

Chlorination of Polyesters*

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Synopsis

By photochemical chlorination chlorine was substituted on the *gem*-dimethyl groups of the polyterephthalate and polycarbonate of 2,2,4,4-tetramethyl-1,3-cyclobutanediol, the polyterephthalate of 2,2-dimethyl-1,3-propanediol, and the polycarbonate of 4,4'-isopropylidenediphenol (bisphenol A). The factors affecting polyester degradation, the efficiency of chlorination, and the degree of chlorination were investigated, and the effects of chlorine content on the solubility, flammability, density, hydrolytic stability, thermal stability, tensile properties, electrical properties, and heat-distortion temperatures of cast films were determined. The chlorinated polyesters of particular interest, because of their properties, are the polycarbonates of 2,2,4,4-tetramethyl-1,3-cyclobutanediol and bisphenol A.

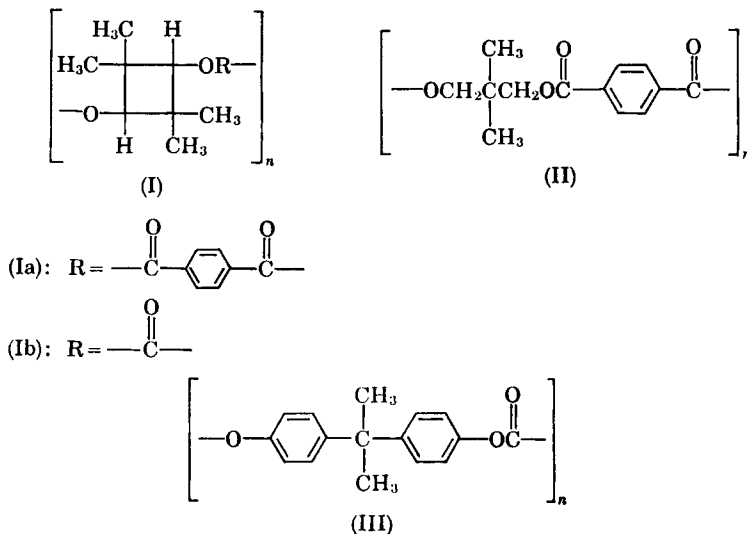
INTRODUCTION

Nonflammable polymers in the form of fibers, films, coatings, and molded objects are in demand today for many uses. Such polymers normally contain fluorine, chlorine, bromine, or phosphorus, or a combination of these elements. From an economical standpoint, however, chlorine is usually the best choice. Theoretically, chlorine-containing polymers can be obtained by polymerizing chlorinated monomers, but it is impractical to prepare many of the chlorinated monomers, particularly the nonaromatic chlorinated diols. Moreover, it is very difficult to obtain polyesters of high molecular weight from nonaromatic chlorinated diols by ester interchange, probably because of a reaction between the catalyst and the chlorine. Miyake and his co-workers¹ reported that only low molecular weight polyesters were obtained by direct esterification or transesterification of 2,2-bis-(chloromethyl)-1,3-propanediol. However, from this diol and dicarboxylic acid chlorides they did obtain polyesters with intrinsic viscosities up to 0.6 (but usually less than 0.4). Another approach to chlorinated polyesters, it appeared, would be chlorination of the polyester itself. Polyester chlorination is unreported except for our recently issued patents.²⁻⁵

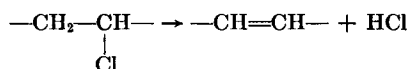
Polyesters chosen for the initial experiments, which are reported in this paper, were prepared from diols containing *gem*-dimethyl groups: 2,2,4,4-tetramethyl-1,3-cyclobutanediol (TMCD) and 2,2-dimethyl-1,3-pro-

* Paper presented at the 154th National Meeting of the American Chemical Society, Chicago, Illinois, September 10-15, 1967.

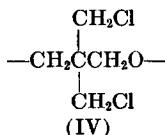
panediol (NPG). The polyesters that were chlorinated were the polyterephthalate (Ia) and polycarbonate (Ib) of TMCD, the polyterephthalate (II) of NPG, and the polycarbonate (III) of 4,4'-isopropylidenediphenol (the latter will be referred to as bisphenol A polycarbonate).



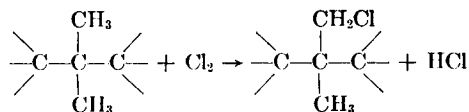
When chlorine is added to these polyesters, it becomes attached to the carbon atoms of the *gem*-dimethyl groups. Since no hydrogen atoms beta to the chlorine atoms are present, hydrogen chloride cannot be eliminated by dehydrohalogenation, as can occur when β hydrogens are present:



The thermal stability of structures containing chlorine atoms attached to *gem*-dimethyl groups is shown by the fact that poly[2,2-bis(chloromethyl)-trimethylene oxide] (IV) can be fabricated at temperatures as high as 550°F..⁶



Furthermore, halogen attached to the geminate carbon atoms is very resistant to $\text{S}_{\text{N}}2$ (but not $\text{S}_{\text{N}}1$) hydrolysis.⁷ In addition, it is known that the polyesters (I) to (III) are resistant to hydrolysis. This factor is important, since hydrogen chloride is the by-product of the chlorination reaction and can cause cleavage of the polyester:



It appeared, therefore, that chlorination of the *gem*-dimethyl groups in these polyesters might yield reasonably stable products if the polyester did not degrade badly during the chlorination process.

The objectives of this investigation were to develop a satisfactory process for chlorinating the polyesters in order to make them self-extinguishing and to determine the effect of chlorine content on their physical properties.

EXPERIMENTAL

Materials

The polyesters TMCD and NPG were prepared by conventional ester interchange methods. The TMCD (Eastman Chemical Products, Inc.) had a *cis/trans* isomer ratio of about 40:60 except where otherwise indicated. The bisphenol A polycarbonate (trademark Lexan) was obtained from the General Electric Co.

The solvents in which the polyesters were dissolved for chlorination were undistilled commercial products. The chlorine was obtained in lecture bottles from Matheson Co. All inorganic compounds were commercial products. A stabilizer, Thermolite 31, which was added to some of the polyesters, was obtained from M&T Chemicals, Inc.

Apparatus

In a well-ventilated hood a three-necked flask was fitted with an efficient stirrer, a thermometer, and a gas-inlet tube. The reaction mixture in the flask was irradiated with a floodlamp (300 w. visible or 275 w. ultraviolet), which was placed about 2 in. from the upper part of the flask, and the temperature of the reaction mixture was controlled with a cold-water bath. The inlet tube, which dipped 2-3 in. below the liquid level in the flask, was attached to a trap. The trap was connected to a sulfuric acid bubbler (for estimating the rate of chlorine addition), and the bubbler was attached to a second trap, which was connected to a chlorine lecture bottle on a balance. The chlorine addition was followed by the loss in weight of the cylinder. When calcium carbonate was not present in the reaction mixture to neutralize the hydrogen chloride that was formed, the outlet of the flask was connected by rubber tubing to a vertical glass tube about 24 in. long. The end of the tube was immersed in a beaker or flask containing water. When chlorine was added too rapidly, bubbles were emitted from the tube. In normal operation the water sometimes rose about 1 in. in the tube (above the water level) because of the rapid take-up of chlorine. When the rubber tubing attached to the chlorine cylinder was removed (and clamped), so that the cylinder could be accurately weighed, water sometimes rose 12-18 in. in

TABLE I
Chlorination of Poly(2,2,4,4-Tetramethyl-1,3-cyclobutanediol Terephthalate)^a

Added, ^b approx. moles per poly- ester unit	Chlorine		Flammability ^c	Temp., °C.	HCl acceptor	Polyester wt., g.	Reaction time, min.	Illum.	Inherent viscosity		Loss, %
	In polyester, %	Found							Init.	Final	
1	11.5	9.1	burned	28-30	H ₂ O	27	85	vis.	0.82	0.65	21
2	19.7	20.4	burned	30-33	H ₂ O	29	50	UV	0.90	0.54	40
3	— ^d	26.3	self-ext.	30-33	H ₂ O	— ^e	80			0.47	48
4	— ^d	35.0	self-ext.	30-33	H ₂ O	— ^e	100			0.37	59
2	19.4	20.3	burned	26-35	CaCO ₃ , H ₂ O	25	40	UV	0.90	0.58	36
3	— ^d	30.8	self-ext.	26-35	CaCO ₃ , H ₂ O	— ^e	65			0.52	42
4	34.5	31.6	self-ext.	30-33	CaCO ₃ , H ₂ O	20	95	UV	0.81	0.32	61

4.5	37.1	25.8	almost self-ext.	30-35	H ₂ O	20	35 ^f	vis.	0.81	0.55	32
4	34.5	26.8	self-ext.	10-15	H ₂ O	20	120	vis.	0.89	0.48	46
4	34.5	24.1	almost self-ext.	5-10	CaCO ₃ , H ₂ O	20	75	vis.	0.89	0.59	45
4	34.5	28.1	almost self-ext.	24-27	None	100	155	vis.	0.83	0.43	48
4	34.5	30.4	self-ext.	24-27	H ₂ O	100	125	vis.	0.83	0.39	53
4	34.5	29.2	self-ext.	19-21	H ₂ O	100	180	vis.	0.83	0.40	52
6	44.3	34.9	self-ext.	35-36	H ₂ O	15	100	UV	0.90	—	—
4	34.5	5.1	burned	40-60	CH ₃ COONa, H ₂ O	15	90	UV	0.64	0.29	55
4	34.5	4.2	burned	7-9	NaHCO ₃ , H ₂ O	20	70	vis.	0.89	—	—
4	34.5	<10	burned	30-35	MgO, H ₂ O	20	60	vis.	0.94	—	—
5	39.8	—	burned	20-25	MgCO ₃ , H ₂ O	20	45	vis.	0.81	—	—

^a Dissolved in 1,1,2,2-tetrachloroethane.

^b Measured as weight loss of cylinder.

^c Polyester was rated as "self-extinguishing" when a 2-mil film stopped burning immediately upon removal from a bunsen burner flame and "almost self-extinguishing" when it burned a few seconds without dripping before going out.

^d Cannot be calculated with accuracy, since earlier portion was removed for analysis and measurement of properties.

^e Part of preceding experiment.

^f Because of this short reaction time the degree of chlorination and the amount of polyester degradation were each less than in similar experiments with longer reaction times.

the vertical tube, as chlorine in the system reacted and the pressure dropped. The tubing attached to the cylinder was always clamped before it was removed from the cylinder, so that there would be no loss of chlorine and no entrance of air.

Chlorination Procedure

Polyterephthalates. The following procedure describes the chlorination of poly(2,2,4,4-tetramethyl-1,3-cyclobutanediol terephthalate) (Ia). The results obtained by a modification of this procedure are given in Table I. Table II shows the results obtained when poly(neopentyl glycol terephthalate) and poly(2,2,4,4-tetramethyl-1,3-cyclobutanediol carbonate) were chlorinated similarly.

A 100-g. amount (0.365 mole, based on the molecular weight of a polyester unit) of the polyester (inherent viscosity 0.83) was dissolved in 1000 ml. of 1,1,2,2-tetrachloroethane with stirring and, when necessary, heating to 100°C. to aid solution. The solution was then cooled to room temperature, and 1000 ml. of deionized water was added. While the mixture was stirred and irradiated with a 300 w. floodlamp, chlorine was slowly passed in. The temperature of the mixture was held at about 25°C. with a water bath. After the chlorination reaction began (10 min. or more were often required for initiation), the chlorine was added at a rate such that bubbles were not emitted from a tube immersed in water at the outlet of the system. The rubber tube attached to the chlorine cylinder was always clamped before it was removed from the cylinder, and the reaction was followed by the weight loss of the cylinder. After 104 g. (1.47 moles) of chlorine had been added, the mixture was stirred about 10 min. longer, to ensure complete reaction. Complete reaction was also indicated by loss of the yellow color due to the chlorine. The total reaction time was about 2 hr.

The aqueous layer was then separated, and the organic layer was washed with sodium bicarbonate solution, to neutralize all of the hydrogen chloride. To remove all of the sodium chloride, the polyester solution was washed thoroughly with water. The washing was accomplished by introducing a stream of deionized water at the bottom of the polyester solution (diluted with methylene chloride) and allowing the water to overflow into the sink for about 8 hr. The polyester solution was then diluted with more methylene chloride and slowly added to methanol with stirring. To remove the tetrachloroethane occluded in the polyester, the fibrous white product was allowed to soak in methanol overnight. The polyester was dried at room temperature and then in a vacuum oven at 70°C. It had an inherent viscosity of 0.39 (measured in chloroform) and contained 30.4% chlorine.

When powdered calcium carbonate was added to the reaction mixture (Table I), the excess was removed at the end of the reaction by filtration or by the addition of acetic acid, which reacted with the excess calcium carbonate.

TABLE II
Chlorination of Poly(neopentyl Glycol Terephthalate) and Poly(2,2,4,4-tetramethyl-1,3-cyclobutanediol Carbonate)^a

Polyester and chlorination solvent	Chlorine		Flam- mability ^c	Temp., °C.	HCl acceptor	Illum.	Inherent viscosity			
	Added, ^b moles per poly- ester unit	In polyester, %					Init.	Final	Loss, %	
										Calcd.
Poly(neopentyl glycol terephthalate)										
CHCl ₃	2	23.4	2.9	burned	7-10	CaCO ₃ , H ₂ O	vis.	1.02	0.77	25
CHCl ₃	4	— ^d	7.2	burned	7-10	CaCO ₃ , H ₂ O	vis.	1.02	0.66	35
CH ₂ Cl ₂	3	31.6	14.9	burned	6-10	CaCO ₃ , H ₂ O	vis.	0.73	0.48	34
Cl ₂ CHCHCl ₂	3	31.6	15.2	self-ext.	5-10	CaCO ₃ , H ₂ O	vis.	1.02	0.60	41
Cl ₂ CHCHCl ₂	3	31.6	25.6	self-ext.	10-12	CaCO ₃ , H ₂ O	UV	0.73	0.42	42
Poly(2,2,4,4-tetramethyl-1,3-cyclobutanediol carbonate):										
Cl ₂ CHCHCl ₂	1	17.4	16.1	burned	21-25	H ₂ O	UV	0.63	0.64	0
Cl ₂ CHCHCl ₂	3	38.9	25.8	burned	24-30	H ₂ O	vis.	0.63	0.56	11
Cl ₂ CHCHCl ₂	4	46.1	39.6	self-ext.	25-35	CaCO ₃ , H ₂ O	UV	0.52	0.36	31

^a Dissolved in 1,1,2,2-tetrachloroethane.

^b Measured as weight loss of cylinder.

^c Polyester was rated as "self-extinguishing" when a 2-mil to 3-mil film stopped burning immediately upon removal from a bunsen burner flame.

^d Cannot be calculated with accuracy, since earlier portion (preceding experiment) was removed for analysis.

TABLE III
Chlorination of Bisphenol A Polycarbonate

Solvent	Added, ^a moles/ poly- ester unit	Chlorine		Flammability	Temp. °C.	HCl acceptor	Illum.	Init.	Inherent viscosity	
		Calcd. ^b	Found						Final	Loss, %
Cl ₂ CHCHCl ₂	4	36.3	22.5	self-ext.	27-32	H ₂ O	vis.	1.04	0.73	30
Cl ₂ CHCHCl ₂	5	—	29.8	self-ext.	27-32	H ₂ O	vis.	1.04	0.62	40
Cl ₂ CHCHCl ₂	4	36.3	23.1	self-ext.	27-33	H ₂ O	UV	1.04	0.75	28
Cl ₂ CHCHCl ₂	4 ^c	36.3	25.8	self-ext.	28-32	H ₂ O	vis.	1.04	0.62	40
Cl ₂ CHCHCl ₂	8	—	29.0	self-ext.	28-32	H ₂ O	vis.	1.04	0.44	58
Cl ₂ CHCHCl ₂	9	—	21.6	self-ext.	28-32	CaCO ₃ , H ₂ O	vis.	1.04	0.35	66
CH ₂ Cl ₂	2	22.0	4.1	burned	28-31	H ₂ O	vis.	1.04	1.12	—
CHCl ₃	4	36.3	5.6	burned	28-33	H ₂ O	vis.	1.04	1.08	—
ClCH ₂ CH ₂ Cl	4	36.3	9.3	burned	28-32	H ₂ O	vis.	1.04	0.88	15
C ₆ H ₅ Cl	4	36.3	17.4	almost self-ext.	30-40	H ₂ O	vis.	1.04	0.71	32

^a Measured as weight loss of cylinder.

^b Courtauld models indicate that only three chlorine atoms per polymer unit (29.8% Cl) can be added.

^c Amount of polymer chlorinated was 127 g. In most other experiments, amount of polymer was 20-25 g.

Bisphenol A Polycarbonate. The following procedure describes the chlorination of bisphenyl A polycarbonate (III). Results obtained by modification of this procedure are given in Table III.

Tetrachloroethane (1400 ml.) was placed in a 3-liter three-necked flask, and 127 g. (0.50 mole, based on the molecular weight of a polyester unit) of Lexan powder (inherent viscosity 1.04) was added. After solution was attained, 800 ml. of deionized water was added. While the mixture was stirred and irradiated with a 300 w. floodlamp, chlorine was slowly passed in. The temperature of the mixture was held at about 30°C. with a water bath. The chlorine was added in 30–40 g. portions (measured as the weight loss of the lecture bottle), and after each portion the mixture was stirred until the yellow color due to chlorine disappeared. The total amount of chlorine added was 142 g. (2.0 moles).

After the aqueous layer was separated, the organic layer was washed with sodium bicarbonate solution. It was then thoroughly washed with water as described in the preceding section. The polyester was precipitated by slowly adding the tetrachloroethane solution to acetone with stirring. Since the polyester was highly swollen because of the tetrachloroethane, it was dissolved in methylene chloride and then precipitated with hexane. The polyester, obtained as a white, fibrous material, was then dried in a vacuum oven at 70°C. It had an inherent viscosity of 0.62 (measured in chloroform) and contained 25.8% chlorine.

Most of the experiments listed in Table III were carried out with 20 to 25 g. of polyester. A small amount of benzoyl peroxide was added in some cases, but it appeared to be of negligible benefit.

Physical Testing Methods

The inherent viscosity of the unchlorinated polyesters was measured in 60:40 phenol/tetrachloroethane solution (0.25 g. per 100 ml.) at 25°C. The inherent viscosity of the chlorinated polyesters was similarly measured in chloroform.

The chlorine analyses were obtained by titration of the chloride ions with silver nitrate after decomposition of the polyesters by combustion in a Schöniger flask.

The hydrolytic stability of the polyesters was determined by heating films at 100% relative humidity and 100°C. and measuring the loss in the inherent viscosity. Each film was placed in a small test tube, and the test tubes were placed upright in a bottle containing a small amount of water. The bottle was then sealed and heated the required length of time in an oven at 110°C.

The thermal stability of the polyesters in air was determined by heating films in a forced-convection oven and measuring the loss in the inherent viscosity.

The tensile properties of the films (tensile strength, elongation, and modulus) were measured with an Instron tensile tester (ASTM D882-64T Method A). The heat-distortion temperatures of the films (2% deflection)

were measured at a load of 50 psi in a forced-convection oven⁸ (ASTM D1637-61). The electrical properties of the films were measured according to standard ASTM procedures (ASTM D150-64T and D257-61).

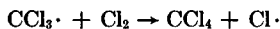
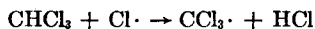
RESULTS AND DISCUSSION

Chlorination of Polyesters

The polyesters were chlorinated photochemically by passing chlorine into the polyester solutions while illuminating them with visible or ultraviolet light (Tables I to III). In most of these experiments water was present, to dissolve the hydrogen chloride that was formed, and in many cases a second component was present for neutralizing the hydrogen chloride. Experimental variables affecting the degree of polyester chlorination and the efficiency of the chlorination were: (1) type of polyester solvent, (2) amount of chlorine added, (3) type of hydrogen chloride acceptor, (4) temperature of reaction mixture, (5) reaction time, and (6) type of illumination. Variables 2-5 also affected the degradation of the polyesters during chlorination.

Effect of Solvent. The solvent in which the polyester was dissolved affected appreciably the efficiency of the chlorination, that is, the amount of chlorine introduced into the polyesters per mole of chlorine added. Since the TMCD polyesters were not soluble in volatile solvents such as methylene chloride or chloroform, they were chlorinated in tetrachloroethane. The other polyesters were soluble in these more volatile solvents (but not in carbon tetrachloride). Chlorination of the polyesters in these solvents, however, was less efficient than in tetrachloroethane; the chlorinations were particularly inefficient in chloroform. Chlorination of the solvent is a competitive reaction, and this is one of the reasons chlorination of the polyesters is less than 100% efficient.

The substitution of chlorine atoms for hydrogen atoms on a carbon atom decreases the bond dissociation energies of the remaining hydrogen atoms.⁹ The carbon-hydrogen bond dissociation energy of chloroform, therefore, should be less than that of methylene chloride and that of tetrachloroethane; consequently, it is not surprising that chloroform is chlorinated more readily than the other two solvents. The mechanism is as follows:¹⁰



The volume of solvent required for chlorination of the polyesters is a function of the inherent viscosity of the polyester; more solvent was used for polyesters with high molecular weights than for those with lower molecular weights, so that the solutions obtained would not be too viscous. It was actually desirable to chlorinate polyesters with high molecular weights so that after breakdown the molecular weight of the chlorinated polyester would still be sufficiently high for the polyester to have good physical properties.

Effect of Amount of Chlorine. As chlorine was added to the various polyesters, their inherent viscosities decreased. Presumably, this was at least partly because more hydrogen chloride formed and caused more hydrolysis.

The amount of chlorine which could be added to a polyester (by replacement of hydrogen atoms) increased, up to a point, as the amount of chlorine added to the reaction mixture increased. Then no further chlorination of the polyesters took place. The maximum amount of chlorine substituted on poly(TMCD terephthalate) (Ia) was about 35%; this corresponds to four chlorine atoms per polyester unit. More chlorine was not substituted, even when 6-7 moles per polyester unit was added to the reaction mixture. Similarly, only three chlorine atoms per polyester unit were substituted on bisphenol A polycarbonate (III) when 6-8 moles of chlorine per polyester unit was added to the reaction mixture (Table III). The limited amount of chlorine that could be substituted on these polyesters was apparently due to a steric effect, which will be discussed later.

The efficiency of the chlorinations (the amount of chlorine introduced into the polyester per mole added to the reaction mixture) is a function of the other variables, which will be discussed independently. The most important of these variables were the solvent in which the polyester was dissolved and the method used for removing the hydrogen chloride that was formed. In general, under favorable chlorination conditions the efficiencies were 80-100% with the TMCD polyesters.

Effect of Hydrogen Chloride Acceptor. Almost all of the chlorinations were carried out in the presence of water, which removed the by-product hydrogen chloride from the polyester dissolved in a water-immiscible solvent. When poly(TMCD terephthalate) was chlorinated in an anhydrous system rather than in an aqueous system, somewhat less chlorination took place (Table I). Apparently some of the chlorine was swept out by the hydrogen chloride that evolved, since bubbles were continuously emitted in the water trap at the outlet of the system. The polyester degradation that took place in this experiment was only slightly less than that in experiments in which water was present.

One approach to the prevention of polyester degradation due to hydrogen chloride is to carry out the chlorinations in the presence of a compound that will neutralize the hydrogen chloride but will not be basic enough to cause alkaline hydrolysis of the polyester. When compounds that gave slightly alkaline solutions were used for this purpose (sodium acetate, sodium bicarbonate, magnesium oxide, magnesium carbonate), very little chlorination of the poly(TMCD terephthalate) occurred (Table I). However, chlorination did take place in the presence of powdered calcium carbonate, which is neutral, rather than slightly alkaline, in the presence of water. This reagent was of some benefit in preventing the degradation of other polyesters,^{2,3} but it was of no help in preventing the breakdown of this polyterephthalate. Moreover, some chlorine was probably swept out by the carbon dioxide that was evolved.

In general, the most efficient chlorinations take place in the presence of

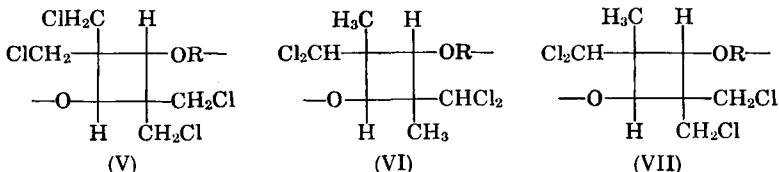
water and without a reagent for neutralizing the hydrogen chloride. If appreciable degradation of the polyester occurs, it is necessary to chlorinate a polyester with a very high molecular weight, so that the molecular weight will still be sufficiently high after chlorination.

Effect of Temperature and Reaction Time. Poly(TMCD terephthalate) was chlorinated at temperatures ranging from 5 to 35°C. (Table I). In general, the efficiency of the chlorination increased with increasing temperature and increasing reaction time. The inherent viscosity of the chlorinated polyester, on the other hand, decreased with increasing temperature and increasing reaction time. To complicate matters further, the required reaction time increased when the reaction temperature was decreased. In one experiment a 50% longer time was required for chlorinating the polyester when the reaction temperature was decreased from 25 to about 20°C. Although temperatures of 5–35°C. could be used, a satisfactory compromise temperature was 20–25°C. The temperatures at which the other polyesters were chlorinated were not varied over a sufficiently wide range for us to draw any conclusions concerning the effect of temperature on chlorination efficiency and polyester breakdown.

Effect of Illumination. Illumination was necessary for chlorination to take place, unless a catalyst was present. It appears that ultraviolet light is somewhat more effective than visible light in effecting chlorination of the polyesters (Tables I–III). The Pyrex reaction flask undoubtedly absorbed a considerable amount of the shorter wavelengths of the ultraviolet light; more efficient chlorinations might be obtained in an apparatus in which the light does not pass through glass.

Structure of Chlorinated Polyesters

A maximum of six chlorine atoms can be forced on the methyl groups of the TMCD (either *cis* or *trans*) polyester units of (Ia) or (Ib) in a Courtauld model (atom sizes are based on Van der Waals radii). Only four chlorine atoms can be added, however, without an appreciable steric effect. This probably explains why a maximum of four chlorine atoms per poly(TMCD terephthalate) unit was observed, even when a large excess of chlorine had been added to the reaction mixture. According to the models, three derivatives of (Ia) and (Ib) containing four chlorine atoms per unit are possible in which there is no steric hindrance:



There is a considerable steric effect when a $-\text{CCl}_3$ group is formed in a model. Moreover, the steric hindrance is very great if either of the two tertiary hydrogens in a polyester unit is replaced with chlorine.

An indication that substantially no chlorination of the aromatic rings took place in a poly(TMCD terephthalate) sample containing four chlorine atoms per polyester unit was given by NMR analysis: the peak for the aromatic protons was very sharp. NMR investigation also indicated that the polyester had about the same number of $-\text{CH}_3$ groups as $-\text{CH}_2\text{Cl}$ groups (the number of $-\text{CHCl}_2$ groups could not be determined because

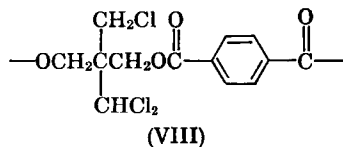
the tertiary hydrogen on the $-\text{CH}$ group to which the oxygen was at-

tached made this peak in the spectrum rather broad). These NMR results can be explained if structures (V) and (VI) are present in a 1:2 ratio or, which is perhaps more probable, if structures (VI) and (VII) are present in a 1:2 ratio. In the latter case one (VI) unit and two (VII) units contain four $-\text{CH}_3$ groups, and two (VII) units contain four $-\text{CH}_2\text{Cl}$ groups; this 1:2 ratio gives an equal number of each group, as indicated by the NMR data.

NMR investigation of a poly(TMCD carbonate) (Ib) sample containing three chlorine atoms per polyester unit revealed the presence of $-\text{CH}_2\text{Cl}$ and $-\text{CH}_3$ groups in a ratio of approximately 3:4. As in the case of the polyterephthalate, most of the chlorine presumably is in $-\text{CHCl}_2$ groups.

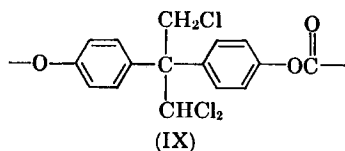
As discussed previously, substitution of chlorine atoms for hydrogen atoms on a carbon atom decreases the bond dissociation energies of the remaining hydrogen atoms. This explains why more of the chlorine in these polyesters is in $-\text{CHCl}_2$ groups rather than $-\text{CH}_2\text{Cl}$ groups. A similar result is obtained in the chlorination of aliphatic hydrocarbons.¹¹ Chloroethane, for example, gives principally 1,1-dichloroethane ($\text{CH}_3\text{-CHCl}_2$) and a little 1,2-dichloroethane ($\text{ClCH}_2\text{CH}_2\text{Cl}$) when chlorinated in sunlight. On continued chlorination 1,1-dichloroethane gives 1,1,1-trichloroethane (CH_3CCl_3) and 1,1,2-trichloroethane ($\text{ClCH}_2\text{CHCl}_2$). Further chlorination leads to hexachloroethane (Cl_3CCCl_3).¹¹

Three chlorine atoms can be substituted on the methyl groups in a Courtauld model of a poly(NPG terephthalate) (VIII) unit:



Models containing a $-\text{CCl}_3$ group or two $-\text{CHCl}_2$ groups can be made, but an appreciable steric effect exists. It is also possible on the model to chlorinate the methylene group attached to the oxygen atom. The maximum amount of chlorine that actually can be added to this polyester is not known, since the chlorination experiments were carried out only with a limited amount of chlorine (Table II).

Only three chlorine atoms can be substituted on the methyl groups in a Courtauld model of an bisphenol A polycarbonate (IX) unit:



Steric hindrance was too great to make a model containing one $-\text{CCl}_3$ group or two $-\text{CHCl}_2$ groups per polymer unit. In two experiments in which excess chlorine (5–8 moles per polymer unit) was added to the reaction mixture polymers were obtained that contained only 2.9–3.0 chlorine atoms per unit (Table III).

According to an infrared analysis of a bisphenol A polycarbonate sample containing exactly three chlorine atoms per polymer unit, a small amount of chlorine was on the aromatic rings, and very few unchlorinated methyl groups were present. According to an NMR study, there were about one half as many $-\text{CH}_3$ groups as $-\text{CH}_2\text{Cl}$ groups in this sample. The absorption peak for the aromatic protons was not sharp, but no conclusions could be drawn concerning whether any chlorination of the aromatic rings had occurred. Presumably, most of the chlorine was in $-\text{CHCl}_2$ groups. The evidence indicates, then, that after the addition of excess chlorine to bisphenol A polycarbonate in the presence of light most of the polymer units have structure (IX); a few $-\text{CH}_3$ groups are present, however, and a small amount of chlorine may be substituted on the aromatic rings.

Physical Properties of Chlorinated Polyesters

Most of the physical properties of the chlorinated polyesters were determined from films cast from methylene chloride. All of these films were tough and transparent.

TABLE IV
Solubility of Chlorinated Polyesters

Polyester		Solvent ^a			
		Toluene	Ethyl acetate	Acetone	MIK ^b
Type	Cl, %				
Poly(2,2,4,4-tetramethyl-1,3-cyclobutanediol terephthalate):	9	swoll.	swoll.	swoll.	sol.
	32	swoll.	sol.	swoll.	sol.
Poly(2,2,4,4-tetramethyl-3-cyclobutanediol carbonate):	16	sol.	sol.	sol.	sol.
	40	sol.	sol.	sol.	sol.
Poly(neopentyl glycol terephthalate):	15	swoll.	sol.	swoll.	sol.
Bisphenol A polycarbonate:	30	swoll.	swoll.	swoll.	swoll.

^a None of the unchlorinated polyesters are soluble in these solvents. All of the listed chlorinated polyesters are also soluble in methylene chloride and dioxane.

^b MIK, methyl isobutyl ketone.

TABLE V
Hydrolytic Stability of Films of Chlorinated Polyesters

Polyester		Cl			Inherent viscosity		
Type	Cl, %	C atoms per unit	Init.	4 days	Loss, %	8 days	Loss, %
Poly(2,2,4,4-tetramethyl-1,3-cyclobutanediol terephthalate)	0	0	0.51	—	—	0.51	0
	31	3.4	0.52	0.13	75	—	—
	32	3.6	0.45	0.14	69	—	—
Poly(2,2,4,4-tetramethyl-1,3-cyclobutanediol carbonate)	0	0	0.63	—	—	0.65	0
	16	0.9	0.64	—	—	0.60	6
	26	1.7	0.56	0.56	0	0.51	9
Bisphenol A polycarbonate	40	3.1	0.36	0.34	0 ^b	0.31	14
	0	0	0.59	0.49	17	0.47	20
	23	2.1	0.73	0.24	67	—	—
	30	3.0	0.62	0.21	66	—	—

^a Heated at 100% relative humidity and 110°C.

^b Listed as zero, since final inherent viscosity is within experimental error of initial value.

Solubility. Except for the polyterephthalate of TMCD and the polycarbonate of TMCD containing over about 60% of the *trans*-diol isomer, the unchlorinated polyesters were soluble in methylene chloride. The TMCD polyesters became soluble when they contained 10–15% chlorine. and poly(TMCD carbonate) also became soluble in lacquer types of solvent such as toluene, ethyl acetate, acetone, and methyl isobutyl ketone. With these solvents tough films and coatings can be formed. The solubilities of the polyesters containing various amounts of chlorine are listed in Table IV.

All of the chlorinated polyesters are insoluble in alcohols, such as methanol and ethyl alcohol, and saturated hydrocarbons, such as hexane and naphtha.

Flammability. In Tables I to III polyesters are described as “self-extinguishing” if their films stopped burning immediately after they were removed from a bunsen burner flame. The polyesters are listed as “almost self-extinguishing” if the films burned a few seconds without dripping before going out. Chlorinated bisphenol A polycarbonate was self-extinguishing when it contained approximately 20–22% chlorine (two chlorine atoms per polymer unit), whereas poly(TMCD terephthalate) was self-extinguishing (when it contained about 28–30% chlorine (three chlorine atoms per polyester unit)).

Hydrolytic Stability. The hydrolytic stability of the chlorinated polyesters was determined by heating films at 100% relative humidity and 110°C. and measuring the loss in inherent viscosity (Table V). For comparison, values for the unchlorinated polyesters are also given in the table. It is apparent that the chlorinated polyesters are less stable than the unchlorinated ones. If the chlorine atom of a $-\text{CH}_2\text{Cl}$ group is displaced on hydrolysis, then a $-\text{CH}_2\text{OH}$ group and hydrogen chloride result. If a chlorine atom in a $-\text{CHCl}_2$ group is displaced, then an unstable $-\text{CH}(\text{OH})\text{Cl}$ group results. This group should immediately eliminate hydrogen chloride and give the more thermodynamically stable aldehyde, $-\text{CHO}$. In either case the hydrogen chloride that is eliminated will catalyze hydrolysis of the carboxylate or carbonate groups in the polyester. Presumably, hydrolysis of the polyesters is due mainly to the formation of hydrogen chloride from chlorine in the $-\text{CHCl}_2$ groups.

Thermal Stability. The thermal stability of the chlorinated polyesters in air was determined by heating films in a forced-convection oven and measuring the resulting loss in inherent viscosity. From Table VI it is apparent that the unchlorinated polyesters were considerably more stable than their chlorinated products. An organotin sulfur compound, Thermolite 31, which is effective in stabilizing poly(vinyl chloride), was added to dopes of some of the polyesters before films were cast. This additive appreciably improved the stability of chlorinated poly(TMCD carbonate), but it caused an increased breakdown to occur in chlorinated bisphenol A polycarbonate.

Chlorinated poly(TMCD terephthalate) was the most unstable polyester. Even in the presence of Thermolite 31 the loss in inherent viscosity

TABLE VI
Thermal Stability in Air of Films of Chlorinated Polyesters

Type	Polyester				Inherent viscosity			
	Cl %	Cl atoms per unit	Amt. of additive, ^a %	Init.	After heating 24 hr.			%
					100°C.	140°C.	Loss, ^b %	
Poly(2,2,4,4-tetramethyl-1,3-cyclobutanediol terephthalate):	0	0	0	0.89	0.99	0	0.96	0
	9	0.8	0	0.65	0.45	31	0.15	77
	9	0.8	4	0.65	0.52	20	<0.1	>80
	32	3.6	0	0.45	0.34	24	<0.1	>70
Poly(2,2,4,4-tetramethyl-1,3-cyclobutanediol carbonate):	32	3.6	4	0.45	0.31	31	<0.1	>70
	0	0	0	0.45	0.46	0	0.48	0
	16	0.9	0	0.64	0.66	0	0.57	11
	16	0.9	2	0.64	—	—	0.65	0
Bisphenol A polycarbonate:	26	1.7	0	0.56	0.54	0	0.24	57
	26	1.7	4	0.56	0.56	0	0.40	28
	40	3.1	0	0.36	—	—	0.25	31
	0	0	0	1.00	0.97	3	0.95	5
	23	2.1	0	0.73	—	—	0.56	23
	23	2.1	0	0.58	0.57	0	—	—
	30	3.0	0	0.53	0.51	0	—	—
	30 ^c	3.0	0	0.62	—	—	—	—
30	3.0	4	0.62	—	—	0.48	23	
							0.26	58

^a Thermolite 31.

^b Listed as zero when the inherent viscosity is 0.02 units (within experimental error) less than the initial inherent viscosity.

^c After 24 hr. at 180°C. film was still tough; inherent viscosity was not measured, since film was insoluble in chloroform.

TABLE VII
Physical and Electrical Properties of Films^a of Chlorinated Polyesters

Polyester		Cl atoms per unit	Inher. viscy.	Dens., g./cm. ³	Tensile properties			Elong. at break, %	Modu- lus, 10 ⁸ psi.	Heat- distort. temp. at 50 psi., °C.	Electrical properties		
Type	Cl, %				Strength, psi	Yield	Break				Dielec. const. ^b	Dissip. factor, ^b %	Vol. resist., ohm-cm.
Poly(2,2,4,4-tetramethyl-1,3-cyclobutanediol terephthalate):													
	0	0	0.89	1.21	7,200	9,000	20	2.5	206	2.9-3.0	0.1	—	2 × 10 ¹⁶
	9	0.8	0.65	1.31	6,900	8,700	30	2.8	186	—	—	—	—
	20	2.0	0.58	1.31	8,400	9,900	16	3.3	196	3.6-3.7	0.9-0.5	—	2.1 × 10 ¹⁶
	31	3.4	0.52	—	8,800	9,800	17	3.4	184	3.6-3.8	1.2-0.6	—	2.7 × 10 ¹⁶
	35	4.1	0.37	1.42	9,700	9,100	11	3.2	170	3.5-3.6	0.9-0.7	—	1.5 × 10 ¹⁷
Poly(2,2,4,4-tetramethyl-1,3-cyclobutanediol carbonate):													
	0	0	0.63	1.13	6,800	7,500	41	2.8	140	1.9-2.0	0.2-0.1	—	1.8 × 10 ¹⁷
	16	0.9	0.64	1.20	7,300	7,100	27	2.7	137	3.4-3.8	2.4-0.3	—	2.0 × 10 ¹⁶

26	1.7	0.56	1.30	8,800	9,000	17	3.2	157	3.5-4.1	2.6-0.5	1.0 × 10 ¹⁶
40	3.1	0.36	1.42	—	9,600	5	4.2	135	3.6-4.2	1.2-1.8	1.3 × 10 ¹⁶
0 ^c	0	1.19	—	6,300	6,800	13	2.1	133	—	—	—
22 ^c	1.4	0.89	—	7,000	7,800	12	2.8	152	—	—	—
37 ^c	2.8	0.77	—	9,300	10,300	10	4.1	163	—	—	—
Poly(neopentyl glycol terephthalate):											
0	0	0.61	—	—	7,500	4	2.8	71	—	—	—
15	1.2	0.60	1.27	—	7,600	3	3.3	73	—	—	—
Bisphenol A polycarbonate:											
0	0	0.88	1.20	8,600	9,300	101	2.8	152	3.2	0.15-0.05	5.7 × 10 ¹⁷
23	2.1	0.73	1.36	11,600	11,900	80	3.8	183	3.4-3.6	1.0-0.4	1.5 × 10 ¹⁷
29	2.9	0.44	—	12,200	11,400	10	4.1	205	—	—	—
30	3.0	0.62	—	12,600	11,400	23	4.0	185	3.6-3.7	0.8-0.5	4.1 × 10 ¹⁶

^a Cast from methylene chloride except for unchlorinated poly(2,2,4,4-tetramethyl-1,3-cyclobutanediol terephthalate), which was cast from 90:15 methylene chloride/trifluoroacetic acid, and unchlorinated poly(2,2,4,4-tetramethyl-1,3-cyclobutanediol) (40:60 *cis/trans* carbonate), which was cast from chloroform. The films were 2-3 mils in thickness.

^b Measured at 1.0 kc. and 25-145°C.

^c The 2,2,4,4-tetramethyl-1,3-cyclobutanediol *cis/trans* ratio was 54:46 instead of 40:60.

during 24 hr. at 110°C. was 20–30%. Chlorinated poly(TMCD carbonate) was appreciably more stable. The films showed no loss in inherent viscosity after 24 hr. at 110°C., and one sample, which also contained the stabilizer, showed no loss after 24 hr. at 140°C. One of the bisphenol A polycarbonate films was still tough after 24 hr. at 180°C. Insolubility of the film in chloroform after this treatment suggests that the film had become cross-linked with loss of chlorine.

Although some of the unstabilized chlorinated polyesters can be subjected to temperatures above 140°C. for short periods of time, they probably are limited to use at temperatures below 100°C. when longer time periods are involved. The TMCD polyesters, for instance, showed no loss in inherent viscosity during 18 mo. at room temperature. By the addition of effective stabilizers it may be possible for some of the chlorinated polyesters to be subjected to temperatures above 100°C. for indefinite periods of time.

Density. The density of the polyesters was determined on cast films (Table VII). As would be expected, the density of a given polyester increased as the chlorine content increased.

Physical and Electrical Properties of Films. In general, the tensile strengths and moduli of the polyesters, measured from cast films, were increased by chlorination, and elongations were decreased (Table VII). Since antiplasticization¹² produces this same effect, these chlorinated polyesters may be considered to be internally antiplasticized.

With the possible exception of chlorinated poly(neopentyl glycol terephthalate), which had a heat-distortion temperature of 73°C., these films had heat-distortion temperatures higher than the temperatures at which they are stable during prolonged use. The heat-distortion temperature of one polymer, bisphenol A polycarbonate, was increased by more than 50°C. (to 205°C.) by chlorination.

When a film is used as a dielectric (insulating material) in a capacitor, it is important that it have a reasonably high dielectric constant. It is also important that the dissipation factor be low, since this is a measure of the power loss in an insulator. Since volume resistivity is a measure of the resistance to the flow of current, this property should have a high value. Chlorination increased the dielectric constants (and the dissipation factors) of some of the polyesters (Table VII). The dielectric constants are moderately high, and the dissipation factors are moderately low. The volume resistivities in general are very high. Because of these properties some of the more stable polymers, such as the chlorinated polycarbonates of TMCD and bisphenol A, could also be of interest as capacitor dielectrics and wire coatings.

CONCLUSIONS

Chlorine was substituted on the *gem*-dimethyl groups in several polyesters by photochemical chlorination. Reaction conditions that gave

efficient chlorination without an excessive amount of polyester degradation consisted of the following:

Solvent:	1,1,2,2-tetrachloroethane
Hydrogen chloride acceptor:	water
Temperature:	20–30°C.
Illumination:	ultraviolet or visible

When an appreciable amount of chlorine was added, most of it was present in $-\text{CHCl}_2$ groups. Substantially no chlorine was substituted on aromatic rings.

The various polyesters became self-extinguishing when they contained about 20–30% chlorine, and polyesters that were insoluble in volatile solvents, such as methylene chloride, became soluble when they contained 10–15% chlorine. When the polyesters were cast from the volatile solvents, clear tough films with good tensile properties and high heat-distortion temperatures were obtained. The chlorinated polyesters of particular interest are the polycarbonates of 2,2,4,4-tetramethyl-1,3-cyclobutanediol and bisphenol A. By using the chlorination procedure discussed here many other types of polyester can be chlorinated to give soluble self-extinguishing products.

We acknowledge the excellent technical assistance of J. L. Beach and J. O. Sharp. We are indebted to V. W. Goodlett for interpretations of the NMR spectra.

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Received November 22, 1967