

Synthesis and Properties of Phosphorus-Containing Polycarbonates

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Synopsis

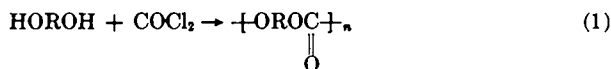
Aromatic polycarbonates were prepared from several dichloroformates with phosphorus-containing bisphenols, such as bis(*p*-hydroxyphenyl)methyl phosphine oxide and bis(*p*-hydroxyphenyl)phenyl phosphine oxide, or with nonphosphorus bisphenols by interfacial, low-temperature solution, and high-temperature solution polycondensation. The interfacial polycondensation gave the best results for polycarbonates, from which colorless, transparent, and fairly tough films were cast. In contrast to analogous nonphosphorus polycarbonates, the phosphorus-containing polycarbonates exhibited lower polymer melt temperatures, greater range of solubility, and better self-extinguishing properties, but less stability to alkali and acid. Thermal degradation of the typical phosphorus polycarbonates proceeded in two steps, and the activation energies for the maximum rates of weight loss range from 29 to 45 kcal/mole.

INTRODUCTION

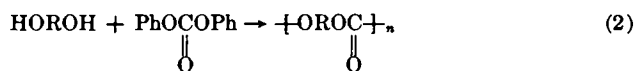
Aromatic polycarbonates are known to be outstanding with respect to stability to heat, light, and numerous chemicals.

Of several known methods for the preparation of polycarbonates, three [eqs. (1)–(3)] are considered to be the most important.

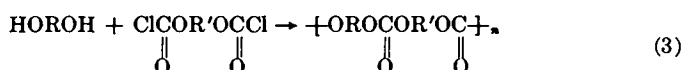
Direct phosgenation:



Ester-exchange reaction:



Dichloroformate method:



Since polycarbonate from bisphenol A has been commercially produced in Germany and United States,¹⁻³ numerous papers on polycarbonates have been published.⁴

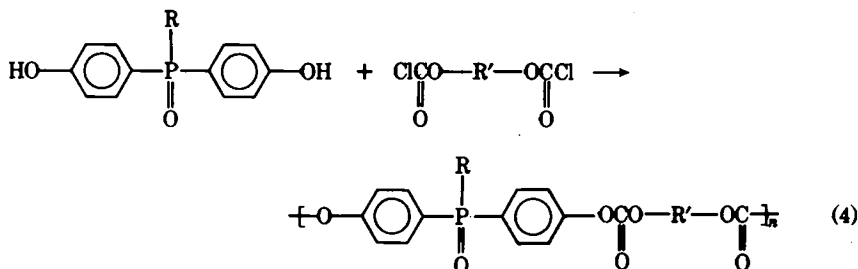
Phosphorus-containing polycarbonates, which have P—O—C, were also prepared from alkyl or arylphosphonic dichloride,^{5,6} arylphosphonothioic dichloride or arylphosphonous dichloride,⁷ arylphosphorodichloridate,⁸ the dichloroanhydride of alkyl or arylphosphinic acid,⁹ or bis(*p*-hydroxyphenyl)alkylphosphonic acid dimethyl ester.¹⁰ However, no work has been reported on polycarbonate with phosphorus-carbon bonds in the backbone.

In this paper, phosphorus-containing bisphenols such as bis(*p*-hydroxyphenyl)methyl phosphine oxide, bis(*p*-hydroxyphenyl)phenyl phosphine oxide, and dichloroformates were used in the preparation of polycarbonates to examine the polymerization conditions and to compare their properties with those of analogous nonphosphorus polycarbonates. Phosphorus-containing bisphenols have been used to prepare polyesters,¹¹ but not polycarbonates.

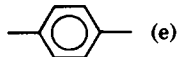
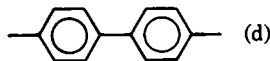
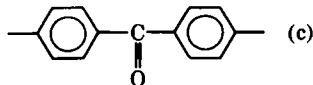
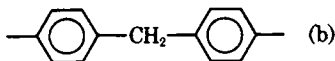
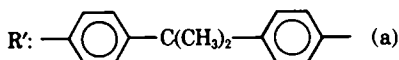
RESULTS AND DISCUSSION

Preparation of Phosphorus-Containing Polycarbonates

Phosphorus-containing polycarbonates were prepared from phosphorus-containing bisphenols and dichloroformates by the interfacial method [eq. (4)].



R: —CH₃ (I)



The addition of an accelerator and/or a detergent generally improves the molecular weight of aromatic polycarbonates prepared by the interfacial method; such additions are usually necessary even in the best solvents.

Table I shows the effects of solvents, the accelerator, and the detergent on the preparation of phosphorus-containing polycarbonate IIa.

The effect of solvent was investigated first. Polycondensation carried out in ethylene dichloride gave a product of reduced viscosity of 0.23, among those carried out in 1,1,2,2-tetrachloroethane, chloroform, trichloroethylene, carbon tetrachloride, and *p*-xylene.

Second, the accelerator and the detergent effects were investigated. Since polycarbonates prepared in the presence of the detergent (sodium laurylsulfate) and the accelerator (triethylbenzylammonium chloride) in ethylene dichloride generally showed low viscosities, $\eta_{sp}/c = 0.06$ –0.22, polycondensation was carried out only in the presence of the accelerator. The polycarbonate of highest viscosity, $\eta_{sp}/c = 0.55$, was obtained in the presence of 1 wt-% of accelerator based on the theoretical weight polymer, and the yields and viscosities decreased in the presence of more than 1 wt-% of the accelerator. This decrease might be explained by reactive impurities in the accelerator.

TABLE I
Effects of Solvents, Detergent, and Accelerator in the Preparation of
Polymer IIa from II and Bisphenol A Dichloroformate^a

Run	Solvent ^b	Deter- gent, wt-% ^c	Acceler- ator, wt-% ^d	Yield, %	η_{sp}/c^e
1	1,1,2,2-Tetrachloroethane	2	—	Trace	—
2	Chloroform	2	—	73	0.12
3	Trichloroethylene	2	—	73	0.18
4	Carbon tetrachloride	2	—	68	0.19
5	<i>p</i> -Xylene	2	—	71	0.21
6	Ethylene dichloride	2	—	72	0.23
7	" "	2	2	48	0.08
8	" "	2	3	80	0.21
9	" "	2	4	84	0.22
10	" "	2	5	49	0.06
11	" "	3	4	86	0.16
12	" "	—	—	93	0.35
13	" "	—	1	100	0.55
14	" "	—	2	100	0.47
15	" "	—	3	100	0.49
16	" "	—	4	97	0.35
17	" "	—	5	99	0.32

^a In each run, 0.001 mole of II and bisphenol A dichloroformate, and 2 ml of 1 *N* NaOH were used.

^b 8 ml was used.

^c Sodium laurylsulfate, wt-% based on 1 *N* NaOH aqueous soln.

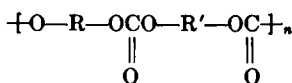
^d Triethylbenzylammonium chloride, wt-% based on the theoretical weight of polymer.

^e $c = 0.5$ g/100 ml in DMF at 30°C.

Table II shows the results of interfacial polycondensation of dichloroformates with phosphorus-containing bisphenols and with nonphosphorus bisphenols. Polycondensation with phosphorus-containing bisphenols gave good yields of considerably high viscosity polycarbonates.

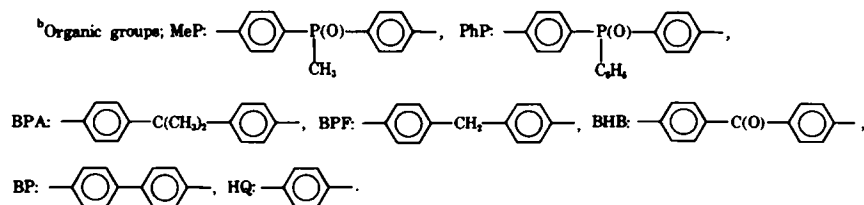
The result of low- and high-temperature solution polycondensations are shown in Tables III and IV. Only low molecular weight polycarbonates, $\eta_{sp}/c = 0.14$, were obtained. Presumably, the low viscosities are due to lower reactivity and poor solubility of phosphorus bisphenols in organic solvents other than aprotic solvents and alcohols.

TABLE II
Interfacial Polycondensation of I, II, and Nonphosphorus Bisphenols
with Several Kinds of Dichloroformates*



Polymer	R ^b	R' ^b	Yield, %	PMT, °C	η_{sp}/c^c	P found (calcd), %
Ia	MeP	BPA	87	208-215	0.32	5.56 (5.86)
IIa	PhP	"	100	248-262	0.55	5.10 (5.24)
III	BPA	"	98	210-219	0.83 ^d	—
Ib	MeP	BPF	100	217-229	0.33	6.01 (6.19)
IIb	PhP	"	98	205-218	0.22	5.01 (5.51)
IV	BPF	"	89	245-250	Insoluble	—
Ic	MeP	BHB	97	188-201	0.23	6.59 (6.10)
IIc	PhP	"	94	160-169	Insoluble	5.73 (5.47)
V	BHB	"	90	>300	"	—
Id	MeP	BP	90	235-244	0.55	6.30 (6.37)
IIId	PhP	"	100	230-242	0.29	5.79 (5.65)
VI	BP	"	95	>300	Insoluble	—
Ie	MeP	HQ	87	205-215	0.27	7.83 (7.55)
IIe	PhP	"	85	215-220	0.23	7.03 (6.53)
VII	HQ	"	72	300	Insoluble	—

* In each run, 0.001 mole of bisphenol and dichloroformate, 2 ml of 1*N* NaOH, 6 ml of water, 0.018 g of triethylbenzylammonium chloride, and 8 ml of ethylene dichloride were used.



^cC = 0.5 g/100 ml in DMF at 30°C.

^dIn CHCl₃.

Properties of Polycarbonates

In contrast to analogous nonphosphorus polycarbonates, the phosphorus-containing polycarbonates exhibited a lower polymer melt temperature, and a greater range of solubilities; they were soluble in DMF, DMSO, nitrobenzene, chloroform, and methylene chloride.

The phosphorus-containing polycarbonates in methylene chloride produced colorless, transparent, and fairly tough films that adhered strongly to metal and glass surfaces.

It has been reported¹² that the polycarbonates prepared from bisphenol A show good self-extinguishing properties. However, according to simple flammability test, the phosphorus-containing polycarbonates prepared in this paper showed better self-extinguishing properties than the nonphosphorus polycarbonates, because the former self-extinguished immediately as soon as the flame was removed, while the latter did within 3 sec.

It has also been reported that polycarbonates are stable in alcohols and acids but not in weak alkalis and strong acids.^{2,13} The effects of sodium hydroxide and hydrochloric acid on polycarbonates IIa and III were investigated, and the results are shown in Table V. The phosphorus-containing polycarbonates exhibited less stability in acid and alkali than did the nonphosphorus polycarbonate.

Thermal Stability of Polycarbonates

The results from thermal gravimetric analysis (TGA), given in Table VI, show that the initial temperature of decomposition of phosphorus-containing polymers differed from that of corresponding nonphosphorus polymers. The introduction of I into the polymer chain lead to increased ease of decomposition, while with II the polymer became more difficult to de-

TABLE III
Low-Temperature Solution Polycondensation^a

Polymer	Solvent ^b	Acid acceptor	Time, hr	Yield, %	PMT, °C	η_{sp}/c^c	Appearance
IIa	NMP	Triethylamine	5	76	164-170	0.09	White
IIa	NMP	"	24	76	151-157	0.12	"
IIa	HMPA	"	24	80	95-102	0.08	"
IIa	DMF	"	24	68	132-139	0.10	Slightly yellow
IIa	DMSO	"	24	Trace	—	—	" "
Ia	NMP	"	24	78	156-164	0.09	White
Ia	NMP	Pyridine	24	47	103-112	0.05	Yellow
Ile	NMP	Triethylamine	24	45	241-251	0.13	Slightly brown
Ie	NMP	"	24	42	300	Insoluble	Brown

^a In each run, 0.001 mole of bisphenol and dichloroformate, 0.002 mole of acid acceptor, and 0.015 g of LiCl were used.

^b 6 ml was used.

^c $c = 0.5$ g/100 ml in DMF at 30°C.

TABLE IV
High-Temperature Solution Polycondensation^a

Polymer	Solvent ^b	Catalyst		Temperature, °C	Time, hr	Yield, %	η_{sp}/c^d	Appearance
		Type	Concn, mole-%					
IIa	<i>o</i> -Dichlorobenzene	Mg	100	180	10	30	0.14	Yellow
IIa	Nitrobenzene	Mg	100	210	10	26	0.07	Slightly brown
Ia	Nitrobenzene	Mg	100	210	10	28	0.07	"
Ia	—	Mg	50	180-230	6	Trace	—	Brown
Ia	DMF	Mg	100	140	10	Trace	—	"
Ia	NMP	Mg	100	160	6	25	0.05	Slightly brown
Ia	NMP	—	—	Room temp.	24	Trace	—	Red
Ia	NMP	ZnCl ₂	50	50	24	Trace	—	"

^a In each run, 0.001 mole of bisphenol and dichloroformate were used.

^b 3 ml was used.

^c Based on I or II.

^d $c = 0.5$ g/100 ml in DMF at 30°C.

TABLE V
Effect of Sodium Hydroxide and Hydrochloric Acid at 60°C on Polymer II and III

Polymer	Time, hr	Medium	Weight recovery, %	Reduced viscosity	
				Original	Recovered
IIa	72	10% NaOH	62	0.49 ^a	0.12 ^a
		1% HCl	80	0.46 ^a	0.25 ^a
IIIa	72	10% NaOH	81	0.83 ^b	0.67 ^b
		1% HCl	98	1.05 ^b	1.03 ^b

^a At a concentration of 0.5 g/100 ml in DMF.

^b At a concentration of 0.5 g/100 ml in CHCl₃.

compose than the analogous nonphosphorus polymers. Usually, thermal degradation of bisphenol A polycarbonate involves breakdown of the carbonate group, followed by decomposition at the isopropylidene linkage.¹⁴ From these facts, it is thought that the introduction of a phosphoryl group effects the decarboxylation in the initial thermal degradation.

The shapes of the TGA curves were somewhat different, as shown in Figure 1. All of the phosphorus-containing polycarbonates, Ia, Ib, IIa, and IIb, showed a region of decreased weight loss after 32–42% decomposition, a behavior not observed with the nonphosphorus polycarbonates (III, IV). This increased stability occurred at a point approaching the theoretical weight loss calculated as carbon dioxide from carbonate groups and C(aromatic)–C(aliphatic) cleavage in phosphorus polycarbonates.

ANAL. Residue Calcd for Ia: 61%; Found: 58% at 420°C. Calcd for IIa: 65%; Found: 62% at 470°C. Calcd for Ib: 64%; Found: 62% at 440°C. Calcd for IIb: 69%; Found: 68% at 470°C.

The mechanism of thermal degradation is shown in eq. (5).

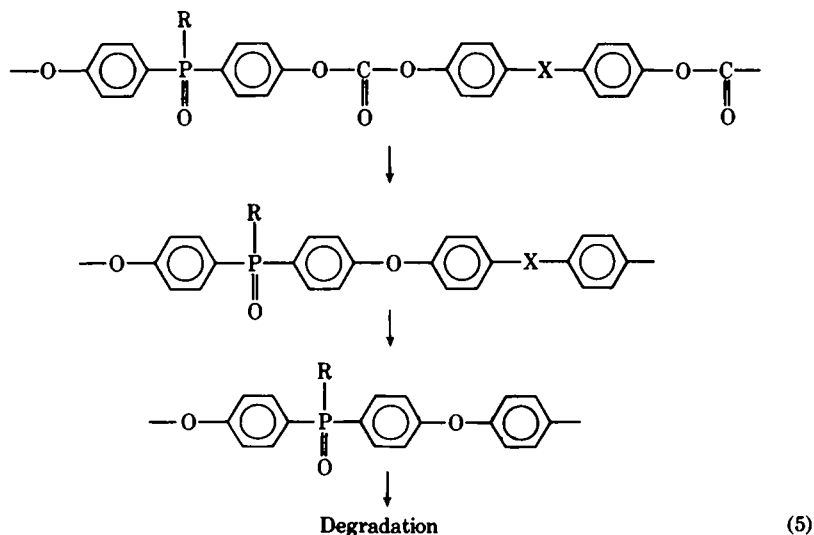


TABLE VI
Initial Temperature of Decomposition and Activation
Energies of Polycarbonate, $\text{-(O-R-OCO-R'-OC)-}_n$

Polymer	R	R'	Decomposition temperature ^a , °C	ΔE , kcal/mole
Ia	MeP	BPA	360	31
IIa	PhP	"	430	45
III	BPA	"	400	32
Ia	MeP	BPF	365	29
IIb	PhP	"	420	39
IV	BPF	"	390	34

^a Heating rate, 10°C/min under nitrogen.

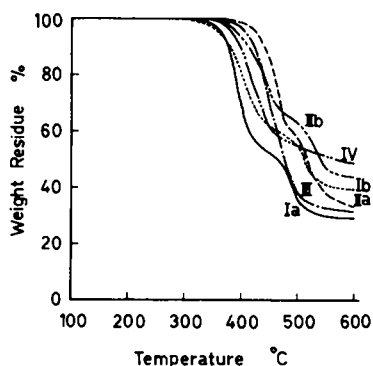


Fig. 1. Thermogravimetric analysis of polycarbonates. Heating rate, 10°C/min under nitrogen.

The formation of polyether groups in phosphorus-containing polycarbonates could explain the subsequent region of slower decomposition in the TGA curves, because polyethers have been shown to decompose more slowly than polycarbonates.

The activation energies (ΔE) of the thermal degradation of polymers from TGA data obtained from the method suggested by Ozawa.¹⁶ Thus, the TGA results at various heating rates are plotted against the reciprocal of absolute temperature. These curves can be superposed on performing lateral shifts. The logarithms of the heating rates are plotted against the reciprocal of absolute temperature, up to the point at which the weight of the sample decreases to a given fraction of its initial weight. Straight lines are drawn by the method of the least squares; from these lines the activation energies are determined.

The ΔE for the phosphorus and nonphosphorus-containing polycarbonates are shown in Table VI. They were between 29 and 45 kcal/mole.

Structure of Phosphorus-Containing Polycarbonates

Infrared spectra of phosphorus-containing polycarbonates showed the following absorption bands: 1300 cm^{-1} ($\nu_{\text{P-O}}$); 1800 cm^{-1} ($\nu_{\text{C=O}}$); 1240 , 1020 cm^{-1} ($\nu_{\text{C-O-C}}$).

NMR spectra were obtained on the typical polycarbonates IIa and Ib.

Polymer IIa showed a singlet for the $\text{CH}_3\text{—C—CH}_3$ protons at $\delta = 1.64$ ppm and a complex splitting pattern for the $\text{C}_6\text{H}_5\text{—P}$ and C_6H_4 protons at $\delta = 7\text{--}8$ ppm. Polymer Ib showed a singlet for the $\text{Ar—CH}_2\text{—Ar}$ protons at $\delta = 3.98$ ppm, a doublet for the $\text{CH}_3\text{—P}$ protons at $\delta = 2.0$ ppm, with $J = 12\text{ Hz}$, as a result of coupling with phosphorus, and a complex splitting pattern for the C_6H_4 protons at $\delta = 7\text{--}8$ ppm.

EXPERIMENTAL

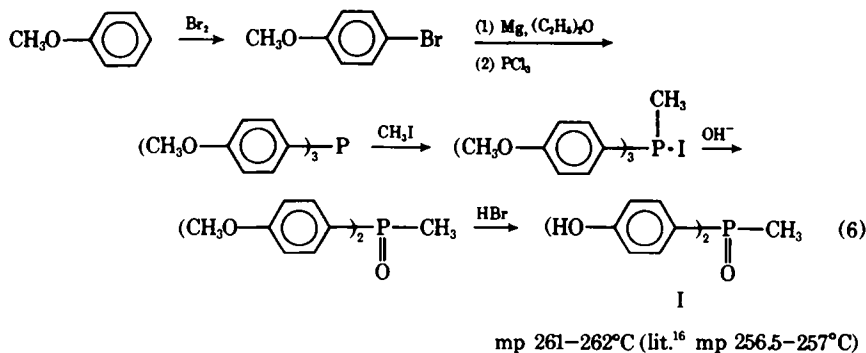
Materials

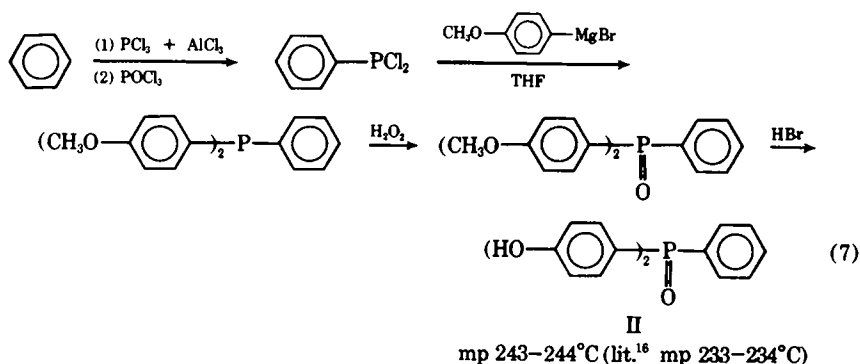
Nonphosphorus bisphenols used were commercial products purified by recrystallization; their melting points were as follows: bisphenol A, mp $156\text{--}157^\circ\text{C}$; bisphenol F, mp $164\text{--}165^\circ\text{C}$; *p,p'*-dihydroxybenzophenone, mp $212\text{--}213^\circ\text{C}$; hydroquinone, mp $170\text{--}170.5^\circ\text{C}$; *p,p'*-bisphenol, mp $274\text{--}275^\circ\text{C}$.

Dichloroformates were obtained according to the usual procedure for phosgenation of the corresponding bisphenols;¹⁷ their melting points were as follows: bisphenol A dichloroformate, mp $95\text{--}96^\circ\text{C}$ (lit.¹⁷ mp $95\text{--}96^\circ\text{C}$); bisphenol F dichloroformate, mp $60\text{--}60.5^\circ\text{C}$; *p,p'*-dihydroxybenzophenone dichloroformate, mp $132\text{--}132.5^\circ\text{C}$; hydroquinone dichloroformate mp $103\text{--}103.5^\circ\text{C}$ (lit.¹⁷ mp $102.5\text{--}103.5^\circ\text{C}$); *p,p'*-bisphenol dichloroformate, mp $132.5\text{--}133^\circ\text{C}$.

Those that have not been described in the literature were identified by Beilstein's method and mass spectra.

Bis(*p*-hydroxyphenyl)methyl phosphine oxide(I) and bis(*p*-hydroxyphenyl)phenyl phosphine oxide(II) were prepared according to the method described by Bride et al.¹⁶ The routes are summarized in eqs. (6) and (7).





Polycondensations

Aromatic polycondensation were prepared by interfacial, low-temperature and high-temperature solution polycondensation. Typical procedures were as follows.

Interfacial Polycondensation Method. II (0.310 g, 0.001 mole), 2 ml of 1N NaOH, 6 ml of water, 0.040 g of sodium laurylsulfate (2 wt-% based on 1N NaOH), and 0.018 g of triethylbenzylammonium chloride (3 wt-% based on the theoretical weight of polymer) were stirred in a homogenizer. Into this mixture, a solution of 0.353 g (0.001 mole) of bisphenol A dichloroformate in 8 ml of ethylene dichloride was added rapidly with vigorous stirring, and then the stirring was continued for 1 hr. The polymer was isolated by filtration, washed sequentially with methanol and water, and dried to constant weight at 100°C in a vacuum oven.

Low-Temperature Solution Polycondensation Method. II (0.310 g, 0.001 mole), 0.015 g of lithium chloride, and 2.02 g (0.002 mole) of triethylamine were dissolved in 3 ml of *N*-methylpyrrolidone (NMP) in a test tube. Into this mixture, solution of 0.353 g (0.001 mole) of bisphenol A dichloroformate in 3 ml of NMP was added with stirring at once, and then the mixture was stirred for 24 hr. The polymer has precipitated by pouring into methanol, washed with water, and dried to constant weight at 100°C in a vacuum oven.

High-Temperature Polycondensation Method. In a test tube with side arm were placed 0.310 g (0.001 mole) of II, 0.353 g (0.001 mole) of bisphenol A dichloroformate, 0.024 g (0.001 g-atom) of magnesium metal, and 3 ml of *o*-dichlorobenzene. This mixture was heated to 180°C in a stream of dry nitrogen. The course of the reaction was followed by observing the evolution of hydrogen chloride. The polymer was precipitated in hexane, washed with water, and dried to constant weight.

Thermal Degradation of Polymers

Thermogravimetric data were secured on a Shimadzu model DT-20B thermal analyzer in an atmosphere of nitrogen. The sample weight used was 10 mg, and heating was at the rate of 10°C/min.

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