

Crosslinked Polymer from *N*-Vinylcarbazole and Formalin

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Synopsis

A crosslinked polymer has been synthesized from the reaction of *N*-vinylcarbazole and formalin in toluene in the presence of dry HCl gas. The copolycondensate is insoluble in all common solvents for poly-*N*-vinylcarbazole, and exhibits higher thermal stability than the unmodified poly-*N*-vinylcarbazole. However, this polymer is less thermally stable than the corresponding furfural modified poly-*N*-vinylcarbazole. A mechanism for the overall reaction has been suggested and the factors affecting the synthesis have been discussed.

INTRODUCTION

In continuation of our research on the chemical modification of *N*-vinylcarbazole polymers¹⁻⁸ we now report the preparation of a crosslinked polymer from *N*-vinylcarbazole and formalin. To our knowledge, formaldehyde copolymers of some vinyl monomers such as isobutylene, a vinyl ether, and a vinyl nitrogen compound were described in a patent,⁹ but the procedure, now suggested by us, is more simple and economic since it uses the readily available and cheap formalin. This article also highlights the relevant physicochemical properties of *N*-vinylcarbazole-formalin crosslinked polymer and compares, in particular, the thermal stability of the polymer with the same for the unmodified poly-*N*-vinylcarbazole and a furfural modified *N*-vinylcarbazole polymer.^{4,5}

EXPERIMENTAL

Materials. *N*-vinylcarbazole (NVC) or its polymer (PNVC, DP = 5750) supplied by BASF, West Germany, were used without further purification. Formalin (FO), a 37% aqueous solution of formaldehyde gas was supplied by B. D. H., India. All other materials were analytical grade certified reagents.

Preparation of NVC-FO and PNVC-FO Crosslinked Polymers. 2 g of NVC or PNVC were dissolved in 50 mL toluene in a two-necked Pyrex flask. Dry HCl gas, generated by adding concentrated H₂SO₄ to solid NH₄Cl in an appropriate glass assembly, was bubbled through the solution to which a measured quantity of formalin (Table I) was added. The reaction was conducted at dif-

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TABLE I
Factors Affecting the Synthesis of NVC-FO Copolycondensates^a

Monomer or polymer	Temp (°C)	Formalin (mL)	Yield ^b (%)
NVC (PNVC)	80	5	— (—)
	90	5	— (—)
	100	5	15 (60-70)
	110	5	17 (80-90)
	110	2.5	12 (85)
	110	7	18 (85)
	110	10	12 (75)

^a 2 g of NVC or PNVC in 50 mL toluene. Reaction time after addition of formalin = 8 h.

^b Figures in parentheses represent the yield data for the PNVC-FO system. In general, the yields reported are reproducible within 1-2%.

ferent temperatures (Table I) for 6-8 h, when a solid product separated out in the reaction medium. This was filtered, the excess formalin was washed out with dilute ammonia solution, and the product was repeatedly washed with deionized water and air-dried. Finally, the material was refluxed with toluene for 12 h, filtered, and subsequently dried off toluene *in vacuo*.

Characterization. Elemental analysis of the polymer was done in a standard C, H, N analyzer. The I.R. spectra of the polymers were recorded on a Perkin-Elmer Model 237 B Spectrophotometer. Thermogravimetric and differential thermal analysis of the polymer was performed in a Shimadzu Model DT-30 Thermal Analyzer.

RESULTS AND DISCUSSION

The material, finally isolated as a faint blue to colorless mass, is insoluble in solvents such as benzene, toluene, dimethylsulfoxide, dimethylformamide or nitrobenzene, mineral acids and alkalis. This feature implies that the material is not a homopolymer of NVC, which is also endorsed by the results of elemental analysis of the product (C = 75.85%, H = 4.76%, and N = 6.75%; the balance 12.69% may be O from the incorporation of FO). The calculated values for C, H, and N in PNVC are, respectively, 86.93%, 5.69% and 7.24%. Further the IR spectra of NVC-FO, PNVC-FO, and of PNVC are very similar. These features imply that the separated polymer is a condensation product of PNVC and formalin.

Factors Affecting the Synthesis of NVC/PNVC-FO

Temperature. Table I clearly shows that the synthesis is most favored in the temperature range 100-110°C, there being no reaction at 90°C even in the course of 24 h. The effect of temperature higher than 110°C on the yield was not investigated.

Formalin Concentration. Table I further suggests that the quantity of formalin used in the synthesis affects the ultimate yield of the polymer. The latter reaches a maximum value at a certain formalin concentration falling thereafter with further increase in the amount of formalin.

TABLE II
Thermal Stability Data for NVC-FO, PNVC, and NVC-Furfural

Polymer	% Decomposition at temperatures (°C)					Maximum decomposition temp
	100	200	300	400	500	
PNVC ^a	7.3	14.6	20.6	66	89	89 (ca. 550°C)
NVC-FO	4.6	12.3	17.9	32.2	52.3	complete (515°C)
NVC-furfural ^b	—	—	—	25.3	40	90 (770°C)

^a NVC polymerized by AIBN in toluene *in vacuo* at 60°C.

^b Reproduced from Ref. 5; measured in a MOM derivatograph.

Another notable feature of this condensation is that the crosslinked polymer is realized in a very high yield when PNVC rather than NVC is used in the reaction. Thus Table I shows that, in general, 80–90% of the insoluble polymer are realized by using PNVC in the reaction with formalin against ca. 20% from the NVC-formalin system. This is attributed to the fact that the resin formation in the system NVC-FO requires the prior formation of PNVC in the system which then enters into condensation reaction with formalin. Relevantly, no solid material has been isolated in the system in which NVC solution in toluene has been refluxed with formalin in the absence of HCl gas. The latter acts both as a polymerization catalyst for NVC¹⁰ as also a typical condensation catalyst.

Thermal Stability Characteristics. Table II presents the relevant data on the thermal stability of the NVC-FO condensation polymer along with the corresponding data for an unmodified polymer of NVC polymerised by AIBN at 60°C and a NVC-furfural resin reported by Biswas and Packirisamy.^{4,5}

It is observed from Table II that NVC-FO copolycondensate exhibits, in general, an improved thermal stability relative to unmodified PNVC. Thus, initially, up to ca. 300°C, both the polymers decompose up to ca. 20%. But, at 400°C, NVC-FO is 50% more stable (32.2% decomposition) than PNVC (66%). Even at 500°C NVC-FO is apparently more stable than PNVC. Above this temperature, the polymers are practically completely decomposed. On the other hand, NVC-furfural copolycondensate is consistently more stable than either NVC-FO or PNVC. Up to ca. 300°C there is no loss in the polymer. Perhaps it is relevant to point out in this context that the experimental conditions maintained, and particularly the catalyst used in the preparation of the NVC-furfural copolymer resin are necessarily different than the same followed in the present context. In the NVC-furfural reaction, the catalyst used was AlCl₃, which is a much more effective polymerization catalyst for NVC and also a condensation catalyst. Accordingly, the resultant polymer matrix in the NVC-furfural system is expected to be more crosslinked than the NVC-FO matrix obtained with the present system, which is possibly the most important factor responsible for the higher thermal stability realized in the former system.

In any case, it seems that incorporation of formalin in the backbone of PNVC favorably modifies the properties of the backbone polymer. Figure 1 schematically explains how condensation and interchain crosslinking may occur in the NVC-FO system. Evidently, the resultant matrix will be a mixture of II and III since oxygen has been detected in the elemental analysis.

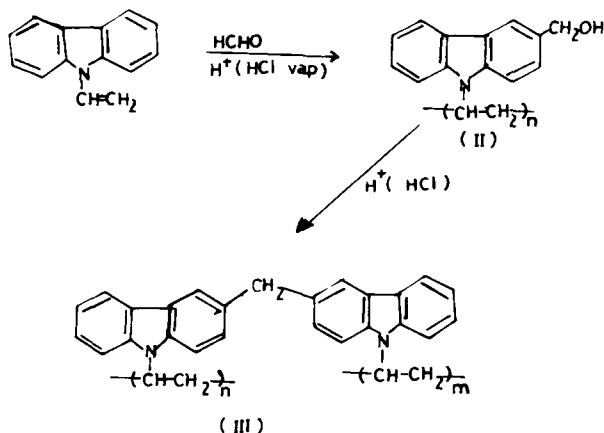


Fig. 1. Scheme for the formation of crosslinked polymer from *N*-vinylcarbazole and formalin.

CONCLUSION

It is possible to prepare a crosslinked polymer by the reaction of NVC with formalin in presence of dry HCl gas. The resultant polymer exhibits impressive thermal stability compared to unmodified PNVC.

Thanks are due to the Authorities of I.I.T., Kharagpur, for facilities, and to Drs. Oshima and Araki and Mr. Higuchi of the Institute of Industrial Science, University of Tokyo, Roppongi, for their help in the thermal analysis measurements. M. B. thanks the Japan Society for the Promotion of Science for a supporting Fellowship at the University of Tokyo.

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Received August 24, 1983

Accepted November 8, 1983