

REVIEW ARTICLE

STATE OF THE ART OF POLYMER RESEARCH IN INDIA
III. PHYSICAL CHEMISTRY OF POLYMERS*

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(Received 04 July 1988; Accepted 28 July 1989)

Work on dilute solution properties as well as thermal, electrical, mechanical and photo-chemical properties of polymers from more than fifty institutions in India during the past about four decades has been reviewed. Various techniques like Viscosity, osmosis, light scattering, DSC, TGA, DTA, UV, IR, NMR, mass spectrometry, X-ray diffraction, SEM, etc. were employed. Thermodynamic parameters of polymer molecules have been evaluated; structure-reactivity, mechanisms for degradation, etc. have been suggested. Reactor designs for various types of polymerization, crystallization, vulcanization, blending of polymers have been covered. In the concluding paragraph a few suggestions for future work have been made.

Key Words : Light scattering; Osmotic; Thermal; Mechanical and Electrical Properties of Polymers; Thermo and Hydro-Dynamics; Reactor Designs, Crystallization of Polymers

INTRODUCTION

MUCH of the work is concerned with thermodynamics and hydrodynamics of dilute solutions by viscosity, osmotic and light scattering techniques and various theories. Flory-Huggins, Kurata-Stockmayer, Plitsyn etc., were examined and many constants and interaction parameters have been evaluated. Thermo-oxidative, degradation and characterization of polymers have been followed by standard techniques such as DTA, DSC, NMR, SEM, X-ray diffraction etc. Aspects of polymers which have received attention are : mechanical and electrical properties, tacticity, crystallization and morphology, vulcanization of rubbers, micro structure determination, heat resistance and fire retardancy, rheology, composites and blends, moisture regain, dye uptake etc. Extensive work has been reported from IIT-Kanpur and NCL-Poona regarding polymer reactor designs. *A few suggestions are made for future work from considerations of relevance, excellence and international standards.*

AHMEDABAD TEXTILES INDUSTRIAL RESEARCH ASSOCIATION, AHMEDABAD

Viscosities of cellulose nitrate solutions in ethyl acetate and methanol-ethyl acetate mixtures being dependent on shear rate was investigated by Chitale.¹ Kulashresta *et al.*² compared newer and native dried cottons with regard to pore size, dye uptake, etc. Studies on streaming potentials of cotton by Madan and

*Parts I & II; *J scient ind Res* 47 (1988) 384, 439

Srivastava³ showed that the former decreased with concentration of the electrolyte. Shah *et al.*'s⁴ work on continuous rope bleaching on a J-box. Raj Kumar and Srivastava's⁵ method based on moisture regain for the composition of blends of fibres and Venkatesh *et al.*'s⁶ studies on shrinkage and stress-strain properties of polythene filaments in various solvents deserve mention. *It is not mentioned whether these studies have helped the textile industry and if so with what results.*

BHABHA ATOMIC RESEARCH CENTRE, BOMBAY

Nair and Vijayendra⁷ developed a perfect and useful 'high vacuum cryoscopic' pumping system for out-gassing the air cardinol-epichloro hydrin, epoxy resin. Bamboocomposites with monomer impregnation under vacuum and gamma-irradiation had improved dimensional stability and reduced moisture swelling, according to Ashok.⁸ Agarwal and Srinivasan's⁹ studies on folding endurance and rot proofing of jute fabrics grafted with monomers deserve mention. *Work on gamma rays as initiators and their effect on polymers and composites at BARC, while good in itself, needs to be exploited to the full for the benefit of the industry.*

DEFENCE RESEARCH AND DEVELOPMENT ORGANISATION LABORATORY, NEW DELHI

Bajaj *et al.*'s¹⁰ work on nitration of substituted polystyrenes led to degradation of the latter but no rational explanation was offered. The studies on importance of Flory's constant for the determination of unperturbed dimension by Deb and Chatterjee¹¹; the evaluation of effective interaction parameter, χ , for the optimum solvent composition of poly (styrene) in cyclohexane-acetone mixtures, and that the binary inter-action parameters being independent of solvent parameters due to Deb *et al.*¹² must be considered as *routine and nothing special.*

INDIAN ASSOCIATION FOR CULTIVATION OF SCIENCE, CALCUTTA

Santi R Palit¹³ developed a method for end group ($-\text{COOH}$, $-\text{NH}_2$, SO_4 , etc) analysis of polymers by two techniques—'dye partition' (DPT) and 'dye interaction'— which are being employed by various laboratories. Bhaumik *et al.*'s¹⁴ studies on the heat of hydrogenation of hard rubber being dependent on sulphur content of the latter, Sen *et al.*'s¹⁵ observation that the trend of chain transfer constants C_n , being related to radical reactivity and Ajit Kumar Chaudhuri *et al.*'s¹⁶ and Chatterjee *et al.*'s¹⁷ studies on the dilute solution properties of polymers and evaluation of thermo and hydrodynamic properties and examination of various theories must be considered as routine. A good finding, however, was that the maximum solvent power in a co-solvent system was also true optimum composition for lateral expansion of the polymer. Mukhopadhyaya, *et al.*'s¹⁸ method of determining monomer reactivity ratios and Vidyarthi *et al.*'s¹⁹ determination of extent of branching and degree of hydrolysis are good but their accuracies could have been tested by other standard methods. Sarkar and Palit²⁰ found that Kurat-Stockmayer and Pritsyn theories rather than of Flory were in better agreement with experimental data. Banthia *et al.*'s^{21,22} attributing polymer association to polar end groups and that in the end group ($-\text{SO}_4$) -

analysis by DPT, polarity of the polymer being irrelevant were reported. Estimation of nitrile end groups in a co-polymer and subsequent evaluations of r_1 and r_2 being accurate, proved the validity of DPT.²³ Co-solvency studies involving polymers and copolymers and determination of optimum solvent compositions for unperturbed dimensions by Vidyanthi *et al.*^{24,25} needs closer scrutiny. Adsorption of organic vapours by a series of naphthyl-polythenes by electrical conductivity by Sircar *et al.*^{26,27} was found to depend on the solvent and vapour pressure. Kanwar and Ghosh²⁸ set up a device for measuring the velocity of compressional ultrasound and elastic constants in poly(styrene). No specific uses of adsorption and ultrasound studies of the polymers were indicated.

INDIAN INSTITUTE OF SCIENCE, BANGALORE

Light scattering and viscosity studies were used for speedy determination of molecular weights and root mean square end-to-end distance of PVA, poly (vinyl acetate), by Ramakrishna Rao *et al.*²⁹ and by Kalpagam and Ramakrishna Rao.³⁰ The depolarization ratios of vertically polarized light and horizontally polarized light for PVA in good solvent methyl-ethyl ketone and poor solvent ethyl acetate were generally in agreement with the values calculated from reciprocity theorem but the relevance of the former to structure and property was not indicated. Studies on chain propagation mechanism and sequence distribution in poly (acrylonitrile)-co-and poly (MMA) random co-polymer by NMR spectroscopy, determination of gamma values (volume fraction of non solvent for incipient phase separation); effect of nature and composition of the solvent on the Huggin's constant were reported by Kashyap *et al.*³¹⁻³⁵ Kishore *et al.*³⁶⁻³⁹ work on thermal degradation of solid, PS, poly(styrene) by DSC, heats and activation energies for the dc-polymerization, burning rates of thermoplastics and thermo-setting resins, transition metal oxides Fe_2O_3 , MnO_2 as suppressors of combustion of PS has to be extended for understanding combustion of solid propellants. Rami Reddy and Kalpagam⁴⁰⁻⁴³ used two parameter theorem to evaluate molecular weights of various fractions, short range and long range interaction parameters, solvent powers, second virial co-efficients and Flory constant for co-polymers of styrene and acrylonitrile and other co-polymers in various solvents were also evaluated. The negative temperature co-efficient of the limiting viscosity number for poly (styrene)-co-poly(acrylonitrile), effect of temperature on the hetero-contact interactions, excess interaction parameters, and solubility parameters were other aspects reported. The photo-degradability of aged low density poly (ethylene) samples was studied by Mathur *et al.*⁴⁴ by TGA and DSC. Effects of molecular weights of polymeric amine/imine perchlorates on thermal properties and impact sensitivity in propellants by DTA and TGA; thermal decomposition of ammonium perchlorate containing 20 per cent of poly (vinyl pyrrolidone) and the carboxy terminated poly (butadiene) were studied by Thomas and Nandi.⁴⁵ Kishore, Vasantha Kumari *et al.*⁴⁶ studies on isothermal melting behaviour of poly (*L*-lactic acid) (hot stage microscopy); Kishore and Sankaralingam's work⁴⁷ on the effect of temperature and humidity

on the aging of poly (butylene terephthalate); Kumar G Saradesi *et al.*'s⁴⁸ work on bio-degradation of gelatin-g-poly (ethylacrylate) in the synthetic medium (pure cultures of pseudoamines); Kishore and Ravindran *et al.*'s⁴⁹ investigation on the effect of transition metal (Fe, Mn) salicylates in the degradation of poly (styrene peroxide); cross linking of 1-1'-bis (glycidoxy methyl) ferrocene (a bonding agent for solid propellants) with carbonyl terminated poly (butadiene), and its wetting effects by Kishore, Vernekar *et al.*⁵⁰; Kishore and Vasantha Kumari's⁵¹ comprehensive review of effect of high temperature and pressure on crystallization, structural changes and melting of the polymers; Kishore and Mattamel's⁵² density, structure correlations and the changes in the average packing density with successive additions of CH₂-groups and a review of ageing and stabilization of PVC and the use of the latter as electrical insulators by Kumar and Nanda⁵³ were various other aspects reported and *these studies are of great significance to our understanding of chemistry of solid and liquid propellants.*

NATIONAL CHEMICAL LABORATORY, PUNE

The temperature dependence of r_1 and r_2 in co-polymerization of MMA and AN was studied by Joshi and Kapur.⁵⁴ Anomalous viscosity behaviour of dilute solutions of natural rubber in mixed solvents, absence of shear effects and expansion and dis-entanglement of rubber chains in benzene and hexane at high dilutions were investigated by Kapur and Gundiah.⁵⁵⁻⁵⁷ Work on the determination of absolute molecular weights of PMMA and PS by an empirical method based on viscosity and the solution properties of poly (ethyl) and poly (isobutyl) methacrylates was due to Gundiah and co-workers.⁵⁸⁻⁵⁹ Joshi's⁶⁰ studies on heats of polymerization of maleic anhydride, MMA, VA with an isothermal distribution calorimeter emphasized influence of association in monomers. The effect of shear on the viscosity of solution of high molecular weight poly (isobutylene) in different solvents was examined by Gundiah and Mohite.⁶¹ Mohite *et al.*⁶² have evaluated Kuhn-Houwink constants for poly (p. chlorostyrene). The work relating polymer extension to adiabatic compressibilities of poly (methacrylic acid) was due to Roy Chowdhury *et al.*⁶³⁻⁶⁵ Dasare and Krishnaswamy⁶⁶ determined the capacities for selective cation uptake; Cu (II), Co(II), Bi(II) by cashewnut shell liquid and tetraethyl pentamine resin. Work on determination of r_1 and r_2 based on binary copolymer composition was due to Joshi *et al.*⁶⁷ and Rao *et al.*⁶⁸ and the effect of pH on their variation by electrostatic repulsive and hydrophobic interactions was due to Ponrathinam and Kapur.⁶⁹⁻⁷⁰ Ghatge *et al.*^{71,72} could offer no rational explanation for electron-beam induced conduction in fluorinated ethylene-propylene copolymer.

Iday *et al.*⁷³ characterized polyurethanes by IR, NMR, X-ray diffraction, SEM, Viscosity, solubility and TGA. Ravindranath and Mashelkar^{74,75} have developed fine mathematical models first of their kind in the country with process and operation variables and temperature profiles for PET polythene terephthalate, reactors which will be dealt with in detail in the 'engineering plastics' in the series. Correlation of the d. c. conductivity of the polymer with free volume by Chand

Navin⁷⁶; the expansion co-efficients of polymers by Kulkarni *et al.*⁷⁷⁻⁷⁸; conformational transitions of poly (methacrylic acid) in dioxane and the decrease in the free energy of transition due to CH₃-CH₃ interactions leading to compact form by Chidambaram and Gundiah⁷⁹ were reported. Work on gas absorption in freely falling films of dilute solutions of hydroxy ethyl cellulose and review of diffusional effects in homogeneous and heterogeneous polymer systems was due to Mashelkar.⁸⁰⁻⁸¹ The design of reactors with a prior prediction of rate constants by Balaraman *et al.*⁸²⁻⁸⁴ and Modelling semi-batch pre-polymerization process of PET by Ravindranath and Mashelkar⁸⁵ will be covered in the 'engineering plastics'.

SHRI RAM INSTITUTE FOR INDUSTRIAL RESEARCH, NEW DELHI

The determination of r_1 and r_2 , composition and microstructure of poly (styrene)-co-poly (methylacrylate) was due to Patnaik and Sawhney.⁸⁶ Work on viscosity, thermal stability, chemical resistance of resins from chlorendic acid and synthesis and characterization of poly (carbonates) was due to Gupta and co-workers.⁸⁷⁻⁸⁸ The rheology and other physical properties and processing characteristics of chlorinated PVC were studied by Krishnan and co-workers.⁸⁹ Thermal degradation and fire retardant efficiency of polyesters from chlorendic and isophthalic acid by Ghosh and Rawat⁹⁰ and resistance to gamma-radiation by unsaturated polyesters with aromatic rings by Gupta and Thampy⁹¹ were other interesting aspects reported.

HART-COURT BUTLER TECHNOLOGY INSTITUTE, KANPUR

Mehta⁹² observed yellowing of the coatings of epoxy resins during storing but no rational explanation was offered. The mechanism of thermo oxidative breakdown of poly-olefines containing metal impurities during processing and their use was explained with no mechanism by Kumar and Srivastava.⁹³ Mathur and coworkers⁹⁴⁻⁹⁶ studied the photo-degradability of additive-free, low density, polyethylene films by DSC etc. The scratch hardness of heat cured films of epoxy resins, Novolacs and bisphenol-A (used for coatings) was discussed by Vasista and Kaushal.⁹⁷ *The use of these coating vis-a-vis conventional coatings, cost-benefit analysis etc. has not been discussed.*

NATIONAL PHYSICAL LABORATORY, NEW DELHI

Mahendru and Jain⁹⁸ observed that charged poly (vinyl acetate) film exposed to a humid atmosphere had decreased magnitudes of thermally stimulated discharge current peaks and the charge regained depended on the level of exposure to humidity. An increase by four orders of magnitude in the electrical conductivity of PVA doped with iodine and the maximum being shifted to lower temperatures was noticed and it was concluded that Poolefrankel effect was operative.⁹⁹ Studies on depolarization current characteristics of thin films of poly (vinyl acetate)-Co-poly (vinyl chloride) based on different relaxation processes by Gupta and co-workers¹⁰⁰; DTA and IR studies on poly (acrylonitrile)-Co-Poly (methyl methacrylate) and PAN fibres by Verma *et al.*,¹⁰¹ Manocha and Bahl¹⁰² and Wasan¹⁰³;

the electrical conduction of polycarbonate films following Richardson-School effect by Chand Suresh and co-workers;¹⁰⁴ effect of pressure and temperature on the secondary relaxation in vinyl chloride and vinyl acetate co-polymer and dielectric measurements on poly (vinyl butyral) following a Debye-type dispersion distribution of relaxation time by Kumar Naresh and Aurora¹⁰⁵ were other investigations reported. *The use and application films with these electrical properties should have been discussed.*

INDIAN INSTITUTE OF TECHNOLOGY, BOMBAY

Deshpande and co-workers¹⁰⁶⁻¹¹² reported that the heats of mixing at infinite dilution of poly (isobutylene) with various solvents varied appreciably with chain lengths¹⁰⁶ and other studies included the anti plasticization effect of cholesteric liquid crystal and isotropic liquid additives;¹⁰⁷ dielectric and dynamic mechanical behaviour of PVC with small amounts of cholesterol;¹⁰⁸ variation of r_1 and r_2 with temperature in the copolymerization of -hydroxy propyl methacrylate with MA, MMA, Ethyl and butyl methacrylate;¹⁰⁹⁻¹¹¹ the effect of reinforcement of poly (butadiene) with BaF_2 and $BaCl_2$ on Young's Moduli, elongation and tensile strength.¹¹² *The special properties of anti plasticization with liquid crystals has not been brought out.*

INDIAN INSTITUTE OF TECHNOLOGY, NEW DELHI

Verma and co-workers¹¹³⁻¹¹⁷ found that the magnitudes of density, moisture regain birefringence of natural and cyano ethylated and formaldehyde cross linked cotton cellulose were greater than those grafted with methyl, ethyl and butyl acrylates and difference was traced to fine structure of the fibre particularly crystallite orientation.

Verma and Patnaik¹¹⁸⁻¹²¹ calculated r_1 and r_2 of co-polymers of 2-hydroxy methacrylate and ethyl (butyl) acrylate and the former's dependence on polarities of monomers, steric factors and resonance stabilization of radicals was stressed. Molecular weight distributions of the copolymers by gel permeation chromatography (GPC); thermal behaviors by dynamic thermogravimetry; photoresistivity potential; cohesive energy densities and composition of the co-polymers (from swelling measurements) were other studies reported. Verma *et al.*'s¹²² investigations are numerous: effect of structure of polyimides and poly (oxadiazoles) on thermal stability, viscosity and density; bathochromic shift and fluorescence;¹²³⁻¹²⁴ study of ternary phase system involving poly (oxadiazoles) and variations in solubility, dielectric constant;¹²⁵ irradiation of poly (vinyl alcohol) fibres in the presence of $CHCl_3$ and CCl_4 leading to discolouration;¹²⁶ thermal degradation of PVC in alkyl maleates and its stabilization in the presence of p-benzoquinone;¹²⁷ thermal stabilities and degradation of alkyl aliphatic poly (sebacamides) and their mechanism;¹²⁸ preparation of polyester fibres¹²⁹ with better drying, moisture regain and dyeability; dilute solution properties and characterization of aliphatic and aromatic poly (benzimidazole)s¹³⁰⁻¹³² and use of crosslinked oligomers for glass-cloth reinforced lamination^{133,134}. Naji Yuvaraj and co-workers¹³⁵ reported

for the copolymer of ethylene terephthalate and hexamethylene terephthalate addition of 1,6-hexanediol resulted in the decrease of tensile strength etc., Chowdhuri and Verma¹³⁶ found improved thermal stability with increase of hydroxy content in the co-polymer of 2-hydroxy ethyl methacrylate and MMA. Padhyal and coworkers^{137,138} made electron microscope studies on plasma etched Nylon-66 film and poly (caprolactam) fibres and concluded that the size of the spherulites in the centre were greater than on the surface. The concept of oriented amorphous (third) phase distribution of crystallites and elastic modulus of the fibres of PET were discussed by Gupta and coworkers.¹³⁹⁻¹⁴³ Pillai and coworkers¹⁴⁴⁻¹⁵⁰ have studied cross linking by thermally stimulated current in poly(vinyl cinnamate); the photoelectric properties (for use xerography) of a double layer of poly (N-vinyl carbazole) film on poly (9-vinyl anthracene) on aluminium substrate; effect of variations in humidity and ambient temperature on electro-thermographic characteristics of polythene, ethyl cellulose and poly (butadiene Co-(acrylo-nitrile)-Co-styrene); polarization in poly (styrene)-chloranil complex; photo conduction of kapton polyimide film in the visible region. Percent orientation in poly (vinyl alcohol) by birefringence and enhanced dye uptake of Nylon-6 grafted by acrylic acid/acrylamide were reported by Gulrajani and co-workers.¹⁵¹⁻¹⁵² Temperature-dependent small angle X-ray scattering from polythene by Rakesh Raman and coworkers;¹⁵³ a rapid method for determination of molecular diffusion co-efficients of polymer solutions by Diwakar Singh and Nigam;¹⁵⁴ a comparative study of thermomechanical and chemo mechanical structuring of Nylon-6 multi filament yarns by Sengupta and co-workers¹⁵⁵; characterization of aromatic, aliphatic polyesters by DSC, X-ray diffraction and density measurements by Khanna and co-workers;¹⁵⁶ photo induced grafting of Nylon-6 fibres with acrylamide and thermal properties of dehydrochlorinated PVC grafted with poly-(styrene) by Mukherjee and coworkers;¹⁵⁷⁻¹⁵⁸ the impact strength and fracture of glass fibre reinforced epoxy composites being maximum are other studies reported.¹⁵⁹ Mani, Gupta and co-workers^{160,161} used IR and SEM studies for structural elucidation of polyester resin concrete containing silane coupling agents; the effect of the latter on mechanical and thermal properties of the former and the role of styrene based shrinkage reducing agent in the resin concrete were also studied. Gupta, Singhal and coworkers^{162,163} studied dielectric relaxation in the glass transition region of poly (acrylonitrile) and poly (methacrylonitrile) and concluded that variations of dielectric increments and relaxation temperatures were related to loss of peak amplitudes. Ahmed Hussain¹⁶⁴ has determined solubility parameters and also dielectric constants of hydroxy poly(acrylamide) by the principle of additivity and molar polarizations. Vasudevan and co-workers¹⁶⁵⁻¹⁶⁸ have carried out studies, on thermal depolarization and DC conductance characteristics of phenol-formaldehyde resins.

Garg and Misra Ashok¹⁶⁹⁻¹⁷¹ have discussed morphology and rate of crystallization in terms of spherulite size, composition of monomers for PET and its block co-polymer. Xavier and co-workers¹⁷² have studied the influence of injection moulding parameters, pressure, speed, temperature, on the morphology and mechanical properties and processing conditions of fibre reinforced poly

(propylene) composites using SEM, Instron testing and polarizing microscopy. Misra and coworkers¹⁷³⁻¹⁷⁶ observed *trans*-crystallinity at glass fibre-polymer interface when glass fibre was under stress. A correlation was obtained between clustering theory and light scattering for water absorption in poly (vinyl butyral) films.

Reviews are reported on fire proofing agents and durable press finishes involving poly (propylene), phosphorylated polyesters and celluloses as blends by Jha and coworkers.¹⁷⁷⁻¹⁷⁹ Bajaj and Chakrapani¹⁸⁰ reported studies variously on crystallinity, denier and thermal behaviour of co-polymer of acrylonitrile with halo-alkyl acrylates by DSC and TGA; halo alkyls in PAN decreased the second order transition temperature; effect of phosphorylated fabrics on flame retardance; configurational sequence, lengths, tacticity; the compatibility and dispersibility of Sb_2O_3 in poly (propylene) giving a product with increased flexural rigidity, diffusion coefficients and uptake of the dyes by the fibres.^{181,182} Bajaj, Chawan and coworkers¹⁸³⁻¹⁸⁶ reported the effect of $Al_2(SO_4)_3$ on cross-linking of ter-polymer of AN by HCHO and suitable for textile printing. Mukherjee and coworkers¹⁸⁷⁻¹⁸⁹ evaluated dye uptake and moisture regain properties of fibres of Nylon-6 grafted with acrylates and reviewed^{188,189} the effect of radiation on crystallinity, thermal and mechanical properties of poly (ethylene) and poly (propylene) and LLDPE, linear low density polythene. *The work covered has a great significance to polymer and textile technology.*

INDIAN INSTITUTE OF TECHNOLOGY, KANPUR

Chaurasia and co-workers¹⁹⁰ made multi-variate regression and perturbation analysis of viscosity, molecular weights and concentration data for poly(MMA), Poly(VA) Poly(S) and studied the effect of chain length, molecular architecture and solvent-polymer interaction energy on second virial co-efficients. A semi-empirical equation was proposed for higher values of solvent-polymer interaction parameter by Gupta and coworkers.¹⁹¹ Anil Kumar, S K Gupta and coworkers¹⁹²⁻²²⁷ and Ray and Gupta²²⁸ have carried out extensive theoretical studies and suggested designs for reactors under diverse conditions of polymerization. This aspect will be elaborated in 'engineering plastics'.

INDIAN INSTITUTE OF TECHNOLOGY, KHARAGPUR

Mooney viscosities and molecular weights of poly (styrene)-poly (butadiene) rubbers were reported by Bhatnagar and Bannerjee.²²⁹⁻²³⁰ Cohesive energy densities (CED) for neutral rubber and poly(styrene) from viscosities and swelling measurements for poly (butadiene) by Mangaraj and coworkers;²³¹⁻²³² electrical and mechanical properties of PMMA - Cu composites and the adverse effect of copper loading on compression strength;²³³ stereo regularity of poly (isobutyl vinyl ether) being inversely proportional to percent conversion of the monomer²³⁴ and with no stereo-regularity if V_2O_5 was the catalyst²³⁵ were other studies reported. Furfural based cation-exchange resin from (N-vinyl carbazole) was characterized.²³⁶⁻²³⁷ It was found that Cu(II) exchanged with zeolitic molecular sieve²³⁸ in the cationic polymerization of NVC and isobutyl vinyl ether.²³⁹⁻²⁴⁰

Biswas and coworkers²⁴¹⁻²⁴³ synthesized a poly (pyro-mellitimide) and elucidated its structure by IR, NMR and elemental analysis, besides studying some thermal and electrical properties. A phosphorylated cation exchange resin from divinyl benzene and NVC was studied for hydro-thermal stability and ion exchange capacity.²⁴³

Bandopadhyay and coworkers²⁴⁴⁻²⁴⁵ studies on adiabatic compressibilities of poly (benzimidiazoles); Maity and Ray's²⁴⁶⁻²⁴⁹ studies on the heat resistance and dielectric properties in relation to structure of polyamide-imide; Atanu Ray *et al.*'s²⁵⁰⁻²⁵² work on heat resistant polyimide²⁵⁰⁻²⁵¹ and their thermal and electrical properties, the needs and durability and fracture morphology of poly (styrene) impregnated with mortar composites by SEM by Bhattacharya and coworkers²⁵³ have been reported.

INDIAN INSTITUTE OF TECHNOLOGY, MADRAS

Radhakrishnamoorthy²⁵⁴ found that thermoluminescence curves of poly (methyl methacrylate) irradiated with gamma rays in the temperature range of 1.0-460 °K showed two glow peaks with maximum at $\lambda = 365\text{nm}$ at 136° and $\lambda = 480\text{nm}$ at 368°. George and Ramamoorthy²⁵⁵ studied the thermal conductance of plasticised PVC containing carbon black or copper powder which increased the hardness but decreased impact strength, tensile strength and elongation. Srinivasan, Gouri Krishna and co-workers²⁵⁶⁻²⁵⁷ synthesized poly (benzimidazoles) - containing cardo and azo groups; characterized isocyanate terminated pre-polymers using polyester polyol and cured with diamines and diols and it was concluded that Maxwell-Wagner-Silars interfacial polarization mechanism was operative. Rajendran and coworkers²⁵⁸⁻²⁶⁰ synthesized low temperature stable poly (tetrahydrofuran urethane) and poly (dimethyl xylol enylamides) and characterized them by viscosity, T_g elongation and crystallinity, S Padma and co-workers²⁶¹ synthesized poly (benzoyl propion amides) and characterized them by DTA, TGA and solubility. Eish, Venkataseshiah and co-workers²⁶²⁻²⁶³ found that the anomalous breakdown voltage of PMMA immersed in transformer of oil decreased when the polarity of the superimposed pulse voltage was opposite to that of direct voltage and increased when the polarities were the same; the polarity of the resultant voltage effected the length of the breakdown path and also discussed the effect of wave shape and polarity of the applied voltage, thickness, and size of the specimen and diameter of the high voltage electrode on anomalous breakdown. Hydrogenation of alkenes and alkynes catalyzed by poly(styrene) bound palladium (II) complexes was reported by Suchita Nayak, and co-workers.²⁶⁴ *The relative merits of electrical and hydrogenation studies have not been brought out.*

M S UNIVERSITY, BARODA

Some new chelating amphoteric ion exchange resins (condensation of epichlorohydrin and catechols) were prepared by Kapadia and co-workers²⁶⁵⁻²⁶⁷ and analysed for thermal stability, moisture retention, Cu exchange capacity. The solubility parameters of polymers were calculated using additivity of molar refraction

constants. Phenol-acetaldehyde polymer chelating resins were prepared by a gel technique, the ligands chosen being salicylic acid, pyro-catechol, dihydroxy quinoline and metal distribution co-efficients (for Ca, Mg, Cu) for the resins were determined as a function of pH by Shah and coworkers.²⁶⁸ *These studies are of great importance for development of polymers as ion exchange resins.*

UNIVERSITY OF BOMBAY, BOMBAY

Terylene polyester fibres and nylon fibres were exposed to various doses of gamma radiation both in vacuum and air, and changes in the melting point, intrinsic viscosity, tensile strength and dye absorption were investigated by Rao and Jaiprakash.²⁶⁹ Electrical and microscopic properties such as static charge, gloss and dye absorption of poly(styrene), poly(amides) and poly(propylene) were studied by Potnis and Shetty.²⁷⁰⁻²⁷² Methods for the qualitative analysis of amino plastic finishing agents were tabulated by Varadarajan and Saraiya.²⁷³ X-ray diffraction of purified cotton treated with ethylene diamine by Lokhande and coworkers²⁷⁴⁻²⁸⁰ showed the presence of cellulose III and a small fraction of cellulose-I; and transformation of cellulose I to II by swelling was found to be complete. Swelling native and mercerised ramie and cotton fibres in ethylene diamine, changed the cellulose I and II lattices into cellulose III and IV lattices respectively and mechanisms for the lattice transformation were discussed by Chidambareswar and coworkers.²⁷⁶ Lokhande *et al.*'s²⁷⁷⁻²⁸⁰ work on swelling of cotton fibres in ethylene diamine-morpholine mixtures; evaluation of X-ray crystallinity index; decrystallinity; dyeability; lattice conversions (cellulose I \rightarrow II \rightarrow III); synergistic effect and correlations between properties; computerized colour matching in dyeing of cotton polyester blended fabrics; correlation of surface charge and zetapotentials of dyes and also mechanism of dyeing with a view to economise energy are noteworthy. Jayanthi and coworkers²⁸¹ observed superior coating properties of copolymers of polyesters from cardanoxyl acetic acid-maleic anhydride-glycerol and from linseed oil terephthalic acid-glycerol. Benzoylation of cotton and viscose by George,²⁸² the role of NaCl in suppressing the ionization of carboxyl groups in and increase of dye uptake by the modified celluloses by Shenai and Mehra²⁸³ and the IR spectra of deuterated Nylon-6 before and after dehydrogenation by Venkataraman and coworkers²⁸⁴ are various studies reported. *It may be emphasized that these contributions have a good bearing on cellulose technology, dyeing of textiles, coatings etc.*

CALCUTTA UNIVERSITY, CALCUTTA

Biswas and Das²⁸⁵ studied the elastic properties of drawn poly(propylene) in terms of phenomenological model involving change of crystallinity and orientation of the crystal. Studies on depolymerization of natural rubber in the presence of sunlight, accompanying changes in viscosity, solubility and molecular weight are due to Iyer and Chaudhury.²⁸⁶ Molecular dimension of poly(vinyl-pyridine) in alcoholic silver nitrate solution by Chatterjee and coworkers.²⁸⁷ Polyelectrolyte behaviour of viscose solutions was studied by light scattering and viscosity by

Ghosh and Chowdhury²⁸⁸ who noticed peculiar viscosity characteristics, and the latter were attributed to ionic interaction and molecular configuration. Studies on unperturbed dimension of sodium cellulose xanthate were made by Das and Raj.²⁸⁹ Sengupta and coworkers²⁹⁰ used the dye partition technique for calculating composition and monomer reactivity ratios of copolymers of methyl (ethyl) methacrylates and allyl alcohol (allyl acetate, vinyl acetate, acrylic and methacrylic acids). Viscometric and osmometric studies of fourteen hymato malonic acids were carried out by Mukherjee.²⁹¹ Studies on molecular association of glycols and determination of the molecular weights and chain flexibility of polyethylene-glycol systems were carried out by Ghosh and coworkers.²⁹² An equation was derived based on statistical approach to rubber elasticity by Mukherjee²⁹³ for calculation of the energy stored in deformation of a rubber elastic polymer network at constant temperature. Ghosh and coworkers²⁹⁴ have studied vulcanization characteristics and physical properties of natural rubber, vulcanized by sulphur in the presence of ZnO, PbP, PbO. Ghosh²⁹⁵ determined the disassociation constant of partly neutralized poly (acrylic acid) from pH at different salt concentration. *While the studies on vulcanization are interesting the real impact (fundamental and applied) has not been brought out.*

UNIVERSITY OF DELHI, DELHI

Titration curves constructed for condensation of HCHO with *para* cresol by Mitra and Chatterjee²⁹⁶ indicated linearity of the product. Details of molecular weight distributions including mechanism in living polymerization were worked out by Jain and Nanda.²⁹⁷ Conductometric titrations involving co-polymers from 2-isomeric methacrylic acid and 2-vinyl pyridine indicated that partial zwitter-ion occurred in the copolymer and equivalents of carboxyl anion, pyridinium cation determined from titration curves agreed closely with those determined from spectrophotometry by Nanda and Jain.²⁹⁸ Expressions for number and weight average chain lengths were obtained from appropriate generating functions developed for living polymers by Chaudry and coworkers.²⁹⁹ A quantum-mechanical version of the cell theory that included the effect of anharmonicity in the cell theory potential was developed by Midha and Nanda³⁰⁰ to explain the volume-temperature relationship of polymer crystals. Co-polymer, poly (*p*-amino-nitrostyrene)-co-poly (formaldehyde) was prepared and separated into 3 fractions in a non-aqueous medium and the potentiometric and conductometric titration curves were correlated with degree of polymerization, basic character and H-bonding in the copolymer by Agarwal and co-workers.³⁰¹ Hyper acidity and stepwise neutralization of functional groups in phenol-formaldehyde oligomers were interpreted in terms of intra molecular hydrogen bonding, homo conjugation and ion association in a medium of low dielectric constant by Chatterjee and coworkers.^{302,303}

Yadav and coworkers³⁰⁴ made a study of isothermal lamellar thickening of crystallization of polythene by DSC and noticed high temperature and low temperature peaks which were attributed to simultaneous molecular fractionation and annealing. The effect of solid state extrusion on crystal density and unit cell parameters of polythene were studied by Dhawan and coworkers.³⁰⁵ Equation

of state for poly (dimethyl siloxane) fluids useful for high pressure work was developed by Sachdeva and coworkers.³⁰⁶ *Conductometric/potentiometric titrations of polyelectrolytes is a well-recognised standard technique.*

KURUKSHETRA UNIVERSITY, KURUKSHETRA

Lal and Bhatnagar^{307,308} studied degradation of poly(ethylene) dissolved in chloronaphthalene as a function of time and calculated and discussed free energy, enthalpy and entropy of activation. A modified semi-empirical Huggin's equation, for calculating thermodynamic interaction parameter was proposed by Sharma and Bhatnagar.³⁰⁹ The intrinsic viscosities of poly (ethylene) solution in decalin and tetralin were determined by Manmohan Singh and Hari.³¹⁰ Kinetic studies of acetylation of cellulose with mono, di, and tribromo acetic acids by Bhatnagar and Satish Agnish³¹¹ indicated that the process was of second order and decomposition temperature of the esters decreased @ 533-119 °K with increasing Br content and Jain, and co-workers³¹²⁻³¹⁴ studied thermal degradation of cellulose and its phosphorylated products (esters, acetate, benzoates and naphthoates) by DTA, mass spectrometry and IR. Physico chemical studies on photo-stabilization of butyl rubber were made by Chandra and Bhatnagar.³¹⁵ *Detailed mechanism and application of photo stabilization is a great need.*

UNIVERSITY OF LUCKNOW, LUCKNOW

Molecular weights of poly(vinyl acetate) were determined by end group analysis by Misra and Gupta.³¹⁶ Studies on dielectric relaxation of isooctyl phenoxy poly(ethoxy ethanol) in dilute solution were made by Dhar and Shukla³¹⁷ and dielectric constant and dielectric loss factors for the former were determined at various temperatures to evaluate polymer dielectric relaxation times but the use of the data has not been spelt out. Shukla and Misra^{318,319} studied solubilities of and suggested mechanisms for thermal decompositions (by DTA 200-580°) of polyamides and polyhydrazides. Shukla and Rastogi and coworkers³²⁰ studied thermal decomposition (DTA) of newer polyamides from *para* iso-phthaloyl chlorides and aromatic diamines between 250-310 °C. *These studies must be considered routine.*

UNIVERSITY OF MADRAS (DEPARTMENT OF PHYSICAL CHEMISTRY), MADRAS

Santappa and co-workers³²¹⁻³⁴⁰ have studied the dilute solution properties of polymers by light scattering, viscosity and osmometry with a view to test various theories such as Fox-Flory; Korata Stockmayer, etc. and have evaluated Flory's constant, unperturbed dimensions, root mean square end to end distances, etc. Mention may be made of Padma Vasudevan and Santappa's investigations on PMMA in iso-amyl acetate; viscosities of dilute solutions of the latter in organic solvents and phase rule studies of the binary and ternary systems involving polymers and organic solvents and of Karunakaran and Santappa's³²⁶⁻³²⁸ studies of the solution properties of poly(ethyl methacrylate) and the co-polymer poly(methyl ethyl acrylate)-CO-poly (styrene). Venkata Rao and Santappa³²⁹ studied molecular weight distribution of poly (acrylamide) prepared by photo-chemical method.

Studies on solution properties of poly [(ethyl (butyl) acrylate)]-CO-poly(styrene), effect of composition on solution properties of poly (styrene)-CO-poly(ethylacrylate) were due to Srinivasan and Santappa.³³⁰⁻³³³ Similar studies on various polymers and copolymers have been reported by Arulsamy and coworkers,³³⁴⁻³³⁵; Venkataramana Reddy and coworkers.³³⁶⁻³³⁸

Co-polyesters were prepared by *trans*-esterification of dimethyl terephthalate with various diols and the kinetic orders, heat and entropy of fusion and activation energies for thermal degradation of the former were determined by DTA by Balakrishnana and coworkers.³³⁹⁻³⁴⁰ *Study of solution properties of various types of polymers by Madras University by light scattering must be considered both extensive and intensive.*

PANJAB UNIVERSITY, CHANDIGARH AND GURUNANAK DEV UNIVERSITY, AMRITSAR

Enthalpies of mixing of poly(tetramethylene-oxide) fractions and dioxane and cyclo hexane were determined by Sharma Subash and coworkers.³⁴¹ Molecular weights of poly (ethylene glycol) determined by differential monometry compared well with those from end group analysis according to Lakhnupal and coworkers.³⁴²⁻³⁴⁴ Heats of mixing of polyethylene glycol-water system; thermodynamic properties of solution of polyethylene glycol in benzene and of polymer-solvent interaction constants in non polar solvents were evaluated. Dhillon³⁴⁵ determined second virial co-efficients for the copolymer of adipic acid and 2-butene-1,4-diol in benzene by light scattering in the temperature range 283-333 °K and that zero temperature was not reached in this range. *Differential monometry as a tool for determination of molecular weights of polymer must be further developed.*

SARDAR PATEL UNIVERSITY, VALLABH VIDHYA NAGAR

R D Patel and coworkers³⁴⁶⁻³⁵² have carried out extensive investigations on the thermodynamic and hydrodynamic properties of the polymers; amylose and its acetate³⁴⁶⁻³⁵⁴ benzoate, propionate,³⁴⁹ palmitate, and nitrate derivatives; trimethyl cellulose,³⁴⁸ cellulose acetate-butyrate, cellulose acetate phthallate, carboxymethyl amylose, amylose sulfate,³⁴⁹ isotactic polybutene-1 poly-(N-phenyl acrylamides) and styrene-grafted amylose acetate, above and below theta conditions.³⁵⁰ Current theories were examined in the light of the experimental data on the polymers,³⁵¹⁻³⁵² modification to Flory's theory was proposed and two new viscosity molecular weight relations for unperturbed dimensions of polymer chains were suggested. Interactions between small ions (counter-ions) and polyions in poly electrolytes were investigated by equilibrium (osmometry, dialysis, etc); and non equilibrium³⁵³⁻³⁵⁵ (polarography, isoionic viscosity etc.) methods which led to the conclusions that the second virial co-efficient, molecular dimensions, and degree of ion-binding were functions of molecular weights and electrostatic interactions.

Attempts were made to crystallise various synthetic and natural polymers,³⁵⁶⁻³⁶³ by a new facile method called 'film formation method' which yielded crystals of different morphological features with perfect symmetry; polythene, poly(butene-1), poly(acrylonitrile), cellulose triacetate etc. The kinetics and growth mechanism

in crystallization involving fibrils, spherulites, sheaves, oval rectangular, hexagonal and rhombic shaped single crystals of different polymers were reported and in Cellulose and carboxy-methyl cellulose which could be perfectly crystallized it was concluded that a stiff backbone chain of cellulose folded back and forth in an ordered array under suitable conditions.

Studies are reported on adsorption of PMMA and cellulose triacetate on to porous adsorbents which facilitated fractionation and diffusion of helium, oxygen, nitrogen and carbon di-oxide. Friedel-crafts condensation of 8-hydroxyquinoline with 1, 2-dichloro ethane (ethylene glycol) yielded polymers which were characterized by IR and UV spectra and their molecular weights were determined by conductometric-titrations in pyridine. It was found that a copolymer of poly (oxymethylenes) and 1,2-dichloroethane-8-hydroxyquinoline was a selective ion exchange resin with the uptake of Cu, Co, and Ni decreasing with increasing NaClO_4 or Na_2SO_4 concentrations but increasing with NaNO_3 or NaCl , whereas the uptake of Zn, Mg and Cd decreased with increasing concentrations of all of these salts; the rates uptake following the order: $\text{Zn} > \text{Cd} > \text{Mg} > \text{Cu} > \text{Co} > \text{Ni}$. Joshi and coworkers³⁶⁹ synthesized a copolymer of salicylic acid—urea—formaldehyde and determined the composition by elemental analysis; number average molecular weights by conductometry; relative thermal stability by TGA and DSC. Patel and coworkers³⁷⁰ studies on uptake of metal ions by an ion exchange resin; Patel and coworkers³⁷¹ synthesis and characterization of other Friedel-crafts polymers and Bhiklu Suthar's synthesis³⁷² and characterization of high temperature polymers are other investigations reported. *Sardar Patel's University's contributions on crystallization of polymers; selective ion-exchange resins must be considered as significant.*

OTHER INSTITUTIONS

Viscosity studies of hydrolysed poly (acrylamide) solution were done by Deb and co-workers³⁷³ and degradation mechanism of copolymer of styrene and polyester by TGA, DTA, IR etc by Das and Baijal³⁷⁴ (Dhanbad School of Mines) are routine type. Ray and coworkers³⁷⁵⁻³⁷⁶ (Jute Research Institute, Calcutta) showed that mercerising jute fibres with 18 per cent sodium hydroxide solution caused an increase in cell wall thickness but has it been put to use? Esterification of aldehydic acids of lac resins both before and after hydrolysis by Sengupta and coworkers³⁷⁷ (Lac Research Institute, Ranchi) indicated that nearly two-third of the former was present in a combined state involving acylal and hemiacetal linkages (to be confirmed by another method). Mathan and Thomas³⁷⁸ (Rubber Research Institute, Kottayam) found that raw blends of natural rubber and emulsion of butadiene rubber (they are done in the industry) had viscosities and tensile properties lower than those of natural rubber. The effects of a static electric field on the formation and annihilation of positronium, in teflon, poly(ethylene), poly(styrene), fused quartz, nylon and perspex were studied by Rama Rao and co-workers³⁷⁹ and ways of eliminating static electricity on the polymers must be given great attention (Saha Institute of Nuclear Physics, Calcutta).

Manjunath and co-workers³⁸⁰ (Bombay Textile Research Association)³⁸⁰⁻³⁸² made routine studies of X-ray diffraction study of water imbibed in cellulose, poly(propylene) and polyester fibres and their diffraction patterns showed similarity in hygroscopic and non-hygroscopic polymers. Dixit³⁸¹ studied scouring of cotton fabrics with tri-chloroethylene obviating the use of caustic soda in a bleaching sequence. Treatment of Nylon-6 with phenol methylol was found to increase the crystallinity and fine structure of the former facilitating dyeing and mechanical behaviour as observed by Subramanian and coworkers³⁸² but has it been adopted by the industry? Doshi and coworkers³⁸² suggested proper selection of temperature, duration and catalyst system for rapid cure and wrinkle resistant finish of cotton textiles. Paralikar and coworkers³⁸³⁻³⁸⁴ (Cotton Technological Research Institute, Bombay)³⁸³⁻³⁸⁵ developed a good electron diffraction technique to study and distinguish crystallinity of various types of celluloses. Pandey and Raju³⁸⁵ studied rate of migration of crosslinking reagents in cotton fabrics during resin finishing treatment and relationship between rates of migration and drying must be further pursued to the advantage of industry and polymer chemist.

Patel and co-workers³⁸⁶ (Indian Petro-chemical Corporation Limited, Baroda)³⁸⁶⁻³⁸⁷ synthesized poly-(N-p-substituted phenyl maleimide and characterized it by elemental analysis and I.R. and also studied the thermal behaviour of the products by DTA and TGA. The use of high resolution C-13 NMR spectra in the analysis of synthetic polymers was reviewed by Nagabhushanam and Salia.³⁸⁷ Addition of rubber dust or crumbs of saw dust to bitumen based sealing compounds gave good workability according to Singh and Agarwal³⁸⁸ (Central Building Research Institute, Roorkee). Gurusamy (Central Electro Chemical Research Institute, Karaikudi)³⁸⁹ measured the electrical resistance per unit deposition charge per unit area anodic deposition of alkyd resin and latex on mild steel and related the former to electrical conductance and electrode material—*good but of limited advantage*. A review was presented on synthesis and application of organic di-iso-cyanates in polymer synthesis by Bhattacharya and Nair³⁹⁰ (Central Fuel Research Institute, Dhanbad). Pitchumani and co-workers³⁹¹⁻³⁹² (Central Leather Research Institute, Madras)³⁹¹⁻³⁹⁴ did routine syntheses of poly(vinyl formate) and poly(vinyl butyrate) from poly(vinyl acetate) and studied the film-forming properties of blends of chlorinated rubbers and co-polymers of acrylates. Co-polymers of sulphated castor oil and acrylic monomers were characterised by viscosity, miscibility, stability for potential use as a fat liquoring agent by Kaniappan and co-workers.³⁹³ But how this fat liquor differs from the conventional ones has not been indicated. Srinivasan and co-workers³⁹⁴ suggested GPC as a tool for distinguishing between graft co-polymers and polymer blends/mixtures involving cellulose nitrate and poly(MMA) and this needs to be further explored.

The low-cycle, high strain fatigue testing of acrylic fibres by Gupta and co-workers³⁹⁵ (Vikram Sarabhai Space Centre, Trivandrum)³⁹⁵⁻³⁹⁹ indicated that the inherent defects in the fibres reduced the fatigue life considerably. Is it not expected? Thomas and coworkers³⁹⁶ found that the decomposition of carboxy terminated poly(butadiene), a binder for solid propellants, was dependent on

heating rate and decomposition products were mainly, low molecular weight hydrocarbons and it would be interesting to pursue work of this nature. Kumar³⁹⁷ has synthesized aromatic polyimides and various side-products in the synthesis were identified and characterized by IR and mass spectra. There is nothing exciting about this. Statistical design studies, many are being done elsewhere, for optimum conditions in the preparation of poly(oxymethylenes) were worked out by Goel and coworkers.³⁹⁸⁻³⁹⁹ Mark-Howink equations were established for the co-polymers of acrylamide, ethyl acrylate and styrene by Khan and coworkers,⁴⁰⁰⁻⁴⁰¹ (Indian Institute of Petroleum, Dehradun), who suggested a suitable modification of Huggins equation for determining the incipient concentration of the polymer solution at which the inter molecular attractions and repulsions cancelled each other. This is a routine study. Gupta and Gupta⁴⁰² (University of Allahabad)⁴⁰²⁻⁴⁰⁴ applied 2-dimensional random walk model for polymers and the Markoff chain model to understand the semi-stretching nature of the polymers. The mathematical treatment was suggested for coiled and ordered helical and crystalline and semi-crystalline region (I) and a generating function for the assymmetric-probability distribution of the end-to-end distance of polymer chain was also derived. Studies of this type have only theoretical significance. Polymeric tetra-dentate chelate from the Schiff base had the well-known octahedral geometry according to Muruga and coworkers.⁴⁰³ Banerjee and Dey⁴⁰⁴ prepared coordination polymers of 1, 2, 5, 8-tetra-hydroxy anthraquinone and Cu(II), Ni(II), Co(II), Mn(II) and Fe(II) and characterized them by reflectance spectra, NMR and TGA but the use of such polymers is limited. In the study of absorption of organic vapours by polymers at constant temperature and pressure, a model was developed that could be used for calculating the diffusion co-efficients and studies of this type must be extended (Banaras Hindu University, Varanasi).⁴⁰⁵⁻⁴⁰⁶ A SEM study of the fatigue failure of carbon-reinforced epoxy resin indicated two distinct zones according to Prakash⁴⁰⁶—one tensile type failure and the second gradual type. An appreciable amount of thermally stimulated, short circuited current was observed during heating and cooling from unpoled plasma-polymerized PAN by Mohana Chandran and Sathianandam⁴⁰⁷ and *this work needs close scrutiny* (Cochin University). The usual light scattering and viscosity data were used to evaluate the degree of molecular entanglement in the sodium alginate and PMMA in different solutions by Sanyal, Rastogi, Gupta and coworkers (University of Gorakhpur).⁴⁰⁸⁻⁴¹⁰ The zeta potential at polyester-water interface estimated by sedimentation potentials was found to decrease with the increase in number of carbon atoms between two carboxyl groups in polymer chain by Rastogi and Prakash.⁴⁰⁹ Thermogravimetric study of copolymer from hydroquinone and phosphorous oxychloride showed that the decomposition was a two-step process according to Gupta and Srivastava.⁴¹⁰

Cheda and Das⁴¹¹ observed that Iron (III)-sulphosalicylate complex retarded the free radical polymerization of styrene. Electrical conductance in PAN films were studied by Chalia and Barne⁴¹² (University of Guwahati). The molecular weight-viscosity relationships were determined for unfractionated and fractionated samples

of PAN by Misra and Mukherjee (University of Jabalpur).⁴¹³ O-acylated anisole, formaldehyde and salicylic acid copolymers, were used as acylating agents for ammonia, amines, alcohols and peptides by Sahni and co-workers⁴¹⁴ (University of Jodhpur). The metachromatic spectra of pinacyanol chloride and sodium salt of poly (methacrylic acid) were broad and multi banded and metachromasia was discussed in relation to stoichiometry by Pal and Ghosh (University of Kalyani).⁴¹⁵ Radiation damage in PAN was studied by thermoluminescence, ESR and optical spectrometry by Masth and Radhakrishna (Kakatiya University).⁴¹⁶ Gupta and Deshmukh⁴¹⁷ found that thermoxidative degradation of poly (lactic acid) in air by DTA and TGA was a first order process (University of Nagpur). Detection of phase transitions in insulators by thin layer chromatography was studied by Walzede and co-workers⁴¹⁸ (University of Poona). Poly electrolytes were prepared from Li polyphosphate and alkylamines and their molecular weights were determined by Vyas and co-workers⁴¹⁹ (University of Rajasthan). *The work described above⁴⁰⁹⁻⁴¹⁹ is of routine type and nothing innovative.*

Bhadani and Gray (Ranchi University)⁴²⁰ reported decrease in the molecular weights of esters from hydroxy propyl cellulose(I) and propionyl (isobutryl) chloride indicating chain scission and the esters of (I) with aliphatic acids showed cholesteric reflection while those with aromatic acids formed a long pitch. The anisotropic-isotropic phase transition occurred at $165 \pm 10^\circ \text{C}$ for all the esters. The mechanism of conductivity in the films of copper-phthalocyanin and iodine doped poly (styrene) was studied by Srivastava and coworkers⁴²¹ and Tiwari and co-workers (University of Saugar).⁴²² Fractionation of TLC (a tool to be explored) of static poly (methyl methacrylate) (I) with good solvents showed that the spots remained, immobile in C_6H_6 and CHCl_3 and the R_f value of (I) depended on the molecular weights according to Jain and co-workers (Vikram University, Ujjain).⁴²³ Usual co-polymerization studies using styrene and drying oils were made by Menon and Agarwal (Regional Research Laboratory, Hyderabad).⁴²⁴ Routine viscosity molecular weight relations for poly(styrene)-CO-poly (butadiene) system at different temperatures were derived and the constants of Mark-Houwink equation were evaluated by Oberoi and Bhatnagar (Regional Engineering College, Kurukshetra).⁴²⁵⁻⁴²⁷ Physico-chemical studies on the photo stabilisation of rubber (an aspect which needs greater study) by allyl phenyl mercury⁴²⁶ and electrical conduction at high electrical fields in the film of Kapton⁴²⁷ were reported.

Araldite (AY-103) containing 18 phv HY-956 hardener, acted as a highly sensitive photo-elastic material according to Rao and Rao⁴²⁸ but has this been done on an extensive scale (Regional Engineering College, Rourkela)? Crystal nucleation and growth rates (needs to be pursued) were studied microscopically by Jain (College of Engineering, Raipur).⁴²⁹ Temperature dependence of dynamic and static young's modulus of polymers such as polyethylene, PVC and PMMA at $0^\circ - 30^\circ \text{C}$ were studied by Yadhar and Dangahu Kar⁴³⁰ (Government Girls' College, Bilaspur). Effect of electrode material on thermally stimulated discharge and dark current in poly (styrene) films were measured by Srivastava and co-workers⁴³¹ (P.V. College, Orai). The partition function due to Bhatnagar was

modified and extended to liquids containing larger and non-spherical molecules by Sharma⁴³² (Rey College of Education, Bhubaneswar). A polyamide-polyimide copolymer was synthesised and characterized by Nitrogen analysis IR, TGA and DTA by Maiti and Maiti,⁴³³ (Ulusia College, Ulusia). PVC of different molecular weights was blended with nitrile rubber and mechanical properties were evaluated before and after vulcanization. Vulcanization with sulphur masked the effect of PVC compatibility with styrene according to Trivedi and Chatterjee⁴³⁴ (Research and Development Centre, NDCIL, Thane). Das and coworkers⁴³⁵ characterized the resins from substituted benzoic acids and formaldehyde by viscosity IR and TG and evaluated the Huggins, Kramers constants and activation parameters for thermal degradation. Lenka and coworkers⁴³⁶ used viscosity technique for determining Flory constant and unperturbed dimension in methylalcohol toluene solvent system for poly(methyl methacrylate) (Utkal University). *There is nothing new or exciting in the work of these various institutions.*⁴³⁰⁻⁴³⁶

CONCLUSIONS

The following few suggestions are being made for further work in this field :-

- (i) Thermodynamics and hydrodynamics of polymer solutions have been studied extensively, various theories tested and many parameters evaluated but no finality has been established towards theory of polymer solutions. Further work in this field should take note of this aspect, otherwise, it might well add to the accumulated repetitive type of work.
- (ii) Work on thermal properties including oxidation/degradation using well-known techniques, DSC, DTA etc. and characterization of the polymers and products by IR, NMR, X-rays, mass spectrometry, SEM, etc. have also been extensive but the use of such data for synthetic organic chemistry, micro-structure determination and morphology and specific utilitarian aspects to industry has been limited. Further work should concentrate on these aspects, particularly on polymers, usefulness in aerospace engineering, electrical and electronics, bio-medicals, fire retardancy, textiles, polymer supports for catalysts; polymer systems, with dopants for super-conductivity; polymers for coatings, anti-corrosion, irrigation, prosthetics, drug release and delivery composites and blends, cation-anion exchange resins, building materials etc.
- (iii) Much useful data on mathematical modelling and reactor designs under diverse conditions of polymerization has been published particularly from NCL Poona and IIT, Kanpur. There is a necessity for consolidating work of this nature by well-known CAD, CAM techniques and with intimate interaction with plastics industry.
- (iv) Study of systems involving composite concrete; networks, membranes, swelling (phase transitions and degree of branching) cross linking and processes like curing, diffusion, sorption-desorption (fractionation of polymers; diffusion of gases and ion exchange resins), rheology, stress-crack resistance will be important from the fundamental and practical aspects.

(v) Liquid crystalline polymers (LCP) which have not received much attention so far must be investigated more extensively. LCP studies may cover molecular design, synthesis, characterization (melt flow and birefringence) melt properties, thermal stabilities, structural and order studies by NMR, order, orientation and crystalline studies by EMS, rheology and processing. More importantly the two important directions in which research may be organised are (i) structural scale ordering (main chain type; molecular and super molecular aspects, oriented systems) and (ii) electro magnetic processes (side chain type multi functional electro magnetic structures with mechanical, thermal and environmental integrity). Studies of this nature would form the basis for designing submicro level devices used in air craft, space vehicles, defence applications, photoresistors, lithographic sources memory storage systems etc.

(vi) There is a vast scope for investigations, covering aspects like fatigue, fracture, anti-corrosion, pyro-electric, dielectric, resistivity and hysteresis behaviour of polymers.

(vii) The entire field of pollution arising out of use of polymers in industry, building, engineering, agriculture, etc is virgin both in India and abroad and researchers might concentrate on aspects like biodegradability, recovery from waste, control of pollution etc.

ACKNOWLEDGEMENT

The author wishes to thank the Indian National Science Academy, New Delhi for providing him with the INSA Senior Scientist's position and to DST for the position of a retired Scientist under USERS Scheme during which tenures this review work has been compiled. His thanks are due to Professor Kameswara Rao of Krishna-deva Raya University, Anantapur for discussion on LCP and to the authorities of Anna University for the necessary facilities for work.

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