University of Nigeria, Nsukka

FROM STUDIES IN POLYMERS AND VEGETABLE OILS TO SANITIZATION OF THE ACADEMIC SYSTEM

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by

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Mr Vice-Chancellor, Members of the Governing Council, Deputy Vice-Chancellors, Other Principal Officers, Fellow Academics, Lions and Lionesses, Ladies and Gentlemen, I feel privileged and pleased to be given the opportunity to give my Inaugural Lecture today. I thank God and the Vice-Chancellor for this.

1.   The Inaugural Lecture

The Inaugural Lecture, which is supposed to formally launch a Professor into his new rank, appears at the moment to be more of a Valedictory Lecture at the University of Nigeria as some very recent ones took place just before the Inaugural Lecturers retired. I too will retire in a few months time. There seems to be a very high inertia for us here to fulfil this academic function; who knows whether it has anything to do with the high barrier energy of promotion most of us have had to overcome to get to the new post. A situation where the promotion of a University of Nigeria Professor, remained in the pipeline for n years, where n could run into two digits, makes the new professor old, and he/she may have run out of academic enthusiasm for waiting too long to be recognized.

Historically, it may be a thing of pride for me to note that I am the first Professor in the Faculty of Physical Sciences to give an Inaugural Lecture, but it is not a history that the Faculty can be proud of. In the light of this, Mr. Vice-Chancellor, sir, it may be necessary to schedule Professors on a routine basis for this important academic function. This suggestion is borne out of the fact that the Inaugural Lecture is also supposed to serve as an opportunity for the Professor to tell the public in a lay-man's language, what he/she professes, the contributions made, problems encountered (including man-made ones) and the prospects for the future. Even though in doing so, there is the risk that it may not be easy for the lay-man to understand some of the technical terms the Professor may inevitably have to use in order to justify being a specialist. Mr. Vice-Chancellor, sir, I profess Physical Chemistry and Polymer Chemistry, since I apply the principles of physical chemistry to the study of polymers. So, please permit me to use chemical terms. In doing so, I shall strive to be as simple as possible so as not bore the expert in the attempt not to bamboozle the non-expert.
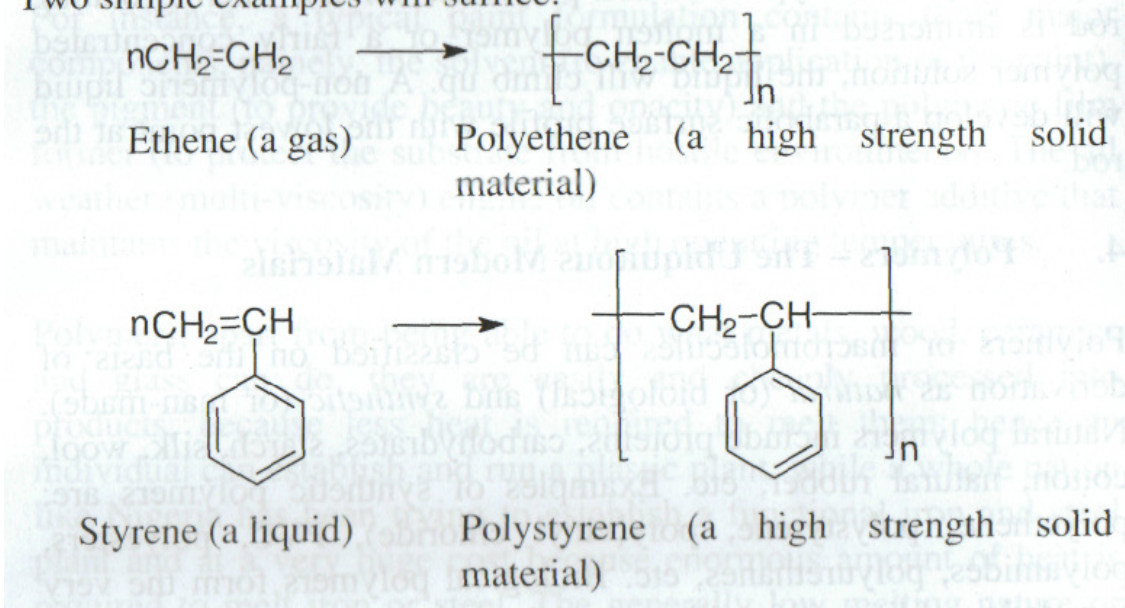.

2.   The Place of Polymer Chemistry In Chemistry

Chemistry as the epicenter of science is concerned with the study of the composition, structure, properties and reactions of matter. Physical chemistry, simply defined, is the application of physical methods and theories to the study of chemical systems. Polymer Chemistry is the study of 'giant' molecules or else called 'macromolecules'. A

molecule is a combination of atoms or group of atoms that are capable of independent existence. The size of a molecule is often expressed in terms of its mass. For instance, water (H_2O) has a mass of 18 using the atom carbon as a reference; this figure is known as its molar mass. The study of molecules with low molar masses, usually below 500, is the concern of 'traditional' chemists, while the study of molecules with molar masses that range from 5000 to some millions, is the concern of polymer chemists. We shall soon see the huge difference this huge difference in mass can make in the properties and applications of low-molecular and macromolecular substances, respectively.

3.   The Unique Behaviour of Polymers.

The high molar mass of a polymer is as a result of its formation by repetitive linkage of a small chemical unit, known as 'monomer'. Two simple examples will suffice:

$$nCH_2=CH_2 \longrightarrow \left[CH_2-CH_2 \right]_n$$

Ethene (a gas)   Polyethene (a high strength solid material)

$$nCH_2=CH \longrightarrow \left[CH_2-CH \right]_n$$

Styrene (a liquid)   Polystyrene (a high strength solid material)

The chemical compositions, that is, the percentages of carbon and hydrogen in ethene and polyethene are exactly the same; thus, it is the size difference that is basically responsible for the change of physical state from gas to solid, with all its ramifications in properties and applications of the two substances. The same goes for styrene and polystyrene, and for any monomer-polymer pair.

Thus, polymers exhibit unique chemical, mechanical, thermal, electrical and optical characteristics as a consequence of their high molar masses. For instance, while a liquid exhibits viscous response to stress or deformational force, a solid (e.g. a steel spring) shows elastic response. A polymer shows both viscous and elastic behaviour, and it is said to be viscoelastic. Some specific examples of UH.S unique behaviour of polymers

include: silly putty *(a* silicone polymer) can bounce like a ball when rolled into a ball and dropped; (he same ball if placed on a table over a long period of time will gradually spread like a viscous liquid; a rubber band carrying a weight contracts on careful heating (thermal *contraction* instead of thermal *expansion* typical of non-polymeric solids); when a rotating rod is immersed in a molten polymer or a fairly concentrated polymer solution, the liquid will climb up. A non-polymeric liquid will develop a parabolic surface profile with the lowest point at the rod.

4.   Polymers - The Ubiquitous Modern Materials

Polymers or **macromolecules** can be classified on the basis of derivation as *natural* (or biological) and *synthetic* (or man-made). Natural polymers include proteins, carbohydrates, starch, silk, wool, cotton, natural rubber, etc. Examples of synthetic polymers are: polyethene, polystyrene, poly(vinyl chloride), PVC, polyesters, polyamides, polyurethanes, etc. Biological polymers form the very foundation of life and intelligence and constitute the bulk of the food we consume and some of the clothes we wear. Synthetic polymers have become the indispensable modern materials, and have replaced in part or in whole, such traditional materials as wood, metal, ceramics, and glass, in many areas of application. This is because polymers possess the thermal conductivity of wood, the hardness of steel, the lightness of aluminium, the optical clarity of glass, the rust resistance of ceramics and the electrical resistance of mica.

The common man encounters polymers as plastics, rubbers and fibres. In these three forms, polymers feature in myriads of industries such as automobile industry, electrical and electronic industry, optics industry, robotics industry, building industry, information and communication industry, aeronautics industry, food and drug industry, water treatment industry, clothing and textile industry, foam industry, paper and pulp industry, packaging industry, oil exploration industry, adhesives industry, paint industry, agricultural industry, etc. In some of these industries, the presence/role of the polymer is often not known to the non-expert. For instance, a typical paint formulation contains three major components, namely, the solvent (to enable application of the paint), the pigment (to provide beauty and opacity) and the polymeric film former (to protect the substrate from hostile environments). The all weather (multi-viscosity) engine oil contains a polymer additive that maintains the viscosity of the oil at high operating temperatures.

Polymers, apart from being able to do what metals, wood, ceramics and glass can do, they are easily and cheaply processed into products, because less heat is required to melt them; hence an individual can establish and run a plastic plant, while a whole nation like Nigeria has been trying to establish a functional iron and steel plant and at a very huge cost because enormous amount of heat is required to melt iron or steel. The generally low melting nature of polymers limits their application to temperatures below the temperature of boiling water (100 °C). However, some specialty polymers, such as silica-fibre-reinforced phenolic polymers are used in nose cones of missiles to protect the inside of the missile from temperatures as high as 2,800 °C for a few seconds, because of their low thermal conductivity and resistance to thermal shock. Again, on a

general note, polymers are inferior to iron and steel in mechanical strength; however, some novel polymer composites, such as polyepoxies reinforced with graphite, surpass steel in mechanical properties, hence they are used in some structural parts of an aircraft to reduce weight.

The foregoing highlights on the unique properties and the unlimited applications of polymers are designed to serve as a 'sweetner' to the actual 'academic meal' we are about to have as I go into the aspects of polymer studies that first caught my fancy and engaged my efforts in the seventies.

5. Fundamental Studies in Polymers: Our General Objectives

5.1 Molecular Structure Effects

The study of molecular structure effects is of fundamental importance in chemistry. This is because (he structure of a molecule, which has to do with how (he component atoms or groups of atoms are linked to each other (chain isomcrism) or arranged in space (stereoisomerism) can have significant effects on the physical and chemical behaviour of a compound. Such effects are usually much more dramatic in polymeric systems. For instance, polypropylene (PP) can be made in three main structural forms (each having the same average molar mass):

Isotactic PP
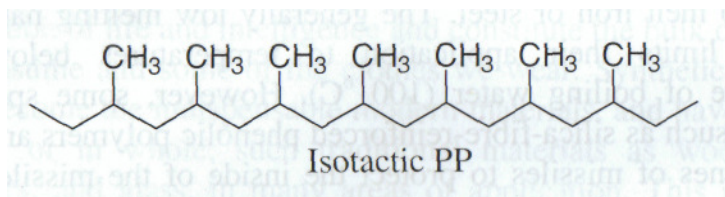
The pendant methyl group (-CH_3) is located on one side of the carbon-carbon backbone. This gives rise to a highly crystalline (ordered) solid material with high tensile (mechanical) strength.

Sydiotactic PP
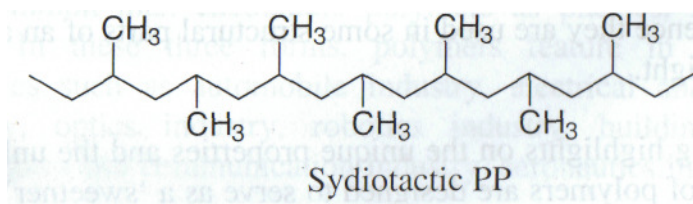
The methyl groups are located alternately in the C-C backbone. This material is also crystalline and with good mechanical strength, but to a lesser degree than the isolaclic isomer.

6. Photophysical Processes in Polymers: Excimer and Exciplex Interactions.

6.1 Photophysical Processes

A molecule can absorb a quantum of light (hv) to transit from a singlet ground state to a singlet or triplet excited state. If the excited electron has a spin antiparallel to that of its mate, the excited state is a *singlet;* but if the spin of the excited electron is parallel to that of its mate, the state is a *triplet.* The energy of an exciled molecule can be dissipated by tour general processes, namely, non-radiative transition (no emission of lighl), radiative transition (emission of light), transfer of absorbed energy to another entity and outright chemical reaction(s) involving the excited molecule. The first three processes are physical in nature (hence they are called*photophysical* processes) since the excited molecule returns to the ground state without losing its nature. In radiative transition, the excited molecule can re-emit a quantum of light to give rise to fluorescence or phosphorescence. The former involves transition from an excited singlet state to a singlet ground state, while the latter involves transition from a triplet excited state to a singlet ground state. Fluorescence is a short-lived emission, while phosphorescence is a long-lived emission.

6.2   Excimers and Exciplexes

Excimers and Exciplexes are 'transient atomic or molecular complexes with associated excited electronic states, dissociative ground state and structureless emission spectra'. Their formation is illustrated in Fig. 1 [1].
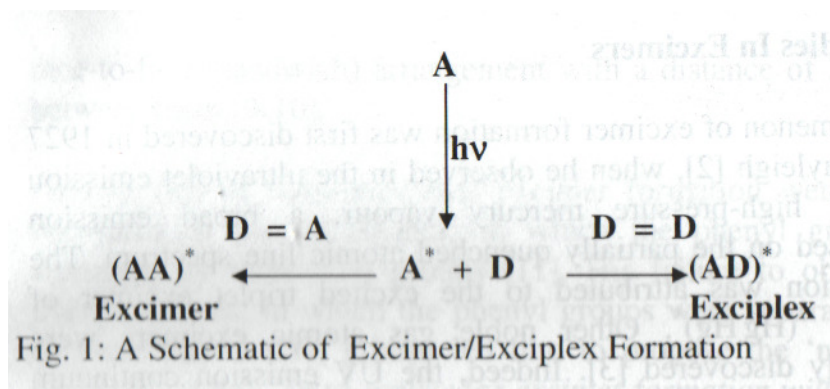

Atactic PP
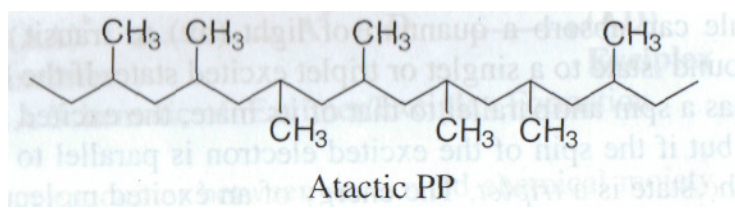
The methyl groups are located randomly (no order) in the C-C backbone. This material is completely amorphous (no order). It is a soft and tacky material, with no mechanical strength. Thus, for a given polymer type, with the same average molar mass, its structure significantly determines its behaviour and hence its ultimate application. Fslablishment of such effects represents one of the general objectives of our research efforts.

5.2   **Molecular Interaction Effects**

On a similar note, intra- and inter-molecular interactions give rise to chemical reactions and/or affect the physical state of matter, including such physical properties as the viscosity and boiling point of a liquid or solution. The high molar of a polymer which in turn gives rise to enormous intra- and inter-molecular interactions render a polymer liquid non-volatile, and therefore incapable of boiling. Instead, the polymer liquid will degrade rather than boil. Consequently, polymer molecules do not exist in the gaseous state. Indeed, changes in physical properties of polymeric systems as a result of intra-

and inter-molecular interactions can be phenomenal. Again, establishment of such effects forms part of the general objectives of our research efforts.

$$A$$
$$\Big\downarrow h\nu$$

$$(AA)^* \xleftarrow{\;\;D\,=\,A\;\;} A^* + D \xrightarrow{\;\;D\,=\,D\;\;} (AD)^*$$

Excimer   Exciplex

Fig. 1: A Schematic of Excimer/Exciplex Formation

Thus, an encounter between an excited chemical moiety, A and an identical or different ground state species leads to an excimer or exciplex, respectively. The emission characteristics of the excited molecule (or monomer) and that of its excited complex (excimer) are shown in Fig. 2. The excimer emission, $h\nu_e$ is structureless because its ground state is repulsive (dissociative) while the monomer emission, $h\nu_m$ is structured because of electronic transitions to various vibrational levels.
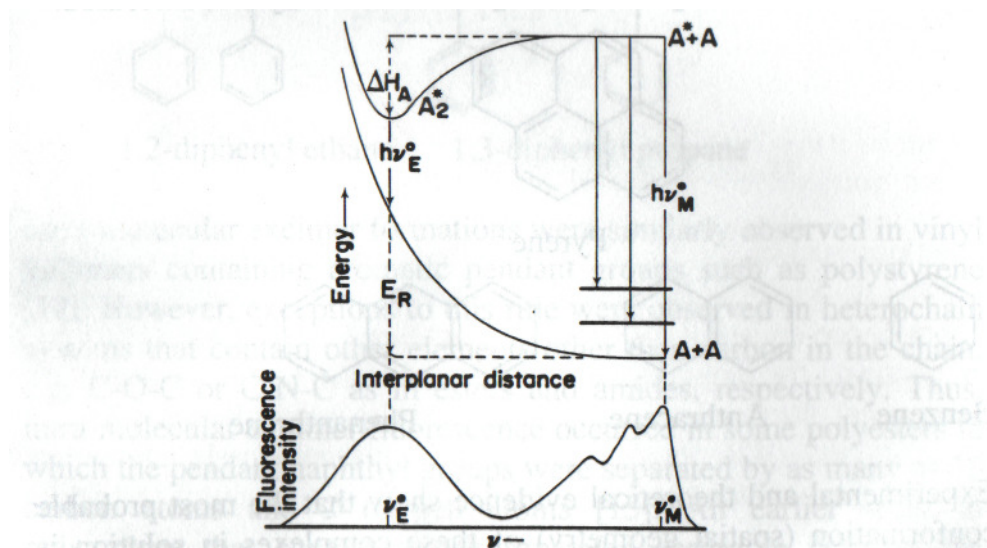

Fig 2. Emission Characteristics of An Excited Chemical Entity and Its Excited Complex (Excimer)

6.3 Studies In Excimers

The phenomenon of excimer formation was first discovered in 1927 by Lord Rayleigh [2], when he observed in the ultraviolet emission spectra of high-pressure mercury vapour, a broad emission superimposed on the partially quenched atomic line

spectrum. The new emission was attributed to the excited triplet excimer of mercury - (Hg Hg)[5]. Other noble gas atomic excimers were subsequently discovered [3]. Indeed, the UV emission continuum from a high-pressure Xenon (Xe) lamp (a widely used light source in optical spectroscopy) originates from xenon excimer (Xe.Xe)*.

Subsequently, **inter-molecular excimers** were observed in condensed phases of many aromatic compounds such as pyrene |4,5j, benzene, naphthalene *[6,1]* and anthracene, phenanthrene [8J. In each case, excimer emission appeared as a broad-structureless band at lower energy than the quenched molecular fluorescence as the concentration of the solution of the aromatic moiety was increased.

Pyrene

Benzene **Anthracene** **Phenanthrene**
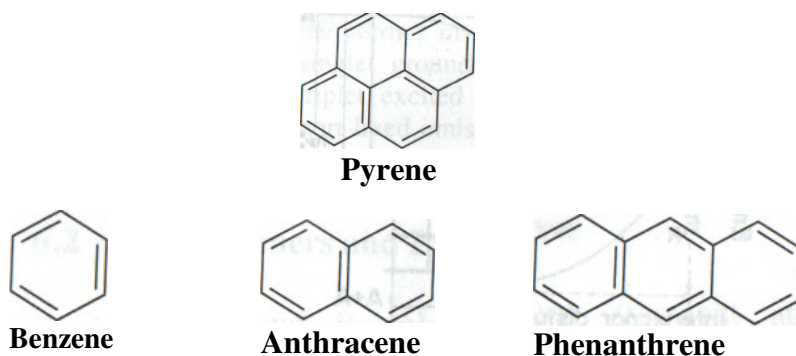
Experimental and theoretical evidence show that the most probable conformation (spatial geometry) of these complexes in solution is one in which the two aromatic components are in parallel-stacked face-to-face (sandwich) arrangement with a distance of 2.5 - 3.5 A between them [9-10].

First reports of intra-molecular excimer formation were made by Hirayama in phcnyl alkancs, in which the phenyl groups were separated by I hive CM. groups 11 11. His failure to observe it in phenyl alkanes, in which the phenyl groups were separated by less or more than 3 Clh groups led him lo propose the 'n = 3' rule, which states that *"intm-molccular cxcimcr formation will occur only when the aromatic chromophores are separated by a chain of three carbon atoms'.* This geometry optimizes the attainment of the required 'sandwich' configuration for excimeric interaction. However, this configuration is not attainable for n = 1 and n = 2 without deforming the tetrahedral bond angle of the alkane chain, while for n > 3, conformational instability due to steric interaction makes the sandwich configuration difficult to reach.

1,2-diphenyl ethane   1,3-diphenyl propane
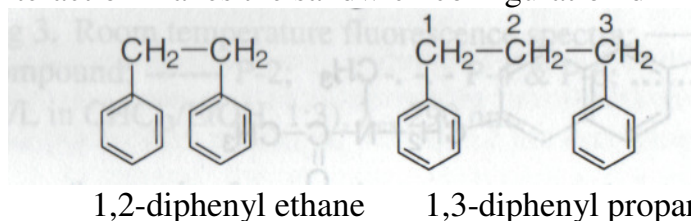
Intra-molecular excimer formations were similarly observed in vinyl polymers containing aromatic pendant groups such as polystyrene [12]. However, exceptions to this rule were observed in heterochain systems that contain other elements other than carbon in the

chain, e.g. C-O-C or C-N-C as in esters and amides, respectively. Thus, intra-molecular excimer fluorescence occurred in some polyesters in which the pendant naphthyl groups were separated by as many as 16 carbon atoms and 2 oxygen atoms [13]. An earlier work in poly amides that contain widely-separated carbazole units in the backbone showed no intra-molecular excimer formation [14], apparently because of the short-lived nature of the carbazole monomer fluorescence

That prompted us to use a different aromatic moiety (naphthalene) in preparing a series of polyamides to explore the possibility of intramolecular excimer formation between widely-separated naphthyl units as shown in the structure below[15].

| x	Polyme
2	P-2
4	P-4
6	P-6
8	P-8
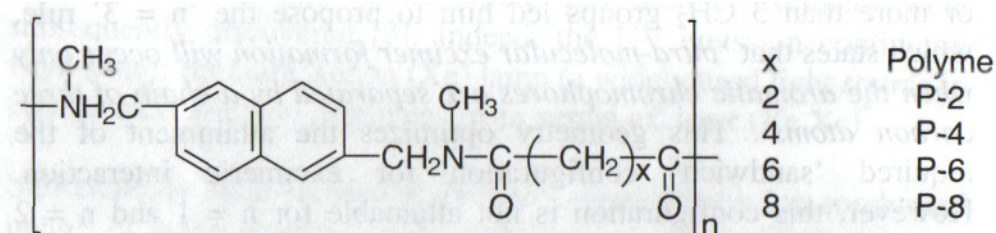
A Polyamide Series with Naphthalene Moiety in the Backbone
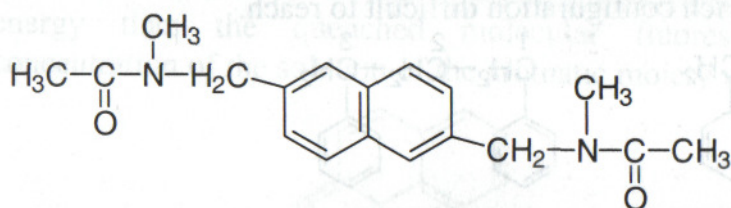
Model Compound (MC)

The fluorescence spectra of MC and the polyamides (P-2 to P-8) are shown in Fig.3. The model compound shows only a single fluorescence emission due to naphthalene emission at $A_{,max}$ ~355nm. In contrast, the polyamides show in addition to the naphthalene (monomer) fluorescence band at 355 nm, a broad band at longer wave length, ~ 425 nm due to intra-molecular excimeric interaction between the naphthalene moieties.
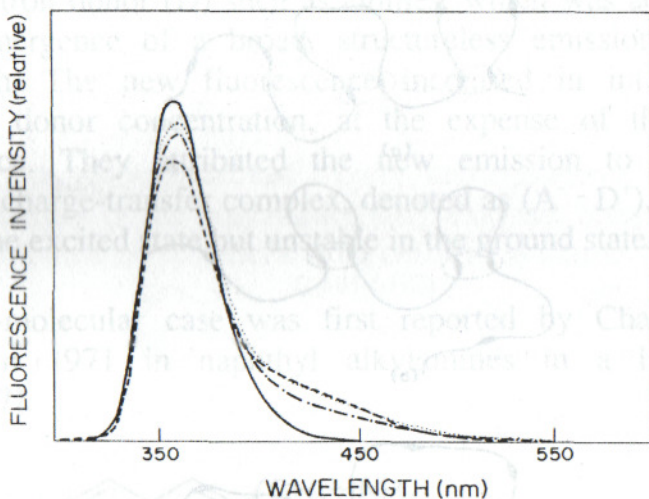
Fig 3. Room temperature fluorescence spectra: -------- model
compound; ....P-2; -. -. -. -. - P-4 & P-6;................P-8 (1 x $10^{"4}$
M/L in CHCb/EtOH, 1:3), X_{ex} 290 nm.

Thus, the result of our study represents another breakdown of the n = 3 rule. Besides, the intensity of the fluorescence emission were found to vary with the distance of separation of the interacting aromatic moieties with maximum intensities shown by P-2 and P-8 (containing 8 and 14 intervening atoms, respectively) and minimum intensities shown by P-4 and P-6 (containing 10 and 12 intervening atoms, respectively). The maxima are attributable to interaction between neighbouring naphthyl goups as illustrated in Fig. 4b while the minima are due to non-neighbouring group interaction, which will be less frequent (Fig 4a). Evidence for the latter interaction was provided by the observed decrease in the fluorescence of P-4 in a good solvent which will tend to expand the polymer chain (Fig 4c), thereby impairing non-neighbouring group interaction.


(a)

(b)

(c)
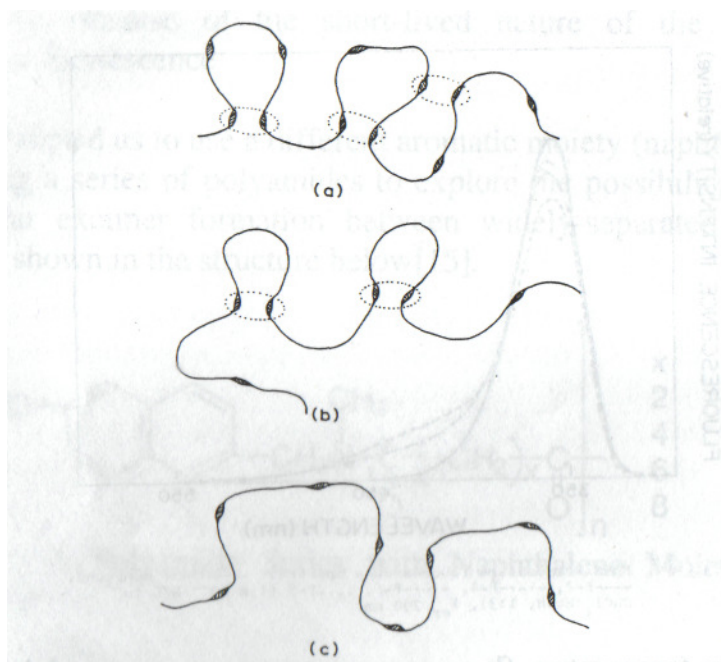
Non-neighbouring and neighbouring group interactions - (a) and (b), respectively. Solvent effect on polymer conformation: compact coil in a poor solvent (a and b), expanded coil in a good solvent (c).

In summary, intra-molccular excimer fluorescence is determined by: the life-time of the fluorescence of the aromatic moiety (the longer the life-time, the better the chances for excimeric interaction) and the length and flexibility of the polymer chain that enable attainment of favourable configuration for the interaction.

6.4   Studies In Exciplexes.

The phenomenon of inter-molecular exciplex fluorescence was first reported in 1963 by Leonhardt and Weller[16] when they observed the quenching of the fluorescence of an excited aromatic moiety (A) by an electron donor (D) such as amines, which was accompanied by the emergence of a broad, structureless emission at longer wavelength. The new fluorescence increased in intensity with increasing donor concentration, at the expense of the acceptor fluorescence. They attributed the new emission to an excited molecular charge-transfer complex, denoted as (A" ~ D$^+$), which was stable in the excited state but unstable in the ground state.

The intra-molecular case was first reported by Chandross and Thomas in 1971 in naphthyl alkylamines in a hydrocarbon medium[17].

$(CH_2)_x NH_2$

x = 1, 2 or 3

Naphthylalkylamines
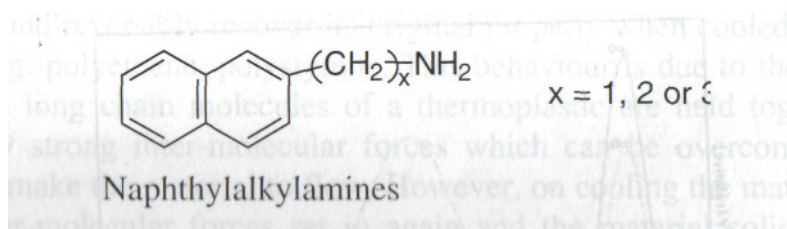
They observed exciplex fluorescence in naphthylethylamine (x = 2) and naphthyl propylamine (x = 3) but not in naphthylmethylamine (n = 1). In general, the geometric requirement for exciplex interaction is not as stringent as in the case of excimer interaction because the former involves a charge transfer interaction which is stronger than the exciton interaction in the latter. However, by taking the fluorescence emission of naphthylmethylamine (NMA) in solvents of different polarity, we discovered remarkable exciplex emissions, the intensity of which showed an initial rise with solvent polarity, followed by a fall at high solvent polarity [18]. The latter was attributed to over stabilization of the exciplex state that led to non-radiative deactivation. We also showed the dramatic effect of N-methylation (i.e. replacement of the amine hydrogen with methyl groups) on the exciplex emission using compounds (I to IV) tailor-made for the purpose [19]. The excimer emission intensities show the following order: IV > III > II (Fig 5). Expectedly, compound I does not show exciplex emission.
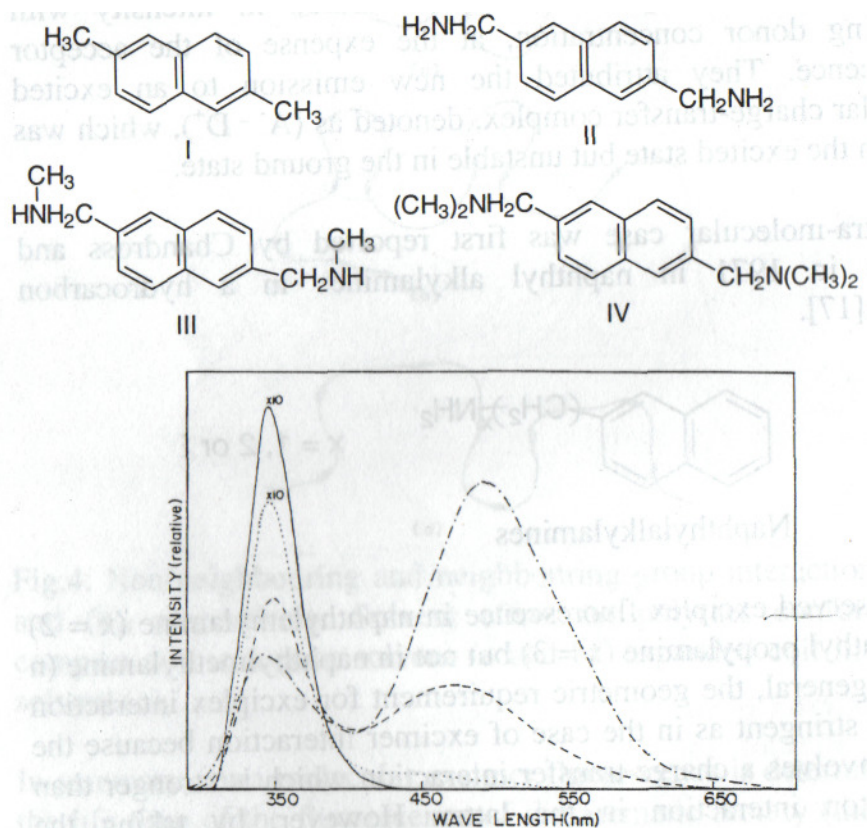
Fig. 5. Enhancement of intra-molecular exciple emission on N-methylation: _____ Cpd I, ... Cpd II; ---------Cpd III, -------- Cpd IV. X_{ex} 290 nm, solvent: ethyl alcohol.

We utilized the specificity of exciplex interaction, involving the formation of a transiently stable and fluorescent complex to study 'polymer effect' on reactivity. The binding of a chemical moiety, such as a reactive group, in a polymer chain, invariably can affect its chemical and physical reactivity. Such effects when contrasted with the behaviour of the moiety in a monomeric carrier is called 'polymer effect'. Using inter-molecular exciplex interaction between triethylamine and the series of polyamides used in the excimer studies, we established the following reactivity order: MC > P -8 > p_6~P-4>P-2, which reflects the relative diffusion rate and accessibility of the naphthalene moiety, and represents the relative chain flexibilities of the polyamides [20]. Polymer effect is utilised in the development of polymeric drug delivery systems.

7.   Studies In Thermoplastic Elastomers

A thermoplastic material is one that can repeatedly soften when heated and reversibly recover its original property when cooled each time, e.g. polyethene, polystyrene. This behaviour is due to the fact that the long chain molecules of a thermoplastic are held together only by strong inter-molecular forces which can be overcome by heat to make the material to flow. However, on cooling the material, the inter-molecular forces set in again and the material solidifies. The process can be repeated over and over again. A thermoplastic material is thus easily transformed into different finished

products.

On the other hand, an elastomer is an amorphous material (no order) in which the molecules are held together by weak inter-molecular forces; consequently, the material when chemically cross-linked can deform extensively and reversibly under stress. However, the hooking up of the molecules by chemical bridges as illustrated in Fig.6, would not permit the material to flow when heated; instead it will degrade, and it is said to be thermosetting (i.e. it is thermally irreversible). This makes the processing of an elastomer or any rubber-like material not as easy as that of a thermoplastic.
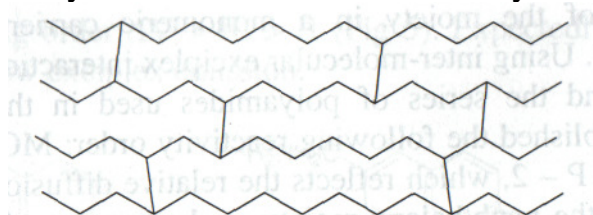
Fig. 6 A Crosslinked Polymer Material

A thermoplastic clastomcric material behaves as a high strength elastomer under service but can be processed as a thermoplastic. It is a copolymer of two monomers, such as butadiene and styrene. Butadiene, if polymerised alone, gives polybutadicne (PB) with rubbery properties; while styrene, if polymerised alone, gives polystyrene (PS) a thermoplastic. But when both are copolymerised to have a PS-PB-PS triblock structure and a composition indicated below, the product will behave as a thermoplastic elastomer (TPE).

PS (10%)   PB (80%)   PS (10%)
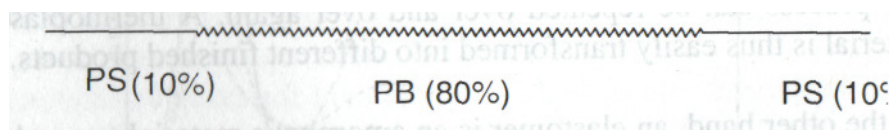
This is due the segregation of similar blocks giving rise to microphase separation and the formation of domains of hard blocks of PS in a matrix of a soft block of PB as shown in Fig.7. The dispersed hard domains then serve, not only as physical cross-links by providing junction points for the elastomeric segments, but also as reinforcing filler [21,22]. During processing, the PTE material will flow when the melting temperature of PS is exceeded and on cooling, the domains/matrix are reformed. TPE materials find extensive use in the shoe industry. It should be noted that a diblock of 20% PS and 80% PB will not behave as a TPE (due to absence of physical cross-links); instead, it will behave as a high impact (non brittle) polystyrene.
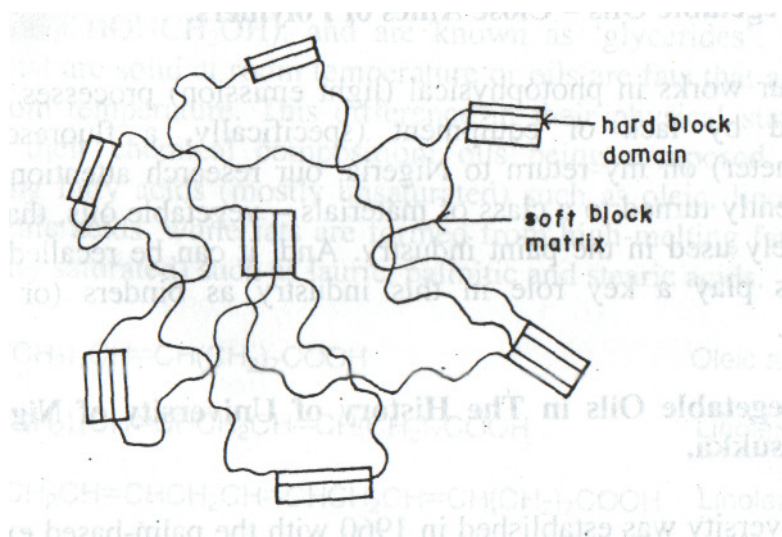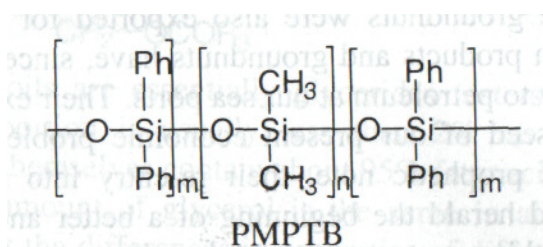
Fg. 7. Domain Morphology in Thermoplastic Elastomers

Our studies in TIM-! involved preparation, characterisation and testing of a polysiloxane: poly(cliphenylsiloxane)-b-poly(dimethylsiloxane)-b poly(diphenylsiloxane), designated PMPTB with the chemical structure shown below [23].

PMPTB

This is a specialty elastomer for use under low and high temperature conditions, under which ordinary rubber would have lost its elasticity. The work was supported by the US Airforce, under a subcontract from Lawerence Livermore Laboratory, California. It thus ended in the United States of America.

8.   Vegetable Oils - Close Allies of Polymers.

When our works in photophysical (light emission) processes were quenched by lack of equipment (specifically, a fluorescence spectrometer) on my return to Nigeria, our research attention was subsequently turned to a class of materials - vegetable oils, that are extensively used in the paint industry. And, it can be recalled that polymers play a key role in this industry as binders (or film formers).

8.1   Vegetable Oils in The History of University of Nigeria, Nsukka.

This University was established in 1960 with the palm-based export earnings of the then Eastern Nigerian Government which instructed its Marketing Board to set aside yearly the sum of £500,000.00 (five hundred thousand pounds) or N 1,000,000.00 (one million naira) from 31st December 1955 to the end of 1964 [24]. The said Marketing Board marketed two products - palm oil and palm kernels, the latter
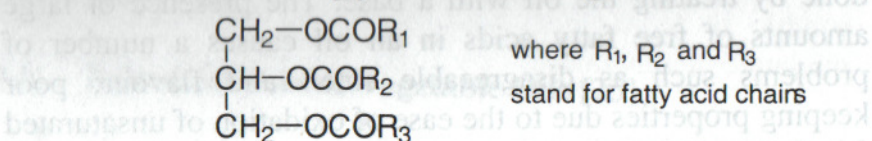
for its oil, which was then extracted overseas. At this time also, there was the groundnut pyramid in the Northern part of the country. The groundnuts were also exported for their oils. Both exports - palm products and groundnuts have, since the early seventies, given way to petroleum at our sea ports. Their exit marked the sewing of the seed of our present economic problems. On a reverse, and indeed prophetic note, their re-entry into the world export market would herald the beginning of a better and brighter economic future for this country.

8.2 Chemistry of Vegetable Oils [25].

Vegetable oils are water-insoluble substances of plant origin which consist predominantly of long-chain fatty acid esters of glycerol ($HOCH_2CHOHCH_2OH$), and are known as 'glycerides'. Fats are oils that are solid at room temperature or oils are fats that are liquid at room temperature. This difference in their physical state arises from their chemical composition: oils being composed of low-melting fatty acids (mostly unsaturated) such as oleic, linoleic and linolenic acids, while fats are formed from high-melting fatty acids (mostly saturated) such as lauric, palmitic and stearic acids.

$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$ Oleic acid

$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$ Linoleic acid

$CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7COOH$ Linolenic acid

$CH_3(CH_2)_{10}COOH$ $CH_3(CH_2)_{14}COOH$ $CH_3(CH_2)_{16}COOH$

Lauric acid   Palmitic Acid   Stearic acid

An oil molecule is a triglyceride with the general structure:

$$CH_2-OCOR_1$$
$$CH-OCOR_2$$
$$CH_2-OCOR_3$$

where R_1, R_2 and R_3 stand for fatty acid chains

Vegetable oils are essentially glycerides (esters of glycerol). The non-ester portion is usually less than 2% of the total oil. The glycerides themselves contain about 95% fatty acid and 5% glycerol. Since the amount of glycerol is the same in all vegetable oils, it follows that the differences in properties of different oils are largely determined by the variations in the fatty acid structure. The minor (non-ester) components of fats and oils include: phospholipids (or phosphatides), sterols, vitamins and their precursors, antioxidants, pigments, free fatty acids and some impurities. These components affect the colour, odour and other qualities of the oil.

Extraction of oil from oil-bearing seeds is generally accomplished by two methods, namely, solvent extraction and mechanical expression. Solvent extraction has the advantage of giving higher oil yields than mechanical expression. However, the choice of solvent is critical because of problems associated with solvent toxicity, flammability

and recovery. The press method is generally more economical, yields better values for oil constants, and requires less equipment, space and time. In industry, a combination of both mechanical expression and solvent extraction is most commonly used.

Fats and oils undergo a number of purification (or refining) processes in order to remove the non-ester (minor) components. Notable among these processes are:

Degumming (to remove some natural gums and phosphatides). This is accomplished by blowing steam into the oil at about 100°C.

- ***Deacidificatipn*** (to remove free fatty acids in the oil). This is done by treating the oil with a base. The presence of large amounts of free fatty acids in an oil causes a number of problems such as disagreeable smell and flavour; poor keeping properties due to the ease of oxidation of unsaturated free fatty acids, etc.

- *Decolorisation* or bleaching (to remove colouring matter in the oil). This usually involves the use of bleaching earth such as fuller's earth and active carbons. Some locally available clays have been found effective [26]. Some saturated oils such as palm oil can be bleached by blowing air into the oil at an elevated temperature.

- *Deodorisation* (to remove odiferous substances and substances with peculiar tastes). This is effected by steaming.

The quality and purity of oils are assessed by determining a number of physical and chemical constants. The physical constants include: melting point, specific gravity, refractive index, viscosity, colour, solubility, etc. The chemical constants are: acid number, iodine value, saponification value, volatile Tally acid content, etc. Of particular interest to us is iodine number, which is a measure of the degree of unsaturation of an oil. It is defined as the *milligrams of iodine absorbed per gram of sample.* The greater the total unsaturation, the higher, in general, is the iodine value. Iodine value determination is important because depending on its value, oils can be classified into *drying, semi-drying and non-drying.* The ability of an oil to be converted into a solid film in the presence of oxygen is known as 'drying'. Drying oils such as linseed, rubber, tung, have iodine values between 150 to 200; these dry to form hard tack-free films and heat polymerize rapidly. Semi-drying oils such as soyabcan, melon, mai/e, sunflower have iodine values between 100 lo 150; Ihc oils in this class form lacky films on drying. Non-drying oils Midi as caslor, olive, palm oil and palm kernel have iodine values below 100.

8.3   Industrial Uses of Vegetable Oils [25]

Vegetable oils have been known and used by man from pre-historic times. Indeed, apart from water, there is no liquid chemical that the common man is more familiar with its uses in the home than vegetable oils. Vegetable oils constitute a major class of agricultural products, with enormous domestic and industrial uses. Their supply is

renewable and hence reliable. Vegetable oils find extensive uses in the following industries:

- Food industry. Vegetable oils and fats, together with carbohydrates and proteins, constitute the three main kinds of foodstuff. Large amounts of fat are consumed in the human diet, and they are the most concentrated source of energy in the diet, yielding 9.3 kcal per gram as compared to 4.1 kcal per gram of protein and carbohydrates. Vegetable oils are important sources of oil-soluble vitamins and of certain essential fatty acids. The edible fat industry is the principal consumer of vegetable oils and fats. Edible fats may be divided into liquid products such as cooking and salad oils and solid materials like margarine, shortenings and confectioneries.

Soap and Detergent Industry. Soaps arc the metal salts of the higher saturated and unsaturated fatty acids obtained by **saponification** or hydrolysis of fats and oils. Fats containing a high percentage of lauric and myristic acids give soaps that are readily soluble in cold water and with good foaming properties. Soaps made from soft fats or oils such as soybean, cotton seed and corn oils, that contain a high percentage of unsaturated acids, are quite soluble in tepid water and are useful for cleaning at moderate temperatures required for washing delicate surfaces and fibres. Fats such as palm oil that contain a high percentage of long-chain saturated acids are useful for detergent operations at elevated temperatures of 60 -85 °C. As a general rule, mixtures of different fats are used rather than a single fat, so as to impart optimum properties to the soap for every specific use.

- Lubricating Industry. Appreciable amounts of fats, fatty acids and substances derived from them are used as lubricants, either alone or more often compounded with mineral oils. Even though mineral oils (from petroleum) are now mostly used as lubricating oils because of their lower cost and greater stability, fatty oils and their derivatives are still used as additives to mineral oils because of their 'oiliness' property (that is, ability of a lubricant to form a tenacious film on metal surfaces). Oiliness is important where rubbing surfaces have small clearance from which the oil may be squeezed out by excessive pressure as on automobile and airplane pistons.

Vegetable oils, as well as mineral oils are used as lubricants for fibres; the former are preferred because of ease and complete removal by saponification. Water repellency in textiles and paper are achieved with zinc, calcium and aluminium stearates (esters of stearic acid). In the leather industry, oils serve primarily as lubricants for trie internal surfaces of fibres.

Lubricating greases are colloidal solutions of soap and other surface-active compounds in mineral oils. The percentage of soap may be as low as 0.25% in textile lubricants or as high as 60% in some rail road greases. Sodium, calcium, aluminium, barium and lead soaps or mixtures of these, are generally used.

Cosmetics Industry. A cosmetic is any substance, preparation or treatment applied by a person to cleanse, alter the appearance or promote the attractiveness of

the person. Oils feature in cosmetics in form of creams (which may be oil in water or water in oil emulsions) and lipsticks which are fatty base products that contain dissolved or suspended colour materials. A highly refined grade of castor oil is one of the most common ingredients of a lipstick.

- *Pharmaceutical Industry.* Fatty oils and waxes, as well as glycerine, are widely used in the preparation of Pharmaceuticals, in the compounding of liniments, ointments (skin blemishes) and demulcents (protection of mucous membrane). The preparations made from them generally have protective softening and lubricating effects. The soap stock from alkali-refining of fats and oils serves as a commercial source of sterols for the manufacture of Pharmaceuticals.

Rubber and Plastic Industries. Vegetable and petroleum oils are added to rubber compounds as softeners to facilitate the addition and dispersion of the other solid compounding ingredients as well as enhance the processing properties for extrusion, calendaring, etc. Tack (stickiness) is another property achieved by adding softeners and it is essential for many applications, such as tyre building. Oil products are used as plasticisers for plastics to render them plastic or flexible during processing.

> *Coatings Industry.* Coatings include paints, varnishes, and printing inks. All three contain three main components as noted earlier, namely, the binder (a liquid polymer or polymer precursor) to form the surface film, the pigment to provide colour and opacity and solvent to enable application. Polymer film formers can be classified into two: 'thermoplastic' and 'convertible' film formers. Thermoplastic film formers, as found in spirit varnishes and emulsion paints, are high molar mass polymers whose molecules simply come together to form the film structure following the departure of the solvent. On the contrary, convertible film formers, as found in oil varnishes and oil paints undergo a chemical reaction to form the cross-linked solid film in the presence of such agents as oxygen, heat/catalyst or curing agent. For instance, oxygen can cause drying- or semi-drying oils, that contain large proportions of unsaturated fatty acids, to harden and form a polymeric film by linking up the oil molecules through their double bonds. Consequently, oils that are rich in linoleic and linolenic acids, such as linseed and soyalu-an oils are major raw materials in the coatings industry.

It is evident from the foregoing that vegetable oils as common as they are, have many uncommon uses which the underemployed 01 the unemployed can take advantage of, to be self-employed. This also underscores our focus on them in our research for some years now.

9.   Studies in Vegetable Oils

For over Iwo decades now, we have carried out fundamental studies on SOUK- locally available vegetable oils, namely, rubber *[Hevca* />mv///<'//.v/,Y(Kimlli) Muell. Arg.|,

melon *Colocynthis vulgaris* Sdiiad l.l, soyabcan \(*il\cinc max* (L.) Merr], fluted pumpkin *iclfuina occidcntalis* Hook f.J and oilbean *[Pentaclethni macrophylla* BenthJ with the general objective to potentialise their use in the coatings industry so as to replace the popular but imported oil of linseed *[Linum usitatissimum* L.]. We have examined their extractability with solvents at different temperatures, their bleachability under different conditions, their dilute solution viscosity behaviour, their autoxidative properties, their performance as components of paint driers, their dimerisability and potential in the preparation of thixotropic paint binders. What follows is a review of the key results of these fundamental cum applied studies.

9.1   Vegetable Oil Extraction Studies [27,28]

Oils were extracted from the seeds of melon, rubber, fluted pumpkin and oilbean at different temperatures using solvents of different dielectric constants (or polarities), namely, petroleum benzene (b.pt 60 - 80 °C), cyclohexane, isopropyl ether, ethyl acetate, tetrahydrofuran, propan-2-ol and acetone. The oil yields of each seed in different solvents ranged as follows: 58.0 - 64.4% (pumpkin), 56.1 - 59.1% (melon), 40.6 - 48.8% (rubber) and 35.4 - 43.3% (oilbean). These figures are based on the mass of the shelled dry seed.

It was observed that for a given seed, solvents of dielectric constant of between 6 and 8 gave higher oil yields than those of either lower or higher dielectric constant. This was attributed to the amphipathic nature of the triglycerides which have both polar and non-polar components. In non -polar solvents (low dielectric constant) solubility will be impaired by the polar ester component of the triglyceride; while in polar solvents, solubility will be adversely affected by the non-polar groups (the fatty acid chains) of the triglycerides. Thus, both cyclohexane and acetone in general exhibited lower oil yields than solvents of intermediate polarity.

Also, the equilibrium extracting capacity of each solvent was found to depend on the nature of the oil. For instance, while ethyl acetate and tetrahydrofuran gave the highest oil yields in rubber, their oil yields in melon were next to the lowest. This oil effect was attributed to differences in the drying nature of the oils as related to the varying levels of unsaturated fatty acid chains.

On temperature effects, oil yield increased with temperature, reaching its maximum value at the boiling point of the solvent. This trend was as a result of increased ease of penetration of the meal matrix by the energised solvent molecules. However, low boiling solvents such as dichloromethane and acetone gave oil yields that were comparable to those of high boiling solvents. This is of industrial importance where energy costs in both the extraction and solvent recovery process must be considered. Also, the use of low boiling solvents minimised the degradation of the oil extract, but at the same time maximised solvent losses. Theoretical oil yields were calculated with the expression:

$$Y_T = Y_s n^{(T-T_s)/10}$$

where Y_T is the oil yield at the required temperature T; Y_s is the oil yield at a known temperature T_s and n is the temperature coefficient with values between 1.02 to 1.10. There was agreement between the observed and calculated oil yields showing the usefulness of our expression for predicting oil yield.

The enthalpy changes in the extraction of rubber and melon seed oils were also determined with values in the range of 4 - 13.5 kJ.mol"[1], indicating the physical nature of the oil extraction process.

9.2   Vegetable Oil Bleaching Studies

Studies on bleaching of vegetable oils with activated clays and charcoal have been shown to be dependent on such factors as the nature of the oil (including type of colouring matter and level of unsaturation), type and quantity of bleaching agent, temperature and time of contact between the oil and the bleaching agent [29,30]. Our aim was to show how some of these factors affected the bleaching of the oils of rubber seed (RS), melon seed (MS) and oilbean seed (OBS). Fuller's earth (FE), activated charcoal (AC) and a mixture of the two (FE/AC) were used. Bleaching was carried out at 80°C (established optimum temperature) and for 40 minutes (also established optimum time). Values of degrees of bleaching monitored by UV/visible absorption measurements showed FE as the most effective bleaching agent for the three oils, followed by FE/AC; on the other hand, oil retention (oil loss) was least with AC, followed by FE. OBS was the most bleached with optimum degree of bleaching in the range of 82 - 93%, while the oils of RS and MS gave comparable bleaching responses which ranged from 43% (using AC) to 88% (using FE). Degrees of bleaching close to the optimum but with considerable reduction in oil loss were achieved by using 75% of optimum amounts of FE/AC and AC for the three oils, and 50% and 17% of the optimum amount of FE for the oils of MS and OBS, respectively [31].

Variation of temperature of bleaching was done, not only to establish the optimum temperature for each oil/bleaching agent system, but also to establish whether the colouring matter was removed by physical adsorption or by chemical adsorption to the bleaching agent. The three oils showed varying optimum bleaching responses in the temperature range of 60 - 105°C, depending on the bleaching agent used. Also, their adsorption enthalpies and activation energies varied but were all under 10 kcal.mor[1], indicating that physical adsorption predominated over chemical adsorption in the bleaching of these oils; the latter usually involves energies of adsorption in the range of 10 -100 **kcaiapl[1].** [32].

9.3   Dilute Viscosity Behaviour of Vegetable Oils

In dilute (low concentration) solution, a polymer molecule is less entangled with its neighbours, so that at infinite dilution (obtainable by extrapolation to zero concentration) the contribution of the individual polymer molecule to the viscosity of the solution can be obtained; this viscosity value is known as the *intrinsic* viscosity of the polymer, and it is a direct measure of its hydrodynamic volume or size in solution. Thus, any significant changes in the size of a polymer molecule is known to cause

dramatic changes in its intrinsic viscosity. It is for this reason that we used intrinsic viscosi measurement to monitor the drying, that is, the conversion of the liquid vegetable oil to a solid film as a result of oxygen-induced cross-linking reaction, with the view to gain insight into the mode-network formation prior to the gel point. The oils of linseed, rubber soybean and melon were used in this study[34].

Intrinsic viscosity values obtained showed a rise-and-fall pattern which   was attributed   to   inter-molecular   cross-linking or polymerization that led to increase in molecular mass and mass. (Fig.8) and intra-molecular cross-linking which led to decrease-size and no change in the molecular mass (Fig 9).
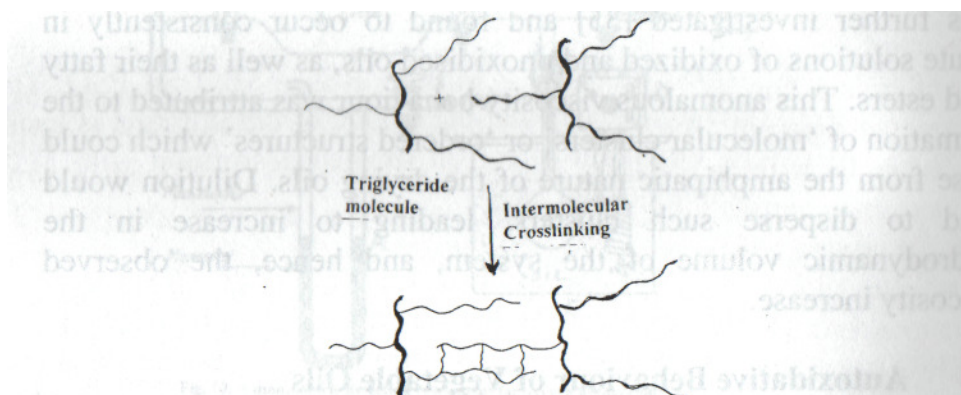
Fig.8 Schematic of network formation in drying oils via inte molecular cross-linking reaction.
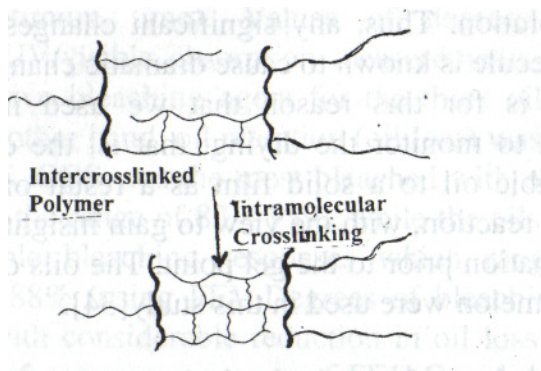
Fig. 9 Schematic of network formation in drying oils via intramolecular cross-linking reaction.

We also observed a steep rise in the reduced viscosity values with dilution, contrary to the expected fall. This anomalous behaviour was further investigated [35] and found to occur consistently in dilute solutions of oxidized and unoxidised oils, as well as their fatty acid esters. This anomalous viscosity behaviour was attributed to the formation of 'molecular clusters' or 'ordered structures' which could arise from the amphipatic nature of the drying oils. Dilution would tend to disperse such clusters, leading to increase in the hydrodynamic volume of the system, and hence, the observed viscosity

increase.

9.4   Autoxidative Behaviour of Vegetable Oils

As noted earlier, unsaturated vegetable oils tend to dry or harden to form a solid film in the presence of oxygen. This is a polymerization reaction involving the oil molecule and forms the basis for their use in convertible coatings. We thus carried out this oxygen-induced polymerization of the oils of linseed, rubber, soyabean, melon and pumpkin seeds to examine the effects of time and temperature on the reaction [36]. A manometric equipment was used to monitor the amount of oxygen consumed in the reaction at temperatures that 'ranged from 30 - 90°C (Fig. 10). This equipment was designed in our laboratory and fabricated by our 'master' Glass Blower, Mr. F.U. Ekezie, of blessed memory. The essential features of the equipment are: a manometer (A), a 3-litre oxygen reservoir (B), reaction flask (C), a thermometer/thermoheater unit (D) and a thermally-lagged bath (E) and control stopcocks numbered 1 to 4.

Oxygen absorption was generally found to be maximum at the 5th hour of reaction. Consequently, the 5th-hour O_2 absorption data were plotted against temperature for each oil as shown in Fig. 11, from which it can be seen that each oil exhibited maximum oxygen absorption at 60°C, followed by a fall and a comparable response at 75 and 90°C.
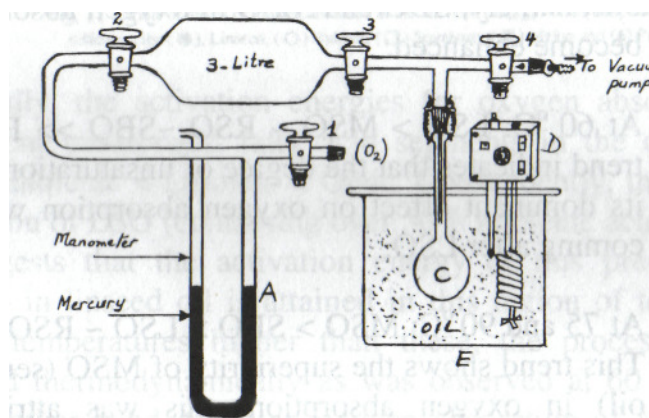
Fig. 10. A manometric detection equipment for oxygen absorption

The observed rise in oxygen absorption with temperature was attributed to increasing number of activated molecules; this number appeared optimized at 60°C. The fall in oxygen absorption observed beyond the optimum temperature was attributed to significant occurrence of the reverse reaction (i.e. oxygen de-absorption) which the reacting oil system might undergo to eliminate the excess heat input at its state of equilibrium (the forward reaction being exothermic).

Significant differences in the oxygen absorption of the oils are also evident from Fig. 11. The graphs show the following order, depending on the temperature region:

1. At 30°C: LSO = RSO > SBO » MSO > PSO. This order is keeping with the degree of unsaturation of the oils.

2. At 45°C: LSO > RSO > SBO » MSO > PSO. This order shows that the performance of the semi-drying oils, namely, SBO and MSO in oxygen absorption has become enhanced.

3. At 60 °C: LSO > MSO ~ RSO -SBO » PSO. This trend indicates that the degree of unsaturation is losing its dominant effect on oxygen absorption with MSO coming after LSO.

4. At 75 and 90 °C: MSO > SBO > LSO ~ RSO » PSO. This trend shows the superiority of MSO (semi-drying oil) in oxygen absorption; this was attributed to possible enhanced activation of the a-methylenic groups for the oxygen attack.
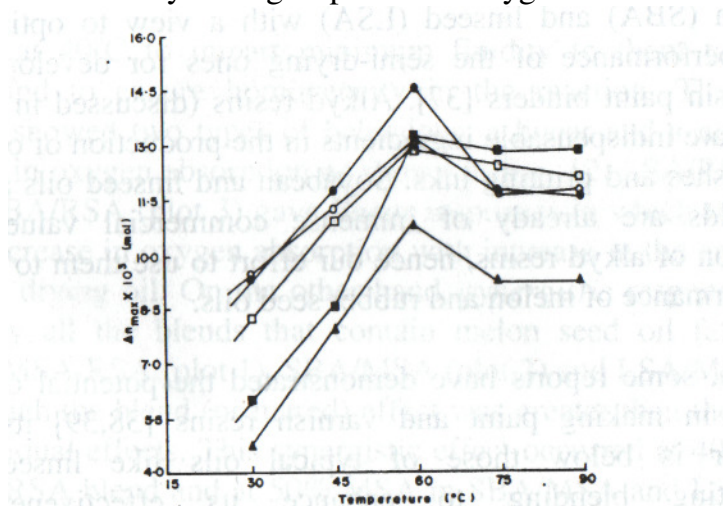
Fig. 11 Plots of moles of oxygen absorbed at the 5th hour (Δn_{max}) versus temperature for different oils: (●), Linseed, (O) Rubber, (□) Soyabean, (■) Melon and (▲) Pumpkin.

Expectedly, the activation energies for oxygen absorption by the constituent unsaturated fatty acid segments in the oils are in the order: Linolenic < Linoleic < Oleic. Consequently, the high oxygen absorption of LSO (containing over 50% linolenic acid) at 30 and 45 °C suggests that the activation energy of this predominant acid segment in linseed oil is attained in this region of temperature, so that at temperatures higher than these, the process will not be favoured thermodynamically as was observed at 60 °C and above. On the other hand, the high oxygen absorption of MSO and SBO (each with over 50% linoleic acid) at 60 °C and above, indicate that the activation energy of this acid segment is reached in the neighbourhood of this temperature. On the whole, these observations indicate that semi-drying oils may prove as useful as drying oils in making oil-modified alkyd resin paint binders that are oven-cured at temperatures above ambient.

Further oxygen-induced polymerisation studies were carried out with blends of fatty acids of rubber seed (RSA), melon seed (MSA), soyabean (SBA) and linseed (LSA) with a view to optimize the drying performance of the semi-drying ones for development of alkyd resin paint binders [37]. Alkyd resins (discussed in the next

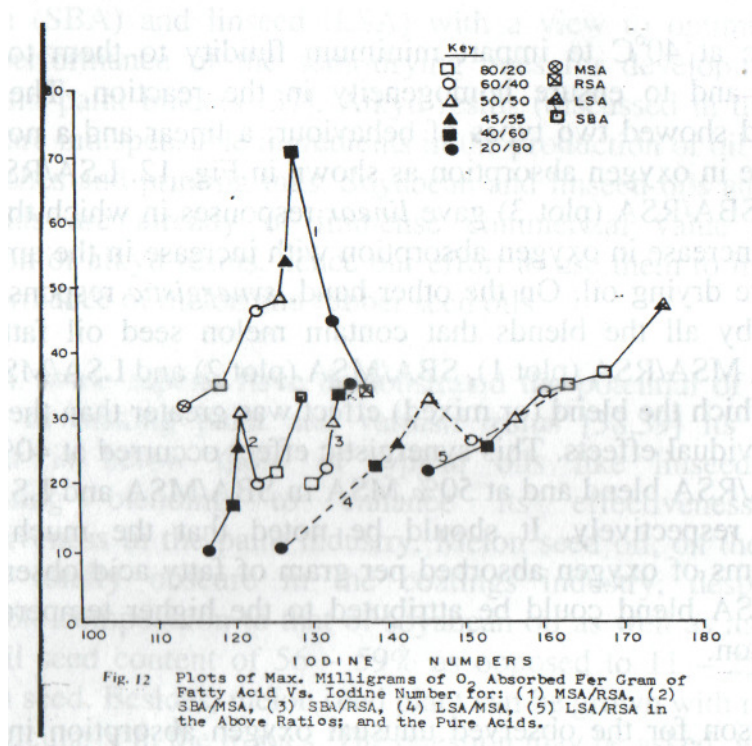section) are indispensable ingredients in the production of oil paints, oil varnishes and printing inks. Soyabean and linseed oils and their fatty acids are already of immense commercial value in the production of alkyd resins, hence our effort to use them to improve the performance of melon and rubber seed oils.

Although, some reports have demonstrated the potential of rubber seed oil in making paint and varnish resins [38,39] its drying behaviour is below those of typical oils like linseed, thus necessitating blending to enhance its effectiveness and competitiveness in the paint industry. Melon seed oil, on the other hand, is totally obscure in the coatings industry, despite its comparable composition to that of soyabean oil as well as its much higher oil seed content of 56 - 59% as opposed to 11 - 25% for soyabean seed. Besides, melon seed plant can be grown with relative ease, particularly in the tropics. The question may be asked: why the scarcely available melon seed as a source of oil for paint making in the country?. This question may be answered with another question: which oil seed or fruit is not currently scarce in the country, including palm fruit? The problem is our near total neglect of agriculture. If we can export cassava now, when a few years ago, we did not have enough of it to make garri for our teaming population, then any time we wake up, we can produce surplus melon seed to meet the domestic and any industrial demand for it. So, in the meantime, our effort to potentialise melon seed oil will go on, in case we wake up in the agricultural sector.

Oxygen absorption measurements with the fatty acids and their blends were done at 30°C for all cases, except for RSA, MSA and MSA/RSA blend, which, because of their semi-solid nature, had to be done at 40°C to impart minimum fluidity to them to enable stirring and to ensure homogeneity in the reaction. The results obtained showed two types of behaviour: a linear and a non-linear response in oxygen absorption as shown in Fig. 12. LSA/RSA (plot 5) and SBA/RSA (plot 3) gave *linear* responses in which there was steady increase in oxygen absorption with increase in the amount of the more drying oil. On the other hand, *synergistic* responses were shown by all the blends that contain melon seed oil fatty acid, namely, MSA/RSA (plot 1). SB A/MS A (plot 2) and LSA/MSA (plot 4), in which the blend (or mixed) effect was greater than the sum of the individual effects. This synergistic effect occurred at 40% MSA in MSA/RSA blend and at 50% MSA in SBA/MSA and LSA/MSA blends, respectively. It should be noted that the much higher milligrams of oxygen absorbed per gram of fatty acid observed for MSA/RSA blend could be attributed to the higher temperature of absorption.

The reason for the observed unusual oxygen absorption in blends involving MSA is not clear. Although, it is invariably and inevitably attributable to its nature and thus composition, it still remains hard to explain bearing in mind that its fatty acid composition is pretty close to that of SBA which does not exhibit the synergistic effect. Thus, this is yet another unique behaviour of melon seed, with its oil showing unusual oxygen absorption at temperatures of 60°C and above, as presented earlier.

Fig. 12 Plots of Max. Milligrams of O_2 Absorbed Per Gram of Fatty Acid Vs. Iodine Number for: (1) MSA/RSA, (2) 3BA/MSA, (3) SBA/RSA, (4) LSA/MSA, (5) LSA/RSA in the Above Ratios; and the Pure Acids.

9.5 New **Alkyd Resin Systems From Blends of Melon and Linseed Oils.**

Alkyd resins are polyesters modified with triglyceride oils or their fatty acids. A reaction between a polyhydric alcohol (e.g. glycerol) and a polyfunctional acid (e.g. phthalic anhydride) would normally give rise to a polyester; but reacting them in the presence of an oil or its fatty acid, the resulting polyester would possess fatty acid segments in its chain as illustrated in Fig. 13.

a trialcohol   a diacid

Oil-modified alkyd resin

$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$
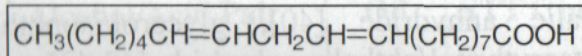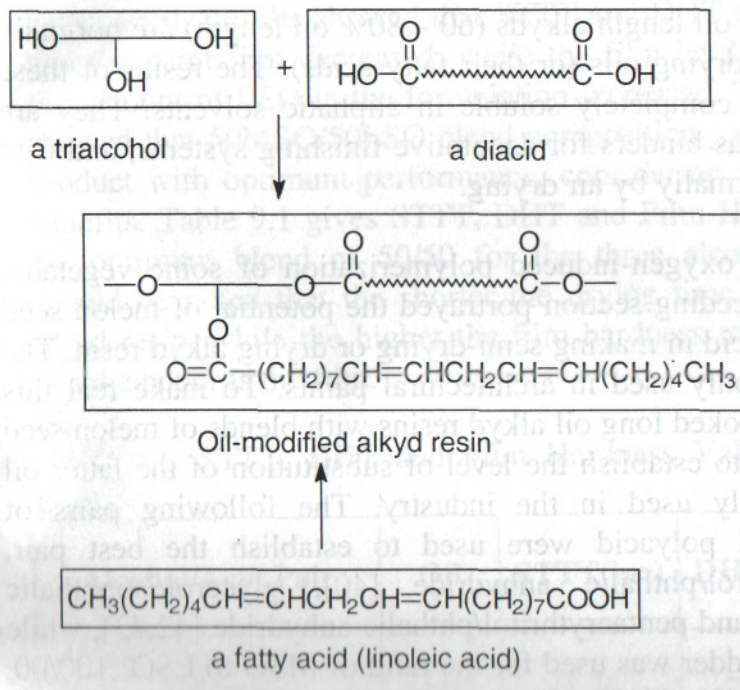
a fatty acid (linoleic acid)

Fig. 13. A schematic for preparation of an oil-modified alkyd resin

Alkyd resins may be classified as drying, semi-drying and non-drying, depending on whether the modifying oil is drying, semi-drying or non-drying. These categories can be subdivided further or the basis of oil length (that is, the amount oil in the alkyd resin) intc short-, medium- and long-oil-length alkyd resins as described under.

Short oil alkyds (contain up to 45% oil length). These are soluble only in aromatic solvents and are cured (i.e. made to form solid film) at high temperatures by baking or stoving.

Medium oil alkyds (45 - 60% oil length) are soluble ir aromatic or aromatic-aliphatic solvent mixtures. These are cured b> either air-drying or high temperature processes. They are frequentl} used as binders in certain types of quick air-drying finishing systems.

Long oil length alkyds (60 - 80% oil length) are normally prepared from drying oils (or their fatty acids). The resins of these oil lengths are completely soluble in aliphatic solvents. They are used primarily as binders for decorative finishing systems, and film formation is normally by air drying.

Our studies in oxygen-induced polymerization of some vegetable oils in the preceeding section portrayed the potential of melon seed oil or its fatty acid in making semi-drying or drying alkyd resin. The latter is commonly used in architectural paints. To make real this potential, we cooked long oil alkyd resins with blends of melon seed and linseed oil to establish the level of substitution of the latter oil that is popularly used in the industry. The following pairs of polyacohol and polyacid were used to establish the best pair, namely, glyccrol/phthalic anhydride [40], glycerol/isophthalic anhydride [41] and pentaerythritol/phthalic anhydride [42,43], while the following ladder was used for the ratio of MSO to LSO: 100/00, 80/20, 60/40, 50/50, 40/60, 20/80 and 00/100.
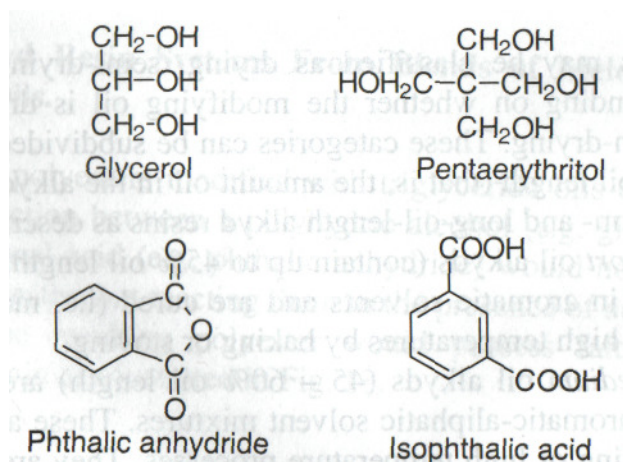
Paints were formulated with the new alkyd resins and their air-drying characteristics, namely, the set-to-touch time (STTT) and the dry-hard time (DHT), as well as their film hardness were determined. Results showed that STTT and DHT of the alkyd resin and the paint film decreased, while the film hardness increased as the amount of

LSO in the formulation increased. These results also showed that 50MSO/50LSO blend composition gave an alkyd resin product with optimum performance, considering raw material cost benefits. Table 9.1 gives STTT, DHT and Film Hardness results at the optimum blend of 50/50 for the three alcohol/acid pairs. It should be noted that the shorter the drying time, the better is the alkyd resin, while the higher the film hardness number, the harder and the better is the film.

Table 9.1. STTT, DHT and Film Hardness Values At Optimum Blend

Alcohol/Acid Pair	Oil	STTT(hr.)	DHT(hr.)	Hardness
Glycerol/l'lilhalic Anhydride	MSO	4.75	20.57 1	89 96
	LSO	1.88	1.95	93.5
	Blend	2.83	15.36	
Glycerol/isophthalic acid	MSO	2.08	15.77	90
	LSO	0.98	6.07	94
	Blend	1.43	7.40	98
Pentaerythritol/Phthalic Anhydride	MSO	2.17	22.17	90
	LSO	1.75	11.40	93.5
	Blend	2.0	13.25	96.5

These results represent significant improvements in the drying characteristics of MSO alkyd resin products. A cost reduction of about 43.75% was calculated at the time of this work for substituting 50% of linseed oil with melon seed oil. The results also show that isophthalic acid alkyd products showed superior behaviour to those of phthalic anhydride products. This was attributed to the reduction in the functionality of the latter acid by intra-molecular cyclisation [44]. Also, pentaerythritol gave better alkyd products than glycerol apparently due to its greater functionality.

9.6   New Paint Drier Systems Using Locally Available Vegetable Oils

We should at this point outline the mechanism of drying of an unsaturated oil or oil-modified alkyd resin in the presence of oxygen. If we represent the fatty acid segment present in each of these as (I), oxygen can attack the double bond to produce a peroxide (II) or attack the -CHU- group to produce a hydroperoxide (III):
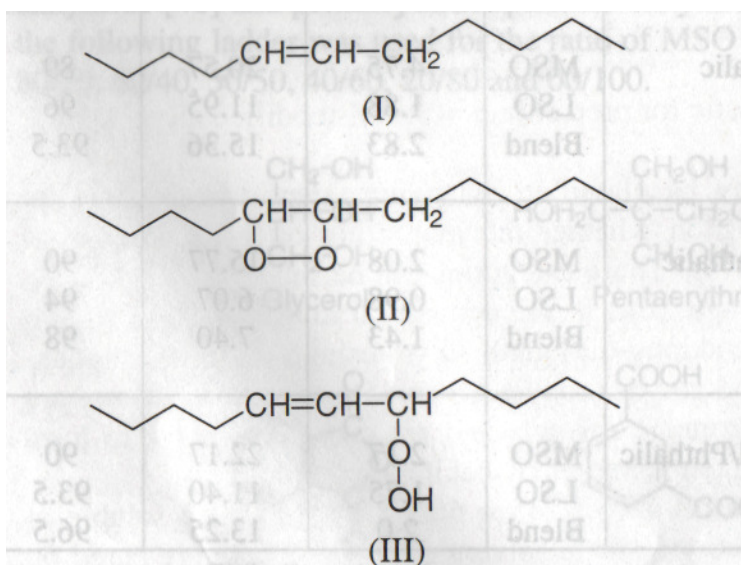
Both the peroxide and the hydroperoxide are unstable and decompose to form free radical on the fatty acid chain such as IV and V, which can combine (cross-link) to give VI.
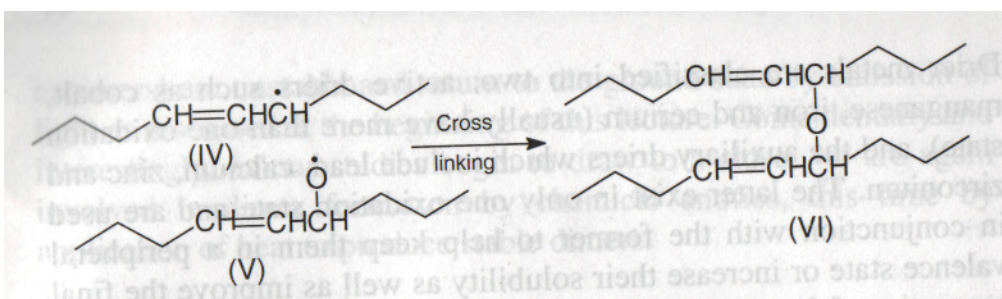
Also, IV and V can each attack the double bond on another oil molecule to form new bridges (cross-links). In this way, a three-dimensional network of chains are formed leading to solid film formation.

The induction period (i.e. the time lag between exposure of oil to the air and the onset of oxygen absorption) can be shortened considerably if a catalyst, called, 'drier' is present. A drier is thus defined as a material that promotes or accelerates the drying process. Driers have the general formula: $(RCOO)_X M$, where R is an aliphatic 01 alicyclu   radical and M is a metal with valence x. The metal component is responsible lor drying acceleration, while the acid segment solubilises the drier in the drying oil or resin, and therefore indirectly affects the efficiency of the drier. The metal accelerates drying by first destroying the anti-oxidants present in the oil. Thereafter, it hastens the rate of peroxide/hydroperoxide formation as well as their decomposition to the free radicals that crosslink to form the film. The action of the drier metal (e.g. cobalt) is illustrated in following scheme for the case of hydroperoxide decomposition:

$$CH_2-O-OH + Co^{++} \longrightarrow CH_2-O^{\bullet} + OH + Co^{+++}$$

$$CH_2-O-OH \longrightarrow CH_2-O-O^{-} + H^{+}$$

$$CH_2-O-O^{-} + Co^{+++} \longrightarrow CH_2-O-O^{\bullet} + Co^{++}$$

$$H^{+} + OH^{-} \longrightarrow H_2O$$
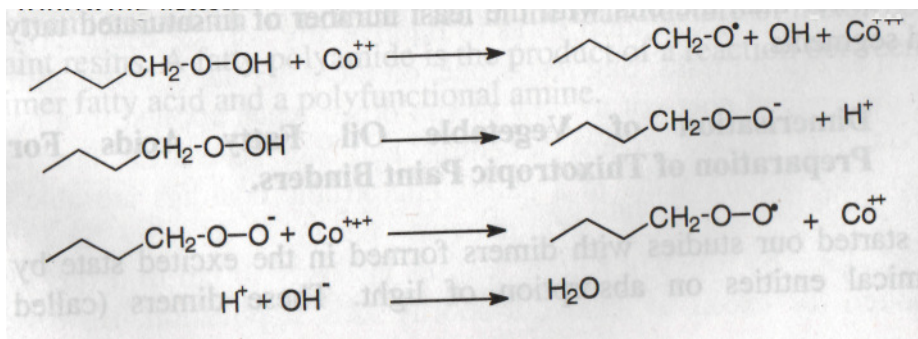
Drier metals are classified into two: active driers such as cobalt, manganese, iron and cerium (usually have more than one oxidation state), and the auxiliary driers which include lead, calcium, zinc and zirconium. The latter exist in only one oxidation state and are used in conjunction with the former to help keep them in a peripheral valence state or increase their solubility as well as improve the final properties of the coatings.

The popular but imported driers are made from naphthenic acids or tall oil fatty acids. It is for this reason that we are currently screening some locally available vegetable oils for use in paint drier preparation. Cobalt and calcium salts of the fatty acids from the oils of oilbean, conophor, fluted pumpkin, groundnut, melon, castor seed, palm kernel and local pear (the flesh) have been prepared and used to dry linseed oil. Set-to-touch-time results showed following ascending order in drying time:

Local pear > palm kernel > castor > melon > groundnut > the pumpkin > conophor > oilbean.

It follows that the drier made from oilbean seed oil showed the lowest drying time and hence enhances drying most. The least performer is local pear oil. This trend suggests that, in general, oils that contain mostly unsaturated fatty acid segments enhanced the solubility or miscibility between the metal drier and the oil being dried better than the oils with the least number of unsaturated fatty acid segments.

9.7 Dimerisation of Vegetable Oil Fatty Acids For Preparation of Thixotropic Paint Binders.

We started our studies with dimers formed in the excited state by chemical entities on absorption of light. These dimers (called excimers) are unstable and return to the ground state by emission of light as discussed at the beginning of this lecture. Coincidentally and interestingly, as our studies begin to draw to a close, we are again involved in dimer formation by chemical entities, this time by application of heat to produce stable dimers.

Specifically, unsaturated oils, when heated in an inert atmosphere to temperatures in the range of 300°C and above, quickly lose their unsaturation, and experience a rise in density and viscosity. Under this condition, the poly unsaturated Qg fatty acids present in the oil dimerise to form mixtures of C^ dibasic acids with some trimers and higher oligomers as well as small amounts of monomeric fatty acids.The relative proportions

of the structures vary with the type of fatty acid present in the feed stock. The crude product of dimerisation reaction usually contains about 60 - 70% dimer. This figure can be increased to up to 97% by standard separation techniques such as vacuum distillation, recrystallization, size exclusion chroinalography, etc. Some structures of the C_{36} dimer acid are given in the scheme on the next page.

Dimer fatty acids (DFAs) are used extensively in adhesives, inks and surface coatings, reactive and non-reactive polyamides, corrosion inhibitors, etc.[46]. DFA imparts to the adhesive: better bond stability, better adhesion and improved durability. Of particular interest to us is the use of DFA in the preparation of fatty polyamides, which in turn are used in the manufacture of *thixotropic* paint resins. A fatty polyamide is

Structures of Some C_{36} Dimer Acid
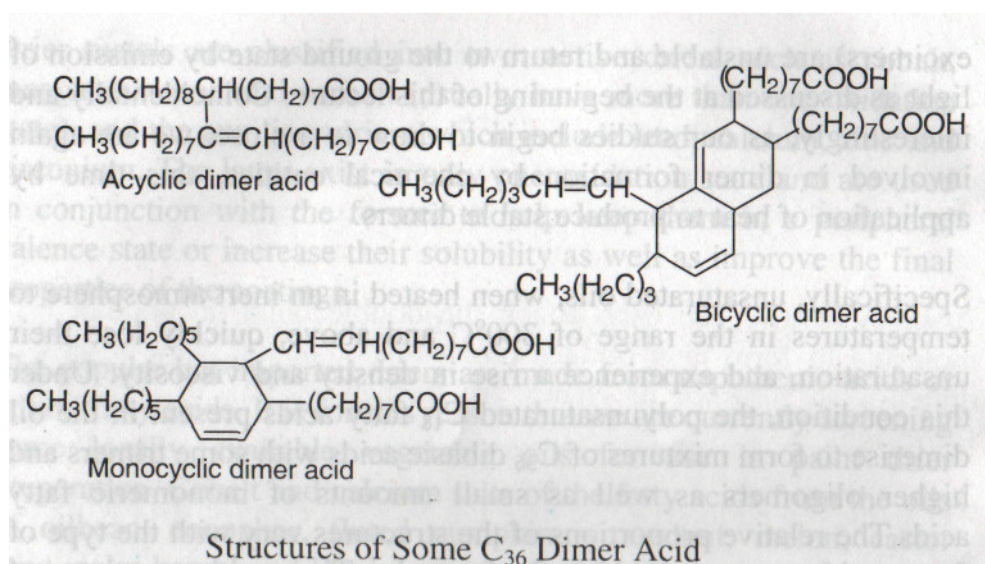
the product of a reaction between a dimer fatty acid and a polyfunctional amine.

A thixotropic fluid, when sheared at constant rate, undergoes decrease in viscosity with time of deformation. If the shearing is stopped for a while, the structure reforms and the experiment may be duplicated. This behaviour occurs when viscosity is partially due to intermolecular structures that take some time to be re-established or destroyed. For instance, ionic polymers tend to be thixotropic since the polymers probably aggregate when relaxed but dispersed and act individually when sheared.

Thixotropic behaviour is important in a paint to ensure good levelling and sag resistance. Levelling is the ability of a coating to flow out after application so as to remove any surface irregularities such as brush marks. Sag resistance, on the other hand, is the ability of the applied coat not to flow or run down when applied to a non-horizontal surface. Thus, levelling and sag resistance are two opposing requirements in a paint. Thixotropic coatings are able to meet these opposing requirements because shearing due to application by brush or rolling, causes viscosity to fall to levels low enough for marks to level out shortly after application. However, upon cessation of shearing after application, the viscosity of the applied coat recovers gradually to prevent 'runs' and 'drips'. Also, during in-can storage, a thixotropic coating assumes a soft gel-like structure

because it is under zero shear. This property eliminates the possibility of pigment settlement (a common problem in non-thixotropic paints), hence thixotropic coatings can be applied without the need for re-dispersion. Also, unlike non-thixotropic coatings, thixotropic coatings can be applied on porous surfaces without the danger of separation of pigment and vehicles caused by absorption of vehicles into the substrate.

It is for these practical considerations that we developed interest in dimer fatty acids. The pioneer work in our laboratory in this direction involved preparation of a fatty polyamide using soyabean oil DFA and 1,2-diphylenediamine. The product obtained was used to impart good thixotropic properties on a commercial non-thixotropic oil-modified alkyd resin [471. Subsequently we have prepared dimer Tally acids of melon seed oil using different catalyst systems, and al different temperatures so as to obtain some kinetic and thermodynamic data on the process. Three catalyst systems were used, namely, sodium hydrogen sulphate, iodine and sulpur [48 -50]. At 350°C, sulphur gave the highest yield (48.67%), followed by iodine (46.1%) after 30 minutes of reaction, and then sodium hydrogen sulphate (40.54%) after 90 minutes of reaction. Molar masses of the dimer products were also in the same order: sulphur (1647.97), iodine (1196.20) and sodium hydrogen sulphate (1141.20).

With these basic information on the dimerisation of melon seed oil fatty acids, work is in progress to use these dimer products to make fatty polyamides using different aromatic diamines with a view to study the effects of molecular structure on thixotropy. Three doctoral students are currently on this assignment.

10.   Sanitization of The Academic System

Mr Vice-Chancellor, sir, I wish at this point to take leave of our efforts and contributions in chemical research to address a subject matter that not only occupied my time and energy as an academic in the past twenty years or more, but also in some instances had posed a threat to one's life. A University is often called an 'Ivory Tower', to reflect an environment where lecturers and students pursue learning without any 'encumbrances'. However, for decades now, the Ivory Tower has come under siege from within and without. The ills of the wider society seem to have spread like wild fire into the Ivory Tower, leaving in their wake all kinds of ills that have continued to stifle the well-being of the system. Consequently, our university system is today beset with such ills as *cultism, examination malpractice and administrative malpractice and/or incompetence*. I will say nothing about cultism because I could do nothing about it. About the other two, I have done something to help sanitise our academic system.

In doing whatever I have done, one has been driven, not only by the discipline and disposition to have things done right, but also by the concern that the real essence of our presence here as students and staff is to ensure advancement of true and enduring knowledge which is made manifest by the quality of our graduates in both character and learning. Even if we have beautiful edifices here, and the cankerworms created by those vices are not eliminated, our academic system may well be described as a 'white

sepulchre'.

10.1 Examination Malpractice.

Examination malpractice is one of the vices or viruses that seem to have become entrenched in the country. Some others are electoral malpractice, bribery and corruption and advanced fee fraud (alias419). Examination malpractice first showed its ugly head on a large scale in WAEC examination in 1970, then captioned, EXPO'70. That was the birth of mass leakage of, and mass cheating in an examination in Nigeria. Since then, examination malpractice has spread to all levels of our educational system, assumed many forms, involving all categories of people that cut across all ages and creed, and so far, has defied all legislation or regulation. Even the supreme punishment, that is, 'expulsion' has not deterred students from cheating in examination. For many students these days, that seems to be the only option for passing; just like electoral malpractice now seems to be the only option for the average Nigerian politician to gain political position. Thus, examination malpractice has become endemic and pandemic. It is both contagious and infectious among our youths and even adults. It has polluted our academic environment, and thus requires 'sanitary' or 'sanitizing' measures than 'punishment' to get rid off. Like the disease that it has become, it is better prevented than cured. It is better to remove the grounds of its occurrence than to write rules to fight it.

10.2 Some Root Causes of Examination Malpractice

Some of the root causes of examination malpractice, particularly in
tertiary institutions, include:
i. Extreme academic weakness and non-academic attitude on the part of many students, a large number of whom have no business being in the University. This crop of students, if shown the examination questions ahead of time, may still not be able^to do well unless they are given the solutions as well. These weak students found their way into tertiary institutions by cheating in WAEC and JAMB examinations. In the latter examination, excellent performances by very poor students are not unusual. And, when a student cheats to come in, and he/she is hollow in the head, the only option is to cheat to go out.

Ladies and gentlemen, this is where the post-jamb test has come as a wonderful remedy to the erstwhile massive invasion of our tertiary institutions by candidates who are neither educatable nor disposed to be educated. The post-jamb test is the greatest sanitization our academic system has received. The dividends are already evident from the summary of the results of students in CHM 112 of this University for 2004/2005 (pre-jamb) and 2005/2006 (post-jamb) shown in Table 10.1.

Table 10.1 A Summary of Student Performance in CHM 112 in 2004/2005 and 2005/2006.

	2004/2005	2005/2006

Population	3306	2481
A	182 (5.5%)	576 (23.3%)
B	309 (9.3%)	465 (18.7%)
C - E	2071 (62.6%)	1241 (50%)
F (total)	902 (27.3)	199 (8%)
F (1st Years)	506 (15.3%)	53 (2.1%)
F(repeat Students)	396(12%)	146 (5.9%)

The figures speak for themselves, but note the massive failure of 1st years (506 no) and repeating students (396 no.) in 2004/2005 compared to 53 and 146, respectively, in2005/2006. The poor performances in 2004/2005 are typical of students' performances in the preceeding years, and we, the lecturers in the course had long been described as wicked, and had also been threatened for their failure. The dramatic excellent performances by the first post-jamb students in the same examination of the same standard can only be attributed to the admission of the right calibre of students.

The huge difference in the performances of the two groups can be illustrated further with the data in Table 10.2, which contains summary results of students in Medicine, Pharmacy, Electronic Engineering and Geology the most subscribed courses in science/applied science areas. Again, the figures speak for themselves. A situation where 83 first-year medical students failed a basic course in chemistry shows the very poor quality of students admitted through the JAMB examination to read this vital course.

Expectedly, the post-jamb test has come under criticism from quarters that had benefited from the old system, giving such excuses that cheating could also occur in the internally administered test. However, no University worth its salt can afford to allow its image to be messed up by allowing cheating in the internal test. In any case, any cheating in the internal test is localized; therefore the agents of such cheating are easily traceable and can be effectively punished, unlike the JAMB situation, where all kinds of faceless agents are involved. And, the usual action by JAMB is outright cancellation of results of candidates, in which many innocent candidates suffer for the sins of others.

Table 10.2 Summary of Students Results in CHM 112 in 2004/2005 and 2005/2006 For Some Selected Department

Department	A	B	C - E	F (1st Yr)	F (repeat)	Total No.
Medicine						
2004/2005	37	52	256	83	25	448
2005/2006	143	64	83	1	3	294
Pharmacy						
2004/2005	31	39	181	29	19	299
2005/2006	82	42	59	4	2	189
Geol						
2004/2005	1	0	45	36	15	97
2005/2006	15	24	79	0	6	124
Electronic Eng.						
2004/2005	8	15	106	33	14	176
2005/2006	31	22	54	3	2	112

ii. Examination malpractice can be encouraged by improper and prolonged registration process, in which students keep away from lectures in the attempt to complete registration. A student who has not been opportuned to listen to the lecturer has not gained knowledge and may be tempted to hire an impersonator.

iii. Improper identification of students in a course, particularly in large classes encourages impersonation.

iv. Improper teaching of students due to few and over-worked teaching hands in the face of large and increasing student population, particularly in the midst of other academic programmes such as sandwich, which involve the same overstretched hands. If on top of this, the teacher is not dedicated and effective, then teaching will surely be impaired and the learning opportunity compromised. A student who has not been taught properly is more likely to be tempted to cheat, more so these days that most students do not buy books to read to gain knowledge, but perhaps to please the lecturer.

v. Lack of lecture halls and public address systems for large classes to ensure that all students in a lecture are seated, see what is written on the board and hear what the lecturer is saying. Where these conditions are lacking, learning is seriously compromised and the temptation to cheat in examination is maximized.

10.3 My Efforts To Help Sanitise Our Examination System a.   Introduction of

the Class Admit Photocard

For five years I taught as a Graduate Teaching Assistant in the Chemistry Department of Michigan State University, USA. I did not encounter any case of examination malpractice nor was I ever threatened by a student. And, for each class I taught, I received from the Registry an authentic list of those who had registered the course.
On my return to Nigeria in 1979, there was no class list for any class from any quarters, neither from the Registry nor from the Department. Instead, the Department supplied us with what was called, 'attendance slips', which the students filled in the examination hall and inserted in their examination scripts. The lecturer, after marking the examination scripts, then generated the class list, or more appropriately the result list, using the information provided by the students on the attendance slips. Thus, the class/result list was generated in the examination hall. This was a very defective system that encouraged examination malpractice that was difficult to detect. At the same time also, the use of the Class Admit Card had been discontinued by the Registry because they were basically useless and were simply dumped in Departmental offices.

Thus, examinations in chemistry large classes increasingly became a nightmare for the invigilators, who faced verbal and physical assault from students, some of whom escaped. There were cases of students jumping from upper floors of storey buildings to escape from invigilators. Often, security men were invited to assist. Some students organized their escape in an embarrassing way: they would request to be escorted to urinate; after urinating, or sometimes without even getting to the make-shift urinary, would wave bye bye to the invigilator. An overzealous and angry invigilator might decide to chase the escapee, forgetting the crowd left in the hall, who would capitalize on his absence to cheat. There were also many incidents of forceful attempts to enter the examination hall by desperate and dangerous impersonators.

In one such incident, I was a co-invigilator with Dr. M.J. Kelleher (an American), and one big guy wanted to enter Chemlll examination hall. Somehow, Dr. Kelleher recognized him as an impostor, and refused him entry. He boldly told Dr. Kelleher that he would deal with him. I looked at this student sternly on the face to scare him; but he returned my stern look and stood menacingly near us. That was in 1994. That brought home to me the danger and other problems posed by lack of identification of students in our examinations. I had to do something about it. consequently, immediately after that incident I wrote to the Head of Department at the time (Prof. S.O. Onyiriuka) and proposed the use of (lass Admit Photocard (CAPC), a Class Register and a Mark and Attendance Sheet (or Class List). The Department accepted and implemented the proposal. The Class Register was filled and signed by students on submission of the CAPC as evidence of submission in case it got lost. At the close of registration, the CAPC was serialized in the order of students' registration numbers and then used to compile the Class List. Part of this proposal involved numbering examination scripts and examination seats to tally with students' serial numbers in the Class List.

This system immediately brought order in chemistry examinations, eliminated incidents of assault on invigilators, escape of students from examination halls. This was because we had in our possession the photos of all '-.indents admitted into the examination hall and no students could afford to misbehave, including registered **impersonators.**

The same year, 1 wrote to the Vice-Chancellor (Prof. O.K. Udeala) to recommend the use of the CAPC in the University as a whole. Apparently, the internal crisis that engulfed him, did not enable my proposal to see the light of day. I re-submitted the proposal under the Sole Administrator (Professor Gonwalk) who passed it to the DVC (Academic) - Professor Ngodi, who was very excited by the idea. He called for details, which I supplied. And by June 1998, after working with the Registry on the format, the present CAPC was introduced in the University.

• In 1997/98, sitting in my office after the examination in Chem. Ill, and using the CAPC, I built an album of impersonators in that examination by comparing previous CAPC submissions by *repeating* students with their present submissions. Females became males and vice versa. The album was submitted to Departmental Academic Board and members were amazed. The following year, impersonation with CAPC dropped drastically in Chem 111. In 1999/2000, Dr. F.C. Chilaka, as co-ordinator of Bio 152, did a similar thing and caught many impersonators who had used the CAPC to impersonate. Again, he reported a drop in this crime the following year following this screening.

In 1999/2000, when some irregular actions were introduced in our registration and admission of students into the examination hall, led to the invasion of Chemlll examination by about 200 suspected impostors, most of whom came from the Engineering Faculty, I was compelled to verify their results and about 100 of them abandoned their results rather than being caught. Later, 24 cases of impersonation involving 48 students were isolated from this group. The following year, the impostors kept away and their clients then came for the examination themselves.

Thus, the point here is for lecturers to take such sanitizing actions in their examinations in order to deter would-be impersonators or other cheats, because a thief would not attempt to steal if he knows he would be caught. It is better to prevent them than to prosecute them. That has been my approach.

b.   **Introduction of Photo Computer Form**

The reason why students used the CAPC to impersonate (particularly in large classes) was because they were allowed to collect them, after they were stamped and signed by the Faculty Officers, to submit to the course lecturers or co-ordinators. They could then superimpose photographs on the CAPC. This was a serious weakness in our registration procedure.

Again, when the Registry started using failed grades in computing a student's GPA,

students countered by withholding their semester computer forms until the results of courses taken in a particular semester were released. This enabled them to upgrade their performance by not entering in the computer form any failed course(s) This practice introduced serious disorder and delay in the computation of students' results, and it became a new form of examination malpractice. This needed to be stopped.

Thus, during my Deanship of the Faculty of Physical Sciences (2004 - 2006), I introduced the use of Photo Computer Forms (PCF) for all I-acuity majors to replace the CAPC. The PCF contained the courses actually registered by the student as certified by the academic adviser, who retained the PCF after the student had submitted it. The student also submitted the original computer form (filled and signed) to there academic adviser al the time of submitting the PCF, failing which (In- slink-ill's name would not appear in the Class List, let alone be allowed lo lake the examination. The PCF, unlike the CAI'C, ensured dial a sliideiil that enrolled in a class actually registered the course. In addition, the PCI[1] was used to identify and admit only registered students into the examination hall. This new system effectively ended late submission of computer forms as well as impersonation with the CAPC by Faculty students for the two years of my Deanship. Unfortunately, we could not apply the new system to guest students because we envisaged that it would be very difficult to collect the PCFs from the many Departments/Faculties involved.

The introduction of online registration this academic year immediately brought to an end the use of PCF and even CAPC in my Faculty. It is my prayer, that online registration be made to work by the operators of the system to ensure that Departments get authentic Class Lists together with the photos of students registered for a course ahead of examination. For the avoidance of doubt, unless the photos of registered students in a large class are made available to the lecturer/invigilator by online registration or by manual submission of CAPC, then there will be massive impersonation in our examinations, the magnitude of which is better imagined than described.

c.   Categorization of Examination Malpractice Offences and Their Punishment.

One major step taken recently by the Senate of the University is to categories examination malpractice and their offences, instead of having 'expulsion' as the only punishment. Experience showed that expulsion for every single offence did not deter students from cheating in examination; instead, there was an increase over the period of this 'capital' punishment; apparently, because lecturers/invigilators were unwilling to report cases either out of mercy for the culprits and/or fear for their lives. In any case, examination malpractice offences surely differ in gravity, more so when some students have resorted to preparing their own examination results. For such students, copying has become a waste of time as it yields little or no dividends. Thus, the two cases, namely, falsification of examination results (a criminal offence as well) and copying in an examination should not attract the same punishment.

[thank Senate for giving me the opportunity to chair the Committee that fine-tuned the examination malpractice offences and their punishment and for accepting most of our recommendations, particularly, for approving my request to restore 'rustication' instead of 'expulsion' as punishment for bringing in unauthorized materials; books, notes, papers, etc. This is already helping in the fight against examination malpractice as many more of such cases are now being reported.

In the same vein, Senate may have to re-visit the issue of making 'expulsion' a punishment for a student caught in an examination with a copy of a leaked examination question paper and/or solutions. We had recommended 'rustication' for one year because we regarded the offence as an indirect involvement since the principal suspects in an examination leakage is the course lecturer and any other person(s) directly involved in the leakage. We thought it was too harsh to expel a student for the failure of a lecturer, whether by design or default, to protect his/her examination questions, more so when the defaulting lecturer may go away unpunished or at worst he/she is merely warned. May be I should do a paper to Senate on Ihis before I retire.

10.4 Running Teachers' Sandwich Programme at UNN Without Disrupting Academic and Educational Programmes.

The above was the subject of a letter I wrote to the Acting Vice-Chancellor (Prof. G.F. Mbanefoh) in January 1998, suggesting that our sandwich programme be taught off campus, if and when it coincided with the regular programme so as to minimize the adverse effects both programmes were having on each other in terms of deep cuts in time required to teach each group of students. We are all living witnesses of the fact that in those years of incessant instability in the University system as a result of student unrest and/or strike action by staff, the university 'long' vacation became 'short' vacation, and often out of phase with the school holiday pattern. Consequently, sandwich students were often called to campus to study when they were supposed to be in school teaching, and the regular students were sent home prematurely in order to accommodate the sandwich programme, which became more sandwiched in the process. These points were raised in my letter to the Chief Executive together with facts and figures on how the sandwich programme could be successfully run in nearby secondary schools. There was no response to my letter.

By 2001, the disruptive effects of the sandwich programme on the regular programme had become much more bitting that a Senator raised the issue on the floor of Senate; that gave me a wonderful opportunity to remind the Chief Executive that I had written him on the matter. I was then asked by Senate to re-submit my proposal to the Director of the Institute of Education. Subsequently, in July 2003, following inaction from the Institute, Senate appointed Professor Eyo (of blessed memory) and myself to liaise with the Director of the Institute of Education to actualize the proposal. The liaising did not yield fruit either, and I decided to go solo.

By November 2003, and with the help of Engr. Nwoji, I successfully secured the permission of Bishop Ilonuba - the Proprietor of St. Cyprain's secondary schools (2 no.) for the use of his schools to run our sandwich programme off campus. I submitted a

report to Senate in December 2003 on my efforts through the Chief Executive. However, because of the way and manner the Report was presented to Senate, nothing came out of it. Apparently, the dragging of feet by the University Authority on the off-campus proposal might be due to its unwillingness to lose the revenue that would accrue from hostel accommodation fees paid by the sandwich students.

By June 2004, following the assumption of office by Prof. C.O. Nebo as Vice-Chancellor in May 2004,1 addressed a letter to him on the urgent need to run the Sandwich programme off-campus during the 2004 long vacation. He accepted the idea. I then led a delegation of Senate Committee to Bishop Okobo and secured his permission for the use of his two secondary schools, namely, St. Teresa's and Queen of the Rosary Secondary Schools. With these initiatives on my part, the stage was set for the first off-campus running of UNN Teachers' sandwich programme in August 2004. And, with that we were able to teach our regular students normally, with the semester running its full course. Our academic system was thus sanitized to run its normal course.

10.5 A New System of Nomination of Heads of Department During My Deanship of the Faculty of Physical Sciences.

In my Inaugural Address to members of the Faculty Board on 12 October, 2004, as the new Dean, I raised the issue of probity in office and stated as follows and I quote: 'Ladies and gentlemen, you know as much as I do that much of the present poor state of **infrastructural** facilities in the Faculty could be attributed to years of mismanagement of manpower, money and material. What do I mean by mismanagement of manpower. It is simply this: when all hands are not encouraged, or not even allowed to be on deck, and those at the helm of affairs run the affairs of the departments/faculty as one-man show, and the rest look on, perhaps waiting for their turn, then, transparency in office is likely to be trampled upon, and probity set aside. When this happens, no matter the amount of money and material made available for academic purposes, there will be little or no positive returns. On the other hand, where there is probity and purposeful leadership, little money, like the 'chemical catalyst', can achieve much', end of quote. Put another way, every unit in the system must be efficiently manned for the system not to suffer setbacks. The present criteria in the University which a Dean of a Faculty uses in nominating two candidates to the Vice-Chancel lor for headship of a Department are: *seniority, academic leadership, merit and rotation.* Experience has shown that seniority tended to compromise academic leadership and hence performance. This is because seniority does not impart competence and ability to deliver on the individual. And, the Dean cannot safely disregard the seniority parameter (even where there are serious grounds to do so) without being accused of victimization or favoritism or both.

It is for these reasons and more, that I worked out and administered a 15-parameter system of assessment of candidates eligible for headship on the basis of seniority and rotation by all members of each Departmental Board in the Faculty. Candidates were scored: 0, 1, 2, 3, 4 or 5 point for each of the following qualities:

Disposition for Transparency and Accountability; Potential for Academic Leadership; Openness with Colleagues; Disposition to Execute Official Duties Promptly, particularly Examination Matters; Effectiveness in Discharge of Official Duties; Organisational Ability; Degree of Participation in Departmental Affairs; Ability to Work with Others; Disposition to Constructive Criticism; Disposition to Use the Departmental Board to Take Decision (if applicable); Disposition to Work to Make Things Better; Display of Administrative Ability, Disposition to Enforce University Academic Regulations and Interest/Effectiveness in Research

The results of the assessment in each Department showed that colleagues knew who would perform and who would not performance. And the Dean's task was made very easy. He forwarded the choice of the people to the Vice-Chancellor, who appointed them as recommended. The dividends of this new system are very apparent at the moment in the Departments in my Faculty. That was a major sanitisation of our academic system in the Faculty of Physical Sciences that helped to ensure collective, responsive and accountable leadership.

10.6 A Measure for Fast Marking and Processing of Examination Results: The System of Fixed Stipend for Postgraduate Demonstrators.

The problem of considerable delay in publishing of students' results remains with us to the extent that the Chief Executive himself has had to issue threats of sanction to defaulters. The situation is particularly bad in large classes. Even though it is understandable in such cases, it is not excusable because it violates the right of our students to have their results published as and when due. Issuance of deadlines for submission of results has not worked, and would not work unless we take fundamental measures to facilitate the process of marking examination scripts.

For five years ol my doctoral programme at Michigan State University, I worked part-time as a Teaching Assistant (TA) in the department of Chemistry. 1 was paid a fixed monthly stipend (or allowance) which was enough to see me through the graduate school. It was a financial assistance given only to graduate students in good academic standing. It was also a cheap way for the Department to hire enough hands to cope with the teaching of large student populations. About ten TAs were usually attached to a Professor who lectured the large class in an auditorium. The class was then broken up into tutorial classes manned by the TAs to answer students' questions in the lecture. The TAs also conducted and marked the quizzes. The three examinations set by the Professor in charge, were marked by the TAs in a conference manner under the supervision of the Professor, and that was done in two days or less because the questions were structured in a way to facilitate marking.

For quite some time in this University, postgraduate students were appointed part-time demonstrators in laboratories. They made claims for hours of demonstration done. Some abuses began to arise and financial claims rose to the sky in some cases. The Personnel Office began to query such claims, and sometimes stopped payments altogether. On the

other hand, processing of approved claims met with both usual and unusual bureaucratic delays. There were allegations of gratification being sought before claims were processed. Thus, the outcome of rejection of claims and/or delay of payments of approved claims was the refusal by many postgraduate students to serve as demonstrators. That was the situation I met as the Dean of the Faculty, and (hat too was in the face of increasing student population and diminishing staff strength. Consequently, results in large classes in the faculty were considerably delayed due to lack of hands. This situation needed urgent sanitisation.

I then wrote to the Vice-Chancellor and proposed the adoption of a system of fixed monthly stipend for graduate demonstrators in the Faculty. Their duty schedule was also outlined to include: conduct of tutorial classes in theory courses, demonstration/supervision in practical courses, invigilation of examinations, marking of tests and quizzes and marking of examination scripts in a conference manner under the supervision of the course lecturer. This proposal was approved by the Vice-Chancellor but not without stiff opposition from the Controller of Personnel Services who argued that the position was not in the University establishment; but the point was made to him that these graduate demonstrators were not permanent workers; in fact could be treated as 'casual workers' in the academic sector. At the end, Senate approved the proposal and the Chief Executive approved a stipend of N8000.00 a month for each graduate demonstrator for the period appointed. With that, in 2004/2005, the Department of Mathematics, as an example, was able four days and to complete the compilation in less than a month. Similar feats have since been recorded in other Departments in the Faculty.

From the Faculty of Physical Sciences experience, it is clear that the only way to solve the problem of late publication of students' results is by engaging more of that category of temporary academic staff. Employing more regular staff will be much more expensive and would not solve the problem. Even, engaging more of the so-called Graduate Assistants (who are regular staff) would be equally expensive and would violate the NUC minimum academic qualification for regular academic position.

" Besides, this system of fixed stipend for postgraduate demonstrators is a vital financial assistance that would enable our bright graduates
*' to undertake postgraduate studies without undue hardship and/or putting their already stressed parents/guardians to further financial stress. Indeed, overseas, postgraduate education/research is paid for through one form of financial assistance or another from either the public or private sector. This is because the Society stands to benefit immensely from postgraduate research outputs. This system of fixed monthly stipend will surely help us attract and keep good quality graduate students in our bid in this University to meet the NUC 60% postgraduate education.

To drive home these points, information was obtained last month on the situation in the Department of Chemistry, MSU, with respect to Academic Staff strength and the total number of students that offered 1st-year chemistry courses in 2005/2006. Table 10.3 gives the big disparity in staff/student ratio in Chemistry Departments at ' UNN and

MSU, particularly with respect to Teaching Assistants. Chemistry Department here therefore needs more TAs to be able to handle the much larger student population. Also, our TAs should be better paid to avoid a slave labour situation, and to attract our bright graduates to take up the offer.

Table 10.3: Staff/Student Ratio at UNN & MSU For 1st-Year Students <u>in Chemistry Courses (2005/2006).</u>

S/No.	Item	UNN	MSU
1	No of Academic Staff	25	48
2	No of Grad. Teaching Assistant (TA)	10	197
3	Total no. of students	16,320	7980
4	Professor's Avg Annual Salary	$24,509	$112,390
5	TA's Annual Allowance	$762	$20,844
6	Percent Difference b/t 4 & 5	96.89	81.45

10.6 Establishment of Polymer Chemistry Programme at University of Nigeria, Nsukka.

Ladies and gentlemen, one of the earliest academic battles I have had to fight to help make the academic programme of this University current and in conformity with National needs was the establishment of an academic programme in Polymer Chemistry. In 1973, a visiting German Chemist in the Department remarked that he would expect most Nigerian chemists to be Polymer Chemists because of the abundance of petroleum in the country, which is a major source of monomers and other intermediates for the Polymer Industry. Apparently, the message in that remark was not to be implemented by the traditional chemists who dominated the Department.

Thus, despite the enormous industrial importance of polymers, some of which have been x-rayed in this lecture, there was no single course in Polymer Chemistry in my undergraduate days in the Department. My interest in polymers arose after reading a book on plastics in my final year in 1972. After graduation, I applied for Commonwealth Scholarship to read Polymer Science and Technology at the University of Aston, UK where I had secured admission. To pass the rigorous interview conducted by such eminent scientists as Professors Chike Obi and Emovon (a chemist), I had to do further readings on polymers in the National Library in Lagos Island some few days before the interview. I secured the scholarship in 1973, but did not take it up because I preferred to study in the United States of America.

After six years of doctoral and postdoctoral training in polymer science, I returned in 1979 to re-join my Department. There was
• another Polymer Chemist who trained in Britain, and had come back two years earlier. And, there was only one course in Polymer

Chemistry in the entire four year undergraduate programme in a Department thai offered al the time two degree options in Pure Chemistry and Industrial Chemistry, respectively. By 1980, I wrote a proposal to add more undergraduate courses in Polymer Chemistry and a postgraduate programme in Polymer Science & Technology leading to a Masters degree. My proposal was turned down by the Head of Department on the ground that I did not consult him before writing so as to ascertain whether there would be hands to teach the courses. I did not consult him because I knew he would not encourage that. Of course, my position was that a programme needed to be in place to justify asking for hands from the University. So, it was a case of giving a dog a bad name to hank it.

By 1982, a student was assigned to me to do a masters degree in industrial chemistry (polymer chemistry option) and there was only * one course in Polymer Chemistry. By this time, the other Polymer Chemist had left out of frustration for another Institution. I refused to leave even though the then Anambra State University of Science& Technology had wanted me badly in their Polymer programme. I chose to serve them on part-time basis.

I did not find it acceptable to educate a student at postgraduate level with only one course in Polymer Chemistry. So, this time I re-submitted my earlier set of courses, and after a stiff debate in the Departmental Board, four core courses and two elective courses were approved on the condition that I would teach them, in addition to the undergraduate polymer course and all my other regular courses in physical chemistry. I accepted the challenge. And, from 1986 till today, I have taught all alone all the postgraduate courses in Polymer Chemistry. They made sure no other Polymer Chemist was employed, even at a time some much younger Chemistry Departments had, on the average, two Polymer Chemists in their staff. I had to bear the teaching/supervision burden for twenty years in order to sustain polymer education in this University. In spite of this sacrifice, and, as if to add insult to injury, the same group of traditional chemists attempted to stop the employment of two Polymer Chemists I had trained. I fought back and they ran of luck, and the two were employed in 2001. Right now, I have been relieved of the undergraduate polymer courses by three of my products, two of them in Chemistry and the other in the Energy Center. *Long live Polymer Education in the University of Nigeria!*

This struggle to start a programme in Polymer Chemistry reminds me of the attempt to start a programme in Chemical Engineering in this University in the late seventies/eighties; perhaps, the traditional engineers did not bother much to have it. Consequently, a whole first generation Engineering Faculty in this country is deficient in that area of modern engineering. The Chief Executive is currently pushing for the establishment of the Department of Chemical Engineering. That will be a nice and more complete engineering education for our children.

Mr. Vice-Chancellor, Ladies and Gentlemen, I have taken you through my studies in polymers (the ubiquitous modern materials) and vegetable oils (the renewable and indispensable agricultural products) to my efforts to help build a virile academic system in this University. It has not been wilhoui llnvals, vilifications, oppositions and even

persecutions. But I have hivn sustained by the urge to do the right thing, guided by the principle of transparency, survived by being open, fair but firm, and above all, protected by God Almighty. Consequently, if 1 were to live my academic life again, I would pursue the same path for it has been challenging and fulfilling, and above all, it was all done in the best interest of the system.

Once again, I thank the Vice-Chancellor for giving me this wonderful opportunity to pontificate, as it were, on these issues on the eve of my retirement. I am equally grateful to the able team of Professor Obioma Njoku - the present organisers of the Inaugural Lecture. They have continued to do a good job. I thank Mr. Paul Ejikeme for his assistance in readily helping me to obtain some urgently needed materials for this lecture, particularly for supplying the data on students' performances in Chem 112. I am ever grateful and loyal to Dr.(Mrs.) Felicia Nneka Ibemesi (my dear wife) for the solid pillar of support she has always been all through my academic career. Indeed, she gingered me into giving my Inaugural Lecture, by asking me one afternoon in January this year, 'man, are these Professors who have given their Inaugural Lectures more professoral than yourself?. I replied immediately in writing by giving her a tentative title for the lecture. So, *we owe today to her.* To all of you who have come to listen to me, from far and near, I say a big thank you for your time and patience. It can be tiring to listen. Finally, *I dedicate this lecture to all my teachers for the water I drank from their fountain of knowledge. May God bless them all.* Thank you all.

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