European Polymer Journal, 1971, Vol. 7, pp. 1621-1628. Pergamon Press. Printed in England.

POLYESTERS—II

THE RATE OF POLYESTERIFICATION OF γ-ARYLITACONIC ANHYDRIDES WITH ETHYLENE GLYCOL

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(*Received* 20 *March* 1971)

Abstract—The polyesterification of γ-phenyl-, γ-*p*-methoxyphenyl-, and γ-*p*-chlorophenyl-itaconic anhydrides (1 mol) with ethylene glycol (1 mol), in the presence or in the absence of *p*-toluenesulphonic acid as catalyst, follows a second order rate equation.

In both the uncatalysed and catalysed polyesterifications, the reaction velocity is enhanced by electron-withdrawing groups and suppressed by electron-donating groups. The unbranched structures of the polyesters have been proved by ozonolysis and by i.r. and NMR spectroscopy.

INTRODUCTION

IN A PREVIOUS publication(1) it was shown that the polyesterifications between γ-arylitaconic acids and ethylene glycol follow second order rate equations. In the present investigation, a similar study is reported for the γ-arylitaconic anhydrides of the acids investigated in part I.

EXPERIMENTAL

γ-Phenylitaconic anhydride,(2) *γ-p-methoxyphenylitaconic anhydride*(3) and *γ-p-chlorophenylitaconic anhydride*(4) were prepared by methods described in the literature and used after two crystallizations. Ethylene glycol was purified as mentioned in Part I.

The apparatus and procedure described in Part I were used. Kinetic runs were taken at 160°, 180° and 200°; phenolphthalein was used as indicator in the titration of the total free carboxyl in samples. (≃ 30 mg) removed from the mixture at suitable intervals.

The i.r. spectra were measured on a Unicam SP 1200 spectrophotometer, using a thin film technique.

Ozonolysis of the polyester

A chloroform solution of the polyester from γ-phenylitaconic anhydride (IIIa) (1·8 g) was treated with ozone for 3 hr, then the ozonide was decomposed with water. The product was steam distilled in a stream of carbon dioxide; the distillate was extracted with ether, dried and the solvent removed to give benzaldehyde (0·8 g), identified and estimated as its 2,4-dinitrophenylhydrazone (2·1 g), m.p. 237°, undepressed with an authentic specimen. The amount of D.N.P. isolated showed that 1·8 g of polyester contained 0·663 g of benzylidene residue.

RESULTS AND DISCUSSION

The unbranched nature of the polyesters produced was established by (i) ozonolysis and (ii) NMR spectrum.

(i) *Ozonolysis.* Isolation of benzaldehyde by ozonolysis of the polyester (IIIa) shows that it contains a benzylidene group. The experimental result shows that the ratio of the polyester (IIIa) or its segmer (s) to the benzylidene

$$\text{residue} = \frac{1 \cdot 8}{0 \cdot 663} = 2 \cdot 7.$$

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$$\text{The calculated ratio} = \frac{\text{M.W. of segmer of IIIa}}{\text{M.W. of } C_7H_6} = \frac{232}{90}$$

$= 2 \cdot 6$, indicating that each segmer contains one benzylidene residue, i.e., there is no branching.

(ii) *NMR spectrum.* The integrated NMR spectrum of IIIa (Fig. 1) shows the following signals: singlet at τ 6·4 (2*p*), triplets at τ 5·6 (4*p*), singlet at τ 2·6 (5*p*) and non-symmetrical singlet at τ 2·1 (1*p*). These signals are characteristic of Ph—C=C—CH_2—CO—,(5a) —CO—O—CH_2—CH_2—O—CO—,(5b) aromatic protons and olefinic proton in Ph—CH=C—CO,(5c) respectively. The low τ value for the olefinic proton is probably due to long range deshielding effect of the *cis*-carboxylate group (cf. the τ value for the olefinic proton in methyl maleate and methyl fumerate).(6) The non-symmetry of the signal for the olefinic proton may be due to weak coupling with the *trans*-CH_2. The sharp signal at τ 6·3 may be due to OH protons.

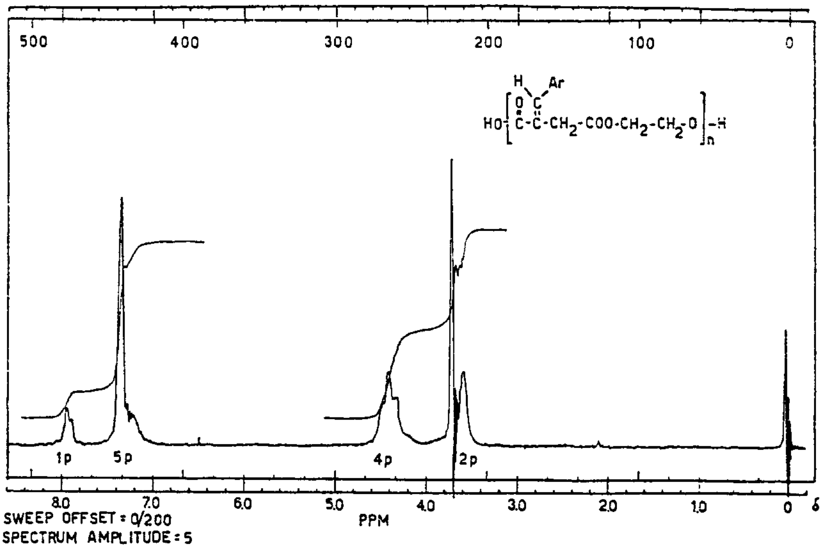


FIG. 1. NMR spectrum of polyester derived from γ-phenylitaconic anhydride and ethylene glycol.

Both these observations substantiate the structure assigned to the polyester and prove that it contains no branching. The absence of branching may be attributed to steric factors. Also, the i.r. spectra of these polyesters show the band characteristic of the bending frequency of the olefinic double bond at 850–860 cm^{-1}.

As in the case of γ-arylitaconic acids and ethylene glycol,(1) the reaction of the corresponding anhydrides with the same glycol is found to be acid catalysed. In the absence of an added foreign acid, a second molecule of the acid (obtained from the hydrolysis of the anhydride with the water, eliminated at the beginning of the reaction) functions as a catalyst and the rate constant is given by the rate expression

$$d\,COOH/dt = k[COOH]^2\,[OH].$$

The hydrogen ion comes from the ionization of the dibasic acid and esterification is supposed to take place according to the mechanism reported by Tang Au Chin.(7) However, in the autocatalysed polyesterification of these anhydrides (1 mol) with ethylene glycol (1 mol), the reaction satisfies second order kinetics. Values k_2 have been calculated using equation (1) (see Table 1).

$$C_0k_2t = 1/(1-p) - 1 \tag{1}$$

where C_0 is the initial concentration in equivalents of OH or COOH group per litre, k_2 is the velocity constant in litres per equivalent per min, t is the time in min and p is the extent of the reaction, i.e. the fraction of the COOH groups which has reacted at time t.

TABLE 1. VELOCITY CONSTANTS, ENERGIES OF ACTIVATION AND ENTROPY OF ACTIVATION FOR THE UNCATALYSED POLYESTERIFICATION OF γ-ARYLITACONIC ANHYDRIDES WITH ETHYLENE GLYCOL

Anhydride	$k_2 \times 10^4$ 160°	180°	200°	ΔE^*	ΔS^*
γ-Phenylitaconic	1·713	5·611	15·66	23	−26·12
γ-p-Methoxyphenylitaconic	1·262	2·400	3·95	12	−51·53
γ-p-Chlorophenylitaconic	1·782	6·858	23·70	26	−17·42

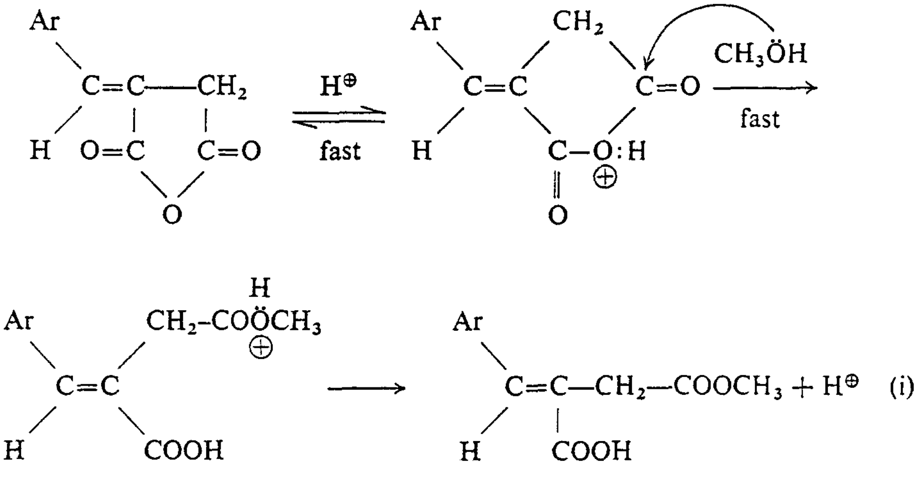
The reactions of γ-arylitaconic anhydrides with ethylene glycol catalysed by a small amount of p-toluenesulphonic acid (0·004 mole per mole of glycol) were also found to satisfy second order kinetics (see Table 2).

TABLE 2. VELOCITY CONSTANTS, ENERGIES OF ACTIVATION AND ENTROPY OF ACTIVATION FOR THE CATALYSED POLYESTERIFICATION OF γ-ARYLITACONIC ANHYDRIDES WITH ETHYLENE GLYCOL

Anhydride	$k_2 \times 10^4$ 160°	180°	200°	ΔE^*	ΔS^*
γ-Phenylitaconic	2·092	6·996	16·085	21·35	−28·76
γ-p-Methoxyphenylitaconic	1·574	3·740	5·345	14·14	−45·96
γ-p-Chlorophenylitaconic	3·754	17·283	53·950	29·79	−10·49

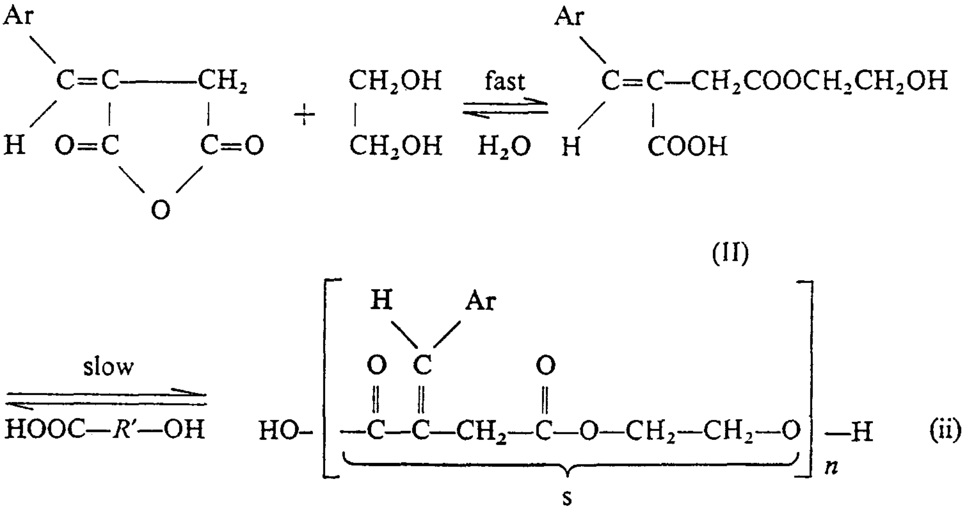
Mechanism of polycondensation

El-Abbady(3,4) reported that substituted γ-arylitaconic anhydrides on simple esterification with methanol gave methyl 4-aryl-3-carboxy-but-3-enoate (I) derivatives and therefore, the esterification of the β-carboxyl group can be considered to be the rate determining step in the diesterification of γ-arylitaconic anhydrides.



(I)

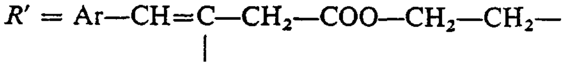
With ethylene glycol, the reaction takes place as follows to give (II)



(II)

(III)

a, Ar = Ph
b, Ar = p—$CH_3O \cdot C_6H_4$
c, Ar = p—$Cl \cdot C_6H_4$



$R' = Ar—CH{=}\underset{|}{C}—CH_2—COO—CH_2—CH_2—$

The rapid nature of the first step is supported by the rapid drop in the acid value in the first 30 min; nearly half of the anhydride is consumed. The above-mentioned steps are similar to those reported in Part I to give (III).

Relation between log k and ΔE^*

As in the case of γ-arylitaconic acids,(1) it is apparent that for the anhydrides studied the range of velocities was not sufficient to permit accurate analysis of the Arrhenius equation. If the changes in the velocity of polyesterification produced by the substituents were entirely due to changes in ΔE^*, the points on the graph for log k vs. ΔE^* would be on a straight line having a slope of $2 \cdot 303$ RT.[8] It was found that the slope differs from the theoretical value, and it may be concluded that the factor P also varies.

ΔS^* for the reaction have very low negative values (see Tables 1 and 2) which may be due to the restricted movement of the molecule due to the high viscosity of the reaction medium and to the bimolecular nature of the mechanism.

Effect of substituents on reaction rate

Baddar *et al.*(1) on studying the effect of substituents on the reaction velocity for γ-arylitaconic acids with ethylene glycol, found that in the uncatalysed reactions the velocity of polyesterification is increased by electron-withdrawing and decreased by electron-donating groups, whereas in catalysed reactions the reverse effect occurs.

The following conclusions can be drawn from the present experimental results.

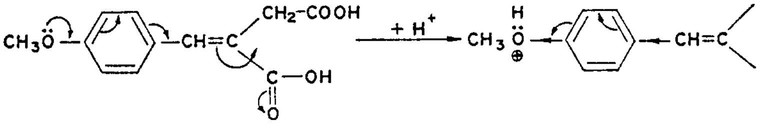
(1) In both the uncatalysed and catalysed polyesterifications of substituted γ-arylitaconic anhydrides, electron-withdrawing groups increase the velocity of polyesterification, whereas electron-donating groups decrease the velocity (see Tables 1 and 2).

(2) The uncatalysed polyesterifications of substituted γ-arylitaconic anhydrides are slower than the catalysed in spite of the fact that the activation energy is not greater. Similarly, in both the uncatalysed and catalysed polyesterifications, the activation energy for γ-chlorophenylitaconic anhydride is higher than that for the p-methoxy derivative in spite of the fact that the rate of the former reaction is much greater than that of the latter. This indicates that the factor P in the Arrhenius equation is much greater for the reaction involving a charged catalyst, and that the polycondensation of γ-p-methoxyphenylitaconic anhydride is less sensitive to variation in temperature. This is reflected in the value of the parameter A in the Arrhenius equation; it is found that $\log_{10} A$ is higher in case of the p-chloro derivative than in case of the p-methoxy compound.

(3) The fact that the anhydrides are known to be more easily monoesterified than the corresponding acids(9) could be taken as a good evidence that the first step in polyesterification is not rate determining, since the rates of polyesterification of the anhydrides are found to be much less than those of the corresponding acids(1) except in the case of the catalysed reaction of p-chlorophenylitaconic anhydride at 180° and 200° which is found to be faster than expected.

(4) The high rate of *catalysed* polyesterification of γ-p-methoxyphenylitaconic acid,(1) and the low value in the case of the corresponding anhydride cannot find a reasonable interpretation, before studying the effects of other electron-donating groups. However, it may possibly be attributed to the ease of protonation of the methoxy group to give an oxonium salt. The positive charge produced on the oxygen atom destroys the $+R$ effect of the methoxy group and increases enormously its

—I effect. In the case of the anhydrides, the proton attacks the anhydride oxygen rather than the methoxy oxygen [see reaction sequence (i)].



(5) The Hammett equation⁽¹⁰⁾ is only obeyed in uncatalysed reaction at 160° and the δ value has a positive sign, which agrees with the experimental fact that the reaction is enhanced by electron-withdrawing groups and retarded by electron-releasing groups. The very low value of ρ (0·14) indicates that this polyesterification, as in case of the corresponding acids, is slightly sensitive to the polar nature of the substituents.⁽¹¹⁾

(6) The slower polyesterification of the anhydrides compared with that of the corresponding acids may be due to the higher hydrogen ion concentration in the latter compounds. The correctness of this idea can be established by studying the effect of hydrogen ion concentration on the rate of polyesterification. This study is in progress.

Properties of the polyesters

The polyesters produced by heating γ-arylitaconic anhydrides with ethylene glycol to an advanced stage of esterification contain at least 4–8 condensation units per mole. Higher molecular weight polyesters have been obtained when the polycondensation was carried out in presence of *p*-toluenesulphonic acid. The polyesters are in the form of crystalline yellow glass-like fibres which can be easily crushed. They are soluble in many organic solvents, but insoluble in carbon tetrachloride, *n*-hexane and light petroleum.

TABLE 3. MOLECULAR WEIGHTS OF SOME POLYESTERS

T (°C)	IIIa	IIIb	IIIc
	Polyesters obtained without catalyst		
160	385	210	563
180	899	551	985
200	1623	797	1653
	Polyesters obtained with catalyst		
160	417	268	612
180	809	933	1628
200	1677	1125	2296
	Polyester obtained with excess of glycol		
180	3553		

These polyesters failed to cure even with styrene or methyl methacrylate in the presence of benzoyl peroxide. No appreciable change in the physical properties was observed when these polyesters were subjected to γ-radiation.

The molecular weights of these polyesters were determined by end group analysis for COOH using KOH; they agreed fairly well with those obtained from u.v. spectral data (see Table 4).

TABLE 4

Compound	M.W.*	(nm) λ_{max}	A_a†	A_p	n	M.W.
γ-Phenylitaconic acid	206	262	0·19	—	—	—
Polymer IIIa at 180°	672	262	—	0·513	2·7	644
γ-*p*-Methoxyphenylitaconic acid	236	292	0·203	—	—	—
Polymer IIIb at 180°	662	292	—	0·487	2·4	646
Polymer IIIb at 180° with catalyst	976	292	—	0·690	3·4	908

* End group method.

† Absorbance of the same molar concentration of γ-arylitaconic acid.

Determination of molecular weight from electronic spectral data⁽¹²⁾

All polyesters show only one absorption band at the wavelengths indicated in Table 4. As mentioned in Part I, the absorbance (A_p) of the polyester at a certain wavelength $= n \times A_s$ (where n is the number of chromophores in the molecule and A_s is the absorbance of a single chromophore at the same molar concentration (10^{-5} M/litre). Table 4 shows the molecular weight of some polyesters found, using the spectral data.

Acknowledgement—The authors thank Dr. F. W. Wehrli (Varian AG, Switzerland) for running the NMR spectrum of the polyester IIIa.

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Résumé—La polyestérification mole à mole des anhydrides γ-phényl-, γ-*p*-méthoxyphényl- et γ-*p*-chlorophényl-itaconique avec l'éthylène glycol se déroule selon une équation du second ordre, que l'on soit en présence ou en absence d'acide *p*-toluènesulfonique comme catalyseur.

Que les polyestérifications soient ou non catalysées, la vitesse de la réaction est accélérée par la présence de groupements attracteurs d'électrons et ralentie par celle de groupements donneurs d'électrons. Par ozonolyse et spectroscopies i.r. et RMN on a montré que les polyesters formés avaient une structure linéaire.

Sommario—La poliesterificazione di γ-fenil-, γ-*p*-metossifenol-, e γ-*p*-clorofenil-itaconico anidride (1 mol) con glicol etilenico (1 mol), in presenza o in assenza di acido *p*-toluensolfonico come catalizzatore, procede secondo un'equazione di secondo ordine.

Sia nella poliesterificazione catalizzata che in quella non, la velocità di reazione viene aumentata da gruppi captatori di elettroni e viceversa diminuita da gruppi donatori di elettroni. Si è provato che la struttura dei poliesteri non è ramificata, mediante ozonolisi e spettroscopia NMR e all'infrarosso.

Zusammenfassung—Die Polyveresterung von γ-Phenyl, γ-*p*-Methoxyphenyl-, und γ-*p*-Chlorphenylitaconsäureanhydriden (1 Mol) mit Athylenglykol (1 Mol) bei Gegenwart oder bei Äbwesenheit von *p*-Toluolsulfonsäure als Katalysator gehorcht einer Reaktion zweiter Ordnung.

In beiden Fällen, der nicht katalysierten und der katalysierten Polyveresterung, wird die Reaktionsgeschwindigkeit erhöht durch Elektronen-abziehende Gruppen und herabgesetzt durch Elektronen-liefernde Gruppen. Die unverzweigten Strukturen der Polyester wurden durch Ozonolyse und durch i.v. und NMR Spektroskopie bewiesen.