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Application of Functionalized Polymers in Organic Synthesis

AHMED AKELAH

Chemistry Department, Faculty of Science, Tanta University, Tanta, Egypt

DAVID C. SHERRINGTON*

Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, Scotland

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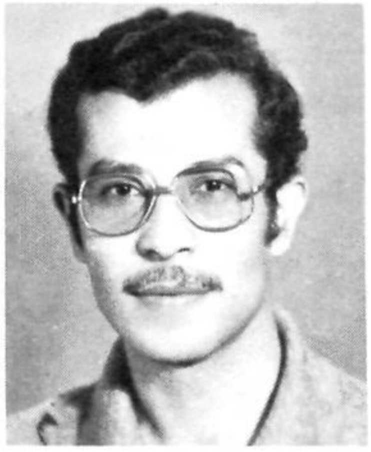
Contents



Ahmed Akelah was born in 1946 and raised in El-Salhia, Egypt. His undergraduate training was at Cairo University (B.Sc. (Honours), 1969) and his M.Sc. was received from Tanta University in 1973. During 1973–1978 he continued his studies at Bonn University where he received his *Dr. rer. nat.* degree with Professor G. Wulff. He joined Tanta University Chemistry staff in 1978. He is now a Visiting Scientist at the Department of Pure and Applied Chemistry, Strathclyde University, Glasgow. His main research interests are polymer science and related organic syntheses.

D. C. Sherrington was born in 1945 and received his B.Sc. (Honours) in 1966 and worked as a Research Assistant with Professors C. E. H. Bawn and A. Ledwith in Liverpool on the physical organic chemistry of ionic polymerizations. He was appointed Lecturer at the University of Strathclyde in 1971, where he continued his work on ionic polymerizations while also developing a research program on polymer-supported reactions, which has become his main interest. He received a Senior Ciba-Geigy Research Fellowship in 1981 and is currently working with Professors E. Chiellini and F. Ciardelli at the Istituto di Chimica Organica Industriale, University of Pisa, on optically active catalysts.

I. Introduction

Until the mid-1960s synthetic polymers were of considerable technological interest largely as materials rather than as organic molecules in their own right. The synthesis of new polymers and the detailed investigation of the mechanisms of existing polymerizations had in the main been directed toward the production of improved materials. At the same time techniques for the characterization of macromolecules had been translated into commercially available instrumentation, leading to a rapid expansion in the material science study of polymers and the search for a molecular understanding of polymer physics which has probably reached a plateau only in the last 2 or 3 years. Since the mid-1960s, synthetic macromolecules have also been increasingly recognized as organic species, capable of behaving as organic reactants and susceptible, under appropriate conditions, to all the chemical transformations of smaller organic species. Ion-exchange resins had previously been widely examined as acid and base catalysts,[1] though no technological application appears to have developed at that time. The rediscovery of polymers as organic molecules and their use in organic synthesis was made by Merrifield in 1963[2] when he introduced his "solid-phase technique" for the synthesis

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of peptides, in which an insoluble cross-linked macromolecule was used as a protecting group, simultaneously providing a facile method for isolating and purifying the product of each condensation step. Since that announcement functionalized polymers have found widespread application in organic synthesis and related fields. They have been employed as stoichiometric reagents, as catalysts, as protecting groups, as substrate carriers, in analytical chemistry, in ion exchange, in the detection of reaction intermediates, in chromatography, in biologically and pharmacologically active systems, in the immobilization of enzymes and cells, in the application of dyes and colorants, and in the field of agricultural chemicals.

The present review will restrict its coverage to those applications specifically in organic synthesis.

The use of inorganic supports in which reactive groups are introduced by covalent bond formation or by sorption phenomena is specifically excluded, and readers are directed to alternative reviews.[3,4]

Our aim has been to distill the literature into four fractions and to present each as an extensive table listing the functionalized polymer involved, along with its relevant application as a reagent, catalyst, etc. In the text we have taken selective examples in order to develop the principle associated with a particular section, and thereafter the remaining members of a section follow that same principle. The reader may therefore search for a particular supported species and ascertain the reactions in which it has been employed, or alternatively pick out a particular reaction type and deduce which supported species have proved useful. We have attempted to be as comprehensive as possible, covering the literature to early 1980, but do not claim to be exhaustive. We hope that this method of presentation will prove a novel and valuable addition to the review articles which precede it.[5-26]

A. Structure and Properties of Functionalized Polymers

A functionalized polymer in the present context is a synthetic macromolecule to which are chemically bound functional groups which can be utilized as reagents, catalysts, protecting groups, etc.

The macromolecule can be a linear species capable of forming a molecular solution in a suitable solvent, or alternatively a cross-linked species, or so-called resin, which though readily being solvated by a suitable solvent remains macroscopically insoluble. Of the two approaches the use of resins has been more widespread because of the practical advantages accruing from their insolubility (see next section). Active functional groups may be incorporated into polymer chains (i) by direct polymerization and copolymerization of monomers containing the desired functional groups, (ii) by chemical modification of a preformed polymer, and (iii) by a combination of (i) and (ii). A difficulty with the first method is that considerable manipulation of the copolymerization procedure may be necessary to ensure a good yield of the required copolymer and, in the case of resins, to ensure also a satisfactory physical form. In the second method commercially available resins of high quality are normally employed and the desired functional groups introduced by using standard organic synthetic procedures. While this generally ensures a product with a good physical form, the derivatization reactions required must be as free of side reactions as possible. Even so the polymers prepared in this way rarely have every repeat unit functionalized, and the distribution of groups may not be uniform. Indeed different methods of preparation may give rise to different functional group distributions, and this still remains an area requiring more detailed investigations and the development of more suitable analytical procedures. Standard elemental analysis with supporting infrared absorption spectra generally provides satisfactory evidence for chemical modification and allows calculation of the degree of substitution or functionalization of a polymeric species, quoted in milliequivalents per gram of polymer. In some circumstances other analytical procedures,[27] including detailed structural analysis by nuclear magnetic resonance spectroscopy,[28] can be applied, depending on the nature of the polymer and the chemical transformations involved.

The ease of chemical modification of a resin, and indeed the level of success in its subsequent application as a reagent or a catalyst, can depend substantially on the physical properties of the resin itself. Functionalized polymeric supports must possess a structure which permits adequate diffusion of reagents into the reactive sites, a phenomenon which depends on the extent of swelling or solvation, the effective pore size and pore volume, and the chemical and mechanical stability of the resins under the conditions of a particular chemical reaction or reaction sequence. These in turn depend on the degree of cross-linking of the resin and the conditions employed during preparation of the resin. Three main types of resin can be identified: (a) microporous or gel-type resins; (b) macroporous resins, and (c) macroreticular resins. These have been described in detail elsewhere,[29] but the essential differences can be summarized as follows.

Microporous species are prepared from a vinyl monomer and a difunctional vinyl comonomer in the absence of any additional solvating media. In the dry state they are microporous, with polymer chains being separated by typical solid-state intermolecular distances. On contact with a good solvent a soft gel network is formed with the generation of considerable porosity depending on the degree of cross-linking. Where the latter is $\leq 1\%$ (i.e., % of difunctional comonomer used in polymerization), swollen resins generally have low mechanical stability and readily fragment even under carefully handling. In contrast, commercially available microporous resins with $>8\%$ cross-linking are mechanically very stable, but unfortunately give rise to acute diffusional limitations resulting in slow and incomplete reactions. In practice, resins of $\sim 2\%$ cross-link ratio provide a satisfactory compromise generally allowing adequate penetration by most reagents and yet retaining sufficient mechanical stability to provide ease of handling. Copolymer beads made by suspension polymerization of 98% styrene and 2% divinylbenzene isomers (in practice $\sim 4\%$ commercial divinylbenzene[29]) have found very wide application as a result of these factors.

Very similar properties can arise with macroporous resins. These are prepared as before but with the inclusion of an inert solvent. Where the solvent solvates both monomer and polymer a fully expanded network is formed with a considerable degree of porosity.[30] Removal of the solvent causes a reversible collapse of the matrix, and in the dry state such materials are similar to microporous resins. In order to achieve mechanical stability in the solvent swollen state it is usual to employ larger quantities of difunctional comonomer in the preparation, up to ~20%. Materials of this type are not readily available from commercial sources.

Where the solvent employed during polymerization is a good solvent for the monomers but a precipitant for the polymer, the term macroreticular is generally employed to describe the product.[31] The latter is a highly porous rigid material which retains its overall shape and volume when the precipitant is removed. Again it is normal to use a larger quantity of difunctional comonomer, and in the case of some chromatographic applications styrene resins with >50% divinylbenzene content are employed.[32] This enables such products to be subjected to high pressures, ~1000 psi, in high-performance liquid chromatography conditions. The structure of these resins is quite different from the previous two. They have a large and permanent pore volume, and reaction sites may be regarded as being located on a permanent interior surface of the resin. Such materials are available from a number of commercial sources. Macroporous species have also been prepared in the presence of large inert molecules which subsequently can be washed away to create permanent voids.[33] The authors are not aware of any commercial source for these products.

The choice of using a microporous or macroreticular resin in preparing a functionalized polymer can be a difficult one and depends very much on the application in question. In a swelling solvent microporous species can often be loaded or functionalized to higher levels than macroreticular ones. However, the latter are generally much less sensitive to the choice of solvent,[34,35] which is not always a readily variable parameter in some chemical reactions. Swollen microporous resins are less sensitive to sudden shock but cannot be subjected to steady and high pressures. Conversely rigid macroreticular species are brittle and fracture under sudden stress, but can withstand considerable steady pressures.

The role of a solvent in the application of a functionalized resin is complex. Ideally it should interact with the polymer matrix to optimize the diffusional mobility of reagent molecules. It should have the correct solvating characteristics to aid any chemical transformations being carried out. It should not limit the reaction conditions which are to be applied (e.g., the temperature), and in the case of bound photosensitizers, for example, it should encourage translucence and not opacity. Naturally it is difficult to satisfy all of these criteria simultaneously, and the selection of a solvent is often a compromise. There have been a number of attempts to quantify the interaction of solvents with a polymer support matrix, and the nitroxide spin-labeling experiments have achieved this with respect to the local motions of the polymer backbone and the associated side-chain substituents.[36,37]

B. Advantages and Disadvantages in Using Functionalized Polymers

Probably the most important advantage in using a functionalized polymer as a reagent or catalyst is the simplification of product work-up, separation, and isolation. In the case of cross-linked polymer resins, simple filtration procedures can be used for isolation and washing, and the need for complex chromatographic techniques can be eliminated. With linear polymers, techniques such as precipitation, sedimentation, and ultrafiltration can be employed, although these are by no means as convenient and readily available in all laboratories. Resins, in addition, provide the possibility of automation in the case of repetitive stepwise syntheses and the facility of carrying out reactions in flow reactors on a commercial scale. Supported reagents may also be used more conveniently in excess to drive reactions to completion, without incurring a penalty in the work-up procedure. Scarce and/or expensive materials can be efficiently retained when attached to a polymer and, if appropriate chemistry is available, they can in principle be recycled many times. The reactivity of an unstable reagent or catalyst may be attenuated when supported on a resin, and the corrosive action of, for example, protonic acids can also be minimized by this effective encapsulation. Finally, toxic and malodorous materials can be rendered environmentally more acceptable.

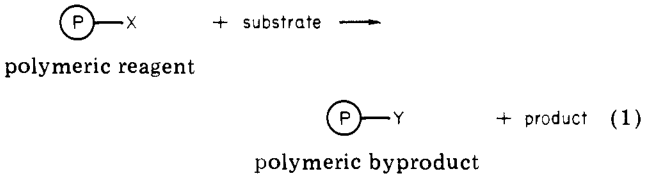
In addition to these factors, a number of potentially important reactivity changes may be induced by the use of a functionalized polymer.[25] When the latter is cross-linked, restricted interaction of functional groups may be achieved. A high degree of cross-linking, a low level of functionalization, low reaction temperatures, and the development of electronic charges near the polymer backbone tend to encourage this situation, which may be regarding as mimicing the solution condition of "infinite dilution". In these circumstances intermolecular reaction of bound molecules is prevented, and such attached residues can be made either to react intramolecularly or to react selectively with an added soluble reagent. Polymer supported metal complexes with vacant coordination sites can be regarded as fulfilling this description, with the resin inhibiting the normal solution oligomerization processes of such species. Under certain circumstances it is also possible to achieve the complementary state of "high concentration" by heavily loading a flexible polymer matrix with one particular moiety in an attempt to force its reaction with a second polymer-bound species.[15]

Balancing the above advantages there are also a number of important disadvantges. Probably the most important of these is the likely additional time and cost in synthesizing a supported reagent or catalyst. This may well be offset by the potential advantages, and certainly in the case of regenerable and recyclable species this objection essentially disappears. The occurrence of slow reactions and poor yields, however, can seldom be accommodated, and these can be a problem. Appropriate choice of support and reaction conditions can overcome this, but most of us in the field have been defeated from time to time. With those applications involving the assembly or modification of a polymer-bound substrate, the final cleavage step releasing the product into solution can be incomplete, or the vigorous conditions employed in cleavage may result in degradation of the polymer. The overall chemical and mechanical stability of the support can often be limiting, and in the case of strongly acidic and basic ion-exchange resins limited temperature stability has hindered their widespread commercial application. The ultimate capacity of a functionalized polymer is also restricted, and may be important in preparative organic chemistry involving stoichiometric quantities of supported reagents. One of the major differences between inorganic supports and polymers is the even lower loading capabilities of the former which, while being suitable for the attachment of catalysts and in polypeptide and oligonucleotide synthesis, is totally unsuitable for high-capacity demands.[4] Difficulty in the characterization of reactions on polymers can also arise. These are maximized in the case of resins, where those techniques relying on the formation of a true homogeneous solution, at best, may be rendered inadequate or insensitive and, at worst, can be completely useless. Finally in the use of functionalized polymers there always exists the additional chemical option of a side reaction with the polymer itself. A number of classic cross-linking side reactions have been identified,[38,39] but many other low yields may well be associated with intrapolymeric reactions, which have never been recognized, let alone characterized.

Despite these potential drawbacks, a large number of systems have been developed, and considerable scope now exists for their exploitation in routine synthetic chemistry. The area need no longer be regarded as a specialized one, and the tables in sections II-V should aid potential users in seeking out appropriate systems for their own needs.

II. Polymeric Reagents

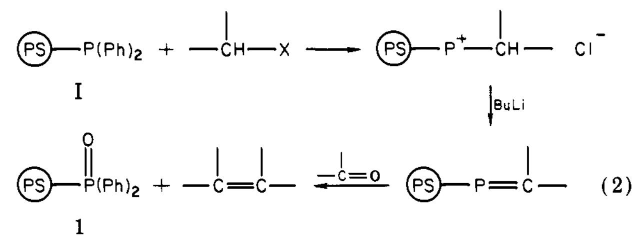
A polymeric reagent is a reactive organic group bound to a macromolecular support and used in stoichiometric quantities to achieve the chemical modification of an added substrate (reaction 1). Such groups may be attached to polymeric carriers by physical adsorption or by chemical bonding. Physically adsorbed species are generally unsatisfactory since in use the components tend to dissociate, and they are therefore unsuitable for column or cyclical application.

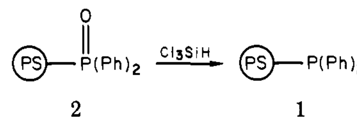


Those chemical reagents covalently attached to polymeric carriers and successfully used in organic synthesis are listed in Table I. Note that after reaction the byproducts remain attached to the insoluble polymer and can be removed by simple filtration. Some of these can be regenerated for repeated use.

A. Polymeric Phosphine Reagents

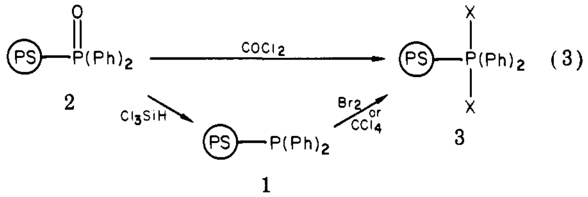
In spite of the widespread application of the Wittig reaction to olefin synthesis, a principle disadvantage of this reaction is the difficulty of separating the main product from the byproduct, triphenylphosphine oxide. In addition, the phosphine itself is a costly reagent. However, by use of the insoluble polymeric phosphine reagent 1 (reaction 2), the byproduct remains attached to the polymer after the reaction and is readily separated from the desired product. Moreover, the polymeric phosphine oxide byproduct, 2, can be readily recycled and reused in further Wittig reactions.[40-42]



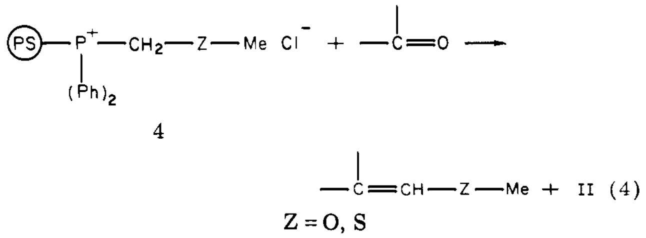


The presence of lithium ions in conventional Wittig reactions, arising during generation of the ylide, lead to the formation of trans olefins due to the preferred complexation of the threo form of the betaine. Polymeric phosphonium reagents can give high yields of cis olefins since inorganic lithium salts may be filtered off before the addition of the carbonyl compound.[40]

In addition to their use in Wittig reactions, polymeric phosphine have been used as their dihalides, 3, X = Cl, Br, and with carbon tetrachloride, 3, X = CCl_4, as mild and efficient reagents for the cleavage of ethers[41] and for the conversion of carboxylic acids, alcohols, and primary amides into the corresponding acid chlorides, alkyl halides, and nitriles, respectively. The recovered polymeric phosphine oxide is readily converted to the polymeric phosphine dihalide for reuse[43] (reaction 3).



Recently, we have used the polymeric phosphine dibromide for the preparation of some compounds which are sensitive to water, column chromatography, and the elevated temperatures required in distillation. These include imidoyl bromide, carbodiimides, and ketenimines.[44] (Polystyryl)diphenyl(methoxymethyl)-phosphonium chloride (4) has also been prepared and used for the synthesis of vinyl ethers and sulfides derivatives from carbonyl compounds[45] (reaction 4).



B. Polymeric Sulfonium Salts

Thiols and thioethers are very useful synthetic reagents because of their low cost and high reactivity, which often allows the use of mild reaction conditions. Unfortunately the noxious odor of sulfide or thiol derivatives and the difficulty of removing sulfide byproduct from reaction mixtures detract from their usefulness. A polymeric sulfide reagent may be used to overcome these disadvantages, and in addition in some applications it can be reused after washing since the original reagent is automatically re-formed.[46] Insoluble polymeric thiol–disulfide systems have been successfully used in a number of oxidation-reduction processes[47,48] (reaction 5).

$$R\text{-}S\text{-}S\text{-}R + 2H^+ + 2e \rightleftharpoons 2R\text{-}SH \qquad (5)$$

If the reactive sites on the polymer maintain separation during reaction, polymeric sulfonium salts may be used for selective monooxidation of diol compounds.[46] In addition, other polymeric reagents have been used in the epoxidation of aldehydes[49,50] and homologation of alkyl iodides and diiodides,[51] as shown in Table I, section 2.

C. Polymeric Halogenating Reagents

Interesting but different polymeric halogenating reagents (Table I, section 3) have been successfully used for the specific addition of halogen to olefins and for allylic halogenation. The success of these functionalized insoluble polymers is attributed to a combination of several advantages, including changes in the specificity and reactivity of the functional group, the ease of removal of excess reagent and product separation, and the facile ability to regenerate the reagents. For example, halogenation of alkyl aromatic compounds with *N*-chlorosuccinimide in the absence of solvents and free-radical initiators leads to the formation of a mixture consisting of side-chain- and aryl-chlorinated compounds. However, with poly(*N*-chloromaleimide) under the same conditions, arylchloro-substituted derivatives are the only product obtained.[52]

D. Polymeric Condensing Reagents

Insoluble polymer-bound carbodiimide derivatives (5) have been prepared and used as condensing agents in the synthesis of peptides.[53,54] Some others were used in the conversion of carboxylic acids to their anhydrides[55] and in the Moffatt oxidation, particularly in the oxidation of highly sensitive alcohols.[56] Polymeric carbodiimides have the advantage that the byproduct, urea 6, remains attached to the polymer and can be readily converted back into the polymeric carbodiimide 5[55] (reaction 6).

$$\underset{6}{\text{(PS)}-NH-CO-NH-R} \xrightarrow{TsCl,\ Et_3N} \underset{5}{\text{(PS)}-N{=}C{=}N-R} \qquad (6)$$

Another polymeric condensing reagent incorporates sulfonyl chloride groups and has been used in oligonucleotide synthesis.[57] The use of a supported reagent has some advantages over the nonsupported system, such as the elimination of emulsion problems and a reduction in the contamination of nucleotide product.

E. Polymeric Redox Reagents

Although many useful procedures for oxidation processes have been reported, the main disadvantage of these is the relative difficulty in the preparation of the reagents and in the working-up of the reaction mixture. Polymeric redox systems were one of the earliest examples of polymeric reagents and alleviate these difficulties. The most important classes of polymeric redox systems are the hydroquinone–quinone, thiol–disulfide, pyridine–dihydropyridine, polymeric dyes, and polymeric metal complex systems.[47,48]

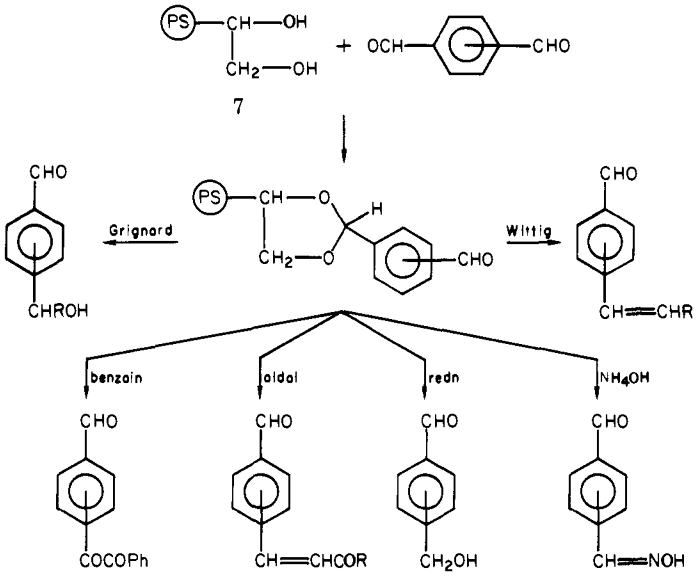
Aliphatic peroxy acids explode very readily on impact, and analogous polymeric reagents based on polyacrylic acids behave similarly.[58-60] Aromatic peroxy acids in contrast are more stable, and the polymer-supported analogues of these have proved very useful indeed.[34,61,62]

Chromic acid is a powerful oxidizing agent, and a supported analogue has been used for the oxidation of alcohols to carbonyl compounds in high yields.[63,64]

Insoluble polymeric organotin dihydride[65] was prepared and used as a selective reducing agent for carbonyl compounds and alkyl halides. This polymeric reagent combines the advantages of both the monomeric dihydride reagent, i.e., its high reactivity, and the monohydride reagent, i.e., its high stability.

F. Polymeric Protecting Groups

There is no group capable of reacting selectively with only one functionality of a completely symmetrical bifunctional compound. However, functionalized insoluble polymers have been used with some success in this role. The selectivity of functional polymer resins for monoblocking utilizes the approximation to "infinite dilution" which can be achieved with a polymer bound group. In this type of reaction a large excess of a symmetrical bifunctional substrate is employed to ensure that only one of the functional groups reacts with the polymer-bound protecting group. Symmetrical diols[35,66-70] and dialdehydes[71-73] have been monoblocked in this way, allowing further reaction at the free alcohol or aldehyde end. For example, Leznoff and his coworkers[71,72] have used a polymer containing a diol functional group, 7, as a monoblocking agent for symmetrical dialdehydes (reaction 7). Other functionalized polymeric reagents used as selective monoblocking groups are listed in Table I, section 6.



(7)

G. Polymeric Acylation and Alkylation Reagents

Several functional polymers have been reported in the literature for use in the acylation and alkylation of

TABLE I. Polymeric Reagents[a]

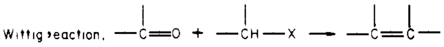
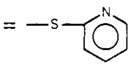
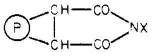
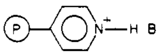
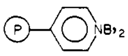
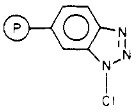
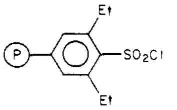
functional polymer	application as reagent	ref
	1. Polymeric Phosphine Reagents	
(PS)—P(Ph)$_2$	Wittig reaction,  $-\overset{|}{C}=O + -\overset{|}{C}H-X \rightarrow -\overset{|}{C}=\overset{|}{C}-$	40, 45, 80-84
(PS)—(CH$_2$)$_n$P(Ph$_2$)$_2$X$_2$		
a, n = 0; X$_2$ = CCl$_4$	conversion of alcohols to chlorides	42, 43, 85-87
	conversion of acids to acid chlorides	43, 85
	conversion of secondary amides to imidoyl chlorides	88
	conversion of acids and amines to amides	85
	conversion of primary amides and aldoximes to nitriles	88
	peptide synthesis	89, 90
	conversion of amides to nitriles	43
b, n = 0; X = Br	conversion of ureas to carbodiimides, amides to imidoyl bromides and ketenimines	44
c, n = 0; X = 	peptide synthesis	91
d, n = 1; X = Cl	conversion of acids to acid chlorides	43, 92
[(PS)—P(Ph)$_2$]$_2$RhCl(CO)	conversion of alkyl lithium and acid chlorides to ketones	93
	2. Polymeric Sulfonium Salts	
(PS)—(CH$_2$)$_n$S$^+$MeR X$^-$		
a, n = 0; R = Me; X = MeSO$_4$	epoxidation of aldehydes	49
b, n = 0; R = Cl; X = Cl	oxidation and selective monooxidation of alcohols	46, 51
c, n = 0; R = Me, Et; X = FSO$_3$	epoxidation of aldehydes	94
d, n = 1; R = Me; X = I	epoxidation of aldehydes	49, 50
e, n = 1; R = alk; X = HCO$_3$	peptide synthesis	95
(PS)—S—CH$_2^-$Li$^+$	homologation of alkyl iodides and diiodides	51
	3. Polymeric Halogenating Reagents	
		
a, X = Br	allylic and aromatic bromination	96-98
b, X = Cl	aromatic chlorination	52
(PS)—I X$_2$		
a, X = F	addition of F$_2$ to olefins to give $-CF_2\overset{|}{C}-$	99
b, X = Cl	addition of Cl$_2$ to olefins	100, 101
	bromination of olefins and ketones	102
	addition of Br$_2$ to olefins	103-105
(PS)—CH$_2$N$^+$Me$_3$Br$_3^-$	α bromination of carbonyl compounds, addition of Br$_2$ to alkenes and alkynes	106, 107
and -BrCl$_2^-$	chlorobromination of alkenes and alkynes	107
(PS)—C(Ph)=NBr	allylic bromination	108
(PS)—COCl	conversion of acids to acid chlorides	109
	chlorination of aromatic compounds	110
	4. Polymeric Condensing Reagents	
-[(CH$_2$)$_6$N=C=N-]$_n$-	peptide synthesis	53
(PS)—CH$_2$N=C=NR		
a, R = i-Pr	conversion of acids to anhydrides	55
b, R = Et	peptide synthesis	56
(PS)—C≡CNEt$_2$	conversion of acids to mixed anhydrides, esters, and amides	111
	oligonucleotide synthesis	54

TABLE I (*Continued*)

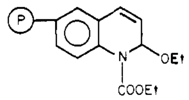
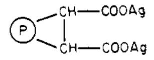
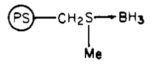
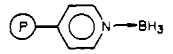
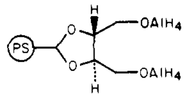
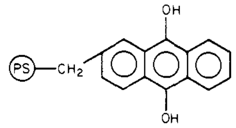
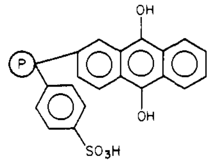
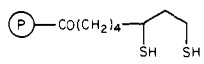
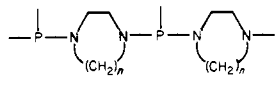
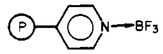
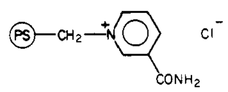
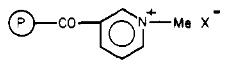
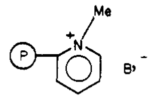
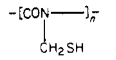
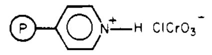
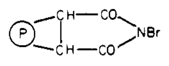
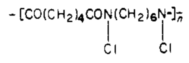
functional polymer	application as reagent	ref
	peptide synthesis	57, 112
	Koenigs-Knorr glycoside synthesis	113
	5. Polymeric Redox Reagents	
$(PS)\text{—}CH_2N^+Me_3\ BH_4^-$	reduction of carbonyl compounds to alcohols	114, 115
 $(PS)\text{—}CH_2\underset{Me}{S}\rightarrow BH_3$	reduction of ketones	116
	reduction of carbonyl compounds	117
$(PS)\text{—}Sn(n\text{-}Bu)H_2$	reduction of carbonyl compounds, selective monoreduction of dials, reduction of alkyl halides to alkanes	65
$(PS)\text{—}CMe_2OAlH_4$	reduction of ketones	118
	reduction of ketones	118
	reduction of quinones to quinols	119
	reduction of quinone to quinols	120
	reduction of disulfide bridges in peptide, proteins, oxidized form of glutathione, and cystine	121
 $n = 2, 3$	desulfurization of polysulfide compounds	122
	reduction of carbonyl compounds	123
	reduction of thionine, benzoquinone, and methylene blue	105, 124
 $X = I^-, SO_4^{2-}$	reducing reagent	101
	redox reagent	104, 105, 125
 $\text{-}[\underset{CH_2SH}{CON}\text{—}]_n\text{-}$	redox reagent	126
	oxidation of alcohols oxidation of alkyl halides to carbonyl compounds	127 128
$(PS)\text{—}CH_2N^+Me_3\ HCrO_3^-$	oxidation of alcohols and alkyl halides to carbonyl compounds	128, 129
	oxidation of alcohols	98
$(PS)\text{—}CH_2N^+Me_3\ IO_4^-$	oxidation of phenols and sulfides	130
 $\text{-}[CO(CH_2)_4CO\underset{Cl}{N}(CH_2)_6\underset{Cl}{N}\text{-}]_n$	oxidation of alcohols and thioethers	131-134

TABLE I (*Continued*)

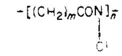
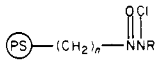
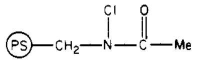
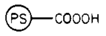
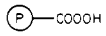
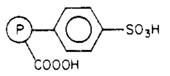
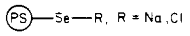
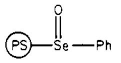
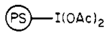
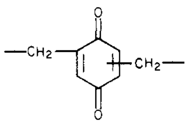
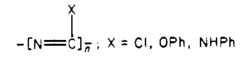
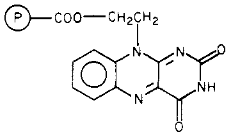
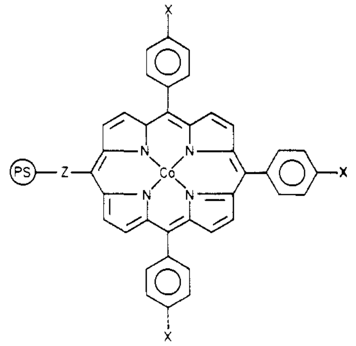
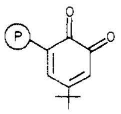
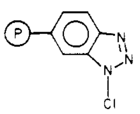
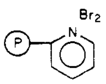
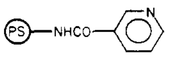
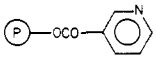
functional polymer	application as reagent	ref
 $-[(CH_2)_mCON(Cl)]_n-$ $m = 3, 6$	oxidation of alcohols and diamines	135
 a, $n = 0$; R = Me, Ph b, $n = 1$; R = Ac	oxidation of alcohols	130
 $(PS)-CH_2-N(Cl)-C(=O)-Me$	oxidation of alcohols	130
	epoxidation of olefins oxidation of thioethers	34, 61 136, 137
	epoxidation	58-60, 138
	hydroxylation of olefins, conversion of acids to peroxy acids	62
	α,β dehydrogenation of carbonyl compounds	139, 140
	oxidation of β-methylnaphthalene to β-naphthaldehyde	139, 140
	oxidation of amines	100
	dehydrogenation, oxidation of amines, cysteine, NADPH, vitamin C oxidation of cycloheptatriene to tropylium cation, Strecker reaction	141 142
 $-[N{=}C(X)]_n-$; X = Cl, OPh, NHPh	peroxidation of alkylaromatic hydrocarbons	143, 144
	dehydrogenation of methyl mandelate	145
 X = NH_2, Z = NH X = COOH, Z = CO	oxidation of thiols to sulfides	146
	oxidation of amines to ketones	147
	oxidation of alcohols, hydrazo compounds, sulfides to carbonyl, azo compounds, and sulfoxides, respectively	110
	oxidation of thiols to sulphides	148
	redox reagent	104
	redox reagent	104

TABLE I (*Continued*)

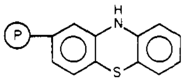
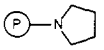
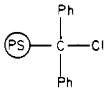
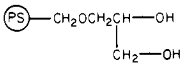
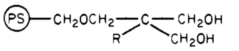
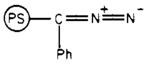
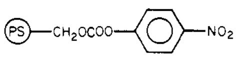
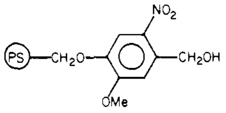
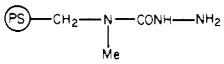
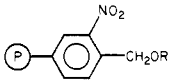
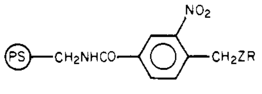
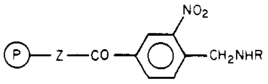
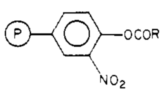
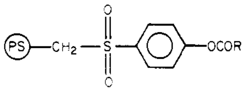
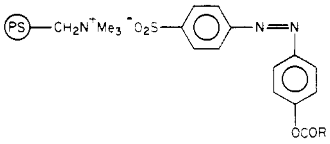
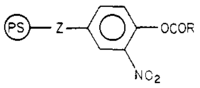
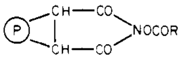
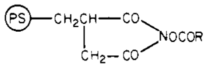
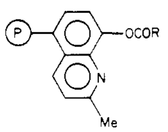
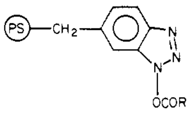
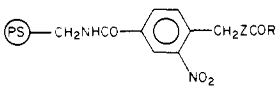
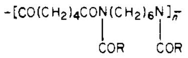
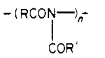
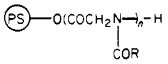
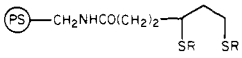
functional polymer	application as reagent	ref
	redox reagent	149, 150
	redox reagent	151
	6. Polymeric Protecting Groups	
 $\text{(PS)—C(Ph)}_2\text{—Cl}$	oligonucleotides synthesis	152
	glycosides synthesis	153, 154
	monoprotection of symmetrical diols	35, 69, 70, 154-157
	monoprotection of triols and tetraols	35
(PS)—COCl	monoprotection of diphenols and diols	68, 155, 34
(PS)—CH_2COCl	monoprotection of symmetrical diols	66, 67
(PS)—CHO	glycoside synthesis	158-161
(PS)—$B(OH)_2$	glycoside synthesis	162
	synthesis of carbohydrate derivatives	163, 164
	partial acylation of acyclic polyols	165, 166
(PS)—CH_2Cl	monoprotection of dithiols	167
 $\text{(PS)—CH}_2\text{OCH}_2\text{CH(—OH)CH}_2\text{—OH}$	monoprotection of symmetrical aromatic dials	71, 72, 168
 R = H, Me	monoprotection of symmetrical aromatic dials	73
(PS)—$(CH_2)_nOH$		
$n = 1$	monoprotection of diacid chlorides	169, 170
$n = 2$	alkylation of acids	80
	synthesis of benzodiazepinone	171
(PS)—$SO_2CH_2CH_2OH$	monoprotection of diacid dichlorides	172
 $\text{(PS)—C(Ph)=N}^+\text{=N}^-$	transformation of penicillin to cephalosporin	173
(PS)—COCl	peptide and oligonucleotide synthesis	174, 175
(PS)—CH_2OCOCl	peptide and oligonucleotide synthesis	176
	monoprotection of symmetrical diamines	177, 178
	oligonucleotide synthesis	179
 $\text{(PS)—CH}_2\text{—N(Me)—CONH—NH}_2$	oligonucleotide synthesis	180
	peptide synthesis	181
 Z = O, NH	peptide synthesis	182, 183
 Z = O, NH	peptide synthesis	184, 185
	7. Polymeric Acylation and Alkylation Reagents	
(PS)—COOCOR	conversion of amines to amides and alcohols to esters	74, 187
(PS)—$CH_2OCOOCOR$		188-190

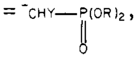
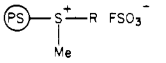
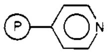
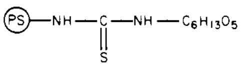
TABLE I *(Continued)*

functional polymer	application as reagent	ref
	peptide synthesis acylation of 6-aminopenicillanic and 7-aminocephalosporanic acids	191 192
	peptide synthesis	193-195
	peptide synthesis	196
 Z = CH_2, $-CH_2OCO-$	peptide synthesis	197, 198
	peptide synthesis	199-205
	peptide synthesis	197
	peptide synthesis	206
	peptide synthesis	207, 208
$\text{(PS)}-COCH_2CH_2COOCOR$	conversion of amines to amides and alcohols to esters	74
 Z = O, NH	peptide synthesis	209-211
$\text{(P)}-COOCH_2CH(OH)CH_2OZR$ Z = CO, NH	peptide synthesis	212
 $-[CO(CH_2)_4CON(COR)(CH_2)_6N(COR)]_n-$	peptide synthesis	213
$\text{(PS)}-CONHOH$	peptide synthesis	203, 204
$\text{(PS)}-SO_2OCOCH_3$	acylation of alcohols and phenols	186
 $-(RCON(COR')-)_n-$		214
 $\text{(PS)}-O(COCH_2N(COR)-)_n-H$		215
 R = $COC_6H_4NO_2$-*p*	acylation of amines	216

8. Polymer-Bound Nucleophiles

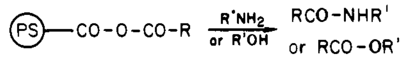
functional polymer	application as reagent	ref
$\text{(PS)}-CH_2N^+Me_3\ X^-$		
X = F^-	conversion of sulfonyl chlorides and tosylate chlorides or bromides to fluorides C-/O-alkylation, sulfenylation, Michael addition	217, 218 219
X = Cl^-, Br, I^-	halogen exchange with alkyl halides	218
X = CN^-	conversion of alkyl halides to nitriles	220, 221
X = SCN^-	conversion of alkyl halides to thiocyanates or isothiocyanate	221, 222
X = OCN^-	conversion of alkyl halides to ureas and urethanes	222
X = NO_2^-	conversion of alkyl halides to nitroalkanes and nitrite esters	223-225
X = $-O\bar{C}OR$	conversion of alkyl halides to esters	226
X = ^-OH	condensation reactions	227

TABLE I (*Continued*)

functional polymer	application as reagent	ref
X = ^-OAr	conversion of alkyl halides to ethers and synthesis of glycosides	225, 228-230
X = ^-O_2SPh	synthesis of alkyl sulfones	78
X = $HFe(CO_4)^-$	conversion of alkyl halides to aldehydes	231
X = $H_3PO_2^-$, $S_2O_3^-$, SO_3^-, $S_2O_4^-$	oxidation of alcohols to carbonyl compounds	232-233
X = $HCrO_3^-$	oxidation of alcohols and alkyl halides to carbonyl compounds	128, 129
X = IO_4^-	oxidation of phenols and sulphides	130
X =  $^-CHY-\underset{O}{\overset{}{\underset{\|}{P}}}(OR)_2$, Y = CN^-, $-COOMe$	conversion of carbonyl compounds and dioxolanes to olefins	234
 $(PS)-\underset{Me}{\underset{\mid}{S^+}}-R\ FSO_3^-$ R = Me, Et	epoxidation of carbonyl compounds	94
	9. Miscellaneous	
$(PS)--SO_2N_3$	diazo transfer to β-dicarbonyl compounds	235
$(PS)-CH_2NMe_2$	acid acceptor	236
	acid acceptor polymeric Girard reagent	237 238
 $(PS)-NH-\underset{S}{\underset{\|}{C}}-NH-C_6H_{13}O_5$	peptide degradation	239-242

[a] (P) = polymer; (PS) = polystyrene

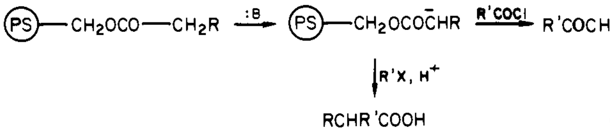
different substrates (Table I, section 7). For example, the insoluble polymer containing the anhydride functional group 8 was used for the conversion of an amine or alcohol to amide or ester[74,75] (reaction 8).



$$(PS)-CO-O-CO-R \xrightarrow[\text{or } R'OH]{R'NH_2} RCO-NHR' \text{ or } RCO-OR' \qquad (8)$$

8

The insolubility of a resin-bound reagent in all common solvents can have the effect of isolating the reactive groups on the polymer from each other. Patchornik and his co-workers[76,77] have used this property in the crossed alkylation of ester derivatives. The reactive carbanion derivative of a bound ester is first generated and self-condensation with unreacted ester inhibited by the rigid matrix. The production of these stable monoanions then allows reaction with acyl or alkyl halides to give selectively monoacylated or monoalkylated products (reaction 9).

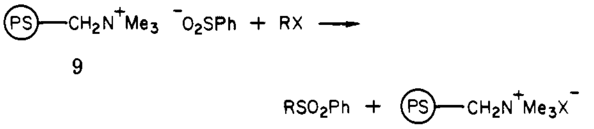


$$(PS)-CH_2OCO-CH_2R \xrightarrow{:B} (PS)-CH_2OCO\bar{C}HR \xrightarrow{R'COCl} R'COCH_2R$$

$$(PS)-CH_2OCO\bar{C}HR \xrightarrow{R'X,\ H^+} RCHR'COOH \qquad (9)$$

H. Polymer-Bound Nucleophiles

Anion-exchange resins in which the bound negative ion is exchanged for a reactive nucleophile prior to use in a reaction have also been employed as polymeric reagents. There exists a close relationship between these systems and polymer-supported onium salts as phase-transfer catalysts, where the anion exchange may be regarded as taking place in situ during reaction (see section IIIE). Where the ion exchange is carried out as a separate process the reagent can be isolated and dried before use under essentially anhydrous conditions. Most applications have employed halide ions as the nucleophile (Table I, section 8), but recently a bound benzenesulfinate anion, 9, has been used in the synthesis of sulfones[78] (reaction 10).

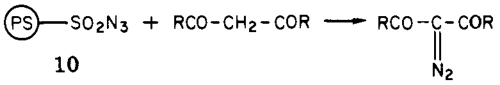


$$(PS)-CH_2\overset{+}{N}Me_3\ {}^-O_2SPh + RX \longrightarrow RSO_2Ph + (PS)-CH_2\overset{+}{N}Me_3X^- \qquad (10)$$

9

I. Miscellaneous

Several reagents do not fall conveniently into any of the previous categories, and these are listed in Table I, section 9. Polymer-bound tosyl azide[79] (**10**) is an important example. This has a useful activity but has greater stability than its monomeric analogue. It can be handled with safety and provides improved yields in diazo transfer reactions to several β-dicarbonyl compounds (reaction 11).



$$(PS)-SO_2N_3 + RCO-CH_2-COR \longrightarrow RCO-\underset{N_2}{\underset{\|}{C}}-COR \qquad (11)$$

10

III. *Polymeric Catalysts*

A polymeric catalyst or polymer-supported catalyst is a conventional catalytic species attached to a macromolecular backbone. As with reagents, the polymer species may be a linear or a cross-linked entity, and again the latter have proved particularly useful. Polymeric catalysts are generally used in catalytic quantities relative to reaction substrates, and can often be reused many times. The attachment of a catalyst to a support may improve its stability and selectivity.[24] On the other hand, increased experimental convenience arising with

TABLE II. Polymeric Catalysts[a]

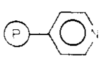
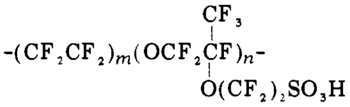
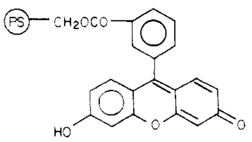
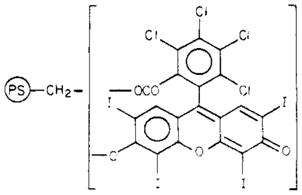
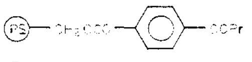
functional polymer	application as catalyst	ref
	1. Ion-Exchange Resin Catalysts	
(PS)—SO_3H	hydrolysis of	
	esters	266-269
	enamines	270
	amides, peptides, proteins	271-281
	glycosylamines	282, 283
	carbohydrates	284-286
	esterification of α-amino acids, fatty acids, olefins, glucose	287-291
	acetal and ketal formation	292-295
	cyclization	296-299
	condensation	299-301
	dehydration	302-307
	alkylation	308-310
	rearrangement	311-313
	decarboxylation	314
	amide formation	315
	hydration	284, 311, 316, 317
(PS)(—SO_3^-)(—X)		
X = SO_3Ag	hydrolysis of esters	318
X = $Me(CH_2)_{15}N^+Me_3$	hydrolysis of esters	319-321
X = $(PhCH_2)_3N^+Me$	hydrolysis of esters	319-321
X = OH	hydrolysis of dextrin	322
X = COOH	hydrolysis of amylose and sucrose	323
(P)—COOH	hydrolysis	324
	esterification	325
(PS)—$CH_2N^+R_3$ OH^-	hydrolysis of esters and peptide blocking group	326-332
	dehydrohalogenation	326, 333
	condensation	300, 334-339
	hydration	328, 329, 340, 341
	cyclization	341
	esterification	226, 339
	acylation	342
	2. Polymeric Lewis Acid and Superacid Catalysts	
(PS) · $AlCl_3$	acetal formation	248
	esterification	247
(PS)—$SO_3H \cdot BF_3$	alkylation of olefins	343, 344
(PS)—$SO_3H \cdot AlCl_3$	isomerization and cracking	250, 345
Nafion-H  $-(CF_2CF_2)_m(OCF_2\underset{O(CF_2)_2SO_3H}{\overset{CF_3}{C}}F)_n-$	transalkylation	252
	dehydration of alcohols	253
	rearrangement	346
	alkylation	347
	hydration of alkynes	348
	esterification	349
	nitration	350
	Friedel-Craft acylation	351
	3. Polymeric Dyes and Photosensitizer Catalysts	
	photosensitized oxidation	255
	photosensitized oxidation	255
	cycloaddition and dimerization of olefins	352, 353
(PS)—COPh	photosensitizer	354

TABLE II (*Continued*)

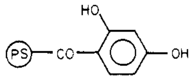
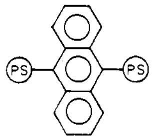
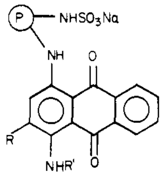
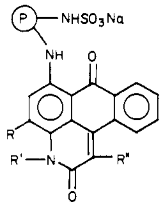
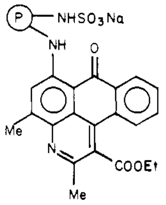
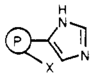
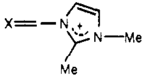
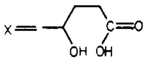
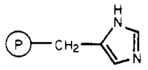
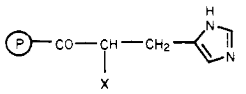
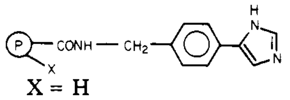
functional polymer	application as catalyst	ref
	UV absorbers	355
		356
 R = H; R' = Me R = Me; R' = H	soluble dye	357
 R = H; R' = Me; R'' = H R = Me; R' = Me; R'' = COOEt R = Me; R' = H; R'' = COOMe	soluble dye	357
	soluble dye	357
	4. Polymeric Hydrolyzing Systems	
		
a, X = H (homopolymer)	hydrolysis of 3-nitro-4-dodecanoyloxybenzoate, p-nitrophenyl acetate, and other ionic esters	358-368
b, X = COOH	hydrolysis of *m*-$MeOOCC_6H_4N^+Me_3$, I^-	369-372
c, X = SO_3^-		370
d, X = SH	hydrolysis of *p*-nitrophenyl acetate	373
e, X = OH		369, 370, 374
f, X = *p*-HOC_6H_4-	hydrolysis of phenyl ester derivatives	374
g, X = CON(Me)OH	hydrolysis of phenyl ester derivatives	375
h, X = -$CONH_2$ + -CON(Ph)OH		376, 377
i, 	hydrolysis of phenyl esters	378
j, 		379
	hydrolysis of phenyl esters	380
 X = NH_2, COOH		381, 382
 X = H	hydrolysis of *p*-acetoxybenzoate	383

TABLE II (*Continued*)

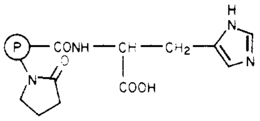
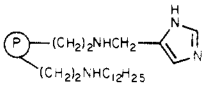
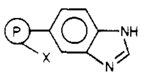
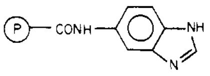
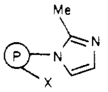
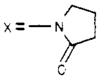
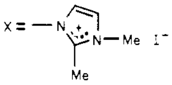
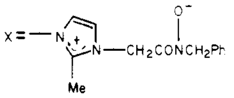
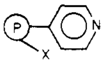
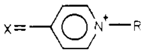
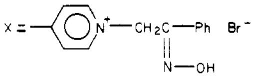
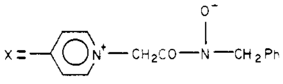
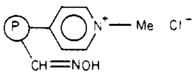
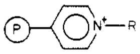
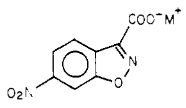
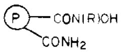
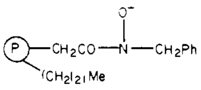
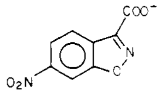
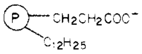
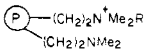
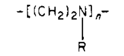
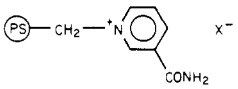
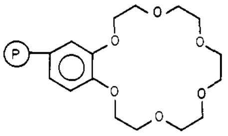
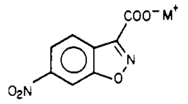
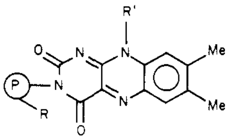
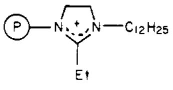
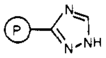
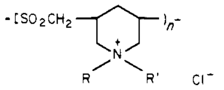
functional polymer	application as catalyst	ref
X = COOH	hydrolysis of m-$Me(CH_2)_nCOOC_6H_4N^+Me_3\ I^-$	384
	hydrolysis of phenyl esters	385
	hydrolysis of p-nitrophenyl acetate hydrolysis of 4-nitrocatechol sulfate	386, 387 388-396
 X = H, COOH	hydrolysis of 3-nitro-4-dodecanoyloxybenzoate esters	397-400
	solvolysis of p-acetoxybenzoate	383
		
a, X = H	hydrolysis of phenyl esters	367
b, X = 	hydrolysis of 3-nitro-4-acetoxybenzoate	401
c, X = 	hydrolysis of 3-nitro-4-acetoxybenzoate	402
d, X = $CONH_2$ + CON(Ph)OH	hydrolysis of p-nitrophenyl acetate	376, 377
e, X = 		403
		
a, X = H	hydrolysis of phenyl esters	404
b, X = 	hydrolysis of phenyl esters	405-410
c, X = 	hydrolysis of p-nitrophenyl acetate	411
d, X = 		403
	hydrolysis of phenyl acetate	412
 R = $Me(CH_2)_{11}$, Et	decarboxylation of 	413, 414
 R = Me, Ph		375, 415
	decarboxylation of 	416
	hydrolysis of Schiff bases	417
 R = C_6, C_8, C_{12}, C_{18}	hydrolysis of p-nitrophenyl acetate	418

TABLE II (*Continued*)

functional polymer	application as catalyst	ref
 $-[(CH_2)_2\underset{R}{N}]_n-$		
R = H	cleavage of *p*-nitrophenyl phosphate	419-421
	hydrolysis of aspirin and phenyl esters	422-424
R = PhCH$_2$	hydrolysis of *p*-nitrophenyl esters and cleavage of disulfide linkage of Ellman's reagent	425, 426
R = C$_{12}$H$_{25}$, C$_{16}$H$_{33}$		427
		428-433
X = Cl, CN, SO$_3$$^{2-}$		
	decarboxylation of 	434
	oxidation of NADPH to NADP$^+$ and thiophenol	435-437
R = H, CH$_2$N$^+$Me$_2$C$_{12}$H$_{25}$		
	proton abstraction from benzoin to give benzil	438
	hydrolysis of phenyl esters	439
	hydrolysis of dinitrophenyl phosphate dianion	440
R = R' = Me, Et R = Me, R' = PhCH$_2$, *p*-O$_2$NC$_6$H$_4$CH$_2$		

5\. Polymeric Phase-Transfer Catalysts

5.1. Ammonium Salts

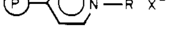
functional polymer	application as catalyst	ref
(PS)—(CH$_2$)$_n$N$^+$R$_2$R' X$^-$		
a, n = 0; R = R' = Me; X = Cl, Br, F, I	RY + Z$^-$ → RZ	218, 441
b, n = 0; R = R' = Me; X = HCrO$_4$	Z$^-$ = Cl, Br, F, I	442, 443
c, n = 0; R = R' = Me; X = OCN		222
d, n = 0; R = R' = Me; X = OH		444
e, n = 1, R = R' = Me; Et, *n*-Bu, *n*-Oct; X = Cl	Z$^-$ = CN, I, $R\text{-}\bar{C}HCN$	222, 232, 259, 260, 445-450, 455, 457
f, n = 1; R = Me; R' = *n*-Bu; *n*-Oct, *n*-C$_{12}$H$_{25}$, *n*-C$_{14}$H$_{29}$, PhCH$_2$, CH$_2$CH$_2$OH, CHMeCHPhOH; X = Cl, Br	Z$^-$ = CN, asymmetric Darzens reaction	232, 259, 454, 448-452
g, n = 1; R = R' = Me; X = SCN		222
h, n = 1; R = R' = Me; X = BH$_4$$^-$		453
i, n = 2,3; R = R' = *n*-Bu; X = Br	Z$^-$ = I, PhS, Br, Cl, N$_3$, ArO, AcO	454, 455
(PS)—Z—N$^+$R$_3$ X$^-$	Z$^-$ = CN, I	261, 447, 456
R = Me; Z = -CH$_2$OCO(CH$_2$)$_n$-; n = 5, 11 R = Me, *n*-Bu; Z = -CH$_2$NHCO(CH$_2$)$_{10}$-		
(Si)—Z—N$^+$R$_3$ X$^-$		457
a, Z = -(CH$_2$)$_3$-; R = H, Me, Et, *n*-Bu, *n*-Oct, *n*-C$_{16}$H$_{33}$ b, Z = -(CH$_2$)$_6$-; R = *n*-Bu c, Z = -C$_6$H$_4$CH$_2$-; R = *n*-Bu		
		
a, R = H; X = ClCrO$_3$		458
b, R = H, *n*-Bu, CH$_2$CHMeEt; X = Br, Cl		459

TABLE II (*Continued*)

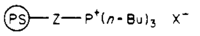
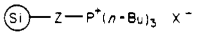
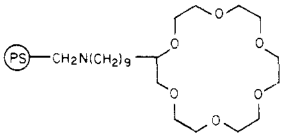
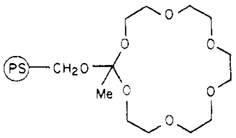
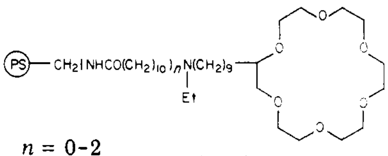
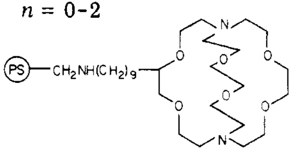
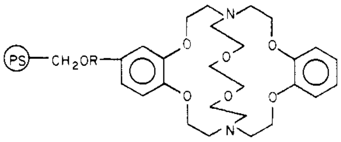
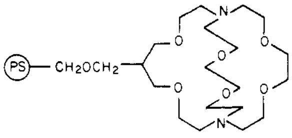
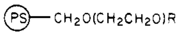
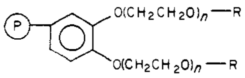
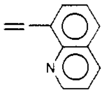
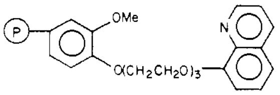
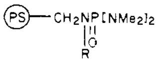
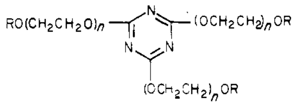
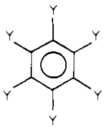
functional polymer	application as catalyst	ref
	5.2. Phosphonium Salts	
 $\text{(PS)}-Z-P^+(n\text{-Bu})_3\ X^-$		
a, Z = $-(CH_2)_n-$; n = 1, 2, 3, 6 b, Z = $-(CH_2)_m[NHCO(CH_2)_x]_n-$; x = 10; m = 1, n = 1, 2, 3	R-Y + Z^- → R-Z Z^- = Cl, I, CN, AcO, ArO, ArS, ArCHCOMe, N_3, SCN, S^{2-}	260, 262, 445-447, 449 454, 455, 460-462
 $\text{(Si)}-Z-P^+(n\text{-Bu})_3\ X^-$		
a, Z = $-(CH_2)_3-$	Z^- = I, PhS, Cl, PhO	447, 461-463
b, Z = $-(CH_2)_3[NHCO(CH_2)_m]_n-$		
m = 2, n = 1	Z^- = I, BH_4, PhO	461
m = 10; n = 1, 2	Z^- = PhO	461, 463
c, Z = $-C_6H_4CH_2-$	Z^- = PhO	457
	5.3. Crown Ethers and Cryptands	
	Z^- = CN	260
		464
 n = 0-2		262
		260
		465
	Z^- = I, CN	466
	5.4. Cosolvents	
 $\text{(PS)}-CH_2O(CH_2CH_2O)R$	Z^- = ArO, Cl, CN, AcO	
a, R = Me; n = 1, 2, 3, 13, 16		264, 445, 446, 467-469
b, R = H; n = 1, 4, 13		446, 467
c, R = Ph		265
	Z^- = AcO	
a, R = Et; n = 4		470
b, R =  ; n = 2, 3		470, 471
	Z^- = AcO	470, 471
 $\text{(PS)}-CH_2N(R)P(=O)[NMe_2]_2$	Z^- = ArO, Cl, CN, AcO	
a, R = H		472-474
b, R = Me		263, 445, 446, 473

TABLE II (*Continued*)

functional polymer	application as catalyst	ref
	5.5. Other Catalysts	
(PS)—$COO^- Na^+$ / (PS)—$COOH$	$Z^- = Cl, CN, AcO$	446
(PS)—$SO_3^- Na^+$	$Z^- = Cl, CN, AcO$	446
(PS)—$S^+Me_2FSO_3^-$	epoxidation of ketones	94
$R[OCH_2CH_2]_nOR$		475-479
		480
 $Y = CH_2(OCH_2CH_2)_nOR$		481
poly(vinyl alcohol)	$Z^- = PhO$	482
poly(vinylpyrrolidone)		482
poly(vinylformal)		482
poly(vinylmethyl ether)		482
poly(methyl vinyl ketone)		482
poly(acrylamide)		482
poly(*N*,*N*-dimethylacrylamide)		482
poly(methoxymethyloxirane)		482
poly(epichlorohydrin)		482
poly(oxyethylene)		482
poly(styrene-*b*-oxyethylene)		482
Span 80		482
Tween 20		482

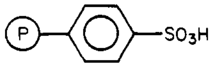
[a] (P) = polymer; (PS) = polystyrene; (Si) = silica.

a polymeric catalyst may be offset by a significant reduction in reactivity associated, for example, with diffusional limitations imposed by resin supports.

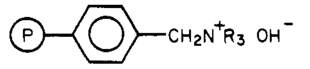
A wide variety of catalysts have been supported in this way, ranging from strong acids and bases (ion-exchange resins), transition-metal complexes, and photosensitizers right through to the highly specific enzymic catalysts. A detailed coverage of the latter, however, lies outside the scope of this review. A systematic listing of polymer-supported transition-metal complex catalysts has also been excluded because this area has been recently reviewed very comprehensively, a similar format to the present review being used. Readers are directed to ref 243 and in particular to the table therein.

A. Ion-Exchange Resin Catalysts

The acid and base forms of ion-exchange resins probably represent the earliest examples of synthetic polymeric catalysts,[1,244] and the use of these materials in this way has been reviewed previously.[245,246] The commercial availability of a series of resins ranging from strongly acid systems based on sulfonated polystyrene (11) to strongly basic ones involving the hydroxyl salts of bound ammonium ions (12) has allowed the study of a great variety of reactions. Virtually all organic syntheses involving catalysis by homogeneous acid or base have also been carried out by use of appropriate polymeric catalysts, and there are now signs of these species being exploited commercially. Table II, section 1, lists the applications.



11



12

B. Polymeric Lewis Acid and Superacid Catalysts

The impregnation of a polystyrene resin with aluminum chloride by use of a suitable carrier solvent produces, on removal of the solvent, a tightly bound complex of insoluble polymer and anhydrous Lewis acid. Furthermore, this can be used very successfully as a mild catalyst for a number of organic preparations.[247,248] The impregnated Lewis acid is readily made available by swelling the resin with an appropriate solvent, while in the dry state the acid is protected from hydrolysis. The polymer appears to attenuate the activity of the catalyst to some extent, and in some reactions undesirable complex condensation side products are virtually eliminated.

When a Lewis acid is introduced into a resin which is already functionalized with strong protonic acid groups, then new acidic functions are generated[249,250] with an acidity approaching that of the so-called superacids.[251] Such resins are capable of protonating paraffins, but where polystyrene is the base polymer, the catalysts are somewhat unstable and are degraded during use. Where, however, a perfluorinated copolymer containing perfluoroalkanesulfonic acid groups is used, much higher stability results, and once again these materials show considerable commercial potential.[252,253] The various systems which have been de-

TABLE III. Separations on Polymeric Carriers[a]

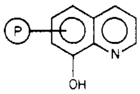
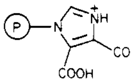
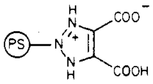
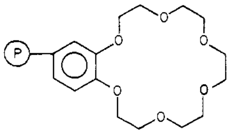
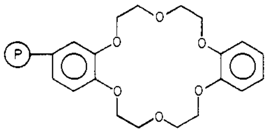
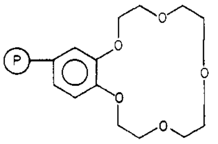
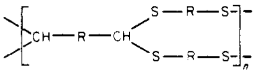
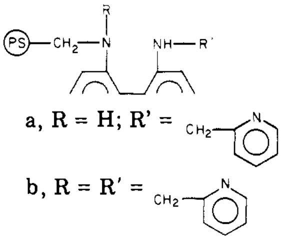
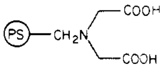
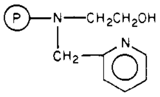
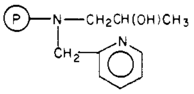
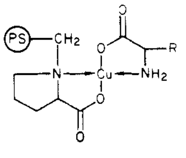
functional polymer	application	ref
	1. Metal Ion Separations	
	extraction of Ni, Cu, Co separation of Cu, Zn, Al	485, 505 487, 506
		507, 508
		507, 508
	complexing of alkali metal ions	509-511
		509-511
		509-511
(PS)—CH_2SH	selective ion exchanger	505
(PS) · β-diphenylglyoxime	selective for Pd	486
(PS) · ethylene diglycol dibutyl ether	selective for Au	512
	selective for Hg	513, 514
	selective separation of Cu, Ag, Ni	484
	separation of transition-metal ions	515
(PS)—COO—$(CH_2)_6$—OCO—CH_2SH	separation of Ag, Hg, Au, Bi, Cu	516
(PS)—$(CH_2)_3$—CON(n-Bu)$_2$	separation of U, Th, Zr, An, Pd	517
	selective for Cu	487, 518
	selective for Cu	488
	2. Resolution of Racemic Mixtures	
 R = H, OH	ligand exchanger for resolution of racemic mixtures	493, 494, 519

TABLE III (*Continued*)

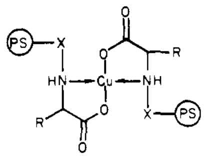
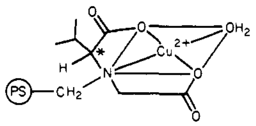
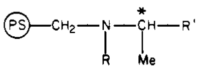
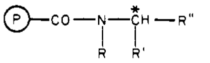
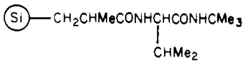
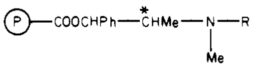
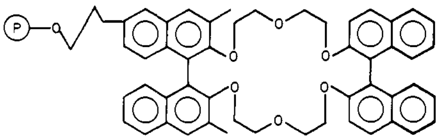
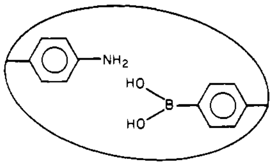
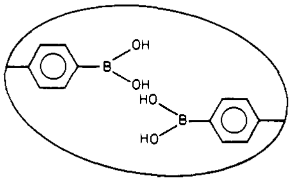
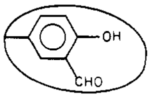
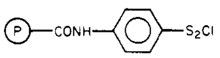
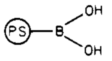
functional polymer	application	ref
 X = -CH$_2$-, -SO$_2$-	ligand exchanger for resolution of racemic amino acids	520
	ligand exchanger for resolution of amino acids	495
 $(PS)\text{—CH}_2\text{—N(R)—C}^{*}\text{H(Me)—R'}$ a, R = H; R' = Ph b, R = Me; R' = Me, CHPhOH, CHPhOAc	resolution of mandelic acid and mandelamide	492, 521
 $(P)\text{—CO—N(R)—C}^{*}\text{H(R')—R''}$	resolution of mandelic acid and mandelamide	
a, R = H; R' = Me; R'' = Ph, c-C$_6$H$_{11}$, *p*-IC$_6$H$_4$, 1-naphthyl		491
b, R = H; R' = COOEt; R'' = Me, Ph, c-C$_6$H$_{11}$CH$_2$, PhCH$_2$, *p*-HOC$_6$H$_4$CH$_2$, *p*-MeOCOC$_6$H$_4$CH$_2$		522
c, R = H; R' = COOBu-*t*; R'' = PhCH$_2$		522
d, R = Me; R' = Me; R'' = CHPhOH		492
 $(Si)\text{—CH}_2\text{CHMeCONHCH(CHMe}_2\text{)CONHCMe}_3$		523-525
 $(P)\text{—COOCHPh—C}^{*}\text{HMe—N(Me)—R}$ R = H; Me, PhCH$_2$, PhCO, MeCO	resolution of mandelic acid and mandelamide	492
(PS)—CH$_2$—N$^+$R$_2$C*HMePh Cl$^-$ R = H, Me	resolution of mandelic acid separation of sugar anomers	526 527
		496
	resolution of glyceric acid	497-499
	resolution of mannopyranoside derivatives	500, 501
	resolution of amino acid esters and anilides	502, 503
	3. Other Separations	
(PS)—NH$_2$ metal complex	removal of oxygen from water	528, 529
(P)—OH	removal of oxygen from solutions selective adsorption of mercaptans and cystine	530 531
(PS)—CH$_2$—NMe—CONH—NH$_2$	trapping aldehyde side products in photochemical reactions	532

TABLE III (*Continued*)

functional polymer	application	ref
	selective separation of tryptophan and tryptophan-containing peptides	533
	separation of glycolipids from natural lipids and phospholipids	534
	separation of diol mixtures	535

[a] (P) = polymer; (PS) = polystyrene.

veloped and their relevant applications are shown in Table II, section 2.

C. Polymeric Dyes and Photosensitizer Catalysts

Several workers[47,48] have examined the possibility of attaching dyes to polymeric supports and using these as indicators in redox reactions or as donor–acceptor substrates in biochemical reactions, since the redox reaction is accompanied by a distinct color change. Because of the variety of properties required in various biological and technological applications, tailor-made polymeric dyes have also been prepared. For example, a water-insoluble chromophore was attached to an amine homopolymer via a portion of the amine groups. The remainder were then converted into solubilizing groups such as sulfonates,[254] making the whole polymeric dye water soluble.

Polymer-bound Rose Bengal[255] has been synthesized and used to sensitize the generation of singlet molecular oxygen for photooxidations of olefins. The singlet oxygen exhibits three modes of reactions with olefins, 1,4-cycloaddition with conjugated dienes to yield cyclic peroxides, an ene-type reaction to form allylic hydroperoxides, and 1,2-cycloaddition to give 1,2-dioxetanes which cleave thermally to carbonyl-containing products. The advantages of using an insoluble photosensitizer lie in the fact that the dye can be readily separated from the product and reused. Supported systems such as these must be translucent. Some examples of polymeric photosensitizers applied as heterogeneous catalysts are shown in Table II, section 3.

D. Polymeric Hydrolyzing Systems

Polymers with an essential functional structure of enzymes have been prepared and used to promote enzyme-type reactions.[48,256,257] Because the imidazole moiety of histidine is present in the active sites of several hydrolyzing enzymes, many synthetic polymers containing imidazole and benzimidazole groups have been prepared and used to catalyze the hydrolysis of esters and amides. The polymeric catalysis is attributed to specific adsorption of the substrate and cooperative interaction of imidazole and other groups of the active center. After hydrolysis, the product is eliminated from the polymer active center which is then available for further catalysis. The functionalized polymers which have been used as hydrolyzing systems are listed in Table II, section 4.

E. Polymeric Phase-Transfer Catalysts

Phase-transfer catalysis[258] is a relatively new phenomenon in which liquid–liquid or solid–liquid phase separated reactions are accelerated by the addition of organophilic onium salts or uncharged species such as crown ethers and cryptands. The catalysts aid the transfer of anions across the phase boundary either by complexing with the attendant metal cation or replacing it in an ion-pair equilibrium. When the same species are supported on a polymer resin, their catalytic action is essentially maintained while problems such as emulsification are eliminated. Costly catalysts such as optically active onium salts, crown ethers, and cryptands are also effectively retained in this manner and can readily be reused. The toxicological problems associated with crown ethers are also overcome. A significant number of quaternary ammonium salts bound to resins have been used in this context,[259] and these are listed in Table II, section 5.1. Far fewer phosphonium salts have been examined,[260] despite their generally higher catalytic activity, and those which have been used appear in section 5.2. Finally, the supported crown ethers and cryptands[260] exploited as phase-transfer catalysts are listed in section 5.3. With all of these species there is evidence for an increase in activity when the catalyst is separated from the polymer backbone by a spacer arm.[261,262] However, the detailed mechanism(s) by which these systems operate is still the subject of much research, and no real consensus has yet emerged.

Problems associated with phase separation of an inorganic reagent and an organic substrate can also be overcome by the use of an appropriate solvent or cosolvent, such as the dipolar aprotic species, dimethyl sulfoxide, hexamethylphosphoramide etc. These have the disadvantage of being costly and difficult to dry and purify and of traces remaining teraciously with reaction products. Perhaps somewhat remarkably, when these species are supported on a resin,[263] they continue to function as solvents or cosolvents and the above difficulties are overcome. Polymer-supported linear oligoethylene oxides have also been used in this context[264,265] (Table II, section 5.4), as well as a number of other linear polymers (section 5.5).

IV. Separations on Polymeric Carriers

Polymeric materials have been used widely as chromatographic column substrates and have proved useful in both gas-phase and liquid-phase separations. A full description of these areas lies outside the scope of this review, but the use of polymeric carriers in metal ion separations and racemate resolutions has involved polymer species with a close structural relationship to many of those systems already described, and hence these are now included.

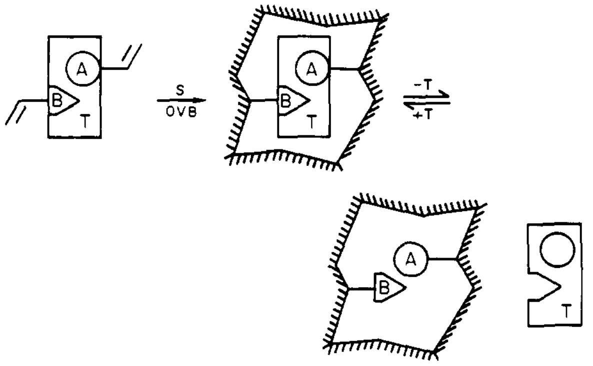
A. Metal Ion Separations

Metal ion separations are important in a number of analytical techniques,[483-486] in metallurgical extraction,[487,488] and in water treatment processes. Simple ion-exchange resins can of course be employed for these purposes, but in general they have poor selectivity. A number of systems with considerably enhanced selectivity have therefore been developed over recent years. These generally have employed neutral ligands, the complexity of which has increased with time. Though at the present moment liquid-liquid ion exchange is used widely in metallurgical extractions, polymer-supported systems will have a significant role to play in the future. Table III, section 1, lists some of the selective separations that have been achieved.

B. Resolution of Racemic Mixtures

In addition to the traditional methods of resolution of racemic mixtures,[489,490] considerable progress has been reported on resolution by chromatographic methods using chiral stationary phases. In principle, enantiomers should move at different rates down a column by forming diastereomeric adsorbates, and indeed column chromatography with synthetic optically active polymer substrates are reported to achieve enhanced resolutions. Blaschke,[491,492] for example, has used *N*-[(*S*)-1-phenylethyl]acrylamides and other optically active polymers as adsorbents for the resolution of racemic mandelic acid and mandelamide. Other resolutions of interest are those which are carried out on columns of asymmetric complex-forming stationary phases by means of ligand-exchange chromatography.[493-495] Chiral crown ethers attached to polymeric supports have also been used to separate mixtures of enantiomers of primary amine salts.[496]

Recently, enzyme-like synthetic polymers containing chiral cavities have been prepared and used for resolution of racemic mixtures.[497-504] The principle is to prepare a synthetic polymer with functional groups in an exact chiral relationship (**13**) by polymerizing vinyl monomers (A and B) attached to an optically active template molecule (T) (reaction 12). Subsequent removal of T leaves behind a chiral cavity, **13**.



(12)

13

The polymer is prepared under conditions that lead to a rigid matrix to avoid the loss of the stereochemistry of the cavity. The functional groups in the cavity must undergo a readily reversible binding and cleavage reaction with the template, analogous to the active site in natural enzymes. Cavities prepared in this way preferentially interact with the enantiomer which has been used as template. Several enzyme-like polymers of this type have been used for resolution of enantiomers and are listed in Table III, section 2.

V. Organic Synthesis on Polymeric Carriers

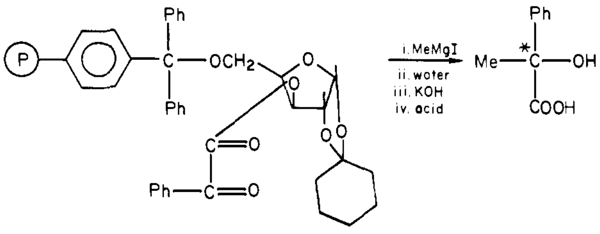
There are a number of areas where polymer molecules have been employed as a convenient support upon which to carry out a synthesis. Completion of the latter is followed by cleavage of the product from the support. One example of this has already been described in section IIF. In principle, the synthesis can be a very complex one involving many steps, and quite clearly a resin support offers a convenient method of isolating and purifying the product at all stages of the synthesis. Merrifield's "solid-phase method" for producing polypeptides[2] initiated this technique, which has been subsequently applied to both oligosaccharide[536] and oligonucleotide synthesis.[537] These are very specialized areas of application of polymer supports, the details of which again lie outside the scope of this review, and interested readers are directed to a number of more specialized reports.[536-540]

The same carrier principle has also been used in a number of asymmetric syntheses, in some cyclization and related reactions, and also in the detection of reaction intermediates.

A. Asymmetric Syntheses

In this technique an optically active compound or functional group is attached to a macromolecular support and then either a synthesis is carried out on the support or the optically active polymer is used as an asymmetric reagent or catalyst. Most applications have used the latter approach, but in principle, in order to achieve significant induction, at some stage in the reaction the substrate must become intimately associated with, or specifically bound to, the optically active center. At this point the polymer acts effectively as an asymmetric carrier species.

One example where the synthesis occurs unambiguously on the support is in the preparation of atrolactic acid[541] using 1,2-*O*-cyclohexylidene-α-D-xylofuranose bound to a polymeric tritylchloride polymer (**14**) (reaction 13). A polymer-supported optically active primary alkoxy amine has been used in a similar role in the synthesis of chiral 2-alkylcyclohexanones.[542]



14

(13)

There are many more examples of polymer-supported optically active metal complexes and chiral bases being employed in asymmetric induction, and also more recently chiral phase-transfer catalysts. Table IV, section 1, lists these and the corresponding reactions in which they have been used.

B. Cyclization Reactions

In conventional cyclization reactions a high dilution technique is used in order to promote intramolecular reaction. When a rigid polymer support is used, the

TABLE IV. Organic Syntheses on Polymeric Carriers

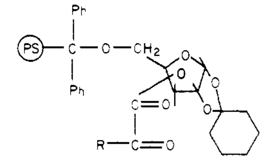
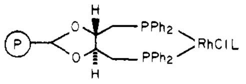
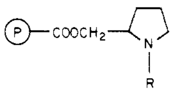
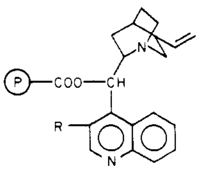
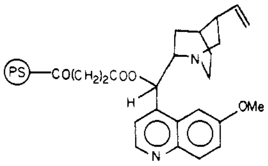
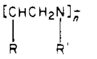
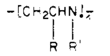
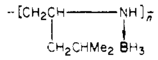
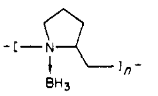
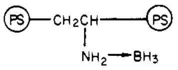
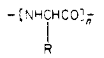
functional polymer	application	ref
	1. Asymmetric Syntheses	
	asymmetric synthesis of α-hydroxy acids by reaction with RMgX, RR'C(OH)COOH	541
R = Me, Ph		
(PS)— $CH_2OCH_2CHMeNH_2$	asymmetric synthesis of 2-alkylcyclohexanones	542
	asymmetric hydrogenation of olefins and hydrosilylation of ketones	550-555
	asymmetric hydroformylation of olefins	556
	asymmetric reduction of $-\overset{\mid}{C}=\overset{\mid}{C}=O$ with MeOH to $-\overset{\mid}{C}H-COOMe$	557, 558
R = Me, $PhCH_2$	asymmetric acetylation of *dl*-1-phenylethanol	558, 559
(P)—COOCHPhCHMeNMeR	asymmetric reduction of ketene with MeOH	557
	asymmetric acylation of *dl*-1-phenylethanol	558, 559
(PS)— $CH_2N^+(Me_2)CHMeC(OH)Ph\ \ Br^-$	asymmetric Darzen reaction	452
	asymmetric reduction of ketene with MeOH	557, 559
	asymmetric acylation of *dl*-1-phenylethanol	558
	asymmetric Michael reaction	560
R = H, MeO		
	asymmetric Michael reaction	560
 $-[\underset{R}{\underset{\mid}{C}}HCH_2\underset{R'}{\underset{\mid}{N}}]_n-$		
a, R = *i*-Bu; R' = H	asymmetric addition of HCN to PhCHO	561
	asymmetric addition of laurylmercaptan to $-\overset{\mid}{C}=\overset{\mid}{C}-C=O$	562
b, R = Me; R' = H	asymmetric hydrogenation of methyl isobutyl ketone and mesityl oxide to 2-methyl-2-pentanol	563
 $-[CH_2\underset{R}{\underset{\mid}{C}}H\underset{R'}{\underset{\mid}{N}}]_n-$	asymmetric synthesis of esters	564
R = *i*-Pr; R' = H, Me R = H; R' = Me		
 $-[CH_2\underset{CH_2CHMe_2}{\underset{\mid}{C}}H-\underset{BH_3}{\underset{\downarrow}{N}}H]_n-$	asymmetric reduction of PhCOMe	565
	asymmetric reduction of ketone	565
	asymmetric reduction of ketone	565
 $-[NH\underset{R}{\underset{\mid}{C}}HCO]_n-$		
R = $-(CH_2)_4NH_2$	asymmetric hydrolysis of phenylalanine ester	566
	asymmetric oxidation of 3,4-dihydroxyphenylalanine to quinone derivative	567, 568
R = CH_2CH_2COOH	asymmetric hydrogenation of methyl acetoacetate and α-acetomidocinnamic acid	569
R = CH_2COOH	asymmetric reduction of α-methyl- and α-acetylaminocinnamic acid	569

TABLE IV (*Continued*)

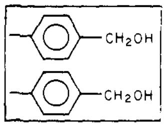
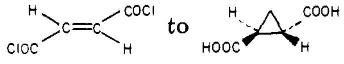
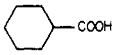
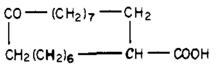
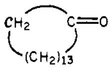
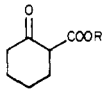
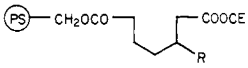
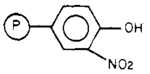
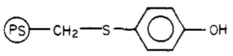
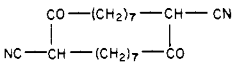
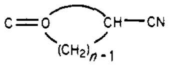
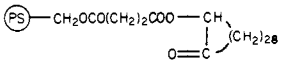
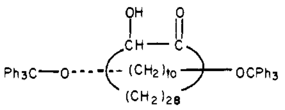
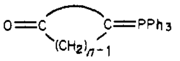
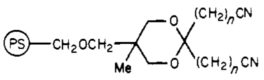
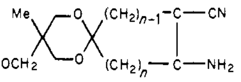
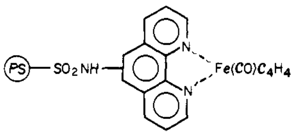
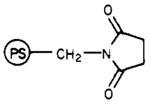
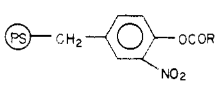
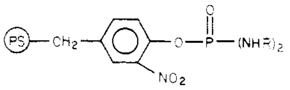
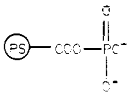
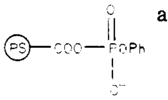
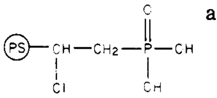
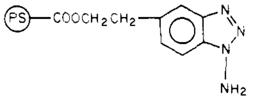
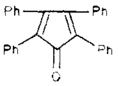
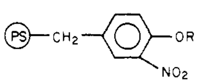
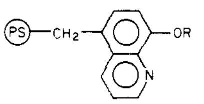
functional polymer	application	ref
	asymmetric conversion of 	570
cell·$CH_2OP(Ph_2)RhCl(PPh_3)_2$	asymmetric hydrogenation of α-phthalimidoacrylic acid derivative to alanine	571
	2. Cyclizations	
(PS)—$CH_2OCO(CH_2)_nCOOR$		
a, $n = 1$	Dieckmann cyclization of $Br(CH_2)_5Br$ to 	572
b, $n = 8$; $R = Me_3C$	synthesis of 	546
c, $n = 14$	Dieckmann cyclization of 	572
d, $n = 5$; R = Et, *t*-Bu, Et_3C	Dieckmann cyclization of 	546
 R = H, Et	Dieckmann cyclization	545, 546
	synthesis of cyclic peptide	191
	synthesis of cyclic peptide	193-195
(PS)—CH_2—Z—$CO(CH_2)_nCN$		
a, Z = S; $n = 8$	synthesis of 	546
b, Z = O	synthesis of 	572
	synthesis of 	544
(PS)—SO_3H	cyclization of aliphatic aldehydes	573
(PS)—COCl	synthesis of unsymmetrical tetraarylporphyrins	574
(PS)—$CH_2OCO(CH_2)_n$—P^+Ph_3 X^-	synthesis of 	572
	synthesis of 	572
	3. Detection of Reactive Intermediates	
 as precursor  as trap	detection of cyclobutadiene	548

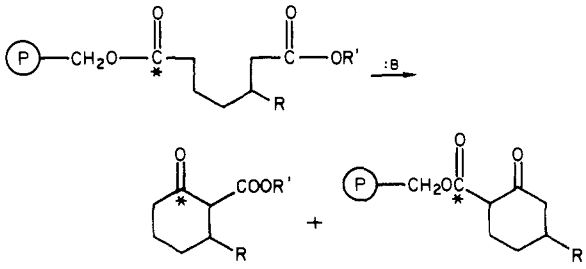
TABLE IV (*Continued*)

functional polymer	application	ref
 as precursor (PS)—CH_2NH_2 as trap	detection of intermediates in nucleophilic and elimination reactions	575
 as precursor; R = c-C_6H_{11} (PS)—$CH_2OCO—CH_2NH_2$ as trap	detection of metaphosphates $\mathrm{RNH}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{P}}{=}\mathrm{NR}$	576, 577
 $\text{(PS)}{-}\mathrm{COO}{-}\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{O^-}}{\vert}}{\mathrm{P}}}\mathrm{O^-}$ as precursor (PS)—$CH_2CCOCH_2NH_2$ as trap	detection of monomeric metaphosphate [PO_3^-]	577, 578
 $\text{(PS)}{-}\mathrm{COO}{-}\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{O^-}}{\vert}}{\mathrm{P}}}\mathrm{OPh}$ as precursor (PS)—$CH_2OCOCH_2NH_2$ as trap	detection of [$\mathrm{Ph{-}O{-}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{P}}{=}\mathrm{O}$]	576
 $\text{(PS)}{-}\underset{\underset{\mathrm{Cl}}{\vert}}{\mathrm{CH}}{-}\mathrm{CH_2}{-}\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{CH}}{\vert}}{\mathrm{P}}}{-}\mathrm{CH}$ as precursor (PS)—$CH_2OCOCH_2NH_2$ as trap	detection of monomeric metaphosphate [PO_3^-]	579
 as precursor  as trap	detection of benzyne	549
(PS)—Rose Bengal sensitizer (PS)—$CH_2OCO(CH_2)_3CH{=}CMe_2$	trapping of $^1O_2$	580
	detection of oxocarbonium ion as intermediate in Fries rearrangement	581
 R = COMe, COPh, *p*-$O_2NC_6H_4CO$-, *p*-ClC_6H_4CO-	detection of oxocarbonium ion	581

[a] (P) = polymer; (PS) = polystyrene; cell = cellulose.

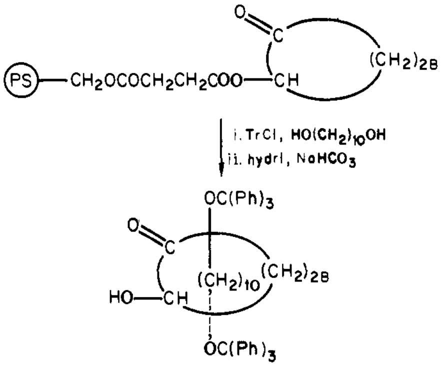
concentration of molecules to be cyclized on the polymer can be made higher than normally used in solution. This has reduced the synthetic problems encountered in the preparation of macrocyclic compounds such as cyclic peptides[191,193,543] and threaded macrocycles.[544] Dieckmann[545] and other cyclizations[546,547] have also been improved by this approach.

Cyclic peptides have been prepared by the stepwise synthesis of the linear peptide on a polymeric carrier followed by intramolecular cyclization. The selective Dieckmann cyclization of mixed esters using conventional techniques has not been reported. However, application of a polymeric support does improve the situation. With such a solid-phase technique, one product remains attached to the polymer whereas the other one is obtained in solution, solving the problem encountered with separation of products in a high-dilution technique (reaction 14).



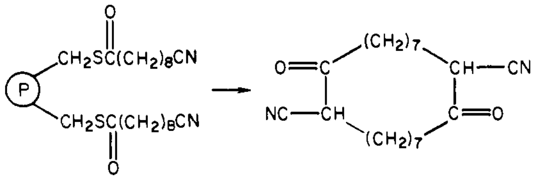
(14)

Insoluble polymer supports have also been used in the synthesis of catenanes and other threaded compounds. Undesirable nonthreaded byproducts are simply washed from the threaded macrocycle itself attached to the polymer.[544] Subsequent cleavage yields the pure threaded compound (reaction 15).



(15)

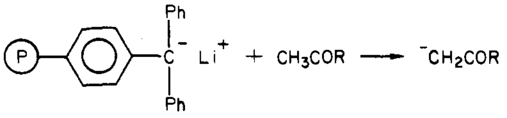
In addition to these intramolecular reactions, intermolecular cyclization of polymer-attached chains have also been reported[546] (reaction 16).



(16)

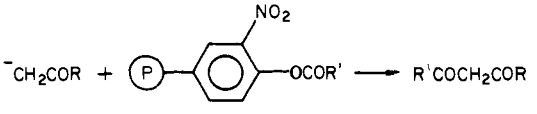
C. Detection of Reactive Intermediates

Among the various advantages associated with functionalized insoluble polymers, the possibility of maintaining mutual separation of reactive functional groups bound to the same polymer support is particularly attractive, and exploitation of this has been described earlier. Derivatized polymeric beads are generally functionalized throughout their interiors, and only a negligible fraction of reactive sites are at the surface of the bead. Hence, two highly reactive compounds may become inert toward each other when attached to two polymers, as was demonstrated in the case of polymeric trityllithium (**15**) and a polymeric active ester (**16**). Upon addition of an enolizable ketone, however, reaction proceeded as in eq 17, because the



(17a)

15



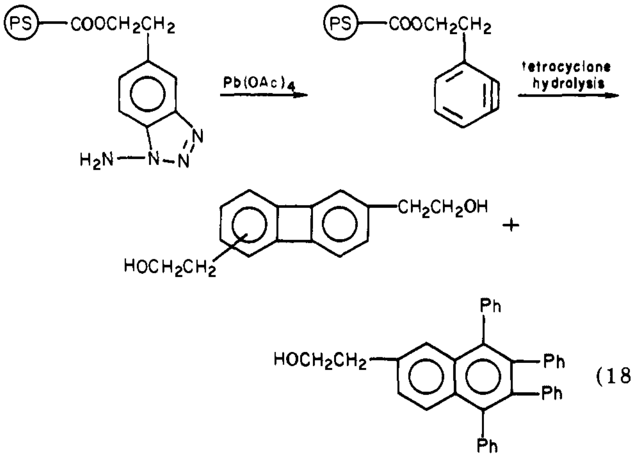
(17b)

16

free carbanion was able to migrate from one resin to the other.[548]

This clear demonstration of the existence of a reactive intermediate has become known as the three-phase test, and other examples are listed in Table IV, section 3. In principle, the technique involves the generation of a reaction intermediate from an insoluble polymeric precursor and its trapping by a second solid-phase reagent. The isolation and detection of an adduct provide positive evidence for the liberated free reactive intermediate.

While benzyne has been isolated as a stable entity in rigid matrices at very low temperature, its lifetime in solution and in the gas phase is limited by dimerization to form biphenylene. However, by generation of benzyne on a functionalized polymer,[549] the ubiquitous dimerization reaction of this reactive molecule is suppressed and its lifetime extended. This allows other products to be made more readily (reaction 18).



(18)

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