polymer reviews

Recent developments in the application of functionalized polymers in organic synthesis

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Functionalized polymers have continued to find increasing use as supports for reagents, catalysts and protecting groups. Recent applications of these are reviewed along with the use of polymeric species in metal ion separations, in racemate resolutions, as specific adsorbents, in organic synthesis (notably in asymmetric reactions) and in the trapping and identification of reactive intermediates. Some indications of developments in the pipeline and areas of importance for the future are also given.

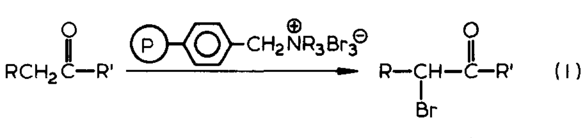
Keywords Polymer supports; polymeric reagents; polymeric catalysts; polymeric separations

INTRODUCTION

In recent years functionalized polymers have found increasing use as supports on which molecular assembly can be carried out[1]. They have been employed as catalysts[2,3], reagents[4–6] and in the immobilization of transition complexes[7–9]. Interest is also growing in their application in asymmetric reactions[10] and in racemate resolution[11,12] as well as in ion-chelation[13], in water treatment[14] and other ecological applications[15], and in the binding of dyes[16]. We have carried out a comprehensive review of the literature to 1980 in the context of organic synthesis[17], and the present review seeks to update that exercise to 1982. It uses a similar format and assumes a knowledge of the work contained in that review.

Polymeric reagents

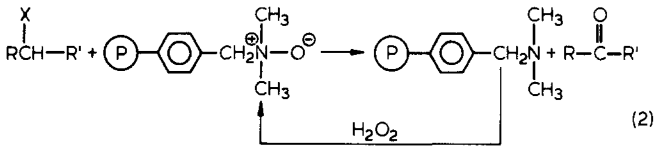
The advances made in this area are summarized in *Table 1*. Further examples of supported phosphines have been described for Wittig reactions[18,19] and in peptide synthesis[20]. In the latter case a careful appraisal has been made of the potentiality for recycling of the reagent. A number of side reactions on the polymer have been identified confirming earlier suggestions that efficient recycling is an unlikely possibility. Polymeric sulphonium salts[21] and halogenating reagents[22,23] are also reported, the latter being employed in the halogenation of carbonyl and other unsaturated compounds. In this case a commercially available anion exchange resin was used to carry ICl^-, Br_3^- and $BrCl_2^-$ species (reaction (1)).



(1)

Polymeric condensing reagents have not been widely employed, but one new species useful in ester formation has emerged[24].

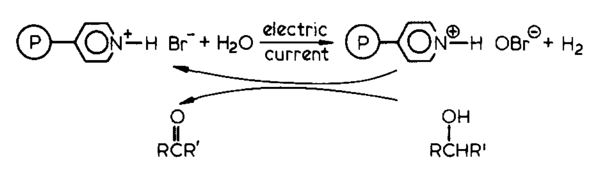
Considerably more interest has been shown in polymeric redox reagents. These have the potentiality for regeneration and re-use, which may well off-set their initial expense. Notable here are some resins with hydroquinone and catechol units as pendant groups used for the oxidation of hydrobenzene to azobenzene[28]. Another interesting oxidizing agent containing an amine oxide moiety has been prepared by modification of a polystyrene resin[29] and employed in the direct oxidation of alkyl halides to carbonyl compounds (reaction (2)).



(2)

This polymeric *N*-oxide eliminates the disadvantages associated with the use of its soluble counterpart, and the polymeric by-product can be recycled by treatment with H_2O_2.

In an attempt to simplify the regeneration of a polymer-bound oxidant, innovative use has been made of electrochemical methods[34]. Thus poly-4-vinylpyridinium hydrobromide readily oxidizes secondary alcohols to ketones in the absence of an electric current and without any contaminating reduced product. This oxidant is then reformed on passage of a current (reaction (3)).



Very closely related is the electrochemical generation of polymer-supported bromite[35]. In this case the starting species was polystyryl trimethylammonium bromide.

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Table 1 Polymeric reagents

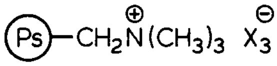
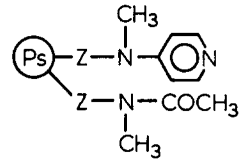
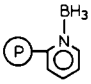
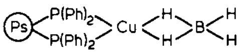
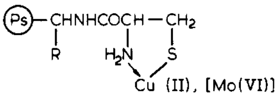
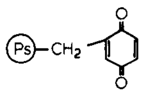
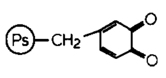
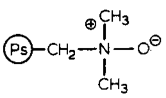
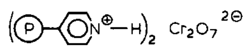
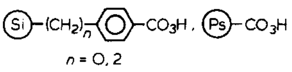
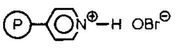
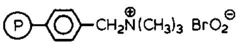
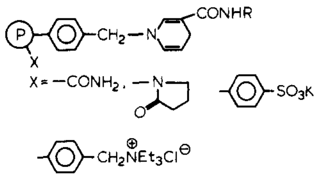
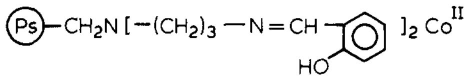
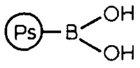
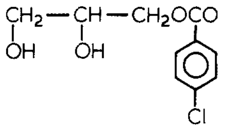
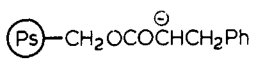
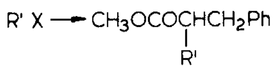
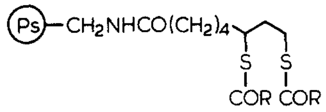
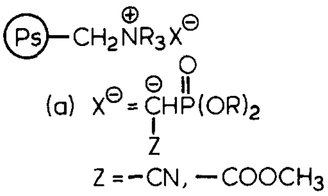
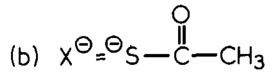
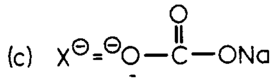
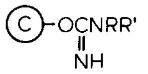
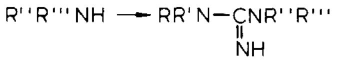
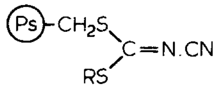
Functional polymer	Application	Reference
1 Polymeric phosphine reagents		
(Ps)$-P(Ph)_2$	Wittig reaction (a) Synthesis of olefins (b) Synthesis of vinyl ethers and thioethers $>C{=}CH{-}Z{-}R$, Z=O, S	 18 19
(Ps)$-P(Ph)_2.CCl_4$	Peptide synthesis	20
2 Polymeric sulphonium salts		
(Ps)$-S(CH_3)_2\ BF_4^{\ominus}$		
3 Polymeric halogenating reagents		
 $\text{(Ps)}-CH_2\overset{\oplus}{N}(CH_3)_3\ \overset{\ominus}{X_3}$		
$X_3^{\ominus} = ICl_2^{\ominus}$	Chlorination of carbonyl and unsaturated compounds	22
$X_3^{\ominus} = Br_3^{\ominus}/BrCl_2^{\ominus}$	Bromination and chlorination of carbonyl compounds	23
4 Polymeric condensing reagents		
 $Z = -CH_2-,\ -CH_2[NHCO(CH_2)_{10}]_2-$	$RCOOH + R'OH \longrightarrow RCOOR'$	24
5 Polymeric redox reagents		
	Reduction of carbonyl compounds to alcohols	25
	Reduction of carboxylic acid chlorides to aldehydes	26
	Reduction of acetylene to ethylene	27
 	Oxidation of hydrazobenzene to azobenzene	28
	Oxidation of alkyl halides and tosylates to carbonyl compounds	29
	Oxidation of alcohols to carbonyl compounds	30–32
	Oxidation of tetrahydrothiophene to sulphoxide and sulphone	33
	Oxidation of alcohols to carbonyl compounds	34
	Synthesis of metal bromites	35

Table 1 **Polymeric reagents** — ***continued***

Functional polymer	Application	Reference
	Oxidation of alloxan, meacridinum iodide, 2,6-dichlorophenol and indophenol	36
	Oxidation of 2,6-dimethylphenol	37
6 Polymeric protecting groups		
	Protecting group for diols 	38
7 Polymeric acylation and alkylation reagents		
	 $R'X \longrightarrow CH_3OCO\underset{R'}{\underset{\mid}{C}}HCH_2Ph$	39
	$RCOCl \longrightarrow RCOCH_2CH_2Ph$ $R'NH_2 \longrightarrow RCONHR'$	40
8 Polymer-bound nucleophiles		
	Conversion of carbonyl compounds to olefin derivatives	41
	Conversion of alkyl halides to thioacetates	42
	Conversion of alkyl halides to alcohols	43
9 Miscellaneous		
(Ps)–SO_2N_3	$RR'CH.CHO \longrightarrow RR'C{=}N_2$	44
 (C)–$O\underset{\underset{NH}{\|}}{C}NRR'$	Synthesis of *N*—alkyl arginines  $R''R'''NH \longrightarrow RR'N{-}\underset{\underset{NH}{\|}}{C}NR''R'''$	45
	Synthesis of *N*—cyanoguanidines $(RNH)_2{-}C{=}N.CN$	46

(Ps) = polystyrene resin

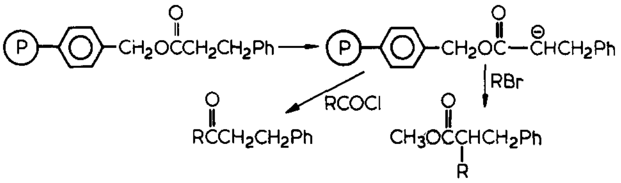
(P) = $-(CH_2-\underset{\mid}{C}H)_n-$

(Si) = silica

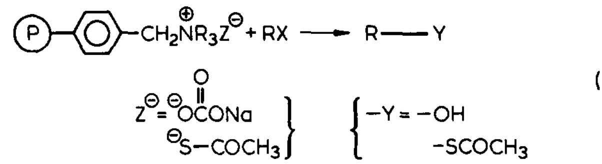
(C) = polysaccharide

Bromite ion is a useful mild oxidizing agent and generated in this way it is apparently stabilized by the macromolecular environment. Elution of the resin with metal hydroxides readily yields solutions of the corresponding metal bromites which can subsequently be isolated as very pure solid salts. Other oxidizing polymer systems have been developed based on transition metal species[30,31,37].

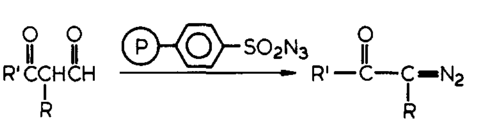
Further examples of the use of polystyrylboronic acid as a protecting group for diols have been reported[38]. Though this is not a new regaent it is a particularly effective one and is, of course, readily re-usable. Additional polymeric acylation and alkylation reagents have also been described[39,40]. Since the 'site isolation' of a reactive species on a polymer support is difficult to achieve with a lightly crosslinked material, these latest reports describe the use of 10 and 20% crosslinked matrices. In this case, enolates 'isolated' in this manner were acylated and alkylated in high yields with no self-condensation products evident (reaction (4)).


(4)

Reactive nucleophilic anions can readily be exchanged with stable species on an anion exchange resin and the polymeric product used as a stoichiometric reagent. Further examples of this procedure have used thioacetate and carbonate anions to convert alkyl halides into thioacetates[42] and alcohols[43] respectively (reaction (5)).


(5)

Finally in this section a polymer-supported sulphonylazide reagent has been applied in the diazo group transfer reaction of tosylazide[44]. In spite of the slightly lower yield than with conventional tosylazide, the greater thermal stability and ease of reaction work-up make this a particularly attractive reagent in synthesis (reaction 6).


(6)

Polymeric catalysts

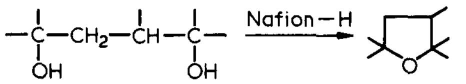
The process reported in this area is summarized in *Table 2*. As in our previous work[17] the specialized area of polymer-supported transition metal complexes has been omitted.

Conventional cationic exchange resins in their acid form continue to be developed as catalytic species in a variety of reactions[47–51], now extended to include the Prins reaction[49] (reaction (7)).


(7)

The hydrochloride of a pyridine containing polymer has also been used as a source of acid in the acetalization of carbonyl compounds and the esterification of carboxylic acids[52]. Perhaps most interesting of all in this particular area, however, is the development of a trifunctional ion exchange catalyst for acetylene hydration by Gates and his coworkers[53]. The concept of introducing more than one type of catalytic function onto a common support to achieve a selective reaction or sequence of reactions is not a new one, and indeed represents an area where considerable technical progress might be achieved in the next few years.

Further examples of the use of polymeric 'superacids' have also been described[48,54–59]. One new application is in the Rupe rearrangement of α-acetylenic tertiary alcohols to α, β-unsaturated ketones[55]. Another potentially important use is the synthesis of substituted tetrahydrofurans from 1,4-butanediols[56] (reaction (8)).


(8)

Closely related to the 'superacid' resins is a polystyrene-supported BF_3 etherate. This has been applied as a catalyst in a range of reactions including the isomerization of alkenes and the rearrangement of limonene epoxide to dihydrocarvone and carvenone[60].

An increasingly important group of supported species, which are effectively catalysts, are the photosensitizers. Far more examples have now been described mainly involving supported carbonyl species[61–69]. Some of these have been used simply as ultraviolet absorbers[61,68,69], while others have been applied specifically as sensitizers[62–67]. In the case of thymine supported on acrylate and methacrylate polymer backbones irradiation induces dimerization of these pendant groups[71].

Another group of polymeric catalysts with considerable commercial potential are the polymer-supported phase transfer catalysts. An increasing number of immobilised quarternary ammonium ions have been used in this context[72–80], as well as phosphonium salts[73,74,77,81–86] and crown ethers and cryptands[83,87–90]. The reactions studied have been mainly S_{N_2} displacements[73,74,76–84,86–89] but the alkylation of phenylacetonitrile[72–75] and the reduction of ketones to secondary alcohols[77,78,83] have received some attention. Considerable progress has been made in the mechanistic understanding of the liquid–liquid systems, particularly those involving supported phosphonium salt catalysts[73,81,82]. In the case where silica is the supporting matrix again a detailed understanding is emerging[84]. On the whole it appears that a delicate balance is required between the hydrophobic and hydrophilic nature of the *entire* supported system in order to achieve maximum catalytic efficiency. Lightly loaded polystyrene resins are too hydrophobic and catalysis seems to be limited by the movement of the aqueous nucleophile through the matrix. On the other hand, hydrophilic supports like cellulose and dextran require a surface hydrophobic treatment before they are effective catalysts, and presumably in this case penetration by the organic phase is the source of the problem[78]. Rather interestingly in the case of cellulose-supported catalysts no such surface treatment is required in the absence of water when the nucleophile is a solid

Table 2 Polymeric catalysts

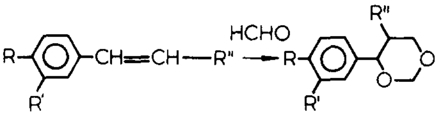
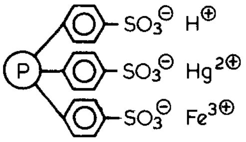
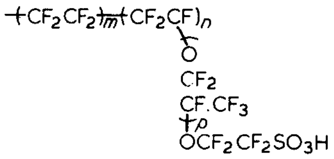
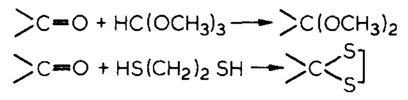
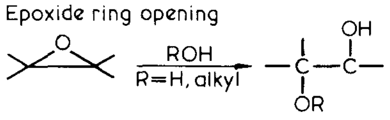
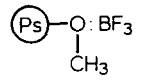
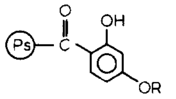
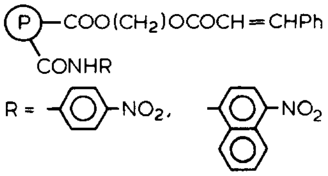
Functional polymer	Application	Reference
1 Ion-exchange resin catalysts		
(Ps)–SO_3H	$RR'C{=}N_2 + EtOH \rightarrow RR'CHOEt$ Alkylation of aromatic hydrocarbons Prins reaction 	47 48 49
(P)–SO_3H partially neutralized with $Fe^{3\oplus}$, $Cr^{3\oplus}$, $Co^{2\oplus}$, $Ni^{2\oplus}$, $Cu^{2\oplus}$ and $Nd^{\oplus}$	Condensation of acetone and phenol Isomerization of cyclohexene. Dehydration of 1-propanol to dipropyl ether and propene	50 51
	Acetalization of carbonyl compounds esterification of carboxylic acids	52
	$HC{\equiv}CH + H_2O \rightarrow CH_3CHO$	53
2 Polymeric 'superacids'		
Nafion — H  $-(CF_2CF_2)_m-(CF_2CF)_n-$; O, CF_2, $CF.CF_3$, $(\ )_p$, $OCF_2CF_2SO_3H$	Friedal–Crafts alkylation of arenes with chloroformates and oxalates Alkylation of aromatic hydrocarbons Rupe rearrangement of α-acetylenic tertiary alcohols to α, β-unsaturated ketones Dehydration of 1,4-butanediols to tetrahydrofurans Preparation of methoxymethyl ethers from alcohols and dimethoxymethane Synthesis of dimethylacetals and ethylene-dithioacetals  Epoxide ring opening 	54 48 55 56 57 58 59
	Isomerization of alkenes, ether formation, rearrangement of limonene epoxide to dihydrocarvone and carvenone	60
3 Polymeric u.v. absorbers and photosensitizers		
 R = H, CH_3, Et, n–Bu, N–Oct, n–$C_{12}H_{23}$	U.v. absorber	61
	Photosensitizer	62

Table 2 Polymeric catalysts – *continued*

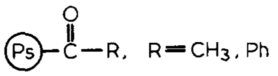
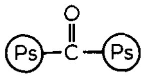
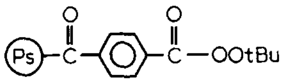
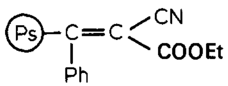
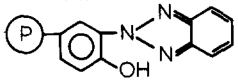
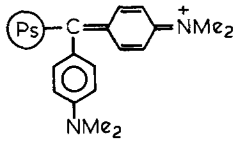
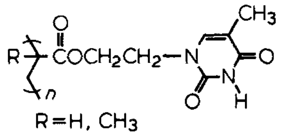
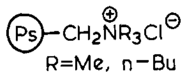
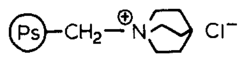
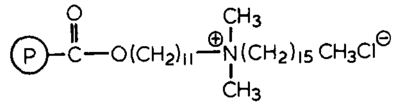
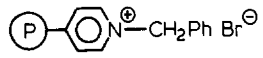
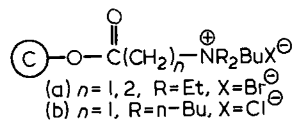
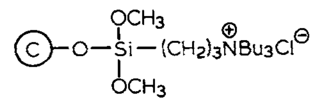
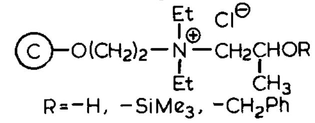
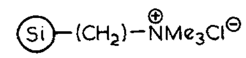
Functional polymer	Application	Reference
	Photosensitizer	63–65
	Photosensitizer	66
	Photoinitiator	67
	U.v. stabilizer	68
	U.v. stabilizer	69
	Photoresponse	70
	Photo-self-dimerization	71
4 Polymer-supported phase transfer catalysts		
(a) Ammonium salts		
	Alkylation of phenylacetonitrile	72–74
	Alkylation of phenylacetonitrile	72
	Displacement reactions	75
	$RBr + PhO^{\ominus} \longrightarrow ROPh$	76
	$R\overset{O}{\overset{\|}{C}}R' \xrightarrow{NaBH_4} R-\overset{O}{\overset{\mid}{C}}HR'$ $RBr + Y^{\ominus} \longrightarrow R-Y$ $Y^{\ominus} = PhO^{\ominus}, AcO^{\ominus}$	77
	$RBr + Y^{\ominus} \longrightarrow R-Y$ $Y = I^{\ominus}, CN^{\ominus}$	78
	$PhCOCH_3 \longrightarrow Ph\overset{OH}{\overset{\mid}{C}}HCH_3$	
	$RBr + AcO^{\ominus} \longrightarrow ROAc$	79

Table 2 Polymeric catalysts — *continued*

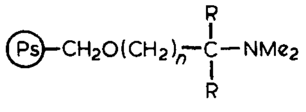
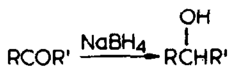
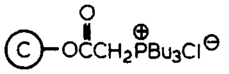
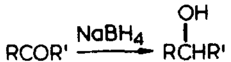
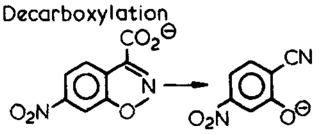
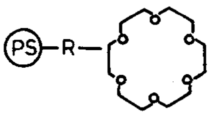
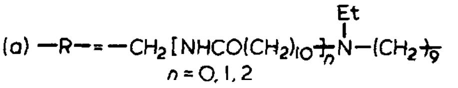
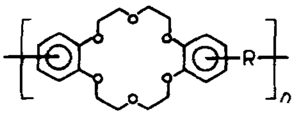
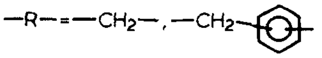
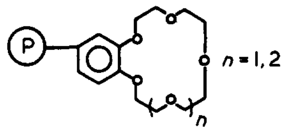
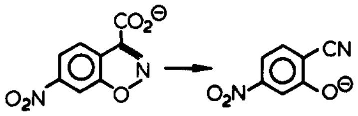
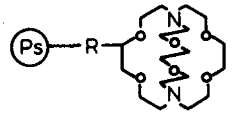
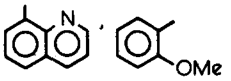
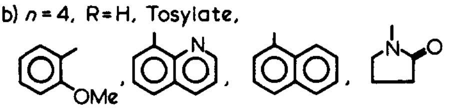
Functional polymer	Application	Reference
 $(\mathrm{Ps})\text{—}CH_2O(CH_2)_n\text{—}\underset{R}{\overset{R}{C}}\text{—}NMe_2$ $n = 1, 2,\ R = H, Me$	$RBr + CN^{\ominus} \rightarrow RCN$	80
(b) Phosphonium salts		
$(\mathrm{Ps})\text{—}CH_2\overset{\oplus}{P}Bu_3\ X^{\ominus}$ $X^{\ominus} = Cl^{\ominus}, {}^{\ominus}OSO_2Me$	$RBr + Y^{\ominus} \rightarrow RY$ $Y = CN^{\ominus}, ArO^{\ominus}$ $R\text{—}OSO_2Me + Cl^{-} \rightarrow RCl$	73,74 81,82
$(\mathrm{Ps})\text{—}(CH_2)_n\text{—}\overset{\oplus}{P}Bu_3\ X^{\ominus}$ $n = 1, 2, 3$	$R\text{—}Br + Y^{\ominus} \rightarrow RY$ $Y^{\ominus} = CN^{\ominus}, I^{\ominus}, Cl^{\ominus}, N_3^{\ominus}, PhS^{\ominus}, PhO^{\ominus}, S^{2\ominus}, SCN^{\ominus}, OAc^{\ominus}$	95
$(\mathrm{Ps})\text{—}CH_2\text{—}[NHCO(CH_2)_{10}]_n\text{—}\overset{\oplus}{P}Bu_3Cl^{\ominus}$ $n = 0, 1$	$R\text{—}Br + Y^{\ominus} \rightarrow RY$ $Y^{\ominus} = I^{\ominus}, CN^{\ominus}, PhS^{\ominus}$  $RCOR' \xrightarrow{NaBH_4} R\overset{OH}{C}HR'$	83
 $(\mathrm{C})\text{—}O\overset{O}{\overset{\Vert}{C}}CH_2\overset{\oplus}{P}Bu_3Cl^{\ominus}$	 $RCOR' \xrightarrow{NaBH_4} R\overset{OH}{C}HR'$ $RBr + Y^{\ominus} \rightarrow RY$ $Y^{\ominus} = PhO^{\ominus}, AcO^{\ominus}$	77
$(\mathrm{Si})\text{—}(CH_2)_3\text{—}\overset{\oplus}{P}Bu_3Br^{\ominus}$	$RBr + I^{\ominus} \rightarrow RI$	84
$(\mathrm{Si})\text{—}(CH_2)_3\text{—}[NHCO(CH_2)_{10}]_n\text{—}\overset{\oplus}{P}Bu_3Br^{\ominus}$ $n = 1, 2$	$RBr + I^{\ominus} \rightarrow RI$ Decarboxylation 	84
$(\mathrm{Al})\text{-----}Bu_4\overset{\oplus}{P}X^{\ominus}$	$CH_2Cl_2 + C_2H_2Br \rightleftharpoons CH_2Br_2 + C_2H_5Cl$	86
(c) Crown ethers and cryptands		
		
 (a) $\text{—}R\text{—} = \text{—}CH_2[NHCO(CH_2)_{10}]_n\overset{Et}{N}\text{—}(CH_2)_9$ $n = 0, 1, 2$ $= \text{—}CH_2OCH_2\text{—}$	$R\text{—}Br + Y^{\ominus} \rightarrow R\text{—}Y'$ $Y^{\ominus} = I^{\ominus}, CN^{\ominus}, PhS^{\ominus}$	83
(b) $\text{—}R\text{—} = \text{—}CH_2\text{—}$	$R\text{—}Br + Y^{\ominus} \rightarrow R\text{—}Y$ $Y^{\ominus} = I^{\ominus}, CN^{\ominus}, PhO^{\ominus}$	87
(c) $\text{—}R\text{—} = \text{—}(CH_2)_n\text{—}OCH_2\text{—}$ $n = 1, 3$	$R\text{—}Cl + Y^{\ominus} \rightarrow R\text{—}Y$ $Y^{\ominus} = F^{\ominus}, CN^{\ominus}, AcO^{\ominus}$	88
 	$R\text{—}Br + Y^{\ominus} \rightarrow R\text{—}Y$ $Y^{\ominus} = I^{\ominus}, CN^{\ominus}, PhO^{\ominus}$	87

Table 2 Polymeric catalysts — *continued*

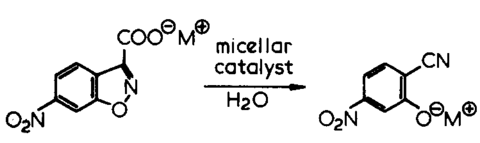
Functional polymer	Application	Reference
	$R-Br + Y^{\ominus} \longrightarrow R-Y$ $Y^{\ominus} = CN^{\ominus}, AcO^{\ominus}$	89
	Decarboxylation 	90
 $-R- = -CH_2OCH_2-, -CH_2NH(CH_2)_9$	$R-Br + Y^{\ominus} \longrightarrow R-Y$ $Y^{\ominus} = I^{\ominus}, CN^{\ominus}, PhS^{\ominus}$ $RCOR'' \xrightarrow{NaBH_4} R\underset{OH}{\underset{\vert}{C}}HR'$	83
(d) 'Cosolvents'		
(Ps)$-CH_2(OCH_2CH_2)_nOR$ (a) $n = 3$, R = H, Me, 	$RBr + PhO^{\ominus} \longrightarrow ROPh$	76, 91, 92
(b) $n = 4$, R = H, Tosylate,  THF—2—yl	$RBr + PhO^{\ominus} \longrightarrow ROPh$	91
(c) $n = 7$, $R = CH_3$	$R-Br + Y^{\ominus} \longrightarrow R-Y$ $Y^{\ominus} = I^{\ominus}, CN^{\ominus}, PhO^{\ominus}$	87
(d) $n = \sim 9$, $R = C_9H_{19}-C_{11}H_{23}$	$R-Br + PhO^{\ominus} \longrightarrow ROPh$	91
(e) $n = 16$, $R = CH_3$	$R-Br + Y^{\ominus} \longrightarrow R-Y$ $Y^{\ominus} = I^{\ominus}, CN^{\ominus}, PhO^{\ominus}$	87
(f) $n = \sim 30$, R = Ph	$R-Br + PhO^{\ominus} \longrightarrow ROPh$	76, 91
(P)$-CONR_2$ R = Me, n—Pr, n—Bu, n—Oct	$R-Br + PhO^{\ominus} \longrightarrow ROPh$	93
$RO(CH_2CH_2O)_nR/NaBH_4$	Reduction of esters to alcohols	94

(Ps) = polystyrene resin
(P) = $+CH_2-\underset{|}{C}H+_n$
(C) = polysaccharide
(Si) = Silica
(Al) = Alumina

metallic salt[77]. The understanding of such solid–liquid phase transfer catalysed systems is still not complete but some advances have been made in the case of resin-supported oligoethers or 'open' crown ethers[92].

Some further attempt has also been made to characterize a substrate selectivity effect in the application of these catalysts[76]. In this case the precursor neutral polymer matrices synthesised from vinyl pyridine displayed a significant reactivity dependence of the size of alkyl halides with which they were reacted. However, when the products of these reactions were subsequently used as catalysts this dependence was no longer observed. Presumably the dramatic change from a purely organic medium to a mixed aqueous/organic one plays a major part in this variation.

Another significant result concerns some of the novel supported crown ether systems[87]. Previously there was fairly general agreement that catalysts removed from the immediate vicinity of the support backbone by use of a 'spacer arm' were more active than conventional species. Indeed even short oligomethylene chains, e.g. $(CH_2)_3$ seem to show a significant enhancement[95]. However, there appears to be little difference in reactivity between crown ether catalysts supported as pendant groups, and those present as an integral part of the polymer backbone[87]. This observation again casts doubt on the molecular understanding of these systems and further investigations are clearly necessary. In passing it is worth noting that onium salts attached by a long spacer, perhaps somewhat predictably, in view of their surfactant-like structure, also function as micellar catalysts in aqueous solutions[85]. Thus the decarboxylation of 6-nitro-benzisoxazole-3-carboxylate (reaction (9)) is often used as a model reaction, characteristically accelerated by micelle species. When supported onium salts attached *via* a spacer arm are used in this reaction the typical rate acceleration is observed. Similarly, supported crown ethers give the same effect[90], the polymer presumably acting as a hydrophobic cavity and the benzisoxazole derivative being bound *via* complexation of the metal counterion, $M^{\oplus}$.



(9)

One particularly exciting development from Tundo's group in Turin is the phenomenon of solid/gas phase transfer catalysis[86]. Whether the mechanism of these reactions has any real parallel with liquid reactions is not yet known, and the designation is purely one of convenience at the moment. In those reactions where the nucleophilic species is a solid salt then the catalyst/salt mixture is gradually consumed and continuous process is difficult to envisage. However, in the case of halogen exchange reactions (reaction (10)) catalysed in this manner, the procedure has exciting technical implications. One clear operating requisite which has emerged is that the onium salt catalyst must be above its melting point for catalysis to ensue.

$$CH_2Cl_2 + C_2H_5Br \underset{\text{gas phase}}{\overset{\text{solid catalyst}}{\rightleftharpoons}} CH_2Br_2 + C_2H_5Cl \quad (10)$$

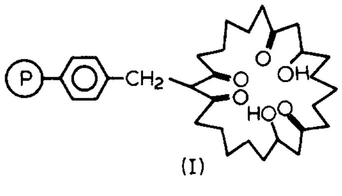
The final group of catalysts in this general area are the so-called supported 'cosolvents'. The solid/liquid catalytic systems developed by Sherrington and his coworkers, and based upon oligoethers, have been extended to include bound polyethers with rigid donor terminal groups[91]. Such species have significantly enhanced catalytic activity, in some instances approaching that of dibenzo-18-crown-6-ether when used in the same reaction. The report of the phase transfer catalytic activity of poly(*N*,*N*-dialkylacrylamide) resins[93] confirms earlier work dealing with a wide range of polar polymeric materials[96]. The dimethyl derivative proved to be the most active on a weight basis in a solid/liquid reaction, while only the di-n-octyl species showed any activity in liquid/liquid reactions.

A few examples of supported optically active phase transfer catalysts have been recorded, and these are dealt with under asymmetric syntheses. Continued interest has been shown in linear polybase catalysis of ester hydrolyses. Most of this work is not appropriate for this review but one new development again involves optically active polymers and this is also described later.

Separations in polymeric carriers

During the last few years this particular area of application of functionalized polymers has received increasing attention and a number of commercial applications already exist. No doubt with the current ecological drive expansion will continue in this field (see *Table 3*).

A great deal of work was completed many years ago on selective metal ion separations using specialized resins, and a host of 'chelating resins' were produced and patented. Interest in these has quickened again recently with the prospect of ore qualities falling progressively in the near future. A large number of alkali metal complexing species have been reported based largely on crown ether and cryptand structures[88,97–100]. Perhaps of more technical interest, however, are a number of resins with some selectivity for $UO_2^{2\oplus}$ [111,115,124,126]. One with a particularly pleasing structure contains a cyclic trimeric β-diketone residue (I) and has been used in recovering $UO_2^{2\oplus}$ from sea-water[111]. Resins have also been described for the extraction and recovery of heavy metal ions like $Pb^{2\oplus}$ and $Hg^{2\oplus}$ [112], and for the isolation of precious metals like silver and gold[119,121,122]. Further developments are also reported in the trapping of $Cu^{2\oplus}$ [114–118].



(I)

The need for optically pure materials in both the pharmaceutical and agro-chemical industry continues to grow. Since traditional methods of racemate resolution are slow and potentially costly in scale-up, there remains considerable interest and activity in chromatographic separations using chiral stationary phases. While virtually all this work has been at the analytical level, preparative spin-off remains a real possibility. The most effective separations of amino acid isomers are those involving diastereomeric copper complex formation, where the attachment to the stationary phase is itself *via* an optically pure amino acid residue[128–131]. Progress has also been made[132] in the resolution of sugar derivatives using stationary phases with an in-built 'chiral cavity'. As before, the cavity is generated by use of a suitable template molecule during formation of the polymeric matrix.

A variety of other interesting separations are reported employing specifically functionalised polymers. Pyridine derivatives have been scavenged from beer[137] and phenolic compounds recovered from water[140]. A Cu(I)Cl, aluminium chloride, polystyrene mixture has been applied successfully in the trapping of carbon monoxide[141]. Finally a very elegant separation of a minor component

Table 3 Separations on polymeric carriers

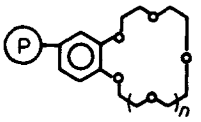
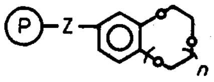
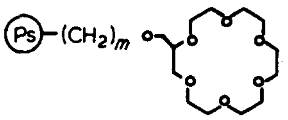
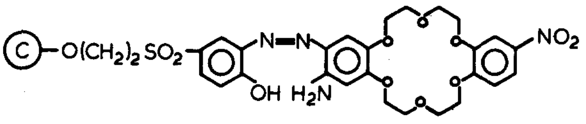
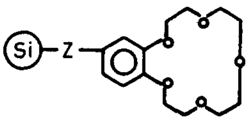
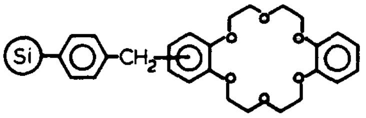
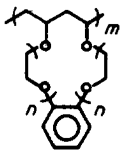
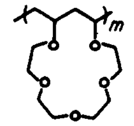
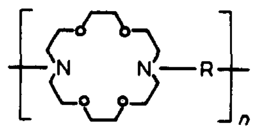
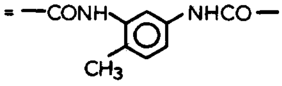
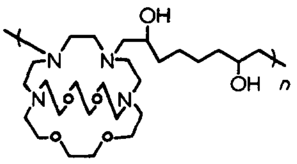
Functional polymer	Application	Reference
1 Metal ion separations		
 $n = 1, 2$	Binding of fluorescent species	97, 98
		
Z = $-CH_2-$, $n = 2, 3, 4, 6$	Cation binding	99
Z = $-COOCH_2-$, $n = 1$	Cation binding	100
 $m = 1, 3$	Alkali metal cation binding	88
	Cation binding	101
	Separation of alkali metal cations	
Z = $-(CH_2)-NHCO-$		102
= $-CH_2-$		103
	$K^{\oplus}$ binding	104
 $n = 0,1$		105
		106
		107
$-R-$ = $-CONH(CH_2)_6NHCO-$		
=  $-CONH-C_6H_3(CH_3)-NHCO-$		
		108

Table 3 Separations on polymeric carriers — *continued*

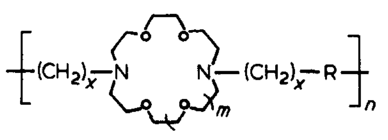
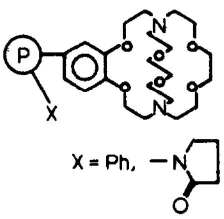
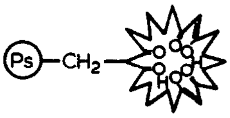
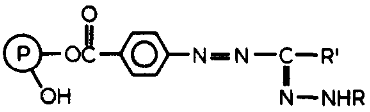
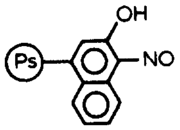
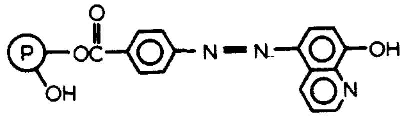
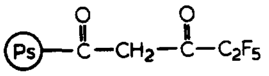
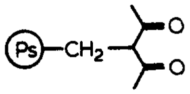
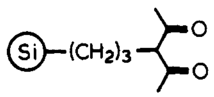
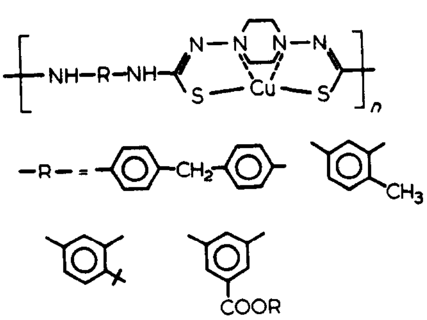
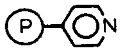
Functional polymer	Application	Reference
 x = 0, 2, 3; m = 0, 1		109
		110
	Extraction of $UO_2^{2\oplus}$ from sea-water	111
	Binding of $Co^{2\oplus}$, $Pb^{2\oplus}$, $Hg^{2\oplus}$	112
	Binding of metal ions	113
	Binding of $Cu^{2\oplus}$, $Fe^{3\oplus}$	114
 $\text{Ps}-\overset{\overset{O}{\Vert}}{C}-CH_2-\overset{\overset{O}{\Vert}}{C}-C_2F_5$	Binding of $Cu^{2\oplus}$, $Ni^{2\oplus}$, $UO_2^{2\oplus}$	115
	Binding of $Cu^{2\oplus}$, $Fe^{3\oplus}$, $Cr^{3\oplus}$	116
		
	Selective separation of $Cu^{2\oplus}$	117
	Selective separation $Cu^{2\oplus}$, $Ni^{2\oplus}$	118
Ⓟ—CONHOH	Separation of $Ag^{\oplus}$ and Au	119
	Determination of trace metals in natural water	120

Table 3 **Separations on polymeric carriers – *continued***

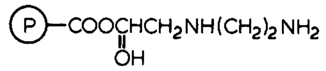
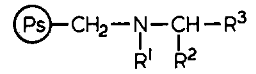
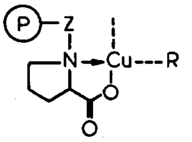
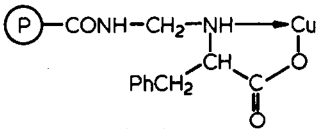
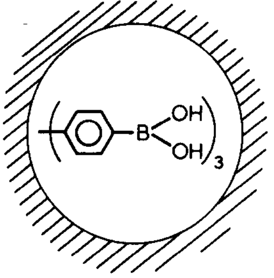
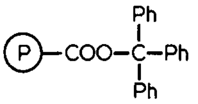
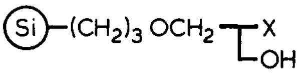
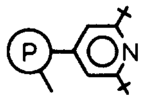
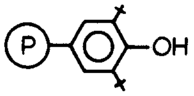
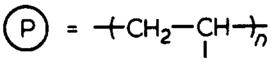
Functional polymer	Application	Reference
 $\text{(P)}-COO\underset{OH}{\underset{\|}{C}}HCH_2NH(CH_2)_2NH_2$	Separation of $Ag^{\oplus}$ and $Ag^{2\oplus}$	121, 122
$\text{(P)}-CONHCH_2NHCOCH_2SH$	Extraction of metal ions	123
$\text{(Si)}-(CH_2)_3NH(CH_2)_2NH_2$	Selective extraction of $UO_2^{2\oplus}$	124
Polyether–polyurethane Polyester–polyurethane	Extraction of tin	125
$\text{(Ps)}-CH_2N(CH_2COOH)_2$	Separation of $UO_2^{2\oplus}$ from natural water	126
2 Resolution of racemic mixtures		
 $\text{(Ps)}-CH_2-\underset{R^1}{N}-\underset{R^2}{CH}-R^3$ $R^1 = H;\ R^2 = CH_3;\ R^3 = Ph,\ -CH_2NH_2$ $R^1 = (CH_2)_2NH\overset{*}{C}HM\ Ph;\ R^2 = Me;\ R^3 = Ph$ $R^1 = -\overset{*}{C}H_2CHMeNH_2;\ R^2 = H;\ R^3 = Ph$	Resolution of racemic amino acids	127
 R = H, OH Z = –CH₂–, –COCH₂–, –(CH₂)₃–	Resolution of racemic amino acids	128–131
	Resolution of racemic amino acids	129
 'Chiral cavity'	Resolution of racemic mannitol	132
 $\text{(P)}-COO-\overset{Ph}{\underset{Ph}{C}}-Ph$	Resolution of racemic mixtures (Tröger's base, menthol, etc)	133
3 Other separations		
$\text{(Ps)}-CH_2\overset{\oplus}{N}Me_3OH^{\ominus}$	Separation of *N*-nitroso-diethanol-amine in cosmetics	134
$\text{(Ps)}-CH_2CH_2NH_2$	Separation of allergens from natural oils	135,136
$\text{(P)}-COOH$	Separation of alkylpyridines in beer	137
 $\text{(Si)}-(CH_2)_3OCH_2\begin{matrix}-X\\-OH\end{matrix}$ X = OH, NH₂ $\text{(Si)}-(CH_2)_3NH(CH_2)_2NH_2$	Separation of polar compounds	138

Table 3 Separations on polymeric carriers — *continued*

Functional polymer	Application	Reference
 X=H, Ph	Separation of HCl from acid chlorides	139
	Separation of amine and pyridine compounds	139
(Ps)—$CH_2N(CH_2COO^{\ominus})_2Fe^{III}$	Recovery of phenolic compounds from water	140
(Ps)----$Cu^{I}AlCl_4$	Separation of CO	141

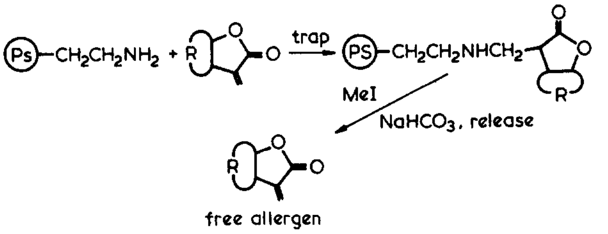
(Ps) = polystyrene


(P) = $-\!\!\left(CH_2-\underset{|}{C}H\right)\!\!-_n$

(Si) = silica

(C) = polysaccharide

from a complex mixture has recently been achieved in the removal of allergenic substances from natural oils used in the cosmetic industry[135,136]. A polystyrene resin functionalized with primary alkyl amine groups reacts stoichiometrically with the allergen and traps it from the oil. Subsequent treatment of the resin with methyl iodide and sodium bicarbonate releases the free allergen (reaction (11)).

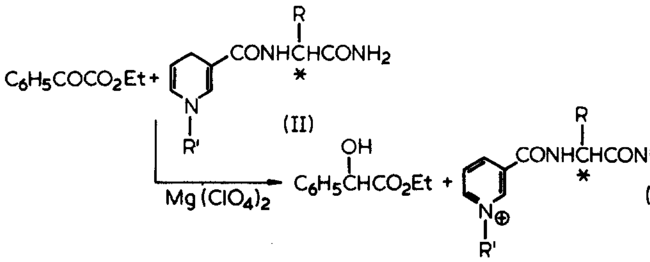


(11)

Organic syntheses on polymeric carriers

Further examples have been reported of the use of polymeric carriers as temporary supports on which an organic synthesis is carried out. By far the most important of these remains the 'solid phase' approach to oligopeptide and oligonucleotide assembly. These specialized areas, however, lie beyond the scope of this review, but some important developments have occurred also in asymmetric syntheses. Included in this summary in *Table 4* are a number of asymmetric phase transfer catalysts.

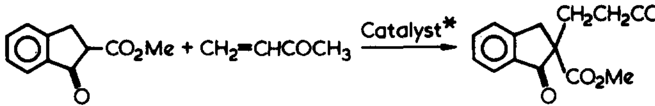
A polystyrene-supported nicotinamide species (II) has been employed as a model for the reduced form of nicotinamide adenine dinucleotide (NADH). By building in asymmetric substituents into the amide group, significant optical yields were obtained[143] in the reduction of ethyl benzoylformate using magnesium perchlorate (reaction (12)).



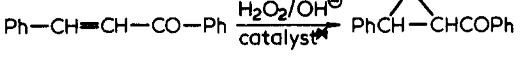
(12)

R' = (Ps)—$CH_2[NHCO(CH_2)_{10}]_n$—

Polymer-bound quinine derivatives have been used with some success in asymmetric Michael additions[142] and chalcone epoxidations[145,148] (reactions (13) and (14) respectively.



(13)



(14)

Progress has also been reported in the selective synthesis of cyclopropane derivatives[146] and in enantioselective ester syntheses[147], again in each case a functional polymer played an important role in directing the stereochemistry of the reaction. Further asymmetric olefin hydrogenations catalysed by polymer-supported optically active rhodium (I) complexes have been carried out[150-152]. These are one of the most successful asymmetric syntheses so far reported. Finally a relatively novel

Table 4 Organic syntheses on polymeric carriers

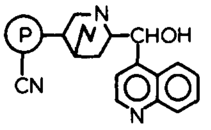
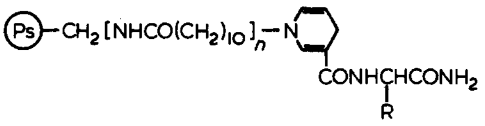
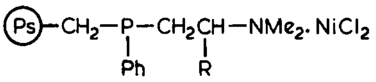
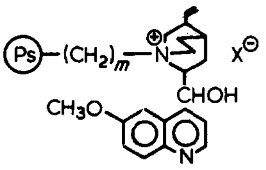
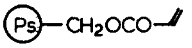
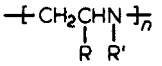
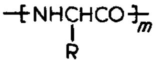
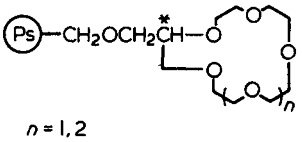
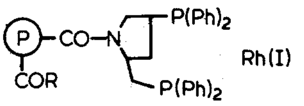
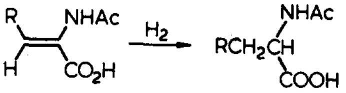
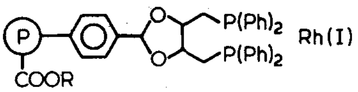
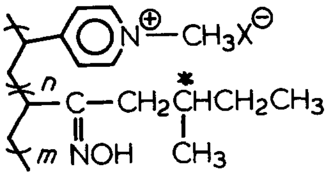
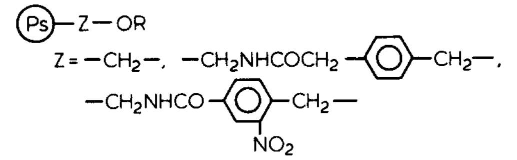
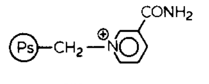
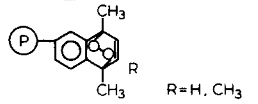
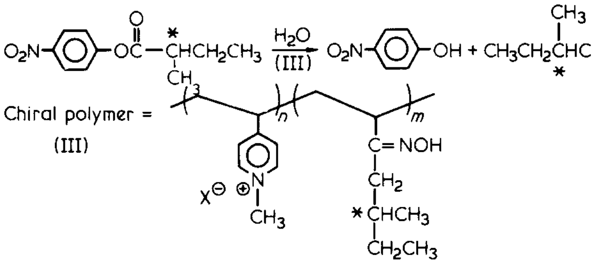
Functional polymer	Application	Reference
1 Asymmetric synthesis		
 R = H, CH_3O	Asymmetric Michael reactions	142
 n = 0, 1; R = Me, $PhCH_2$—	Asymmetric reduction of carbonyl compounds to alcohols	143
 $(Ps)\text{—}CH_2\text{—}\underset{Ph}{P}\text{—}CH_2\underset{R}{CH}\text{—}NMe_2 \cdot NiCl_2$ R = i — Pr, $PhCH_2$	Asymmetric cross-coupling of secondary alkyl Grignard reagent with vinyl bromide	144
 m = 1, 12; $X^{\ominus} = Cl^{\ominus}$, $Br^{\ominus}$	Asymmetric epoxidation of chalcones	145
 	Stereoselective preparation of cyclopropyl derivatives	146
 $\text{—}[CH_2\underset{R}{CH}\underset{R'}{N}]_n\text{—}$ R = i — Pr, H; R' = H, CH_3	Enantioselective ester syntheses from acid salts, chlorides and anhydrides	147
 $\text{—}[NH\underset{R}{CH}CO]_m\text{—}$	Asymmetric epoxidation of chalcone	148
 n = 1, 2		149
 R = $\text{—}O\overset{*}{C}HCH_3\overset{*}{C}HOHCH_3$, $\text{—}O(CH_2)_2OH$, $\text{—}CONMe_2$	Asymmetric hydrogenation 	150–152
 R = $\text{—}(CH_2)_2OH$, $\text{—}\overset{*}{C}HCH_3\overset{*}{C}HOHCH_3$		152
	Enantioselective ester hydrolyses	156

Table 4 Organic syntheses on polymeric carriers — *continued*

Functional polymer	Application	Reference
2 Cyclizations		
	Synthesis of diketopiperazines—cyclic dipeptide	153
3 Detection and isolation of reactive intermediates		
	Trapping of alloxan and ninhydrin radical anions — use in reduction reactions	154
	Thermal source of $^1O_2$	155

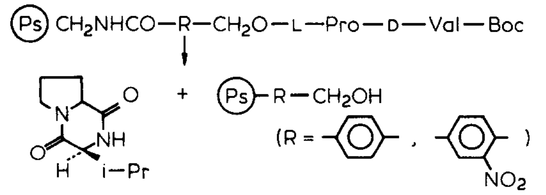
(Ps) = polystyrene (P) = $-(CH_2-CH)_n-$

development is the polymeric esterolysis catalysts prepared by Ciardelli and his coworkers[156]. These contain both pyridinium ions and oxime groups and are known to function as cooperative catalysts in the hydrolysis of activated esters. In this case a moderate chiral discrimination was obtained in the hydrolysis of (±) *p*-nitro phenyl 2-methylbutanoate using a copolymer of 4-vinylpyridine and the oxime of (+)-(S)-5-methyl-1-hepten-3-one (III) (reaction (15)).



(15)

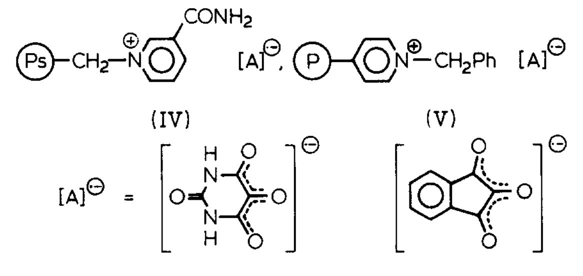
Another group of reactions in which polymer supports can be enormously helpful are intramolecular cyclizations. Here the advantage lies in isolating the species to be cyclized in low dilution on a polymer matrix. This naturally favours intra- *versus* inter-molecular reaction. Another successful example of this is reported involving synthesis of a cyclic dipeptide, diketopiperazine (reaction (16)).

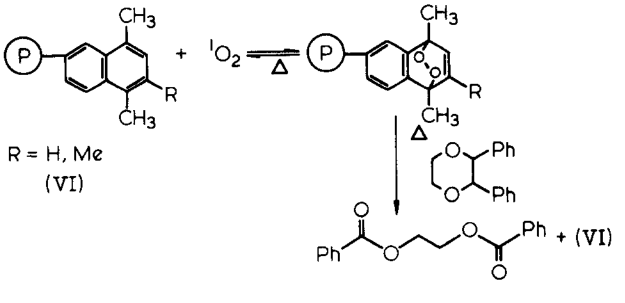


(16)

No doubt similar factors play an important role in the cross-condensation reactions[39,40] already described in the Polymeric reagents section.

One final and important application of functional polymers is in the demonstration of the existence of a reactive intermediate, the so-called 'three phase' test. Further examples of this have been described in that polymeric nicotinamide and pyridinium salt derivatives (IV and V) have been used to trap alloxan and ninhydrin radical anions[154]. These polymer trapped intermediates were then used for the reduction of a number of substrates. Polymeric naphthalene derivatives (VI) have been similarly employed to absorb singlet oxygen, $^1O_2$, generating endoperoxide polymers[155]. On heating, these release $^1O_2$ again, hence this is a facility for storing excited oxygen. In this case the released oxygen readily converted 2,3-diphenyl-*p*-dioxene to citronellol (reaction (16)).





FUTURE DEVELOPMENTS

The field of polymer-supported organic reactions is rapidly maturing, and specific areas of application will no doubt continue to proliferate as experimentalists realize the advantages that polymer-supported species can bring to their own systems. The use in asymmetric syntheses will certainly be expanded, as will their application in the synthesis of asymmetrically substituted symmetric molecules, e.g. porphoryns. With regard to polymeric reagents, the question of cheap and efficient regeneration remains a vital one and the use of electrochemical methods represents a novel step forward and highlights the close relationship with the developing field of polymer surface-modified electrodes[157].

In catalysis the use of the gas phase is particularly attractive, and the emergence of gas/solid phase transfer catalysis is a significant development[86]. Again more is likely to be seen of this type of system, perhaps extended to other classes of organic reaction. Supported transition metal complexes will also continue to attract considerable attention because of their tremendous industrial potential. Immobilized cluster compounds[158] and coordinately unsaturated species with no true analogue under homogeneous conditions will probably prove of immense synthetic utility.

More and more examples of the use of polar (and/or hydrophilic) supports are already in the pipeline, as the inherent disadvantages of conventional polystyrene resins are recognized. Such systems themselves have considerable potential disadvantages especially with regard to side reactions involving the support itself, and time may well prove the tremendous versatility of the lowly styrene based systems.

Whether polymer-supported systems finally develop and become accepted as routine organic synthetic procedures remains a debatable point. On a laboratory scale more and more researchers are being convinced but are deterred by the absence of any significant range of proprietary polymer reagents available 'off the shelf'. A number of companies are aware of this void and are planning to remedy the situation. Of crucial importance in this argument is the question of large scale industrial application. Polymeric acids and bases in the form of appropriate ion exchange resins have been available in large quantities for many years and despite the enormous literature on the very effective use of these as catalysts[159] only a few large scale industrial applications seem to have materialized. A particular drawback in this context is the limited chemical and thermal stability of such resins. While their application as acids and bases at temperatures ~200°–300°C probably represents the most extreme conditions in which a polymer-supported species is likely to be applied, nevertheless it sets a useful limit which might be aimed for in setting the specification for an industrial reagent/catalyst. With the present range of supports available the use of such temperatures is inconceivable except for very short periods, and considerable scope remains for novel developments in this context. We as polymer chemists are acutely aware of this problem and are currently looking at potential candidates for this high temperature regime.

REFERENCES

1 Geckeler, W., Pillai, V. N. R. and Mutter, M. *Adv. Polym. Sci.* 1981, **39**, 65

2 Sherrington, D. C. *Br. Polym. J.* 1980, **12**, 70

3 Chiellini, E., Solaro, R. and D'Antone, S. *Makromol. Chem., Suppl.* **5**, 1981, 82

4 Frechet, J. M. F. *Tetrahedron* 1981, **37**, 663

5 Kraus, M. A. and Patchornik, A. *J. Polym. Sci., Macromol. Rev.* 1980, **15**, 55

6 Cainelli, G., Manescalchi, F. and Contento, M. in 'Organic Synthesis Today and Tomorrow', Eds. B. M. Trost and C. R. Hutchinson, Pergamon Press Ltd., 1981

7 Kaneko, M. and Tsuchida, E. *J. Polym. Sci., Macromol. Rev.* 1981, **16**, 397

8 Bailey, D. C. and Langer, S. H. *Chem. Rev.* 1981, **81**, 109

9 Hagihara, N., Sonogashira, K. and Takahashi, S. *Adv. Polym. Sci.* 1981, **41**, 149

10 Kobayashi, N. *J. Synth. Org. Chem. Jpn.* 1981, **39**, 181

11 Davankov, V. A. *Adv. Chromatography* 1980, **18**, 139

12 Blaschke, G. *Angew Chem. Int. Edn.* 1980, **19**, 13

13 Smid, J. *Makromol. Chem., Suppl.* 1981, **5**, 203

14 Bolto, B. A. *J. Macromol. Sci. Chem.* 1980, **A14**, 107

15 Klein, J. *Makromol. Chem., Suppl.* 1981, **5**, 155

16 Dawson, D. J. *Aldrichimica Acta* 1981, **14**, 23

17 Akelah, A. and Sherrington, D. C. *Chem. Rev.* 1981, **81**, 557

18 Clarke, S. D., Harrison, C. R. and Hodge, P. *Tetrahedron Lett.* 1980, **21**, 1375

19 Akelah, A. *Eur. Polym. J.* submitted for publication

20 Appel, R. and Willms, L. *Chem. Ber.* 1981, **114**, 858

21 Ogura, K. Kondo, S. and Tsuda, K. *J. Polym. Sci., Polym. Chem. Edn.* 1981, **19**, 843

22 Bongini, A., Cainelli, G., Contento, M. and Manescalchi, F. *J. Chem. Soc. Chem. Commun.* 1980, 1278

23 Bongini, A., Cainelli, G., Contento, M. and Manescalchi, F. *Synthesis* 1980, 143

24 Shinkai, S., Tsuji, H., Hara, Y. and Manabe, O. *Bull. Chem. Soc. Jpn.* 1981, **54**, 631

25 Menger, F. M., Sinozaki, H. and Lee, L. C. *J. Org. Chem.* 1980, **45**, 2724

26 Amaratungs, W. and Frechet, J. M. F. *A.C.S. Polym. Prepr.* 1981, **22**, 151

27 Huche, M., Savignac, M. and Pourcelot, G. *Nouv. J. Chim.* 1981, **5**, 109

28 Iwabuchi, S., Nakahira, T., Fukushima, Y., Saito, O. and Kojima, K. *J. Polym. Sci., Polym. Chem. Edn.* 1981, **19**, 785

29 Frechet, J. M. F., Darling, P. and Farrall, M. J. *ACS, Polym. Prep.* 1980, **21**, 270

30 Frechet, J. M. J., Darling, P. and Farrall, M. J. *A.C.S., Polym. Prepr.* 1980, **21**, 270

30 Frechet, J. M. F., Darling, P. and Farrall, M. J. *A.C.S., Polym. Prepr.* 1980, **21**, 272

31 Frechet, J. M. J., Darling, P. and Farrall, M. J. *J. Org. Chem.* 1981, **46**, 1728

32 Brunelet, T., Gelbard, G. and Guyot, A. *Polym. Bull.* 1981, **5**, 145

33 Greig, J. A., Hancock, R. D. and Sherrington, D. C. *Eur. Polym. J.* 1980, **16**, 293

34 Yoshida, J., Nakai, R. and Kawabata, N. *J. Org. Chem.* 1980, **45**, 5269

35 Kageyama, T. and Yamamoto, T. *Makromol. Chem.* 1981, **182**, 705

36 Endo, T., Hawasaki, H. and Okawara, M. *A.C.S., Polym. Prepr.* 1979, **20**, 617

37 Drago, R. S., Gaul, J., Zombeck, A. and Straub, D. K. *J. Am. Chem. Soc.* 1980, **102**, 1033

38 Bullen, N. P., Hodge, P. and Thrope, F. G. *J. Chem. Soc. Perkin I* 1981, 1863

39 Chang, Y. H. and Ford, W. T. *J. Org. Chem.* 1981, **46**, 3756

40 Nambu, Y., Endo, T. and Okawara, M. *J. Polym. Sci., Polym. Chem. Edn.* 1980, **18**, 2793

41 Cainelli, G., Contento, M., Manascalchi, F. and Regnoli, R. *J. Chem. Soc. Perkin I* 1980, 2516

42 Cainelli, G., Contento, M., Manescalchi, F. and Mussatto, M. S. *Synthesis* 1981, 302

43 Cardillo, G., Orena, M., Porzi, G. and Sandri, S. *Synthesis* 1981, 793

44 Durr, H., Hanck, G., Bruck, W. and Kober, H. *Z. Naturforsch.* 1981, **36**, 1149

45 Pundak, S. and Wilchek, W. *J. Org. Chem.* 1981, **46**, 808

46 Zupan, M., Sket, B., Vodopivec, J., Zupet, P., Molan, S. and Japelj, M. *Synth. Commun.* 1981, **11**, 147

47 Misic-Vukovic, M. M., Vukovic, D. V. and Hadzismajlovic, D. E. *J. Chem. Res. (S)* 1980, 258

48 Hasegawa, H. and Higashimura, T. *Polym. J.* 1981, **13**, 915

49 Delmas, M. and Gaset, A. *Synthesis* 1980, 871

50 Jerabek, K. *J. Polym. Sci., Polym. Chem. Edn.* 1980, **18**, 65

51 Kmosťak, S. and Setinek, K. *Coll. Czech. Chem. Comm.* 1981, **46**, 2354

52 Yoshida, J. I., Hashimoto, J. and Kawabata, N. *Bull. Chem. Soc. Jpn.* 1981, **54**, 309

53 Moxley, T. T. and Gates, B. C. *J. Mol. Catal.* 1981, **12**, 389

54 Olah, G. A., Meidar, D., Malhotra, R., Olah, J. A. and Narang, S. C. *J. Catal.* 1980, **61**, 96

55 Olah, G. A. and Fung, A. P. *Synthesis* 1981, 473

56 Olah, G. A., Fund, A. P. and Malhotra, R. *Synthesis* 1981, 474

57 Olah, G. A., Husain, H., Gupta, B. G. B. and Narang, S. C. *Synthesis* 1981, 471

58 Olah, G. A., Narang, S. C., Meidar, D. and Salem, G. F. *Synthesis* 1981, 282

59 Olah, G. A., Fung, A. P. and Meidar, D. *Synthesis* 1981, 280

60 Kinstle, J. F. and Quinlan, G. L. *A.C.S., Polym. Prepr.* 1981, **22**, 166

61 Kamogawa, H., Takayanagi, Y. and Nanasawa, M. *J. Polym. Sci., Polym. Chem. Edn.* 1981, **19**, 2947

62 Nishikubo, T., Iizawa, T. and Yamada, M. *J. Polym. Sci., Polym. Chem. Edn.* 1981, **19**, 177

63 Asai, N. and Neckers, D. C. *J. Org. Chem.* 1980, **45**, 2903

64 Neckers, D. C., Gupta, S., Gupta, I., Thijs, L. and Damen, J. *A.C.S., Polym. Prepr.* 1981, **22**, 167

65 Bourdelande, J. L., Font, J. and Sanchez-ferrando, F. *Tetrahedron Lett.*, 1980, 3805

66 Gupta, S. N., Thijs, L. and Neckers, D. C. *Macromolecules* 1980, **13**, 1037

67 Gupta, S. N., Thijs, L. and Neckers, D. C. *J. Polym. Sci., Polym. Chem. Edn.* 1981, **19**, 855

68 Sumida, Y., Yoshida, S. and Vogl, O. *A.C.S., Polym. Prepr. 1980*, **21**, 201

69 Yoshida, S. and Vogl, O. *A.C.S., Polym. Prepr.* 1980, **21**, 203

70 Negishi, N., Tsunemitsu, K. and Shinohara, I. *Polym. J.* 1981, **13**, 411

71 Kita, Y., Uno, T., Inake, Y. and Takemoto, K. *J. Polym. Sci., Polym. Chem. Edn.* 1981, **19**, 477

72 Balakrishnan, T. and Ford, W. T. *Tetrahedron Lett.*1981, 4377

73 Tomoi, M. and Ford, W. T. *J. Am. Chem. Soc.* 1981, **103**, 3821, 3828

74 Tomoi, M. and Ford, W. T. *J. Am. Chem. Soc.* 1980, **102**, 7140

75 Regen, S. L., Czech, B. and Singh, A. *J. Am. Chem. Soc.* 1980, **102**, 6638

76 MacKenzie, W. M. and Sherrington, D. C. *Polymer* 1981, **22**, 431

77 Akelah, A. and Sherrington, D. C. *Eur. Polym. J.* 1982, **18**, 301

78 Kise, H., Arakai, K. and Seno, M. *Tetrahedron Lett.* 1981, 1017

79 Bram, G. and Decodts, G. *Tetrahedron Lett.* 1980, 5011

80 Maeda, H., Hayashi, Y. and Teramura, K. *Chem. Lett.* 1980, 677

81 Ohtani, N., Wilkie, C. A., Nigam, A. and Regen, S. L. *Macromolecules* 1981, **14**, 516

82 Regen, S. L., Bolikal, D. and Barcelon, C. *J. Org. Chem.* 1981, **46**, 2511

83 Montanari, F. and Tundo, P. *J. Org. Chem.* 1981, **46**, 2125

84 Tundo, P. and Venturello, P. *J. Am. Chem. Soc.* 1981, **103**, 856

85 Tundo, P. and Venturello, P. *Tetrahedron Lett.* 1980, 2581

86 Angelitti, E., Tundo, P. and Venturello, P. *J. Chem. Soc., Chem. Commun.* 1980, 1127

87 Fukunishi, K., Czech, B. and Regen, S. L. *J. Org. Chem.* 1981, **46**, 1218

88 Manecke, G. and Kramer, A. *Makromol. Chem.* 1981, **182**, 3017

89 Cook, F. L., Robertson, J. R. and Ernst, W. A. *A.C.S., Polym. Prepr.* 1981, **22**, 161

90 Smid, J., Kimura, K., Shirai, M. and Sinta, R. *A.C.S., Polym. Prepr.* 1981, **22**, 163

91 Heffernan, J. G., MacKenzie, W. M. and Sherrington, D. C. *J. Chem. Soc., Perkin II* 1981, 514

92 MacKenzie, W. M. and Sherrington, D. C. *Polymer*, 1980, **21**, 791

93 Regen, S. L., Mehotra, A. and Singh, A. *J. Org. Chem.* 1981, **46**, 2182

94 Santaniello, E., Ferraboschi, P. and Sozzani, P. *J. Org. Chem.* 1981, **46**, 4584

95 Chiles, M. S., Jackson, D. D. and Reeves, P. C. *J. Org. Chem.* 1980, **45**, 2915

96 Kelly, J., MacKenzie, W. M., Sherrington, D. C. and Riess, G. *Polymer* 1979, **20**, 1048

97 Kimura, K. and Smid, J. *Makromol. Chem., Rapid Commun.* 1981, **2**, 235

98 Jaycox, G. D. and Smid, J. *Makromol. Chem., Rapid Commun.* 1981, **2**, 299

99 Warshawsky, A. and Kahana, N. *A.C.S., Polym. Prepr.* 1980, **21**, 114

100 Kimura, K., Maeda, T. and Shono, T. *Makromol. Chem.* 1981, **182**, 1579

101 Pjamali, M. G., Burba, P. and Lieser, K. H. *Angew, Makromol. Chem.* 1980, **92**, 145

102 Kimura, K., Nakajima, M. and Shono, T. *Anal. Lett.* 1980, **13**, 741

103 Blasius, E., Janzen, K. P., Klein, W., Klotz, H., Ngyen, V. B., Tien, T. N., Pfeiffer, R., Scholten, G., Simon, H., Stockemer, H. and Toussaint, A. *J. Chromotography* 1980, **201**, 147

104 Waddell, T. G. and Leyden, D. E. *J. Org. Chem.* 1981, **46**, 2406

105 Butter, G. B. and Lien, Q. S. *A.C.S., Polym. Prepr.* 1981, **22**, 54

106 Mathias, L. F. and Canterbarry, J. B. *A.C.S., Polym. Prepr.* 1981, **22**, 38

107 Mathias, L. J. and Al-Jumah, K. *J. Polym. Sci., Polym. Chem. Edn.* 1980, **18**, 2911

108 Gramain, P. and Frere, Y. *Makromol. Chem., Rapid Commun.* 1981, **2**, 161

109 Cho, I. and Chang, S. K. *Makromol. Chem., Rapid Commun.* 1981, **2**, 155

110 Manecke, G. and Reuter, P. *Makromol. Chem.* 1981, **182**, 1973

111 Tabushi, I., Kobuke, Y. and Nishiya, T. *Nature* 1979, **280**, 665

112 Gruber, H. *Monatsheft. Chem.* 1981, **112**, 587

113 Ghosh, J. P., Pramanick, J. and Das, H. R. *Talanta* 1981, **28**, 274, 957

114 Gruber, H. *Monatsheft Chem.* 1981, **112**, 445

115 Phillips, H., Kinstle, J. F. and Adcock, J. L. *J. Polym. Sci., Polym. Chem. Edn.* 1981, **19**, 175

116 Yeh, H. C., Eichinger, B. E. and Andersen, N. H. *A.C.S., Polym. Prepr.* 1981, **22**, 184

117 Donaruma, L. G., Kitoh, S., Walsworth, G., Edzwald, J. K., Depinto, J. V., Maslyn, M. J. and Niles, R. A. *A.C.S., Polym. Prepr.* 1981, **22**, 149

118 Sugii, A., Ogawa, N., Iinuma, Y. and Yamamura, H. *Talanta* 1981, **28**, 551

119 Vernon, F. and Zin, W. M. *Anal. Chim. Acta* 1981, **123**, 309

120 Colella, M. B., Siggia, S. and Barnes, R. M. *Anal. Chem.* 1980, **52**, 967, 2347

121 Svec, F., Kalalova, E., Tlustakova, M. and Kalal, J. *Angew. Makromol. Chem.* 1980, **92**, 133

122 Schmidt, E. M., Inczedy, J., Laki, Z. and Szabadka, O. *J. Chromatography* 1980, **201**, 73

123 Deratani, A. and Selville, B. *Anal. Chem.* 1981, **53**, 1742

124 Northcott, S. E. and Leyden, D. E. *Anal. Chim. Acta.* 1981, **126**, 117

125 Lo, V. S. K. and Chow, A. *Talanta* 1981, **28**, 157

126 Pakalns, P. *Anal. Chim. Acta* 1980, **120**, 289

127 Kurganov, A. A., Zhuchkova, L. Y. and Davankov, V. A. *Makromol. Chem.* 1979, **180**, 2101

128 Zolotarev, Y. A., Myasoedov, N. F., Penkina, V. I., Dostovalov, I. N., Petrenik, O. V. and Davankov, V. A. *J. Chromatography* 1981, **207**, 231

129 Zolotarev, Y. A., Myasoedov, N. F., Penkina, V. I., Petrenik, O. V. and Davankov, V. A. *J. Chromatography* 1981, **207**, 63

130 Boue, J., Andebert, R. and Quivoron, C. *J. Chromatography* 1981, **204**, 185

131 Sugden, K., Hunter, C. and Jones, G. L. *J. Chromatography* 1980, **192**, 228

132 Wulff, G., Schulze, I. and Zabrocki, K. *Makromol. Chem.* 1980, **181**, 531

133 Yuki, H., Okamoto, Y. and Okamoto, I. *J. Am. Chem. Soc.* 1980, **102**, 6356

134 Fukuda, Y., Morikawa, Y. and Matsumoto, I. *Anal. Chem.* 1981, **53**, 2000

135 Cheminat, A., Benezra, C., Farrell, M. J. and Frechet, J. M. J. *Tetrahedron Lett.*, 1980, 617

136 Frechet, J. M. J., Farrell, M. J., Benezra, C. and Cheminat, A. *A.C.S., Polym. Prepr.* 1980, **21**, 101

137 Peppard, T. L. and Halsey, S. A. *J. Chromatography* 1980, **202**, 271

138 Becker, N. and Unger, K. *Z. Anal. Chem.* 1980, **304**, 374

139 Okamoto, Y., Khojasteh, M., Hou, C. J. and Rice, J. *A.C.S., Polym. Prepr.* 1980, **21**, 99

140 Petronio, B. M., Lagaua, A. and Russo, M. V. *Talanta* 1981, **28**, 215

141 Hirai, H., Komiyama, M. and Hara, S. *Makromol. Chem., Rapid Commun.* 1981, **2**, 495

142 Kobayashi, N. and Iwai, K. *J. Polym. Sci., Polym. Chem. Edn.* 1980, **18**, 923

143 Shinkai, S., Tsuji, H., Sone, T. and Manabe, O. *J. Polym. Sci., Polym. Lett. Edn.* 1981, **19**, 17

144 Hayashi, T., Nugashima, N. and Kumada, M. *Tetrahedron Lett.* 1980, 4623

145 Kobayashi, N. and Iwai, K. *Makromol. Chem., Rapid Commun.* 1981, **2**, 105

146 Artaud, I. and Viout, P. *Tetrahedron Lett.* 1981, 1009

147 Kawakami, Y., Suguira, T., Mizutani, Y. and Yamashita, Y. *J. Polym. Sci., Polym. Chem. Edn.* 1980, **18**, 3009

148 Julia, S., Masona, J. and Vega, J. C. *Angew Chem. Int. Edn.* 1980, **19**, 929

149 Manecke, G. and Winter, H. J. *Makromol. Chem., Rapid Commun.* 1981, **2**, 569

150 Baker, G. L., Fritschel, S. J. and Stille, J. K. *A.C.S., Polym. Prepr.* 1981, **22**, 155

151 Baker, G. L., Fritschel, S. J., Stille, J. R. and Stille, J. K. *J. Org. Chem.* 1981, **46**, 2954

152 Baker, G. L., Fritschel, S. J. and Stille, J. K. *J. Org. Chem.* 1981, **46**, 2960

153 Girault, E., Eritja, R. and Pedroso, E. *Tetrahedron Lett.* 1981, 3779

154 Endo, T. and Okawara, M. *J. Polym. Sci., Polym. Chem. Edn.* 1980, **18**, 2121

155 Saito, I., Nagata, R. and Matsuura, T. *Tetrahedron Lett.* 1981, 4231

156 Aglietto, M., Ruggeri, G., Tarqunini, B. and Ciardelli, F. *Polymer* 1980, **21**, 541

157 Murray, R. W. *Acc. Chem. Res.* 1980, **13**, 135

158 N'Guini, J. B., Lieto, J. and Aune, J. P. *J. Molec. Catal.* 1982, **15**, 367

159 Sherrington, D. C. in 'Polymer-supported Reactions in Organic Synthesis', Eds. P. Hodge and D. C. Sherrington, Wiley, Chichester, 1980, Ch. 3, p 157