polymer communications

Linear polymers and block copolymers as solid-liquid phase transfer catalysts

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Introduction

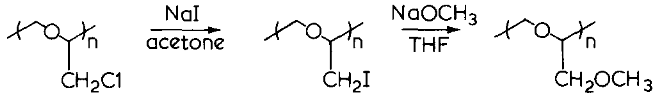
Soluble linear polymers have been used widely as catalysts in esterolyses where considerable rate enhancements arising from cooperative effects have been demonstrated[1,2]. There are also a few reports of polymeric catalysts being employed in homogeneous reactions other than ester hydrolyses[3–6]. In addition polyelectrolytes have been investigated in some depth with regard to their influence on reactions involving ions[7–9]. Resin supported phase transfer catalysts have also attracted some attention[10–13] and while soluble linear analogues of some of these have been reported[14–16], no attempt has previously been made to assess the range of readily available polymers which might be useful in this context. A few examples of the use of linear polymers as catalysts in displacement reactions are available[17–20], though the solvents employed are largely such that reaction mixtures are essentially homogeneous, and under these circumstances the description 'phase transfer' is not really applicable.

The present report deals with our preliminary investigation of linear vinyl and ethereal polymers and block copolymers as phase transfer catalysts in the Williamson synthesis of n-butyl phenyl ether, using a two phase system involving solid potassium phenoxide and a solution of n-butyl bromide in toluene. As far as we are aware this is the first example of the use of block copolymers as catalysts in an organic reaction.

Experimental

Materials. Potassium phenoxide was prepared as recorded in the literature[21]. The following materials were used as supplied: poly(vinylalcohol) (Aldrich), PVA1, 100% hydrolysed, M.W. ~115 000; PVA2, 88% hydrolysed, M.W. 10 000; poly(vinyl pyrrolidone) (Koch–Light), PVP, M.W. ~25 000; poly(vinyl formal) (Aldrich), PVF; poly(vinyl methylether) (Aldrich), PVME1, 50% aqueous solution; poly(epichlorohydrin) (Aldrich), PECH; Span 80 and Tween 20 (Koch–Light), non-ionic surfactants based on sorbitol; 2-(2-(2-methoxyethoxy) ethoxy) ethanol (Fluka), MEEE; poly(ethylene oxide), PEO, M.W. ~300 000 (gift from ICI).

Anhydrous poly(methyl vinyl ether), PMVE2, was obtained from PMVE1 by extraction with methylene chloride. The latter solution was dried over anhydrous $CaCl_2$ and then evaporated to dryness. Poly(methyl vinyl ketone), PMVK, poly(acrylamide), PA, and poly(N,N-dimethyl acrylamide), PDMA, were prepared by free radical polymerization of their respective monomers in aqueous solutions, using ammonium persulphate and tetramethyl ethylene diamine as the redox initiator. Poly(methoxy methyloxirane), PMMO, was obtained from PECH by reaction with sodium iodide in dry acetone, to produce initially the corresponding iodinated polymer, followed by treatment with sodium methoxide in tetrahydrofuran.



Finally the two block copolymers PSE and PESE were supplied by Professor G. Reiss of 'Ecole Superiereur de Chemie de Mulhouse'. PSE is a poly(styrene-b-ethyleneoxide), $M_N \sim 126\,000$, containing ~51% polystyrene. PESE is a poly(ethyleneoxide-b-styrene-b-ethyleneoxide), $M_N \sim 64\,000$ containing ~ 56% polystyrene. They were prepared and characterized as described previously in the literature[25].

Williamson Syntheses. These were performed on a small scale as previously described[13]. Known weights of catalysts were added to the heterogeneous

$$K^{\oplus}OPh^{\ominus}\ (\text{solid}) + \text{nBuBr(toluene)} \xrightarrow[\text{reflux}]{\text{catalyst}} \text{nBuOPH} + K^{\oplus}Br^{\ominus}$$

mixtures of reagents stirred at ~600 r.p.m. and the reactions monitored as before by quantitative g.l.c methods. Initial rates of reaction were calculated from n-butyl bromide decay curves, and the final yields of the product ether were determined on termination of reactions, generally after 3 h.

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Table 1 Linear vinyl polymers as solid/liquid phase transfer catalysts in Williamson syntheses of n-butyl phenyl ether

Catalyst	Weight of catalyst (*g*)	Initial rate of reaction $10^5\,M^{-1}s^{-1}$	Yield of ether[a] (%)
None	–	1.9	–
PVA1	0.1	2.1	27
PVA2	0.1	slow	–
PVP	0.1	12	72
PDMA	0.1	6.7	83[b]
PDMA	0.01	4.2	71
PA	0.1	5.2	78
PA	0.01	2.5	60
PMVE1	0.01	slow	18
PMVE2	0.1	slow	–
PMVK	0.1	slow	29
PVF	0.1	2.1	12

[a] after 3 hours; [b] after 1 hour

Results and discussion

The results of experiments using vinyl polymers are shown in *Table 1*, while those from the polyethers and block copolymers are summarized in *Table 2*. The most relevant features which emerge from these are as follows. As a group the polyethers and block copolymers are superior catalysts to the vinyl polymers. The most effective of the latter is poly(vinylpyrrolidone) which confirms the results of other workers[19,20]. With dioxane and ethanol as the solvent catalysis by this macromolecule is more effective than the monomeric analogue N-methyl-pyrrolidone and has been attributed to a cooperative action of pendant groups facilitating dissociation of the alkali metal phenoxide ion pair. In the present work the polymer certainly displays a capacity to solubilise or phase transfer the phenoxide into toluene, although nothing can be said about the degree of dissociation of the ion pairs therein. Likewise both poly(acrylamide) and poly(N,N-dimethyl acrylamide) display significant catalytic action again indicating an ability specifically to solvate the alkali metal cation. The dimethyl derivative appears to be consistently better than poly(acrylamide) itself, and this may be due to an inhibiting effect arising from the known internal hydrogen bonding characteristics of the latter, which are absent in its dialkyl derivatives. Both poly(vinylalcohols) displayed virtually no catalytic effect at all, and once again it seems most likely that intramolecular hydrogen bonding precludes the possibility of these species solvating alkali metal ions. Poly(methyl vinyl ether) maybe regarded as the methylated derivative of poly(vinyl alcohol) and all possibility of hydrogen bond formation is thus removed. Nevertheless this polymer also shows no phase transfer properties and seems that the 1,3 ethereal structure has poor donor character with regard to binding metal cations. This observation supports the findings that poly(oxetane), poly(tetrahydrofuran) and poly(ethyl vinyl ether) are poor catalysts for the Williamson reaction carried out homogeneously in dioxane[18]. Similar conclusions may be drawn about the ketone functionality of poly(vinyl methyl ketone). Poly(vinyl formal) might have been expected to display some activity since it can be regarded as a macromolecular analogue of tetrahydropyran. In spite of this, however, it performed very poorly and one possible explanation is that this polymeric structure is likely to be relatively rigid, perhaps making it impossible for adjacent tetrahydropyran moities to coordinate simultaneously with the same metal ion.

All of the polyethers and the two block copolymers displayed some catalytic action, and since all possess the basic 1,2 ethereal structure, $\left(\mathrm{OCH_2CH_2O}\right)$, or its variants, it is not surprising that these are able to coordinate with some efficiency to potassium ions and hence effect a phase transfer process. Poly(epichlorohydrin) and its derivative poly(methoxymethyloxirane) were the poorest of the group, and it appears that substitution of the ethylene bridge between respective oxygen atoms inhibits formation of the conformation most favourable for multiple coordination with metal ions.

Oligomers and polymers of ethylene oxide itself are known to be strong cation donors and to enhance the solubility and dissociation of salts in organic media[22–24]. Increasing the molecular weight of the macromolecule enhances its catalytic action in dioxane solvent[18], though a limiting effect is reached at a molecular weight of ~10 000. Similarly in this work the high molecular weight poly(ethyleneoxide) performed no better than the oligomer, MEEE, though a direct comparison is not possible because of the different weights employed. With toluene as the solvent the relatively highly crystalline nature of the sample of poly(ethylene oxide) used may be a factor in limiting its effectiveness.

The two block copolymers proved to be the best catalysts based upon the relative number of moles of 'O' donor present Yields of n-butyl phenyl ether are consistently high, and virtually quantitative for weights of catalyst > 0.01 g. The triblock species, PESE, is more effective than the diblock, PSE, and a direct comparison is appropriate since the poly(styrene) and poly(ethylene oxide) contents of each are about the same. It is by no means clear why these materials should be such good catalysts but the presence of the styrene components may enhance the solubility in the toluene phase, and simultaneously give rise to highly expanded polymer conformations. Such a situation would aid the interaction of the poly(ethylene oxide) components with the solid potassium phenoxide and enhance the transport of these ion pairs into the liquid phase. In the presence of a discrete aqueous phase these materials are known to func-

Table 2 Linear polyethers and block copolymers as solid/liquid phase transfer catalysts in Williamson syntheses of n-butyl phenyl ether

Catalyst	Weight of catalyst (*g*)	Initial rate of reaction $10^5M^{-1}s^{-1}$	Yield of ether[a] (%)
MEEE	0.05	13	71
Span 80	0.1	14	67
Tween 20	0.1	20	85[b]
PECH	0.1	3.1	32
PMMO	0.05	4.3	42
PEO	0.01	5.8	76
PEO[e]	0.01	1.4	18
PEO[d]	0.01	slow	–
PSE	0.1	56	94[c]
PSE	0.02	13	90
PSE	0.01	5.0	79
PSE[e]	0.01	4.2	51
PSE[d]	0.01	slow	–
PESE	0.1	33	97[b]
PESE	0.02	20	93
PESE	0.01	9.5	94
PESE[e]	0.01	2.7	71
PESE[d]	0.01	slow	–

[a] after 3 h; [b] after 1 h; [c] after 2 h; [d] discrete aqueous phase present (2 ml H_2O) [e] no stirring

tion highly efficiently as emulsifiers capable of stabilising both water-in-oil and oil-in-water systems. These properties have been characterised in some detail[25] and may also have relevance in the present catalytic studies.

More detailed investigations are required to achieve a full understanding of these systems and our work in this area is continuing.

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A 'Feathered' polymer resin

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In the course of our on-going syntheses of new macromolecular supports for application in the solid phase method[1] of peptide and oligonucleotide assembly, we have prepared a crosslinked poly(*N*,*N*-dipropylacrylamide) with a remarkable macroscopic structure, which to the authors' knowledge has never been reported before. Polymerization was carried out in suspension as described below, in anticipation of producing a beaded polymer in the usual way. After the reaction was completed a sample of the suspended product was examined under an optical microscope. While the polymeric material did indeed consist of particles with essentially spherically symmetric cores, ($\sim$50 μm diameter), in addition, protruding in all directions from their surfaces were feather-like appendages (*Figure 1*). On leaving part of the reaction mixture to stand in a stoppered storage bottle the 'feathered' resin beads gradually settled. However, the volume occupied by the polymer was considerably larger than with conventional resins, presumably because the protrusions preclude close packing.

Examination of a sample allowed to dry out on a microscope slide showed that the 'plumage' had become detached from the central cores, and therefore has poor mechanical stability. Indeed when another sample was left in a shaker for 1 h many of the 'feathers' once again were detached. By repeatedly diluting this suspension with acetone followed, after settling, by decantation, the suspension medium was gradually changed. In this solvent the detached 'feathers' tend to remain in suspension much longer, and hence their separation from the remaining polymer fraction was readily effected. Infra-red analysis of the dried 'feathers' confirmed them to consist of an acrylamide-type polymer. Although no weight fractions were measured, the polymer 'plumage' appears to constitute a relatively minor fraction of the total mass of polymer.

The mechanism by which these structures are formed is not known, but a crucial factor may be the extent to which

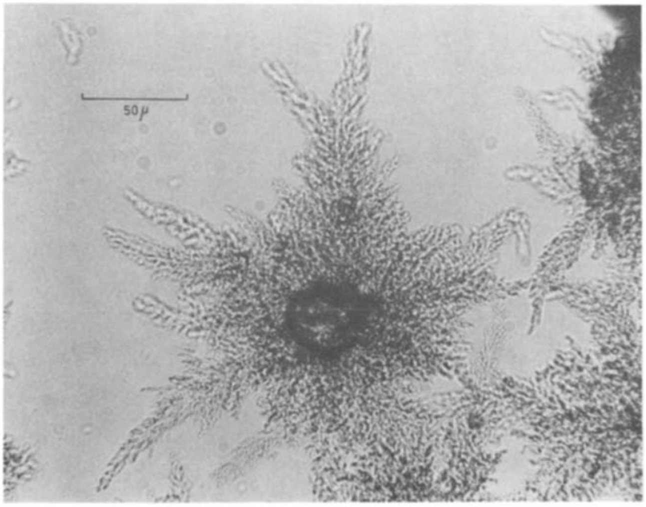

Figure 1 Optical photograph of a 'feathered' resin bead in suspension in water

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