# Poly(ethyleneoxide-b-styrene) copolymers as solid–liquid phase transfer catalysts

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Di- and tri-block copolymers of ethylene oxide and styrene function as effective phase transfer catalysts in the reaction of solid potassium phenoxide with n-butylbromide in refluxing toluene to give virtually quantitative yields of n-butyl phenyl ether. A wide range of copolymer structures have been examined and the catalytic activity is found to increase with $\bar{M}_n$ of both the styrene and the ethylene oxide segments levelling off at $\bar{M}_n$ styrene block ~30 000 and $\bar{M}_n$ ethylene oxide block ~60 000. Beyond $\bar{M}_n$ ethylene oxide block ~100 000 rates of reaction drop again towards the value for a high molecular weight homopolymer of ethylene oxide. Kinetic analysis suggests the rate controlling process to be the bimolecular reaction between complexed potassium phenoxide and n-butyl bromide, and the activation energy for the reaction is the same as that for reactions catalysed by low molecular weight oligoethers. From the kinetic dependence of the concentration of copolymer catalysts, the dependence on the structure of individual copolymers and from the known physical behaviour of these copolymers in toluene solution, catalysis appears to involve micellar aggregates of copolymer chains.

**Keywords** Catalysis; phase transfer catalysis; block copolymers; polyethyleneoxide

## INTRODUCTION

In our preliminary communication[1] we showed that a number of common linear vinyl polymers will function as effective phase transfer catalysts in the reaction of solid potassium phenoxide with n-butyl bromide in toluene solvent. Furthermore we also demonstrated for the first time that block copolymers of styrene and ethylene oxide are effective catalysts in this system, and indeed are more efficient than poly(ethylene oxide) itself. We have now looked at these reactions in more detail and in particular have examined a wide range of block copolymers of varying structure in order to understand the mechanism of catalysis and to optimize the catalytic effect.

## EXPERIMENTAL

### *Materials*

Potassium phenoxide was prepared by a literature procedure[2], poly(ethyleneoxide), PEO, $\bar{M}_n \sim 300000$ was a gift from ICI and PEO $\bar{M}_n$ 5700 was from Polymer Laboratories Ltd. All of the di- and tri-block copolymers of ethylene oxide and styrene were supplied by Professor G. Reiss of 'Ecole Supérieure de Chimie de Mulhouse'. They were prepared and characterized as described previously in the literature[3]. A summary of their structures is shown in *Table 1*. Copolymers labelled D are poly(ethylene oxide-b-styrene) di-blocks while those labelled T are poly(ethylene oxide-b-styrene-b-ethylene oxide) tri-blocks. In the case of the tri-blocks the number average molecular weight of the poly(ethylene oxide) segment, $\bar{M}_n$ PEO, refers to a single block only.

All other materials were used essentially as supplied.

### *Williamson syntheses*

These were carried out as before[4] and initial rates of reaction calculated from n-butyl bromide decay curves. Even the slowest reactions gave virtually quantitative yields when left to react for three hours at 110°C.

$$K^+ OPh^- \text{(solid)} + nBuBr \text{ (toluene)} \xrightarrow[110^\circ C]{\text{catalyst}} nBuOPh + K^+ Br^-$$

## RESULTS AND DISCUSSION

### *Effect of copolymer structure*

Copolymers were examined in a series of groups A to E such that within a group some structural property was kept constant or approximately constant. Thus within A, $\bar{M}_n$ PS was constant while $\bar{M}_n$ PEO was increased. In B, the weight % PS was constant while $\bar{M}_n$ PS and $\bar{M}_n$ PEO simultaneously decreased. In C, $\bar{M}_n$ PEO was approximately constant while $\bar{M}_n$ PS decreased. In D, diblock and triblock copolymers of similar structure were employed, and E contains miscellaneous structures. The results appear in *Table 2*.

From these it is clear that many of the copolymers are better catalysts than poly(ethylene oxide) itself, and this confirms our earlier findings[1]. Some of the groupings also show some clear trends; for example in B, simultaneous decrease of $\bar{M}_n$ PS and $\bar{M}_n$ PEO leads to a fall in activity.

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*Table 1* Structure of block copolymers employed as solid/liquid phase transfer catalysts in Williamson syntheses of n-butylphenylether

| Copolymer | Weight % PS[a] | $\bar{M}_n$ PS block | $\bar{M}_n$ PEO[b] block[c] | $\bar{M}_n$ COP[d] |
|---|---|---|---|---|
| 1D | 30.4 | 4200 | 9600 | 13 800 |
| 2D | 10.8 | 4200 | 34 700 | 38 900 |
| 3D | 8.0 | 15 800 | 181 700 | 197 500 |
| 4D | 10.5 | 11 800 | 100 200 | 112 000 |
| 5D | 15.6 | 3700 | 19 900 | 23 600 |
| 6D | 23.8 | 15 800 | 49 600 | 65 400 |
| 7D | 20.0 | 14 200 | 56 800 | 71 000 |
| 8D | 23.2 | 11 800 | 39 000 | 50 800 |
| 9D | 42.0 | 15 800 | 21 800 | 37 600 |
| 10D | 32.5 | 14 200 | 29 400 | 43 600 |
| 11D | 34.5 | 31 300 | 59 400 | 90 700 |
| 12D | 43.2 | 31 100 | 41 200 | 72 500 |
| 13D | 78.0 | 168 500 | 47 500 | 216 000 |
| 1T | 35.3 | 1800 | 1700 | 5200 |
| 2T | 21.0 | 1800 | 3400 | 8600 |
| 3T | 9.1 | 1800 | 9000 | 19 800 |
| 4T | 33.0 | 36 100 | 36 000 | 109 300 |
| 5T | 36.5 | 19 100 | 16 600 | 52 300 |
| 6T | 40.0 | 3800 | 2900 | 9600 |

[a] PS = polystyrene
[b] PEO = poly(ethylene oxide)
[c] Refers to a single block only
[d] Overall molecular weight of copolymer

However, the overall picture is made much clearer when the rate is plotted both as a function of $\bar{M}_n$ PEO (*Figure 1*) and $\bar{M}_n$ PS (*Figure 2*). In *Figure 1* if the $\bar{M}_n$ PEO block for the tri-block series is taken as twice the value of a single block then all the data fall within the same envelope, indicated by the two solid curves, as the di-block series. Within this envelope rates also increase with $\bar{M}_n$ PS at a constant value of $\bar{M}_n$ PEO and this leads to a broadening of the data. The same pattern is confirmed in *Figure 2*, and all the data fall within a second broad envelope indicated by the solid curves. Rates increase with $\bar{M}_n$ PS and again, at constant $\bar{M}_n$ PS, with $\bar{M}_n$ PEO. Both dependences show a trend to a limiting rate value, and in the case of $\bar{M}_n$ PEO there is good evidence for a maximum value being achieved, and an approximately linear fall off with $\bar{M}_n$ PEO above 100 000 (*Figure 1*).

### *Kinetics*

Copolymer 4T was used in deriving an experimental rate law. The usual technique of varying the concentration of one component while keeping the other concentrations fixed was employed. A fixed quantity of solid $K^+OPh^-$ of 2.0 mmol was used throughout. *Figure 3* shows the catalyst dependence and *Figure 4* the alkylhalide dependence. Thus, for an excess of solid $K^+OPh^-$, the rate law is:—

$$\frac{-d[\mathrm{nBuBr}]}{dt} = k_{\mathrm{expl}}[\mathrm{nBuBr}]^1[\mathrm{copolymer}]^{1.8}$$

This has a similar form to the equations deduced for catalysis by free and resin-supported oligo (ethylene oxides)[5], although the catalyst exponent is different. Furthermore, the activation energy (*Figure 5*) of ~40 kJ $\mathrm{mol}^{-1}$ also corresponds to the previous value. These observations strongly suggest that the rate controlling process is the bimolecular displacement reaction between n-butylbromide and copolymer associated $K^+OPh^-$.

### *Mechanism*

PEO itself has only a low solubility in toluene and it could be argued that the improvement in catalysis using styrene block copolymers might be due simply to improved compatibility with the solvent. Expanded PEO chains might then complex and solubilize $K^+OPh^-$ (*via*

*Table 2* Effect of block copolymer structure on rate of catalysis of Williamson ether syntheses in refluxing toluene

| Group[a] | Copolymer | Weight of[b] copolymer (g) | Initial rate[c] $\times 10^4$ ($M^{-1}$ $s^{-1}$) |
|---|---|---|---|
| A1 | 1D | 0.0257 | 0.967 |
| | 2D | 0.0201 | 0.871 |
| A2 | 1T | 0.0277 | 0.563 |
| | 2T | 0.0267 | 0.537 |
| | 3T | 0.0195 | 0.688 |
| B1 | 3D | 0.0193 | 1.02 |
| | 4D | 0.0199 | 1.31 |
| | 2D | 0.0201 | 0.871 |
| | 5D | 0.0211 | 0.746 |
| B2 | 6D | 0.0235 | 1.53 |
| | 7D | 0.0227 | 1.33 |
| | 8D | 0.0232 | 1.00 |
| B3 | 4T | 0.0266 | 1.73 |
| | 5T | 0.0280 | 1.43 |
| | 1T | 0.0277 | 0.563 |
| C | 9D | 0.0321 | 0.800 |
| | 10D | 0.0275 | 1.07 |
| | 8D | 0.0232 | 1.00 |
| | 2D | 0.0201 | 0.871 |
| D | 4T | 0.0266 | 1.73 |
| | 11D | 0.0264 | 1.08 |
| E | 12D | 0.0310 | 1.28 |
| | 13D | 0.0810 | 1.11 |
| | 6T | 0.0297 | 0.683 |
| PEO ($M_n$ 300 000) | | 0.020[d] | 0.828 |
| PEO ($M_n$ 5 700) | | 0.020[d] | 0.734 |

[a] A, $\bar{M}_n$ PS constant, $\bar{M}_n$ PEO increasing; B, weight % PS constant, $\bar{M}_n$ PEO and $\bar{M}_n$ PS decreasing; C, $\bar{M}_n$ PEO constant, $\bar{M}_n$ PS decreasing; D, diblock and triblock of similar structure; E, miscellaneous
[b] Corresponds to ~0.41 mmol of 'O' donor in catalyst
[c] $[\mathrm{nBuBr}]_{\mathrm{initial}} = 0.24\mathrm{M}$ (2 ml). $K^{\oplus}OPh^{\ominus} = 2.0$ mmol
[d] Corresponds to 0.45 mmol of 'O' donor

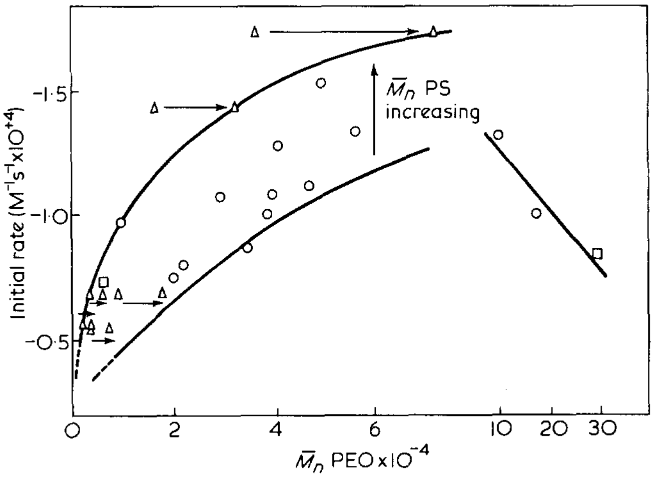

*Figure 1* Initial rate dependence on $\bar{M}_n$ PEO block. ⊙ di-block copolymers; △ tri-block copolymers; ⊡ homopolyethylene oxide. Overall $\bar{M}_n$ PEO in tri-block series = 2 x $\bar{M}_n$ PEO for single block (→). Conditions as shown in *Table 2*

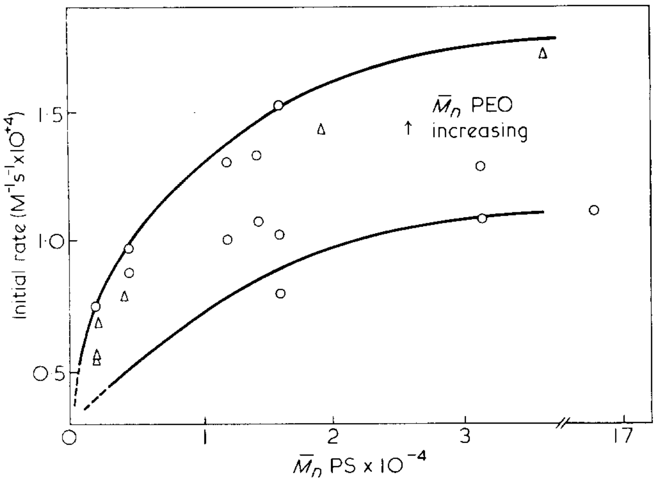

*Figure 2* Initial rate dependence on $\bar{M}_n$ PS block. ⊙ di-block copolymers; △ tri-block copolymers. Conditions as shown in *Table 2*

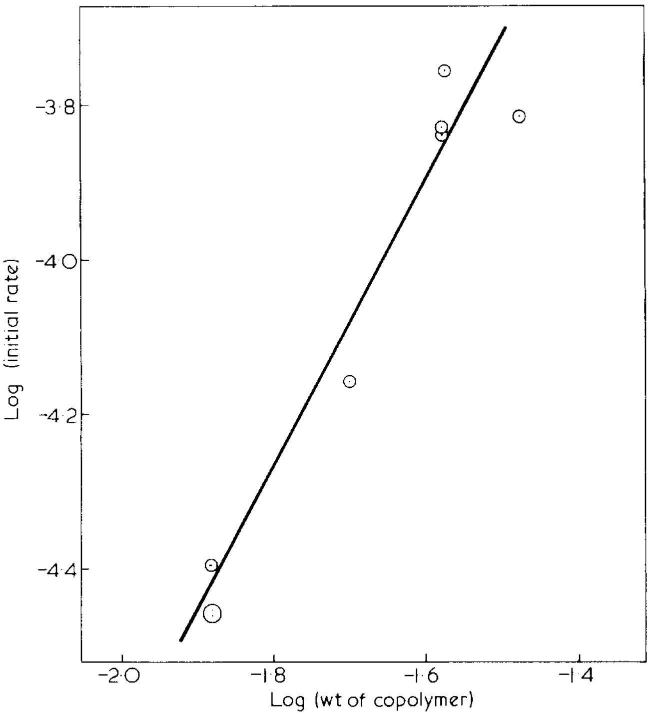

*Figure 3* Initial rate dependence on the weight of copolymer 4T. [n-BuBr]$_{initial}$ = 0.24M; K$^{\oplus}$OPh$^{\ominus}$ = 2.0 mmol

the K $^+$ ion) and allow displacement on the alkyl halide to occur as the rate controlling process. This cannot be the whole story, however, because solubilization of K $^+$ OPh $^-$ by individual block copolymer chains would give rise to a catalyst kinetic exponent of unity. Also with a minimal $\bar{M}_n$ PS block to improve the solubility of PEO the rate should be virtually independent of $\bar{M}_n$ PEO block for a total fixed amount of 'O' donor. In practice the rate increases.

A similar molecular weight dependence has been reported previously[6] though a limiting effect was reached at a molecular weight of ~10000. We have previously made the same observations with oligo(ethylene oxides) with molecular weights up to ~1500, and have tentatively attributed it to enhanced shielding of the K $^+$ ion[7]. German workers have used a wider range of oligomers in a related system and demonstrated the existence of a distinct maximum in their rate *versus* $\bar{M}_n$ PEO relationship[8]. In the present case different levels of cation shielding, and therefore anion activation, may also make some contribution, but a more important factor may be the degree of aggregation of copolymer chains. These materials are well known to form microemulsions in oil–water mixtures because of their inherent hydrophilic hydrophobic structural units[3,9]. Furthermore, in view of the poor compatibility of homo-poly(ethylene oxide) with toluene some aggregation of these copolymer molecules via their PEO blocks might be expected in toluene. This effect would, of course, depend on the $\bar{M}_n$ of the PEO block. Cloud points in water have been measured[10]

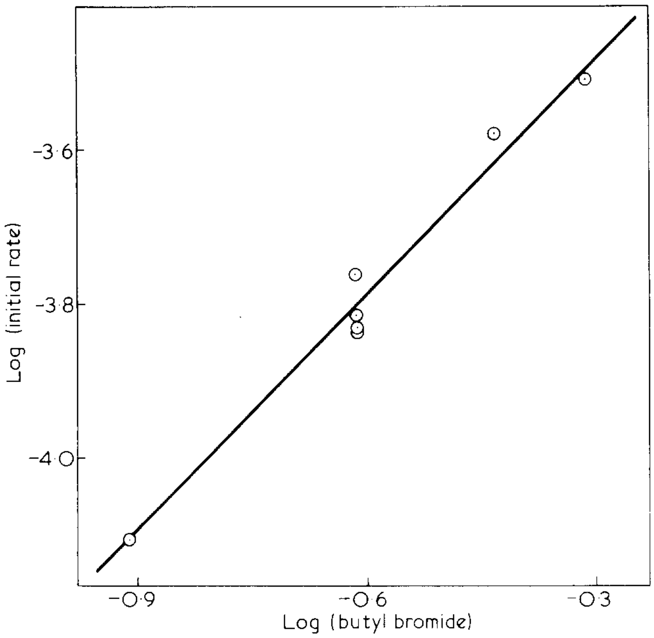

*Figure 4* Initial rate dependence on initial concentration of n-butyl bromide. 0.41 mmol of 'O' donor in catalyst 4T. K$^{\oplus}$OPh$^{\ominus}$ = 2.0 mmol

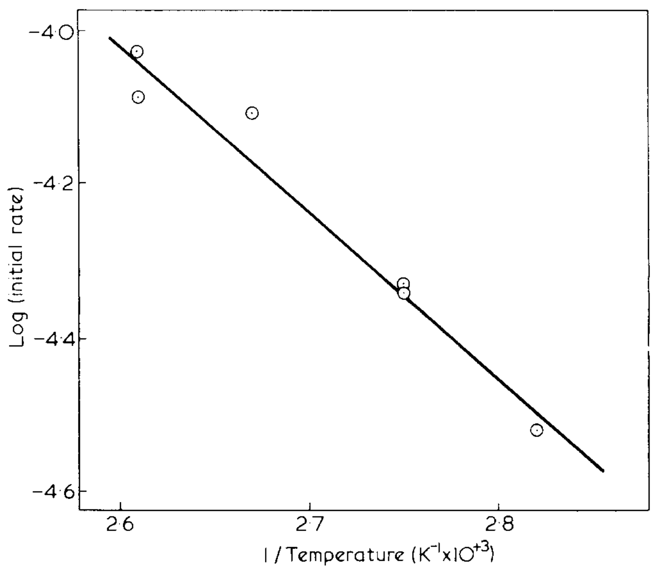

*Figure 5* Arrhenius plot for catalyses using 4T. Conditions as shown in *Table 2*

although quantitative evaluation of toluene solutions has not yet been carried out. Typically the solutions contain ~1% by weight of copolymer and hence the occurrence of micellar aggregates is not unreasonable, and would be consistent with the unusual kinetic exponent for the copolymer rate dependence. Detailed structural information at the molecular level is not available, but the process of micellization itself would be dependent on copolymer composition and structure and in turn the latter would be expected to influence the binding of the $K^+$ ions to oligoether segments in the PEO block, and hence the catalytic performance.

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