for the methine and methylene carbon spectra as a measure of tacticity. Kawamura and Matsuzaki[9,10] analyzed in detail the ^{13}C NMR spectra of PNVCs obtained by AIBN, $BF_3.Et_2O$ and various charge transfer catalysts. On the basis of the relative peak areas of the methine peaks in PNVC, several distinct categories of spectral types were proposed. AIBN initiated PNVC showing characteristics as in Table 2 has been assigned an atactic structure. $BF_3.Et_2O$ initiated PNVC, however, exhibiting methine carbon peaks and areas as in Table 2 is syndiotactic. The highest peak area of 49.71% for the 49.55 ppm peak is ascribed to the isotactic rich configuration of $BF_3.Et_2O$ initiated PNVC. Data of Table 2 clearly show that for both AIBN and Co(II)-13X initiated PNVC, the 49.50 and 48.42 ppm peaks reveal lowest peak areas in marked contrast to the highest isotactic peak area of 49.71% for the 49.55 ppm peak of $BF_3.Et_2O$ initiated PNVC. It may then be concluded that the PNVC obtained with both Co(II)-13X and AIBN catalysts shows a ^{13}C NMR methine peak pattern typical of an atactic configuration.

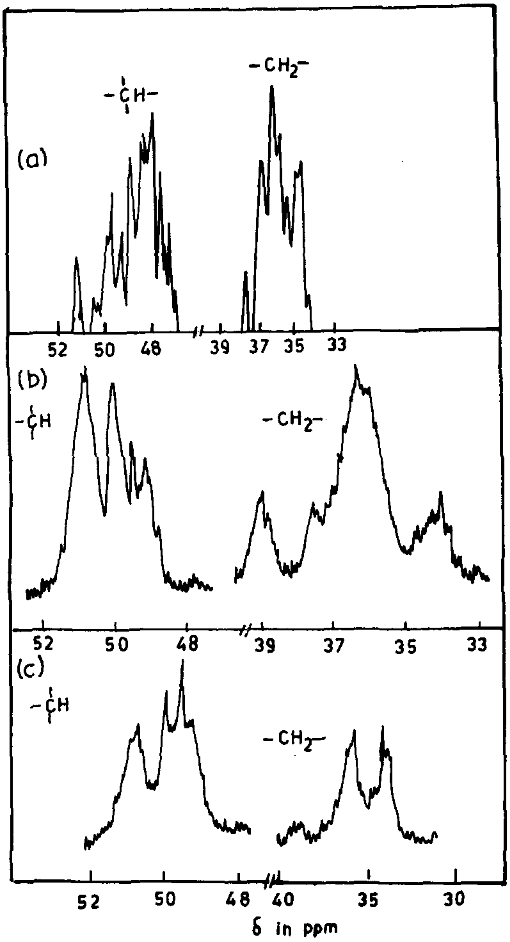

Figure 1.

^{13}C NMR spectra of methine ($-\overset{|}{\underset{|}{C}}H-$) and methylene($-CH_2-$)carbons of PNVC prepared with

(a) Co(II)-13X ;

(b) 2-2'-azobisiso-butyronitrile and

(c) $BF_3(C_2H_5)_2$ O.

Table 1

Solubility characteristics of PNVC[a] in MEK obtained from Co(II)-13X-NVC system

PNVC in MEK		PNVC insoluble in MEK
Temperature (°C)	Time (h)	(%)
32 (stirring)	25	91.67
32 (stirring)	50	89.91
32 (stirring)	50	86.00[b]
80 (reflux)	5	81.67

[a] Polymerization condition : [NVC] = 0.15 M : exchange level of Co(II) in 13X = 30% : solvent, toluene $\overline{M}_w$ and MWD : as described in text.

[b] Duplicate set of experiment.

Table 2

Comparison of relative peak areas for methine and methylene carbon spectra of PNVC prepared by different catalysts

Catalyst	Chemical shift		Relative peak area
	$-\overset{|}{\underset{|}{C}}H$ (ppm)	$-CH_2$ (ppm)	(%)
AIBN[a]	50.95	-	55.04
	50.04	-	32.79
	49.50	-	12.74
	-	39.05	11.44
	-	37.76	7.74
	-	36.38	64.41
	-	33.94	16.41
Co(II)-13X	50.04	-	48.81
	48.96	-	28.38
	48.42	-	22.82
	-	37.00	36.63
	-	35.74	31.39
	-	35.05	31.97
$BF_3(C_2H_5)_2O$[a]	50.70	-	31.59
	50.01	-	18.69
	49.55	-	49.71
	-	35.82	58.19
	-	34.25	41.77

[a] Reproduced from Refs. [9,10].

In conclusion, these results suggest that partial solubility of polymers in ketonic solvents need not necessarily be regarded as a criterion for stereoregularity. However in the present instance as in earlier cases of NVC polymerization by carbon black $\overline{M}_n$ (PNVC) = 8900, by soluble Ziegler type of catalyst system Co-(Py)-ZnEt$_2$/benzene, $\overline{M}_n$ (PNVC) = 6500, the molecular weights of the resultant PNVC are not high enough to render the polymer insoluble in MEK. The precise reason for this behavior is yet obscure.

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