BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 650—654 (1966)

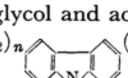
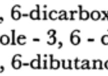
Polyesters Containing Carbazole Rings in the Main Chain. III. Syntheses of New Polyesters from Carbazole-dibasic Acids

By Yoshio NAGAI and Chin-Chuan HUANG

Institute of Industrial Science, The University of Tokyo, Azabu, Tokyo

(Received May 18, 1965)

Several new polyesters were synthesized by the reaction of ethylene glycol with such carbazoledicarboxylic acids as carbazole-3, 6-dicarboxylic, 9-ethylcarbazole-3, 6-dicarboxylic, carbazole-3, 6-dibutanoic and 9-methylcarbazole-3, 6-dibutanoic acid in the presence of various catalysts.

Several new polyesters were prepared from ethylene glycol and acids of the general formula $HO_2C\text{-}(CH_2)_n$  $(CH_2)_nCO_2H$,[1,2] in which n is 0 or 3, and R indicates –H or alkyl groups ($-CH_3$ or $-C_2H_5$). With respect to the polymer-melt temperature, intrinsic viscosity, color, and resistance to organic solvents, the new polyesters have, in general, better properties than those derived from ethylene glycol and carbazole keto acids $HO_2C\text{-}(CH_2)_2OC$  $(CH_2)_2CO_2H$, in which R indicates –H or $-CH_3$ group.

Experimental

Preparation of Monomers.—The syntheses of carbazole-3, 6-dicarboxylic acid (CDA), diethyl carbazole-3, 6-dicarboxylate (diEtCD), 9-ethylcarbazole-3, 6-dicarboxylic acid (9-EtCDA), diethyl 9-ethylcarbazole-3, 6-dicarboxylate (diEt 9-EtCD), carbazole-3, 6-dibutanoic acid (CDBA), and 9-methylcarbazole-3, 6-dibutanoic acid (9-MeCDBA) were described in previous papers.[1,2] Ethylene glycol was purified according to the previous method.[2]

Polycondensation. — *Preparation of Poly(ethylene carbazole-3, 6-dibutanoate) (PECB) and Poly(ethylene 8-Methylcarbazole-3, 6-dibutanoate) (9-MePECB).* — A highly polymeric PECB or 9-MePECB can be made by heating ethylene glycol with CDBA or 9-MeCDBA, in which the molar ratio of ethylene glycol and CDBA or 9-MeCDBA is 2 : 1. Preferably the higher molar ratios of ethylene glycol for the simple ester of the acid or the acid are used. During the ester interchange period the temperature advantageously approaches the boiling point of the glycol. In the first stage, in the preparation of β-hydroxyethyl carbazole-3, 6-dibutanoate or β-hydroxyethyl 9-methylcarbazole-3, 6-dibutanoate, there is no particular need to add the catalysts. Once all of the acid has reacted with glycol, the temperature is raised and the excess glycol is removed from the reaction mixture in the presence of various catalysts by distillation under reduced pressure. During this process of heating the viscosity of reaction mixture gradually increases. The heating may be effected in an inert atmosphere, for instance, in a stream of nitrogen gas.

Preparation of Poly(ethylene Carqazole-3, 6-dicarboxylate) (PECC) and Poly(ethylene 8-Ethylcarbazole-3, 6-dicarboxylate) (9-EtPECC).—Since CDA and 9-EtCDA sparingly dissolve in most organic solvents, diEtCD and diEt 9-EtCD are used in the polycondensation. The reaction is carried out under conditions in which the displaced ethanol can be removed by distillation. At least two moles of ethylene glycol per mole of diEtCD or diEt 9-alkylCD should be used. Preferably the heating is effected in an inert atmospher, and is continued until the distillation of the displaced ethanol ceases.

The low polymeric product can be converted into the highly polymeric polyester by heating it above 280°C for several hours under reduced pressure.

Examples of Polycondensation.—*PX-11*—One gram of ethylene glycol and 2.5 g. of CDBA were heated in the presence of 0.0026 g. of germanium dioxide in a stream of oxygen-free nitrogen for about 2 hr. at 194°C. The resulting β-hydroxyethyl carbazole-3, 6-dibutanoate was further heated in a stream of nitrogen for three hours at 237°C, and finally at 285°C for 30 min. The low polymeric product was then heated at 285°C for an additional 30 min. under reduced pressure (0.2 mmHg). The polycondensation product showed an intrinsic viscosity of 0.54 in *m*-cresol at

---

* A part of this paper was presented at the 13th Annual Meeting of the Society of High Polymers of Japan, June, 1964.

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

2) Y. Nagai and C.-C. Huamg, ibid., **38**. 1136 (1965).

30°C; the color of the polymer was light yellow and transparent.

Found: C, 71.97; H, 6.39; O, 17.75. Calcd. for $-(C_{22}H_{23}O_4N)-$ or $-OC(CH_2)_3\text{-}C_{12}H_7N\text{-}(CH_2)_3CO_2\text{-}(CH_2)_2O-$, where $C_{12}H_9N$ is the carbazole ring: C, 72,23; H, 6.3; O, 17.53%.

9-MePECB.—A mixture consisting of 2.0 g. of 9-MeCDBA, 1.0 g. of ethylene glycol, and 0.003 g. of germanium dioxide was heated in a hard glass flask under the same conditions as in the previous example, thus giving a polyester which is light amber color and shows an intrinsic viscosity of 0.41 in *m*-cresol at 30°C.

Found: C, 72.01; H, 6.73; O, 17.20. Calcd. for $-(C_{23}H_{25}O_4N)-$ or $-OC(CH_2)_3\text{-}C_{13}H_9N\text{-}(CH_2)_3CO_2\text{-}(CH_2)_2O-$, where $C_{13}H_9N$ is the 9-methylcarbazole ring: C, 72.83; H, 6.59; O, 16.89%.

PX-5.—Two grams of diEtCD, 1.0 g. of ethylene glycol, and a blended catalyst of 0.005 g. of cobaltous acetate and 0.003 g. of calcium hydride were heated in a hard glass flask at 194°C for 1 hr. in a stream of oxygen-free nitrogen. The resulting β-hydroxyethyl carbazole-3, 6-dicarboxylate was heated at 235°C for 2 hr. in the same inert atmosphere and finally at 285°C for 30 min., while the pressure of the system was gradually reduced to 0.2 mmHg. Heating at 285°C was then continued for an additional hour under the same pressure. The product was a light yellowish-white opaque solid showing an intrinsic viscosity of 0.51 in *m*-cresol at 30°C; the polymer-melt point was above 210°C.

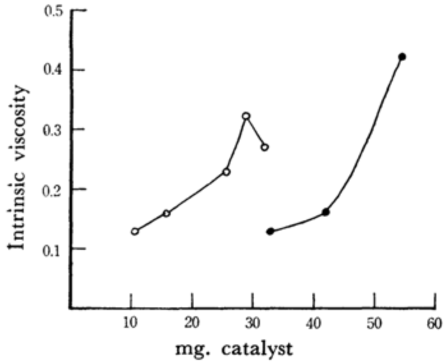


Fig. 1. Intrinsic viscosity of poly(ethylene carbazole-3, 6-dibutanoate) vs. catalysts.
○ $Ca(CH_3CO_2)\cdot H_2O$ and Sb_2O_3
● $Ca(CH_3CO_2)_2\cdot H_2O$

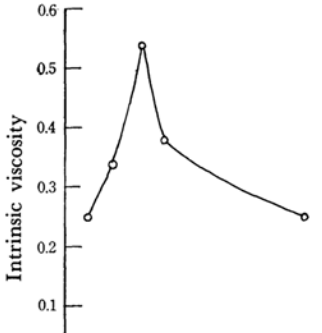


Fig. 2. Intrinsic viscosity of poly(ethylene carbazole-3, 6-dibutanoate) vs. weight of GeO_2.

Found: C, 63.52; H, 4.08; O, 23.21. Calcd. for $-CO\text{-}C_{12}H_7N\text{-}CO_2(CO)_2O-$: C, 64.77; H, 3.91; O, 22.81%.

9-EtPECC.—A mixture consisting of 2.0 g. of diEt 9-EtCD, 1.0 g. of ethylene glycol, 0.005 g. of cobaltous acetate, and 0.002 g. of calcium hydride was allowed to react under the same conditions and over the same period as in the synthesis of PECC. The polycondensation product showed an intrinsic viscosity of 0.34 in *m*-cresol at 30°C.

Found: C, 69.57; H, 4.95; O, 21.48. Calcd. for $-(C_{18}H_{15}O_4N)-$ or $-OC\text{-}C_{14}H_{11}N\text{-}CO_2(CH_2)_2O-$, in which $C_{14}H_{11}N$ is the 9-ethylcarbazole ring: C, 69.90; H, 4.85; O, 20.71%.

Results and Discussion

As has been described previously²⁾ polyesters obtained from ethylene glycol and diethyl carbazole-3, 6-γ, γ′-diketobutanoate, diEtCDKB, or diethyl 9-methylcarbazole-3, 6-γ, γ′-diketobutanoate, diEt 9-MeCDKB, suffer from the defects of dark color

TABLE I. RELATION BETWEEN WEIGHT OF CATALYST AND INTRINSIC VISCOSITY

Polymer code	Catalyst		Intrinsic[a] viscosity
	Fromula	Wt., g.	
PX-1	$Ca(CH_3CO_2)_2\cdot H_2O$	0.042	0.16
PX-2	$Ca(CH_3CO_2)_2\cdot H_2O$	0.033	0.13
PX-3	$Ca(CH_3CO_2)_2\cdot H_2O$	0.055	0.42
PX-4	$Ca(CH_3CO_2)_2\cdot H_2O$	0.011	0.13
	Sb_2O_3	0.003	
PX-5	$Ca(CH_3CO_2)_2\cdot H_2O$	0.016	0.16
	Sb_2O_3	0.004	
PX-6	$Ca(CH_3CO_2)_2\cdot H_2O$	0.026	0.23
	Sb_2O_3	0.006	
PX-7	$Ca(CH_3CO_2)_2\cdot H_2O$	0.029	0.32
	Sb_2O_3	0.007	
PX-8	$Ca(CH_3CO_2)_2\cdot H_2O$	0.032	0.27
	Sb_2O_3	0.003	
PX-9	GeO_2	0.0008	0.25
PX-10	GeO_2	0.0016	0.34
PX-11	GeO_2	0.0026	0.54
PX-12	GeO_2	0.0033	0.38
PX-13	GeO_2	0.0079	0.25
PX-14	Mg	0.0473	0.22
PX-15	B_2O_3	0.0025	0.27
PX-16	ZnO	0.007	0.31
	B_2O_3	0.005	
PX-17	Sb_2O_3	0.0057	0.13
PX-18	Sb_2O_3	0.0053	0.29
	CaH_2	0.0610	
PX-19	Control	—	0.11

a) Viscosity was measured with Cannon-Fenske viscometer in *m*-cresol at 30°C.

TABLE II. COLOR AND SOFTENING TEMPERATURE OF POLY(ETHYLENE CARBAZOLE-3, 6-DIBUTANOATE)

Polymer code	Color[a]	Softening temp.[b]
PX-1	IIIa	80 (285)
PX-2	IIIa	82 (285)
PX-3	IIIb	100 (293)
PX-4	IIIa	83 (290)
PX-5	IIIa	85 (290)
PX-6	IIIa	80 (285)
PX-7	IV	98 (290)
PX-8	IV	85 (290)
PX-9	II	83 (290)
PX-10	II	110 (293)
PX-11	II	122 (295)
PX-12	II	112 (295)
PX-13	IIIa	83 (285)
PX-14	V	80 (285)
PX-15	IV	82 (290)
PX-16	IV	90 (292)
PX-17	IIIa	80 (285)
PX-18	IV	90 (290)
PX-19	IIIa	80 (285)

a) Color of crude product was classified in six grades as follows: I, water white; II, light yellow (transparent); IIIa, light amber (transparent); IIIb, light amber (opaque); IV, amber; V, dark amber.

b) Temperature at which polyester becomes rubbery or soften without melting. Numbers in parentheses are temperatures above which the polymer decomposed.

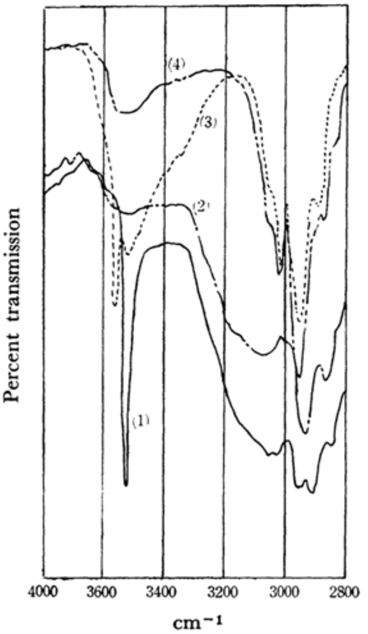


Fig. 3. Infrared spectra of 1, CDBA (——); 2, 9-MeCDBA (—·—); 3, low polymeric PECB (······, in $CHCl_3$); and 4, low polymeric 9-MePECB (–––, in $CHCl_3$).

and brittleness, though they have rather good resistance to many organic solvents. It seems that the dark color of poly(ethylene CDKB) or poly-(ethylene 9-MeCDKB) can be partly ascribed to carbonyl groups which attach directly to two benzene rings of the carbazole molecule and which may serve as possible chromophores, because PECB or 9-MePECB, which has no such groups, is in general a lighter color. Such catalysts as lead and cobaltous acetate or alkali metals can also exert a marked effect on the color of PECKB and PECB when added in large amounts. Blended catalysts

TABLE III. SOLUBILITY PROPERTIES[a] OF POLY-(ETHYLENE CARBAZOLE-3, 6-DIBUTANOATE) AND POLY(ETHYLENE CARBAZOLE-3, 6-DICARBOXYLATE)

Polymer solvent	PX-3	PX-7	PX′-5	PX-14	PX-16
Benzene	4	4	4	4	4
Cyclohexane	4	4	4	4	4
Dioxane	4	4	4	4	4
Toluene	6	4	4	4	4
Pyridine	1	3	4	3	4
n-Butyl acetate	4	4	4	4	4
Phenol	3	3	4	6	6
o-Cresol	1	1	1	1	1
m-Cresol	1	1	1	1	1
Nitrobenzene	2	2	4	2	6
Dichlorobenzene	3	2	4	6	6
DMF	2	2	4	6	3

a) The solubility is indicated by the numbers as follows[2]: 1, soluble in hot solvent and remains soluble when the solution becomes cold; 2, very low solubility, or little solvent action on solute; 3, absorption of solvent produces gelling; 4, insoluble; 5, soluble in hot solvent, precipitated when the solution becomes cold; 6, melted or sticky in hot solvent.

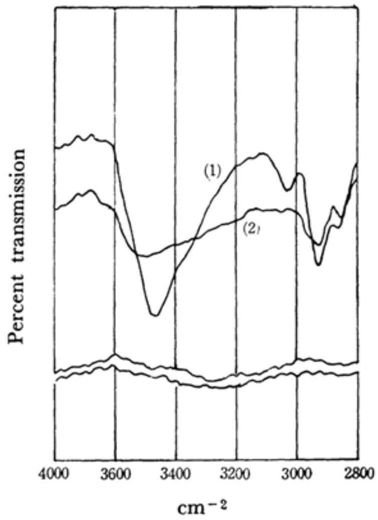


Fig. 4. Infrared spectra of 1, PECB (in KBr); and 2, N MePECB (in KBr).

TABLE IV. RELATION BETWEEN CATALYSTS AND INTRINSIC VISCOSITY OF POLY(ETHYLENE CARBAZOLE-3,6-DICARBOXYLATE)

Polymer code	Catalyst			Intrinsic viscosity[a)]
	Formula		Wt., g.	
PX′-1	Control		—	0.06[p)]
PX′-2	Na_2CO_3		0.005	0.08[p)]
PX′-3	$Pb(C_2H_3O_2)_2 \cdot 3H_2O$	1)	0.005	0.08[p)]
		2)	0.013	0.15[c)]
PX′-4	$Pb(C_2H_3O_2)_2 \cdot 3H_2O$		0.005	
	CaH_2		0.003	0.23[c)]
PX′-5	$Co(CH_3CO_2)_2 \cdot 4H_2O$		0.005	
	CaH_2		0.003	0.51[c)]
PX′-6	Sb_2O_3		0.005	
	CaH_2		0.001	0.50[c)]

a) Viscosity was measured with Cannon-Fenske viscometer and intrinsic viscosity obtained by plotting inherent viscosity numbers vs. concentration and extrapolating to zero concentration.

c) In *m*-cresol at 30°C.

p) In pyridine at 30°C.

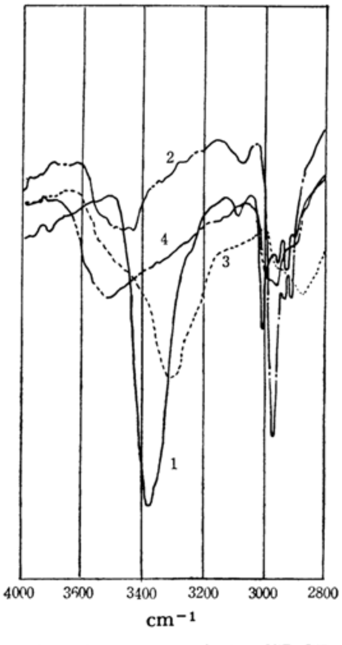
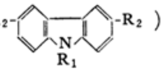


Fig. 5. Infrared spectra of 1, diEtCD (——); 2, diEt9-EtCD (—·—); 3, PECC (……); 4, 9-Et PECC (---).

TABLE V. DEPENDENCE OF POLYMER-MELT TEMPERATURE ON STRUCTURE OF ACID COMPONENT (ACID OR SIMPLE ESTER OF GENERAL FORMULA



)

		R_2	PMT (°C)
A	$R_1 = -H$	-COEt	above 200
		$-(CO_2)_3COOH$	below 100*
		$-CO(CH_2)_2COOEt$	above 165
B	$R_1 = -CH_3$	$-(CH_2)_3COOH$	below 120*
		$-CO(CH_2)_2COOEt$	above 190
C	$R_1 = -C_2H_5$	-COOEt	above 280

* Polymer softening temperature

are prone to give a darker polycondensation products, as is shown in Table II.

Numerous PECB by adding different amount of germanium dioxide, ranging from 0.03 to 0.32% by weight of CDBA, exhibited a light yellow color, and the crude product was transparent. Figure 2 shows that the viscosity of the resulting PECB tended to decrease when more than 0.13% of germanium dioxide (based on the weight of CDBA) was added in a polycondensation. As is shown in Fig. 1, calcium acetate, used singly, was equally as effective as the combined catalyst ($Ca(CH_3CO_2)_2 \cdot H_2O/Sb_2O_3 = 4/1$). The antimony trioxide in combination with calcium hydride exerted a good effect, whereas it did not enhance the marked catalyst effect when used together with calcium acetate, as is shown in Table I.

The catalysts effective in the syntheses of PECKB and PECB were mostly ineffective in the preparation of PECC (for instance, calcium acetate or germanium dioxide). In the absence of calcium halide, the reaction of diEtCD and ethylene glycol at the early stage did not proceed smoothly, so that β-hydroxyethyl carbazole-3,6-dicarboxylate was obtained in only a low yield. On the other hand the reaction proceeded readily in the presence of calcium hydride.

In the synthesis of PECC, calcium acetate as a single catalyst proved to be ineffective, whereas lead acetate was suitable. Under the influence of blended catalysts, such as lead acetate and antimony trioxide, an infusible and insoluble PECC was obtained. However, a mixture of lead acetate and calcium hydride or cobaltous acetate and calcium hydride was revealed to be a good catalyst blend in preparing PECC.

The polymer melt temperature or the polymer softening temperature depends greatly on the structure of the acid component, as is shown in Table V. In contrast to PECB, which was more susceptible to deformation by heat, PECC showed a fairly high polymer melt temperature.

The infrared spectra of the starting monomers and the polyesters (PECC, 9-EtPECC, PECB, and 9-MePECB) were compared in order to establish the structures of polycondensation products. Figures. 3, 4 and 5 show the characteristic N–H stretching absorptions. As is illustrated in the figures, these absorptions are apparently absent in the spectra of 9-MeCDBA, 9-MePECB, 9-EtCDA, and 9-EtPECC. The presence of an aromatic-type structure is also evidenced by the absorption near 3030 cm⁻¹, as shown in Figs. 3, 4, and 5. These characteristic absorptions, as well as other absorptions in the lower regions of the charts (arising from the C=O and C=C groups), together with the data of the elementary analyses of the polyesters, indicated that PECB and PECC are linear polyesters with the following recurring units:

PECB, $-(OCOC_3H_6-C_{12}H_7N-C_3H_6CO_2C_2H_4O)-$, in which $-C_{12}H_7N-$ is the carbazole ring; PECC, $-(OC-C_{12}H_7N-CO_2C_2H_4O)-$. in which $-C_{12}H_7N-$ is the carbazole ring.