

State-of-the-Art of Polymer Research in India: Part I—Modification of Polymers by Grafting

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Introduction

Extensive work has been carried out on 'grafting' of cellulose, rubber, PVC, synthetic copolymers, collagen, wool, jute, silk fibre, etc. with various vinyl monomers with a view to improving the physical and mechanical properties of the polymers. Initiation of grafting has been effected by heavy metal ions like Ce(IV), Co(III) and V(V); complexes of Co(III), Mn(III) and Fe(III); redox pairs such as Ce(IV)-alcohols, V(V)-glycols, peroxydisulphate-ascorbic acid, peroxodiphosphate-ascorbic acid and peroxy compounds, benzoyl peroxide, H_2O_2 , $S_2O_8^{2-}$ and $P_2O_8^{4-}$, etc. Graft copolymers synthesized have been characterized by different techniques such as IR, NMR, dye-partition, electron microscopy, and thermogravimetry. This article reviews, institution-wise, the work on grafting in India. Some suggestions for further work in this field are also given.

Ahmedabad Textile Industry's Research Association, Ahmedabad

Kulkarni and Mehta¹⁻⁴ found that graft copolymerization of acrylonitrile to cellulose and cellulosic materials initiated by Ce(IV) by the solution polymerization technique depended upon temperature, adsorption of monomers within the fibre, etc. In general, the rates and yields of grafting were higher with Ce(IV) than with persulphate-thiosulphate redox system. A lower graft yield was obtained at 60°C than at 20°C and 40°C. Traces of Cu(II) in the reaction mixture did not increase grafting yield. A theoretical method was developed for calculating the number-average molecular weights of polymers. Hebeish and Mehta⁵⁻⁷ concluded that the presence of water was essential for grafting mercerized cotton with acrylonitrile by γ -rays. However, practical applications of graft copolymers in industry and the precise roles of agents like Cu(II) and water have not been identified.

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Agarwal and Sreenivasan⁸ grafted vinyl acetate, styrene, acrylonitrile, methyl methacrylate and their mixtures to jute fabrics swollen by water or methanol by γ -irradiation. The extent of grafting decreased the tensile strength and folding endurance, a limiting factor influencing the degree of optimum polymer loading. The folding endurance was least affected when grafting was done with acrylonitrile, while it decreased significantly when jute was grafted with vinyl acetate. No rational explanation based on polymer structure has been offered. Work on cross-linking and grafting of jute with plastics, rubbers, composites and fibres has been reviewed by Iya and Majali⁹. Rao *et al.*¹⁰ determined graft polymerization rates, moisture regain, dye uptake, surface charge densities, yarn spinnability and costs of different radiation sources for grafting of (i) vinyl acetate, acrylonitrile and acrylic acid onto polyester fibres; (ii) vinyl acetate, acrylic acid and methacrylic acid onto polypropylene fibres; and (iii) acrylonitrile, acrylic acid and acrylamide onto polyformaldehyde fibres. Attempts have been made to improve anti-static and dyeability by grafting polyester fibres with 4-vinylpyridine and by adding retarders like ferrous ammonium sulphate and copper sulphate. The rate of grafting of acrylic acid to polypropylene fibres was higher at higher temperatures of swelling and irradiation¹¹⁻¹³. In all these studies, no attempts were made to explain the mechanism of grafting; the relevance of such studies to textile industry with relative merits and cost-benefit analysis has not been stated.

Bombay Textile Research Association, Bombay

Graft copolymerization of cellulose with acrylonitrile was carried out by Sharma and Daruwalla¹⁴⁻¹⁸ employing different initiation techniques, viz. ceric ion, γ -irradiation, Fe(II)- H_2O_2 and anionic; the molecular weights of grafted chains were determined and the solubility behaviour of copo-

ymers was explained. Graft copolymerizations of cotton and vinyl monomers, acrylamide, acrylonitrile, methyl methacrylate, methyl acrylate and ethyl acrylate singly and in mixtures have been carried out by pad-batch method. The effects of concentrations of monomer, catalyst, pH, temperature and duration of reaction on the graft yields, crease recovery, tensile strength, tear strength, abrasion resistance, etc. have been determined. Betrabet¹⁹ has discussed the use of transmission electron microscopy to study the cotton finishes with emphasis on replication, fibrillation, ultrathin-sectioning and cellulose dissolution technique for evaluating chemically modified cotton. Although these studies do not relate the properties to structure, they would be of significance to a practical cellulose technologist.

Central Leather Research Institute, Madras

Studies on grafting of vinyl monomers to collagen, hide powder, hides and skins under diverse conditions are due to Nayudamma, Santappa and coworkers. Panduranga Rao *et al.*²⁰⁻²⁸ grafted vinyl monomers to collagen and studied the extent of grafting efficiency, effect of redox catalysts, etc. Grafting sites²⁰ increased when collagen was thiolated, N-brominated, vinylated, cyano-ethylated or methylated, indicating that hydroxy, amino and peptide groups on collagen backbone provided sites for initiation of grafting. The number of grafting sites decreased when acetylated collagen or collagen treated with oxidized starch was used²¹⁻²⁴. The vinyl polymer chains grafted to collagen and to goat skins and isolated both by acid and enzymatic hydrolysis showed IR absorption for the amide group. Electron microscopic observation of grafted collagen fibrils did not show any cross-striation, indicating that the polymers were probably bound chemically to collagen molecules²⁵⁻²⁸. The turbidimetric titration curves²⁹ were characteristic of different polymer types, grafted to collagen. Pickled skins and chrome-tanned leathers singly grafted with methyl methacrylate, methyl acrylate, butyl acrylate, acrylonitrile or mixtures of monomers by the use of ceric ammonium sulphate as initiator showed superior physical properties³⁰.

The effect of composition of water/methanol in the preparation of collagen grafted with poly(methyl methacrylate) has been studied and the molecular weights of branches were higher with 25% methanol and the number of branches were always more in aqueous alcohol media than in pure aqueous medium, but no explanation has been given for this observation. Satish Babu *et al.*^{31,32} found

the order of the rate of grafting to collagen by Mn(III) to be similar to that by Ce(IV), viz. methyl methacrylate > methyl acrylate > acrylonitrile. Photochemically induced grafting of vinyl monomers to collagen by using dye sensitizers like phloxine, benzophenone, fluorescein and Rose Bengal was investigated in detail by Nagabhushanam *et al.*³³⁻³⁸. These workers have suggested a mechanism based on excitation of the dye to the singlet state followed by the transition to the triplet state, which abstracted hydrogen atoms from the collagen and created active centres on it for the initiation of grafting. Liquid polysulphides grafted to leathers (tanned by acrolein and formaldehyde) yielded soft and supple leathers^{39,40}.

The ion-binding capacity of grafted phosphorylated collagen and gelatin was found to increase⁴¹. The grafts from the caesin-g-poly(methyl methacrylate) and caesin-g-poly(acrylonitrile) copolymers showed positive ninhydrin test and characteristic IR amide group absorption⁴². Analyses of amino acids of the caesin-g-poly(acrylonitrile) and pure caesin⁴³ indicated that 7 out of 11 amino acids served^{44,45} as grafting sites. The per cent grafting of methyl methacrylate on gelatin with ceric ammonium nitrate⁴⁵ plus azobisisobutyronitrile was found to be higher than with the individual initiators. Vasudevan *et al.*⁴⁶ studied the kinetics and mechanism of benzoyl peroxide initiated grafting of methyl acrylate and methyl methacrylate to copolymers of vinyl acetate and vinyl chloride and suggested the use of such graft copolymer as a coating material for leather. Ethyl acrylate and *n*-butyl methacrylate grafted to chlorinated rubber in the presence of benzoyl peroxide showed that the increase in the concentration of the latter decreased the yield of homopolymer and the grafting efficiency. Lacquers based on the graft copolymers of chlorinated rubber with poly(methyl acrylate) were found to be better film-forming materials for leather finishes^{47,48}. Satish Babu *et al.*⁴⁹ found that syntans and vegetable tannins decreased the per cent grafting, while the mineral tannins, Al(III), Cr(III) and Zn(II) increased it; such differences were attributed to different levels of hydrophobicity, swelling characteristics of fibres, etc. KMnO₄ could be used as a grafting catalyst for skins and might be preferred to Mn(III) as initiator in the grafting of leathers. Sudhakar *et al.*⁵⁰⁻⁵² and Srinivasan *et al.*⁵³ studied grafting of methyl methacrylate to nitrocellulose with Ce(IV) as initiator and to poly(vinyl chloride)-co-poly(vinyl acetate) in non-aqueous media with benzoyl peroxide and azobisisobutyronitrile as initiators and provided evidence for grafting through the IR spectra of grafts for

C=O peak at $1,740\text{ cm}^{-1}$. A probable mechanism based on grafting at the α -carbon atom of the primary alcohol or at C_2 - C_3 glycol group of the anhydro glucose unit or at the hemiacetal group of the end unit of nitro-cellulose was suggested. Santappa⁵⁴ reviewed the work on grafting of vinyl monomers to chlorinated rubber, PVC, collagen fibres, cellulose nitrate and caesin and their applications in leather industry. Sudhakar⁵⁵ used gel permeation chromatography to differentiate cellulose nitrate, poly(methyl methacrylate) and cellulose nitrate grafted with poly(methyl methacrylate). Grafting of collagen also yielded prosthetic material^{56,57}, 'fill-up leathers'⁵⁸, 'glaze finish leathers'^{59,60} and full leathers with grafts of very high molecular weights⁶¹⁻⁶⁶.

Poly(vinyl acetate) and poly(butyl acrylate) were grafted separately to caesin by Mohan *et al.*⁶⁷⁻⁷⁰ in the presence of potassium persulphate-ascorbic acid; increase in the concentration of the latter and temperature favoured homopolymerization, and grafting efficiency was greater in the presence of potassium persulphate alone. Chlorinated rubber grafted with acrylic ester in toluene was used as a good top-coat for football leathers⁷¹. The work on grafting of skins, hides and leathers under varied initiator conditions with elucidation of reaction mechanisms and improved properties of leathers *per se* is excellent but the main lacunae are that this has not been extended to pilot plant level and to the industry and with practically no data on cost-benefit analysis.

Defence Science Laboratory, Delhi; and Naval Chemical and Metallurgical Laboratory, Bombay

In the grafting of acrylic acid to methylcellulose with $S_2O_8^{2-}$, Bajaj and Chatterjee⁷² found that the rheology of the graft copolymer depended on the degree of grafting but they did not indicate to what effect this was used. The percentage of methyl acrylic acid in its graft copolymer with poly(vinyl alcohol) increased significantly when sodium methacrylate was used for grafting or when mercapto-modified poly(vinyl alcohol) was grafted^{73,74}. A graft copolymer of masticated natural rubber with poly(styrene) together with motor oil and dibutyl sebacate was suggested as a rocket fuel⁷⁵, its present status, however, not being known.

Indian Association for the Cultivation of Science, Calcutta

Gupta and Nandi⁷⁶ grafted poly(acrylonitrile) (I); poly(methacrylamide) (II) to 1:1 poly(methyl methacrylate)-co-(polystyrene-sulphonyl chloride) (III). Sengupta and Palit⁷⁷ studied graft polymeri-

zation of III with I via thioamide group formation. Mukhopadhyay *et al.*^{78,79} studied grafting of acrylic acid to poly(vinyl alcohol) and methylcellulose separately with permanganate as initiator and suggested a mechanism of grafting based on the reactivity of -OH groups on the backbone. There is no novelty in the mechanism; neither is there mention of the possible uses of the graft polymers.

Indian Lac Research Institute, Ranchi

Improved film-forming properties of graft-copolymers of shellac with acrylates, styrene and acrylonitrile individually and with mixtures were noticed and the best results were observed when shellac was grafted with ethyl methacrylate⁸⁰. No detailed mechanism or any particular use of the graft copolymers was suggested.

Indian Institute of Technology, Delhi

Varma and coworkers⁸¹⁻⁹¹ grafted various acrylates with $S_2O_8^{2-}$ - $S_2O_3^{2-}$ redox initiator on (i) wool, (ii) oxidized and reduced wool, (iii) cotton, and (iv) nylon and determined the order of thermal stabilities of copolymers; they did not suggest any practical applications. Scattering intensity studies showed that the average crystallite size increased with the extent of grafting and scanning electron micrographs of the peeled surface and the cross-sections of the grafted fibres showed that a significant amount of polymer was deposited in the medullae of the fibres⁹². Mukherjee and coworkers⁹³⁻¹⁰⁴ have studied graft copolymerization of (i) poly(vinyl chloride) partially dehydrochlorinated and styrene⁹³ with anhydrous $AlCl_3$ as cationic initiator, (ii) nylon-6 fibres with methyl methacrylate⁹⁴⁻⁹⁸ in the presence of fructose, (iii) polypropylene fibres with methacrylic acid and (iv) starch^{99,100} with acrylamide and Ce(IV) initiator. TGA and DSC studies have described the thermal stabilities of copolymers, photochemical grafting¹⁰¹ of acrylamide on nylon-6 monofilaments in aqueous fructose, liquid inhibition properties of cellulose via graft copolymerization of vinyl monomers to cellulose^{102,103} and moisture regain, viscosity, dye uptake¹⁰⁴ of nylon-g-poly(acrylamide). These studies are bound to benefit the practical technologist in the long run.

Indian Institute of Petroleum, Dehra Dun

Bhargava and Bhattacharya^{105,106} reviewed the work on butadiene rubber-g-poly(styrene) copolymers; their IR analysis of the graft copolymer showed that the microstructure of the rubber was unchanged. During polymerization, 80% of styrene was converted constantly to homopoly(styrene).

and 20% to graft polymer; grafting was initiated by proton abstraction from the α -C of butadiene. The grafted chains were shorter than free homopolymer chains¹⁰⁷.

**Indian Petrochemicals Corporation Limited,
Baroda**

Bharadwaj and Hensinger¹⁰⁸ irradiated polypropylene fibres with different doses of electron beams in the presence of acrylic acid and 2-, and 4-vinylpyridine and found that the grafted fibres had increased tenacity, dye uptake, solubility and crystallinity. UV stabilizers, 2-hydroxy-4-methacryloxybenzophenone (I) and 4-acryloxy-2-hydroxybenzophenone (II) were synthesized and grafted to the backbone of polypropylene (III), low density polyethylene (IV) and polystyrene (V) by melt processing. The extent of additive grafting on the polymer backbone was determined by IR spectra and found to be in the order: V > IV > III (ref. 109). The order of degree of grafting¹¹⁰ with 2-hydroxy-4-(acryloxy)benzophenone and its methacryloxy analogue was also similar. The absence of mechanism of UV stabilizers and antioxidants and extension of the results to factories are the lacunae in this work.

**Indian Jute Industries Research Association,
Calcutta**

IR spectra of methyl methacrylate grafted to jute fibres showed that the major portions of grafting was associated with the lignin fraction of the jute fibres¹¹¹. The possible use of the grafted polymer has not been indicated.

National Chemical Laboratory, Pune

Joshi¹¹² prepared carboxylic rubber by chloro-carboxylation of linear high-density poly(ethylene) with maleic anhydride or maleimide in tetrachloroethane at 90-110°C for 3-5 h. The carboxylic rubbers contained 32.5-57.1% Cl and 0.59-4.05% COOH groups. The chloro-carboxylate polyethylene resembled chlorosulphonated polyethylene in physicochemical properties. The mechanisms and the relative merits vis-a-vis conventional rubbers need to be studied further.

National Metallurgical Laboratory, Jamshedpur

Deb and Sankolkar¹¹³ grafted poly(methyl methacrylate) to partially thiolated poly(vinyl chloride) in cyclohexane at 60°C with Me₂SO as catalyst and the grafting efficiency (~75%) was found to be a function of Me₂SO concentration; the mechanism and use of copolymer have not been indicated.

Saha Institute of Nuclear Physics, Calcutta

Bhattacharya and Maldas^{114, 116} grafted poly(styrene) and poly(acrylamide) to cellulose acetate film by γ -ray post-irradiation grafting technique. The effects of solvents, water and MeOH were studied and it was found that the composition of binary mixtures as well as the type of solvent had a strong influence on grafting. The results were discussed in terms of relative molar reactivities. The grafts formed were also examined by SEM. No mention, however, was made of the application of the graft copolymers.

State Forensic Science Laboratory, Bhubaneswar

Mohanty *et al.*^{117, 118} grafted poly(methyl methacrylate) to tussah silk fibres using Ce(IV) as initiator and studied the properties such as thermal conductivity, shrinkage, breaking load, tenacity, tensile strength, Young's modulus and electrical resistance of grafted silk fibres¹¹⁸. Similar studies of grafting of poly(acrylonitrile) to coir were made by Mohanty and coworkers¹¹⁹ with no mention of the mechanism of initiation or uses of polymers being mentioned.

Shri Ram Institute for Industrial Research, Delhi

Grafting of methyl methacrylate to cellulose by the use of pentavalent vanadium nitrate by Harcharan Singh *et al.*^{120, 121} yielded a graft copolymer insoluble in cuprammonium solution. Grafting of poly(styrene) to poly(butadiene)-copoly(acrylonitrile) in emulsion yielded polymers with improved mechanical properties¹²².

Patra *et al.*¹²³ grafted poly(methyl acrylate) and poly(methyl methacrylate) using Mn₂(SO₄)₃ as catalyst under de-aerated conditions and determined the structural factors which influence the solution properties. The equilibrium swelling of the insoluble graft copolymer fraction in a series of esters, ketone, and chlorinated hydrocarbon solvents showed that the grafting of poly(methyl acrylate) occurred inside the amylose structure with increased cross-linking and the resultant swelling. Their work did not discuss the mechanism leading to cross-linking.

Allahabad University, Allahabad

Srivastava *et al.*¹²⁴ worked out a new method of determining the percentage grafting in starch-g-poly(acrylonitrile) copolymers based on acidic hydrolysis of graft copolymer and estimating the glucose content of the hydrolysate. This method has not yet been put to extensive use.

Bombay University, Bombay

Lokhande *et al.*¹²⁵ and Achwal and Nagar¹²⁶ studied the electrokinetic properties such as zeta-potential, surface charge density and surface conductivity of polyester fibres grafted with acrylic acid and acrylonitrile. The effect of cationic dyes on the surface of the fibres lowered zeta-potential. The change in the electrokinetic properties of the grafted samples with the percentage grafting showed the formation of three-dimensional network. The light-fastness of polyamide fibres, wool or nylon fibres pre-dyed with cationic dyes was improved by grafting with acrylonitrile or acrylamide and attained a low add-on graft (~3%) to maintain the physical and mechanical properties of the dyed fibres. Moisture regain levels and dyeability of polyester, polyamide, polypropylene and poly(oxymethylene) fibres were improved by γ -irradiation grafting with vinyl monomers but there was some loss in strength of the fibres and also increased cross-linking¹²⁷. Faterpeker and Potnis¹²⁸⁻¹³³ grafted acrylonitrile/acrylamide/methyl methacrylate to cotton fibres and studied their thermal stabilities. The acrylamide and acrylonitrile mixtures grafted to cotton at different monomer compositions by keeping the total monomer concentrations constant slowed down the synergistic action. Lokhande *et al.*¹³⁴⁻¹³⁶ grafted polyethylene terephthalate fibres with vinyl acetate which showed improved dyeing characteristics; in the acid and alkaline hydrolyses no appreciable conversion of acetate to hydroxyl group occurred and with no change in the tensile properties of the grafted fibres. A synergistic effect was observed when acrylamide, acrylic acid and acrylonitrile-acrylic acid mixtures were grafted to polyester fibres by using benzoyl peroxide as initiator; the results were explained in terms of the reactivity ratios of the monomers. Electrokinetic properties, zeta-potential, surface charge density and surface conductivity of polypropylene fibres and those grafted with acrylic acid and methacrylic acid were studied by using the streaming potential method; the results on surface charge density and surface conductivity showed the hydrophilic character of the grafted polypropylene. Polyethylene-terephthalate fibres grafted with vinyl acetate were selectively hydrolysed and the effects of graft on morphological characters such as crystallinity index, X-ray orientation function and unit cell parameters were determined. Crystallite size, birefringence and amorphous orientation functions have been determined. The amorphous orientation function decreased with increasing vinyl acetate grafting. The results obtained by Lokhande *et al.* have a consid-

erable significance to dyeing of textiles even though no extensive application appears to have been made at present.

Calcutta University, Calcutta

Ghosh and Sengupta¹³⁷ grafted methyl methacrylate to natural rubber with benzoyl peroxide/azobisisobutyronitrile as initiators or by 'photolysis' in the presence of H₂O₂ or benzophenone and the efficiencies of grafting under different conditions were calculated. Graft copolymerization of methyl methacrylate and styrene to polychloroprene was investigated and the results of grafting efficiencies and chain-transfer constants were reported¹³⁸. Graft copolymerization of methyl methacrylate to bleached jute in the presence of Mn(III) or Fe₂(SO₄)₃ under visible radiation was carried out and the mechanism of grafting was explained¹³⁹ on the basis of formation of ligand radical with a concomitant reduction of Mn(III) to Mn(II). Graft copolymerization^{140,141} of methyl methacrylate to cellulose/oxy-cellulose under photo-activation by visible light in the presence of KMnO₄-oxalic redox system was investigated and the percentage grafting and efficiency were evaluated. Photo-grafting of MMA to reduced wool with Ce(IV)-oxalic acid redox system as initiator in aqueous medium producing optimum grafting effects was reported. While photo-grafting of rubber, according to Ghosh and Ghosh¹⁴¹, has some merits, the feasibility of its application in industry has not been considered.

Delhi University, Delhi

Chatterjee *et al.*^{142,143} grafted a dehalogenated phenolic copolymer (from *p*-chlorophenol, *p*-cresol and HCHO) with substituted monomers and oligomers of known structures at specific sites previously occupied by chlorine atoms. The percentage of halogen of the grafted polymers could be calculated on the assumption that all the available reactive positions were attached to the grafting monomers.

Himachal Pradesh University, Shimla

Extensive work on grafting by Misra and co-workers¹⁴⁴⁻¹⁸⁹ has been reported. Various vinyl and other monomers were used for grafting. The initiators used were Ce(IV)-redox systems, benzoyl peroxide, azobisisobutyronitrile, acetylacetonates of Cr(III), Fe(III), VO(II), γ -rays, etc. The backbone polymers for grafting were wool¹⁴⁴⁻¹⁶⁷ and reduced wool¹⁶⁸⁻¹⁷⁰, gelatin¹⁷¹⁻¹⁷⁶, cellulose¹⁷⁷⁻¹⁸⁴, starch^{185,186}, rubber¹⁸⁷, polypropylene¹⁸⁸, and po-

ly(vinyl alcohol)¹⁸⁹. All these studies have suggested conditions for maximum grafting and effects of various variables, monomers, catalysts on percentage and efficiency of grafting and mechanisms of grafting. The grafts were separated from graft copolymers by the selective solvent extraction method or by acid/alkaline hydrolysis. An unambiguous proof for covalent bond formation between backbones and grafts has not been established even in a single case. The work is of repetitive type and is not of much relevance either from the fundamental or applied aspects.

Jadavpur University, Calcutta

Mukherjee and Sanyal¹⁹⁰ found that shellac grafted with poly(styrene) or poly(methyl methacrylate) by the catalyst KMnO_4 in NH_3 solution possessed improved water and solvent resistance; the degree of grafting increased considerably and graft copolymers of shellac with styrene, methyl methacrylate or ethyl acrylate possessed superior film-forming properties, adhesion, flexibility and scratch and solvent and water resistance compared with those of the pure shellac films. The chain transfer constants of shellac with the poly(methyl methacrylate) radical at 60°C showed that very little, if any, grafting occurred via polymer radical transfer to shellac¹⁹¹. Special uses of such shellac products, if any, have not been mentioned.

Lucknow University, Lucknow

Shukla, *et al.*¹⁹² grafted methyl methacrylate to wool with peroxodisulphate-thiomaleic acid redox system initiator and the graft yield ranged from 25 to 70% depending upon the concentration of redox system, duration of reaction and temperature. The authors have discussed neither the mechanism nor the use of the graft copolymer.

Madras University, Madras

Santappa *et al.*¹⁹³⁻¹⁹⁹ grafted methyl methacrylate to chlorinated rubber in toluene solution with benzoyl peroxide as initiator at 80°C. The mechanism involving chain transfer reaction between rubber molecule and polymethyl methacrylate radicals was suggested¹⁹³. This was the first ever work reported (1965) in India on grafting. The backbone and the graft copolymers were characterized by light scattering and viscosity data. Poly(vinyl chloride), chlorinated rubber and bromo-polystyrene were also found¹⁹⁴⁻¹⁹⁶ to be good backbone materials for synthesis of graft polymers owing to the presence of halogen atoms as reactive sites for grafting. The grafts were characterized by elemental analysis, IR, NMR and, particularly, by light

scattering method, the only foolproof and unambiguous method which proved the chemical binding of the backbone polymer to the grafts. Works in this field reported from the country have so far not determined molecular weights. The graft polymers, besides showing higher molecular weights, differed greatly in the values of second virial coefficients from those of either the backbone or the homopolymer. Poly(vinyl alcohol) was grafted with acrylamide and the extent of grafting was estimated¹⁹⁷. Graft copolymerization of MMA to wool fibres^{198,199} was carried out with potassium peroxodiphosphate (PDP) and PDP plus Fe(II) initiators; the grafts were characterized by IR, NMR, dye uptake, alkaline solubility and tensile strength, etc.

Sardar Patel University, Vallabh Vidyanagar

Patel *et al.*²⁰⁰⁻²⁰⁵ grafted styrene to amylose in the presence of H_2O_2 and metal ions such as Fe(II), Cr(III), Co(II), and Ag(I) individually as catalysts. Maximum graft yield was obtained with Fe(II). Neither the mechanism nor the practical use of the polymers has been discussed.

Utkal University, Bhubaneswar

Nayak and coworkers²⁰⁶⁻²¹⁴ grafted methyl methacrylate to cellulose with peroxydiphosphate; acrylamide to nylon-6 with V(V), and methyl methacrylate to wool and silk with $\text{P}_2\text{O}_8^{4-}$ under different conditions. These workers have carried out very extensive studies on graft copolymerization using various types of backbone polymers, monomers and the usual initiator systems with all possible permutations and combinations. The backbone polymers used were: Chokla wool²⁰⁶⁻²¹⁴, reduced wool²¹⁵⁻²²⁴, wool²²⁵⁻²²⁸, wool fibres²²⁹⁻²³¹, silk fibres²³²⁻²⁴⁷, cellulose²⁴⁸⁻²⁵⁶ modified cellulose²⁵⁷⁻²⁶⁷, nylon²⁶⁸⁻²⁸², PET²⁸³⁻²⁸⁷, rubber²⁸⁸⁻²⁹¹ and polysaccharides²⁹². In almost all the studies, rates of polymerization, activation energies for rate initiation and percentage and efficiency of grafting, etc. were evaluated. From the IR spectra of copolymers, it was erroneously inferred that grafting had taken place. The effect of various process variables on rate was studied and mechanisms of grafting were arrived at. This work and that from Himachal Pradesh University are good examples of 'Parkinson's Law' operating in R&D. Mechanisms suggested are not novel; neither is there any discussion on thermodynamic parameters. This is also an instance of indiscriminate and *ad nauseam* use of redox systems, additives, inhibitors, etc. In the voluminous work reported, not a single instance of practical application has been men-

tioned. In short, research work of this nature is unrewarding.

Summary and Conclusions

For over two decades in the country, a number of natural, bio- and synthetic polymers and copolymers have been used for grafting. A multiplicity of thermal as well as photoactive initiator systems, sometimes for a single backbone polymer, has been employed. Work on the evaluation of kinetic parameters, separation and characterization of grafts by chemical as well as by IR, NMR, etc. is so voluminous that it cannot but be described as routine.

Physical properties, thermal stabilities and electrical properties of grafted synthetic fibres have been evaluated to a limited extent, but their use in fabrics is conspicuous by its absence. Also, work on applications of grafted collagen/hides and skins/leathers has been limited.

It is surprising that except the Madras school, no group has determined the molecular weights of grafted polymers (surest method of chemical bond formation of the grafts with backbone and, therefore, of increase in molecular weights). Hence, the need for carrying out further work in this direction.

Studies are also called for on the use of graft copolymers in synthetic organic chemistry, on characterization of graft copolymers by X-ray and other instrumental techniques, on the determination of properties like crystallinity and tenacity, and on the applications of grafting in industry. The entire field needs a firm foundation and proper orientation with a view to achieving excellence and international standards.

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State-of-the-Art of Polymer Research in India: Part II: Kinetics of Polymerization

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Introduction

In a brief period of about four decades of growth of polymer science in India, no field has received as much attention as kinetics of polymerization. Work has been carried out in more than forty laboratories/institutions/universities. Various aspects of kinetics of polymerization have been covered (per cent publications in the brackets); (i) Red-ox (47.7); (ii) Graft polymerization and copolymerization (12.9); (iii) Photo (9.3); (iv) Ziegler-Natta and metal alkyls (3.6); (v) Phase/charge transfer (1.8); (vi) Electro-initiated (1.1); and (vii) Miscellaneous (12.2). Investigations on these aspects have been briefly and critically reviewed in this article institution-wise. The kinetics of condensation polymerization has received much less attention than it deserves. Some suggestions have also been made for carrying out future work in this field.

INSTITUTION-WISE WORK

Bhabha Atomic Research Centre, Bombay

Kinetics of polymerization (aqueous, solution, emulsion, solid) of vinyl benzoate, diallylphthalate, vinylidene chloride, trioxane, phenyl acrylates and phenyl methacrylates by γ -rays was reported by Rao, Panajkar and coworkers^{1,2}. The feasibility of obtaining controlled molecular weights of the polymers was suggested. The effect of solvents like C_6H_6 , $CHCl_3$ and $CHBr_3$ was studied. However, extension of the work to industry, cost-benefit analysis and unambiguous nature of initiating and terminating species have not been spelt out.

Central Leather Research Institute, Madras

The preparation of *m*-cresol-formaldehyde and polyamide resins by interfacial and solution polymerization was reported by Sivarami Reddy *et al.*³, but the specific utilization of these polymers was not indicated. Reddy *et al.*⁴ determined the reactivity ratios in the copolymerization of acrylic acid and acrylonitrile.

They also studied the kinetics and mechanism of polymerization of methyl methacrylate and acrylonitrile by the initiator system, M-ascorbic acid-O₂ [$M = Cu(II), Fe(III), VO(II)$]. The system of metal ion-ascorbic acid-oxygen as initiating system is noteworthy, particularly when oxygen is generally, an inhibitor. The role of oxygen as suggested is conjectural and hence a more systematic investigation supported by experimental evidence is needed. Copolymerization of methyl acrylate in the presence of poly(vinyl chloride)-co-poly(vinyl acetate) was also reported.

Defence Research and Development Organization, Delhi

Nitration of polystyrene was studied by Bajaj *et al.*⁵. The work of Deb and Kapoor⁶ on polymerization of methyl methacrylate, styrene and vinyl acetate initiated by benzoyl peroxide (Bz_2O_2) and azo-bis-isobutyronitrile (AIBN) at different concentrations of the latter indicated that two different kinetic paths—non-ideal and anomalous—were operative. A detailed mathematical analysis of retarded polymerization of tributyltin-methyl methacrylate yielding all rate constants was made and this needs to be extended to other retarders, if any, to prove its general validity.

Harcourt-Butler Technological Institute, Kanpur

Srivastava and Mathur⁷ investigated the effect of various initiators in the copolymerization of styrene with methyl methacrylate. Polystyrene with living ends was copolymerized with bis-phenol-A and after phosgenation, block copolymers were separated. Methylene blue and crystal violet retarded the polymerization of styrene and methyl methacrylate. Results of Y-lides (β -picolinium *p*-chlorophenacylide) catalyzing the polymerization of α -methyl styrene and cationic polymerization of methyl acrylate and $AsCl_3$ by Srivastava⁸; effect of zinc bromide on copolymerization of styrene and methyl acrylate and kinetics of al-

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