

**215.** *Reactions of Macromolecules. Part III.*<sup>1</sup> *Formation of n-Alkyl Hydrogen Esters from Styrene-Maleic Anhydride Copolymer.*

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Styrene-maleic anhydride copolymer, with pyridine and the first nine alkan-1-ols, yields the corresponding alkyl hydrogen maleate copolymers. Reaction of the anhydride units is virtually complete and is not inhibited by increase in length of the alkyl group.

THE formation of esters by heating styrene-maleic anhydride copolymer with alcohols is described in patents;<sup>2</sup> octyl<sup>3</sup> and octadecyl<sup>4</sup> esters having equivalent weights approximating to those of alkyl hydrogen esters have been prepared. In no instance was esterification effected in the presence of a base, but many examples of the preparation, from phthalic anhydride, of alkyl hydrogen phthalates by Kenyon and his co-workers have shown that base-catalysed esterification proceeds readily and is free from side reactions. This method has now been applied to the reaction of the first nine alkan-1-ols with styrene-maleic anhydride copolymer.

Two aspects of the esterification are of interest. First, it provides information on the reactivity of side-groups of a macromolecule towards a set of reagents bearing a homologous series of alkyl groups. There are no systematic data on this point, and it was possibly the case that, at a critical side-chain length, the attachment of an alkoxy side chain becomes obstructed by those already combined with the main chain to such an extent that reaction cannot be forced beyond a certain degree of alkoxylation. Secondly, the reaction provides a method of preparation, from a single stock of parent anhydride-copolymer, of a sequence of polymers bearing side chains in homologous series.

The copolymer, prepared from equimolar amounts of styrene ( $M_1$ ) and maleic anhydride ( $M_2$ ) with initiation by benzoyl peroxide, is known to be highly alternating: the monomer reactivity ratios are  $r_1 = 0.01$  at  $60^\circ$ ,  $0.04$  at  $80^\circ$ , and  $r_2 = 0$ .<sup>5,6</sup> In our work a large excess of the alcohol was used, and two molecules of pyridine were present to each anhydride unit.

From the equivalents and analyses of the derived copolymers (Table), conversion of the anhydride units into alkyl hydrogen ester units is seen to be nearly complete. No inhibition of alkoxylation with increasing length of the alkyl group occurs under the conditions investigated.

There are two modes of reaction of the alcohol with the anhydride-copolymer, leading to alkyl hydrogen ester units as in (I) and (II). It is not known which is the predominant structure. The mechanism is probably as in (A). The carbonyl group which is nearer the

<sup>1</sup> Part II, Arcus and Halliwell, *J.*, 1962, 2187.

<sup>2</sup> U.S.P. 2,570,846, 2,615,843.

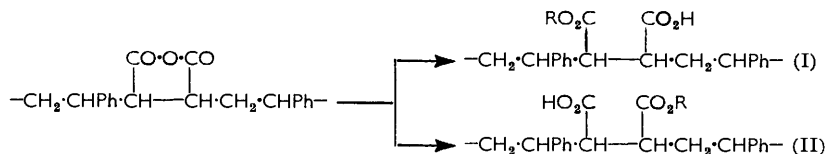
<sup>3</sup> Drinberg, Fundyler, Gorelik, and Frost, *Zhur. priklad Khim.*, 1959, **32**, 1348; *Chem. Abs.*, 1959, **53**, 18,540.

<sup>4</sup> U.S.P. 2,698,297.

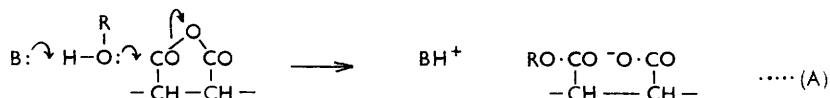
<sup>5</sup> Mayo, Lewis, and Walling, *J. Amer. Chem. Soc.*, 1948, **70**, 1529.

<sup>6</sup> Alfrey and Lavin, *J. Amer. Chem. Soc.*, 1945, **67**, 2044.

phenyl group is subject to the greater electron-withdrawal but also to the greater steric hindrance, and these factors favour (I) and (II), respectively.



The yields of the alkyl hydrogen ester copolymers from the anhydride-copolymer are high (80—97%, Table), and the losses are of the more soluble, mainly low-molecular-weight polymer. Probably, therefore, the weight-average molecular weights of the main chains



of the ester-copolymers differ little from that of the main chain of the anhydride-copolymer from which they were prepared. The alkyl hydrogen ester copolymers thus form a series of macromolecules having approximately the same weight-average chain length but with side chains of which the length increases homologically. The series is expected to be of value in the study of the relation of side-chain length to molecular shape and main-chain flexibility, and, to clarify this relationship, a detailed study of solution viscosities and of unimolecular film characteristics has been undertaken. In order to characterise the present copolymers, viscosity numbers of solutions in acetone are recorded (Table).

#### EXPERIMENTAL

*Styrene-Maleic Anhydride Copolymer.*—Maleic anhydride was recrystallised from chloroform and distilled; it had b. p. 94—96°/20 mm., m. p. 53°. Styrene was thrice washed with *n*-sodium hydroxide and with water, dried (Na<sub>2</sub>SO<sub>4</sub>), and distilled under nitrogen; it had b. p. 48·5—49·5°/24 mm.

Styrene (104 g.), maleic anhydride (98 g.), and benzoyl peroxide (2·42 g.) in “AnalaR” benzene (2·5 l.) were heated under reflux for 1 hr. The copolymer was precipitated; it was filtered off, washed with benzene until the washings no longer decolorised a solution of bromine in carbon tetrachloride, and dried for 5 hr. at 110°. In order to protect the copolymer (182 g.) from moisture, 4-g. portions were sealed in glass tubes, which were opened immediately before use (Found: C, 71·15; H, 5·2. Calc. for C<sub>8</sub>H<sub>8</sub> : C<sub>4</sub>H<sub>2</sub>O<sub>3</sub> = 1 : 1, C, 71·3; H, 5·0%).

*Alkyl Hydrogen Maleate Copolymers.*—Methanol, ethanol, and propanol were dried by treatment with magnesium and a little iodine, and distilled. The other alcohols were dried by potassium carbonate and distilled through a Vigreux column. The identity of each higher alcohol was checked by the preparation of the *N-p*-nitrophenyl- or *N-1*-naphthyl-carbamate. The alcohols had the b. p. and *n*<sub>D</sub><sup>25</sup>, and the carbamates the m. p.s., recorded in the literature.

Pyridine was dried (KOH), distilled (b. p. 115—116°), and kept over potassium hydroxide.

#### 1 : 1 Styrene-alkyl hydrogen maleate copolymers.

Alkyl Group (R)	Yield (g.)	Equivalent (%) *	Equivalent		Found (%)		Required (%) **		Viscosity number
			Found	Calc.**	C	H	C	H	
Methyl .....	8·0	86	234	234	66·35	6·15	66·65	6·0	0·36
Ethyl .....	9·1	92	252	248	66·75	6·4	67·7	6·5	0·47
Propyl .....	10·1	97	259	262	68·2	6·8	68·7	6·9	0·57
Butyl .....	10·0	92	276	276	69·45	7·3	69·55	7·3	0·67
Pentyl .....	10·1	88	293	290	70·3	7·65	70·3	7·65	0·71
Hexyl .....	10·7	89	305	304	71·55	7·9	71·05	7·95	0·73
Heptyl .....	12·1	93	316	318	71·55	8·1	71·65	8·25	0·77
Octyl .....	11·4	87	334	332	72·15	8·35	72·3	8·5	0·76
Nonyl .....	11·0	80	340	346	72·4	8·55	72·8	8·75	0·77

\* On anhydride-copolymer. \*\* For C<sub>8</sub>H<sub>8</sub>, C<sub>2</sub>H<sub>2</sub>(CO<sub>2</sub>R)·CO<sub>2</sub>H.

Styrene-maleic anhydride copolymer (8.0 g.) was heated with pyridine (6.4 g.) and the alcohol (50 ml.) in a flask fitted with a reflux condenser and protected by a drying-tube. The mixtures with methanol were refluxed for 10 hr., and that with ethanol for 24 hr.; those with other alcohols were heated for 12 hr. on a steam-bath. The copolymer dissolved, and in all instances a homogeneous solution was eventually formed.

In order to remove pyridine completely, and to obtain the alkyl hydrogen ester in a satisfactory physical form, it was necessary to alter the method of isolation as the molecular weight increased. For the methyl, ethyl, and propyl esters, the reaction solution was added dropwise with vigorous stirring to *n*-hydrochloric acid (500 ml.). The ester was collected, dissolved in acetone (100 ml.), and precipitated as before. The reaction solutions of the other esters were each diluted with acetone (50 ml.). The butyl ester was precipitated by addition to *n*-hydrochloric acid (1 l.), dissolved in acetone (100 ml.), and reprecipitated as above. The solutions of the higher esters were added dropwise with vigorous stirring to light petroleum (b. p. 60–80°); the precipitate, swollen with petroleum, was dissolved in acetone (100 ml.) and reprecipitated by addition to 0.5*N*-hydrochloric acid (1 l.); dissolution and precipitation were repeated; the product was filtered off, and thrice washed with very dilute hydrochloric acid and with water. The 1:1 *styrene-alkyl hydrogen maleate copolymers*, which formed white powders, required prolonged drying. On being kept for several weeks over sulphuric acid at 20 mm., the methyl-hexyl esters dried to constant weight. This did not suffice for the three higher esters which, however, dried almost completely on being kept adjacent to phosphoric oxide at 40–50°/ < 1 mm. Specimens for analyses and viscosity determinations were finally dried to constant weight at 80°/0.1 mm. (P<sub>2</sub>O<sub>5</sub>).

Equivalent weights were determined by titration against 0.1*N*-sodium methoxide in benzene-methanol, with Thymol Blue, by the method of Fritz and Lisicki<sup>7</sup> as modified by Bamford and Barb,<sup>8</sup> except that the specimen (0.1–0.2 g.) was dissolved in acetone (40 ml.). The end-point was taken at the first blue colour persisting for 1 min.

The viscosity number,  $(\eta_{\text{soln.}}/\eta_{\text{solv.}} - 1)/c$ , ( $c = \text{g. of solute in 100 ml. of solution}$ ) was determined for the alkyl hydrogen maleate copolymer in solution in acetone at 25° and  $c$  1.0.

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<sup>7</sup> Fritz and Lisicki, *Analyt. Chem.*, 1951, **23**, 589.

<sup>8</sup> Bamford and Barb, *Discuss. Faraday Soc.*, 1953, **14**, 208.