INTRODUCTION

In spite of the vast importance of the polymeric material little appropriate emphasis has been placed to determine and understand its structure prior to 19th century. Now-a-days a rapid development of polymer industries has made it necessary to study the molecular structure of these materials and the relationship that exist between the structure, properties and applications.

The overgrowing development of the chemistry of high molecular weight compounds in past 20 or 30 years due to the fact that polymeric material withstand high temperature without impairment of their characteristic advantage and distinct properties. These characteristics led the macromolecule towards the extensive and varied applications as constructive material such fiber forming material, ion-exchange resins, insulative materials, protective membranes and in number of other branches of national economy.

In solid polymers the intermolecular interactions are very complex which prohibit the characterisation of the molecular properties, moreover as the polymer cannot be transformed in gaseous from the intrinsic
properties of the polymer molecules are studied in dilute solutions. In dilute solution the interactions are minimised, therefore, the characterisation of polymers could be done in dilute solutions.

In retrospect it seems very strange that it was not until mid 1930's that serious investigation of the 'Dilute solution properties' were taken into account for those macromolecules. At about this time physical and physico-chemical methods to estimate these properties were developed and were achieving more importance comparable to more classical methods.

From the survey of literature, it appears that maleimides have been studied from different aspects. A great deal of research work on maleimides in the form of patents reflects their commercial importance. Polyimides are known for their distinguish properties viz. high melting temperature, selected solubility in specific solvents, rigidity and stiffness. Combination of maleimides with other monomer enhanced its applicability for various purposes.

The work incorporated in the present investigation deals with the synthesis and study the solution
properties of co-polymers, free radical initiation in particular N-arylmaleimides with methyl methacrylate, which is widely used monomer in modern plastic technology.

Maleimide monomer with a structure of 1:2 ethylenic-type five membered ring which completely hinders the rotation of imide residue around the backbone of the macromolecule which imparts stiffness when maleimide unit is introduced into a flexible vinyl polymer chain, the intra- and inter-molecular interaction different from those of homopolymer are expected to play an important role on the properties, such as chain stiffness, thermal stability of co-polymers. Thus the following co-polymers have been synthesised for their characterisation.

\[ \text{CO} \quad \text{Cl} \]
Some references on the synthesis of maleimide and its derivatives are summarised below:

Berson/1/ reported the synthesis of maleimides from furan - maleic anhydride adduct.

Searle/2/ obtained N-aryl maleimide by heating N-aryl-maleic acid with excess Ac₂O and about 5-10% by weight fused sodium acetate at 80-100°C.

Kratom/3/ treated N-phenyl maleic acid with P₂O₅ at 100-130°C in dioxan to yield N-phenyl maleimide. Other substituted N-phenyl maleimides were prepared similarly/4/.

Carol/5/ prepared N-substituted maleimides in satisfactory yield by treating N-substituted isomaleimides with an anion of lower fatty acid bringing about an isomerisation.

Schamalz/6/ obtained N-substituted maleimides with improved purity and high yields by heating the corresponding maleic acids at 100-160°C in presence of H₂SO₄ and paraffin oil under reduced pressure.

Barrales - Riande/7/ prepared N-(fluorophenyl)maleimide from fluorophenyl amines and maleic anhydride by a modified method. Similarly the keto derivatives of N-phenyl maleimide were obtained by fusing the mixture
of \(C_6X_5NH_2\) \((X = H, Cl, Br)\), maleic anhydride and \(ZnCl_2\) at 150-210°C/8%. Rakočevica - Maksudova/9/ prepared twenty eight maleimides with 25-94% yield by reaction of maleic anhydride with \(R-NH_2\) \((R = Ph, p-tolyl, \alpha, \beta\) naphthyl, p-chlorophenyl, p-bromophenyl).

Fahmy - Aly - Elkomy/10/ prepared \(N\)-aryl maleimides from acid azides. Refluxing succinic, maleic 1,2,3,6 tetrahydrophthalic, 1,8-naphthalene dicarboxylic and propionic anhydride with \(p-RC_6H_4CON_3\) \((R = H, Me, MeO, Cl, NO_2)\) in pyridine for 3 hrs gave the corresponding \(N\)-aryl maleimides with 64-83% yields.

Ihara chemical industries/11/ prepared \(N-(p\)-chlorophenyl) maleimide from maleic anhydride by stirring with \(p\)-chloroaniline and \(H_2SO_4\) (135-138°C) for 4 hrs in xylene. Similarly other \(N\)-substituted maleimides were also prepared by the condensation of corresponding amines with maleic anhydride.

The commercial importance of maleimides has been summarised by its uses in multifield fields:

A) Maleimides in Biosciences

1) Bioicides: Large number of maleimide derivatives are reported to have very good fungicidal, insecticidal,
bacterial and herbicidal activity. The survey of literature has been given in the following references.

N-substituted, 2,3-dichloromalimidides exhibit fungicidal effectiveness against a variety of organisms/12-17/. N-(Alkyl-cyclohexyl) dichloro maleimidides are efficient, oil soluble fungicides/18/.

Torgeson/19/ evaluated a group of N-phenyl maleimide, chloromalimidides and succinimidides as soil fungicides.

Maksudov, N. Kh, Mukhtaroyev, D.Z., and coworkers/20/ compared the fungicidal activity of some compounds from the series of N-substituted maleimides.

These compounds tested on agar against verticillium dahliae mycelium, N-(p-chlorophenyl) maleimide, N-(o-bromophenyl) maleimide, N-(p-nitrophenyl) maleimide, N-N'-p-phenylenedimalmid, N,N'-m-phenylenedimalmid, N-α naphthylmaleimide, N-β-naphthyl maleimide were found the most effective suppressors for the fungus growth with 0.005% concentration. The imide structure was found to be essential for fungicidal activity. The greatest increase in activity was obtained by methyl, ethyl or ethoxy substitution at ortho position of the phenyl ring.
N-alkyl- or cycloalkyl substituted mono or dichloro maleimides had insecticidal properties/21/. N-(Dichlorophenyl)-imides are industrial antimicrobial agents/22-26/. N-(2-methyl-1-naphthyl) maleimide showed its effectiveness as bactericide for the protection of polyvinylchloride polymer, cotton textiles, wood and as a fungicide in paints/27,28/. N-(p-phenoxophenyl) maleimide and its dichloro analogue, are industrial biocides effective when added to cotton fabrics or PVC films/29/.

Synergistic bactericidal and fungicidal activities have been observed with N-(4-fluorophenyl)-2,3-dichloro maleimide/30/. Other antibacterial compositions consist of N-(p-thiocyanatophenyl)-2,3-dichloro maleimide/31/. N-(p-acetoxyphenethyl)-maleimide/32/. 2-(4-maleimidophenyl)-6-methyl benzothiazole/33/.


Several maleimide derivatives e.g. N-substituted halo-maleimides, N-di-substituted N-amino maleimides,
N-alkyl maleimides, etc. possess herbicidal action and operate as defoliants and desiccants/43-46/.

Rubin, Beruch, Kirino, Osamu, Casida/47/ tested the action of N-substituted maleimides on plant growth. N-alkyl maleimide were inactive but N-(p-chlorophenyl) maleimide protected sorghum for injury caused by alachlor without reducing its herbicidal activity. N-(p-chlorophenyl) maleimide passed both botanical and chemical specificity protecting sorghum among the 6 crops evaluated and only against alachlor. It had no antidote activity or effects on EPTS or chlorosulfuron toxicity. Structural activity showed that the maleimide ring of the N-phenylmaleimide conferred the highest antidotal activity when it was unsubstituted. Chloride or methyl substituted at number four position was also favourable. The effect of the phenyl substitution on the antidotal activity was identical for N-Ph-maleimides, iso-maleimides and maleamic acids. N-(p-chlorophenyl) maleimide and corresponding isomaleimides hydrolysed to N-(p-chlorophenyl) maleamic acid which slightly modified the translocation pattern of alachlor in sorghum. This antidote increased the GSH level or content in sorghum roots by 1.6 to 2.5 times as compared to controls.
ii) Antifouling Agents

Certain N-aryl maleimides and their mono- or disubstituted analogue are part of antifouling coatings for inhibiting adhesion of shellfish and algae to submerged bodies, e.g. ships, hulls and fishing nets/48-53/. The application of mixture of N-aryl maleimides with an organotin compound to underwater installation or fish nets is effective antifouling agent/54/.

iii) Analytical Reagent

Determination of water in thiols by Karl-Fisher titration can be done using N-ethylmaleimide which reacts with the thiol to give a thiol ether/54a/. A group of maleimides/55-60/ are used as fluorescent thiol reagent for the detection of sulfhydryl groups particularly in protein and in cancer cells. N-(3-pyrenyl) maleimide, a long life time fluorescent adduct with organic compounds and proteins containing sulfhydryl groups/55,56/. Fluorescent tracer method for protein containing sulfhydryl group utilizes N-(7-dimethylamino-4-methyl coumarinyl) maleimide or N-naphthylmaleimide derivatives with a dimethylamine or a methoxy group as an auxochrome/57-60/. Liu/61/ reported some N-substituted maleimides as potential antineoplastic sulfhydryl agents.
B) Maleimides in Chemistry and Industry

Versatility of maleimides in various aspects of chemistry and industry has created more and more interest towards them.

i) Dyes

N-methylmaleimide is reported as useful intermediate in the synthesis of dyes/62/. The dyes prepared from N-aryl maleimides and 1,3,3-trimethyl-2-methylenesindolenine/63/ are used to dye polyester and polyamide fibres from neutral solutions. Fluorescent maleimide dyes/64/ are used to dye polystyrenes, poly(methylmethacrylate), polycarbonates and polyester fibres fast yellow to red shades. Zahn/65,66/ prepared fibre-reactive maleimide dyes applicable to wool, silk and nylon. Finnis/more/67,68/ has described the fixation mechanism and a novel method for determining the fixation ratio of maleimides containing dyes on wool. Thermal discolouration of polyacrylonitrile is inhibited by N-aryl maleimides/69,70/.

ii) Additives for Fuels and Lubricants

William/71/ utilized maleimides as a component
of detergent and antiwear additives for engine lubricants. Nandi/72/ reported substituted maleimide lubricant additive. Other miscellaneous typical applications of maleimides includes:

- As blocking agent for poly(isocyanates)/73/
- As nickel electroplating brighteners/74/
- As components for ion-exchange, antistatic agents/75/
- As polymerisation catalyst of epoxy compounds/76a,b/
- As starting material for photosensitive resins/77a,b/
- As rubber antioxidant and modifiers/78,a,b,c/
- As heat stabilizers for polymers/79,a,b,c,d/
- As reactive carriers for enzyme immobilization/80/
- As controller of photographic development inhibitors/81/.

iii) Crosslinkers

On account of ethylenic double bond in maleimides several physical properties can be improved by incorporating maleimides. Pinazzi/82/ confirmed the radical type mechanism for reaction of N-methylmaleimide and maleic anhydride with cis & trans polyisoprene. There are reports of vulcanisation of elastomers with maleimide in the literature/83–88/.

In radiation induced vulcanisation of natural rubber and other hydrocarbon polymers, aromatic
mono maleimides especially substituted one are more effective than bis-maleimides/89/.

Baumann/90/prepared photocrosslinking polymers having pendant maleimide groups; useful in the manufacture of printed electric circuits.

Stevens/91/ studied photocrosslinking, as well as free radical, thermal and Diels – Alder crosslinking of maleimide pendant group – containing polystyrenes.

Previous work on N-aryl maleimide as homopolymer

Maleimides constitute an important class of monomers which are used for the synthesis of thermally stable polymers. Their homopolymerisation is carried out by both radical and anionic mechanism.

Radical polymerisation

Radical – initiation to homopolymerize maleimide is noticed both by thermal initiators and irradiation. Unlike poly(maleic anhydride), poly-(maleimide) of high molecular weight (10^6) was obtained by solution polymerisation for 4-6 hrs at 60°C using benzoyl peroxide or AIBN as catalyst/91a/.
Influence of the structure of N-alkyl, N-aryl maleimides and N-alkylmaleimidoacides on their polymerizability and on the polymer properties is described in radical polymerisation in bulk or in DMF at 60% using AIBN/92-94/.

Yamada et al. studied (A) polymerisation of maleimides having hydroxy radical as the substituent initiated (i) by K$_2$S$_2$O$_8$ in water or water-dioxan mixture (ii) by AIBN in DMF, (iii) by BuLi in tetrahydrofuran/95/ (B) solvent effect in radical polymerisation of N-phenyl maleimide/96/ (C) homopolymerisation of maleimides by radical and anionic mechanisms/97/.

Block, H., Groves, R. et al. studied the dielectric relaxation in polymaleimides and N-substituted polymaleimides. The α, γ relaxations process were observed in solid polyimide and in most N-alkyl and N-aryl maleimides studied at 10$^5$ to 10$^6$ Hz and -80° to 230°C and were assigned to the second order glass rubber transition/98/.

Ivanov and co-workers have explored intensive research data on γ -radiation (from 60 Co) polymerisation as a function of dose strength, temperature, the medium and the presence of sensitizers of -
i) N-phenyl maleimide in solid or liquid state/99,100/
iin) N-Hydroxy maleimide in bulk/101/
iii) N-(p-chlorophenyl)maleimide in solid (at 20-107°C) or liquid (at 112-157°C) phase and N(m-chlorophenyl) maleimide with accelerated electrons/102/
iv) N-(p-tolyl maleimide) in solid phase at 120°, 130°, 140°C/103/
v) N-(p-nitrophenyl)maleimide in solid or liquid phase/104/
vi) N-(2,4-dimethylphenyl)maleimide in solid or liquid phase/105/
vii) N-benzyl maleimide/106/
viii) N-methylolmaleimide in solid state/107/
ix) N-(carboxyphenyl)maleimide in DMF or acetic acid at 85°C/108/

Polymer yields in the radiation induced solid state polymerisation of maleimides were found in the following order in liquid or solid state:
N-benzyl maleimide I < N-(2,4-dimethyl phenyl)maleimide < N-(o-tolyl) maleimide < N-phenyl maleimide II < N-methylol maleimide < maleimide < N-(p-chlorophenyl) maleimide < N-(m-chlorophenyl) maleimide < N-(p-tolyl) maleimide < N-p-(nitrophenyl maleimide. The polymerisation rates of I & II increased with increasing
purity of monomers. The poly maleimides molecular weights were independent of the dose rate, dose and monomer purity.

I.R. spectroscopy of the photopolymer based on N-phenyl-, N-p-tolyl-, N-(2,4-dimethyl phenyl)-, N-benzyl-, N-(p-chlorophenyl)- and N-carbamoylmaleimide showed that the polymerisation proceeds with opening of the C=C bond of the imide ring.

Yamada/111/ investigated the photopolymerisation of maleimide and its N-substituted derivatives in both solid state and the solution. The polymers prepared in solution were soluble in DMF and cyclohexanone but those from solid were soluble only in DMF. The IR spectra obtained by solution polymerisation and by radical initiators (AIBN) were very similar to each other.

**Anionic Polymerisation** Basic catalyst e.g., n-butyl-lithium, sodium and potassium salts of n-butanol and t-butanol, n-butyl magnesium chloride and tributylboron in dimethyl acetamide (ACNMe₂) solution initiated the polymerisation of maleimides to yield a low molecular weight polymer. Several maleimido derivatives have been synthesized and polymerised by basic catalyst but none gave high molecular weight polymer/112/.
Yamada et al./113/ investigated the anionic polymerization of N-phenyl maleimide and its N-4-substituted derivatives. The molecular weight of the polymer obtained by anionic polymerization of N-phenyl maleimide in presence of sodium ethoxide at -70° in THF was higher than that of the polymer obtained in the presence of butyllithium. The initial rate of the polymerization in presence of sodium ethoxide was proportional to the concentration of the initiator and the monomer. The polymerization with sodium propionate as catalyst in DMF also gave polymer with higher molecular weight and the polymer yield increased with increased atm of EtOC₂Na powder. Effects of substituents in N-(4-substituted phenyl) maleimide on the polymer was also studied.

Bezdek M., Herbak F./114/ had studied the thermogravimetry (10 min. heating rate under N₂ atmospheres) of co-polymers of styrene with N-(halo-phenyl maleimide) and showed the order of decreasing heat resistance:

\[
\text{Cl} > \text{Br} > \text{Cl}_3 \quad \text{Br}_3 \quad \text{Cl}_3
\]

Urushizaki, Michio, Aida, Hiroshi, Shimazaki, Masanobu, Fujii, Yukio, Onizuka, Kunio, Nomura, Sadayoshi/115/ Poly(N-phenyl) maleimide (I) and
p-substituted derivatives of (I) are prepared by polymerisation of corresponding N-phenyl maleimides with "Azo bis isobutyronitrile" under N$_2$ at 70°C. Each polymer was stable in N$_2$ stream at 300°C but degraded rapidly from 350°C. Weight losses at 420°C were 40-20% in the order (p-substituents given) OMe, Me, H, Cl, OAc, CO$_2$Et and AC, which agree with electron donating ability to stabilize imide ring. All soluble initially in Me$_2$NAC and given an insoluble fraction on heating.

Patel R.D., Patel N.R., Bhardwaj I.S./116/ studied the polymerisation of N-(p-halophenyl) maleimide (F, Cl, Br) at 80°C with BZ$_2$O$_2$ initiator and found that it was slow initially with an induction period of 30 min, but give high yield after 6 hrs. The initial decomposition temp. (TGA) of the homopolymer was F - 355°C, Cl - 320°C, Br - 325°C. The thermal degradation of all polymers was the 1st order kinetically and followed essentially the same mechanism. The activation energy for most sample has 42-93 Kcal/mol. The I.R. spectra of the polymers were also discussed.
Previous work on co-polymers of N-\((p\)-chlorophenyl maleimide)  

Masumori, Yamada/117-119/ investigated radical polymerisation of N-(4-substituted) maleimides (I) with vinyl acetate (II). The effect of the substituents of (I) on the co-polymerisation reaction with vinyl acetate (II) in presence of radical initiator were investigated. The relative reactivities \((1/x_1)\) of (I) towards vinyl acetate (II) radicals, no reasonable order was obtained for all the substituents but the reactivity of (II) towards (I) radicals \((1/x_2)\) decreased in the following order of the substituents: \(\text{Ac} > \text{COOEt} > \text{OAc} > \text{Cl} > \text{H} > \text{OMe}\). The order can be explained largely in terms of polar effects and the differences in homopolymerisation reactivity.

Otsuka, Michio/120/ have calculated the reactivity ratio of the co-polymer of N-\((4\)-substituted phenyl) maleimide derivatives with vinyl chloride. The co-polymerisation of vinyl chloride \((M_2)\) with N-(4-substituted phenyl) maleimide viz. N-(4-methyl phenyl) maleimide, N-phenyl maleimide, N-(4-chlorophenyl) maleimide were carried out at 60\(^\circ\) with AIBN as an initiator. The monomer reactivity ratios at 60\(^\circ\) were \((0.03, 4.37)\), \((0.03, 3.92)\), \((0.03, 3.66)\) respectively for the monomers.
The co-polymers obtained were colourless powders but turned brown when N-(4-substituted phenyl) maleimide content in the polymer increased.

Kuehne, G., Andrasche H.J./121/ have modified the PVC with increased heat distortion temperature. Vinyl chloride was co-polymerised with N-(4-substituted phenyl) maleimides to give products those exhibited heat distortion temperature generally higher than PVC, good workability and higher resistance to heat fatigue and were useful in hot-packing of food.

Dedovets, G.S., Ivanov, V.S./122/ have investigated the co-polymerisation reaction of N-aryl maleimide with styrene. In homo-polymerisation of N-aryl maleimides and its co-polymerisation with styrene in polar solvent in presence of lauryl peroxide, the polymerisation rate was lower in electron donor solvents than electron acceptor solvents. The co-polymerisation rate was influenced by the composition of the monomer mixture and to less extent by the position of the substituents in the phenyl ring. The Mayo-Lewis integral equation was used to calculate co-polymerisation constant as well as "Alfrey-Price" and Schwom-Pricing constant. The statistical distribution of monomer units was also calculated.
Trofimove, V.A. Ermolova, A.N./123/ synthesized the co-polymer based on higher ester of methyl acrylic acid and N-substituted maleimides. Bezdok M. Harbak F/124/ carried out the polymerisation of N-(monochlorophenyl) maleimides with styrene and butadine. N-(bromophenyl)(I) and N-(chlorophenyl)(II) maleimide with halogen atom at 2, 3 or 4 position of phenyl ring were polymerised with styrene and butadine using AIBN as initiator. The thermogram of the polymer showed the alternating co-polymers of all N-(monochlorophenyl) phenyl maleimides with (I) and (II) started to decompose spontaneously in air at 340-70°. The limiting index value of co-polymers varied between 22 and 40.

Recently Patel J.D., Patel M.R./125/ have synthesised the co-polymer of N-(p-chlorophenyl) maleimide with methyl acrylate. Free radical polymerisation of methyl-acrylate with N-(p-chlorophenyl) maleimide initiated by AIBN in cyclohexanone at 75° was studied. The co-polymerisation was detected by nitrogen content and NMR spectra. Reactivity ratio was calculated by Mayo-Lewis, Fineman-Ross, Kelen-Tudos and Joshi-Joshi method. The Q and e values were selected by Alfrey-Price scheme.
Previous work on (N-p-chlorophenyl maleimide-co-MMA)

N-arylmaleimide with Me-methacrylate(I) and (optional) other monomer (II) were co-polymerised in presence of 0.05 - 2% (of monomers) catalyst at 0-120°C to give products containing 80-95 wt % of (I), 5-20 wt % of maleimide and 0-15 wt % (II) which can be used as moulding compounds/126/. Thus a mixture of 90 parts (I), 10 parts N-arylmaleimide (N-p-chlorophenyl maleimide) and 0-1 part B2O2 is heated to give a syrup and a syrup is placed in a long glass cell (0.32 cm wide) and heated 65 hrs at 70°C and 1 hr at 110°C to give a polymer having reduced viscosity 6.2 (0.5% in CHCl3 at 25°C), Vicat softening point 129°C, Vicat softening point (after saturation with H2O) 114°C as compared with 10.6, 123.5°, 104.1 respectively for the control poly(MMA).

Yamada/127-128/ studied the relation between reactivities of N-p-chlorophenyl maleimide in co-polymerisation with Me-methacrylate or vinyl acetate. Imperial chemical industries ltd./129/ synthesised a co-polymer of Me-methacrylate (I) with 5-20% N-arylmaleimide (N-p-chlorophenyl maleimide) having better softening point, water absorption and impact strength than poly (Me-methacrylate).
Bezděc, Milan, Hasebeck/130/ prepared N(monohalo phenyl) maleimide (I), isomaleimide (II) with Br or Cl in position 2, 3 or 4 and co-polymerised with styrene, butadine, and Me-methacrylate in presence of 'AIBN' and 'Diisopropyle peroxid carbonate' to give self-extinguish co-polymer. The reactivity ratio indicates the formation of alternating co-polymer in all cases except for the co-polymer with Me-methacrylate. A solvent effect on reactivity ratio was observed and the polymer are thermally stable up to 300-350°C.
Theories of dilute polymer solutions

Since the polymers do not exist in gaseous state, the intrinsic properties of polymer molecules are studied in dilute solutions. The solutions are non-ideal due to gaint size of polymer chains. However, the molecular and thermodynamic parameters, characteristic of polymer-solvent interactions, are determined by light-scattering, osmometry, sedimentation and viscometry techniques. Studies on polymer solutions encounter the problems arising from solvent-polymer interactions, intramolecular interactions (generally absent in small molecules) and intermolecular interactions of tortuous nature.

A well known excluded volume effect, firstly recognized by Flory/131/arises from so called long-range intramolecular and solvent-polymer interactions; the thermodynamic effects arise from intermolecular interactions. Besides the finite volume occupied by a polymer chain in solution, two or more chain elements belonging to the same chain may compete for the same volume element which in turn may result into repulsive interactions between two remote chain elements. Thus, the volume occupied by one chain element is not available to other elements, resulting in dilation of a chain(coil)
occupying additional volume. The above effects depend on the molecular weight of the polymers, however, such dependency is never observed in solutions of low-molecular weight compounds.

Kuhn/132/ was the first to advance a statistical treatment of the configurational description of a polymer chain. He arrived at a significant conclusion that the mean square end-to-end distance \( \langle R^2 \rangle \) of the chain is proportional to the number of chain elements (or molecular weight, \( M \)) of the molecule. This provided a foundation for presently accepted random-flight chain model in the theory of dilute polymer solutions. The notable results of statistical treatment are represented by the theory of light-scattering by Debye/133/ and Zimm/134/, the theory of intrinsic viscosity by Debye/135/, Kirkwood and Riseman/136/, and the theory of virial coefficient by Zimm/137/. On the other hand, using statistical thermodynamics, Flory/138/ and Huggins/139/ represented a lattice theory of concentrated solutions to explain non-ideality of polymer solutions.

Development in the theory of excluded volume is extensive and Yamakawa/140/ has critically reviewed it in his recent book on Modern Theory of Polymer Solutions.
The perturbation theory based on cluster expansion method is the foundation of all the theories. The potential of mean force, arising from non-bonded interactions in the chain with fixed end-to-end distance, has been utilized in deriving several closed approximate equations for the excluded volume assuming (i) the validity of superposition approximation (pair-wise decomposability of the potential energy) and (ii) the form of the binary cluster integral which represents the effective volume excluded to one segment by the presence of another. All the three proposed models: random-flight, spherical and ellipsoidal smoothed density, have been considered. Differential equation approach is also followed with due consideration of non-Gaussian distribution of segments around the center of a polymer molecule.

The excluded volume theory which was first developed by Flory gave impetus to the understanding of excluded volume problem. Flory defined a theta temperature, corresponding to Boyle's temperature for a non-ideal gas where the repulsive interactions (excluded volume effect) are balanced by attractive ones and polymer solution becomes ideal one. Above theta temperature, the excluded volume effect overrides the attractive
interactions and expands the polymer coil. Consequently \( \langle \Gamma^2 \rangle / M \) increases with \( M \) without limit in contrast to that of a random flight chain. For the first time Flory's theory could explain reasonably the variation of the exponent \( \gamma \) in \( [\gamma] = K M^{\gamma} \) equation between the limits 0.5 and 0.8. Further the theory predicts that in case of solid amorphous polymers the end-to-end distance is that of the ideal state. Although the theory rightly predicts the trend of polymer behaviour, the quantitative agreement is found to be inadequate.

The later developments in excluded volume theory are due to Bueche and James, Kurata, Stockmayer and Roig, Kurata, Fixman, Ptitsyn, and Yamakawa and Tanaka. These theories are within the frame work of a two parameter theory correlating expansion factor (\( \alpha \)) and excluded volume (\( z \)). Since these two parameters constitute the theories, they are known as two parameter theories. These two parameter theories may be generalized in the following form for their asymptotic behaviour:

\[
\lim_{z \to \infty} \alpha^x = \text{const. } z
\]

where \( x \) decides the power type equation. The following table shows the power type equation against the corresponding theory.
Characteristics of some excluded volume theories

<table>
<thead>
<tr>
<th>Theory</th>
<th>Power type equation</th>
<th>$\gamma^*$ max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Busche-James</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>First order perturbation</td>
<td>2</td>
<td>1.25</td>
</tr>
<tr>
<td>Fixman</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Kurata-Stockmayer-Roig</td>
<td>4</td>
<td>0.875</td>
</tr>
<tr>
<td>Ptitsyn</td>
<td>5</td>
<td>0.8</td>
</tr>
<tr>
<td>Yamakawa-Tanaka</td>
<td>6.67</td>
<td>0.575</td>
</tr>
</tbody>
</table>

* $\gamma \ln[\gamma] = KM^\gamma$ ... Mark-Houwink-Kuhn-Sakurada equation

The controversy is disputed since long between the fifth power type equation of Flory and the third power type equations of Fixman, Ptitsyn and Kurata-Stockmayer and Roig. The available Monte-Carlo data (for small chains) indicated a linear relation between $M^3$ and $\gamma^2$, and there exists similar relationship between the intrinsic viscosity and molecular weight. These indicated superiority of third-power type equation over fifth-power type. However, the recent Monte Carlo
data for longer chains show that $\alpha^3$ is not linear in $z$. Moreover, the asymptotic solution at large $z$ using the self-consistent-field approach shows that the fifth power type equation is more plausible than the third power type.

The theories of second virial coefficient (measure of solvent-polymer and intermolecular interactions) within the framework of the two parameter theory when combined with corresponding excluded volume theories reveal the fact that fifth power type equation is favoured for large number of polymers.

Very recently, Domb and Barrett/141/ have proposed a new formula for the excluded volume which turns out to be fifth power type equation. In the derivation, numerical data on self avoiding (nonintersecting) walks on three dimensional lattices are combined with the well known virial expansion theory. Hence the form of the theory becomes universal (free from assumptions of superposition approximation and binary cluster integral), that is, the same form for all three dimensional lattices and continuum models.

The Mark-Houwink exponent $\alpha$ is generally observed in the range 0.5–2 covering variety of polymers. The
fifth power type equation is adequate upto $\gamma_{\text{max}} = 0.8$ only and the third power type equations upto $\gamma_{\text{max}} = 1.0$ as shown in the above Table. If similar arguments are extended, then first order perturbation and Bueche-James theory respectively cover the value of $\gamma$ upto 1.25 and 2.0 which may explain the behaviour of semi-rigid to rigid polymer chains. However, the problem of excluded volume is yet not completely solved. More efforts are required in that direction.

On the other hand some of the viscosity theories are put forward to explain the behaviour of semi-flexible polymer chains. Amongst these, the notable theories are due to Ptitsyn and Eizner/142/ and Yamakawa Fujii/143/. These theories adequately explain rigid character of polymer chains.

Bohdanecky H./144/ proposed a new method for estimating the parameters of the worm like chain model from the intrinsic viscosity of stiff-chain polymers. He simplified the term $\Phi_0$ in the Yamakawa-Fujii equation (1974) for the intrinsic viscosity of the worm like continuous cylinder model.

$$[\eta]_0 = \frac{\Phi_0 \left( \lambda^{-1} \right)^{3/2} L^{7/2}}{K_L}$$
The term can be given a simple form valid over a broad range of the chain contour length \( (L) \).

\[
\Phi_0 = \Phi_\infty \left[ B_0 + A_0 \left( \frac{\lambda^{-1}}{L} \right)^{\frac{1}{2}} \right]^{-3}
\]

The parameter \( A_0 \) is a function of the ratio \( d/\lambda^{-1} \) while \( B_0 \) is nearly constant. New methods are proposed for the evaluating the model parameters (Kuhn segment length \( \lambda^{-1} \), relative molecular mass per unit, contour length \( M_L \) and chain diameter \( d \)) from the intrinsic viscosity data for stiff chain polymers. The possibilities of estimating \( M_L \) and \( d \), either from their combination with partial specific volume of the polymer are discussed. When applied to nine typical stiff-chain polymers, the results agreed with those obtained by more complicated procedures.
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