STUDIES IN CHLOROCARBOXYLATION OF POLYETHYLENE

A THESIS
SUBMITTED TO THE
UNIVERSITY OF POONA
FOR THE DEGREE OF
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BY

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Dedicated to My Parents

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S.G. JOSHI

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GENERAL REMARKS

1. The figure (graphs, spectra etc.) numbers, reference numbers etc. given in each section refer to particular section only. The references are given at the end of each section.

2. The temperatures are given in centigrade scale and wherever it was necessary to have the temperature to be constant (e.g. kinetic study experiments in section III), thermostatic bath was used. The temperature variation in such a bath was $\pm$ 0.05^{o}C.

3. All the solvents were distilled before use and were dried wherever necessary. The purity of the solvents was checked by VPC.

4. The visible spectra were recorded on a Carl Zeiss 'Specord' UV-visible spectrophotometer.

5. The IR spectra of the polymer samples were recorded by casting the film by evaporation of the solution in a suitable solvent. Wherever film casting or isolation of the film was not possible, the spectra were recorded in nujol mull or the film was deposited on sodium chloride optics (windows) by evaporation of the polymer solution; solvent (dry CTC) in such cases were removed as far as possible before recording the spectra.

6. The IR spectra were recorded on 'Perkin-Elmer 599B', Perkin Elmer 'Infracord' 137B and 283B models.

7. All the ^{1}H NMR spectra were recorded in CTC solutions of suitable concentration using TMS as internal standard ^{1}H NMR shifts are given in δ -scale, and recorded at 60 MH$_{Z}$ on a varian T-60 spectrometer.

8. Abbreviations, notations etc. are freely used wherever necessary, and are as follows:

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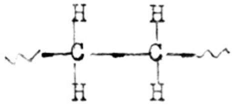
PE = polyethylene, LDPE = low density polyethylene, HDPE = high density polyethylene

$Cl^{\bullet}$ = radical chlorine (dot used to indicate radicals of the concerned species).

CTC = carbon tetra chloride, TCE = tetra chloro ethane, MA = maleic anhydride, PMA = polymaleic anhydride, CPE = chlorinated polyethylene, CCPE = chlorocarboxylated polyethylene, CSPE = chloro sulfonated polyethylene.

$P^{\bullet}$ (CPE, PE or CCPE macro radical and chain segments of these). This was used to facilitate complicated typing of some reactions of polymeric chains.

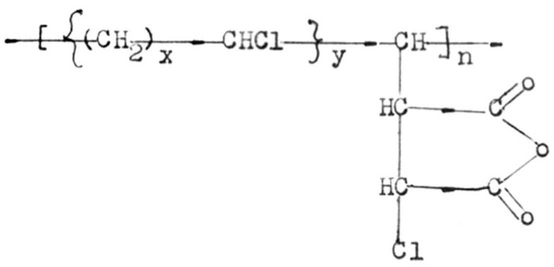
9. 

$$\sim\!\!\sim CH_2-CH_2 \sim\!\!\sim$$

This structure is typed frequently to indicate the polymer chain segments of PE, CPE or CCPE.

10. In section-V 'parts' in various formulations means parts by weight.

11. General formula of CCPE is typed as:



The numerical values of x and y are not mentioned unless necessary.

12. Other notations and abbreviations (θ_{Cl}, θ_{MA} etc.) are defined at the proper places in the text.

SECTION I

INTRODUCTION AND HISTORICAL SURVEY

SECTION-I

INTRODUCTION AND HISTORICAL SURVEY

1.1 General Characteristics of Polymeric Materials

The polymeric substances exist in many forms such as fibers, rubbers, plastics. This is a very broad group of materials. Individually these materials are having diverse range of properties. The reason why all these substances are put in the same main category is that, they all have very high molecular weights, as compared to many organic and inorganic compounds. The molecular weights of these polymers are usually more than 20,000, often it is more than 100,000. In some cases it is more than one million and in few cases it exceeds 30 to 50 millions. These macromolecules are held together by strong covalent bonds. The chemical bonds in macromolecules are strong enough so that the material withstands all kinds of drastic conditions, such as action of chemicals, high and low temperatures, mechanical stresses.

The properties of the polymeric materials are in a broad sense governed by the following factors.[1]

1.1.1 Molecular weight and molecular weight distribution

Molecular weight is of great importance in the synthesis and application of polymers, as can be seen from Table 1.1. It singularly affects the properties of polyethylene monotonically.[1]

Table: 1.1

Relation Between Molecular Weight and Properties of Polyethylene (Density: 0.92)

Molecular weight (Number average)	14,000 to 18,000	20,000 to 22,000	26,000 to 28,000	30,000 to 32,000
Yield strength at 25°C(psi)	1430	1490	1700	1720
Tensile strength at 25°C(psi)	1430	1965	2965	3060
Ultimate elongation %	305	550	580	625
Tear strength in (psi)	440	540	580	691
Abresion volume loss (100 = butyl rubber)	85	50	40	30

The term degree of polymerization ($\overline{DP}$) is used to describe the chain length of a polymer and this is related to molecular weight by

$$\bar{M}_w = \overline{DP} \times (M_w)_n \qquad [1]$$

where $\bar{M}_w$ is the average molecular weight of the polymer and $(M_w)_n$ is the molecular weight of the repeating unit in the chain.

Many properties of the polymeric materials are dependent on $\overline{DP}$, the average degree of polymerization. The relation between $\overline{DP}$ and mechanical strength (MS) of polymer is depicted in Figure 1.1. This typical behaviour is observed for all the polymers and differs for each individual material only in numerical details.

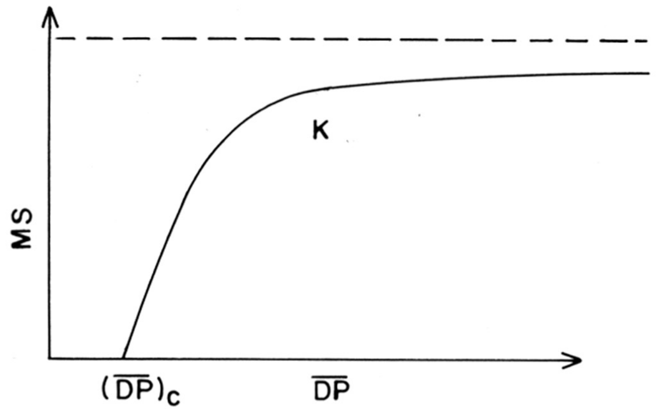


Fig. 1·1 (Ref. 1)

In this diagram $(\overline{DP})_c$ is the critical degree of polymerization and upto this point polymer does not show any appreciable strength. The knee at K of the curve indicates that ($\overline{DP}_K$) corresponding to this point is the critical degree of polymerization. It may be seen from the curve that above this value of ($\overline{DP}_K$) further increase in the degree of polymerization does not appreciably increase the mechanical strength of the polymer.

The curve in the Figure 1.1 can be represented by the equation of the type

$$MS = (MS)_j - \frac{A}{(\overline{DP})} \qquad [2]$$

where $(MS)_j$ is the mechanical strength of the polymer having infinitely long chain. MS is the mechanical strength for the given ($\overline{DP}$) and A is a constant.

The parameters A and $(MS)_j$ are characteristic for any given polymer. These are connected with $(\overline{DP})_c$, the critical degree of polymerization through equation (3),

$$(\overline{DP})_c = \frac{A}{(MS)_j} \qquad [3]$$

Equation (2) then becomes,

$$MS = (MS)_j \left[1 - \frac{(\overline{DP})_c}{\overline{DP}}\right] \qquad [4]$$

It is obvious that equation (4) loses its significance when $\overline{DP}$ becomes smaller than $(\overline{DP})_c$

1.1.2 Crystallinity of the polymers [2]

The next important parameter which governs the properties of polymer to a very great extent, is crystallinity. This is one of the basic properties of polymeric chains. The polymer chains do exhibit the tendency to form crystal like bundles or aggregates.

In crystalline polymers certain volume of the polymeric chain units reaches a three dimensional order. In certain respect, this ordered arrangement approaches normal crystalline materials. However, crystalline domains in polymeric materials do not have regular shape like normal crystals. These are much smaller in size and contain many more imperfections, disorders and amorphous areas. The defects are created by 'through going chains'. There is no distinct boundary between three dimensionally ordered (crystalline) and disordered (amorphous) parts of the system.

Factors which favour the crystalline structure of the polymeric materials are:

a) Structural regularity of the chain, which can readily lead to the establishment of progressive periodicity.

b) Free vibrational and rotational motions of the segments, so that different conformations can be assumed without overcoming high energy barriers.

c) Presence of specific groups which produce strong lateral (intermolecular) bonds (Hydrogen bonds or Van der Waals bonds) and regular periodic arrangement of such groups, and

d) Absence of bulky and irregularly spaced substituents. These substituents inhibit the chain segments from fitting into a crystal lattice. This in turn, prevents the latteral bonding groups from approaching each other to the distance of best interaction.

Progress in the field of polymer science and technology is going on at a tremendous rate. More and more new members are joining this group of materials, and presently sufficient advances are made in the synthesis of these materials. The properties of the polymeric materials can be predicted on the basis of (a) the structure of the monomeric units, (b) the pattern in which these units are fitted in the chain and (c) how these will interact with each other if the units belong to different chains. Thus, one can save considerable experimentation on the polymeric material having desired properties.

1.2 Various Routes of Obtaining Polymeric Materials[3]

In the synthesis of polymeric materials there are mainly three approaches. One is to synthesize newer monomers having different reactive groups with different reactivities. This can be done by incorporating groups such as carboxyl, hydroxyl etc. in the monomer structure and then polymerize it. Thus the characteristic properties of monomeric units can be endowed in the polymer according to the planned structure of the macromolecule.

The other approach is to work with the known monomers like ethylene, propylene, styrene. These monomers can be polymerized using new methods, new catalysts, which would give 'controlled molecular weight and crystallinity' polymers. This particular approach is very much successful in last few decades, due to the discovery of Ziggler-Natta catalysts.[4]

Another way of obtaining polymeric materials is the conversion of existing polymers to newer type of polymers with desired properties. This can be achieved by grafting of different monomers or by carrying out some well known reactions on the polymeric materials. Especially, rather inert materials like polyethylene, polypropylene can be reacted with suitable substances having reactive groups such as hydroxyl, carboxyl, halogens etc. The reactivity of these groups can be used for further conversion of these rather inactive polymers to a material having specific enduse.

Some of the commercially well established processes in this category are:

i) Production of poly(vinyl alcohol) from poly(vinyl acetate).

ii) Preparation of various derivatives of cellulose - cellulose acetate, nitrate etc.

iii) Chlorination of rubbers

iv) Chlorination and chlorosulfonation of polyethylene etc.

1.3 Rubbery State of the Polymeric Materials [5]

One of the aims of the present investigation was to derive elastomeric material from polyethylene, a polymer having fairly high degree of crystallinity. This crystalline material was converted to rubbery state through the reaction of chlorine and maleic anhydride simultaneously. The rubbery state of the material is a peculiar feature of the polymeric substances and it will be worthwhile to consider this state on molecular level but in a rather qualitative fashion. [5]

At sufficiently low temperature the polymeric materials behave like ordinary crystalline solids. These materials have the following characteristics:

i) Long range order of atoms or atomic groups (l.r.o.) of the chain molecules.

ii) It can transfer stress when mechanical forces are applied.

iii) Individual atoms or group of atoms are virtually at rest, i.e. Brownian motion is negative.

When temperature of such a solid is raised sufficiently high (above melting point) it has following characteristics:

i) No long range order of the atomic groups.

ii) It flows when stress is applied even though the viscosity is very high as compared to normal low molecular weight substances.

iii) It has positive Brownian movement and this corresponds to liquid state (plastic) of the low molecular weight substances.

In case of polymeric materials due to long chain nature of macromolecules, consisting of large number of small units, the macromolecule as a whole has many degrees of freedom. And as the temperature of such material is increased, only few of these degrees of freedom can get activated. These more active segments of the chain can move considerably from the normal equilibrium position. The macromolecule as a whole is still at rest and in case of polymeric materials, there are two types of Brownian motions - internal Brownian motion (iBM) which is restricted to local movement of segments and small groups of the chain, and external Brownian motion (eBM), wherein overall movement of macromolecules is possible together with the local movement of segments. The on-set of iBM corresponds to the brittle point temperature (T_b) of the polymer and T_m corresponds to the melting point of the polymeric materials, when the flow of the material is possible. The material exists in the rubbery state in this temperature range i.e.

in the range T_b to T_m . Various states of the polymeric materials are summarized in the Table 1.2 as follows:

Table: 1.2

Various States of Polymeric Materials and Characteristics of each State

	Crystalline solids (fibre like)	Rubbery	Liquid (plastics)
int. Brownian movement	-ve	+ve	+ve
ext. Brownian movement	-ve	-ve	+ve
long range order	+ve		-ve

These states of polymeric materials can be represented in the form of phase diagram as shown in Figure 1.5.[5]

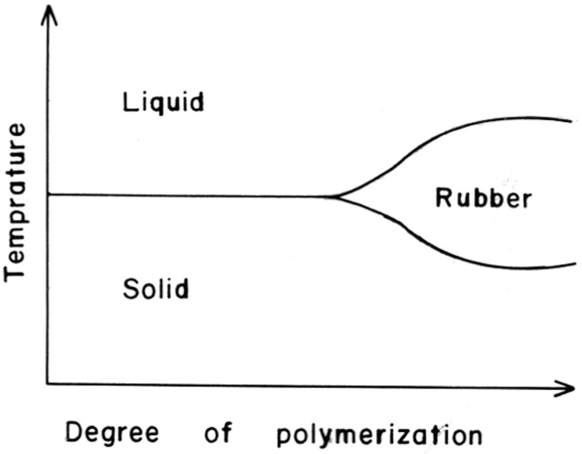


Fig. 1.2

Degree of polymerization as a function of temperature describing liquid, solid and rubbery state[5]

The rubbery range of the polymer can be widened by:

i) Plasticization - This can be done by adding plasticizing monomer to form a copolymer, or

ii) A liquid which is compatible with polymer and softens, can be added to the system as a plasticizer.

By this process local motion of small segments of polymer can be favoured and positive sign of iBM can be maintained even at lower temperatures.

In the second step, on-set temperature of external Brownian motion is to be moved to higher temperature and this can be done by crosslinking. Crosslinking and plasticization together widen the rubbery range of the polymeric materials. Plasticization refers to the internal Brownian motion and crosslinking refers to external Brownian motion.

All work in rubber technology is the combination of plasticization and crosslinking. Calendering, milling and mastication of rubber is plasticization and vulcanization is crosslinking. Rubbery state is thus the combination of liquid and solid state. The liquid state with superimposed system of fixed points or it is a solid with very accentuated local motion of molecular segments.

At present, understanding of rubbery state of the polymeric material is based on better theoretical foundation. This is mostly due to the excellent theoretical analysis of this state, carried out by Flory [6], Treloar [7] and many others.[8] But if one looks at the historical developments of the synthetic elastomers one sees that, till the period just before world war II, the scientists and technologists working in this field were trying to immitate the structure of natural rubber. And it was thought that synthetic elastomer can be prepared by such immitations. The discovery of several saturated polymers with elastomeric character, just after world war II changed the long assumed concept of duplicating the structure of natural rubber.

The chemical derivative of polyethylene namely chlorinated polyethylene (CPE) was discovered just after world war II. These grades of chlorinated polyethylene were very carefully studied, which revealed:[9-11]

i) Chlorination of these highly crystalline hydrocarbons polymers, introduces enough heterogenuity into their structure, and

ii) This heterogenuity prevents crystallization of these polymers in the relaxed state, which gives the rubbery character to these chlorinated derivatives.

These chlorinated polyethylenes, the Thiokol rubbers and polyisobutylenes represented a distinct break from the concept of duplicating the structure of natural rubber. It is now known that any polymer that is non-crystalline, non-glassy and crosslinkable, will show elastomeric character.

Chlorinated polyethylene and polyisobutylene elastomers have a typical property of being able to crystallise under stress. These elastomers with saturated chemical structure have the distinct advantage of showing both high strength in non-reinforced systems and have excellent stability towards weathering, thermal aging and chemical attack.

Elastomeric chlorinated polyethylene can be cross-linked by somewhat drastic reactions of breaking relatively strong C-Cl or C-H covalent bonds.[12] However, to achieve ready crosslinkability, sulfonyl chloride ($-SO_2Cl$) groups are introduced in a low concentration into the polymer chain during chlorination. The resulting class of polymers is commonly known as 'chlorosulfonated polyethylene' and sold under the trade name 'Hypalon' synthetic rubbers.[13] The sulphonyl groups may be reacted with alkyl- di or polymines, aromatic di or polyamines, divalent metal oxides etc. in vulcanization to a commercial rubber.

The purpose of the present studies is to explore the possibility of modifying polyethylene by introducing carboxyl (-COOH) groups randomly in the polymer chain simultaneously during chlorination. The process may be termed as the 'chlorocarboxylation' of polyethylene, and the reaction product 'chloro-carboxylated polyethylene (CCPE)' fulfilling the requirements of an elastomer. Hydrogen atoms in the parent polyethylene being randomly replaced by chlorine atoms , destroying the crystallinity and a low percentage of carboxyl groups can act as the crosslinking sites during vulcanization. Thus it is a combination of two types of elastomers i.e. chlorinated polyethylenes (CPE) and carboxylic elastomers, and it will be interesting to review briefly the chemistry and technology of such elastomers separately before going into the investigations of CCPE elastomers viz. the combination.

1.4 Chlorinated Polyethylene Elastomers [14]

Chlorinated polyethylene (CPE) first became commercially available in early 1940s and were made by dissolving low density polyethylene (LDPE) in highly chlorinated solvents and chlorinated by gaseous chlorine. These resins were expensive and did not offer impressive physical properties as a thermoplast. [15]

1.4.1 Chemistry and structure of CPE [14,16]

CPE is a product of random chemical substitution of hydrogen atoms on polyethylene chain. Because of random placement of chlorine, chlorinated polyethylene (CPE) unlike PVC has better stability in regard to dehydrochlorination. The better chain flexibility of CPE is a result of random chlorination which destroys the crystallinity of polyethylene by inter chain separation through bulky chlorine atoms.

The chlorinated polyethylenes range in properties from elastomers with low glass transition temperature (-20°C) at low chlorine contents, to rigids with high glass transition temperature (180°C) at high chlorine contents. In the range of 20 to 40 weight-percent chlorine, there is a series of CPE whose glass transition temperatures are in the range of 20°C to 30°C. These materials are amorphous and rubbery in nature.

The effect of chlorination on PE can be seen from Table 1.3. Initially it reduces the crystallinity and at higher levels of chlorination increase in stiffness is observed.[17]

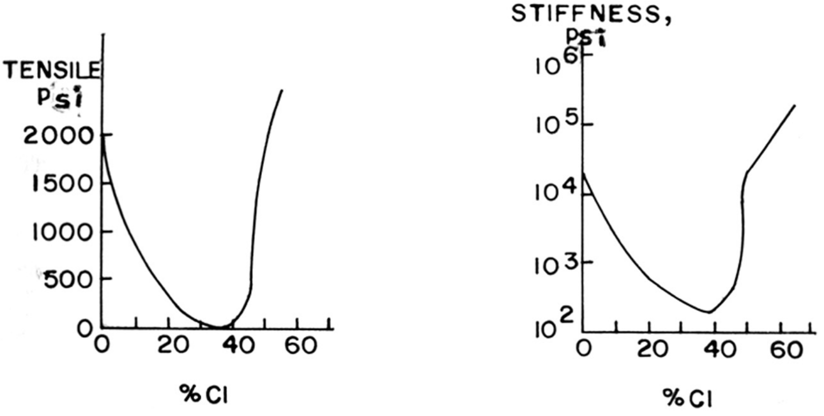
Figs. 1.3(a) and 1.3(b) show the effect of chlorination on the stiffness and tensile strength of PE.[17]

Table: 1.3

The Effect of Chlorination on the Properties of Polyethylene(PE)*

Chlorine % w/w	Brittle point °C	Softening point °C	Descriptions
2		82	
8		69	
25		<20	Rubbery
40		20	Soft sluggish
45	-20	30	Leathery
54	+20	52	Rigid
60	+40	67	Brittle

[* **This data is reported by Oakes W.G. and Richards R.B. - Ref. Trans. Faraday Soc. 42(A), 197 (1946)**]



(a) (b)

Fig. 1.3

Effect of Chlorination on Stiffness and Tensile Strength of PE (Ref. 17).

The properties of CPE not only depend upon the overall amount of chlorine introduced but also on the method of chlorination. Different results are obtained on chlorination in solution than in suspension due to the different distribution of chlorine atoms along the polymer chain.

In the case of polyethylene, all three types of hydrogen atoms i.e. primary, secondary and tertiary are present but most of the hydrogens are secondary, as on the main repeating segment ($-CH_2-$) of the polymeric chain. For low density PE relative amounts of each being as follows:[18]

5.8% primary
92.5% secondary
1.7% tertiary

The relative rates of chlorination[19] of primary, secondary and tertiary hydrogens are 1.0:2.3$\sim$2.9:3.6$\sim$3.9. This would result in the chlorine distribution in PE chain as follows:

2% primary chloride
95% secondary chloride
3% tertiary chloride in CPE

Even though most of the chlorine present in CPE is of secondary chloride type, it is necessary to know the relative position of the chlorine atoms with respect to each other. Infra red spectra (IR) have been used for the detailed analysis of the chlorine distribution in CPE and it is found that $-CH_2Cl-$ and $-CHCl-CHCl-$ type of units are present but no $-CCl_2-$ units. [20,21]

1.4.2 Manufacture of CPE [14,16]

Raw materials for the manufacture of CPE are high or low density polyethylene powder, chlorine gas, chlorinated hydrocarbons as solvents - generally tetrachloroethane (TCE) or carbon tetrachloride (CTC) - and a free radical initiator source or photo initiation system. Chlorination processes are classified as:

i) Chlorination in solution
ii) Aqueous chlorination or suspension chlorination, and
iii) Fluidized bed chlorination

A variety of CPE are produced ranging from soft flexible to extremely rigid and tough thermoplastics. The commercial product is characterized, virtually by the following four product variables:

i) Melt viscosity
ii) Chlorine contents
iii) Residual percent crystallinity
iv) Product additives, stabilizers, etc.

1.4.3 CPE elastomers [14,16]

CPE produced from HDPE or LDPE having 25 to 40% chlorine are rubbery in nature. These can be cured by amine or peroxide curing systems.

The outstanding properties of CPE vulcanizates are:

a) Compounds are ozone proof independent of loading,
b) Excellent heat aging properties,
c) Resistance to hydrocarbons, oils, fuels and gasoline,
d) Chemical resistance in aqueous media,
e) Excellent flex-crack resistance,
f) Excellent flame resistance and self extinguishing nature,
g) Good colourability and colour stability,
h) High filler loadings.

1.5 Carboxylic Elastomers

The degree to which a polymer is rubbery is influenced by the detailed shape and chemical composition of the polymer.[22] Rubbery polymers possess relatively weak interchain forces and lack linear symmetry and orderly arrangements. Copolymerization and graft copolymerization destroy regularity and symmetry, and favour rubbery characteristics. Interchain forces can be introduced by incorporation of polar groups into polymers. Carboxylic groups in the copolymerization or graft copolymerization tend to destroy the regularity of the polymer chains favouring rubbery properties over crystallinity.

Strong polar nature of the carboxylic groups increases the interchain forces imparting increased strength to the polymer. When carboxylic groups function in this way the resulting rubber can be regarded as a polar elastomer.[23] The chemical reactions,characteristic of carboxylic functional groups may be employed to alter the properties of elastomers. Thus carboxylic elastomers can be regarded as functional elastomers also.[23]

1.5.1 Preparation of carboxylic elastomers [24]

The first preparation of carboxylic elastomers was recorded in a French patent in 1933, under which butadiene was copolymerized with acrylic acid in emulsion.[25] The product was vulcanized by a sulphur recipe, accelerated with zinc chloride and dithiocarbamate of decahydroquinalidine using carbon black as a filler. The reported good properties of the vulcanizates are attributed to the reactions of carboxylic groups.

Three methods are generally used for the preparation of carboxylic elastomers:

(1) Copolymerization of unsaturated carboxylic acids, e.g. acrylic acid, with olefins and dienes[26],

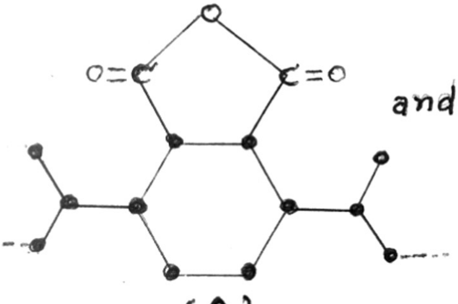
(2) Converting groups such as esters, nitriles, amides etc. to carboxylic groups by hydrolysis, and

(3) Reactions of carboxylic compounds such as maleic anhydride, β-mercapto propionic acid etc. with elastomers through latex solutions or directly on a mill.[24]

In the present investigation MA was used as a carboxylating agent during the process of chlorocarboxylation and it will be worthwhile to review the chemistry and technology of the MA modified natural and synthetic elastomers briefly.

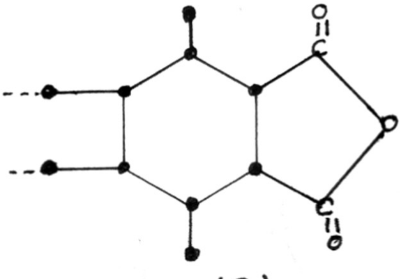
1.5.2 Structure and chemistry of MA modified elastomers

Reactions of MA with rubber hydrocarbon are very well documented in the literature.[27-29] Bacon[26] and Farmer[28] had shown that MA can be added to rubber hydrocarbon in presence of radical initiator. The proposed structures of the adduct were:



(A)

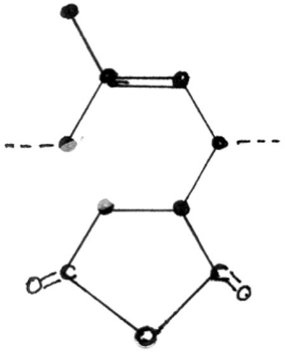
and



(B)

corresponding to inter and intra molecular reactions.

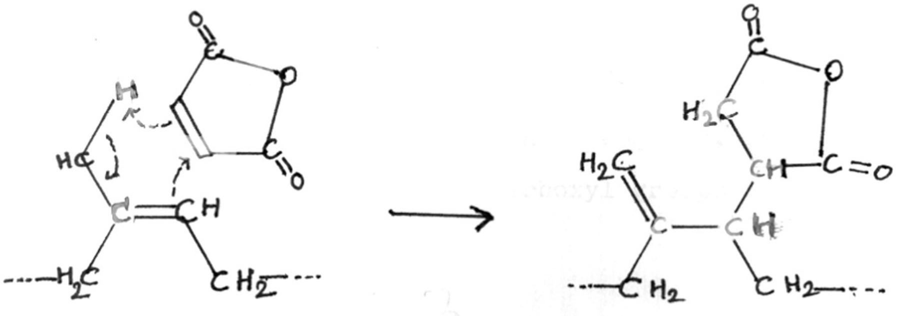
Alder et al. [27] and Farmer [28,29] studied the reactions of MA with simple olefins and proposed a mechanism that consists of a substituting addition of MA on one of the adjacent methylenes of isoprenic double bond. The initiation is essentially due to radical sources (e.g. benzoyl peroxide) or eventually due to heat. The proposed structure is:



(C)

(D)

The product obtained from radical initiators (D) is different from that obtained by thermal (C) initiation. In this thermal addition process, elevation in the temperature induces the appearance of active sites on the chain. According to electron transfer mechanism addition of MA can be according to reaction (1).



(1)

The supply of thermal energy induces the circular displacement of electrons without the appearance of any radical sites. [30]

The reactions of MA and other polymeric dienes with analogous structure are also studied. These are briefly reviewed in Table 1.4.

Table: 1.4

Reactions Between Maleic Anhydride and Various Diene Polymers[31]

Diene polymers	Degree of addition, $\bar{n}$ per chain	
	Radical reaction	Thermal reaction
cis 1,4-polyisoprene (rubber)	14	9
cis 1,4-polyisoprene (synthetic)	9	6
trans 1,4-polyisoprene (gutta-purcha)	7	8
cis 1,4-polybutadiene (synthetic)	12	5

Reaction conditions:
Thermal 45 mins at 220°C
Radical 2 hrs at 130°C, 3% AIBN (Azobisisobutyronitrile)
$\bar{n}$ = degree of addition of MA onto chain

The carboxyl contents of the elastomer can be determined by direct titrations with alcoholic alkali in an appropriate solvent such as benzene, pyridine etc. [24] The distribution of the carboxyl groups in the polymer chains obtained by grafting of carboxyl containing molecules to the polymer chain can be very different from the distribution obtained by copolymerization. However, acceptable carboxylic elastomers can be obtained from all the aforesaid processes.

Carboxylic elastomers prepared by copolymerization method were analysed by IR spectroscopy and it was found that small amounts of carboxyl groups did not have much effect on overall polymer chain structure. [32]

1.5.3 Vulcanization of carboxylic elastomers [23,33]

Carboxylic elastomers and MA modified carboxylic elastomers in particular [34] can be crosslinked through the reactions of carboxyl groups. Divalent metal oxides, di- and polyamines, polyols and epoxy compounds etc. are commonly used as curing agents. The vulcanization can also be achieved by combination of any of these curing agents.

Carboxyl groups alone in the elastomer molecules have been shown to contribute to the crosslinking of the polymer molecules, through hydrogen bonding, anhydride formation, salt formation, reactions of di- and polyamines etc. [23, 33]

1.5.4 Properties and applications of carboxylic elastomers[33]

Incorporation of carboxyl groups in the elastomer causes elevation of the elasticity temperature range, improvement of film forming properties and increases the resistance to swelling by hydrocarbon solvents. Important qualities of gum stock and lightly filled carboxylic rubber compounds are: (a) good mechanical and elastic properties, (b) high cut growth resistance and (c) good resistance to heat aging.

The main drawback of carboxylic rubbers is the tendency to scorch.

Adhesives for metal to rubber, artificial silk, nylon to rubber etc. can be prepared from carboxylic elastomers together with other synthetic and natural resins.[23]

Carboxylic rubbers are of considerable interest for the preparation of general and special purpose rubber compounds.[33]

1.6 Objectives of Present Studies

In the present studies, a reaction combination is attempted in which during radical chlorination of PE, maleic anhydride can also be anchored to polymer chain simultaneously. This is feasible via radical mechanism by virtue of high chain transfer and radical scavenging action of the latter.[37] The reaction combination is termed as 'chlorocarboxylation'. The prime objective of this investigation is to study the reaction mechanism and kinetics of the chlorocarboxylation process. This is very much essential for preparing elastomeric vulcanizable polymer through the process of 'chlorocarboxylation of PE.'

Throughout an exhaustive literature survey, only one sketchy reference [35] was found wherein maleic anhydride in excessive quantities was employed to introduce carboxylic sites after pre-chlorination of polyethylene to 25% chlorine. No scientific details i.e. reaction mechanism, kinetics, characterization of the reaction products etc. are reported for this reaction combination.

In this work chlorocarboxylation of PE has been studied by varying the following two parameters: temperature and ratio of PE:MA in the reaction medium.

The reaction products CCPE were characterized by using the same techniques as used in the earlier work by the author.[36] These techniques include:

(A) Analytical methods - (i) Elemental analysis, (ii) Dye partition technique and (iii) Non-aqueous and alcoholic alkali titrimetry.

(B) Spectroscopy - IR and NMR.

The results of characterization are evaluated to elucidate the reaction mechanism and kinetics of the process.

The reaction mechanism was confirmed by preparing the derivatives of the CCPE. Well known reaction of the carboxyl groups were carried out for CCPE polymers.

In order to analyse the kinetics of the chlorocarboxylation process, the following equations were derived.

(a) Rate equation for the chlorination of PE:

$$\frac{d\theta_{Cl}}{dt} = k_{Cl}\,[Cl_2]\,[1-\theta_{Cl}-\theta_{MA\ poly}]$$

(b) Rate equation for the carboxylation of PE (i.e. reaction of MA with PE):

$$\frac{d\theta_{MA}}{dt} = k_{MA}\,[MA][1-\theta_{Cl}-\theta_{MA\ poly}]$$

(c) The composition equation for the product-chloro-carboxylated PE:

$$\theta_{Cl} = \frac{k_{Cl}}{k_{MA}}\cdot[Cl_2].\ \ln\frac{\theta_{MA_o}}{\theta_{MA_o}-\theta_{MA\ poly}}$$

These equations are derived in terms of the fraction of the total number of reaction sites occupied by 'chlorine atoms' and 'maleic anhydride moities'.

The data generated by kinetic study experiments is treated for evaluating kinetic rate constants k_{Cl} and k_{MA} and for the composition of the CCPE formed using above equations.

CCPE applications development work

Some screening experimental work was carried out with elastomeric CCPE polymer, in order to evaluate the polymer for some specific applications.

CCPE was evaluated for the following applications:

i) A base material for surface coatings: Few paint and varnish formulations were prepared which included CCPE as a film forming material along with some other ingradients.

The coatings were evaluated in the usual manner in order to check the utility of paints and varnishes.

ii) CCPE vulcanizates: Vulcanization systems were developed based on di- and polyamines, and metal oxides for CCPE. Stress strain properties have also been studied in order to evaluate the elastomeric CCPE for its practical use.

However, it seems essential to point out that 'applications development' section is a preliminary report and many parameters connected with these applications are yet to be optimized.

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SECTION II

A : EXPERIMENTAL

B : ANALYSIS OF CCPE

SECTION-II

(A) EXPERIMENTAL

2.0 Chlorocarboxylation of Polyethylene

Following reactions were studied experimentally:

1. Chlorocarboxylation of polyethylene
2. Chlorination of polyethylene
3. Chlorination of maleic anhydride
4. Carboxylation of polyethylene

Materials

Low density polyethylene (LDPE) was used for the present studies. The properties of the PE are listed in Table 2.1. The polymer was treated with boiling acetone for 72 hrs. to remove antioxidants and other additives if any. This was further powdered by the procedure described by Joshi [1] using n-hexane as the borderline solvent. This procedure also causes the removal of the additives.

PE and n-hexane (1:10 w/v) were mixed and heated in an autoclave at temperature 150°C (above the melting point of PE) while stirring for an hour. The contents were cooled slowly and powdered PE was dried under vacuum at room temperature for 24 hours.

Maleic anhydride (C.P. grade, B.D.H. make) was purified by crystallization from distilled chloroform.

Table: 2.1

Properties of Low Density Polyethylene

1.	Melt flow index	7.0
2.	Density at 23°C	0.928 g/cc
3.	Type and the manufacturer	WNG-14 M/s. ICI (India) Ltd.

Tetrachloroethane (TCE) technical grade was purified by ordinary distillation and fraction boiling at 142°C was collected and used.

Chlorine gas supplied in cylinders (99.9% minimum purity) was bubbled through concentrated sulphuric acid traps for drying, before it entered the reaction vessel.

2.1 Chlorocarboxylation of PE

In a suitable capacity all glass resin kettle, fitted with condenser and stirrer, 25 gms of purified polyethylene was dissolved in 500 ml of TCE under stirring at the boiling point of the solvent so as to get 5% w/v solution. After complete dissolution of PE, the contents were cooled to the reaction temperature, maleic anhydride was added and dissolved. The reactor was flushed with dry nitrogen gas, and dry chlorine gas was bubbled at a rate of 10 lit/hr. for various pre-set reaction periods. The product was recovered by vacuum distillation of the excess solvent followed by precipitation in methanol.

The elastomeric CCPE was hydrolyzed by prolonged contact with alkaline warm water (60°C) followed by neutralization, and was vacuum dried. This product was used for vulcanization and stress-strain and surface coating studies. For chemical analysis, kinetic studies, spectroscopy and dye interaction technique [2], the CCPE was purified without the hydrolysis treatment, by the repeated dissolution (in distilled tetrahydrofuran - THF) and precipitations in methanol. It was filtered and further purified in a soxhlet extractor using methanol and was dried under vacuum at 40°C for 72 hours.

In order to study the various parameters of the chlorocarboxylation process, following sets of experiments were conducted:

<u>Set A</u>
  i) PE 5% solution w/v in TCE
  ii) MA in the feed 5% to 25% (w/w of PE)
  iii) Temperature, 90°C
  iv) Chlorine flow rate 10 lit/hr
  v) Reaction time 1 to 5 hours

<u>Set B</u>
  i) PE 5% solution w/v in TCE
  ii) MA to the feed 5 to 25% (w/w of PE)
  iii) Temperature 100°C
  iv) Chlorine flow rate 10 lit/hr
  v) Reaction time 1 to 5 hours

<u>Set C</u>
  i) PE 5% solution w/v in TCE
  ii) MA in the feed 5% to 25% (w/w of PE)
  iii) Temperature 110°C
  iv) Chlorine flow rate 10 lit/hr
  v) Reaction time 1 to 5 hours

Results of analysis of each set are given in Table Nos 2.2 (A, B and C). The detailed analytical techniques are discussed in the Part-B of this Section. Fig. 2.1 (A) shows percentage chlorine in the product (CCPE), and percentage MA in CCPE vs. time of reaction under the experimental conditions in the Set A. While Figs. 2.1 (B) and 2.1 (C) indicate the corresponding plots for Set B and Set C respectively.

Chlorocarboxylation of PE, being a simultaneous reaction, the following sets of reactions were also studied for the proper evaluation of the process.

2.1.1 Chlorination of PE

Experimental conditions are same as in the Sets A, B and C except that there was no feed of MA in the reaction system. The results of analysis are shown in Table 2.2 (A, B and C) and the variation of chlorine percentage with time is shown in the Fig. 2.1 which is the curve corresponding to zero feed of MA in the system.

2.1.2 Chlorination of MA

Quantity of MA in the feed was same as that in the Sets A, B and C of the chlorocarboxylation reactions. The chlorination was done in an identical manner (10 lit/hr chlorine flow etc.) for a period of 5 hrs. The final reaction product was recovered and analysed for chlorine, which indicated that only traces of chlorine were present in the product. Also vapour phase chromatography (VPC) and

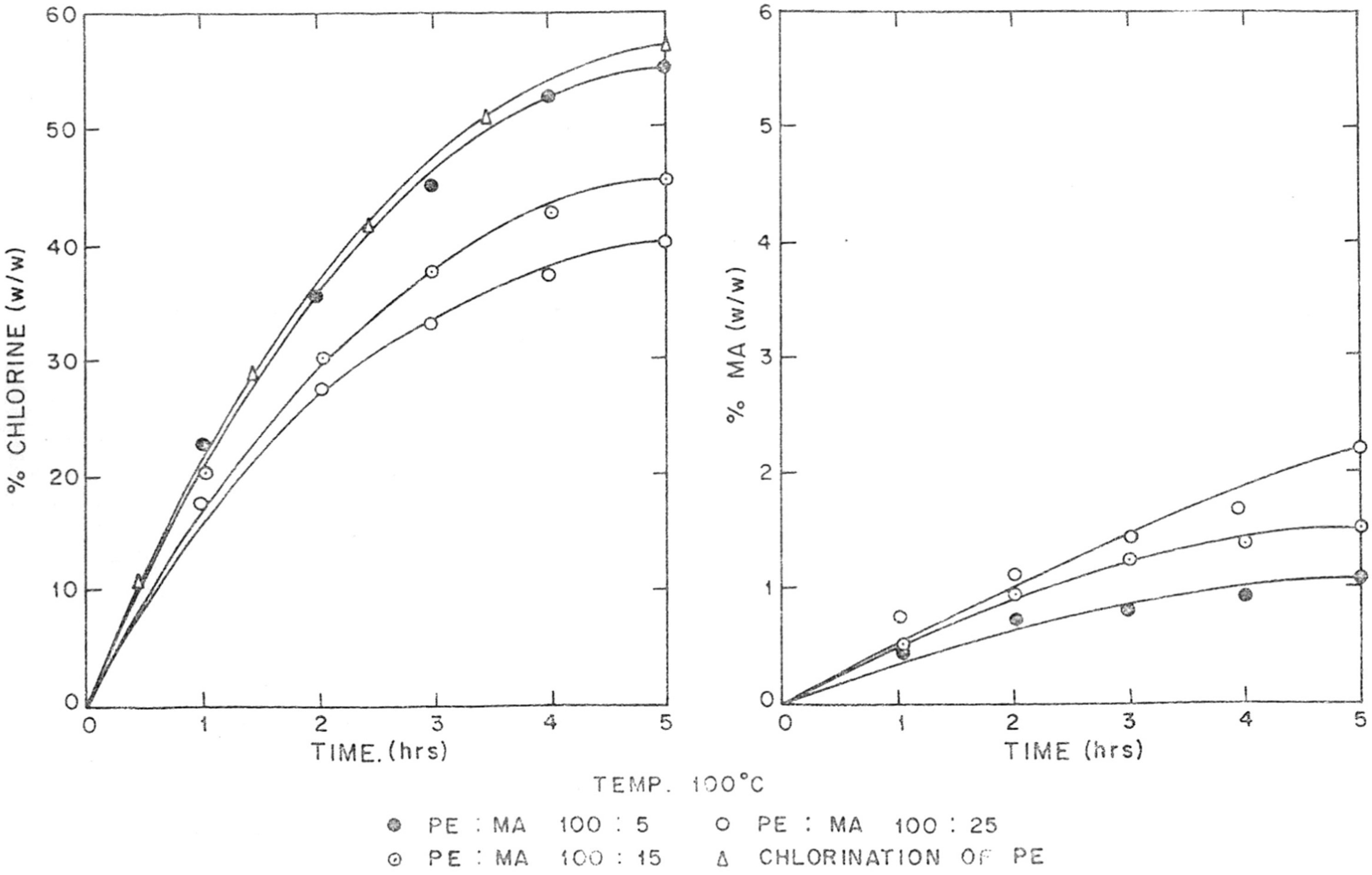

FIG. 2·1(A) : CHLOROCARBOXYLATION OF PE EXPERIMENTAL CONDITIONS AS IN SET A.

Table: 2.2 (A)

Chlorocarboxylation of PE

(Reaction Conditions as in Set A)

Time	% Chlorine	% MA
(Temp. 90°C, MA 2.5 g/lit. in the feed)		
1.	22.5	0.40
2.	35.2	0.70
3.	45.0	0.80
4.	52.5	0.90
5.	55.0	1.10
(Temp. 90°C, MA 7.5 g/lit. in the feed)		
1.	20.5	0.45
2.	30.0	0.95
3.	37.5	1.20
4.	42.5	1.35
5.	45.0	1.50
(Temp. 90°C, MA 12.5 g/lit. in the feed)		
1.	17.5	0.70
2.	27.5	1.10
3.	33.0	1.40
4.	36.0	1.70
5.	40.0	2.2

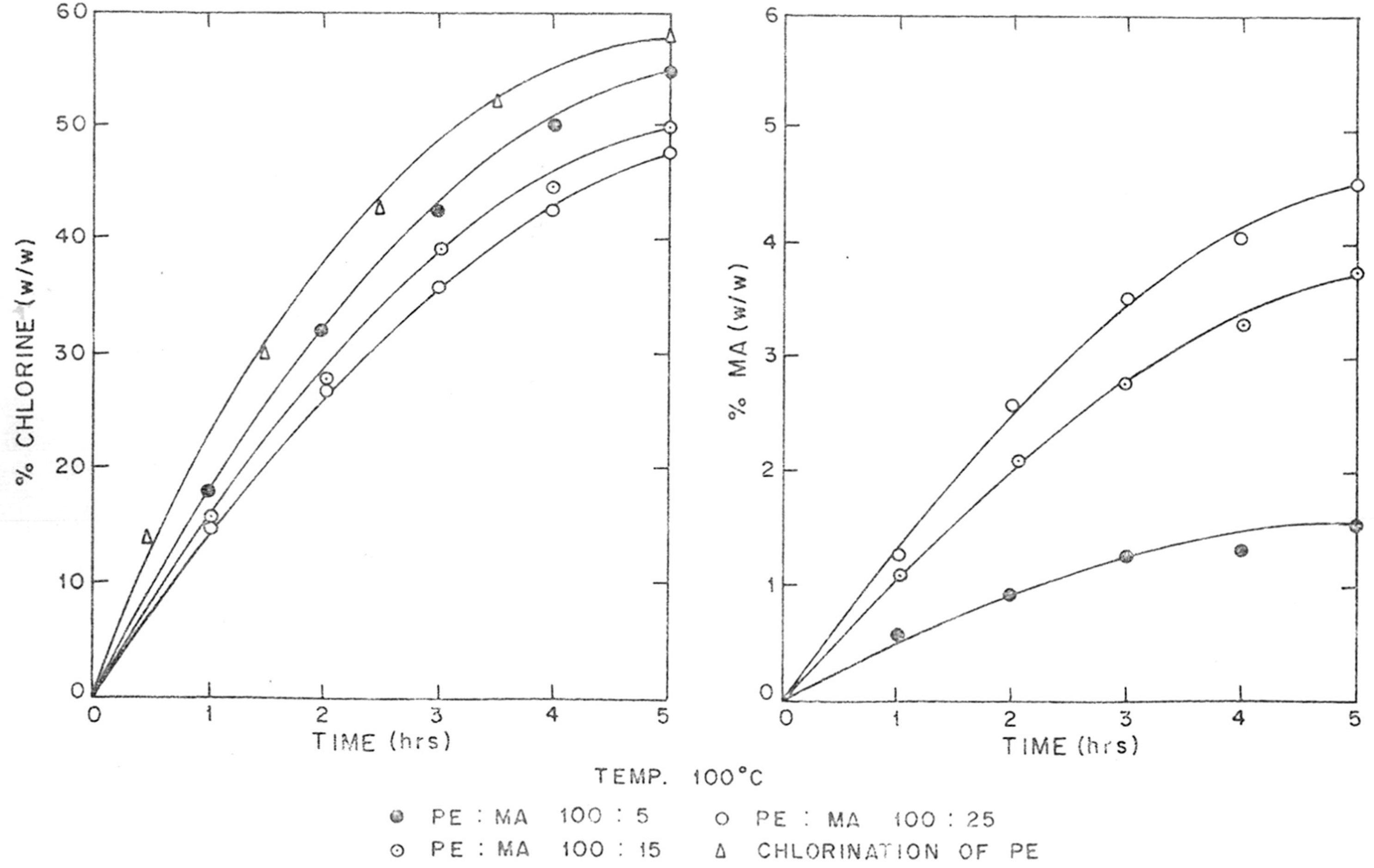

FIG. 2·1(B) : CHLOROCARBOXYLATION OF PE EXPERIMENTAL CONDITIONS AS IN SET B.

Table: 2.2 (B)

Chlorocarboxylation of PE

(Reaction Conditions as in Set B)

Time	% Chlorine	% MA
(Temp. 100°C, MA 2.5 g/lit. in the feed)		
1.	18.0	0.60
2.	32.0	0.90
3.	42.5	1.25
4.	50.0	1.30
5.	55.0	1.50
(Temp. 100°C, MA 7.5 g/lit. in the feed)		
1.	16.0	1.20
2.	28.0	2.10
3.	39.0	2.75
4.	44.0	3.30
5.	50.0	3.75
(Temp. 100°C, MA 12.5 g/lit. in the feed)		
1.	15.0	1.30
2.	27.0	2.60
3.	36.0	3.50
4.	42.5	4.10
5.	47.6	4.50

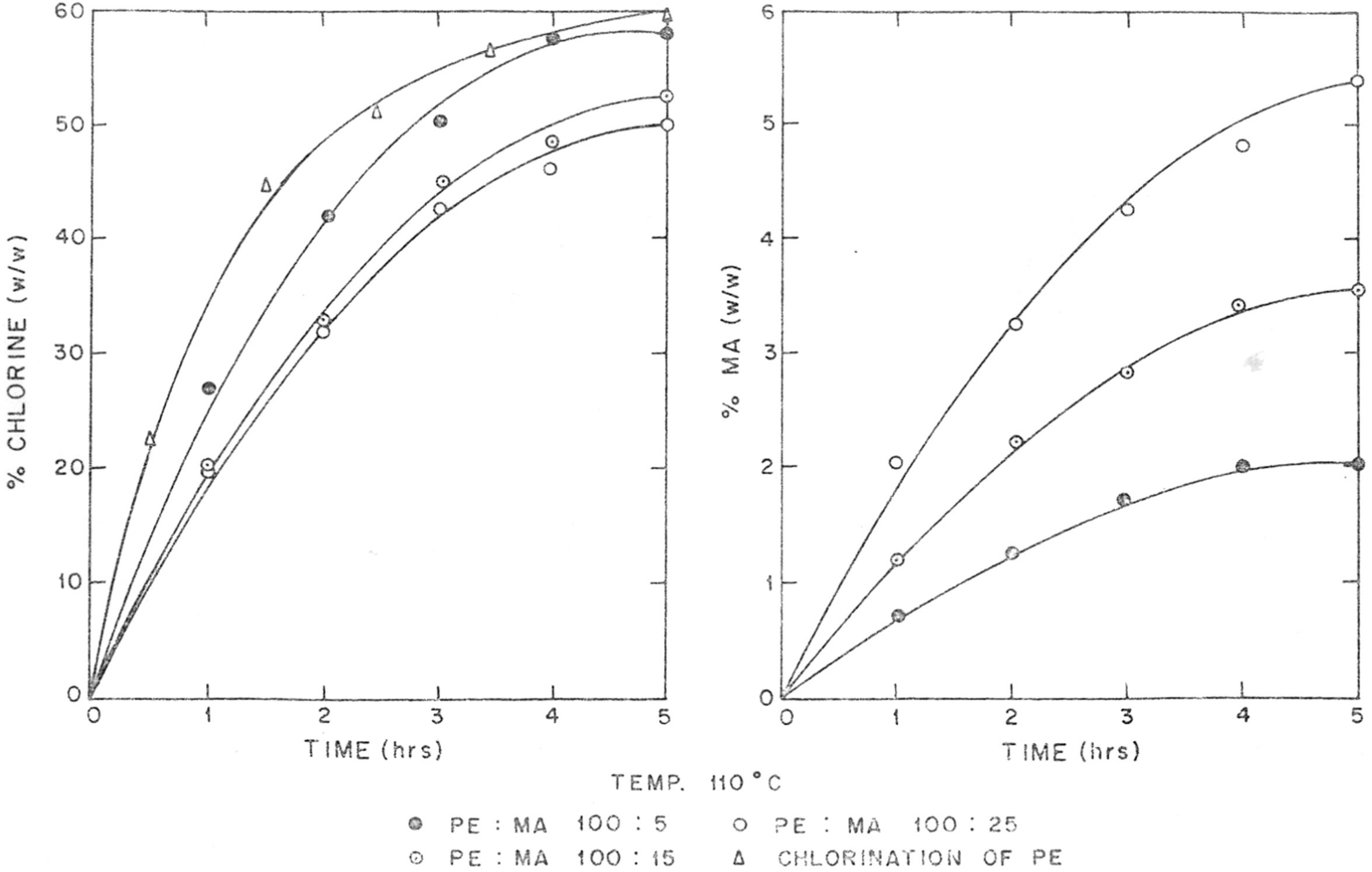

FIG. 2·1(C) : CHLOROCARBOXYLATION OF PE EXPERIMENTAL CONDITIONS AS IN SET C.

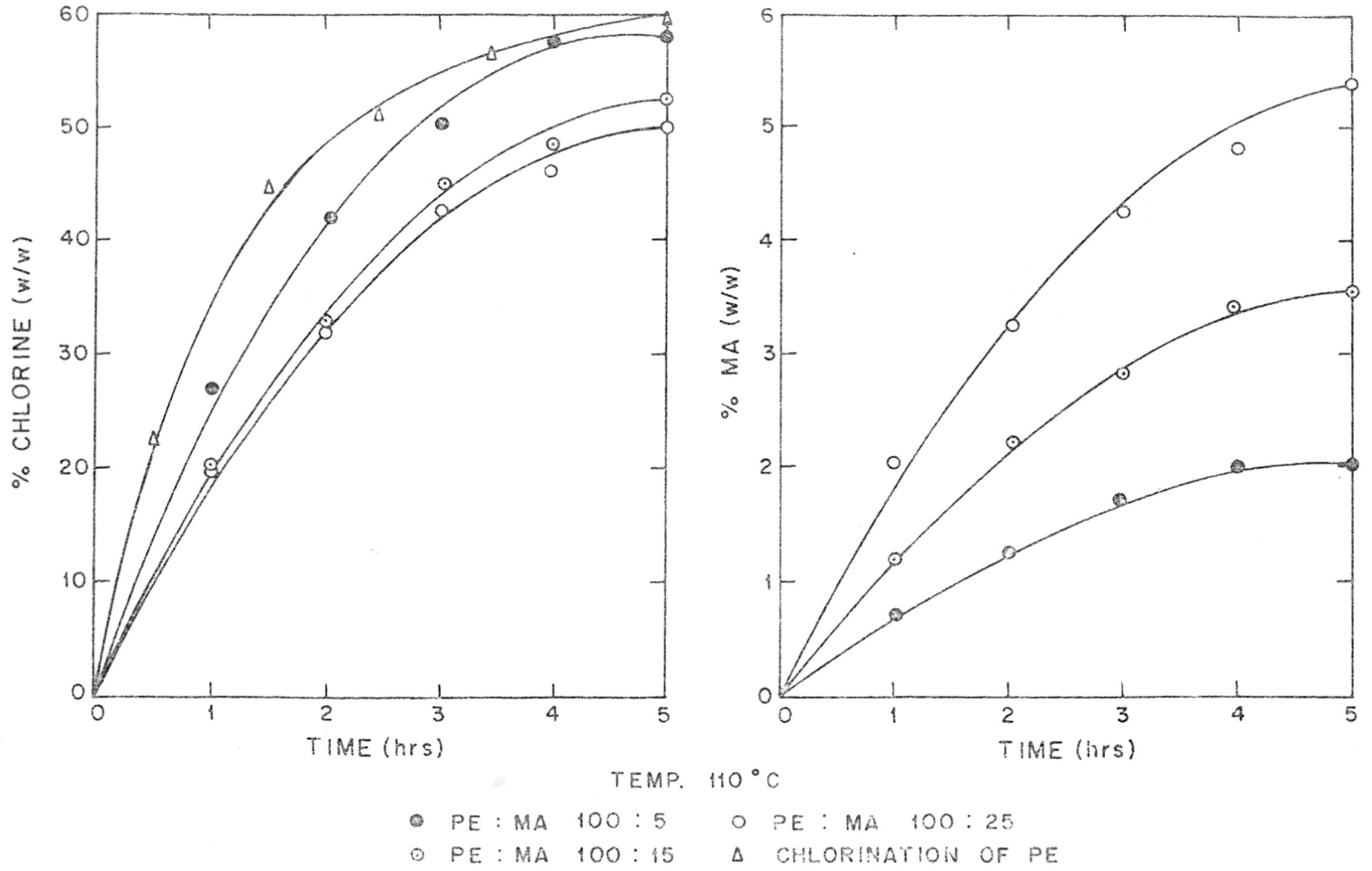

FIG. 2·1(C) : CHLOROCARBOXYLATION OF PE EXPERIMENTAL CONDITIONS AS IN SET C.

Table: 2.2 (C)

Chlorocarboxylation of PE

(Reaction Conditions as in Set C)

Time	% Chlorine	% MA
(Temp. 110°C, MA 2.5 g/lit. in the feed)		
1.	27.0	0.70
2.	42.0	1.25
3.	50.0	1.70
4.	57.5	2.00
5.	58.0	2.05
(Temp. 110°C, MA 7.5 g/lit. in the feed)		
1.	20.0	1.2
2.	32.0	2.2
3.	45.0	2.8
4.	50.0	3.4
5.	52.5	3.5
(Temp. 110°C, MA 12.5 g/lit. in the feed)		
1.	20.0	2.05
2.	32.0	3.25
3.	42.0	4.25
4.	46.0	4.80
5.	50.0	5.40

thin layer chromatography (TLC) were used to analyse the product, using MA as the blank. This VPC and TLC showed the presence of essentially one component in the final reaction product, viz. the unreacted MA corroborating with chlorine analysis.

2.1.3 Reaction of MA with PE

This set of experiments was conducted at 110°C for 5 hours using 5% solution of PE and adding 25% MA (of PE w/w) in the reaction mixture. Final purified product was analysed for MA contents. The elemental analysis (C, H, O) and the dye interaction technique showed only traces of chemically combined MA present in the final product.

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SECTION-II

(B) ANALYSIS OF CCPE

2.2 Purification of Samples for Analysis

The samples of CCPE were purified by repeated dissolution in THF and precipitations in methanol. The purification was finally completed in a soxhlet extractor using methanol for 24 hours. The purified polymers were dried under vacuum for 72 hours.

2.2.1 Chlorine contents in CCPE

Chlorine analysis of polymer samples was carried out by Carius method [3], which is a well known and standard procedure for quantitative chlorine determination in polymers.

2.2.2 Carboxyl contents in CCPE

Carboxyl contents in the polymer were determined by three different methods:

i) Non-aqueous titrimetry [4]
ii) Alcoholic alkali titrimetry [5]
iii) Dye interaction method [2]

2.2.2 (A) Non-aqueous titrimetry [4]

This method is used for the determination of the acidic groups in the polymers and copolymers (e.g. styrene-MA) [6] and consists of titrating the polymer solutions in a non-aqueous medium with standard sodium methoxide solution using bromothymol blue (BTB) as the indicator.

Reagents

Bromothymol blue 0.3 gm in 100 ml distilled methanol was used as indicator.

0.1 N sodium methoxide

About 5 gms of freshly cut sodium metal was washed in methanol, then dissolved in 100 ml methanol. The reaction was controlled by cooling the flask in ice water. When all the sodium metal is reacted, 150 ml of methanol and 1500 ml of benzene were added and the reagent stored in a pyrex container protected from carbondioxide and moisture.

Procedure

Known weight of CCPE was dissolved in benzene and the solution was titrated against sodium methoxide reagent delivered by 3 ml syringe type micro burette reading 0.01 ml, using bromothymol blue as the indicator to a sharp blue end point.

Sodium methoxide solution was standardised using 100 mg of A.R. maleic anhydride per 100 ml of benzene and titrating 10 ml of this solution as above. From this reading carboxyl contents of the CCPE sample can be directly found out as the (equivalent) percent maleic anhydride in CCPE. The results of analysis are given in Table 2.3.

2.2.2 (B) Alcoholic KOH titrimetry[5]

Weighed sample of polymer was dissolved in a suitable solvent (benzene, pyridine etc.) and excess of aqueous standard KOH (0.1 N) was added to this solution and shaken for 1-2 hours while slightly warm. Excess of alkali was back titrated using standard HCl (0.1 N) and phenolphthalin as indicator. The results of CCPE analysis are given in Table 2.3.

2.2.2 (C) Dye interaction method [2]

The method is based on the observation that the benzene extract of some basic and acid dyes from their aqueous solution of suitable pH value can be successfully employed for the detection of micronormal concentrations of benzene soluble acids, bases and salts. This has been used for the detection of ionizable end groups of high polymers and the quantitative determination of acidic and basic groups in polymers and copolymers by colorimetric method even at the micronormal range of concentrations in benzene. For the quantitative determination of traces of acid in particular, Rhodamine B or Rhodamine 6G dyes are found to be most satisfactory. [2]

Procedure

Preparation of the sample

CCPE samples were refluxed for 30 minutes over alcoholic caustic soda solution (2%) on a water bath, the solution was then just acidified with HCl (2%) and refluxed similarly. The treated polymer was purified by the methods as mentioned earlier.

The dye reagent

A 3-4 mg portion of the Rhodamine-B dye was dissolved in 4 cc of a phosphate buffer (pH 10-12) and the solution was immediately extracted with 100 ml benzene with efficient shaking in a stoppered Earlen mayer flask. The yellowish benzene extract is the dye reagent. It was preserved over solid caustic alkali in dark at room temperature. The reagent is reported to exhibit maximum efficiency at temperature 25°-30°C.[2]

The carboxylic compounds and the polymers containing carboxylic groups change the yellowish colour of the dye reagent 'Rhodamine' to pink even at very low concentrations (10^{-6} N).

The development of the pink colour was measured in a Beckman spectrophotometer at 570 nm; the frequency at which the optical density of the specimen is maximum (Fig. 2.2) using a standard 1 cm stoppered cell.

Equal volumes of polymer solution (containing known amount of CCPE) and dye reagent were mixed and allowed to stand for about half an hour. The optical density readings were taken after proper dilution so that the optical density was within the range (of the calibration curve) 0.40 to 0.80. Concentrations of succinic acid moiety in the hydrolyzed CCPE at such high dilutions was of the order of few ppm of benzene.

Calibration curve for the carboxyl analysis

A.R. grade maleic acid was used for the calibration purpose. Solutions of maleic acid of concentrations ranging

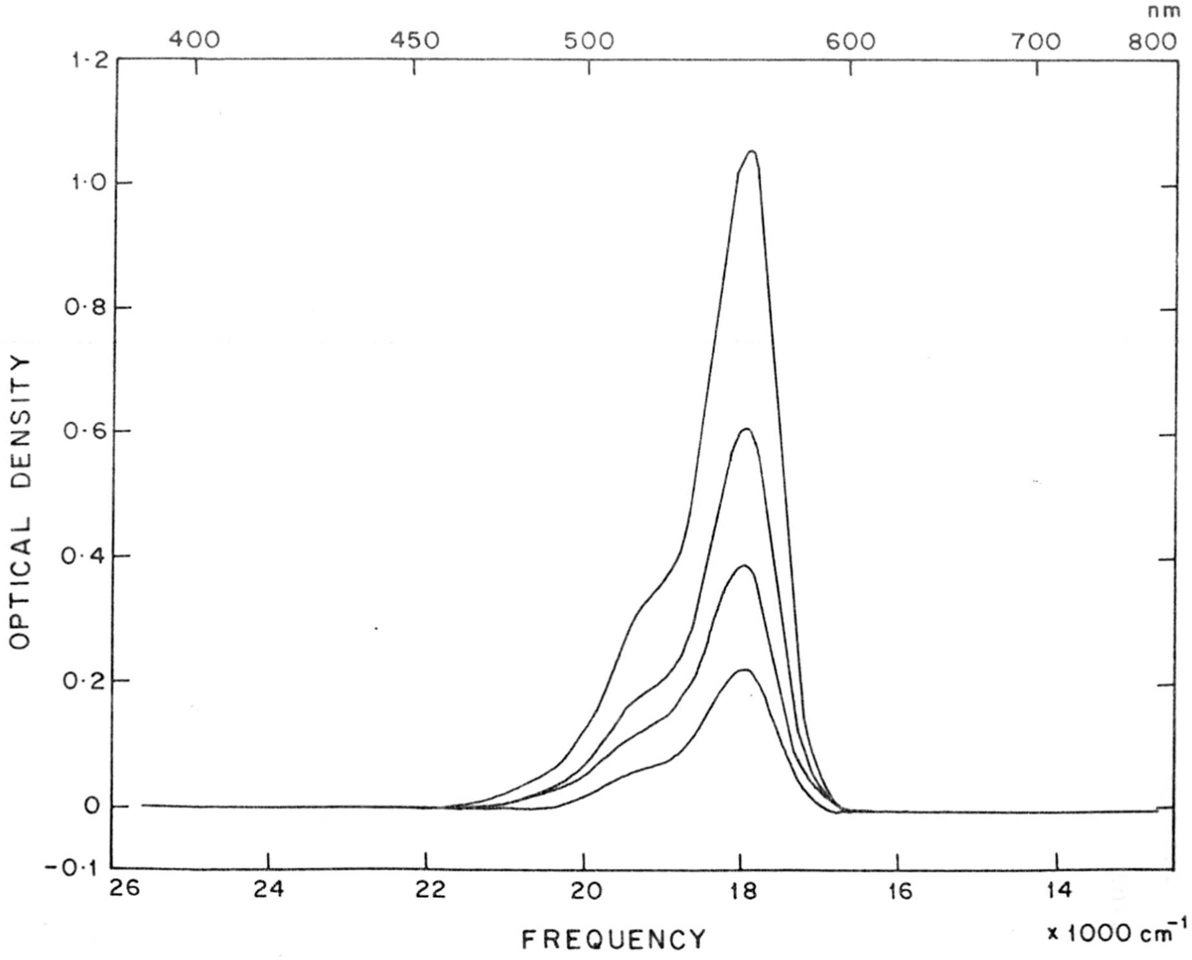


FIG. 2·2 : SCANNING OF SOME CCPE SAMPLES FOR SPECTROPHOTOMETRIC MEASUREMENTS.

between 1 ppm to 10 ppm were prepared in benzene. These solutions were used as standards for the dye interaction procedure as above and optical density measurements were recorded.

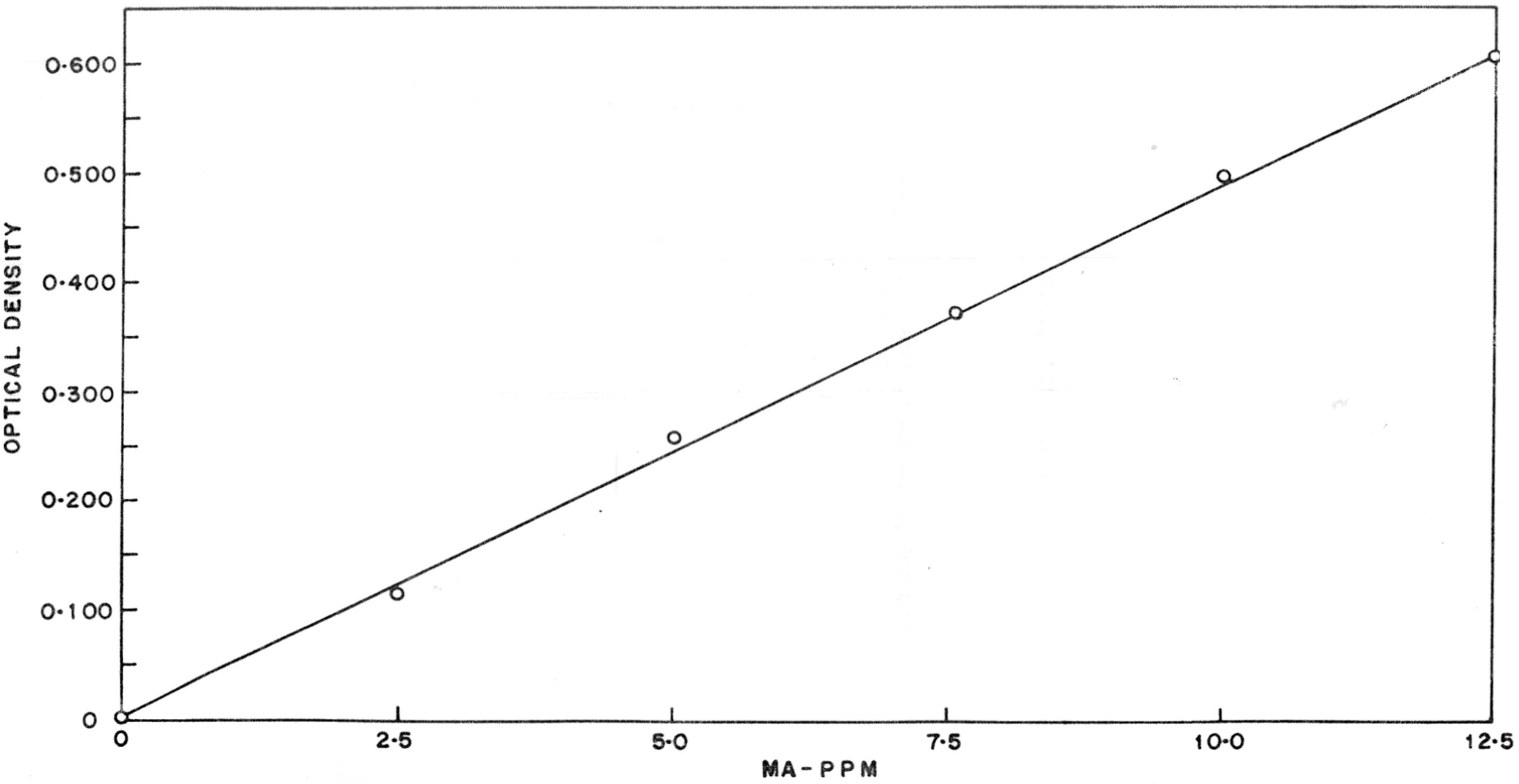
Optical density vs. concentration plot is shown in Fig. 2.3 which is linear passing through origin (carboxyl contents of polymer are expressed as the equivalent ppm of MA). This was used as the reference curve for determining the unknown MA contents of CCPE. Results of analysis are shown in Table 2.3.

Table: 2.3

Chlorocarboxylation of polyethylene: Results of analysis of a typical CCPE by different methods

	Methods for the determination of MA	% MA	% chlorine (by Carius method[3])
1.	Alcoholic alkali titrimetry[5]	1.92	56.6
2.	Non-aqueous titrimetry[4]	2.20	56.6
3.	Dye-interaction method[2]	2.22	56.6

Methods (2) and (3) were followed throughout the course of this work for the analysis of MA in CCPE.



CALIBRATION CURVE FOR SPECTRO-PHOTOMETRIC ANALYSIS. OPTICAL DENSITY vs CONCENTRATION (ppm) IN BENZENE

OPTICAL DENSITY MEASURED AT 570 (nm)

FIG. 2·3

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SECTION III

A : STRUCTURE OF CCPE.

B : REACTION MECHANISM FOR THE CHLOROCARBOXYLATION OF PE.

C : REACTIONS OF CHLOROCARBOXYLATED PE.

SECTION-III

(A) STRUCTURE OF CCPE

3.0 General Characteristics of CCPE

The effect of chlorocarboxylation reaction on polyethylene is in broad sense similar to that of chlorination reaction. Especially when carboxyl contents, i.e. MA reacted with PE during chlorocarboxylation is less than 5%. In this case also probably, it reduces crystallinity of PE initially and at the higher levels of chlorination the stiffness of CCPE increases. At the same chlorine contents, CCPE appears to be more stiff than CPE. The stiffness increases with the increased level of carboxylation for the same chlorine contents.

The rubbery range of CCPE products is observed (for varying amounts of MA reacted with PE) when chlorine contents were in the range 27 to 47%. The rubbery range in case of CPE is observed above 25% chlorine and upto 45% chlorine contents.[1,2] The CCPE elastomeric products appear to be more stiff with higher strength than corresponding CPE products. This is probably due to the incorporation of MA which favours inter molecular interactions of the polymeric chains.

CCPE films when casted from solutions for IR studies showed much higher adhesion over metal substrates (aluminium) and even on glass substrates. This type of adhesion was not shown by PE films and very slight adhesion was shown by CPE films. It was not possible to remove CCPE films from the substrates unless silicon emulsions were used as the release agents. This is probably due to the highly polar carboxyl groups incorporated in CCPE. The nature of CCPE products of varying amounts of chlorine and maleic anhydride can be seen from Table 3.1. The table also contains properties of CPE for comparison.[3]

Table: 3.1

Effect of Chlorination and Chlorocarboxylation on Polyethylene

% Chlorine	Nature of CPE	% Chlorine	% Maleic anhydride	Nature of CCPE
15	Plastic	18	0.7	Plastic
16 to 24	Plastic elastomeric	19 to 27	0.7 to 1.3	Plastic elastomeric
25 to 50	Elastomeric	28 to 52	1.1 to 4.5	Elastomeric
51 to 60	Semi-elastic leathery tough	53 to 60	4.5 to 6.4	Semi-elastic leathery tough

The pattern of chlorocarboxylation reaction is depicted in Fig. 3.1. The chlorination reaction shows a peculiar behaviour during chlorocarboxylation process. As the initial feed quantity of MA in the reaction mixture is increased the rate of chlorination of PE is reduced . This can be seen from various curves for chlorination reactions.

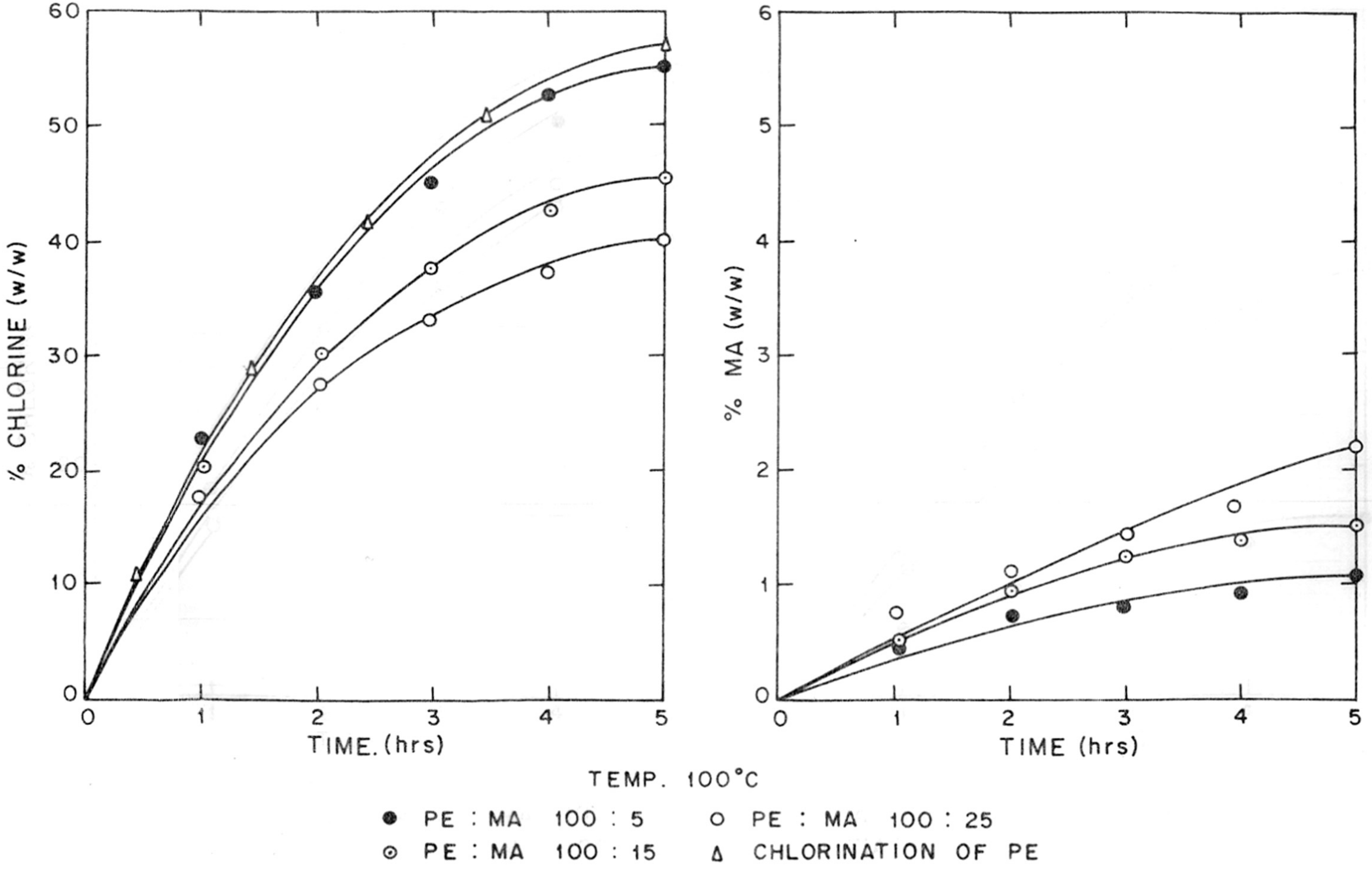


FIG. 3·1 (A) : CHLOROCARBOXYLATION OF PE EXPERIMENTAL CONDITIONS AS IN SET A SEC. II

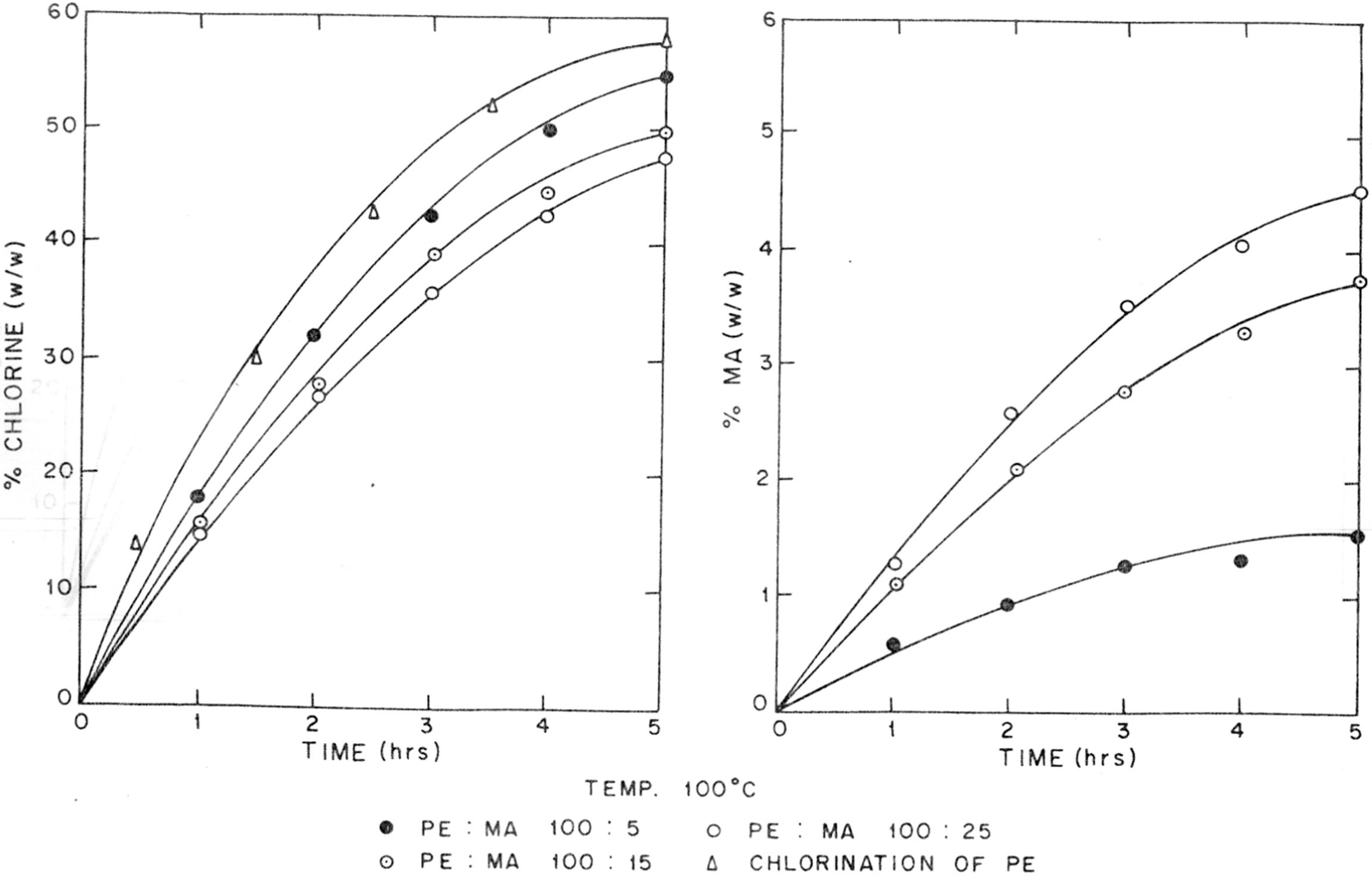


FIG. 3·1(B) : CHLOROCARBOXYLATION OF PE EXPERIMENTAL CONDITIONS AS IN SET B SEC.I

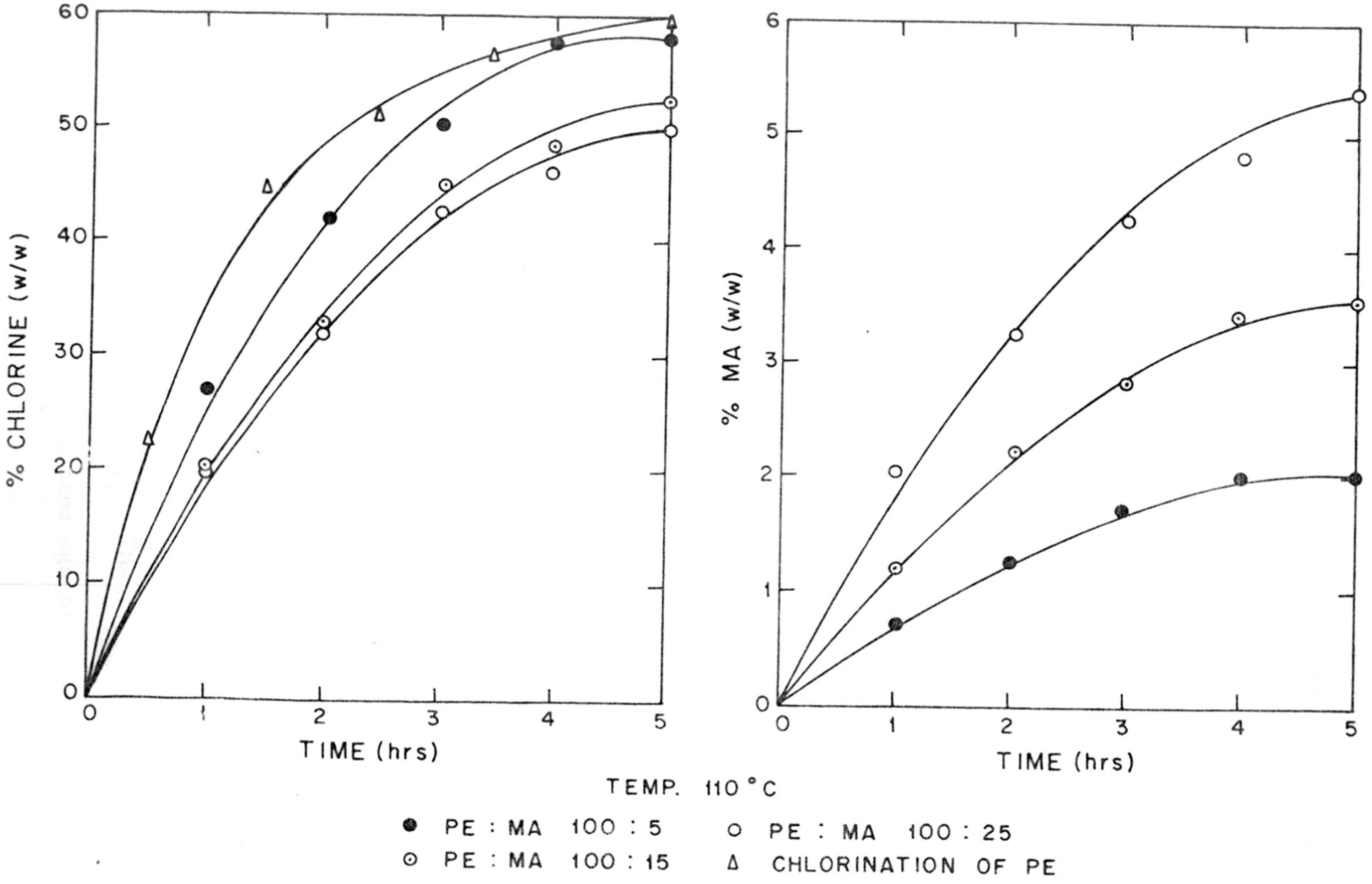


FIG. 3·1 (C) : CHLOROCARBOXYLATION OF PE EXPERIMENTAL CONDITIONS AS IN SET C SEC.I

The reduction in the rate of chlorination indicates the competitive nature of the chlorocarboxylation process. The reduction in the rate of chlorination is also due to the radical scavenging action of maleic anhydride. This will be discussed in more details in section III(B), which deals with the reaction mechanism of CCPE process.

Chlorocarboxylation of PE is a substitution type of reaction. The hydrogen atoms of PE chain being replaced either by chlorine or by maleic anhydride moities. As more and more hydrogens are replaced either by chlorine or by MA, the overall rate of chlorocarboxylation falls down. When this substitution process approaches the situation such that, there is one substituent (either Cl or MA) on every two carbon atoms of PE (i.e. PVC type configuration), further replacement of hydrogen atoms of PE becomes very difficult due to neighbouring substituent effect.[4]

As the temperature of the CCPE process is increased, more MA moities can be incorporated in PE. Further, at higher initial feed quantities of MA, more MA moities can be substituted in PE chain, but in this case unreacted MA left in the reaction mixture is also more. This can be seen from the Figure 3.2.

The variation of the composition of CCPE is depicted in Figure 3.3. In this case $\frac{\bar{N}_{Cl}}{\bar{N}_{MA}}$ (i.e. average number of PE hydrogens substituted by chlorine atoms or MA moities per chain) is plotted against time. As seen in these

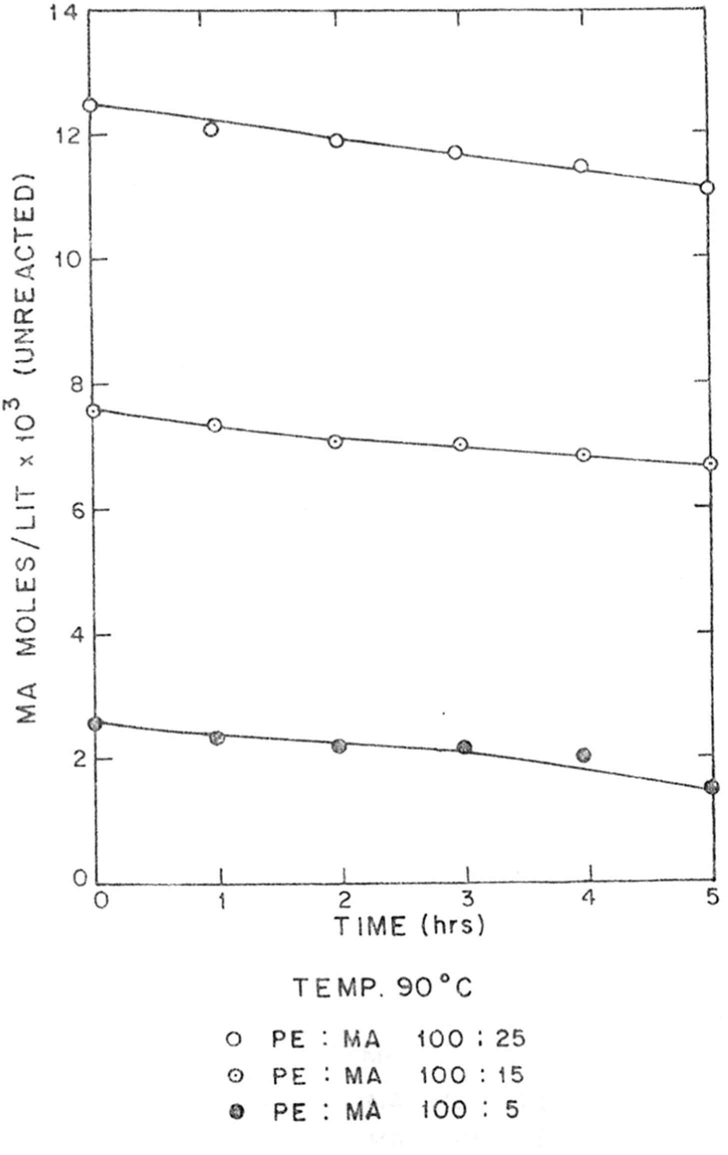


FIG. 3·2(A) : MA UNREACTED IN THE REACTION MIXTURE AS A FUNCTION OF TIME.

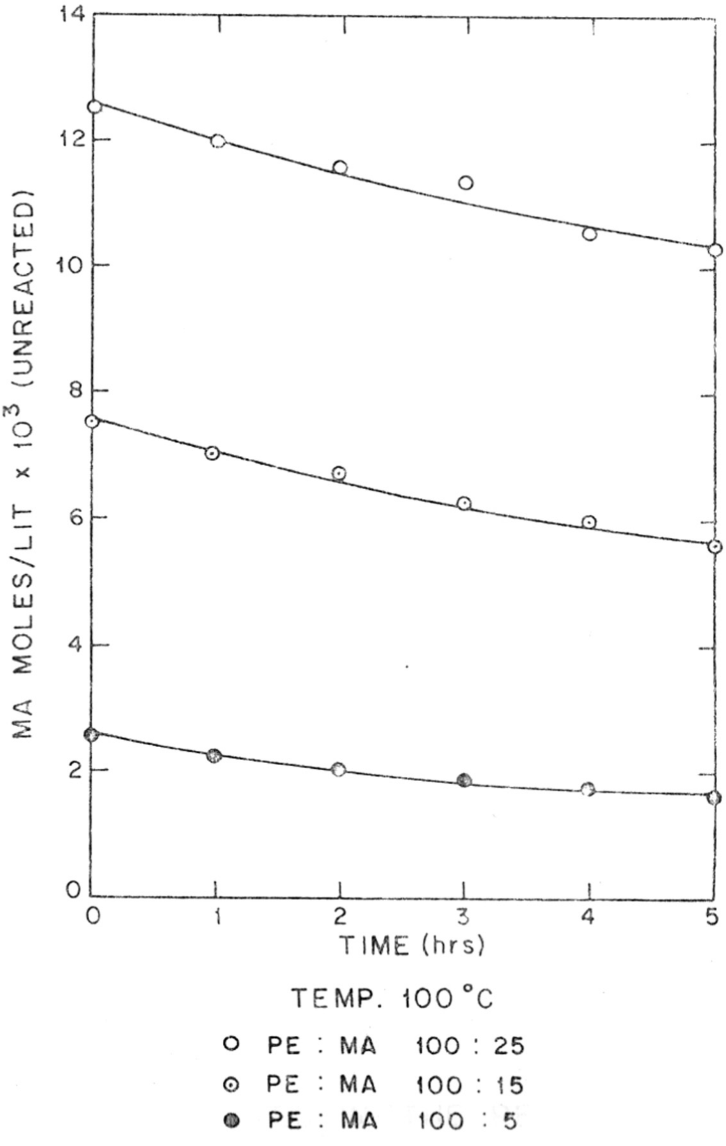


FIG. 3·2(B) : MA UNREACTED IN THE REACTION MIXTURE AS A FUNCTION OF TIME.

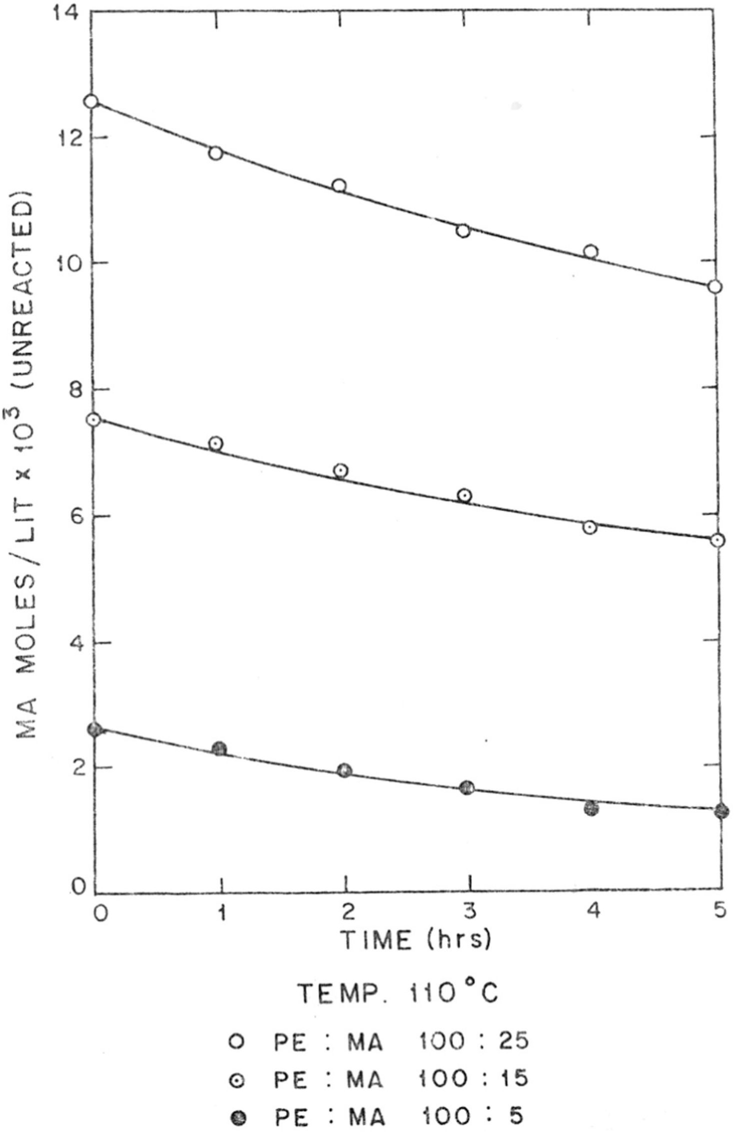


FIG. 3·2(C) : MA UNREACTED IN THE REACTION MIXTURE AS A FUNCTION OF TIME.

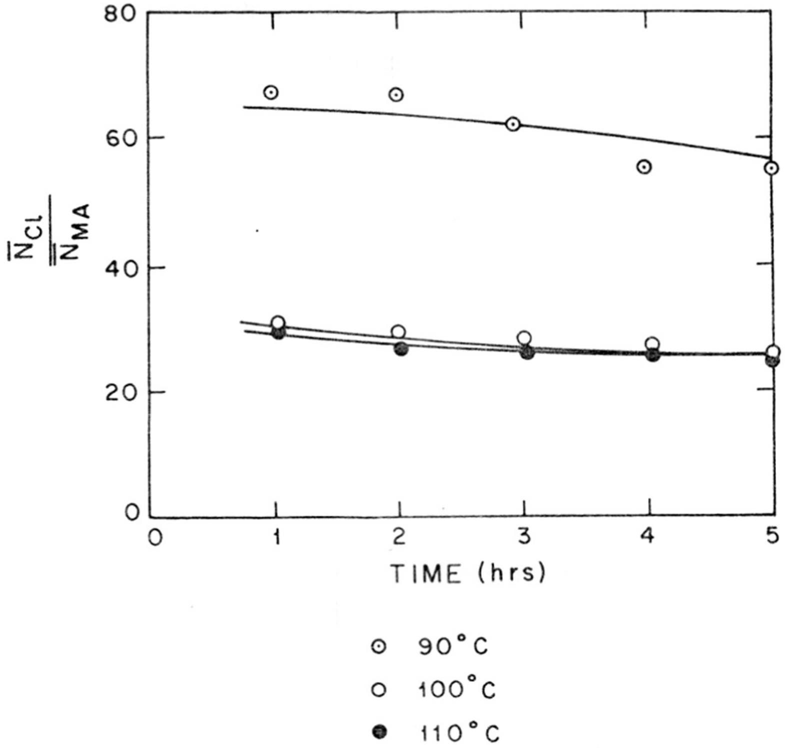


FIG. 3·3 : VARIATION OF COMPOSITION OF CCPE WITH TIME.

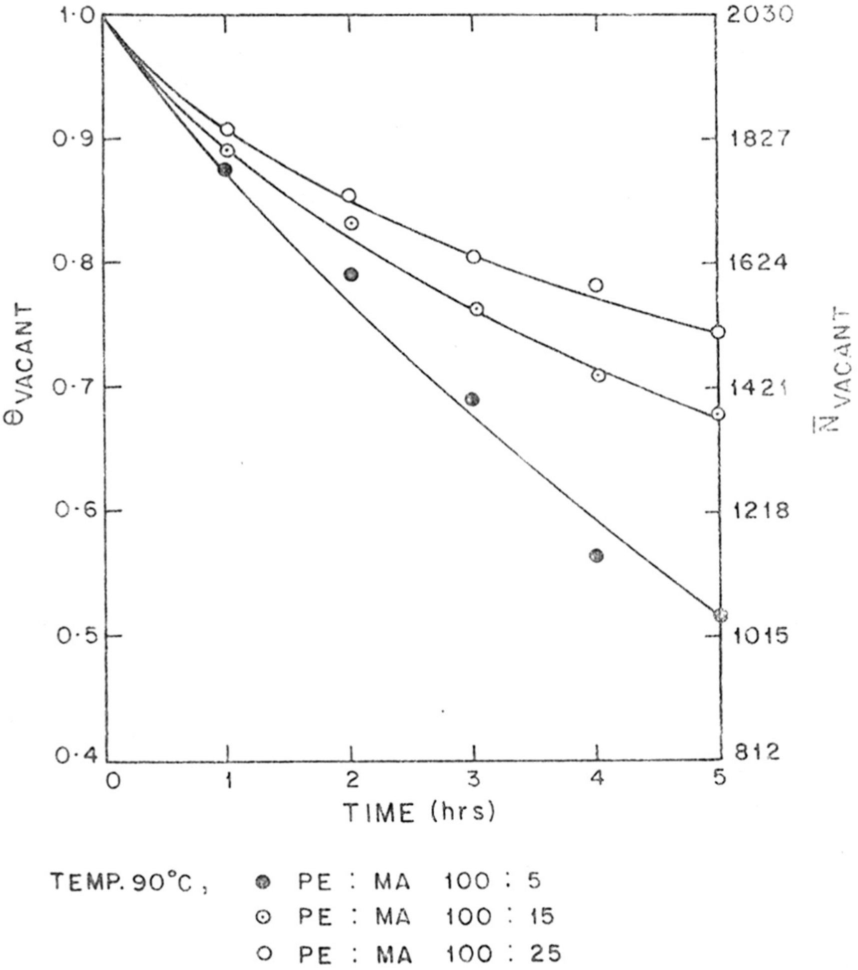


FIG. 3·4(A) : VARIATION OF UNSUBSTITUTED SITES DURING CHLOROCARBOXYLATION OF PE

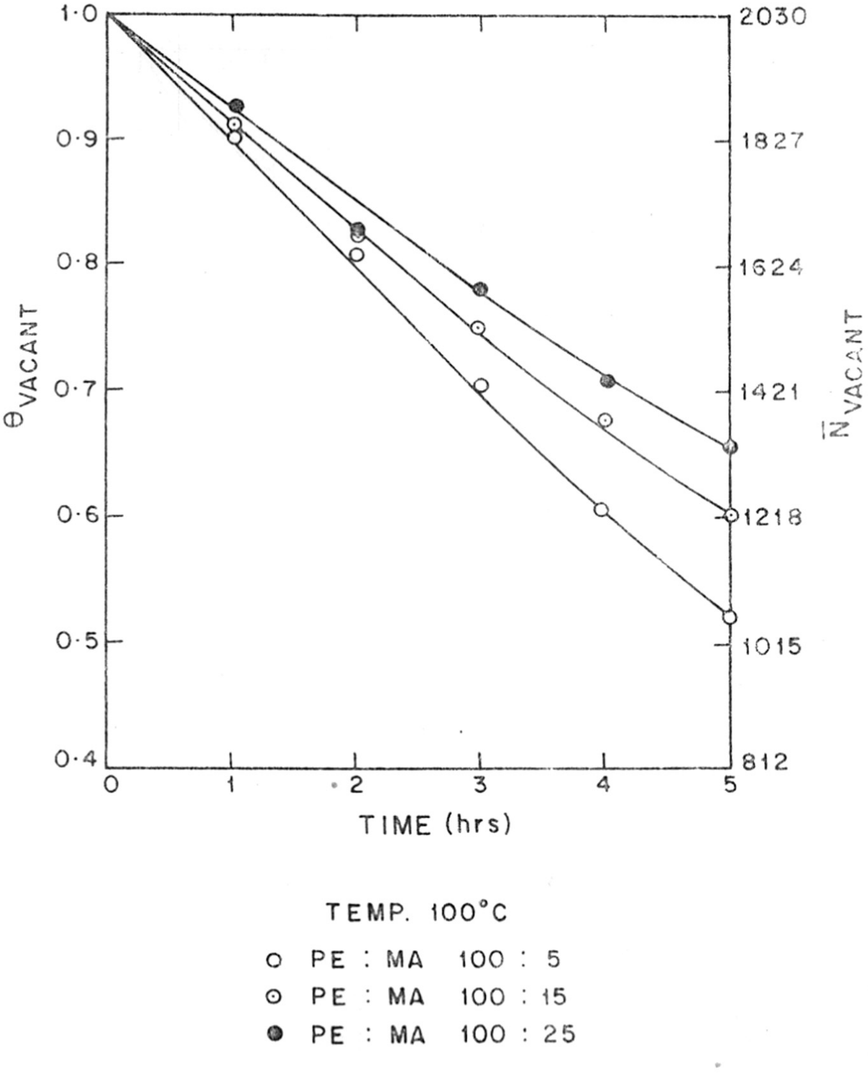


FIG. 3·4(B) : VARIATION OF UNSUBSTITUTED SITES DURING CHLOROCARBOXYLATION OF PE.

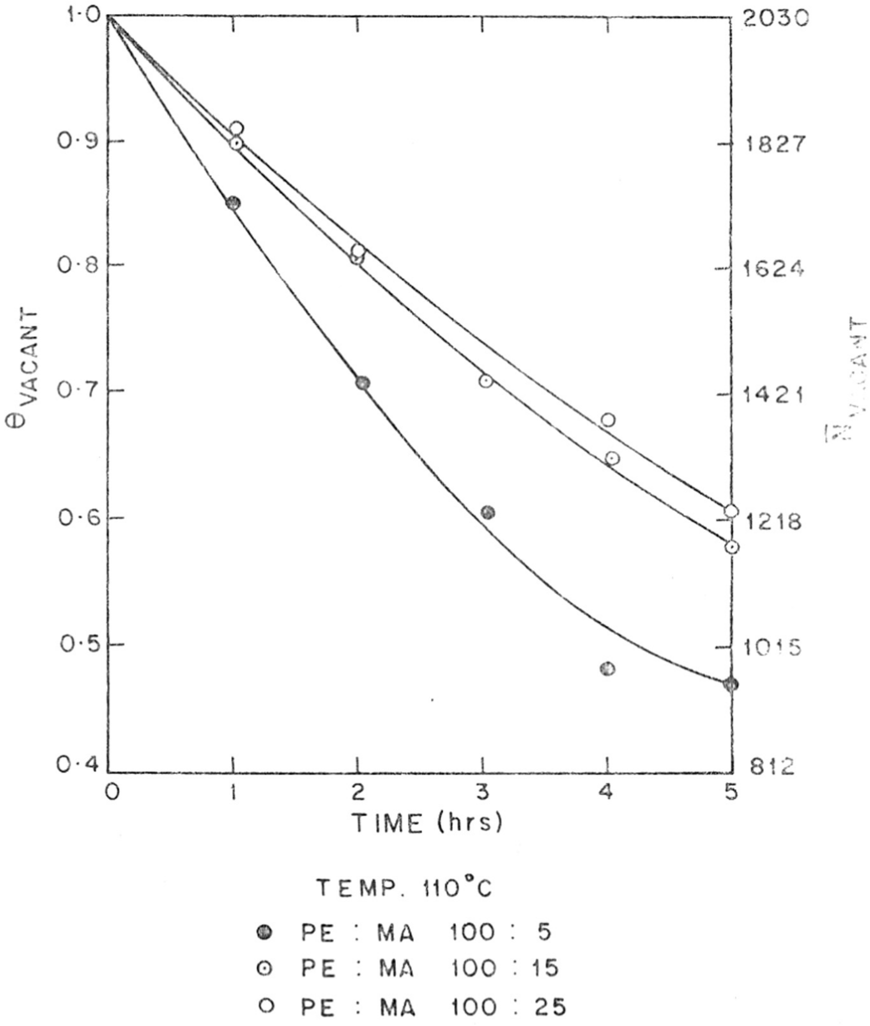


FIG. 3·4(C) : VARIATION OF UNSUBSTITUTED SITES DURING CHLOROCARBOXYLATION OF PE.

3.1 IR and NMR Studies of CCPE

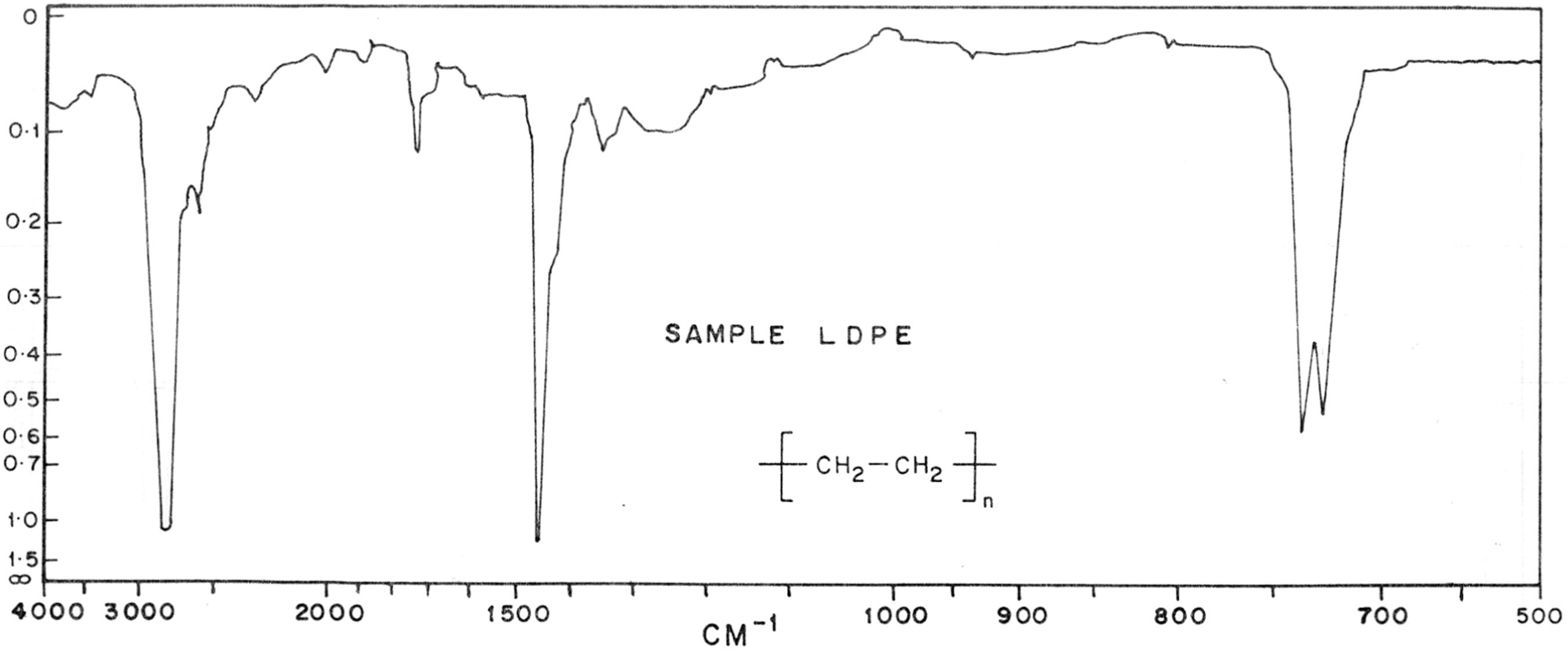
The pioneering work on IR studies of chlorinated high polymers was done by Thompson and Torkington.[6] The first important IR study on CPE was published in 1960 by Nambu.[7] The detailed studies on IR and NMR of CPE were carried out by Quenum et al.[8], in which they studied the conformational and configurational changes occurring while chlorinating PE by various methods. Since 1970 micro structural NMR analysis of CPE have been published indicating that NMR is a very effective tool for investigations,[9-12] though IR analysis is still a fast and routine method.

3.1.1 IR studies of CCPE

Experimental: The films used as the experimental samples were obtained by evaporation of carbon tetrachloride (CTC) solutions of CCPE and CPE, taken from mercury surface at room temperature. For polyethylene the film was obtained from CTC solution in a similar manner by evaporating CTC at elevated temperature. The cooled film was immersed in methanol for 24 hours and vacuum dried at 45°C for 72 hours.

(i) General features of the infrared spectrum [7,8] : The IR spectra are shown in Figs. 3.5 (A,B,C).

500 cm^{-1} to 800 cm^{-1} region: As a rule C-Cl stretching mode appears in this region. A strong band assigned to $C\text{-}Cl_2$ stretching appears at 527 cm^{-1} in the spectrum of polyvinylidine chloride (PVDC) (Figure 3.6-B). No such bands have been reported in the spectra of CPE even in the range of 73% chlorine.[7,8]



IR SPECTRUM OF LDPE

FIG. 3·5(A)

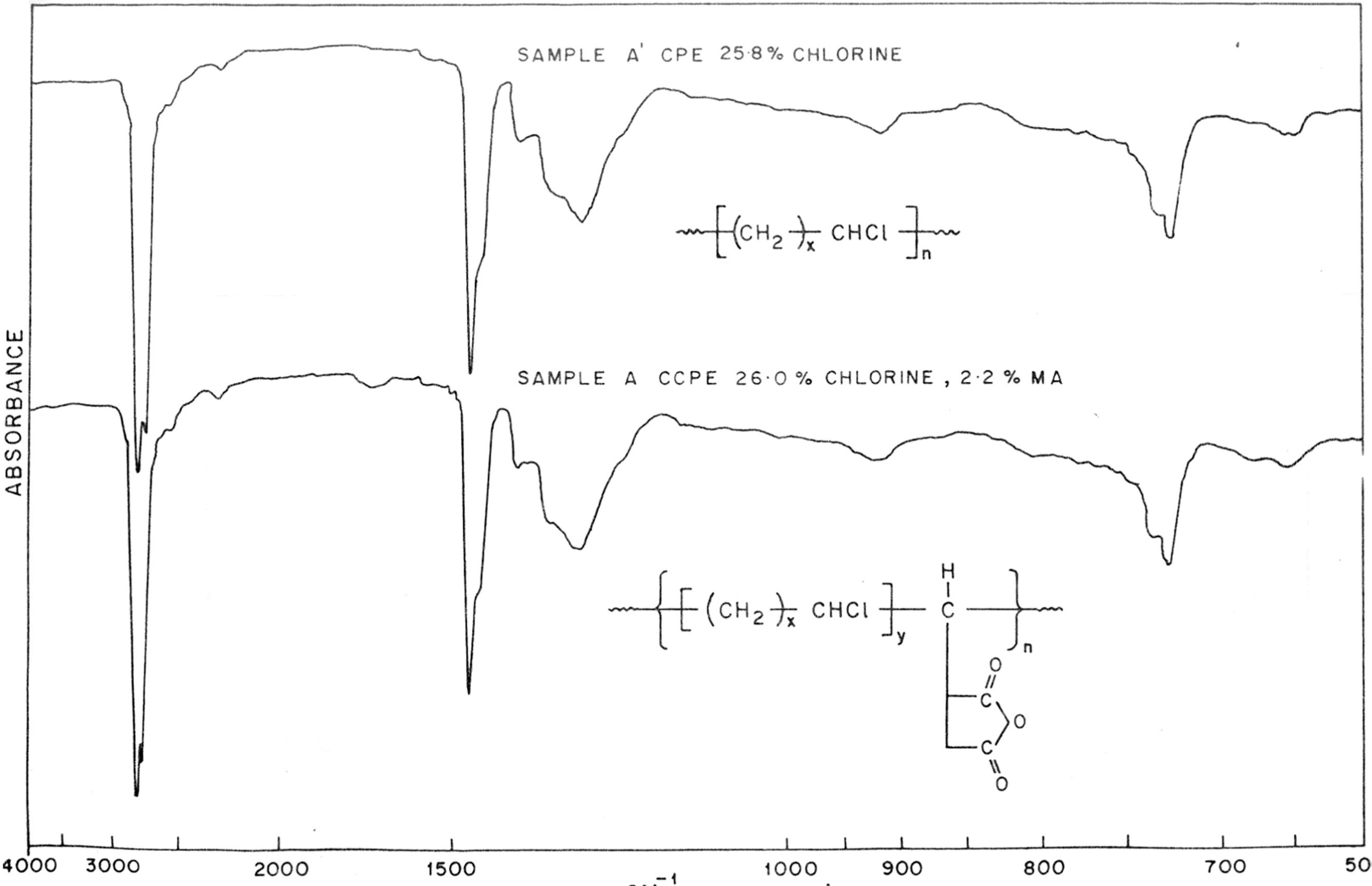
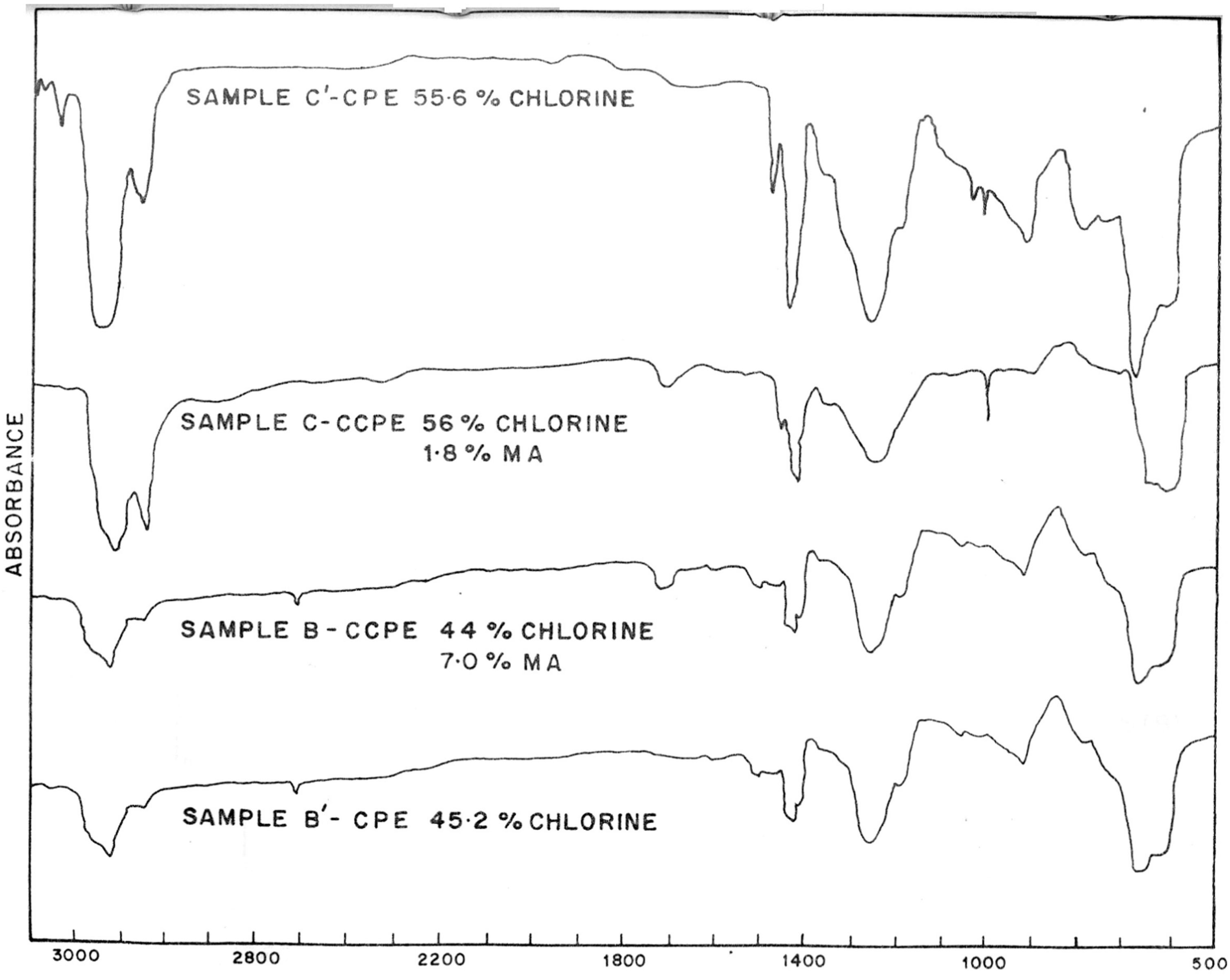
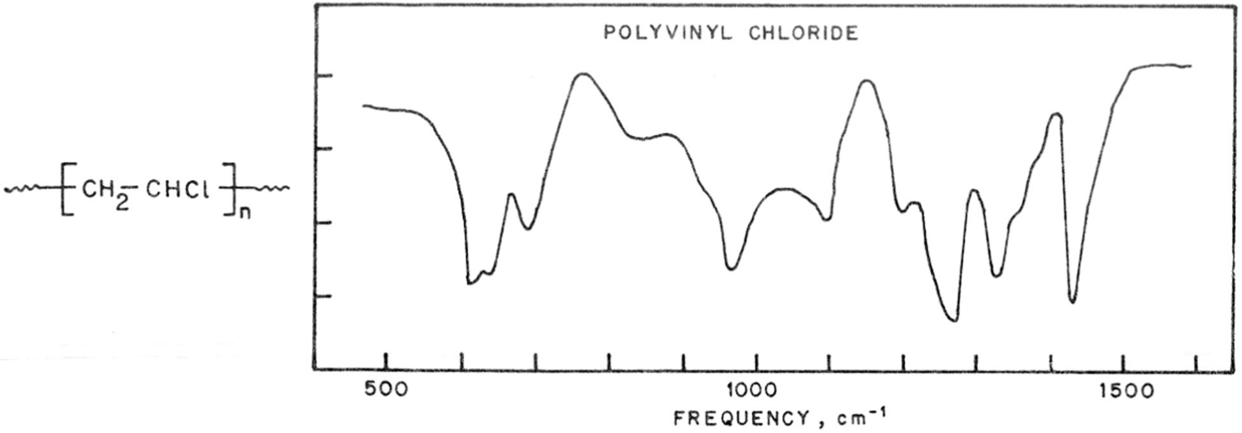


FIG. 3·5(B) : IR SPECTRA OF CPE AND CCPE.

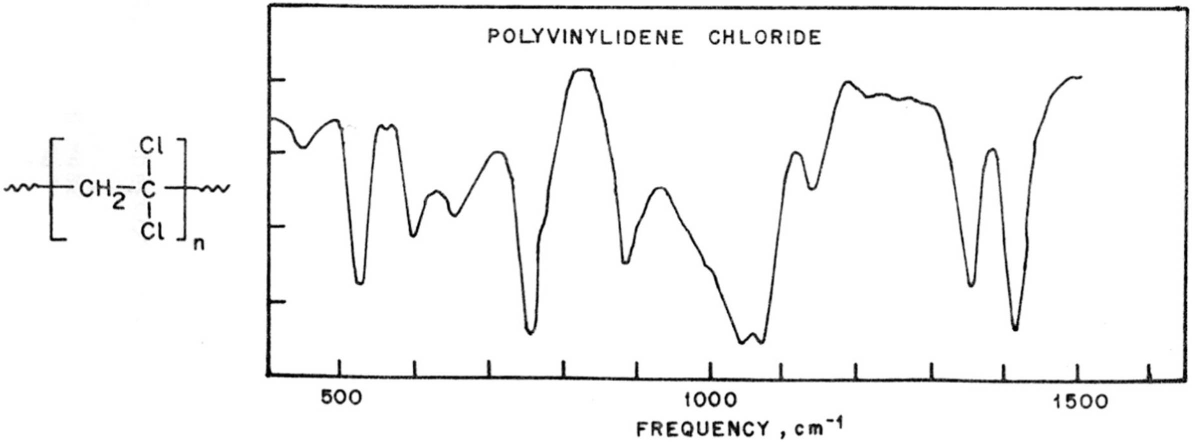


I R SPECTRA OF CPE AND CCPE
FIG. 3·5 (C)



$$\sim\!\!\left[CH_2-CHCl \right]_n\!\!\sim$$

FIG. 3·6 (A)



$$\sim\!\!\left[CH_2-\underset{Cl}{\overset{Cl}{C}} \right]_n\!\!\sim$$

FIG. 3·6 (B)

INFRARED SPECTRA OF POLYVINYL CHLORIDE AND POLYVINYLIDENE CHLORIDE.[13,14]

FIG. 3·6

The $-CH_2-$ rocking mode of polyethylene is found at about 725 cm^{-1} in the spectrum of PE and CCPE having low chlorine content. This peak disappears as the chlorine and carboxyl content of PE is increased.[7,8]

800 cm^{-1} to 1100 cm^{-1} region[7,8]: The carbon-carbon skeletal mode generally appears in this region. This mode appears rather weakly but a few new bands which are not in the spectrum of PE appear now in the spectra of both CPE and CCPE. Two such bands are at 910-930 cm^{-1} and 1060-1080 cm^{-1}. PVC has two carbon-carbon skeletal modes at 960 cm^{-1} and 1090 cm^{-1} (Figure 3.6-A). The bands at 910-930 cm^{-1} and 1060-1080 cm^{-1} in the spectra of CCPE and CPE probably resemble the bands at 960 cm^{-1} and 1090 cm^{-1} in the spectra of PVC.[13]

1100 cm^{-1} to 1300 cm^{-1} region[7,8]: The band at about 1180-1190 cm^{-1} in the spectra of CPE and CCPE which could not be found in the spectrum of original PE, probably corresponds to a weak band at 1196 cm^{-1} in the spectrum of PVC.[13]

The -CH- deformation mode appears strongly at 1255 cm^{-1} in the spectra of PVC [13], which is not found in the spectra of PVDC [14] (Figure 3.6-B). A similar strong band appears at about 1250-1260 cm^{-1} in the spectra of CPE and CCPE. The band becomes stronger as the degree of chlorination of PE in CPE or CCPE goes beyond 45%.

The IR spectra of CPE and CCPE resemble PVC in the region 500-1300 cm^{-1} than that of PVDC.[7] This observation suggests that the PE is chlorinated as -CHCl- and hardly any $-CCl_2-$ units are formed during chlorination or chlorocarboxylation.

Some of the important bands of CCPE are shown in Table 3.2.[7] These bands are due to chlorination part of CCPE and the assignment is based on comparing the spectra of CPE and CCPE.

Table: 3.2

Some Important Bands in the IR Spectra of CPE and CCPE and their assignment [7]

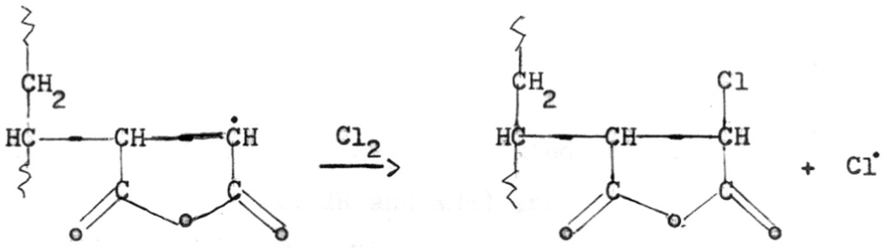
Frequency cm^{-1}	Resonance mode	Atoms concerned	Unit concerned	Structure concerned in CPE and/or CCPE chain
600-615	Stretching	C,Cl	-CHCl-	PVC syndiotactic sequence
720-730	Rocking	C,H	$-CH_2-$	$-(CH_2)_n - (n \geq 4)$
730-740-760	Bending	C,Cl	-CHCl-	$(CH_2$-CHCl-CHCl) or (CHCl-CHCl-CHCl)
780-800	Bending	C,Cl	-CHCl-	$(CH_2$-CHCl-CHCl) or (CHCl-CHCl-CHCl)
1180-1210	Deformation	-	-CHCl-	(CHCl-CHCl-CHCl) and PVC sequences
1375-1380	Deformation	-	$-CH_3-$	$-CH_2-\underset{R}{CH}-CH_2-$
1420-1430-1440	Bending	-	$-CH_2-$	PVC syndiotactic sequences
1450-1455-1440	Bending	-	$-CH_2-$	PVC isotactic sequences
1475-1480	Bending	-	$-CH_2-$	CHCl-$(CH_2)_x$-CHCl) with $x > y > z$
1465	Bending	-	$-CH_2-$	CHCl-$(CH_2)_y$-CHCl)
1455-1460	Bending	-	$-CH_2-$	CHCl-$(CH_2)_z$-CHCl)

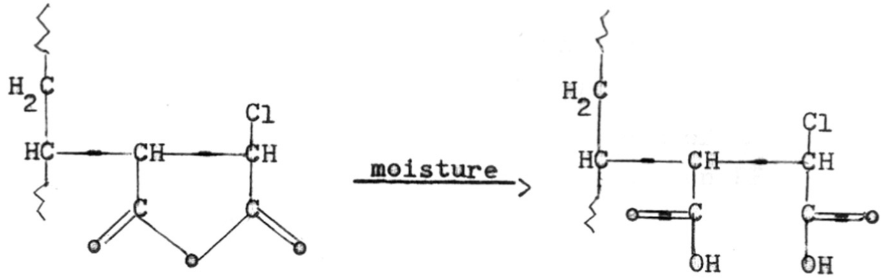
(ii) The absorption bands due to carboxylic groups (Fig.3.5)

The band in the region 3500 cm^{-1} to 2750 cm^{-1} is probably due to hydroxyl groups of dicarboxylic acids.[15] This peak which is very weak is probably due to hydrogen bonds of different lengths.[16]

The bands at 1750 cm^{-1} and 1720 cm^{-1} are due to the carbonyl $>C=O$ stretch present in the dicarboxylic acid.[15] Succinic acid shows a strong absorption band at 1700 cm^{-1} and the substitution of halogen[15] atom in the α position is indicated by the band at 1720 cm^{-1}, which shifts the low frequency band to higher frequency by $\approx$ 20 cm^{-1}.

It appears that in CCPE the substituted maleic anhydride (actually succinic anhydride) gets chlorinated at α position and further hydrolysis takes place due to the precipitation using excess methanol. Methanol used for precipitation may contain traces of moisture even after thorough drying and this moisture may be responsible for the conversion of anhydride to acid. α chloro maleic anhydride is very much sensitive to moisture and gets converted to acid. The reaction may be represented by :





Separate chlorocarboxylation reactions were carried out in order to avoid the hydrolysis of the MA moities reacted with PE. LDPE was used as the starting material for these reactions for the following reasons.

i) LDPE being a branched polymer will contain more number of tertiary and primary hydrogens. These hydrogens will be more probable sites for the substitution, either by MA or by chlorine.[17,18]

ii) The solution viscosity of the reaction mixture could be lower when LDPE is used (due to low molecular weight) as starting material for the given reaction temperatures.

iii) Due to the low viscosity of the system the reaction conditions could be properly chosen (i.e. no high temperature, initial high feed quantities of MA). This could give CCPE with higher quantities of MA (and chlorine) substituted within the reasonable time.

It was thought essential to prepare CCPE with high (more than 5%) quantities of MA substituted in polymer chain for structural studies (by IR and NMR) and to know the mode in which MA reacts with PE. **i.e.**

i) whether it reacts with PE as a single unit (as succinic acid derivative),

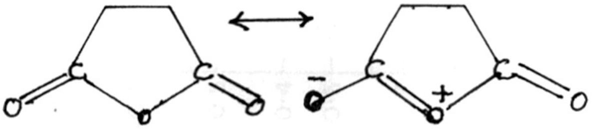
or ii) it reacts and forms short branches of poly (maleic anhydride) graft copolymer on PE chains.

CCPE was prepared using extremely dry solvent (TCE) and reaction was carried out under extremely anhydrous conditions at 143°C (B.P. of solvent) using excess quantities of MA in the initial feed (PE:MA ratio in the feed 100:25).

Pet-ether (boiling range 40°-60°C) dry distilled- was used for precipitation and the product was dried under high vacuum (less than 1 mm) at 60°C for several hours. Benzene solution of this CCPE gave negative results when treated for dye interaction test using Rhodamine dye [19], indicating the absence of free carboxyl groups. (-COOH).

The films for IR studies were prepared, as described earlier, under extremely anhydrous conditions. IR spectra of this film is shown in Figure 3.7(A) and also the IR spectra of the same film after exposing it to atmosphere for few hours (Figure 3.7-B). As can be seen it is very sensitive to moisture and shows both acid and anhydride bands due to partial hydrolysis.

IR spectra of CCPE (Figure 3.7-A) shows carbonyl ($>C=O$) bands at 1800 and 1845 cm^{-1}. The two bands are due to the following structures:[20]



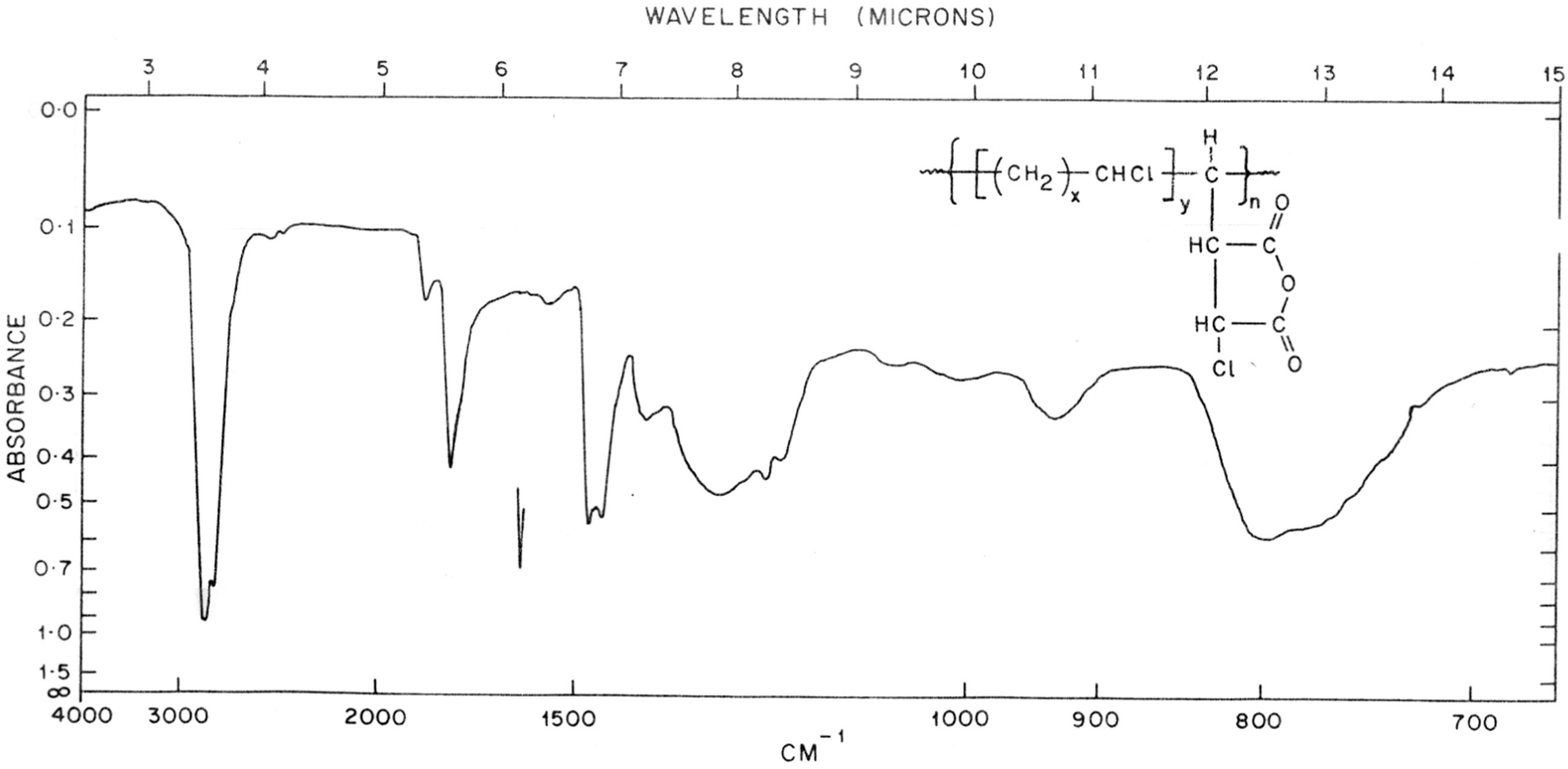


FIG. 3·7(A) : IR SPECTRUM OF CCPE (ANHYDRIDE FORM).

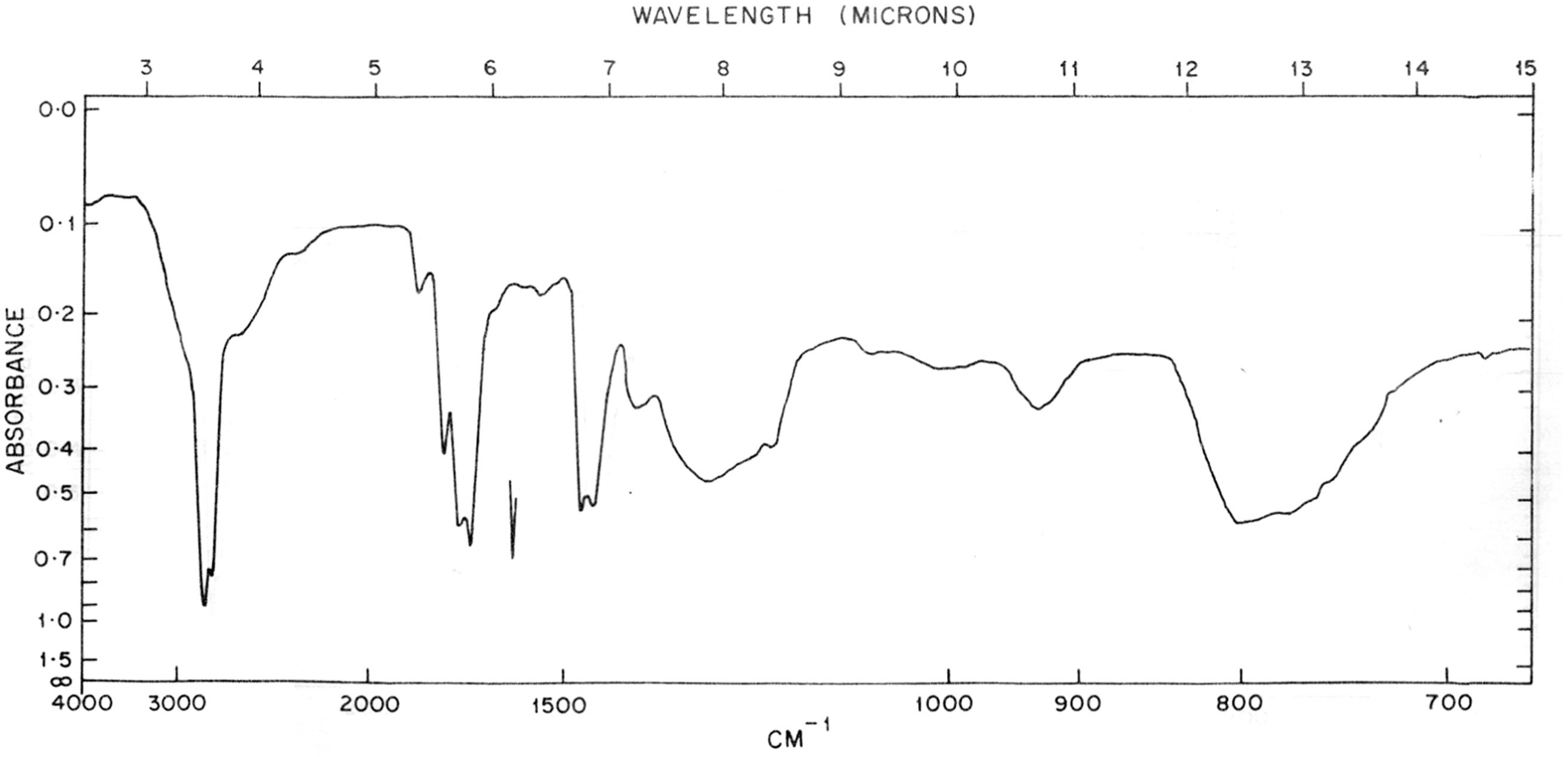


FIG. 3·7(B) : IR SPECTRUM OF CCPE (ACID AND ANHYDRIDE MIXED FORM).

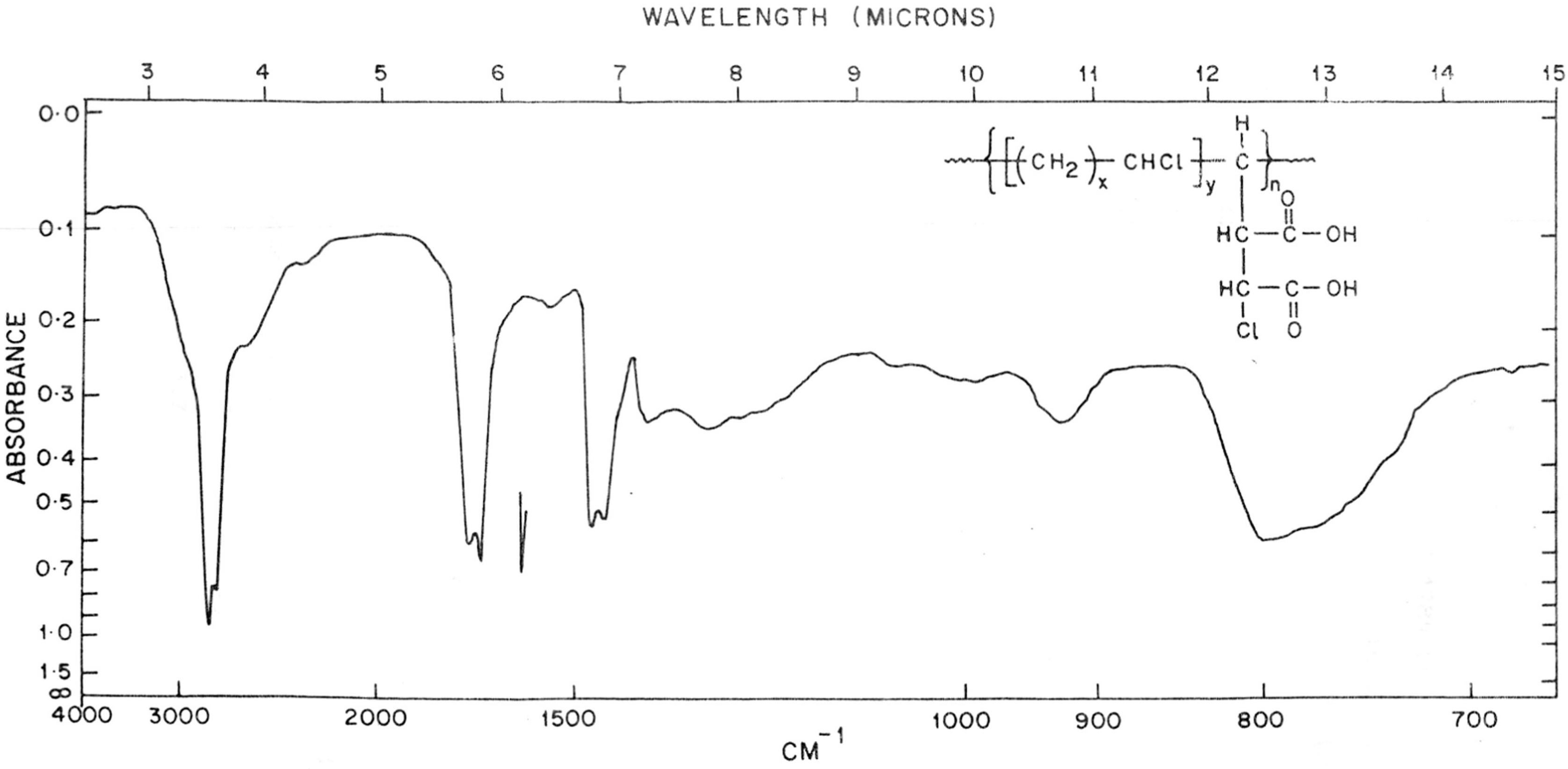


FIG. 3·7 (C) : IR SPECTRUM OF CCPE (ACID FORM).

These bands are seen at 1855 (m) and 1784 (s) cm^{-1} in the IR spectra of maleic anhydride, and in the IR spectra of succinic anhydride these can be seen at 1876 (m) and 1782 (s) cm^{-1} [21] (Figures 3.8 (A) and (B)).

The shift of the low frequency band (1782 cm^{-1}) to higher frequency by $\approx$20 cm^{-1} is probably due to the presence of chlorine atom at the α position of the anhydride ring.[21,22]

Figure 3.7 (A) also shows -C-O-C-(ester) band at 1220 cm^{-1}. This band appears in the IR spectra of MA at 1240 cm^{-1}. The shift of this band to the lower frequency (by 20 cm^{-1}) is probably due to the absence of conjugation with -C=C- bond.[21]

In the reaction of MA with PE in the presence of chlorine the -C=C- double bond of MA obviously forms covalent bond with PE. This changes MA into succinic anhydride derivative which is probably chlorinated at α position.

The IR spectrum of MA (Figure 3.8-A) shows a medium intensity band at 1660 cm^{-1} arising due to a -C=C- function.[22] This band is absent in the IR spectrum of CCPE and confirms the above prediction.

IR spectrum of MA was investigated in detail by **Mirone & Chiroboli.**[22] Some of the important bands of MA are listed in Table 3.3. These bands are particularly absent in the IR spectrum of CCPE (Fig. 3.7).

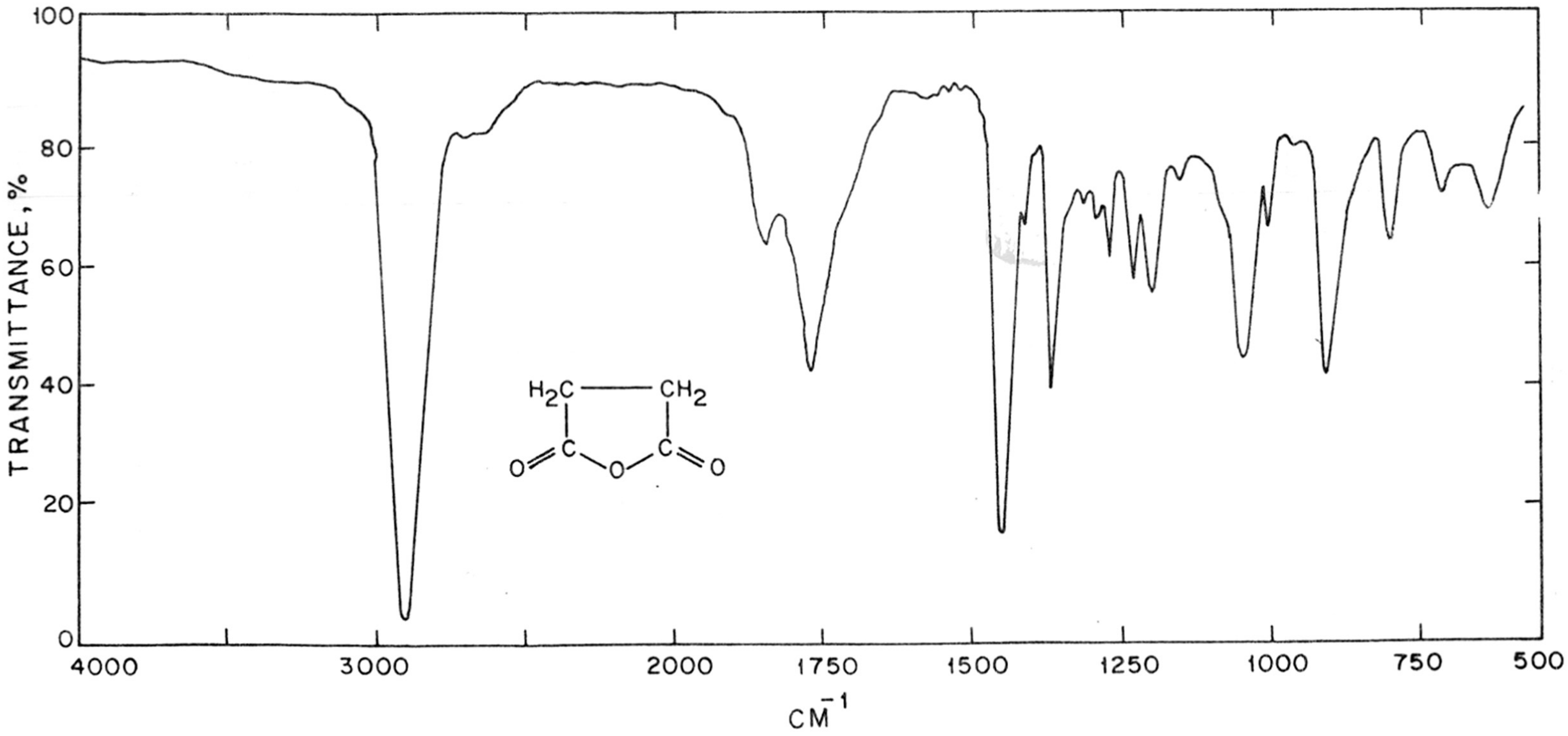


FIG. 3·8 (A) : IR SPECTRUM OF SUCCINIC ANHYDRIDE (NUJOL MULL).

Table: 3.3

Some Peculiar Bands in the IR Spectra of MA which are absent in IR spectra of CCPE

	Frequency cm^{-1}	Assignment and remarks	
1.	3130	-C=C-H	This band is absent
2.	1590	-C=C-	This band comes in conjugation with -C=O at 885 cm^{-1} is absent
3.	840		This band is absent, which comes in association with -C=C- double bond
4.	695	H atoms	in cis position to -C=C- double bond

IR spectra of CCPE does not show the typical bands at 1720 and 3300 cm^{-1} which are present in the homopolymer of MA or in the graft copolymer of MA (Fig. 3.8-C). On the other hand a band 1060 cm^{-1} is present in the IR spectra of pure α chloro MA and also in the IR spectra of CCPE. It appears therefore, MA, when reacting with PE does not form any graft copolymer.

Reactions of MA with polyethylene were investigated in detail by Braun et al.[18] They have established that MA reacts with PE as monomeric unit (succinic anhydride derivative) without forming any graft copolymer as short chains.

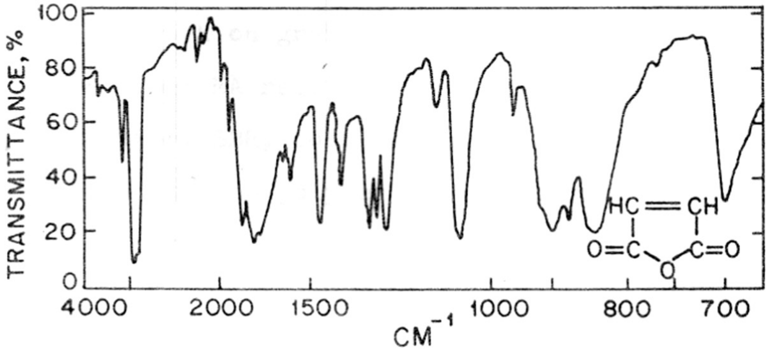


FIG. 3·8 (B)

IR SPECTRUM OF MALEIC ANHYDRIDE (NUJOL MULL).

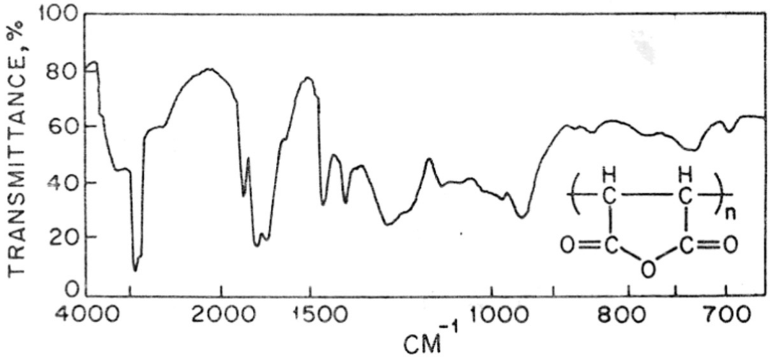
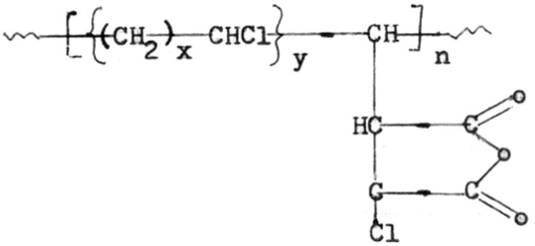


FIG. 3·8 (C)

IR SPECTRUM OF POLY-MALEIC ANHYDRIDE (NUJOL MULL) TAKEN FROM REFERENCE 29.

In a review on 'polymaleic anhydride' by Gaylord [23] the reaction mechanism for the formation of polymaleic anhydride is discussed in detail. The author has also reviewed the work on graft copolymers of MA.[23] It is stated that when MA reacts with flexible chain polymers (natural rubber, SBR, polyisoprene), it reacts as a single unit anchored to the polymer without forming any graft copolymer of short chains (of polymaleic anhydride).[23,24]

In the reactions of PE, when chlorine and MA simultaneously react, MA also reacts probably, as a single monomeric unit. The formation of any graft copolymer of MA does not appear probable from these findings. The probable structure of CCPE can be represented by:



3.1.2 NMR studies of CCPE

The study of NMR spectrum of CPE is the topic of research interest since 1970.[9-12] The detailed studies of IR and NMR spectra of CPE were carried out by Quenum et al.[9] In this work the conformational and configurational changes occurring while chlorinating PE by various methods were studied. NMR analysis was used to determine chlorine distribution in chlorosulfonated PE (CSPE) by Brame.[25]

Most of the NMR work on CPE (or CSPE)[25] are concerned with microstructural analysis and sequence distribution studies.[9-12] In these characterisations the following substances are used as model compounds for the assignment of various units in CPE chain:[9-12,25]

a) 1-chloro pentane
b) 1-4 dichloro butane
c) Syndiotactic poly(vinyl chloride) and
d) Isotactic poly(vinyl chloride)

The NMR measurements were further compared with the statistical predictions made for substitution polymers.[26]

The NMR spectra of CPE and CCPE is shown in Figure 3.9 (A) and (B). This was obtained at 60 MHz. The assignment of various structures in CPE and CCPE is rather broad and is based on the comparison of the assignments for various structural sequences, made by Quenum et al.[9-12], Brame [25] and the reported NMR shifts of the model compound as listed earlier. Table 3.4 shows the various structures which can be detected by NMR.

In Table 3.4 chemical shifts (in δ ppm from TMS) for various structural units in CPE and CCPE are given. The chlorine contents of these polymers were almost same (46%) corresponding to about 540 chlorine atoms per chain. CCPE chains contained additional equivalent maleic anhydride (4.8%) i.e. 27 MA moities per chain of the polymer.

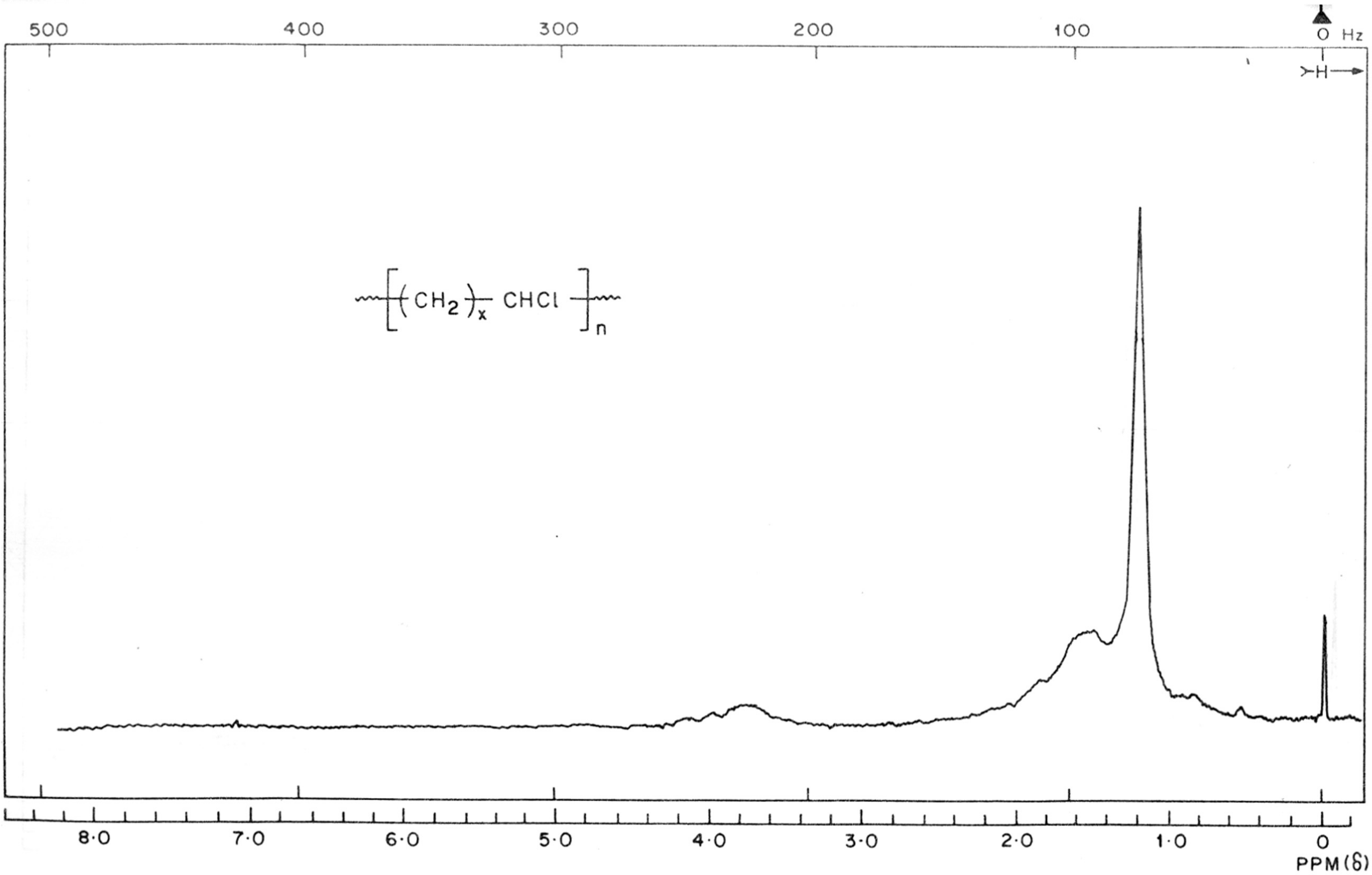


FIG. 3·9 (A): NMR SPECTRUM OF CPE.

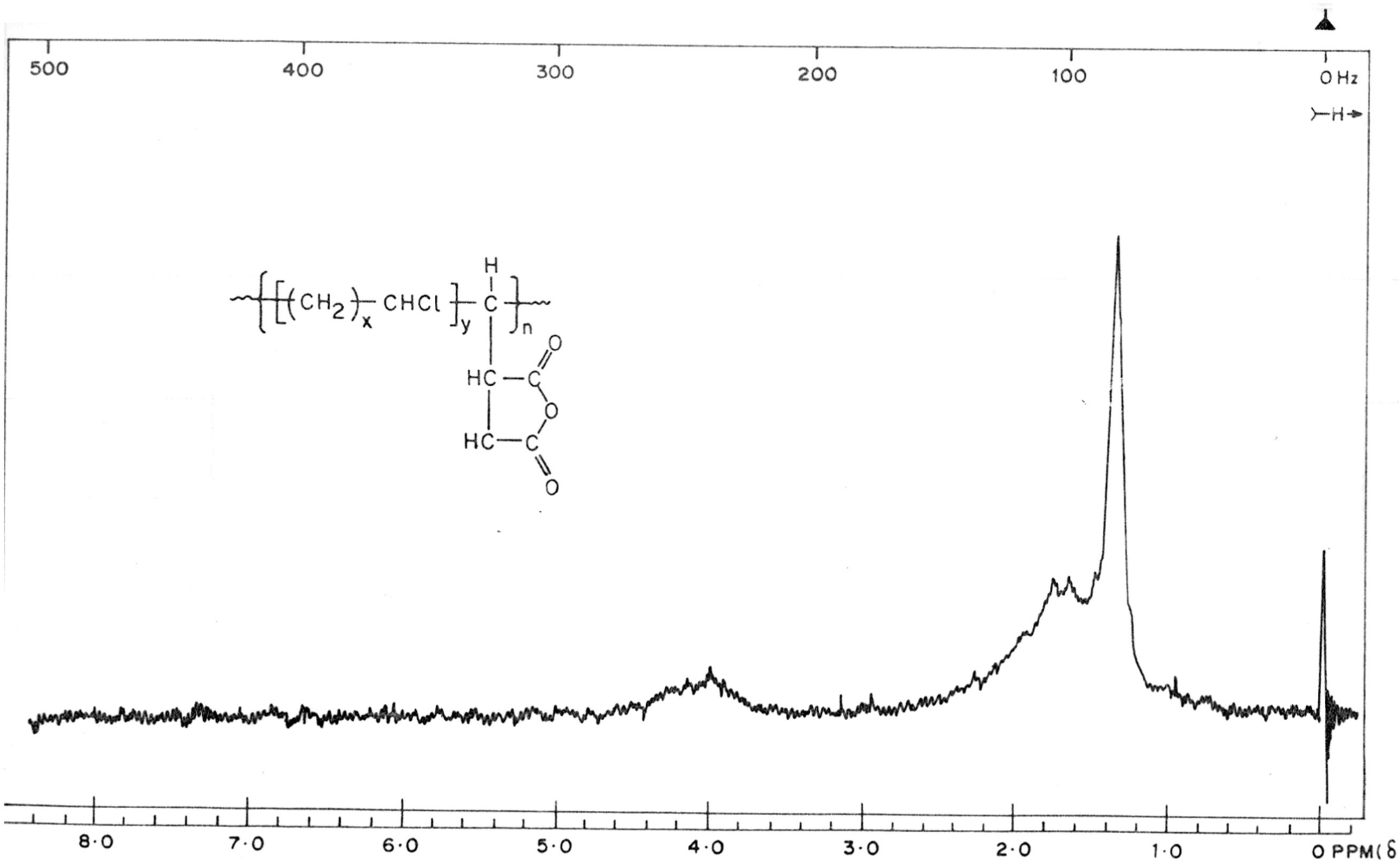
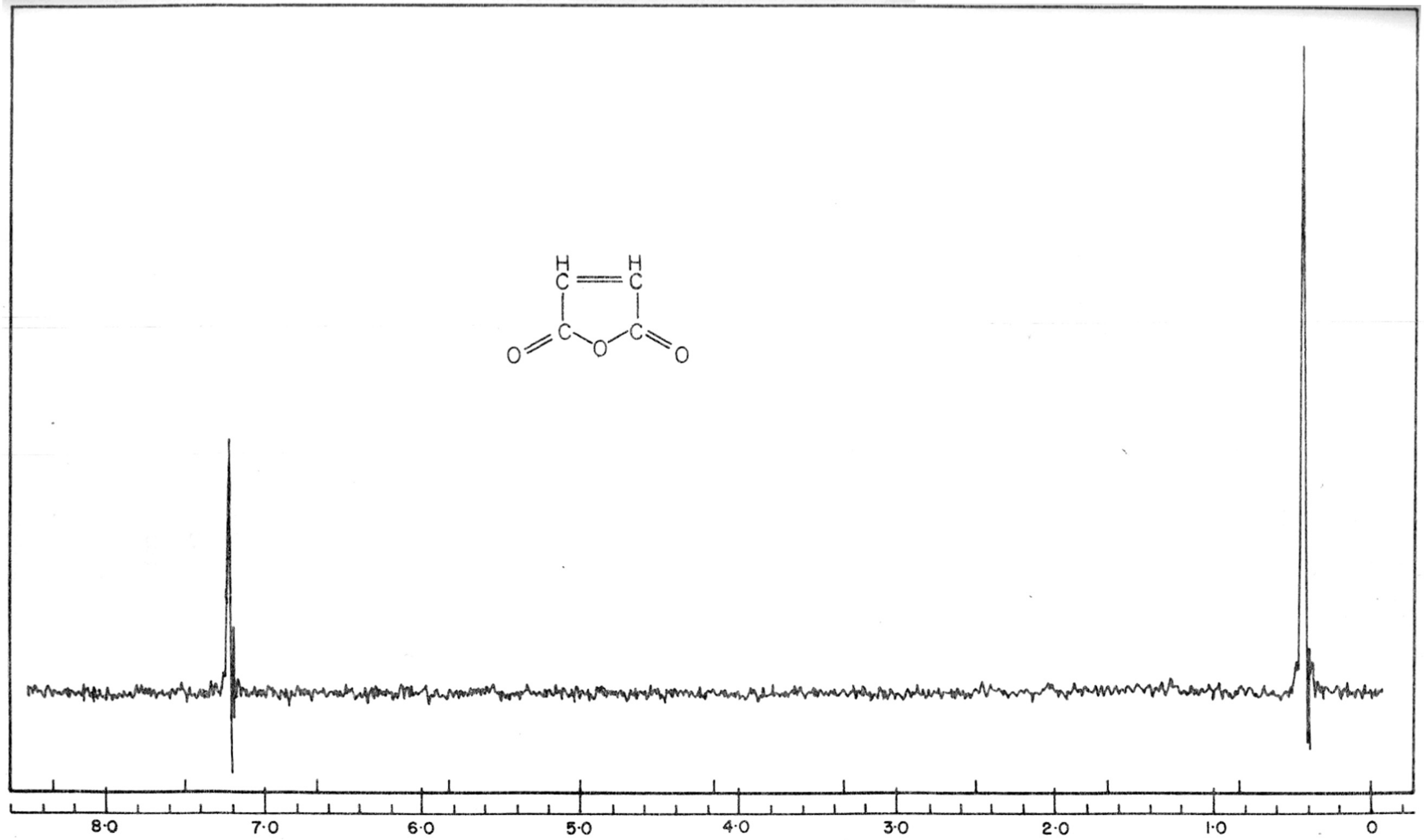


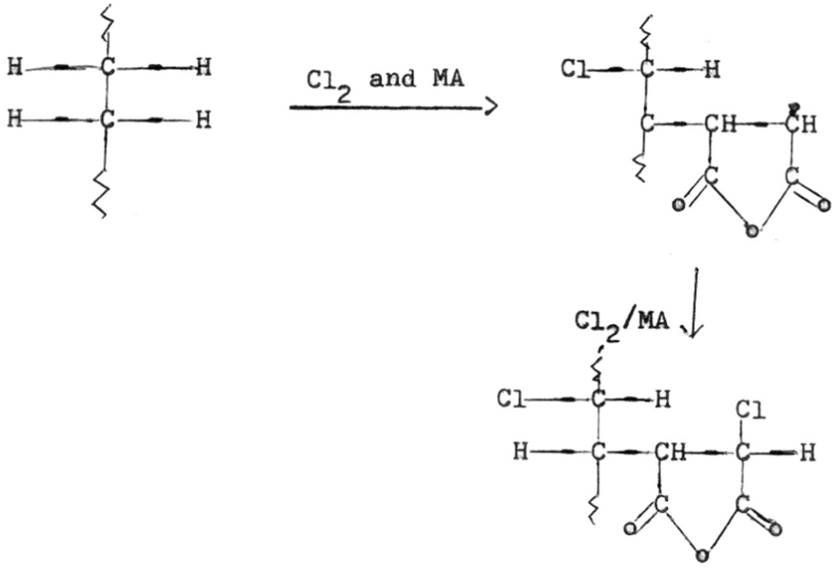
FIG. 3·9(B) : NMR SPECTRUM OF CPE.



NMR SPECTRUM OF MALEIC ANHYDRIDE

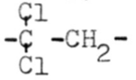
FIG. 3·9(C)

Formation of these units (I) can be explained by:

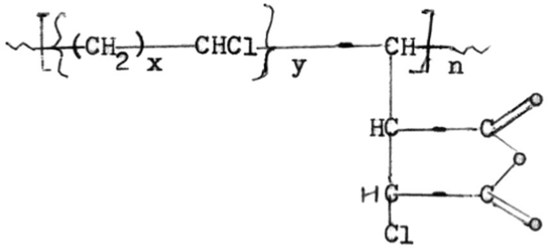


(I)

According to the IR and NMR characterization, chlorination (and chlorocarboxylation) of the PE chains seems to occur as follows.

At the beginning of chlorination some of $-CH_2-CH_2-$ units; and primary and tertiary hydrogens of PE, due to relatively higher rates of chlorination gets chlorinated, these are the units near the chain ends of PE which gets converted to $-CHCl-CH_2-$ (sample A IR) (Fig. 3.6).[8,9] As the chlorination proceeds, more secondary hydrogens (which are present upto 90% of the total hydrogens of PE) get converted to $-CH_2-CHCl-$ units (sample B of IR) (Fig.3.6-C). As chlorination exceeds 56.7% (that is of PVC), $-CHCl-CHCl-$ units are formed but no di substitution  $-\overset{Cl}{\underset{Cl}{C}}-CH_2-$ seems to occur. [8,9]

Chlorocarboxylation reaction also proceeds almost in the similar manner as far as chlorination is concerned except that the rate of chlorination is affected due to high chain transfer and radical scavenging action of maleic anhydride. [29] The detailed reaction mechanism will be discussed in section III(B). Based on these findings structure of CCPE can be represented by:



SECTION-III

(B) REACTION MECHANISM FOR THE CHLOROCARBOXYLATION OF PE

3.2.1 Introduction

This is the combination of two simultaneous reactions, namely:

a) Chlorination of PE , and

b) Reaction of MA with PE (carboxylation)

Chlorination of PE is a well established commercial process since early fourties. The studies in the structure and reaction mechanism of this process was carried out by many scientists till last decade (e.g. Nabu, Quenum et al. [7,8]). On the other hand, Gabara et al. [30] have studied the reactions of MA with PE in sixties. This reaction of MA and PE was studied in detail by Braun et al. [18] recently (1976) and have proposed the reaction mechanism for the same. In the proposed reaction mechanism for chlorocarboxylation of PE, various steps involved in both these reactions are taken into account.

The most probable reactions are summarised in Table 3.5 and will be discussed separately.[31]

Table: 3.5

Reaction 1	Remarks 2
1. $Cl_2 \longrightarrow Cl^\bullet + Cl^\bullet$	Thermal, photochemical or peroxide initiation
2. $P\text{-}H + Cl^\bullet \longrightarrow P^\bullet + HCl$	P-H means PE, $P^\bullet$ macro radical
3. $P^\bullet + Cl_2 \longrightarrow P\text{-}Cl + Cl^\bullet$	Chlorination of PE

contd...

Table: 3.5 contd..

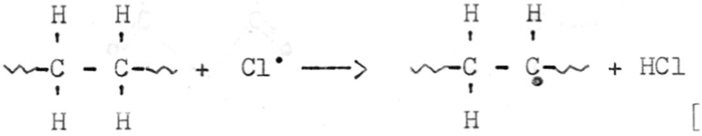
	1	2
4.	$\overset{\bullet}{P} + M \xrightarrow{\text{fast}} P\text{-}M^{\bullet}$	Carboxyl grafting with maleic anhydride (M) and its propagation
5.	$P\text{-}M^{\bullet} + P \xrightarrow{\text{slow}} P\text{-}M+P^{\bullet}$	
6.	$P^{\bullet} + N \xrightarrow{\text{fast}} P\text{-}H + M^{\bullet}$	chain transfer
7.	$M^{\circ} + M^{\bullet} \longrightarrow M\text{-}M$	dimerization of M
8.	$Cl^{\bullet} + M^{\bullet} \xrightarrow{\text{slow}} M\text{-}Cl$	chlorination of M
9.	$M^{\bullet} + n\,M \xrightarrow{\text{slow}} (M)_n\text{-}M^{\bullet}$	homopolymerization of M
10.	$P\text{-}M^{\bullet} + P\text{-}M^{\bullet} \xrightarrow{\text{fast}} P{=}M+PM$	termination by disproportionation

3.2.2 Discussion

Chlorine gas, when bubbled through the reaction mixture in solution of chlorinated solvent (CTC or TCE) at sufficiently high rate (about 10 lit/hr) attains quickly equilibrium concentration (saturation point). These dissolved chlorine molecules dissociate into chlorine radicals.

i.e. $$Cl_2 \rightleftharpoons Cl^{\bullet} + Cl^{\bullet} \qquad [1]$$

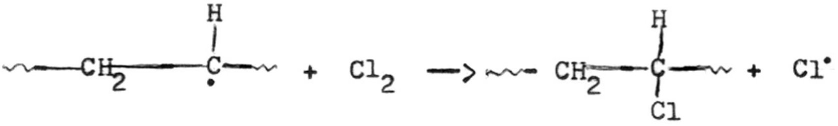
These chlorine radicals abstract hydrogen from PE generating PE macroradical (I).



$$\sim\!\!\underset{H}{\overset{H}{C}} - \underset{H}{\overset{H}{C}}\!\!\sim + Cl^{\bullet} \longrightarrow \sim\!\!\underset{H}{\overset{H}{C}} - \overset{H}{\dot{C}}\!\!\sim + HCl \qquad [2]$$

(I)

This may be regarded as the initiation of the reaction. This macroradical (I) can react with chlorine or maleic anhydride present in the solution of reaction mixture. When it reacts with chlorine molecule it will form chlorinated PE like segments in the polymer chain and in turn will generate chlorine radicals according to reaction (3):

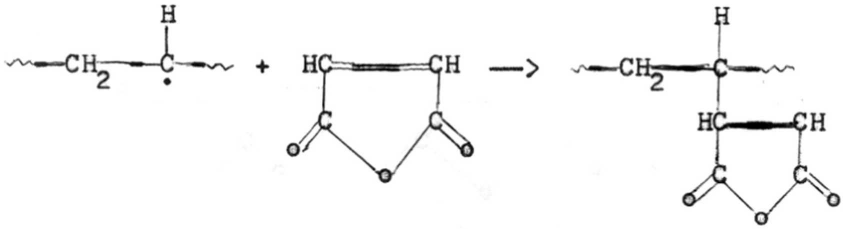


[3]

(I)

Reaction (3) being the usual radical chlorination of alkane,[32] macro radical generation through thermal initiation is assumed by Nabu et al.[7] and Quenum et al.[8] while proposing the reaction mechanism for the chlorination of PE.

Macro radical (I) can react with MA as in reaction (4):



[4]

(I)

(II)

In reaction (4) a new macro radical is generated. As discussed in Section III(A) (under the topic - structure of CCPE) this macro radical (II) probably does not react with further MA molecules. In addition to the earlier discussion, homopolymerization of MA or formation of graft copolymer on PE (or CPE) chain does not take place probably due to the following reasons:

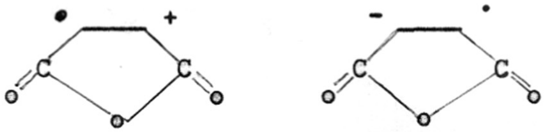
(1) MA reacts with PE (or CPE) in the same manner probably as it reacts with the other flexible chain macro molecules i.e. reacts as a single unit without forming any graft copolymer.[23]

(2) The temperature and dilution effects in radical polymerization of MA are discussed by Gaylord in a recent publication.[24] It is stated that polymerization of MA is possible in bulk and highly concentrated solutions. The homopolymerization requires excess free radicals.

In dilute solutions yield of polymaleic anhydride is reduced considerably. This is attributed to:

a) Short half life of MA excimer:

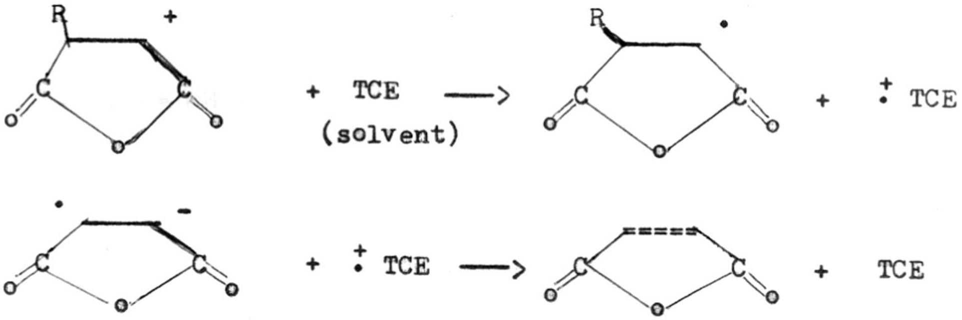
i.e.



and/or

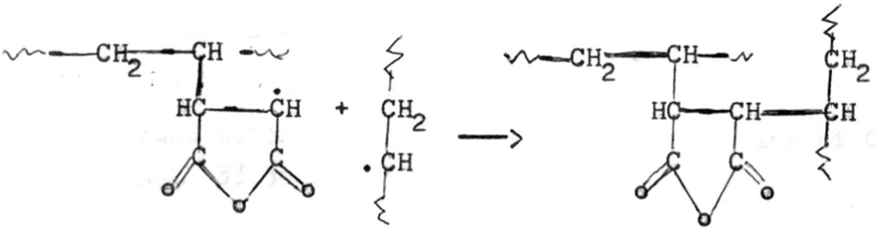
b) Interaction of this excimer with solvent:

e.g.



In this situation then there can be following probable reaction paths for macro radical (II).

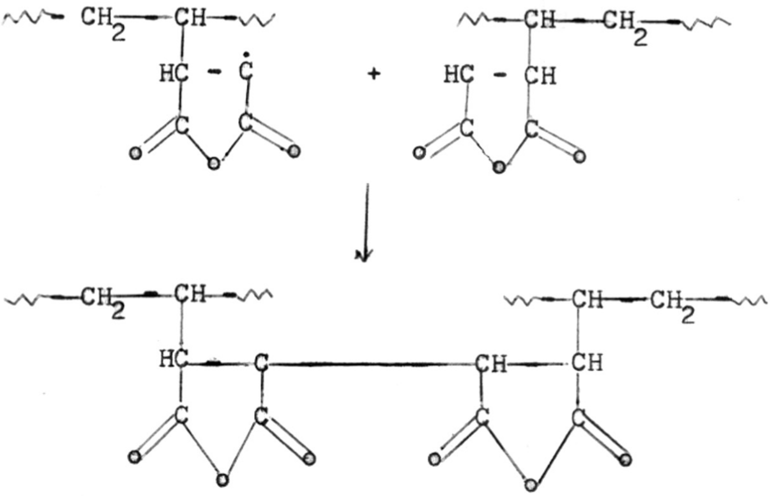
1. Macro radical (II) can combine with polyethylene macro radical (I) by expansion of CCPE chain through reaction (5) or two such macro radicals (II) can combine as in reaction (6), which will also cause the expansion of CCPE.



[5]

(II)

OR ....

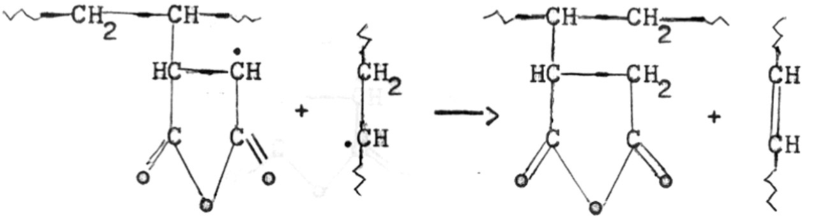


[6]

If this type of reaction mechanism is assumed the reaction product CCPE should show some crosslinking or gelling. The reaction mixture does not show any abnormal rise in solution viscosity. The product CCPE is soluble in solvents CTC, TCE, benzene etc.

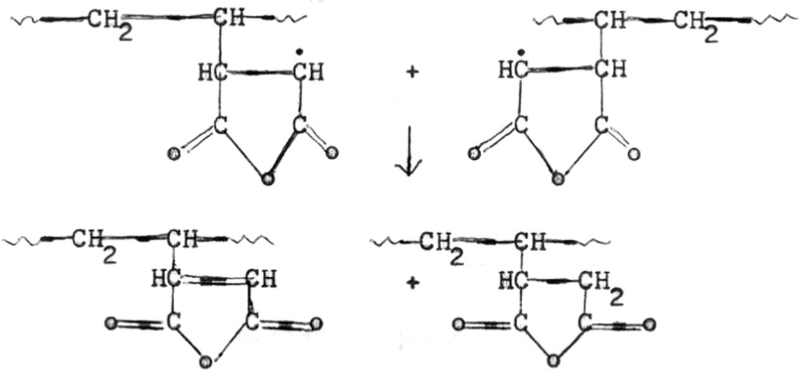
Solution viscosity measurements of CCPE, containing varying amounts of chlorine and MA does not show any abnormal rise in the viscosity. This was confirmed by comparing the solution viscosities of CPE and CCPE.[33,34]

2. Macroradical (II) can react by disproportionation with macroradical (I). The resultant -C = C- double bond will then be borne by PE through reaction (7).



[7]

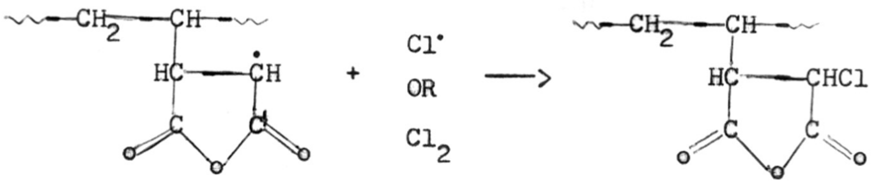
If the disproportionation of the two macroradicals (II) is assumed then double bond will be borne by one of the two anhydride groups by reaction (8).



[8]

If these disproportionations (as in reactions 7 and 8) are assumed, then the IR spectra (Fig. 3.7) of CCPE will show the bands corresponding to -C=C- double bonds at 889 cm^{-1} and 1643 cm^{-1}. The absence of these bands makes such disproportionations unlikely.

3. The macroradical (II) can react with chlorine radical or chlorine molecule.



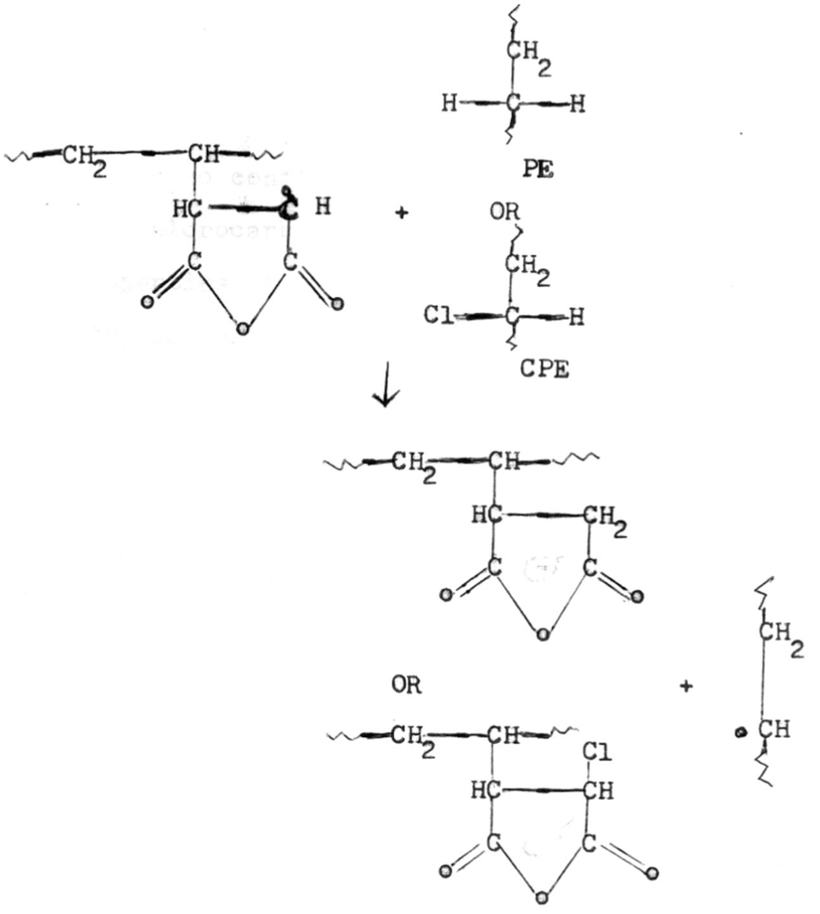
(II) (III)

[9]

In both these reactions there is loss of macroradical concentrations by termination and by disproportionation. These reactions also reduce the probability of forming graft copolymer on PE (or CPE) chains.

IR spectroscopic data supports this type of structure (III) formation. IR spectra of CCPE and hydrolysed CCPE shows the shift of low frequency carbonyl band (20) to higher frequency (1782 cm^{-1} to 1800 cm^{-1} and 1700 to 1720 cm^{-1}) which is probably due to the presence of chlorine atoms in the α position of the anhydride ring.[21,15] This is also confirmed by NMR spectra of CCPE and that of MA. However, formation of structure (III) is also possible as follows.

4. Macroradical (II) can react with PE or CPE segments by transfer of hydrogen or chlorine to CCPE, generating new macroradical.



[10]

This fragmentation appears more probable because MA is known to be easily ameable to the transfer reactions.[35,29]

Marked reduction in the rate of chlorination is always observed (Fig. 3.1, Section II(A)) during chlorocarboxylation process due to the presence of MA. This can be explained by the competitive nature of reactions (3) and (4) and radical scavenging [29] and termination reactions which are discussed earlier.

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SECTION-III

(C) REACTIONS OF CHLOROCARBOXYLATED PE

In order to confirm the structure and reaction mechanism of chlorocarboxylation of PE, and to see the chemical properties of CCPE, some of the well established reactions typical of carboxyl groups were carried out.[36] CCPE used for these reactions had composition as follows:

% chlorine (w/w)	31.2
% equivalent MA(w/w)	7.3

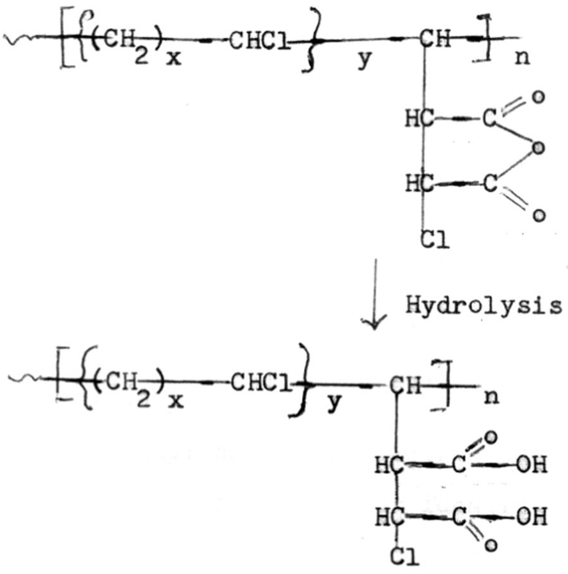
These reactions confirm the structure of the chlorocarboxylated polymers, besides being helpful to indicate the suitability of the polymer for various applications namely:[1,2,30]

1) as an elastomer, and
2) as a base for surface coatings.

3.3.1 Acid derivative of CCPE

The reaction product CCPE was dissolved in benzene and hydrolysed with mild alkali solution in benzene. It can also be hydrolysed by putting small rubbery crumbs of CCPE in boiling water. In fact, CCPE polymers are found to be sensitive to moisture, anhydride groups slowly getting converted to acids in humid environments.

The hydrolysed product showed positive test for (Palits) Dye interaction reagent[19] and negative test was shown by unhydrolysed starting material CCPE. Its IR spectrum (Fig. 3.7, Section III(**A**)) showed the absence of twin anhydride bonds at 1800 and 1848 cm^{-1} which are seen in the IR spectrum of CCPE (Fig. 3.7-A) and presence of twin bands at 1710-1740 cm^{-1} & 2750-3500 cm^{-1} representing ketonic and hydroxyl groups of carboxylic acids.[15] IR spectra of maleic acid and succinic acid shows these twin bands at 1705-1780 cm^{-1} and 1700,1725 cm^{-1} respectively. The shift of these bands at higher frequency in the spectrum of hydrolysed CCPE also confirms the presence of chlorine at α position of the carboxylic acid in CCPE. The spectrum also shows the typical pattern of carboxylic acid 'OH' groups in the range 2780 to 3500 cm^{-1}. Based on this IR data, CCPE can be represented by structure III and its hydrolysed product by structure IV.

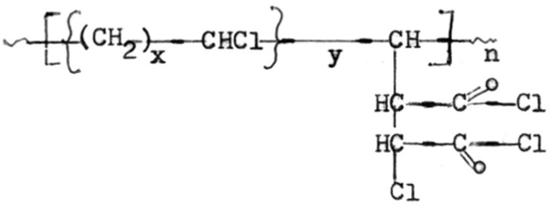


(IV)

3.3.2 Acid chloride derivative of CCPE

The dicarboxylic acid CCPE (IV) was further treated in solution with thionyl chloride in CTC at room temperature for three hours. After removing the excess thionyl chloride and the solvent by vacuum distillation yielded a product which showed negative test for Palit's dye interaction reagent.[19] Its IR spectra (Fig. 3.10) showed the shift of twin ketonic bands from 1705,1730 cm^{-1} to 1735,1780 cm^{-1}. This shift is attributed to the presence of electron withdrawing chlorine atom. This indicates that carboxylic acid is converted into its acid chloride.[21]

The broad hydroxyl band present in the IR spectra (Fig. 3.9) of dicarboxylic acid at 2700-3500 cm^{-1} (IV) is also absent in the IR spectra of acid chloride (Fig. 3.10). This all suggests that structure of acid chloride polymer can be represented by:



(V)

Thionyl chloride reaction was also carried out on chlorinated PE and PE under identical conditions. The chlorine analysis of these products revealed that backbone -C-C- chain of polyethylene does not get chlorinated under these conditions by reaction of thionyl chloride.

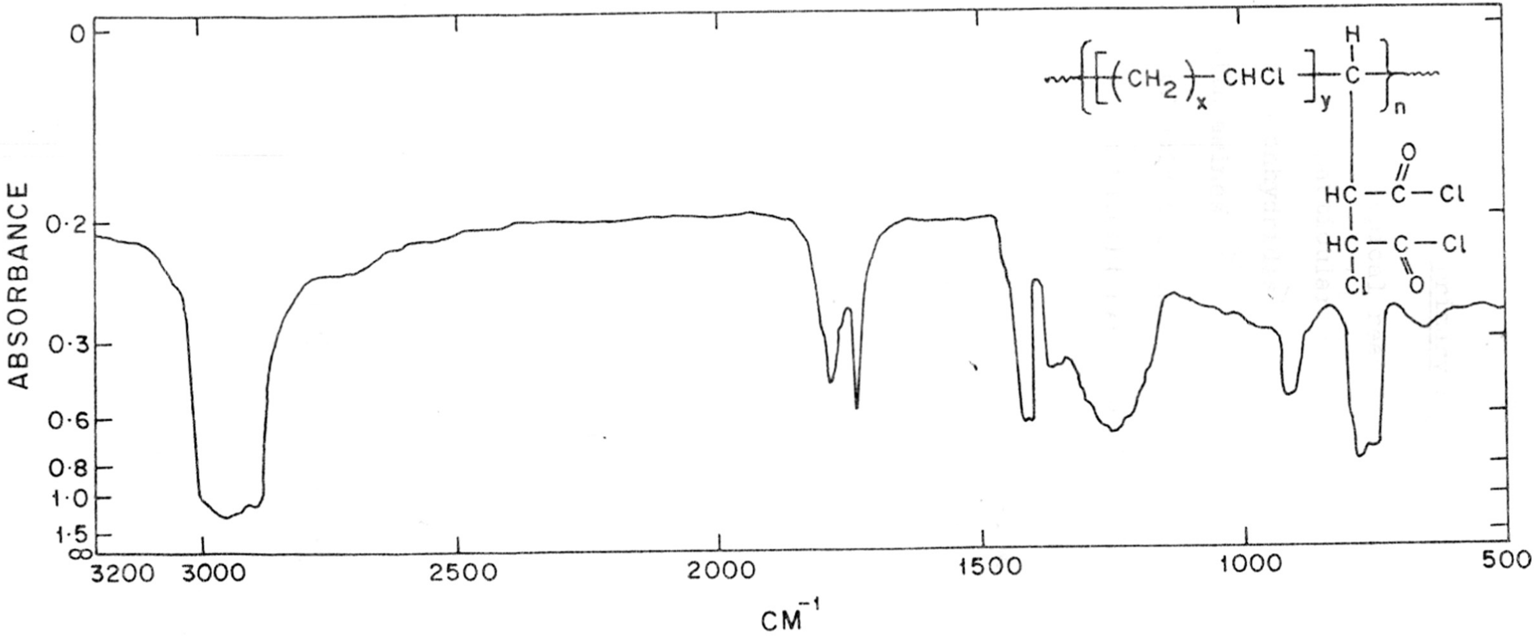
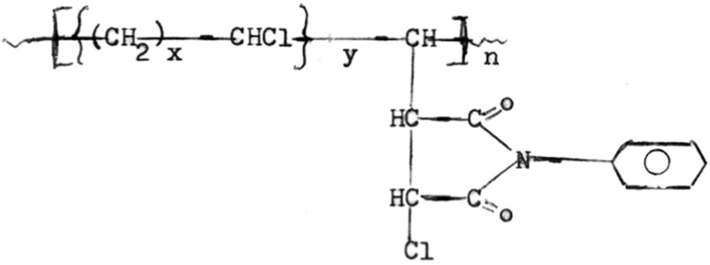


FIG. 3·10 : IR SPECTRUM OF CCPE : ACIDCHLORIDE DERIVATIVE (V).

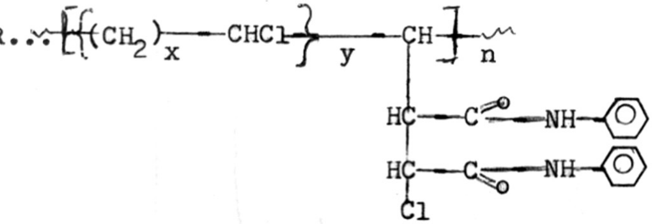
3.3.3 Reactions with primary and secondary amines

These are typical reactions of carboxyl groups. Organic acids, particularly dicarboxylic acids (acid chlorides and anhydrides), give typical products when treated with amines.[35,36] In order to confirm the structure of acid chloride (V) and in turn that of CCPE polymer, it was thought desirable to react acid chloride(V) with different amines. Elimination of hydrochloric acid and formation of new imide was realized when solution of this acid chloride (V) in CTC was treated with aniline[37,38] at b.p. of CTC (75°C). It gave a product whose structure can be depicted by (VI)



(VI)

OR..



(VII)

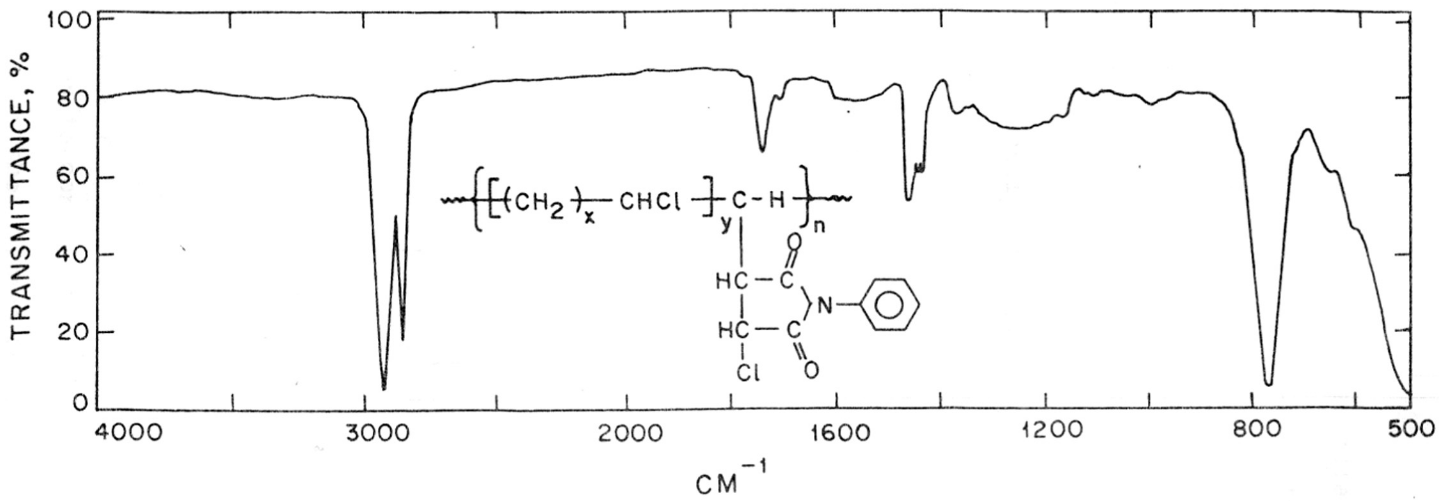
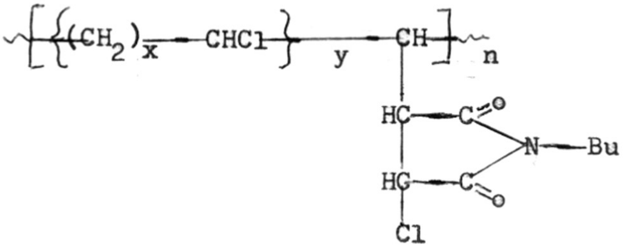


FIG. 3·11 : IR SPECTRUM OF CCPE : IMIDE DERIVATIVE (ANILINE) (VI).

Since slightly excess than required molar proportions of aniline was used - but not two moles - the possibility of the structure VII does not appear probable.[36,37]

The imide formation as depicted in structure (VI) from dicarboxylic acids is well documented in the literature.[37,38] This was also supported by IR spectrum which showed bands at 1757 cm^{-1} corresponding to imides and a band at 1550 cm^{-1} due to phenyl ring (Fig. 3.11). The spectrum does not show the twin bands at 1735,1780 cm^{-1} which are present in the IR spectrum of acid chlorides.[20]

Similar product was obtained when dilute solution of the acid chloride (in CTC)-(V) was treated with N-butylamine. Spectral data (Fig. 3.12) (imide band at 1750 cm^{-1}) and in anology with the above reaction with aniline, obviously the structure of the reaction product can be represented by (VIII):



(VIII)

In order to confirm the presence of anchored anhydride ring in the polymer chain and rule out the possibility of any free carboxylic groups which can be

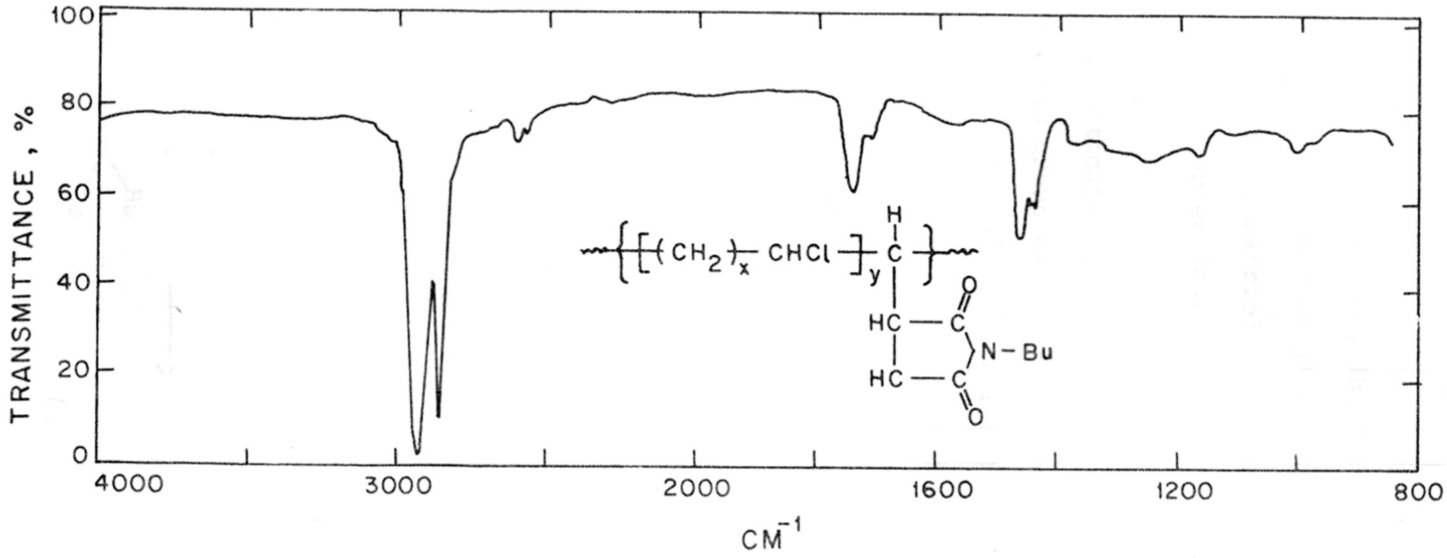
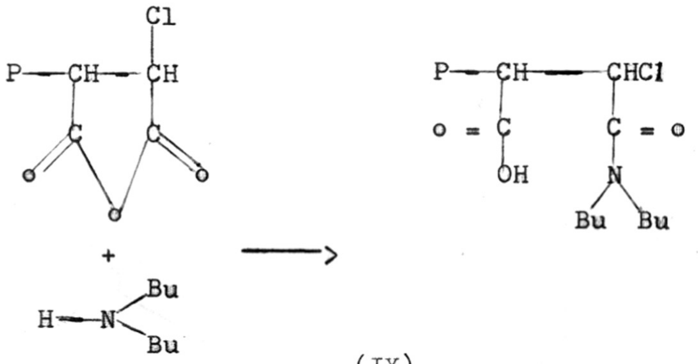


FIG. 3·12 : IR SPECTRUM OF CCPE : IMIDE DERIVATIVE (n-BUTYL AMINE) (VIII).

some times undetectable by IR, CCPE solution inCTC, was reacted with secondary butyl amine [36] at b.p. of CTC (75°C). This reaction was carried out under extremely anhydrous conditions in order to prevent the conversion of anhydride to acid.

As anticipated the IR (Fig. 3.13) of product showed a carboxylic group at 1700-1760 cm^{-1} in the IR and another ketonic band at 1640 cm^{-1} corresponding to amide groups.[15,20] The presence of one hydroxyl group was also revealed by the visible spectra of the reaction product plus Rhodamine B complex [19] (Palits dye interaction reagent) which showed the optical density of 0.05 at 570 nm (Fig. 3.14) as against the O.D. of 0.08 for the dicarboxylic acid (IV) Rhodamine B complex which corresponds to double the amount of carboxyl moities present as compared to the former one.

This peculiar behaviour of ring anhydrides is well documented in the literature [36,37] and thus the reaction of CCPE can be represented by:



(IX)

Here P- represents the chlorinated PE segment of CCPE.

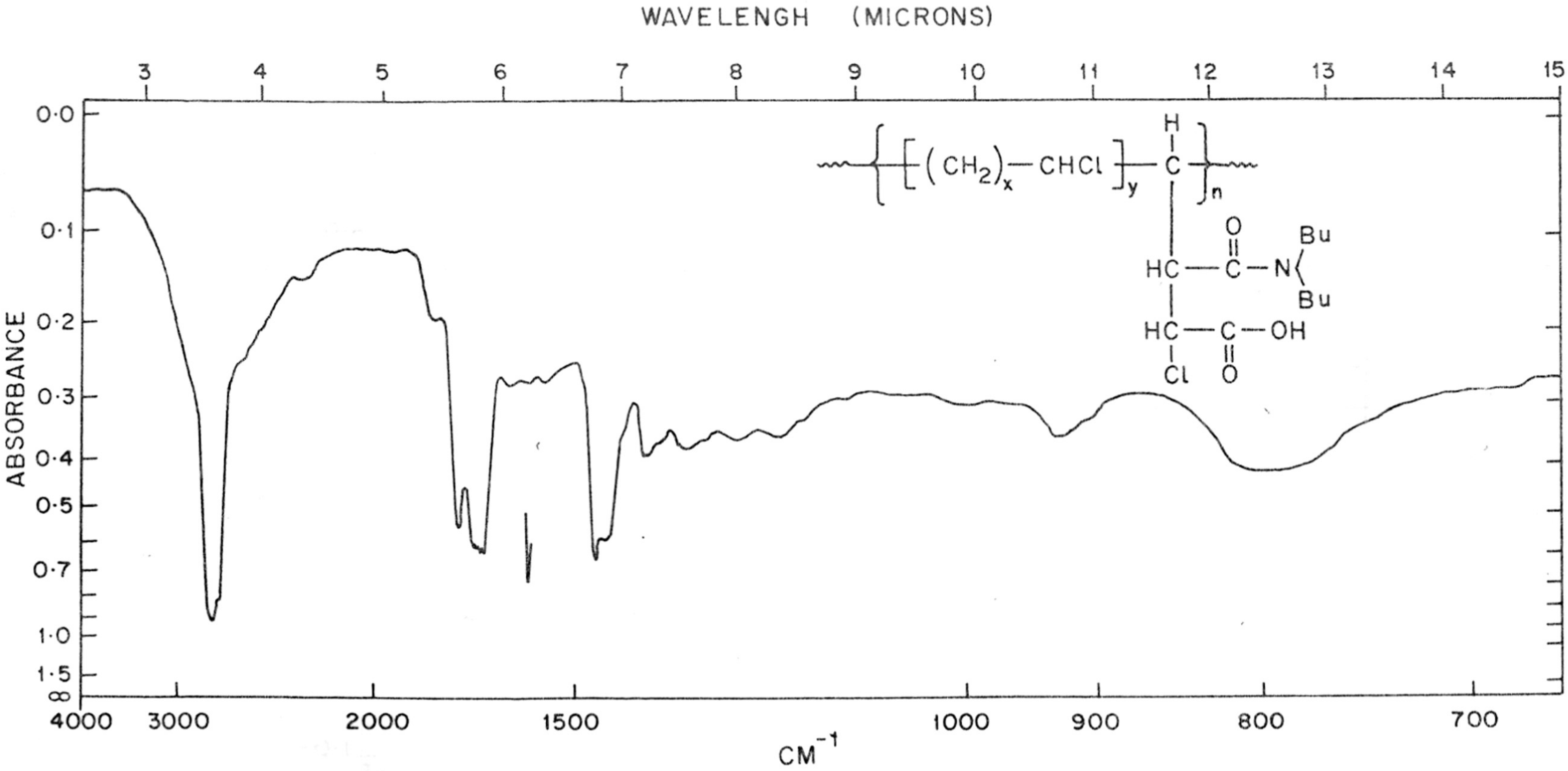


FIG. 3·13 : IR SPECTRA OF CCPE : AMIDE DERIVATIVE (SECONDARY BUTYL AMINE) (IX).

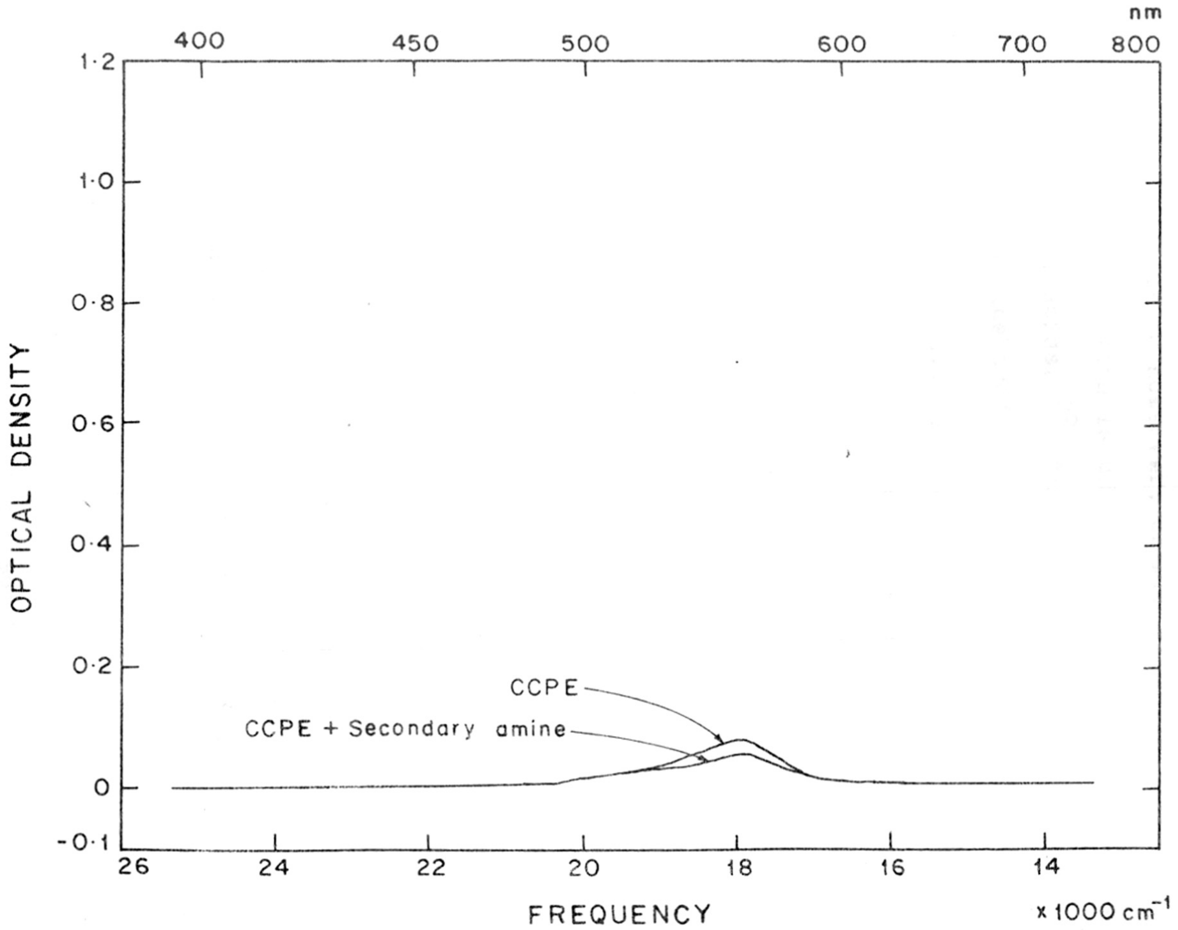
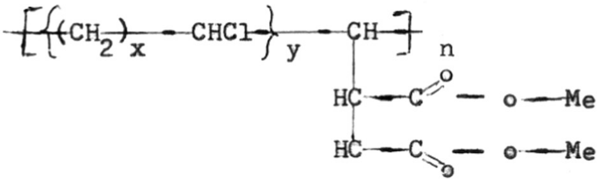


FIG. 3·14 : VISIBLE SPECTRA OF CCPE AND AMIDE DERIVATIVE (IX) FOR CARBOXYL DETERMINATIONS.[19]

3.3.4 Esters of CCPE

Carboxylic acids and acid anhydrides can be converted to esters using some very common alcohols. Especially sodium methoxide reaction is used for quantitative estimation of carboxylic acids.[39] This ester can be isolated by little warming of the product with distilled water.

Figure 3.15 shows the IR spectra of ester obtained by reaction of CCPE with sodium methoxide. It shows typical ketonic bands at 1730-1695 cm^{-1} and new bands at 1190 cm^{-1} corresponding to ester linkage.



(X)

Reactions of carboxylic elastomers with polyhydric alcohols are well established. In this case, for the formation of ester crosslinks carboxyl groups are converted to acylhalids and then these can be reacted with diols.[41,42] This reaction i.e. reaction of polymer acid chloride (V) and ethane diol was carried out for CCPE in order to confirm the structure of CCPE. Acid chloride (V) solution in CTC was treated with ethane diol at 75°C (b.p. of CTC).

The reaction product of polymer acid chloride (V) and ethane diol was partly soluble in CTC. IR spectra (Fig. 3.16) of the soluble part showed the shift of ketonic band from 1780, 1735 cm^{-1} to 1725, 1690 cm^{-1} and a new band at 1160-1180 cm^{-1} corresponding to ester linkage. It also

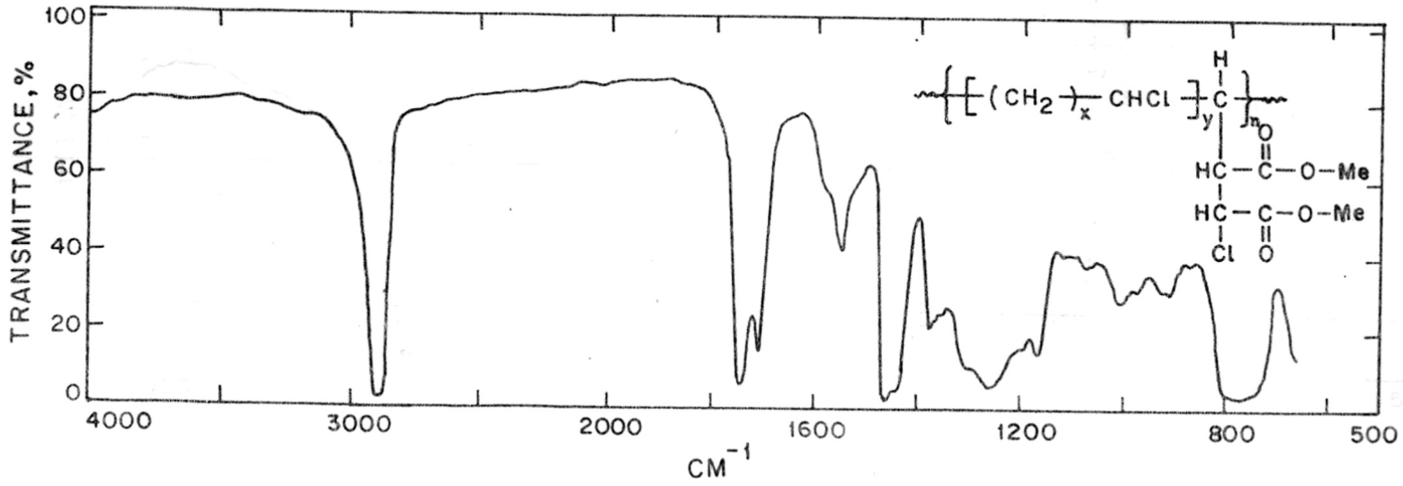


FIG. 3·15 : IR SPECTRUM OF CCPE : ESTER DERIVATIVE (METHYLESTER) (X).

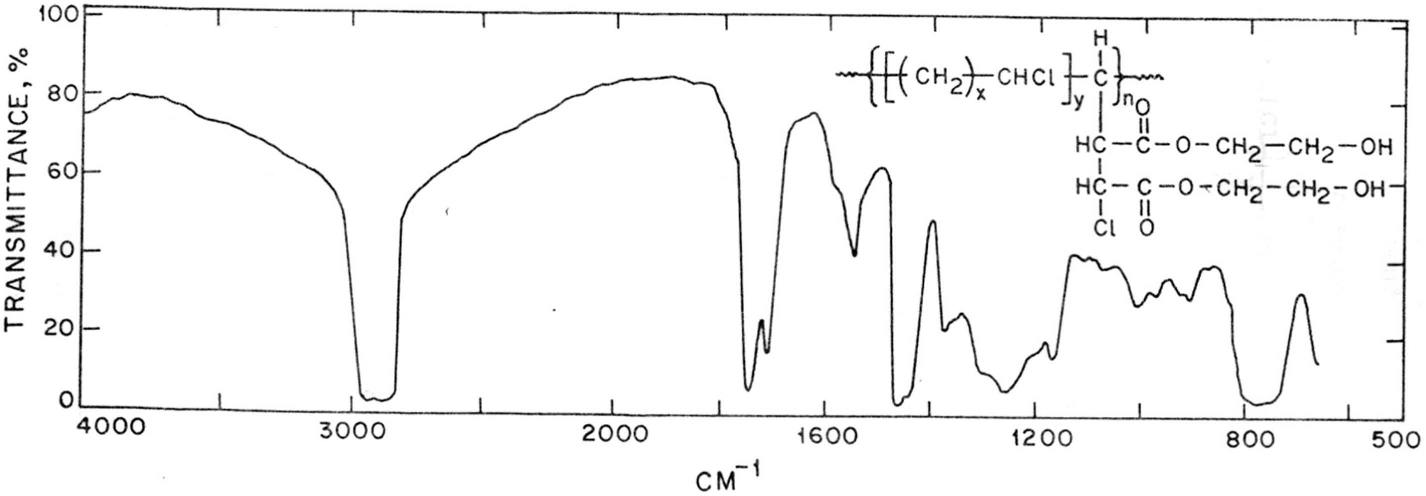
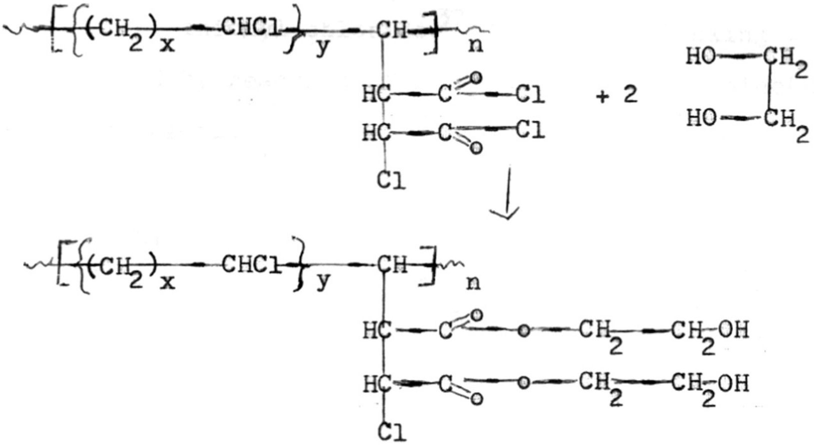


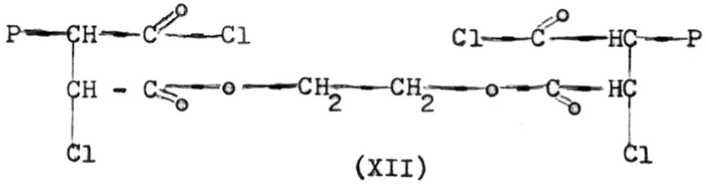
FIG. 3 16 : IR SPECTRUM OF CCPE ESTER DERIVATIVE (ETHANE DIOL)(XI).

showed the broad hydroxyl band in the region 2700-3500 cm^{-1}. The reaction can be represented by:



(XI)

and the crosslinked product can be represented by (XII):

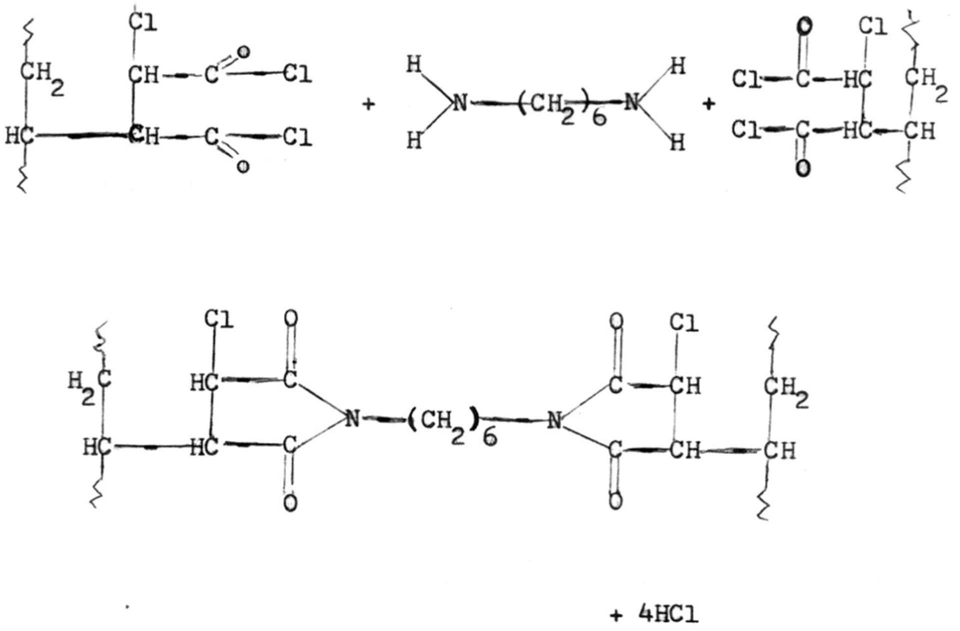


(XII)

Here P represents CPE segment of CCPE

3.3.5 Crosslinking reactions of CCPE

Finally, the presence of anhydride structure was established when a crosslinking between the two anhydride groups (or dicarboxylic acids or dicarboxyl acid chlorides) with a dibridge of diamines was obtained.[39] This was achieved by reacting CCPE (in dilute solution of CCl_4) with different diamines e.g. hexamethylene diamine (HMD), diphenyl methane diamine in presence of catalytic quantities of thionyl chloride.[37,38] The crosslinking was also achieved by reaction of hexamethylene tetraamine(HMT). One of the reactions can be represented by:



where P- is chlorinated PE segment of CCPE

These gelation reactions are characteristic of the amines used and reaction products, which can be recovered from boiling methanol, are also having well defined elastomeric nature. These are summarized in Table 3.6.[43]

Table: 3.6

Gelation of CCPE with Amines

CCPE+HMD	CCPE+HMT	CCPE+Diphenyl-methane diamine
i) Gels reasonably high within 15 min. at room temperature	i) Gels very slowly at room temperature	i) Does not gel much at room temperature
ii) Reaction product elastomeric with better flexibility	ii) Reaction product stiff but rubbery	ii) Better gelling at 100°C
		iii) Reaction product stiff but rubbery with good strength

CPE was also treated for gelation reactions under identical conditions. It did not show any (appreciable) gelation with these amines.

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SECTION IV

CHLOROCARBOXYLATION OF POLYETHYLENE
KINETICS OF THE PROCESS.

SECTION-IV

CHLOROCARBOXYLATION OF POLYETHYLENE: KINETICS OF THE PROCESS

4.1 Introduction

Many organic reactions involving polymeric substances can be compared with those of low molecular weight substances of similar structure i.e. low molecular weight analogues. There are some examples in which the reaction of a polymeric substance shows abnormal behaviour compared to the reaction of its low molecular weight analogue. The rates of these reactions are orders of magnitude slower or sometimes orders of magnitude faster. The following reactions involving polymeric molecules are examples.

a) Catalytic (heterogeneous) hydrogenation of an unsaturated polymer in solution can be much slower than the corresponding low molecular weight analogue.[1]

b) The copolymers of acrylic acid and p-nitrophenyl methacrylate are hydrolysed many orders of magnitude more rapidly than p-nitro phenyl ester of a monocarboxylic acid.[2]

The principle of equal reactivity was postulated by Flory[3], to explain the kinetics of polymerization and reactions of polymers. It was shown that reactions of polymer chain can be compared to those of low molecular weight analogue.

Through the investigation of polyesterification reactions by Flory, [4] it was established that the rates of reactions of carboxyl[5] and hydroxyl groups do not depend upon the size or shape of polymeric chains to which they are attached. [6] Furthermore, Flory has developed theoretical arguments supporting the principle of equal reactivity for a broad range of polymeric reactions.[4,5]

This principle states in a qualitative manner that 'reactions of functional group' do not depend on the size of the molecule to which it is attached.

The chemical transformations of polymers can be carried out by taking into account the reactive nature of certain sites on the polymer chains. The reaction sites would exhibit essentially equal reactivity as that of the same groups on analogous low molecular weight substances, if the following conditions are met.[4,5]

i) The reaction occurs in homogeneous fluid medium; all the reactants, intermediates and products being soluble in medium.

ii) Each elementary step of the reaction involves no more than one macromolecule attached to functional groups, all other reacting species being small and mobile.

iii) The choice of low molecular weight 'homologue' is made carefully, attention being given to the steric hindrance that can arise in the immediate vicinity of a polymer chain.

The above are the sufficient conditions for equal reactivity of polymer and its small homologue. Equal reactivity may be observed even in cases where one or another of these conditions is not met. The real requirement in condition (i) being high diffusional mobility of low molecular weight reactants. The macroscopic viscosity of polymer solution can be very high without resulting in 'diffusion-controlled kinetics' as long as the small molecules are mobile. Even in a three dimensional network polymer with zero macroscopic shear fludity the small molecules may often exhibit sufficient mobility to meet this requirement. At very high concentrations of polymer, the multicomponent system can be in glassy state, which immobilises even the small molecules. This, however, is a very unusual situation not encountered in the polymer reaction kinetic studies. The reacting medium can be extremely viscous and yet retain the characteristic 'fluidity' in the sense of condition (i).

Practically, all useful replacement reactions of aliphatic hydrocarbons are chain reactions involving free radical mechanisms with a few exceptions which appear to be ionic, e.g. sulfonation and iodination of PE at moderate temperature.[7] In these substitution reactions (replacement of H atom) the side reactions which may occur are cross-linking and scission. By proper choice of experimental conditions, these reactions can be avoided and also neatly utilized to get desired properties in the reaction product.

The principle of equal reactivity can be extended to free radical reactions involving saturated hydrocarbon polymers and the 'normal' low molecular weight analogue pattern for the reactions[5,8] can be expected. The potential reactivity of free radical which is attached to polymer can be considered to be similar to that of small analogue radical as per the equal reactivity concept. But in actual cases many times the rate of reaction with a polymeric substrate or with a second polymeric radical, may be very low (or high) because of geometrical restraints.[1,9-11]

Another type of deviation is due to the situation when more than one reaction site on polymer chain is available for a low molecular weight substance for reaction. If one compares this situation with parallel reactions of low molecular weight analogue, appreciable deviation is observed in the kinetic behaviour. This is due to the low collision probability associated with different sites of chain molecules (due to low mobility).[1]

Chlorocarboxylation of PE is the reaction (in solution) in which chlorine and MA react simultaneously with the polymer.

In this reaction, conditions mentioned in the principle of equal reactivity are met. i.e.

i) Small molecules chlorine and MA react with polyethylene.

ii) Macro radical PE is reacting with small mobile chlorine and MA molecules.

iii) Reactions are carried out in dilute solutions and viscosity of the medium should not affect the mobility of reaction species.

The kinetics of the chlorocarboxylation process can therefore be carried out in the usual manner. The rates of the reactions can be expressed in terms of concentrations of reacting and product species and various rate constants, no special significance being given to the polymeric species while analysing the kinetics of the process.

4.2 Experimental

The detailed preparation purification analysis of CCPE is described in section II (A). For the evaluation of the kinetics of the process following sets of experiments as stated in the Table 4.1 were conducted.

Table: 4.1

Set of Experiments for the Evaluation of the Kinetics of Chlorocarboxylation of polyethylene

		Set A	Set B	Set C
1)	PE	50 g/lit	50 g/lit	50 g/lit
2)	MA	a) 2.5 g/lit b) 7.5 g/lit c) 12.5 g/lit	a) 2.5 g/lit b) 7.5 g/lit c) 12.5 g/lit	a) 2.5 g/lit b) 7.5 g/lit c) 12.5 g/lit
3)	Temperature	$90^{o}C$	$100^{o}C$	$110^{o}C$
4)	Solvent -	TCE	TCE	TCE
5)	Time of reaction:	1 to 5 hours	1 to 5 hours	1 to 5 hours

The starting material PE used for this study was low density PE (WNG-14). The properties of this PE are given in the Table 4.2.

Table: 4.2

Properties of LDPE

1.	MFI	7.0
2.	Mol. wt. (viscosity average in xylene)	2.863×10^4
3.	Density at 23°C	0.928 g/cc
4.	Type of manufacturer	WNG-14 M/s. ICI India Ltd.

4.3 Derivation of Kinetic and Composition Equations

The free radical reaction mechanism for chlorination in solution is established for chlorine substitution reactions of saturated aliphatic hydrocarbons.[8] In chlorocarboxylation reaction the detailed reaction mechanism is discussed in section III (B), for the kinetic analysis of the process, the following main steps can be considered.

a) Thermal dissociation of dissolved chlorine molecule to chlorine radicals

$$Cl_2 \rightleftharpoons Cl^{\bullet} + Cl^{\bullet}$$

b) Abstraction of hydrogen from PE chain and generation of $P^{\bullet}$ macro radical

$$P - H + Cl^{\circ} \longrightarrow P^{\bullet} + HCl$$

c) Reaction of macro radical $P^{\bullet}$ generated in (b) with chlorine molecules or MA molecules

i) $$P^{\circ} + Cl_2 \longrightarrow PCl + Cl^{\bullet} \qquad (I)$$

ii) $$P^{\circ} + MA \longrightarrow PMA^{\bullet} \qquad (II)$$

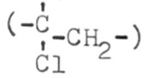
It is already shown that macro radical PMA° terminates through reaction with chlorine molecules. Termination of macro radical by hydrogen abstraction from PE molecules is less probable.

It can be seen that overall composition of CCPE formed during the chloro-carboxylation process is controlled by reactions (I) and (II). The reaction is carried out in single phase (solution) and in fairly dilute state so that the kinetics of the process is not affected by the viscosity of the system. Under these conditions it can be assumed that all the polymer chains are uniformly chlorocarboxylated. And for kinetic analysis of the process only one chain can be considered.

The kinetic equation can be written in terms of the number of sites occupied by chlorine and MA at a given time 't'.[12]

Suppose that $\bar{N}_o$ is the average number of sites on the PE which can be substituted during chlorocarboxylation either by chlorine atoms or by maleic anhydride. Here, in CCPE MA reacts with PE in the form of chloro derivative of succinic anhydride, the quantities incorporated in the polymer can be expressed as the equivalent of MA.

This number ($\bar{N}_o$) will be equal to average number of carbon atoms per chain of the PE. Since the purpose of this investigations was to make elastomeric CCPE, the maximum level of chlorination during chlorocarboxylation was kept low, less than 30% of the total sites available. Under these conditions, as reported by Quenum[13] et al. and Nambu,[14] the formation of dichloride type structure



$(-\overset{Cl}{\underset{Cl}{C}}-CH_2-)$ or any other di substitution is not probable, so that there can be only one probable substitution site for each carbon atom of the chain.

Let $\bar{N}_{Cl}$ and $\bar{N}_{MA}$ be the number of sites occupied by chlorine and maleic (equivalent) anhydride moities respectively and $\bar{N}_v$ the vacant sites.

Therefore,

$$\bar{N}_o = \bar{N}_{Cl} + \bar{N}_{MA} + \bar{N}_v \qquad [1]$$

This equation can be normalized with respect to $\bar{N}_o$ the total number of sites and the fractions $\frac{\bar{N}_{Cl}}{\bar{N}_o}$, $\frac{\bar{N}_{MA}}{\bar{N}_o}$ and $\bar{N}_v/\bar{N}_o$ can be designated by θ_{Cl}, θ_{MA} and θ_v respectively. The equation (1) reduces to:

$$1 = \theta_{Cl} + \theta_{MA} + \theta_v \qquad [2]$$

and the rate of change of θ_{Cl} and θ_{MA} fractions with respect to 't' can be expressed by equations:

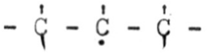
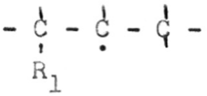
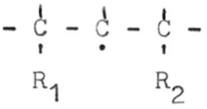
$$\frac{d\,\theta_{Cl}}{dt} = k_{Cl}\,[Cl_2]\,[1 - \theta_{Cl} - \theta_{MA}] \qquad [3]$$

$$\frac{d\,\theta_{MA}}{dt} = k_{MA}\,[MA]\,[1 - \theta_{Cl} - \theta_{MA}] \qquad [4]$$

It is assumed that rates of substitution of chlorine and MA are proportional to the concentration of each and to $\bar{N}_o$, and k_{Cl} and k_{MA} are the rate constants for reactions (I) and (II) respectively.

Alfrey et al.[12] have suggested that if two sites of substituents are neighbouring elements, then the rates of reactions are different and separate rate constants have to be incorporated into the rate equations as shown in Table 4.3.

Table: 4.3

	Reaction site	Rate constant
i)	 $-\underset{\mid}{\overset{\mid}{C}}-\underset{\bullet}{\overset{\mid}{C}}-\underset{\mid}{\overset{\mid}{C}}-$	k_1
ii)	 $-\underset{\underset{R_1}{\mid}}{\overset{\mid}{C}}-\underset{\bullet}{\overset{\mid}{C}}-\underset{\mid}{\overset{\mid}{C}}-$	k_2
iii)	 $-\underset{\underset{R_1}{\mid}}{\overset{\mid}{C}}-\underset{\bullet}{\overset{\mid}{C}}-\underset{\underset{R_2}{\mid}}{\overset{\mid}{C}}-$	k_3

Reaction rates are affected by the substituent on the neighbouring carbon atoms. The effect will depend upon the substituents R_1 and R_2, but generally $k_1 > k_2 > k_3$. This is probably due to steric hindrance.

However, in the present case one rate equation (with one rate constant for each reaction) can be assumed since total number of sites occupied by chlorine and MA are not more than 50% (even much less than 50%) and substituents Cl or MA are fairly distant from each other on PE chain.

Dividing equation (3) by equation (4), equation (5) is obtained

$$\frac{d\,\theta_{Cl}}{d\,\theta_{MA}} = \frac{k_{Cl}}{k_{MA}}\,\frac{[Cl_2]}{[MA]} \qquad [5]$$

Equation (5) gives the composition of CCPE formed in the time interval between t and $(t+\delta t)(\delta t \longrightarrow 0)$.

In equation (5) concentration of chlorine $[Cl_2]$ is not a function of time 't', since in the chlorocarboxylation reaction chlorine gas was bubbled at sufficiently high rates (10 l/hr) in order to maintain the solubility of chlorine at saturation level, at the reaction temperature (at atmospheric pressure). The solubility data for chlorine in TCE is reported in Table 4.5.The concentration of chlorine was also checked by pouring known volume of reaction mixture (5/10 ml) in ice cold methanol and estimating the dissolved chlorine iodimetrically.[15]

In equation (5) k_{Cl}, k_{MA} and $[Cl_2]$ are constants. However, [MA] is time dependent since as reaction proceeds, more and more MA gets incorporated in

PE and its concentration in the system drops. Concentration of MA in the system can be found out from:

$$[MA]_t = [MA]_o - [MA]_{poly\ at\ 't'} \qquad [6]$$

$[MA]_o$ is the feed MA concentration added at the beginning of the reaction and $[MA]_{poly}$ can be found out from analysis of the polymer sample collected at time 't'.[16,17]

$[MA]_{poly\ at\ t}$ is already expressed in terms of N_{MA} or θ_{MA} .

$[MA]_o$ can be expressed in terms of the average number of molecules available for reaction per polymer chain (N_{MA}). This will be constant for a given set of experiments, since the amount of PE taken is constant for constant feed of MA. This can be further expressed normalising with respect to the total number of sites available for the reaction at t=0, (N_o). This can be designated as θ_{MA_o} and this is a constant quantity.

Therefore equation (6) reduces to

$$\theta_{MA_t} = \theta_{MA_o} - \theta_{MA\ poly\ at\ 't'}$$

and equation (5) can be rewritten as:

$$\frac{d\theta_{Cl}}{d\theta_{MA\ poly}} = \frac{k_{Cl}}{k_{MA}} \frac{[Cl_2]}{N_o} \times \frac{1}{(\theta_{MA_o} - \theta_{MA_{poly}})} \qquad [7]$$

In equation (7), variables are separable and boundary conditions of equation (8) are θ_{1MA} and θ_{MA} on the right and θ_{1Cl} and θ_{2Cl} on the left. Then,

$$\int_{\theta_{1Cl}}^{\theta_{2Cl}} d\theta_{Cl} = \frac{k_{Cl}}{k_{MA}}[Cl_2] \int_{\theta_{1MA}}^{\theta_{2MA}} \frac{d\theta_{MA_{poly}}}{(\theta_{oMA} - \theta_{MA_{poly}})} \qquad [8]$$

and

$$\theta_{2Cl} - \theta_{1Cl} = \frac{k_{Cl}}{k_{MA}}[Cl_2]\Big[-\ln(\theta_{o\,MA} - \theta_{MA_{poly}})\Big]_{\theta_{1\,MA_{poly}}}^{\theta_{2\,MA_{poly}}} \qquad [9]$$

or

$$\theta_{2Cl} - \theta_{1Cl} = \frac{k_{Cl}}{k_{MA}}[Cl_2] \ln \frac{[\theta_{oMA} - \theta_{1MA_{poly}}]}{[\theta_{oMA} - \theta_{2MA_{poly}}]} \qquad [10]$$

In equation (10) $\frac{k_{Cl}}{k_{MA}}[Cl_2]$ is a constant factor, the remaining factor is the natural logarithm of the ratio, which is equal to

$$\frac{\text{unreacted MA at time } t_1}{\text{unreacted MA at time } t_2}$$

and is always positive since the ratio is greater than unity.

In equation (10) suitable boundary conditions can be chosen for θ fractions (corresponding to time t) and the plot of $(\theta_{2Cl} - \theta_{1Cl})$ Vs. ln $\frac{[\theta_o MA - \theta_{2MA_{poly}}]}{[\theta_o MA - \theta_{2MA_{ply}}]}$ will be a straight line passing through the origin with $[Cl_2] \times \frac{k_{Cl}}{k_{MA}}$ as the slope.

Equation (10) can be further simplified by choosing boundary values of θ corresponding to the time variable t=0 and t=t , where t represents any time in the course of reaction for which θ_{Cl} and θ_{MA} values are found out from polymer analysis.[16-18]

for $t = 0, \quad \theta_{1Cl} = 0, \quad \theta_{1MA_{poly}} = 0$

and equation (11) simplifies to

$$\theta_t\, Cl = \frac{k_{Cl}}{k_{MA}} [Cl_2] \ln \frac{\theta_o\, MA}{\theta_o\, MA - \theta_t\, MA_{poly}} \qquad [11]$$

In equation (11) $\theta_{t\ Cl}$, $\theta_{t\ MA_{poly}}$ can be found out from the analysis of polymer and these quantities are related to percentage of chlorine and maleic anhydride incorporated in PE respectively.[16-18] Concentration of chlorine can be found out from the known volume of reaction mixture and analysing for chlorine iodimetrically.[15]

The plot of $\theta_{t\ Cl}$ Vs. ln $\frac{\theta_o\, MA}{\theta_o\, MA - \theta_{t\ poly}}$ gives a straight line passing through the origin and from the slope $\frac{k_{Cl}}{k_{MA}} \times [Cl_2]$ the ratio of rate constants can be found out.

and the plot of $(\theta_{2Cl} - \theta_{1Cl})$ Vs. ln $\frac{[\theta_o MA - \theta_{2MA_{poly}}]}{[\theta_o MA - \theta_2 MA_{ply}]}$ will be a straight line passing through the origin with $[Cl_2] \times \frac{k_{Cl}}{k_{MA}}$ as the slope.

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for $t = 0$, $\theta_{1Cl} = 0$, $\theta_{1MA_{poly}} = 0$

and equation (11) simplifies to

$$\theta_t\, Cl = \frac{k_{Cl}}{k_{MA}} [Cl_2] \ln \frac{\theta_o\, MA}{\theta_o\, MA - \theta_t\, MA_{poly}} \qquad [11]$$

In equation (11) $\theta_{t\,Cl}$, $\theta_{t\,MA_{poly}}$ can be found out from the analysis of polymer and these quantities are related to percentage of chlorine and maleic anhydride incorporated in PE respectively.[16-18] Concentration of chlorine can be found out from the known volume of reaction mixture and analysing for chlorine iodimetrically.[15]

The plot of $\theta_{t\,Cl}$ Vs. ln $\frac{\theta_o\, MA}{\theta_o\, MA - \theta_{t\,poly}}$ gives a straight line passing through the origin and from the slope $\frac{k_{Cl}}{k_{MA}} \times [Cl_2]$ the ratio of rate constants can be found out.

Table: 4.5 (A)

Chlorocarboxylation of PE

(Reaction Conditions as in Set A)

Time (hrs)	%Chlorine(w/w) in CCPE	% MA (equivalent) w/w in CCPE	θ_{Cl}	$\theta_{MA}x10^3$	$\ln\frac{\theta_{MA_o}}{\theta_{MA_o} - \theta_{MA\ poly}}$	Remarks
(Temp. 90°C, MA in the feed 2.5 g/lit)						
1.	22.5	0.40	0.114	0.746	0.053	Concentration of chlorine $[Cl_2]$ in the reaction mixture was almost constant for all the experiments = 0.106 ± .0007 moles/lit and was dependent on temperature only (90oC) in pure solvent (FCE) it was 0.1055 moles/lit.
2.	35.2	0.70	0.213	1.570	0.115	
3.	45.0	0.80	0.321	2.110	0.122	
4.	52.5	0.90	0.433	2.700	0.212	
5.	55.0	1.10	0.478	3.560	0.284	
(Temp. 90°C, MA in the feed 7.5 g/lit)						
1.	20.5	0.45	0.101	0.820	0.0191	
2.	30.0	0.95	0.167	1.970	0.0467	
3.	37.5	1.20	0.224	2.800	0.0670	
4.	42.5	1.35	0.288	8.420	0.0826	
5.	45.0	1.50	0.318	4.000	0.0968	
(Temp. 90°C, MA in the feed 12.5 g/lit)						
1.	17.5	0.70	0.083	1.230	0.0172	
2.	27.5	1.10	0.148	2.210	0.0311	
3.	33.0	1.40	0.191	3.050	0.0434	
4.	36.0	1.70	0.217	3.890	0.0556	
5.	40.0	2.20	0.256	5.390	0.078	

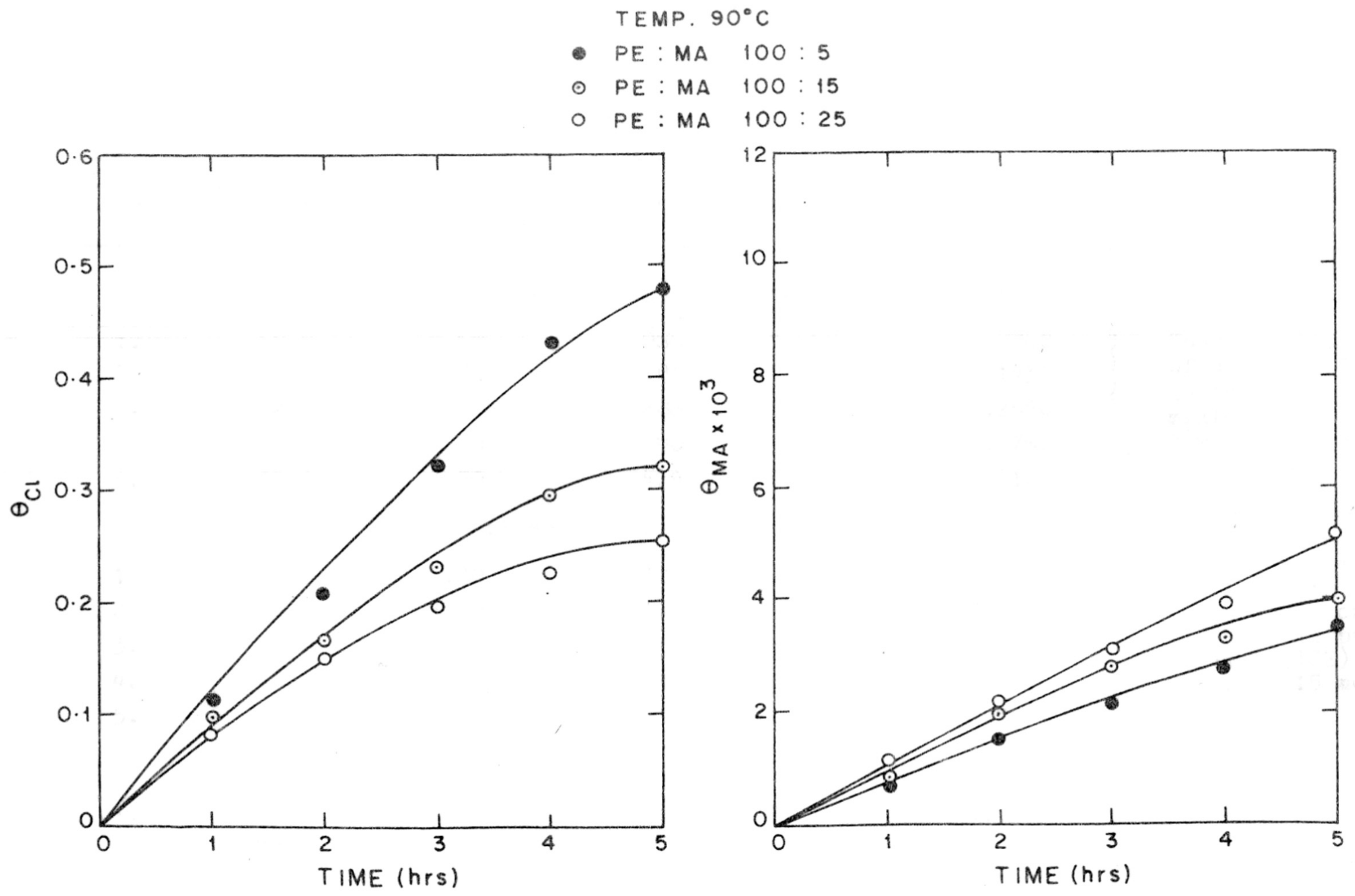


FIG. 4·1(A) : CHLOROCAROXYLATION OF PE : θ_{Cl} AND θ_{MA} FRACTIONS AS FUNCTION OF TIME. EXPERIMENTAL CONDITIONS AS IN SET(A).(TABLE 4·1)

Table: 4.5(B)

Chlorocarboxylation of PE

(Reaction conditions as in Set B)

Time (hrs)	%Chlorine(w/w) in CCPE	%MA (equivalent) w/w in CCPE	θ_{Cl}	$\theta_{MA}x10^3$	$\ln \frac{\theta_{MA_o}}{\theta_{MA_o} - \theta_{MA\ poly}}$	Remarks
(Temp. 100°C, MA in the feed 2.5 g/lit)						Concentration of chlorine $[Cl_2]$ in the reaction mixture was almost constant for all the experiments = 0.014 ± .0007 moles/lit and was dependent on reaction temperature only (100°C), in pure solvent (TCE) it was = 0.015 moles/lit.
1.	18.0	0.60	0.086	1.660	0.0760	
2.	32.0	0.90	0.184	1.920	0.1430	
3.	42.5	1.25	0.288	3.170	0.2480	
4.	50.0	1.30	0.390	3.790	0.3760	
5.	55.0	1.50	0.478	4.870	0.4140	
(Temp. 100°C, MA in the feed 7.5 g/lit)						
1.	16.0	1.20	0.073	2.080	0.0490	
2.	28.0	2.10	0.149	4.300	0.1043	
3.	39.0	2.75	0.233	6.560	0.1655	
4.	44.0	3.30	0.297	8.770	0.2250	
5.	50.0	3.75	0.376	11.210	0.3001	
(Temp. 100°C, MA in the feed 12.5 g/lit)						
1.	15.0	1.30	0.068	2.230	0.0313	
2.	27.0	2.60	0.140	5.260	0.0759	
3.	36.0	3.50	0.211	8.150	0.1200	
4.	42.5	4.10	0.276	10.690	0.1600	
5.	47.6	4.50	0.337	12.910	0.1970	

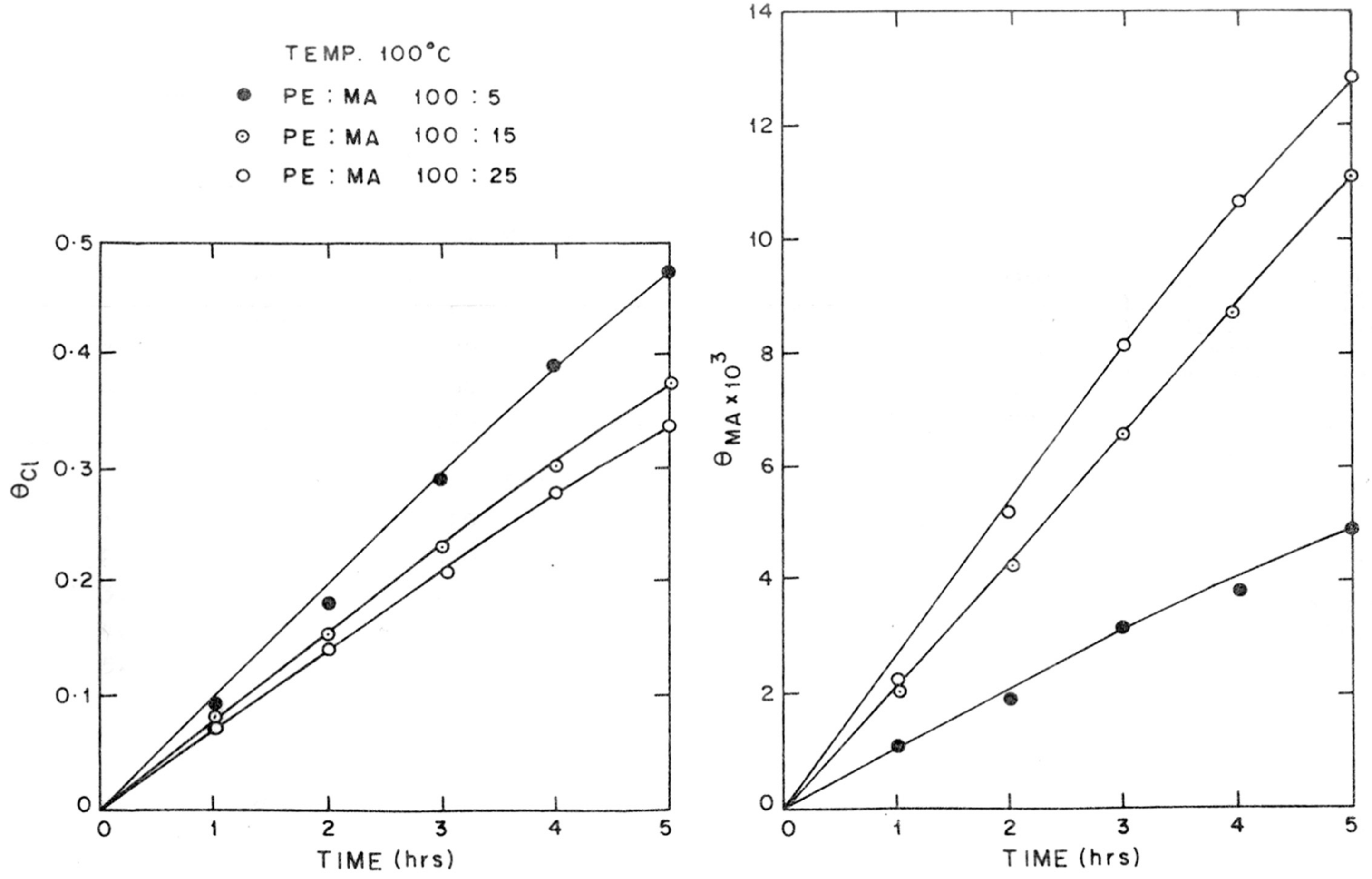


FIG. 4·1(B) : CHLOROCARBOXYLATION OF PE:EXPERIMENTAL CONDITIONS AS IN SET (B). θ_{Cl} AND θ_{MA} FRACTIONS AS FUNCTION OF TIME.(TABLE 4·1)

Table: 4.5(C)

Chlorocarboxylation of PE

(Reaction conditions as in Set C)

Time (hrs)	%Chlorine(w/w) in CCPE	%MA (equivalent) w/w in CCPE	θ_{Cl}	$\theta_{MA}x10^3$	$\ln \frac{\theta_{MA_o}}{\theta_{MA_o} - \theta_{MA\ poly}}$	Remarks
(Temp. 110°C, MA in theffeed 2.5 g/lit)						
1.	27.0	0.70	0.145	1.390	0.0950	Concentration of chlorine[Cl_2] in the reaction mixture was almost constant for all the experiments = 0.0071 ± .0005 moles/lit and was dependent on temperature (110°C) only, in pure solvent (TCE) it was 0.008 moles/lit.
2.	42.0	1.25	0.282	3.140	0.2460	
3.	50.0	1.70	0.387	4.980	0.4250	
4.	57.5	2.00	0.522	6.910	0.6540	
5.	58.0	2.05	0.532	7.170	0.6890	
(Temp. 110°C, MA in the feed 7.5 g/lit)						
1.	20.0	1.20	0.097	2.200	0.0525	
2.	32.0	2.20	0.180	4.750	0.1172	
3.	45.0	2.80	0.276	7.150	0.1820	
4.	50.0	3.40	0.349	9.740	0.2620	
5.	52.5	3.50	0.417	10.980	0.3220	
(Temp. 110°C, MA in the feed 12.5 g/lit)						
1.	20.0	2.05	0.095	3.760	0.0530	
2.	32.0	3.25	0.177	7.107	0.1040	
3.	42.0	4.25	0.270	11.010	0.1660	
4.	46.0	4.80	0.315	13.430	0.2070	
5.	50.0	5.40	0.367	16.425	0.2590	

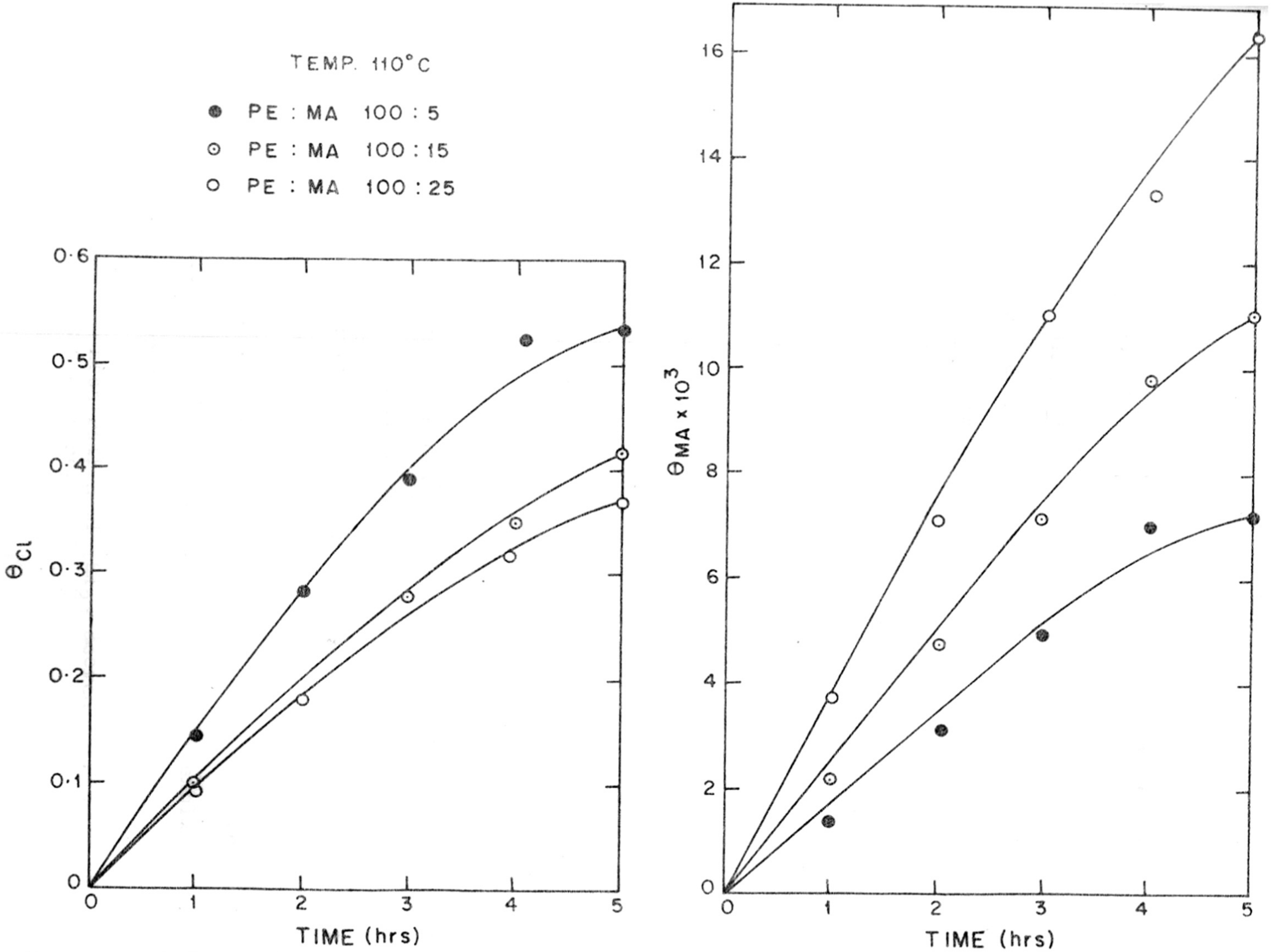


FIG. 4 : 1 (C) : CHLOROCARBOXYLATION OF PE : EXPERIMENTAL CONDITIONS AS IN SET (C) (TABAL 4·1) θ_{Cl} AND θ_{MA} FRACTIONS AS FUNCTION OF TIME.

Equation (11) gives the composition of the CCPE formed at any time 't'.

4.4 Results and Discussion

Table 4.5 shows the results of chlorocarboxylation at temperature 90,100,110^{o}C in TCE. From the analysis of polymer, various quantities required in the equation (11) can be derived (Appendix-1). These are listed in Table 4.4.

Figure 4.2 shows the least square fit straight line plots of $\theta_{Cl\ t}$ Vs. $\ln \dfrac{\theta_o\ MA}{\theta_o\ MA - \theta_t\ MA_{poly}}$. Values of k_{Cl}/k_{MA} calculated from slope are given in Table 4.6.

The following quantities are computed from the analysis of chlorine and equivalent MA incorporated in CCPE.

Table: 4.4

$\bar{N}_{Cl}$	Average number of sites occupied by chlorine atoms per PE chain
$\bar{N}_{MA}$	Average number of sites occupied by (equivalent) maleic anhydride per PE chain
$\bar{\theta}_{Cl}$	Fraction of total number of sites occupied by chlorine
$\bar{\theta}_{MA}$	Fraction of total number of sites occupied by (equivalent) MA
$\bar{N}_o-(\bar{N}_{Cl}+\bar{N}_{MA})$	Vacant sites of PE not occupied by chlorine or MA
$(1-\theta_{Cl}-\theta_{MA})$	Fraction:(vacant sites/total number of sites per chain)
$\ln \dfrac{\theta_o MA}{\theta_o\ MA - \theta_{MA\ poly\ at\ t}}$	Factor in R.H.S. of equation (11)

These computations were carried out on 'Hewlett-Packard' Computer (Model 9830A) and the computer programme was written in BASIC language, which is given in Appendix-1.

Though the curves θ_{Cl} Vs. t, θ_{MA} Vs. t (Fig. 4.1) are different for each initial feed quantity of MA, only one straight line is obtained for each temperature even for different quantities of feed maleic anhydride (or θ_o MA).

The slope of the line is given by $k_{Cl}/k_{MA}\ [Cl_2]$ which is independent of feed MA (or $\theta_{o\,MA}$) and origin is always the point on the line - slope and origin determine unique straight line.

It is seen from the plots θ_{Cl} Vs. ln $\dfrac{\theta_{MA_o}}{\theta_{MA_o} - \theta_{MA\ poly}}$ (Fig. 4.2) that chlorine is very highly reactive as compared to MA towards PE macro radical. k_{Cl}/k_{MA} is always greater than unity and this ratio increases with temperature the rate of increase of k_{Cl} is high as compared to k_{MA} . In spite of decreasing solubility of chlorine at higher temperatures, chlorine incorporated in PE is much more than MA. This can be seen from Tables 4.5 and 4.6.

Temperature will have pronounced effect on the composition of CCPE formed. This can be well explained by the various terms of equation (11).

i) Concentration of $[Cl_2]$ decreases with temperature,

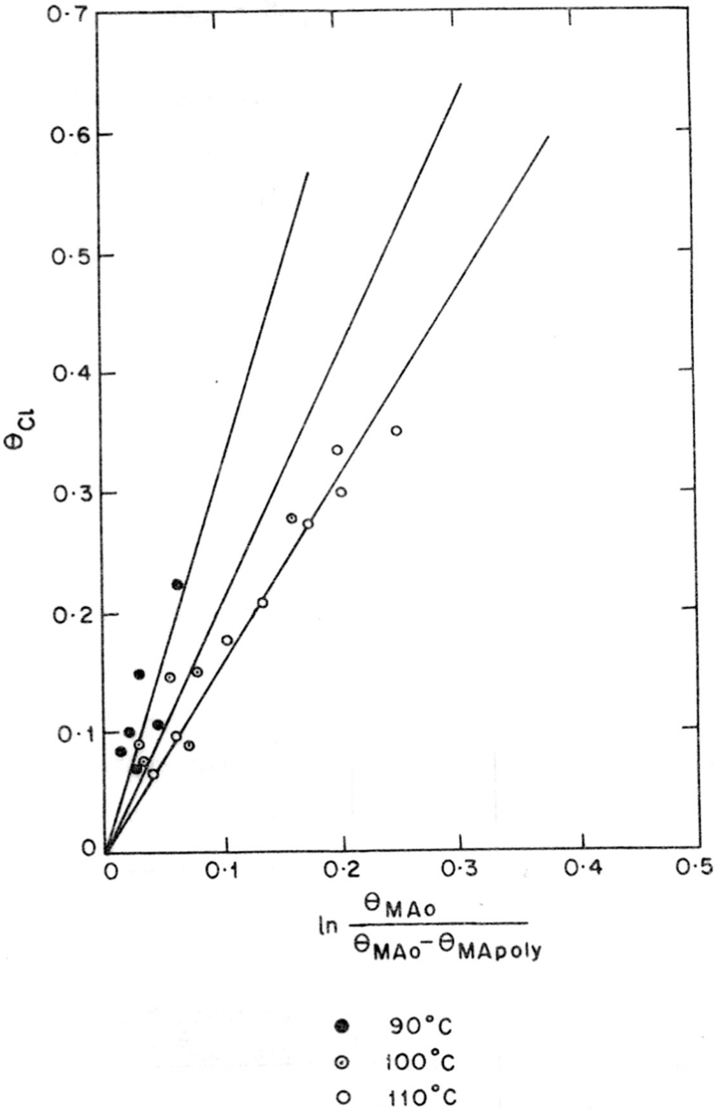


FIG. 4·2 : θ_{Cl} FRACTION AS FUNCTION OF $\ln \frac{\theta_{MAo}}{\theta_{MAo}-\theta_{MApoly}}$ (EQN. 11) (TABLE 4·5).

All points are not shown due to large overlap near origin.

ii) $\frac{k_{Cl}}{k_{MA}}$ increases with temperature as seen from Fig. 4.2 and Table 4.6.

iii) $\frac{MA_o}{MA_o - MA_{poly}}$ increases with temperature.

In Figures 4.1 (A,B and C) variation of θ_{Cl} and θ_{MA} fractions is depicted at temperatures 90, 100 and 110°C. Individual rate constants k_{Cl}, k_{MA} can be evaluated using these plots and the equations:(by differential procedure)

$$\frac{d\,\theta_{Cl}}{dt} = k_{Cl}\,[Cl_2]\,[1 - \theta_{Cl} - \theta_{MA}] \qquad [3]$$

$$\frac{d\,\theta_{MA}}{dt} = k_{MA}\,[MA]\,[1 - \theta_{Cl} - \theta_{MA}] \qquad [4]$$

Kinetic analysis was restricted to low conversion of PE to CCPE [less than 0.4 of value of $(\theta_{Cl} + \theta_{MA})$]. At higher conversion the kinetics of the process changes due to the configuration changes and steric hindrances, and it becomes complicated due to the incorporation of additional rate constants in the equations (3) and (4) as suggested by Alfrey et al. [12]

In equations (3) and (4), $\frac{d\theta}{dt}$ can be evaluated from differential procedure i.e. by evaluating $\frac{d\,\theta_{Cl}}{dt}$ or $\frac{d\,\theta_{MA\ poly}}{dt}$ at various times from the plots of θ_{Cl} or $\theta_{MA\ poly}$ Vs. time (Fig. 4.1) and is almost constant in the region considered. The other quantities required to evaluate k_{Cl} and k_{MA} can also be found out as follows:

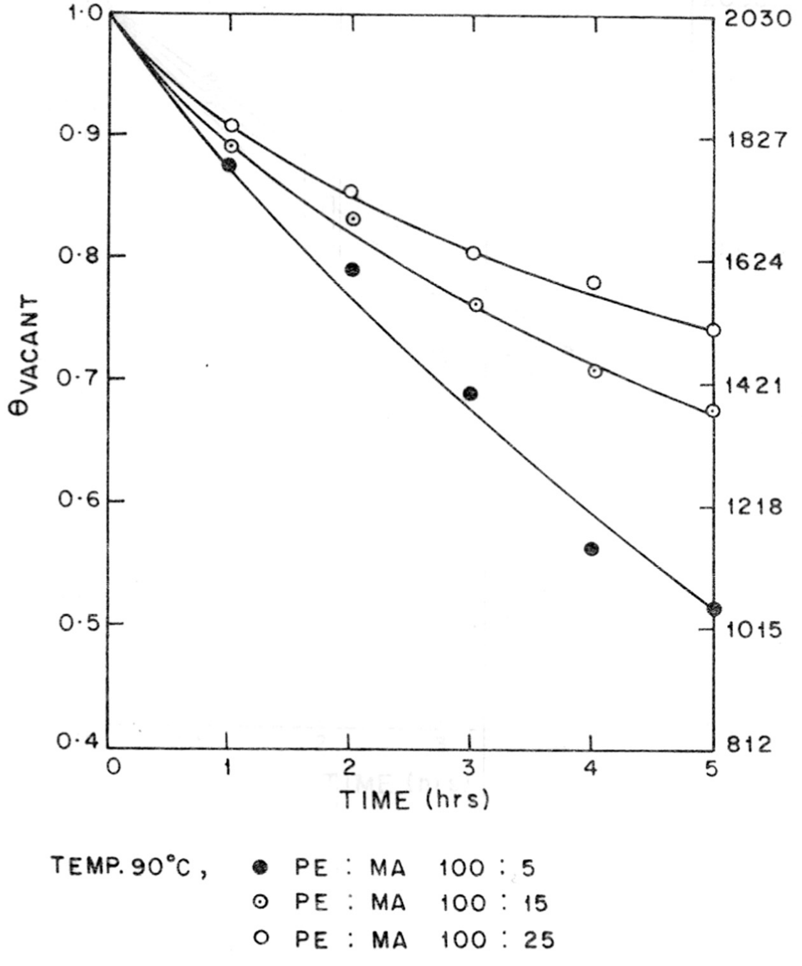


FIG. 4·3 (A) : VARIATION OF UNSUBSTITUTED SITES DURING CHLOROCARBOXYLATION OF PE.

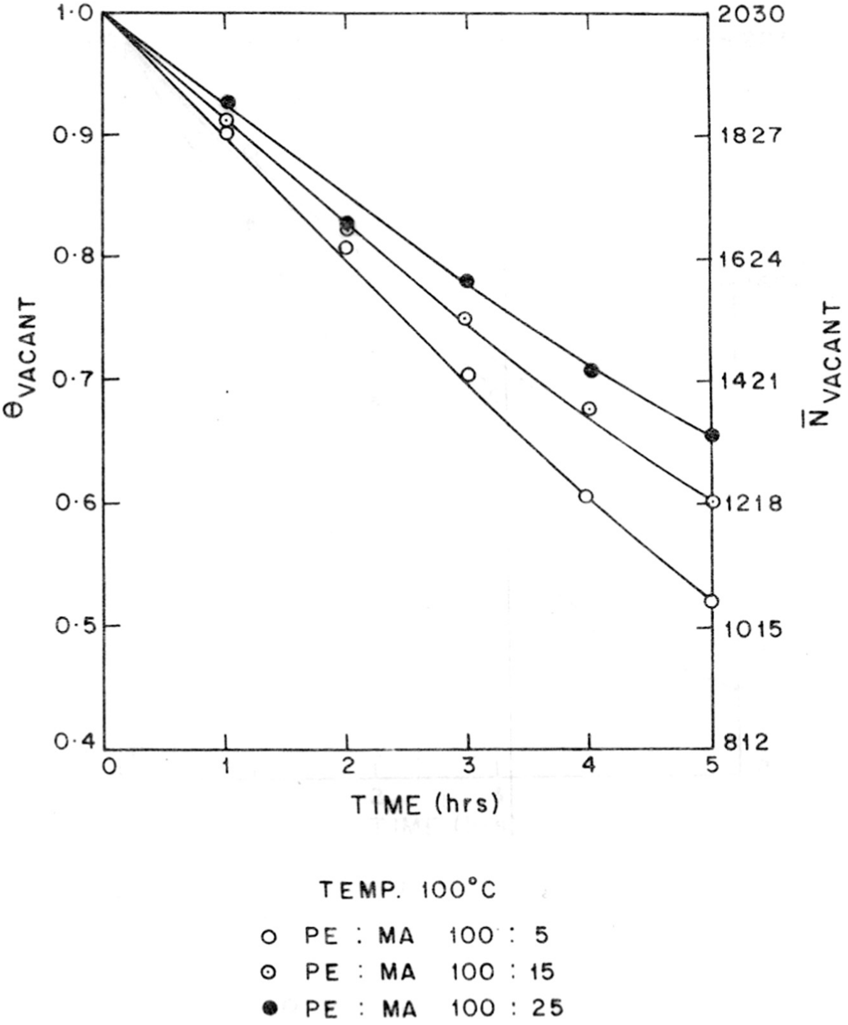


FIG. 4·3(B) : VARIATION OF UNSUBSTITUTED SITES DURING CHLOROCARBOXYLATION OF PE.

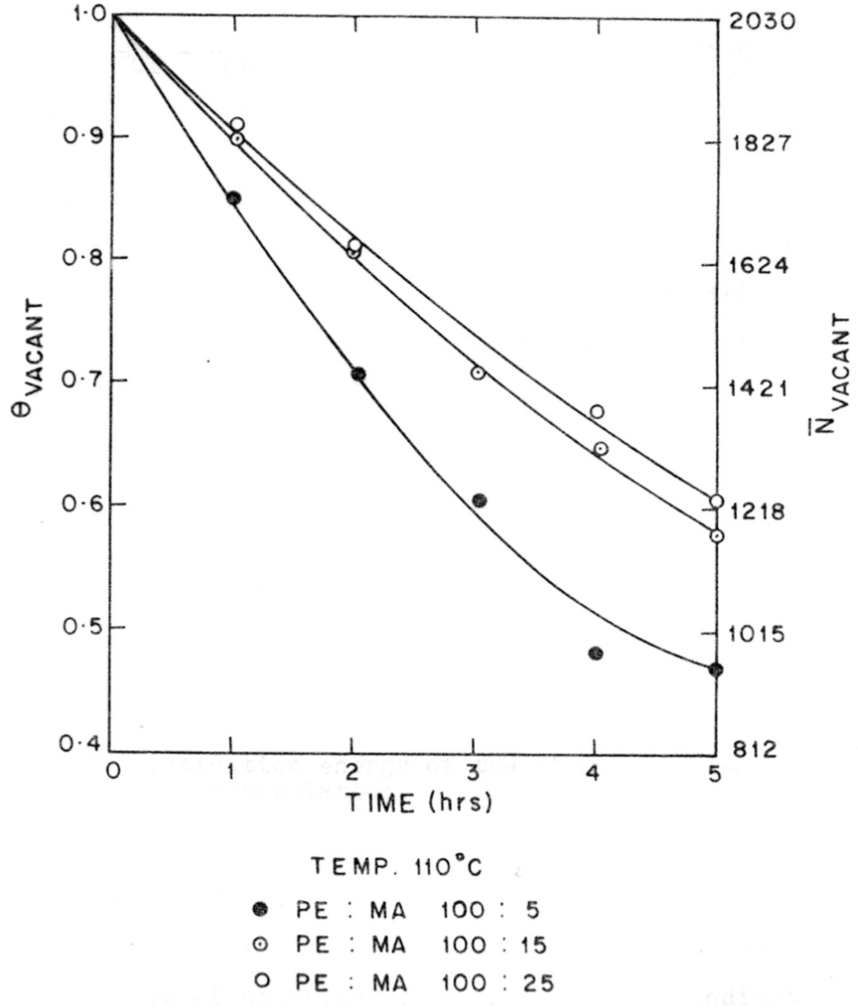


FIG. 4·3(C) : VARIATION OF UNSUBSTITUTED SITES DURING CHLOROCARBOXYLATION OF PE.

$[Cl_2]$ —> iodimetrically [15]

$[MA]$ —> from feed MA and MA incorporated by analysis of CCPE [16-17]

$[1-\theta_{Cl}-\theta_{MA}]$ —> from analysis of CCPE samples collected at the corresponding times in the plots [16-18]
or from plots of θ_{vacant} Vs. time (Fig. 4.3)

As seen from the plots θ fractions Vs. time (Fig. 4.1), the rate appears to be constant for low conversion i.e. for low values of $(\theta_{Cl}+\theta_{MA\ poly})$.

The values of rate constants k_{Cl} and k_{MA} are (differential procedure) given in Table 4.6. The dependence of k_{Cl} and k_{MA} on temperature is given by Arrhenius equation.

$$k = A\ e^{-E/RT} \qquad [12]$$

where E = activation energy of the either chlorination or carboxylation

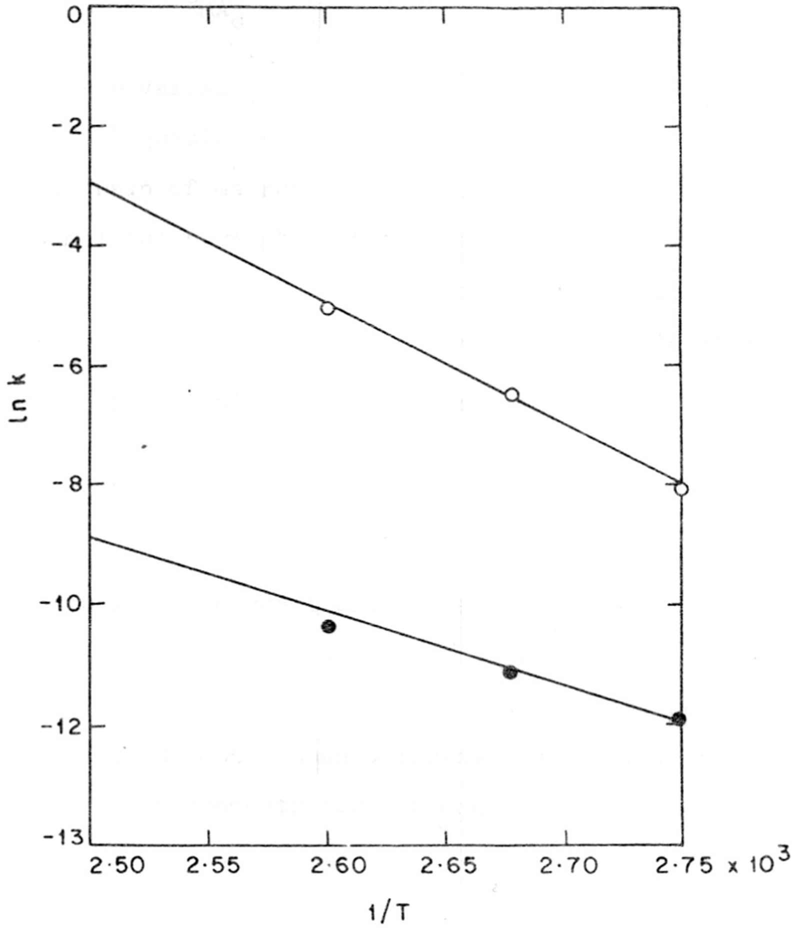
A = pre-exponential factor

These (A and E) can be evaluated graphically from plot [Fig.4.4] lnk Vs 1/T The activation energy for chlorination process and reaction of MA with PE is 41.6 and 25.7 Kcal/mol respectively. Reactive nature of chlorine molecule with PE is indicated by A values as compared to A_{Cl}, A_{MA} is very low. The relative ratio of the effective collisions of reacting species A_{Cl}/A_{MA} is of the order of 20.5.

Table: 4.6

Kinetic rate Constants k_{Cl} and k_{MA} as Evaluated from Eqn. (3) and Eqn. (4) and Comparison of the Ratios as Evaluated by Eqn. (11)

Temp. °C	k_{Cl} lit/mol $\times 10^5$ (Eqn. 3)	k_{MA} lit/mol $\times 10^5$ (Eqn. 4)	k_{Cl}/k_{MA}		Activation energy	Pre-exp. factor ratio A_{Cl}/A_{MA}
			Eqn.(3) and (4)	Eqn.(11)	from ln k Vs. 1/T plot	
90	125.8	0.51	50.77	36.29	For chlorination of PE 41.6 Kcal/mol	
100	200.0	1.50	133.30	142.00		20.5
110	504.0	1.82	276.90	218.50	For reaction of MA and PE 25.7 Kcal/mol (carboxylation)	



○ CHLORINATION OF PE.

● REACTION OF MA WITH PE (CARBOXYLATION)

FIG. 4·4 : ARRHENIUS PLOT FOR CHLORINATION AND CARBOXYLATION OF PE.

The $\frac{k_{Cl}}{k_{MA}}$ values are also computed from the plots of θ_{Cl} Vs. $\ln \frac{\theta_{MA_o}}{\theta_{MA_o} - \theta_{MApoly}}$ using equation (11).

These values are comparable and it appears that composition equation (11) derived by taking into account a single chain of macromolecule and its reactions with two low molecular weight substances (e.g. chlorine and MA in the present case) in terms of the number of sites occupied by each is supported by experimental findings.

It is possible to predict the composition of CCPE using equation (11) and reaction conditions (temperature, solvent, feed MA concentration etc.).

This method of analysis can be extended to the chlorocarboxylation reactions of many other polymers wherein the reaction mechanism can be broadly described by reactions of type (I) and (II). It can also be extended to the reactants other than chlorine and MA i.e. in a situation where concentration of one of the reactants remains constant and that of the other decreases with time, if reactions are of the type I and II.

In the reaction of macromolecule wherein the concentrations of both the reactants are decreasing with time, or remains constant, the terms in equation (9) can be suitably expressed and the composition equation can be derived with slight modification, **but** overall scheme of analysis will remain the same (e.g. CSPE process using SO_2 and Cl_2 gases).

The yield of chlorocarboxylated PE depends upon both temperature of the reaction and feed quantity of MA for given quantity of PE.

The variation of yield with time (and its composition) is given in Table 4.7 and is depicted in Fig. 4.5. The main features of the process can be summarised as follows:

1. At higher temperature the yield of CCPE is more at a given time, this is due to higher values of k_{Cl} and k_{MA}.
2. At a given temperature for low feed quantities of MA in the reaction system, higher yields are obtained. This is because of more reactive nature of chlorine. In this situation chlorination process is more dominant and CCPE obtained is richer in its chlorine contents.
3. At a given temperature the yield of CCPE is reduced if high initial feed quantities of MA are employed. The probable reason for low yield is, the radical scavenging reactions (discussed in section III (B)) are dominant in chlorocarboxylation process.[19,20]

MA at higher concentrations can reduce yield of CCPE by scavenging $Cl^{\bullet}$ radicals and prevent macro radical formation,

$$P - H + Cl^{\bullet} \longrightarrow P^{\bullet} + HCl$$

As the temperature of CCPE process is increased more MA is getting reacted with PE and at higher feed quantities of MA, the MA reacted with PE increases, but in this case more unreacted MA is also left the reaction mixture. This is depicted in Figures 4.6

Table: 4.7 (A)

Chlorocarboxylation of PE
Yield of CCPE and its Composition

(Reaction Conditions as in Set A)

Time	% Chlorine w/w in CCPE	% MA	Yield gms (PE 25 gms)	MA unreacted (gms)
(Temp. 90°C, MA 2.5 g/lit. in the feed)				
1.	22.5	0.40	32.5	2.320
2.	35.2	0.70	38.9	2.228
3.	45.0	0.80	45.9	2.213
4.	52.5	0.90	53.1	2.220
5.	55.0	1.10	56.2	1.880
(Temp. 90°C, MA 7.5 g/lit. in the feed)				
1.	20.5	0.45	31.6	7.360
2.	30.0	0.95	36.2	7.156
3.	37.5	1.20	40.6	7.010
4.	42.5	1.35	44.5	6.900
5.	45.0	1.50	46.2	
(Temp. 90°C, MA 12.5 g/lit. in the feed)				
1.	17.5	0.70	31.0	12.283
2.	27.5	1.10	35.0	12.115
3.	33.0	1.40	38.5	11.961
4.	36.0	1.70	40.0	11.820
5.	40.0	2.20	43.0	11.550

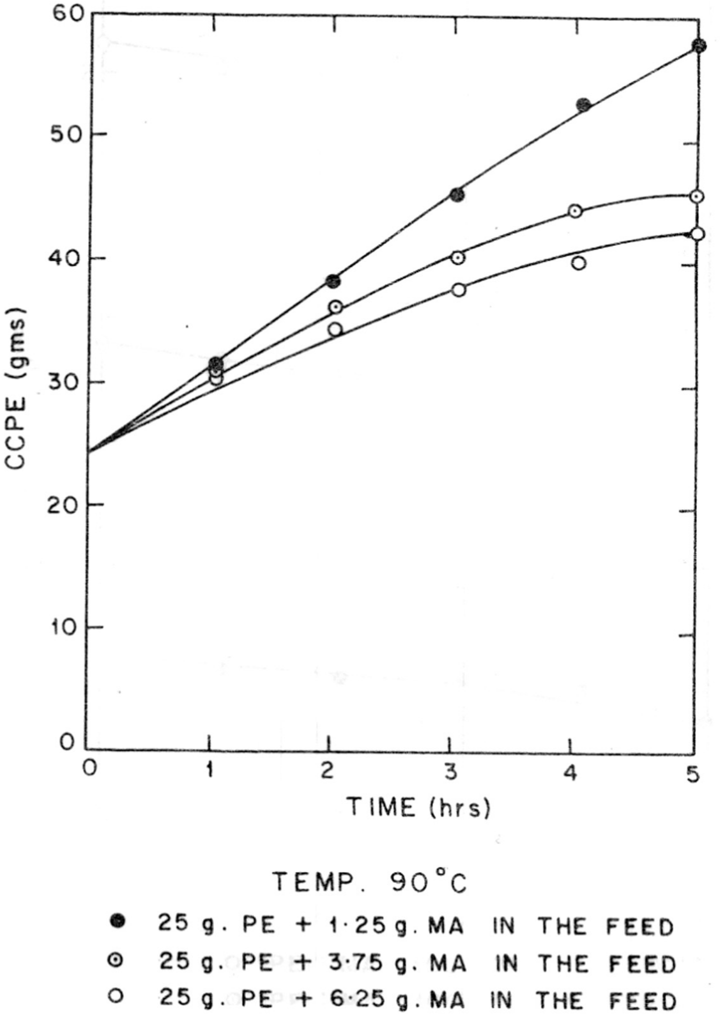


FIG. 4·5(A) : CHLOROCARBOXYLATION OF PE VARIATION OF YIELD WITH TIME.

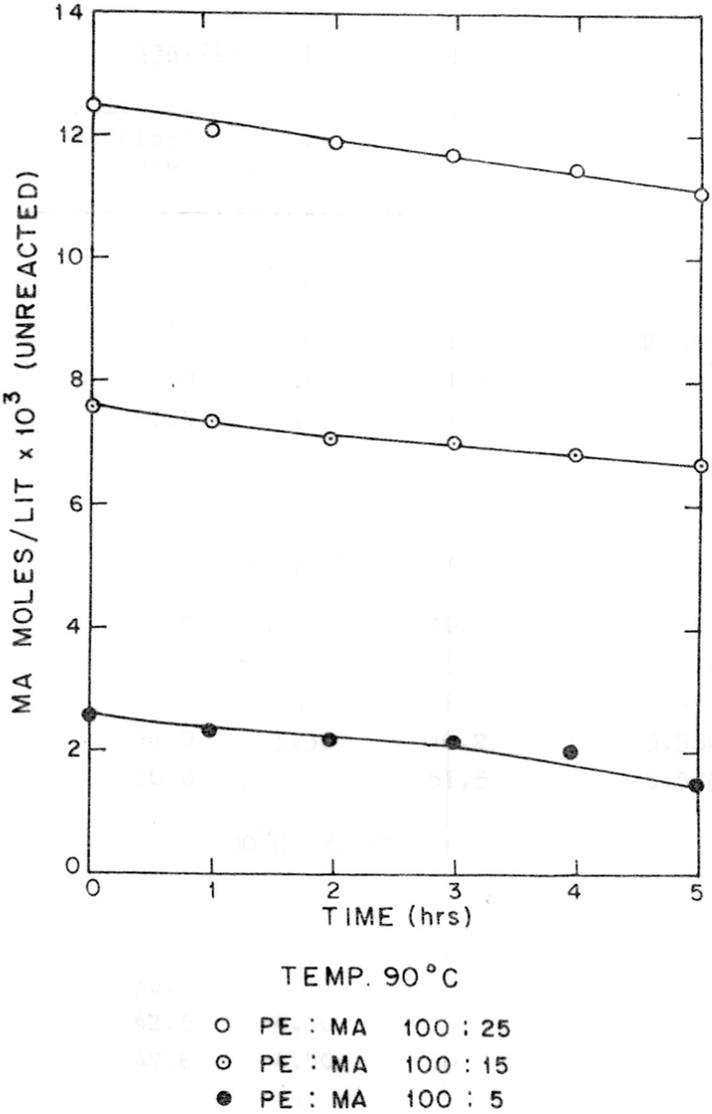


FIG. 4·6(A) : MA UNREACTED IN THE REACTION MIXTURE AS A FUNCTION OF TIME.

Table: 4.7 (B)

Chlorocarboxylation of PE: Yield of CCPE and its Composition

(Reaction Conditions as in Set B)

Time	% Chlorine w/w in CCPE	% MA	Yield gms PE: 25 gms	MA unreacted (gms)
(Temp.100°C,MA 2.5 g/lit. in the feed)				
1.	18.0	0.60	30.7	2.316
2.	32.0	0.90	37.2	2.165
3.	42.5	1.25	44.5	1.940
4.	50.0	1.30	50.7	1.840
5.	55.0	1.50	56.5	1.650
(Temp. 100°C, MA 7.5 g/lit. in the feed)				
1.	16.0	1.20	30.2	7.100
2.	28.0	2.10	35.5	6.750
3.	39.0	2.75	42.0	6.350
4.	44.0	3.30	46.2	5.980
5.	50.0		51.5	5.570
(Temp. 100°C, MA 12.5 g/lit. in the feed)				
1.	15.0	1.30	30.0	12.110
2.	27.0	2.60	35.5	11.560
3.	36.0	3.50	40.5	11.430
4.	42.5	4.10	45.5	10.630
5.	47.6	4.50	50.0	10.250

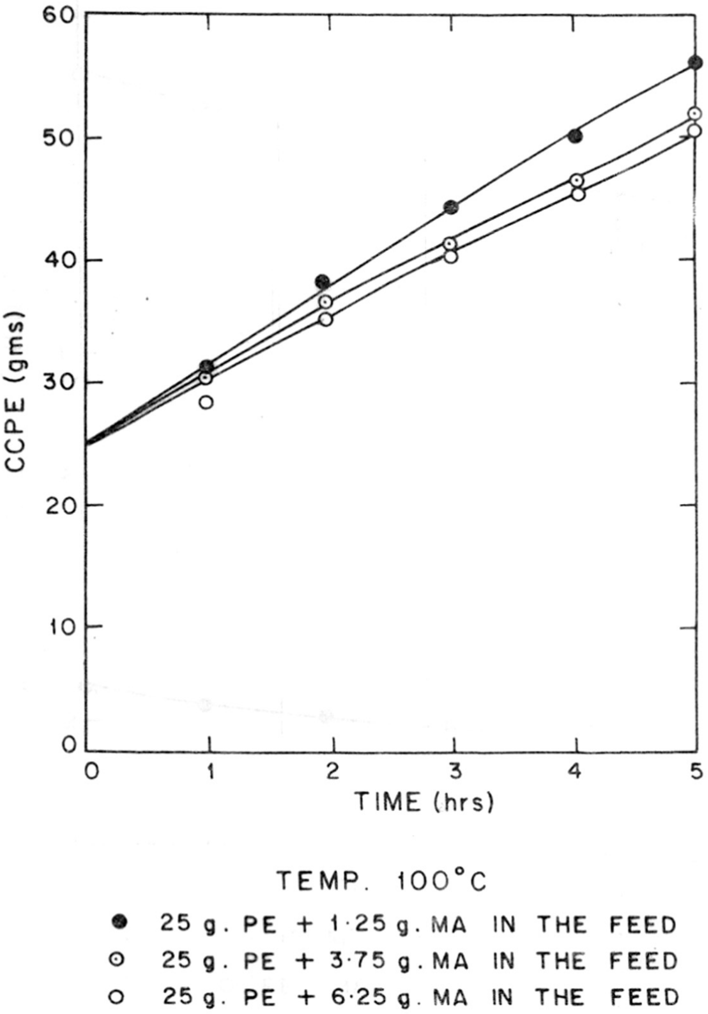
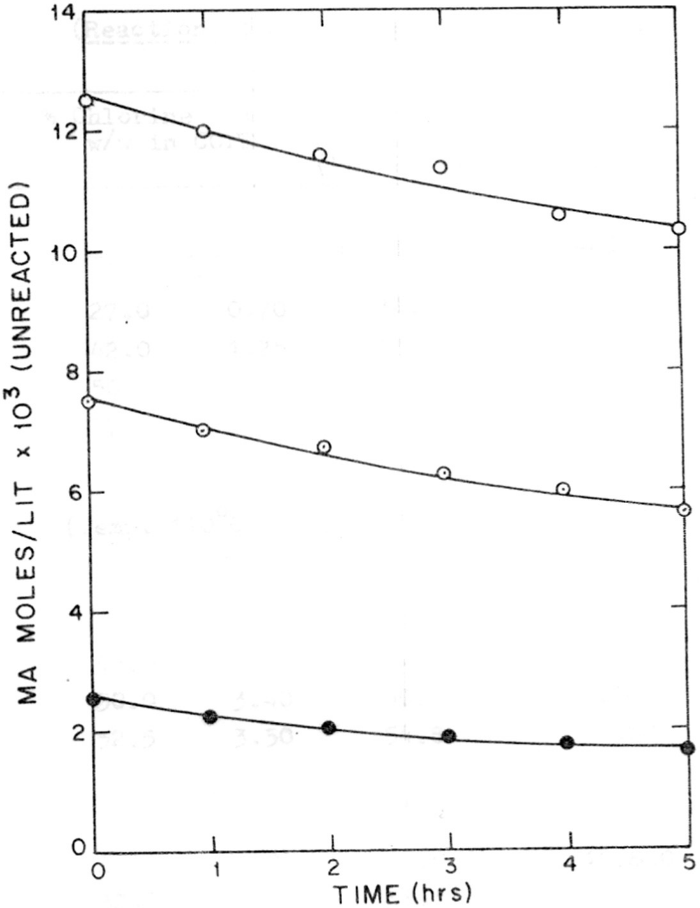


FIG. 4·5(B) : CHLOROCARBOXYLATION OF PE VARIATION OF YIELD WITH TIME.



TEMP. 100 °C

○ PE : MA 100 : 25

⊙ PE : MA 100 : 15

● PE : MA 100 : 5

FIG. 4·6(B) : MA UNREACTED IN THE REACTION MIXTURE AS A FUNCTION OF TIME .

Table: 4.7 (C)

Chlorocarboxylation of PE: Yield of CCPE and its Composition

(Reaction Conditions as in Set C)

Time	% Chlorine w/w in CCPE	% MA	Yield gms (PE: 25 gms)	MA unreacted (gms)
(Temp. 110°C, MA 2.5 g/lit. in the feed)				
1.	27.0	0.70	34.6	2.270
2.	42.0	1.25	43.7	1.960
3.	50.0	1.70	50.9	1.630
4.	57.5	2.00	60.2	1.300
5.	58.0	2.05	60.8	1.250
(Temp. 110°C, MA 7.5 g/lit. in the feed)				
1.	20.0	1.20	31.8	7.120
2.	32.0	2.20	37.9	6.670
3.	45.0	2.80	44.6	6.250
4.	50.0	3.40	50.0	5.800
5.	52.5	3.50	54.8	5.600
(Temp. 110°C, MA 12.5 g/lit. in the feed)				
1.	20.0	2.05	32.0	11.800
2.	32.0	3.25	38.5	11.240
3.	42.0	4.25	45.5	10.567
4.	46.0	4.80	49.0	10.148
5.	50.0	5.40	52.9	9.650

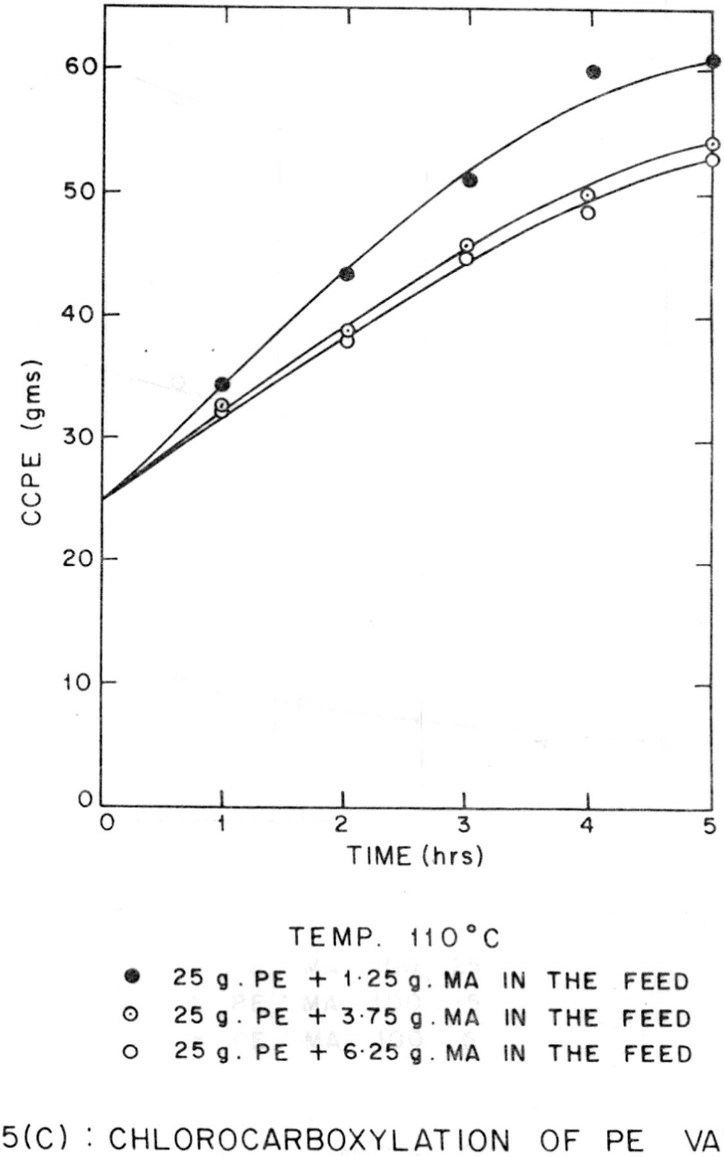


FIG. 4·5(C) : CHLOROCARBOXYLATION OF PE VARIATION OF YIELD WITH TIME.

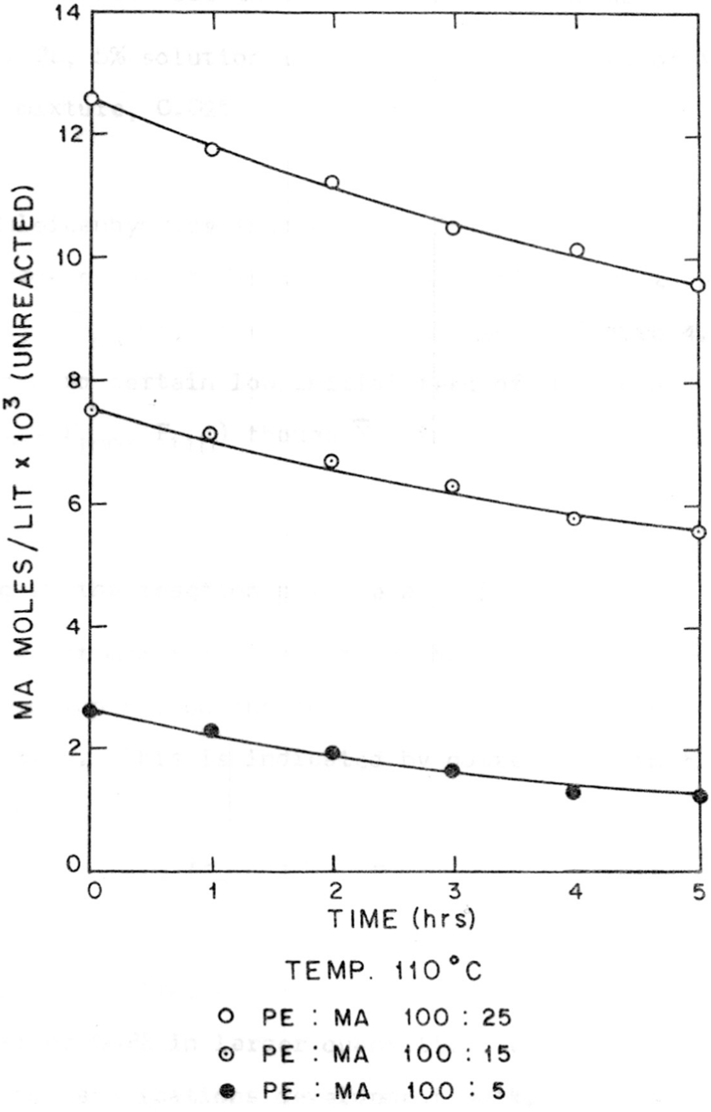


FIG. 4·6(C) : MA UNREACTED IN THE REACTION MIXTURE AS A FUNCTION OF TIME.

In order to work out optimum conditions for the reaction of maleicanhydride with PE during chlorocarboxylation, experiments were carried out under following conditions:

a) PE, 5% solution in TCE (b) initial feed of MA in the reaction mixture, 0.025 to 0.125 moles/lit (c) reaction period 5 hours.

Maleicanhydride incorporated in PE was expressed as $\overline{N}_{MA}$ (average number of equivalent MA moities per PE chain). Variation of $\overline{N}_{MA}$ with feed MA is depicted in Figure 4.7. $\overline{N}_{MA}$ increases upto certain low initial feed of MA beyond this point (F_{90}, F_{100}, F_{110}) though $\overline{N}_{MA}$ increases with initial feed of MA, this change in $\overline{N}_{MA}$ is fairly low. Large initial feed quantities of MA have to be employed and unreacted maleicanhydride remaining in the reaction mixture also increases.

The optimum feed quantity of MA (for given temperature, preset reaction period and conc. of PE) can be found out by interpolation. This is indicated by dotted line in Figure 4.7 (Table 4.8).

These points (F_{90}, F_{100}, F_{110}) give $\overline{N}_{MA}$ optimum and MA unreacted remaining in the system minimum.

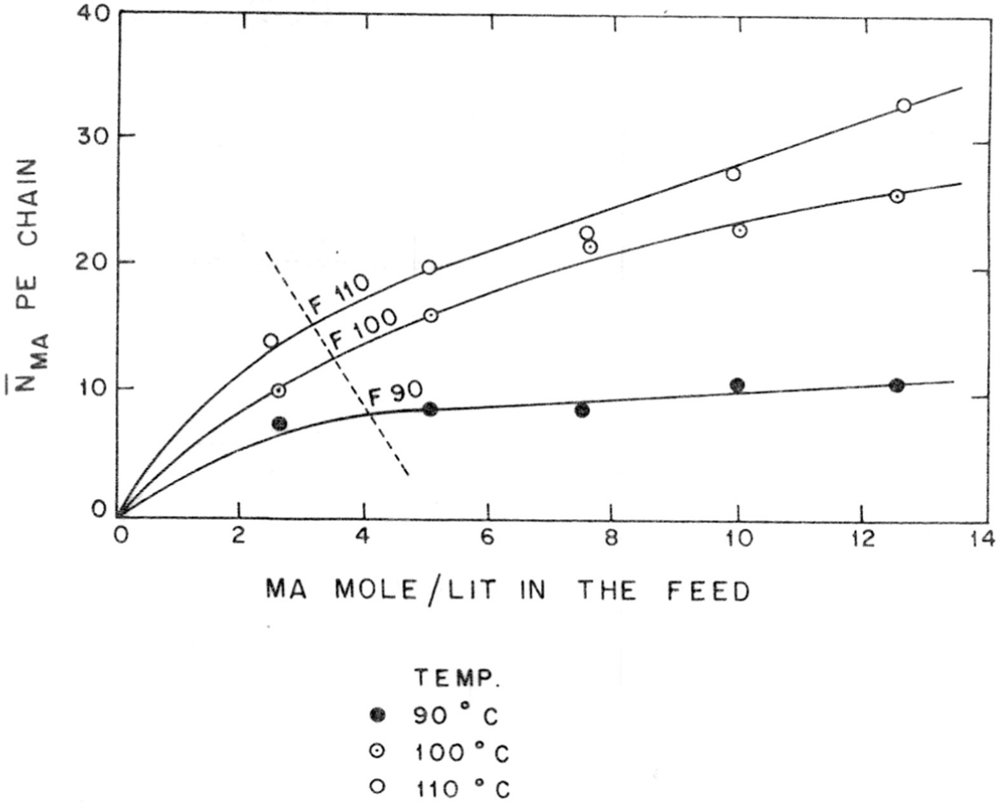
This data (Table 4.8) can be utilized as the guideline for preparing CCPE in larger quantities, especially CCPE required for applications development work.

Table: 4.8

Optimization of Initial MA feed for CCPE Process*

MA initial feed of mol/ lit x 10^2	$\bar{N}_{MA}$ Average MA (equivalent) moities per chain of PE	Optimum feed MA g/mol/lit x 10^2
	Temp. of Reaction 90°C	
2.5	7.2	4.0 for 90°C
5.0	8.0	
7.5	8.09	
10.0	10.2	
12.5	11.0	
	Temp. of Reaction 100°C	
2.5	10.02	3.5 for 100°C
5.0	16.4	
7.5	22.8	
10.0	23.8	
12.5	26.22	
	Temp. of Reaction 110°C	
2.5	14.5	3.0 for 110°C
5.0	20.0	
7.5	23.2	
10.0	27.58	
12.5	32.52	

* Reaction Period 5 hrs., PE 50 g/lit.



(CONC. OF PE 50 g/lit, REACTION PERIOD 5 hrs.)

FIG. 4·7 : OPTIMISATION OF INITIAL MA FEED IN CHLOROCARBOXYLATION PROCESS.(TABLE 4·8)

APPENDIX -I

```
10 REM  COMPUTER PROGRAM IN BASIC LANGUAGE TO PROCESS KINETIC DATA FOR THE
20 REM  CHLOROCARBOXYLATION OF PE
30 REM  DEFININTIONS OF VARIABLES USED IN THE PROGRAM FOLLOWS :
40 REM   N = NUMBER OF PAIRS OF % Cl AND % MA IN CCPE
50 REM        (ALSO EQUALS TO NUMBER OF EXPERIMENTS PER SET)
60 REM   X = % Cl  IN CCPE SAMPLE
70 REM   Y = % MA IN CCPE SAMPLE
80 REM  M1 = CHANGED MOLECULAR WEIGHT OF PE DUE TO CHLORINATION
90 REM  M2 = CORRECTION DUE TO ALPHA Cl  SUBSTITUTION
100 REM N1 = AVERAGE NUMBER OF SITES OCCUPIED BY Cl ON PE CHAIN
110 REM T1 = N1/K4
120 REM M3 = CHANGED MOLECULAR WEIGHT OF PE DUE TO
130 REM      CHLOROCARBOXYLATION
140 REM N2 = AVERAGE NUMBER OF SITES OCCUPIED BY MA ON PE CHAIN
150 REM T2 = N2/K4
160 REM M6 = UNREACTED MA AT THE END OF THE REACTION PERIOD
170 REM      FOR GIVEN PAIR OF X,Y, VALUES
180 REM M7 = FACTOR IN R.H.S OF EQUATION 11
190 REM M8 = N1/N2 , CL TO MA SITE RATIO
200 REM M9 = VACANT SITE
210 REM K1 = MOLECULAR WEIGHT OF PE
220 REM K2 = ATOMIC WEIGHT OF Cl
230 REM K3 = MOLECULAR WEIGHT OF MA
240 REM K4 = AVERAGE NUMBER OF SITES AVAILABLE FOR SUBSTITUTION BY
250 REM      Cl OR MA ON PE CHAIN
260 REM F1 = CONCENTRATION OF PE IN REACTION MIXTURE (g/Lit.)
270 REM F2 = INITIAL CONCENTRATION OF MA IN REACTION MIXTURE (g/Lit.)
280 DIM X[100],Y[100]
290 K1=2.8633E+04
300 K2=35.5
310 K3=98
320 K4=2030.8
330 F1=25
340 F2=1.25
350 DISP "NUMBER OF SETS";
360 INPUT N
370 FOR I=1 TO N
380 READ X[I],Y[I]
390 X=X[I]
400 Y=Y[I]
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CONTD...

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410 M1=K1/(1-(X/100))
420 X2=X-(Y*K2/K3)
430 M2=K1/(1-(X2/100))
440 N1=(M2-K1)/K2
450 T1=N1/K4
460 M3=M1/(1-(Y/100))
470 N2=(M3-M1)/K3
480 T2=N2/K4
490 M4=(F1*M3)/K1
500 M5=M4*Y/100
510 M6=(F2-M5)*2
520 M7=LOG(F2/M6)
530 M8=T1/T2
540 M9=(1-T1-T2)
550 PRINT X,Y,M1,N1,T1,M2,N2,T2,M3,M4,M5,M6,M7,M8,M9
560 NEXT I
570 END
580 DATA 20,1.2
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SECTION V

APPLICATIONS DEVELOPMENT WORK.

A : VALCANIZATION AND VISCOELASTIC STUDIES ON CCPE.

B : SURFACE COATINGS BASED ON CCPE.

SECTION-V

APPLICATIONS DEVELOPMENT WORK

(A) VULCANIZATION AND VISCO-ELASTIC STUDIES ON CCPE

5.1.1 Vulcanization

Vulcanization is a common process to bring about desired stress-strain properties for raw elastomers and dates back to Goodyear's early experiments (1839) with natural rubber, heated with small amounts of sulphur. Chemical reactions associated with vulcanization process are ideally limited to a minor reaction at very few sites and brings about large changes in the properties of the long chain elastomer molecule. Depending upon the reactive groups, the vulcanization reactions are varied in nature. Vulcanization may be defined [1] in terms of the physical properties of the elastomer as the process which:

a) decreases the flow of the elastomer
b) increases the tensile strength and the modulus
c) but preserves its extensibility

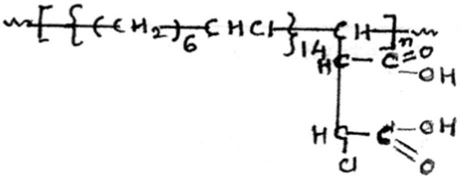
The vulcanization systems for various elastomers are broadly classified in two groups: (a) sulphur vulcanization and (b) non-sulphur vulcanization.

Sulfur vulcanization is related to the unsaturation in the elastomer, while non-sulfur vulcanization adopted for saturated polymers/elastomers is a process in which peroxides, nitrosocompounds, quinones or azocompounds are added as curing agents.

Vulcanization of CPE by the conventional sulphur cure is ineffective since it is a saturated polymer. It can be readily cured, however, through amine or peroxide curing systems.[2,3]

Several curing systems including metal oxides, di- and polyamines, polyisocyanates, etc. are used for vulcanization of carboxylic elastomers,[4,5] metal oxides and diamine systems being studied in detail, as revealed by published work.[6] Metal oxides play a major role in the vulcanization of chlorinated polyethylene and sulphochlorinated polyethylene.[7] Organic diamines are potential cross linking agents for 'maleic' rubber.[8]

The product CCPE studied for vulcanization in this work, has the following structure:



which corresponds to about 30% chlorine and 2.2% (equivalent) MA. The overall distribution of chlorine and MA on the polymer chain is one chlorine atom for every seven carbon atoms and one anchored MA group for about 96-110 carbon atoms of the polymer chain.

It is apparent that the vulcanization of CCPE, will proceed through carboxylic groups, chlorine atoms on the chain being relatively stable as in the case of poly (vinyl chloride)[9]. Systems based on ZnO, MgO and amines were studied in the present work.

5.1.2 Experimental

Compounding ingredients for the gum stock vulcanization of CCPE as indicated in Table 5.1 were mixed on a laboratory rubber mill at room temperature, time not exceeding five minutes. The milled product was vulcanized at the temperature of 120°C.

The properties of the vulcanized product are given in Table 5.3.

Table: 5.1

Compounding Ingredients for CCPE

	System A	System A'	System B	System B'
CCPE (30% Cl, 2.2% MA)	100 parts	100 parts	100 parts	100 parts
Stearic acid	2 parts	2 parts	2 parts	2 parts
ZnO	5 parts	4 parts	4 parts	4 parts
MgO	5 parts	4 parts	4 parts	4 parts
Hexamine	-	2 parts	-	2 parts
Hexamethylene diamine(HMD)	-	-	2 parts	-
Secondary butylamine	-	2 parts	-	2 parts

5.1.3 Melt-viscosity or plasticity test[10,11]

These tests provide the basis for the rheological behaviour of unvulcanized compounds. An important factor for successful processing of the rubber compound is the plasticity (viscosity) of the elastomer base. There are various types of plastometers used to measure plasticity. Williams Plastomer, in which a single pellet of rubber or stock is placed between the parallel plates, a pressure is applied and the distance between the plates is measured at specified time intervals. In Mooney plastomer, a disc of definite dimensions is rotated in the mass of the rubber and the torque required to turn the rotor is measured. A number (M) proportional to this torque is taken as an index of the viscosity of the rubber. Mooney viscometer can be used for determining Scorch time and cure rate for the compounded rubber and is extremely useful for studying vulcanization rate and optimum cure time of the compounded elastomer.

Mooney viscosity measurements were carried out at 100°C (212°F) for the raw CCPE. For the compounded system A (metal oxide cured) systems A', B and B' (metal oxides + amine cured), the measurements were carried out at 120°C (248°F) using large rotor. The variation of Mooney viscosity with time for systems A, A', B and B' is shown in Fig. 5.1.

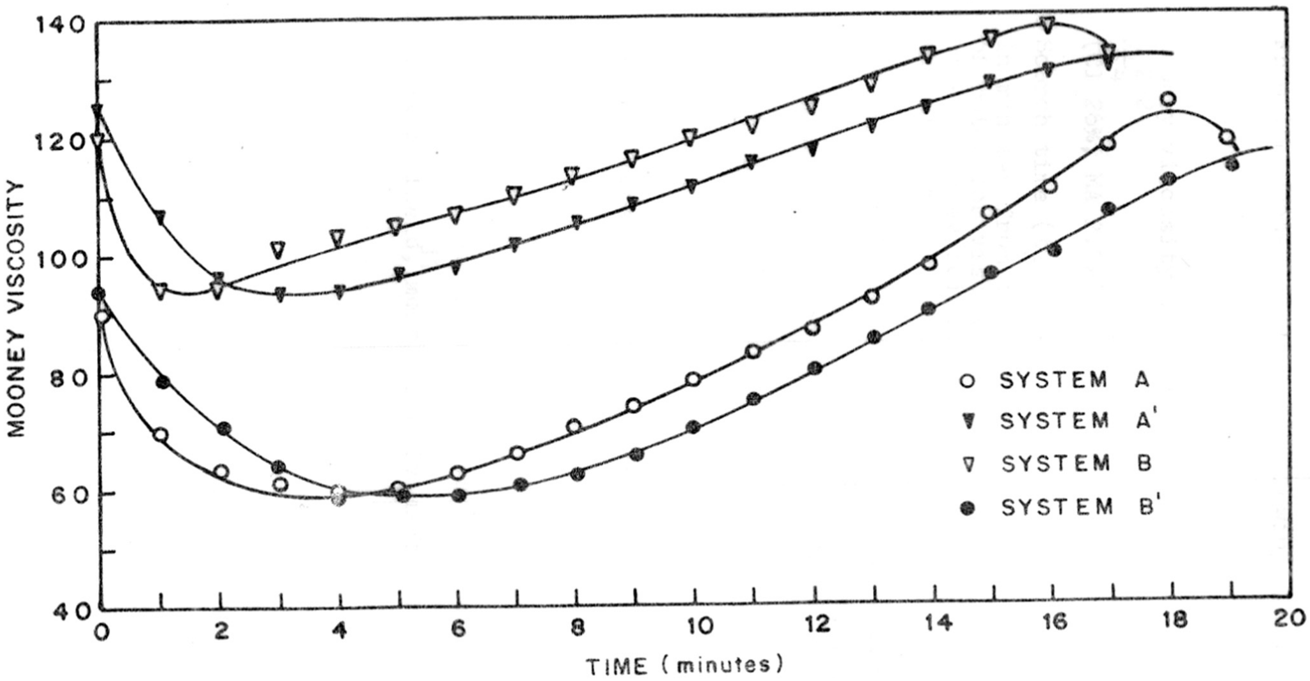


FIG. 5·1 (TABLE 5·2)

From the Mooney curve the following determinations are made(Table-5.2):

(1) Mooney viscosity of CCPE ML_4^{212} (Cl 26%, MA 2.2%) = 29.0

(2) Scorch time (t_s) i.e. time in minutes from the start of rotor for viscosity to rise 5 Mooney points above the minimum = t_5

(3) Time of cure (t_c) = t_{35} (time from the start, for viscosity to rise 35 Mooney points above the minimum viscosity reading)

(4) Cure index = $t_{35} - t_5$

(5) Rate of cure = $\frac{30}{t_c - t_s}$ Mooney units per min.

From this data it is possible to extrapolate actual optimum cure time. Among various formulae suggested by many workers in this field[11], most commonly used formula for optimum cure is:

Optimum cure time = Time required for $(0.9 \times M_{max})$ Mooney units

5.1.4 Stress-strain studies

The stress strain studies of CCPE vulcanisates were carried out on the Scott Tester (floor model) with an automatic recorder. The dumbbell shaped specimen was placed in the two grips of the machine and the lower grip of

Table: 5.2

Results of Mooney Viscosity Measurements

	Characteristics	System A	System A'	System B	System B'	
(1)	Minimum viscosity (M_V)	60 Mooney units	58 Mooney units	95 Mooney units	94 Mooney units	70
(2)	Time to scorch (t_s)	7 minutes	8 minutes	3.5 minutes	6 minutes	5
(3)	Time to cure (t_c)	14 minutes	16 minutes	13.5 minutes	15 minutes	17
(4)	Rate of cure	4.3 Mooney units/ minute	3.55 Mooney units/ minute	3.0 Mooney units/ minute	3.33 Mooney units/ minute	
(5)	Cure index ($t_c - t_s$)	7 minutes	8.5 minutes	10 minutes	9 minutes	12
(6)	Optimum cure time	14.5 minutes	15.0 minutes	12.5 minutes	15.5 minutes	

13-

Table: 5.3

Properties of the Vulcanized Products

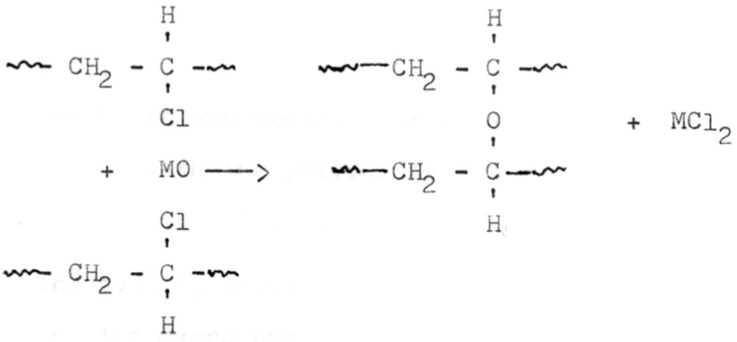
	Characteristics	System A	System A$'$	System B	System B$'$
(1)	Vulcanization time (optimum cure)	14.5 minutes	15.0 minutes	12.5 minutes	15.5 minutes
(2)	Vulcanization temperature	120°C	120°C	120°C	120°C
(3)	Modulus at 100% elongation	22.1 kg/cm^2	20.6 kg/cm^2	24.5 kg/cm^2	23.0 kg/cm^2
(4)	Modulus at 300% elongation	38.5 kg/cm^2	35.0 kg/cm^2	42.0 kg/cm^2	40.3 kg/cm^2
(5)	Tensile strength	93.0 kg/cm^2	85.5 kg/cm^2	121 kg/cm^2	115 kg/cm^2
(6)	Ultimate elongation	580 %	620 %	600 %	650 %
(7)	Shore A Hardness	72	70	70	70

the dumbbell was driven downwards at the rate of 50 cms per minute.

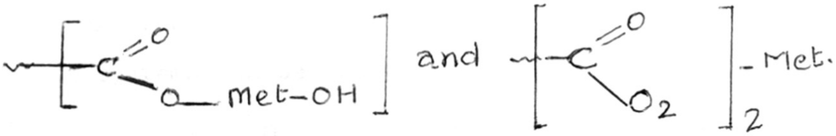
Results of the stress-strain behaviour of CCPE are shown in Table 5.3.

5.1.5 Discussion

Vulcanization of CPE can be achieved with difficulty by the reaction that involves breaking of relatively strong C-H or C-Cl covalent bonds.[2,3] This is achieved through the peroxide or amine curing systems. The mechanism of such crosslinking is essentially free radical with peroxides, and chlorine displacement with amines.[2,3] Metal oxides which are also included in the curing systems act as[7] acid acceptors, being commonly used for this purpose and for chlorinated rubbers as the crosslinking agents.[12]



Several curing systems are used to vulcanize carboxylic elastomers. Simplest and most extensively studied are those based on divalent metal oxides. Oxides of Zn, Mg, Ca, Al etc. are commonly used. It is found that low molecular weight fatty acids react quantitatively with oxides of Zn, Mg, Ca.[6] Only partial reaction of carboxylic elastomers occurs due to localized insolubility of metal oxides, indicating the heterogeneity of the reaction. After formation of the network structure remaining component of the carboxyl group in the chain becomes immobilised. Chemically two types of salts, basic (I) and neutral (II) are possible.[6]



(I) (II)

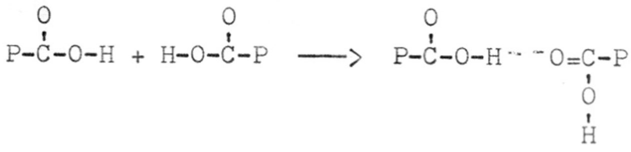
The basic and neutral salts possess limited compatibility with the polymer fluid and crystallize out when cooled to normal working temperature.

The bonding between polymer chains occurs at the surface of the macro particles of the metal oxides or the crystals of basic or neutral salts. In both the cases, intermolecular bond strength is proportional to the ionic forces of corresponding basic and neutral salts of the organic acids. This explains the stress orientation and hysterisis, compression set etc. in such ionically crosslinked elastomers.[6]

Carboxylic elastomers react with di- and poly amines to give covalent crosslinks.[5,13,14] If HMD, or HMDC is used with stearic acid to liberate the diamine, then vulcanization depends upon the aminolysis of the elastomer.[15] Diamines cause gelation of maleic anhydride grafted elastomers even in solution which indicates that diamines are potential crosslinking agents for carboxylic elastomers.[8]

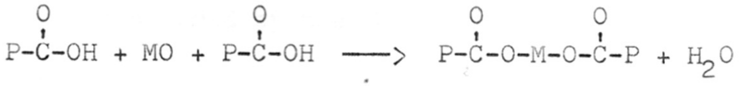
The important reactions which may cause crosslinking of CCPE by metal oxide and combined metal oxides diamines systems can be summarised as (P = polymer chain):

(1) Thermal (hydrogen bonding)



$$P-\overset{O}{C}-O-H + H-O-\overset{O}{C}-P \longrightarrow P-\overset{O}{C}-O-H\cdots O=\underset{\underset{H}{O}}{C}-P$$

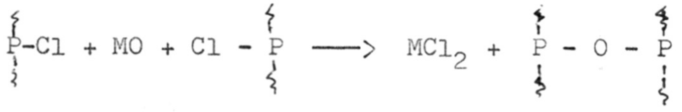
(2) Salt formation due to metal oxides



$$P-\overset{O}{C}-OH + MO + P-\overset{O}{C}-OH \longrightarrow P-\overset{O}{C}-O-M-O-\overset{O}{C}-P + H_2O$$

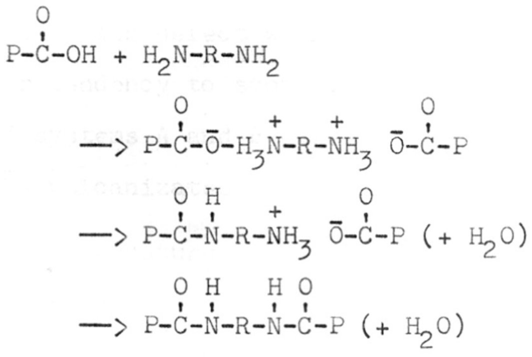
$M = Mg, Zn$

and to some degree with the chlorinated segment of CCPE metal oxides may react as:



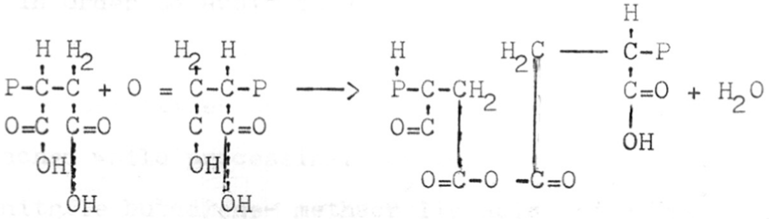
$$P-Cl + MO + Cl-P \longrightarrow MCl_2 + P-O-P$$

(3) Crosslinking due to diamines



$$\mathrm{P{-}\overset{O}{C}{-}OH + H_2N{-}R{-}NH_2}$$
$$\longrightarrow \mathrm{P{-}\overset{O}{C}{-}\bar{O}{-}H_3\overset{+}{N}{-}R{-}\overset{+}{N}H_3\ \bar{O}{-}\overset{O}{C}{-}P}$$
$$\longrightarrow \mathrm{P{-}\overset{O}{C}{-}\overset{H}{N}{-}R{-}\overset{+}{N}H_3\ \bar{O}{-}\overset{O}{C}{-}P\ (+\ H_2O)}$$
$$\longrightarrow \mathrm{P{-}\overset{O}{C}{-}\overset{H}{N}{-}R{-}\overset{H}{N}{-}\overset{O}{C}{-}P\ (+\ H_2O)}$$

(4) Anhydride crosslinking at higher vulcanization temperature



Combined metal oxide and diamine curing systems have been found to be better for carboxylic elastomers. This fact is confirmed by the good balance of stress strain properties. As seen from the properties of the vulcanizates (Table 5.3), the combined metal oxides-diamine system appears to be superior to metal oxide system alone in respect of tensile strength and elongation.

5.1.6 Modification of curing system to avoid scorching of CCPE elastomers

The main defect with most of the carboxylic rubbers is their tendency to scorch. While studying the vulcanization of systems A and B based on CCPE it was also observed that the vulcanizates are having tendency to scorch.[5]

The premature vulcanization of carboxylic elastomers is due to the high affinity of metal oxides (ZnO in particular), towards carboxyl groups. This scorching tendency also affects the shelf life of the compounds.[16]

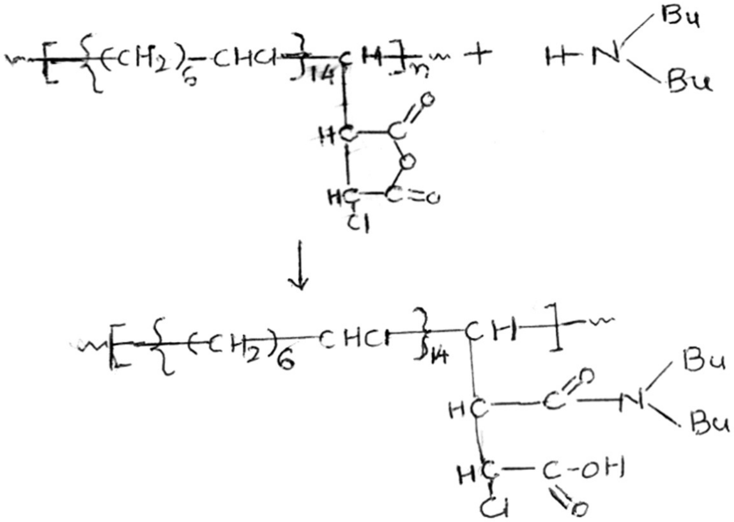
In order to avoid this scorch due to the high affinity of metal oxide, carboxylic groups must be protected from the metal oxides until desired vulcanization conditions are reached while processing. Carboxylic rubbers i.e. acrylonitrile butadiene- methacrylic acid ter polymer, and butadiene metacrylic acid copolymer were cured by Hallenbeck[16] using zinc sulfide coated ZnO. The compounds did not show any tendency to scorch. Carboxyl groups in the polymer are supposed to be isolated from ZnO until desired vulcanization temperature is reached due to ZnS coating. ZnO coated with zinc phosphate also functions in similar way. ZnO in the system can be replaced by alkoxides (aluminium ethxide or aluminium isopropoxide) to give non-scorchy compounds.[16]

In an attempt to avoid scorching tendency of CCPE compounds the vulcanization system was modified as follows.

a) HMD was replaced by hexamine (HMT). This probably acts as the delayed action curing agent as compared to HMD as found out from gelling reactions of CCPE (Section III-C) .

b) Secondary butyl amine was also included in the system. This probably protects the vulcanization sites and retards the undue high curing rates caused by the presence of metal oxides (ZnO in particular) in the vulcanization system.

As reported earlier (Section III-C), secondary butyl amine probably reacts with CCPE according to reaction (5) during vulcanizations and blocks one of the carboxyl groups.[17] It also provides hinderance to the crosslinking reactions of the remaining carboxyl group due to anchored 'butyl moities.'[7]



[5]

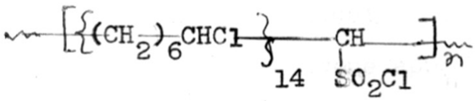
The properties of the vulcanizates based on HMT and secondary butyl amine (Systems A' and B') are given in Table 5.3 and as can be seen from figure 5.1 and table 5.2, it also increases scorch time. This system reduces scorching tendency, without appreciable loss of properties of the vulcanizates.

Section-V

(B) Surface Coatings Based On CCPE

Chlorinated PE (CPE) and chlorosulfonated PE (CSPE) are used as base material for surface coatings.[2,18] These coatings are having very good chemical and solvent resistance properties. The ozone resistant properties of these coatings are excellent. Poor resistance towards the action of ozone is the drawback of many rubber based coatings.

CPE or CSPE manufactured from low density branched polyethylene (LDPE) are suitable for coating applications. The chlorine and sulfonyl chloride group distribution of CSPE used for applications is as follows.



$$\sim\left[\left\{(CH_2)_6CHCl\right\}_{14}\underset{SO_2Cl}{\underset{|}{CH}}\right]_n\sim$$

i.e. 1 chlorine atom for every 7 to 8 carbon atoms of PE chain and one anchored SO_2Cl group for every 90 to 100 carbon atoms.[19] In CSPE, chlorine atoms gives the flexibility to the polymer chain and SO_2Cl groups act as the crosslinking sites.

Since coating applications of CPE and CSPE are well-established commercial processes, it was thought desirable to make CCPE which probably will be suitable for coating applications.

CCPE prepared for coating applications was based on LDPE. Its chlorine distribution was similar to that of CSPE coating grade polymer, i.e. one chlorine atom for every 7 to 8 carbon atoms of PE and one anchored MA moity for every 90 to 100 carbon atoms, which will act as the crosslinking site. Thus CCPE used for coating developments was similar to CSPE except that carboxyl groups of hydrolysed MA were the crosslinking sites instead of SO_2Cl groups.

5.2.1 Factors affecting the performance of coating

a) Solvent

Selection of solvent system is the critical parameter for the coating applications. To develop coatings based on CCPE, xylene and toluene appear to be suitable solvents because the solubility parameter of these solvents and that of CCPE is of the same order. Here solubility parameter of CCPE is assumed to be 9.1 i.e. of the same order as that of CSPE. [18]

Table 5.4 lists the properties of some solvents which can be used for coatings. Toluene and xylene are true solvents for CCPE, since solubility parameters of these are 8.9 and 8.8 respectively. [18]

Table: 5.4

Properties of Solvents Which can be used for CCPE Coatings 18,20

Solvent	Solubility parameter	Molar volume	Specific gravity 15°C	Evaporation rate* minutes
Acetone	10.0	73	0.791	0.8
Methyl ethyl ketone	9.3	89	0.807	1.5
Isopropyl alcohol	11.5	76	0.790	2.2
Toluene	8.9	116	0.867	2.7
Xylene	8.8	122	0.870	7.3
Hexane	7.3	130	0.659	0.6

* minutes required for 0.5 cc to evaporate from filter paper at 25°C temperature

A blend of solvents can be used even though each individual component may not be the solvent for polymer, and the solubility parameter of the blend can be controlled by adjusting the composition of the blend. And this value of the solubility parameter can be adjusted to that of polymer solubility parameter.

Usually solvent blend gives effective solution if solubility parameter is within 1 or 2 units of that of the polymer.

The solubility parameter δ of the blend is related to the mole fraction X, molar volume V (molecular weight/density) by the following equation.[20]

$$\delta_{blend} = \frac{X_1V_1\ \ _1 + X_2V_2\ \ _2 + ---- + X_nV_n\ \ _n}{X_1V_1 + X_2V_2 + -------- + X_nV_n}$$

Using this relation many other solvent systems can be formulated for CCPE coatings.

Viscosity and shelf life are also important properties which affect the behaviour of coatings. Viscosity is related to the shape of the polymer chain in solution.[18]

b) <u>Viscosity</u>[18]

In good solvent polymer chains are elongated. In poor solvent polymer chains are irregularly folded into more or less tight spheres. This means in good solvent for a given concentration the viscosity of the solution is more than the viscosity in poor solvent. Toluene and xylene are good solvents for CCPE (than other combination e.g. acetone and xylene)[18].

c) <u>Shelf life</u>[18]

The concentration at which polymer chains are separate and discrete in good solvent, the spherical molecules in poor solvent under identical conditions are associate into clusters. Within these clusters the opportunities for crosslinking are very good and polymer tends to gel. The presence of accelerators or crosslinking agent in solution tends to increase the rate of gelation. All these factors were taken into account before selecting xylene and toluene as the solvents for CCPE coating.

5.2.2 CCPE coatings

CCPE coating was prepared as follows:

PART-I : CCPE - resin solution

	Parts(by weight)
CCPE	90
Hydrogenated wood resin	3
SF-69 silicone fluid (2% in toluene)	3
Xylene	297
Isopropyl alcohol (99%)	45

These ingredients were dissolved at room temperature (or temperature less than 60°C) using mechanical stirrer.

PART-II : Dispersion of compound ingredients

	Parts (by weight)
Toluene	225
Isopropyl alcohol (99%)	30
Bantone 34 clay	3
Zinc oxide	20
Magnecium oxide	20
Titamin dioxide (Rutile)	125
Isophthalic acid	2
HMD (Hexamethylene di amine)	2

These ingredients were ground in a peble mill to Hegman fineness 8. Suitable coloured pigments can also be incorporated (less than 2 parts by weight). In this work no pigments were used.

PART-III : CCPE solution

	Parts (by weight)
CCPE	10
Toluene	40

These components were dissolved at 60°C using mechanical agitator and cooled to room temperature.

5.2.3 Preparation of the coating

Part-III was added to Part-II and grinding in pebble mill was continued for 15 minutes. This mixture was added to part-I while stirring.

The properties of the formulation are given in Table 5.5.

Table: 5.5

Properties of CCPE Coating Formulation

1.	Total solids weight %	30
2.	Density	0.88 g/cm^2
3.	Ford cup-viscosity, No. 4 cup	52 seconds

5.2.4 Functions of the various ingredients incoatings.[19,21]

In this coating formulation ZnO and MgO act as crosslinking agents. The crosslinking reaction can be facilitated by organic acids. Hydrogenated wood Rosin and isophthalic acid are included for this purpose.

HMD acts as an accelerator.

Isopropyl alcohol together with xylene and toluene gives solvent system. Actually, isopropyl alcohol is the precipitant for CCPE. Due to different rates of evaporation of solvents (xylene and toluene) and isopropyl alcohol film formation process is accelerated due to partial precipitation.

Bentone 34 is usually used in ionic coating systems and this helps the formation of stable gels and facilitates film formation process.[19]

Silicon fluid acts as an antifoam and antifloat agent and keeps the pigment dispersion in a stable condition.

Titanium dioxide (rutile) is a well known pigment having very good covering power and is extensively used for coating applications.

CCPE coatings can be applied on various substrates (metal, wood, masonary surfaces etc.) by brush or by standard spray guns.

Properties of coating are shown in Table 5.6.

CSPE coatings based on similar formulation were used for the comparison.[18]

Table: 5.6

Properties of CCPE Coating

	Test	CSPE coating	CCPE coating
A)	Film drying and curing		
	i) Dry to the torch at room temperature	5 minutes	7 minutes
	ii) at 70°C	complete drying in 3 minutes	complete drying in 4.5 minutes
	iii) Curing time at room temperature	4 days	5 days
B)	Weight of coating per sq.ft. (covering)	9 gms	10 gms
C)	Dry adhesion	Very good**	Very good
		Very little coating removed from scored portion by cellophane tape	
D)	Wet adhesion (as above but film was treated for 1 hour in boiling water)	Very good	Very good
E)	Water resistance		
	a) 72 hrs in hot water at 60°C	Very good	Good *
	b) 72 hrs in hot water at its B.P.	Good	Poor +
F)	Acid resistance 24 hrs in 1 N $H_2 SO_4$	Very good	Good
G)	Alkali resistance 24 hrs in 1 N NaOH	Very good	Good

** Traces of coating affected

* 3-5% of coated surface affected

\+ More than 10% of coated surface affected[19,21]

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SECTION VI

SUMMARY AND CONCLUSIONS.

SECTION-VI

SUMMARY AND CONCLUSIONS

Chlorocarboxylation of polyethylene is a reaction combination in which the chlorination of PE and reaction of maleic anhydride may proceed simultaneously via radical mechanism. The anchoring of MA on PE chain is possible due to its high chain transfer and radical scavenging action. This reaction combination was realized experimentally and the process is termed 'chlorocarboxytion' of polyethylene. The reaction product fulfills the requirements of an elastomer. Hydrogen atoms in the parent polyethylene are randomly replaced by chlorine, destroying the crystallinity of PE and low percentage of carboxyl groups can act as the crosslinking sites during vulcanization. In order to get a suitable vulcanizable chlorocarboxylated polyethylene (CCPE), the following aspects of the process were studied: (i) structural characterization of CCPE, (ii) reaction mechanism of the process, (iii) kinetics of the process and factors affecting the composition of CCPE formed and (iv) suitability of the product for applications as an elastomer and as a base material for surface coating.

In the present work chlorocarboxylation of low density PE at three temperatures (90°, 100° and 110°C) has been studied. LDPE dissolved in tetrachloroethane (TCE) was chlorinated by gaseous chlorine, the reaction mixture also containing varying amounts of MA. The thermal initiation was adequate and addition of usual free radical initiators was unnecessary.

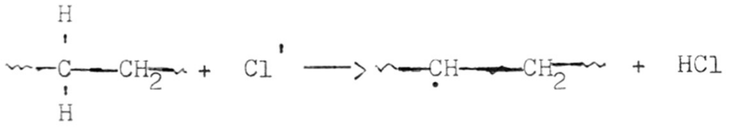
The CCPE samples were characterized in regard to chemical composition by using the following techniques: (a) elemental analysis (b) dye interaction technique and (c) non-aqueous titrimetric procedure.

IR and NMR spectroscopic data is presented for the structural characterization of CCPE. The reaction mechanism of the process consists of the following main kinetic steps:

i) Formation of chlorine radicals from molecular chlorine by various processes, e.g. thermal, photo, etc.

$$Cl_2 \overset{thermal}{\rightleftharpoons} Cl^{\cdot} + Cl^{\cdot}$$

ii) Abstraction of PE hydrogen by chlorine radicals



$$\sim\overset{H}{\underset{H}{C}}-CH_2\sim + Cl^{\cdot} \longrightarrow \sim\underset{\bullet}{C}H-CH_2\sim + HCl$$

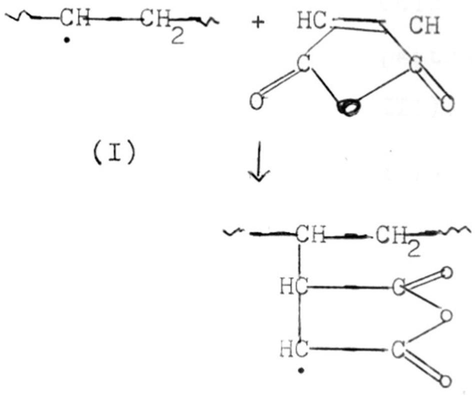
(I)

iii) Reaction of macroradical (I) with chlorine or maleic anhydride

a) $\sim\underset{\bullet}{C}H-CH_2\sim + Cl_2 \longrightarrow \sim CHCl-CH_2\sim + Cl^{\bullet}$

(I)

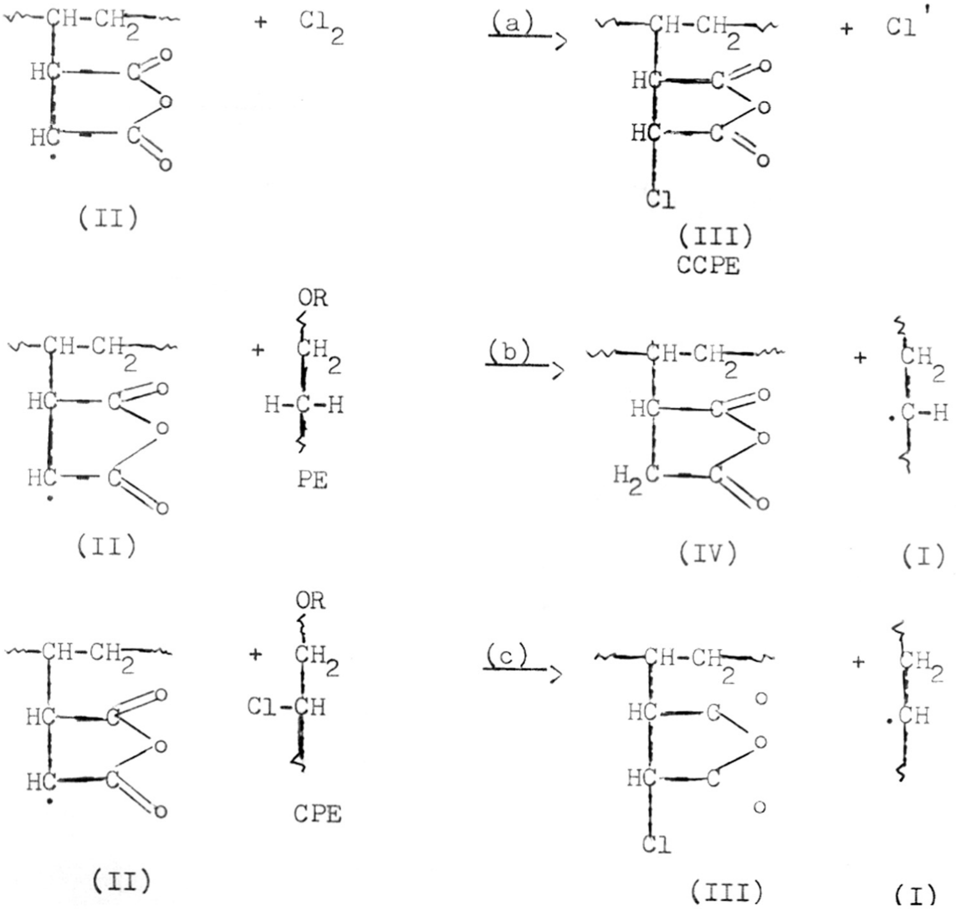
formation of CPE segments and generation of new radicals b)



(I)

(II)

iv) Macroradical (II) generated in (iii.b) terminates by the following probable reactions:



(II) (III)

(II) (IV) (I)

(II) (III) (I)

In all these reactions either chlorine radical or new macroradical (I) is generated. Spectroscopic evidence supports the formation of structure (III).

Other reaction routes, possible in the mechanism have been found to be less probable on the basis of experimental observations and CCPE characterization results. Some well-known reactions of carboxyl group are also studied on the macromolecule to support its structure and hence the reaction mechanism of CCPE process.

Kinetic equations are derived to fitin the observed relative rates of reactions of maleic anhydride and chlorine with PE. Mathematical expressions are also derived to predict the composition of CCPE formed in the reactions.

Rate equations:

$$\frac{d\theta_{Cl}}{dt} = k_{Cl}\,[Cl_2]\,[1 - \theta_{Cl} - \theta_{MA\ poly}] \qquad [1]$$

$$\frac{d\theta_{MA}}{dt} = k_{MA}\,[MA]\,[1 - \theta_{Cl} - \theta_{MA\ poly}] \qquad [2]$$

Composition equations:

$$\theta_{Cl} = \frac{k_{Cl}}{k_{MA}} \cdot [Cl_2] \cdot \ln \frac{\theta_{MA_o}}{\theta_{MA_o} - \theta_{MA\ poly}} \qquad [3]$$

where θ_{Cl} and $\theta_{MA\ poly}$ are the fractions of the total number of sites occupied by chlorine atoms or by maleic anhydride moities respectively and θ_{MA_o} is the fraction of feed maleic anhydride moles available for a reaction site on PE chain.

k_{Cl} and k_{MA} are the rate constants for chlorination and carboxylation (MA substitution) reactions.

Reaction kinetics study was carried out at three temperatures and corresponding values of k_{Cl} and k_{MA} were evaluated from kinetic equations (i) and (ii). From the data, activation energy 'E' for chlorination and carboxylation (maleic anhydride substitution reaction) was determined from the Arrhenius plots, and is of the order of 41.6 and 25.7 Kcal/mol respectively.

Some well-known vulcanization systems used for CPE and carboxylic elastomers (combined metal oxides and diamine, systems) were adopted for vulcanization of CCPE. These systems gave elastomers of reasonable mechanical strength but were associated with scorchiness, a defect usually observed in carboxylic elastomers. A successful attempt was made to avoid scorchiness by modifying the vulcanization systems using secondary amines and Hexamine that delayed curing action.

As a possible application, preparation of a paint based on CCPE is described. The properties of this paint when applied on metal substrate (mild steel) are studied and compared with the standard Hypalon-based paint coatings.

Conclusions

Vulcanizable chlorocarboxylated polyethylene (CCPE) elastomers can be obtained by simultaneous reaction of chlorine and maleic anhydride with PE. Low concentrations (less than 3%) of carboxyl groups have been detected by IR and NMR spectroscopy and further quantitatively estimated by dye interaction and non-aqueous titrimetry procedure.

Spectroscopic data is presented for the structural characterization of macromolecule CCPE and to elucidate the reaction mechanism of the process. During chlorocarboxylation process maleic anhydride can be anchored to backbone CPE chain as a single monomeric unit of chloro derivative without forming any graft copolymer of short branches. Some well-known reactions of carboxyl groups were carried out with CCPE to confirm structure and reaction mechanism of CCPE.

The relative rates of chlorination and carboxylation can be expressed in terms of the fractions of the sites occupied by each on PE chain in the form of differential equations (1) and (2) and composition of CCPE can be expressed by equation (3). Relative rate constants k_{Cl} and k_{MA} have been evaluated using equations (1) and (2). The composition of CCPE can be predicted by application of equation (3).

This scheme of studying kinetics of CCPE may be generalized and extended to the reactions of polymers involving similar reaction mechanisms.

Vulcanizability of CCPE of CCPE has been checked using modified 'metal-oxides-amines', curing system to avoid scorching (a defect usually associated with carboxylic rubbers) of CCPE. A possible application of CCPE as a base material for surface coatings has been discussed.

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