

Mechanism and Side Reactions of the Anionic Condensation of Styrene with Alkyl Halides

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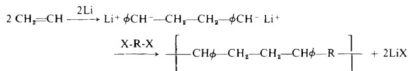
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The reactions occurring in the system styrene + butyl bromide + lithium in tetrahydrofuran are studied as a model for olefine/dihalide reactions pioneered by Richards and co-workers for the purpose of synthesising highly regular copolymers. Computer fittings of a kinetic scheme and of gel permeation chromatographs of the products leads to the conclusion that homopolymerisation of styrene tends to be a serious side reaction to the desired condensation between the styrene dianion and two moles of butyl bromide. As expected from previous work, this is found to be much less serious in the analogous system with alpha methyl styrene in place of styrene.

I. Introduction

In recent years, a new method has been proposed by Richards and co-workers¹ to synthesize a group of hydrocarbon copolymers from vinyl compounds and difunctional halides. The reaction, conducted in THF at room temperature with the aid of metallic lithium, has been considered to involve a dimer-dianion formation, well known in anionic polymerization, followed immediately by condensation with halide. In the case of styrene, e.g.,



Thus, the formation of a regular sequence with head-to-head/tail-to-tail dimeric unit has been envisaged. This should be true as a first approximation. Possible side reactions which, if present, would cause structural irregularity, would clearly be of importance. It was therefore planned to study the kinetics and statistics and the detailed mechanism, and how these are reflected in the regularity of the polymer structure. Styrene has been chosen as the vinyl material; as the "comonomer", mono-functional

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butyl bromide has been used, instead of dihalide, in order to simplify the system. This type of approach with monohalide has been made for other monomers by Davis *et al.*^{2,3,4} and by Pemberton *et al.*⁵ From a kinetic study it became likely that the system involves some unwanted side-reactions, which give rise to various copolymerised units. This has now unfortunately been confirmed also by the analysis of the products by means of G.P.C. Comparison of the kinetic calculation with the experimental results, both of kinetics and of fractionation, has been made using computer calculations. From this, a reaction second-order in the vinyl concentration has been proved more likely in the initiation step which gives the dimeric dianion.

2. Experimental

2.1. Materials

Styrene: Commercial styrene (BDH, Ltd.) was purified by the usual distillation in vacuo after drying with calcium hydride.

Butyl bromide: Commercial material (BDH, Ltd.), dried with molecular sieve and with phosphorus pentoxide, was distilled fractionally.

Tetrahydrofuran (THF): THF, after reflux over sodium-potassium alloy in a flow of argon, was distilled, discarding the first and a (major) last portion.

Lithium: The metal was supplied commercially (BDH, Ltd.) in the form of rod. Immediately before use, the metal, cut into pieces of c. 0.2 inches,⁶ was immersed in dry ethanol to remove surface contamination, and washed with petroleum ether, followed by dry THF.

2.2. Kinetic experiments

The method of carrying out the reaction is basically similar to the earlier work.¹

A 500-ml four-necked flask was equipped with a stirrer, condenser, gas inlet, thermometer and a stop cock, through which THF solution containing the required amount of styrene and butyl bromide were introduced. The temperature was controlled with an external bath normally at $25 \pm 0.5^\circ\text{C}$. Under stirring and with argon bubbling through cleaned pieces of lithium (of sufficient weight to allow the reaction between styrene and halide, even if they happened without side reactions) were added. Aliquots of 1 ml were taken out at fixed intervals to serve for quantitative g.l.c. analysis of the residual concentration of styrene and halide, using a silicone oil-chromorp P column, at 120°C . The initial molar ratio of styrene to halide was not fixed at the possible stoichiometric ratio, but the concentrations of the two materials were varied. A system using α -methyl styrene has been studied in this way by Cunliffe^{6,7} and also by us (see later).

2.3. Gel-permeation chromatography

Analytical fractionation of the product was carried out by g.p.c. (Waters Assoc. Model 200) using a high-resolution column elaborated by Dr C. J. Devoy. THF was used as solvent.

⁶Throughout this paper 1 in = 2.540 cm, 1 mmHg = (101.325/760) kN/m².

The reaction mixture, containing lithium bromide, was first purified as follows. Benzene and water were added to separate the product into two layers. The water layer was extracted several times with benzene and the extract added to the first benzene solution. Benzene was evaporated off from this and the residue, a viscous oil, redissolved in THF for use in g.p.c. This treatment for removal of lithium bromide was important since the salt shows a peak within the elution-volume range of the compounds.

3. The isolation and the confirmation of phenyl decane and diphenyl dodecane

The reaction mixture, obtained with 1 mol/l of butyl bromide and 0.5 mol/l of styrene, purified as above, was distilled *in vacuo* and two fractions obtained. These compounds were examined and compared with the presumed structures, 5-phenyl decane and diphenyl dodecane (a mixture of 5,8- and 5,7- isomers). The first fraction (5-phenyl decane) gave the following results:

b.p.: 94°C/0.1 mmHg (yield c. 50%)

m.w. from cryoscopy: 223 (calc. 218.4)

Aliphatic to aromatic hydrogen ratio from proton n.m.r.: 4.20 (calc. 21/5 = 4.20)

Elemental analysis: C(%), 88.21 (calc. 88.00); H(%), 11.83 (calc. 12.00)

The second fraction (diphenyl dodecane) gave:

b.p.: 158 ~ 163°C/0.1 mmHg (yield c. 20%, and its major fraction crystallised from petroleum ether, m.p. 38–42°C)

m.w. from cryoscopy: 325 (calc. 322.5)

aliphatic to aromatic hydrogen ratio: 2.51 (calc. 24/10 = 2.40)

elemental analysis: C(%), 89.24 (calc. 89.37); H(%), 10.52 (calc. 10.63).

4. Schemes of the reaction for the styrene-butyl bromide system

The existence of some measure of side reactions was first noticed by plotting a set of kinetic data for the styrene-butyl bromide system shown in Figure 1, where the residual concentrations of the two substances, for several runs with various initial concentrations, are correlated. When the reaction starts with equimolar amounts of styrene and the halide, the relation traces approximately a straight line down to the origin, implying that the rates of consumption of the two compounds are essentially consistent with each other. This, then, does not conflict with the desired mechanism which should yield a single product, 5,8-diphenyl dodecane (generally $R(M)_2R$), in analogy to the desired formation of a regular copolymer structure when monohalide is replaced by dihalide. With different (non-stoichiometric) starting-points, however, the curves deviate seriously from the linear relation with a slope of 45°C which should be realised in absence of side reaction. The rate of styrene consumption is higher at higher styrene/bromide ratio, whereas butyl bromide is consumed faster at lower ratio. In any case, the curves have a tendency to end near the origin, where both styrene and halide are consumed. These observations led to the assumption of two types of side reaction: a polymerisation (or anionic addition) for the monomer and a Wurtz-type reaction for the halide, the former being favourable at high monomer

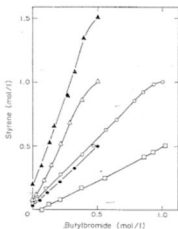


Figure 1. Relation between the residual concentration of styrene and butyl bromide for runs with various initial concentrations indicated by the terminal points of the plots.

concentration and vice versa. The occurrence of these types of side reactions have, in fact, been observed and discussed in the system involving α -methyl styrene.^{2,7} With these side reactions, are anticipated numerous by-products. They may be classified into two groups. One is of compounds derived from the head-to-head dimer dianion, represented by $R M_n R$ ($n \geq 2$), including 5,8-diphenyl dodecane, 5,8,10-triphenyl tetradecane, tetraphenyl hexadecane (two isomers), etc. The other group is initiated by butyl lithium and does not contain head-to-head units, $R M'_n R$ ($n \geq 1$), 5-phenyl decane, 5,7-diphenyl dodecane, 5,7,9-triphenyl tetradecane, 5,7,9,11-tetraphenyl hexadecane, etc. In fact the formation of such types of by-products has been observed by g.p.c., as will be seen later. Octane, the expected Wurtz-reaction product, has not been observed in the product of any runs made with various initial concentrations. G.p.c. with THF is not a sensitive method to detect octane because of the similarity of its refractive index to that of the solvent. However, no octane peak has been observed by g.l.c. either. Instead, a new peak has appeared at shorter retention time indicating butane and/or butene. The peak has been relatively small in general, but of a significant magnitude at the later stage of reactions particularly when the reaction is carried out with high bromide concentrations. This may be attributed to the disproportionation⁸ which could occur between butyl lithium and butyl bromide.

The reactions discussed above may be summarised in Fig. 2.

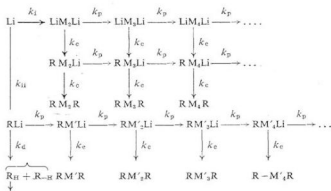


Figure 2. Scheme of the reaction involved in styrene-butyl-bromide-lithium system.

In this scheme, the heavy arrows show the main reaction steps to give a head-to-head type unit, as envisaged in the original work.

As for the generation of the dimer-dianion, there are two options, a first-order and a second-order reaction in the monomer concentration. Physically, the first order should arise if a monomer molecule reacts with metallic lithium to form a monomeric radical anion, which dimerises after diffusing from the original reaction site. On the other hand, the second order case occurs if two monomers are directly required to form a dimer-dianion or the coupling of the radical anion formed takes place instantaneously. In any case, the dimerisation process which is naturally diffusion controlled,^{2,3} is regarded as much faster than the following reactions, i.e. the condensation with halide or the polymerisation. That the generation of dianion perhaps follows a second order law is suggested by examining the experimental results in the light of calculations (see below). However, we meanwhile retain the two possibilities.

5. Derivation of the kinetic equations

When we assume a first order reaction, the rate of generation of the dimer dianion, ignoring its disappearance, is given.

$$\frac{d[\text{LiM}_2\text{Li}]}{dt} = \frac{1}{2} k_i [\text{M}] A = {}_1C_1 \quad (1)$$

where k_i is a rate constant and A , a term related to the reactive surface of lithium which may be a function of time. With the second-order assumption,

$$\frac{d[\text{LiM}_2\text{Li}]}{dt} = \frac{1}{2} k_i [\text{M}]^2 A = {}_2C_1 \quad (2)$$

For the other initiation step which gives alkyl lithium, the rate, again ignoring the disappearance, is given with another constant k_d :

$$\frac{d[\text{RLi}]}{dt} = k_{it} [\text{RX}] \cdot A = C_2 \quad (3)$$

Among the subsequent steps in Figure 2, reactions involving anionic intermediates, such as LiM_jLi , RM_jLi and $\text{RM}'_j\text{Li}$, may be treated with a steady state condition. In other words, these intermediate molecules at any step should disappear immediately after their generation, reacting with either monomer or halide. Even as a whole, the concentration of anions should be very low: the specific red colour of the anion has not been observed during the reaction.

To describe these reactions, as a first approximation, a single constant k_p has been assumed for the addition of monomer to anion, and k_c , for the condensation with alkyl halide, irrespective of the molecular size or structure. Thus, denoting the rate of the generation of dimeric dianion, given by Equations (1) or (2), by C_2 , one can write:

$$\frac{d[\text{RM}_2\text{R}]}{dt} = C_1 \left[\frac{k_c[\text{RX}]}{k_c[\text{RX}] + k_p[\text{M}]} \right]^2 \quad (1a)$$

$$\frac{d[\text{RM}_3\text{R}]}{dt} = C_1 \times 2 \left[\frac{k_c[\text{RX}]}{k_c[\text{RX}] + k_p[\text{M}]} \right] \left[\frac{k_p[\text{M}]}{k_c[\text{RX}] + k_p[\text{M}]} \right] \quad (2a)$$

And, in general,

$$\frac{d[\text{RM}_n\text{R}]}{dt} = C_1 \times (n-1) \left[\frac{k_c[\text{RX}]}{k_c[\text{RX}] + k_p[\text{M}]} \right]^{n-2} \left[\frac{k_p[\text{M}]}{k_c[\text{RX}] + k_p[\text{M}]} \right] \quad (4)$$

$(n \geq 2)$

Defining another constant k_d , for the disproportionation of alkyl lithium, the total rate of formation of alkane and alkene is written:

$$\frac{d[\text{Rane} + \text{Rene}]}{dt} = C_2 \times \frac{k_d[\text{RX}]}{k_d[\text{RX}] + k_p[\text{M}]} \quad (5)$$

where C_2 is the rate of alkyl lithium generation given by Equation (3).

For the following series of products, similar treatment gives:

$$\frac{d[\text{RM}'_n\text{R}]}{dt} = C_2 \left[\frac{k_p[\text{M}]}{k_d[\text{RX}] + k_p[\text{M}]} \right] \left[\frac{k_c[\text{RX}]}{k_c[\text{RX}] + k_p[\text{M}]} \right] \left[\frac{k_p[\text{M}]}{k_c[\text{RX}] + k_p[\text{M}]} \right]^{n-1} \quad (6)$$

$(n \geq 1)$

As each product has two alkyl groups irrespective of the number of its monomer units, the total rate of halide consumption is obtained from:

$$-\frac{d[\text{RX}]}{dt} = \sum_{j=2}^{\infty} \left[2 \frac{d[\text{RM}_j\text{R}]}{dt} \right] + 2 \frac{d[\text{Rene} + \text{Rane}]}{dt} + \sum_{j=1}^{\infty} \left[2 \frac{d[\text{RM}'_j\text{R}]}{dt} \right] \quad (7)$$

Applying Equations (4), (5) and (6) to (7), this reduces to:

$$-\frac{d[\text{RX}]}{dt} = 2C_1 + 2C_2 \quad (8)$$

The result simply adds the total rate of the two types of initiations, on the assumption that the concentration of intermediates is negligibly small.

The rate of monomer consumption is similarly given:

$$-\frac{d[\text{M}]}{dt} = \sum_{j=2}^{\infty} \left[j \frac{d[\text{RM}_j\text{R}]}{dt} \right] + \sum_{j=1}^{\infty} \left[j \frac{d[\text{RM}'_j\text{R}]}{dt} \right] \quad (9)$$

Using Equation (4) and (6),

$$-\frac{d[\text{M}]}{dt} = \left[2C_1 + C_2 \frac{k_p[\text{M}]}{k_p[\text{M}] + k_d[\text{RX}]} \right] \left[1 + \frac{k_p[\text{M}]}{k_c[\text{RX}]} \right] \quad (10)$$

The equations derived above contain a parameter A , relating to the effective surface area of lithium which, in practice may well change with time. However, time as well as A can be eliminated, provided any interaction of metallic lithium with styrene and halide is included in k_i and k_{ii} , respectively.

When the first-order initiation is assumed for the dimer-dianion generation. The division of Equation (8) by (10) with substitution by Equations (1) and (3) gives:

$$\frac{d[\text{RX}]}{d[\text{M}]} = \frac{\left[-\frac{d[\text{RX}]}{dt} \right]}{\left[-\frac{d[\text{M}]}{dt} \right]} = \frac{(k_i[\text{M}] + 2k_{ii}[\text{RX}])}{\left[k_i[\text{M}] + k_{ii}[\text{RX}] \frac{k_p[\text{M}]}{k_p[\text{M}] + k_d[\text{RX}]} \right]} \left[1 + \frac{k_p[\text{M}]}{k_c[\text{RX}]} \right] \quad (11)$$

This shows the relation between the residual concentration of monomer and that of alkyl halide, whose integration should correspond to the plot in Figure 1.

The change of weight fraction of the product in terms of monomer concentration is obtained from Equations (1), (3), (4) and (10)

$$n \times d[\text{RM}_n\text{R}] = n \times n \times d[\text{RM}_n\text{R}] = n \times Sd[\text{RM}_n\text{R}]S$$

$$n \times \frac{d[\text{RM}_n\text{R}]}{-d[\text{M}]} = n \times \frac{\left[\frac{d[\text{RM}_n\text{R}]}{dt} \right]}{\left[-\frac{d[\text{M}]}{dt} \right]} = \frac{\frac{1}{2}k_i[\text{M}]n(n-1) \left[\frac{k_c[\text{RX}]}{k_c[\text{RX}] + k_p[\text{M}]} \right]^2 \left[\frac{k_p[\text{M}]}{k_c[\text{RX}] + k_p[\text{M}]} \right]}{D_1} \quad (12)$$

and from Equations (1), (3), (6) and (10)

$$\begin{aligned}
 n \times \frac{d[\text{RM}'_n\text{R}]}{-d[\text{M}]} &= n \times \frac{\left[\frac{d[\text{RM}'_n\text{R}]}{dt} \right]}{\left[-\frac{d[\text{M}]}{dt} \right]} \\
 &= \frac{k_{ii}[\text{RX}]n \left[\frac{k_p[\text{M}]}{k_d[\text{RX}] + k_p[\text{M}]} \right] \left[\frac{k_c[\text{RX}]}{k_c[\text{RX}] + k_p[\text{M}]} \right] \left[\frac{k_p[\text{M}]}{k_c[\text{RX}] + k_p[\text{M}]} \right]^{n-1}}{D_1} \quad (13)
 \end{aligned}$$

where the denominator, D_1 , is the same as appeared in Equation (11). From Equation (12) and (13), one may calculate, with various integers n , the figures which correspond to concentrations measured by g.p.c.

In the case of second-order initiation, expressions similar to Equation (11), (12) and (13) are obtained with Equation (2) in place of Equation (1).

$$\frac{d[\text{RX}]}{d[\text{M}]} = \frac{(k_i[\text{M}]^2 + 2k_{ii}[\text{RX}])}{\left[k_i[\text{M}] + k_{ii}[\text{RX}] \frac{k_p[\text{M}]}{k_p[\text{M}] + k_d[\text{RX}]} \right] \left[1 + \frac{k_p[\text{M}]}{k_c[\text{RX}]} \right]} \quad (14)$$

$$n \times \frac{d[\text{RM}_n\text{R}]}{-d[\text{M}]} = \frac{\frac{1}{2}k_i[\text{M}]n(n-1) \left[\frac{k_c[\text{RX}]}{k_c[\text{RX}] + k_p[\text{M}]} \right]^n \left[\frac{k_p[\text{M}]}{k_c[\text{RX}] + k_p[\text{M}]} \right]^{n-2}}{D_2} \quad (15)$$

$$\begin{aligned}
 n \times \frac{d[\text{RM}'_n\text{R}]}{-d[\text{M}]} &= \\
 &= \frac{k_{ii}[\text{RX}]n \left[\frac{k_p[\text{M}]}{k_d[\text{RX}] + k_p[\text{M}]} \right] \left[\frac{k_c[\text{RX}]}{k_c[\text{RX}] + k_p[\text{M}]} \right] \left[\frac{k_p[\text{M}]}{k_c[\text{RX}] + k_p[\text{M}]} \right]^{n-1}}{D_2} \quad (16)
 \end{aligned}$$

D_2 is the same denominator which appeared in Equation (14). In these equations numbered from (11) to (16), of the kinetic constants involved, only the three ratios k_{ii}/k_i , k_p/k_c and k_d/k_p are significant. The absolute value of any constant is not important, when time is not involved. If the unwanted side reactions do not occur in the system, one can set $k_{ii}/k_i = k_p/k_c = k_d/k_p \equiv 0$.

6. Fractionation of the products

In order to examine the extent of the side reactions and accordingly, the inhomogeneity of the products of the reaction with various initial concentrations have been analysed by g.p.c. Gas chromatography was also tried but was not convenient for high oligomers. Higher temperatures might have improved this method, but could lead to errors arising from pyrolysis. g.p.c. is much more favourable in any case

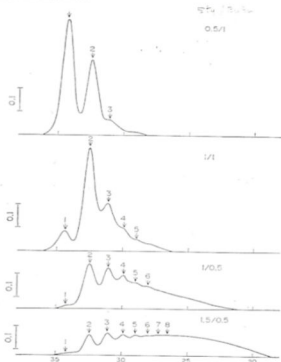


Figure 3. Gel permeation chromatographs of styrene/butyl bromide products obtained at the end of runs with four different initial concentrations shown. Numbers with arrow show the number of styrene units in components having a general formula, butyl-(styrene)_n-butyl.

since the total structure of the spectrum of compounds including any high molecular weight species, ought to be fitted to the kinetic calculations.

In Figure 3 the g.p.c. curves are shown for the styrene-butyl bromide products obtained at the ends of the runs in Figure 1. As mentioned previously, using equimolar styrene and butyl bromide at 1 mol/l each, leads to essentially equal rates of consumption by the end of the reaction. The product, as seen in Figure 3(b), consists of several compounds, and not, as was hoped, of the unique substance, 5,8-diphenyl dodecane.

When the concentration of styrene is twice that of the bromide, the fractions with higher molecular weight have increased extensively, suggesting occurrence of the polymerisation reaction, and the tendency is even more obvious with still higher styrene concentration [Figure 3(b) and (c)]. In the system with an excess amount of

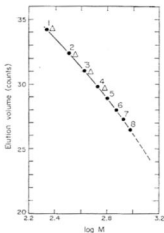


Figure 4. The elution volume of peaks in Figure 3 (styrene/butyl bromide) plotted against the log. molecular weight of *n*-metric compounds. The first two points, 1 and 2, have been assigned with pure compounds; the molecular weights of the rest are deduced from successive peaks (assuming increments of one monomer unit). The triangles are from α -methyl-styrene/butyl bromide products.

halide, the peak at the longest elution volume has enlarged very much, while those at shorter elution volume, are depressed.

In order to identify the peaks, a fractional distillation was undertaken as described in the experimental section. Two compounds were isolated and identified as 5-phenyl decane and diphenyl dodecane, the latter being possibly a mixture of 5,8- and 5,7-isomers. The distillation of the higher molecular weight compounds has not been successful, but a reasonable estimation of these has been possible from the graph shown in Figure 4.

The elution volume of the unknown peaks in Figure 3 are plotted against the logarithm of the molecular weight calculated from the expected molecular structure, together with the identified two peaks. An exactly linear relation between these quantities, proposed⁹ in general, has not been obtained possibly because of the effect of the end group. The curve, however, is quite smooth tending to be linear at larger molecular weights. Therefore, it is not unnatural to regard the peaks following those of mono- and diphenyl- compound, as belonging to triphenyl tetradecane, tetraphenyl hexadecane and so on. The area of peaks in Figure 3 may be taken to represent the weight distribution of styrene in each component which can be calculated from the kinetic equations, if the contribution to the refractive index of the end group is ignored. The correction factor has been calculated from the area of peaks obtained with known quantities of phenyl decane, diphenyl dodecane and high molecular weight polystyrene. The linear relation in Figure 5 is fitted by

$$f = 1 + (0.214/n)$$

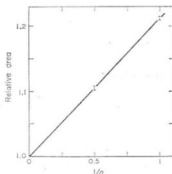


Figure 5. Relative peak area, i.e. the ratio of area from 1 mol of n -meric compound to that from a base mole of polystyrene plotted against the reciprocal of n .

in terms of the number n of styrene units per molecule.

Figure 3 can be converted to the true weight distribution of styrene dividing the area of each peak by this factor, though the corrected figure is not shown.

It is seen in Figure 3 that the formation of the dimeric unit is sensitive to the initial concentration of the two materials, styrene and butyl bromide. When the two materials are used in stoichiometric ratio, styrene incorporated in the dimeric unit is as high as 46%. Whereas it is only 32% at the smaller styrene/butyl bromide ratio of 0.5 mol/1 mol, and 19% and 8% at the large ratios, 1.0 mol/0.5 mol, 1.5 mol/0.5 mol, respectively. Thus the yield decreases markedly when the concentration ratio deviates in either direction, from the stoichiometric ratio for the dimeric unit.

7. Fitting of the kinetic calculations to experimental result

Two equations, Equations (11) and (14), give relations between the concentrations of monomer and halide. The former is based on the first-order generation of the dimer dianion and has been solved mathematically by direct integration. The result is given, however, only as an implicit function. Equation (14) for the second-order initiation reaction is not homogeneous. Thus, the integration was only carried out by a numerical method, the trapezoidal rule. Fitting of the theory to the experimental data by the choice of a set of constants was by trial and error methods on the PDP-10 computer. The weight fraction of n -meric units has been calculated simultaneously using the styrene-halide relation thus obtained.

The hypothesis of *first-order* formation of the dimer dianion has not proved successful. It is true that for the styrene-butyl bromide relation, a set of curves similar to Figure 1 can be calculated from Equation (11), with $k_{i1}/k_i = 0.2$, $k_p/k_c = 0.2$, $k_d/k_p = 0$. However, the weight distribution of the n -meric units, calculated from Equations (12) and (13), does not fit the g.p.c. data at all well. The results are specially unsatisfactory to explain the sensitivity of the ratio of monomeric to dimeric units,

to the initial concentrations of styrene and halide. In fact, this sensitivity has been one of the puzzling problems in previous work in the literature.¹

On the other hand, a much better fit to the experiment (Figures 1 and 3) has been obtained from Equations (14), (15) and (16) derived by assuming *second-order* formation of the dimer dianion, choosing the kinetic constants as, e.g., $k_{ii}/k_i = 0.2$, $k_p/k_c = 0.3$ and $k_d/k_p = 0.2$. The fit is still not perfect but reveals some systematic deviations. The rate of the consumption of styrene relative to that of bromide is too slow, particularly at high styrene concentrations, and the dimeric fraction is relatively too small compared with that of the higher products. These deviations are attributed to failure of the simplifying assumption that any anion, without regard to its structure, has fixed kinetic constants for the polymerisation (k_p) and the condensation (k_c). As a next approach, the disappearance of the dimeric dianion among the numerous steps in Figure 2, has been treated with different constants, k_{p_2} and k_{c_2} . Thus, Equations (14), (15) and (16) are modified, respectively as (17), (18) and (19):

$$\frac{d[\text{RX}]}{d[M]} = \frac{(k_{ii}[M]^2 + 2k_{i_2}[\text{RX}])}{\left[k_i[M]^2 \left\{ 1 + \frac{(k_{p_2}/k_{c_2} - k_p/k_c)[M][\text{RX}]}{2(k_{p_2}[M]/k_{c_2} + [\text{RX}])(k_p[M]/k_c + [\text{RX}])} \right\} + k_{ii} \frac{k_p[M]}{k_p[M] + k_d[\text{RX}]} \right]} \left[1 + \frac{k_p[M]}{k_c[\text{RX}]} \right] \quad (17)$$

$$n \times \frac{d[\text{RM}_n\text{R}]}{d[M]} = \frac{\frac{1}{2}k_i[M]^2 n \left[\frac{k_c[\text{RX}]}{k_p[M] + k_c[\text{RX}]} \right] \left[\frac{k_{c_2}[\text{RX}]}{k_{p_2}[M] + k_{c_2}[\text{RX}]} \right] \left[\frac{k_p[M]}{k_p[M] + k_c[\text{RX}]} \right]^{n-2}}{D_3} + (n-2) \left[\frac{k_{p_2}[M]}{k_{p_2}[M] + k_{c_2}[\text{RX}]} \right] \left[\frac{k_p[M]}{k_p[M] + k_c[\text{RX}]} \right]^{n-3}}{D_3} \quad (18)$$

$$n \times \frac{d[\text{RM}'_n\text{R}]}{d[M]} = \frac{k_{ii}[\text{RX}] n \left[\frac{k_p[M]}{k_d[\text{RX}] + k_p[M]} \right] \left[\frac{k_c[\text{RX}]}{k_c[\text{RX}] + k_p[M]} \right] \left[\frac{k_p[M]}{k_c[\text{RX}] + k_p[M]} \right]^{n-1}}{D_3} \quad (19)$$

Again, D_3 is the denominator occurring in Equation (17).

The result of the calculation from Equations (17), (18) and (19) are illustrated in Figure 6, where the kinetic constants are set $k_{ii}/k_i = 0.25$, $k_{p_2}/k_{c_2} = 0.1$, $k_p/k_c = 0.5$, $k_d/k_p = 0.2$. These constants have been adjusted merely by trial-and-error methods.

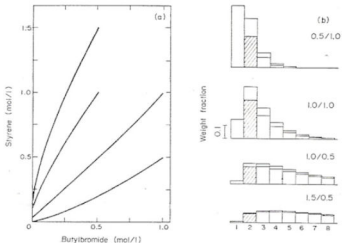


Figure 6. Calculated relation between the concentrations of styrene and butyl bromide for four initial conditions (a) and the calculated weight distribution of styrene in n -meric compounds (up to octamer) at the end of each run (b). The shadowed part is the fraction of head-to-head dimeric unit. The constants used for the calculation are:

$$k_{po}/k_{eo} = 0.1, k_p/k_e = 0.5, k_{ii}/k_i = 0.25 \text{ and } k_d/k_p = 0.2.$$

The figures, both of the styrene-halide concentration and of the fraction of the products, explain the corresponding experiments (Figures 1 and 3) very reasonably. The model is still not sufficient to fit the experimental result in every detail. The weak points of the calculation are: first, that the assumption of steady state has been made throughout the reaction from the beginning, which seems inadequate when the first stage of the runs in Figure 1 is compared with that in Figure 6. Secondly, the law of mass action has been applied to this complicated system which involves a heterogeneous (surface) reaction and a substantial increase of viscosity in the system at the later stages of the reaction. The solvent effect may vary between runs, or even within a run, since experiments have been carried out at fairly high initial concentrations, which is not taken into account in the calculations. The effect of lithium bromide, which is produced during the run, may have been responsible for the deviation particularly observed at the initial stage.

A suggestion obtained from the calculation is that with the second-order initiation, the relative weight fractions of the units change considerably as a function of total conversion, or of the styrene concentration in the system. Figure 7 is an example, where the reaction begins with equimolar styrene-bromide, 1 mol/l. The decrease in the head-to-head dimeric unit (or the increase in the Wurtz-initiated units) is remarkable at the later stage of the reaction. Similarly, the weight fraction of dimeric units may vary with the initial concentration of styrene even when the ratio of styrene to halide is constant. Higher styrene concentration is, conceivably, advisable to

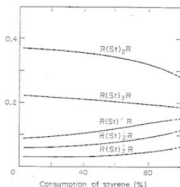


Figure 7. Change in the weight fraction of units with conversion, calculated for the run with initial concentration of styrene and halide, 1 mol/l each (cf. Figure 6).

depress one of the side-reactions, Wurtz-type initiation, but not promising in this system because the overall concentration is already high from the practical point of view.

8. Conclusions

In a normal bimolecular reaction between two different species, the stoichiometry ensures that both reagents disappear at the same rate, whatever their concentrations. It is a characteristic feature of the present system that, because of side reactions, a self-regulating effect develops. Whichever is in excess, styrene or halide, disappears at a faster relative rate, so that both become exhausted at the end of the reaction, over a wide range of initial mole ratios. Equally, if the monohalide/styrene reaction is replaced by dihalide/styrene, we may expect to get polymers over a wide range of mole ratios. However, a very high regularity of structure is then not to be expected. Of course, the results obtained in this study are not to be applied in general to this type of polymer-forming system. Higher percentage of dimeric unit has been reported when α -methyl styrene^{2,3} or butadiene^{1,3} was used as the vinyl material. For α -methyl styrene this situation is well confirmed by Figure 8. This reports g.p.c. results for α -methyl styrene butyl bromide reaction products, which can be compared with the analogous results in Figure 3 for styrene butyl bromide. It is immediately apparent that the side reaction leading to higher oligomers and polymers is very much reduced in the α -methyl styrene system.

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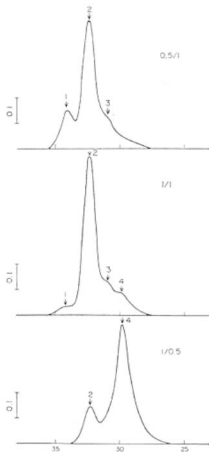


Figure 8. Gel permeation chromatographs of α -methyl styrene/butyl bromide products obtained at the ends of runs with three different initial concentration shown. For details compare Figure 3 for the analogous system with styrene in place of α -methyl styrene.

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