# POLYESTERIFICATION OF HALOGEN CONTAINING DIFUNCTIONAL COMPOUNDS B.BOUTEVIN, E.B. DONGALA and Y. PIÉTRASANTA

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## SUMMARY

The increasing interest in halogen containing polymers has led us to re-evaluate the different methods for the polycondensation of fluorinated and chlorinated monomers to form polyesters. The use of acid chlorides easily gives polymers with relatively high molecular weights (above 3000). We also describe in this work a new method of polytransesterification from the bishydroxyethyl esters of fluorinated and chlorinated diacids at temperatures below 200°C.

## Résumé

L'intérêt croissant pour les polymères halogénés nous a amené à reconsidérer les diverses méthodes de polycondensation de monomères fluorés et chlorés. Seule, l'utilisation des chlorures d'acide conduit aisément à des polymères de poids moléculaires relativement élevés (supérieurs à 3000). Nous avons également mis au point une méthode originale de polytransesterification à partir des bis hydroxyéthylesters des acides fluorés et chlorés à des températures n'excédant pas 200°C.

## INTRODUCTION

The polycondensation of halogen containing monomers-especially fluoro derivatives is presently subject to active investigation because of the special physical and chemical properties of these compounds which offer excellent resistance to high temperatures and corrosive chemical reagents and possess specific surface properties such as hydrophobic and oleophobic character. New requirements brought upon by the progress of aeronautics (e.g. the need for macromolecules which will be stable under extreme conditions) have created new interest in the search for polymers which can stand a very wide temperature variation and do not become brittle at very low temperatures ; moreover, their chemical reactivity make them potential good solid fuel binders for rockets (1).

A bibliographic survey shows that all the classical methods of polyesterification. reactions with diacids (2-4), acid anhydrides (5), diesters (6-8) and especially diacid chlorides (9-13), have been tried for the synthesis of these polyesters ; in each case, the halogen atoms may be present in both or in only one of the difunctional compounds. These studies show that the reaction of fluorinated diols with fluorinated or hydrocarbon acids is very difficult although after an extremely long time, low molecular weight polyesters are obtained. SCHWEICKER et al. (4) explain this low reactivity by the fact that fluorinated diols are  $10^4$  to  $10^6$  times more acidic than their hydrocarbon homologs, and the same reason is given for the sluggishness of transesterification reactions of fluorinated or hydrocarbon diesters with fluorine-containing diols; thus, EVERS and EHLERS (6) have been unable to obtain high molecular weight polymers even under drastic conditions (reaction temperature between 200 and 300°C, reaction time exceeding 100 hours). The polyesterification of fluorinated anhydrides with diols also requires very drastic conditions (3).

The use of acid chlorides is the only reported method which gives satisfactory results, many polyesters have been synthetized this way and one may easily get polymers with an average molecular weight  $\overline{M}_n$  greater than 5000. However, many of these results are on the one hand disparate and non conclusive, and on the other, to the best of our knowledge, only fluorinated monomers have been investigated and there is no study of chlorine containing monomers. This had led us to reconsider the three methods of polyesterification of both chlorine and fluorine-containing monomers : polycondensation in homogeneous solution, polycondensation in heterogeneous media (interfacial polycondensation) and polytransesterification.

## RESULTS AND DISCUSSION

We have used a series of chlorine-(14) and fluorine-(15) containing compounds prepared by telomerization including the diol (I) and diesters (II) and (III) :

 $HOCH_2-CF_2-CFH-CF_2-CH_2OH RO_2C-(CF_2-CFC1)_n-CF_2-CO_2R$ (I)
(II) n= 2,3 ; R= nBu,CH\_3  $CH_3O_2C-CC1_2-CH_2-CHC1-CH_2-CHC1-CH_2-CC1_2-CO_2CH_3$ (III)

Each of these compounds contains two halogen atoms  $\alpha$  to the reactive function; moreover, because of their symmetrical structures, the ester group as well as the hydroxyl of each one of these monomers have exactly the same reactivity. Finally, the use of both chlorofluorinated and chlorohydrogenated compounds makes possible the assessment of differences in reactivity which may be caused by the halogen present.

## I. POLYCONDENSATION IN HOMOGENOUS SOLUTION

## SYNTHESIS OF FLUORINATED POLYESTERS BY REACTION OF AN ACID DICHLORIDE WITH A DIOL

We first investigated the polycondensation of diol (I) with adipic acid dichloride in dichlorobenzene. It is necessary to use an excess of one of the compounds in order to know unambiguously the chain ends of the polyesters. FLORY (16) has shown that the degree of polymerization is related to the excess diol accoding to the equation.

$$\overline{DP}_n = \frac{r+1}{r+1-2pr}$$

p is the extent of reaction of the reaction and r the molar ratio of the reactants (adipoyl chloride)/(diol) (I)) < 1.

When an excess of diol (I) is used, a dihydroxy polyester (IV) is obtained according to the reaction :

(I) + C1OC-(CH<sub>2</sub>)<sub>$$A$$</sub>-COC1  $\longrightarrow$ 

$$HOCH_2 - CF_2 - CFH - CF_2 - CH_2 - 0 - (CO - (CH_2)_4 - CO - 0 - CH_2 - CF_2 - CFH - CF_2 - CH_2 - 0)_x - H$$
(IV)

Different reactions were run with r, equal to 0.8; 0.9; 0.97 and 1. The average molecular weight  $\overline{M}_n$  was determined by titration of the chain ends after acetylation in pyridine. The  $\overline{M}_n$  values obtained were checked by NMR spectroscopy (shown in Figs.1 and 2) as will be explained further below.

The intrinsic viscosity (n) of each polyester was determined at 30°C in chloroform. The results are collected in the table below.  $\overline{M}_n$  is related to the viscosity by the Staudinger equation : (n) =  $K.\overline{M}_n^a$ ; a is nearly equal to 1, and k = 2.5 x 10<sup>-3</sup>. This gives : (n) cm<sup>3</sup>/g = 2.5 x 10<sup>-3</sup> \overline{M}\_n; in similar studies, SCHWEICKER et al. (9) use the values k = 3.2.10<sup>-3</sup> and a = 1.

r	0.8	0.9	0.97	1
(1) cm <sup>3</sup> /g	4.05	8.55	17.4	27.2
Mn experimental	1375	2900	5900	9200

Variation of (n) as a function of r for the polyester (IV)

We have thus obtained polyesters with a fluorinated alcohol,  $-CF_2CH_2OH$  as the end group. As stated previously such groups are not very reactive. In order to have fluorinated polyesters with comparable molecular weight and the same reactivity it is necessary to prepare polyesters having a hydrocarbon alcohol group as its chain end groups. For this, the use of an excess diacid chloride is necessary ; at the end of the reaction, an excess of butanediol is added :

$$(I) + Cloc-(CH_2)_4-COC1 (excess) \longrightarrow$$

$$Cloc-(CH_2)_4-CO-\{0-CH_2-CF_2-CFH-CF_2-CH_2-0-CO-(CH_2)_4-CO\}_x-C1 \xrightarrow{butanediol} (V)$$

$$HO-(CH_2)_4-O-CO-(CH_2)_4-CO-\{0-CH_2-CF_2-CFH-CF_2-CH_2-0_2C-(CH_2)_4-CO\}-O-(CH_2)_4-OH$$

(VI)

The structure of the polyesters and the average molecular weight were determined by NMR and by titration of the end groups after acetylation.

## II. POLYCONDENSATION IN HETEROGENEOUS SOLUTION

We have investigated the interfacial polyesterification of the fluorinated diacid chlorides  $C10C-CF_2-CFC1-CF_2-COC1$  (VII) with butanediol. The polyester obtained has the basic structure :

Figs 3 and 4 show the NMR spectra of butanediol and polyester (VIII). The respective intensities of the CH\_2-OH (3.6 x  $10^{-6})$  protons and of the methy-





lene at the  $\alpha$  position of the ester groups (4.4 x 10<sup>-6</sup>) allow the calculation of  $\overline{M}_n$ . The low value of the  $\overline{M}_n$  obtained (1450) and the fact that the nature of the chain end groups are not precisely known limit the use of this method.

From diols and acid dichlorides we have prepared fluorinated polyesters with precisely known chain end groups. The molecular weights are between 1000 and 10000 which is comparable to those obtained previously in similar studies (4)(7). However, the synthesis of acid dichlorides and fluorinated diols is very laborious and working with acid chlorides is rather hazardous. We have therefore investigated a different method for the synthesis of polyesters starting from easily obtained monomers such as (I) and (II). These monomers are easy to synthesize and to purify and are very stable.

## III. SYNTHESIS OF HALOGEN-CONTAINING POLYESTERS BY POLYTRANSESTERIFICATION

It is surprising to see from the literature that the synthesis of halogen-containing polyesters by transesterification has been so little studied. EVERS and EHLERS (6) have studied the reaction of perfluoropentandiol with isophthaloyl chloride and various substitued isophthalic esters under drastic conditions (temperature above 300°C, reaction time < 30h) the final product is dark brown and insoluble in DMF SCHWEICKER et al. (4) write that the transesterification of fluorinated diethylesters with fluorinated diols is not a satisfactory method of synthesis. GOSNELL et al. (7) have reported the polytransesterification of diethyl malonate with hexafluoropentanediol and do not mention any special difficulty.

However, to our knowledge, there is no report in the literature of the transesterification of a halogenated diester with a hydrocarbon diol, even though this would seem to be quite practicable.

We first examined the possibility of transesterification to the halogenated diesters (II) and (III). This is a two-step reaction : 1) substitution of the diester group by the chosen diol 2) elimination of the substituted alcohol group which is the polycondensation step proper. The usual catalysts for the reaction are calcium acetate for the first step and butyl orthotitanate for the second (17).

The first transesterification investigated was that of diester (II) with ethyleneglycol ; the reaction was followed by NMR spectroscopy and gas chromatography. After 30 hours at 200-220 $^{\circ}$ C, a compound (IX), was formed in very small quantities :

(IX)  $HO-CH_2-CH_2-O_2C-CF_2-(CFC1-CF_2)_n-CO_2-CH_2-CH_2OH$ 

The presence of an  $A_2B_2$  system in the <sup>1</sup>H NMR spectrum.is characteristic of the bishydroxyethyl ester. After 72 hours, product (IX) is totally transformed into polyester (X).

(X) 
$$HO-CH_2-CH_2-O-(CO-CF_2(CFC1-CF_2)_n-CO_2-CH_2-CH_2-O)_p-H$$

The average molecular weight (by vapor pressure osmometry) is 2500. However only 20% of the diester (II) has been transformed; the nature of the diester has no influence on the reaction since we found similar results with methyl and n-butylesters.

The same type of reaction was carried out with the chlorohydrogenated diester (III) and different diols. There is no polyester formation with ethyleneglycol and butanediol ; instead, there is formation of dioxane and tetrahydrofuran. To avoid the cyclization of the diol, hexanediol was used in excess and compound (XI) was obtained in about 10% yield :

(XI) 
$$HO-(CH_2)_6 - O_2C-CC1_2 - CH_2 - CHC1 - CH_2 - CHC1 - CH_2 - CC1_2 - CC1_2 - CO_2 - (CH_2)_6 - OH_2 - OH_2$$

These reactions show that the first step of transesterification of fluorine or chlorine containing monomers leading to the bishydroxyalkylesters is very difficult and always incomplete ; however once this step is achieved, the polyesterification goes easily to completion. This had led us to synthesize the bishydroxyalkylesters by a different method.

Saponification of the fluorine-containing diesters (II) leads to the corresponding diacids ; their direct esterification in the presence of excess ethyleneglycol gives the bishydroxyalkylesters (IX).

The chlorine-containing diester (XII) was synthetised by direct telomerization of 1,5 hexadiene with hydroxyethyl trichloroacetate since it was impossible to obtain the corresponding acids by saponification because of their instability in a basic medium :

$$CC1_3-CO_2-CH_2-CH_2-OH + CH_2=CH-(CH_2)_2-CH=CH_2$$

$$HO-(CH_2)_{2}-O_2C-CC1_2-CH_2-CHC1-CH_2-CH_2-CHC1-CH_2-CC1_2-CO_2-(CH_2)_2-OH$$
(XII)

The bishydroxyalkylesters (IX) and (XII) condense together at temperatures below 200  $^{\circ}C$  to give polyesters (X) and (XIII) :

$$H-(-O-(CH_2)_2-O_2C-CC1_2-CH_2-CHC1-(CH_2)_2-CHC1-CH_2-CC1_2-CO)_x-O-(CH_2)_2-OH_2$$
(XIII)

A titration of the end groups after acetylation gives an average molecular weight of 2500 for polyester (XIII) ; the intrinsic viscosity (n) in chloroform is 5.8 cm<sup>3</sup>/g. The polyester has a slight brown coloration ; there was no degradation and no emission of hydrochloric acid during the reaction. The product contains about 50% chlorine which may give it fire-proofing properties.

The bishydroxyalkylester (IX) which is a mixture of n=2 (90%) and n=3 (10%) was first heated to 190°C (0.1 torr) without a catalyst for 2 hours. When the ethylene glycol stopped distilling off, 1% of Ti(OBu)<sub>4</sub> by weight was added and the reaction carried on at 200°C for 2 hours. Fig.5 shows the G.L.C. and the NMR spectra of the starting monomers, those of the pre-polyester without catalyst and those of the final polyester. The G.L.C. curve shows the progressive disappearance of the two starting diesters, and the NMR, spectrum shows the transformation of the  $A_2B_2$  into an  $A_4$  system. The relative intensities of the signals at 3.8 and 4.6.10<sup>-6</sup> allow the calculation of the  $\overline{DP}_n$  of the polyester ; the same values can also be obtained form G.L.C. curve by tracing a calibration curve starting with p = 1,2,3 ... for (X,n=2).

Ve	33.5	31	29.8	28.6	28
M <sub>n</sub>	461	860	1259	1658	2057
р	1	2	3	4	5

A value of p=2,5 ( $\overline{M}_n \approx 1000$ ) for the prepolyester obtained without catalyst is obtained similarly. At the end of the reaction p is nearly equal to 10 ( $\overline{M}_n \approx 4000$ ).

## CONCLUSION

Polycondensation reactions from halogen-containing diols and diesters are difficult reactions and have been little studied. SCHWEICKER and al. (4) attribute this low reactivity to the presence of two halogen atoms  $\alpha$  to the hydroxy function which gives them a relatively strong acid character. However, this explanation cannot apply in the case of halogen-containing diesters, since the two halogen atoms should increase the electrophilic character of the carbonyl, and increase their reactivity toward nucleophiles. We have shown this increase in reactivity of halogenated diesters in the case of reactions with amines (14).





The low reactivity of diesters with two halogen atoms  $\alpha$  to the carbonyl may be the reason for the lack of published work on polycondensation by transesterification. The method of polytransesterification we have proposed in this paper makes it possible to prepare under reasonably mild conditions halogencontaining polymers. The novelty of the method resides in the fact that the nature of the leaving group (ethyleneglycol) and that of the attacking group (éthyleneglycol ester) are very similar ; this favors the transesterification. In this way we have prepared without major difficulty, not only fluorinated polyesters from fluorinated monomers which are very stable even at high temperatures, but we have also synthetised chlorine-containing polyesters from chlorinated monomers which usually are not stable under the drastic conditions of classical polycondensations.

#### EXPERIMENTAL

All structures were confirmed by IR, NMR and elemental analysis. Only the main characteristics are given below, further details can be obtained from the authors. In NMR, s,d,t,m, stand for singlet, doublet, triplet and multiplet.

#### Preparation of monomers

Diol (I) and diesters (II) and (III) were prepared according to the method described by BOUTEVIN et al. (14,15,18).

# SYNTHESIS OF 2,2,3,44,5,6,6-OCTAFLUORO-3,5-DICHLOROBISHYDROXYETHYL PIMELATE (IX) :

To 0,5 mole of diacid obtained from the saponification of diester (II) and 1,5 mole of ethyleneglycol was added 100 to 150cc of chloroform. After reflux for 4h,the solution was washed with warm water to remove excess water and made neutral. After evaporation of the chloroform product (IX) was obtained in a 90% yield.

IR (CHCl<sub>3</sub>) :  $\gamma_{OH}$  : 3600 ;  $\gamma_{C=0}$  : 1780. N.M.R. (CDCl<sub>3</sub>.10<sup>-6</sup>) : 3.9 and 4.5 (A<sub>2</sub>B<sub>2</sub> system) ; 3.0 (s,shifts with dilution).

#### SYNTHESIS OF 2,2,4,7,9,9-HEXACHLORO BISHYDROXYETHYL DECANEDIOATE (XII):

The telogen  $CC1_3-CO_2-CH_2-CH_2OH$  was prepared from trichloroacetic chloride and ethylene glycol. The telomerization reaction was carried as in (II) (15). Yield : 60%. IR (CHCl\_3) :  $\gamma_{OH}$  : 3600 ;  $\gamma_{C=0}$  : 1760 N.M.R. (CDCl\_3.10^{-6}) ; 2.0 (large signal 2.55 (s) ; 3.10 (m) ; 3.9 and 4.5 (A\_2B\_2 system) ; 4.7 (m).

#### Polycondensation

#### A POLYCONDENSATION IN HOMOGENEOUS SOLUTION

#### SYNTHESIS OF POLYESTER

$$HO-CH_2-CF_2-CFH-CF_2-CH_2-0-\{CO-(CH_2)_4-CO_2-CH_2-CF_2-CFH-CF_2-CH_2-O-\}_{x}-H$$
 (IV)

This synthesis was carried out in dichlorobenzene with an excess of diol (I), after two recrystallisations of the latter in benzene (m.p. :  $69^{\circ}$ C). The adipoyl chloride was freshly distilled (b.p. :  $70-75^{\circ}$ C/1mm) as was the orthodichlorobenzene, the latter over P<sub>2</sub>O<sub>5</sub> (b.p. :  $72^{\circ}/20$ mm). During the reaction a flow of nitrogen (purified through sodium pyrogallate, concentrated H<sub>2</sub>SO<sub>4</sub> and a colum of P<sub>2</sub>O<sub>5</sub>) was passed in order to remove the hydrochloric acid formed as the reaction proceeds.

The diol and the diacid chloride in dichlorobenzene were heated at  $120^{\circ}$  for 5h. The fluorinated diol, insoluble in the dichlorobenzene, disappeared as HCl, was evolved. The temperature was then raised to  $170-180^{\circ}$ C and kept there for 15h. The mixture was then cooled concentrated and extracted with chloroform. It was finally dried for 48h under 0.1 torr.

IR (CHCl<sub>3</sub>) :  $\gamma_{OH}$  : 3600 (weak) ;  $\gamma_{C=0}$  : 1750 ; NMR (acetone-d<sub>6</sub>.10<sup>-6</sup>) : 1.8 and 2.5 (m) ; 4.56 (t ; 14Hz) ; 5.33 (m,J<sub>HF</sub><sub>gem</sub> = 45Hz ; J<sub>HF</sub><sub>vic</sub> = 14Hz) ; 6.5 (s).

ACETYLATION OF POLYESTER (IV) ; 
$$r = 0, 8$$
. DP CALCULATION

The acetylation solution (45ml of pyridine for 5ml of acetic anhydride) was added to 1.95g of polyester (IV). It was refluxed for 1/2hr and hydrolyzed at room temperature, and rinsed with acetone. Potentiometric titration (Metrohm E 336 with automatic burette) was with 0.9M NaOH (v= 9.25cc). The volume for the acetylating solution gives v'= 12.55cc. From these results  $\overline{M}_n = \frac{2m.10^{-3}}{N(v'-v)} = 1375$  which gives an x of approximately 4 and  $\overline{DP}_n$  of 9 according to the formula  $\overline{DP}_n = 2x + 1$ .

This method gives good results for molecular weights below 5000, but above that, experimental errors become great.

# 

$$\begin{array}{cccccccccccc} & \gamma & \delta & \alpha & \beta & \gamma & \varepsilon \\ & CH_3-O-CO-CH_2-CF_2-CFH-CF_2-CH_2-O(CO-CH_2-(CH_2)_2-CO_2-CH_2-CF_2-CFH-CF_2-CH_2-O)_{\mathbf{x}}-COCH_3 \end{array}$$

H protons	α	β	γ	δ.	ε
δ chemicalshift	4.56	4.8-6.0	2.5	1.8	2.1
Number of H	4x+4	x+1	4x	4x	6

The table above shows the different chemical shifts of the acetylated polyester (IV) protons. Comparison of the relative intensities of the six  $\varepsilon$  protons and the 4x  $\gamma$  protons allows a determination of x.

#### SYNTHESIS OF POLYESTER

 $\mathsf{HO-(CH}_2)_4 - \mathsf{O-CO-(CH}_2)_4 - \mathsf{CO-\{O-CH}_2 - \mathsf{CF}_2 - \mathsf{CFH} - \mathsf{CF}_2 - \mathsf{CH}_2 - \mathsf{O}_2\mathsf{C-(CH}_2)_4 - \mathsf{CO}\} - \mathsf{O-(CH}_2)_4 - \mathsf{OH}_2 - \mathsf{OH}_$ 

This synthesis was carried out in dichlorobenzene solution with an excess of adipoyl chloride as for polyester (IV). However, after 20h, a large excess of butanediol was added. After 5h, the polymer was worked up as previously described.

NMR  $(CDCl_3.10^{-6})$ : 2 large signals at 1.7 and 2.45. At 3.65 a not well-defined triplet; at 3.43 a singlet which shifts with dilution; centered at 5.3 a triplet (J : 14Hz) and a multiplet of very weak intensity.

CALCULATION OF THE DP OF POLYESTER (VI) FROM ITS NMR SPECTRUM

$$γ$$
 δ  $γ$   $χ$  δ ε  
CO-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-CO<sub>2</sub>-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-OH

The difference of intensities between the signals at  $1.7.10^{-6}$  (corresponding to the 4x+8  $\delta$  protons) and the signals at 2.45 (corresponding to the 4x  $\gamma$  protons) is equivalent to the 8 central protons of the butanediol. Comparison with the 4x  $\alpha$  protons allows the determination of  $\overline{\text{DP}}_n$  =18 (19 by using Flory's formula).

## B POLYMERIZATION IN HETEREGENEOUS SOLUTION

## INTERFACIAL POLYMERIZATION OF DIACID CHLORIDE (VII) WITH BUTANEDIOL TO GIVE POLYESTER (VIII)

A slightly basic solution of butanediol in water was carefully added to a vessel containing the diacid chloride in trichloro-1,1,2 trifluoro ethane solution. After standing for 20h, the polyester formed was extracted with ether and chloroform. Excess butanediol was distilled off under vacuum to give a colorless viscous liquid.

IR (CDCl<sub>3</sub>) : <sub>OH</sub> : 3600 ; <sub>OH</sub> : 1750 (strong). NMR CDCl<sub>3</sub>.10<sup>-6</sup>) : 1.95 (large signal) ; 3.6 (t) ; 4.43 (large) ; 7.1 (s, shifts with dilution). Calculation gives x = 4.5 which gives a  $\overline{DP}_{p}$  of 9.

## C POLYTRANSESTERIFICATION

# SYNTHESIS OF POLYESTER H-{O-(CH<sub>2</sub>)<sub>2</sub>- $\frac{O_2C-(CF_2-CFC1)}{2}$ 2- $\frac{CF_2-CO)-}{2}$ x $\frac{-O(CH_2)_2-OH-(X)}{2}$

15g of monomer (IX) was placed in a reactor with 0.1% by weight of calcium acetate and antimony oxide. The reaction was heated at  $180^{\circ}$ C under 20 torr for two hours and then raised to  $200^{\circ}$ C under  $10^{-1}$  torr for one hour. After cooling to room temperature, the polymer was dissolved in chloroform, washed with warm water and dried. The chloroform was distilled off and the polymer dried at  $10^{-1}$  torr for several hours.

NMR (CDCl<sub>3</sub>.10<sup>-6</sup>) : 3.9 and 4.5 (A<sub>2</sub>B<sub>2</sub> system) ; 4.7 (s, A<sub>4</sub> system).

G.L.C. were determined with a WATERS Associates Apparatus with 100, 100,500 and 1000Å columns. The solvent was THF, at 2ml/mn and a differential refractometer detector was used.

$$\mathsf{H-\{0-(CH_2)_2-0_2C-CC1_2-CH_2-CHC1-CH_2-CH_2-CH_2-CHC1-CH_2-CC1_2-CO\}_x-0-(CH_2)_2-OH}$$

The synthesis was carried out as for polyester (X).

NMR (CDCl\_3.10<sup>-6</sup>) : 2.0 (large signal) ; 3.1 (m) ; 3.9 and 4.3 (A\_2B\_2 system) ; 4.5 (m) ; 4.6 (s, A\_4 system).

The potentiometric titration method mentioned (page 13) for the acetylation of polyester (IV) gives with v = 8.5cc of 0.98N NaOH, v'= 10.25cc of the acetylating solution, which leads to  $\overline{M}_{n}$  = 2332.

Viscosity in chloroform gives for  $(\eta) = 5.80 \text{cc/g}$ .

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SYNTHESIS OF CHLORINE-CONTAINING POLYESTER (XIII)