STUDIES IN VINYL POLYMERIZATION ON BENTONITE

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A C K N O W L E D G E M E N T

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P R E F A C E

The thesis embodied the results of the investigations carried out by the author at the Department of Chemistry, University of North Bengal, Darjeeling, India.

The thesis presents the results of the aqueous polymerization of Methylmethacrylate, Methacrylonitrile and acrylonitrile and their co-polymerizations in presence of a trace amount of ethanol and the bentonite clay mineral, particularly hydrogen bentonite in the aqueous suspension. Considerable attention has been devoted to establish the hydrogen bentonite-ethanol system as the free radical initiator for the polymerization reactions. Spectral and Kinetic data have been produced in support of the view. The failure of both Methacrylonitrile and Acrylonitrile to homopolymerize and the success of each of them to copolymerise with Methylmethacrylate have been accounted for. The mechanism for the polymerization process has been put forward.

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CHAPTER - I

Section IA : Historical : The clay mineral

Clay minerals are, in general, silicates of either magnesium or aluminium. Oxygens are arranged tetrahedrally around silicon atoms and octahedrally around aluminium atoms; the silicon layers and the aluminium layers are linked through some oxygen atoms of either layer. X-ray diffractions of mica, talc, pyrophyllite , chlorite and kaolinite[1,2] Pauling had suggested an essential similarity between these materials regarding the dimension of their unit cell in the plane of cleavage and suggested that these materials have a layer structure composed of sheets of cristobalite, SiO_2 and either gibbsite, $Al_2(OH)_6$ or brucite $Mg_3(OH)_6$. The layer of silicates or phyllosilicates are believed to form by condensation of sheets of linked $Si(O,OH)_4$ tetrahedra with $M_{2-3}(OH)_6$ octahedra, where M is either a divalent or trivalent cation. According to the type of condensation the clay minerals may be classified in three distinct categories:

(i) 1:1 type or dimorphic minerals with a general layer formula $M_{2-3}Si_2O_5(OH)_4$. The species are : Kaolinite, Halloysite etc.

(ii) 2:1 type of trimorphic minerals where the octahedral sheet is sandwiched between two sheets of inward pointing tetrahedra (the mica type layer structure). The species are: monmorillonite or bentonite, talc, mica, etc.

(iii) 2:1:1 type or tetramorphic minerals. The species are : Chlorite, etc.

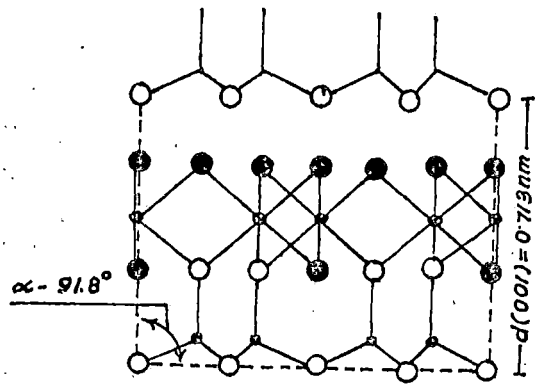
We restrict our choice of clay minerals only to those used for polymerization reaction. Due to unsymmetric cleavage of the sheet of clay minerals charges may grow in them and the charges are neutralised by the absorption of opposite ions that are abundant in the local soil[3]. The kaolinite clay with zero charge per formula unit falls in the 1:1 type of the above classification. With 2:1 type of clay mineral the charge per formula unit is found to be zero for pyrophylite and talc and the charge 0.25 to 0.6 are found for montmorillonite and saponite of different origins. The clay minerals vermiculite and chlorite have the basic unit structure of 2:1:1 type. While the former has 0.6-0.9 charge per formula unit, the later has much varied charge. Depending upon the abundance of the cations in the soil, the exchange of one by another could change the physical properties of the clay minerals. There is scope, in these structures, for isomorphous replacement, i.e. for substitution of Si^{+4} and/or $M^{+2/+3}$ for cations of similar size but different (usually lower) valency. Thus if 3 Mg^{+2} ions replace 2 Al^{+3} ions in the octahedral sheet of pyrophyllite, the mineral is talc. Structural varieties or polymerphism are found in many of the groups (i.e. among any of the variety, say 2:1) because the crystals are composed of discrete layers which can be stacked in a number of different ways.

Interstratification of two or more types of layers within a single crystal is also possible.

A few clay minerals among the three classes, used so far in the polymerization reactions need individual attention.

Kaolinite

Dioctahedral species kaolinite and halloysite of the kaolinite group are the examples of 1:1 type of minerals. The structure of the kaolinite layer, together with the manner of stacking of successive layers within a crystal are shown below:



O Oxygen
o Aluminium
• Silicon
● Hydroxyl

Fig. 1 Kaolinite layer viewed along a axis

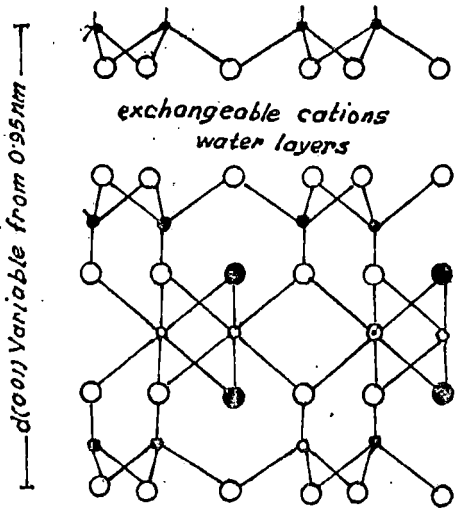
Each layer occupies a thickness of ~ 0.72 nm, a value equal to the basal $\overline{d(001)}$ spacing of kaolinite. As shown in the figure, the kaolinite is electrically neutral but in reality

it carries a small negative charge due to a small amount of isomorphous replacement[4]. This 'permanent' - as opposed to the 'pH dependent' negative charge is responsible for the small but measurable (< 0.1 mole kg^{-1}, monovalent cation) exchange capacity of kaolinite sample in acidic condition. Hoffmann[5] et al proposed that the exchange sites of kaolinite are situated only on the tetrahedral surface.

The superposition of oxygen and hydroxyl planes of successive layers within a single kaolinite crystal facilitates pairing of O and OH ions and inter layer O...HO hydrogen bond formation. In other words, the forces arising from H bonding and those due to vander Waals' interactions holding adjacent layers together, must be overcome if interlayer sorption (intercalation) of extraneous species is to occur. It can now be recognised that the edges of kaolinite crystals are of particular importance. This is because the edges containing unsatisfied valencies ('broken bonds') occupy an appreciable proportion (10-20%) of the total crystal.

Bentonite/Montmorillonite.

This is a 2:1 type condensate.



○ Oxygen
● Hydroxyl
○ Aluminium
• Silicon
⊙ Magnesium, Iron

Fig. 2 The Hoffmann-Endell-Wilm-Marshall-Maegdefrau-Hendricks structure of a montmorillonite layer viewed along the axis. Basal spacing is given in nm units.

The structure of montmorillonite was first given by Hoffmann, Endell and Wilm[6] on the basis of its similarity with that of pyrophyllite. This basic structure into which modification by Marshall, Maegdefrau and Hoffmann[7] and Hendricks[8] were subsequently incorporated, is now generally accepted. The montmorillonite layer differs from that of pyrophyllite in that the substitution of Al^{+3} for other cations (e.g. Mg^{+2}, Fe^{+2}) in octahedral positions, and

less frequently of Si^{+4} and Al^{+3} in the tetrahedral sheet always occurs. Although some internal compensating substitution may occur the final result of the isomorphous replacement in the pyrophyllite structure is a layer which carries a permanent negative charge[7]. The positive charge deficiency is balanced by sorption of exchangeable cations which, apart from those associated with external crystal surfaces, are situated between the randomly superposed layers within a crystal. Water is also readily adsorbed in the interlayer space[9,10]. These concepts are illustrated in figure 2. Water appears to enter the interlayer region as an integral number of complete layers of molecules. This number depends on the nature of the exchangeable cation. The d(001) spacing of montmorillonite can thus vary over a wide range, the minimum corresponding to the fully collapsed state being 0.95 nm. With large monovalent and divalent cations occupying interlayer exchangeable sites, interlayer (or intracrystalline) swelling is limited to a d(001) spacing of about 1.9 nm. On the other hand, montmorillonite samples saturated with small, monovalent cations (Li^+, Na^+) may show extensive interlayer expansion in dilute aqueous solutions (< 0.3 N) of their respective cation salt and in water, and under optimum conditions the layers can dissociate completely. The charge density on the clay surface as well as the nature of the exchangeable cation has a profound influence on the hydration properties of 2:1 type phyllosilicates and in consequence the hydration properties are affected more by the interlayer cation than by the silicate

surface. Since uncharged polar organic molecules are adsorbed essentially by replacement of the interlayer water, the behaviour of such molecules is likewise strongly influenced by the exchangeable cation. Evidence is accumulating to show that, at least at low water contents, cation-dipole interactions are of paramount importance in their effect on the adsorption of polar molecules by clay minerals.

An alternative and completely different structure (Fig. 3) for montmorillonite has been suggested by Edelman and Favejee[11]. The main aspect of the present structure is that every alternate SiO_4 tetrahedron in the tetrahedral sheet is inverted. The apicel oxygens of such inverted tetrahedra, now pointing away from the surface, are replaced by hydroxyl groups which also fill the gaps left in the octahedral sheet. No isomorphous replacement within the structure is envisaged and the observed cation exchange capacity being solely ascribed to the dissociation of apical hydroxyl groups. Somewhat similar structure in which excess hydroxyls are present due to the replacement of some Si^{+4} ions by $4H^{+}$ or Al^{+3} H^{+} ions in the tetrahedral sheet has been suggested by McConnell[12].

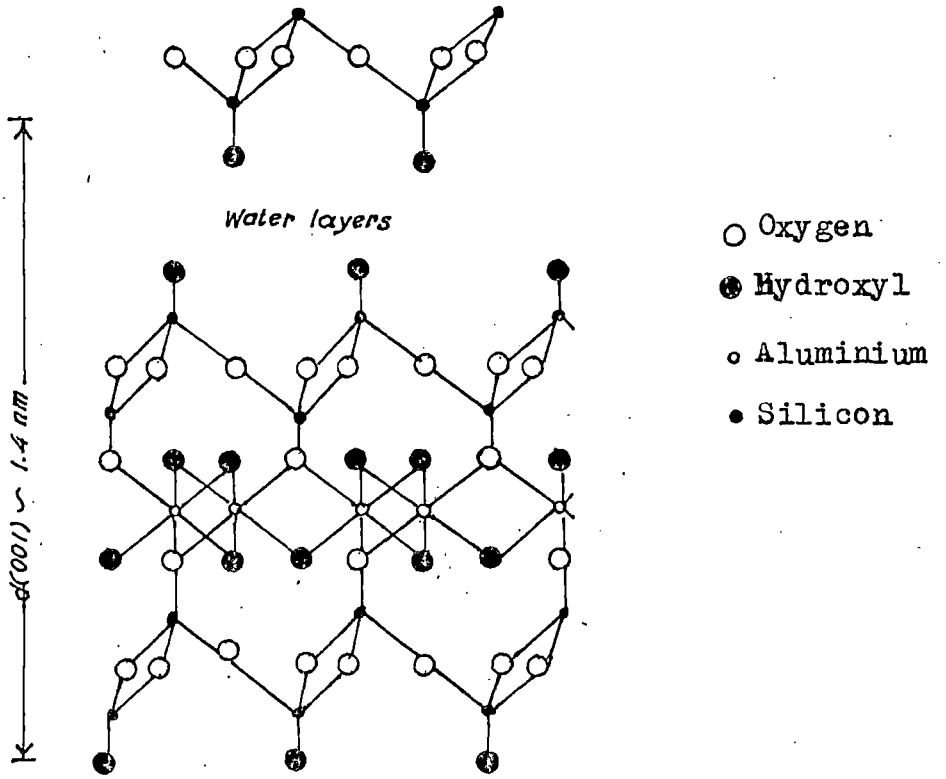


Fig. 3 The montmorillonite layer structure viewed along the axis according to Edelman and Favejee.

On the other hand, Grim and Kulbicki[13] postulated the existence of two types of montmorillonite, one confirming to the Hofmann-Endell-Wilm-Marshall-Maegdefrau-Hendricks structure and the other to the Delman-Favejee structure. Because of the poorly crystalline nature of the clay mineral, X-ray diffraction patterns are generally broad and diffuse. Moreover, obtaining homogeneous and uncontaminated samples is not an easy task. These facts make it difficult to

discriminate between the various possibilities using X-ray analysis alone. By a combination of X-ray, DTA, TGA and chemical analysis, it has been possible to distinguish between four types of montmorillonite and 'non-ideal' types and between 'ideal' and 'non-ideal' beidellites. The 'ideal' type has 4OH groups per unit layer cell (a unit cell being twice the formula unit).

Studies on the surface esterification of montmorillonite and related silicate minerals by Berger[14] and specially by Deuel[15] and co-workers have been explained in terms of the existence of surface silanol groups, thus favouring the Edelman-Favejee concept. Apart from restrictions imposed by accessibility and steric factors, these hydroxyl groups are capable of reacting with certain organic compounds (e.g. CH_2N_2, $SOCl_2$, alkyl chlorosilanes) to yield covalently bonded organic complexes.

In montmorillonite less than 10% and more commonly only 2-3% of the total (external crystal and inter layer) area of $\sim 760 \times 10^3$ m^2kg^{-1} is apportioned to the crystal edges. Hence, the influence of the crystal edges on the pH-dependent charge and sorption of anions,. electron transfer reactions involving organic compounds, and the initiation and/or inhibition of polymerization of organic monomers is much more in evidence with kaolinite than with montmorillonite and mica-type minerals.

The inter layer expansion and collapse of vermiculite are influenced by the nature of the exchangeable cation as well as by

that of the inter layer liquid. In this respect and in its ability to form inter layer complexes with organic compounds,[16] vermiculite bears a striking resemblance to montmorillonite. Any subtle difference between vermiculite and montmorillonite, such as their respective response to contact with organic liquids, are usually ascribable to differences in the amount and location of isomorphous replacement. Thus, Mg -saturated vermiculites fail to expand beyond a basal spacing of $\sim$ 1.45 nm with glycerol (single-layer complex) where as Mg^{+2} -montmorillonite appears to give a double-layer complex with glycerol [d(001)~1.78 nm]. By the same token, the replacement of inter layer inorganic cations by alkylammonium ions in montmorillonite is complete in presence of appreciable amount of aqueous alkylammonium chloride in two hours at room temperature where as much longer period of contact and elevated temperatures are usually required to effect similar exchange in vermiculite crystals.

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SECTION IB

CLAY-ORGANIC INTERACTIONS

The establishment of structure and crystallinity of the main groups of layer silicates related to clay minerals initiated studies on the clay-organic complexes. It was postulated that complex formation between the clay fraction and the organic constituents of soils is responsible for the stability of the microbial [1-2]. Till 1960's X-ray diffraction was used almost exclusively to study the structure of the complexes formed between expanding 2:1 type layer silicate and organic compounds. The development of infrared spectroscopy along with improved methods of sample preparation has provided means to study the nature of the clay organic bond[3].

Water is perhaps the most common polar compound present in the interlayer space of bentonites and vermiculites. It is now established that water is also intimately involved in the binding and exchange of polar organic compounds on the surface of the mineral[4-6]. Walker and co-workers demonstrated, from X-ray diffraction studies, the existence of two distinct types of interlayer water in vermiculite crystals[7]. The first type (I) constitutes the inner (or primary) hydration shell around the exchangeable cation, i.e., the water is directly co-ordimated to the cation. The second type (II) being the outer (or secondary) co-ordination sphere of the cation where water is indirectly linked to the cation

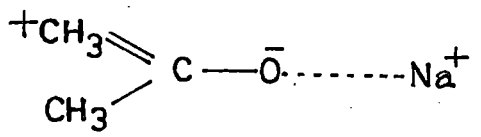
possessing greater mobility. It is now well accepted that the size and valency and hence the polarizing power of the exchangeable cation plays a decisive role in water absorption. This has been further supported by the infrared spectra of water adsorbed on layer silicates[8-11]. The broadening of the absorption band below 3500 cm^{-1} has been assigned to OH groups associated with the inter molecular hydrogen bonds. The preferential adsorption of polar organic compounds on the clay surface occurs due to the interaction between adsorbate and exchangeable cation. It might thus be expected that the removal of much of water from the clay surface would cause the cation to polarize the residual water molecules in the primary hydration shell. This results in the dissociation of water molecules and the protons generated are involved in the initiation of Color[12], polymerization[13] and decomposition reactions[14,15].

Hoffmann and Brindley[16] reported appreciable adsorption of non ionic aliphatic compounds of chain length C_5 to C_{10} on calcium-bentonite. But little or no adsorption of short chain organic compounds on bentonite from dilute solution (< 0.5 M) occurred. However, German and Harding[17] have reported that calcium and sodium bentonites adsorbed adequate amounts of primary n-alcohols viz. ethanol, propanol and butanol. This deviation from chain length rule of Hoffman and Brindley has been supported by Bradley for adsorption of some aliphatic amines[18]. The complex formation between clay minerals and organic compounds (other than alcohols)

of lower boiling points than water is limited due to the evaporation of both the solute and the solvent. In addition, the adsorption on clay surface is greatly influenced by the chemical character of the organic molecules. For many aliphatic compounds, a useful index of character is their 'CH activity' arising from the activation of methylene groups by neighbouring electron withdrawing substituents like $>C = O$ and $-C\equiv N$. At equilibrium concentration (m moles) the amount (m mole gm^{-1}) of C_6 - C_7 organic compounds of different functional groups adsorbed on the clay mineral in the order : α-methoxy-acetylacetone > acetoacetic ethyl ester > β-ethoxy propionitrile > hexanedione-2,5 > hexane diol-1,6 > 2,4-hexadiyne-diol-1,6[16].

Complex formation with polar organic compounds is profoundly affected by the nature of exchangeable cation and by the water content (hydration status) of the clay. Apparently, hydration of the clay facilitated acetone uptake, presumably due to the expansion of mineral interlayers. In an attempt to prepare acetone complex, it was found that dehydrated calcium bentonite invariably yielded a double-layer complex whereas the corresponding sodium clay gave either a single or a double layer complex[19]. This difference between calcium and sodium bentonites in their behaviour towards polar organic liquids accords with later findings of German and Harding[17] and Bissada et al[20] for ethanol-bentonite and acetone -bentonite systems and is ascribable to the greater

solvation energy of the calcium ion compared to that of sodium ion. The IR spectrospopic observation for the adsorption of acetone on sodium bentonite suggests an electrostatic interaction with sodium ion probably through the formation of the following resonance structure[21]



Similar observation has been reported for the complex formation between a number of aldehydes and clay minerals like halloysite and bentonite[19,22].

The formation of double layer complexes of bentonite with some ethers and polyethers and one-layer complexes of halloysite with some alcohol ethers has been reported[18,19]. From X-ray data the basal spacings of 1.31 - 1.34 and 1.57 - 1.76 nm were suggested for both single and double layer complexes respectively[16].

A comparative study for the adsorption of acetoacetic ethyl ester, $\beta:\beta'$-oxydipropionitrile, 2,5-hexanedione and triethylene glycoldiacetate from aqueous solutions on gibbsite, kaolinite and bentonite showed the expected highest adsorption on bentonite due to its largest surface area compared to all other

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minerals[23]. Gibbsite, on the other hand, showed the highest adsorption when the results are expressed per unit surface area or as an equivalent number of packed organic layers. In the absence of any exchangeable cation in gibbsite, cation-dipole interactions cannot be responsible for the uptake of polar organic molecules. As gibbsite is composed of hydroxyl ions, it would seem that O -H - O bonding is important.

Apart from alcohols, the complex formation between aliphatic or aromatic amines and 2:1 type clay minerals has received much attention. The basic information available are (i) the amines can exist in the cationic form like the corresponding alkylammonium ions which can replace the inorganic cations occupying exchange sites at the clay surface, (ii) adsorption of some primary n-amines by hydrogen bentonite is influenced by the pH of the system and by the size (chain length) of the organic molecule.

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SECTION IC

CLAY CATALYZED POLYMERIZATION

Clay minerals, due to their favourable structures, have found extensive use as fillers; catalysts for cracking, polymerization etc. In 1960's and earlier clay initiated polymerixations of vinyl monomers emphaized on the use of dry clay minerals and non polar solvents[1-3]. The choice of such reaction conditions was based on the observation that the activity of the dry clay minerals increased in non polar reaction media. Butadiene, trans and cis-butene-2 spontaneously polymerized on the external surface of neutral and acidic bentonites at room temperature and atmospheric pressure without additional catalysts[1]. The olefins were adsorbed on dry clay from systems like (i) solid-gas at reduced pressure at various temperatures (ii) solid-gas at room temperature and equilibrium pressure and (iii) solid-liquid at -78 or $0^{o}C$ for neat monomer or monomer dissolved in solvent.

Although the carbocationic polymerizations of vinyl monomers have been investigated extensively with Lewis acids such as BF_3, $BF_3.Et_2O$, BCl_3, $AlCl_3$, $TiCl_4$, $SnCl_4$, alkyl aluminiums etc[4-10], the first report on such polymerizations of styrene with acid clays (an alumino silicate with Lewis acid sites) came in 1964[11]. Almost 100% yield of polystyrene of molecular weights 500 to 2000 was achieved. The catalytic activity of the clay has been shown to be due to active protons associated with tetrahedral (due to

dehydration of the mineral) aluminium[12,13]. The formation of carbenium ion* following surface adsorption of olefins on acid sites caused subsequent polymerization. Proton accepting contaminants such as water, amines etc., being preferentially adsorbed over styrene, suppressed the polymerization. Styrene polymerized also on the surface of homoionic clays[14]. From the comparison of mineral structure and catalytic activity, it has been shown that dry kaolinite $\lceil Al_4Si_4O_{10}(OH)_8 \rfloor$ and attapulgite $\lceil (Si_{3.9}Al_{0.1})(Al_{0.68}FeMg_{1.22})O_{1.05} \rfloor$ were more active than bentonite $\lceil Al_{2-x}Mg_x)Si_4O_{10}(OH)_2 \rfloor$ or pyrophyllite $\lceil Al_2Si_4O_{10}(OH)_2 \rfloor$. Talc $\lceil Mg_3Si_4O_{10}(OH)_2 \rfloor$ failed to initiate the polymerization. On the other hand, bentonite (2:1 type structure), inspite of coating the edges with sodium hexametaphosphate, yielded traces of polystyrene; whereas kaolinite (1:1 type structure), under similar conditions failed to do so. The polymerization reaction characterizes a free radical as well as an ionic mechanism. It is, therefore, thought that an electron transfer from adsorbed styrene to the aluminium produced radical cations which rapidly dimerized. Both radical cations and dimers are involved in the initiation step but the propagation being cationic. Using activated clay minerals, however, styrene did not polymerize in the presence of ethanol, dioxane,

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* Such nomenclature has been put forward by J.P.Kennedy in "Cationic Polymerization of Olefins: A Critical Inventory", Wiley Interscience, New York, 1975.

ethylacetate and MMA within 30 minutes of the reaction. All these data lead to postulate that the active sites are the octahedral aluminiums at the crystal edges. These aluminiums act as electron acceptors.

Matsumoto, Sakai and Arihara[15] preferred the concept of Bronsted acidity rather than Lewis acidity responsible for the initiation of the polymerization of styrene on bentonite. The inconsistency in their experiments, however, is in the reduction of polymer yield in the presence of Trityl chloride which selectively adsorbs on Lewis acid sites. They argued in favour of the Bronsted acidity due to the fact that the replacement of exchangeable hydrogen ions by sodium or ammonium ions almost completely inhibited the polymerization. On reacidifying the mineral, however, the activity to polymerize styrene was restored. Since the degree of polymerization increased with the dielectric constant of the medium and almost independent of the initial monomer concentration, cationic mechanism for the initiation process was favoured[16]. This would apply equally well to the propagation process and, therefore, the initiation by a radical ion mechanism cannot be ruled out[14]. The possibility of proton transfer to monomer leading to decreased average degree of polymerization,similar to conventional cationic mechanism, has also been discussed[12].

The work of Matsumoto et al[15] along with Solomon and Rosser[14] lead to infer that acidity of clay cannot be solely ascribable to either Bronsted acidity or Lewis acidity. It has to

be understood that dry mineral surface is very acidic due to the polarisation of residual water molecules by the exchangeable cations. Such acidity is influenced by the solvent as evident from the blue coloration of aqueous benzidine in the presence of oxidized bentonite. Instead a yellow color appeared when a benzene solution of benzidine was treated with dry clay mineral[16,17]. Solomon and Rosser failed to find evidence of styrene interacting with the clay mineral which led to assume that styrene is either incapable of moving into the interlayer space or do so with difficulty.

The polymerization of MMA on such clay minerals has not yet received much attention. The failure of MMA to polymerize can be accounted for in the light of well accepted mechanism of charge transfer from the monomer to the clay mineral to produce a radical cation which is a non-propagating species for the polymerization of MMA. However, Dekking could prepare MMA bentonite complex using the conventional free radical initiator, 2-2'-azobis isobutyramidine AIBA[24]. The polymerization of MMA and methyl acrylate in bentonite interlayer induced by γ-radiation has been studied by Blumstein and co-workers[18-21]. The interlayer polymers were difficult to isolate by the usual solvent extraction and could only be isolated by treating the clay-polymer complex with hydrofluoric acid which damaged most polymers. Glavati et al[22] found that polymerization of acrylonitrile/bentonite complex by γ-radiation produced stereospecific polymers.

Thermal polymerization of a number of vinyl monomers e.g., MMA, acrylamide, vinyl acetate, 4-vinyl pyridine could be induced by bentonite if AIBA was previously introduced to the clay mineral[23]. The cationic form of AIBA goes to the exchange sites in kaolinite and bentonite to form AIBA-clay complex which decomposes thermally to generate free radicals. The complex has high initiating efficiency. The rate of polymerization with the AIBA-bentonite complex initiator was greater than that for AIBA alone[24]. It has been proposed that the free radicals remain attached to the adjacent planes of AIBA-bentonite dispersed in water, and on heating, these planes move away from each other allowing more water to penetrate. This can be represented as:

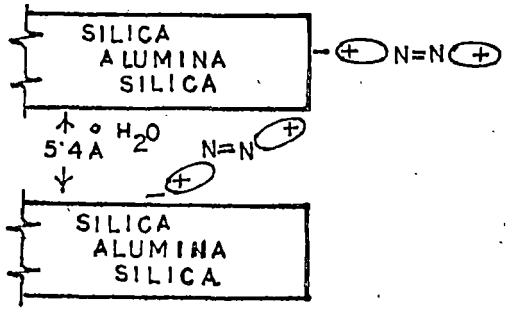


FIG-4

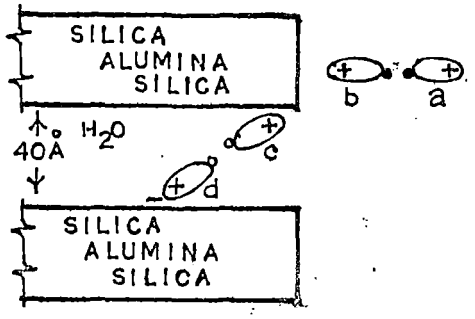
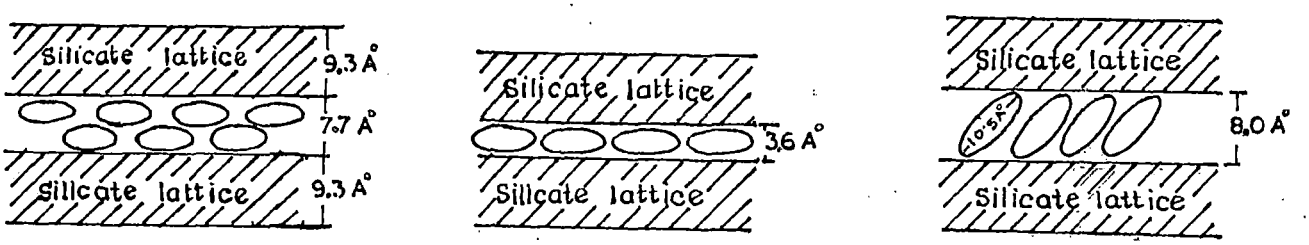


FIG-5

From X-ray studies it was concluded that type 'c' and 'd' radicals do not recombine but move apart due to driving force of water. Once the radicals are separated by some 30Å, they can initiate the polymerization. Of the three types of free radicals formed during the decomposition of the AIBA-clay complex, only type 'a' (Fig. 5) can form homopolymer, and type 'a' radicals are free to be deactivated through recombination with type 'b'. Fig. 5 also explains how the formation of homopolymer may be greatly decreased while the formation of graft polymer (from clay) is increased by decomposing the AIBA-bentonite complex. If the clay is dispersed in methanol, latter surrounds the intercalated free radicals inhibiting their separation and thus facilitating the graft polymer formation.

Solomon and Loft[25] worked with a series of acrylates and methacrylates and, from X-ray data suggested an interlamellar complex formation between monomer and bentonite. This can be illustrated by Fig. 6.



TYPE I

Two monolayers lying flat (spacing shown is for MMA)

TYPE II

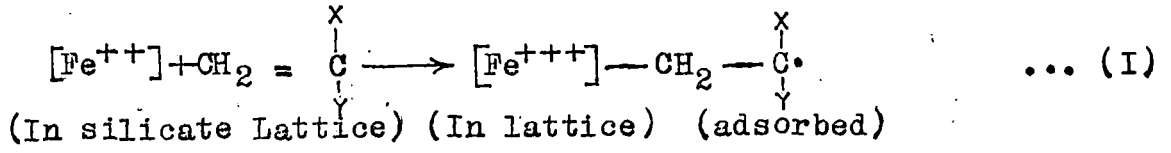
One monomer layer lying flat (spacing shown is for dimethyl amino ethyl methacrylate)

TYPE III

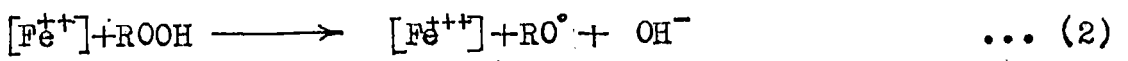
One layer of inclined monomer molecules (spacing shown is for hydroxy ethyl methacrylate)

Fig. 6

Only type III is responsible for spontaneous polymerization of acrylic monomers in presence of a peroxide initiator[25]. The polymerization of hydroxy methacrylates has been suggested to be due to the presence of electron donating sites within the silicate lamellas. The inclined orientation of the hydroxyl groups gave a favourable orientation for initiation, and the propagation involved radical anions. The following mechanisms have been forwarded:



(In silicate Lattice) (In lattice) (adsorbed) ... (I)



(In lattice) (In lattice) ... (2)

Iron is shown as the oxidizable atom in the silicate lattice although other transition metals may be present. In mechanism I the radical anion is formed via electron transfer from the mineral to the double bond. The mechanism is similar to that proposed for the polymerization of olefins by transition metal catalysts.

The influence of aluminosilicates and magnesium silicates on the free radical polymerization of MMA has been studied in terms of termination reaction and supported by studies of the reaction of stable free radicals with the minerals. It has been shown that the ability of a mineral to inhibit polymerization follows the

order: attapulgite > kaolinite > montmorillonite > talc. In the absence of clay mineral the yield of polymethylmethacrylate PMMA was 3.68% (Mol. wt. 1.36×10^{-6}) whereas with kaolinite and montmorillonite the yields were 0.51% (Mol. wt. 2.81×10^{-6}) and 0.68% (Mol. wt. 3.05×10^{-6}) respectively. That the decreased amount of polymer in the presence of the mineral is not due to the depolymerization has been established by heating PMMA with kaolinite and determining the viscosity average molecular weight before and after the treatment.

A recent study[30] on the polymerization of vinyl monomers on clay surfaces shows that MMA, vinyl chloride, and acrylonitrile were homopolymerised and co-polymerised with 2-dimethyl amino ethyl methacrylate in the presence of halloysite. The polymer yield can be increased by preheating the mineral with 50% sulphuric acid. The polymerization rate dropped for solution polymerization and, among different solvents tested the highest polymerization rate was obtained with benzene in the presence of benzoyl peroxide. In redox polymerization in the presence of N-N-dimethyl aniline and benzoyl peroxide, the adherence of the polymer to the clay surface was noticed for both homopolymer and copolymer formed. Among the monomers tested acrylonitrile gave the lowest yield and among the clay minerals, talc was found to be more active for polymerization to occur. However, bonding between the mineral and polymer is least with talc. One more recent work[33] involved ESR study to assess the state of Fe in bentonites. The absorption bands in the weak field

as g values 7.6, 4.2 and 3.9 were assigned to Fe^{+3} ions in the octahedral layer of montmorillonite. The intensities of the wide bands of the spectra remained unchanged when the cations were altered at the exchanging sites. This indicated that the montmorillonite had practically no iron in the ion exchangeable positions. When the clay mineral was treated with sulphuric acid there was a decrease of the amplitude of the bands for structural iron. The decreased intensities of the narrow bands in the weak field (g = 3.9 - 7.6) with an increase in sulphuric acid concentration provided a measure of the break down of the clay mineral during acid activation.

Studies on the structural properties of the polymers from clay catalysed polymerizations of vinyl monomers have been made by several workers. Blumstein and co-workers[10,18], noted that the thermal stability and dilute solution properties of the polymers prepared in the presence of clay minerals differed significantly from those obtained using conventional free radical technique and suggested that the interlayer PMMA developed a two-dimensional sheet structure in the presence of a cross linking agent during the polymerization. Analysing the n.m.r. data they concluded that PMMA probably, consisted predominantly of short isotactic sequences. Small scale stereoregularity of this kind could be ascribed to the orientation induced in the intercalated monomer by ion-dipole interactions between the interlayer sodium cations of the bentonite and the ester carbonyl group of the monomer. Earlier, Glavati et al[22] reported to have oriented stereoregular poly(acrylonitrile) and

poly (acrylic acid) using similar procedures.

Theng reported[31,32] that the influence of clay minerals on the polymerization reactions extends beyond direct action on the monomers. The chemical compounds used as polymerization initiators may also be modified by the minerals. It has been observed that clay minerals could affect both the rate and products of decomposition of initiators.

A mere recent work[33] reported that PVC or a vinyl acetate vinyl chloride copolymer modified by a latex of Butyl acrylate - Methylmethacrylate copolymer, Butadiene-Styrene copolymer, poly (Methylacrylate) or a similar polymer was prepared by adding the latex to the reactor during the suspension polymerization. The addition was made after 30-95% conversion of monomers. If inorganic compounds such as silica, bentonite, or Ca phosphate was added before or during the addition, the polymers with satisfactory particle size separated out from the aqueous suspension.

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CHAPTER - II

Object and Scope

Majority of the polymerization systems with clay minerals comprises of non polar solvents along with free radical initiators. Limited data are available, on the other hand, for aqueous polymerizations in the presence of clay minerals.

During scouting experiments it was observed that polymerization of monomer like methylmethacrylate can be initated by aqueous suspension of hydrogen, Na, Cu etc. bentonites only in the presence of alcohols and thiols. The present investigation, therefore, was directed to understand

1. the new initiating system
2. limitations

and establish the feasibility of its application.

Hydrogen bentonite/alcohol initiating system is characterised by 33% initiated efficiency (with respect to total weight of clay), negligible transfer to monomer and alcohol with an apparent activation energy of ~ 15 KCal $mole^{-1}$. Not only the aqueous suspension but also dry clay impregnated with alcohol is as effective in polymerizing methylmethacrylate. Easy operational conditions and high molecular weight product could be favourable for this initiating system.

This initiating system, however, suffers from apparent drawbacks.

1. Inability to induce polymerization of monomers like acrylonitrile,

methacrylonitrile etc.

2. The polymers molecules are trapped within the clay layer and cannot be totally separated. These drawbacks, however, are advantageous for certain applications.

1. The ability of this initiating system to produce copolymer of acrylonitrile or methacrylonitrile with other monomers with almost negligible amount of homopolymers of the first two monomers. The copolymers of acrylates e.g. ethylacrylate and acrylonitrile have important applications in coating and also to resist soiling and aging.

2. Clay-Polymer adduct obtained from this polymerization system can be efficiently used in agriculture because of its water repelling nature. Because of the incorporation of polymer molecules into the clay mineral matrix, the exchange capacity of the latter is changed significantly. This might find application in obtaining membrane electrodes of different standard potentials. Furthermore, the clay-polymer adduct having reduced surface area than the present clay mineral would certainly influence clay catalyzed reactions.

Other future scopes for this system have to be established by polymerizing other monomers and finding specificity, if any.

CHAPTER - III

EXPERIMENTAL

IIIA. Materials and Purification

i) Bentonite (Evans Medical Co., England) : An aqueous suspension of 25 lit. was prepared by stirring continuously 100 gms of bentonite in distilled water. The suspension was maintained at pH ~ 8 with NaOH solution. After every 24 hours, 10 cm layer of the suspension (from the top) was siphoned out and each time the original volume was restored by adding water. This process resulted in particle size less than 2μ. The clay collected, on acidification with HCl to pH ~ 4, settled at the bottom of the container by coagulation. This coagulated portion was stirred continuously with 30% (v/v) H_2O_2 (2 ml per 3 lit. suspension) in a large beaker followed by heating on a water bath for a long time with occasional stirring to ensure complete removal of H_2O_2. On cooling, the suspension was passed successively through columns packed with Amberlite IR-120 and Amberlite IRA-400. The hydrogen bentonite HB suspension, thus obtained, was stored at 5-10°C.

ii) Monomers: Methylmethacrylate MMA (BDH) was washed repeatedly with 2% NaOH solution, water to remove NaOH, dried over fused $CaCl_2$ at 0°C. It was distilled before use under reduced pressure (~ 2 mm) and the middle fraction was collected (35°C).

Acrylonitrile ACN (BDH) was washed with 5% Na_2CO_3 solution followed by acidifying with dilute H_2SO_4. The monomer was acid freed

by repeated washing with water. It was dried over fused $CaCl_2$ for 24 hours at $0^{\circ}C$ and pure ACN was obtained by distillation just before use.

Methacrylonitrile MACN (Gift Sample) was washed and dried following similar method as for ACN. It was distilled fractionally under reduced pressure (~ 1 mm) before use and the middle fraction ($30^{\circ}C$) was collected.

iii) Solvents: Benzene (C.P) was thiophene freed with conc. H_2SO_4, neutralised with aqueous $KHCO_3$, washed several times with water, and finally dried over P_2O_5. It was filtered and distilled into a brown bottle.

Rectified Spirit (C.P) was treated with proportional amount of freshly burnt quicklime and kept overnight. Absolute ethanol was obtained on distillation and the middle fraction ($78^{\circ}C$) was stored in a sealed brown bottle.

n-propanol, n-butanol, isobutanol and tert-butanol were dried over anhydrous K_2CO_3, filtered and fractionally distilled.

N,N'-dimethylformamide DMF (B.D.H) was stored over P_2O_5 for nearly 10 hours and distilled.

Methanol (E. Merck, Analytical Reagent), tetrahydrofurane THF (Fluka, AG), diphenyl-picryl hydrazyl DPPH (Sigma), petroleum ether (C.P) and sodium hexametaphosphate (obtained from Prof. B.K. Theng, New Zealand) were used as received.

Water was distilled with alkaline $KMnO_4$.

iv) Nitrogen: The commercial grade (Indian Oxygen Ltd) was passed through a series of bubblers containing Fiesser's solution[2]. The oxygen free nitrogen was dried by passing through 2 bubblers containing conc. H_2SO_4.

IIIB. Polymerizations

i) Homopolymerization: The polymerization of MMA was carried out in 100 ml ground joint pyrex bottled (outside painted black). Measured amount of alcohol was added, under N_2, to known volume of HB suspension in the bottles, stoppered, shaken vigorously and allowed to equilibrate at the polymerization temperature. The polymerization was started by adding MMA under N_2 and shaking well. Control runs were carried out side by side without alcohol. The bottles were withdrawn from time to time and the reaction was arrested with alcoholic solution of DPPH followed by chilling. The solid mass was separated by centrifugation ($16-17 \times 10^3$ r.p.m), dried in a vacuum oven at $40^{\circ}C$ and weighed.

ii) Copolymerizations:

The copolymerization was carried out in 100 ml standard joint stoppered bottles with different monomer compositions. The process was similar for reactions with both the monomers (MMA and MACN). The copolymers separated out when the reaction were carried out at the same time intervals but different monomer compositions and were separated by centrifugation ($\sim$ 16000 r.p.m)

dried in vacuum oven at the room temperature. The purification was made from dimethyl formamide in which the copolymer was soluble. The pptn. of the copolymer was made from petroleum ether. Such a purification of the copolymer is carried out three to four times and then dried in the vacuum oven at the room temperature. The infrared spectroscopy reading of the copolymer and its glass transition temperature confirmed the formation of the copolymer.

III C. Polymer Separation

i) Polymethylmethacrylates

Non-extractable (polymer bonded to bentonite) and extractable polymethylmethacrylates PMMA's were separated by repeated extraction (Soxhlet) of the whole mass with benzene followed by centrifugation. Benzene extracted PMMA was purified by repeated precipitation into a mixture of methanol and petroleum ether followed by drying under vacuum at 40°C.

ii) Copolymers:

The copolymers of MMA - MACN and MMA - ACN are very hard and sticky due to characteristic nature of the nitrile polymers. The copolymers are found to be hardly soluble in DMF and THF and almost insoluble in benzene. Moreover, the copolymers are degraded at the higher temperature (at 40°C and above) to a significant extent. Such a property makes the separation of the copolymer a formidable task. Of the solvents used, THF has been found to be suitable one for the separation of the copolymer at or below 35°C. Still there remains a large amount of the copolymer intimately adhered to the mineral

particles. Repeated extraction with the solvent produces about 80% of the total copolymer formed. The copolymer is precipitated from petroleum ether. The pure copolymer is obtained by dissolving it in THF and then precipitating from petroleum ether for three to four times.

III D. Fractionation:

The polymer, PMMA, is made free from the extraneous admixtures like, clay mineral, unreacted monomer etc. before going for fractionation. Extraction, washing with Benzene or DMF, reprecipitation from Petroleum ether/methanol mixture are carried out for this purpose. After the above treatments the sample is dried to constant weight by putting the sample in vacuo at room temperatures. The fractional precipitation is then carried out by the procedure given as follows. The polymer solution in benzene is placed in a constant temperature water bath in a beaker at 30°C. When the solution has attained the temperature of the bath, Methanol as used for the precipitation of the lower molecular weight fraction is gradually added from a burette and the solution is stirred thoroughly but gently until the faint turbidity redissolves. The stirring with high speed is avoided to prohibit the degradation of the polymer. The degree of turbidity of the solution serves as an indicator of the amount of the precipitant required to redissolve the precipitate a given fraction. The solution with the precipitant (methanol) is gently warmed to

redissolve the precipitate, and then gradually cooled in the thirmostat. Phase separation occurs after a while, and the phases are isolated from each other by filtration. The first two fractions are isolated in the same way by further successive addition of methanol to the solution. The last fraction is isolated by addition of large volume of petroleum ether (B.P. 60^{o} - 80^{o}C). Sometimes each fraction is refractioned to get more narrow range of molecular weight fragments.

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CHAPTER - IV

IVA. Introduction

Polymerization of MMA is found to be successful only with alcohols in combination with bentonites in H^+, Na^+ and Cu^{+2} forms. The alcohols are, however, the chain transfer agents. The molecular weights of PMMA's obtained in these systems are as high as obtained in conventional free radical polymerizations. Detail studies of polymerization has been done with MMA and H^+ form of bentonite in conjunction with ethanol. Molecular weights, molecular weight distributions, thermodynamic parameters, spectroscopic and other qualitative data suggest a free radical mechanism.

IVB. Results

IVB (i) Effect of Alcohols: The polymerization reaction is sensitive to impurities and, therefore, purification of alcohols, normaly containing traces of aldehydes, is essential. The polymerization of MMA with aqueous suspension of HB alone at $60^{o}C$ under N_2 results in nearly 2% PMMA. Under identical conditions, but in the presence of alcohols, significant amounts of PMMAs are obtained. M_vs' of PMMAs' harvested with HB and alcohols of chain lengths C_1 to C_4 are essentially the same for similar conversions of 49-57% inspite of their different chain transfer constants. Not only alcohols but also thiols produces high molecular weight PMMAs' in reasonably good yields. Higher polymer yields are obtained with an increase in ethanol concentration [Table - 1]. Detail

investigation of polymerization of MMA with HB/alcohol is conducted with ethanol because of its low toxicity and relatively high boiling point. A 500 fold increase in ethanol concentration increased the conversion from 25% to 68% (Table 2). 100% conversion, however, could not be achieved even after a week. M_vs' decreased initially but attained a constant value afterwards. N_vs' increased parallely

Table - 1

Polymerization of MMA in the presence of different alcohols: $[HB] = 0.8\%$ (w/v), $[MMA] = 0.374M$, $[Alcohol] = 0.34M$; Total volume : 50 ml, 60°C, 6 hrs.

Alcohol	a	$C_A^b \times 10^4$	Conversion (%)	$\bar{M}_v \times 10^{-6}$	$\bar{N}_v^d \times 10^6$
Methanol	32.70	0.24	54	1.92	0.52
Ethanol	24.25	0.40	57	1.98	0.54
n-propanol	20.13	0.69	50	2.00	0.50
Isopropanol	18.41	0.58	49	1.98	0.46
n-butanol	17.51	0.25[c]	51	1.80	0.52
Benzene thiol	-	-	50	1.96	0.51
Control	-	-	1.5	-	-

a: Dielectric constant at 25°C; b: Chain transfer constant to alcohol for the free radical polymerization of MMA at 60°C; c: Data at 80°C; d : Viscosity average moles of PMMA.

and remained constant at $\sim 5 \times 10^{-7}$. Complete inhibition of the polymerization reaction is observed with Diphenyl picryl hydrazyl (DPPH) an inhibitor for such reactions. The molecular weight distributions

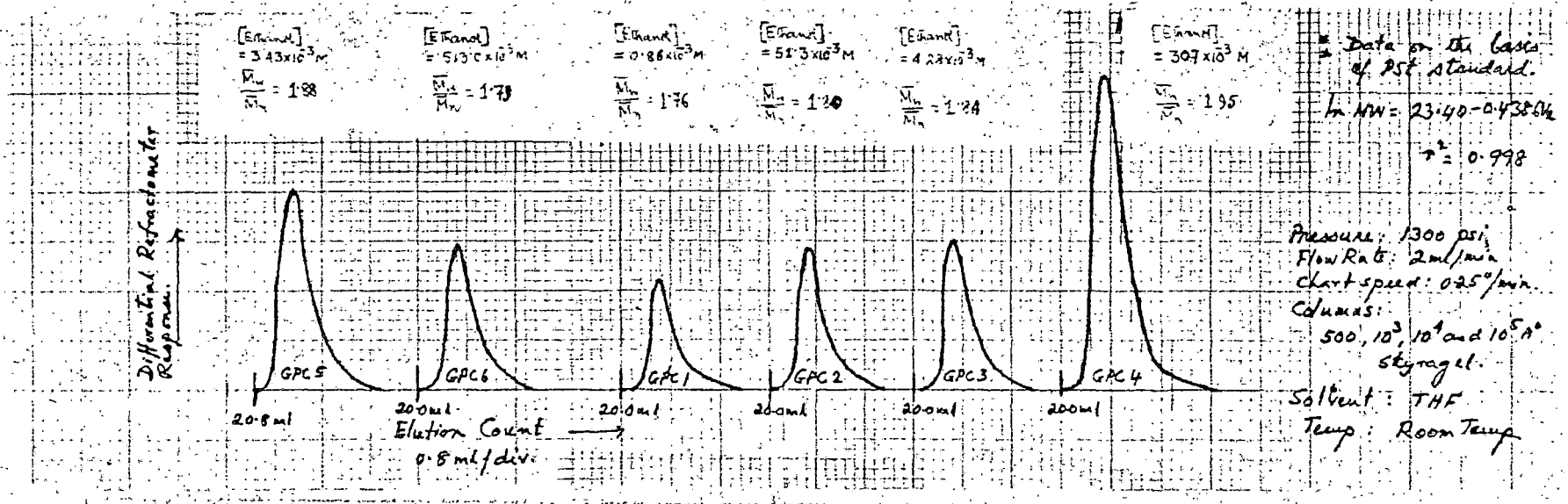
($\bar{M}_w / \bar{M}_n$) calculated from Gel Permeation Chromatograms (Figure 7) were nearly constamt in the ethanol concentration range studied. Such studies are necessary to ascertain the mode of termination in the polymerization process.

Table - 2

Polymerization of MMA in the presence of varying amounts of ethanol : $[HB] = 1.08\%$ (w/v), $[MMA] = 0.374$ M; Total volume : 50 ml, 60°C, 12 hrs.

Ethanol , M x 10^3	Conversion (%)	$\bar{M}_v \times 10^{-6}$	$\bar{N}_v \times 10^6$	$\bar{M}_w / \bar{M}_n$
-	2.0	-	-	-
0.86	25.2	4.13	0.11	1.76
3.43	30.7	3.70	0.15	1.88
4.28	35.8	3.12	0.21	1.84
5.13	42.25	2.73	0.29	-
21.40	48.3	2.60	0.35	-
51.30	55.6	2.33	0.45	1.80
102.60	62.9	2.15	0.55	-
307.80	65.4	2.20	0.55	1.95
513.00	68.2	2.40	0.53	1.79

In all polymerizations an induction period of ~ 90 mins. is observed. Once the polymerization is started it increased rapidly with time. Higher overall initial rate is associated with



of PMMA obtained

Fig.7. G.P.C. at different ethanol concentrations; [MMA] = 0·374 M; [HB] = 1·08% (W/V); 60°C, 12 hrs.

higher ethanol concentration (Figure 8). The conversions, after 13 hours of polymerization, with 0.8% HB and 0.68, 1.03 and 1.37M ethanol are 55, 65 and 75% respectively. Distinguishable differences in $\bar{M}_v$s' and conversions are registered for reactions carried out in shaken and unshaken conditions. A vigorous shaking of the reaction mixture at the desired temperature increases the amount of PMMA and the $\bar{M}_v$. The time-conversion plots are shown in Figure 9 . With similar reactant concentrations and temperature the conversions after six hours for shaken and unshaken PMMA's are discussed later.

IVB(ii) Effect of clay concentration: It has already been pointed out in the preceeding section that the polymerization of MMA occurs only in the presence of combined HB and ethanol. No conventional initiator is necessary to induce the reaction. The rates are dependent on the concentration of HB. The polymerization almost ceases with 0.3% (w/v) or less HB when ethanol and monomer concentration are kept at 0.34M and 0.562M respectively. The conversions after 12 hours of polymerization with 12.1 gm, 10.0 gm, 7.5 gm, 5.0 gm and 3.5 gm per litre of the HB suspension have been found to be 62.15%, 53.04%, 44.75%, 26.31% and 14.55% respectively. Both $\bar{M}_n$ and $\bar{N}_n$ increases with increasing HB concentration and have been shown in Table 3 . The induction period is found to be strongly dependent on HB concentration. Thus, induction periods of 55, 65, 95, 120, 145 minutes are observed with the above concentrations of HB (Figure 10).

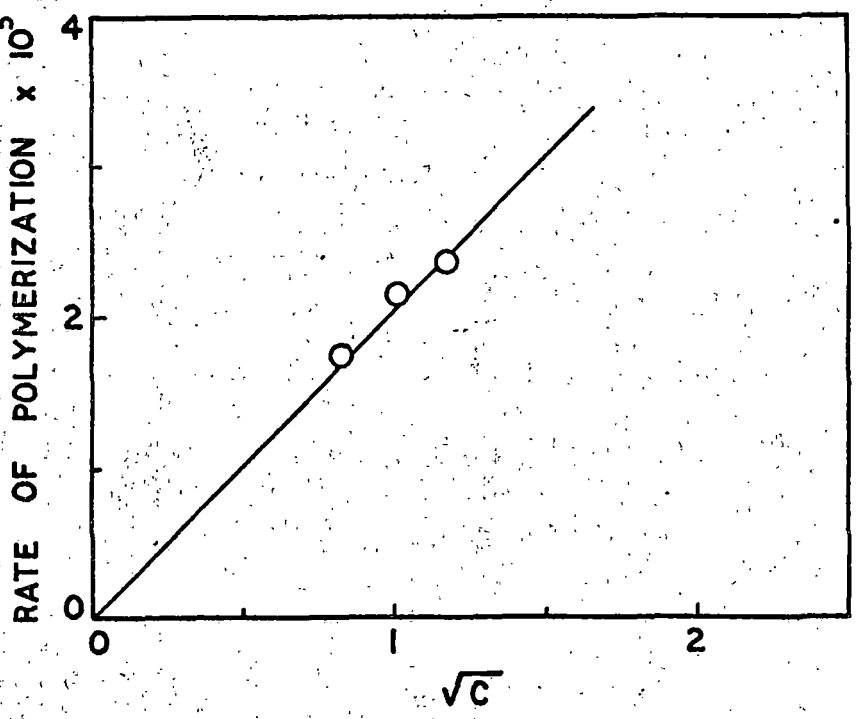


FIG.8. RATE OF POLYMERIZATION AS A FUNCTION OF (ETHANOL CONCENTRATION IN MOLES / LIT.)$^{0.5}$

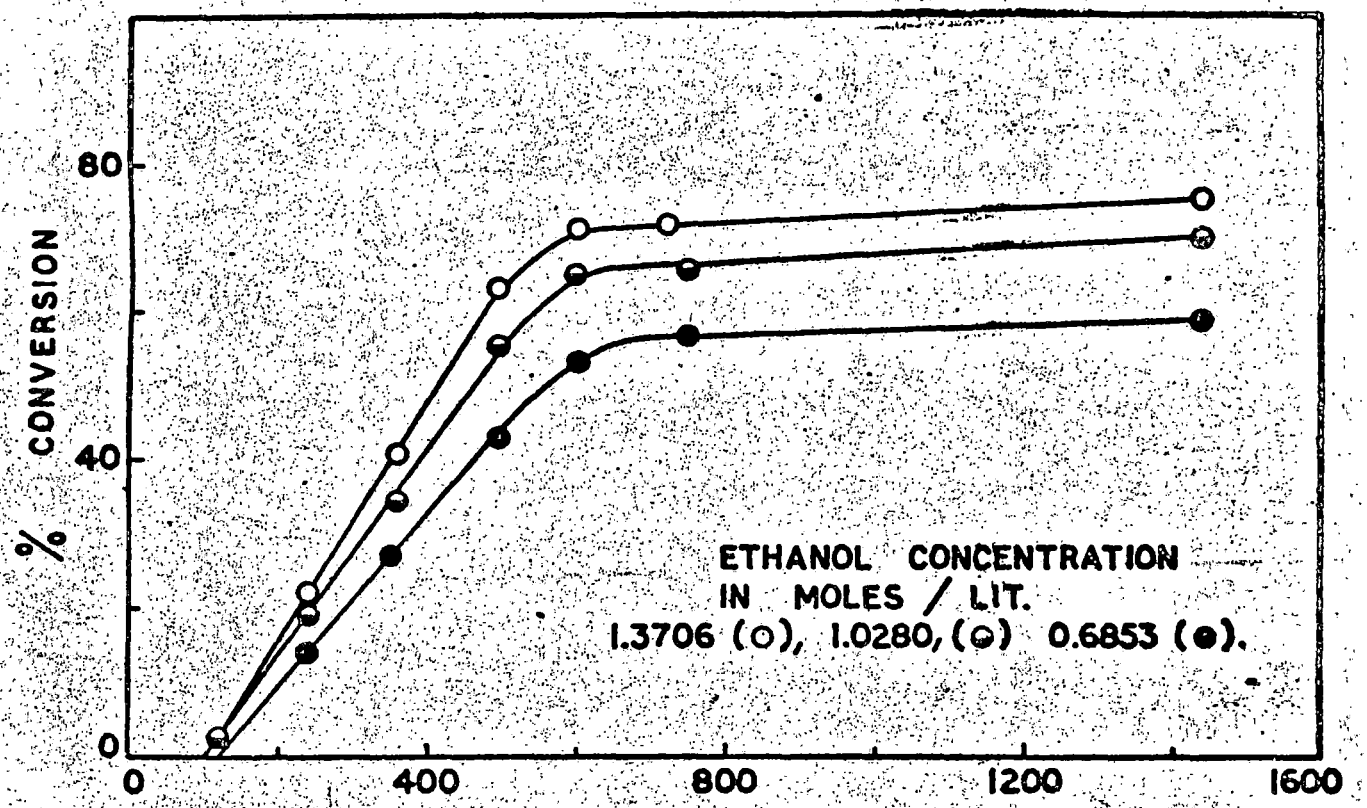
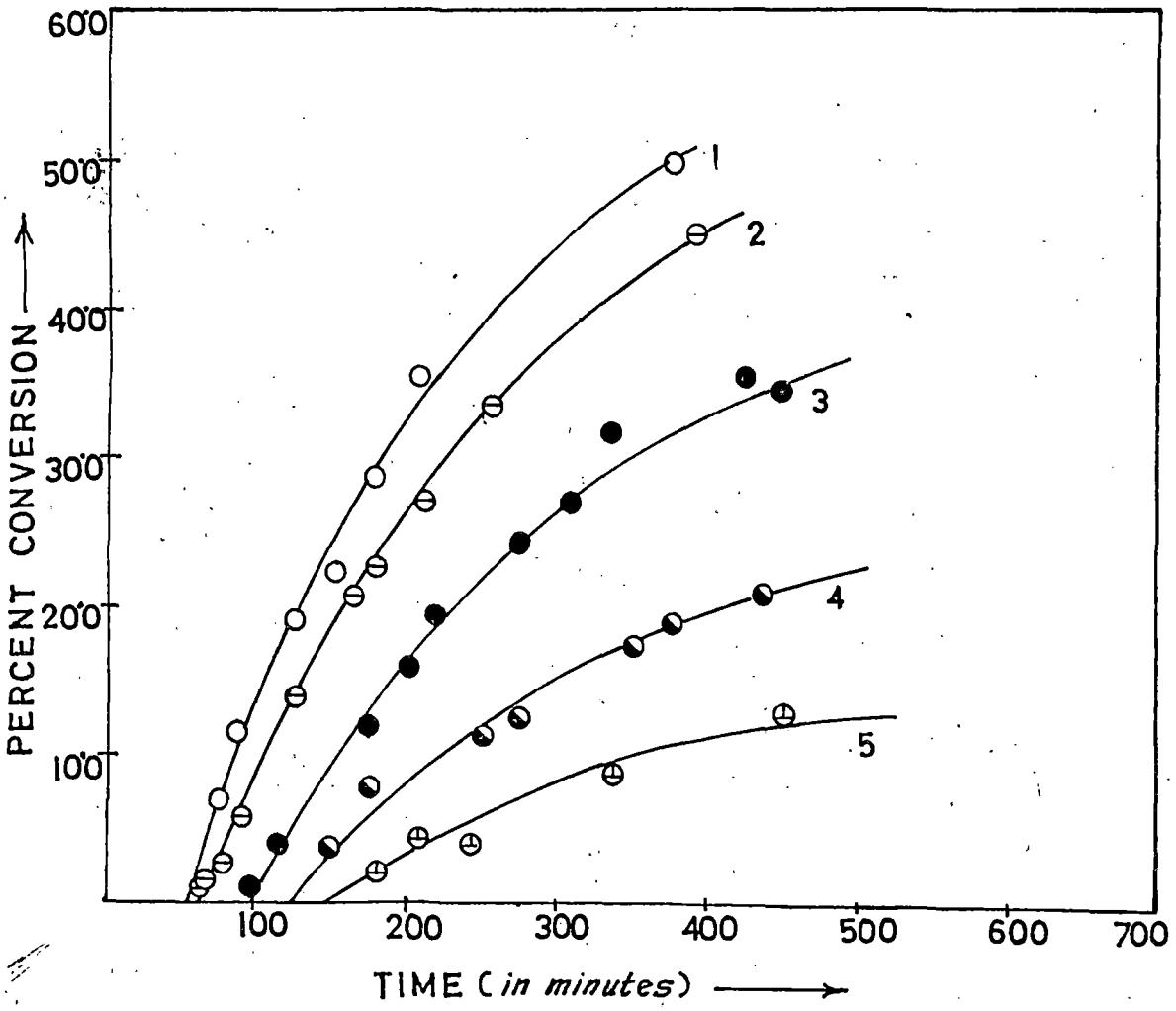


FIG. 9. TIME CONVERSION PLOT FOR DIFFERENT ETHANOL CONCENTRATIONS.

FIG. - 10.



Time-conversion plots for aqueous polymerization of MMA at 60°C with HB/Ethanol.; (MMA) = 0.562M; (Ethanol)=0.34M; and(HB) in W/V = 1.21%(1); 1.00%(2); 0.75%(3); 0.50%(4) and 0.35%(5).

Table -3

Polymerization of MMA in the presence of different amounts of HB : [MMA] = 0.562 M; [Ethanol] = 0.34 M; 60°C, 12 hrs. Total Volume : 50 ml.

Clay concentration (gms lit^{-1})	Maximum conversion (%)	$R_o \times 10^5$ (Moles Lit^{-1} Sec^{-1})	$\bar{M}_n \times 10^{-6}$	$\bar{N}_n{}^a \times 10^6$
12.1	62.15	2.248	2.01	0.87
10.0	53.04	1.99	1.92	0.78
7.5	44.75	1.592	1.83	0.69
5.0	26.31	0.781	1.75	0.42
3.5	14.55	0.527	1.52	0.27
*Controls	-	-	-	-

*Four control runs with four HB concentrations, without alcohol.

a Number average moles of PMMA : $\bar{N}_n = \frac{\text{gms of PMMA}}{\bar{M}_n}$

Not only the hydrogen form of bentonite but also Na^+, and Cu^{+2} forms are almost equally efficient in initiating the polymerization with ethanol. Once again, either form of bentonite is ineffective when used alone. The results of such polymerisation are tabulated below (Table 4).

Table - 4

Influence of cations of clay mineral for the polymerization of MMA in the presence of Ethanol: $[\text{Clay}] = 0.632\%$ (w/v); $[\text{Ethanol}] = 0.343$ M; $[\text{MMA}] = 0.374$ M; 60°C; 12 hrs. Total volume = 50 ml

Nature of cation	Maximum conversion (%)	$R_o \times 10^5$* Moles Lit^{-1} Sec^{-1}	$\bar{M}_v \times 10^{-6}$
H^{+1}	55.11	1.29	1.12
Na^{+1}	56.02	1.33	1.14
Cu^{+2}	43.24	1.22	1.03
Control**	-	-	-

* Calculated from time-conversion plot at conversions below 20%

** Control runs are done with H^{+1}, Na^{+1}, Cu^{+2}-bentonites in the absence of ethanol.

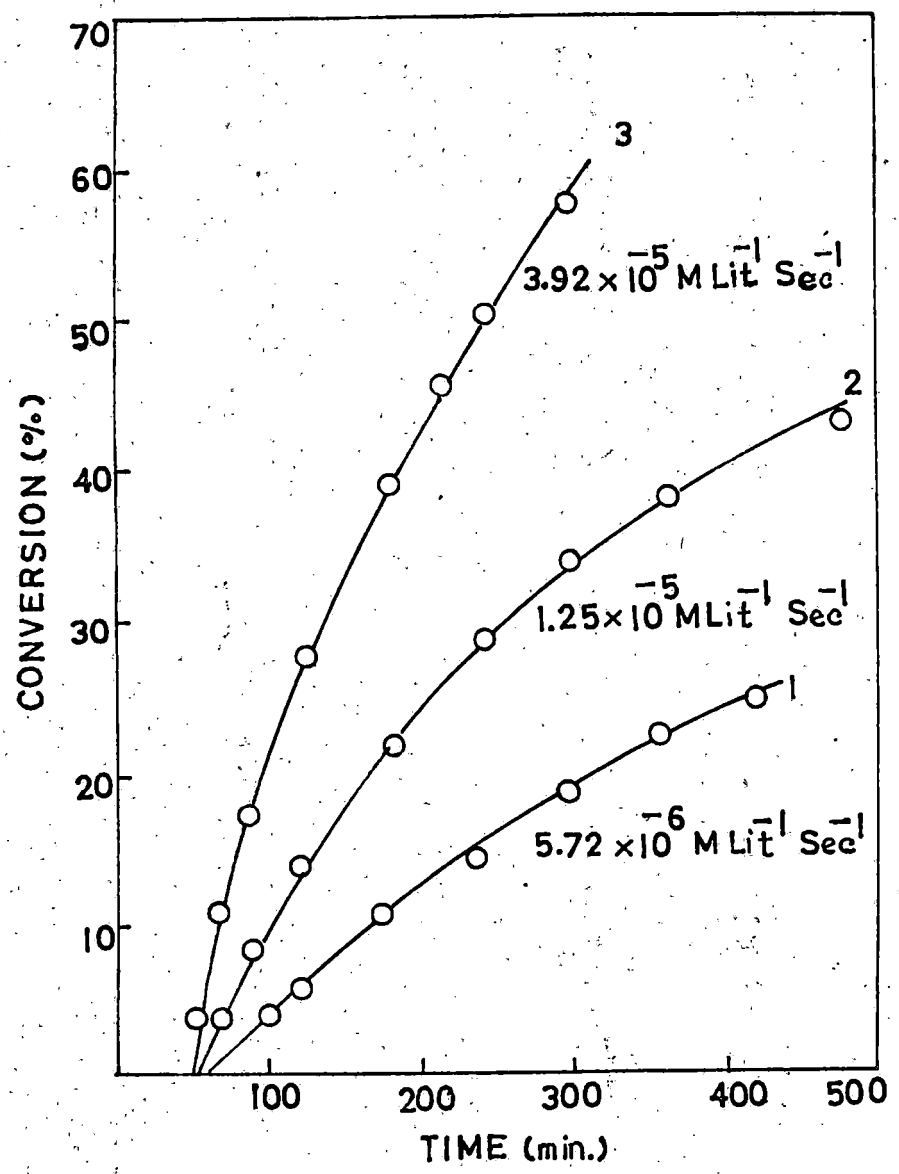
It is clear from the table that the overall initial rates of polymerization with H^{+}, Na^{+} or Cu^{+2} bentonites are quite comparable.

IVB(iii) Effect of Temperature:

For an approach towards suggesting a mechanism for the polymerization of MMA with HB/ethanol system, the study of the effect of temperature is necessary. It will give different energy parameters like, enthalpy change, entropy change etc. for the reaction. It is known that the specific reaction rates depend on the reaction temperature.

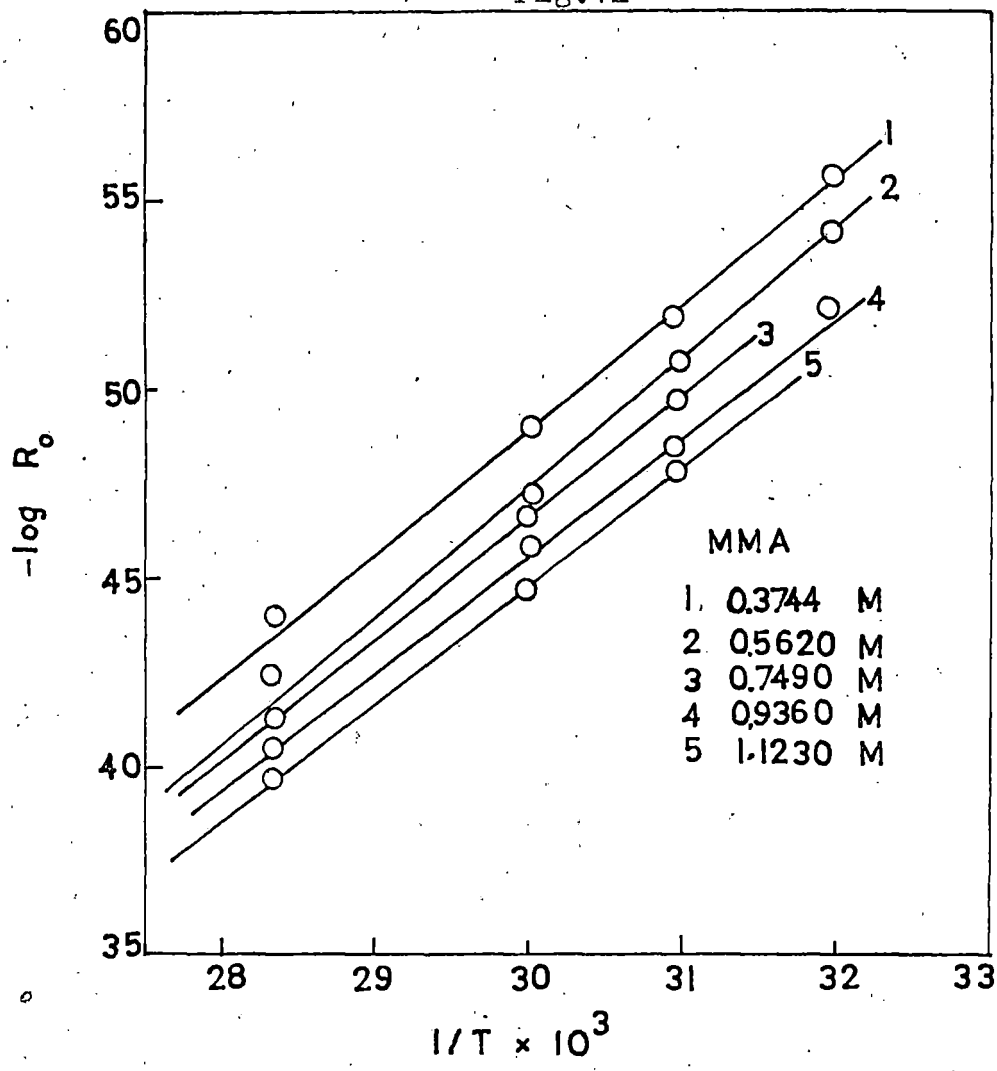
With HB/ethanol system as the initiator, the polymerization of MMA is studied over 12 hours. The amount of PMMA and R_os' increase with increasing temperature. Increase in overall initial rate of polymerization from 5.72×10^{-6} moles lit^{-1} sec^{-1} at 50°C through 1.25×10^{-5} moles lit^{-1} sec^{-1} at 60°C to 3.92×10^{-5} moles $lit^{-1} sec^{-1}$ at 80°C is significant (Figure 11). An approximately rate of polymerization is very low at 40°C, no polymerization is observed to occur within 48 hours. The activation energy can be obtained from the Arrhenins equation $k = A \exp(-E_a/RT)$ where symbols have their usual meaning. The overall activation energy E_a has been from the slopes of plots of $-\log R_o$ vs I/T for various MMA concentrations (Figure 12). A value of 15.0 Kcal $mole^{-1}$ is lower than usually obtained for aqueous polymerization of MMA with redox initiators. This is, however, is apparent activation energy since correction due to the heats of adsorption of MMA on HB has not been made. Other activation parameters, $2E_p - E_t$, E_d have been determined from K_p^2/K_t values at 50, 60 and 80°C and calculated using the relation $E_a = E_d/2 + (E_p - E_t)/2$. These values are shown in Table 5. The value of E_d is 17.0 Kcal $mole^{-1}$ and is comparable to the conventional initiators. Activation energy for $\overline{DP}_n$, calculated from the plot of $\log \bar{M}_n$ vs I/T (Figure 13) is -3.2 Kcal $mole^{-1}$. This suggests that transfer is insignificant. Other thermodynamic parameters for the polymerization have been tabulated (Table - 6).

FIG. - 11.



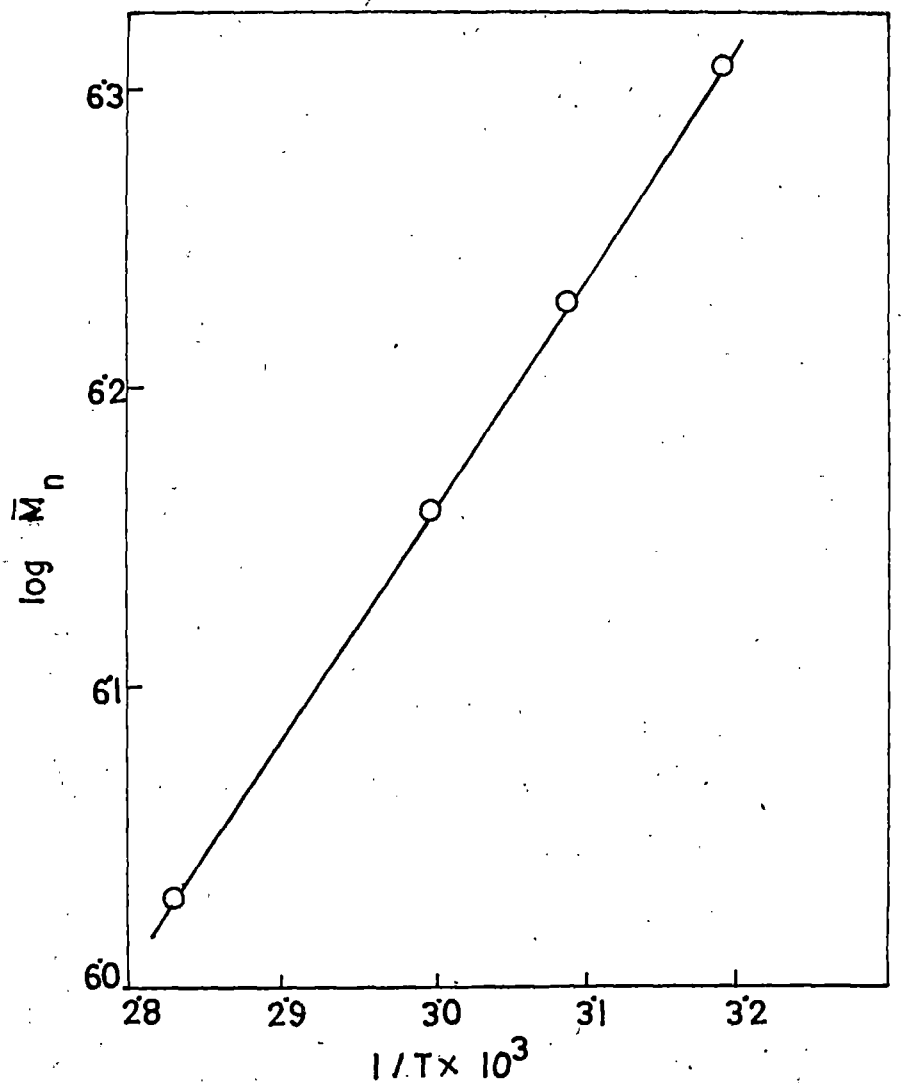
Time-conversion plots for aqueous polymerization of MMA at 50^{0}C (1), 60^{0}C (2) and 80^{0}C (3); (MMA) =0.374 M; (HB)=0.887% (W/V) and (Ethanol)=0.343M.

Fig.12



Arrhenius plots;-log R_o Vs.1/T with various amounts of MMA with 0.887% (W/V) HB and 0.343 M Ethanol.

FIG. - 13.



Arrhenius plots for $\overline{M}_n$ of PMMA; (MMA)=0.374 M; (HB)=0.887% (W/V); (Ethanol) = 0.343 M.

Table - 5

Kinetic and energy parameters for the aqueous polymerization of MMA with 0.343M Ethanol and 0.887% (w/v) HB at various temperatures.

Temp. °C	K_p^2/K_t Lit/mole.Sec	$K_{tr,M}/K_p$ x 10^5	E_a	$2E_p-E_t$	E_d	E_{DP_n}
			K Cal $mole^{-1}$			
50	0.84	1.54				
			15.0	12.2	17.0	-3.2
60	1.67	2.44				
80	4.20	3.36				

Other thermodynamic parameters for the polymerization have been tabulated (Table - 6).

Table - 6

Thermodynamic quantities for the polymerization of MMA in ethanol treated clay suspension: [Clay] = 0.85%; [Ethanol] = 0.343M; [MMA] = 0.75M; 60°C, 6 hrs. Total volume : 50 ml.

Temperature(°K)	$\Delta H^{\neq}$ Kcal/mole	$\Delta G^{\neq}$ Kcal0mole	$\Delta S^{\neq}$ cal/deg.K.-mole
40°			
50°	15.0	26.65	-353.0
60°			
80°			

$\neq$ sign indicates the energy parameters for activation.

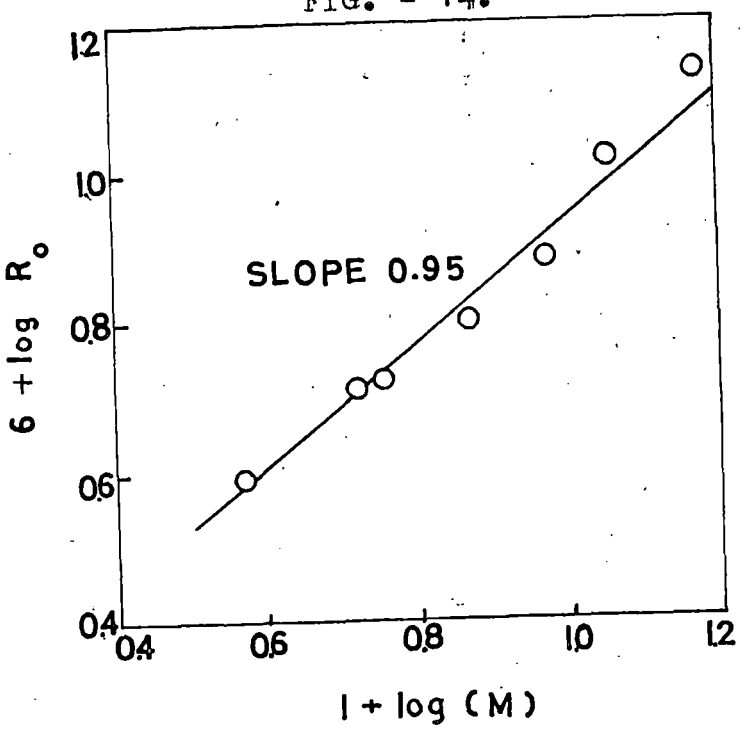
IVB(iv) Effect of monomer concentration:

Since MMA has low solubility in the aqueous medium and the system is heterogeneous in nature sufficient care is taken to get reproducible data. In the presence of HB and ethanol the polymerization of MMA shows an increase in the overall initial rate with an increase in the monomer concentration. The dependence is first order with respect to the monomer concentration (Figure 14). Such a dependence is sensitive to the experimental conditions. The data obtained for shaken and unshaken systems while all other factors remaining unaltered are presented below the time of polymerization being 6 hours with HB = 0.532% (w/v) and $[\text{Ethanol}] = 0.34M$

$[\text{MMA}]$ M	Percent yield	
	Shaken	Unshaken
0.3744	33%	5.1%
0.5620	41.1%	6.7%
0.7490	49.2%	7.6%
1.1230	52.4%	9.2%

Table 7 records the conversion, $\bar{M}_n$, $\bar{N}_n$ and the overall initial rates (at conversion below 15%). R_o increases from 0.512×10^{-6} to 1.04×10^{-6} moles lit^{-1} sec^{-1} when the monomer concentration is varied from 0.5616M to 1.1232M. The number average molecular weights increases with the increase in monomer concentration. However, very high monomer concentration can not be used because of its limited solubility and, therefore, any effect on $\bar{M}_n$ beyond 1.1232M remained unchecked.

FIG. - 14.



Plot of log R_o Vs. log(M) for the aqueous polymerization of MMA at 60°C with 0.887% (W/V) HB and 0.334 M Ethanol.

Table - 7

Rates of Polymerization and $\bar{M}_n$ at different temperatures for various MMA concentration with 0.343M ethanol and 0.887% (w/v)

MMA M	Temp. °C	$R_o \times 10^5$ M lit^{-1} sec^{-1}	$\bar{M}_n \times 10^{-6}$	E_a
0.3744	40	0.26	1.55	
0.5620	40	0.394	-	
0.7490	40	-	-	
0.9360	40	0.611	-	
1.1230	40	-	-	
0.3744	50	0.572	- -	
0.5620	50	0.850	1.35	15.0 Kcal mole^{-1}
0.7490	50	1.080	1.70	
0.9360	50	1.370	1.97	
1.1230	50	1.590	2.37	

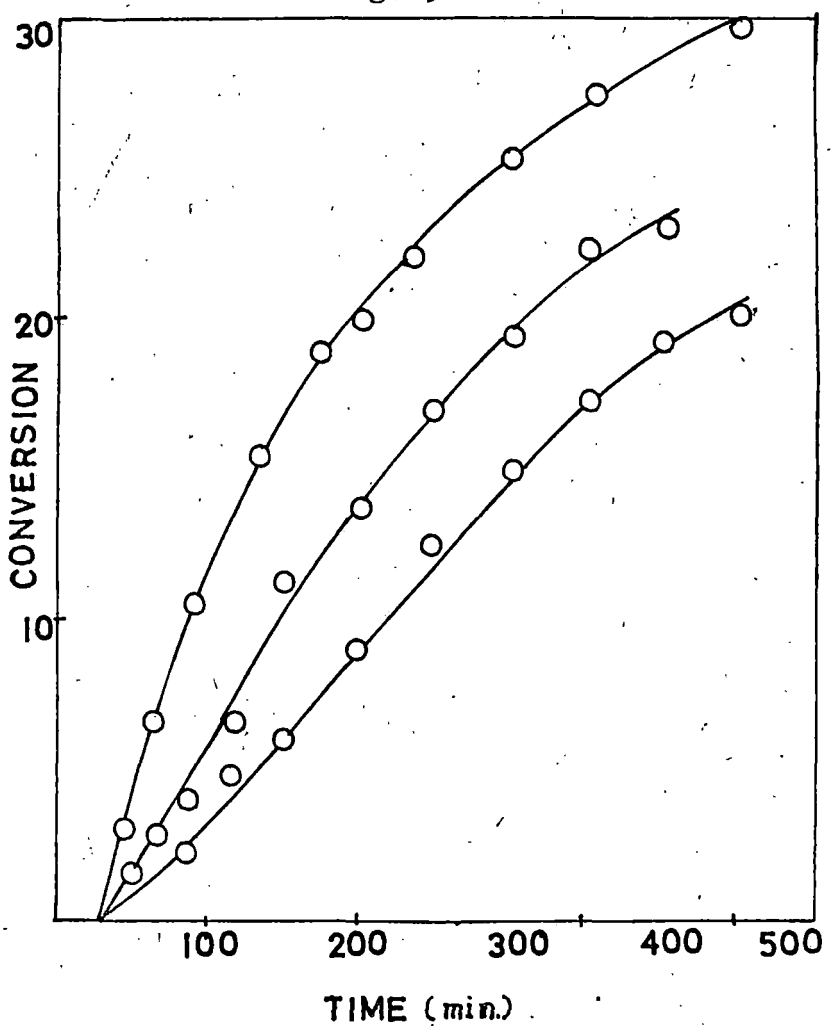
Contd..

Table - 7 (Contd..)

MMA M	Temp. °C	$R_o \times 10^5$ M lit^{-1} sec^{-1}	$\bar{M}_n \times 10^{-6}$	E_a Kcal. mole^{-1}
0.3744	60	1.250	1.01	
0.5620	60	1.860	1.13	
0.7490	60	2.110	1.45	
0.9360	60	2.880	1.63	
1.1230	60	3.150	2.00	15.0
0.3744	80	3.920	1.22	
0.5620	80	5.580	-	
0.7490	80	7.400	1.09	
0.9360	80	9.120	1.26	
1.1230	80	10.750	1.42	

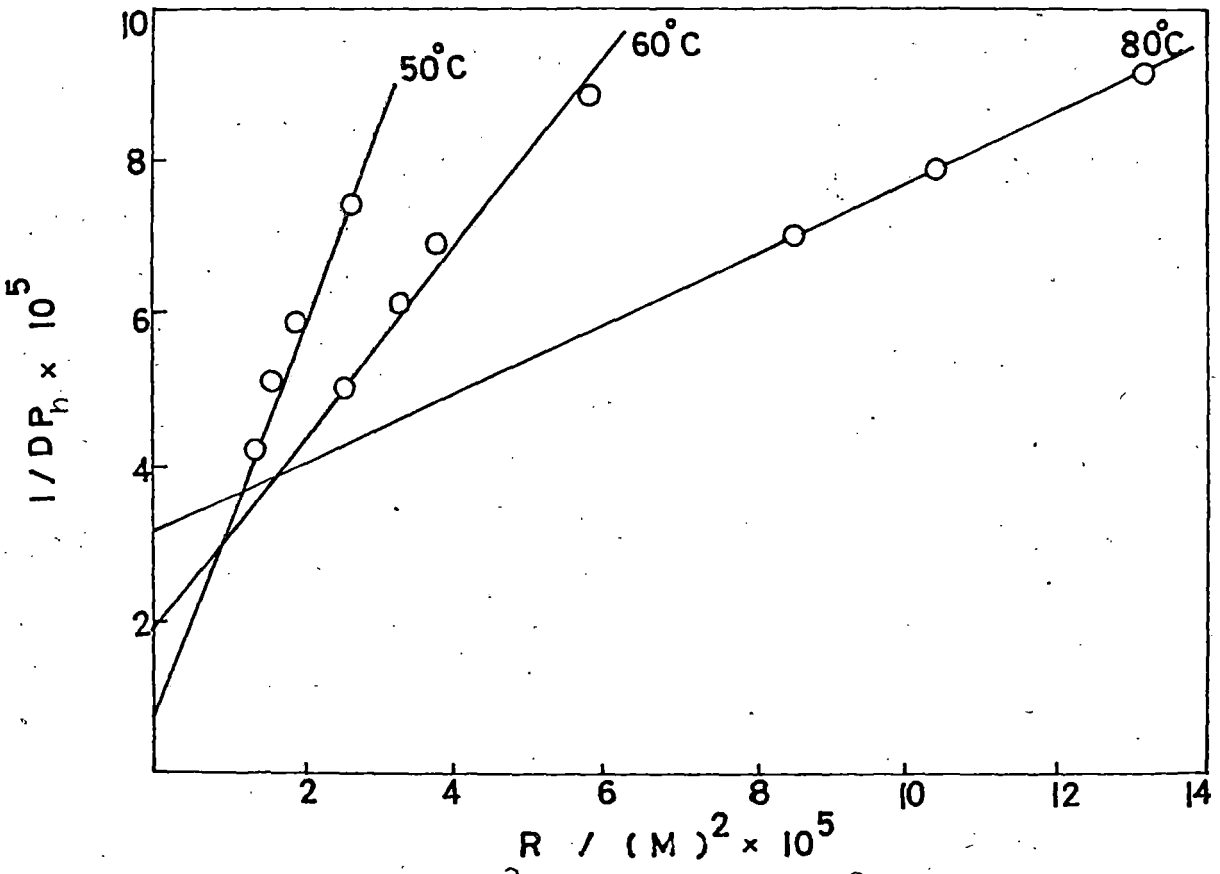
The time-conversion plots for aqueous polymerizations at different concentrations of MMA at 60°C have been shown in figure 15. After 5 hours of polymerization the conversions are found to be 15, 20 and 25% for 0.749, 1.112 and 1.495M MMA respectively. However, higher conversions result for longer reaction time . In all polymerizations an induction period is found to be independent of monomer concentration. In figure 15A, $1/DP_n$ has been plotted against $R_o/[M]^2$ for the determination of transfer to monomer which is found to be very small.

Fig.15



Time-conversion plots for the aquaous Polymerization of MMA at 60°C with HB/Ethanol.(HB)= 0.887%(W/V); (Ethanol)= 0.343 M.

FIG. - 15 A.



Plots of 1/ $\overline{DP}_n$ Vs. R_o/ M^2 at 50, 60, and 80°C for the aqueous polymerization of MMA with HB/ Ethanol.

IVC. Spectral analyses of polymethylmethacrylate:

IVC.(i). X-rays: The X-ray data for HB and HB - PMMA adduct have been tabulated (Table - 8). The first band (d_{001} spacing) of both the samples have been taken for analytical purpose. The diffraction pattern of both the samples have been shown in figure 16 .

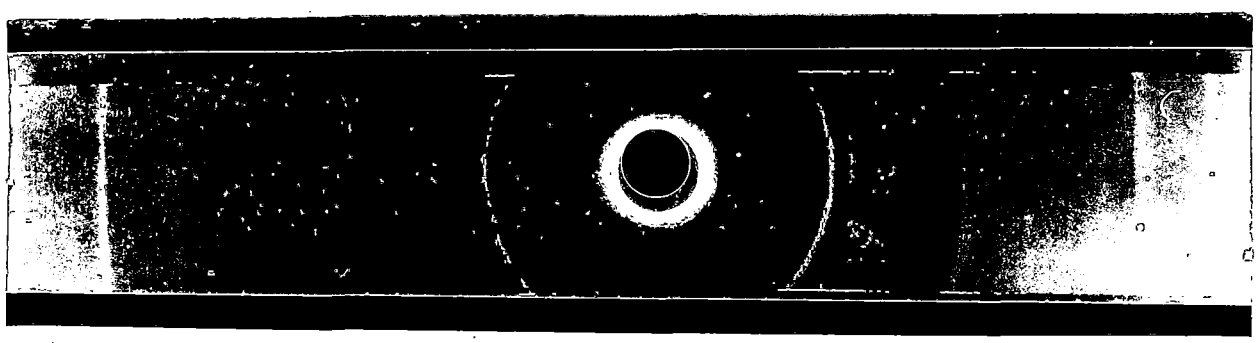
Table - 8

X-ray diffraction parameters of H-bentonite (HB) and H-Bentonite-polymer adduct after extraction of the polymer.

H-Bentonite		H-Bentonite-PMMA adduct	
d_c in Å	I	d_c in Å	I
14.00	S(B)	17.9	S(B)
4.45	S	4.45	S(B)
4.05	M	4.03	SM
3.32	W	3.30	WM
3.12	WW	3.11	M
2.85	VVW	2.76	W
2.79	VVW	2.70	W
2.56	W(B)	2.40	VW(B)
2.47	VW(B)	2.21	VVW(B)
2.22	VVW(B)	2.01	VVW(B)
2.21	VVW(B)	1.82	VVW(B)
2.01	VVW(B)		

Contd..

(A)



(B)

(C)

FIG. 16: X-ray diffraction pattern of (A): Pure Bentonite, (B) Ethanol treated H-Bentonite and (C) Free polymer free HB-PMMA addinct.

Table - 8 (Contd..)

H-Bentonite		H-Bentonite-PMMA adduct	
d_c in Å	I	d_c in Å	I
1.865	VVW(B)		
1.820	VVW		
1.820	VVW		
1.685	W(B)		
1.605	VVW		
1.540	VVW		
1.492	M(B)		
1.290	VW(B)		
1.245	VW(B)		

S = Strong, MS = Medium strong, M = Medium, WM = Weak Medium, W = Weak, MW = Medium weak, VW = Very weak, VVW = Very very weak, B = Broad, I = Intensities.

IVC.(ii). Infrared spectroscopy:

The infrared spectroscopic data has been obtained for pure monomer MMA, the polymer PMMA, ethanol treated hydrogen bentonite HB and the clay-polymer adduct. The data have been recorded in Table - 9 and a comparative diagram has been given in figure 17, 18 and 19.

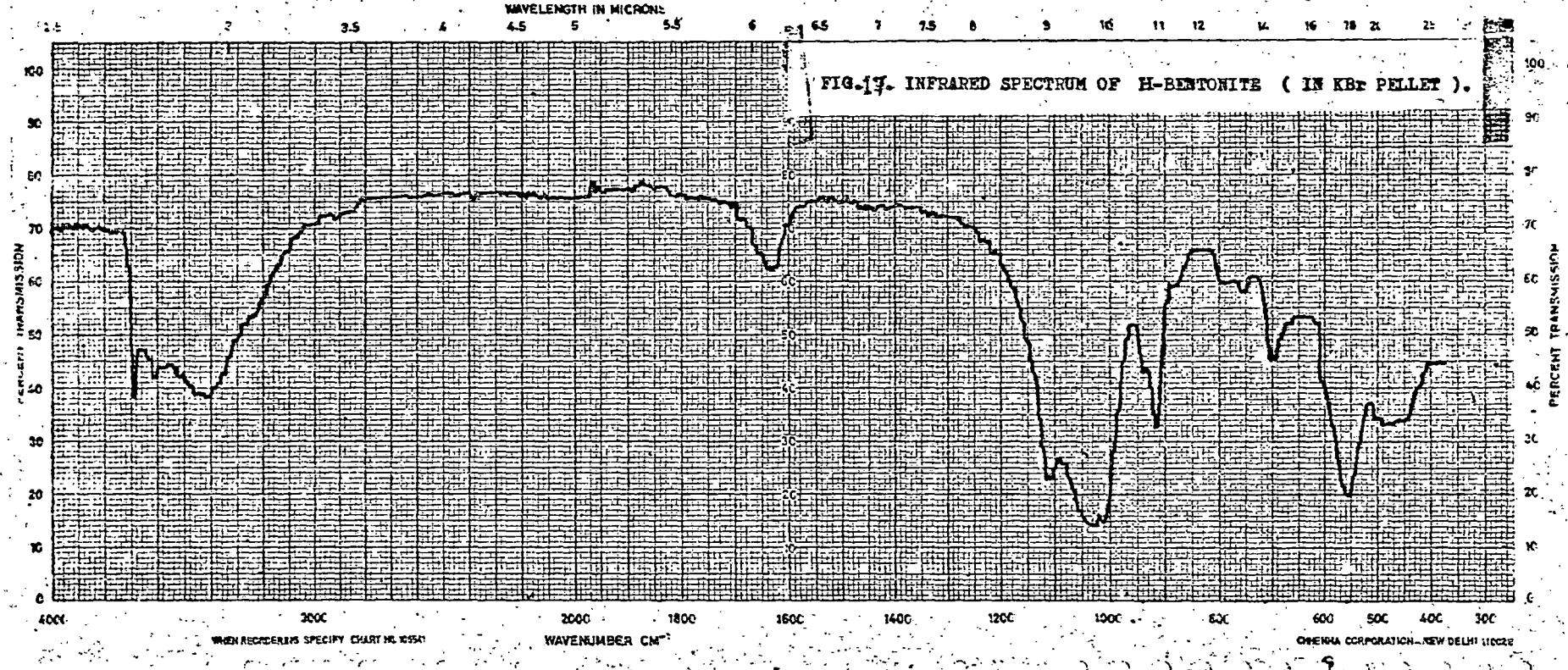


FIG. 17. INFRARED SPECTRUM OF H-BENTONITE (IN KBr PELLET).

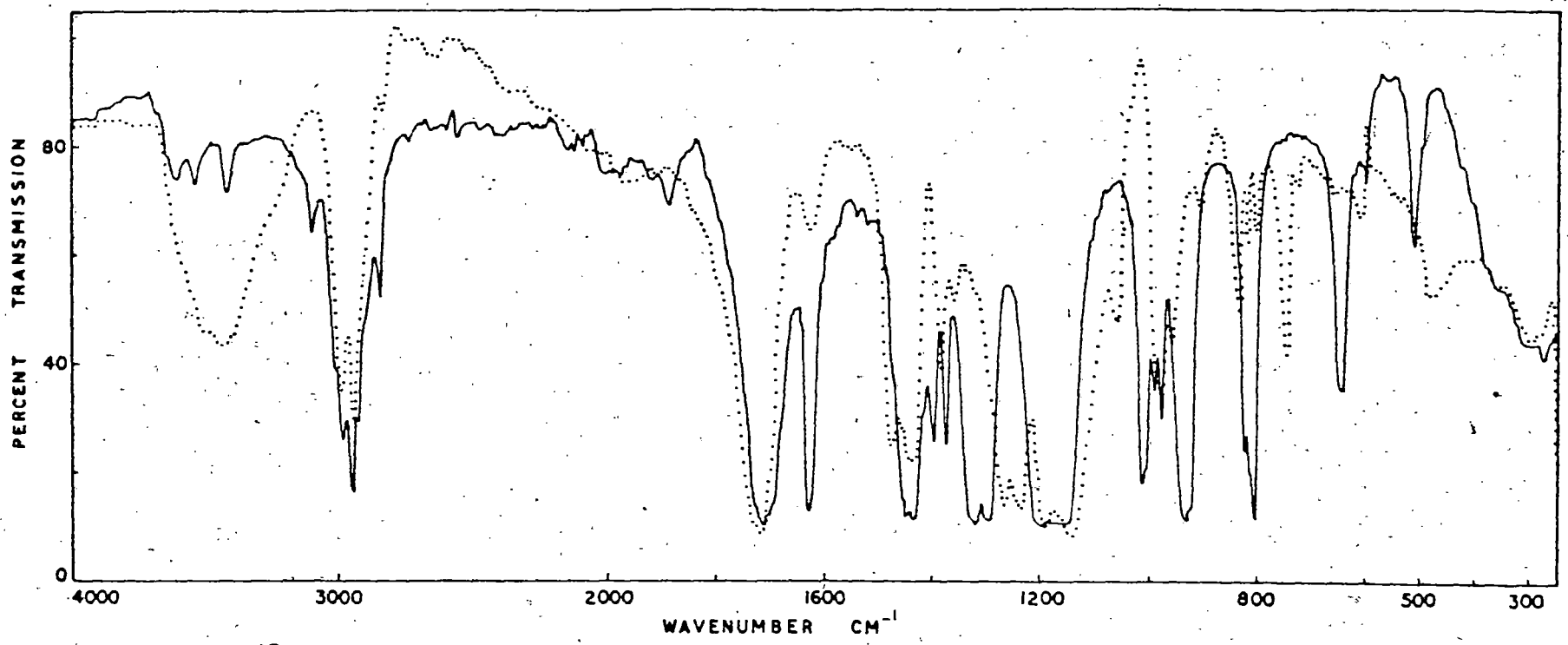


FIG. 18. I. R. SPECTRUM OF PURE MMA —— AND FOR PMMA ····· [KBr PELLET].

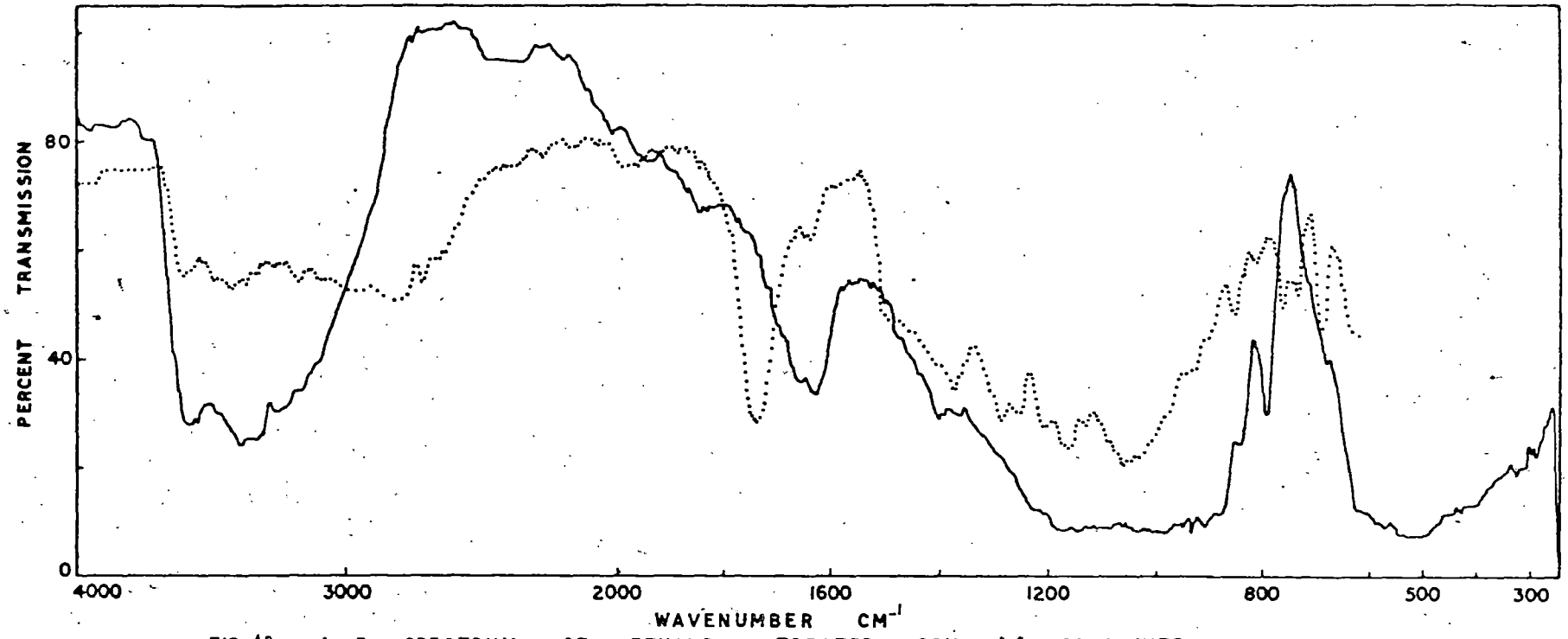


FIG. 19. I. R. SPECTRUM OF ETHANOL TREATED DRY "H" BENTONITE —— AND CLAY-POLYMER MMA ····· [KBr PELLET].

Table - 9

I.R absorption frequencies for different samples

Sample	Sampling technique	I.R. absorption frequencies, cm^{-1}
Pure MMA	Liquid film	2990(s), 2960(s), 2930(s), 2850(m), 1730-40(s), 1630(m), 1450-70(bs), 1385(s), 1280(s), 1245(s), 1200(m), 1140(m), 1050(m), 850(m), 755(m), 725 (w)
PMMA	Kbr pellet	3000(s), 2960(s), 2840(w), 1720-35(s), 1628(w), 1440-50(s), 1480(s), 1385(m), 1360(w), 1280(s), 1240(s), 1190(s), 1140(s), 900(m), 840(m), 820(w), 800(w), 750(m)
HB-ethanol	KBr pellet	3580-3600(b,s), 3400(b,s), 1665(m), 1630(m), 1370-1400(b,m), 900-1200(b,s), 840(s), 800(s), 685(m)
HB-Polymer adduct	KBr pellet	3585(m), 3400-3450(m,b), 2700(w), 2280(w), 1720-40(s), 1630(w), 1370(m),1290(m),1250(m),1220(m), 1160-80(b,m),1060(m),850(m), 765(m),730(w),690(m)

b:broad; s: strong; m:medium; w: weak.

The far infrared spectroscopic study of the clay polymer adduct has done to identify any Si-O or Al-C bond which might have been present in the adduct. Apart from this, the spectra will also show stereoregularity (if any) of the polymer associated with the clay mineral (Figure 20). Table - 10 records the far i.r. absorption frequency bands for the clay-polymer adduct.

Table - 10

Sample	Sampling technique	Absorption frequencies, cm^{-1}
Clay-polymer adduct	KBr pellet	120(s), 122(m), 126(sh), 132(s), 145(m), 154(m), 170(sh), 175(m), 182(s), 200(s), 300(w), 350(s), 380(s), 455(m), 480-85(s), 5575(w), 520(m)

where 'sh' stands for shoulder; other notations are same as in table - 9.

IVC(iii). Proton magnetic resonance spectroscopy:

The n.m.r. spectral study concerns primarily to understand the stereoregularity of the polymer. Different resonance peaks for PMMA in $CDCl_3$ and in dichloro benzene have been recorded in Figure and Figure 21. The comparison of the figures indicates that the position of the resonances for PMMA are not identical in al solvents

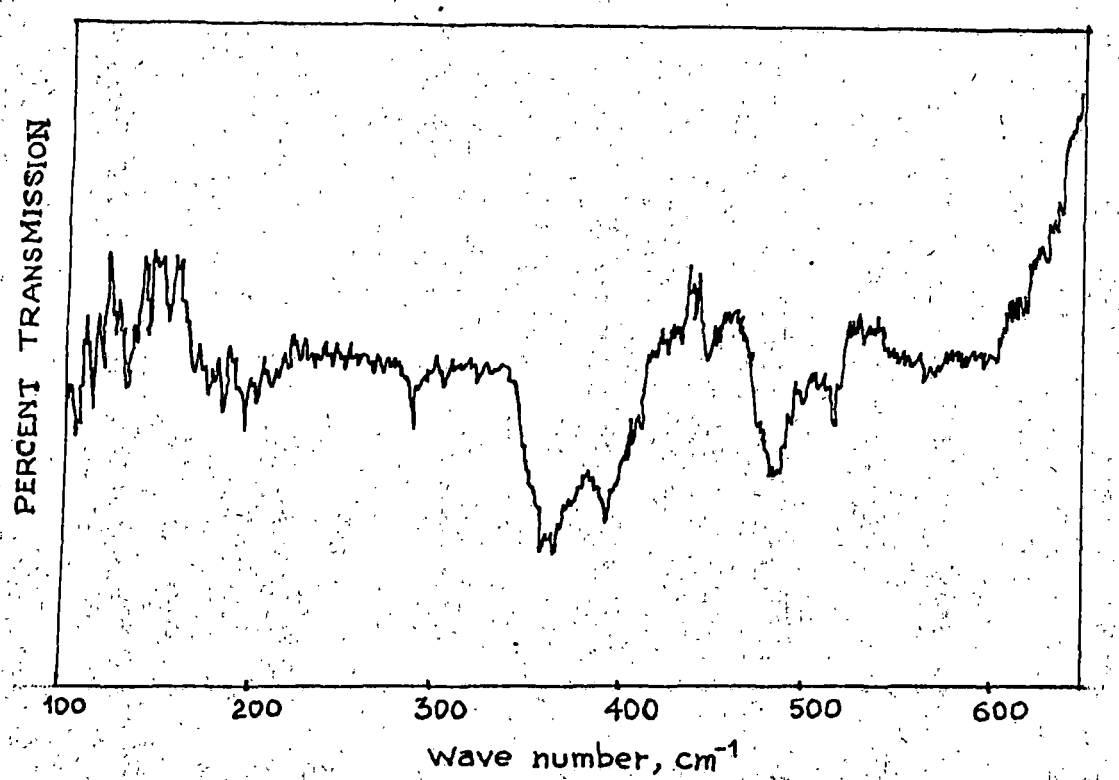


Fig. 20. Far I.R. of HB-PMMA adduct.

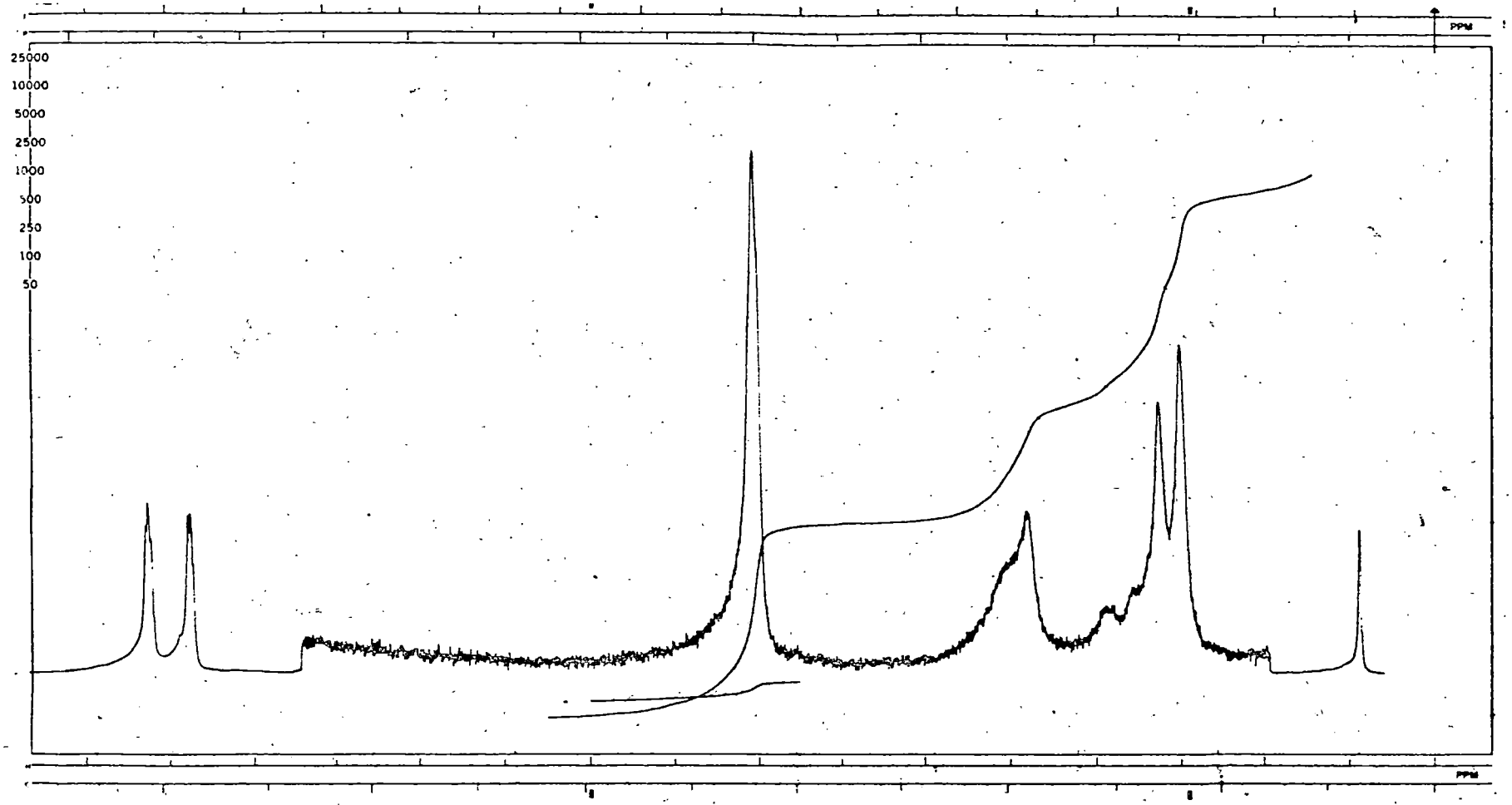


FIG. - 21. P.M.R. Spectrum of Poly-methyl-methacrylate produced from HB-Ethanol initiating system (In Dichloro Benzene); 300 MHz.

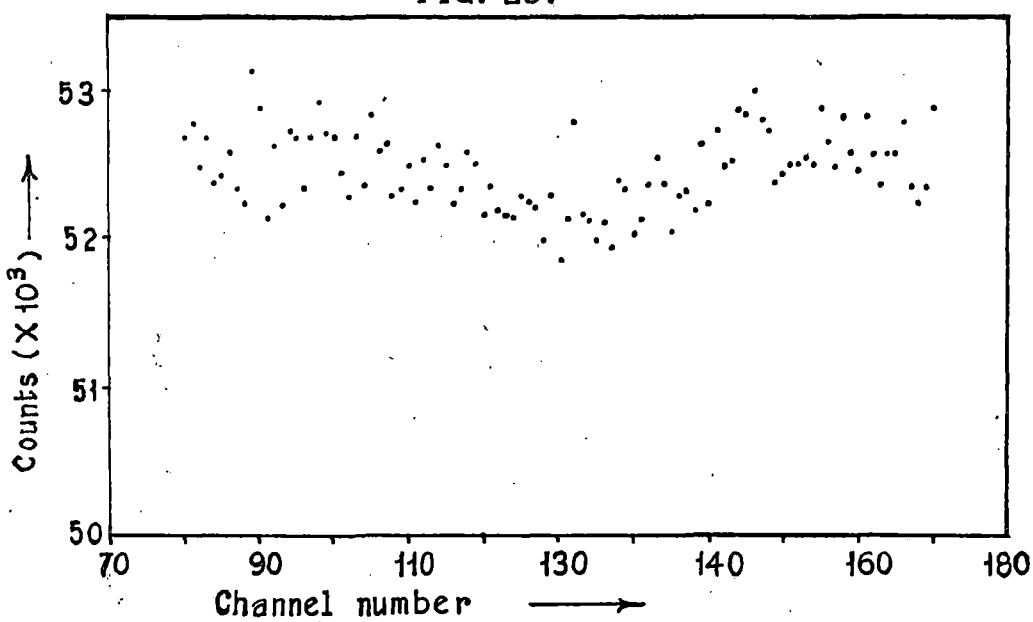
and, there is a shift of τ values in the higher τ value regions.

IVC(iv). Electron spin resonance and Mossbauer spectroscopy:

The Mossbauer spectrum of the clay sample (HB) is taken with $^{57}C_o$ (in Palladium matrix, strength $2mC_i$) source using 14.4 Kev gamma ray (Figure 23).

The e.s.r. spectra (Figures 24,25,26and 27) of the samples dry HB; dry HB treated with ethanol, HB suspension (in nitrogen atmosphere) and HB suspension treated with ethanol (in nitrogen atmosphere) provided valuable information regarding the mechanism of the polymerization process.

FIG. 23.



Mössbauer Spectrum of hydrogen Bentonite

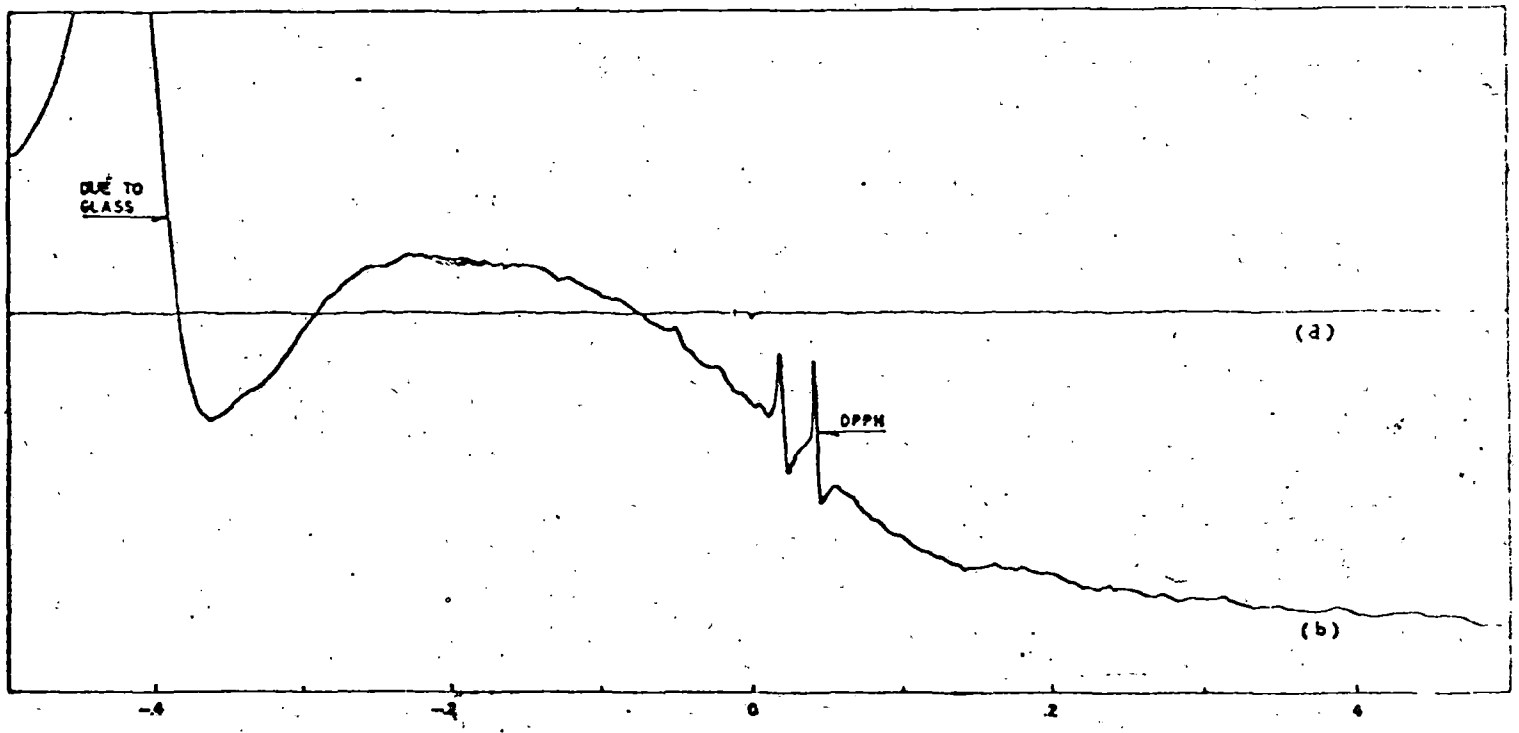


FIG. 24 ESR SPECTRA OF (a) H-BENTONITE CLAY AND (b) ETHANOL TREATED DRY H-BENTONITE.

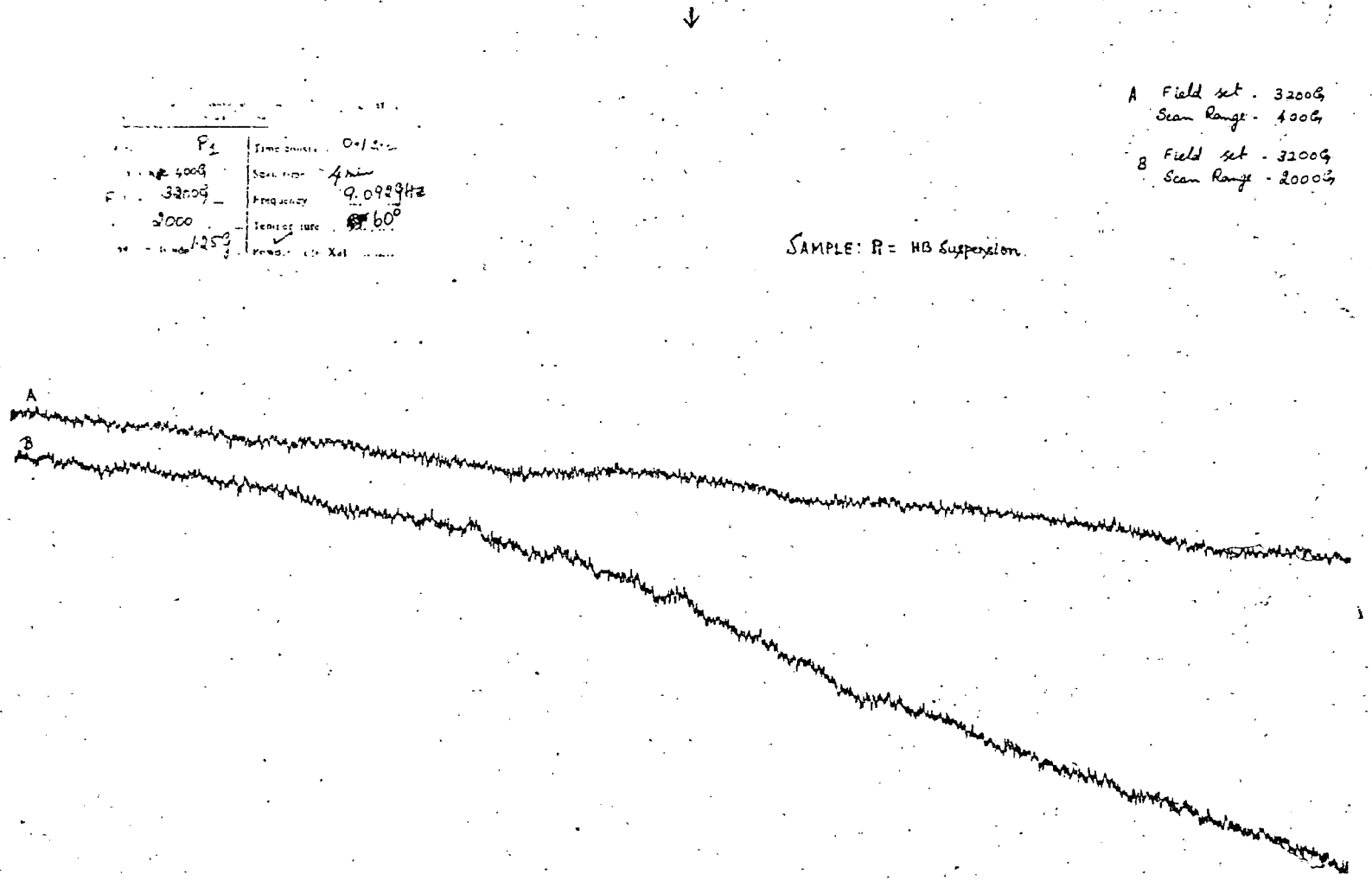


FIG. - 25. E.S.R. Spectrum of Hydrogen Bentonite in water suspension

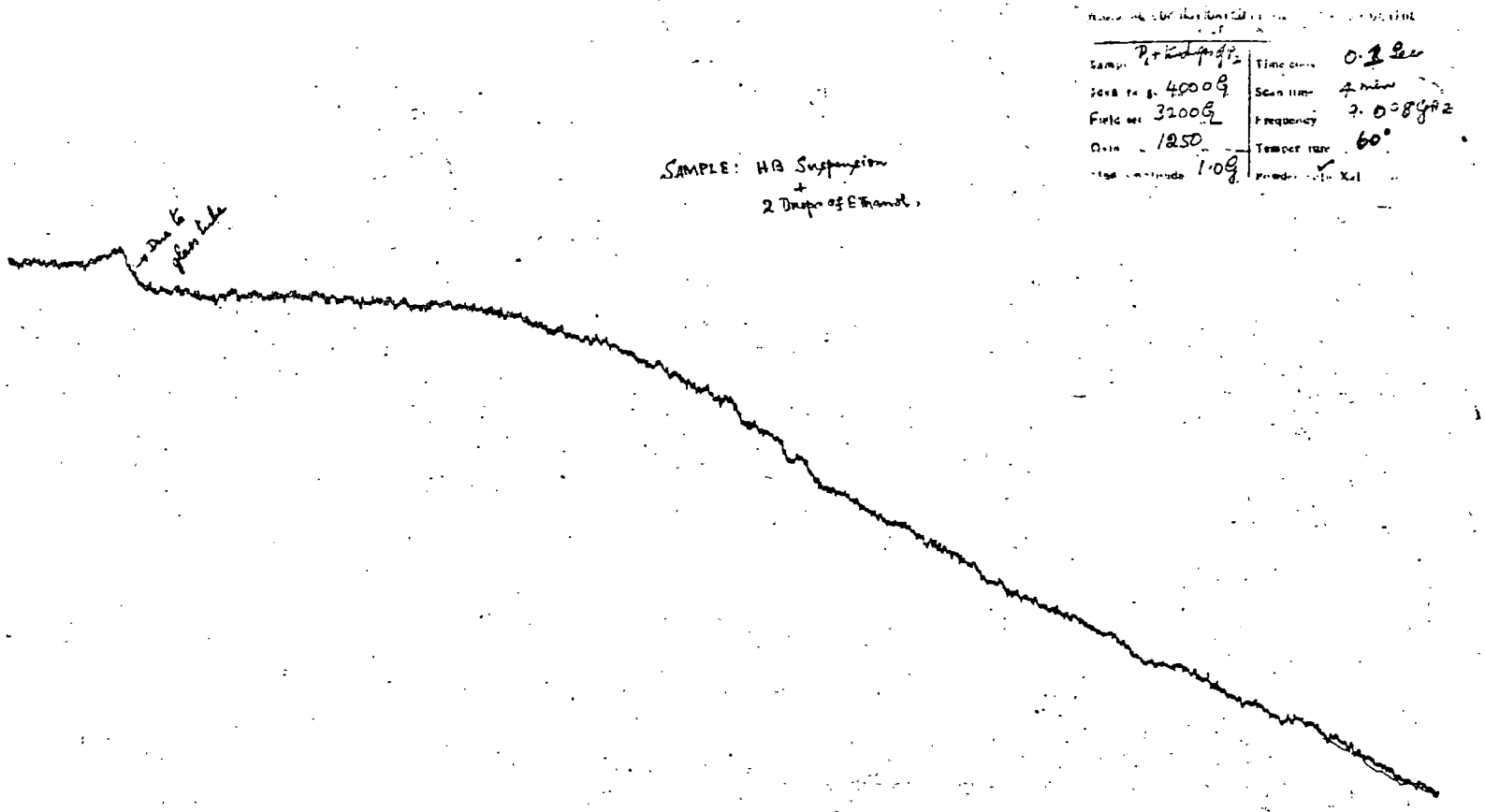


FIG. - 26. E.S.R. Spectrum of HB Suspension and Ethanol (In aqueous medium).

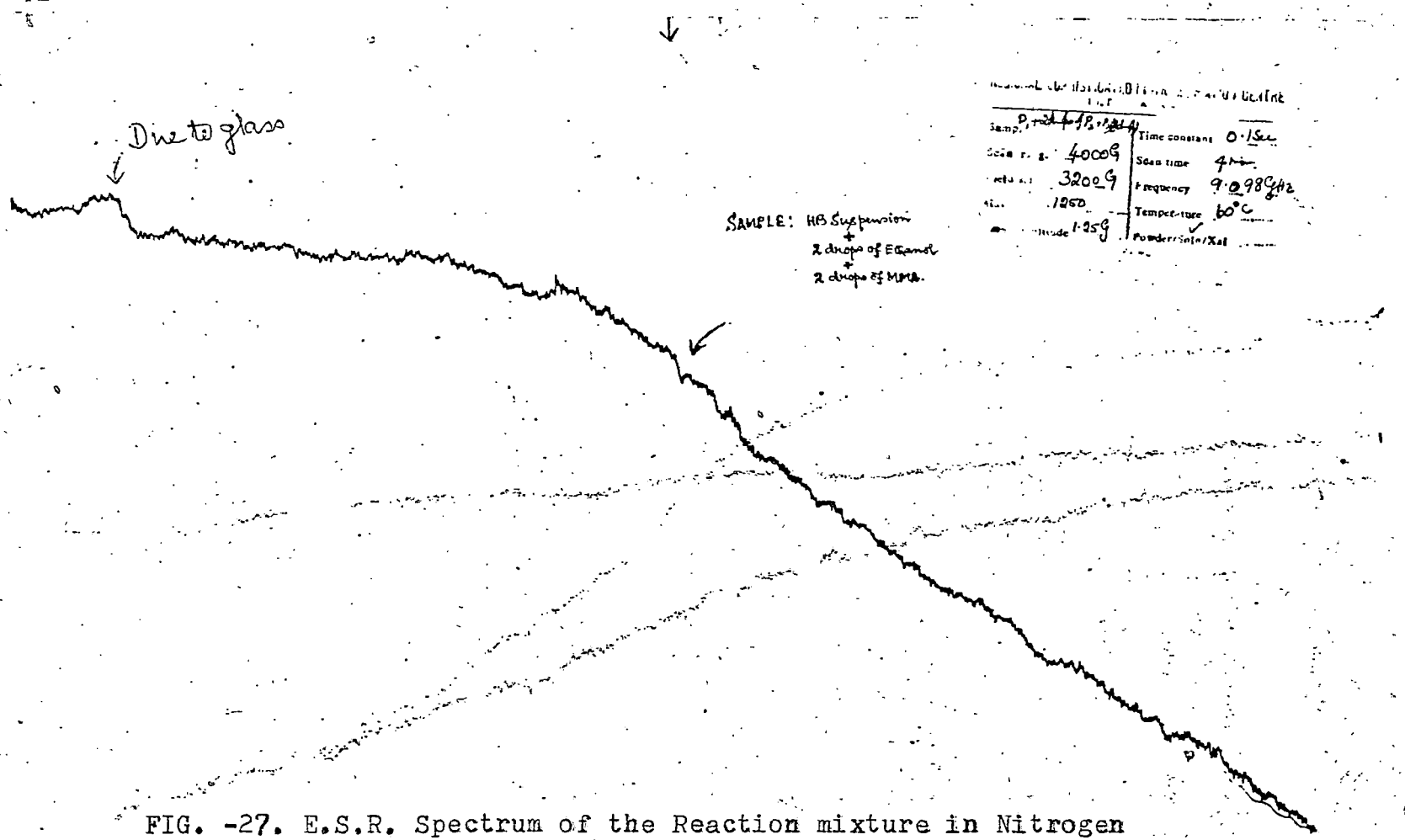


FIG. -27. E.S.R. Spectrum of the Reaction mixture in Nitrogen Atmosphere at 60°C (Arrow shows a little concentration of spin).

Section IVD : Discussion:

The effect of alcohols on the aqueous polymerization of MMA in the presence of HB is unusual one from the point of view that alcohols are known as telomerizing agents in the conventional free radical polymerization reactions. The production of PMMA in the absence of any conventional free radical initiator, but in the presence of the clay mineral treated with ethanol, may be explained by systematic analysis of the experimental results which has been recorded in the previous section.

The near constancy of the viscosity average molecular weights, $\bar{M}_v$s' of PMMAs harvested with alcohols of different chain lengths and transfer constants, strongly suggest that these alcohols do not behave as chain transfer agents in HB/alcohol/MMA polymerization systems. The high molecular weight PMMAs' produced with HB/thiol/MMA system further supports this view. Thiols are known to have very high chain transfer constants and they were not expected to produce polymers of molecular weights as high as 10^6. Alcohols, in the present investigation (Table - 1) thus, are not acting as they do in conventional free radical polymerization. Instead, their interaction with the clay mineral helps to produce active species, the initiator, for the polymerization. In the present investigation it has been established that without alcohol, clay mineral could not initiate the polymerization. The effect of ethanol concentration on

the rate of polymerization has been established. The overall initial rate varied linearly with 0.5th order of ethanol (Figure 8). This can be attributed to the involvement of ethanol in generating the initiating species for the polymerization of MMA in the presence of HB. Such a dependence is obeyed for most free radical polymerizations as recorded in the literature[1,2]. Moreover, the quenching of the polymerization with DPPH supported the free radical mechanism involved in the present investigation. As has been discussed in Section IB, alcohols can penetrate the near surface of the clay mineral and be adsorbed there. Such a process might generate free radicals. Both the alcohols and the clay mineral are responsible for generating the initiating species, for, when the amount of clay mineral is decreased the amount of polymer decreases parallely. To confirm the nature of the polymerization, it is carried out in the presence of DPPH. The reaction, under identical conditions of a successful process, is found to be completely inhibited by DPPH. Further, support for the involvement of free radical in the polymerization is established from the e.s.r. spectra (Figure 24A). Dry HB soaked with ethanol responds for the presence of odd electrons. In polymerizing conditions, without MMA, we failed to detect radical species. This is probably due to their extreme low concentration in the suspension (Figures 24,25,26).

To ascertain the exact location of the radical generating sites experiments were performed by blocking the octahedral aluminiums

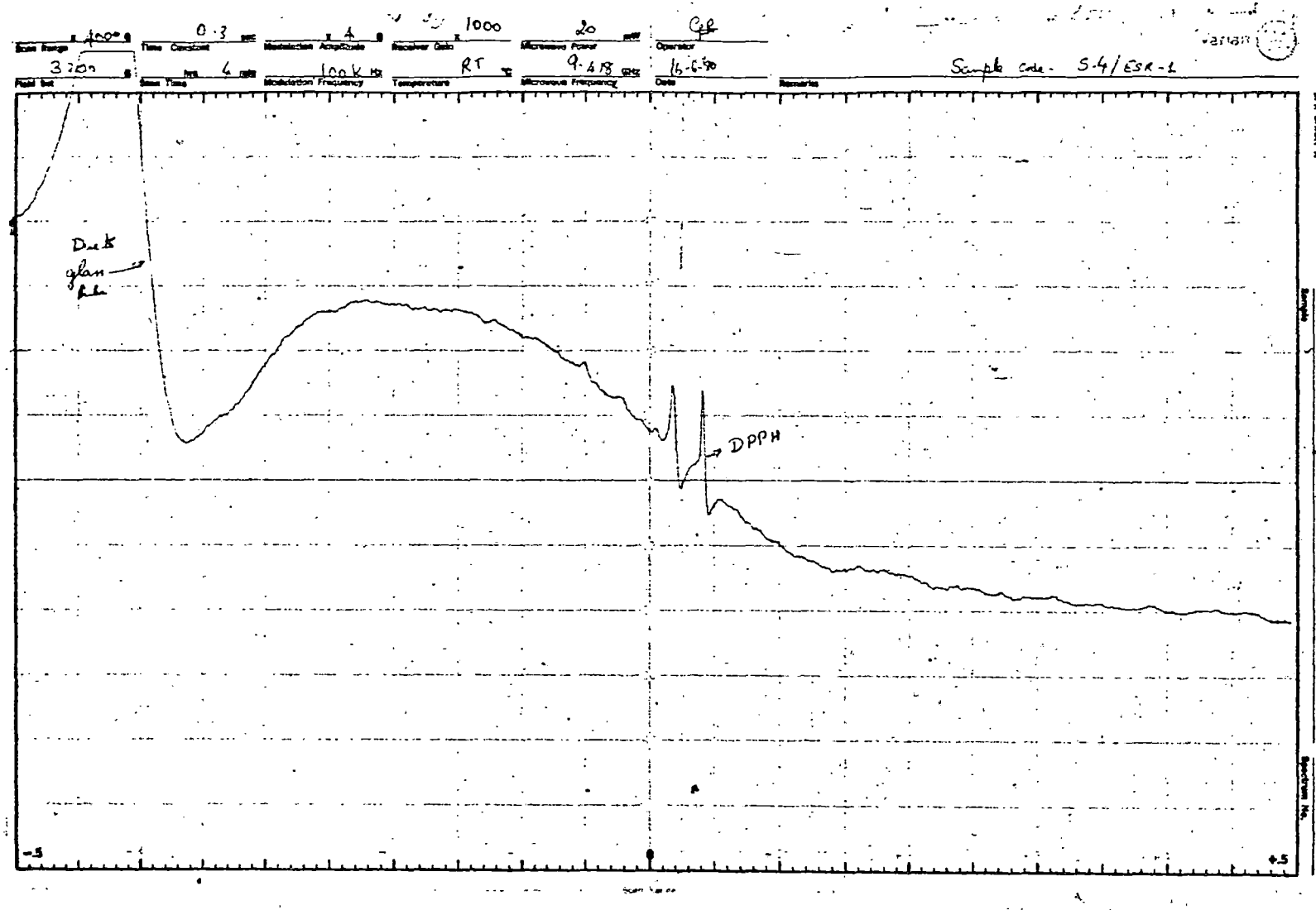


FIG. - 24A. E.S.R. Spectrum of Hydrogen Bentonite (HB).

of HB with sodium hexametaphosphate SHMP. The conversions and molecular weights remain unchanged. As has been pointed out in Table 4, H^+, Na^+ and Cu^{+2} bentonites were equally effective in polymerizing MMA with alcohols. Thus the availability of H^+ in clay mineral is not the essential criterion for polymerization. The course of the reaction remains unaltered by varying the cation exchangers in clay mineral. Such a claim is made, however, by some authors[3] for clay catalysed (dry H-montmorillonite) polymerization of MMA. It could be, however, thought that the free radicals are generated by any transition metal present in the clay as impurity. The examination of the Mossbauer spectrum of HB (Figure-23) showed beyond doubt that this was not true and the presence of even traces of transition metals (Iron) could not be surmised. The results, therefore, strongly suggest the free radical generation via the complex formation between alcohol and Si-sites of HB. Dowdy and Mortland also suggested that alcohols can penetrate the near surface of clay crystal lattice[4]. This has been further corroborated by the polymerization of MMA on quartz surface (200 mesh) in the presence of alcohols. It may be noted that quartz alone failed to do so.

The Figure 9 we have showed that at conversions below 20%, the overall initial rates of polymerization were 0.89×10^{-5}, 1.28×10^{-5}, 1.66×10^{-5} and 1.81×10^{-5} moles lit^{-1} sec^{-1} for 0.39, 0.68, 1.028 and 1.37M ethanol respectively. These values are much lower than those for the aqueous polymerization of MMA using conventional free radical initiators.

That the octahedral aluminium in bentonite are not responsible for the initiation in conjunction with alcohol has been established by using sodium hexametaphosphate to block these aluminium sites. The examination of the dependence of the overall initial rate of polymerization is limited because of the limited variation of the clay minerals. The increase in the amount of clay mineral ought to increase the viscosity of the medium and consequently, the reaction fundamentals would have been changed to greater extent. Low clay concentration i.e., less than 0.30% (w/v) can hardly produce polymer probably because of very low active initiator concentration and/or destruction of the same by some unknown reactions. Interestingly, the increase in clay resulted in higher conversion with parallel increase in $\bar{M}_n$ and $\bar{N}_n$ (Table-3). For a 3.5 fold increase in HB, $\bar{M}_n$ increased 1.32 fold while $\bar{N}_n$ increased 3.2 fold. The increase in $\bar{M}_n$ is probably due to the increase in viscosity of the medium. But the increase in $\bar{N}_n$ is definitely due to the increased number of active species. The overall initial rates increased from 0.527×10^{-5} moles lit^{-1} sec^{-1} to 2.25×10^{-5} Moles lit^{-1} sec^{-1} for increase in HB concentration from 0.35% (w/v) to 1.21% (w/v). This is probably the combined effect of viscosity and adsorption of larger amounts of MMA on the clay surface (the surface area increased on increasing the amount of clay). The increase in molecular weight (Table 3) of PMMAs' for higher amount of clay mineral indicates that the mineral surface is not a transfer agent.

Initial increase in viscosity on increasing HB concentration might have caused a change in rate because of trapping of free radicals in radicals in submicroscopic agglomerates of PMMA plus HB. MMA is slightly soluble in water. HB forms a suspension and, PMMA produced are suspended by HB to a great extent. Due to this complex nature it is rather difficult to suggest rigid kinetic treatment and evaluate quantitative data at this stage. Norrish and Smith suggested that diffusion effect may be important in growing radical termination[5]. Later on Tomsdorff explained the auto-acceleration, observed in many free radical polymerizations, was due to the termination process being diffusion controlled[6]. Although it is generally assumed that propagation and termination rates are independent of radical chain length, the particular problem of termination has been investigated by Benson and North[7]. Using an extension of Herrington and Robertson[8] common kinetic relationships are derived. In the absence of any transfer reaction

$$R_p = k_p [M] R_i^{1/2} / (2k_{t_{11}})^{1/2} F^{1/2} \quad \ldots (1)$$

$$DP = k_p [M] / R_i^{1/2} (2k_{t_{11}})^{1/2} F^{1/2} \quad \ldots (2)$$

$$\nu = R_i^{1/2} / (2k_{t_{11}})^{1/2} F^{1/2} \quad \ldots (3)$$

where R_p = rate of polymerization

DP = Degree of polymerization

ν = Kinetic chain length

$k_{t_{11}}$ = Hypothetical termination rate constant and

F = dimensionless parameter defined by

where $f_n = f_{nm} X_m$ and $f_{nm} = k_{tnm} / k_{t_{11}}$, X_i being the mole fraction of 'i' mer radicals, k_{tnm} is termination rate constant for the reaction between radicals of chain lengths n and m .

With large amount of transfer to monomer in the system the kinetic orders with respect to monomer and initiator are normally first order and half order respectively.

In this system of polymerization the overall initial rate has been found to be first order and half order with respect to MMA and ethanol . It has, however, been shown with the Mayo plot (Figure 15A) that transfer to MMA is not significant. Although the measurement of viscosity with varying concentrations of HB was not done, it can be stated from the literature[9] that the change in viscosity was more compared to the change in R_o values (Table - 3) . Moreover, for a reaction to be diffusion controlled the value of the rate constant would be of the order of 10^7 lit mol^{-1} sec^{-1} or greater and the energy of activation in normal liquids would be approximately 3 Kcal $mole^{-1}$ which is much less than our experimental value of 15.0 Kcal mol^{-1}. We, therefore, conclude that with all probability the systems, where clay concentrations were increased, are not

diffusion controlled. The increase in rate is due to the participation of larger number of initiating sites as is evident from $\bar{M}_v$ (Table - 3).

The remarkable feature of the temperature dependence of the rate of polymerization is that the rate increased rapidly from $R_o = 0.572 \times 10^{-5}$ moles lit^{-1} sec^{-1} at 50^oC to $R_o = 3.195 \times 10^{-5}$ moles lit^{-1} sec^{-1} at 80^oC. The rate is found to be very low at temperatures 30^oC and 40^oC. At 30^oC the conversion of PMMA is about 10% after about a month. Such data is not reproducible since other necessary conditions like shaking etc. could not be maintained evenly for every observation. Literature records the overall activation energy for MMA polymerization by AIBN as 18.8 Kcal/mole[10]. The corrected activation energy obtained for the present polymerization system from Arrhenins plot (Figure 12) is 15.0 Kcal/mole. Such a value would definitely be significant. The existence of monomer layer within interlamellar clay surface and any adsorption of alcohol on the Si-site of the clay mineral would definitely lower the activation energy barrier for the polymerization. The $\bar{M}_v$ being numerically nearer to $\bar{M}_w$ and $\bar{M}_w / \bar{M}_n$ being very near to constant, $\bar{M}_v$ would decrease in the process. It can be expected that at higher temperature the number of molecules crossing the energy barrier may be greater and thus will decrease $\bar{M}_v$. Assuming energy of activation E_a to be equal to the enthalpy of activation, $\Delta H^{\neq}$, and using the relations:

$$\Delta S^{\neq} = R\left\{\ln\left(\frac{kA}{KT}\right) - 2\right\} \qquad \ldots (4)$$

and $$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \qquad \ldots (5)$$

('A' is the frequency factor).

The other thermodynamic parameters have been calculated. The term 'h' in the above equation stands for Planck's constant and 'A' the collision frequency of the reaction is obtained from Arrhenins plot.

The entropy of activation as has been determined is found to be -0.353 Kcal K^{-1} Mol^{-1}. This value of entropy of activation can be accounted for the monomer molecules being trapped by the silicate layers in well arranged manner in close distance.

The rate of polymerization increased with increasing monomer concentration (Fig. 15). In Fig. 14 , the first order dependence of rate on monomer concentration provides the validity of the following rate equation for the present polymerization system.

$$R_p = k_p \cdot [M] \cdot \left(\frac{f k_d [I]}{k_t}\right)^{1/2} \qquad \ldots (6)$$

where $[M]$ and $[I]$ are monomer and initiator concentrations respectively. We have discussed earlier that the overall initial rate depends on $[\text{Ethanol}]^{\frac{1}{2}}$. This is also in accordance with the above general equation for free radical polymerization. The increase

in $\bar{M}_v$ as well as $\bar{M}_n$ (Table - 7) is consistent with such a view. This can be explained on the basis of greater adsorption of monomer on the clay surface within the interlamellar space. Also MMA being insoluble in water and HB suspension in water being a heterogeneous phase, the increase in $\bar{M}_n$ indicates that the free radical is soluble in the monomer phase and it exists little or not all in the aqueous phase.

One of the most important way to study the mode of the polymerization reaction is to study the initiator efficiency. The initiator efficiency could not be calculated with respect to clay mineral due to experimental difficulties such as problems in calculating the exact hydration status of the clay mineral in the reaction medium. The initiator efficiency with respect to ethanol has been calculated using the very simple relation[11]. Thus the initiator efficiency has been expressed as $I_{eff} = \frac{\text{Conversion of monomer to polymer in M}}{\text{Concentration of } C_2H_5OH \text{ in M}}$. With clay concentration 0.45% (w/v) and ethanol concentration 0.34M , I_{eff} was calculated to be 0.33 and, found to be true for other combinations. The value of I_{eff} with respect to clay concentration appeared to be very different to calculate in the present experimental conditions due to our lack in knowledge of exact number of available Si-sites. The increase in conversion of PMMA with the increasing amount of ethanol might indicate that the active species are grown out of clay-ethanol interaction lying in the near vicinity of the clay mineral. The monomer, being less soluble in the aqueous phase, required a

vigorous shaking for their trapping within the interspaces of the silicate layers of the clay mineral. On the basis of the basic composition of bentonite $\angle Al_2Si_4O_{10}(OH)_2 _/$, the weight of Si-site is $\backsim$30% and Al $\backsim$ 15% of the total weight of the clay mineral. The clay mineral, on interaction with ethanol, produces the initiator, and the active sites are the Si-sites. The value of I_{eff} ($\gtrsim$33%) calculated with respect to ethanol lies close to the total number of Si-sites. Assuming 1:1 type of ineraction between the primary units of Si-sites of clay mineral with the alcohol molecules, the initiator efficiency with respect to Si-surface alone is 100%.

Mechanism:

The most reliable and important observation came from Mossbauer (Figure 23), e.s.r. (Figure 24), X-ray (Figure 16) as discussed in Section IVE. These led to understand the mechanism of the polymerization of MMA with HB/ethanol as the initiating species. The e.s.r. spectrum of dry HB soaked with ethanol indicated the presence of odd electrons. The response to e.s.r. signal of ethanol treated clay mineral is dependent upon the spin concentration. The suspended clay ethanol system had either very small or no response to the e.s.r. signal (Figure 25).

X-ray diffraction data suggested a basal spacings of 14Å for HB dried at 100-105°C and water occupies 4.4Å. Dekking[1] reported that in a 3.3% (w/v) bentonite suspension swelling to an extent of

31Å occurred. The spacing in HB-PMMA adduct was found to be 17.9Å. In all probability two MMA layers may be conjectured within the interlamellar Si-layers arising from approximately 30Å C-axis expansion in aqueous phase. Such an explanation requires free radical initiation to exist on the Si-layer. With such knowledge the following radical forming steps have been proposed.

$$\text{Si-lattice} + \text{R-OH} \longrightarrow \dot{\text{R}}\dot{\text{O}} + \dot{\text{H}}$$

$$\dot{\text{R}}\dot{\text{O}} + \text{ROH} \longrightarrow \text{R-O-R} + \dot{\text{O}}\text{H}$$

$$\dot{\text{O}}\text{H} + \text{ROH} \longrightarrow \text{H}_2\text{O} + \dot{\text{R}}\dot{\text{O}}$$

'or'

$$\text{Si-lattice} + \text{R-OH} \longrightarrow \dot{\text{R}} + \dot{\text{O}}\text{H}$$

$$\dot{\text{O}}\text{H} + \text{R-OH} \longrightarrow \text{H}_2\text{O} + \dot{\text{R}}\dot{\text{O}}$$

It might be possible that the vacant d-orbital of Si in the lattice stretched the unsymmetrical alcohol molecule to form the radical. The radicals then attacked the monomer molecules in the initiation step in the interlamellar space of the clay mineral. The frequency of termination between growing chains will be low due to the separation of interlamellar Si-layers by nearly 30Å.

On the homopolymerization of Acrylonitrile ACN, Methacrylonitrile MACN and Styrene ST.

The successful homopolymerization of MMA in the present investigation foresees the possibility of homopolymerization of ACN, MACN and Styrene. Except styrene both ACN and MACN have similar

type of substitients at the vinyl group. Styrene can be polymerized by any of the free radical or ionic paths. We have observed that HB/ethanol failed to polymerize both ACN and MACN although they were copolymerized each with MMA. This observation confirmed the proposed mechanism for the homopolymerization of MMA.

The reason for the failure of ACN and MACN homopolymerization may be accounted for by the interference of the metal ions through the -CN group of the monomers. The -CN group being attached to the vinyl group, the latter has helped to polarize the former by the metal ion. The vinyl group in the process is thereby deactivated. The monomers, however, go to copolymerization possibly due to their solubility in the MMA layer. The deactivation of the nitrile group by the cations on the clay surface may be represented as shown below:

drift of electron

$$CH_2 = CH - C \equiv N \cdots\cdots Na^+$$

This certainly explains the disruption in symmetry of the electronic arrangement on the vinyl group that is essentially required for free radical generation and propagation through the monomer molecules.

Section B:

i) Infrared spectra

The application of infrared spectroscopy has become increasingly important for the study of the nature of interaction of organic molecules with the clay minerals[12]. The organic molecules has to compete with the water molecules to come to the near surface of the clay minerals.

One of the earliest observations of hydroxyl absorption bands in the spectra of mineral sample is found that was reported in 1937 for montmorillonite by Buswell, Kerbs and Rodebush. The spectrum as shown in Fig. 17A is of the sample evaluated at 100°C. By comparing absorbate species the absorption bands with those of an alcohol in non-polar solvent, it is concluded that the high-frequency band is due to hydroxyl groups which are not involved in hydrogen bonding, while the low frequency band demonstrated hydrogen bonding. Later studies[13-15] have shown that the high frequency band is due to structural hydroxyl groups in the bulk of the clay laminae, and that the hydrogen bonding arises from absorbed water[16].

With quartz particles (1 micron diameter) Soda[17] has observed the absorption bands at about 3400, 1100 and 950 cm^{-1}. The high frequency band is assigned to the oxygen-hydrogen stretching vibration of surface hydroxyl groups. However, there exists some uncertainity concerning the assignment of the hydroxyl deformation vibration to the low frequency bands and the 1100 cm^{-1} band is

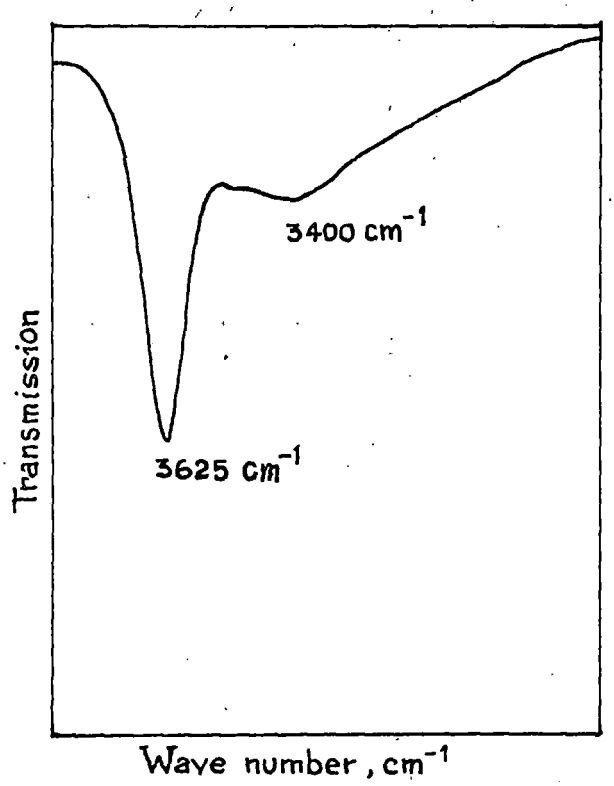
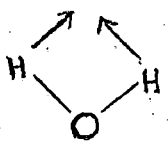


Fig.17A. I.R. spectrum of montmorillonite, dried at 100°C for 36 hours.

preferred for this vibrational assignment. The highest frequency bands at 3750-3730 cm^{-1} for silica and 3795 cm^{-1} for alumina have been attributed to the stretching vibration of hydroxyl groups which are free and not involved in hydrogen bonding on the surface. A broad band at lower frequencies ($\sim$3650 cm^{-1}) is thought to be responsible for the hydroxyl groups involved in hydrogen bonding on the oxide surface.

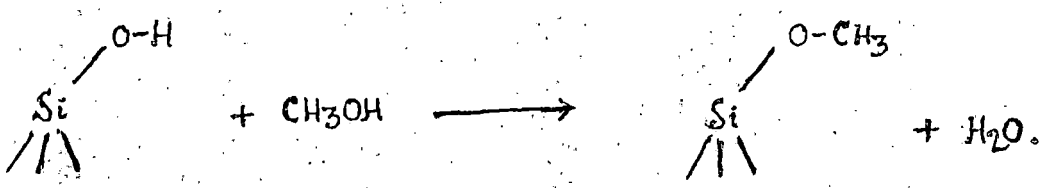
It is possible to distinguish between hydroxyl groups and water molecules adsorbed on the surface of the Silica powder and alumina gel by observing the spectrum in the regions 3800-3300 cm^{-1} and 1650-1600 cm^{-1}. Molecular water gives rise to an infrared active deformation vibration with movement of the hydrogen atoms in the plane of the molecule.



The absorption band at $\sim$1630 cm^{-1} is produced for this mode in liquid water[18]. In comparison to the high frequency hydroxyl component at about 3750-3740 cm^{-1} for the evacuated silica sample at 300°C, the hydroxyl stretching frequency of liquid water occurs at about 3450 cm^{-1} and this shows maked evidence for hydrogen bonding. The absorption bands in the hydroxyl stretching region of the spectrum cannot differentiate between strongly hydrogen bonded hydroxyls and

adsorbed water. The deformation vibration band at 1650-1600 cm^{-1}, of the water molecule has been used to distinguish adsorbed water from surface hydroxyl groups. Kiselev and Lygin[19] and Lygin[20] have observed that the absorption spectrum of the OH hydroxyl stretching mode is much wider and assymetrical when the silicas are evaculated at lower temperatures (below 400°C) but the absorption band becomes sharp when the sample is evacuated at elevated temperatures.

Dzhigit et al[21] observed that the hydrophilic silica surface becomes hydrophobic on treatment with methanol. This is due to the incorporation of the methyl group on the silica surface. The reaction is studied by infrared spectroscopic methods[22]. The intensity of the free hydroxyl band at 3750 cm^{-1} decreased and the bands appeared at 2965 and 2862 cm^{-1}, corresponding to the CH-stretching modes of methyl groups on the surface. The reaction occurred has been considered to be as follows:



The surface methoxyl groups are stable to heat and the i.r. shows that they are not removed from the surface by heating to 400°C. The group may be slowly replaced by hydroxyls when the sample is reacted with water. It has been suggested that the methylation of the surface does not proceed to completion due to steric hindrance by $-OCH_3$ groups on the surface which prevent from the reaction between remaining hydroxyl groups and alcohol.

The infrared spectroscopic technique to determine the orientation of structural hydroxyl groups in the aluminosilicate laminea may be employed if the sample is in the form of an extended single sheet as in the case of micas. Alternatively, a powdered sample may be used if the individual particles can be aligned by deposition from an aqueous suspension. After drying to remove the excess water, the spectrum of the oriented deposit may be recorded.

A vibration which involves a changing dipole-moment along the direction of the incident radiation will not interact with the electric vector of the radiation, since this is oriented perpendicular to the direction of the beam. The change in dipolemoment for the hydroxyl stretching vibration is directed along the oxygen-hydrogen internuclear axis. If this direction is normal to the plane of the silicate laminae (001 plane), no hydroxyl absorption band will be recorded for radiation normal to this plane. Including the clay deposit at an angle to the infrared beam will result in a component of the dipolemoment change being directed parallel to

the electric vector. An infrared absorption band will ensue in the spectrum, the intensity of which will increase with increased inclination of the sample to the infrared beam. For hydroxyls directed at angles other than normal to the silicate planes, the band intensities will be proportional to the component of the dipole moment change that is perpendicular to the beam direction.

The octahedral positions are only two-thirds filled with aluminium and magnesium for the bentonites. The absorption at 3620-30 cm^{-1} is due to the hydroxyls directed towards the octahedral vaccancies (Fig. 17) in pure bentonite. The sample, not being sufficiently dry at 105°C shows a broad hydroxyl stretching band at 3400 cm^{-1} and an associated deformation band at 1640 cm^{-1}, both due to absorbed water molecules. The absorption of ethanol in bentonite on the surface of bentonite is evident from the absorption band at 1660 cm^{-1} (Fig. 19) in ethanol treated bentonite. In pure HB (Fig. 17) the O - H deformation (coupled) band at 1120 cm^{-1} is being broadened when the clay mineral is treated with ethanol. For the later (Fig. 19) a broad band appears at 1230 cm^{-1} - 1000 cm^{-1} due to coherent existence of C-O stretching vibration O-H deformation (coupled) vibration on the surface of the clay mineral. The interaction of the alcohol molecule with the clay mineral is thus established from i.r. studies and as the conditions are explained the alcohol molecules are successfully competing to reach to the surface of the clay mineral when sufficient water molecules are present.

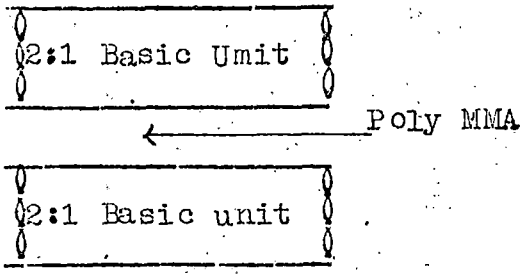
The analysis of i.r. spectrum of polymethylmethacrylate (PMMA) helps to distinguish the characteristic configurational isomers. It has been reported[23] that polymers of different tacticity usually give different absorption spectra. One of the major differences of i.r. spectra of a purely isotactic and a purely syndiotactic polymer is reflected by the characteristic band at 1058 cm^{-1}, which remains absent for the purely isotactic product. The purity of the istotactic form is usually determined with the help of this band. The i.r. spectrum of PMMA as is obtained from the clay ethanol system as indicator has been shown in figure 18 and the analysis of the spectrum leads to the conclusion that the polymer has either a syndiotactic or atactic configuration. The i,r. analysis, however, helps little in distinguishing these two.

The far infrared spectroscopic study of PMMA helps in establishing a particular configuration corresponding to a particular model of isotactic or syndiotactic configuration[24]. The spectrum (Fig. 20) corresponds to six i.r. active band related to a point group C_{2v} with the alternating aspect of syndiotactic model. The low energy region of the spectrum (100-200 cm^{-1}) as shown in the figure has a noise which may be eliminated by a check up with interferometer.

ii) X-ray studies:

All who have reported the polymerization of vinyl monomers on the dry clay minerals emphasized the initiation of polymerization through the 'Al-sites' of the aluminosilicates[25,26]. In all the observations some amount of unextractable polymers retains with the mineral. This reuiqres a direct interaction of the active Al-site of the mineral and the monomer. Dry clay mineral at the elevated temperatures makes its 'Al-sites' acidic (Lewis) in nature which produces the radical cation on the monomer (e.g., Styrene) that propagates. In aqueous suspension of bentonite such as initiation process is quite unacceptable due to deactivation of 'Al-sites' by water molecules. Some authors[27] have showed that the Si-sites are also active in catalysing a dissociation of the conventional initiators like AIBN or Benzoyl peroxide. In our present investigation we have not used any initiator. Still it has been established that the HB ethanol system can be used successfully to initiate polymerization of MMA through a free radical mechanism. The X-ray study has been undertaken to find out whether the polymer layer is adhered to the Si-surface in the interpsaces of the clay mineral or it remained free that can be completely separated by the solvents (like Benzene, DMF etc). The adherence to the Si-surface means the interaction of the monomer directly with the free radical on the Si-atom on the surface. The bentonite mineral has a basic unit structure in which the alumina octahedra is standwiched between the Silicon tetrahedra. Thus, after the polymerization the polymer

will reside in the interspaces of the basic units (Fig. Shown below). This will increase the basal spacing of HB even in its collapsed state.



The clay sample (HB) is dried at 100-105°C in the air oven and gives a basic spacing of 14Å. The treatment of the clay mineral with ethanol and dried at the same temperature increases the basal spacing to 17.0 Å , a value which is due to the formation of double layer complex of the alcohol with the mineral (Fig. 16) Dekking[27] reported that a 3.3% (w/v) bentonite suspension has a water layer of 35.4Å. Therefore, in aqueous suspension swelling to an extent of 31Å occurs. On close examination a spacing of 17.9Å has been found in dry HB-PMMA adduct. This allows two MMA layers (each attached to Si-layer) within the interlamellar space. In consequence, it can be expected that the frequency of termination between the growing chains would be low since that would involve two interlamellar Si-layers separated by nearly 30Å. Such an explanation requires free radical initiation to exist on the Si-layer.

Glaeser and Mering[28] examined the relative stabilities of hydrogen, calcium and sodium montmorillonite complexes with methanol, ethanol, n-propanol, isopropanol, n-butanol and cyclohexanol. They observed that the hydrogen and calcium forms could retain a monolayer against prolonged evacuation, but sodium form could not retain the organic compound. For the polymerization reaction with HB-ethanol system we have observed that vacuum dried hydrogen bentonite in solid aggregation can polymerize MMA but sodium clay failed if the latter kept for prolonged evacuation at 60°C. This indicates that ethanol is very much involved with the clay surface (HB) in effecting the polymerization of MMA.

iii) Electron spin resonance spectra:

The electron spin resonance spectra of different samples related to the present investigation are studied to trace out whether any odd electron was present to initiate the polymerization process. The Mössbauer spectrum (Fig. 23) of the dry clay sample (Hydrogen Bentonite) has been examined with $^{57}C_o$ in Palladium matrix of strength 2 mC_i and using a γ-ray source of 14.4 Kev. The spectrum showed a flat base line and thus indicating the absence of iron. The data did not fit to a doublet of Lorentzian curve which is necessary for absorption due to iron atom. This observation rules out any possibility of iron atom as a source of odd electron transfer in the process of polymerization as observed by Solomon and Loft[29].

The figure24,show the e.s.r. spectra of dry Hydrogen Bentonite (HB) and ethanol treated dry Hydrogen Bentonite in reference to DPPH. All the clay samples has been taken in solid aggregation and are obtained from the suspension of HB in water-ethanol mixture. The sample was dried from the mixture of the solvents at 100-105^{o}C and finally evacuated at room temperature for 48 hours. Dry Hydrogen Bentonite has no e.s.r. signal but HB-ethanol responds to it indicating that HB-ethanol has odd electron within the sample whereas the pure clay mineral has no odd electron at all. As iron is absent in the clay matrix it is obvious that the origin of the odd electron in HB-ethanol lies with the interaction of alcohol molecule with the clay mineral.

The e.s.r. spectral study lies with the property of unpaired electrons. Such electrons in the transition metal ions are found in incomplete inner orbitals. The other source of unpaired electrons comes from the free radicals. The electron in free radicals are found in the outer orbital and they are produced from the homolytic fission of a covalent bond. The electrons possess angular momentum only in integral multiples. It follows that the associated magnetic moment must also be quantized, according to fundamental postulates of quantum theory, corresponding to a finite number of possible orientations with respect to an external magnetic field. Each orientation represents a discrete energy level and transitions between these levels may be induced by interaction with electromagnetic radiation. In essence, it can be said that

the electromagnetic field reversing the direction of the magnetic dipole and hence reversing the spin of the electron by the net absorption of energy from the field. This is the basis of the e.s.r. observation. The frequency ν_0 of the electromagnetic radiation which causes the transitions of the unpaired electron spin is related to the magnetic field H' in which the sample is placed is given by the simple equation

$$h\nu_0 = g\beta H_0 \qquad \text{--------(7)}$$

where 'h' is the Planck's constant, is the Bohr magneton (a) factor for converting angular momentum to magnetic moment), and g is a factor, called Lande 'g' factor, which is numerically close to two for free electron on the radial.

In reference to a standard (Say DPPH) of known 'g' value (2.0036) and microwave frequency the H_0 value of the standard material becomes known. Therefore from the 'scan range' and the field set as recorded in the instrument the 'H_0' value of the investigating sample can be calculated easily. If ' H' is the field separation between the standard and the unknown samples, the 'g' factor for the unknown is given by

$$g = 2.0036\left[1 - (\delta H/H_0)\right] \qquad \text{... (8)}$$

'δH' is positive if the unknown sample has its centre at the higher field.

For the HB sample the average 'g' factor is calculated from the equation (2) and is found to be 'g_{av}' = 2.018. Undoubtedly the value comes from the electron on a radical of thealcohol. The work of Sullivan and Koski[30,31] has positively identified the following species with methanol.

$\dot{C}H_3$ (quartet, a^H = 23.5 Gauss), $\dot{C}H_2OH$ (triplet, a^H = 18 (Gauss) $\dot{C}HO$ (assymetric doublet, a^H = 130 Gauss) and $CH_3\dot{O}$ (singlet with nearly axially symmetric g-tensor, g_x = 2.007, g_y = 2.002, g_z = 2.034). The $CH_3\dot{O}$ radical believed to be present in u.v. irridiated methanol has g_{av} = 2.014 and may well be the peroxy radical also. Since the 'g' value of $C_2H_5\dot{O}$ and $C_2H_5O\dot{O}$ lies very close to $CH_3\dot{O}$, it can be inferred from the above 'g' value of clay ethanol system that $C_2H_5\dot{O}$ active radical which is responsible for occurring the free system. The spin concentration of the sample has been detected to be as low as 10^{12} spin with the line width for the HB-ethanol sample is approximately 20 Gauss.

iv) Nuclear magnetic resonance spectrum:

The proton magnetic resonance of polymethylmethacrylate has been discussed much in several literatures[32,33]. In the discussion Bovey has shown that the isotactic methylene signal in PMMA is a quartet whereas that for the syndiotactic is a singlet. The observation of the quartet methylene signal (for two different H environment) is an absolute determination of the presence of

isotactic structure and is independent of any type of evidence. Bovey further has observed that PMMA obtained from an anionic initiator is predominantly isotactic whereas free radically initiated polymerization is found to produce PMMA of a predominantly syndiotactic form (Fig. 21)

The PMMA obtained from the initiation of Hydrogen Bentonite-ethanol system in aqueous medium has been shown in figure 21. The 2-methyl peak at 8.98 τ is characteristic of the predominantly atatactic form over the syndiotactic form of PMMA. The peak at 8.78 τ corresponds to the α-methyl group in isotactic form. The methylene peak is found to be singlet and appeared at 7.94 τ.

The spectrum of the α-substituents does not in itself provide an absolute indication of configuration, but must be correlated with the β-methylene resonance or some other absolute measurement. If this is done, the α-substituent spectrum may give more detailed configurational information than the β-methylene spectrum. The chemical shifts of α-substituents commonly vary appreciably with the relative configurations of the nearest neighbouring monomer units, but this is not always the case is found in the spectrum of polymethylmethacrylate. The 2-methyl group resonance in PMMA is markedly dependent on configuration, whereas the ester methyl resonance (peak at 5.66 in $CDCl_3$) is (Fig. 22)

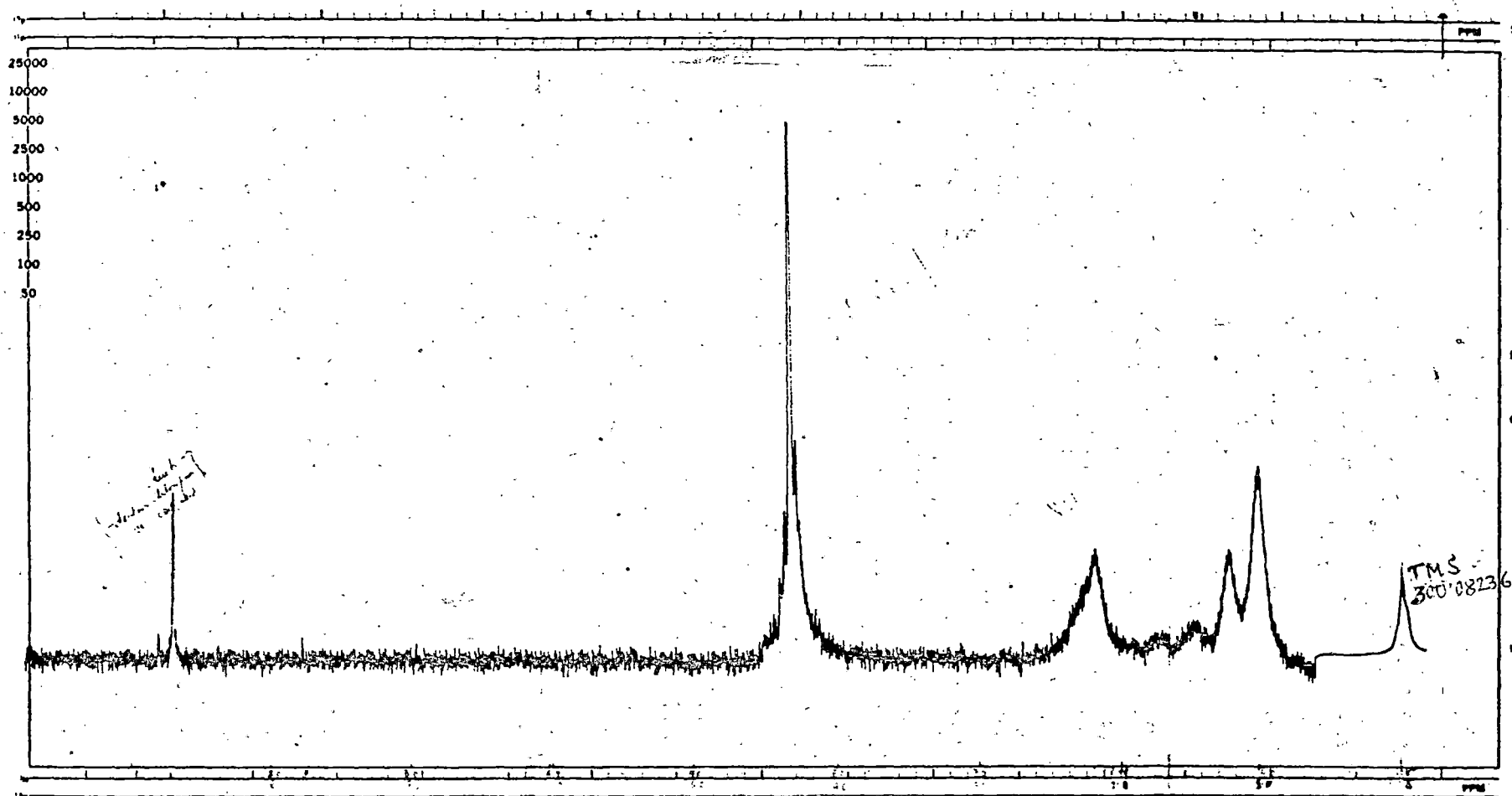


FIG. - 22. P.M.R. Spectrum of Poly-methyl-methacrylate (In $CDCl_3$) produced from HB-Ethanol initiating system: 300 MHz.

not. When such discrimination is possible one can observe three species of α-substituents in a polymer which is not stereochemically pure. Whereas preradically initiated PMMA is found to have an approximate i:h:s ratio of 10:30:60 (i = isotactic, h = heterotactic and s = syndiotactic), anionic initiated polymers can be made having either 100% isotactic or 90% syndiotactic. The PMMA obtained from the HB-ethanol initiating system has the i:h:s ratio 14:47:39, the spectrum is being taken in dichlorobenzene (Fig. 21). The structural information regarding the PMMA obtained from the present investigating system thus infers that though heterotactic isomer and syndiotactic isomers are present in almost equal amounts, the tendency to form heterotactic isomer is more. In a study of the effect of solvent on the appearance of spectra, it has been shown[34] that in benzene solution the ester methyl group appears as three close resonances which have been assigned to isotactic, heterotactic and syndiotactic, in order of increasing field strength. The separation of the 2-methyl resonance were less in aromatic solvents.

Though the stereoregularity of anionically produced polymers has been shown[35] to be dependent on the solvent, the syndiotacticity of the free radically initiated polymer has been claimed to be independent of the nature of the solvent[36]. The relative peak heights of isotactic and syndiotactic resonances, however, changed markedly when the measurement temperature raised from 35° to 90°C,

and this is attributed to the narrowing of the isotactic signal occurring at a lower temperature than that for the syndiotactic signal. This is paralled by the difference in glass transition temperature of isotactic polymer at 45°C and syndiotactic at 110°C.

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CHAPTER - V

COPOLYMERIZATION

VA. Introduction

After successful polymerization of MMA with HB/ethanol initiating system, attempts have been made to homopolymerize other acrylic monomers like acrylonitrile ACN and methacrylonitrile MACN with the same system. The attempts were, however, unsuccessful due to the formation of non propagating species following an interaction between HB and monomer molecule. This has been discussed in Chapter IV. Consequently it was thought that ACN or MACN could be polymerized following the polymerization of MMA with HB/ethanol resulting in copolymers/block copolymers.

Copolymers of acrylates and acrylonitrile are of tremendous industrial importance and have been used in various ways. Several methods like solution[1], suspension[2,3] and emulsion[4,5] polymerization are known to prepare MMA-ACN copolymers. The emulsion technique, however, is frequently used for its reproducibility, low cost and simplicity. Granular copolymers of ethyl acrylate EAC and ACN have been prepared by Thomas[3] with dispersed bentonite. When EAC and ACN were dissolved in ethanol and heated under reflux condition with benzoyl peroxide for six hours copolymers were obtained[2]. The physical properties of the copolymers, in some cases, are dependent on the method of preparation. Improved fibers have been obtained when ACN polymers or copolymers were prepared

in aqueous solution rather than in emulsion. Emulsion copolymers of 90:10 EAC : ACN provide adherant, flexible spray coatings for PVC prestheses and resisted soiling, aging etc[8].

Copolymers of acrylates having 5-15% ACN are known to yield high resistant synthetic rubber after vulcunization[6,7]. Rubbers prepared from ternary copolymers of methyl or ethyl acrylate, 2-8% ACN and ~ 60% butadiene have also been discussed[9]. Flexible resilient coatings for rubbers were obtained from a ternary copolymer of EAC : ACN : 2-methyl styrene (75:12:10)[10]. Copolymers of 75-78 : 25-22:: MMA : ACN were blended with GRS and nitrile rubber[11] and with PVC[12] and found to be impact resistant. Acrylate - ACN copolymers have found applications as binder. Paper coatings in which they were used to bind inorganic pigments were reported to possess excellent flexibility, gloss, fold and water resistance and printability[13].

In copolymers comprising of MMA and ACN the methacrylate contributes toughness and flexibility whereas ACN adds hardness, higher softening temperature, greater strength and decreased water absorption. For MMA-ACN copolymer prepared free radically with benzoyl peroxide at 60°C the reactivity ratios are 1.35± 0.1 and 0.18 ± 0.1 respectively[14]. Anionically (sodamide in liquid ammonia at -30°C) produced copolymer, however, resulted in reactivity ratios of 0.25 ± 0.25 and 7.9± 1.6 respectively[15]. Other investigations on anionic copolymerizations of MMA and ACN

reported small amounts of MMA in the copolymer indicating its reactivity ratio close to zero[16,17]. The termination constant for free radical copolymerization of MMA and ACN has been calculated to be 200[18]. This indicates a strong preferential cross termination rather than termination by like radicals.

It has been theorized that the inability of HB/ethanol system to polymerize ACN or MACN might control the formation of homopolymer in the copolymerization of MMA with either of the monomers. The propagation of ACN or MACN polymerization in the copolymer would occur from the methacrylate radicals. Any small but negligible amount of homopoly ACN or MACN, if produced, would result through transfer to monomer. The success in copolymerization would result in relatively pure copolymer without subsequent solvent extractions. Moreover, the structure of the clay mineral would, perhaps, control the structure and property of the copolymer. This chapter deals with the copolymerization of MMA with ACN and MACN and determination of reactivity ratios.

Copolymerizations of vinyl monomers on clay surface have not been studied in details. We, therefore, took advantage of the present initial system in copolymerizing MMA and other non polymerizable monomers.

VB. Experimental

The copolymerizations are carried out in well cleaned stoppered glass bottles made of corning glass at 60°C with HB/ ethanol system as has been mentioned in Chapter III. The copolymers are extracted from the clay polymer adduct by THF, centrifuged and is precipitated from petroleum ether. The process is repated three to four times to get the pure product. The analysis for carbon, hydrogen and nitrogen of the copolymer are made from C.D.R.I, Lucknow, India. The molecular weight distribution pattern (M_w / M_n) of MMA-Co-MACN and MMA-Co-ACN are obtained from Akron, OHIO, U.S.A. The C^{13} n.m.r. spectrum of MMA-Co-MACN and the p.m.r. spectra of MMA-Co-ACN are obtained from Akron, OHIO, U.S.A. The p.m.r. spectrum of MMA-Co-MACN is obtained from C.D.R.I. Lucknow, India .

The compositions of the monomers in the copolymer have been determined from the analysis values for carbon, hydrogen and nitrogen in the samples.

VC. Results:

The study of copolymerization involves the calculation of reactivity ratio of the monomers. Several authors have put forward different methods for the calculation of the reactivity ratios[19,20,21]. A reliable, simple but convenient method is the linear graphical method of Kelen and Tüdős[22]. The present investigation involved the copolymers of acrylonitrile and methacrylonitrile with methyl methacrylate. Such monomer conjugates have been chosen because (i) the groups attached to the vinyl groups are electron withdrawing (i.e., the ester group in MMA and nitrile group in MACN and ACN), (ii) the position occupied by the methyl group in both the monomers (MMA and MACN) is similar with respect to the vinyl carbon atom. The homopolymerization of acrylonitrile and methacrylonitrile failed with clay-ethanol initiating system and this has already been accounted for in Chapter IV. The unique feature with these two monomers lies in that their copolymerizations were possible with the clay-ethanol initiating system. It provides an elegant method of preparing the copolymers because the purification does not involve the laborious procedure of separating the copolymer from the homopolymer of MMA.

The determination of reactivity ratios involve the expression:

$$\frac{dM_1}{dM_2} = \frac{M_1}{M_2} \cdot \frac{r_1 M_1 + M_2}{r_2 M_2 + M_1} \quad \cdots\cdots (1)$$

where M_1 and M_2 are concentrations of the monomers in the feed and $\frac{dM_1}{dM_2}$ is the ratio of the concentrations of the corresponding constituents in the polymer yield. The quantities r_1 and r_2 are the reactivity ratios expressed as the ratio of the monomers 1 and 2 and is expressed as

$$r = \frac{\text{Specific rate constant for the homopolymer formation}}{\text{Specific rate constant for the copolymer formation}}$$

Kelen-Tüdős[21] presentation involves the graphically evaluable linear equation derived from equation (1)

$$\eta = \left(r_1 + \frac{r_2}{\alpha}\right)\xi - \frac{r_2}{\alpha} \quad \text{--- --- --- --- ... (2)}$$

where the transormed variables are

$$\eta = \frac{G}{\alpha+F} \text{ and } \xi = \frac{F}{\alpha+F}, \; G = \frac{X(Y-1)}{Y} \text{ and } F = \frac{X^2}{Y};$$

$$X = \frac{M_1}{M_2} \text{ and } Y = \frac{dM_1}{dM_2}$$

and α denotes an arbitrary constant ($a > o$). The variable ξ cannot take any positive value, only these in the internal $(0,1)$.

Though the above equation (2) has been reported to yield an easily evaluable and dependable values of r_1 and r_2, we

adopted a different equation using the advantage of the present investigation that neither acrylonitrile nor methacrylonitrile forms homopolymers and hence $r_2 = 0$ (where the subscript '2' is assigned to the nitrile monomers). We can write equation (1) as

$$Y = \frac{r_1 X + 1}{r_2 + X} \times X \text{ , where the transformed}$$

variables are $\frac{M_1}{M_2} = X$, and $\frac{dM_1}{dM_2} = Y$

Therefore, $\frac{Y}{X} = \frac{r_1 X + 1}{r_2 + X}$, and when $r_2 = 0$,

$$r_1 = \frac{Y - 1}{X}, \text{since } X \neq 0 \quad \text{--- --- --- ... (3)}$$

The C, H, N and thereby O of the (i) poly (MMA-Co-MACN) and (ii) Poly (MMA-Co-ACN) have been shown in Table 1. The composition of the constituents in the copolymers are calculated from the analytical data of C, H, N and O. The value of $Y = (dM_1 / dM_2)$ thus becomes known from which the reactivity ratio of monomer, MMA is calculated for Poly (MMA-Co-MACN) (Table - 2) and Poly (MMA-Co-ACN)(Table - 3) have been calculated from graphical plots. The reactivity ratio of MMA has been calculated to be 1.27 for the former and 1.31 for the latter.

Table - 11

The analytical values of C, H, N for different copolymer compositions

M_1 = Methyl Methacrylate; M_2 = Methacrylonitrile or Acrylonitrile.

Nature of Copolymer	Chemical Composition (M_1) in moles lit^{-1}	(M_2) in moles lit^{-1}	Analytical composition of the copolymer % C	% H	% N	% O
MMA-Co-MACN	1.50	0.50	62.58	7.68	2.79	26.95
	1.25	0.75	57.48	7.61	4.68	30.23
	1.00	1.00	63.00	7.79	5.20	24.01
	0.50	1.50	68.19	7.49	5.99	18.33
	0.25	1.75	69.12	7.19	7.36	16.33
MMA-Co-ACN	1.50	0.50	60.88	7.65	2.84	28.63
	1.25	0.75	59.83	7.58	4.77	27.82
	1.00	1.00	61.93	7.52	5.50	25.05
	0.50	1.50	64.42	7.38	6.98	21.22
	0.25	1.75	68.36	7.21	7.59	16.84

Table - 12

$[\text{Clay}]$ = 0.834% (w/v); $[\text{Ethanol}]$ = 0.34M; Time : 12 hours

Temp. 60°C

Reactivity ratio of MACN (r_2) = 0

MMA Conc. in the feed, (M_1) in moles lit^{-1}	MACN Conc. in the feed, (M_2) in moles lit^{-1}	Relative MMA Conc. (% Oxygen) in the product	Relative MACN Conc. (% Nitrogen) in the product	$\frac{(M_1)}{(M_2)} = \frac{\%O}{2\times\%N}$	$[dM_1]/[dM_2]$	Reactivity ratio of MMA ($= r_1$)
2.0	0.00	32.16	-	-	-	
1.75	0.25	-	-	7.00	-	
1.50	0.50	26.95	2.79	3.00	4.83	
1.25	0.75	30.23	4.68	1.67	3.23	
1.00	1.00	24.01	5.20	1.00	2.30	1.27
0.75	1.25	-	-	0.60	-	
0.50	1.50	18.33	5.99	0.33	1.53	
0.25	1.75	16.33	7.36	0.14	1.11	
0	2.0	-	-	0	-	

Table -13

$[\text{Clay}]$ = 0.834% (w/v); $[\text{Ethanol}]$ = 0.34M; Time : 12 hours

Temp. 60°C

Reactivity ratio of ACN (r_2) = 0

MMA Conc. in the feed, (M_1) in moles lit^{-1}	ACN Conc. in the feed, (M_2) in moles lit^{-1}	Relative MMA Conc. (% Oxygen) in the product	Relative ACN Conc. (% Nitrogen) in the product	$\frac{(M_1)}{(M_2)}$	$\frac{[dM_1]}{[dM_2]} = \frac{\%O}{2\times\%N}$	Reactivity ratio of MMA (r_1)
2.0	0	32.16	-	-	-	
1.75	0.25	-	-	7.00	-	
1.50	0.50	28.63	2.84	3.00	5.04	
1.25	0.75	27.82	4.77	1.67	2.91	
1.00	1.00	25.05	5.50	1.00	2.28	1.31
0.75	1.25	-	-	0.60	-	
0.50	1.50	21.22	6.98	0.33	1.52	
0.25	1.75	16.84	7.59	0.14	1.11	
0	2.0	-	-	0	-	

An attempt has been made to calculate the reactivity ratio of MMA from the p.m.r. spectra of the copolymers shown in Fig.28&29&30. The relative monomer concentrations in the copolymer are calculated from the proton counts of the integration curves. The proton counts are corrected for the number of protons for methylene (Fig.28&29) and methine peak intensities for Poly (MMA-Co-ACN). Methylene peak, being overlaped with the methine peak, is again standarised with the relative intensities of the ester methyl group with the correction for number of protons. The reactivity ratio of MMA by this method has been calculated to be 1.30 which is close to the value mentioned earlier. Similarly, the comparison of relative intensities of methyl peaks of MMA and MACN, the reactivity ratio of MMA has been calculated to be 1.21. The copolymers (Fig.30&29) are prepared from 1:1 molar ratio of the monomers. The copolymer of figure 28 has 1.25: 0.75 molar ratio of MMA and ACN.

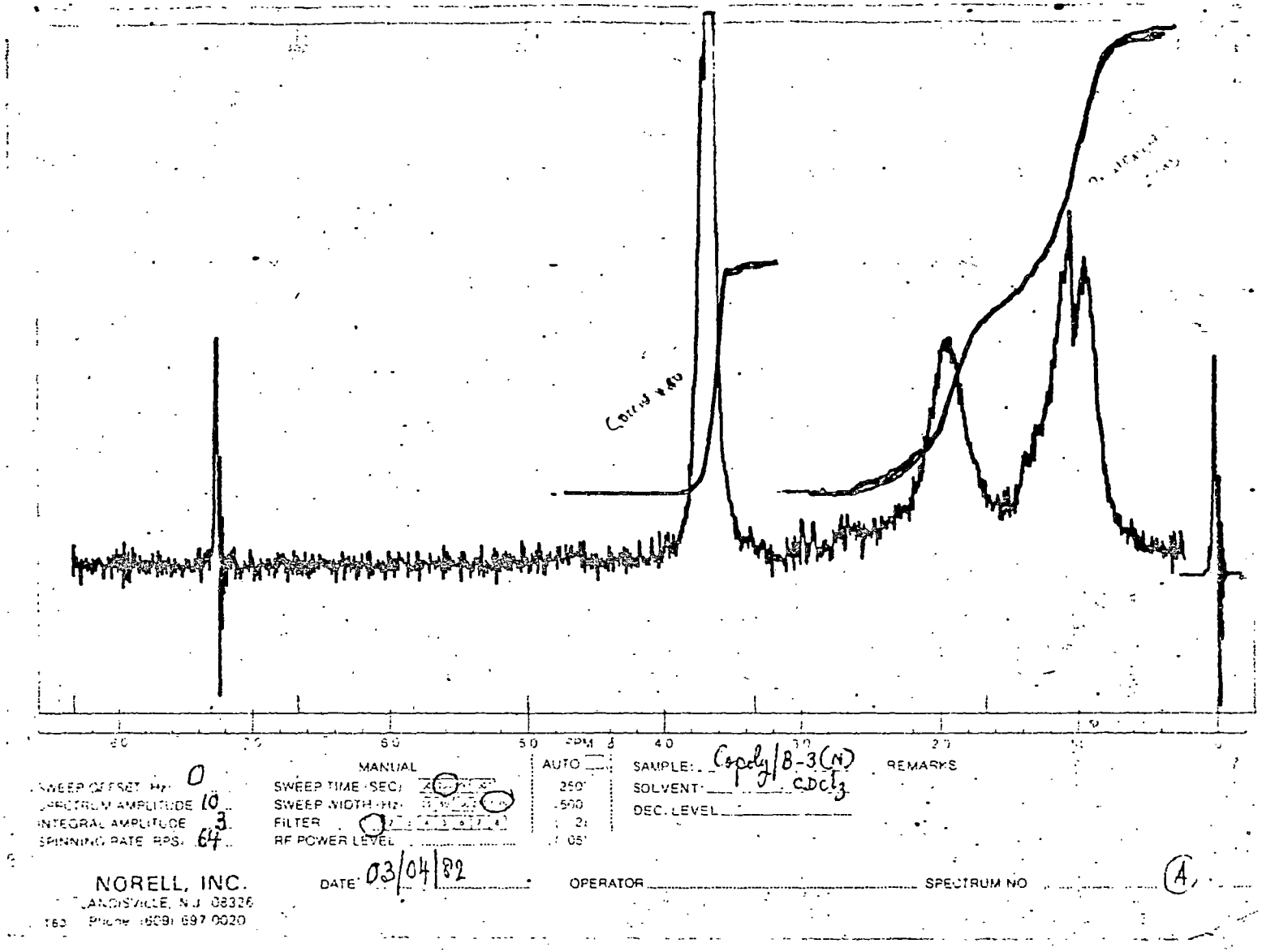
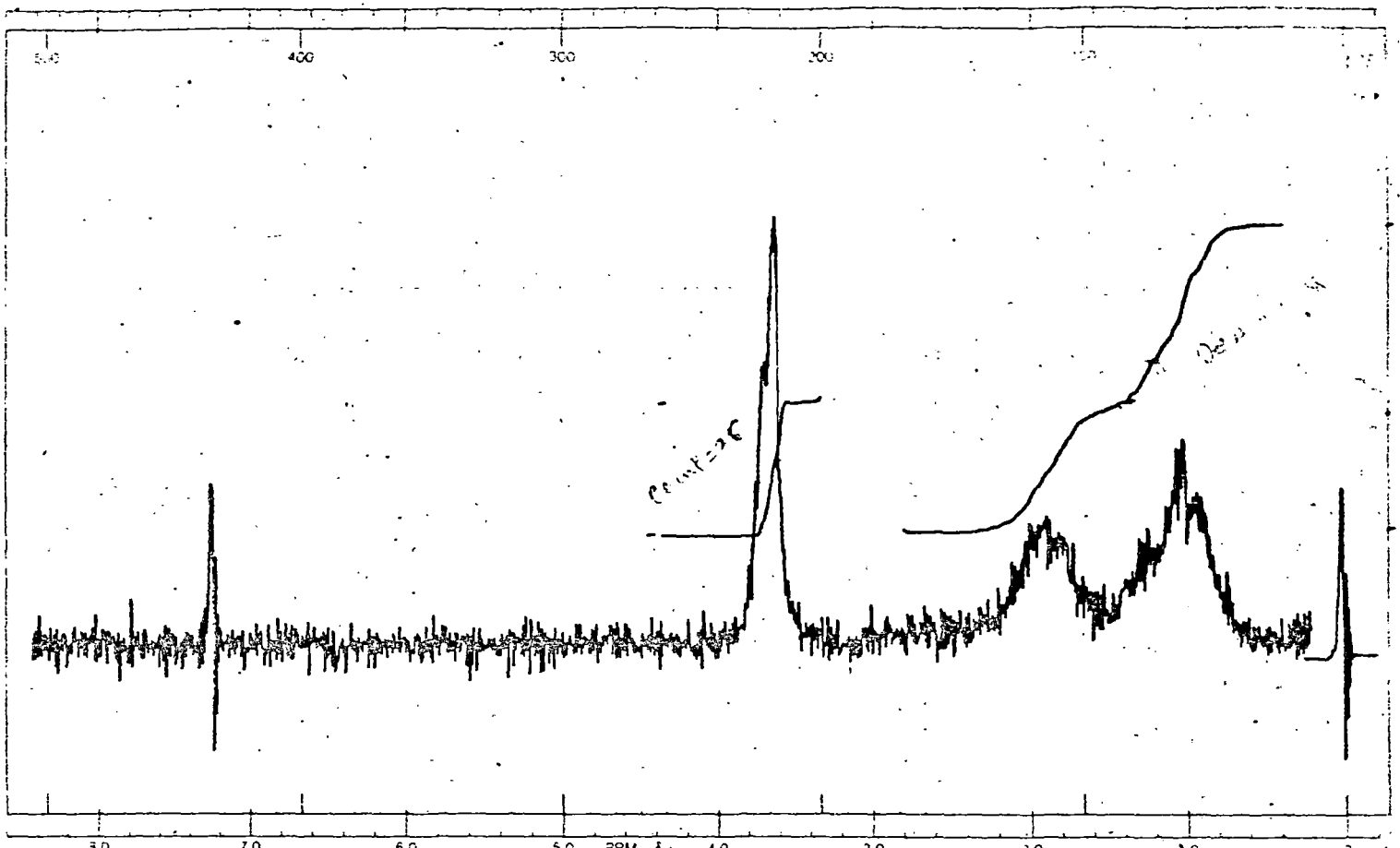


FIG. - 28. P.M.R. Spectrum of Poly (MMA - Co - ACN) in $CDCl_3$; 60 MHz; produced from (MMA):(ACN) = M/ M.



MANUAL ✓ AUTO ☐

SWEEP OFFSET (Hz)	0	SWEEP TIME (SEC)	(250)
SPECTRUM AMPLITUDE	12.5	SWEEP WIDTH (Hz)	500
INTEGRAL AMPLITUDE	4	FILTER	(2)
SPINNING RATE (RPS)	60	RF POWER LEVEL	0.07 (05)

SAMPLE: Copcl2/B-4 REMARKS

SOLVENT: $CDCl_3$

DEC. LEVEL

NORELL, INC.
LANDISVILLE, N.J. 08326
Phone (609) 697-0020

DATE 03/02... OPERATOR SPECTRUM NO

FIG. - 29 . P.M.R. Spectrum of Poly (MMA - Co - ACN) in $CDCl_3$; 60 MHz; produced from (MMA):(ACN) = M/ M.

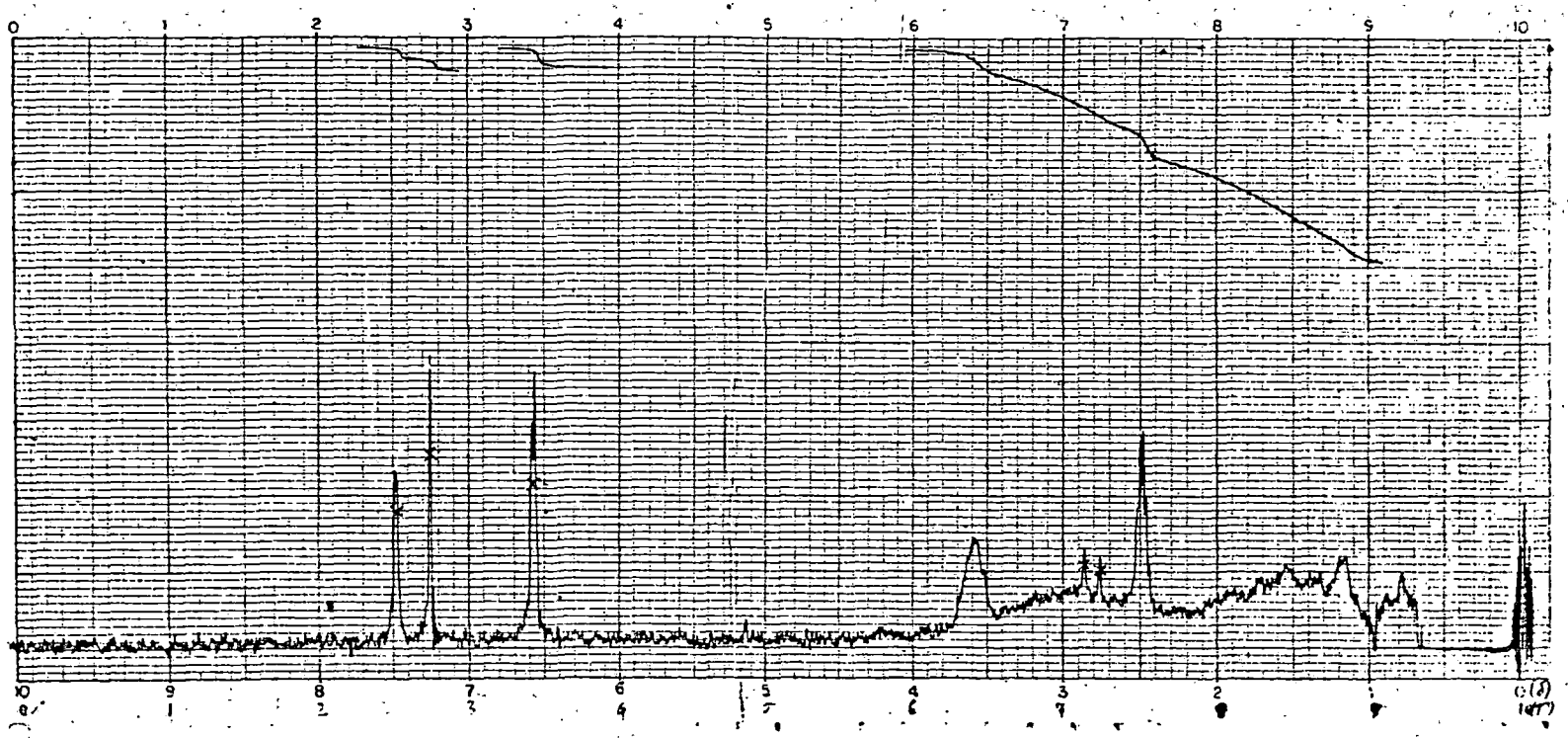
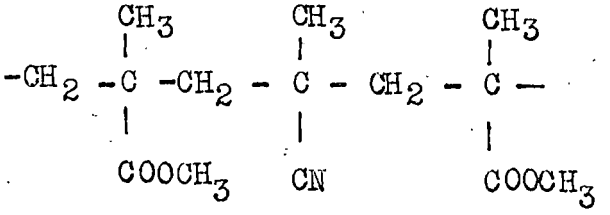


FIG. - 30 . P.M.R. Spectrum of Poly (MMA -Co - MACN) in $CDCl_3$ and DMSO-D_6 mixture (90 MHz).

VD. Discussion:

The C, H, N and O analysis of the copolymers produced from the reactions of MMA/MACN (1:1 molar ratio) and MMA/ACN (1:1 molar ratio) have been tabulated (Table -1) in VB. A comparison between experimental and theoretical values requires a model of triad sequence of the copolymer. We can discuss the model with the copolymer MMA-MACN by the following figures

Fig. (i)

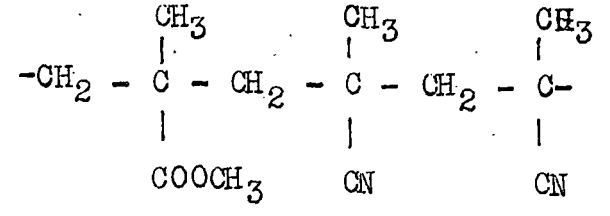


Triad Sequence

Theoretical values : C = 62.92%, H = 7.84%, N = 5.24%, O = 23.94%

Analytical values : C = 63.00%, H = 7.79%, N = 5.20%, O = 24.01%

Fig. (ii)

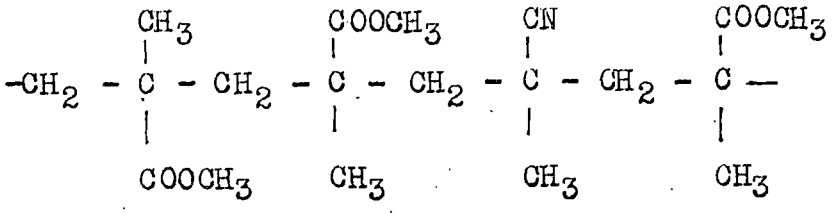


Triad sequence

Theoretical values : C = 66.67%, H = 7.69%, N = 11.97%, O = 13.68%

Analytical values : C = 63.00%, H = 7.79%, N = 5.20%, O = 24.01%

Fig. (iii)

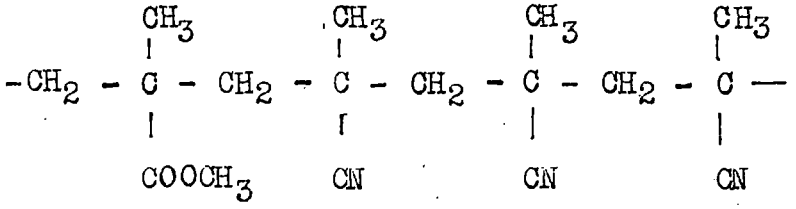


Triad sequence

Theoretical values : C = 62.13%, H = 7.9%, N = 3.81%, O = 26.16%

Analytical values : C = 63.00%, H = 7.79% , N = 5.20%, O = 24.01%

Fig. (iv)



Tetrad sequence

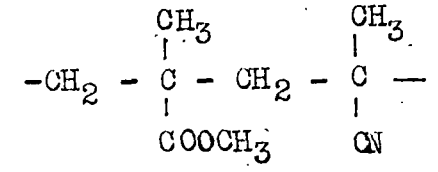
Theoretical values : C = 67.77%, H = 7.64%, N = 13.95%, O = 10.63%

Analytical values : C = 63.00%, H = 7.79%, N = 5.20%, O = 24.01%

The dyad sequence, if exists at all, will have an alternating sequence. The nitrile group being present in small amounts, the block copolymerization for the present copolymer requires higher

energy due to the steric hindrance of the bulky ester group in the close pack. The dyad sequence represented by Fig. V has the following composition:

Fig. (v)



Dyad Sequence

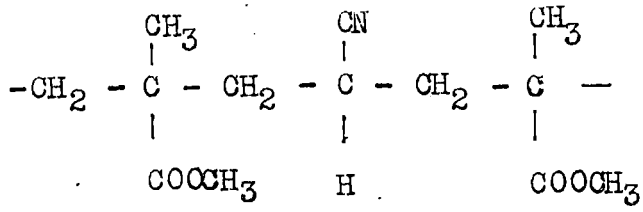
Theoretical values : C = 64.67%, H = 7.78%, N = 8.38%, O = 19.16%

Analytical values : C = 63.00%, H = 7.79%, N = 5.20%, O = 24.01%.

Thus the models considered above help to assign the copolymer structure in which for two molecules of MMA, there is one unit of MACN

Similarly, for the copolymer MMA-Co-ACN, the C, H, N and O analytical values (C = 61.95%, H = 7.52%, N = 5.50%, O = 25.05%) are obtained for a particular composition of 1:1 molar ratio of MMA and ACN reactants and the analytical values are compared with the theoretical values of different trial sequences. Again the analytical values were close to the theoretical values of triad sequence with alteration of the components.

Fig. (vi)



Theoretical values: C = 61.66%, H = 7.50%, N = 5.53%, O = 25.29%

Analytical values : C = 61.93%, H = 7.52%, N = 5.50% , O = 25.05%

Though with the above discussion we have reached to the sequencial structure of the copolymer, but the method as discussed is not sufficient to point towards the configurational structure. The later can be solved by the n.m.r. spectroscopic analysis of copolymers.

VD.1. NMR studies of Poly(MMA-Co-MACN) and Poly(MMA-Co-ACN):

i) C^{13} -magnetic resonance spectrum of Poly (MMA-Co-MACN)

Results of the ^{13}C n.m.r. spectral analysis of the copolymer as prepared with 1:1 molar ratio of MMA and MACN is given in Table 4. The values of chemical shifts for different carbon atoms have been obtained by applying the proton decoupling technique. The very sharp signals are obtained for the positional carbon atoms, there are two peaks at $\delta = 67.39$ and $\delta = 64.15$ with relative peak intensities 19 and 21 respectively, are neglected. These two peaks appears due to consideration of a relatively low intense peak

(δ = 41.10) of 20 for the methyl carbon of MACN. Obviously, the MACN component in the copolymer is present in low amount. The main peaks at the left of $CDCl_3$ and at the right of $CDCl_3$ have been

Table - 4

^{13}C Chemical shifts for Poly(MMA-Co-MACN) system. Reference: $CDCl_3$ (ppm)

Carbon atom incorporated in the Group	Line assigned δ	Relative peak intensities
Ester Carbon ($-\bar{C}OOCH_3$) of	137.69	27
MMA unit	137.19	22
Nitrile ($-\bar{C}N$) carbon of MACN unit	130.18	39
	67.39	19
Methylene ($-\bar{C}H_2$) carbon of the copolymer	66.31	55
	66.12	54
Not considered	64.15	21
Ester methyl ($-COO\bar{C}H_3$)	59.29	46
Carbon of MMA unit	58.98	59
	58.50	25
Methyl carbon ($-\bar{C}H_3$) of MMA unit	46.87	92
Methyl carbon ($-\bar{C}H_3$) of MACN unit	41.10	20

$\bar{C}$ = the resonating carbon

expanded. This shows that a line at $\delta \sim 137.70$ has been missed in the main spectrum due to its very low intensity. Thus the ester carbon peak is a triplet actually. Both the triplets, one for (Fig:32) ester carbon and the other for ester methyl, are due to the three possible configurational structures of the copolymer.

The CMR studies for the characterization of the copolymer, however, often very difficult since they may be arranged in three types of stereoregular units viz. mm, mr, rr where 'm' and 'r' indicated the meso- and racemic forms respectively. In the table No. 4, the line assignments at 137.69, 137.19 have been made for heterotactic (mr) and syndiotactic (rr) triads in order of increasing field. The isotactic form, being in very small amount is not detected in the original spectrum. However, it is clear from thespectrum (Figs: 31-33) that the heterotactic triad has a little predominance over the syndiotactic form. The observed relative intensities of approximately 2:5:4 for mm :mr:rr are consistent with the free radically generated polymers having a structure like $\leftarrow CH_2CHR\rightarrow_n$ and the same steric configuration, the conformation in solution is qualitatively the same. Thus the assignment of the nitrile carbon lies of the spectrum has been made from their similarities with the relative positions of carbon in the main chain, for which definite line assignments already exist. For instance, polypropylene has been chosen for a suitable comparison since ^{13}C nmr spectra of known isotactic and atactic

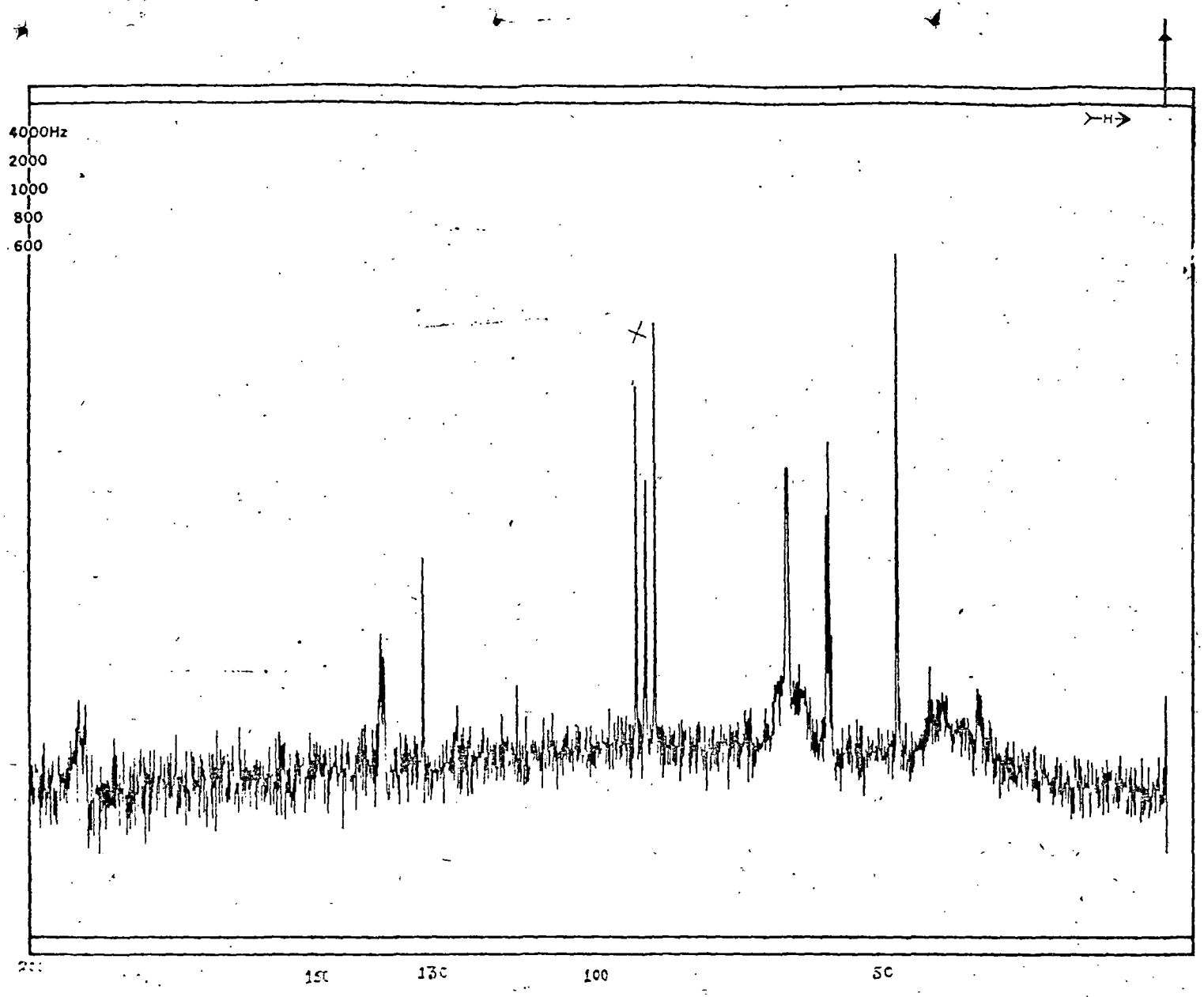


FIG. - 31. C.M.R. Spectrum of Poly (MMA - Co - MACN) in $CDCl_3$.

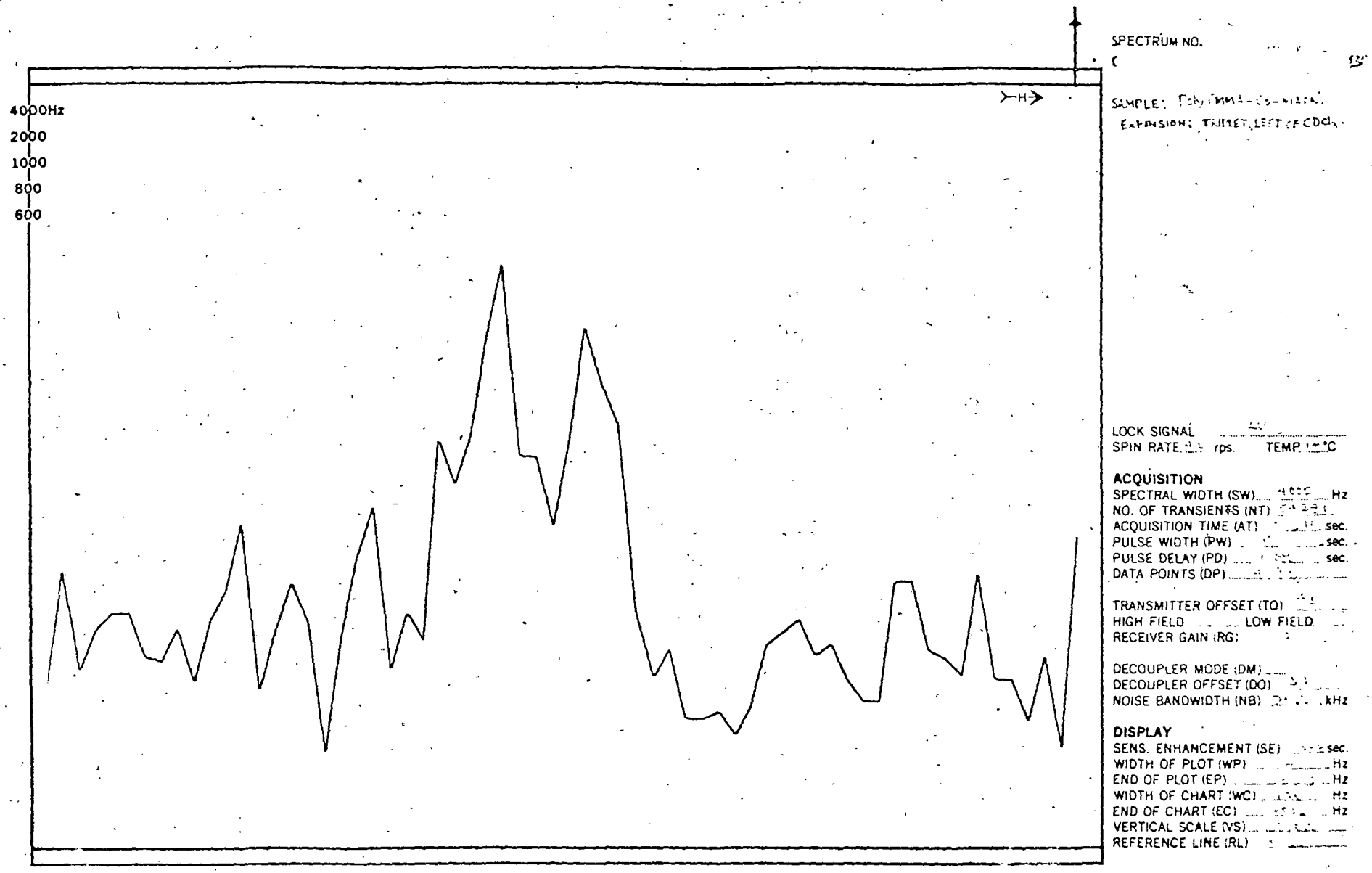


FIG. - 32 . C.M.R. Spectrum of Poly (MMA - Co - MACN) in $CDCl_3$; Expansion: Triplet, left of $CDCl_3$.

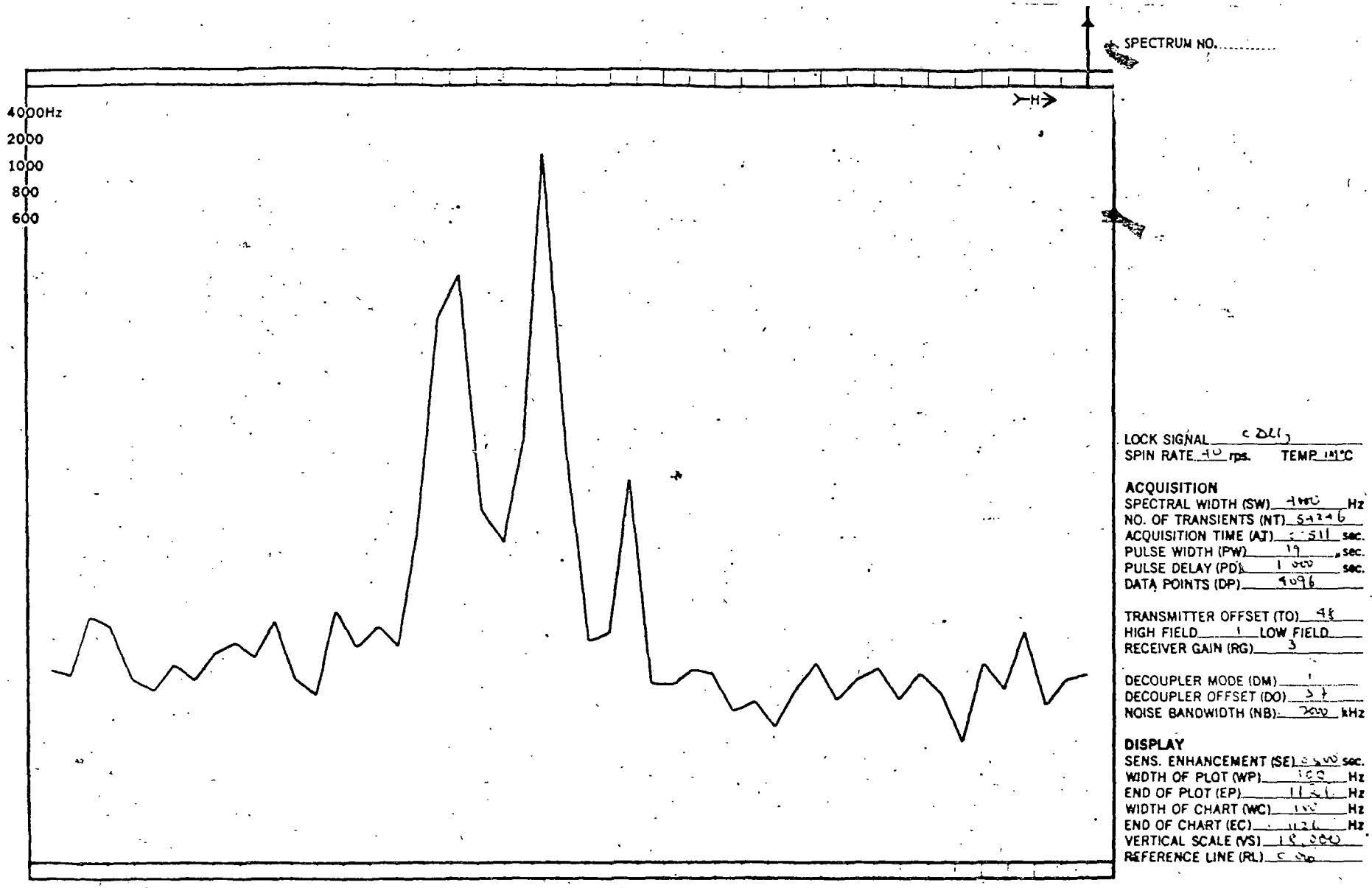


FIG. - 33 . C.M.R. Spectrum of Poly (MMA - Co - MACN) in $CDCl_3$; Expansion: Triplet, Right of $CDCl_3$.

versions of these polymers do exist with definitive assignments.

One of the important points to note is that the chain termination did not occur either through the water molecule (where $-CH_2-OH$ signal exists) or through the water molecule (where $-CH_2-O-R$ signal comes) since for both the cases the ^{13}C nmr would show theline beyond $\delta = 140$. It is thus highly probable that the chain termination occurred through recombination. The high molecular weight ($\sim 4.5 \times 10^6$) of the copolymers is quite consistent with this argument. The distribution pattern for the copolymer ($\frac{M_w}{M_n} = 1.92$) also (Fig. 34) supports above termination mechanism.

The inference drawn in the above discussion on the basis of the reliability of comparative study with a standard or reference spectrum implies that the methylene carbon line of an isotactic dyad should appear at low field relative to that of a syndiotactic dyad. The methylene signal at $\delta = 66.31$ and $\delta = 66.12$ (in Fig. 31) with the peak intensities 55 and 54 respectively, however, depicted that isotactic and syndiotactic dyads are present almost inequal amounts in the polymer chain. The heterotactic sequence is present in small amount and is insignificant.

ii) ^1H -magnetic resonance spectrum of Poly (MMA-Co-MACN)

As we have seen that the sequential pattern of Poly (MMA-Co-MACN) and Poly (MMA-Co-ACN) are same, it is expected that their configurational sequence will also be the same. Since, the molecule

Fig: 34

SAMPLE:

Poly (MMA-MACN)

$\bar{M}_w/\bar{M}_n = 1.92$

Flow Rate: 1 ml/min

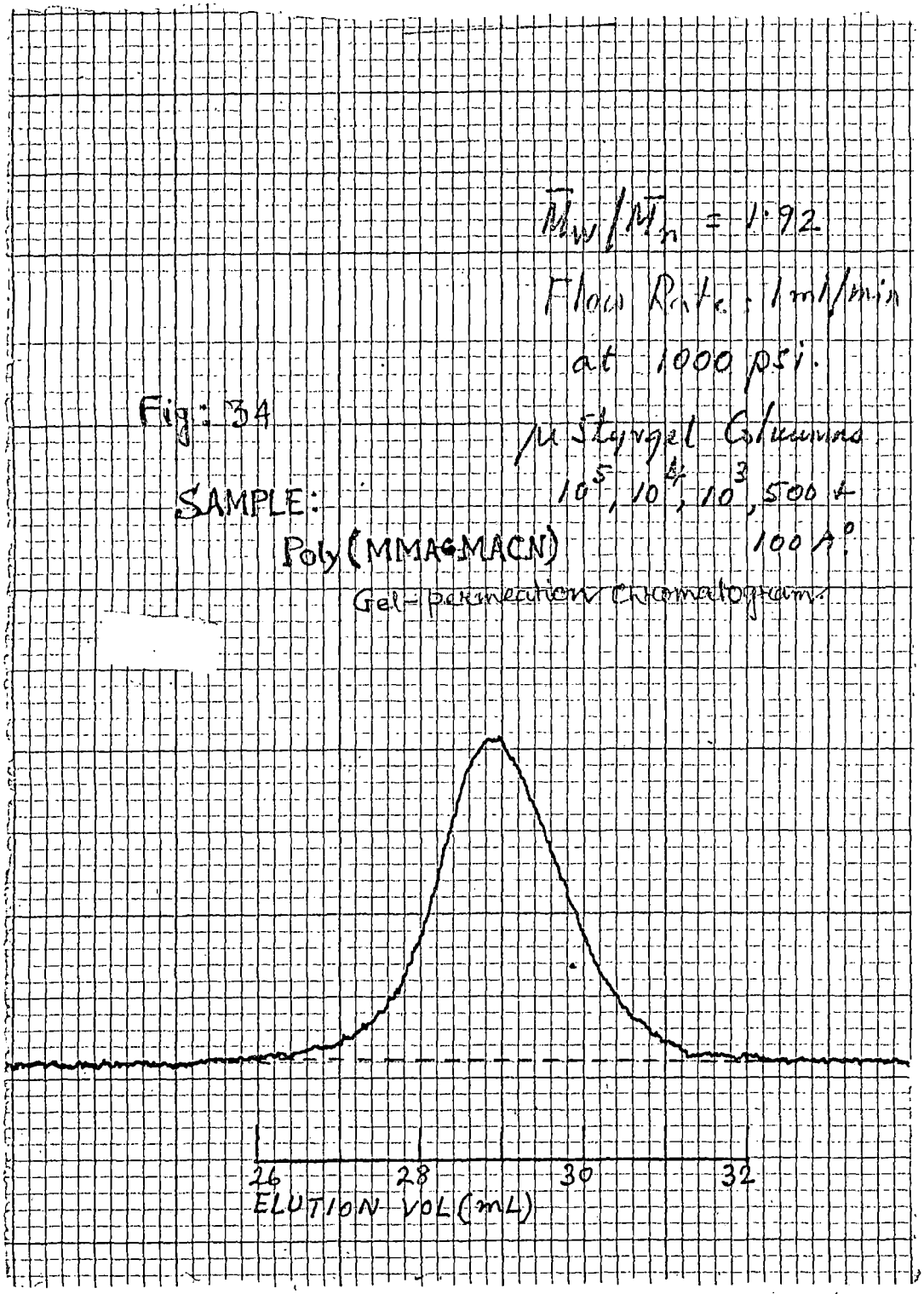
at 1000 psi.

μ Styragel Columns

$10^5, 10^4, 10^3$, 500 Å

100 Å

Gel-permeation Chromatogram



will tend to lie on the lowest energy state and thus would try to avoid the steric repulsion of the bulky substituents on the carbon atoms. Such a situation has been discussed above and is true also for Poly (MMA-Co-ACN). The p.m.r. of the latter copolymer has been discussed in the next section and will held true for the configurational analysis of Poly (MMA-Co-MACN) also. The spectrum has been shown in figure 30.

iii) ^{1}H - magnetic resonance spectrum of Poly (MMA-Co-ACN)

The p.m.r spectra of Poly (MMA-ACN) copolymers have been recorded with polymers produced with different concentrations of monomers to find out and to provide knowledge on the configurational structure and the reactivity ratio of the monomers from n.m.r. spectra. The n.m.r spectra of the copolymer are shown in Figures 28 and 29 . The methylene and methine protons have appeared as a single peak with a hump. The β -methylene resonance (saturated) appeared at τ = 7.4-8.6 and the methine resonance (saturated) appeared at τ = 8.35-8.60. The position is shifted compared to PMMA, due to the effect of substituents. As discussed for PMMA, that 2-methyl resonance appeared at 8.78, 8.95 and 9.09 τ for isotactic, heterotactic and syndiotactic forms, and since such a sequence holds good, the spectrum (figures 28 and 29) predicts that the methyl methacrylate unit in major part, is oriented in isotactic form. Moreover, the heterotactic and

syndiotactic parts are present in almost equal amounts although less than the isotactic form with such a configuration, the co-polymer is expected to be present in somewhat crystalline form. This has been corroborated by the X-ray diffraction pattern of the copolymer (Fig. 35). However, detailed X-ray study to estimate the percentage of the crystalline form of thePoly (MMA-Co-MACN) is not done. The formation of thecopolymer has caused the methylene group resonance of the homopolymer (PMMA) block to shift to the higher field which may be explained by the fact that $-CH_2-$ group is shielded by the ester and the nitrile groups from the adjacent carbons. However, it is not clear from the spectrum whether the ester group and the nitrile groups are on the same side or on the different sides of the carbon chain.

The p.m.r. spectrum of poly (MMA-Co-MACN) were complex in nature and is difficult to interpret due to the large number of substituents in the polymer chain. However, the $-CH_2-$ resonance has split into quintet which is not symmetrical about mid point.

VD. 2. Discussion on glass transition temperature (Tg):

The formation of the copolymer has been confirmed from the glass transition temperature which has been shown in figure 36.

The T_g and Tm for PMMA have been reported[24] to be 105°C & 200°C. We have shown in figure 36 that the T_g value for the copolymer of MMA and ACN is 110°C, where an inflexion exists for 20°/min and 10°/min conditions . But as shown in the figure such

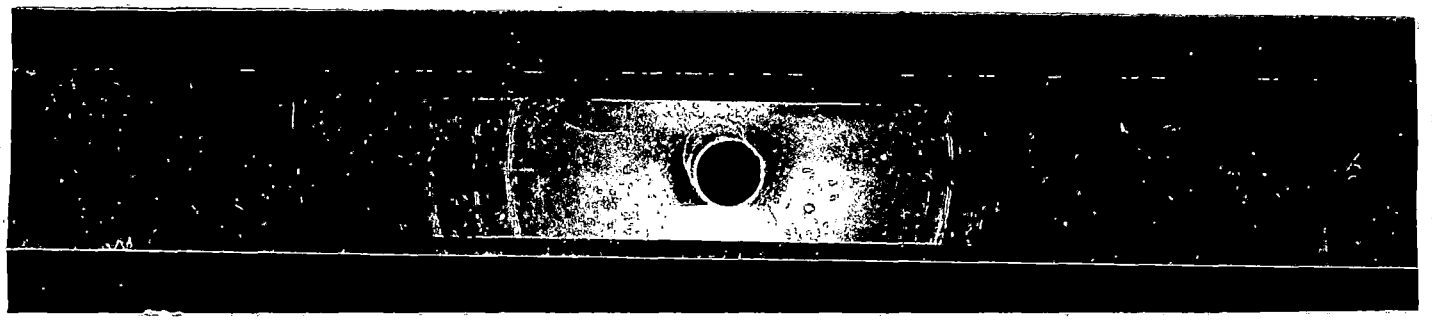


FIG. 35. X-ray diffraction pattern of poly (MMA-CO-ACN.

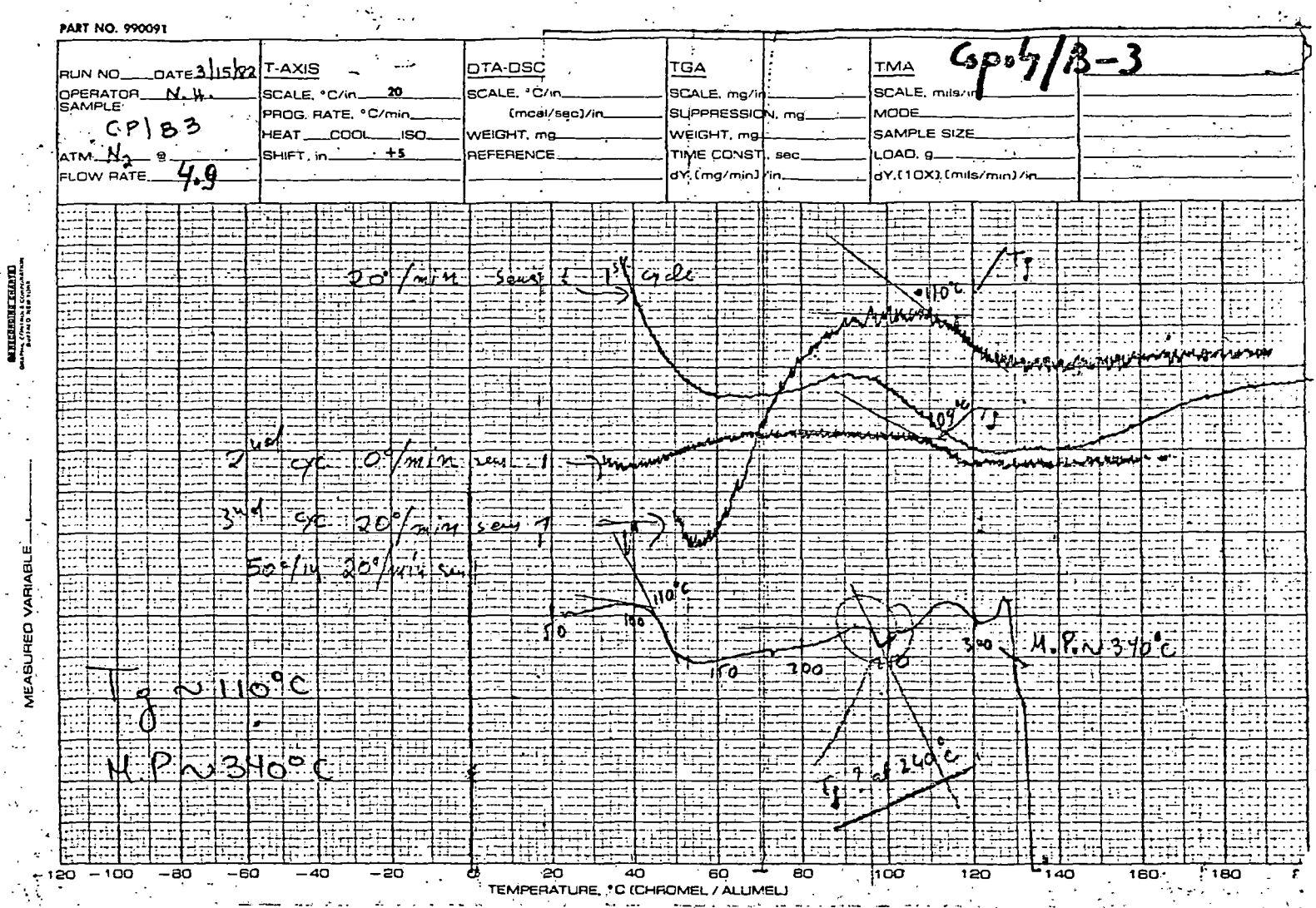


FIG. - 36 . Thermomechanical analysis (TMA) of (MMA - Co - ACN) for determination of Tg and Tm.

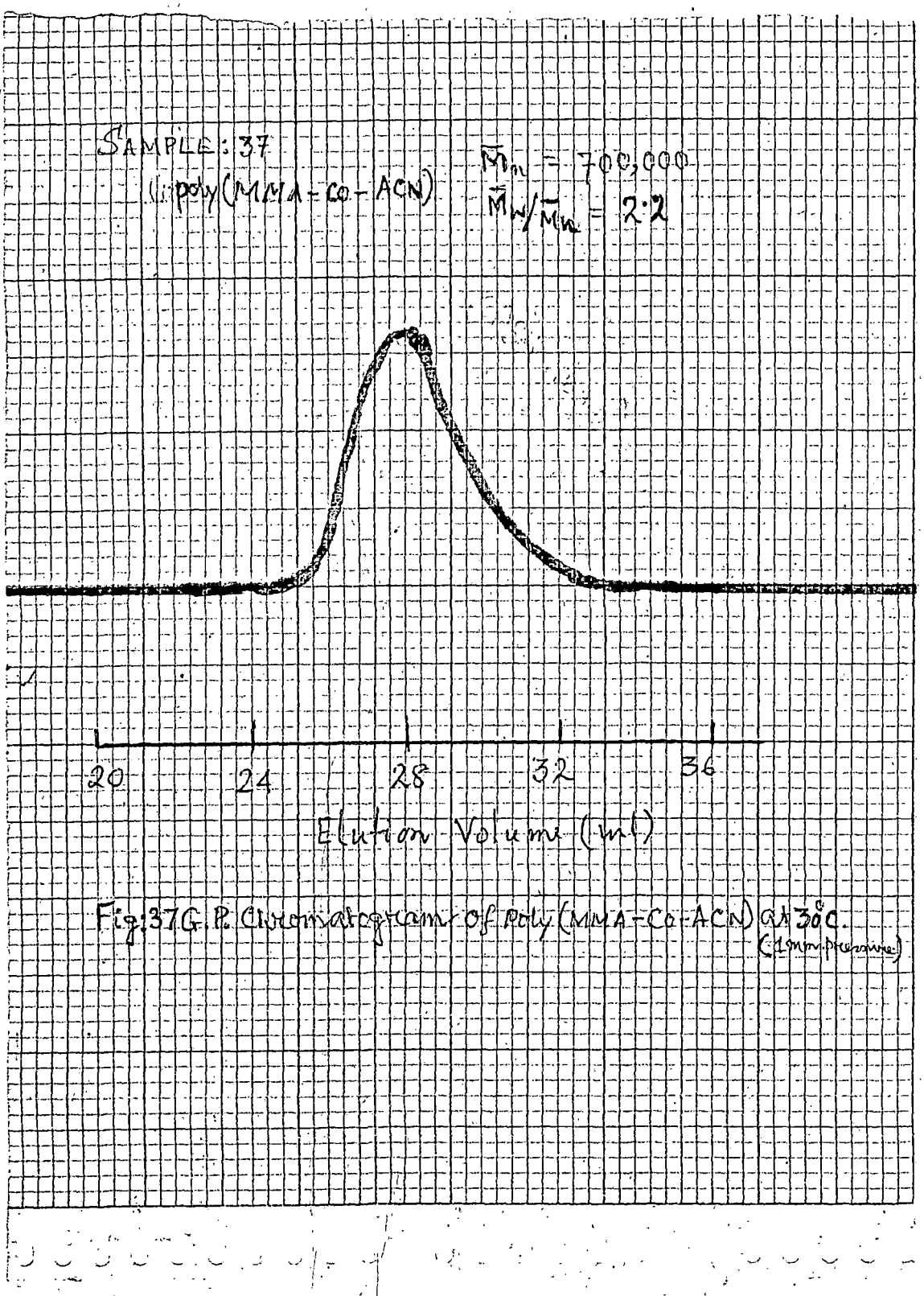


Fig: 37 G.P. Chromatogram of Poly(MMA-co-ACN) at 30°C.
(Programme)

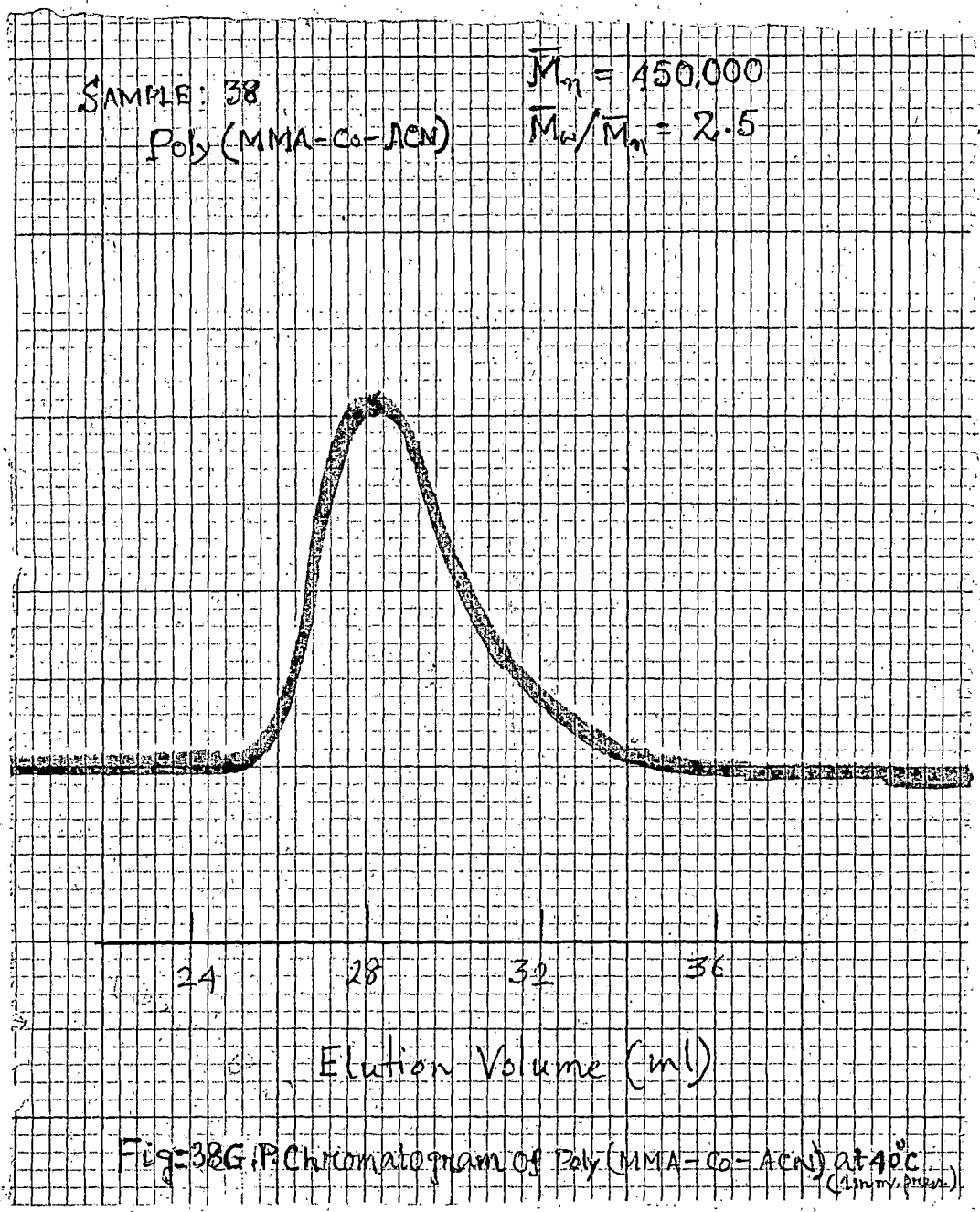
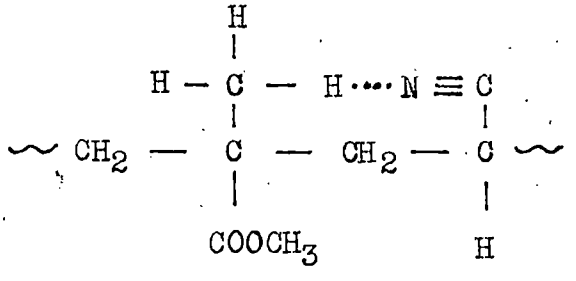


Fig-38G; P. Chromatogram of Poly (MMA-Co-ACN) at 40°C (1 mm/ml, Press.)

a value of T_g is not conclusive. On its way to reach the melting temperature (T_m) we have one more inflexion at 240°C. There are sufficient reason to believe that this temperature may also be the glass transition temperature. The value of T_m has, however, been shown to be 340°C.

The incorporation of the acrylonitrile monomer to the PMMA increases the T_g and T_m -values. This is quite consistent with the previous discussion that the copolymer has the crystalline character where as PMMA is amorphous. The two thermal transitions are generally affected in the same manner by the molecular symmetry, structural rigidity, and secondary forces of the polymer chains like hydrogen bonding or high polarity etc. If 240°C (the higher value) is T_g then it would be reasonable to think that -CN and $-COOCH_3$ were in opposite sides of the polymer chains and the C-C rotation about the chain is restricted due to (i) the steric strain involved in bringing -CN to the same side of $-COOCH_3$ and (ii) the -CN group with its environment of $-CH_3$ group on the same side may involve weak hydrogen bonding as shown below:



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S U M M A R Y

CHAPTER - I : The present investigation embodies aqueous homo- and copolymerization of methylmethacrylate, acrylonitrile and methacrylonitrile, using hydrogen bentonite/alcohol initiating system. Clay minerals are essentially aluminosilicates in which the silicate layer exists in polymeric straight chain bridged by O atoms of the basic SiO_2 unit. Silicon is in tetrahedral form whereas the alumina layers have octahedral geometry with either O or -OH groups. Each alumina layer as $\overline{Al(OH)_6}$ is followed by a silica layer $\overline{as\ Si(OH)_4}$. The layers are held by some O atoms. In bentonite one alumina layer is sandwiched between two silica layers. The other forms are kaolinite - one silica layer attached to one alumina layer and, vermiculite in which sheets of linked tetrahedra of $(Si,Al)_4$ are pointed inward. Polymerizations of vinyl monomers with clay minerals were studied in nom polar media in whuch the aluminium sites (Lewis acidity) were responsible in the generation of cation radicals. Cation radicals of monomers like styrene are stable enough for propagation whereas those of methyl-metahcrylate and the like, because of the instability of the cation radical, could not propagate. However, theories concerning the Bronsted acidity of the clay minerals were also put forward for the initiation of polymerization. The catalytic activity of the clay minerals in inducing polymerization in conjunction with free radical initiators like 2-2' -azobis-isobutyronitrile has already been shown by other authors. In a study with clay mineral it is found that aqueous polymerization of vinyl monomers, 2-2'-azobis-iso

butyra amidine formed complex with clay which, consequently, decomposed easily to polymerize methylmethacrylate, acrylamide, vinyl acetate etc. with much higher efficiency than the free radical initiator alone. The presence of transition metals in clay minerals are known to generate radicals with peroxy acids. Interlamellar complex formation between monomer and clay favoured the propagation. Other polymerization systems involving dry clay minerals in non polar solvent are also available in the literature.

CHAPTER - II

A new initiating system, comprising of hydrogen, sodium or copper forms of bentonite and alcohol, is proposed. This initiating system is incapable of homopolymerizing either acrylonitrile or methacrylonitrile but efficiently polymerized methylmethacrylate and copolymerized these monomers in aqueous medium. The system is, therefore, interesting and provides an easy, inexpensive, and elegant method to prepare copolymers exclusively when acrylo- or methacrylonitrile is used. This initating has only been tested with water insoluble monomers. Thus the scope of future work with water soluble monomers is still left, that the polymer which is produced with insoluble monomers are not all soluble in solvents and are either chemically or physically associated with the clay minerals. This results are helpful in organizing plans to change the surface property of the clay minerals

following adsorption/chemical bond of any polar polymer molecule.

CHAPTER - III

Bentonite suspension was prepared by withdrawing suspension of the clay mineral at pH ~ 8 at a regular interval of 24 hrs, acidifying, treating with H_2O_2 and heating for a long time on a water bath (~ 100°C) till complete decomposition of H_2O_2 was achieved. For the hydrogen form the so formed suspension was treated with cation and anion exchangers.

Monomers and other chemicals were purified adapting standard procedures.

The homopolymerization and copolymerizations were carried out in 100 ml. dark, well stoppered pyrex bottles under nitrogen blanket. Polymethylmethacrylate/clay was centrifuged and the polymer was separated by benzene extraction and purified following repeated precipitation into a mixture of petroleum ether and methanol (50 : 50). The crude copolymers were extracted with tetra hydro furan followed by high speed centrifugation to separate traces of clay particles and finally precipitated from petroleum ether.

CHAPTER - IV

The polymerization of methylmethacrylate occurred with aqueous suspension of bentonites (H^+, Na^+, or Cu^{2+}) only in the presence of alcohols and thiols. The conversions are dependent

on both clay, alcohol concentrations and temperature. In all polymerizations induction period of 60-185 minutes were observed depending upon the reaction conditions. Usually high molecular weight polymers $\sim 10^6$ and moderate to high conversions were obtained. With 1.08% (w/v) hydrogen bentonite (HB) and 0.374M Methyl Methacrylate the conversions at 60°C were 25.2%, 30.7%, 42.25%, 55.6%, 62.9% and 68.2% for 0.86×10^{-3}, 3.43×10^{-3}, 5.13×10^{-3}, 51.30×10^{-3}, 102.60×10^{-3}, 513.00×10^{-3} M ethanol respectively and with varied clay concentrations the conversion were 14.55%, 26.31%, 44.75%, 53.04% and 62.15% corresponding to 3.5, 5.0, 7.5, 10.0 and 12.1 gms per litre of the clay suspension when 0.562 M Methyl methacrylate and 0.34 M ethanol were used for the polymerization at 60°C for 12 hours.

The initial overall rate has 0.5 th order dependance on ethanol concentration. Such dependence is followed by most aqueous free radical polymerization. Free radical nature of this system has been established by e.s.r. spectra and inhibiting effect by diphenyl picryl hydrazyl. Silicon sites are responsible for the free radical generation and has been established by blocking all the octahedral aluminiums of the clay mineral with sodium hexameta phosphate and by successful polymerization of MMA with ethanol treated quartz (200 mesh). It has been suggested that lower alcohols and thiols penetrate the clay surface beyond the first hydration layer and interact with the silicon. The free radicals are

presumably generated by the stetching of the unsymmetrical alcohol molecule by the d-orbital of the silicon.

Transfer to monomer is negligible. The M_n's increased with increasing monomyer concentration. The M_n's increased with increasing monomer concentration. It has been suggested that the conversion and molecular weight increase are due to the adsorption of monomer molecules on the clay surface. The depletion of monomer concentration on the clay surface dictates for fresh monomer adsorption. This is probably because no measurable polymerization took place without intermittent shakings. The overall initial rate of polymerization is first order with respect to monomer. This, along with the 0.5 th order dependence or ethanol concentration and the free radical nature of the reaction suggest that classical equation is applicable.

$$R_P = k_P [M]. \left[\frac{f k_d [I]}{k_t}\right]^{1/2}$$

The conversion of 55.11%, 56.02% of MMA and $\bar{M}_v$ values of the product (PMMA) of 1.12×10^6 and 1.14×10^6 for HB and sodium bentonite (Na-B) under identical conditions concluded that the nature of the cation on the clay mineral is not going to influence the mechanistic behaviour of the polymerization reaction. The PMMA yield of 33% and 41.1% for shaken and 5.1% and 6.7% for the unshaken conditions for 0.3744 and 0.5620 M Methyl

methacrylate concentrations respectively leads to the view that the monomer has to come to the near surface of Si-surface for the polymerization to proceed.

Similar results have been obtained with increasing clay concentration. Parallel increase in molecular weight of the polymers is probable due to the increased viscosity, higher concentration of adsorbed monomer and lower termination rate. The failure of the polymerization with lower clay concentrations viz. 0.3% (w/v) or below is probably due to the very low concentration of radicals generated and some unknown side reactions.

The initiator efficiency of hydrogen bentonite/ethanol has been calculated with respect to ethanol from conversion, molecular weight and concentration of the alcohol. The initiator efficiency accounts for 33% with respect to ethanol. The value with respect to clay was not possible to determine because of the uncertainity in the calculation of hydration number of the clay mineral in the polymerizing system. However, with a knowledge of the basic composition of bentonite, Si sites are $\sim 30\%$ which, assuming 1:1 type of interaction between Si and alcohol, suggests 100% initiator efficiency.

Temperature has positive effect on the polymerization with this initiating system and the rate increased with increasing temperature. The polymerization was extremely slow at and below $40^{o}C$ and hardly measurable amount of polymer could be isolated in 48 hrs. However, the rate increased significantly at higher

temperatures. Thus the rate increased from 5.72×10^{-6} Moles lit.$^{-1}$ sec.$^{-1}$ to 3.92×10^{-5} Moles lit.$^{-1}$ sec.$^{-1}$ at 50 and 80°C respectively. The apprent acivation energy of 15.0 Kcal mole^{-1} is slightly lower than that observed in homogeneous polymerization of methylmethacrylate with azo-bis-isobutyronitrile but higher than usually obtained for aqueous polymerization using various redox initiators.

This is probably due to the preoccupation of the monomer layer im the interlamellar space of the clay mineral before the propagation starts. The monomer reaches the near vicinity og the clay surface where it gets free radicals already produced on the surface.

CHAPTER - V.

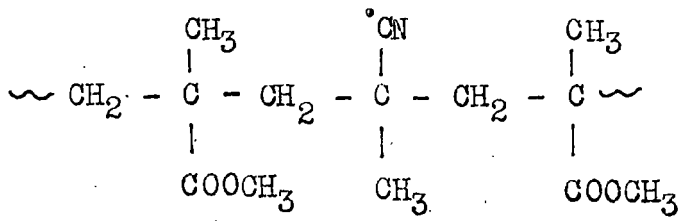
The copolymerization of acrylonitrile (ACN) and methacrylonitrile (MACN) with methylmethacrylate (MMA) under the present investigating HB-ethanol initiating system were important in respect to the failure of both the former monomers (ACN amd MACN) to homopolymerize. The purification of the copolymer avoided a step for the separation of the copolymer from one of its homopolymer i.e. poly acrylomitrile or poly methacrylomitrile.

The copolymers, poly (MMA-Co-ACN) amd poly (MMA-Co-MACN), were mot much stable and degraded considerably with rise in temperature beyond 50°C. Gel permeation chromatographic study with poly (MMA-Co-ACN) showed that $\bar{M}_w/\bar{M}_n$ value of 2.2 changed to 2.5 when the conditioming values of the sample changed from 30°C (1 mm pressure) to 40°C (1 mm pressure). Both $\bar{M}_w$ and $\bar{M}_n$ changes. When $\bar{M}_n$ changes from 7×10^5 to 4.5×10^5 , the $\bar{M}_w$ changes from

1.54×10^6 to 1.125×10^6 (Figs. 37&38). An examination of the nmr spectra of the samples showed that it is the polymeric acrylonitrile group which is degraded from the copolymer chain.

The reactivity ratio of the nitrile monomers in both the copolymers being zero, the same for the other monomer i.e., MMA is calculated from the analysis data for carbon, hydrogen and nitrogen in the copolymer prepared from different monomer concentrations. The compositions of monomers were then known to both in the monomer feed and the copolymer and the reactivity ratios were calculated to be 1.28 and 1.35 for Poly (MMA-Co-MACN) and poly (MMA-Co-ACN) respectively.

The analysis of carbon, hydrogen and nitrogen of both the copolymers further suggested the tirad sequence in the copolymer and having the following structure:



Such a sequence is also a best fit from the nmr spectral observations. Of the two copolymers, poly (MMA-Co-MACN) was taken as a model for the configurational study by ^{13}C nmr spectrum. The analysis of the spectrum leads to the conclusion that the heterotactic triad had a little predominance over the syndiotactic form.

The observed relative intensities of the peaks of approximately 2:5:4 are consistent with the free radical generated copolymer having essentially a random configuration. Furthermore, the chain termination did not occur either through the water molecule or through the alcohol molecule because in that case both the copolymers would produce the line segments beyond 140 for ^{13}C nmr spectrum. It is then reasonable that the chain termination occurred through recombination. This is consistent with the high molecular weight ($\bar{M}_w \sim 1.5 \times 10^6$) of the copolymer yield.

List of Publications

1. Aqueous Polymerization of clay surface 1. The Polymerization of methyl methacrylate on Hydrogen Bentonite : Effect of alcohols.

S. Talapatra, S.K.Saha, S.K.Chakravarti and S.C.Guhamiyogi

Polymer Bulletin, 10, 21-27 (1983)

2. Aqueous Polymerization on clay surface 2. The Polymerization of methyl methacrylate on Hydrogen Bentonite : Effect of monomer concentration and temperatures.

S. Talapatra, S.K.Chakravarti, S.C.Guhaniyogi

Communicated to J. Macromolecular Sci. Chem.

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