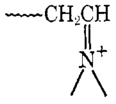
The following tentative suggestion is offered. The polyvinylcarbazole cation is very inert; it may be represented as an ammonium ion E. Consequently,



E

it is incapable of initiating propagation in the absence of some additional driving force. Such a force may be provided by the polarizability of the planar vinylcarbazole molecule by the planar carbonium ion of polyvinylcarbazole. This additional driving force does not operate in the addition of oxetane. Hence, homopropagation of vinylcarbazole, but not its copolymerization with oxetane, is feasible.

The importance of polarizability in some reactions of planar aromatic molecules was demonstrated elsewhere.[5]

Acknowledgment. We gratefully acknowledge the financial support of this investigation by the National Science Foundation and the Petroleum Research Fund administered by the American Chemical Society.

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Polymerization and Copolymerization of N-Vinylindole and N-Vinylmethylindoles

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Received April 7, 1968

ABSTRACT: Polymers and copolymers of N-vinylindole, N-vinyl-2-methylindole and N-vinyl-3-methylindole have been synthesized. The synthetic procedures for preparing the monomers and the polymers are described.

As part of an investigation of the polymerizability of N-vinyl heterocyclic compounds, the homopolymerization and copolymerization of N-vinylindole, N-vinyl-2-methylindole, and N-vinyl-3-methylindole were studied. The polymerization of N-vinylindole with stannic chloride[1] and with organic electron acceptors[2] to give polymers in the molecular weight range 600–1800 and 5400, respectively, has recently been reported. The polymer was described as a white powder softening between 169 and 177°.[1]

The monomers N-vinylindole, N-vinyl-2-methylindole, and N-vinyl-3-methylindole were prepared by the vinylation of indole,[3] 2-methylindole,[4] and 3-methylindole, respectively, at 150–190° and 20–30 atm pressure. The three monomers were successfully polymerized thermally without added catalyst and with cationic, free-radical, radical-cation and Ziegler–Natta catalysts. The number average molecular weight of several of these polymers were greater than 10,000 as determined by vapor phase osmometry and confirmed by gel permeation chromatography.

The polymerization data which are summarized in Table I indicated that N-vinylindole is polymerized more readily than the 2- or 3-methyl derivatives. Apparently α and β substituents on the indole ring affect the monomer reactivity in a manner similar to that of *ortho* and *meta* substituents on styrene.[5] This is further substantiated by the unsuccessful attempts to copolymerize N-vinyl-2-methylindole with N-vinyl-3-methylindole and by the poor yields obtained in attempting to copolymerize N-vinylindole with either monomer.

Of considerable interest was the copolymerization of N-vinylindole with monomers having a reactive double bond within the ring structure. It was found that copolymers could be prepared with indole, N-methylindole, indene, coumarin and maleic anhydride (Table II). Elemental analyses (Table III) suggest that approximate 1:1 copolymers were prepared using 1:1 molar quantities of monomers. Copolymer formation was confirmed by the following experimental evidence: the C, H, and N analyses and the infrared spectra of the copolymers were unchanged after Soxhlet extraction with boiling methanol for 144 hr. Attempts to homopolymerize the comonomers indole, N-methylindole, coumarin, and indene under the same conditions used for the copolymerization and for the homopolymerization of N-vinylindole were unsuccessful. Each monomer was recovered quantitatively, unchanged. The single gel permeation chromatographic distribution peaks obtained for each copolymer were examined by computer programmed analysis.[6] These results gave

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(6) We wish to thank Dr. Edward M. Barrall, II, of the Chevron Research Co. for the gel permeation programmed analysis of the copolymers and for the interpretation of these results.

TABLE I
HOMOPOLYMERIZATION OF N-VINYLINDOLE MONOMERS

Expt no.	Monomer, g	Solvent	Temp, °C	Initiator, g	Time, hr	Yield, %	Softening pt, °C	Intrinsic viscosity, η^a
1	N-Vinylindole, 7.5	None	150	Δ	48	89	315–325	Insoluble[b]
2	N-Vinylindole, 5.0	Acetonitrile	40	DDQ,[c] 0.09	4	66	170–182	Insoluble[b]
3	N-Vinylindole, 5.0	SO_2	−33	H_2O, SO_2, 15	4	52	204–215	0.05
4	N-Vinylindole, 7.3	Toluene	−78	Et_2AlCl, 0.32	5	11	204–215	0.12
5	N-Vinylindole, 5.0	Methylene chloride	−70	$BF_3 \cdot (C_2H_5)_2O$, 0.05	2.5	11.5	202–215	0.05
6	N-Vinylindole, 11.2	Benzene	80	AIBN,[d] 0.13	24	58	204–215	0.14
7	N-Vinylindole, 10	Benzene	55	$TiCl_3$, 1.1 Et_2AlCl, 2.1	56	99	202–216	Insoluble[b]
8	N-Vinyl-2-methylindole, 5.0	None	150–200	Δ	96	8	212–225	0.16
9	N-Vinyl-2-methylindole, 10.0	Benzene	80	AIBN, 0.10	42	76	212–225	0.14[e]
10	N-Vinyl-3- 5.0 methylindole	None	150–200	Δ	96	24	137–158	0.05
11	N-Vinyl-3-methylindole, 10.0	Benzene	80	AIBN, 0.10	42	<1	192–202	

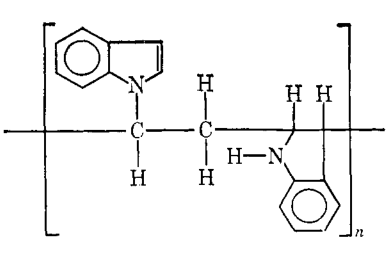
[a] Determined at 37° in benzene. [b] Insoluble in the common organic solvents and in DMF, hexamethylphosphoramide, hexafluoracetone, α-chloronaphthalene, and H_2SO_4 at elevated temperatures. [c] 2,3-Dichloro-5,6-Dicyano-*p*-benzoquinone. [d] Azobisisobutyronitrile. [e] Number average molecular weight in benzene at 37° determined by vapor phase osmometry was 12,000.

TABLE II
COPOLYMERIZATION OF N-VINYLINDOLE[a] WITH VARIOUS MONOMERS

Expt no.	Comonomer, g	Solvent	Temp, °C	Initiator, g	Time, hr	Yield, %[b]	Softening pt, °C	Intrinsic viscosity, η^c	$\bar{A}_w/\bar{A}_n$[d]
1	Indole, 4.1[e]	None	150	Δ	24	45	>300	0.20	3.1
2	N-Methyl-indole, 4.6[e]	None	150	Δ	24	17.5	220–230	0.24	1.4
3	Indene, 4.1[e]	None	150–200	Δ	116	78	165–173	0.05	1.4
4	Coumarin, 5.1[e]	None	200	Δ	48	44.5	>300	0.24	3.1
5	Maleic anhydride, 11	Methylene chloride	40	Benzoyl peroxide, 0.09	22	68	146–153	0.10	
6	N-Vinylcarbo-zole, 6.8	None	150	Δ	24	85	>300	Insoluble	
7	Styrene, 3.6	None	150–200	Δ	116	99	178–193	Insoluble	
8	N-Vinyl-2-methylindole, 13.1	Benzene	70	AIBN, 0.33	24	11	198–216	0.07	
9	N-Vinyl-3-methylindole, 13.1	Benzene	70	AIBN, 0.33	24	0			

[a] N-Vinylindole (5 g) was used in all experiments except in 5, 8, and 9 where 10.9, 14.3, and 14.3 g, respectively, were used. [b] Yield is based on purified polymer. [c] Determined at 37° in benzene. [d] Glpc analysis. [e] Homopolymerizations of indole, N-methylindole, indene and coumarin carried out under the experimental conditions of Tables I and II were unsuccessful.

no evidence for bimodality. The infrared spectroscopic data suggest the repeat unit shown for these polymers. The weak double bond at 6.1 μ and the bond at 14.0 μ, indicative of some *cis* configuration in the indole monomer, are diminished in the vinylindole–indole copolymer. Confirming evidence for the presence of indole in the copolymer is the sharp, single N–H band near 2.9 μ, indicative of a secondary amine. The infrared spectra of the copolymers shows that the strong C═C stretching band at 6.2 μ, characteristic of the vinylindole monomer, has essentially disappeared. The absorption bands at 10.2–10.5 and 11.7–12.2 μ, assigned to the terminal vinyl group on a nitrogen in the monomer, are no longer present in the polymers.



The nmr spectra of the copolymers in deuteriobenzene were poorly resolved yielding only a limited amount

TABLE III
ELEMENTAL ANALYSES FOR N-VINYLINDOLE COPOLYMERS

Comonomer	Polymer repeat unit (1:1)	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
Indole[a]	$(C_{18}H_{16}N_2)_n$	83.04	6.19	10.76	82.82	5.98	10.41
					83.01	5.10	10.46
N-Methylindole[a]	$(C_{19}H_{18}N_2)_n$	83.17	6.61	10.21	83.19	6.42	10.17
					83.06	6.58	10.31
Indene[a]	$(C_{19}H_{17}N)_n$	88.03	6.56	5.41	87.54	6.33	5.99
					87.72	6.50	6.05
Coumarin[a]	$(C_{19}H_{15}NO_2)_n$	78.89	5.19		80.98	5.78	
					81.13	5.94	
Maleic anhydride[b]	$(C_{14}H_{11}NO_3)_n$	69.70	4.60	5.81	78.46	5.81	7.90
					78.51	5.89	7.94
N-Vinylcarbazole	$(C_{24}H_{20}N_2)_n$	85.67	5.99	8.33	84.67	6.42	7.83
					84.58	6.60	7.95
Styrene	$(C_{18}H_{17}N)_n$	87.41	6.93	5.66	86.83	6.66	6.33
					86.66	6.56	6.42
N-Vinyl-2-methylindole	$(C_{21}H_{20}N_2)_n$	83.96	6.71	9.33	83.72	6.29	9.72
					83.76	6.72	9.74

[a] Elemental analyses for C, H, N before and after 144 hr Soxhlet extraction in boiling methanol. [b] Analysis indicates polymer is approximately an 85:15 copolymer: C, 78.65; H, 5.70; N, 8.31.

of information. However, the aromatic to aliphatic proton ratios appear to be consistent for the suggested structures.

Experimental Section

The vinylindole monomers were prepared from the corresponding indoles (Eastman Organic Chemicals) by the following procedure. The indole (150 g) was dissolved with 5 g of KOH in 250 ml of toluene in a 1-l. stainless steel "Magnedrive" pressure reactor (Autoclave Engineers, Inc.). The reactor was pressurized at ambient temperature to 200 psi with acetylene, 99.5% (The Matheson Co., Inc.), and diluted with 200 psi of dry nitrogen. The temperature was slowly raised to 150° for the 2- and 3-methylindoles and 190° for indole and held constant for 24 hr. The extent of reaction was monitored on a pressure-temperature recorder. The crude mixture was washed with water, extracted with ether and the ether extract washed with cold alkaline methyl alcohol (pH 9). The organic layer was separated, dried over Na_2SO_4 and fractionated through a glass-helix packed column under vacuum to give the following monomers: N-vinylindole, bp 70–72° (1 mm) [lit.[1,4] bp 70–72° (1 mm)], mp 31.5–32.0° (lit.[2] mp 28.7°); N-vinyl-2-methylindole, bp 105° (2 mm) [lit.[4] 105 bp (2 mm)]; and N-vinyl-3-methylindole, bp 94° (1 mm), $n^{25}D$ 1.6204. The N-vinyl-2- and -3-methylindoles are liquids at ambient temperature.

Thin layer chromatography confirmed the purity of the monomers showing only one spot in several solvent mixtures for each compound.[7] The infrared spectra showed no N–H absorption at 2.94 μ. *Anal.* Calcd for $C_{10}H_9N$ (N-vinylindole): C, 83.88; H, 6.34; N, 9.78. Found: C, 83.43, 83.64; H, 6.38, 6.15; N, 9.71, 9.89. *Anal.* Calcd for $C_{11}H_{11}N$ (N-vinyl-2-methylindole): C, 84.04, H, 7.05, N, 705, N, 8.91. Found: C, 84.13, 84.16; H, 7.05, 7.14; N, 8.72, 8.88. *Anal.* Calcd for $C_{11}H_{11}N$ (N-vinyl-3-methylindole): C, 84.04, H, 7.05, N, 8.91. Found: C, 83.97, 84.09; H, 7.15, 7.15; N, 8.71, 8.73.

Polymerizations. A. Monomers. The distilled vinylindole monomers were kept at 0° under nitrogen prior to their use. Indole and coumarin (Eastman Organic Chemicals) were recrystallized from benzene; N-vinylcarbazole (Fluka) was recrystallized once from methanol and further purified by vacuum sublimation; N-methylindole and indene (Eastman) were fractionally distilled prior to use; styrene (Eastman) was passed through a chromatographic column of alumina (Al_2O_3, Fluka-type 5016A) to remove inhibitor and then distilled at reduced pressure. The purity of the monomers was checked by gas chromatography and tlc.

B. Catalysts. Benzoyl peroxide, boron trifluoride etherate (Eastman), azobisisobutyronitrile (K & K Chemicals), titanium trichloride (Stauffer Chemical), sulfur dioxide, 99.9% (Matheson), and 2,3-dichloro-5,6-dicano-*p*-benzoquinone (DDQ, Aldrich Chemicals) were used as received. Aluminum alkyls (Texal Alkyls, Inc.) were used without purification as 25% solutions in benzene or toluene.

C. Solvents. Solvents used were of spectrograde purity. Benzene and toluene were dried over sodium wire.

D. Polymerization Method. Bulk polymerizations were carried out with degassed monomers in heavy-walled glass polymerization tubes sealed at 10^{-5} to 10^{-6} mm pressure. Solution polymerizations were carried out under nitrogen or argon either in pressure bottles or in small three-necked flasks. Typical experimental procedures are as follows.

1. Bottle Method. Into a serum-capped 100-ml narrow-necked pressure bottle, which had been previously baked overnight at 100° and flushed with nitrogen for 1 hr, was added 30 ml of solvent, the catalyst, and 20 ml of solvent containing 5–10 g of monomer. The bottle was then placed in a shaker bath at the desired temperature. At the conclusion of the reaction, the bottle was vented with a hypodermic needle and 25 ml of a 10% hydrogen chloride–methyl alcohol solution was added to destroy the catalyst. The bottle was shaken for an additional 15 min, opened and its contents were added to a large excess of methanol. The polymer was filtered, then purified by repeated precipitation from benzene with methanol. The polymer was then dried in a vacuum oven at 40–50° for 12–16 hr.

2. Three-Necked Flask Method. Into a 200-ml three-necked flask equipped with a stirrer, reflux condenser, thermometer and gas inlet was added the monomer and 50 ml of solvent. Moisture was rigorously excluded by flaming the entire apparatus prior to introduction of solvent and monomer. Oxygen was excluded by maintaining a blanket of purified nitrogen or argon over the solution. To

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(7) E. V. Truter, "Thin Film Chromatography," Interscience Publishers, New York, N. Y. 1963, p 49 ff.

this stirred mixture was added the catalyst. At the termination of the reaction several milliliters of isopropyl alcohol was added to destroy the catalyst and the entire reaction mixture was added to a large excess of methanol. The poylmer was filtered, washed with methanol and purified by repeated precipitation from benzene or toluene with methanol. After repeated washing with fresh methanol the polymer was dried in a vacuum oven at 40–50° for 12 hr.

E. Analysis. Infrared spectra[8a] were obtained with a Perkin-Elmer 521 grating spectrophotometer. Nuclear magnetic resonance spectra were obtained with a Varian AR-100 instrument. Glpc analyses[8b] were carried out in THF at ambient temperature with 1.5×10^5-, 1.5×10^4-, 8000-, and 800-Å columns. $\bar{A}_w$ and $\bar{A}_n$ values corresponding to molecular sizes were determined from the chromatograms. Melting points are uncorrected and were taken on a Hoover Unimelt apparatus.

Acknowledgment. We wish to acknowledge Mr. O. Need for his assistance in the synthesis of the vinyl indole monomers and Mr. G. Shrout for his aid in the interpretation of the infrared spectra.

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(8) (a) The ir spectra of all polymers are available from the authors on request. (b) ArRo Laboratories, Inc., Joliet, Ill.

Diels–Alder Polymerizations. VI.[1] Phenylated Polyphenylenes from Bis-2-pyrones and *p*-Diethynylbenzene[2]

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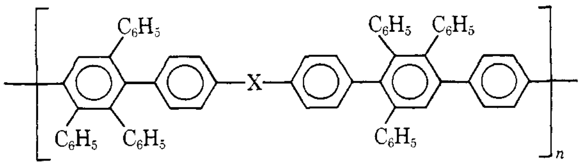
ABSTRACT: Phenylated polyphenylenes (**10**, **11**) were obtained from the reactions of *p*-diethynylbenzene with 5,5′-*p*-phenylenebis-4,6-diphenyl-2-pyrone (**4**) or 6,6′-*p*-phenylenebis-4,5-diphenyl-2-pyrone (**5**), respectively, at 210–300° in toluene. The low molecular weight polymers ($[\eta] = 0.04$–0.13) obtained showed approximately the same thermal stability (TGA break = 550°, air or nitrogen) as those high molecular weight polyphenylenes obtained from the reaction of diethynylbenzenes with bistetracyclones. The polymer backbones probably have both *meta* and *para* linkages in **10** and *ortho* and *meta* linkages in **11** as demonstrated by the model reaction of 4,5,6-triphenyl-2-pyrone (**7**) with phenylacetylene which affords a 5:1 mixture of 1,2,3,4-tetraphenylbenzene (**8**) and 1,2,3,5-tetraphenylbenzene (**9**).

High molecular weight, thermally stable phenylated polyphenylenes of the general structure **1** have been prepared through Diels–Alder reactions of biscyclopentadienones and diethynylbenzenes.[3] For those polyphenylenes which do not contain methylene linkages, the pendant phenyl groups have been shown to be responsible for the initial weight loss at 550° in air or 575° in nitrogen.[3b] Since the cyclopentadienone ring must be tetrasubstituted to ensure that the cyclopentadienone will not undergo spontaneous dimerization,[4] an alternate approach was necessary for the preparation of polyphenylenes with fewer pendant phenyl groups and possibly higher thermal stability. Diels–Alder reactions of 2-pyrones and acetylenes are known to yield benzene derivatives,[5] and although 2-pyrone itself polymerizes on standing, monophenyl- and monocarboxyl-substituted 2-pyrones are stable in the monomeric form.[6] Accordingly, Diels–Alder reactions of bis-2-pyrones with *p*-diethynylbenzene were examined.



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The bis-2-pyrones which have been reported[7,8] were unsuitable for this work since they contained aliphatic (alkylene, ether, or ester) groups linking the pyrone moieties and could not be expected to produce thermally stable polymers. Of the few general methods for the synthesis of 2-pyrones,[9] the base-catalyzed condensation of desoxybenzoin with ethyl phenylpropiolate[10] seemed suited for modification to the preparation of bis-2-pyrones fro bisdesmoxybenzoins. Thus, bis-2-pyrones **4** and **5** were prepared from 1,4-di(phenacyl)benzene (**2**) and 1,4-di(phenylacetyl)benzene (**3**).[11] Compound

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(1) For the previous paper in this series, see F. W. Harris and J. K. Stille, *Macromolecules*, **1**, 463 (1968).

(2) Reported in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968. This research was supported by the U. S. Army Research Office, Durham, N. C.

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