CHAPTER - I

INTRODUCTION

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CHEMICAL KINETICS

The chemical kinetics deals with the quantitative study of rate of chemical reactions and the various factors upon which it depends, such studies may through light on the general principles of reactivity or may be useful in arriving at a probable reaction mechanism. Chemical kinetics might very well be called chemical dynamics.

Thermodynamics gives little information about the mechanism of chemical reactions, but chemical kinetics provides an approach for establishing a reaction mechanism. The reaction mechanism may be regarded as detailed and pictorial representation of the reaction from spectroscopic methods; such as NMR, ESR techniques; stereochemical methods; the isolation and characterization of intermediates; the use of isotopes etc. The relation between reaction scheme and reaction mechanism has been expressed by R.S. Nyhohm[1] saying "Kinetics of mechanism equals facts to fiction."

To suggest the mechanism of given chemical process with the help of kinetic study; we should get additional information such as the products of the reaction; stereochemical evidences; use of isotopes; detection of short-lived intermediates and refinement of kinetic methods. The

determination of reaction rates by conventional methods reduces to a study of concentration as a function of time. In general analytical procedures may be divided into two broad categories; chemical and physical. It is found that physical methods of analysis are usually much more convenient than chemical methods. Common among physical methods are pressure or measurement of volume changes, optical methods such as polarimetry, refractometry calorimetry and spectrophotometry, electrical methods such as conductometry, potentiometry, polarography and mass spectrometry.

Chemical kinetics covers wide range of processes. It includes the imperial study of the effects of concentration, temperature, catalyst, solvent, hydrostatic pressure and ionic strength on the reaction, when a reaction has more than one elementary steps, the kinetics is limited by the slowest step, which is known as the rate determining step. There are different types of reactions and a wide variety of experimental techniques are used to investigate them. For the reaction in solution, the most common method for investigating the rate, involves the chemical analysis of one of the products or reactants at various stages during the course of the reaction, the time corresponding to each analysis being determined accurately.

For identification of the reaction mechanism, the following two general methods are used.

i) Kinetic method and

ii) Non-kinetic method

In these kinetic methods the amounts of the reactants or products are estimated by any well known method, at different time intervals. This is because the chemical kinetics is the study of relationship between the speed or the rate of a reaction and temperature and concentration of the participating reactants. In exceptional cases other factors are also to be taken into consideration.

Thus for kinetic study carried in liquid phase reactions, we have to find out the different kinetic parameters, the most important being the order of a reaction with respect to the different reactants, the effect of the concentration of the catalyst; ionic strength, solvent[2], dielectric constant[3] of the medium and temperature on the reaction rate. Determination of stoichiometry of the reaction, detection and estimation of the products, effect of the substituents on the rate of reaction are also valuable factors which throw considerable light on the mechanism of the intermediates, if possible has also proved to be great importance in visualising the possible reaction mechanism.

OXIDISING AGENTS

In the realm of organic reaction in solution, oxidation reactions are perhaps the most important. A large number of oxidizing agents have been utilised for overall as well as step by step oxidation process. Kinetics of such reactions have been investigated[4-6]. The well known oxidizing agents are nitric acid, chromic acid, permangnates, cerric sulphate, lead tetracetate, Cr(VI) oxide, peroxydisulphate, Mn(II) Pyrophosphate, Mn(III) acetate, Mn(III) sulphate, hexacyanoferrate, chloramine-T, bromamine-I etc.

HALOAMINES AS AN OXIDISING REAGENTS

Haloamines :

Compounds, both inorganic and organic containing one or more halogen atoms attached to a nitrogen atom are classified as haloamines. From electronegativity considerations, the N-X bond (X=halogen) is polar, with the halogen at the positive end, except in the N-fluoro compounds. The inorganic chloramines, viz. NH_2Cl, $NHCl_2$ and NCl_3 are formed when dilute hypochlorous acid reacts with ammonia.

The important organic haloamines may be considered to be N-halo derivatives of the following groups of compounds.

i) Alkyl or aryl sulphonamides

ii) Amides/imides

iii) Carbamates

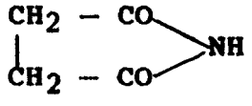
iv) condensed amines from cyanamide derivatives.

Amongest these N-metallo-N haloaryl sulphonamides have received considerable attention. These reagents furnish halonium cation with halogen in +1 oxidation state, and are amongst the most potential oxidation state.

N-chloro derivatives of the following group of compounds may be considered as an important organic chloramines.

i) Sulphonamides $R\text{-}SO_2\text{-}NH_2$

ii) Heterocyclic chloramines with chloramines with chlorine attached to nitrogen in the ring



iii) Condensed amines from cyanamide derivative

$$H_2NC(NH)N : NC (:NH) NH_2$$

iv) Anilides $C_6H_5.NH.CO.CH_3$

Commercial chloramines such as chloramine - T(CAT) and chloramine - B(CAB) are more stable than hypochlorite and they have been used as disinfectants and antiseptic (in tooth pastes, mouth washes and soaps and in the treatment of infected woulds) in preference to hypochlorites, especially

from the point of view of stability. The germicidal action has been attributed to the labile N-Cl bond[7]. Chloramine-T has also been used as fungicide and showed in vitro effectiveness equivalent to that of sodium o-phenylphenate[8].

Chloramine-T is a versatile oxidizing agent, hence it is useful as oxidant and it appears to be suitable substituent for hypochlorites, hypochlorous acid and monochloramines, which are less stable. Since the hydrolysis constant of chloramine-T is very low[9]. It does not liberate chlorine in acid solution and does not chlorinate many compounds which are attacked by chlorine water. However, chloramine-T liberates iodine from acidified potassium iodide solution.

$$ArSO_2NCl^-Na^+ + 2I^- + 2H^+ \longrightarrow ArSO_2NH_2 + I_2 - NaCl \quad ...(I.1)$$

(The molecule $P\text{-}CH_3C_6H_4SO_2$, is designated as $ArSO_2$ hereafter)

The equivalent weight of chloramine - T is half of its molecular weight because the reaction (I.1) involves two electron charge. Since the extent of hydrolysis is very low, the 0.05 M aqueous solution will have the pH value equal to 7.7 giving an apparent value for ionization constant as 2.38×10^{-5}, for the free acid $ArSO_2NHCl$.

Nature of Chloramine - T In Aqueous Solution :

The various species in acidified aqueous solution of chloramine-T have been investigated[9], and the equilibrium constants have been determined. Chloramine - T is a strong electrolyte and dissociates according to the equilibrium (I.2) in aqueous solution.

$$ArSO_2NClNa \xrightleftharpoons{K_1} ArSO_2NCl^- + Na^+ \qquad ...(I.2)$$

$$ArSO_2NCl^- + H_3O^+ \xrightleftharpoons{Ka} ArSO_2NHCl + H_2O \qquad ...(I.3)$$

(Ka of $ArSO_2NHCl$ is 2.8×10^{-5})

$$2ArSO_2NHCl \xrightleftharpoons{Kd} ArSO_2NH_2 + ArSO_2NCl_2 \qquad ...(I.4)$$

($Kd = 5.8 \times 10^{-2}$)

$$ArSO_2NHCl + H_2O \xrightleftharpoons{Kh} ArSO_2NH_2 + HOCl \qquad ...(I.5)$$

($Kh = 4.9 \times 10^{-8}$)

$$ArSO_2NCl_2 + H_2O \xrightleftharpoons{K'h} ArSO_2NHCl + HOCl \qquad ...(I.6)$$

($K'h = 8.0 \times 10^{-7}$)

$$HOCl + H_2O \xrightleftharpoons{K_7} H_3O^+ + OCl^- \qquad ...(I.7)$$

($K_7 = 3.3 \times 10^{-8}$)

The anion picks up a proton in acid (reaction I.3) to give the free acid, $ArSO_2NHCl$. Although the free acid has not been isolated, there are experimental evidences for its formation[10,11]. It undergoes disproportionation[12] via reaction (I.4) giving rise to chloramine-T and the parent

amide. Dichloramine-T and the free acid undergo hydrolysis [reaction (I.5) and (I.6)]. Finally hypochlorous acid ionises according to reaction (I.7). The values of equillibrium constants, viz. Ka, Kd, Kh, K'h and K_7 are at 298^0K.

Soper[13] determined the composition of chloramine-T solution, acidified with acids other than HCl. He observed that [HOCl] is very small and is independent of [CAT]. The predominant species is $ArSO_2NHCl$. Morris et. al.[12] have determined the ionisation constant of $ArSO_2NHCl$ as 4.55 PKa units at 298^0K by two methods (i) by measuring the apparent solubility of dichloramine-T in solution buffered to pH 4-5 and containing known amount of added p-toluene sulphonamide and by (ii) potentiometric titration of chloramine-T with standard hydrochloric acid. Bishop and Jennings[9] found that the $[ArSO_2NHCl]$ in acid solution ($[H^+]$ 0.33 mol dm^{-3}) is almost constant. Recently evidences for further protonation of $ArSO_2NHCl$ have been reported[14] (I.8).

$$ArSO_2NHCl + H_3O^+ \underset{}{\overset{K_8}{\rightleftharpoons}} (ArSO_2NH_2Cl)^+ + H_2O \quad ...(I.8)$$
$$(K_8 = 103)$$

Between pH 3 and 11, the main reactive species are $ArSO_2NHCl$ and HOCl and in more alkaline solution[15], the dominant oxidizing species are $ArSO_2NCl^-$ and OCl^-.

Oxidation of Alcohols by Chloramine - T :

Chloramine - T is a good oxidising agent and its oxidizing properties are well reviewed by no. of authors[16-19]. Chloramine - T was introduced as an analytical reagent by Noll[20] and a large number of papers have been published on the use of chloramine - T in analytical chemistry. The behaviour of chloramine - T as a titrimetric reagent and standardisation methods have been critically examined by Bishop and Jennings[9] and Jennings[21].

In earlier work and even in some recent reports, on the widely investigated oxidation of various types of alcohols by N-metallo. N-haloaryl - Sulphonamides in acid solution, the linear dependence of reaction rate on $[H^+]$ was explained on the basis of equilibrium (I.9) and the neutral N-haloaryl-sulphonamide was postulated as the reactive oxidising species.

$$ArSO_2\bar{N}X + H_3O^+ \longrightarrow ArSO_2NHX + H_2O \qquad ...(I.9)$$

However, N-haloarylsuphonamides are weak acids and exist almost completely as the undissociated molecules in solution of pH 2. A further increase in the acidity of the solution does not cause any significant increase in $[ArSO_2NHX]$. Hence the postulation of neutral N-haloaryl sulphonamide as the reactive species in solutions of pH 2, is an error. The increase in rate with acidity observed in many reactions, can be attributed to further protonation of

N-halogenoaryl sulphonamide (I.10) to give a stronger electrophile and oxidant.

$$ArSO_2NHX + H_3O^+ \longrightarrow (ArSO_2NH_2X)^+ + H_2O \quad ...(I.10)$$

Physico-chemical evidences for the existance of such species have recently been reported[22].

The oxidation of some primary alcohols[23] (n-butanol, iso-butanol and iso-pentanol) and cyclo-alkanols[24,25] by chloramine - T in the pH range 4.0 to 5.7 was shown to be first order in [CAT] and $[H^+]$ but was independent of the [alcohol]. Hydrolysis of $ArSO_2NHCl$, in the rate-determining step, to give hypochlorous acid has been postulated. The alcohol reacts with HOCl in a fast step, and forms corresponding aldehyde. The rate law is of type.

$$-\frac{d[CAT]}{dt} = K\,[CAT]\,[H^+]$$

The oxidation of unsaturated alcohols like allyl alcohol, crotyl alcohol and phenylallyl alcohol by chloramine - T[26-28] in HCl medium was investigated by Mahadevappa et.al., the reactions showed zero order dependence in [alcohol] and first order dependence in [CAT] and [acidity]. The reactions were shown to be catalysed by chloride ion also. In the above oxidation, the rate law, at low acid concentration is

$$-\frac{d[CAT]}{dt} = K\,[CAT]\,[H^+]$$

HOCl is assumed to be reactive oxidizing species. In the allyl alcohol oxidation by chloramine - T at higher acid concentration, the rate law becomes

$$-\frac{d[CAT]}{dt} = K\,[CAT]\,[H^+]^2$$

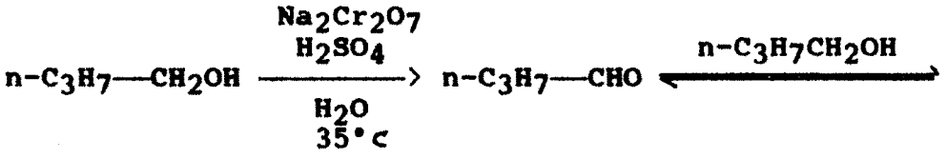
The stepwise addition of two protons to chloramine - T melecule, to generate the chlorinium ion (Cl^+) is envisaged. The (Cl^+) ion on hydrolysis in a rapid step produces the protonated hypochlorous acid (H_2OCl^+), which then attacks the substarate in a fast step giving the oxidation product, allyl aldehyde. A similar behaviour is noticed in the oxidation of crotyl and cinnamyl alcohol by chloramine - T in hydrochloric acid medium[26-28]. Herlihy[29] reinvestigated the oxidation of allyl alcohol by chloramine - T in HCl medium and obtained the rate law (I.11)

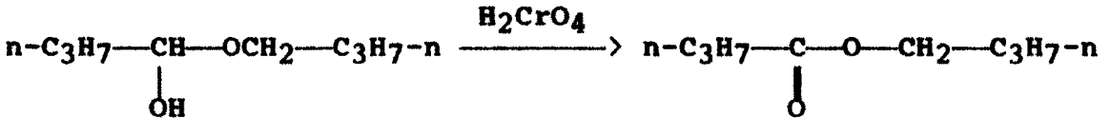
$$d[CAT]/dt = K[H^+]\,[Cl^-]\,[CAT]\,[Alcohol]^0 \qquad ...(I.11)$$

The oxidation of benzyl alcohol and primary aliphatic alcohols by chloramine - T[30-31] in the presence of acids other than HCl, have been studied. The reactions were shown to be first order each in [alcohol] and [CAT] and were catalysed by H^+ ions.

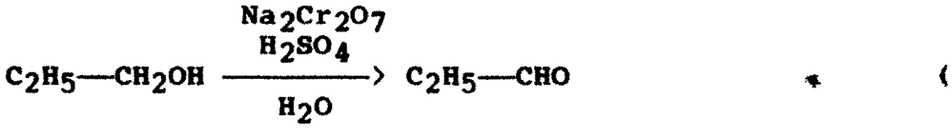
CHROMIUM COMPOUNDS AS AN OXIDIZING REAGENTS

Although the oxidation of primary alcohols to aldehydes may be accomplished [redacted] by chromic acid, the reaction may be corresponding carboxylic acid, though at a rate slower than that of the oxidation of the alcohol[32a]. A more serious complication is the reaction of the aldehyde and the alcohol in the reaction mixture to form a hemiacetal (e.g., [I-12], which is oxidized rapidly to an ester. However, moderate yields of aldehydes have been obtained from oxidations of primary alcohols with chromic acid, especially in such cases as [I-13] and [I-14] where the volatile aldehyde can be distilled from the preparation of sterically hindered aldehydes such as those obtained from alcohols of the neopentyl type[34].

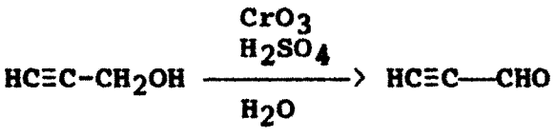




[I-12] (41-47%) (Ref.33a)



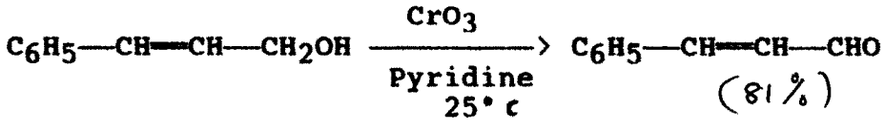
[I-14] (45-49%, distilled from mixture as formed) (Ref.35a)



(Ref. 35b)

[I-15] (35-41% distilled from mixture as formed)

Reasonable yields of aldehydes have been obtained by the oxidation of primary alcohols with chromium trioxide in pyridine, especially in cases where the alcohol is allylic or benzylic. The use of a methylene chloride solution of the chromium trioxide-dipyridine complex appears to be the method of choice for the oxidation of primary alcohols to aldehydes[32b]. The success of these procedures may be attributable in part to the fact that the oxidation is done in the absence of an appreciable concentration of water, a necessary reactant for at least one of the mechanistic pathways for the conversion of an aldehyde to an acid.



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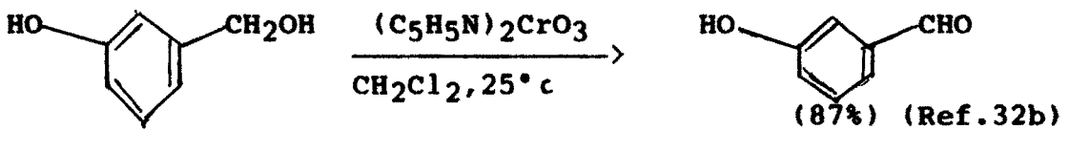

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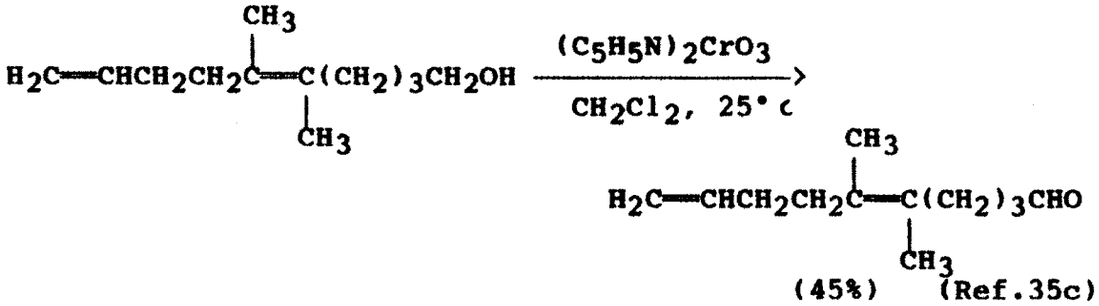


(Ref.35c)

POLYMER SUPPORTED REAGENTS AS AN OXIDISING REAGENTS

The last fifteen to twenty years have seen the rise in popularity of functionalised polymer, in polymer chemistry. This use of functionalised polymer focuses essentially on the attachment of reactive and interactive - functional groups to polymer backbones, and subsequent application of the supported or immobilized species in some chemical or biochemical process. The use of polymeric reagents dates back to the mid 30's when ion exchangers made by condensation processes became available[36]. The advantages of polymer - supported reactions were fully recognized after the work of Merrifield and Letsinger in 1963 on peptide synthesis using crosslinked polymer - supports[37-38]. Since the introduction of this technique a large number of authoritative books[39-45] and reviews[46-60] have appeared in the literature. In addition to this, a series of international symposia have been held on this subject and the proceedings of each of these have also been published[61-65].

The most of the polymer - supported species consists of spherical beads as the supporting polymer, in principle the polymer support might be a linear soluble species, a porous crosslinked resin, or indeed a macroscopic polymeric object. Immobilization of a reactive species on a support might provide a number of important advantages some of these are listed below.

Potential advantages in using a polymer support.

1) Simply converting the reactive function to a macromolecular species immediately aids separation, isolation and purification procedures involving the bound species.
2) Convenient use of excess reagent.
3) Retention of precious species.
4) Reuse or recycling possibilities.
5) Encapsulation of corrosive, noxious or toxic species.
6) Batch or column reactors.
7) A number of processing gains may also be made since supported species tend themselves for use in gas and liquid phase reactions.
8) Immobilized groups are essentially siteisolated and so such groups can behave as if present in infinite dilution.
9) Enhanced selectivity.
10) Reduced side reactions.
11) Enhanced reactivity.
12) Stabilization of reactive species.

It is also important of course to be realistic and appreciate that some disadvantages can arise and these are listed below. The first two are very obvious and very important. In any useful application, these two factors must be more than balanced by one or more of the advantages given

above. In addition the possible disadvantages are as listed below.

Disadvantages in using a polymer support.

1) Initial extra cost.
2) Not available "off - the - shelf".
3) Reduced reactivity - slower reactions.
4) Increased side - reactions.
5) Greater difficulty of analysis of the structure of supported species and of impurities.
6) Inability of separate polymer bound impurities.
7) Lesser stability of organic supports than of inorganic supports.

SYNTHESIS OF POLYMER

Although in principle a wide variety of physical forms of a polymer might be employed as the basis of supported species, in practice most useful applications have employed spherical crosslinked participate resin beads. These are prepared in the laboratory and on an industrial scale by suspension polymerization techniques[66]. Typically, an organic phase, consisting of a vinyl monomer and divinyl crosslinking comonomer, is dispersed as droplets by stirring in an aqueous phase containing a water soluble polymer as a suspension stabilizer. (Fig. I.1). A free radical initiator is dissolved in the monomer droplets and so when the

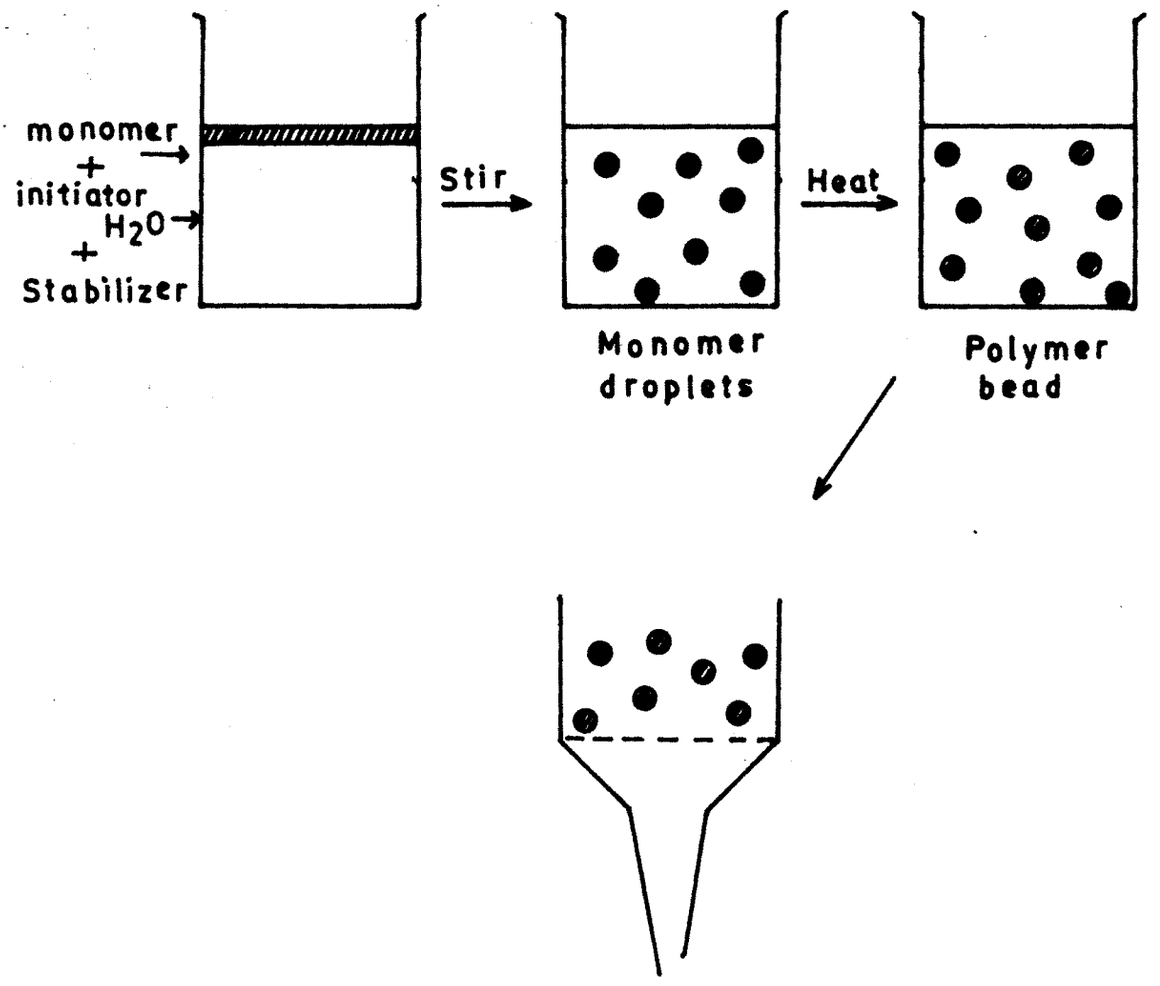


Fig. I·1 — SUSPENSION POLYMERIZATION SCHEME .

suspension is heated, polymerization droplets into rigid, solid polymer particles or "beads". These can be collected by filtration and washed free of the aqueous phase. They can also be readily freed of residual comonomers by extraction with a swelling solvent in a soxhlet extractor. On drying free flowing polymer resin beads are obtained.

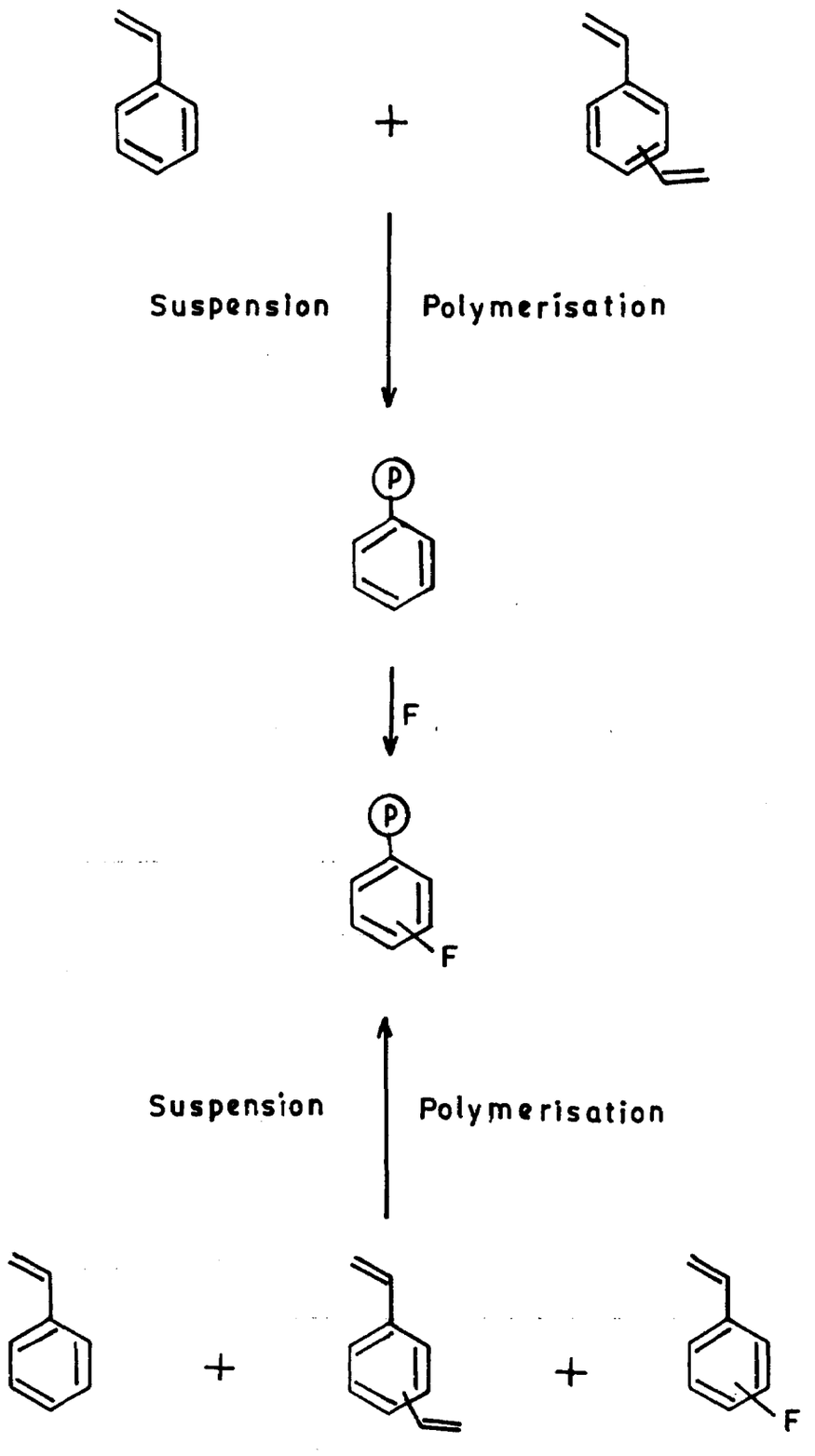
In practice the suspension polymerisation process can be quite tricky and the water-soluble suspension stabilizer can be very important for success with some comonomer species. The process is also aided by use of a flat-bottomed reactor with flanged sides. This arrangement maximises the level of turbulence produced for a given energy input from the stirrer system.

IMMOBILIZATION OF REACTIVE SPECIES

A reactive functional group can be introduced onto a polymer resin matrix using two ways. A non functional resin can be synthesised then in separate procedure the required chemical functionality can be introduced by chemical modification (one or more steps) of the polymer matrix. This is called "chemical modification route". Alternatively the required functionality can be introduced into a polymerisable monomer and then this functional comonomer can be used as one component of the polymerising mixture during resin preparation. This is called the "functional comonomer" route. Combination of these

approaches is also possible. These two strategies are shown in Fig. I.2.

Each strategy has some advantages and some disadvantages and the various factors are listed in Table I.1. Summarising these it is apparent that the comonomer route allows the structure of the functional group to be clearly defined and offers more control over the number and distribution of groups. Over all the chemistry is better defined. The chemical modification route offers an overall easier strategy, enabling off-the shelf resins to be employed, and provides groups which are less likely to be located in inaccessible region of the resin coupled with lower cost. These factors have meant that the chemical modification route is the one which has been most widely employed. This strategy has to be used carefully, if resin groups with even a reasonable level of purity are to be obtained.



F = Functional Group

Fig. I·2 – SYNTHESIS OF POLYMER SUPPORTED SPECIES.

Table I.1 **Derivatization of Resins Via Chemical Modification and Use of Functional Comonomers.**

Factor	Chemical Modification Route	Functional Comonomer Route
Availability	Off-the-shelf product	Comonomer and polymer to be prepared
Structure of the groups	may be nuclear	well defined
Number of groups	poor control	better control
Distribution groups	poor control poorly defined	better control better defined
overall chemistry	may be poorly defined	generally clearcut
Access to groups	generally good	possibly limited
cost/ convenience	low/high	higher/lower

Having made or purchased a non-functional precursor resin a wide variety of chemistry is available to generate specific functionality by chemical modification. In principle any chemical transformation which has been carried out on small molecules in solution can be achieved on analogous macromolecular structures. In practice extra care may be required in selecting suitable reaction conditions and sometimes much experimentation is required before

success is achieved. Typically for polystyrene-based resins, however, the various electrophilic substitutions shown in Fig I.3 can be achieved quite readily. Some of these, for example, the chloromethylation and sulphonation yield cation exchange resins, whereas amination of the chloromethylated species using trimethylamine yields anion exchange resin[67]. The latter is an example of an attack by a nucleophile, and this is the second important group of reactions used for introducing functionality into the polystyrene-based resins. Some other examples are shown in Fig. I.4[68]. Though the chemistry of polystyrene is by the most well developed, great scope remains with other polymers. For example, rubber chemists have examined the derivatization of polydienes in great detail and a considerable literature exists on the derivatization of main chain alkene residues.

POLYMERIC REAGENTS : CONCEPT AND CHARACTERISTICS

Polymeric reagents are reactive species bound to a polymeric back-bone. These macromolecules are often tailor-made to perform specific functions and are sought for these properties rather than for the mechanical bulk properties of the polymers. The attachment of the reagent function to the macromolecules may be via chemical methods or physical interactions. The polymer may be organic or inorganic in nature. Thus, the polymeric reagent is a novel type of substance possessing a combination of the physical

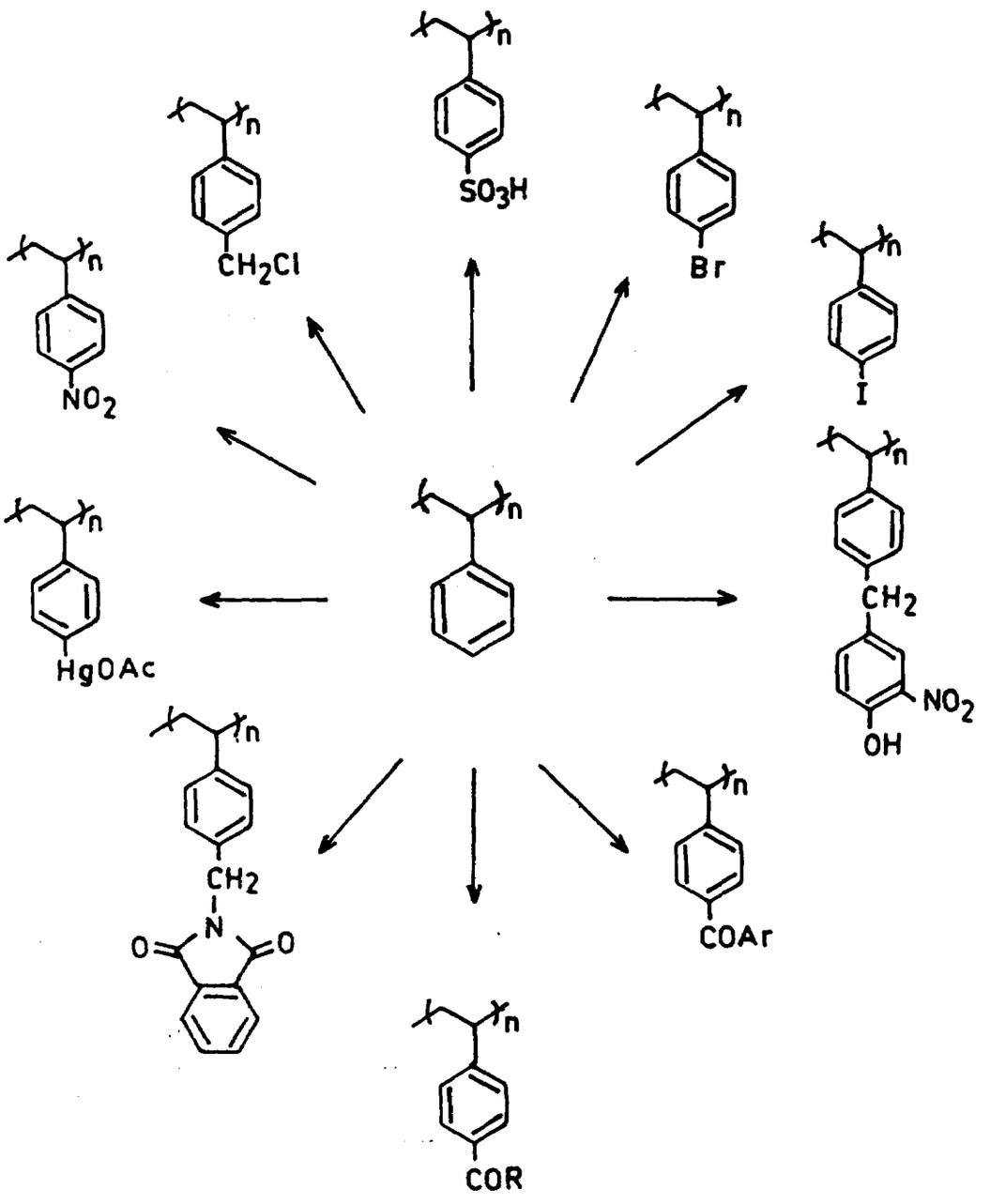


Fig. I-3 — ELECTROPHILIC SUBSTITUTION REACTION OF POLYSTYRENE .

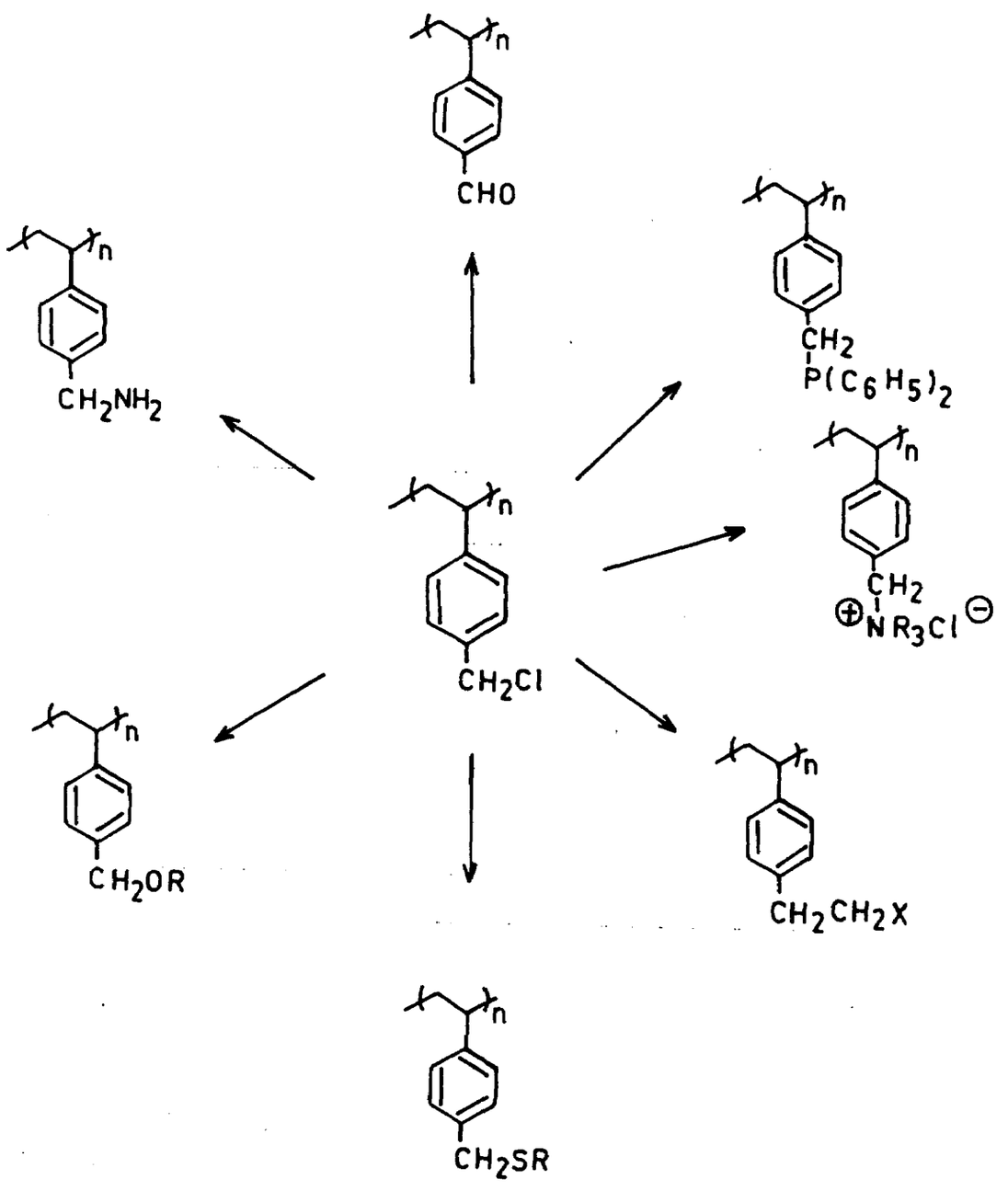


Fig. I·4 — NUCLEOPHILIC SUBSTITUTION REACTION OF POLY (CHLOROMETHYLSTYRENE).

properties of the high polymer and the chemical properties of the attached reagent.

The polymer may be organic or inorganic reagent attachment may via chemical bonds or physical interactions. Physically adsorbed species are generally unsatisfactory since in use, the compound tend to dissociate, and they are therefore unsuitable for column or cyclical application. Polymeric reagent may be used as reactants in conventional or unconventional chemical or biochemical processes. A general scheme whereby a polymeric reagent would be used in synthesis is presented in Fig. I.5.

In this type of synthesis the reagent is linked to polymeric material to form the functionalized reagent polymer [P - R]. The low molecular weight substrate (A) is then added to the reaction mixture containing the polymeric reagent. Upon completion of the reaction the spent reagent byproduct polymer P - B is removed from solution and the desired product (C) is isolated.

During the reaction a transitory polymeric reagent - substrate complex[69] may be formed which need not be isolated. In such cases the substrate is generally bound to the polymer via a labile bond and is then transformed by a nucleophile into the desired product[70]. The polymeric reagent can also act by direct transforming the substrate (S) into the product. Examples of reactions using such

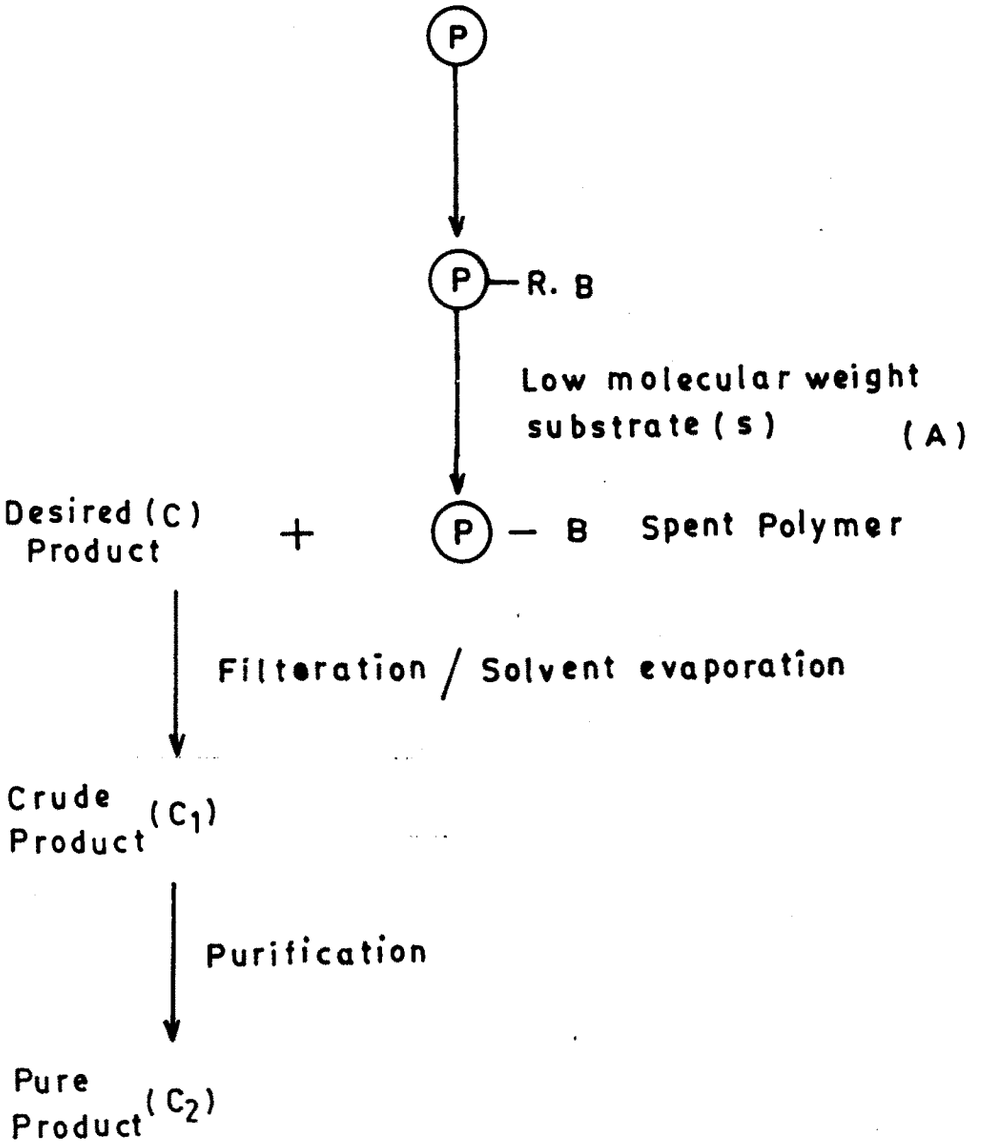


Fig. I·5 — POLYMERIC REAGENT IN SYNTHESIS

polymeric reagents have included those incorporating the polymeric peptide coupling agents. Carbodiimide[71] and the reactive function found in EDDQ (2-ethoxy-1-ethoxy carbonyl-1,2 dihydroquinoline). Other examples include epoxidations, brominations[72] and hydrogenations[73].

The second type of polymeric reagent mediated reactions include reaction in which a low molecular weight substance is covalently bound to the polymer support and then reacted with a low molecular weight reagent solution. The product remains attached to the support. While the by-product, excess of reagent and solvent all remain in solution and can be removed by filteration. The last stage in such synthesis involves cleavages of the product from the polymer back-bone.

The third type includes reactions of polymeric reagents carrying catalytic groups. These reactions are not basically different from the above type of (second) reactions. In this the by-product polymer is the same as functionalized polymer.

TYPES OF SUPPORTS

There are many organic and inorganic materials have been investigated as support matrices. The use of a particular polymer as a reagent or catalyst depends on the physical properties and chemical constitution of the

polymer. The use of functionalized polymer demands a structure which permits adequate diffusion of reagents to the reactive sites which in turn is dependent on the extent of solvation, the effective pore-size and pore volume. The support material should be chemically and mechanically stable under the reaction conditions.

The supports may be either a linear polymer or a cross linked one. In the case of linear polymers, the separation is effected by precipitation or ultrafilteration. The cross-linked organic macromolecular species in particular are experimentally very attractive because of their ease of filteration and purification. Various structurally different organic supports employed in polymer-supported reactions can be given as below.

The earlier supports experimented were those of poly (methyl-methacrylate), poly (vinyl alcohol) and cellulose. But they were later rejected due to the synthetic inconvenience associated with them. Merrifield used 1-2% cross linked styrenedivinyl benzene copolymers as supports. These types of supports were found to be incompatible with polar solvents nature of the polystyrene matrices. For overcoming these difficulties, polyamide supports were introduced by Sheppard and co-workers[74]. These solved some of the problems related to incompatibility of solvents and substrates; yet some other remained concerning the

difficulties with functionalization and stability of the supports.

Majority of the polymeric reagents prepared so far utilize crosslinked polystyrene as the product material on account of its commercial availability and ease of functionalization by a variety of substitution reactions in the aromatic ring. Reagents based on polyamides[75]. Poly (vinyl pyridines)[76] and poly (N-acrylylpyridine)[77] were also introduced to study the effect of the nature of the macromolecular support on the reactions using supported were found to be much superior to those based on polystyrene due to the better hydrophilic hydrophobic balance they could provide,[78,79] polysaccharides were also found to be able to act as immobilizing group conversions[80].

The advantages of linear group conversions[80]. Supports for polymeric reagents were demonstrated by the use of N-chloronylons as oxidising and halogenating reagents[81]. The linear polymers are soluble in good solvents, hence diffusion restrictions are small, high conversions can be obtained, because homogeneous accessibility of functional groups is possible. They dissolve to form true molecular solution[78], in which state, the polymer chain exhibits a random coil. The solubility of a polymer in a solvent depends on the nature of the polymer backbone and it has been observed that attaching a reactive function to a

polymer alters the microstructure of the polymer backbone. Hence, the solvation behaviour of a functional polymer and not the parent backbone should be considered for planning a synthesis.

Crosslinked polymer supports are used widely when compared to linear supports. Crosslinked polymers consist of infinite networks in which linear chains are interconnected. When crosslinking sites are introduced the molecular coil size and the viscosity is increased. The pore-size of the support material, which is a predominant factor that affects the reactions using the supported reagent, is controlled by the "Comb model" in which increasing the molecular weight by branching does not produce a rapid transition from a soluble gel to the insoluble one. Free rotation of the branched chain around the primary chain may be the factor which favours the increased solubility of this type of branched polymers. At higher concentrations of divinyl compound, diffusional restrictions come into play[82].

Extent of crosslinking in a polymerisation is dependent on the rate of polymerisation of each species and their ratio of molar concentrations[83]. Large beads from a single reaction mixture have lower degree of crossing than small beads from the same mixture when the percentage of the divinyl monomer is high[84]. In such cases the growing polymer is propagated as a helix in the presence of a high

concentration of monomer. The different reactive sites along a crosslinked polymer metrix have varying reactivity, reflecting heterogenity at the molecular level[85]. The active sites can be made available by increasing the surface area of the particle. So that diffusion into the gel metrix is not an important factor rather than swelling. Such a case is achieved with macroreticular and macroporous resins containing large pores fixed by a high degree of crosslinking. With an effective surface area hundred times that of suspension polymers[86,87]. These polymer are prepared by using a high degree of crosslinking agent and diluting the monomer phase by an inset solvent. Large amount of crosslinking agent leads to increased number of intramolecular crosslinking steps which result in highly crosslinked nuclei. When the nuclei grow in size, the cavities between the particles are filled with inert solvent. The resulting polymer may be porous even in the dry state. Macroporous polymers having a high interior surface can be functionalized as a kind of monolayer.

SOLVATION - BEHAVIOUR OF FUNCTIONAL POLYMERS

A polymeric reagent can provide an effective alternative to its low-molecular weight counterpart, if the reactive functional groups anchored on it are easily accessible to the low molecular weight substrates. Linear polymers are soluble in good sovlent. But the crosslinked

polymers are macroscopically insoluble in almost all solvents. The crosslinked polymer absorb considerable amount of solvent and become extremely porous forming a pseudo gel. At low crosslink density (>2%) the solvent swollen polymer may resemble a homogeneous solution such that the gel network consists of largely of a solvent with only a small fraction of the total mass being polymer backbone. But with increasing crosslink density, the polymer backbone becomes more and more rigid and available free space in between crosslinks for penetration of solvents is reduced diminishing the ability for the intake of solvents. In the presence of solvents which are not able to swell the polymer network, movement of reagents within such a network may become diffusion controlled. At higher concentration of the crosslinking, considerable chain entanglement can also occur. This reduces the extent of swelling in presence of good solvents[88].

Cases are observed when resins showed selective uptake of solvents with inclusion of the solute pointing out the phenomenon of distribution in polymer aided reactions[89]. Flory has suggested that for dissolving a linear polymer or for swelling a crosslinked polymer, the driving force is due to contributions of normal entropy and enthalpy changes associated with mixing of solvents and solute molecules added with configurational entropy resulting from dilution

of flexible chain molecules[90]. For linear molecules, the contribution from configurational entropy change is favourable until complete dissolution occurs when the entire solvent volume is uniformly filled with polymer. In the case of crosslinked polymers, the tendency to disperse is opposed by a decreased configurational entropy of polymer chains held between crosslink points where they are forced to assume more elongated, less probable configuration of the network expands. Thus, at higher crosslink ratio, the swollen volume is lower.

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