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# STRUCTURAL ANALYSIS OF REGULAR COPOLYMERS OF BUTADIENE AND METHYLENE WITH REPEAT UNIT [But—$(CH_2)_n$—But] BY THE USE OF MODEL COMPOUNDS—II

## AN ANALYSIS OF FACTORS WHICH INFLUENCE THE PROPORTION OF 1,2-ADDITION

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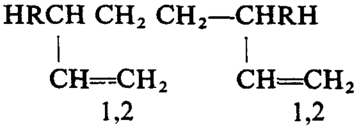
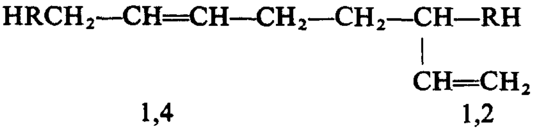
**Abstract**—The structures of regular copolymers of butadiene of repeat unit —[But—R—But]—, where R is an alkyl ligand, are studied by the preparation of model compounds HR—But—But—RH under identical experimental conditions. The effect of varying experimental parameters, such as temperature, ligand, etc., on the probability of 1,2-addition is examined; the differences in activation energy between 1,2 and 1,4 addition are considered.

IN A PREVIOUS PAPER,⁽¹⁾ we described a method for preparing regular copolymers with repeat unit —[MRM]— by the reaction of a diene or vinyl monomer, M, with excess alkali metal and an alkyl dihalide, $RX_2$, in tetrahydrofuran. The process involves the formation from the monomer of a dimer dianion which immediately reacts with the dihalide to produce a polymer of the above repeat unit. Thus, for styrene, the dianion is of the structure $^-CHPhCH_2CH_2CH^-Ph$ and the polymer formed consequently has the repeat unit $-[-CH_2CHPhR\ CHPhCH_2-]-$. Substitution of a monohalide, RHX, for the dihalide produces alkyl terminated dimers of structure HR—M—M—RH,⁽²⁾ which may be regarded as model compounds of the equivalent polymers. The butadiene dimer dianion, however, can be regarded as a mixture of three canonical forms which, on termination with alkyl halide, gives three products (I, II and III).



$$\underset{\substack{|\\ CH{=}CH_2\\ 1,2}}{HRCH}\ CH_2\ CH_2\text{—}\underset{\substack{|\\ CH{=}CH_2\\ 1,2}}{CHRH}$$

I



$$\underset{1,4}{HRCH_2\text{—}CH{=}CH\text{—}CH_2}\text{—}CH_2\text{—}\underset{\substack{|\\ CH{=}CH_2\\ 1,2}}{CH}\text{—}RH$$

II

$$\underset{1,4}{HRCH_2\text{—}CH{=}CH\text{—}CH_2}\text{—}\underset{1,4}{CH_2\text{—}CH{=}CH\text{—}CH_2}\text{—}RN$$

III

Use was made of this in Part I⁽³⁾ to determine the vinyl content of copolymers formed from butadiene, alkyl dihalides and lithium at −15°. The equivalent monohalide was used to terminate the dianion under conditions similar to those used for the polymer preparation and the relative amounts of the three products so formed were estimated by g.l.c. Analysis of the three separated components by $^1H$ n.m.r. spectroscopy showed them to correspond to the structures I, II and III in increasing order of retention times. Separation of the *cis* and *trans* 1,4 isomers was not readily achievable by g.l.c. and so the relative areas of the three peaks were used to determine the probability of 1,2 addition. The results obtained were in good agreement with the values obtained from the n.m.r. spectra of the equivalent polymers and when $n \geqslant 2$ were independent both of the value of $n$ and the nature of the halogen in the alkyl halide.

Since the g.l.c. estimation of the model compounds is more sensitive to small changes in the proportions of 1,2 and 1,4 links, and is probably more accurate, we describe its use in this paper to study the effect of experimental parameters such as temperature, alkali metal, etc., on the structures of the regular copolymers.

## EXPERIMENTAL

The experimental techniques used were very similar to those given in Part I and are only briefly described here. All reactions were carried out under nitrogen and with purified materials. The reaction temperature was selected and maintained at ± 1° by use of a Thermo-watch and Jack-o-matic manufactured by Instruments for Research and Industry. Gas–liquid chromatography analyses were carried out using a Pye–Unicam 104 chromatograph with 7 ft by 0·25 in. outside diameter columns containing embacel coated with 10 per cent Apiezon K by weight.

In a typical reaction, butadiene (0·2 moles) was distilled into a solution of alkyl halide (0·2 moles) in tetrahydrofuran (200 ml) containing excess alkali metal (at least 0·4 moles). The reaction was allowed to proceed at the required temperature for about 4 hr when the solution was filtered and the solvent removed by vacuum distillation. The residue was extracted with an ether–water mixture and the ether solution dried with anhydrous sodium sulphate before removal of the ether to yield pale straw-coloured oils which were then subjected to g.l.c. analysis.

## RESULTS AND DISCUSSION

In Part I it was shown that the mode of reaction of one anionic end of the butadiene dimer is independent of the fate of the other so that in these circumstances simple statistics apply. Thus, if $p$ = probability of 1,2 addition, the probabilities of forming the 1,2–1,2; 1,2–1,4; and 1,4–1,4 adducts are respectively given by $p^2 : 2p(1-p) : (1-p)^2$ and the relative areas of their g.l.c. peaks should consequently be in these ratios. This relationship has been found to hold and so has been used to determine the values of $p$ quoted in this paper.

Table 1 lists the variation with temperature of the relative areas corresponding to the three dimeric products obtained from the reactions of butadiene and lithium with each of the primary alkyl halides, methyl iodide, *n*-propyl iodide and *n*-pentyl bromide. The $p$ values obtained from these results are also listed. Table 2 illustrates the effect of the change of alkali metal counter ion on the proportions of products; Table 3 shows the mode of reaction of secondary and tertiary alkyl halides. Arrhenius plots for the calculated $p$ values gave good linear relationships from which the activation energy differences between 1,2 and 1,4 addition ($\Delta E$) were calculated. These are listed in Table 4.

The $\Delta E$ values obtained are all negative indicating that, in all the reactions studied, the activation energy for 1,2 addition is less than that for 1,4 addition. With the exception of the methyl iodide–lithium reaction, the differences are quite small and so the mode of reaction is relatively insensitive to temperature changes. These observations are in general agreement with the results obtained for the anionic homopolymerization

TABLE 1. INFLUENCE OF TEMPERATURE ON THE PROPORTION OF 1,2 ADDITION FOR PRIMARY HALIDES

| T (°C) | $C_5H_{11}$ Br | | | | $C_3H_7I$ | | | | $CH_3I$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Peak areas | | | $p\times100$ | Peak areas | | | $p\times100$ | Peak areas | | | $p\times100$ |
| | I | II | III | | I | II | III | | I | II | III | |
| +15 | 12·8 | 47·1 | 40·1 | 36·4 | 12·5 | 45·8 | 41·7 | 35·4 | | | | |
| + 5 | 12·7 | 46·8 | 40·5 | 36·1 | 13·2 | 46·0 | 40·8 | 36·2 | | | | |
| − 5 | 14·0 | 48·8 | 37·2 | 38·4 | 13·4 | 46·1 | 40·5 | 36·6 | 3·4 | 37·5 | 59·1 | 22·2 |
| −15 | 16·0 | 50·1 | 33·9 | 41·4 | 15·2 | 47·3 | 37·4 | 38·9 | 4·7 | 41·5 | 53·8 | 25·5 |
| −30 | 15·7 | 49·6 | 34·7 | 40·5 | 15·1 | 46·8 | 38·1 | 38·5 | 8·5 | 41·4 | 50·1 | 29·2 |
| −45 | 16·3 | 49·5 | 34·2 | 41·1 | 16·4 | 47·6 | 36·0 | 40·2 | 10·1 | 43·4 | 46·5 | 31·8 |

I = 1,2 − 1,2 addition
II = 1,2 − 1,4 addition
III = 1,4 − 1,4 addition

TABLE 2. THE EFFECT OF ALKALI METAL ON THE MODE OF REACTION OF BUTADIENE WITH PRIMARY HALIDES

| T (°C) | Alkali metal | $C_3H_7I$ | | | | $CH_3I$ | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Peak areas | | | $p \times 100$ | Peak areas | | | $p \times 100$ |
| | | I | II | III | | I | II | III | |
| +10 | Na | 10·7 | 45·5 | 43·8 | 33·5 | 4·1 | 34·1 | 61·8 | 21·2 |
| −15 | Na | 11·7 | 45·2 | 43·1 | 34·3 | 5·1 | 34·5 | 60·4 | 22·4 |
| −45 | Na | 12·5 | 46·1 | 41·4 | 35·6 | 5·1 | 37·0 | 57·9 | 23·6 |
| +10 | K | 7·7 | 46·1 | 46·2 | 30·8 | | | | |
| −15 | K | 8·2 | 45·9 | 45·9 | 31·1 | 4·2 | 30·3 | 65·5 | 19·4 |
| −45 | K | 9·3 | 45·0 | 45·7 | 31·8 | | | | |

TABLE 3. MODE OF REACTION OF SECONDARY AND TERTIARY HALIDES WITH BUTADIENE

| T (°C) | Halide | Alkali metal | Peak areas | | | $p \times 100$ |
|---|---|---|---|---|---|---|
| | | | I | II | III | |
| −15 | $(CH_3)_3CBr$ | Li | 8·9 | 36·4 | 54·7 | 27·1 |
| −15 | $(CH_3)_3CBr$ | Na | 5·8 | 30·8 | 63·4 | 21·2 |
| −15 | $C_2H_5CH(CH_3)Br$ | Li | 24·4 | 50·8 | 24·8 | 49·8 |
| −15 | $(CH_3)_2CHI$ | Li | 22·9 | 49·7 | 27·4 | 47·8 |
| −15 | $(CH_3)_2CHI$ | Na | 20·5 | 51·2 | 28·3 | 46·1 |
| +10 | $(CH_3)_2CHBr$ | Li | 27·1 | 51·4 | 21·5 | 52·8 |
| −15 | $(CH_3)_2CHBr$ | Li | 28·2 | 51·9 | 19·9 | 54·2 |
| −45 | $(CH_3)_2CHBr$ | Li | 31·0 | 51·8 | 17·2 | 56·9 |

of butadiene(4) and *iso*prene(5) in tetrahydrofuran although the percentage of 1,2 linking is very much greater in the polymerization processes than in the alkyl halide reactions. Within the small activation energy differences obtained, however, it may be seen that on change of alkali metal, $\Delta E$ lithium > $\Delta E$ sodium > $\Delta E$ potassium.

Table 1 supports the observation in Part I that the percentage of 1,2 addition is independent of the halogen and ligand in the series $H(CH_2)_nX$ when $n > 2$, and shows

TABLE 4. ACTIVATION ENERGY DIFFERENCES BETWEEN 1,2 AND 1,4 ADDITION

| Halide | Alkali | $\Delta E$ (kcal/mole) |
|---|---|---|
| $CH_3I$ | Li | (−1·54) |
| $n$-$C_3H_7I$ | Li | (−0·44) |
| $n$-$C_5H_{11}Br$ | Li | (−0·49) |
| $CH_3I$ | Na | (−0·29) |
| $n$-$C_3H_7I$ | Na | (−0·25) |
| $n$-$C_3H_7I$ | K | (−0·11) |
| $(CH_3)_2CHBr$ | Li | (−0·36) |

that this independence holds over a wide temperature range. The reaction between butadiene, lithium and methyl iodide results in smaller $p$ values than the other primary alkyl halides and a much larger activation energy difference, supporting the suggestion that a differently shaped transition state is involved.

The influence of the dimer counter ion on the relative proportion of products obtained is illustrated in Tables 1 and 2. As the size of the counter ion increases, the proportion of 1,2 addition decreases. This trend is observed with both the secondary and tertiary alkyl halides (Table 3) and is also found in the homopolymerization of butadiene$^{(4)}$ when the complete range of alkali naphthalene complexes were used as initiators and the structures of the resulting polymers analysed.

It is interesting to note that the replacement of lithium by sodium in the reaction involving methyl iodide results in a fall in the activation energy difference from −1·5 kcal/mole to the more generally observed value of −0·2 kcal/mole, although the percentage of vinyl linking remains significantly lower than for other primary halides. We are unable to explain this difference at this stage.

Table 3 clearly shows that the mode of reaction depends markedly on the structure of the halide employed. At constant temperature and alkali metal, the probability of 1,2-placement changes in the order secondary > primary > tertiary. Furthermore, variation of the secondary halide structure shows that this probability is to a lesser degree dependent on the nature of the ligand and of the halogen, in contrast to the independence observed for the straight chain primary halides.

The effect of solvents other than tetrahydrofuran on the reaction path has been studied, but no other solvent so far used has allowed the reaction to proceed smoothly. Dimethoxyethane and tetramethylenediamine have been used as co-solvents with tetrahydrofuran but, as expected, have had no effect on the percentage of 1,2- linkages formed.

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**Résumé**—On étudie les structures des copolymères réguliers du butadiène dont le motif de répétition est —[But—R—But]—, R étant un liant alcoylé, en préparant des composés modèles HR—But—But—RH dans des conditions expérimentales identiques. On examine l'effet de la variation des paramètres expérimentaux, tels que la température, le liant, etc., sur la probabilité de l'addition 1–2; on tient compte des différences d'énergie d'activation entre les additions 1,2 et 1,4.

**Sommario**—Si è studiata la struttura di copolimeri regolari di butadiene con gruppo ripetitivo —[But—R—But]—, in cui R rappresenta un legante alchilico, mediante la preparazione, in condizioni sperimentali identiche, di modelli di composti HR—But—But—RH. Si è esaminato l'effetto della variazione di parametri sperimentali, come temperatura, legante, ecc, sulla probabilità d'addizione 1,2; si prendono in considerazione le differenze in energia d'attivazione tra l'addizione 1,2 e quella 1,4.

**Zusammenfassung**—Die Strukturen von regelmäßigen Copolymeren des Butadiens mit der wiederkehrenden Einheit —[But—R—But]—, wobei R ein Alkylligand ist, werden untersucht durch Herstellung von Modellsubstanzen HR—But—But—RH unter gleichen experimentellen Bedingungen. Der Einfluß der experimentellen Parameter, wie Temperatur, Ligand ect. auf die Wahrscheinlichkeit einer 1,2-Addition wird geprüft; die Unterschiede in der Aktivierungsenergie zwischen 1,2 und 1,4 Addition werden berücksichtigt.