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Studies in Pyrolysis. Part XXVI.¹ Model Systems for the Pyrolysis of Poly(ethylene Fumarate) and Allied Polyesters

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Pyrolysis of ethyl maleate leads to $cis \rightarrow trans$ inversion, with concurrent alkyl-oxygen scission (A¹; predominating), acyl-oxygen scission (B²), and decarboxylation (C²). For methyl maleate, A^{T} scission is structurally precluded; there is cis \rightarrow trans inversion, with concurrent B^2 and C^2 scission. Ethylene diacrylate and dimethacrylate both undergo a predominating double C^2 scission, in competition with A^1 scission and a minor B^2 scission : the products of the primary A¹ scission partially interact to give an ethylidene diester, followed by disproportionation and further breakdown. All pyrolyses were at ca. 450-500° in the vapour phase. The bearing of these results on the pyrolysis of poly(ethylene fumarate) is discussed.

WORK on the thermal breakdown of poly(ethylene terephthalate) described in previous Parts² has now been extended³ to poly(ethylene fumarate) and its industrial modifications. The polyester component of

these materials is prepared by polycondensation of an unsaturated dibasic acid or anhydride (usually maleic)

³ Some of the results have been summarised in outline elsewhere (P. D. Ritchie, in 'Thermal Degradation of Polymers,' Soc. Chem. Ind. Monograph No. 13, 1961, p. 107; P. D. Ritchie, 4th Internat. Reinforced Plastics Conf., Brit. Plast. Fed., 1964, Paper No. 6). Certain of the published conclusions are now slightly modified, in the light of more recent work.

¹ Part XXV, R. L. Forman, H. M. Mackinnon, and P. D. Ritchie, preceding paper. ² P. D. Ritchie et al., J. Chem. Soc., 1955, 2717; 1956, 3563;

^{1957, 524, 2107, 2556.}

with a glycol (e.g., ethylene or propylene glycol): a proportion of a saturated dibasic acid or anhydride (e.g., adipic, sebacic, or phthalic) is commonly added as a third component of the polycondensate, to control the spacing of the CC groupings along the initial chain. This polyester, dissolved in an olefinic monomer (usually styrene) and 'cured,' gives a cross-linked heteropolymer network. The idealised section of such a network shown in the Figure indicates the type of structure which has been suggested 4,5 and widely accepted. Here B represents a segment where cross-linking is achieved by incorporation of an unsaturated acid residue of type A into the growing polyvinyl chain derived from CH2:CR1R2, with the formation of an $\alpha\beta$ -disubstituted succinic acid residue. The work to be described was intended to determine (i) where overall thermal breakdown commences (within the copolyester chain of A and C residues; and this paper describes the pyrolytic behaviour of models (II) and (III), related to the formal segment A(1), and (IV), related to segment A(2). Succeeding papers will describe the pyrolysis of models related to the cross-linking segment B and the saturated segment C.

RESULTS AND DISCUSSION

Preliminary pyrolyses (liquid phase: ca. 400-500°) of molten poly(ethylene fumarate) (DP_n ca. 2-9) showed the breakdown to be complex: its immediately striking features were (i) that the gaseous pyrolysate contains ca. 60-75% of carbon dioxide, and little carbon monoxide, the complete reverse of the results² for poly(ethylene terephthalate), and (ii) that no maleic anhydride is detectable in the non-gaseous pyrolysate. At first this result is surprising, since simple esters of certain other dibasic acids (e.g., alkyl phthalates⁶



within the polyvinyl chain; at their point of junction B; or competitively at all three sites); (ii) whether any breakdown within the copolyester chain occurs preferentially at an unsaturated (A) or a saturated (C) residue (for various values of x), or competitively at both; and (iii) what is the mechanism of each operative mode of breakdown. and monomeric ethylene succinate 7) yield the appropriate cyclic anhydride on pyrolysis. It is explained, however, by the fact that during polycondensation of maleic anhydride with glycols there is strong $cis \longrightarrow$ trans geometrical inversion, ^{5,8} with formation of what is essentially poly(ethylene fumarate), though a minor content of maleic groupings may persist.

$$\begin{array}{c} A(1) \\ (I) & & & \\ & & \\ (I) & & & \\ & & \\ & & \\ (II) & & \\ & & \\ & & \\ (II) & CH \cdot CO_2 Alk \\ & & \\$$

As in previous work,² the problem was approached by studying the breakdown of simple model esters representing specific segments of the polymer. Poly-(ethylene fumarate) (I) is a sequence of type A residues, In view of the complexity of the pyrolysate from polyester (I), attention was turned to models (II)—(IV).*

Alkyl Maleates (II) and Fumarates (III).—Ethyl maleate and fumarate. The maleate was studied in some detail, but only one run (Table 1, Run 6) was made with the fumarate before the work was suspended. In Run 3

1955, **18**, 497. ⁶ W. Nagel and R. H. Abelsdorff, Wiss. Veröff. Siemens, 1926, 5, 193. P. D. Bitchie, *J. Chem. Soc.* 1935, 400.

5, 193; P. D. Ritchie, J. Chem. Soc., 1935, 400. ⁷ M. Tilicheev, J. Soc. phys.-chem. russe, 1925, 57, 143.

⁸ H. Batzer and B. Mohr, *Makromol. Chem.*, 1953, **8**, 217; S. S. Feuer, T. E. Bockstahler, C. A. Brown, and I. Rosenthal, *Ind. Eng. Chem.*, 1954, **46**, 1643; B. T. Hayes and R. F. Hunter, *Chem. and Ind.*, 1957, 559; I. V. Szmercsányi, K. Maros, and A. A. Zahran, 4th Internat. Reinforced Plastics Conf., Brit. Plast. Fed., 1964, Paper No. 6A.

^{*} The programme had to be curtailed abruptly before the trans-models (III) were fully investigated, because three separate workers on the problem developed severe dermatitis. Their work overlapped, so that the substance or substances responsible could not be identified with certainty: nevertheless, it seems desirable to record a general caveat on this health hazard. One worker handled maleic and fumaric esters (mainly ethyl) and their pyrolysis products for over a year without trouble, and then suddenly contracted a dermatitis on the hands. Once sensitised, he appeared to become susceptible to an unspecific range of common chemicals, but was little troubled by acrylic esters: whereas a second worker developed a severe rash on handling the latter and their pyrolysis products. The third worker developed a similar rash only a few days after first handling methyl maleate and fumarate. The use of proprietary barrier creams was only a partial safeguard and palliative.

B. Berndtsson and L. Turunen, Kunststoffe, 1954, 44, 430.
M. Gordon and B. M. Grieveson, J. Polymer Sci., 1955, 17, 107; M. Gordon, B. M. Grieveson, and I. D. McMillan, *ibid.*,

TABLE 1Pyrolysis of ethyl maleate (II; Alk = Et), methyl maleate (II; Alk = Me), ethyl fumarate (III; Alk = Et), methyl fumarate (III; Alk = Me), and fumaric acid

	•	·				(III:	(III:	Fumaric
Pyrolysand	(II; $Alk = E$	t)	(II; Alk	x = Me	Alk = Et	Alk = Me	acid
Run no.	1	2	3	4	5	6	7	8
Temperature	400°	450°	500°	500°	500°	500°	500°	400°
Reaction vessel	V/176	V/176	V/176	P/220	P/220	V/176	P/220	P/220
Feed-rate (g./min.)	0.70	0.70	0.80	0.36	0.13	0.66	0.13	0.43
Residence time (sec.)	31	31	36	83	23	43	23	63
Wt. pyrolysed (g.)	77.5	100.0	172.0	55.0	20.0	40.0	20.0	15.0
(a) Liquid pyrolysate (g.)	49.0	61.0	134.5	16.0	3.0	14.9	$3 \cdot 0$	t
(b) Solid pyrolysate (g.)	Nil	Nil	Nil	9.0	11.0	f 14·2	11.0	14.0
(c) In cold trap (g.)	Nil	Nil	Nil	$1 \cdot 0$	0.5	Nil	0.5	t
(d) Gaseous pyrolysate (l.)	11.8	$24 \cdot 9$	27.0	16.4	$5 \cdot 3$	12.9	$2 \cdot 0$	0.2
Composition (%) of (d) $(approx.)$:								
со	t	0.5	2.5	32	41	4	20	t
со,	14	16	18	57	45	15	57	83
Alkvne	0.5	1	2	t	t	3		Nil
СН, СН,	85	83	78	t	t	77		17
СН, СНМе	Nil	Nil	Nil	11	14	Nil		Nil
Unsaturated (total)	85.5	84	80	11	14	80	7	17
Alkane	t	t	t	t	t	t	9	Nil
Н	Nil	Nil	Nil	t	t	Nil	7	Nil
Decomposition (%)			89	95	95		40	t
Carbonisation in vessel (g.)	—-			12	5		3	1
	,	T 1	11.1.4		-			

(the most detailed experiment) ethyl maleate gave at $ca.500^{\circ}$ a pyrolysate containing some 11% of unchanged ester, together with a complex mixture of products whose formation is best interpreted by Scheme 1. The



predictable A^1 scission of ethyl esters is the predominant primary route (ca. 66%), in competition with C^2 scission

t = Trace, l = light, - = not observed.

(ca. 27%), B^2 scission (ca. 2-3%), and cis \rightarrow trans inversion (ca. 4-5%). All the substances shown were actually identified, except for two postulated intermediates shown in square brackets, which are likely to be highly labile. Scheme 1 is simplified by the omission of ethylene, carbon monoxide, and carbon dioxide (from A^1 , C^1 , and C^2 scission respectively) and acetaldehyde (from any of the CO₂Et groups, by minor B^2 scission). Accurate quantitative analysis of such a complex pyrolysate being almost impracticable, the percentage figures shown should be regarded as approximate.

The true extent of $cis \longrightarrow trans$ inversion during pyrolysis is unknown, though it is certainly incomplete under the conditions used. The figure of 4-5% is based on the observed amount of fumaric acid (which as indicated by the broken arrows may have more than one immediate precursor), but must be regarded as a minimum, since the observed A^1 , B^2 , and C^2 scission products must have arisen in part from the rearranged (trans) ester as well as the original *cis*-ester. (Also, as shown later, there is more than 60% of *cis* \longrightarrow *trans* inversion in the pyrolysis of methyl maleate.)

The observed primary C^2 scissions, and the secondary C^2 scissions of some of the primary products, provide further examples of the known decarboxylation ^{2,9} of esters having unsaturation immediately adjacent to the $\cdot CO_2$ grouping. They are, however, novel in that previous examples have concerned either alkenyl esters (where A^2 scission requires higher temperatures than does C^2 scission ¹⁰) or phenyl esters (where A^1 scission is structurally precluded). With the maleic ester, A^1 scission is such a strong competitor that it predominates

⁹ H. M. Mackinnon and P. D. Ritchie, J. Chem. Soc., 1957, 2564.
¹⁰ P. E. Reininger and P. D. Ritchie, I. Chem. Soc., 1963.

¹⁰ P. E. Reininger and P. D. Ritchie, *J. Chem. Soc.*, 1963, 2678.

to the extent of ca. 66%: nevertheless, C^2 scission still occurs markedly in the competition (ca. 27%).

The configurations of the observed β -ethylacrylic acid and ester are not known: but the hex-3-ene produced from the latter showed the i.r. absorption characteristics of the *trans*-olefin.

Methyl maleate and fumarate. Here the easy A^1 scission is structurally precluded, although primary scission to acid and ethylene may still formally occur at

by the omission of carbon monoxide, carbon dioxide, and formaldehyde (from C^1 , C^2 , and B^2 scissions respectively).

It is possible that, before its inversion, part of the original maleate may make some direct minor contribution to the primary C^2 and B^2 scissions. Nevertheless, in summary, the facts as a whole indicate (i) that for ethyl maleate, A^1 scission dominates the competitive primary breakdown, but (ii) that for methyl maleate the



higher temperatures by the A^0 scission ¹¹ undergone by other alkyl esters lacking a β -hydrogen atom (presumably via a transient carbene). This absence of A^1 scission gives a relatively uncomplicated pyrolysate from methyl maleate: and *direct* observation of any cis \longrightarrow trans inversion is facilitated by the fact that here the fumarate is a solid. At ca. 500° (Runs 4 and 5), the pyrolysate contains at least 60% of methyl fumarate, and since no methyl maleate could be detected, it is probable that primary thermal inversion is complete, or nearly so. Scheme 2 appears to be the best interpretation of the results obtained before the work had to be suspended: it is again simplified, this time

¹¹ For nomenclature, see E. Jones and P. D. Ritchie, *J. Chem. Soc.*, 1960, 4141.

dominating primary reaction is the rearrangement (R), so that the C^2 and B^2 products arise chiefly by secondary breakdown of the inverted (*trans*) ester.

Various intermediates are shown in Schemes 1 and 2, e.g., acrylic, β -ethylacrylic, and crotonic esters, and most of the corresponding acids and aldehydes. Several of these observed intermediates (and related models) have been prepared and pyrolysed separately,¹ to find whether their partial secondary breakdown contributes significant minor components to the total complex pyrolysates, and to confirm that the suggested reaction schemes are realistic.

Ethylene Diacrylate (IV; R = H) and Dimethacrylate (IV; R = Me).—These models were selected in order to find whether A^1 scission of poly(ethylene

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fumarate) (I), with formation of vinyl ester end-groups, plays the same governing role in the pyrolysis as in the known case ² of poly(ethylene terephthalate). It was found that at *ca.* $450-500^{\circ} A^{1}$ scission is an important primary reaction in the competition, but that C^{2} scission is the predominating route. Scheme 3 is the best interpretation of the results. Like Schemes 1 and 2, it has been simplified by the omission of carbon monoxide and dioxide, and, in addition, by limiting the listed products to those of the three competing primary scissions and of one major secondary reaction of each primary product: it should be remembered that several of these undergo minor competing scissions which contribute further minor components to each pyrolysate. minor B^2 scission observed for the latter ¹⁰ could not be detected (Scheme 4). The competing routes differed in quantitative importance from those of vinyl benzoate: the gaseous pyrolysate from the latter contained carbon monoxide (ca. 75%), carbon dioxide (ca. 15%), and unsaturated hydrocarbons (ca. 5%) (cf. 39, 39, and 22% respectively for vinyl acrylate). In other words, for vinyl acrylate C^2 scission is at least as important qualitatively as the R/C^1 sequence.

Application of Results to Poly(ethylene Fumarate) (I).— The variation of the behaviour of polyester (I) over the temperature range $ca. 250-400^{\circ}$ can now be considered in the light of the foregoing results. At $ca. 250^{\circ}$, in an atmosphere of oxygen-free nitrogen, there is further

TABLE 2

Pyrolysis of ethylene diacrylate (IV; R = H), ethylene dimethacrylate (IV; R = Me), and vinyl acrylate (V)

Pyrolysand	(IV; $R = H$)			(IV; $R = Me$)			(V)	
Run no.	9	10	11	12	13	14	15	16
Temperature	400°	450°	500°	500°	500°	500°	500°	500°
Reaction vessel	P/20	P/220	P/220	P/220	V/176	V/176	V/176	P/20
Feed-rate (g./min.)	0.26	0.31	0.21	0.31	0.38	0.32	Ó·31	0.23
Residence time (sec.)	14	122	180	122	75	90	93	8
Wt. pyrolysed (g.)	25.0	30.0	25.0	20.0	100.0	100.0	156.0	$7 \cdot 0$
(a) Liquid pyrolysate (g.)	24.0	19.0	11.0	7.0	63.6	61.9	97.0	5.0
(b) Solid pyrolysate (g.)	Nil	Nil	t	t	Nil	Nil	Nil	Nil
(c) In cold trap (g.) \dots	Nil	t	t	t	Nil	Nil	Nil	t
(d) Gaseous pyrolysate (l.)	t	4.6	$6 \cdot 2$	4 ·8	25.8	$22 \cdot 6$	35.3	0.3
Composition (%) of (d) (approx.):								
со	t	40	46	44	39	30	29	39
CO,	Nil	34	32	35	36.5	35.5	37	39
Alkyne	t	4	2	3	2	2	2	
CH ₂ :CH ₂	t	22	19	18	Nil	Nil	Nil	
CH ₂ :CHMe	t	t	t	t	12	11	12	—
CH ₂ :CMe ₂	Nil	Nil	Nil	Nil	8	9	8	
Unsaturated (total)	t	26	21	21	22	22	22	22
Alkane	Nil	t	t	t	12	12	11	t
Decomposition (%)	t	63	84	85		<u></u>	85	57
Carbonisation in vessel (g.)	1	6	7	8				1

Qualitatively, Scheme 3 represents the results for both the diacrylate (R = H) and the dimethacrylate (R = Me): but the pyrolysates are so complex that quantitative results are difficult to obtain. The approximate percentage figures given refer to the dimethacrylate (Table 2, Run 15): equally significant figures could not be obtained for the diacrylate, but again the primary C^2 and A^1 scissions predominated.

The lower part of Scheme 3 was confirmed by separate studies on the A^1 scission products of ethylene diacrylate (vinyl acrylate and acrylic acid). These compounds, refluxed together at 90—100°, yielded acetaldehyde and acrylic anhydride (just as vinyl benzoate and benzoic acid yield acetaldehyde and benzoic anhydride ¹²) by addition-disproportionation (D): at this temperature, acrylic anhydride is sufficiently stable to survive, though at higher temperatures it is destroyed ¹³ by intra-acyl scission (E) followed by further breakdown of the labile products. Pyrolysed alone (ca. 500°: Table 2, Run 16), vinyl acrylate (V) gave results qualitatively parallel to those of vinyl benzoate, though the very

¹² R. J. P. Allan, E. Jones, and P. D. Ritchie, J. Chem. Soc., 1957, 524.

progressive polycondensation with elimination of water: the DP_n rises smoothly from *ca*. 5 to *ca*. 48 after 60 min., and after a further 15 min. the polymer becomes insoluble, presumably owing to cross-linking *via* the

	$\stackrel{\text{Minor}}{\longrightarrow} \text{CH}_2:\text{CH}\cdot\text{CO}_2\text{H} + \text{CH}:\text{CH}$	A²
CH2:CH·CO2·CH:CH2-	Major [CH ₂ :CH·CO·CH ₂ ·CHO]	R
(V)	$\mathbf{H}_{2}:CH\cdot COMe + CO$	C1
	$\stackrel{\text{Major}}{\longrightarrow} \text{CH}_2:\text{CH-CH:CH}_2 + \text{CO}_2$	C²
	Scheme 4	

•CH:CH• groups. (At *ca.* 300°, insolubility is produced after only 10 min., and there is much darkening.) Up to this point, there is little breakdown of polymer backbone, but at *ca.* 350° (15 min.) carbon monoxide and dioxide, and unsaturated hydrocarbons, are evolved (Table 3). If molten polyester (I) is allowed to flow into

¹³ Part XXIV, A. L. Brown and P. D. Ritchie, *J. Chem. Soc.* (C), 1968, 2007.

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a vapour-phase reaction vessel at $ca. 400^{\circ}$, all tendency towards further polycondensation is completely overcome by A^1 chain-scission, with complicated secondary breakdown of the new end-groups, as demonstrated by the behaviour of models (II)—(IV); there is also marked carbonisation. C^2 Scission competes strongly with this A^1 scission, and the polymeric product completely loses its original fumarate structure, as shown by the disappearance of the characteristic i.r. absorption band at ca. 975 cm.⁻¹. To account for its complete ultimate absence, it is not necessary to postulate the C^2 elimination of all $\cdot CO_2$ groups: the DP_n of polyester (I) is usually only ca. 2-9, and random elimination of about half of the •CO₂• groups in this short chain, on average about one from each neighbouring pair, would bring about the observed result. Scheme 5, in which three (marked *) of six $\cdot CO_2$ groups in a short polyester chain are eliminated at random, illustrates the resulting loss of fumarate structure.

Poly(2,2-dimethyltrimethylene Fumarate) (VI) and Poly(p-phenylene Fumarate) (VII).—These polyesters were prepared and pyrolysed to demonstrate that

EXPERIMENTAL

Apparatus and Procedure.-Vapour-phase flow-pyrolyses were run, and the pyrolysates analysed, as described in the preceding paper,¹ except that in certain runs (Table 1, Runs 1-3, 6) the reaction vessel was used pre-carbonised, without burning-off after the previous run. Tables 1 and 2 summarise the general experimental conditions and gas analyses for 16 such runs. Two static reaction vessels were also used for melt-phase pyrolyses, S.1 consisting of a Pyrex test-tube (5 in. by 1 in.) supported in a vertical electric furnace, and S.2 consisting of a three-necked 50 ml. Pyrex flask with nitrogen inlet, thermocouple pocket, and take-off condenser, heated in a Wood's-metal bath.

Materials Pyrolysed.—Maleic and fumaric esters (II, III). These were pure compounds from British Drug Houses Ltd.

Ethylene diacrylate. Prepared in 33% yield by a standard method,¹⁶ this ester had b.p. 65°/1 mm., 90-94°/3 mm., $n_{\rm D}^{20}$ 1·455 (lit.,¹⁶ b.p. 90—94°/2—3 mm., $n_{\rm D}^{20}$ 1·455: lit.,¹⁷ b.p. 62-65°/0.9 mm., $n_{\rm D}^{20}$ 1.455-1.457).

Ethylene dimethacrylate. This ester, containing 1% quinol, was obtained from Imperial Chemical Industries Limited. Freed from stabiliser by washing with alkali, and redistilled, this yielded a main fraction, b.p. $122-126^{\circ}/$ 15 mm. (lit.,¹⁸ b.p. 122-126°/15 mm.).

HO·CH₂·CH₂·ČO₂·CH:CH·CO₂·CH₂·CH₂·O₂C·CH:CH·ČO₂·CH₂·CH₂·O₂C·CH:CH·CO₂·CH₂·CH₂·CH₂·OH

HO·CH₃·CH₃·CH:CH·CO₃·CH₃·CH₃·O₃C·CH:CH·CH₂·CH₂·O₂C·CH:CH·CH₂·CH₂·OH SCHEME 5

although A^1 scission is here structurally precluded, other types of breakdown still occur in both polyesters by C^2 scission, and in (VI) probably also by B^2 scission (cf. Golomb and Ritchie¹⁴). It has been shown that poly(2,2-dimethyltrimethylene terephthalate), lacking a β -hydrogen atom, is more thermostable than poly-(ethylene terephthalate),¹⁵ and that of the corresponding models 2,2-dimethyltrimethylene dibenzoate and ethylene dibenzoate the former, also lacking a β -hydrogen atom, is the more thermostable.¹⁴ Nevertheless, polyesters (I), (VI), and (VII) all eliminate carbon dioxide

$H \cdot [O_2 C \cdot CH : CH \cdot CO_2 \cdot CH_2 \cdot CMe_2 \cdot CH_2]_n \cdot OH$ (VI) $H \cdot [O_2 C \cdot CH: CH \cdot CO_2 \cdot C_6 H_4]_n \cdot OH$ (VII)

with roughly equal facility, as shown in Table 3. The fact that the three onset temperatures $T(CO_2)$, $T(R \cdot CHO)$, and T(unsats.) for polyester (I) are not affected by the incorporation of various inhibitors of free-radical reactions agrees with the previous conclusion ¹⁰ that (with the exception of intra-acyl scission ⁹) the reactions observed to compete in the pyrolysis of esters are not free-radical in character.

¹⁶ Imperial Chemical Industries Ltd. and R. Hill, B.P. 423,790/1933.

¹⁷ J. G. Burtle, J. C. Saam, and L. C. Mokrasch, J. Org. Chem., 1952, 17, 1302.

Vinyl acrylate. Prepared in 15% yield by Adelmann's method,¹⁹ this ester had b.p. 94-96° (lit.,²⁰ b.p. 94-96°).

Poly(ethylene fumarate). Polyester with DP_n ca. 5 was prepared and purified as described by Gordon et al.5

Poly(2,2-dimethyltrimethylene fumarate). This was prepared similarly from 2,2-dimethylpropan-1,3-diol and maleic anhydride, as a clear colourless resin, more viscous and softening more readily than polyester (I), for samples prepared by similar periods of heating.

Poly (p-phenylene fumarate). This was similarly prepared from quinol and maleic anhydride. The polymer was very dark, and was hard and brittle, but softened at ca. 100°. It was of low DP_n , being soluble in 5% aqueous sodium hydroxide, from which it was precipitated unchanged on acidification.

Reference Standards.-The following compounds were prepared for use as reference standards in i.r. spectrometric analysis of the pyrolysates.

β-Ethylacrylic acid. Prepared from propionaldehyde and malonic acid in presence of pyridine, the acid had b.p. 195-201° (lit.,²¹ b.p. 195-197°: lit.,²² b.p. 200-201°).

Ethyl β-ethylacrylate. Esterification of the foregoing acid yielded the ester, b.p. 155-160° (lit.,²¹ b.p. 155-160°).

Vinyl methacrylate. Interaction of vinyl acetate and methacrylic acid (Adelmann's method 19) gave the ester in fair yield, b.p. 110° (lit., 20 b.p. 112°).

2,5-Dimethylhexa-1,5-diene. The hydrocarbon, b.p.

¹⁸ T. L. White, J. Chem. Soc., 1943, 238.

²¹ A. W. Crossley and H. R. Le Sueur, J. Chem. Soc., 1899, 75, 166.
²² R. Fittig and J. E. Mackenzie, Annalen, 1894, 283, 85.

¹⁴ A. Golomb and P. D. Ritchie, J. Chem. Soc., 1958, 4515.

¹⁵ H. A. Pohl, J. Amer. Chem. Soc., 1951, 73, 5660.

R. L. Adelmann, J. Org. Chem., 1949, 14, 1057.
W. Bauer and C. T. Kautter, U.S.P. 2,363,286/1944.

113-114°, $n_{\rm D}^{22}$ 1.4306, was prepared by the action of metallic sodium on 3-chloro-2-methylprop-1-ene (lit.,²⁵ b.p. 114°, $n_{\rm p}^{20}$ 1·4293).

2-Methylbut-1-ene-4-ol. This compound, b.p. 130°, was prepared in poor yield, on the lines described by Linsted and Rydon ²⁴ for the lower homologue but-1-ene-4-ol.

Pyrolyses.—Ethyl maleate (Runs 1-3). These three runs were made in a pre-carbonised reaction vessel, and gave very consistent gas analyses. Run 3 (the largest) gave a liquid pyrolysate (134.5 g.) from which a few crystals of fumaric acid separated: filtered and distilled, it yielded (i) 0.5 g., b.p. 20°/660 mm., (ii) 16.8 g., b.p. 60-85°, (iii) 0.5 g., b.p. 95-105°, (iv) 4.5 g., b.p. 135-145°, (v) 0.9 g., b.p. 155-160°, (vi) 72.0 g., b.p. 190-205°, (vii) 23.2 g., b.p. 205-220°, and (viii) 16.6 g., solid brown residue. Fraction (i) was mainly acetaldehyde. Fraction (ii), redistilled, yielded 2.0 g. of crude hex-3-ene, b.p. 65-70°. Further fractionation yielded a purer specimen, b.p. 67.5°, n_D²⁰ 1.388 (lit.,²⁵ cis, b.p. 66.8-66.9°/741 mm., $n_{\rm D}^{20}$ 1·3934; trans, b.p. 67·4—67·6°/741 mm., $n_{\rm D}^{20}$ 1·3938): its i.r. absorption spectrum included bands characteristic of both the cis and the trans isomer.26 Fraction (iii) contained water (giving sym-diphenylurea on treatment with phenyl isocyanate): dried (CaCl₂), the residue consisted of ethyl acrylate (i.r.). Fraction (iv), redistilled, yielded acrylic acid, b.p. 140° (i.r.). Fraction (v), redistilled, yielded ethyl β -ethylacrylate, b.p. 155—160° (lit.,²¹ b.p. 155—160°), and fraction (vi) similarly yielded β -ethylacrylic acid, b.p. 197-201° (lit.,22 b.p. 195-197°; lit.,22 b.p. 200-201°), both identified by i.r. spectra with synthetic reference specimens. Fraction (vii), filtered, washed with alkali, and redistilled, yielded a mixture, b.p. 210-214°, of ethyl maleate and ethyl fumarate (molar ratio ca. 3:1; i.r.). Residue (viii), combined with solids removed by filtration from fractions (vi) and (vii), and sublimed, yielded a mixture of maleic acid and fumaric acid. No acraldehyde could be detected in fractions (ii)-(vii).

Methyl maleate (Runs 4, 5). Run 4 (the larger) gave a liquid pyrolysate (16 g.) from which crystalline methyl fumarate (ca. 6.5 g.) was removed by filtration, and gaseous formaldehyde by passing a gentle current of carbon dioxide; the remainder on distillation yielded five fractions: (i) b.p. 45-63° (crude acraldehyde, polymerising in the condenser on redistillation), (ii) b.p. 75-90° (yielding methyl acrylate, b.p. 80-85°, on redistillation), (iii) b.p. 100-110° (vielding crotonaldehyde, b.p. 104-105°, on redistillation), (iv) b.p. 115-125° (largely methyl crotonate, b.p. 121°), and (v), b.p. 200-250°, mainly methyl fumarate (solidifying in the condenser) but containing no methyl maleate. Run 5 was made for the purpose of measuring the extent of $cis \rightarrow trans$ inversion as accurately as possible; the non-gaseous pyrolysate, carefully fractionated, gave methyl fumarate (ca. 61% of theory).

Ethyl fumarate (Run 6). The liquid pyrolysate was not fractionated, the work being suspended at this point for the reason stated earlier. The gaseous pyrolysate was very similar in composition to that from ethyl maleate.

Methyl fumarate (Run 7). A trace of propene was identified in the cold trap. The main liquid pyrolysate contained formaldehyde, acraldehyde, methanol, methyl acrylate,

²³ A. L. Henne, H. Chanan, and A. Turk, J. Amer. Chem. Soc., 1941, 63, 3474.

 R. P. Linstead and H. N. Rydon, J. Chem. Soc., 1934, 1995.
K. N. Campbell and L. T. Eby, J. Amer. Chem. Soc., 1941, 63, 216.

water, crotonaldehyde, and methyl crotonate. The solid pyrolysate was crude methyl fumarate.

Ethylene diacrylate (Runs 9-12). The results from Run 10 are typical The cold trap contained propene, buta-1,3-diene, and acetaldehyde. The liquid pyrolysate (19.0 g.), distilled, yielded (i) 0.3 g., b.p. 114°, (ii) 0.2 g., b.p. 114-120°, (iii) 2.5 g., b.p. 120-150°, (iv) 0.7 g., b.p. 25-65°/1.5 mm., (v) 3.5 g., b.p. 65-70°/1.5 mm., and (vi) 11.0 g., b.p. 70°/1.5 mm. There was a very small residue. Fractions (i)-(iii) contained acraldehyde: fractions (ii) and (iii) also contained hexa-1,5-diene and methyl vinyl ketone (i.r.). Fraction (iv) contained vinyl acrylate (yielding acrylic acid and acetaldehyde on alkaline hydrolysis) and water. Fractions (v) and (vi) were mainly unchanged pyrolysand.

Ethylene dimethacrylate (Runs 13-15). The results from Run 15 are typical. On distillation, the liquid pyrolysate yielded eleven fractions: (i) b.p. 20°/660 mm. (mainly acetaldehyde), (ii) b.p. 30-40° (mainly isoprene: i.r.), (iii) b.p. 50-60° (mainly acetone), (iv) b.p. 60-76° (mainly methacraldehyde), (v) b.p. 95-105° [contained water, and on redistillation after drying (CaCl₂) yielded methyl isopropenyl ketone, b.p. 98-102°: i.r.], (vi) b.p. 105-120° (on further fractionation yielded a mixture, b.p. 110-114°, of vinyl methacrylate and 2,5-dimethylhexa-1,5-diene: i.r.), (vii) b.p. 120-145° (small: gave traces of a crude 2,4-dinitrophenylhydrazone, but not characterised), (viii) b.p. 155-165° (methacrylic acid), (ix) b.p. 70-80°/20 mm. (mainly 3-methylbut-3-enyl methacrylate: on alkaline hydrolysis yielded methacrylic acid and a liquid, b.p. 130°, identified as 2-methylbut-1-ene-4-ol by comparison with the i.r. spectrum of a synthetic specimen), (x) b.p. 110-125°/ 13 mm. (mainly unchanged pyrolysand), and (xi) b.p. 80-100°/11 mm. (probably contained methacrylic anhydride: polymerised on standing).

Vinyl acrylate (Run 16). The cold trap contained buta-1,3-diene and acetaldehyde. The liquid pyrolysate, distilled, yielded (i) 1.5 g., b.p. 66-74° (acetaldehyde and

Γа	BLE	3
LA	DLF	J

Thermal breakdown of polyesters	(I),	(VI), and	(VII)
Pyrolysand	(I)	(VI)	(VII)
	~ ~	94	90

Gas evolved (ml./mg. of pyrolysand)	55	34	30
Composition (%) of gas:			
CO	52	50	57
CO,	32	30	39
Unsat. hydrocarbons	16	20	4
Onset temperatures:			
T (CO ₂)	295° *	290°	280°
$T (\mathbf{R} \cdot \mathbf{C} \mathbf{HO})$	305 *	290	†
			1

$T (CO_2)$ $T (R \cdot CHO)$ T (unsats.)		295° * 305 * 305 *	290° 290 335	280° † †

* Not affected by addition of phenanthraquinone, t-butyl-catechol, o-phenylenediamine (1%), quinol (1 and 10%), or benzaldehyde (5%). † No evolution up to ca. 500°.

methyl vinyl ketone), (ii) 1.5 g., b.p. 76-86° (methyl vinyl ketone and unchanged vinyl acrylate), (iii) 1.0 g., b.p. 88-94° (vinyl acrylate), (iv) 2.0 g., b.p. 95-142° (water and acrylic acid), and (v) 1.0 g., b.p. >142° (uncharacterised). Methyl vinyl ketone, treated with phenylhydrazine, yields 27 1-phenyl-3-methylpyrazoline: similarly,

26 Amer. Petroleum Inst. Research Project 44, Nat. Bur. Standards Catalog of Infra-Red Spectral Data, No. 1059 and 621

(1948). ²⁷ E. E. Blaise and M. Maire, Bull. Soc. chim. France, 1908, 3, 270.

treated with 2,4-dinitrophenylhydrazine, it yields 1-(2,4-dinitrophenyl)-3-methylpyrazoline, m.p. 172—174° (Found: C, 48·4; H, 3·8. $C_{10}H_{10}N_4O_4$ requires C, 48·0; H, 4·0%). Poly(ethylene Fumarate) (I), Poly(2,2-dimethyltrimethylene Fumarate) (VI), and Poly(p-phenylene Fumarate) (VII).— In the static reaction vessel S.1 at ca. 250°, in a current of oxygen-free nitrogen, the DP_n of polyester (I) rose from ca. 5 (zero time) to ca. 16 (30 min.) to ca. 48 (60 min.). After 75 min. (or, in a separate run at ca. 300°, after 10 min.) the polymer became insoluble and DP_n could no longer be measured by end-group analysis. Polyesters (I), (VI), and (VII) evolved gases as shown in Table 3, during pyrolysis in static reaction vessel S.2 for 15 min. at ca. 350°. Table 3 includes onset temperatures for the evolution of carbon dioxide, aldehyde, and unsaturated hydrocarbons. These were measured by the apparatus and under the standardised conditions previously described.¹⁰ It must be emphasised that the present pyrolysands are all solid polymers, so that while their onset temperatures form a self-consistent set of comparative figures, they bear no necessary direct relationship to corresponding onset temperatures previously measured ¹⁰ for a group of simple liquid esters.

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