Polymer Bulletin 1, 383-388 (1979)

Polymer Bulletin

Syntheses of Aromatic Polyesters from Silylated Monomers

New Polymer Syntheses II.

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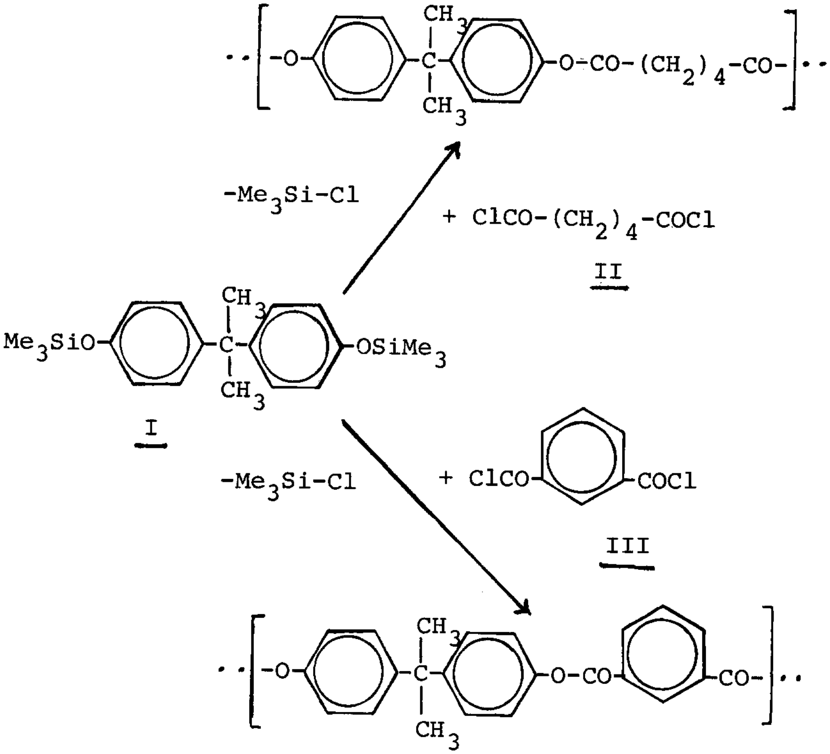
SUMMARY

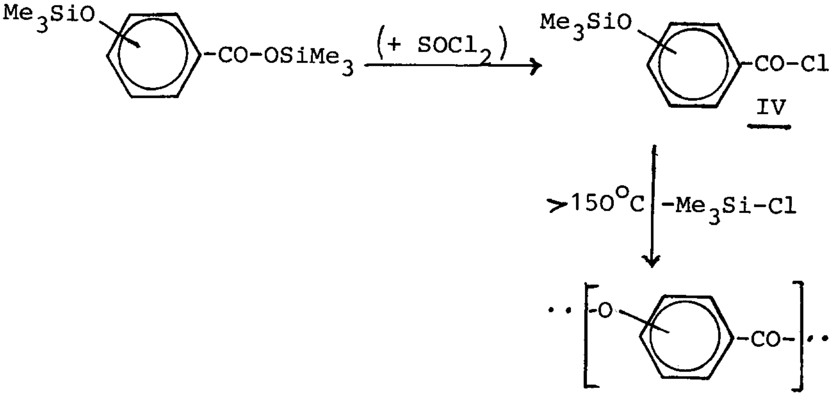
Aromatic polyesters were synthesized either from silylated bisphenols and diacid chlorides or from trimethyl siloxy benzoyl chlorides by thermal condensation at 200-300°C. Yields and molecular weights were compared with those obtained by other condensation methods. The "Silyl Method" seems to be most useful for the synthesis of polyesters of aromatic ω-hydroxy acids.

RESULTS and DISCUSSION

Polyesters with aromatic components have found growing interest during the last twenty years, and some polymers, e.g. polyethylene, terephthalate and poly-p-hydroxy benzoic acid,are industrially produced. Our studies on the use of silylated amino acids for the synthesis of polypeptides and polyamides prompted us to investigate the usefulnes of silylated bisphenols and silylated hydroxybenzoic acids for the synthesis of polyesters. In contrast to silylated aliphatic alcohols silylated phenols are stable against the attack of most acid chlorides at room temperature. However, upon heating above 100-140°C the siloxy group is acylated and trimethyl chlorosilane is splitt off. Thus, it was possible to obtain polyesters by thermal condensation of bistrimethylsilyl Bisphenol A (I) with adipoyl chloride (II) or isophthaloyl chloride (III). The less reactive aromatic diacid chloride requires higher temperatures than the aliphatic one (s.Tab.1). An analogous polycondensation can be carried out with aromatic trimethylsiloxy carboxylic acid chlorides (IV). These monomers are nearly quantitatively formed when silylated aromatic hydroxy carboxylic acids are treated with distilled thionylchloride in boiling methylene chloride.The monomers IV are stable at room temperature, but condense partially in the course of the distillation at temperatures $\gg$ 100°C.Syntheses and properties of numerous trimethylsiloxy aroyl-chlorides will be described elsewhere.

0170-0839/79/0001/0383/$01.20


-Me$_3$Si-Cl
+ ClCO-(CH$_2$)$_4$-COCl
II
Me$_3$SiO
CH$_3$
C
CH$_3$
OSiMe$_3$
I
-Me$_3$Si-Cl
+ ClCO
COCl
III
-O-
-O-CO-(CH$_2$)$_4$-CO-
-O-CO
CO-


Me$_3$SiO
-CO-OSiMe$_3$
(+ SOCl$_2$)
Me$_3$SiO
-CO-Cl
IV
>150°C
-Me$_3$Si-Cl
-O
-CO-

Since our new synthetic method requires silylated monomers, it is certainly a relatively costly procedure. However, it must be emphasized, that the trimethylchlorosilane split off in the course of the polycondensation is easy to condense and to recycle. To see how worthwile are the results of our method the same polyesters were prepared by various procedures, and several experiments were repeated under identical conditions (s.Tab.I) or under slightly varied conditions (s.Tab.II) to test the reproducibility of the experiments. The results of Table I demonstrate that for polyesters built up by diphenols and diacids the "interface-method" gives the best results with respect to the polymerization degree. However, the "silyl-method" is superior to other thermal polycondensations so far studied. In this connection it should be pointed out that all thermal condensations of two different monomers suffer from distillation or sublimation of the most volatile monomer, since the stoichometry of the reaction mixture is changed. This disadvantage is obviously avoided, if the trimethylsiloxy aroyl chlorides IV are used as monomers. Thus, it is not surprising that the molecular weights obtained with the m-hydroxy benzoic derivative are higher than those obtained with silylated Bisphenol A and adipoylchloride. Furthermore, it must be emphasized that for the synthesis of polyesters of aromatic hydroxy carboxylic acids several methods, such as the "interface condensation" are principally not applicable. The thermal condensation of free hydroxy benzoic acids as well as the polycondensation of hydroxy benzoic acid phenylesters has been shown by other authors to be inferior to the thermal condensation of acetoxy benzoic acids[1,2] The data of Table II show on the other hand that the "silyl-method" yields molecular weights two to three times higher than those obtained with the "acetoxy-method". In this connection it must be mentioned that for the polyester of m-hydroxy benzoic acid molecular weights (Mn) of 11 - 25 000 were reported [2]. These values were determined by titration of the carboxyl end groups in benzylalcohol solution. However, no experimental evidence was given that all polyester chains really possess carboxyl endgroups. It is well known that the thermal polycondensation of ω-hydroxy benzoic acids leads to decarboxylation [3]. Hence, we suppose that the molecular weights reported in reference 3 are by far to high, because a part of the polymer chains was devoid of carboxyl groups. Finally we come to the conclusion that the merits of the new synthetic method described in this work lies mainly in the field of polyesters derived from aromatic hydroxy acids. A detailed description of syntheses and properties of various aromatic homo- and copolyesters will follow in a succeeding paper.

Table I. Synthesis of polyesters containing Bisphenol A and Adipic Acid or Isophtalic Acid.

Reaction Partners	Reaction Conditions	Yield[a)] (%)	$\frac{\eta_{sp}}{c}$[b)] cm^3g^{-1}	Mn[c)]
Bisphenol A adipoyl chloride	"Interface polycondensation" with CH_2Cl_2 and 1 n sodium hydroxide at 0°C	74 76	33.4 27.9	5.800 5.000
Bisphenol A adipoyl chloride	homogeneous reaction in CH_2Cl_2 with pyridine at 20-25°C	73 78	20.4 19.3	3.800 3.600
bistrimethylsilyl Bisphenol A adipoyl chloride	polycondensation in the melt; 0,5h/150°C and 1.5h/200°C	89 95	34.1 27.5	5.800 4.900
bisacetyl Bisphenol A adipic acid	polycondensation in the melt catalyzed by Mg; 3.0h/220°C (1.5h in vacuo)	65	16.3	3.100
Bisphenol A isophthaloyl chloride	"Interface polycondensation" in CH_2Cl_2 and 1 M sodiumhydroxide at 0°C	89	71.7	--
Bisphenol A isophthaloyl chloride	homogeneous polycondensation in CH_2Cl_2 with triethylamine at 20-25°C	93	35.2	--
bistrimethylsilyl Bisphenol A isophthaloyl chloride	polycondensation in the melt; 1h/200°C +4h/250°C	77	34.1	--
bisacetyl Bisphenol A isophthalic acid	polycondensation in the melt; catalyzed by Mg; 1h/250°C + 4.5h/300°C (1.5h vacuum)	78	27.7	--
Bisphenol A dimethyl isophthalate	polycondensation in the melt; catalyzed by $NaOCH_3$; 0.5h/150°C+ 2h/250°C	0	-	--

a) After reprecipitation b) c = 2,3 g/l in phenol/carbontetrachloride (3:2 by weight) at 20°C
c) Vapor pressure osmometry in chloroform

Table II Reaction conditions and results of the synthesis of poly-m- and poly-p-hydroxybenzoic acid

Monomers		Reaction Conditions	Yield a) (%)	$\frac{\eta_{sp}}{c}$ (cm^{3}g^{-1})	Mn b)
m-Trimethylsiloxy benzoyl chloride c)		3h/200°C	88	16.7	4 000
" c)		3h/250°C	99 98	83.5 60.5	13 300 10 600
" d)		3h/250°C	95	58.5	10 000
" c)		10h/250°C	89	75.0	11 800
" c)		3h/350°C	93	72.5	11 800
m-Acetoxy-benzoic acid + catalytic amount of Mg		2h/220°C (1h vacuum) 0.25h/300°C	89	19.5 e)	3 850
"		10h/220°C (8h vacuum) 0.25h/300°C	90	17.0	3 700
m-Trimethyl-siloxybenzoyl chloride c) + p-Trimethyl-siloxybenzoyl chloride c)	90/10	3h/250°C	99	46.5	8 400
	80/20	3h/250°C	99	76.0	8 800
	70/30	3h/250°C	95	81.0	8 850

a) after reprecipitation

b) vapor pressure osmometry in chloroform

c) distilled

d) two times concentrated in vacuo after dilution with toluene

e) a direct comparison with the values of ref. is not possible because the dimension of the viscosity values and the temperatur are not reported

EXPERIMENTAL

Poly (Bisphenol-A adipate)

25 mmol bistrimethylsilyl Bisphenol-A and 25 mmol adipoyl-chloride were heated under a slow stream of nitrogen at 150°C for 0.5h and then at 200°C for 1.5h. After cooling the polymer was dissolved in formic acid/methylene chloride (1:4 by volume) and precipitated from 600 ml methanol.Final drying was carried out at 65°C/10^{-1} mbar.

Poly-m-hydroxybenzoic acid

50 mmol of distilled m-trimethylsiloxy benzoylchloride were heated under a slow stream of nitro en at 180°C for 0.2h and then at 250°C for 3h. After cooling the polymer was dissolved in 180 ml of a 1:1 mixture of pyridine and benzene at 60-80°C, precipitated from 1 l methanol, and dried at 135°C/10^{-1} mbar.

Acknowlegement

We thank the Deutsche Forschungsgemeinschaft for financial support.

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Received February 2o, 1979