

**POLY (N-VINYL-
CARBAZOLE)**

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POLY(N-VINYLCARBAZOLE)

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POLY(N-VINYLCARBAZOLE)

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Edited by M. B. Huglin, University of Salford

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DEDICATION

*We dedicate this book to our families; without
their help and understanding the task of writing it
would have been quite impossible.*

*Hilary, Dean and Jill
Dana, Jarmila and Helena*

Series Editor's Preface

"If a book is worth reading, it is worth buying." (John Ruskin)

Two trends, which are not especially favourable to a series such as this have become noticeable in recent years, *viz*—first, the reluctance of the polymer industry to invest in the development of entirely new homopolymers and, secondly, the increasing costs of scientific book production. Enquiry and feed-back revealed, perhaps surprisingly, but nonetheless emphatically, a genuine need for authoritative up-to-date treatments on several existing polymers. Consequently, each volume is devoted to one specified polymer. The interests of an industry or an institution usually dictate that research and/or development be conducted over an extended period of time on the particular polymer of relevance. It is hoped that individuals will be able to select their specific volume from Polymer Monographs and thus be freed from the inconvenient and unfair obligation to pick sections out of the commoner, large treatises devoted to classes of polymer.

With regard to the topics themselves, proven useful application is considered a *sine qua non*, and hence macromolecules of purely academic interest are excluded from this series. An innovation is the inclusion of biopolymers and their synthetic prototypes. Since polymer science has now become truly interdisciplinary in scope, the monographs are addressed to a broad spectrum of potential readers.

These volumes are short, the aim being to present the maximum of current information in the minimum of space. Fortunately the authors, who are all pre-eminent in their respective fields, have not only complied with this difficult and stringent condition, but have succeeded in doing so without

POLY(N-VINYLCARBAZOLE)

sacrificing readability. The publishers have endeavoured to make these books available at a price which is reasonable by present standards. They and I trust these volumes will prove useful and welcome comments and suggestions for future topics.

MALCOLM B. HUGLIN

Preface

In comparison to the other polymers covered in this monograph series, poly(N-vinylcarbazole) must be considered as a specialty rather than a bulk product. The early motivation for its production and study lay in its utility as a high temperature dielectric. Although it served as a replacement for mica in capacitors and other electrical components in the 1940s, its extreme brittleness and poor mechanical and processing characteristics severely limited its applications, and the polymer was eventually replaced by other improved materials. After the discovery in 1957 of its unique photoelectric properties, the polymer again became a focus of attention.

For a specialty polymer, poly(N-vinylcarbazole) has an impressive listing in the patent and scientific literature. Most of the patent references relate to photoelectronic properties and applications. In the general scientific literature, the synthesis, the structure and the properties of the polymer have all been widely investigated in laboratories throughout the world. These studies have played a key role in advancing our understanding of photoelectronic phenomena in organic and polymeric solids and in stimulating a continuing interest in the development of organic materials for specialized electronic and photoelectronic applications.

The authors express their thanks to Xerox Corporation and Eastman Kodak Co. for permission to publish this book. The use of their excellent facilities greatly simplified the preparation of the manuscript. We owe a debt of gratitude to our many colleagues, particularly for their advice on unfamiliar subject matter, to Dr M. B. Huglin for the invitation to write this book and to Professor A. Ledwith for his enthusiastic assistance, his

PREFACE

insights into carbazole and vinylcarbazole chemistry and his review of the final manuscript.

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J. M. PEARSON
M. STOLKA

Contents

	Series Editor's Preface	xi
	Preface	xiii
	Introduction	1
1	The Monomer	4
	1.1 Synthesis	4
	1.2 Purification	7
	1.3 Properties	7
	1.4 Toxicity	9
	References	9
2	Polymerization	11
	2.1 Radical	11
	2.2 Cationic	17
	2.3 Photocationic	22
	2.4 Ziegler-Natta	22
	2.5 Anionic	22
	2.6 Charge Transfer	23
	2.7 Photoinduced Charge Transfer	28
	2.8 Cyclodimerization of NVK	32
	2.9 Electrochemical	34
	2.10 Solid State	34
	References	39
3	Physical Properties	43
	3.1 Mechanical and Rheological Properties	43
	3.2 Glass Transition Temperature	45
	3.3 Oriented PVK	47

3.4	Solution Behavior	50
3.5	Crystallinity	52
3.6	NMR Spectroscopy	60
	References	66
4	Electrical Properties	68
4.1	Dielectric	68
4.2	Photoconductivity	73
4.2.1	Definitions and measurements	74
4.2.2	Carrier generation	78
4.2.3	Carrier transport	91
4.2.4	Recombination of carriers	101
4.3	Conductivity	102
4.4	Persistent Conductivity	103
	References	104
5	Chemical Reactions.	108
	References	110
6	Thermal Degradation	111
	References	114
7	Charge Transfer Complexes	115
	References	129
8	Optical Spectroscopy	130
8.1	Absorption Spectra	130
8.2	Emission Spectra	131
8.3	Energy Transfer	138
8.4	Other Carbazole-Containing Vinyl Polymers .	140
	References	146
9	Other Carbazole-Containing Polymers and Copolymers	149
9.1	Copolymers of NVK	149
9.1.1	Random copolymers	149
9.1.2	Block and graft copolymers	153
9.1.3	Alternating copolymers	154
9.2	Other Carbazole-Containing Polymers . . .	155
	References	156

10	Miscellaneous Applications	159
	References		162
	Subject Index	163

Introduction

Poly(N-vinylcarbazole) (PVK) is a vinyl aromatic polymer produced by polymerization of the monomer, N-vinylcarbazole (NVK). Although there are several acronyms for this monomer-polymer, e.g., NVC-PVC, $\text{NVC}_z\text{-PVC}_z$, we have chosen to use NVK-PVK, which presumably comes from the German "Karbazol".



The polymerization reaction and the structure and properties of the polymer are largely controlled by the electronic and steric influence of the carbazole function. NVK is a strongly basic monomer which polymerizes readily by cationic initiation. Free radical polymerization is also effective and was used to manufacture the polymer. The nucleophilicity of the propagating free radical, however, can introduce unusual complexities into the polymerization reaction. NVK does not polymerize anionically. The discovery in 1963 of the spontaneous polymerization of the donor NVK monomer in the presence of suitable electron acceptor species stimulated a flurry of activity in the so-called charge transfer polymerization. NVK proved to be an ideal system and contributed much to the mechanistic understanding of these unique polymerization reactions.

The polymer PVK is a glassy, brittle material. It was produced commercially in the 1940s in both Germany and the US, primarily for application as a high temperature capacitor dielectric. The discovery in 1957 of its photoelectronic behavior created a strong industrial interest in finding a com-

mercial utilization for this interesting property. This was in fact realized in 1970 when IBM Corporation introduced the first commercial organic polymeric photoconductor, based on PVK, in its Copier I series of electrophotographic (photocopying) machines.

The bulkiness of the pendant carbazole group and the hindered rotation around the C—N bond linking it to the backbone dominate the structural and physical properties of the material. The polymer chains are rigid and rod-like in nature. In the solid, the polymer forms ordered paracrystalline structures induced by the pendant group packing rather than stereoregularity in the chain, a phenomenon not encountered in other vinyl polymers. The T_g for PVK is $\sim 227^\circ\text{C}$, among the highest known for a vinyl polymer, and the material exhibits excellent thermal stability. Unfortunately, this property has never been exploited because of the extreme brittleness of the polymer. Attempts to improve the mechanical and processing properties by conventional techniques (plasticization, orientation, copolymerization) have not been successful enough to overcome this limitation.

Dielectric and nmr studies have been the most successful in elucidating the polymer structure and morphology and also the dynamic aspects of the polymeric solid. The polymer, independent of its mode of polymerization, is best described as atactic, with some slight preference for isotactic placement in cationic samples. Main chain and side group motions are severely limited in the polymer as a result of steric constraints.

Perhaps the most intriguing properties of the polymer are its photophysical and photoconductive characteristics and its ability to form charge transfer complexes with suitable electron acceptor molecules. The spectroscopic behavior of PVK (absorption, emission and energy transfer phenomena) has been investigated in detail both in solution and in the solid state. PVK is the only known vinyl aromatic polymer which exhibits emission from two characteristic excimer states, reflecting its unique structure and interchromophoric effects. Photoconductivity studies on the polymer have contributed significantly to the understanding of the mechanism of the

photogeneration and transport of electronic charge carriers in organic and polymeric solids. PVK based materials have been the most extensively studied and are among the best understood polymeric semi- and photo-conductors.

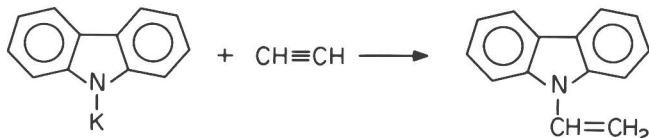
CHAPTER 1

The Monomer

1.1 SYNTHESIS

Most published synthetic routes utilize carbazole as starting material since it is readily available as a by-product from coal-tar distillation. N-Vinylcarbazole is easily synthesized in moderate to high yields by a variety of vinylation techniques.

The most straightforward, high yield process (up to 99%) is the reaction of carbazole and alkali metal hydroxide or pre-formed alkali metal salt of carbazole with acetylene in polar solvents.¹⁻¹⁵



Although most of the syntheses are carried out at slight pressures, the reaction can proceed in high yields at atmospheric pressure in anhydrous polar solvents such as dimethylformamide, dimethylsulfoxide and N,N'-dimethylacetamide.^{13, 15} Another convenient method is dehydration of N-(2-hydroxyethyl)carbazole,¹⁶⁻¹⁸ which can be obtained by the reaction of potassium carbazole with ethylene oxide^{16, 17} or 2-chloroethanol.¹⁸ The dehydration is carried out with sodium or potassium hydroxide.

