Chapter-II
Literature Review
LITERATURE ON YLIDES

Compounds in which a carbon atom is attached directly to a heteroatom $X^+$ (which could be nitrogen, phosphorus, sulphur, arsonium, stibonium, bismuthonium, selenium, tellurium) carrying a positive formal charge are termed ylides. These are 1,2 dipolar compounds represented as:

\[
R_mX\equiv CR_n \quad \text{(I)}
\]

\[
Ylide
\]

\[
R_mX\rightarrow CR_n \quad \text{(II)}
\]

\[
Ylene
\]

If heteroatom (X) is an element from the first row of the periodic system, the ylide is commonly represented by charge separated form (I) whereas if the heteroatom is from second, third etc. row then it can also be written in the canonical form (II) with neutral double bond.

The term 'ylide' was first coined in German language by George Wittig in 1944. It was derived by the use of the ending –yl to imply an open valence and the ending –id to imply anionicity on a carbon atom. Thus, ‘Yl-ide’ describes both the covalent ‘yl’ and ionic ‘ide’ nature of the bonding, between the heteroatom and the neighboring carbon atom. The ylide in charge separated form (I) emphasizes the dipolar zwitterionic nature involving anonium centre at elements like P, S, N, As, Sb, Bi, Se which may be at least partially delocalized into suitable substituents. The ylene (II), however, contains a double bond between the onium centre and the ylidic carbon. The advent of modern physical techniques and the theoretical calculations suggest that ylide formula predominates in the ground state of these and related molecules.

The property of ylide depends on the identity of the heteroatom. The dipolar and nucleophilic character of the ylide increases and the stability decreases as heteroatom goes down the periodic table which may be attributed to less efficient $\pi - \pi$ overlap between the C-sp$^2$ orbitals of heteroatom in $>\text{C} - X$.

In 1894, Michaelis and Gimborn prepared the first phosphonium ylide. Later in 1920s, Staudinger (Nobel laureate 1953) carried out research on phosphonium ylides and iminophosphoranes. Wittig (Nobel laureate 1979) and his
collaborators synthesized nitrogen ylide\textsuperscript{41} and phosphonium ylide\textsuperscript{42}, which on treating with aldehyde or ketone formed alkene. Sulphonium ylide was first made by C.K. Ingold\textsuperscript{43} and propagated by Corey\textsuperscript{44,45} (Nobel laureate 1990). Olah\textsuperscript{46} (Nobel laureate 1994) showed that oxonium ylides were obtained as intermediates during conversion of methanol to ethane and higher hydrocarbons, at high temperature over a catalyst.

The reaction of carbenes and carbenoids with heteroatoms continues to draw attention both mechanistically and synthetically\textsuperscript{47}. The recent method for ylide generation has been accomplished by the transition metal catalyzed decomposition of diazo compounds in the presence of a heteroatom.

\[
R\equiv R + R_2CN_2 \xrightarrow{\text{Transition Metal}} R\equiv R
\]

Ylide formation employing the transition metal catalyzed decomposition of diazo compounds depends on the catalyst, diazo species, the nature of the heteroatom and competition with other processes. The ylide generation has also been achieved using rhodium (II) carboxylate\textsuperscript{48} catalyst which offers better yield than alternative catalysts.

1. NITROGEN YLIDES:

The first nitrogen ylide was synthesized by Wittig in what he called an ‘absurd experiment’ to demonstrate the existence of nitrogen by preparing pentamethylnitrogen. Wittig and Wetterling\textsuperscript{41} in 1947, treated tetramethylammonium bromide with phenyllithium to prepare tetramethylammonium phenyl. The reaction resulted in the deprotonation adjacent to the nitrogen atom forming a substance insoluble in ether but soluble in tetrahydrofuran with typical nucleophilic properties. The substance formed was lithium bromide complex of trimethylammonium methylide (I) along with benzene.

\[
\begin{align*}
\equiv \equiv \equiv \equiv & \quad \text{\textsuperscript{13}Li} \\
\equiv \equiv \equiv \equiv & \quad \text{LiBr}
\end{align*}
\]

(1)
Nitrogen ylides can be classified as below:

1(a). Ammonium ylides:

Wittig and Polster\textsuperscript{49} proposed that when trimethylammonium methylide (I) was complexed with lithium bromide, the ylide was stable whereas the free radical (II) quickly decomposed into trimethylamine and methylene. Weygand \textit{et al.}\textsuperscript{50} further examined the nucleophilic properties of trimethylammonium methylide (II) in tetrahydrofuran solution. The ylide was difficult to alkylate as it decomposed to trimethylamine and affected eliminations with the alkyl halides.

\[
\begin{array}{c}
\begin{array}{c}
\text{N} \\
\Theta
\end{array}
\end{array}
\xrightarrow{\text{LiBr}}
\begin{array}{c}
\begin{array}{c}
\text{N} \\
\Theta
\end{array}
\end{array} + \text{Solvent. LiBr}
\]

\[
\begin{array}{c}
\begin{array}{c}
\text{N} \\
\Theta
\end{array}
\end{array} + [\text{CH}_3^+] \rightarrow (\text{CH}_2)_n
\]

Trimethylammonium dicyanomethylylide (III) is the most stable ammonium ylide isolated from its conjugate acid and aqueous hydroxide with m.p.-153°C. It was found to be stable in the presence of oxygen and water for indefinite periods. The ammonium ylide (III) is stabilized through resonance involving delocalization of carbanion lone pairs through two cyano groups along with electrostatic stabilization by the ammonium group. Ammonium ylides are found to be less stable than phosphonium ylides in terms of reactivity and thermodynamically.

\[
\begin{array}{c}
\begin{array}{c}
\text{N} \\
\Theta
\end{array}
\end{array}
\xrightarrow{\text{CN}}
\begin{array}{c}
\begin{array}{c}
\text{N} \\
\Theta
\end{array}
\end{array} \text{CN}
\]

Some of other ammonium ylides\textsuperscript{51,52} obtained as an intermediate are:

\[
\begin{array}{c}
(C_2H_5)_3\text{N} \xrightarrow{\Theta} \begin{array}{c}
\text{CH}_2\text{CH} \equiv \text{C}
\end{array}
\end{array}
\]

(V)

\[
\begin{array}{c}
\text{Ph}
\end{array}
\xrightarrow{\Theta}
\begin{array}{c}
\text{CHCO}_2\text{Et}
\end{array}
\]

(VI)
1(b). Pyridinium ylides:

In 1935, Krohnke\textsuperscript{53} discovered pyridinium ylide by treating N-phenacyl pyridinium bromide with potassium carbonate.

\begin{equation}
\begin{array}{c}
\text{N-} \text{CH} = \text{C}-\text{C}_6\text{H}_5 \text{Br} \\
\text{K}_2\text{CO}_3 \\
\text{N-} \text{CH} = \text{C}-\text{C}_6\text{H}_5 \\
m.p. 74^\circ\text{C}
\end{array}
\end{equation}

Krohnke reported series of ylide with general structure (II) over a period of nearly thirty years.

Out of several pyridinium ylides reported, only few have been isolated. The isolated ylide contains one of the groups $R_1$ and/or $R_2$ in structure (II) that is capable of stabilizing the carbanion by resonance.

Lloyd and Sneezum\textsuperscript{54} in 1955, prepared and isolated a red-brown, high melting solid, pyridiniumcyclopentadienylide (III) by treating 3,5 dibromocyclopentene with excess pyridine followed by sodium hydroxide. The pyridinium ylide (III) was insoluble in water but dissolved in dilute acid forming a colourless solution.
In 1960s, pyridinium tetraphenylcyclopentadienyide (IV) was prepared by heating 2,3,4,5-tetraphenyl diazopentadien (IV) at reflux in pyridine. Addition of water precipitated high yields of purple ylide.

Later, pyridinium ylide was also synthesized by heating diazomethanedicarbonitrile in pyridine. Pyridinium ylide (IV, V) was also prepared photochemically.

Laser flash photolysis of diphenyl diazomethane in the presence of pyridine resulted in the pyridinium ylide (VI).

Pyridinium ylides were also prepared from quinoline and isoquinolinium salts. Isoquinoline-carboethoxymethyl ylide (VII) was prepared by the thermal decomposition of ethyl diazoacetate in the presence of isoquinoline.

\[
\begin{align*}
\text{Pyridine} &+ \text{Ph} &\rightarrow &\text{Ph} \\
\text{Pyridine} &+ \text{N}_{2}\text{C(CN)}_{2} &\rightarrow &\text{Ph} \\
\text{Ph} &+ \text{N}_{2}\text{CCH}_{2}\text{CO}_{2}\text{Et} &\rightarrow &\text{Ph}
\end{align*}
\]
Pyridinium ylides undergo wide range of reactions typical of nucleophiles in general and carbanions in particular. Pyridinium ylides are more stable than ammonium ylide as the carbanion is stabilized by resonance with pyridinium ring. These ylides undergo carbanionic reactions such as alkylation and acylation.

1(c). Nitrile ylides:

The reaction of a carbene or carbenoid with a nitrile to produce an intermediate nitrile ylide has been a useful method for preparing these dipoles. Nitrile ylides are versatile intermediates which undergo 1,3-dipolar cycloaddition to give complex heterocycles.\(^{61}\)

The first stable nitrile ylide was prepared by Arduengo and coworkers\(^ {62}\) in 1984 via carbene addition to a nitrile. Irradiation of diazotetrakis (trifluoromethyl) cyclopentadiene in the presence of 1-adamantyl nitrile resulted in the formation of a stable crystalline solid nitrile ylide (I).

Kende and coworkers\(^ {63}\) prepared nitrile ylide intermediate from carbenes and methacrylonitrile. Thermolysis of p-diazo oxide in methacrylonitrile as solvent generated nitrile ylide (II) as intermediate followed by 1,3 dipolar cycloaddition.
The traditional methods used to prepare nitrile ylide include the thermal elimination of hydrogen chloride from imidoyl chlorides\textsuperscript{64}, cycloelimination of carbon dioxide from oxazolin-5-ones\textsuperscript{65}, photolytic ring opening of 2H-aziridines\textsuperscript{66,67}.

Some of the other nitrile ylides\textsuperscript{68-70} reported to be formed as an intermediate during the course of reaction are given below:

\[ \text{CH}_3C\equiv\text{NCH}_2\text{Ph} \quad \text{PhC\equivC-NH}_2 \]

Here are some images of nitrogen imines:

\begin{enumerate}
\item [1(d)]. \textbf{Nitrogen Imines:}
\end{enumerate}

Discovery of nitrogen imines dates back to the year 1949 when Wittig and Rieber\textsuperscript{42} found that reaction of 1,1,1-trimethyl hydrazinium iodide with phenyl lithium gave an intermediate ammonium imine (I) that could not be isolated and on further alkylation by benzyl bromide yielded 1,1,1-trimethyl 2-benzylhydrazinium iodide.

\[ \text{CH}_3\text{C\equivN-NH}_2\text{I} \xrightarrow{\text{Ph-Li}} [\text{CH}_3\text{C\equivN-NH}] \xrightarrow{\text{Ph-Br}} \text{CH}_3\text{C\equivN-NH-C}_6\text{H}_5\text{I} \]

Schneider and Seebach\textsuperscript{71} carried out the conversion of pyrrollium salts to pyridines by ammonolysis using phenyl hydrazine as the base. The resulting pyridinium salt was treated with sodium hydroxide to dark blue anhydrous base (II) which was reconverted to the salt with dilute acids.
Structure (II) was corrected to (III) as the anhydro base undergoes methylation with methyl iodide on nitrogen instead of carbon.

![Chemical structure](image)

(III)

Nitrogen imines are less basic than nitrogen ylides and their chemical and physical properties have not been extensively studied.

1(e). Diazo compounds:

Diazo compounds are used as precursors to carbenes, which are generated by thermolysis or photolysis. Diazo compound may be considered a special form of nitrogen ylide in many reactions and are more stable than corresponding ammonium and pyridinium ylides. They are represented in canonical form (I) as:

![Canonical form](image)

(I)

The diazo compound is stable and isolable if the substituents attached to the carbon provide maximum stability for carbanion. The diazo compounds that have been isolated, purified and characterized include diazofluorene, diphenyldiazomethane, diazoketone and phenyldiazomethane. Diazo compounds react with aldehyde and ketone giving three products whose ratio depends on the structure of both the reactants as well as reaction conditions. The reaction starts with the initial attack of diazo compound, through its carbanionic carbon, on the carbonyl carbon to form betaine (II) as an intermediate. Carbonyl compounds with electron withdrawing substituents tend to form oxide as major product.
In 1952, Bamford and Stevens\textsuperscript{73} for the first time examined the reaction of aliphatic diazo compounds with tertiary amines. They treated diazofluorene with benzyldimethylamine to form $\alpha$-benzyl-$\alpha$ (dimethylamino) fluorene. Diazofluorene decomposed to fluorenylidene which reacted with amine resulting in the generation of ammonium ylide as an intermediate which later underwent stevens rearrangement.

Nitrogen ylides have been successfully used as the radical initiators to bring about the polymerization. Srivastava and coworkers synthesized the following homopolymers and copolymers with nitrogen ylides:

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Polymers</th>
<th>Ylide</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>Homopolymers</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>Polyacrylamide</td>
<td>PDMY</td>
<td>74</td>
</tr>
<tr>
<td>2.</td>
<td>Polyethyl methacrylate</td>
<td>4-PCPY</td>
<td>75</td>
</tr>
<tr>
<td>3.</td>
<td>Polymethyl acrylate</td>
<td>$\beta$-PCPY</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\alpha$-PCPY</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MNY</td>
<td>78</td>
</tr>
<tr>
<td>4.</td>
<td>Polymethyl methacrylate</td>
<td>PDMY</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ICPY</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\beta$-PCPY</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td>Polystyrene</td>
<td>PDMY</td>
<td>82</td>
</tr>
<tr>
<td>---</td>
<td>-------------</td>
<td>------</td>
<td>----</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ICPY</td>
<td>83</td>
</tr>
<tr>
<td></td>
<td></td>
<td>β-PCPY</td>
<td>84</td>
</tr>
<tr>
<td>6.</td>
<td>Poly N-vinyl pyrrolidone</td>
<td>β-PCPY</td>
<td>85</td>
</tr>
<tr>
<td>7.</td>
<td>Polyvinyl acetate</td>
<td>β-PCPY</td>
<td>86</td>
</tr>
<tr>
<td><strong>Copolymers</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.</td>
<td>Poly(acrylonitrile-co-styrene)</td>
<td>β-PCPY</td>
<td>87</td>
</tr>
<tr>
<td>9.</td>
<td>Poly(acrylonitrile-co-α-methyl styrene)</td>
<td>β-PCPY</td>
<td>88</td>
</tr>
<tr>
<td>10.</td>
<td>Poly(methyl acrylate-co-styrene)</td>
<td>ICPY</td>
<td>89</td>
</tr>
<tr>
<td>11.</td>
<td>Poly(methyl methacrylate-co-styrene)</td>
<td>β-PCPY</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PDMY</td>
<td>91</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ICPY</td>
<td>92</td>
</tr>
<tr>
<td>12.</td>
<td>Poly(methyl methacrylate-co-4-vinyl pyridine)</td>
<td>β-PCPY</td>
<td>93</td>
</tr>
<tr>
<td>13.</td>
<td>Poly(styrene-co-4-vinyl pyridine)</td>
<td>β-PCPY</td>
<td>94</td>
</tr>
</tbody>
</table>

![Chemical structures](image)

**2. PHOSPHORUS YLIDES:**

Although the history of phosphonium ylide dates back to 1890’s, but very little was known of the general chemistry and physical properties of the ylide until
1950's with the exception of a brief study in 1920. The first phosphonium ylide (I) appears to have been prepared in 1894 by Michaelis and Gimborn by treating an aqueous solution of triphenyl (carboethoxymethyl) phosphonium chloride with cold potassium hydroxide solution, but not assigned its correct structure.

\[(C_5H_5)_3P\equiv CH\equiv COOC_2H_5\]  

(I)

Phosphonium ylides are reactive and are usually not capable of isolation unless some special structures have been incorporated. Staudinger conducted research on various substances closely related to ylides but could isolate only one ylide, benzhydrylidene triphenylphosphorane in 1919 by pyrolysis of the corresponding phosphinazine. The pioneering work of Staudinger laid the foundation for the important synthetic applications of phosphonium ylides, taken up by Wittig. The importance of the chemistry of phosphorus ylides was demonstrated by Wittig and Geissler through the reaction between methylene triphenylphosphorane with benzophenone to give 1,1,-diphenylethene and triphenylphosphine oxide.

\[(C_5H_5)_3P\equiv CH_2 + (C_5H_5)_2C\equiv O \rightarrow (C_5H_5)_2C\equiv CH_2 + (C_5H_5)_3PO\]

The Wittig reaction was thus discovered with this experiment which became the most simple and common way of constructing alkene moieties in organic compounds requiring either an acetaldehyde or ketone as the starting material. It was only after the discovery of Wittig reaction that phosphorus ylides were introduced as reagents in organic synthesis and today they rank among the most important tools of the preparative organic chemist both in research and in industry. The phosphonium ylide is usually prepared from a phosphonium salt which can be made readily by treatment of an alkyl halide with triphenylphosphine and the salts thus formed is suspended in the solvent such as diethyl ether or THF and a strong base e.g. phenyllithium or n-butyllithium is added to generate phosphonium ylide.
The phosphorus ylide, thus obtained is a strong base. Like other strongly basic organic reagents, it is protonated by water and alcohols, and is sensitive to oxygen. Water decomposes alkylidene phosphoranes to hydrocarbons and phosphine oxide.

\[
R_3P\equiv CR'_2 + H_2O \rightarrow [R_3P(OH)\equiv CHR'_2]
\]

\[
R_3P\equiv O + R'_2CH_2
\]

Oxygen cleaves these ylides in a similar fashion, converting the alkylidene moiety to a carbonyl compound.

\[
R_3P\equiv CR'_2 + O_2 \rightarrow R_3P\equiv O + R'_2C\equiv O
\]

There are considerable experimental evidences suggesting that phosphorus can use its 3d-orbital in σ bonding and that a phosphorus atom can be pentavalent. Staudinger and Meyer\(^\text{40}\) proposed the pentavalent phosphorus atoms to account for the formation of pentaphenylmethylene phosphorane (II) and by Meyer to account for the properties of a phosphonium betaine (III).

\[
(C_6H_5)_2C\equiv P(C_6H_5)_3 \quad (\text{II}) \quad (C_6H_5)_3P\equiv C\equiv O \quad (\text{III})
\]
The experimental evidences available and the theoretical conclusions drawn by Craig and Magnusson\textsuperscript{97} indicated that any phosphorus system which carries hydrogen atom on the carbon atom alpha to phosphorus atom with a positive charge gives phosphorus ylide i.e. when the bonding stabilization extend to the carbanions alpha to phosphonium centre, the zwitterionic conjugate bases derived from such cations yield phosphonium ylide.

The recent research includes the synthesis of ylides containing fluorine atoms on the phosphorus atom of the P=C group\textsuperscript{98}. These compounds are found to be convenient reagents for preparing various organic and organo-phosphorus compounds hardly available by other methods. The chemistry of these compounds is significantly different from the chemistry of triphenylphosphonium ylides.

Large amount of work has been conducted by Srivastava and Varshney on polymerization of monomers with phosphorus ylide as radical initiator.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Polymer</th>
<th>Ylide</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Homopolymers</td>
<td>Polyvinyl acetate</td>
<td>p-NBTPY</td>
</tr>
<tr>
<td>2.</td>
<td>Polymethyl methacrylate</td>
<td>p-NBTPY</td>
<td>100</td>
</tr>
<tr>
<td>3.</td>
<td>Polystyrene</td>
<td>p-NBTPY</td>
<td>101</td>
</tr>
<tr>
<td>4.</td>
<td>Copolymers</td>
<td>Poly(acrylonitrile-co-methacrylic acid)</td>
<td>p-NBTPY</td>
</tr>
<tr>
<td>5.</td>
<td></td>
<td>Poly(styrene-co-methyl methacrylate)</td>
<td>p-NBTPY</td>
</tr>
<tr>
<td>6.</td>
<td></td>
<td>Poly(methyl methacrylate-co-N-vinyl pyrrolidone)</td>
<td>p-NBTPY</td>
</tr>
<tr>
<td>7.</td>
<td>Terpolymer</td>
<td>Poly(styrene–methyl methacrylate–acrylonitrile)</td>
<td>p-NBTPY</td>
</tr>
</tbody>
</table>

\[
\text{C}_6\text{H}_5\text{P}<\Theta\text{CH}-\text{NO}_2
\]

p-NBTPY
(p-nitrobenzyl triphenylphosphonium ylide)
3. SULPHUR YLIDES:

Sulphur ylides\(^{106}\) due to synthetic ease in its preparation and the interesting rearrangement have been widely studied in synthetic organic chemistry. These find application in biochemical processes and synthesis of β-lactam antibiotic\(^{107}\), pyrrolizidine alkaloids\(^{108}\) and other natural products\(^{109}\). Sulphur ylide can be prepared by reaction of a carbene (or carbenoid) with a sulphide.

\[
\text{RSR} + \text{R}_2\text{C}' \rightarrow \text{R}_2\text{C}=\text{S} \quad \Theta
\]

3(a). Sulphonium ylides:

The carbene approach to sulphur ylide formation has been studied by Ando\(^{110}\), who used carbenes with strongly electron withdrawing substituents that stabilized the sulphonium ylides facilitating their isolation. The sulphonium ylides are prepared and isolated with much ease than analogous ylides involving other heteroatoms due to the stabilizing effect of the d-orbitals of the sulphur atom. The earliest report of a stable sulphonium ylide formed by this method was by Diekmann\(^{111}\) in 1965. The reaction of bis (phenylsulphonyl) diazomethane with dibutyl sulphide gave a stable sulphonium ylide (I).

\[
\text{Ph(SO}_2\text{)}_2\text{CN}_2 + n \text{Bu}_2\text{S} \xrightarrow{\text{hv}} n \text{Bu}_2\text{S} \quad \Theta \quad \text{C(SO}_2\text{Ph}_2)
\]

(I)

There are two methods proposed for the synthesis of sulphonium ylides namely the ‘salt method’ and the ‘benzyne method’\(^{112}\). The ‘salt method’ is accompanied by the base mediated removal of α-hydrogen from a sulphonium salt\(^{113}\). Therefore, any sulphonium salt with atleast one α – hydrogen forms ylide. The most widely used bases are alkyl or aryllithiums. Bases like triphenylmethyl anion, tert-butoxide anion, other alkoxides and sodium hydroxide have also been reported to be used for sulphonium ylide generation. Corey\(^{114}\) prepared variety of ylides from their corresponding salts using methylsulphinyl carbanion as a base.
A number of sulphonium ylides\textsuperscript{115-120} was synthesized photochemically, thermally or through catalytic decomposition. The reaction progresses with the conversion of electrophilic singlet carbene or carbenoid which is attacked by the non bonding electron pair of sulphur atom resulting in sulphonium ylide.

\[
\begin{align*}
\text{H}_3\text{C} & \xrightarrow{\text{NaH, DMSO}} \text{CH}_3 \Theta \text{S}^\Theta \text{H}_2 \\
\text{H}_3 \text{C} & \xrightarrow{\text{NaH, DMSO}} \text{CH}_3 \Theta \text{S}^\Theta \text{H}_2 \\
\end{align*}
\]

where \( R = \text{alkyl or aryl group} \)

\[\textbf{3(b). Sulphoxonium ylide :}\]

In comparison to vast literature available on sulphonium ylides, very few data is available on sulphoxonium ylides. The stable sulphoxonium ylide has been prepared by silver oxide decomposition of dimethyl diazomalonate in dimethyl sulfoxide in 85% yield\textsuperscript{121,122}.

\[
\begin{align*}
\text{(p-ClC}_{6}\text{H}_{5})_2\text{S} & \xrightarrow{\text{N}_2\text{CHCOPh, Cu(acac)}_4} \text{(p-ClC}_{6}\text{H}_{5})_2\text{S} + \text{CHCOPh} \\
\text{Cu} & \xrightarrow{\text{0}, \text{h}_\nu \text{ or CuSO}_4} \text{C}_{6}\text{H}_{5}-\text{p-Cl} \text{C}(\text{CO}_2\text{CH}_3)_2 \\
\text{CH}_3 & \text{CH}_3 \\
\end{align*}
\]

The copper (I) cyanide decomposition of diazo ester in dimethyl sulfoxide also resulted in the formation of stable sulphoxonium ylide in 93% yield\textsuperscript{123}.

\[
\begin{align*}
\text{(CH}_3\text{)}_2\text{S} & \xrightarrow{\text{N}_2\text{C(CO}_2\text{CH}_3)_2, \text{Ag}_2\text{O, h}_\nu} \text{CH}_3 \Theta \text{S}^\Theta \text{C}(\text{CO}_2\text{CH}_3)_2 \\
\text{CH}_3 & \text{CH}_3 \\
\end{align*}
\]

Reaction of \( \alpha \)-diazoacetophenone with copper (II) acetylacetonato at 50°C in the presence of bis (p-chlorophenyl) sulphoxides formed sulphoxonium ylide\textsuperscript{124} in 30% yield along with bis (p-chlorophenyl) sulphide.
Another way to prepare sulfoxonium ylide is by treating carbenes with sulfoxide but it is complicated by a competing attack of the carbene on oxygen causing deoxygenation of the sulfoxide\textsuperscript{125}.

\[
\begin{align*}
R_2S&=O + \overset{\text{CCl}_2}{} \rightarrow \left[ R_2S\overset{\Theta}{}=O\overset{\Theta}{}\text{CCl}_2 \right] \rightarrow R_2S + \text{COCl}_2 \\
\end{align*}
\]

3(c). Sulphinyl ylides:

Corey and Chaykovsky\textsuperscript{126} found that dimethylsulphoxide was readily metallated by sodium hydroxide and the resulting methysulphinyl carbamion (I) adds to the carbonyl compounds like benzophenone under mild conditions to give simple hydroxysulphoxide addition product.

\[
\begin{align*}
\text{RSR} + \overset{\text{N}_2\text{C(CN)}_2}{} \rightarrow \overset{\text{hv}}{} \rightarrow R_2S\overset{\Theta}{}=\overset{\Theta}{}\text{C(CN)}_2 \\
\end{align*}
\]

It was later found by the same group of workers along with Walling and Bollyky\textsuperscript{127} that under severe conditions the reaction followed a different course although it may have proceeded via the same initial step, the addition of the carbanion to the carbonyl group.

Sulphonium ylides have been widely used by Srivastava and coworkers for the polymerization of various vinyl monomers.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Polymer</th>
<th>Ylide</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>\textit{Homopolymers}</td>
<td>Ypy-s</td>
<td>128</td>
</tr>
<tr>
<td>2.</td>
<td>Polystyrene</td>
<td>p-BPDSY</td>
<td>129</td>
</tr>
<tr>
<td>3.</td>
<td>Polymethyl acrylate</td>
<td>p-BPDSY</td>
<td>130</td>
</tr>
<tr>
<td>4.</td>
<td>Poly(methyl methacrylate-co-N-vinyl pyrrolidone)</td>
<td>p-BPDSY</td>
<td>131</td>
</tr>
</tbody>
</table>
4. ARSONIUM YLIDES:

X-ray crystallography\textsuperscript{132}, IR\textsuperscript{133,134}, NMR\textsuperscript{135} results show that arsonium ylides are stronger nucleophiles than phosphorus due to larger contribution of zwitterionic resonance form in arsonium ylides and their use in organic synthesis is accompanied by mild reaction with high yield and stereoselectivity. Arsonium ylides may be prepared by deprotonation of an arsonium salt\textsuperscript{136}, reverse Wittig process\textsuperscript{137} (sch.1) and methods involving arsine dihalides\textsuperscript{138} (sch. 2), arsine oxides\textsuperscript{139} (sch. 3) or diazo compounds\textsuperscript{140} (sch. 4).

\[
\text{Ph}_3\text{AsO} + \text{RC}≡\text{CR}^2 \rightarrow \text{Ph}_3\text{As}≡\text{CR}^1\text{COR}^2
\]

(sch.1)

\[
\text{Ph}_3\text{AsCl}_2 + \text{CH}_2\text{XY} \xrightarrow{\text{Et}_3\text{N}} \text{Ph}_3\text{As}≡\text{CXY}
\]

(sch.2)

\[
\text{Ph} \quad \text{Ph} \quad \text{Ph} + \text{Ph}_3\text{AsO} \xrightarrow{\text{Ac}_2\text{O}} \text{Ph}_3\text{As}\_\text{AsPh}_3
\]

(sch.3)

\[
\text{Ph} \quad \text{Ph} \quad \text{N}_2 \xrightarrow{\text{heat}} \text{Ph}_3\text{As} \_\text{AsPh}_3
\]

(sch.4)
The first arsonium ylide was prepared in 1902 by Michaelis. He used the 'salt method' for the preparation of arsonium ylide in which an arsonium salt obtained by reaction of an organosulphate or halide with a tertiary arsine, is treated with a suitable base to get ylide. Krohne assigned the correct structure (II) for arsonium ylide in 1950. Survey of literature reveals that 16 ylides have been reported so far but only half have been isolated.

\[
\begin{align*}
\text{Ph}_3\text{As} + \text{PhCOCH}_2\text{Br} & \rightarrow \text{Ph}_3\text{As}-\text{CH}-\text{COC}_6\text{H}_5\text{Br} \\
& \xrightarrow{\text{NaOH}} \text{Ph}_3\text{As} \rightleftharpoons \text{CH}-\text{COPh} \\
& \text{(II)}
\end{align*}
\]

Suzuki and Murafuji for the first time formed arsonium ylide (III) in moderate yields from transylidation of bismuthonium ylide with triphenylarsine in the presence of copper (I) salt catalyst in benzene at room temperature.

\[
\begin{align*}
\text{MeOC} \rightleftharpoons \text{BiPh}_3 + \text{Ph}_3\text{As} & \xrightarrow{\text{CuCl}} \text{MeOC} \rightleftharpoons \text{AsPh}_3 \\
& \text{(III)}
\end{align*}
\]

Huang et al. reported α-acyl arsonium ylides (IV), α-organoseleno arsonium ylide (V), α-phenylthioethylene arsonium ylide (VI), iodonium arsenium ylide (VII) and α-thio arsonium ylides (VIII).

\[
\begin{align*}
\text{R}' = \text{-COMe, -COPh, -COOMe, -COOEt, -CN} & \quad \text{R} = \text{-OMe, -Ph, -Me, -C}_6\text{H}_5\text{-p-Cl, -C}_6\text{H}_5\text{-p-Br} \\
\text{R}'' = \text{-Me, -(CH}_3\text{)}_2\text{Me, -Ph} & \\
& \text{R}''\text{= (IV) (V)}
\end{align*}
\]
Kim and Kim\textsuperscript{149} prepared arsonium ylides (IX) with triisopropylsilyl enol ether groups.

Mitsumoto and Nitta\textsuperscript{150} reported the first stable arsonium ylide derivative (X) in low yields containing cyclohepta-2,4,6-trienyl and electron withdrawing COOC\textsubscript{2}H\textsubscript{5} and CN groups.

Arsonium ylides undergo wide range of addition and substitution reactions\textsuperscript{151}, most of which involve electrophilic carbonyl compounds. These are used in alkene synthesis, heterocycle synthesis, carbocycle synthesis and polymerization reactions.

Srivastava \textit{et al.}\textsuperscript{152-156,158} and Varshney\textsuperscript{157} have carried out various polymerizations using \( p \)-acetylbenzylidene triphenylarsonium ylide (XI) as a radical initiator.
<table>
<thead>
<tr>
<th>S.No.</th>
<th>Polymers</th>
<th>Ylide</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td><strong>Homopolymers</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Polymethyl methacrylate</td>
<td>p-ABTAY</td>
<td>152</td>
</tr>
<tr>
<td>2.</td>
<td>Polystyrene</td>
<td>p-ABTAY</td>
<td>153</td>
</tr>
<tr>
<td></td>
<td>Thermal</td>
<td></td>
<td>154</td>
</tr>
<tr>
<td></td>
<td>Photo</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>Polyvinyl acetate</td>
<td>p-ABTAY</td>
<td>155</td>
</tr>
<tr>
<td></td>
<td><strong>Copolymers</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>Poly(styrene-co-vinyl acetate)</td>
<td>p-ABTAY</td>
<td>156</td>
</tr>
<tr>
<td>5.</td>
<td>Poly(styrene-co-acrylonitrile)</td>
<td>p-ABTAY</td>
<td>157</td>
</tr>
<tr>
<td></td>
<td><strong>Terpolymer</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>Poly(styrene-acrylonitrile-copper acrylate)</td>
<td>p-ABTAY</td>
<td>158</td>
</tr>
</tbody>
</table>

![Structure of p-ABTAY](image)

**5. STIBONIUM YLIDES:**

Stibonium is placed at 15\textsuperscript{th} group and 5\textsuperscript{th} period in the periodic table. The nucleophilic and dipolar character of the stibonium ylide increases on going down the periodic table. Stibonium ylide was difficult to prepare because of the solubility and stability problems. Lloyd\textsuperscript{159} proposed the preparation of the ylides from diazo compounds that enabled the preparation and isolation of stibonium ylides.

![Structure of stibonium ylide](image)
Wittig and Laib\textsuperscript{160} were the first to conduct studies on stibonium ylides. They prepared dimethyldibenzylstibonium bromide and treated it with an ether solution of phenyllithium which gave a yellow colouration that faded rapidly. Henry and Wittig\textsuperscript{161} prepared triphenylmethyl salts by alkylating triphenylstibine with tetrafluoroborate. The corresponding ylide, triphenylstibonium methylide (A), was then synthesized in solution by treating the salt with ethereal phenyllithium. The methylide (A) further reacted with benzophenone forming very high yields of triphenylstibine and diphenylacetaldehyde.

\[ \begin{align*}
(C_6H_5)_2CO & \quad \rightarrow \quad \left(\begin{array}{c}
(C_6H_5)_3Sb \rightarrow \overset{\Theta}{\text{CH}_2} \\
\Theta \quad O \quad C(C_6H_5)_2
\end{array}\right) \quad \rightarrow \quad -(C_6H_5)_2Sb \\
(C_6H_5)_3Sb \rightarrow \Theta \quad \text{CH}_2 & \quad \rightarrow \quad (C_6H_5)_3Sb \rightarrow \Theta \quad \text{CH}_3 \\
\text{C}_6\text{H}_5\text{Li} & \quad \rightarrow \quad (C_6H_5)_3Sb \rightarrow \Theta \quad \text{CH}_2 \\
(C_6H_5)_2C \rightarrow \Theta \quad \text{CH}_2 & \quad \rightarrow \quad (C_6H_5)_2CH \rightarrow \Theta \quad \text{CHO}
\end{align*} \]

The recent improvement in the method of preparation of ylides from diazo compounds has led to the preparation and isolation of a number of stibonium ylides (II-VIII).

\[ \begin{align*}
\text{Ph(PhCH}_2\text{SO}_2)\text{C} \rightarrow \text{SbPh}_3 & \quad (\text{PhSO}_2)_2\text{C} \rightarrow \text{SbPh}_3 \\
(\text{III}) & \quad (\text{IV}) \\
\text{Ac(PhCO)}\text{C} \rightarrow \text{SbPh}_3 & \quad \text{Ac}_2\text{C} \rightarrow \text{SbPh}_3 \\
(\text{V}) & \quad (\text{VI}) \\
\text{SbPh}_3 & \quad \text{SbPh}_3 \\
(\text{VII}) & \quad (\text{VIII})
\end{align*} \]

Srivastava and his group has carried out polymerization with several vinyl monomers using triphenylstibonium 1,2,3,4-tetraphenylecyclopentadienylide as radical initiator.
### Homopolymers

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Polymers</th>
<th>Ylide</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Polymethyl acrylate</td>
<td>TPS 1,2,3,4-TPCPDY</td>
<td>162</td>
</tr>
<tr>
<td>2.</td>
<td>Polymethyl methacrylate</td>
<td>TPS 1,2,3,4-TPCPDY</td>
<td>163</td>
</tr>
<tr>
<td>3.</td>
<td>Poly n-butyl methacrylate</td>
<td>TPS 1,2,3,4-TPCPDY</td>
<td>164</td>
</tr>
</tbody>
</table>

#### 6. BISMUTHONIUM YLIDE:

In contrast with the large amount of information available for ylides of nitrogen, sulphur and phosphorus, only meager information is presently available of the general chemistry and physical properties of bismuthonium ylide. This is mainly because of the limited number of approaches to this class of compounds. Only few examples of quaternary bismuth salts are known, while the trivalent organobismuth compounds have rarely been used as ligands in the transition metal complexes. An unsuccessful attempt was made by Henry and Wittig\(^{161}\) to quaternize a trivalent bismuth compound of triphenylbismuth with trimethyloxonium tetrafluoroborate. On the other hand, the pentacovalent compounds, triphenylbismuth dichloride and pentaphenylbismuth have been prepared, although pentaphenylbismuth could not be characterized properly\(^{165}\). Wittig and Hellwinkel\(^{166}\) prepared triphenylbismuthonium-N-tosylimine (I) on reacting triphenylbismuth with chloramines-T.

\[
(C_6H_5)_3Bi\text{---N---SO}_2\text{---C}_6\text{H}_4\text{-p-CH}_3
\]

(I)

There are very less evidences that bismuth can expand its valence shell. Lloyd\(^{167}\) put forth the method for preparation of ylides by treating diazotetraphenylcyclopentadiene with triphenylbismuth resulting in a deep blue solid, bismuthonium ylide (II).
Other bismuthonium ylides\textsuperscript{168} (III, IV) are also reported in the literature. The bismuthonium ylide (III) decomposes slowly in the solid state giving bis(phenylsulphonyl) methane whereas bismuthonium ylide (IV) appears to be fairly stable and remains unchanged for several months. Bismuthonium ylide (III) and (IV) are extremely insoluble in organic solvents. A major difference between bismuthonium ylide (II), (III) and (IV) is their colour where (III) and (IV) is khaki while (II) is deep blue solid.

Ogawa, Murafui and Suzuki\textsuperscript{169} prepared triphenylbismuthonio-4,4-dimethyl-2,6-dioxocyclohexane-1-ide (V) and triphenylbismuthonio-4,4-dimethyl-2,6-dioxo-3,5-dioxan-1-ide (VI) in pure crystalline form.

Later, Matano, Yoshimune and Suzuki\textsuperscript{170} reported triphenylbismuthonium-2-oxoalkylides generated from the 2-oxoalkylbismuthonium tetrafluoroborates and a base in THF at -78°C.
Few publications are credited to Srivastava and group for executing work on triphenylbismuthonium 1,2,3,4-tetraphenylcyclopentadienyliide (TPB 1,2,3,4-TPCPDY).

<table>
<thead>
<tr>
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<th>Ylide</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Polymethyl acrylate</td>
<td>TPB 1,2,3,4-TPCPDY</td>
<td>171</td>
</tr>
<tr>
<td>2.</td>
<td>Polymethyl methacrylate</td>
<td>TPB 1,2,3,4-TPCPDY</td>
<td>172</td>
</tr>
<tr>
<td>3.</td>
<td>Polystyrene</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Thermal</td>
<td>TPB 1,2,3,4-TPCPDY</td>
<td>173</td>
</tr>
<tr>
<td></td>
<td>Photo</td>
<td></td>
<td>174</td>
</tr>
<tr>
<td>4.</td>
<td>Poly(methyl methacrylate-co-styrene)</td>
<td>TPB 1,2,3,4-TPCPDY</td>
<td>175</td>
</tr>
</tbody>
</table>
Polymerization in which only one species of monomer is involved is called homopolymerization. Homopolymer is categorized into:

**Isotactic polymer** comprising of only one species of configurational base unit which has atoms in the main chain in unique arrangement with respect to its adjacent constitutional units.

![Isotactic polymer structure]

**Syndiotactic polymer** comprising alternating enantiomeric configurational base units which has atoms in the main chain in a unique arrangement with respect to their adjacent constitutional units.

![Syndiotactic polymer structure]

**Atactic polymers** are the homopolymers in which the configurational units are not all identical.

![Atactic polymer structure]

A vast literature is available on the homopolymerization of n-butylmethacrylate (n-BMA) and methylmethacrylate (MMA). Free radical polymerization of MMA was carried out using N,N-dimethylaniline\textsuperscript{176} as initiator.
The rate of polymerization was determined at 40, 50 and 60°C. The rate equation was obtained as \( R_p \alpha [DMA]^{1/2} [MMA]^{3/2} \) and the polymerization was inhibited by benzoquinone. The activation enthalpy and activation entropy of polymerization was calculated as 63.2 kJ mol\(^{-1}\) and 153 mol\(^{-1}\) K\(^{-1}\) at 60°C. Vinyl polymerization of MMA with enolizable ketone (\( R_1\text{-CO-CH}_2\text{-CO-R}_2 \)) carbon black system\(^{177}\) was investigated. The enol form of the ketone and quinonic oxygen groups on the carbon black surface played an important role in the initiation system.

Radical polymerization of MMA was also studied in the presence of cellulose triacetate (CTA)\(^{178}\). The system obeyed ideal kinetics (\( R_p \alpha [CTA]^{0.5} [MMA] \)). The overall activation energy for polymerization was calculated as 7.9Kcal/mole. The molecular weight of the extracted PMMA decreased slightly upon increasing the polymerization temperature and was independent of the concentration of CTA. These results suggested that the molecular weight of PMMA was affected by the transfer of growing radical to monomer molecule.

Penlidis et al.\(^{179}\) studied the bulk free radical polymerization of MMA with tetrafunctional peroxide initiator. The results revealed that the new tetrafunctional peroxide initiator produced a faster rate of polymerization than that of a monofunctional counterpart (tert-butylyperoxy 2-ethylhexyl carbonate (TBEC)) and also produced low molecular weight polymers.

Polymerization of MMA, initiated by azibenzil\(^{180}\), was also examined kinetically. The polymerization reaction proceeded through radical mechanism. The kinetic expression was \( R_p \alpha [AB]^{0.47} [MMA]^{0.97} \). The overall energy of activation for the polymerization was calculated as 16.1 Kcal mol\(^{-1}\).

Mechanisms of initiation of MMA by lithium tert-alkoxides\(^{181}\) were also investigated. Polymerization of MMA in the presence of methyl, butyl, tert-butyl isobutyrate and methyl pivalate showed that the order of the initiation reaction with respect to the monomer (about 2) has its cause in the ability of the ester group in the monomer and of methyl or butyl isobutyrate to activate lithium tert-alkoxide.
Controlled / ‘living’ radical polymerization of MMA with p-TsCl / CuBr\textsuperscript{182} as the initiator were studied under microwave irradiation (MI). The polymerization of MMA under MI showed linear first order rate plots, linear increase in the number average molecular weight with conversion and low polydispersities. The MI process increased the rate of polymerization and narrowed the polydispersity index of polymers as compared to conventional heating process.

Photopolymerization of MMA\textsuperscript{183} was investigated kinetically using arsonium ylide. The free radical mode of polymerization was confirmed by the inhibitory effect of hydroquinone and by ESR spectroscopy. Photodecomposition was suggested to take place by phenyl radical generation.

Srivastava \textit{et al.} examined the polymerization of MMA using α-picolinium-p-chlorophenacyl ylide\textsuperscript{184} in CCl\textsubscript{4} at 30, 35 and 40°C for 4 hrs. The orders of reaction with respect to the concentration of ylide and MMA were 0.22 ± 0.01 and 1.0 respectively. The overall activation energy of polymerization and $k_p/k_i$ was calculated as 21.0 kJ mol\textsuperscript{-1} and 0.37 x 10\textsuperscript{-2} L mol\textsuperscript{-1} s\textsuperscript{-1} respectively.

Polymerization of MMA was investigated using 4-dimethyl-4'-isopropylbenzophenone\textsuperscript{185} (PI) as photoinitiator. It was found that the nature of polymerization initiating radicals depended on the type of solvent and the photoinitiator concentration. In cyclohexane solution and at low PI, only cyclohexyl radical was responsible to initiate polymerization while at higher PI, both cyclohexyl and aminoalkyl radicals derived from the PI brought about initiation, increasing the participation of the latter as the PI increases.

Kinetic aspects of the radical polymerization of MMA with 1,2,3,10a-tetrahydrophenanthrene-1,2 dicarboxylic anhydride\textsuperscript{186} (TH) was examined. The rate of polymerization of methyl methacrylate revealed non-ideal kinetics ($R_p \propto [TH]^{0.3} [MMA]^{1.6}$). The overall energy of activation of polymerization and chain transfer to TH was determined to be 47.7 kJ/mole and 0.52 respectively.
Imoto reported the polymerization of MMA initiated by 4,4'-diazidoazobenzene (DAAB) in benzene solution. The rate equation \( R_p \propto [\text{DAAB}]^{0.62} [\text{MMA}]^{1.17} \) indicated non-ideal kinetics with the overall activation energy for polymerization to be 20.5 Kcal/mole.

The polymerization of MMA in the presence of ferric nitrate was examined kinetically. The rate of polymerization was found to increase with increasing concentration of ferric nitrate in the range below \( 1.0 \times 10^{-3} \) mol L\(^{-1}\). The kinetic expression was \( R_p \propto [\text{Fe(NO}_3\text{)}_3]^{1/2} [\text{MMA}]^{3/2} \). It was proposed that the ferric salt initiates the polymerization within the range of its lower concentrations while at higher concentrations; the ferric salt terminates the polymerization.

Kinetics of polymerization of MMA using 9-diazofluorene at 75°C in benzene was investigated. The system obeyed ideal kinetics with overall activation energy estimated to be 21.9 Kcal/mole.

Polymerization of MMA was also carried out dilatometrically using trichloroacetyl chloride and water. The reaction followed radical mode of polymerization and rate equation was determined as \( R_p \propto [\text{TAC-H}_2\text{O}]^{0.45} [\text{MMA}] \). The activation energy of initiation was calculated to be 4.8 Kcal/mole.

The homogenous photopolymerization of MMA by colloidal cadmium sulfide was carried out by Popović et al. A polymerization mechanism involving an existing CdS particle in both the initiation and termination steps was proposed. During initiation, MMA molecule was oxidized by a positive hole photogenerated in a CdS particle resulting in a novel chain end structure of PMMA. Chain termination occurred by degradative chain transfer to a reduced excited cadmium sulfide particles. Thus, for the first time, a detailed polymerization mechanism for the polymerization of vinyl monomers initiated by semiconductors was proposed.

Ho et al. investigated the kinetics of the free radical polymerization of MMA initiated by azo-containing polydimethylsiloxane (PSMAI) and AIBN. It
was suggested that the greater polymerization rate ($R_p$) in MMA/PSMAI systems may be due to the higher value of the initiation rate ($R_i$) and lower value of the termination rate constant ($k_t$) than that in MMA/AIBN system. The order of the reaction with respect to initiator PSMAI decreased with increase in polydimethylsiloxane chain length (SCL) in PSMAI. The deviation in rate of polymerization was explained in terms of primary radical termination. The photoinitiator efficiency $\Phi$ of initiators decreased with increase in SCL and the ratio of rate constants for chain termination and chain initiation by primary radical increased with SCL.

Srivastava and Srivastava\textsuperscript{164} studied the radical polymerization of n-butyl methacrylate with 1,2,3,4-tetraphenylcyclopentadiene triphenylstibonium ylide in dioxan at 60°C for 90 min. The system followed non-ideal kinetics i.e. $R_p \propto [\text{ylide}]^{0.2} [\text{BMA}]^{1.8}$. The overall activation energy of polymerization and $k_p/k_t$ was calculated as 33 kJ/mole and $0.133 \times 10^{-2}$ L mol$^{-1}$ s$^{-1}$. ESR studies confirmed the radical mode of polymerization brought about by phenyl radical.

Kárpátyová and Bartoň\textsuperscript{193} investigated the effect on kinetics and mechanism of emulsion polymerization of BMA with AIBN in the presence of anionic emulsifier disodium dodecylphenoxybenzene at 60°C. The exponent for the concentration of AIBN over the conversion range between 0 and 30% was 0.34. 2-cyanoisopropyl radicals, generated from AIBN in water phase were assumed to carry out the initiation of polymerization.

The free radical polymerization of tert-butyl methacrylate ($t$-BMA), MMA, ethyl methacrylate (EMA) and isopropyl methacrylate (IPMA) was examined under various conditions to obtain stereoregularity\textsuperscript{194} with fluoroalcohols. MMA polymerization by fluoroalcohols showed enhanced syndiotactic specificity, including (CF$_3$)$_3$COH as a solvent or an additive attaining highest syndiotacticity at -98°C. Similar effects were noticed for polymerization of EMA whereas the negligible effect was observed in IPMA polymerization. $t$-BMA polymerization
showed decreased syndiotactic specificity with the use of \((\text{CF}_3)_3\text{COH}\). The stereoeffects of fluoroalcohols were accounted due to the hydrogen bonding interaction of the alcohols with monomers and growing species.

Varshney and Prajapati\(^{100}\) carried out the free radical homo-polymerization of MMA using p-nitrobenzyl triphenylphosphonium ylide at 65°C for 2 hrs. The system obeyed ideal kinetics with an activation energy of 75.7 kJ/mole and \(k_p^2/k_i\) as \(1.14 \times 10^2\) L mol\(^{-1}\) s\(^{-1}\). The copolymer was characterized using FTIR, \(^1\)HNMR and \(^{13}\)CNMR. TGDTA analysis confirmed the atactic nature of the polymer and its thermal stability up to 120°C.
While homopolymerization of vinyl monomers has produced many useful and commercially successful polymers, the addition of a second monomer to produce a copolymer immediately increases the range of possible structures that can be formed, and also, therefore the range of properties obtained thus facilitating the production of new materials.

Polymerization in which two monomers are incorporated into the same polymer chain is termed as copolymerization. The copolymers, therefore, contain two repeating unit. The monomers may be linked to each other in head to head, tail to tail or head to tail manner. The variation in monomers causes change in copolymer properties like solubility, glass transition temperature, crystallinity, elasticity etc. as it affects intramolecular and intermolecular forces as well as the symmetry of the polymer chain. There are large number of commercially available copolymers such as styrene–butadiene copolymer obtained from styrene and butadiene.

Copolymers have been classified on the basis of the arrangement of comonomers as well as the ratio of monomers present in the polymer chain. These include:

**Random copolymers or statistical copolymers** in which probability of finding a given monomeric unit at any given site in the chain is independent of the nature of adjacent units.


**Alternating copolymers** consisting of two species of monomeric units arranged in alternating sequence.

Block copolymers are a linear polymers in which adjacent blocks are constitutionally different i.e. long linear sequences of comonomer A are joined to long linear sequences of comonomer B.

\[ \sim A\sim A\sim A\sim B\sim B\sim B\sim A\sim A\sim B\sim B\sim B \sim \]

Graft copolymers are branched polymers where adjacent blocks in the main chain or side chain, or both, are constitutionally different.

\[ \sim A\sim A\sim A\sim A\sim A\sim A\sim A\sim A\sim A\sim A\sim A\sim A\sim A\sim A\sim A\sim A\sim A\sim A\sim A\sim B\sim B\sim B\sim B\sim B \sim \]

Copolymerization of multiple monomers allows the synthesis of new polymeric material that are often substantially different from the homopolymers obtained from the individual monomers e.g. polystyrene is brittle, but hard enough to be made into a high performance product unless the properties of a stretchable material like butadiene rubber is added. The two such materials can not be mixed due to the amplified effect of intermolecular forces on polymer insolubility, but if polybutadiene is added during polymerization, it gets chemically bonded to the polystyrene forming a graft copolymer called high impact polystyrene or HIPS which is less brittle and more impact resistant and is used in toys, product castings etc.

Copolymerization is mostly concerned with chain growth process where chain growth takes place by successive additions of the comonomers to the active site i.e. radical, ionic or organometallic. The relative ratio of incorporation of monomers A and B are generally different from their relative concentrations in the initial reaction from the feed mixture, and the feed composition changes continuously from the beginning to the end of the reaction.

The chain growth polymerization products are mostly kinetically determined. By the end of 1930s, it was clear that chain growth copolymers obtained from olefinic monomers differ in composition from the monomer feed.
Copolymers of equimolar composition were obtained from copolymerization of maleic anhydride with stilbene, benzalfluorene or anisalfluorene. Efforts to interpret radical copolymerization dates back to 1941 by Wall and Marvel further used the Wall treatment for calculations, but the experimental studies were too restricted in terms of feed composition. Later, based on the hypothesis of Dostal, Norrish and Brookman and Jencket, Mayo and Lewis put forward the first successful kinetic analysis of copolymerization reaction in which the rate of addition of a monomer to a radical chain end depends only on the nature of the radical end group and not on the length or chemical composition of the chain to which the radical is attached. The Mayo and Lewis treatment is referred to as the ‘terminal model’.

Mayo Lewis equation gave the equation:

\[ y = x \frac{1 + r_1 x}{r_2 + x} \]  \hspace{1cm} (II.1)

where,

\[ \frac{[M_1]}{[M_2]} = x \hspace{1cm} \frac{d[M_1]}{d[M_2]} = y \]  \hspace{1cm} (II.2)

Later, Finemann and Ross gave equation:

\[ G = r_1 F - r_2 \]  \hspace{1cm} (II.3)

and/or

\[ \frac{G}{F} = - r_2 \frac{1}{F} + r_1 \]  \hspace{1cm} (II.4)

where, the transformed variables are:

\[ G = x (y - 1) \hspace{1cm} \text{and} \hspace{1cm} F = \frac{x^2}{y} \]  \hspace{1cm} (II.5)

Graphical plotting of eq (II.4) give \( r_1 \) as slope and \( r_2 \) as intercept while the plot of eq (II.5) give \( r_1 \) as intercept and \( r_2 \) as slope. Disadvantage of the FR method was that the experimental data were unequally weighed. The data
obtained under extreme experimental conditions (i.e. at low comonomer concentrations) had the greatest influence on the slope of the line.

Kelen - Tüdos\textsuperscript{204} improvised the equation as-

\[
\frac{G}{\alpha+F} = \left( \frac{r_1 + \frac{r_2}{\alpha}}{\alpha+F} \right) \frac{F}{\alpha+F} - \frac{r_2}{\alpha} = (r_1 + \frac{r_2}{\alpha}) F \frac{1}{\alpha} - \frac{r_2}{\alpha} = (r_1 + \frac{r_2}{\alpha}) F \frac{1}{\alpha} - \frac{r_2}{\alpha} \tag{II.6}
\]

\[
\eta = \frac{G}{\alpha+F} \quad \text{and} \quad \xi = \frac{F}{\alpha+F} \tag{II.7}
\]

Thus, eq (II.6) may be written as

\[
\eta \left( \frac{r_1 + \frac{r_2}{\alpha}}{\xi} \right) - \frac{r_2}{\alpha} \tag{II.8}
\]

and/or

\[
\eta = r_1 \xi - \frac{r_2}{\alpha} (1-\xi) \tag{II.9}
\]

where,

\[
\alpha = \sqrt{F_m F_M} \tag{II.10}
\]

i.e. of the series of F values calculated from the series of measurement, F\textsubscript{m} stands for the lowest and F\textsubscript{M} for the highest value.

A search of literature showed that kinetic study of free radical copolymerization of styrene with butyl methacrylate was studied by Rodriguez et al. The initiator used was 1-phenyl-1-(2',2',6',6'-tetramethyl-1'-piperidinyl-oxy) ethane\textsuperscript{205} in bulk at 125°C. The kinetic analysis of the copolymerization system indicated an apparent propagation rate coefficient independent of the monomer feed composition as well as a limiting conversion that decreased upon decreasing the styrene monomer feed. The number average molecular weight linearly increased with conversion and copolymers showed narrow molecular weight distribution.
Microemulsion (ME) and conventional emulsion (CE) copolymerization of styrene and n-butyl methacrylate (n-BMA)\textsuperscript{206} were studied at 70°C in an inert atmosphere by employing sodium lauryl sulfate as a surfactant, n-heptanol as a cosurfactant and potassium persulfate as a free radical initiator. The reactivity ratios for the ME and CE of Sty-co-nBMA were determined by Fineman-Ross (F-R), Kelen-Tudos (K-T) and Mayo-Lewis (M-L) methods. The F-R for ME polymerized copolymer yielded the reactivity ratios of Sty (\(r_{\text{Sty}}\)) and n-BMA (\(r_{\text{BMA}}\)) as 0.17±0.02 and 0.60±0.02 respectively while the CE polymerization gave the reactivity ratios of \(r_{\text{Sty}}\) and \(r_{\text{BMA}}\) as 0.31±0.02 and 0.55±0.02 respectively.

Yousi et al.\textsuperscript{207} investigated the living free radical copolymerization of styrene with the polar monomers including BMA, MMA and methyl acrylate (MA). Monomer reactivity ratios determined by Kelen-Tudos method were \(r_{\text{Sty}}=1.27, r_{\text{BMA}}=0.59, r_{\text{Sty}}=0.74, r_{\text{MMA}}=0.25, r_{\text{Sty}}=1.32, r_{\text{MA}}=0.14\) for Sty-BMA, Sty-MMA and Sty-MA copolymers respectively. It was observed that the copolymerization of styrene with acrylates resulted in decreased monomer reactivity ratio \(r_1(\text{Sty})\) and in the copolymerization of Sty with methacrylates the monomer reactivity ratio \(r_1(\text{Sty})\) increases while the length of the substituted group increases.

Raghavan et al.\textsuperscript{208} synthesized copolymer of styrene with BMA, MMA and ethylmethacrylate (EMA) at 60°C by employing a mixture of n-butylamine and carbon tetrachloride as charge transfer (CT) initiators in dimethylsulfoxide (DMSO). Copolymers were characterized by IR and \(^1\text{HNMR}\) spectroscopy. The copolymer compositions were determined by \(^1\text{HNMR}\) spectroscopy and reactivity ratios were calculated by F-R and K-T methods. The reactivity ratios of Sty-MMA and Sty-EMA copolymers showed the incorporation of styrene in higher proportions in the copolymer. The copolymer of Sty-BMA showed higher level of BMA than styrene in the copolymer chain. In Sty-MMA and Sty-BMA systems, the product of \(r_1\) and \(r_2\) was greater than 1, representing the formation of high degree of random copolymers while the product of \(r_1\) and \(r_2\) is less than 1 in Sty-EMA copolymer, indicating the formation of alternating copolymers.
The copolymerization in bulk of Sty with BMA and EMA at 50°C, in presence of ZnCl₂ was examined. The complexing agent determined the formation of copolymers with high alternating tendencies which was proved by the copolymer composition and distribution of the diads.

Free radical induced copolymerization of Sty with BMA was investigated using BPO as initiator. Kinetic studies and optical microscopy of the reaction mixture showed that the reaction exhibits autoacceleration behaviour, which could be suppressed by reducing the reaction temperature. The monomer reactivity ratios at various temperatures were calculated from the experimental data.

Copolymerization of MA, ethyl acrylate (EA) and n-butyl acrylate (BA) with styrene in the presence of zinc chloride at 300K was carried out. The complexes formed were found to be polar in nature. The viscosity and density of the complexes increased while the tendency to form binary complex decreased on increasing the size of the alkyl substituents of the acrylate monomer. The copolymerization of MA and BA with styrene occurred by cross propagation mechanism and the copolymerization of EA with Sty followed radical complex mechanism in the presence of their complexes with ZnCl₂.

Furthermore, free radical copolymerization of MA with Sty using imidazolium p-chlorophenacylde89 (ICPY) as initiator at 60°C for 3hrs. in dioxan was reported by Srivastava and Nigam. The exponent values with respect to initiator and monomer was 0.5 and 1.0 respectively indicating ideal kinetics. The molar fraction of Sty and MA obtained from phenyl and methoxy protons respectively, were nearly equal suggesting alternating nature of the copolymer formed. NMR spectra confirmed alternating copolymer by showing three peaks for methoxy protons at δ=3.2-3.6 ppm, δ=2.7-2.9 ppm, δ=2.2 ppm and singlet for phenyl protons at δ=7.0 ppm. The stereochemistry of the copolymer was explained by the formation of triad.

Kinetics and mechanism of copolymerization of Sty with MA catalyzed by cyclopentadienyltitanium trichloride – MAO (CpTiCl₃-MAO)₂ system was investigated. A mechanism resulting in a slow formation of random copolymer
was proposed. The complexation ability of styrene and insertion ability of methyl acrylate resulted in a 1:1 copolymer.

Thoenes and coworkers\textsuperscript{213} carried out the emulsion copolymerization of Sty with MA. Studies revealed that the homogenous copolymer was formed.

Copolymerization propagation kinetics of Sty with alkyl acrylates\textsuperscript{214} viz. MA and BA was investigated at 298K and 323K over a range of monomer feed compositions with pulsed UV laser as source of initiation. Products were analyzed using gel permeation chromatography (GPC). In addition Mark-Houwink constants (K and $\alpha$) were determined as $7.88 \times 10^{-3}$, 0.885 and $8.57 \times 10^{-3}$, 0.865 for PMA and PBA respectively.

Radical induced copolymerization of Sty with methyl $\alpha$-acetylaminoacrylate\textsuperscript{215} at 50°C in tetrahydrofuran with AIBN as initiator was examined. The reactivity ratios were $r_1=3.04$, $r_2=0.058$, $Q=6.03$ and $e=0.52$ in the copolymerization of methyl $\alpha$-acetylaminoacrylate ($M_1$) and styrene ($M_2$). The values of $Q$ and $e$ suggested that the $\alpha$-acetylamino group has no polarizing action and significant resonance effect.

Radical copolymerization of styrene with methyl cis-\textbeta{cyanoacrylate}\textsuperscript{216} formed charge transfer complex with styrene and behaved as a weak electron acceptor. The reactivity ratios were determined using K-T method.

Copolymer of n-butyl methacrylate with vinyl pyrrolidone\textsuperscript{217} was prepared by microemulsion polymerization technique with a nonionic surfactant of Tween-80 as emulsifier and n-butanol as coemulsifier. The polymerization was initiated by BPO, potassium persulfate (KPS), KPS/ferric sulfate ($\text{FeSO}_4$) and BPO/$\text{FeSO}_4$ respectively, where the initiation with BPO/$\text{FeSO}_4$ occurred at the interphase between the oil phase and the reaction media. This interfacial-initiated microemulsion polymerization resulted in larger particles with relatively narrower particle size distribution as well as higher limiting monomer conversion but lower polymerization rate than the polymerization initiated by KPS/$\text{FeSO}_4$.

Copolymerization of N-VP with glycidyl methacrylate (GMA)\textsuperscript{218} was carried out at 60°C in chloroform using AIBN as initiator. The copolymers were
characterized by IR and $^{13}$CNMR spectroscopy. The copolymer compositions were established by microelemental analysis and $^{13}$CNMR spectroscopy. The reactivity ratios were calculated using F-R and K-T methods. GPC measurements were used to determine molecular weights of the copolymer. Another publication reporting the synthesis of N-VP and GMA was studied at 50°C using 3.0 mol L$^{-1}$ of N,N'-dimethylformamide solution and 9.0 x $10^{-3}$ mol L$^{-1}$ of AIBN as initiator.

Free radical copolymerization of N-vinyl pyrrolidone (N-VP) and MA in bulk with BPO as initiator was studied by Brar and Kumar. The copolymer composition was determined by $^1$HNMR spectra. The reactivity ratios calculated by K-T and non-linear least square error in variable method were $r_1=0.09$ and $r_2=0.44$ for N-VP and MA respectively.

Varshney and Prajapati carried out the synthesis and characterization of MMA and N-VP using p-nitrobenzyl triphenylphosphonium ylide at 60°C for 1 hr. The kinetic expression obtained through kinetic studies was $R_p \alpha [I]^{0.75} [\text{MMA}]^{1.2} [\text{N-VP}]^{1.2}$. The activation energy calculated was 45.4 kJ/mole. The FTIR spectra showed bands of $-\text{OCH}_3$ of MMA at 1725 cm$^{-1}$ and $>\text{C}=\text{O}$ of N-VP at 1679 cm$^{-1}$. The glass transition temperature of the copolymer was 133°C and GPC data revealed polydispersity index of about 1.5. ESR studies revealed phenyl radical initiated polymerization.
A heteropolymer formed when three monomer are linked in the same polymer chain is termed terpolymer and the process is called terpolymerization. Terpolymerization provides the information on reactivity of certain class of monomers not otherwise available. Terpolymerization is an effective method to modify the polymer properties through proper choice of monomers\textsuperscript{221}. In a terpolymer system, the two monomers provide heat resistance, tensile strength, elasticity, transparency, solvent resistance and dimensional stability whereas the third monomer gives the added features that include vulcanizability, dyeing ability, modified flow properties, etc.

Alfrey and Goldfinger\textsuperscript{222} showed the importance of nine propagating reactions in determining composition of the three component system. Further, extension to multicomponent systems was carried out by Wallings and Briggs\textsuperscript{223,224}. In 1957, Slocombe\textsuperscript{225} performed work on three component system and discovered a method by which a range of high clarity terpolymers could be easily located in many three component systems.

Literature survey reveals that terpolymerization of benzyl methacrylate, styrene and methyl methacrylate was investigated by Disselho\textsuperscript{226} using dilatometer. Nadir \textit{et al.}\textsuperscript{227} examined the terpolymerization of polar vinyl monomers like AN, MA, MMA with butadiene and Sty in the presence of Lewis acids. The yield and contents of monomer units of the terpolymer were determined.

Guillot \textit{et al.}\textsuperscript{228} used an emulsion polymerization technique for terpolymerization of AN, Sty, MA. The polymerization was done using potassium persulfate as initiator and sodium lauryl sulfate as emulsifier. Kinetic studies showed that styrene was much more reactive than AN and MA. Rios found that after the conversion limit is attained, the addition of the more rapidly consumed monomer resulted in reinitiation of polymerization.
In 1980, Jenner and Kellou\textsuperscript{229} carried out the free radical terpolymerization of maleic anhydride, MA and Sty at 50-60°C using lauryl peroxide as initiator and chloroform as diluent. In another publication Groebel et al.\textsuperscript{230} studied the terpolymerization of AN, Sty, maleic anhydride.

Shaaban et al.\textsuperscript{231} examined the organotin polymer using binary and ternary copolymerization method. Ternary polymerization of the system, butyl methacrylate / tributyltinmethacrylate / AN was carried out and the terpolymer composition of each system was calculated through tin and hydrogen analysis.

Kobayashi and Schikizar\textsuperscript{232} studied the sequence distribution of the terpolymer of Sty, MMA and butyl acrylate (BA). They examined the sequence distribution by \textsuperscript{1}H NMR and glass transition temperature of acrylic resins by thermochemical analysis, for industrial paints.

Zanovic, Saric and Vogel\textsuperscript{233} formed the terpolymer of AN, Sty, 2,3 dibromopropyl acrylate in emulsion and in solution of dimethylformamide (DMF). The polymerization at low conversions yielded terpolymers whose thermal stability was measured by TGA and DTG measurements.

The literature is further enriched by the work of Wiss et al.\textsuperscript{234} who experimentally determined the terpolymerization kinetic equation for the terpolymerization of donor (e.g. styrene, \(\alpha\)-methyl styrene), acceptor (e.g. maleic anhydride) and neutral monomers (e.g. acrylonitrile).

The physicochemical analysis of the initial stage of the terpolymerization of styrene, methyl methacrylate, acrylonitrile was examined at 60, 75 and 80°C by Kucher et al.\textsuperscript{235}. In 1988, Nikiforenko et al.\textsuperscript{236} determined the rate of AIBN initiated polymerization of Sty, MMA and AN system in the presence of 2,2',6,6' tetramethylpiperidine oxide. Furthermore, the free radical co and terpolymerization of acrylic monomers with olefins using Lewis acid as a complexing agent for the acrylic monomer was studied by Lieberth et al.\textsuperscript{237}. Khalil et al.\textsuperscript{238} carried out the free radical initiated terpolymerization of N-acryloyl oxypythalimide (NAP) or N-methacryloxyphthalimide (NMP) and acrylonitrile with methyl acrylate at 60°C. In 1992, Bartur\textsuperscript{239} carried out the bulk
polymerization of maleic anhydride, 2-ethylhexylacrylate and styrene in benzene at 70°C under nitrogen blanket. Remphrey et al.\textsuperscript{240} studied the analysis of terpolymerization of AN, Sty and 2,4,6-tribromophenyl acrylate in DMF at 60°C.

The complex radical terpolymerization of two acceptor – donor – acceptor systems, maleic anhydride / styrene / acrylonitrile and n-butyl methacrylate / styrene / acrylonitrile in low and high conversion conditions was examined by Kibarer et al.\textsuperscript{241}. It was found that the terpolymerization occurred through a ‘complex mechanism’ in a state of near binary copolymerization of Sty-BMA and AN-Sty complexes. The terpolymer had high thermal stabilities (295-325°C) due to intermolecular fragmentation of AN units through cyclization and crosslinking reactions.

Terpolymerization of maleic anhydride, Sty and AN was carried out in benzene at 60°C with AIBN as initiator\textsuperscript{242}. Polymerizations were performed with total initial monomer concentrations of 0.25 g/mL. Although the ternary system comprised of one electron donor monomer and two electron acceptor monomers, maleic anhydride was the most reactive monomer as it was incorporated in higher proportions than other monomers.

Terpolymerization of AN / Sty / MA system were examined by emulsion polymerization using sodium lauryl sulfate as emulsifier and potassium persulfate as initiator\textsuperscript{243}. Kinetic studies of the reaction mixture by gas chromatography and calculation of the copolymer composition versus conversion showed that the classical theory of copolymerization (propagation rate by Markov chain 1\textsuperscript{st} order) can be applied to the emulsion polymerization. It was found that when a conversion limit is obtained, the polymerization can be restarted by addition of more rapidly consumed monomer (Sty in this case).

Furthermore, Varshney and Prajapati prepared the terpolymer of Sty / AN / MMA initiated by p-nitrobenzyl triphenylphosphonium ylide\textsuperscript{105} at 65°C for 120 min in dioxan. The kinetic expression was $R_p \propto [\text{ylide}]^{0.45} [\text{Sty}]^{0.8} [\text{MMA}]^{1.2} [\text{AN}]^{1.2}$. The overall activation energy for polymerization was 42 kJmol\textsuperscript{-1}. The reactivity ratios calculated from $^1$HNMR and elemental analysis by Kelen-Tüdos
method was $r_1(MMA+AN)=0.06$ and $r_2(Sty)=0.005$ confirming the alternating nature of the terpolymer. ESR studies confirmed the presence of phenyl radical responsible for initiation.

Terpolymerization of acrylonitrile(N)-Styrene(S)-acrylic acid(A) were prepared by Brar and Pathan\textsuperscript{244}. The terpolymers were characterized using NMR spectroscopy. The terpolymer compositions were determined by $^{13}$CNMR spectra. The comonomer reactivity ratios calculated were $r_{NS}=0.04$, $r_{SN}=0.35$, $r_{NA}=0.81$, $r_{AN}=2.99$, $r_{SA}=0.80$ and $r_{AS}=0.10$.

In another experiment, Brar and Pathan\textsuperscript{245} carried out the terpolymerization of acrylonitrile(N)-styrene(S)-glycidyl methacrylate(G) using BPO as initiator. The terpolymer compositions were determined by $^1$HNMR and $^{13}$CNMR spectroscopy. The comonomer reactivity ratios were determined as $r_{NS}=0.04$, $r_{SN}=0.40$, $r_{NG}=0.22$, $r_{GN}=1.37$, $r_{SG}=0.44$ and $r_{GS}=0.53$.

Kinetic investigations were carried out for terpolymerization of MMA-dodecyl methacrylate(DDMA)-octadecyl methacrylate(ODMA) and Sty-DDMA-ODMA systems\textsuperscript{246}. Terpolymerization runs were performed at 70-105°C, in xylene solutions, using bifunctional peroxide initiator, 1,1-di(tert-butylperoxy)-3,3,5-trimethylcyclohexane or monofunctional tert-butylperoxy-2-ethylhexanoate. Terpolymers were characterized with respect to composition and molar mass distribution. In the MMA-DDMA-ODMA system, experimental terpolymer compositions were found to be similar to the initial monomer feed compositions.
Photopolymerization is a term denoting initiation of a chain polymerization process by light, thereby, resulting in increase in molecular weight. Photopolymerization involves exposure of monomers to ultraviolet light at 10-40°C. Almost all photopolymerization reactions are initiated by free radicals. Photopolymerization is an effective way for detection and identification of photochemically produced free radicals as the reaction can be interrupted at will by merely turning on or off the light. Photopolymerization also provides subtle control on molecular weight and molecular weight distribution by varying the intensity of light. The primary radicals produced photochemically are essentially independent of temperature contrary to thermal free radical initiators. Photopolymerization is the best method to polymerize monomers with low ceiling temperature. The energy difference for stereospecific polymers (syndiotactic and isotactic) is about 1 Kcal/mole, hence photopolymerization at low temperature favours syndiotactic polymers. Photopolymerization finds application in biochemistry like disc electrophoresis.

The earlier methods of photopolymerization include exposure of vinyl monomers to sunlight. In 1845, Blyth and Hoffmann prepared clear glass-like product from styrene in sunlight. Bertholet and Guadechon for the first time polymerized ethylene to a solid form with ultraviolet light. Ostromislenski in 1912 demonstrated the chain reaction nature of vinyl polymerization.

Primary radicals are formed by photolytic decomposition of initiator(s) by absorbing light of intensity $I_a$. The initiators absorb light and goes to higher electronic state called excited state. The excited species may either react with another substance to give radicals or may itself decompose to form radicals ($R'$). The rate of radical formation is given by Beer’s law:

$$v_R = \phi I_o = \phi I_o \left(1 - e^{-\varepsilon I [S]}\right)$$

where $\phi$ is the quantum yield, $I_o$ is the incident light, $I$ is the path length of the system, and $[S]$ is the concentration of the initiator of extinction coefficient $\varepsilon$. 

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A number of light sources of high intensity are available for photo illumination. These lamps have mercury and mercury-xenon high pressure point arc sources. The xenon lamp gives spectral emission from 300µm through visible region superimposed with mercury spectral lines. Furthermore, lasers e.g. argon lasers, helium neon lasers are also used as light sources in photopolymerization as they do not show any divergence.

Various methods are available to monitor the course of photopolymerization. Photopolymerization can be followed by studying the disappearance of the monomer, the appearance of the polymer or by determining the concentration of radicals in the system at every moment through E.S.R. The disappearance of the monomer is determined by observing a loss in the property of monomer like density, infrared absorption, and refractive index while the appearance of the polymer is monitored by viscometry and light scattering.

All free radicals do not initiate polymerization. For a free radical to initiate, the chain radical formed must be sufficiently stable relative to the primary radical. The initiators used for photopolymerization include organic carbonyls (benzophenone), peroxides (benzoyl peroxide), organic sulphur compounds (S-aryldithiocarbamate derivatives), azo compounds (α,α'-azobisisobutyronitrile), halogen containing compounds (chloroform, carbon tetrachloride), metal carbonyls (manganese carbonyl [Mn₂(CO)₁₀], rhenium carbonyl [Re₂(CO)₁₀]), inorganic solids (zinc oxide, silver halide), inorganic ions (ferrous and ferric complexes), dye sensitization (riboflavin) and ylides etc.

A search of literature reveals that Timpe and Kronfeld studied the kinetics and initiator mechanism of photochemical polymerization of methyl methacrylate in CH₃CN in the presence of benzophenone, xanthone, fluorenone, thioxanthone, acridone or N-methyl acridone as photoinitiator using fluorescence measurements. Kinetics and photophysics measurements showed that the triplet states of some ketone initiators reacted well with MMA yielding diradicals that decomposed to the starting compounds whereas some initiated MMA
polymerization. The studies showed that the polymers contained the corresponding ketone moiety.

Another study of photoinduced polymerization of methylmethacrylate with pyrene in the presence of triethylamine was conducted by Lissi et al.\textsuperscript{270}. It was proposed that the active free radicals were formed as a result of the interaction of the monomer with the pyrene-triethylamine complex and/or the pyrene radical.

Ghosh and Pal\textsuperscript{271} investigated the photopolymerization of methylmethacrylate at 40°C using pyridinium chloromate as the photoinitiator. The kinetic expression \( R_p \alpha [I]^{0.21} [\text{MMA}] \) revealed that initiator exponent value is 0.21. Ghosh and Mukherjee\textsuperscript{272} studied the kinetics of the photopolymerization of MMA at 40°C employing photoinitiator systems containing a chloro derivative of acetic acid in combination with dimethylaniline.

Photopolymerization of MMA with 4,4'-dithio-bis-morpholine as photoinitiator was studied dilatometrically at 40 ± 0.5°C under the light of a mercury vapour lamp by Nag\textsuperscript{273}. The system obeyed ideal kinetics \( R_p \alpha [I]^{0.5} [\text{MMA}] \).

Uri et al.\textsuperscript{274} for the first time conducted studies on photoinduced polymerization of vinyl monomers like acrylonitrile, MMA or methacrylic acid by an ion-pair complex. Aliwi and Bamford\textsuperscript{275} studied the hydroxo-oxabis(8-quinolyloxo) vanadium - n-butylamine ion pair complex initiated free radical photopolymerization of MMA at 25°C at 365nm wavelength.

Bulk polymerization of MMA was carried out using N-(p-benzoylbenzene-sulfonyl) benzene sulfonamide\textsuperscript{276} as a photoinitiator. An ideal kinetics was obeyed by the system.

PMMA was prepared using UV-visible light at 40°C and morpholine-iodine charge transfer complex as photoinitiator in benzene diluted system by Shimose et al.\textsuperscript{277} The system followed non-ideal kinetics \( R_p \alpha [I]^{0.09} [\text{MMA}]^{1.15} \). Ghosh and Pal\textsuperscript{278} also conducted bulk photopolymerization of MMA with morpholine-chlorine charge transfer complex as photoinitiator. A non ideal kinetics \( R_p \alpha [I]^{0.071} [\text{MMA}]^{1.10} \) was obtained for the system.
Tsunooka et al.\textsuperscript{279} carried out the photopolymerization of N-acetyl pyridinium chloride-KSCN-CCl\textsubscript{4} in an aqueous system. Photopolymerization of MMA was also carried out in the presence of benzyl and phenylpropanedione monoxime esters\textsuperscript{280}. Crivells et al.\textsuperscript{281} carried out the synthesis and evolution of S-aryl-S,S'-cycloalkyl sulfonium salts as cationic photoinitiators.

Allen and Edge\textsuperscript{282} conducted bulk photopolymerization of MMA employing a variety of radical and cationic initiators along with amine cosynergistics. Photoinduced cationic polymerization of cyclohexene oxide using phenacyl benzoylpyridinium salts\textsuperscript{283} was also studied. Synthesis and characterization of PMMA by photoinduced polymerization were carried out using atom radical transfer polymerization\textsuperscript{284}.

Photopolymerization of acrylate derivatives initiated by hexaarylbiimidazole with ether groups were examined by Yori et al.\textsuperscript{285}. A novel natural photoinitiator, Curcumin, was reported for the copolymerization of styrene and MMA by Mishra and Daswal\textsuperscript{286}. In another study conducted by Mishra and Daswal\textsuperscript{287}, polymerization of n-butyl acrylate employing 1-(bromoacetyl) pyrene and its arsonium salt was investigated.
Although ample of literature is available on the research of ylides but their use as a ligands has not been explored much to this date. Ylide complexes enhance our knowledge of structural chemistry, in addition, several exhibit exceptional catalytic activities or are of pharmacological importance.

Phosphorus ylides are powerful electron donors and therefore, form wide range of complexes having stable metal-carbon bonds. Series of carbonyl complexes with Group VI A metals and the adducts\textsuperscript{288-290} of triphenylphosphonium cyclopentadienylide have been formed.

Wilkinson and coworkers\textsuperscript{291} synthesized a series of zwitterionic complexes (I) from the Group VI A metal hexacarbonyls and the ylidylic ligand triphenylphosphonium cyclopentadienylide\textsuperscript{292}. It was found that the considerable stability of the complexes contrasted sharply with the reactivity of the parent anionic carbonyl complexes. Following the Dahl-Ballhausen-Green\textsuperscript{293} interpretation of the bonding in \(\pi\)-cyclopentadienyl metal tricarbonyls, Kotz and Pedrotty\textsuperscript{289} proposed that the bonding in complexes involved the presence of three filled non-bonding orbitals on the metal nucleus. The increased stability of the complexes to their anionic analogue was attained by reduction of excess electron density on the metal nucleus by the interaction of one of the filled non-bonding orbitals with the vacant d orbital of the phosphonium centre. It was found that carbonium\textsuperscript{294} and phosphonium centres\textsuperscript{295} alpha to the metal complexed cyclopentadienyl ring interacted strongly with the metal atom, either directly or through the cyclopentadienyl ring.
A series of substituted analogues of triphenylphosphonium cyclopentadienylide containing phosphorus, arsenic and antimony at the positively charged centre are available\textsuperscript{296}. The degree of ring heteroatom p-d bonding in these ligands decreased in the order: P > As > Sb.

![Diagram](image)

Treatment of tetrakis (methoxycarbonyl) palladiacyclopentadiene (A) with neutral ligands has been reported to yield monomeric palladiacyclopentadiene complexes\textsuperscript{297-299}. Ishii \textit{et al.}\textsuperscript{300} prepared triphenylphosphonium cyclopentadienylide adduct of tetrakis (methoxycarbonyl) palladiacyclopentadiene in 79\% yield.

![Diagram](image)

Sulphur ylide complexes have become indispensable reagents to the organic chemist\textsuperscript{301}. Open chain sulphur ylides can be coordinated as terminal ligands to the metal centre\textsuperscript{302} (III) in a similar way as the phosphorus ylides. Their monoanions can coordinate as bridging double ylides (IV) or as chelating ligands\textsuperscript{303} (V). Chelate complexes are also formed if the molecule contains a donor atom in addition to the ylide function\textsuperscript{304} (VI). In another method for formation of sulphur ylide complexes, the ylide function itself may be substituted.
with metal atoms at the carbanionic centre\textsuperscript{305} (VII) or a complexed metal may additionally act as substituent at the sulphonium centre\textsuperscript{306} (VIII).

\[
\begin{align*}
\text{(III)} & \quad \text{(IV)} & \quad \text{(V)} \\
\text{(VI)} & \quad \text{(VII)} & \quad \text{(VIII)}
\end{align*}
\]

Ylides stabilized by a carbonyl group adjacent to an ylide carbon atom can also interact with metal ions through the carbonyl oxygen atom. Several ylide tungsten(0) carbonyl complexes\textsuperscript{307-309} with dimethylsulphonium, triphenylphosphonium and 4-methylpyridinium phenacylides (VIII) and the corresponding 2-pyridylcarbonylmethylides (IX) have been reported in the literature.

\[
\begin{align*}
\text{(IX)} & \quad \text{(X)} \\
Z = \text{SMe}, \text{PPh}_3, \text{and NC}_3\text{H}_4\text{Me}-4
\end{align*}
\]

Srivastava and Bhatnagar\textsuperscript{310} reported phenacyl dimethylsulphoxonium ylide complex of mercuric chloride (X) initiated radical copolymerization of styrene and methyl methacrylate at 85°C in dioxan diluent. The system followed ideal kinetics.
They also carried out the homopolymerization of styrene at 85°C in dioxan. The kinetic expression \( R_p \propto [\text{PDSY-HgCl}_2]^{0.3} [\text{Sty}]^{1.11} \) revealed non ideal kinetics. Other publications using [PDSY-HgCl₂] as the initiator includes polymerization of 4-vinyl pyridine and methyl methacrylate. Styrene has also been photopolymerized with [PDSY-CuCl₂] as initiator.
LITERATURE ON INTERPENETRATING POLYMER NETWORK

An Interpenetrating Polymer Network (IPN) is any material consisting of two polymers, each in network form i.e. it contains two kinds of chains forming two separate networks, but in juxtaposition or interpenetrating. History of IPN goes back to 1914 when Jonas Alysworth, Thomas Adison’s chief chemist made first IPN material in an attempt to make phonograph records with phenol formaldehyde resin, although Alysworth did not called this material an IPN. Later, in 1920, Herman Staudinger confirmed the existence of chain like polymeric structure with molecular weights exceeding 5000 grams/mole. IPNs were not studied as a class of heterogeneous materials until the late 1950s to early 1960s. J. Millar was the first researcher to investigate the IPN properties and coined the term “interpenetrating polymer network”.

IPNs are classified on the basis of geometry and structure. On the basis of geometry they are classified into:

1) Sequential IPNs- IPNs formed by polymerizing the first mixture of monomer, cross-linking agent and initiator or catalyst to form a network. The network is swollen with a second combination of monomer and cross linking agent and polymerized to form an IPN.

2) Simultaneous Interpenetrating Networks (SINs)- An IPN formed by polymerizing two different monomer and cross linking agent that pairs together in one step.

On the basis of structure IPNs are classified into:

1) Full IPNs- It is comprised of two networks that are ideally juxtaposed, which generate a lot of entanglements and interaction between the networks.

2) Homo IPNs- It is a special type of full IPNs, where both polymers used in the networks are same. They are usually sequential IPNs.

3) Semi- or Pseudo IPNs- One of the components of these IPNs has a linear structure instead of a network structure. These type of IPNs can be formed by either a sequential or simultaneous process.
4) **Latex IPNs**- It is formed by an emulsion polymerization where both monomers can be added at once or in stages.

5) **Thermoplastic IPNs**- These IPNs are moldable and can be extruded and recycled. One component of these IPNs is usually a block copolymer while the other component is a semi-crystalline polymer.

\[
\text{Network A} \quad + \quad \text{Network B} = \quad \text{IPN=A+B}
\]

The conditions for eligibility as an IPN are-

1) the two polymers are synthesized and / or crosslinked in the immediate presence of the other, and

2) the polymers have similar kinetics.

However, these are loosely held guidelines. There are IPNs that have only one polymer crosslinked (where the polymers are synthesized separately) or where the polymers have vastly different kinetics.

An IPN can be distinguished from other multipolymer material in three ways:

1) IPN swells in the presence of solvents but does not dissolve.

2) Creep and flow are suppressed, and

3) IPN show characteristic morphologies due to mutual incompatibility and thus it influence the physical and mechanical behaviour of the material.

The IPN synthesized till now show varying degree of phase separation. The phase varies in size, shape, sharpness at the interfaces and degree of continuity. There is no direct method to show the existence of interpenetration or to measure the quantitative level of interpenetration. L.H.Sperling\(^{320}\), K.C.Frisch, Liptov and coworkers have done pioneering research of Interpenetrating Polymer Network.
An IPN differs from simple polymer blends by equilibrium swelling and crosslink density measurements. The classical way of polymer mixing usually leads to multiphase morphology but IPNs via crosslinking reactions are immiscible and form more homogenous systems. In some cases it is the only method facilitating the formation of a blend from completely immiscible polymers. The IPN structure differs from the systems prepared by physical mixing mainly in the fact that both polymers form continuous phases in the whole volume of IPNs.

The main problem of the IPNs is the miscibility of the individual components and the existence of phase separation. IPNs exhibit different degree of phase separation which depends on the compatibility of the components. IPN shows improvement of other properties like tensile strength, impact strength, and adhesion and, in some cases, greater sound and shock absorption.

Many kinds of IPN architecture exist which differ in number and type of crosslinks that exist in the system. Survey of literature reveals that a vast amount of literature is available on synthesis and characterization of interpenetrating polymer network. Srivastava et al.\textsuperscript{321} carried out the synthesis of IPN based on polystyrene and poly(citronellol-alt-methyl methacrylate) in xylene, using BPO as initiator and divinyl benzene (DVB) as cross linking agent. Scanning electron microscopy (SEM) showed two distinct phases. The percentage swelling, average molecular weight between the cross links ($M_c$) were the direct function of concentration of copolymer and BPO while inverse function of concentration of styrene and DVB. Differential Scanning Calorimetry (DSC) gave two transition temperatures ($T_g$) at 64.09 and 159.79°C. The activation energy calculated from thermogravimetric analysis (TGA) was 20 kJ mol\textsuperscript{-1}.

Synthesis of IPNs based on poly(vinyl chloride-co-vinyl acetate) and poly (alkyl methacrylates) was carried out by Deb and Mathew\textsuperscript{322}. The semi IPNs were transparent, high strength materials and showed only one glass transition temperature.
Semi IPNs based on polyvinyl alcohol and polyacrylamide was prepared using N, N'-methylene bis acrylamide (MBA) as cross linking agent and suitable redox system comprising of potassium persulfate and metabisulfite. The IPNs were characterized by FTIR, SEM and X-ray diffraction (XRD) methods.

Varshney and Prajapati synthesized semi IPNs based on poly(α-terpineol-co-styrene) and ethyl acrylate using DVB as cross-linking agent and p-nitro triphenylphosphonium ylide as initiator. An FTIR spectrum was used to characterize IPN. DSC showed two T_g at 15 and 59°C. SEM micrographs showed phase separation. The TGA curve showed IPN to be thermally stable and activation energy calculated from Coats-Redfern equation was 23 kJ mol^{-1}. The percentage swelling and M_c were direct function of copolymer as well as ylide and inverse function of monomer and DVB.