Study by Means of Computerized Spectroscopy of Copolymerization Grafting

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SYNOPSIS

Experiments were performed in an attempt to explain the probable mechanism present in the polymeric grafting process and to determine the percentual ratio between N-4-[4-(dietylamine) fenil] fenilmetilene-2-5-cyclohexadiene-1-ilidene-N-etil ammonium monomer and the sulfate (1 : 1) (Green Vinyl Malachite: GVM) in poly-N-vinylcarbazole/Green Vinyl Malachite, PNVC/GVM, specimens of the copolymerization product. Computerized spectroscopic techniques, optimized for maximum absorption and minimum effect noise, were utilized to subtract the spectral information of the GVM monomer noncopolymerized species from the macromolecular base with no special sampling techniques. The samples were processed using the standard PECDS software with the infrared Data Station. The copolymerization process resulted in a 52.91% concentration of a noncopolymerized fraction consisting of dimerized structures of the reactant monomer.

INTRODUCTION

Vibrational spectroscopy has proved to be both a convenient and effective method in the identification and in the conformational study of polymers. The technique is applied to determine polymeric structures of additives, adhesives, and latex as well as in the assay of contaminants.[1-5] An advantage possessed by this technique over others, such as chromatography of gel permeation, is that the absorption bands, revealing functional groups, bonding characteristics, and stereochemical configurations, can be evaluated by means of data processing routines not possible with conventional spectroscopic techniques.

EXPERIMENTAL

A PNVC/GVM copolymerization system was set up to be studied experimentally, for which both the PNVC,[6,7] to be used as the macromolecular homopolymeric base, and the GVM,[8,9] as the monomer reactant, were obtained in analytical grade from the Aldrich Chemical Co. The solvents, of Merck analytical grade, were dichlorometane and 1,4-dioxane. Preparation consisted in dissolving, through constant agitation and at a temperature of approximately 70°C, 20 g of PNVC in equal volumes of solvents in a sufficient amount, then in dissolving 0.5 g of GVM in a second volume of the solvent mixture, which was then incorporated into the first-prepared homopolymeric system. The same temperature was maintained and shaking kept constant until homogeneity was achieved. The product was then adjusted to 300 mL with added amounts of the same solvent mixture for sampling.

The spectrophotometer utilized was a computerized IR Perkin-Elmer Model 283B. Samples of the product in the form of alkaline haluride pellets or as depositions placed directly on KRS-5 windows were examined for copolymerized material. Computerized examinations were performed using the PECDS application program, and the TAAT, DIFF, ABEX, FLAT, and SMOOTH routines, to retrieve the spectral information, to optimize absorption bands, and to minimize level noise.

Despite its optimal resolution and freedom from interference, the absorption associated with aromatic structures could not be utilized to precisely

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differentiate the reactant monomer absorption band. Therefore, to determine the noncopolymerized portion of the monomer reactant, as well as to deduce the insoluble fraction present in the macromolecule base, the absorption band stretching of the CCN group was used.

RESULTS AND DISCUSSION

Noted in our experiments on copolymerization grafting of the PNVC/GVM system in the presence of polar solvent systems was that the macromolecular homopolymeric PNVC (Fig. 1) strongly conserved its $n\pi$ character, thereby enhancing its capacity to ionically copolymerize more energetically than do π doner systems. Although the propagation mechanism generally accepted in the case of heterocyclic monomers is that of a nucleophilical substituent, in the basic vinyl colorant cationically polymerizable GVM (Fig. 2), it becomes an anionic monomer whose aromatic substituent acts to repel the double-bond π electron. The positively charged tricovalent carbon atom GVM mechanism induces a cationic polymerization requiring the presence of carbon ions as polar systems. The GVM ion in this process copolymerized cationically with the PNVC, which then acted as a comonomer electron doner. During the copolymerization, the double-bonding polymerization induced the formation of head–tail copolymers, rather than of head–head or tail–tail homopolymeric macromolecules.

The primary process came about through interaction of the monomer with the acid entity that formed in preparing the solvent system (CH_2Cl_2, solvent, and the $C_4H_8O_2$, ether, Lewis base), the initiator in the cationic polymerization, and displaced the hexocyclic double-bonding π electrons toward the quinonic ring. This displacement added protonated species and polarized the charges.

The migrating positive charge of the carbon atom adjacent to the aromatic rings was stabilized by the resonance. The resulting cation, which added itself
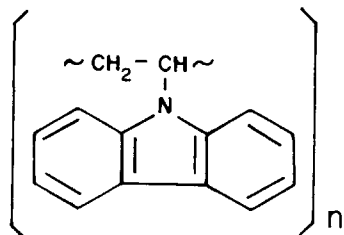
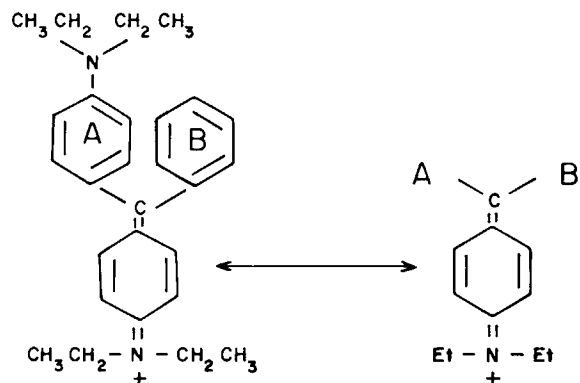**Figure 1**   Homopolymeric macromolecule of PNVC.

Figure 2   Monomeric unit of GVM: A, B, aromatic rest; Et, ethyl group.

to the polarized end of another monomeric molecule, then behaved as a highly stable nucleophilic species.

The positive charge at the end of these dimeric structures interacts with the comonomer nucleophilic zone to produce a branched copolymer intermixed with dimeric residue. During this reaction, the $n\pi$ doners, which are characterized by C=C insaturations combined with an n electron doner atom,[10-12] exchange basicity with the π system, thus bringing about more effective cationic dimerization. In this reaction involving a macromolecular base and a monomer dimerizing in its presence, the dimer displaces a hydrogen atom from the polymeric base, thus creating an active center in which a covalent bond is established. The dimeric species in this copolymerized conformation are arranged as masses of low molecular weight (Fig. 3). Figure 3, gives the suggested structure for the copolymeric compound PNVC/GVM.

Knowledge was gained from the best-defined spectra of the macromolecular structure, as to the bonding characteristics of the chromophoric groups as well as to the correlations between specific chemical group frequencies.

The absorption used to characterize these structures corresponded to the chemical groups —C =N+, CCN, —C=C—C=, and —CH2—N+. The absorption bands of the GVM vibrational spectrum observed for the —C=N+ group (Fig. 4) appeared within the 2500–2400 cm^{-1} range, whereas the intense band at 1581 cm^{-1} appeared only when the ring was conjugated with unsaturation-extending conjugations. The pronounced band at 1414 cm^{-1} corresponding to the methylene group was shifted under the influence of the positively charged nitrogen atom, —CH2—N+, whereas the CCN group absorption at 1152 cm^{-1} characterized the structure as a monomeric unit.
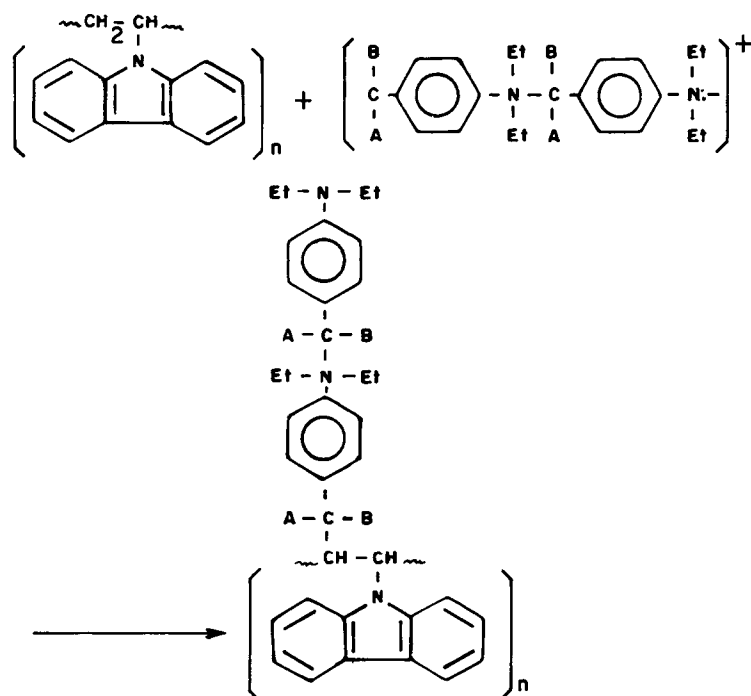
Figure 3   Possible version of the copolymeric structure PNVC/GVM.

Repetitions in the chemical units was the basis for spectroscopic interpretation of the PNVC vibrational spectrum. These spectra provided information as to the doubly substituted aromatic unsaturations in *orto* and as to the CCN group at 1154 cm^{-1} that was associated solely with the monomeric base (Fig. 5).

The clearly differentiated absorption stretching of the copolymerized product, whose macromolec-

ular base composed the major component, could be readily seen at 1623 and 1593 cm^{-1} (Fig. 6). In contrast, the polycyclic component being present in such reduced proportions was not readily identifiable. Presumably, these molecules are so tightly compressed as to render vibration stretching undiscernible. Completely absence from the spectra are the absorptions corresponding to the positively charged aromatic carbon $-$ nitrogen bonding, ϕ $-$ N^{+}, at the
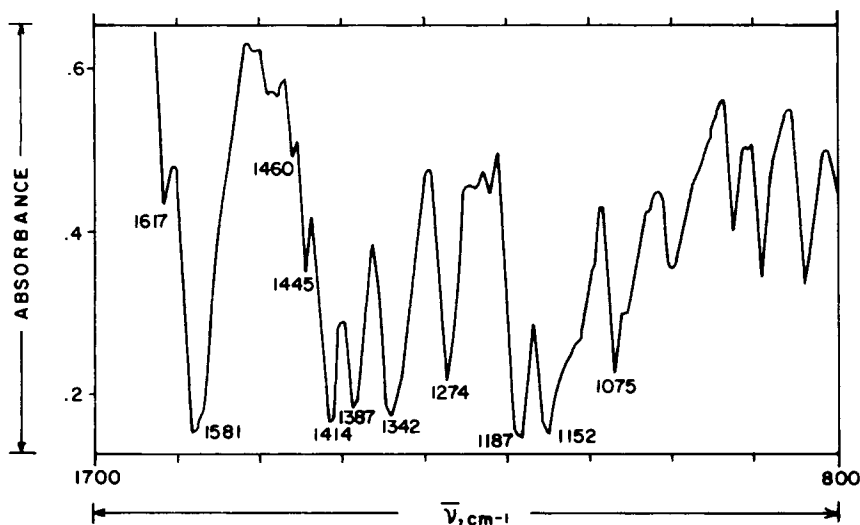

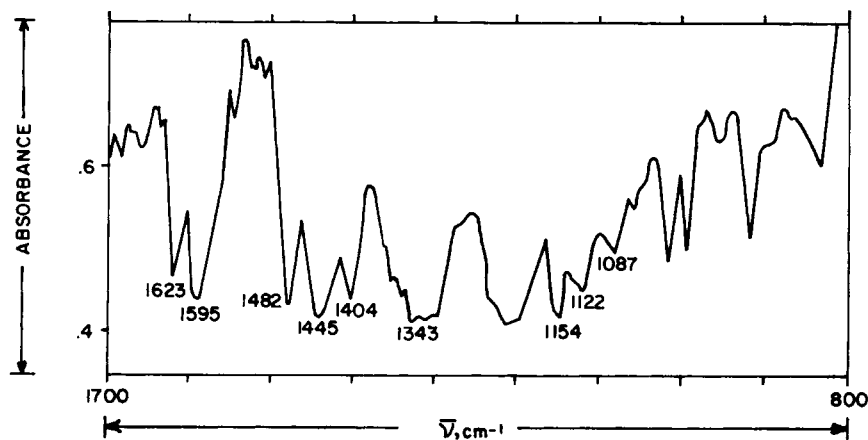**Figure 4**   Vibrational absorption spectrum of the GVM monomeric unit.

Figure 5 Vibrational absorption spectrum of the PNVC homopolymeric macromolecule.

2500–2400 cm⁻¹ interval, the unsaturated groups conjugated at 1581 cm⁻¹, and the —CH₂═N⁺ groups at 1414 cm⁻¹. This lack of presence provides evidence of a conformation structurally distinct from that of the reactant comonomers.

Indicative of a stereochemical conformation, in which the hexocyclic chromophoric group of the comonomeric reactant dislocates electronically to form a simple bonding structure from which both the extended conjugation system and the nitrogen atom positive charges disappear, are the intense absorption associated with the aromatic carbon — nitrogen bonding, φ — N, at 1329 cm⁻¹, with the alliphatic stretching vibrations C═N at 1252, 1233, and 1221 cm⁻¹ and with the stretching vibra-

tions of the CCN group at 1156 cm⁻¹. Related specifically to the CCN group in the copolymerization product are the vibrational frequency and the intense absorption band.

Once the vibrational spectrum was substracted from the spectrum of the original copolymerization system, the noncopolymerized dimeric component could be identified and assayed. Without duplicating specimen thicknesses, normalization was achieved by manipulating computerized routines so that the system automatically distinguished the spectral frequencies of the differentiated noncopolymerized dimer structures.

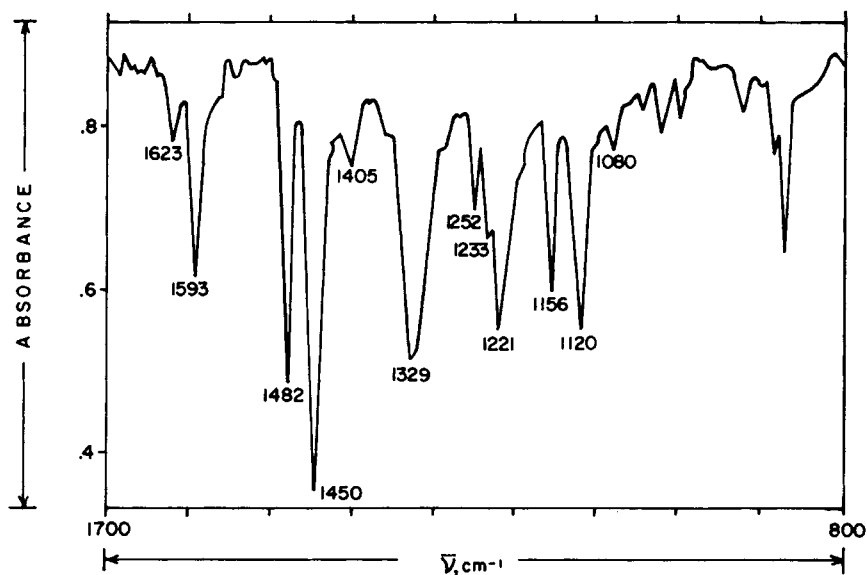The absorption band corresponding to the CCN group served to differentiate the dimeric portion in

Figure 6 Vibrational absorption spectrum of PNVC/GVM copolymerization system.
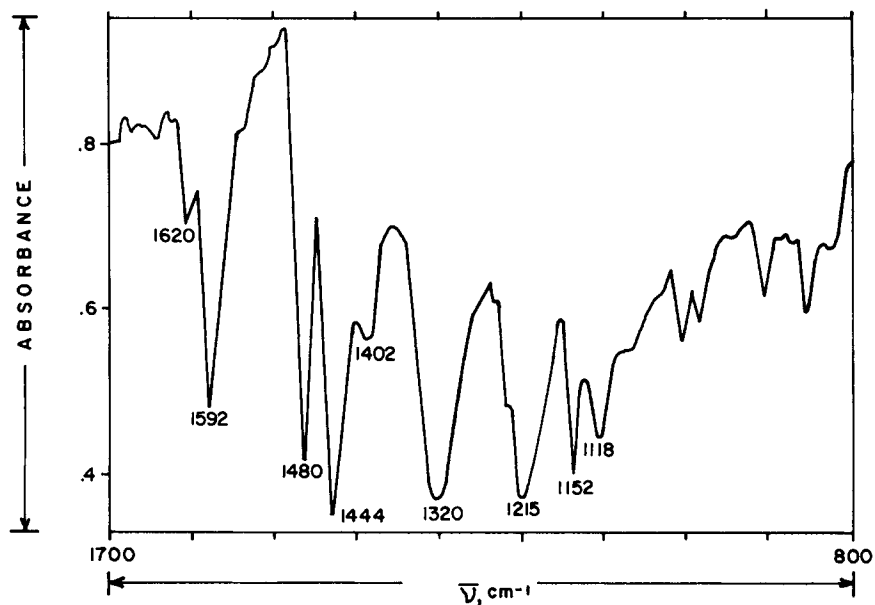
Figure 7   Vibrational absorption spectrum of the insoluble dry fraction.

the copolymerized structure from the noncopolymerized portion. Specimens of the copolymerized product immersed in sufficient water yielded both a soluble and an insoluble fraction. Once dried, the insoluble residuum generated, presumably, the copolymerized material of spectral information B (Fig. 7), which was similar in many respects to the original copolymerization product A (Fig. 6). The DIFF
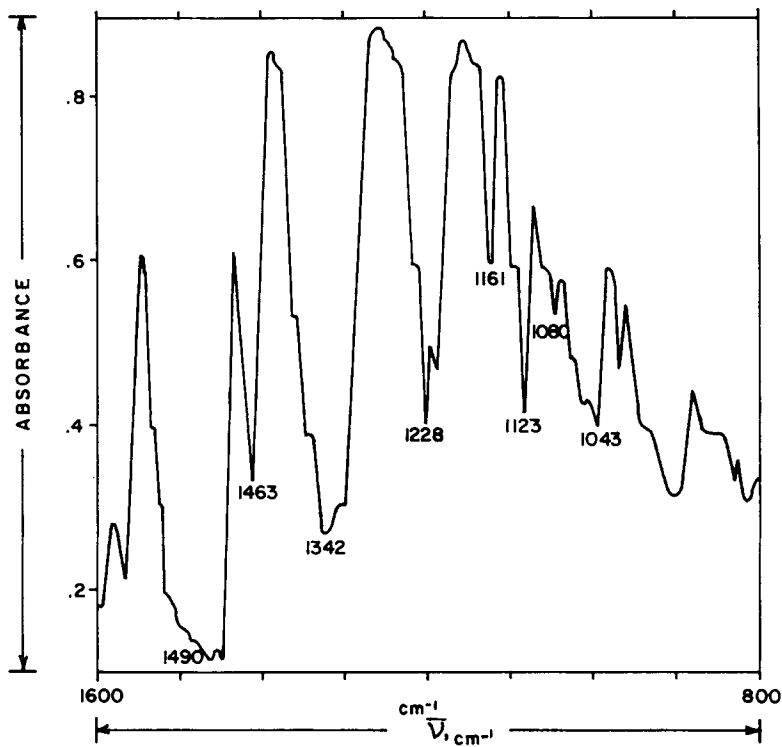

Figure 8   Vibrational absorption spectrum of the nonpolymerized fraction obtained by computerized differentiation of the insoluble sample.
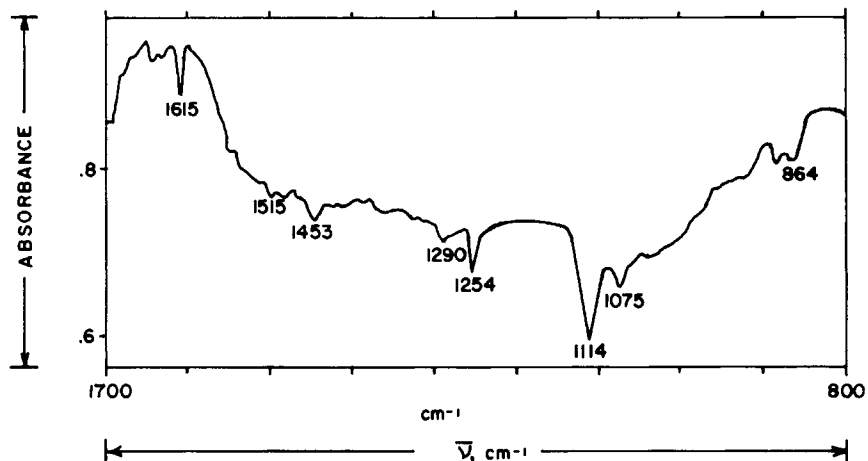
Figure 9 Vibrational absorption spectrum of the nonpolymerized fraction obtained by computerized differentiation of the soluble sample.

routine substracted spectral information B from A by means of a computer-determined factor. This factor normalized the absorption bands in different concentrations of specimens. The spectral information of noncopolymerized C (Fig. 8) substracted from A and B resulted in an interference-free spectrum far more representative of this fraction. The C spectral information characterized the dimer as an aromatic configuration without unsaturation-extended conjugations and without groups in which positively charged nitrogen was present. The chromophoric groups of the C spectrum appeared and could be identified as such by the following: intense absorptions at 1490, 1463, 1080, and 1043 cm^{-1}; the aromatic carbon — nitrogen bond at 1342 cm^{-1}; C — N alliphatic vibrational at 1228 and 1123 cm^{-1}; and a CCN group at 1161 cm^{-1}. The D soluble fraction spectral information (Fig. 9) differed in structural conformation from the dry sample B (Fig. 7). The vibrational frequency at 1114 cm^{-1} (Fig. 9) characterized the *tert*-hydroxyl group bonded to the α-unsaturated group. The C = C stretching of double-substituted aromatic groups at 1615, 1515, 1075, and 864 cm^{-1}, and that of the C — N aromatic and

alliphatic vibrations shown at 1290 and 1254 cm^{-1} seen in the same figure, make up the remaining absorptions. Spectral interpretation of the D soluble fraction supports the assumption that the dimeric species in solution are stabilized by their interaction with the reactive groups of the solvent, which accounts for the vanishing of the CCN group vibrational contribution from the spectrum (Fig. 9). The CCN group vibrational contribution from this spectrum is markedly affected, which explains the absence of a detectable absorption. Assay of this soluble species was based on the aromatic vibrational stretching at 1075 cm^{-1}.

To substract B from A, a band common to both spectra was chosen and its measures the band absorbance, whose value is equivalent to 100%. The difference command automatically places the computed difference spectrum in file C. Its absorbance is related to that of the common band and the equivalent percentage is obtained. The results obtained for the percentage concentration in the C substraction spectrum (Fig. 8) was consistent with those of spectrum D (Fig. 9). The results are shown in Tables I and II.

Table I   Noncopolymerized GVM in Insoluble Dry Fraction

CCN	Copolymerization Product (A)	Insoluble Residuum (B)	Noncopolymerized Fraction (C)
$\eta_{cm^{-1}}$	1156	1152	1161
A*	0.206	0.096	0.109
%	100.0	46.60	52.91

Table II Noncopolymerized GVM in Soluble Fraction

$p - \phi$	Copolymerization Product (A)	Noncopolymerized Fraction (D)
$\eta_{cm^{-1}}$	1080	1075
A*	0.321	0.166
%	100.0	51.71

CCN, chemical group to be evaluated, alliphatic stretching; $\eta_{cm^{-1}}$, vibrational absorption stretching; A*, absorbance; %, percentual ratio; $p - \phi$, chemical group to be evaluated, aromatic stretching. An undesirably high production of free dimeric species in the PNVC/GVM copolymerization of these experiments did not allow a greater yield of the copolymerized product.

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