from that formed by coordination catalysts in the configuration of the asymmetric centers and not merely in molecular weight, since we have now been able to compare directly samples with the two different configurations of essentially the same molecular weight.

Since base-catalyzed polymerization of phenylglycidyl ether has been reported to give crystalline isotactic polymer of low molecular weight,[3] we had hoped to compare this material directly to degraded samples from high molecular weight isotactic polymer formed by coordination catalysts. The recovered degraded polymer proved to be rubbery rather than a crystalline solid. This has to date frustrated this hope. Perhaps one reason for this is the fact that in poly(phenylglycidyl ether) there are both backbone and side-chain ether bonds which may cleave.

Preparation and Properties of a Polymer Formed from Propargyl Azide

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During the investigation of the preparation and properties of new organic azides, it was found that when an alcohol–water solution of propargyl bromide and sodium azide was refluxed, an insoluble polymeric product was formed. It appeared that intermolecular addition had taken place after the propargyl azide was formed by displacement of the bromide, resulting in a polytriazole product. Because of an interest in high nitrogen containing polymers for certain solid rocket propellant applications, the properties of this product, including the heat of combustion, were determined.[1]

Experimental Section

Propargyl Azide; Formation and Polymerization. Solutions of 8.3 g (0.128 mol) of sodium azide in 30 ml of water and 10 ml (0.128 mol) of propargyl bromide in 15 ml of ethanol were mixed in a round-bottom flask; two layers were formed. Heat was evolved upon mixing, and as the displacement reaction proceeded before refluxing an inversion of the layers was observed.

Refluxing of the mixture was initiated and after about 1 hr, the liquid had become one phase and had turned orange; shortly thereafter, a precipitate started to form. After refluxing for about 2 days, 2.7 g (26%) of tan solid was collected and washed with water; a small additional amount of polymer could be precipitated by adding water to the filtrate.[2] The product was dried under vacuum at about 100° before analysis. *Anal.* Calcd for $C_3H_3N_3$: C, 44.45; H, 3.73; N, 51.84. Found: C, 44.04; H, 4.07; N, 49.57; O, 1.97. The oxygen is presumably due to water which had been occluded or chemically bound.

The insolubility of the product in nonreactive organic solvents precluded an exact determination of a molecular weight. It was quite soluble in concentrated sulfuric or hydrochloric acids, and could be reprecipitated by diluting with water. The infrared spectrum and appearance of the reprecipitated product was identical with that of the original material, thus, the solution process in acid did not permanently alter the product. Viscosity measurements were made on an hydrochloric acid solution of the product, from which an intrinsic viscosity was estimated.

Table I
Infrared Data (cm^{-1})

3125 (m)	1325 (m)	1028 (m)
2980 (w)	1220 (s)	975 (w)
1552 (m)	1153 (w)	843 (w)
1450 (m)	1127 (m)	787 (s)
1420 (m)	1050 (s)	

Table II
Energy of Combustion of the Polytriazole

Wt of Sample (g)	Temp Change (°C)	Energy from Fuse Wire (cal)	HNO_3 Formed (mol × 10^4)	$-\Delta E_c{}^a$ (cal/g)
0.6687	1.476	16.5	1.5	5233
0.4503	1.001	15.5	0.9	5262
0.5610	1.246	17.9	1.1	5260
			Av	5252 ± 12

[a] These values have been corrected for HNO_3 formation; the ΔH_f and ΔH_{sol} for HNO_3 were taken as 42.4 and 7.2 kcal per mol, respectively.[3]

The substance was thermally stable up to 200° but darkened above that temperature; the darkening was accompanied by slow gas evolution, and no sign of melting was observed.

Heat of Combustion. The energies of combustion (ΔE_c) were determined using a Parr, Series 1230, Model 1115, oxygen bomb calorimeter equipped with a Model 2611 adiabatic control system. The standard procedure for a nonvolatile solid was followed. The polymer samples were ground to a fine powder, dried under vacuum, pressed into a soft pellet, weighed, and placed in the bomb. One milliliter of water was placed in the bomb also to saturate the atmosphere with water vapor and to ensure that any HNO_3 formed in the combustion would go into dilute solution. The bomb was evacuated (to the vapor pressure of water), pressurized to 20 atm with oxygen, evacuated again, then repressurized for combustion (30 atm ensured essentially complete combustion).

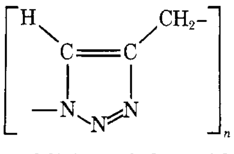
The assembled adiabatic calorimeter was allowed approximately 15 min to equilibrate before temperature readings were taken; temperature readings were taken exactly 4 min before ignition, at ignition, and 9 min after ignition. The uncertainty of the thermometer readings was ±0.0005°.

The calibration of the calorimeter was made with benzoic acid supplied by Parr; the energy of combustion was taken as 6317.8 cal/g. Five samples of benzoic acid were used to determine the energy equivalent of the calorimeter system. The Washburn corrections were applied to the raw data using the methods in Hubbard, Scott, and Waldington.[3] The resulting mean energy equivalent was 2386.9 ± 1.2 cal/deg (±average deviation).

The bomb was carefully rinsed out after combustion of the polymer and the solution titrated with NaOH to determine the HNO_3 content. It was assumed that the HNO_3 was formed exclusively from the nitrogen in the polymer because of the precautions taken to prepare the bomb. This assumption was checked by titrating a solution after combusting a hydrocarbon under similar conditions; no acid was found.

Discussion Section

From the observed properties and composition, the product appears to be primarily a polymer of 4-methylene-1,2,3-triazole



formed by 1,3-cycloaddition of the azido group of one molecule of propargyl azide to the acetylenic bond of another (the 5-methylene configuration is a possibility also and

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(1) The product appears to be similar to that reported by M. C. Baldwin, K. E. Johnson, J. A. Lovinger, and C. O. Parker, *J. Polym. Sci., Part B*, 5, 803 (1967). However, the method of synthesis reported herein is much less hazardous and the polymer has been more fully characterized.

(2) Professor P. A. S. Smith (University of Michigan) has reported to us that if the reaction mixture is stirred for about 1 hr then diluted with water, without having been heated, a liquid product, apparently monomeric propargyl azide is obtained. It distilled near 80°, but exploded with destructive violence before distillation could be completed. The shock sensitivity of propargyl azide has been reported to be greater than that of nitroglycerine.[1]

(3) W. N. Hubbard, D. W. Scott, and C. Waldington in "Experimental Thermochemistry," F. D. Rossini, Ed., Interscience, Inc., New York, N. Y., 1956, pp 75-104.

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.

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

(5) L. W. Hartzel and F. R. Benson, *J. Amer. Chem. Soc.*, **76**, 667 (1954).

(6) E. Lieber, C. N. Rao, T. S. Chao, and H. Rubinstein, *Can. J. Chem.*, **36**, 1441 (1958).

(7) C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy," Academic Press, New York, N. Y., 1963, pp 323–329.

(8) G. B. Borlin and T. J. Batterham, *J. Chem. Soc., B*, 516 (1967).

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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(1) W. Klöpffer, *J. Chem. Phys.*, **50**, 2337 (1969).

(2) T. Holstein, *Ann. Phys.*, **8**, 343 (1959).

(3) D. J. Williams, *Macromolecules*, **3**, 602 (1970).

(4) V. Lopatinskii and E. E. Sirotkina, *Metody Poluch. Khim. Reactivov Prep.*, **11**, 40 (1964); *Chem. Abstr.*, **65**, 2203 (1966).