

# Polymerization of *N*-Vinylcarbazole by Gaseous Initiators

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## SYNOPSIS

The polymerization of *N*-vinylcarbazole initiated with  $\text{NO}_2$  and  $\text{SO}_2$  in dichloroethane has been studied. The kinetics of polymerization were followed gravimetrically. The polymerization is fast with  $\text{NO}_2$  but a relatively slow rate was obtained with  $\text{SO}_2$ . The polymerization with these gases appears to be initiated by a charge transfer mechanism.

## INTRODUCTION

Nitrogen dioxide<sup>1-4</sup> and sulphur dioxide<sup>5,6</sup> initiate polymerization of some vinyl monomers. In this article, we briefly describe the polymerization of *N*-vinylcarbazole (*N*-VCZ) initiated by these two gaseous compounds in dichloroethane (DCE).

## EXPERIMENTAL

### Materials

DCE was properly dried and purified by fractional distillation, collecting only the middle fraction. *N*-VCZ was analytical grade and used after drying. Pure and dry  $\text{NO}_2$  was conveniently prepared by heating lead nitrate. The concentration of  $\text{NO}_2$  in DCE was determined volumetrically by treating the solution with an excess of sodium hydroxide solution and titrating the resulting nitrite solution with acidified standard potassium permanganate solution.<sup>1</sup>  $\text{SO}_2$  was prepared by reacting sodium sulfite with dilute HCl. Its concentration in DCE was determined volumetrically by treating the solution with a standard aqueous alkali solution.

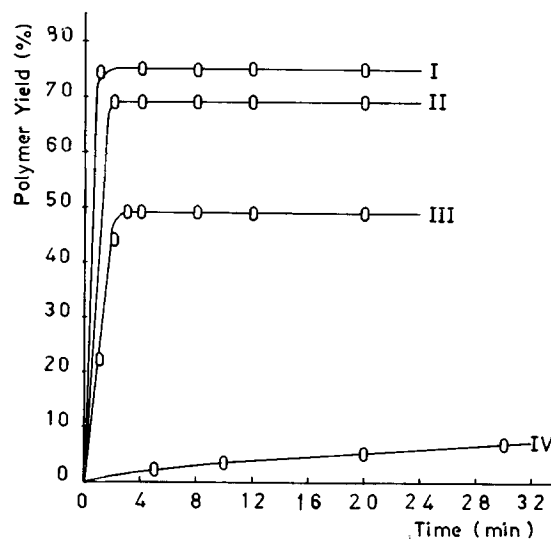
### Polymerization

The polymerization of *N*-VCZ was carried out under nitrogen atmosphere in glass vials tightly stoppered

and thermostated. The kinetics of polymerization were followed gravimetrically. After known periods of time, the polymerizing mixture in each vial was poured into an excess of methanol to precipitate the polymers that were then filtered off, washed, dried, and weighed.

## RESULTS AND DISCUSSION

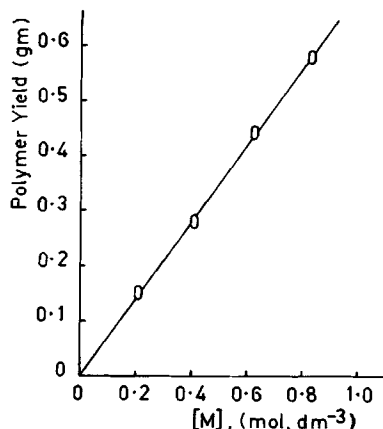
A reaction profile as a function of  $\text{NO}_2$  concentration is presented in Figure 1, which shows that the rate



**Figure 1** Polymer yield as a function of  $\text{NO}_2$  concentration and reaction time within fixed concentration of *N*-VCZ ( $0.207 \text{ mol dm}^{-3}$ ) in DCE at  $40^\circ\text{C}$ . (I),  $10 \times 10^{-3} \text{ mol dm}^{-3}$ ; (II),  $1 \times 10^{-3} \text{ mol dm}^{-3}$ ; (III),  $0.1 \times 10^{-3} \text{ mol dm}^{-3}$ ; (IV),  $0.01 \times 10^{-3} \text{ mol dm}^{-3}$ .

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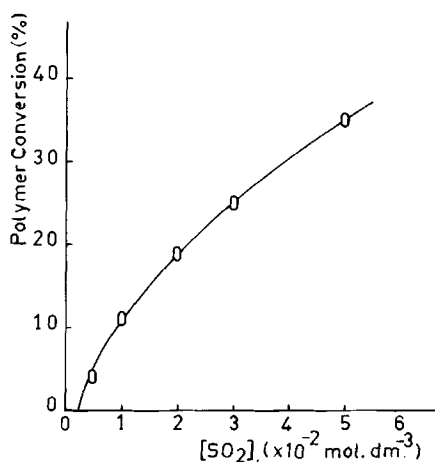


**Figure 2** Polymer yield as a function of *N*-VCZ concentration for 1 h polymerization time with a fixed concentration of  $\text{NO}_2$  (conc.:  $1 \times 10^{-2} \text{ mol dm}^{-3}$ ) in DCM at  $40^\circ\text{C}$ .

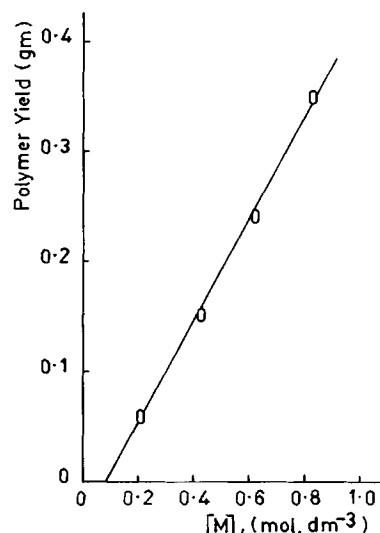
of polymer formation increases rapidly with increasing  $\text{NO}_2$  concentration, giving a maximum 75% monomer conversion to polymer within a few minutes of polymerization (curve I of Fig. 1). The polymer yields monotonically increase with increasing *N*-VCZ concentration as seen from Figure 2.

Similar to  $\text{NO}_2$ ,  $\text{SO}_2$  also causes the successful polymerization of *N*-VCZ but with a relatively slow rate. Some pertinent results are shown in Figures 3 and 4.

The average molecular weight of the resulting polymers was not high as indicated by the limiting viscosities, the average value being  $0.101 \text{ dL g}^{-1}$  in DCE at  $30^\circ\text{C}$ . The high degree of termination pos-



**Figure 3** Polymer conversion as a function of  $\text{SO}_2$  concentration for 24 h polymerization time with a fixed concentration of *N*-VCZ ( $0.207 \text{ mol dm}^{-3}$ ) in DCE at  $40^\circ\text{C}$ .

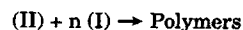
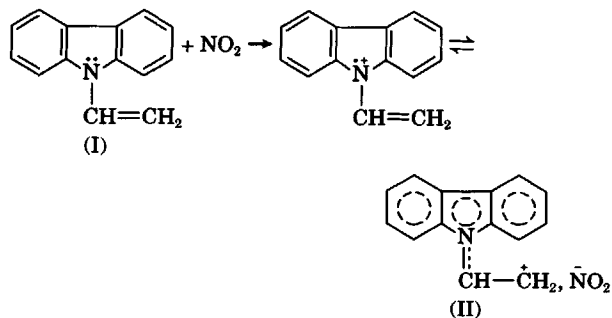


**Figure 4** Polymer yield as a function of *N*-VCZ concentration for 24 h polymerization time with a fixed concentration of  $\text{SO}_2$  in DCM at  $40^\circ\text{C}$ .

sibly due to *N*-VCZ, which is a basic compound, might be responsible for low molecular weight.<sup>7</sup>

The free radical inhibitor, 2,2'-diphenyl-1-picrylhydrazyl did not inhibit the polymerization of *N*-VCZ by  $\text{NO}_2$ . The polymer formation also does not occur in basic solvents such as *N,N'*-dimethyl formamide.

A characteristic feature of the *N*-VCZ polymerization is the initiation by electron-accepting compounds. The electron-releasing effect of nitrogen in the carbazole ring may induce high nucleophilicity on the vinyl group and cationic propagating species may be stabilized by conjugation with carbazole group.  $\text{NO}_2$  is a Lewis acid and thus may accept an electron from *N*-VCZ (I) to cause cationic polymerization.<sup>8,9</sup> The possible mechanism of polymerization might be cationic propagation by the species (II) that was due to radical delocalization over the carbazole ring as shown below.

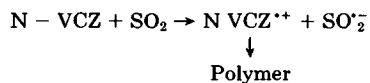


**Table I** Color Formation from *N*-VCZ and poly(*N*-VCZ) with NO<sub>2</sub> in DCE at 25°C

Acceptor	Donor: <i>N</i> -VCZ	Donor: poly( <i>N</i> -VCZ)
NO <sub>2</sub>	Brown	Yellow
SO <sub>2</sub>	Colorless	Yellow
SbCl <sub>5</sub>	Green	Green
BF <sub>3</sub>	Blue	Blue

The IR spectrum of the polymers did not display absorption peak for vinyl group (near 600 and 880 cm<sup>-1</sup>), suggesting that the polymerization took place only at the vinyl sites and carbazyl groups were not involved in the polymer formation.

SO<sub>2</sub> is also a charge transfer electron acceptor like NO<sub>2</sub> and initiates the polymerization through a charge transfer mechanism.<sup>7</sup>



The color formation from monomer *N*-VCZ and poly(*N*-VCZ), was prepared by NO<sub>2</sub> initiation process, in DCE is presented in Table I.

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