Polyesters Containing Carbazole Rings in the Main Chain. II. The Syntheses of Polyesters from Carbazole Keto Acids*

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As has been described previously,[1] to prepare polyesters containing carbazole rings in the main chain, the authors first synthesized several carbazole- and *N*-alkylcarbazole-dicarboxylic acids. Carbazole-dibasic acids of the general formula X-R-X, where X is $-COC_2H_4CO_2H$ or $-(CH_2)_3CO_2H$ and R is carbazole or a 9-methylcarbazole ring, were also synthesized in better yields by a modification of the method of Mitchell and Plant.[2]

New polyesters were derived from diethyl carbazole- and diethyl 9-methylcarbazole-3, 6-γ,γ'-diketobutanoates in the presence of various catalysts.

Experimental

The Preparation of Monomers. — *Carbazole-3,6-γ,γ'-diketobutanoic Acid (I).*—The succinoylation of carbazole according to the method of Mitchell and Plant[2] gave I in yields lower than 40 per cent. These results indicated that the use of at least 2.5 molecular proportions of aluminum chloride per mole of succinic anhydride is a requisite and that the extension of the reaction time up to 16 hr. is preferable in increasing the yield of I. Table I shows the molecular proportions of aluminum chloride per mole of succinic anhydride and the relative per cent yields of keto acid.

Found: C, 65.71; H, 4.65. Calcd. for $C_{20}H_{17}O_6N$: C, 65.32; H, 4.64%.

Carbazole-3,6-dibutanoic Acid (II).[7] — Reducing I also by the Clemmensen method, Mitchell and Plant[2] prepared II in a 50 per cent yield. As Table II shows that, when I was reduced in an aqueous acetic acid, II was obtained in a more than 80 per cent yield. II can be alternatively synthesized from the ethyl ester of I by the Clemmensen method. A zinc amalgam was prepared by mixing 300 g. of zinc powder, 300 cc. of a 10% aqueous mercuric chloride solution, and 10 cc. of concentrated hydrochloric acid. The mixture was stirred for 5 min., and then the residue which remained after the decantation of the aqueous solution was covered with 300 cc. of water. To this mixture was added 30 g. of I and 300 cc. of glacial acetic acid; then the

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[1] Y. Nagai and C.-C. Huang, This Bulletin, **38**, 951 (1965).

[2] D. R. Mitchell and G. P. Plant, *J. Chem. Soc.*, **1936**, 1295.

[3] U. S. Pat. 2534028 (1948).

[4] U. S. Pat. 2647885 (1951).

[5] U. S. Pat. 2578660 (1949).

[6] British Pat. 727790 (1952).

[7] Syntheses of polyesters from II and V will be described in the succeeding paper, "III. Syntheses of Polyesters from Carbazoledicarboxylic and Carbazoledibutanoic Acid."

TABLE I. SYNTHESIS OF CARBAZOLE-3,6-γ,γ'-DIKETOBUTANOIC ACID

Carbazole g.	Nitrobenzene cc.	$AlCl_3$ g.	Succinic anhydride g.	Reaction		Yield	
				Time hr.	Temp. °C	g.	%
30.0	420	102.0 (4.3)	36.0 (2.0)	6	0±2	24.0	36.4
30.0	420	102.0	36.0	7	0±2	25.2	38.2
30.0	420	102.0	36.0	8	0±2	24.8	37.5
30.0	420	102.0	36.0	8	0±2	25.1	38.0
30.0	420	128.0 (5.3)	36.0 (2.0)	6	0±2	32.2	48.8
30.0	420	144.0 (6.0)	36.0 (2.0)	6	0±2	33.6	50.9
30.0	420	192.0 (8.0)	36.0 (2.0)	6	0±2	34.5	52.3
30.0	420	216.0 (9.0)	36.0 (2.0)	6	0±2	33.8	51.8
30.0	420	128.0	36.0	12	0±2	35.8	54.3
30.0	420	128.0	36.0	16	0±2	41.6	63.2

Numbers in the parentheses are molecular proportions of aluminum chloride or succinic anhydride per mole of carbazole.

TABLE II. SYNTHESIS OF CARBAZOLE-3,6-DIBUTANOIC ACID

I g.	Zinc amalgam g.	Glacial AcOH cc.	Other solvent cc.	Concd. HCl[a] cc.	Reaction		Yield	
					Time hr.	Temp. °C	g.	%
30.0	300	300	40[b]	300	4	90—95	13.2	47.6
30.0	300	300	25[b]	300	4	90—95	12.0	43.3
30.0	300	300	75[b]	300	4	90—95	9.0	32.5
30.0	300	300	40[c]	300	4	90—95	12.8	46.0
30.0	300	300	60[c]	300	4	90—95	12.9	46.2
30.0	300	300	300[d]	300	4	90—95	22.4	80.7
30.0	300	300	300[d]	300	4	90—95	22.6	81.3
30.0	300	300	—	300	4	90—95	14.5	52.3
30.0[e]	300	300	—	300	4	90—95	15.0	62.5

a) $d=1.175$ g./cc. b) Toluene c) Xylene d) Water e) Diethyl ester of I.
I, Carbazole-3,6-γ,γ'-diketobutanoic acid.

whole was refluxed and stirred while 300 cc. of concentrated hydrochloric acid was added, drop by drop, over a 4-hr. period. After the completion of the reaction, the upper layer of the product was decanted and the residual amalgamated zinc was refluxed with glacial acetic acid to take up any product remaining on the top of the amalgam or on the wall of the flask. On cooling, the combined solution of the filtrate and the decanted layer yielded II as white flakes; 22.5 g., m. p. 198—200°C.

Found: C, 70.59; H, 6.20; N, 5.73. Calcd. for $C_{20}H_{21}O_4N$: C, 70.80; H, 6.19; N, 5.81%.

Diethyl Carbazole-3,6-γ,γ'-diketobutanoate (III).—The reaction of I with a mixture of ethanol and concentrated sulfuric acid for 6 hr. gave III as white plates; m. p. 175—176°C after crystallization from ethanol (decolorizing charcoal added).

Found: C, 68.12; H, 5.92. Calcd. for $C_{24}H_{25}O_6N$: C, 68.10; H, 5.92%.

Diethyl 9-Methylcarbazole-3,6-γ,γ'-diketobutanoate (IV).—A solution of 1.5 g. of III in 300 cc. of acetone was poured into a flask containing 1.5 g. of an aqueous potassium hydroxide in 1.0 cc. of water, and to this mixture was added 2.0 cc. of dimethyl sulfate. The mixture was then stirred for 12 min. at 25°C, and the product was poured into 2 l. of water to give white precipitates which yielded IV as white crystals (1.5 g.; m. p. 145—146°C after recrystallization from ethanol).

Found: C, 67.37; H, 6.11. Calcd. for $C_{25}H_{27}O_6N$: C, 67.09; H, 6.04%.

9-Methylcarbazole-3,6-dibutanoic Acid (V).[7]—For this synthesis, a zinc amalgam was prepared as has been described in the preparation of II. The procedure was also essentially the same except that IV was reduced instead of I. The melting point of V is 227—229°C.

Found: C, 71.06; H, 6.58. Calcd. for $C_{21}H_{17}O_4N$: C, 71.35; H, 6.52%.

Polycondensation. — *General Procedure.* — Polyesters were obtained by heating a mixture of ethylene glycol and III or IV in a glass flask. The ester exchange reaction in the presence or in the absence of a catalyst was effected under such condition that the displaced alcohol could be removed by distillation; this involved the use of a reaction temperature below the boiling point of ethylene glycol, but well above that of the alcohol to be displaced. In carrying out the reaction, at least two molecular proportions of ethylene glycol per molecular proportion of III or IV were used, and the heating in a stream of nitrogen was continued until the distillation of the displaced alcohol ceased. The resulting low polymeric products could be converted to polyesters by heating them, at a temperature above the boiling point of ethylene glycol, under reduced pressure (below 1 mmHg). The polyesters thus prepared were reprecipitated several times in order to increase the homogeneity.

For the following polycondensations, ethylene glycol was first dried over anhydrous sodium sulfate and then purified by dissolving metallic sodium in it (1.0 g. per 100 cc.) and refluxing it in an atmosphere of nitrogen for 1 hr. and then distilling it (b. p. 99—100°C/15 mmHg).

TABLE III. POLYESTERS BASED ON DIETHYL CARBAZOLE-3, 6-γ, γ'-DIKETOBUTANOATE

Polyester code	Catalyst	Weight g.	$[\eta]$[a)]	PMT[b)] °C
PX-1	Na	0.0014	0.12[p)]	160(9)
PX-2	Na_2CO_3	0.0150	0.09[p)]	115(5)
PX-3	PbO	0.0600	0.14[p)]	166(9)
PX-4	$Ca(CH_3CO_2)_2 \cdot H_2O$ Sb_2O_3	0.0410 0.0100	0.18[c)]	170(9)
PX-5	$Ca(CH_3CO_2)_2 \cdot H_2O$ Sb_2O_3	0.0120 0.0031	0.11[p)]	160(8)
PX-6	$Ca(CH_3CO_2)_2 \cdot H_2O$ Sb_2O_3	0.0500 0.0120	0.18[c)]	172(8)
PX-7	$Ca(CH_3CO_2)_2 \cdot H_2O$ Sb_2O_3	0.0210 0.0050	0.15[c)]	
PX-8	$Ca(CH_3CO_2)_2 \cdot H_2O$ Sb_2O_3	0.0250 0.0062	0.16[c)]	170(7)
PX-9	$Ca(CH_3CO_2)_2 \cdot H_2O$ Sb_2O_3	0.0330 0.0076	0.18[c)]	
PX-10	$Co(CH_3CO_2)_2 \cdot 4H_2O$	0.0047	0.21[c)]	175(7)
PX-11	$Co(CH_3CO_2)_2 \cdot 4H_2O$	0.0063	0.21[c)]	
PX-12	$Co(CH_3CO_2)_2 \cdot 4H_2O$	0.0018	0.19[c)]	172(9)
PX-13	$Pb(C_2H_3O_2)_2 \cdot 3H_2O$	0.0050	0.23[c)]	180(10)
PX-14	$Pb(C_2H_3O_2)_2 \cdot 3H_2O$	0.0060	0.24[c)]	183(10)
PX-15	$Pb(C_2H_3O_2)_2 \cdot 3H_2O$	0.0092	0.24[c)]	
PX-16	GeO_2	0.0040	0.18[c)]	171(7)
PX-17	GeO_2	0.0020	0.16[c)]	168(8)
PX-18	GeO_2	0.0083	0.23[c)]	178(8)
PX-19	GeO_2	0.0061	0.23[c)]	
PX-20	GeO_2	0.0102	0.23[c)]	
PX-21	Control	—	0.08[p)]	106(5)

a) The intrinsic viscosity, $[\eta]$, was obtained from plotting inherent viscosity numbers versus concentration and extrapolating to zero concentration.

b) PMT, polymer melting temperature; Numbers in the parentheses are PMT temperature range.

c) Measured in *m*-cresol at 30°C.

p) Measured in pyridine at 30°C.

In syntheses of the polyesters PX-1 to PX-18, 10 g. of III and 3 g. of ethylene glycol were used. Various catalysts and the corresponding weights for each preparation are shown in Table III. Two preparations will be described as examples; the rest are essentially the same.

PX-4.—The following ingredients were introduced into a hard glass flask: III, 10.0 g.; ethylene glycol, 3.0 g.; calcium acetate, 0.041 g. and antimony trioxide, 0.01 g. The mixture was then heated in a stream of oxygen-free nitrogen in a vapor bath of 195°C for 2 hr., until most of the ethanol distilled off. The low polymeric product was then heated further at an elevated temperature, 210°C at the early stage and finally at 280°C, over a period of 5 hr. in the full vacuum used at the last phase of the reaction. The resulting condensation product exhibited an intrinsic viscosity of 0.18 in *m*-cresol at 30°C.

PX'-1. — A mixture of 10.5 g. of IV, 3.0 g. of ethylene glycol, and 0.005 g. of lead acetate was allowed to react in a stream of oxygen-free nitrogen for 2 hr., while the ethanol was being continuously removed; then it was polycondensed under the same conditions as in the previous example and over the same period to give, in *m*-cresol at 30°C a polyester with the intrinsic viscosity of 0.23.

Results and Discussion

Since I and 9-methylcarbazole-3, 6-γ, γ'-diketobutanoic acid dissolve sparingly in most organic

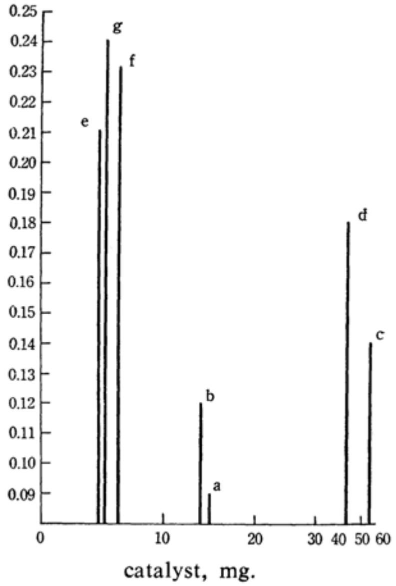

Fig. 1. Maximum intrinsic viscosity attained with various catalysts.

a	Sodium carbonate	b	Sodium
c	Lead monoxide	d	Calcium acetate
e	Cobaltous acetate	f	Germanium-dioxide
g	Lead acetate		

TABLE IV. SOLUBILITY OF POLY(ETHYLENE CARBAZOLE-3,6-γ,γ'-DIKETOBUTANOATE) IN VARIOUS SOLVENTS

Solvent	Polymer					
	PX-1	PX-3	PX-6	PX-10	PX-14	PX-18
Acetone	4	4	4	4	4	4
Chloroform	4	4	4	4	4	4
cis-1,2-Dichloroethylene	4	4	4	4	4	4
Methanol	4	4	4	4	4	4
Carbon tetrachloride	4	4	4	4	4	4
Benzene	4	4	4	4	4	4
Cyclohexane	4	4	4	4	4	4
Toluene	4	4	4	4	4	4
Pyridine	1	1	2	4	4	4
Phenol	1	1	1	1	1	1
o-Cresol	1	1	1	1	1	1
m-Cresol	1	1	1	1	1	1
Nitrobenzene	6	6	6	6	6	6
DMF	1	1	1	2	2	2
Dichlorobenzene	3	3	3	6	6	6
Concd. H_2SO_4	7	7	7	7	7	7

1: Soluble in hot solvent and remains soluble cold.
2: Very low solubility, or little solvent action on solute.
3: Inbives hot solvent and swells.
4: No effect of solvent on solute.
5: Soluble in hot solvent, precipitated cold.
6: Melted or sticky in hot solvent.
7: Soluble in cold solvent.

TABLE V. ELEMENTARY ANALYSES OF PECKB AND 9-MePECKB

Polymer code	C, %	H, %	O, %
PX-4	66.18	5.03	25.49
PX-6	66.44	4.99	24.28
PX-10	66.72	5.01	24.65
PX-15	66.65	5.01	25.43
PX-18	66.72	5.03	24.54
PX'-1	67.03	5.22	23.81
Calcd. for $-(C_{22}H_{19}O_6N)-$	67.18	4.84	24.43
Calcd. for $-(C_{23}H_{21}O_6N)-$	67.82	5.16	23.59

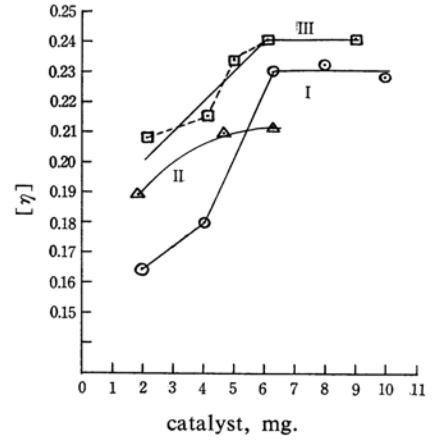

Fig. 2. Relation between the weight of catalyst and the intrinsic viscosity.
I Germanium dioxide II Cobaltous acetate
III Lead acetate

solvents, III and IV were used in the practical polycondensation.

In the absence of a catalyst, merely a low polymeric condensation product was obtained. Among several catalysts, e. g., lead monoxide,[3)] calcium acetate,[4)] germanium dioxide,[5)] and antimony trioxide,[3)] which have been proclaimed as excellent catalysts for preparing white aromatic polyesters when applied either singly or in combination, lead monoxide has proved to be inadequate in the synthesis of poly(ethylene carbazole-3,6-γ,γ'-diketobutanoate) (PECKB) from the viewpoint of the color of the product. The use of lead monoxide less than 0.6% by weight of III yielded only a low polymeric product, and an attempt to synthesize high polymeric PECKB by adding more lead monoxide resulted in a product the color of which was usually very dark amber. In preparations of PECKB and 9-MePECKB, the catalytic effect of germanium dioxide compared favorably with that of cobaltous acetate or lead acetate, which is generally considered to be a good accelerator in polycondensation. In the presence of about 0.6% by weight of lead acetate, a relatively high polymeric PECKB was obtained, as is illustrated in Fig. 2, though a rather irregular increase in viscosity in accordance with the increment of the catalyst was observed. The color of PECKB or 9-MePECKB tends to become darker upon the addition of more than 0.1% by weight of lead acetate or germanium dioxide; the addition of more than 0.06% by weight of cobaltous acetate to the reaction mixture also is apt to give a polyester of a very dark amber color. The use of more than 5 times by weight of calcium acetate in comparison with other catalysts was necessary, as is clearly shown in Figs. 1 and 3; otherwise, the viscosity increased steadily up to 0.18 with the increase in the weight of the catalyst.

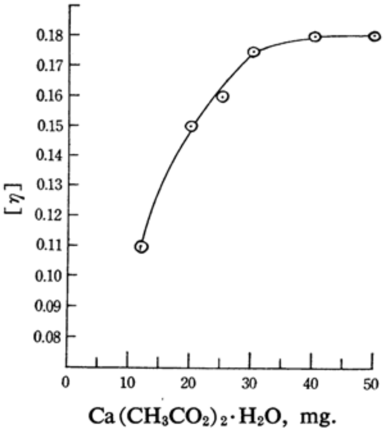

Fig. 3. Relation between the weight of catalyst and the intrinsic viscosity.

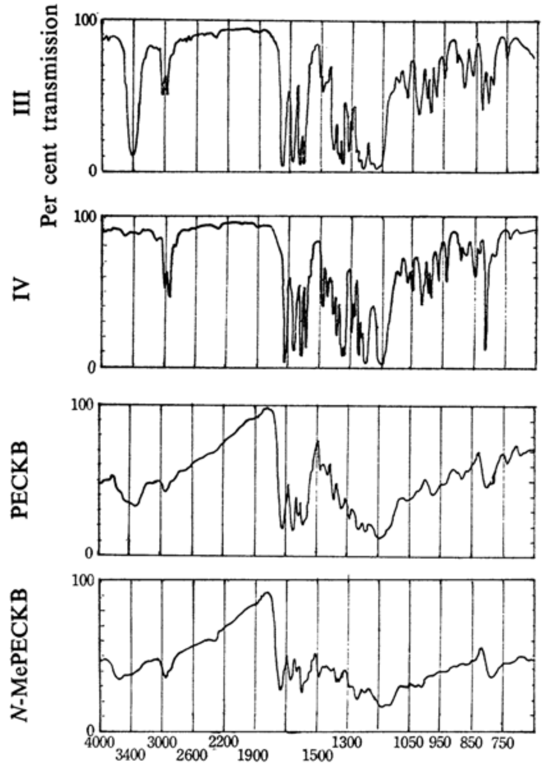

Fig. 4. Infrared spectra of III, IV, PECKB, *N*-MePECKB.

Infrared spectrum of III was obtained on the pressed disk of 3.8 mg. of III/700 mg. KBr; and that of IV on the pressed disk of 3.9 mg. of IV/700 mg. KBr.

Infrared spectra of PECKB and 9-MePECKB were obtained on the pressed disks of 4.5 mg. of PECKB/700 mg. KBr and 5.5 mg. of 9-MePECKB/700 mg. KBr respectively.

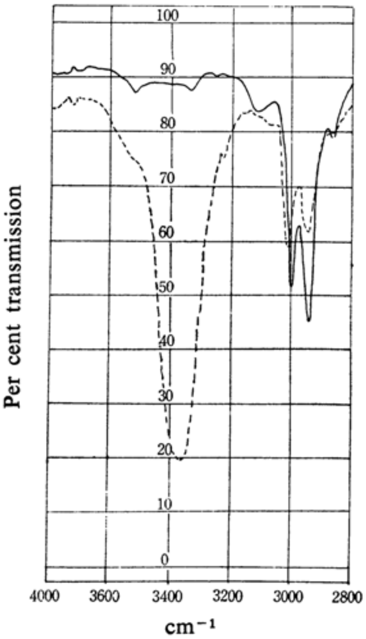

Fig. 5. Infrared spectra of III* and IV**.
* On pressed disk of 3.5 mg. III/700 mg. KBr.
** On pressed disk of 3.5 mg. IV/700 mg. KBr.

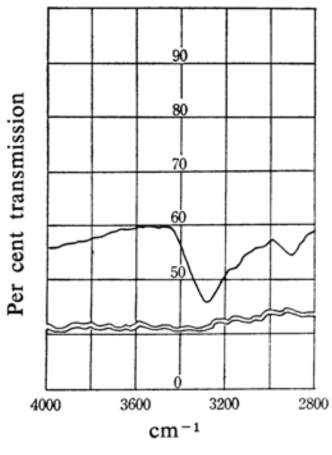

Fig. 6. Infrared spectrum of poly(ethylene carbazole-3,6-γ,γ'-diketobutanoate)*, PECKB.
* On pressed disk of 3.5 mg. PECKB/700 mg. KBr.

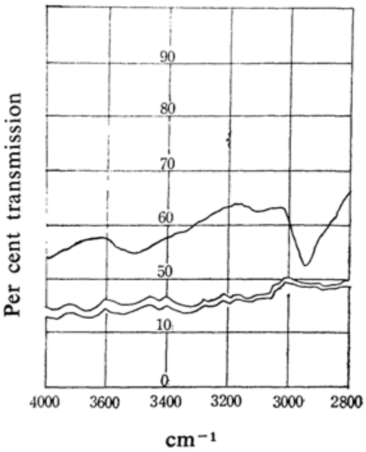

Fig. 7. Infrared spectrum of poly(ethylene 9-methylcarbazole-3, 6-γ, γ'-diketobutanoate)*, 9-MePECKB.

* On pressed disk of 3.5 mg. 9-MePECKB/700 mg. KBr.

PECKB and 9-MePECKB have, in general, good resistance to many organic solvents, though not to pyridine, phenol and cresol. Condensation products exhibiting an intrinsic viscosity lower than 0.14 dissolve in pyridine at the boiling point of the solvent, whereas PECKB and 9-MePECKB, which show an intrinsic viscosity of 0.15 or higher, dissolve in only phenol or cresol at the boiling point of the solvent; all the polyesters synthesized dissolve slowly in concentrated sulfuric acid.

The wide temperature range of polymer melting points shown in Table III seems to indicate that polyesters based on III or IV are largely amorphous. Figures 4, 5, 6, and 7 show the infrared spectra of III, IV, PECKB, and 9-MePECKB. The data from elementary analyses of the polycondensation product and the characteristic absorption bands shown in these figures indicate that synthesized PECKB and 9-MePECKB are linear plyesters with the following recurring units:

PECKB,

$-(OCC_2H_4CO\text{-}C_{12}H_7N\text{-}COC_2H_4CO_2C_2H_4O)-$

9-MePECKB,

$-(OCC_2H_4CO\text{-}C_{13}H_9N\text{-}COC_2H_4CO_2C_2H_4O)-$

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