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Synthesis of Poly-5-vinylindole Derivatives

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ABSTRACT

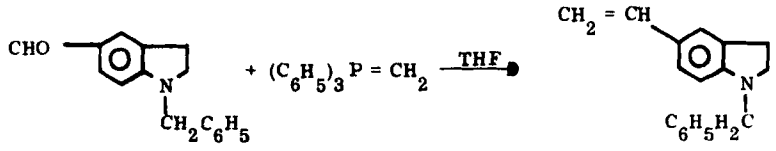
5-Vinyl-N-benzylindoline and 5-vinyl-N-benzylindole were synthesized starting from the corresponding 5-formyl derivative, by utilizing the Wittig or Wittig-Horner reactions. The monomers were polymerized by free-radical (AIBN) and anionic (BuLi) catalysts. Poly-5-vinyl-N-benzylindole was converted through suitable reactions to the tryptamine and indole acetic acid derivatives. Poly-5-vinyl-N-benzyltryptophane was synthesized by malonic ester synthesis by utilizing the condensation of poly-5-vinyl-N-benzylgramine and diethyl formamidomalonate.

INTRODUCTION

Many indole derivatives possess important biological activities. Indole acetic acid is a plant growth hormone [1, 2], tryptophane is an essential amino acid, while tryptamine and especially its 5-hydroxy derivative (serotonin) as well as other indole derivatives substituted at the 5-position [3-6] possess a variety of pharmacological activities.

Since the type of derivatization is responsible for the biological as well as the different physical and chemical characteristics of the products, such as their solubility and permeation through biological membranes, it was of interest to prepare 5-vinylindoline and 5-vinylindole and their polymers and to utilize them for the synthesis of polymers of 5-vinylindoleacetic acid, tryptamine, and tryptophane. Due to the reactivity of the -NH- group, it was blocked by an N-benzyl protecting group to minimize side reactions during the synthesis of the monomers and their polymerization.

Several routes were investigated for the preparation of 5-vinyl-N-benzylindoline (II). 5-Formyl-N-benzylindoline (I) was synthesized by the reaction of N-benzylindoline with phosphorus oxychloride and dimethylformamide and reacted with triphenyl phosphine methylene [7, 8] (Wittig reaction) as follows:



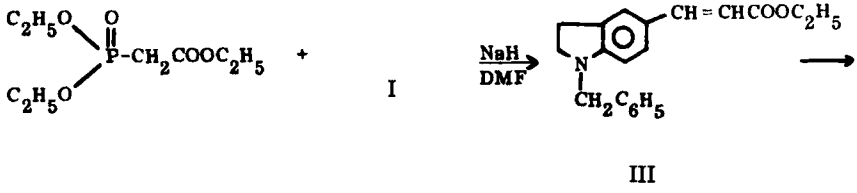
I II

Compound II was obtained in 30% yield, but its separation from triphenylphosphonium oxide was not trivial. Most of the latter was separated by controlled dissolution of the crude reaction product in cold benzene, and finally by preparative tlc. Running the reaction in dry DMSO according to Corey and Chaykovsky [9] did not lead to a better yield.

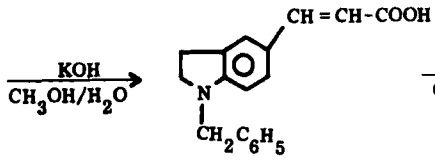
Better yields of II were obtained by using the Wittig-Horner reaction. Triethyl phosphonoacetate was reacted with I [10], and the resulting ester derivative III was hydrolyzed to the α,β-unsaturated acid IV and decarboxylated.

The decarboxylation can be carried out in the presence of copper metal in quinoline [11] or copper chromite in quinoline [12]. The copper has to be freshly prepared from cupric sulfate solution using zinc metal and then dried for 1 hr at 40°C. The overall yield of II by this procedure was 40%.

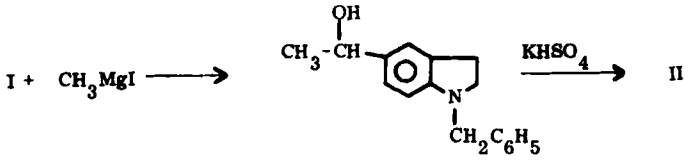
By another route, II was obtained in low yield by treating I with methylmagnesium iodide in dry ether (the reaction is unsatisfactory in THF) to give N-benzyl-5-(α-hydroxyethyl)indoline (V), followed by dehydration with fused potassium bisulfate at about 200°C for 2-3 min [13, 14].



I III



IV II



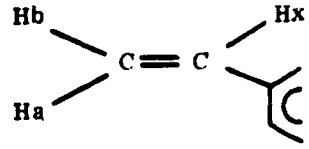
V

II was extracted from the reaction mixture. This procedure was found to give better yields than distillation. Relatively low yields were obtained in the dehydration due to polymerization of the product.

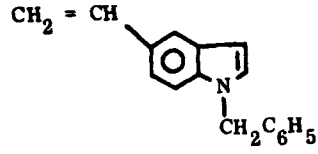
Attempts to increase the yield by exchanging the secondary alcoholic group of V with halogen, followed by dehydrohalogenation were unsatisfactory.

The vinylic protons of II can readily be related to an AMX pattern. The protons H_a and H_b are not chemically equivalent, and H_a is about 30 cps downfield compared with H_b because of its relative proximity to the ring. The proton H_x is strongly deshielded by the ring, and it splits H_a ($J \simeq 16$ cps). H_a is splitted also by H_b ($J \simeq 2$ cps). H_b is splitted by H_x ($J \simeq 11$ cps) and by H_a ($J \simeq 2$ cps).

The synthesis of N-benzyl-5-vinylindole (VI) was analogous to that of the indoline derivative. The starting material was N-benzyl-5-formylindole which was obtained by dehydrogenation of the



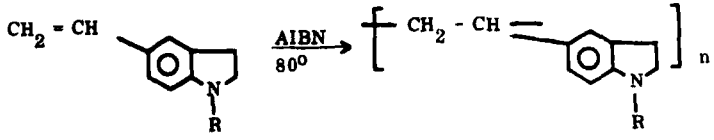
corresponding indoline derivative (I) by chloranil in refluxing xylene. Dehydrogenation by Pd/C catalyst could not be used, since it led to simultaneous decarbonylation of the aldehyde [15].



VI

Polymerization of II was carried out both radically and by anionic initiation.

The radical polymerization was carried out in bulk or in solution by use of toluene or DMF as solvent and azo bis isobutyronitrile (AIBN) as catalyst [Eq. (1)].



(1)

The molecular weight of the polymers decreased on increasing the amount of initiator or the temperature (Table 1).

The anionic polymerization of II as well as VI was carried out in benzene at room temperature using butyl lithium. The molecular weights increased on increasing the [monomer]/[butyllithium] ratio in accordance with a living polymerization (Table 2).

The synthesis of poly-5-vinyl-N-benzylindoleacetic acid and poly-5-vinyl-N-benzyltryptamine was carried out according to the scheme (2). Poly-5-vinyl-N-benzylindole (VII) gave a smooth Mannich

TABLE 1. Radical Polymerization of II[a]

Temperature (° C)	AIBN (%)	$[\eta]$ (dl/g)[b]
60	4	0.225
90	4	0.126
120	4	0.090
60	2	0.275
60	10	0.180

[a]The monomer (0.2 g) was polymerized in DMF (1 ml) under a nitrogen atmosphere for 3 days. The polymers were precipitated with MeOH, purified from DMF-methanol; mp 110-135° C.

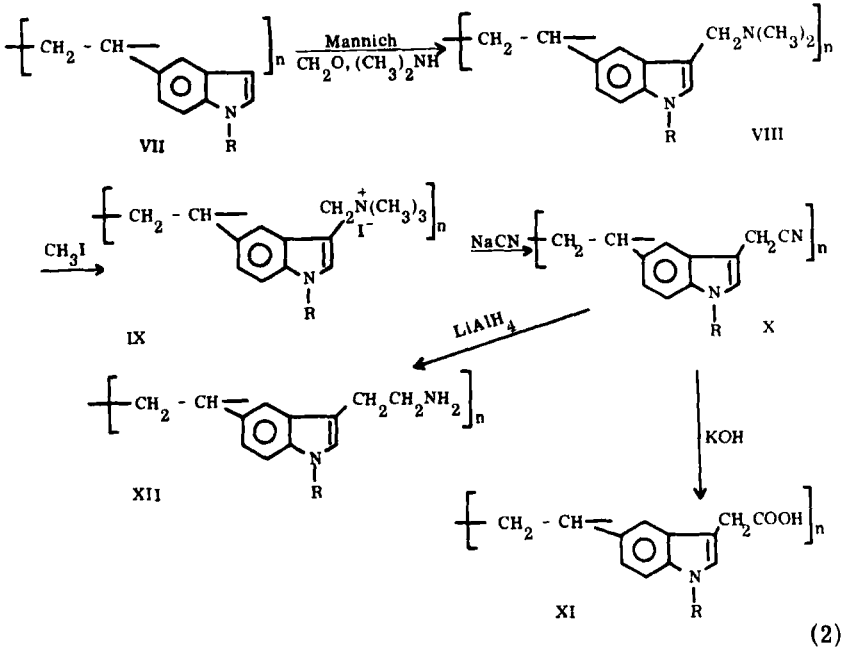
[b]The intrinsic viscosities were determined in DMF at 30° C.

TABLE 2. Anionic Polymerization of II and VI[a]

Monomer	$\frac{[\text{Monomer}]}{[\text{BuLi}]}$	$[\eta]$ (dl/g)[b]
II	4	0.435
	7	0.762
	15	0.895
	50	1.310
IV	4	0.290
	7	0.410
	15	0.460
	50	0.520

[a]Experimental conditions. To a solution of monomer (0.15 g, 0.62 mole/liter) in benzene (1 ml), BuLi in hexane was added, and the mixture was stirred for 16 hr at room temperature. The polymers precipitated by methanol and purified from DMF-methanol, mp 110-135° C.

[b]Intrinsic viscosities were determined in DMF at 30° C.

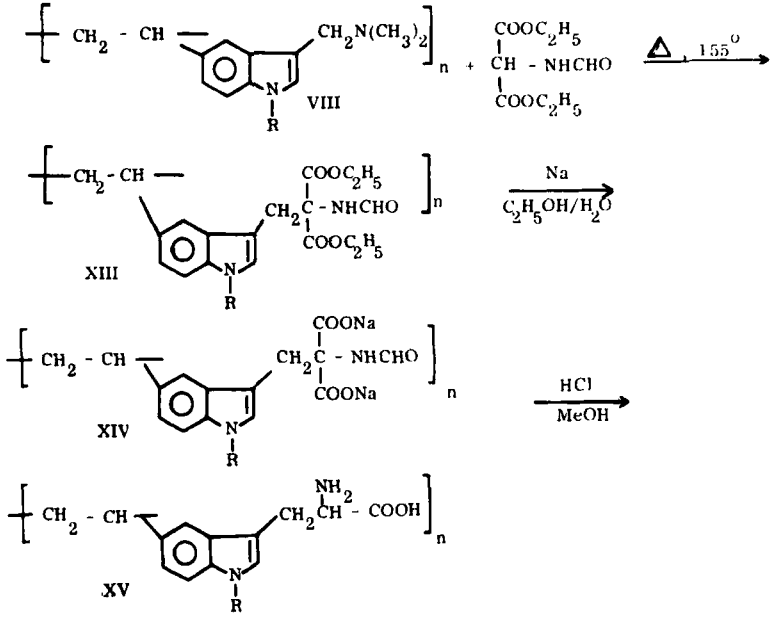


(2)

reaction on heating with formaldehyde and dimethylamine in dioxane-acetic acid to give the polygramine derivative (VIII). This was methylated and converted to the quaternary ammonium derivative (IX), which in turn, on nucleophilic substitution by CN^- gave the nitrile (X). The hydrolysis of the nitrile to the indoleacetic acid derivative (XI) went smoothly on heating with KOH in diethylene glycol/water. The nitrile was reduced by lithium aluminum hydride in THF to poly-5-vinyl-N-benzyltryptamine (XII). All the compounds were obtained in good yields and in a high degree of purity, as seen from elemental analysis and spectroscopic tests.

The synthesis of poly-5-vinyl-N-benzyltryptophane (XV) was carried out starting from poly-5-vinylgramine (VIII) according to the scheme (3).

The alkylation of diethyl formamidomalonate with the polymeric gramine derivative was not satisfactory when carried out in the presence of sodium ethoxide in refluxing toluene or xylene. Better yields were obtained when carrying out the alkylation in boiling pyridine. Optimal yields were obtained on heating equimolar amounts of the reactants at 155°C in a sand bath for 40 min. Hydrolysis of the malonic ester derivative (XIII) to the sodium salt



(3)

(XIV) was carried out by sodium ethoxide in the presence of water. Deformylation and decarboxylation of XIV was carried out in one step by HCl-dry methanol [16]. Partial esterification of the amino acid (XV) occurred, so the crude polymer was subjected to mild hydrolysis by dilute sodium hydroxide to obtain pure poly-5-vinyl-N-benzyltryptophane.

EXPERIMENTAL

NMR spectra were taken on Varian T60 and IR on Perkin-Elmer 457 instruments.

5-Formyl-N-benzylindoline (I)

Phosphorus oxychloride (3.07 g, 0.02 mole) was added dropwise with stirring at 0°C to dry DMF (5.4 g, 0.074 mole) followed by N-benzylindoline [17] (4.18 g, 0.02 mole). The mixture was heated for 2 hr on a steam bath, and the green-yellow precipitate that

formed, dissolved completely. The colored mixture was decanted onto crushed ice (30 g), cautiously neutralized with dilute sodium hydroxide to pH 6-8, so that the temperature did not rise above 10°C, and left overnight at 0°C. The product crystallized, was filtered, washed with water, dried, and recrystallized from heptane to give 3.7 g (78%) of yellow needles, mp 92°C.

NMR ($CDCl_3$): δ, 3.30 (m, 4, CH_2CH_2N); 4.29 (s, 2, NCH_2): 7.12 (s, 5, C_6H_5); 9.56 (s, 1, CHO).

IR (Nujol); 1655 (Ar-CHO); 692, 730 cm^{-1} (C_6H_5).

UV_{max}(EtOH): 249 nm ($\epsilon = 6.5 \times 10^3$); 355 nm ($\epsilon = 2.67 \times 10^4$).

Analysis. Calcd for $C_{16}H_{15}NO$: C, 80.98%; H, 6.37%; N, 5.90%. Found: C, 80.88%; H, 6.05%; N, 6.04%.

N-Benzyl-5-vinylindoline (II) by Wittig Reaction

n-Butyllithium (0.003 mole, as 25% solution in hexane) was added dropwise under nitrogen at room temperature to a stirred solution of methyltriphenylphosphonium bromide [5] (1.068 g, 0.003 mole) dried overnight in a vacuum oven at 100°C. After 30 min, N-benzyl-5-formylindoline (0.71 g, 0.003 mole) in dry THF (5 ml) was added, followed by tert-butyl hydroquinone inhibitor (0.005 g), and the solution was stirred for 40 hr, filtered and evaporated in vacuo. The yellow oil residue was taken up in the minimum amount of cold benzene and the triphenyl phosphine oxide was filtered. This procedure was repeated 4 times and the product finally purified by using preparative TLC (silica gel G) and eluting with benzene-n-hexane (1:1); yield 0.34 g (48%).

NMR ($CDCl_3$): δ, 3.0 (m, 4, CH_2CH_2N); 4.04 (s, 2, NCH_2); 4.70-5.50 (4d, 2, $=CH_2$).

UV_{max} (EtOH): 321 nm ($\epsilon = 2.5 \times 10^4$), 347 ($\epsilon = 3.0 \times 10^4$).

Analysis. Calcd for $C_{17}H_{17}N$: C, 86.77%; H, 7.28%; N, 5.95%. Found: C, 86.51%; H, 7.06%; N, 5.78%.

Ethyl β-(N-benzyl)-5-indolylacrylate (III)

To a suspension of sodium hydride (60% dispersion in paraffin, 0.4 g, 0.01 mole) in dry DMF (freshly distilled over P_2O_5), triethyl phosphonoacetate (2.24 g, 0.01 mole) in DMF (5 ml) was added. After 1 hr stirring, N-benzyl-5-formylindoline (2.37 g, 0.01 mole) in DMF (25 ml) was added to the yellow-green solution. The reaction mixture was heated to 75-80°C for 2 hr, cooled, and filtered. The

filtrate was diluted with water and extracted with methylene chloride. The organic layer was washed with water, bicarbonate, dried over magnesium sulfate, and evaporated. The product crystallized out on standing and was washed with cold methanol; yield, 2.65 g (86%), mp 88°C.

NMR ($CDCl_3$): δ, 1.22 (t, 3, C-CH_3); 4.10 (q, 2, CH_2-O); 4.14 (s, 2, NCH_2-).

IR (Nujol): 1680 cm^{-1} (OCO).

UV_{max} (EtOH): 249 nm ($\epsilon = 9.2 \times 10^3$); 3.62 nm ($\epsilon = 2.6 \times 10^4$).

Analysis. Calcd for $C_{20}H_{21}NO_2$: C, 78.15%; H, 6.89%; N, 4.56%. Found: C, 78.06%; H. 6.80%; N, 4.53%.

β-(N-Benzyl)-5-indolylacrylic Acid (IV)

Ethyl β-(N-benzyl)-5-indolyl acrylate (2.0 g, 0.0065 mole) was added to potassium hydroxide (1 g) in methanol (30 ml) and water (1 ml) and heated under reflux for 1 hr. Additional water (2 ml) was added, and the reflux was continued for 30 min. The mixture was diluted with water, the methanol evaporated in vacuo, and the residue extracted with methylene chloride. The aqueous layer was acidified to pH 2-3 with dilute sulfuric acid, extracted with methylene chloride, dried, and evaporated. The crude product was dissolved in 5% sodium hydroxide, extracted with methylene chloride, and the aqueous layer was again acidified. The product was taken up in methylene chloride, and recovered on evaporation of the solvent and trituration with dry ether; yield 1.5 g (83%), greenish needles, mp 182°C.

NMR (CF_3COOH): δ, 4.15 (s, 2, CH_2N); 5.90 (d, 1, H_α); 7.22 (d, 1, H_β).

IR (Nujol): 1650 cm^{-1} (COOH).

UV_{max} (EtOH): 245 nm ($\epsilon = 9.4 \times 10^3$); 359 nm ($\epsilon = 2.28 \times 10^4$).

Analysis. Calcd for $C_{18}H_{17}NO_2$: C, 77.40%; H, 6.13%; N, 5.01%, Found: C, 77.26%; H, 6.05%; N, 4.95%.

N-Benzyl-5-vinylindoline from IV

β-(N-Benzyl)-5-indolylacrylic acid (IV) (0.56 g, 0.002 mole) was dissolved in quinoline (2 ml). Copper powder (0.15 g), freshly precipitated from copper sulfate solution by zinc metal and dried at 40°C, and tert-butyl hydroquinone inhibitor were added and the mixture was heated under reflux for 50 min. The cold reaction mixture was filtered,

the filtrate acidified with 5% HCl and extracted with chloroform. The extract was washed with bicarbonate and water, dried over magnesium sulfate, and evaporated to yield 0.26 g (55%) of the product.

N-Benzyl-5-(α-hydroxyethyl)indoline (V)

N-Benzyl-5-formylindoline (0.95 g, 0.004 mole) in dry benzene (3 ml) was added to an ethereal solution of methylmagnesium iodide prepared from methyl iodide (0.004 mole), and heated under reflux for 4 hr. The reaction mixture was added to ammonium chloride (20 g) in water (40 ml) and crushed ice (50 g), and the organic layer was washed with water, dried over sodium sulfate, and distilled.

The product passed at 184°C/0.5 mm Hg, with some decomposition. It was possible to proceed with the synthesis without distillation; yield 0.91 g (90%).

NMR ($CDCl_3$): δ, 1.37 (d, 3, CH_3); 2.02 (br.s, 1, OH); 4.06 (s, 2, CH_2N), 4.55 (q, 1, CH-O).

IR (Neat); 3380 cm^{-1} (OH).

UV_{max} (EtOH): 261 nm ($\epsilon = 1.68 \times 10^4$), 305 nm ($\epsilon = 3.67 \times 10^3$).

Analysis. Calcd for $C_{17}H_{19}NO$: C, 80.60%; H, 7.56%; N, 5.53%. Found: C, 80.42%; H, 7.41%; N, 5.61%.

N-Benzyl-5-vinylindoline from V

N-Benzyl-5-(α-hydroxyethyl)indoline (V) (2.53 g, 0.01 mole) was dropped slowly onto freshly fused potassium bisulfate (1.0 g) and tert-butyl hydroquinone (0.05 g) held at 220-230°C and the system attached to a vacuum pump (125 Torr). Towards the end of the addition the vacuum was lowered to 20 Torr, but most of the product did not distill, and the residue was extracted with chloroform, washed with water, and dried ($MgSO_4$). The product was recovered on evaporation of the chloroform and further purified on TLC; yield 0.09 g (19%).

N-Benzyl-5-formylindole

N-Benzyl-5-formylindoline (1.2 g, 0.005 mole) and chloranil (1.35 g, 0.0055 mole) in xylene (25 ml) were heated under reflux for 7 hr. The solution was cooled and washed twice with 10% NaOH, water, 15% HCl and water. The organic layer was dried, evaporated to dryness, and the residual yellow-red oil crystallized on refrigeration.

It was recrystallized from chloroform-petroleum ether (40-60°C), yield 0.47 g (40%), mp 132°C.

NMR ($CDCl_3$): δ, 5.08 (d, 2, NCH_2); 6.54 (d, 1, Ph–CH=); 9.73 (s, 1, CHO).

IR (Nujol): 1652 cm^{-1} (Ar-CHO).

UV_{max} (EtOH): 264 nm ($\delta = 4.25 \times 10^3$).

Analysis. Calcd for $C_{16}H_{13}NO$: C, 81.68%; H, 5.57%; N, 5.95%. Found: C, 81.51%; H, 5.48%; N, 5.94%.

N-Benzyl-5-vinylindole (VI)

The compound was prepared by the reaction of N-benzyl-5-formylindole with triphenylmethylphosphonium bromide in dry THF (Wittig reaction), as described before in the case of respective indoline derivative. The oily product was purified by TLC with benzene-hexane (1:1), yield 61%.

NMR ($CDCl_3$): δ, 5.52-5.95 (4d, 2, $=CH_2$); 5.25 (s, 2, $N-CH_2$); 6.50 (d, 1, Ph–CH=).

UV_{max} (EtOH): 258 nm ($\epsilon = 4.21 \times 10^4$), 353 nm ($\epsilon = 2.16 \times 10^4$).

Analysis. Calcd for $C_{17}H_{15}N$: C. 87.52%; H, 6.48%; N, 6.00%. Found: C, 87.32%; H, 6.52%; N, 6.17%.

Poly-5-vinyl-N-benzylgramine (VIII)

To a solution of acetic acid (5 ml) and dioxane (25 ml), 37% formaldehyde solution (0.4 g, 0.005 mole), and 28% dimethylamine solution (0.8 g, 0.005 mole) were added. The mixture was cooled to 0°C and poly-5-vinyl-N-benzylindole (VII) (1.16 g, 0.005 mole) in dioxane (25 ml) was added dropwise. The solution allowed to stand overnight at room temperature, diluted with water to 75 ml, filtered, and made strongly basic with sodium hydroxide. The mixture was kept at 0°C for 4 hr for quantitative separation of the product, which was extracted with chloroform, dried, evaporated and recrystallized from $CHCl_3$-petroleum ether (40-60°C); yield 70%, mp 99-112°C.

NMR ($CDCl_3$): δ, 4.17 (s, 6, $N(CH_3)_2$, 5.06 (s, 2, CH_2N), 1.12 (m, 3, $CHCH_2$).

UV_{max} (EtOH): 221 nm ($\epsilon = 1.9 \times 10^4$); 289 nm ($\epsilon = 4.41 \times 10^3$).

Analysis. Calcd for $C_{20}H_{22}N_2$: C, 82.72%; H, 7.64%; N, 9.65%. Found: C, 82.55%; H, 7.51%; N, 9.56%.

Poly-5-vinyl-N-benzylgramine Methiodide (IX)

To a solution of poly-5-vinyl-N-benzylgramine (VIII) (0.725 g, 0.0025 mole) in benzene (30 ml), methyl iodide (2 ml, 0.032 mole) in benzene (5 ml) was added dropwise with vigorous stirring at room temperature. The stirring was continued for 2 hr, and the methiodide was filtered and air-dried, mp 185-188°C ($CHCl_3$-petroleum ether, 40-60°C).

Poly-5-vinyl-N-benzylindole-3-acetonitrile (X)

To a solution of poly-5-vinyl-N-benzylgramine methiodide (IX) (0.54 g, 0.0012 mole) in ethanol-water (7:3) (25 ml), sodium cyanide (0.75 g, 0.015 mole) was added. The solution was heated with stirring on a steam bath at 80-90°C for 2 hr. The mixture was cooled, water (25 ml) was added, and the mixture was extracted by chloroform. The organic phase was washed with water, dried and evaporated. The polymer was recrystallized from $CHCl_3$-petroleum ether (40-60°C); yield 80%, mp 130-142°C.

NMR ($CDCl_3$): δ, 3.15 (s, 2, CH_2CN).

IR (Nujol): 2210 cm^{-1} (CN).

UV_{max} (EtOH): 225 nm ($\epsilon = 2.6 \times 10^4$), 280 nm ($\epsilon = 5.4 \times 10^3$), 291 nm ($\epsilon = 5.2 \times 10^3$), 330 nm ($\epsilon = 4.65 \times 10^2$).

Analysis. Calcd for $C_{19}H_{16}N_2$: C, 83.79%; H, 5.92%; N, 10.29%. Found: C, 83.77%; H, 5.73%; N, 10.05%.

Poly-5-vinyl-N-benzylindole-3-acetic Acid (XI)

To a solution of poly-5-vinyl-N-benzylindole-3-acetonitrile (X) (0.47 g, 0.0017 mole) in diethylene glycol (2 ml), a solution of KOH (1.5 g) in water (1.5 ml) was added. The solution was heated at 160°C for 16 hr, cooled, diluted to 20 ml with water, filtered, acidified with 5% HCl solution to pH 1, and extracted three times with chloroform. The organic layer was extracted with 4% NaOH, and the aqueous solution was acidified with dilute HCl, extracted with chloroform, dried, and evaporated. The polymer was recrystallized from $CHCl_3$-petroleum ether (40-60°C); yield 70%, mp 95-130°C.

IR (Nujol): 1708 cm^{-1} (COOH).

UV_{max} (EtOH): 231 nm ($\epsilon = 3.02 \times 10^4$), 282 nm ($\epsilon = 5.95 \times 10^3$).

Analysis. Calcd for $C_{19}H_{17}NO_2$: C, 78.33%; H, 5.88%; N, 4.81%. Foun d: C, 78.02%; H, 5.77%; N, 4.60%.

Poly-5-vinyl-N-benzyltryptamine (XII)

To a solution of poly-5-vinyl-N-benzylindole-3-acetonitrile (X) (0.475 g, 0.00175 mole) in dry THF (40 ml) under nitrogen, $LiAlH_4$ (1.0 g, 0.026 mole) was added. The mixture was heated under reflux with stirring for 16 hr. To the cold mixture, aqueous ammonium chloride solution was added, the mixture extracted with methylene chloride, dried and evaporated. The polymer was recrystallized from $CHCl_3$-petroleum ether (40-60°C); yield 61%, mp 102-107°C.

IR (Nujol): 3300, 3420 cm^{-1} (NH_2).

UV_{max} (EtOH): 230 nm ($\epsilon = 2.97 \times 10^4$), 283 nm ($\epsilon = 6.05 \times 10^3$).

Analysis. Calcd for $C_{19}H_{20}N_2$: C, 82.57%; H, 7.29%; N, 10.14%. Found: C, 82.51%; H, 7.00%; N, 10.06%.

Poly-5-N-benzylindole 3-Methylenediethylformamidomalonate (XIII)

Poly-5-vinyl-N-benzylgramine (VIII) (0.64 g, 0.0022 mole) and diethyl formamidomalonate (0.52 g, 0.0025 mole) were heated slowly to 155°C in a sand bath and kept at this temperature for 40 min. Dimethylamine was evolved. The mixture was cooled, taken up in chloroform, and precipitated with petroleum ether (40-60°C; yield 63%, mp 85-95°C.

NMR ($CDCl_3$): 1.16 (t, 6, CH_3), 4.15 (q, 4, CH_2O), 5.1 (s, 2, NCH_2).

IR ($CHCl_3$): 1740 (OCO), 3360 cm^{-1} (–NH).

UV_{max} (EtOH): 244 nm ($\epsilon = 7.77 \times 10^3$), 295 nm ($\epsilon = 4.03 \times 10^3$).

Analysis. Calcd for $C_{26}H_{28}N_2O_5$: C, 69.63%; H, 6.29%; N, 6.25%. Found: C, 69.40%; H, 6.07%; N, 6.16%.

Disodium Poly-5-vinyl-N-benzylindole-3-methyleneformamidomalonate (XIV)

XIII (0.45 g, 0.001 mole) was added to a solution of sodium (0.046 g, 0.002 mole) in absolute ethanol (3 ml) followed by two drops of water, and the mixture was heated under reflux for 15 min. The disodium salt partially precipitated out and was completely recovered on evaporation of the reaction mixture to dryness; yield 87%.

Poly-5-vinyl-N-benzyltryptophane (XV)

Disodium salt (XIV) (0.44 g, 0.001 mole) was added to a solution (20 ml, 7.2 N) of dry HCl in absolute methanol, and the mixture was stirred for 48 hr at room temperature. The mixture was evaporated to dryness. Aqueous NaOH (5%) was added to the residue, stirred for 45 min, to hydrolyze the ester groups formed. The solution was filtered and acidified to pH 7. The polymer (0.11 g, 35%) was collected; mp 120-153°C.

NMR (CF_3COOH): δ, 7.2 (m, 4, C_6H_4), 7.1 (s, 1, CH=).

IR (Nujol): 1755 (COOH), 1218 (C–COO), ~ 3000 cm^{-1} (NH_3^+, br).

Analysis. Calcd for $C_{20}H_{20}N_2O_2$: C, 74.98%; H, 6.29%; N, 8.74%. Found: C, 74.59%; H, 6.01%; N, 8.55%.

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