the product probably is a combination of both). The viscosity measurements yielded a value of 0.058 for the intrinsic viscosity which indicates a low molecular weight, probably in the range of 10^3–10^4 g/mol.[4] In order to confirm the postulated structure, ir and nmr data were obtained.

Table I lists the ir absorption frequencies, including their relative strength, that were observed using mineral oil and fluorolube slurries, and a KBr pellet. This spectrum appears consistent with that expected from the proposed structure. The three absorptions at 1552, 1450, and 1420 are close to the ring stretching vibrations of 1,2,3-triazole.[5] Similarly, the absorptions at 1127, 1050, and 975 are in the ranges reported for ring skeletal vibrations of triazoles[5,6] and the absorption at 1325 is very close to the range (1300–1270) assigned to the cyclic -N–N=N- linkage in vicinal triazoles.[6] Finally, the absorptions at 1220, 1153, and 1028 are in the range of vibrations attributed to CH in-plane deformations and those at 843 and 787 are in the range of vibrations attributed to CH out-of-plane deformations for nitrogen containing heterocyclic compounds.[7] Thus, the observed ir absorptions are consistent with the proposed structure for the product.

The nmr spectrum was obtained with the polymer dissolved in D_2SO_4; sodium 2,2-dimethyl-2-silapentane-5-sufonate in D_2O was used as the reference. There were only three significant peaks observed; the acid proton (isotopic impurity) appeared at δ 11.6 downfield from the reference, the other two were at δ 8.8 and 6.2 with an area ratio of about 1.9 (the latter resonance being the larger). The relative shifts and areas are about what would be predicted from the proposed structure (assuming the ring was protonated), with the vinyl proton resonance occurring further downfield than that of the methylene protons. The nmr spectrum for 1-methyltriazole in trifluoroacetic acid had a resonance at δ 8.5 for the proton in the 5 position and at 4.5 δ for the methyl protons,[8] which is consistent with the spectrum of the product. Based on the above information it was concluded that the product consists of a polymer with the proposed triazole structure.

The results of the energy of combustion determinations are listed in Table II. The calculated enthalpy of combustion (ΔH_c) is within 0.1% of the value of ΔE_c. By using the determined composition the heat of formation was calculated to be 414 ± 2 cal/g.

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(4) Because of the solvents necessary to dissolve the polymer, the acquisition of a more exact value was not attempted.

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Variation in Inter-Ring Interactions in a Series of Carbazyl Group Containing Polymers

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The interactions between neighboring chromophores in aromatic group-containing vinyl polymers can be expected to be extremely important in controlling the electrical and optical properties of the polymers. One of the most widely cited photoconductive polymers is poly(*N*-vinylcarbazole) (PNVC), and the question of its uniqueness in terms of structure property relationships has not been discussed previously in the literature.

The electronic absorption spectrum of PNVC[1] is virtually identical with that of *N*-isopropylcarbazole indicating very little mixing of the wave functions in the ground or low-lying excited states of the polymer. In weakly interacting systems such as this it is reasonable to expect electronic conduction will occur *via* a hopping mechanism. Charge-carrier mobilities in such systems have been shown by Holstein[2] to be proportional to the square of the transfer integral between hopping sites. The average molecular overlap should therefore be a controlling factor in determining the carrier mobilities in such systems. In a previous study[3] it was shown that PNVC exhibits unusually large shielding of one or more aromatic protons. Although the perturbation of the electronic spectrum is weak[1] the protons act as very sensitive magnetic probes of inter-ring interactions. We would expect that polymers which exhibit the largest inter-ring interactions will exhibit the largest mobilities. In order to examine the effect of conformational differences on electrical and electronic properties of a series of structurally related polymers we have synthesized poly(*N*-ethyl-2-vinylcabazole) (PNE2VC) and poly(*N*-ethyl-3-vinylcarbazole) (PNE3VC). In this communication the synthesis of polymers, their nmr spectra, and the interpretation of these spectra are described. Subsequent papers will relate the electrical and optical properties to the macromolecular structure.

Materials

***N*-Ethyl-3-vinylcarbazole.** Triphenylmethylphosphonium bromide (35.72 g; 0.1 mol) and anhydrous H_4furan (300 ml) were placed in a 2-l. three-necked flask. The contents of the flask were protected by a blanket of argon and then 46 ml of a 2.18 *M* solution of butyllithium in hexane (0.1 mol) was added to the vigorously stirred solution over a period of 15 min. The reaction mixture was allowed to react for 2 hr and then *N*-ethylcarbazole-3-carboxaldehyde (22.33 g; 0.1 mol) in H_4furan (150 ml) was added to the reaction flask over a period of 10 min. After heating to reflux temperature for 1.5 hr the reaction mixture was cooled to room temperature and treated with 750 ml of hexane. After the precipitate which forms was discarded, the solvents were removed to yield a crude product which crystallized on standing. Recrystallization was accomplished with a minimum amount of ethanol containing a drop of ammonium hydroxide: yield 11.5 g (52%); mp 66–67°, lit.[4] mp 66–67°.

Poly(*N*-ethyl-3-vinylcarbazole). *N*-Ethyl-3-vinylcarbazole was purified on a silica gel column and eluted with hexane. The polymerization solvent, Spectrograde methylene chloride, was passed through a neutral alumina column and was used immediately. *N*-Ethyl-3-vinylcarbazole (4.0 g) in 80 ml of methylene chloride was placed in a 100-ml two-necked flask and protected with a blanket of dry nitrogen. The solution was cooled to −60° and then 8 μl of boron trifluoride etherate in 2 ml of methylene chloride was added to the monomer solution which was rapidly stirred with a magnetic stirring bar. After a few minutes the viscosity of the solution increased to the point at which stirring was difficult. The reaction mixture was then quickly quenched in 400 ml of methanol. The H_4furan-soluble polymer was reprecipitated several times with methanol: yield 2.8 g; M_n 330,000, M_{WD} 2.97.

Poly(*N*-ethyl-2-vinylcarbazole) was prepared by conventional free-radical methods using monomer prepared

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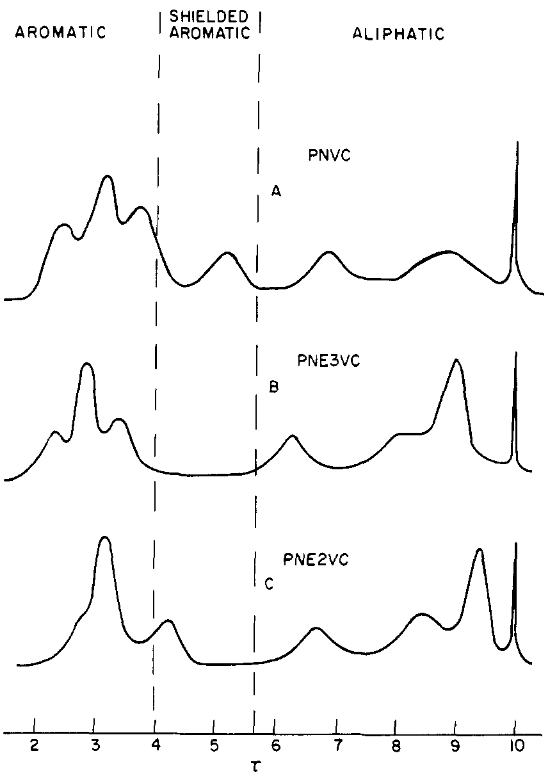

Figure 1. 60-MHz proton nmr spectrum of PNVC, PNE3VC, and PNE2VC at room temperature in $CDCl_3$.

Table I
Chemical Shifts (τ) and Approximate Numbers of Protons

	Aromatic	Shielded Aromatic	Aliphatic
PNVC	2.4, 7.2, 7.8 (~1)	5.0 (~1)	6.8, 8.6
PNE2VC	2.7, 3.1 (~6)	4.1 (~1)	6.7, 8.3, 9.4 (5)
PNE3VC	2.3, 2.7, 3.4 (7)		6.3, 8.0, 9.0 (5)

according to the method of Ledwith.[5] The polymer was precipitated by methanol: M_n 19,400, M_{WD} 2.13.

Poly(*N*-vinylcarbazole) was obtained commercially, and purified repeatedly from H_4furan with methanol: M_n 202,000, M_{WD} 5.1.

The 60-MHz room-temperature proton nmr spectra of PNVC, PNE2VC, and PNE3VC are shown in Figure 1. The various peaks in the proton nmr spectrum are arbitrarily grouped into three regions: aromatic, shielded aromatic, and aliphatic. The assignment of the peaks and numbers of protons are given in Table I. Because of the broadness of the peaks it is difficult to assign individual peaks to their corresponding protons in the molecules. It is possible, however, to distinguish aliphatic from aromatic protons and also to estimate the number of protons in the region designated as shielded aromatic. For PNVC and PNE2VC there is approximately one proton in this shielded aromatic proton region and for PNE3VC none. The intense peak at τ 9.0 in PNE3VC and τ 9.4 in PNE2VC is easily identified as belonging to the methyl group in the *N*-ethyl substituent. These differences in chemical shifts are very significant and will be interpreted below.

In an earlier detailed study of the nmr spectrum of PNVC[3] it was shown that at 220 MHz the shielded aromatic peak could be resolved into a number of peaks whose relative intensities appeared to be temperature dependent. This multiplicity could possibly have been due to contributions from several different positions in the molecule in the different stereochemical sequences and reflect the unusually high steric and spacial constraint in that polymeric environment resulting in large magnetic anisotropies. A further confirmation of this interpretation was obtained when the nmr spectra of a series of *N*-vinylcarbazole–ethyl acrylate, copolymers, were examined. It was shown that the shielded aromatic peak gradually disappeared as the vinylcarbazole concentration was changed from 84 to 54 mol % (Figure 4).[6] For a 1:1 copolymer the nmr spectrum of the aromatic region was very similar to *N*-isopropylcarbazole (Figure 5),[6] where no such steric constraints are possible.

The variations in the degree of shielding in the different polymers contain significant information on the conformation and overall structure of the polymer chain. PNVC appears to represent the polymeric environment in which the carbazole rings are the most tightly packed of any of the carbazyl group containing polymers. PNE2VC appears to be less tightly packed than PNVC but much more so than PNE3VC. On this basis it would seem likely that PNVC should exhibit the largest electronic mobilities and PNE3VC the least. If this correlation can be verified through mobility studies an important relationship between the tertiary structure of the polymer and the electronic properties has been obtained.

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Spectrophotometric Detection of Acylimidazole Poly(ethylenimine), an Intermediate in Catalytic Hydrolysis

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In a previous publication[1] we described derivatives of poly(ethylenimine) (PEI) with catalytic activity toward hydrolysis of nitrophenyl esters. In these derivatives hydrocarbon residues attached to PEI served as binding groups and imidazole residues provided potential catalytic groups. The hydrolytic rate curves in the presence of these polymers indicated that the nitrophenyl esters were cleaved in a two-step kinetic mechanism. Following a fast preequilibrium binding, the first kinetic step was attributed to acylation by substrate of the polymer imidazole residue, accompanied by simultaneous release of nitrophenol(ate). The succeeding kinetic step was ascribed to hydrolysis of the acylimidazole leading to carboxylate ion and regenerated imidazole.

It has seemed desirable to try to detect the postulated acylimidazole intermediate by spectroscopic probing. Acetylimidazole has been shown[2] to have an absorbance maximum at 245 nm with an extinction coefficient of 3000. This absorbance should provide a basis for detection of the intermediate. However, in practice the strong absorbances due to the aromatic ester substrate (nitrophenyl caproate) and the product (nitrophenol(ate)), added to the light scattering from the polymer, have made the spectrophotometric observation of the acylimidazole intermediate unfeasible under the reaction conditions previously described.[1]

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