

CHAPTER - 1

GENERAL INTRODUCTION

## GENERAL INTRODUCTION

Since its foundation by the pioneering work of Studinger (1920-30), the subject of polymer science has diversified both conceptually and materially. Following the recognition of two broad classes of polymer viz. condensation and addition, significant developments have taken place in the domain of these two types of polymers.

During these years, the scientific world has seen a variety of spectacular achievements in polymer science and technology through : (a) the synthesis of new monomers and polymers with outstanding physico-chemical properties, (b) developments of new catalyst systems, Ziegler (1955), Natta (1955), charge transfer catalysts, Ellinger (1963), Scott (1963), living polymerization catalysts, Swarzo and Henderson (1968), Phillips catalysts (1930) and many other heterogeneous catalysts.

Despite these many sided progress research still is warranted in the domain of synthetic polymer science along the following directions : (a) synthesis of fresh monomers and polymers with novel properties, (b) development of new/novel/cheap catalyst systems unmodified as well as modified by various chemical means, (c) mechanistic interpretation and supporting kinetic characterization and (d) technological exploitation of the various polymers synthesized.

The work highlighted in this thesis an endeavour to develop a heterogeneous catalyst system based on a very cheap and abundant material carbon black - which is indigenously produced in India and which yet has not found any other potential channel of utilization excepting its key role in rubber industry as fillers, and the like. A detailed literature search to be highlighted in a later section indicates that recently almost parallel to our research here some Japanese workers have become active in developing carbon black catalysts. However, it is gratifying to place on record here that our results are significantly distinct from any published information on more than one aspect and we consider this research to have acquired a very encouraging status at the moment.

The major accomplishments of this research presented here may be summarized as under : (a) carbon black is an efficient catalyst for cationic polymerization as revealed by the experimental work, (b) a novel electron transfer mechanism has been shown to be operative, (c) enhancement of catalytic activity of carbon black is possible by appropriate chemical modification, (d) under selective conditions it is possible to produce novel carbon black grafted poly (N-vinylcarbazole) composites.

The work highlighted in this thesis attempts to focus some new and useful observations along the four points featured as

above in respect to the polymerization of N-vinylcarbazole with modified and unmodified carbon blacks.

For a critical appraisal of these aforementioned features, it is necessary to keep in view the relevant developments in this field and the conclusion reached there of. The first chapter, Introduction, is devoted to a brief survey of cationic polymerization of vinylmonomers and the available knowledge of the modified and unmodified carbon blacks vis-a-vis their role in the cationic polymerization.

SECTION I. PRESENT STATUS OF THE CHEMISTRY OF CATIONIC  
POLYMERIZATION OF VINYL MONOMERS

Since our research is mainly concerned with cationic polymerization reactions, it is intended to highlight the present status of this field. A typical cationic polymerization is affected by the monomer structure, nature of the catalyst, co-catalyst, solvent, temperature and other related factors. In the following sections a general discussion is presented summarizing the significant basic conclusions that can be drawn from the mammoth literature in the field.

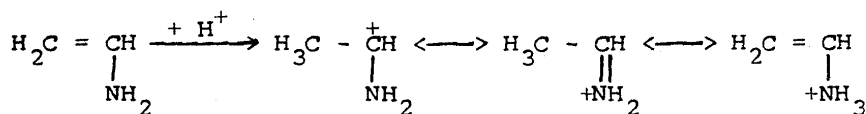
I.1 Monomer Structure

The structure of monomer molecules influences the reaction mechanism significantly. The polarity, basicity of the monomer and also the steric effects can play a dominant role<sup>1</sup> in the cationic polymerization of vinyl monomer.

Cationic vinyl monomers are in general electron rich in their double bonds which are the sites of highest nucleophilicity. Naturally, the vinyl monomers containing electron releasing substituents are much more suitable in producing high polymers. The initiated cationic species tend to seek most nucleophilic site of the molecule which must be a double bond of the vinyl monomer in order to continue the propagation

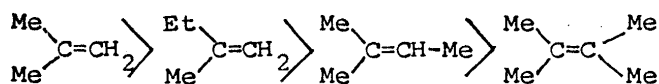
reaction. If the nucleophilic site of the molecule be other than double bond then non-propagating complexes may form which will make the reaction to come to an end.

The stability of the cationic species due to the electron rich double bond is also important for the propagation of the reaction. The high molecular weight polymer product is rather dependent on the ease of propagation of the cationic species formed in the reaction which furthermore depends on the structure of the monomer. There are in fact many vinyl monomers which readily undergo cationic initiation but can not produce high molecular weight product. For example, acrylamide can be initiated cationically but propagation does not proceed because of prohibitively high stability of the species formed<sup>2</sup> :



#### Alkyl substituted olefins

The reactivity of alkyl substituted olefins decreases with the increasing molecular weight of the substituent. However, the reactivity of the unsymmetrically substituted olefin is higher than symmetrically substituted olefins. The reactivity order is shown as below :



The steric effect also significantly disturbs the cationic polymerization<sup>3,4</sup>. For example, the methyl groups<sup>1</sup> in isobutene are not so bulky but cause a considerable steric hinderence.

High basicity of the monomer species, due to varying electronic affinities of the substituents, can also influence the polymerization reaction. Ethylene can not produce any polymer at  $-100^{\circ}\text{C}$  in the presence of  $\text{AlCl}_3$  in methylene chloride solvent, while, under the same condition<sup>5</sup>, propene gives a low molecular weight product and isobutene produces a high molecular weight polymer.

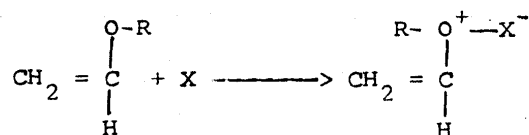
#### Aryl substituted olefins

The reactivity of aryl substituted olefins is also influenced by the basicity of the monomer. However, the basicity is governed by the aromatic substituent<sup>6</sup> and not by the electron density on the vinyl double bond. The steric factor plays an important role in the propagation step<sup>7</sup>.

#### Alkoxy substituted olefins

Alkoxy substituted olefins such as vinyl ethers are readily polymerizable by cationic processes. The polymerizability of the alkoxy substituted olefins can be widely influenced by their structural factors. In alkyl vinyl ether, the vinylic double

bonds are linked with a heteroatom, oxygen, having unshared electron pairs through which they form complexes with the aprotic acids by a dative bond.



The vinyl ethers differ from the alkyl or aryl substituted olefins in that they can form complexes with the aprotic acids through a dative bond. These are more basic than aryl substituted olefins because of their high electron density on the double bond.

Vinyl ethers are capable of acting as their own cocatalysts. This capability is strongly limited and even suppressed with more reactive alkyl vinyl ethers (cyclohexyl, isopropyl etc.) which form an inactive  $\pi$ -complex with the acceptors and consequently require the presence of a 'third component' (co-catalyst) to undergo polymerization<sup>8</sup>.

#### Styrene and its derivatives

The reactivity of these monomers is also governed by the basicity factor. The aromatic substituent enhances the basicity and in some cases the basicity of aromatic substituents enables



the monomer to the formation or ionization of the active complexes leading to higher reaction orders with respect to the monomer<sup>9,10</sup>.

### N-vinylcarbazole

N-vinylcarbazole (NVC) is by far the most reactive monomer among the nitrogen vinyls. NVC is a crystalline monomer<sup>11</sup> (m.p. 65°C) that can be polymerized by thermal<sup>12</sup>, free radical<sup>13</sup> and cationic initiation<sup>14</sup>. It consists of a carbazole ring with a vinylic substituent at the nitrogen atom. The lone pair of electrons on nitrogen atom makes it basic. This lone pair of electrons is delocalized over the carbazole ring and, as a whole, the monomer is a conjugated double bond system. The high concentration of negative charges ( $\pi$ -electron density) around the vinyl double bond makes the monomer adverse towards anionic polymerization. The cationic polymerization is also adversely affected by organic bases, such as aniline, N,N-dimethylaniline (DMA) and by water. In linear head-to-tail addition polymerization, NVC also undergoes reactions like the formation of complexes with the catalysts.

Lately, there is a voluminous literature on carbazole polymers which have been recognized as photoconductive polymers. Many carbazole polymers have appreciable thermal stability and find use as thermostable polymers. The dielectric properties of these polymers have also been studied.

## I.2 Types of Catalysts

Like the monomer and even in a more extensive measure, the catalyst can influence the mechanism of cationic polymerization. Electrophillic substances which under certain conditions are capable of inducing cationic polymerization fall into five groups :

- a) Protonic acids and acid surfaces
- b) Aprotic acids
- c) Carbonium salts
- d) Cationogenic substances
- e) Heterogeneous catalyst systems.

Since our research is mainly concerned with polymerization mainly by heterogeneous catalysts we intend to focus the pertinent achievements in this field.

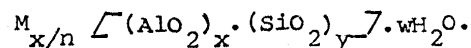
### Heterogeneous catalyst (solid phase)

During recent years, considerable interest has developed in the use of solid phase heterogeneous catalysts systems where the catalyst exists as a separate phase in the polymeric medium. Thus, for example, the developments on the Phillip's catalyst and its supports which grew out of the discoveries in England in 1930's, are still continuing and polymers prepared by Phillip's process are known to be distinctly

different with respect to density, crystallinity, and improved properties of the prepared polymers. Metal oxide catalysts<sup>15</sup> are also of immense importance for their use as heterogeneous catalyst. Very recently molecular sieves and carbon blacks have been used as heterogeneous catalyst for vinyl polymerization and hence a brief discussion is presented below for these two types of catalyst.

#### Molecular sieve

Molecular sieves are crystalline aluminosilicates or zeolites honey-combed with cavities which are interconnected by pores of diameter varying from 3-10 Å units<sup>16</sup>. These cavities are occupied by ions or water. The ions are comprised of group I and II elements, in particular, Na, K, Mg and Ca. The structural formula of a zeolite is best expressed for crystallographic unit cell as :



Where M is cation of valency n, w = number of water molecules and the ratio y/x usually has value of 1-5 depending upon the structure. The framework of molecular sieve contains channels and interconnected voids occupied by water molecules and cations which are thought to be source of its many and diverse properties which have been responsible for the successful

utilization of these molecular sieves as catalysts in the polymerization reactions. The catalytic activity of the molecular sieves is mainly due to cations only. However, Brönsted acids<sup>17,18</sup> and Lewis acid<sup>19,20</sup> sites and further electrostatic fields (and potentials)<sup>21,22</sup> have been reported to be responsible for the catalytic activity.

Among numerous molecular sieves and zeolites, the 13X and SK-500 molecular sieves have been extensively studied in relation to their polymerization characteristics. Barson et al.<sup>23</sup> reported the polymerization of styrene by a 13X molecular sieve. However, most of the vinyl polymerization by 13X and SK-500 molecular sieves and by their metal-exchanged variety have been studied and reviewed by Biswas, Maity<sup>16</sup> and Banerjee<sup>24</sup>.

#### Carbon black

Literature reveals some reports on vinyl polymerization catalyzed by carbon black with various functional groups and unpaired electrons present on the surface of carbon black which are responsible for the initiation and inhibition effect in different polymerization systems. It is usually believed that surface functional groups on the carbon black are mainly responsible for the initiation process<sup>25-27</sup>. However, the role of unpaired electrons and other surface properties on

the polymerization reaction by carbon blacks has so far been overlooked in earlier study<sup>28-30</sup>. The present study has been carried out considering the surface properties of carbon blacks and their role on the polymerization activity. A detailed discussion of this topic will be presented in a later section.

### I.3 Parameters Affecting Cationic Polymerization

In cationic polymerizations, besides the monomer and catalyst moiety, important roles are played by co-catalysts, solvents and of course temperature. However, instances have also been reported where the presence of co-catalyst is not necessary<sup>31-34</sup> for the initiation reaction. Detailed discussions are beyond the context of this work and hence not attempted.

#### Solvent

The role of solvents in the polymerization reactions manifests through polarity and basicity which have decisive effect on initiation, propagation and termination.

The degree of ionization or dissociation of the primary complex formed by the catalyst and/or monomer and the stabilization of the anionic counterpart do depend on the solvent.

Thus, the solvation power is an important factor in the activation of the primary complex. However, excess solvation of the primary complex and especially solvation of the cation causes a decreased polymerization rate or in some cases total inhibition of the polymerization reaction. The polarity of the solvent also plays an important role in the polymerization reaction. The dielectric and dipolar properties of the solvent influence the energy of charge separation and affect the solvation energy of ion or ion-pairs. Usually, as the dielectric constant of the solvent increases, the rate of cationic polymerization<sup>35</sup> increases markedly but not the molecular weight of the product. Besides the above two factors of the solvent, there are some instances where the solvents take part in reactions resulting in chain breaking<sup>36</sup> and effecting the molecular weight of the polymer.

#### I.4 Temperature

The effect of temperature on the cationic polymerization is quite significant. Generally, the fast reactions at low temperature and a negative temperature co-efficient of reaction rate are characteristics of cationic polymerizations. The radical and anionic polymerizations can be fast at temperatures well below 0°C, and that the rate of many cationic polymerizations has a positive temperature co-efficient<sup>37</sup>.

Beyond a temperature limit, the normal linear polymerization turns into a conjugated one<sup>38</sup>. This reveals the occurrence of maxima in the dependence of reaction rate and molecular weight. The overall reaction rate is a complex quantity and the partial elementary reactions composing it do not necessarily have the same turning temperature, so that the maximum is either blurred or not exhibited<sup>39</sup>.

In most cationic polymerization, the molecular weight increases with decreasing temperature. A plot of  $\log \bar{P}_n$  vs  $1/T$  follows straight line. The slope of this curve gives the apparent activation energy of  $\bar{P}_n$ . The dependence of  $\log \bar{P}_n$  on  $1/T$  can be linear only if the activation energies of all the chain breaking process are same. Otherwise,  $E_{\bar{P}_n}$  varies with temperature depending on which reaction predominates in the given condition.

#### I.5 Mechanism and Kinetic Aspects

It is indeed difficult to suggest a general valid reaction scheme or a mathematical formulation describing the kinetics of the cationic polymerization process because of the large impact of the concentration of reaction components, the composition of the solvents, and other reaction conditions on mechanism of these processes<sup>40</sup>.

The kinetic formulation is much more difficult for a heterogeneous catalytic system. Generally, the initiation occurs at a 'proton site' and the reaction propagates on the heterogeneous surface of the catalyst. In some heterogeneous catalytic polymerizations, transfer of an electron from the monomer moiety to the unpaired electron sites or the vacant sites of the catalyst initiate a polymerization reaction. In any case, adsorption of monomer moiety on the surface of the catalyst is an important aspect for the heterogeneous systems. However, kinetic formulations fall into three basic types<sup>40</sup> which appear to describe the behaviour of all the systems commonly met with :

(I) The rate of polymerization can be represented as follows<sup>41</sup>:

$$-\frac{d[M]}{dt} = k[M]^a [AB]^b \quad \dots (1)$$

where,  $[M]$  = monomer concentration,  $[AB]$  = concentration of the active complex, 'a' and 'b' are the orders with respect to monomer and active complex respectively.

When a cocatalyst is involved in the active complex formation, the rate expression follows :

$$-\frac{d[M]}{dt} = k[M]^a [catalyst]^b [cocatalyst]^c \quad \dots (2)$$

In case of monomer taking part in complex formation, 'a'



equals to 2. If solvation and stabilization of chain carrier involve monomer aids, the kinetic order may be still higher. Same is the case with the exponents 'b' and 'c'.

II. The second type of kinetic expressions are those which involve non-stoichiometric course of reaction. Such reactions have been discussed in relation to styrene -  $H_2SO_4$  system<sup>42,43</sup>.

III. Third type of reactions comprise of the cationic polymerization in which the equilibrium reaction is the rate determining step. The expression for the overall reaction rates is given by :

$$-\frac{d[M]}{dt} = \frac{KK'[C][M]}{1 + K'[M]} \quad \dots (3)$$

where,  $[C]$  = catalyst concentration and  $K'$  = equilibrium constant.

#### The degree of polymerization

The degree of polymerization  $\bar{P}_n$  of the polymer is determined by the ratio of the rate of chain growth to the sum of the rates of all chain breaking processes and of course the steady state concept is assumed,

$$\bar{P}_n = \frac{k_p[M]}{k_t + k_m[M] + [k_z][z_i]^{z_i}} \quad \dots (4)$$

where,  $K_Z$  = rate constant for transfer with impurities,  $Z_i$  and  $z_i$  = order with respect to  $Z_i$ . The equation (4) can be represented in the Mayo equation form :

$$\frac{1}{\bar{P}_n} = \frac{k_M}{k_p} + \frac{k_t + k_Z [Z_i]^{z_i}}{k_p [M]} \quad \dots (5)$$

$z_i$  is usually unity. The degree of polymerization should be linear function of  $[Z_i]$  if the composition of the active complex and the degree of dissociation of the ion-pairs remain same.

In order to explain non-linearity, the equation (5) can be written as :

$$\frac{1}{\bar{P}_n} = \frac{k_t}{k_p [M]} + \frac{k_Z [Z_i]^{z_i}}{k_p [M]} + \frac{k_Z \cdot \gamma_i [Y_i]^{y_i}}{k_p [M]} \quad \dots (6)$$

where,  $[Y_i]$  = concentration of ionized impurities,  $y_i$  = reaction order and  $\gamma_i$  = degree of dissociation.

The first term in equation (6) corresponds to the idea of closely conjugated ion pair at the growing end of macron . Chain breaking is then monomolecular reaction. The second term includes all bimolecular mechanism resulting in chain breaking, including chain transfer with monomer. The third term represents contribution of free anions and determines linearity of equation (5).

SECTION II : CARBON BLACK STRUCTURE-COMPOSITION AND  
GENERAL CHARACTERISTICS

Introduction

Carbon black, an industrial commodity of considerable technological and economical importance, is a component of many heterogeneous systems. It consists of spherical particles formed by pseudocrystallites of graphite and a certain amount of 'unorganized' carbon.

All varieties of carbon black contain significant amount of surface oxides which is definitely responsible for its chemical reactivity. Small quantities of oxygen are always found even in carbon black which has been graphitized at 3000°C. However, heating above 1500°C reduces the oxygen level to amounts which challenge the abilities of the analysts.

Besides the surface oxides, there are always a number of other elements present in carbon black which significantly influence its properties. Most carbon blacks contain materials extractable with organic solvents such as acetone, benzene, toluene etc. Particularly, thermal and furnace black may contain large quantities of extractables, usually dark colored materials.

Carbon black also contains a large amount of unpaired electrons which have been detected by electron spin resonance (ESR) in a number of carbon blacks of different origin<sup>44, 45</sup>. The possibility that these carbon blacks contain unpaired electrons on the surface has been the subject of speculation in recent years, primarily because such unpaired electrons might be expected to affect materially the reinforcement of high polymer, particularly elastomers, and possibly their resistance to oxidative attack.

The mechanism of carbon black reinforcement of elastomers has been the subject of intensive research, at times, of considerable controversy. General nonspecific Van der Waals adsorption, physical adsorption at active centres, chemisorption through functional groups on the carbon black surface, reaction with rubber involving vulcanizing agent, and reaction with rubber through the unpaired electrons (free radical acceptor) sites have all been proposed as explanations for the outstanding reinforcing qualities of carbon black<sup>44, 45</sup>. Lately, some attention has also been paid to a proper utilization of carbon black of active grades as potentially polymerization catalysts in which these systems show interesting variations from free radical to ionic mechanism involving the functional groups<sup>25, 26, 30</sup> as well as the unpaired electrons<sup>46</sup> on the surface of carbon black.

### Structure and Composition

The basic structural unit of carbon black is carbon element, present as partially broken crystallites of hexagonal layer type, somewhat similar to graphite crystals but much smaller. The building block, microstructure, of carbon black refers to the internal organization of the carbon within the particles of the solid which have been considered to be paracrystalline solids. Certain amount of "unorganized" carbon makes the crystallitic structure to be defective and distorted and as a whole carbon black is partially crystalline<sup>47</sup>. During the formation of carbon black by high temperature cracking process, small amounts of oxygen and hydrogen interact with the surface which is also partially responsible for destruction of crystalline structure.

The size or geometry, of the carbon black particles is important in regards to the structure. The minute size of the particles is a major factor for its unique reinforcing character. The openings or pores in the frame work are also important since for the use of carbon black as polymerization catalyst, they must be larger than the reactant and product molecules to allow these molecules to freely diffuse to and from the internal surface of carbon black.

Small amounts of surface oxides, detected as functional groups, are in fact much responsible for the unique structure

of carbon black differing from that of pure carbon, graphite and diamond. These functional groups determine the elemental composition of carbon black. In the subsequent paragraphs the structure, composition and the surface chemistry arising out of the functional groups and the other surface properties of carbon black have been discussed briefly.

(A) Microstructure

Carbon black is paracrystalline, an intermediate structural form between the graphite and a nontridimensional structure. Fig. 1.II.1(a) represents the well known structure of graphite. However, degenerate structures of lower degree of symmetry can be constructed from graphite structure. The degenerate forms, (a) turbostratic structure and (b) lubricostratic structure, are paracrystalline form whereas "amorphous" condition is that where carbon atoms are no longer located on the plane.

Investigation of microstructure of carbon blacks by X-ray diffraction study shows that three degenerate graphitic forms actually coexist in carbon black. Later studies show that certain amount of turbostratic structure<sup>50</sup>, and certain amount of "unorganized" carbon particles, which do not participate in the periodic structure<sup>51</sup>, are infact building block of the microstructure. However, the structure varies from grade to grade of carbon blacks. Austin<sup>52</sup> remarked

that the carbon microstructure depends essentially on the initial hydrocarbon and on the method of manufacture. The effect of heat treatment is an ordering and limited growth of crystallites of carbon black<sup>53</sup>.

An extensive study by the electron diffraction method<sup>54</sup> confirms the structure of carbon black to be the same as has been obtained by X-ray diffraction analysis of various grades of carbon black. Fig. 1.II.1(b) shows the microstructural model derived from the above studies.

(B) Surface Area

Surface area is an important characteristics of carbon black, particularly since the particles are very small and the specific surface area is very high. Following are the methods generally employed for surface area measurement of carbon black:

(a) Gas adsorption

(b) Iodine number

(c) Cetyltrimethylammoniumbromide (CTAB) adsorption.

Of these, gas adsorption is the best method to determine the total surface area precisely.

(a) Gas adsorption

This method is based on Langmuir's adsorption isotherm model in which monolayer of gas is adsorbed at low temperature

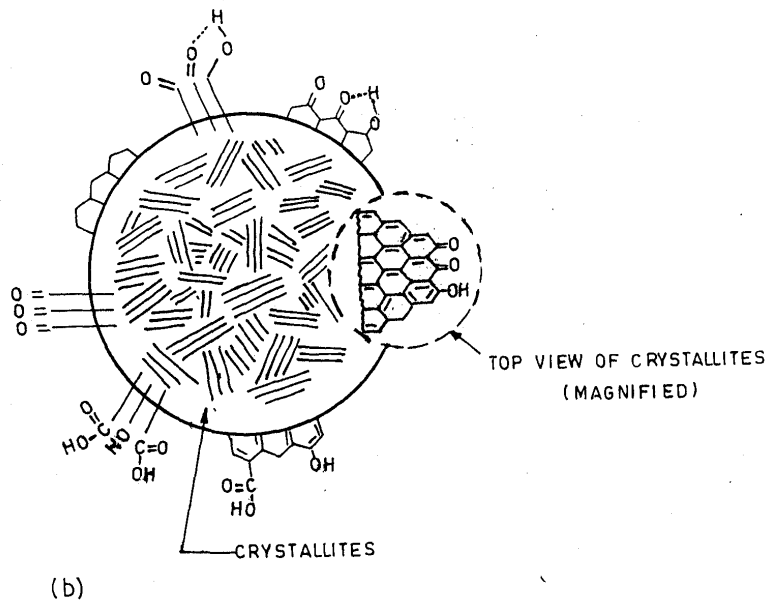
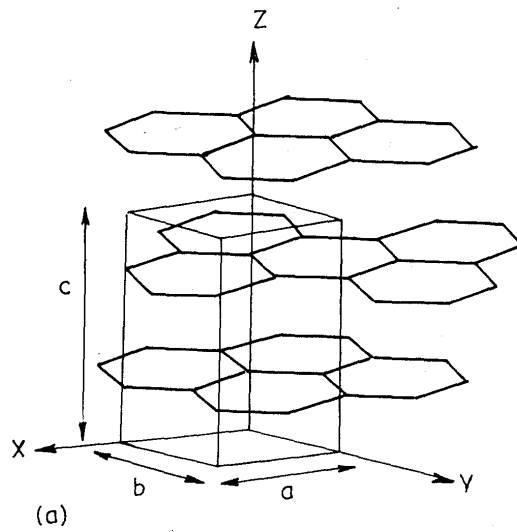


FIG. 1.II.1. (a) GRAPHITE STRUCTURE  
 (b) STRUCTURE OF CARBON BLACK  
 (WITH SURFACE OXIDES)



and the surface area is determined from the study of the adsorption isotherm. Langmuir's model of monolayer gas adsorption limits on perfectly smooth surface only. When the system is under equilibrium i.e. adsorption and desorption are equal, then :

$$b = \frac{kp}{1 + kp} \quad \dots (1)$$

where,  $b$  = surface covered by the adsorbed gas

$p$  = equilibrium pressure and

$k$  = constant.

Equation (1) can be transformed to the proper form of BET<sup>55</sup> equation (shown in Experimental Chapter) which can be employed successfully for carbon black surface area measurement. The samples which have significant porosity do not generally give good results of surface area measurement<sup>56, 57</sup>. The surface area of the presently studied carbon blacks have been measured by  $N_2$ -BET method.

(b) Iodine number

The amount of iodine adsorbed from a solution in mg per gram of carbon black is the iodine number. It is related to the surface area of carbon black and generally agree with the  $N_2$ -BET surface area for a number of carbon blacks. The presence of volatiles, high porosity and extractable materials influence the iodine adsorption number. The iodine number of

nonoxidized samples is almost equal to  $N_2$ -BET surface area but differs widely for oxidized samples<sup>58, 59</sup>.

Iodine number also decreases to great extent for the carbon black with high porosity. The large iodine molecule can not penetrate to the small pores of the sample and hence lowers the iodine number value than  $N_2$ -BET surface area value.

(c) CTAB adsorption

The CTAB adsorption by carbon black is independent of residual tar and surface oxides. Furthermore, CTAB molecules are much bigger than iodine and hence it excludes totally the internal surface. Janzen and Kraus<sup>58</sup> showed that smooth surface area calculated for a number of carbon blacks relates satisfactorily to the values obtained by correcting  $N_2$ -BET surface area for the calculated pores.

Composition

Carbon black contains significant amounts of noncarbon materials - hydrogen, oxygen, sulfur etc. The composition varies depending on the types of carbon black.

Elemental composition : Hydrogen is always associated with all grades of carbon black which varies one to ten atoms of hydrogen per hundred atoms of carbon. Both hydrogen and

oxygen have been regarded as potentially much more than innocuous impurities. Sulfur is partly free and partly chemically bound on carbon black surface. Table 1.II.1 shows elemental composition of a few of various grades of carbon black.

Ash content : Chemical analysis of ash shows that it contains sodium and magnesium chlorides and sulfates as water soluble component, and calcium carbonates and sulfates, and iron oxides and carbonates as water insoluble component<sup>60</sup>. Carbon black also contains very little amount of water<sup>61,62</sup> which decreases on relatively high temperature heat treatment<sup>63,64</sup>.

Extractable materials : Carbon black contains oily materials and tars as extractable materials and can easily be extracted with toluene, benzene etc. The nature of the tars have been studied and found to contain fused ring aromatics of relatively high molecular weight<sup>65</sup>. Non-aromatic compounds have also been found to present and they are identified as alkenes, dienes and related compound<sup>65</sup>.

#### Surface functional groups

Extensive studies have been done on the analysis, characterization and chemical reactivity of the surface oxides. The surface reactivity of carbon black, in particular, is for

TABLE 1. II. 1

ELEMENTAL COMPOSITION OF CARBON BLACKS

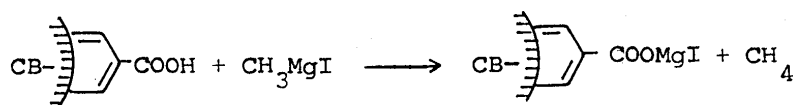
Designation	Code	C(%)	H(%)	O(%)	S(%)
Thermal black					
MT	N990	99.3	0.3	0.1	0.01
FT	N880	99.4	0.5	0.1	0.01
Furnace black					
SRF	N770	99.2	0.4	0.2	0.01
GPF	N660	98.7	0.4	0.2	0.50
HMF	N601	98.8	0.4	0.2	0.20
FEF	N550	98.4	0.4	0.6	0.60
Channel black					
High color	HCC1	84.0	11.0	-	-
Medium color	MCC1	95.0	3.3	-	-
EPC	S300	95.0	3.1	-	-
Lamp black	-	97.0	2.6	-	-

a large part dependent on the superficial chemical groups constituted by the surface oxides. In 1963 Smith<sup>65</sup> pointed out the presence of surface oxides from the adsorption and desorption behaviour of carbon black and later the study<sup>66,67</sup> of the nature of these oxides proved to be of two types, namely: (a) acidic oxides and (b) basic oxides. The nature, however, depends on the temperature of reaction with oxygen<sup>68</sup>.

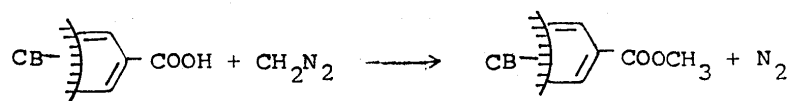
(a) Acidic oxides

Acidic surface oxides are formed when the reaction with oxygen takes place at high temperature. Mainly four acidic functional groups constitute the surface oxides. These are carboxyl, phenolic-OH, quinone and lactone groups. They are all chemically reactive and some of the reactions are unambiguous.

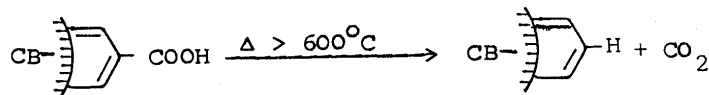
(1) Carboxyl groups: Both qualitative<sup>69-72</sup> and quantitative<sup>73,74</sup> reactions of carboxyl groups have been reported. Some typical chemical reactions are presented below:



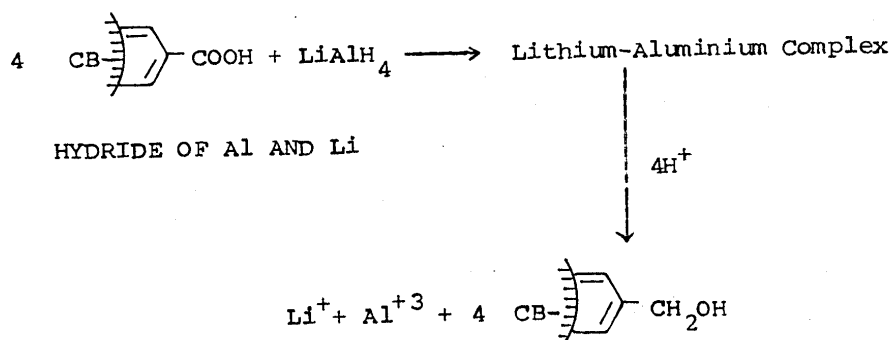
ORGANOMAGNESIUM COMPOUND



DIAZOMETHANE



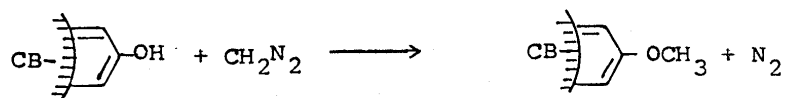
DECARBOXYLATION



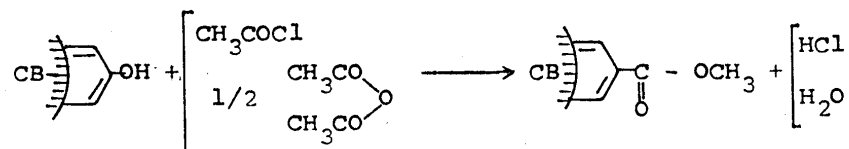
Puri and Bansal<sup>75</sup> studied titration curves of carbon black and suggested the presence of "frozen CO<sub>2</sub>" which behave more or less as carboxyl group. They also pointed out the heterogeneous characteristics of titration reaction caused by the influence of the diffusion of the reagent at the point of carboxyl group.

The presence of carboxyl groups confers hydrophilic character to carbon black.

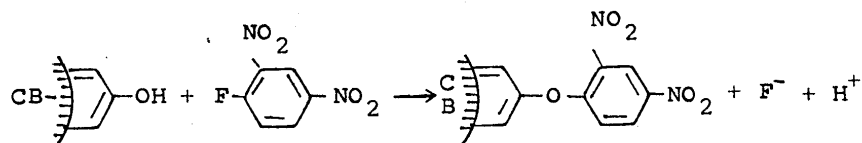
(2) Phenolic -OH groups : A relatively good amount of reactive phenolic -OH groups is present on carbon black surface. Some characteristic reactions<sup>71,73,76-78</sup> involving phenolic -OH groups are :



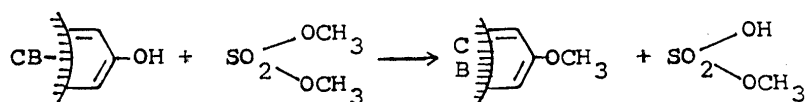
DIAZOMETHANE



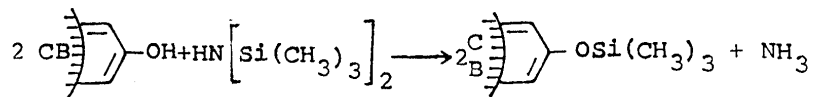
ACETYLATION



2,4-DINITROFLUOROBENZENE



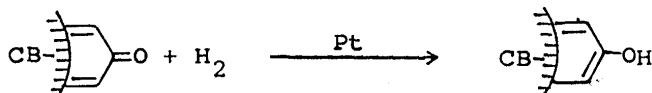
DIMETHYLSULFATE



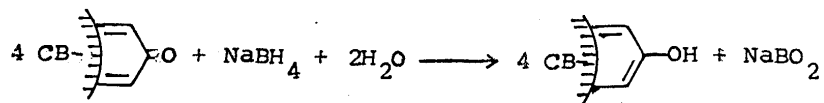
HEXAMETHYLDISILANE

Total acidity of carbon black surface is determined by direct titration of carboxyl and phenolic -OH group. However, the methylation with diazomethane and dimethyl-sulfate yields ethers which are easily differentiated from hydrolyzable esters formed simultaneously from carboxylic acid groups.

(3) Quinonic groups: Small amount of quinonic groups on carbon black surface behave somewhat like free quinones. Polarographic study permits the identification and characterization of this functional group<sup>79</sup>. Some characteristic reactions of quinonic groups<sup>71,79-82</sup> are :

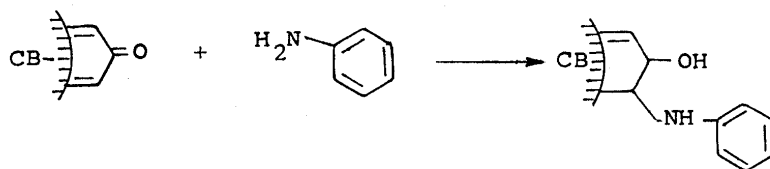


CATALYTIC HYDROGENATION



SODIUM BOROHYDRIDE





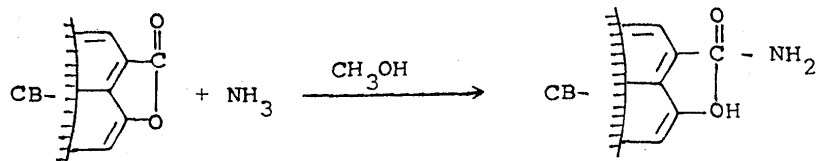
CONDENSATION OF ANILINE



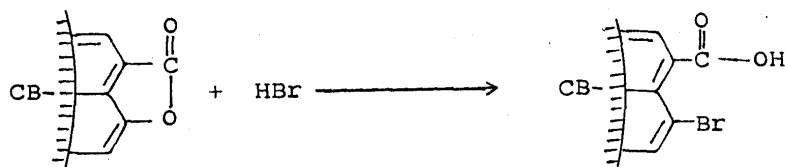
HYDROXYLAMINE

Quinonic functional groups favor the adsorption of benzene, probably due to interaction of  $\pi$ -electrons of benzene with the electrons of quinone functional groups.

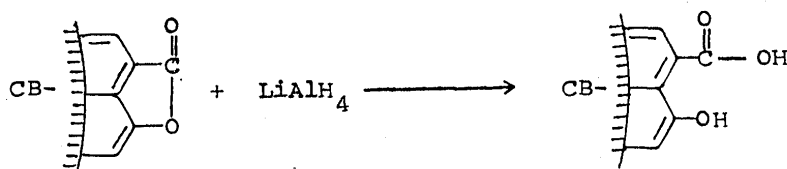
(4) Lactone groups : Minute quantities of lactone groups are present on carbon black surface. A few of the characteristic reactions<sup>70,82</sup> are :



AMMONIA



HYDROBROMIC ACID

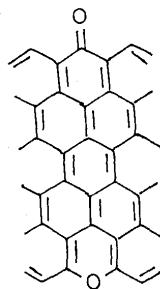
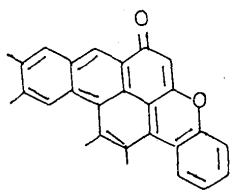
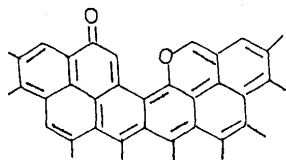


LITHIUM-ALUMINIUM HYDRIDE

Quantitative measurement of lactone group is difficult.

(b) Basic oxides

Very little is known about the oxides which are formed only at low temperature reaction of oxygen on carbon black surface. Boehm and Voll<sup>83</sup> proposed the following pyrone type structure for these oxides.



### Unpaired electrons

All grades of carbon black contain appreciable amounts of unpaired electrons, a large portion of which may be expected to reside in crystallites exposed to the surface. It is more likely that the spins possess mobility within each quasi-graphitic molecules making up the crystallites. Since, such mobility is the characteristics of  $\pi$ -electrons, it is concluded that the unpaired spins on the carbon black surface are most likely  $\pi$ -electrons<sup>84,85</sup>. A little amount of unpaired electrons resides in the bulk and do not possess any mobility. They have  $\sigma$ -characteristics<sup>85</sup> and are not available for superficial reactions. On heat treatment, very little oxygen sensitivity to unpaired electrons is found, and this suggests immobile unpaired electrons distribute through the bulk phase<sup>85</sup>.

SECTION III. RESUME OF SIGNIFICANT DEVELOPMENTS ON THE USE  
OF CARBON BLACK AS A POLYMERIZATION CATALYST

The discovery, that the carbon blacks possess catalytic activity, has added new dimensions to the field of heterogeneous catalysis and catalytic processing for the simple reason that their activity and selectivity can be tailored to produce specific desired reactions. Again the discovery that various grades of carbon black can act as polymerization catalyst has tremendously enhanced the scope and importance of these materials.

Ohkita et al.<sup>28-30</sup> carried out the polymerization reactions employing carbon black as a catalyst. They studied the relative catalytic activities of modified and unmodified carbon blacks. When carbon black is oxidized by  $H_2O_2$ , which increases the acidic functional groups on the carbon black surface, the reaction rate of polymerization is increased<sup>30</sup>. However, treatment of oxidized carbon black with 2-2'-diphenylpicryl hydrazil (DPPH) reduces the catalytic activity which may be encountered due to loss of unpaired electrons capable of initiating a polymerization reaction<sup>46</sup>.

In the study of free radical polymerization of vinyl monomers by carbon black, the latter is invariably used along with the other free radical initiators<sup>29, 30</sup>. Hence, such

reactions do not provide any specific information about the capabilities of carbon black itself in initiating a free radical polymerization but they show the effect of carbon black surface on the free radical polymerization. The polymerization of vinyl monomers has been studied in the presence of carbon black employing different free radical initiators such as benzoyl peroxide, phthaloyl peroxide and others<sup>28-30</sup>, and the results show that a change of the initiator in the reaction has a significant effect on the rate of polymerization. For example, in the bulk polymerization of styrene<sup>28</sup> at 45°C in the presence of phthaloyl peroxide and carbon black (Philblack O HAF), the conversion is higher than that with the use of benzoyl peroxide in place of phthaloyl peroxide. The polymerization of methyl methacrylate (MMA) has been found to be reverse, indicating that the polymerization depends not only on the initiator used but also upon the monomer. In all cases the reactions are found to possess lower rate of polymerization in the presence of carbon black than in its absence. Also a comparative study of the polymerization reactions of different monomers, initiated by benzoyl peroxide in the presence of carbon black has revealed that carbon black has significant effect on retarding the reaction rate<sup>86</sup>. Thus, the polymerization of styrene and MMA initiated by benzoyl peroxide in the presence of carbon black is retarded sufficiently because carbon black undergoes reaction with benzoyl peroxide and

hinders homopolymerization. The presence of inherent unpaired electrons on the surface of carbon black is responsible for the electron accepting and donating properties, which might have caused the inhibition of benzoyl peroxide initiated polymerization of styrene and to less extent of MMA. Similar findings have also been observed in the free radical polymerization of chloroprene by p-benzoquinone in the presence of carbon black<sup>64</sup>. In this case, the inhibition of radical polymerization is assumed to be due to quinone groups on the surface of carbon black. It is possible to relate the concentration of carbon black and the inhibition factor in the way that the logarithm of the inhibition factor<sup>64</sup> increases linearly with the amount of carbon black during the bulk polymerization of chloroprene in the presence of an amount of p-benzoquinone equal to that on the carbon black surface.

The oxygen containing groups on the carbon black surface have tremendous influence on the rate of polymerization reaction. The thermal polymerization of styrene in the presence of carbon black, untreated and treated with azobisisobutyronitrile (AIBN) or diazomethane, reveals that in case of untreated carbon black, the rate of polymerization is inhibited, suggesting that quinone type oxygen on carbon black surface probably inhibits the thermal polymerization<sup>28</sup>. When carbon black is treated with AIBN or diazomethane, quinonic group loses reac-

tivity and the thermal polymerization is found to be accelerated. This reaction has also shorter induction period than the untreated carbon black catalyzed polymerization. The thermal polymerization is found to have higher induction period if carbon black is reduced with sodium borohydride. However, acceleration occurs in the later stage of polymerization. These observations suggest that decreased rate of the polymerization in the presence of carbon black is most probably due to the presence of -O- containing groups. When strong reducing agents such as diazomethane, AIBN,  $\text{NaBH}_4$  are added, the quinonic oxygen groups are converted to phenolic -OH groups<sup>70</sup> which may be mainly responsible for the acceleration of the reaction in the later stages.

All free radical polymerizations in the presence of carbon black are inhibited due to the inhibition effect arising from quinonic groups present on the carbon black surface. Furthermore, the free radicals interact with the unpaired electrons on the surface of carbon black due to which the rate of polymerization decreases.

Useful information on the polymerization of NVC catalyzed by carbon black is provided by the copolymerization reaction with styrene and MMA. Styrene gives copolymer with NVC while MMA does not produce copolymer during the early stage of polymerization. It is proposed that phenolic -OH

groups on the surface of carbon black have no ability to initiate the polymerization and increase the dielectric constant of the solvent (solvent-catalyst interactions), which further enhances the rate of polymerization. The prior treatment of carbon black surface by  $\text{NaBH}_4$  which reduces quinonic functional groups<sup>70</sup> to phenolic -OH groups, enhances the copolymerization. On the contrary, the polymerization of NVC by diazomethane treated carbon black is seriously impaired due to the loss of accelerating effect of the phenolic -OH groups which decrease on treatment with diazomethane, as endorsed by DPPH determination of phenolic -OH groups.

Highly acidic channel black initiates the polymerization at low temperature ( $20^\circ\text{C}$ ), whereas furnace black containing relatively low amount of carboxyl groups can initiate the polymerization only at elevated temperature<sup>90</sup>. Given et al.<sup>91</sup> also reported that 2-methyl propene and isobutene can be polymerized by channel black and the surface acidic functional groups of the channel black have been considered to be mainly responsible for the initiation of the polymerization. The treatment of channel black with acid neutralizing agents causes retardation in the polymerization. Diazomethane reacts with carboxyl and phenolic -OH groups on the surface to produce methoxy groups and such treatment inhibits polymerization. It is clear that a cationic mecha-



nism is probably operative in which initiation is believed<sup>e 88-91</sup> to occur through acidic sites, especially carboxyl groups, on the surface of channel black.

In all these cases, initiation of polymerization is believed to occur through acidic functional groups on the surface of carbon black. However, these mechanisms ignore the role of surface unpaired electrons of carbon black. Further, surface area plays an important role in heterogeneous catalytic reactions. Lowest activity of Philblack O (HAF) may be due to low surface area ( $79.6 \text{ m}^2/\text{g}$ ) as compared to acidic channel blacks (Carbolac-I HCC,  $839.2 \text{ m}^2/\text{g}$ ). Ohkita et al.<sup>29,30</sup> attributed the inhibitory effect of DPPH for the polymerization of NVC to a decrease in the number of acidic functional groups through reaction of functional groups with DPPH. According to our proposal to be highlighted in the thesis such observation can be reinterpreted in terms of the radical scavenging action of DPPH on the unpaired electrons of carbon black surface. However, the acidic functional groups are inherently too weak<sup>46</sup> to initiate a cationic polymerization, nevertheless they have been assumed to be the major chain initiating entities. We<sup>46</sup> have concentrated on this point in our work and have tried to bring out the role of unpaired electrons in such polymerization.

SECTION IV. SOME GENERAL ASPECTS OF CHEMICAL MODIFICATION OF CARBON BLACK

Since a major part of the research presented in the thesis involves reactions with modified carbon black, we intend to have a brief discussion on the present status of research in this direction.

The most important chemical modification is oxidation of carbon black which is characterized by fixation of oxygen on the particles and the formation of oxidation products, such as carbon dioxide and carbon monoxide. Consequently, the surface area, porosity, surface functional groups, unpaired electrons and even electrical conductivity of carbon black change due to oxidation. The nature of oxidized products depends on the type of the reagent used for this purpose. The oxidation method can be classified in two categories: (a) gas phase oxidation, (b) liquid phase oxidation.

(a) Gas phase oxidation : In this method, carbon black oxidation is carried out by oxidizing gases. Molecular oxygen<sup>92,93</sup>, atomic oxygen<sup>94</sup>, ozone<sup>95,96</sup> and dry or humid air<sup>97</sup> are used for oxidation. Mixture of gases<sup>98</sup> can also be used for this purpose. The amount of oxygen containing groups increases<sup>92</sup> continuously during oxidation until to the saturation point.

The oxidation is affected by temperature of reaction and relative oxygen pressure<sup>92</sup>.

As the amount of surface functional groups increases by oxidation, carbon black becomes more hydrophilic in character<sup>99</sup> and the pH of carbon black changes to acidic region<sup>100</sup>. In general, the BET surface area increases more rapidly than the geometric surface area, due to formation of pores<sup>92,93</sup>. Which are created probably due to removal of one or more layer planes by oxidation.

The ash content of carbon black influences the oxidation process<sup>101</sup>. If the ash contains catalytically active substances such as alkali salts, the oxidation reaction with carbon black is catalyzed. Otherwise, the oxidation follows non-catalytic process.

(b) Liquid phase oxidation : Most carbon blacks are oxidized in liquid phase in which liquid oxidizing agents are used. The oxidation in liquid phase is characterized by the formation of carbon dioxide and the creation of surface oxides groups on carbon black. These surface oxides are mainly carbonyl, hydroxyl and carboxyl groups. A little amount of soluble degradation product is also formed by oxidation. Numerous oxidizing agents have been used for carbon black oxidation. Of them, nitric acid<sup>102</sup>, potassium permanganate<sup>102</sup>, chlorite,

chlorate and perchlorate of sodium<sup>102</sup>, aqueous solution of oxone<sup>103</sup> and bromine<sup>104</sup>, mixtures of aqueous solution of potassium chromate and phosphoric acid<sup>105</sup>, and Simon's reagent<sup>106</sup> (mixture of sulfuric acid and silver bichromate) have been extensively used.

The oxidation proceeds in three steps<sup>103</sup>. First, chemical functions are created on the surface and some degradation products which are an intricate mixture of chemicals, mainly consisting of complex polyphenols with short aliphatic side chains, are also formed. Second, less organized carbon particles are oxidized to carbon dioxide. Third, the oxidation of organized particles proceeds slowly. The formation of carbon dioxide does not originate from decarboxylation<sup>107</sup> unless at elevated temperature. Degradation products are formed from "unorganized" carbon particles, and hence direct formation of carbon dioxide is an excellent indicator of the degree of organization of the carbon particles. Voet and coworkers<sup>108</sup> found that prolonged oxidation by nitric acid causes the carbon black particles cemented together by the degradation products to form huge, micron size lamellae.

The properties of oxidized carbon blacks differ from those of nonoxidized carbon blacks, especially in their application. Oxidized channel blacks are used in high grade printing inks and lacquers. The reinforcement of butyl rubber with

oxidized carbon black is superior to nonoxidized carbon black<sup>109</sup>, due to large amount of functional groups in the former. However, it is not clearly known what surface groups play an important role in the formation of polymer-filler bonds. An increase in oxygen containing groups decreases the risk of premature vulcanization. Oxidized furnace black is super reinforcing fillers for butyl rubber.

Keeping these developments in view we have attempted to suitably modify some grades of carbon black with a view to improving their polymerization initiating activity.

SECTION V. SOME GENERAL ASPECTS OF SYNTHESIS OF  
POLYMER GRAFTED ON CARBON BLACK

A part of the work highlighted in the thesis is concerned with preparation of carbon black grafted polymer through a novel but simple procedure, developed by us. In order that the significance of the work may be assumed in the proper prospective - it is thought worthwhile to focus in this section some developments in the synthesis of polymer grafted on carbon black. Attempts have been made to produce polymer grafted carbon black using varieties of monomer and various grades of carbon black. The formation of polymer graft carbon black is ascertained by the formation of stable colloidal solution formed after the reaction. High speed centrifugation and standing the solution for indefinite period can not separate the carbon black particles from the solution. During the polymerization reaction, some portion of the formed polymer undergoes grafting and some portion remains ungrafted which can be easily separated by soxhlet extraction with suitable solvent. The grafting ratio and graft efficiency are determined by using the following equations :

$$\text{Grafting ratio (\%)} = \frac{\text{Weight of polymer grafted}}{\text{Weight of carbon black used}} \times 100$$

$$\text{Grafting efficiency(\%)} = \frac{\text{Weight of polymer grafted}}{\text{Weight of total polymer produced}} \times 100$$

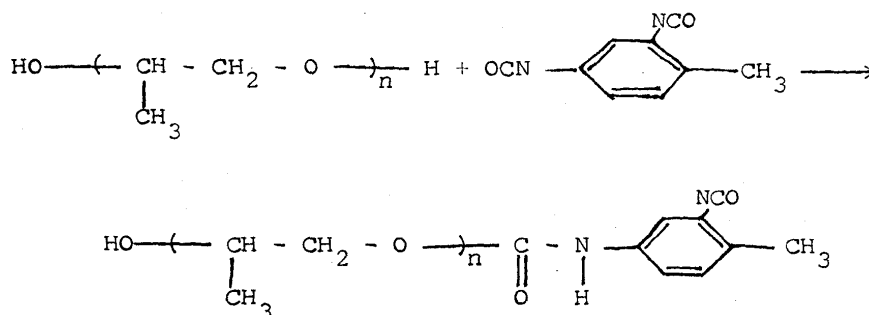
Both the grafting ratio and grafting efficiency depend on the monomer and the nature of the carbon black. Grafting mainly occurs due to interaction of the surface functional groups on the carbon black and the polymer. So, carbon black enriched with surface functional groups are preferred for grafting. However, other surface properties may influence the grafting but those are not exclusively studied so far.

Grafting involving carbon black/polymer systems can be classified into three types depending on the process :

- (a) Grafting of a prepolymer
- (b) Grafting of polymer in carbon black-initiator system
- (c) Grafting of polymer in carbon black system.

Basic difference is the process of grafting otherwise the grafting characteristics remain same in all cases.

(a) Grafting of prepolymer : In this process the polymer is prepared first and then treated with carbon black, the unreacted carbon black being centrifuged out using suitable solvent for the polymer. Tsubokawa et al.<sup>110</sup> reported the grafting of urethane on channel black. The grafting occurs as :



(Prepolymer)

First, the urethane is prepared by heating poly-propylene-glycol (PPG) and toluene diisocyanate (TDI) and grafting is performed with carbon black at 120°C under nitrogen atmosphere. The grafting ratio in this case is determined from the amount of prepolymer irreversibly fixed on the surface of carbon black by the following equation :

Grafting ratio (%) =

$$\frac{\text{Weight of carbon black obtained from the reaction} - \text{Weight of carbon black used}}{\text{Carbon black used}} \times 100$$

Grafting ratio is independent on the amount of carbon black.

It is suggested that prepolymer interacts with the surface



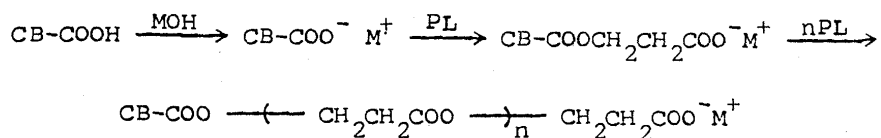
carboxyl and phenolic -OH groups on carbon black resulting into grafting of polymer. Minoura and Katano<sup>87</sup> reported that Polystyrene can be grafted onto the carbon black surface. They obtained the graft polymer using the reaction of living anionic polystyrene with carbon black and believed the reaction to be due to interaction of acidic functional groups on black surface with the living polymer.

(b) Grafting of polymer in carbon black-initiator system : In general, grafting of vinyl monomers onto the surface of carbon black occurs during the polymerization by radical<sup>25</sup>, anionic<sup>26,27,111</sup> or cationic initiators<sup>112</sup> in the presence of carbon black. However, the grafting ratio in these systems is not too high, less than 10% in a radical polymerization system.

Tsubokawa et al.<sup>113</sup> reported the polymer graft-carbon black during the polymerization of MMA with enolizable ketone ( $R_1-CO-CH_2-O-R_2$ )-carbon black system. The polymer grafted carbon black gives stable colloidal dispersion in organic solvents such as benzene, acetone and chloroform. The grafting ratio of poly-MMA-grafted carbon black is large in enolizable ketone-carbon black initiation system.

Carbon black containing alkali metal carboxylate group can initiate the anionic ring opening polymerization of  $\beta$ -propiolactone (PL). The product polyester grafts efficiently on

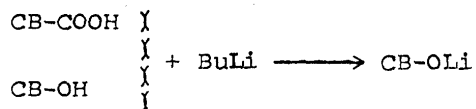
the surface of carbon black<sup>114,115</sup>. The reaction occurs through the functional groups.

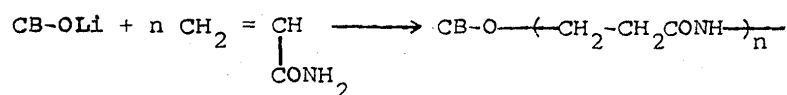


where, M = Na, K, Cs, etc.

The rate of polymerization and grafting depends on the ionic nature of the alkali metal. In this anionic polymerization system, the grafted polyester propagates from  $\text{-COO}^- \text{M}^+$  groups and shows profound effect on temperature and solvent. High grafting ratio is obtained by controlling chain transfer reaction which can be brought by lowering the reaction temperature. The high dielectric constant of the solvent increases the separation of negative charge of  $\text{-COO}^- \text{M}^+$  ion enhancing chain transfer reaction and thus leads to lower grafting ratio.

Grafting of poly- $\beta$ -alanine occurs during the polymerization of acrylamide initiated by lithium phenolate group on the surface of carbon black<sup>116</sup>. The reaction scheme can be shown as :

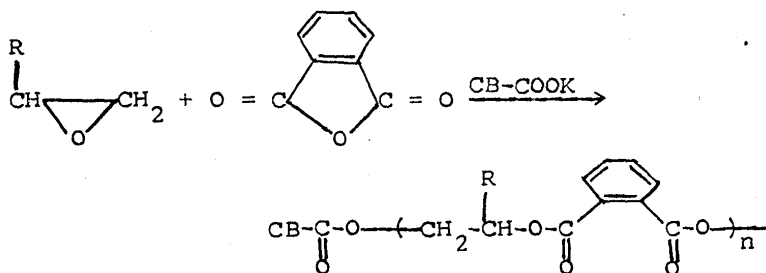




Poly-β-alanine grafted carbon black

The polymerization reaction occurs by hydrogen transfer of β-alanine by -OLi group on the carbon black surface.

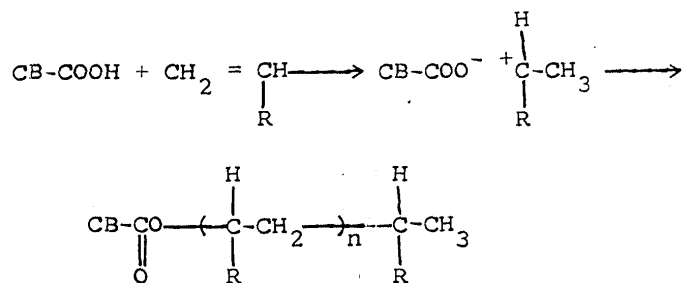
The grafting of polyester dicarboxylic acid anhydride copolymer onto carbon black through polyester end during copolymerization of epoxide with phthalic anhydride has been reported by Tsubokawa et al.<sup>117</sup>



The grafting ratio is lower than that obtained from anionic ring opening polymerization of β-propiolactone. It is apparent that -COOK groups have an ability to initiate copolymerization of epoxides with dicarboxylic acid anhydrides and that various kinds of polyester can be grafted onto carbon black surface.

(c) Grafting of polymer in carbon black system : During polymerization of vinyl monomers by carbon black, some portion of

product polymer may be grafted on carbon black surface. The polymerization of NVP with highly acidic channel black results in polymer grafted carbon black, though the yield is very low<sup>118</sup>. The grafting efficiency is only about 1%. The amount of poly-NVP grafted carbon black decreases by hydrolysis, suggesting the role of acidic functional groups in grafting which may occur as :



In the light of these foregoing discussions it appears that grafting essentially involve interaction of surface functional groups of carbon black and the monomer moiety. However, our observations on the NVC-carbon black graft systems are somewhat novel in the sense that grafting occurs during polymerization of NVC in presence of acid modified N220 without any selective catalyst, Detailed discussions will follow in due course.

SECTION VI. OBJECT AND SCOPE OF THE PRESENT INVESTIGATION

The work embodied in this thesis attempts to elucidate the polymerization initiation characteristics of modified and unmodified (Furnace Black, N220 and N110, N330, N660 and N774) carbon black in respect of the solution polymerization of NVC. The survey of the relevant literature on carbon black and its role as a polymerization catalyst, as out-lined in the previous sections, indicates that earlier research is mainly concerned with channel black or high acid carbon blacks as the polymerization catalyst. In many cases carbon black has been used in conjunction with other initiators (AIBN etc.) and in these studies the surface functional groups are regarded to be mainly responsible for initiating the polymerization reaction. Thus, many of these results are confusing as to the specific contribution of carbon black to the polymerization initiation mechanism.

In a few cases, carbon black alone has been used to induce the polymerization of cation active monomers. The popular mechanism set forth for these polymerizations involves the participation of -COOH and phenolic -OH groups of carbon black in the initiation process. However, the contention is acceptable only partially because it is well known that the Brönsted acidity of surface -COOH groups or phenolic -OH groups

is certainly not very strong so that facile polymerization with high conversion and molecular weight can be achieved as claimed by these authors. These observations imply that there must be a more fundamental process of initiation mechanism involved in these reactions.

Yet another draw back of above mechanism is that they do not consider a very fundamental fact about the nature of active carbon black surface, that is, the fact that carbon blacks contain a significant concentration of unpaired electrons<sup>84,85</sup>. The well known chemical nature of the heteroatom containing monomers such as NVC, NVPD and IBVE to undergo facile charge transfer reaction with electron deficient compounds has therefore been ignored in formulating the generalized mechanism explaining the initiation of polymerization by surface groups of carbon black.

It has therefore been the most significant objective of the present research to focus the role of surface unpaired electrons in the initiation process of such polymerizations.

The second objective of this research has been to assess the various grades of furnace blacks (at least five different grades, N110, N220, N330, N660 and N774) in regard to their efficiency as initiators of the cationic polymerization of NVC. So far, no such clear cut attempt appears to have been

made in correlating the activities of these various grades of carbon blacks. The result of such study will establish the best catalyst to be chosen for a particular polymerization process.

The third objective of this work has been to explore the feasibility of improving the catalytic activity of these conventional carbon black grades by appropriate chemical modification. In the introductory section, it has been discussed in the light of existing literature how it is possible to subject carbon black to various chemical treatments leading to modified products with different catalytic activity from the unmodified substance. In view of this, attempts have been made in the present study to chemically modify carbon black through simple treatment with oxidizing acids. The improved catalytic reactivity of the oxidized carbon black thus obtained has been utilized in the polymerization of NVC and the features have been compared with those derived from the usual unmodified carbon black as the catalyst.

In a novel attempt to modify carbon black to a stereoregulating catalyst, the reaction of dialkyl zinc with carbon black has been examined in regard to NVC polymerization. The guiding idea has been that carbon black might provide a selective environment for stereoregular propagation of the polymerization. Of course, it is imperative that the carbon

black be halogenated by treatment with thionylchloride so as to replicate a metal halide-alkyl halide type of catalyst system (as in conventional stereoregular catalyst system).

The fourth objective of this work has been to draw a suitable mechanism of polymerization by carbon black taking into account all possible kinetic features. The later necessarily includes a typical evaluation of the essential kinetic parameters such as dependence of the rate of polymerization on monomer and catalyst concentration, temperature, additive, preheating temperature and solvent effect. On the basis of these kinetic conclusions thus achieved, attempts have been made to formulate a kinetic expression accounting for the observed characteristics.

The final objective of the work has been to explore the feasibility of preparing polymers grafted onto carbon black surface. This necessitated the formulation of the appropriate reactants and fixing up of the appropriate reaction conditions such as modification of catalyst surface, concentration of the reactants, solvent and temperature. The unique feature of the study has been the use of a modified carbon black alone as a catalyst and it is in this respect that the work reported is distinctly different from the conventional grafting procedures used by the contemporary research workers in this field.



Perhaps, it may be relevant to conclude the discussion with the observation that this study has revealed several features (mechanistic as well as kinetic) not hitherto focussed by any other studies in this or related field.

R E F E R E N C E S

1. Zlamal, Z. Vinyl Polymerization, Part II, Vol. 1, Ed. George E. Ham, Marcel Dekker, N.Y., 1969, p. 243.
2. Kennedy, J.P. Cationic Polymerization of Olefins - A Critical Inventory, Wiley-Interscience, N.Y., 1975, p.29.
3. Roberts, D.E. J. Res. Natl. Bur. Std., 44, 221 (1950).
4. Evans, A.G. and Polanyi, M. Nature, 152, 738 (1943).
5. Zlamal, Z. Vinyl Polymerization, Part II, Vol. 1, Ed. George E. Ham, Marcel Dekker, N.Y., 1969, p. 244.
6. Elliot, B., Evans, A.G. and Owen, E.D. J. Chem. Soc., 689 (1962).
7. Kennedy, J.P. Cationic Polymerization of Olefins - A Critical Inventory, Wiley-Interscience, N.Y., 1975, p.35.
8. Eley, D.D. and Johnson, A.F. J. Chem. Soc., 2238 (1964).
9. Colclough, R.O. and Dainton, F.S. Trans. Faraday Soc., 54, 886 (1958).
10. Reppe, W. and Keyssner, E. German Pat., 618,120 (1935); Chem. Abst., 30, 110 (1936).

11. Gandini, A. and Plesch, P.H. J. Chem. Soc., B, 7 (1966).
12. Reppe, W. U.S. Department Commerce, Office of Technical Service, B.D. Rep., 18, 852S (1949).
13. Ellinger, L.P. J. Appl. Polym. Sci., 9, 3939 (1965).
14. Jones, G.D. Cationic Polymerization, Ed. P.H. Plesch, Pergamon Press, Oxford, 1963, p.542.
15. Biswas, M., Maiti, M.M. and Ganguli, N.D. Die Makromol. Chem., 124, 263 (1969).
16. Biswas, M. and Maity, N.C. Adv. Polym. Sci., 31, 47 (1979).
17. Ward, J.W. J. Catal., 9, 225, 396 (1967).
18. Ward, J.W. and Hansford, R.C. J. Catal., 13, 364 (1969).
19. Tung, S.E. and Melninch, E. J. Catal., 10, 166, 175 (1968).
20. Turkevich, J., Nozaki, F. and Stamires, D.N. International Congress of Catalysis, Amsterdam, North Holland, Amsterdam, 1965, p.586.
21. Pickent, P.E., Rabo, J.A., Dempsy, E. and Schomaker, V. International Congress of Catalysis, Amsterdam, North Holland, Amsterdam, 1965, p.714.
22. Rabo, J.A., Angell, C.L., Kasai, P.H. and Schomaker, V. Discuss. Faraday Soc., 41, 328 (1966).



23. Barson, C.A., Knight, J.R. and Robb, J.C. Brit. Polym. J., 4, 427 (1972).
24. Biswas, M., Banerjee, M. and Maiti, M.M. J. Polym. Sci. Polym. Chem. Ed., 22, 1979 (1984).
25. Ohkita, K., Tsubokawa, N. and Saitoh, E. Carbon, 16, 41 (1978).
26. Ohkita, K., Nakayama, N. and Shimomura, M. Carbon, 18, 277 (1980).
27. Ohkita, K., Nakayama, N. and Tsujita, T. Carbon, 16, 155 (1978).
28. Ohkita, K., Tsubokawa, N., Saitoh, E., Noda, M. and Takashina, N. Carbon, 13, 443 (1975).
29. Ohkita, K., Uchiyama, M. and Nishioka, H. Carbon, 16, 195 (1978).
30. Ohkita, K., Tsubokawa, N., Noda, M. and Uchiyama, M. Carbon, 15, 195 (1977).
31. Biswas, M. and Chakravorty, D. Macromol. Chem., 163, 37 (1973).
32. Biswas, M. and Kamannarayana, P. J. Polym. Sci., Polym. Chem. Ed., 13, 2035 (1975).
33. Ellinger, L.P. Chem. Ind., 1982 (1963).
34. Pac, J. and Plesch, P.H. Polymer, 8, 237 (1967).
35. Zlamal, Z. and Kazda, A. J. Polym. Sci., 53, 203 (1961).

36. Flesch, P.H. J. Chem. Soc., 1953 (1953).
37. Allen, P.E.M. and Plesch, P.H. Cationic Polymerization, Ed. P.H. Flesch, Pergamon Press, Oxford, 1963, p.542.
38. Schmerling, L. and Ipatieff, V.N. Adv. Cat., 2, 21 (1950).
39. Zlamal, Z., Vinyl Polymerization, Part II, Vol. 1, Ed. George E. Ham, Marcel Dekker, N.Y., 1969, p. 234.
40. Zlamal, Z. Vinyl Polymerization, Part II, Vol. 1, Ed. George E. Ham, Marcel Dekker, N.Y., 1969, p. 294.
41. Imoto, M. Kobunshi Kagaku, 13, 295 (1956).
42. Burton, R.E. and Pepper, D.C. Proc. Roy Soc., A 263, 58 (1961).
43. Hayes, M.J. and Pepper, D.C. Proc. Roy Soc., A 263, 63 (1961).
44. Johnson, P.J. and Eberline, C.R. Encyclopedia of Chemical Processing and Design, Eds. J.J. McKetta and W.A. Cunningham, Marcel Dekker, Inc., N.Y., 1977, Vol. 6, pp. 187-257.
45. Dannenberg, E.M. Kirk-Othmar Encyclopedia of Chemical Technology, 3rd Edn., Eds., M. Grayson and D. Eckroth, Wiley-Interscience, , 1978, Vol. 4, pp. 631-666.

46. Biswas, M. and Haque, S.A. J. Polym. Sci. Polym. Chem. Ed., 21, 1861 (1983).
47. Warren, B.E. J. Chim. Phys., 2, 551 (1934).
48. Maire, J. and Mering, J. Proc. 4th Conf. on Carbon, p. 345 (1960).
49. Maring, J. and Maire, J. Les Carbones, Mason, Paris, Vol. 1, p. 162 (1965).
50. Hoffman, U. and Wilm, D. Z. Electrochem., 42, 504 (1936).
51. Franklin, R.E. Proc. Roy Soc. (London), 209, 196 (1950).
52. Austin, A.E. Proc. 3rd Conf. on Carbon, p. 389 (1958).
53. Kotlensky, W.V. and Walker, Jr., P.L. Proc. 4th Conf. on Carbon, p. 423 (1960).
54. Kasatotshkin, V.L., Lukianovitch, V.M., Popov, N.M. and Tschmutov, K.V. J. Chim. Phys., 52, 822 (1964).
55. Brunauer, S., Emmett, P.H. and Teller, E. J. Am. Chem. Soc., 59, 1553 (1938).
56. Kodera, K. and Onishi, V. Bull. Chem. Soc. Japan, 32, 356 (1959) and 33, 338 (1960).
57. Haul, R.A.W. Angew. Chem., 68, 238 (1956).
58. Janzen, J. and Kraus, G. Rub. Chem. Technol., 44, 1287 (1971).

59. Janzen, J. and Goodarz-Nia, I. J. Coll. Interf. Sci., 69, 473 (1976).
60. Lewis, J.E., Deviney, Jr., M.L. and McNabb, C.F. Rub. Chem. Technol., 43, 449 (1970).
61. Pierce, C. and Smith, R.N. J. Phys. Chem., 57, 64 (1953).
62. Kiselev, A.K. Rev. Gen. Caout., 41, 377 (1964).
63. Dannenberg, E.M. and Opie, W.H. Rub. World, 139(3), 1 (1958).
64. Walker, Jr., P.L. and Janov, J. J. Coll. Interf. Sci., 15, 449 (1968).
65. Smith, A. Proc. Roy. Soc. (London), A12, 424 (1863).
66. Ogawa, I. Biochem. Z., 172, 249 (1926).
67. Kruyt, H.R. and de Kadt, G.S. Kolloid Z., 47, 44 (1929).
68. Fedorov, G.G., Zarif'yants, Yu. A. and Kiselev, V.F. Zh. Fiz. Khim., 37, 2344 (1963).
69. Villars, D.S. J. Am. Chem. Soc., 70, 3655 (1948).
70. Rivin, D. Rub. Chem. Technol., 36, 729 (1963).
71. Studebaker, M.L. Rub. Age, 77, 69 (1955).
72. Donnet, J.B. and Marguier, P. C.R. Acad. Sci. Paris, 242, 771 (1956).
73. Boehm, H.P., Diehl, E., Heck, W. and Sappok, R. Angew. Chem., 76, 742 (1964).

74. Boehm, H.P., Diehl, E. and Heck, W. Rev. Gen. Caout., 41, 461 (1964).
75. Puri, B.R. and Bansal, R.C. Carbon, 1, 451 (1964).
76. Donnet, J.B. and Papirer, E. Rev. Gen. Caout., 42, 389 (1965).
77. Friedman, S., Kaufman, M.L., Steiner, W.A. and Wedner, I. Fuel, 40, 33 (1961).
78. Given, P.H. and Hill, L.W. Carbon, 7, 649 (1969).
79. Hallum, J.V. and Drushel, H.V. J. Phys. Chem., 62, 110 (1958).
80. Studebaker, M.L., Huffman, E.W.D., Wolfe, A.C. and Nabors, L.G. Ind. Eng. Chem., 48, 162 (1956).
81. Donnet, J.B. and Henrich, G. Bull. Soc. Chim. France, 1609 (1960).
82. deBruin, W.J. and Vander Plas, Th. Rev. Gen. Caout., 41, 452 (1964).
83. Boehm, H.P. and Voll, M. Carbon, 8, 227 (1970).
84. Collins, R.L., Bell, M.D. and Kraus, G. J. Appl. Phys., 30, 56 (1959).
85. Kraus, G. and Collins, R.L. Rub. World, 139, 219 (1958).
86. Tsubokawa, N. J. Polym. Sci. Polym. Lett. Ed., 18, 461 (1980).
87. Minoura, Y. and Katano, M. J. Appl. Polym. Sci., 13, 2057 (1969).



88. Tsubokawa, N.,  
Takeda, N. and  
Kudoh, K. Carbon, 18, 163 (1980).
89. Tsubokawa, N.,  
Takeda, N. and  
Kanamaru, A. J. Polym. Sci. Poly. Lett. Ed.,  
18, 625 (1980).
90. Tsubokawa, N.,  
Takeda, N. and  
Kudoh, K. Nippon Kagaku Kaishi, 8, 1264 (1980).
91. Given, P.H. and  
Hill, L.W. Carbon, 6, 525 (1968).