Journal of Scientific & Industrial Research
Vol. 47, August 1988, pp 439-447

360

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

M SANTAPPA*
Anna University, Madras 600 025, India

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-O_2 [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 Kapoor[6] 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 Mathur[7] 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 Srivastava[8]; effect of zinc bromide on copolymerization of styrene and methyl acrylate and kinetics of al-

---

* INSA Senior Scientist

kali-catalyzed polymerization of cardanol and formaldehyde were reported. The work on Y-lides as initiators needs to be extended for understanding the mechanism and, possibly, the use of the former in industry and synthetic organic chemistry.

Indian Association for Cultivation of Science, Calcutta

Palit and coworkers have carried out pioneering work on various aspects of polymerization and the credit for heralding polymer research in India during the past more than four decades should go to this group to a great extent. Initiators used by Palit *et al.*[9] were: Bz_2O_2; $S_2O_8^{2-}$; H_2O_2; acyl peroxides, complexes of Co(III), Mn(III), Fe(III)-amine, Ce(IV), Cr(III), Cu(II)-amine and various red-ox systems. Studies on dye sensitization involving amine activators and thermal initiators, metal ions and metallic soaps were carried out by Sen *et al.*[10] and Nandi *et al.*[11]. Kinetics of the rates of hydration of poly(vinyl acetate)-co-(poly maleic anhydride); effect of ketonic substitution of double bond; chain-transfer studies in organic solvents catalyzed by Bz_2O_2 and AIBN were reported by Gupta and Palit[12] and Roy *et al.*[13]. Studies were carried out on the diffusion controlled copolymerization and the effect of monomer feed on the termination constants by Maiti *et al.*[14] and Kar *et al.*[15]. Evaluation of chain transfer constants in the binary system of solvents; retardation by red-ox dyes; photochemical polymerization of methyl methacrylate in bulk with systems like CCl_4 + anthracene (phenanthrene; Bu_3N) or H_2O_2 + sulphonates was also reported. Chain transfer constants were evaluated for polymerization in the solid state by dye technique; industrial applications were cited and the limitations of Mayo's equation were pointed out. Hydrogen abstraction and electron transfers in the polymerization of methyl methacrylate by hydrogen peroxide; determination of cross constants and Melvilles constants in copolymerizations by Das, Palit and coworkers[16] and equations for distribution of molecular weights of polymers by Chatterjee, Palit *et al.*[17]; detection and estimation of polymer end groups (SO_4; COOH, OH, halogens, SO_2OH, amines) and modes of termination by 'dye partition' and 'dye interaction' techniques are some other studies reported. 'Reverse dye-partition' technique was employed to study hydrolysis of amides and parameters like reactivity ratios, efficiency of grafting and of initiators, degrees of substitution, and branching were evaluated. Kinetics of emulsion and heterogeneous polymerization were studied and the effects of miscible blends and immiscible diluents on termination rates were reported. Deviations from normal kinetics were explained when red-ox systems like PCl_5-SO_2Cl_2; $S_2O_8^{2-}$-thiolactic acid are used. N-bromosuccinimide-reducing metal as a phot chemical initiator, methylene blue as a retarder an ferric laurate-organic amine as an efficient initiat non-aqueous systems were the other studies repor ed. The estimation of end groups by dye partition technique has been recognized internationally as fine tool.

Indian Institute of Petroleum, Dehra Dun

Sagu and Bhattacharya[18] have carried out γ radiation-induced polymerization of trioxane with and without penta-acetyl glucose and tetrahydrofuran and reported the correlation of various parameters by a polynomial equation. Step-wise reactions in *m* cresol-formaldehyde reactions were reported by Gupta and coworkers[19]. The bulk copolymerization of styrene and methyl methacrylate, together with the determination of molecular weights from interaction parameters, were studied. It has not been indicated whether the accuracies of the molecular weights have been verified by other independent methods.

Indian Institute of Science, Bangalore

Hydropolymerization of acetylene in flow system under pressure over ZnO-chromium oxide incorporated Kieselguhr catalyst; solution polymerization of furfuryl alcohol in dioxane with HCl as catalyst; kinetics of formation of poly(vinyl formal); thermal decomposition of polystyrene peroxide and the role of cupric dipivaloylmethide in vinyl polymerization are some of the studies reported by Chanda and coworkers[20] and Kishore and coworkers[21]. Polymerization of methyl methacrylate catalyzed by the complexes of Co(III) and of acrylonitrile by Cu(II)-imine chelates; solid state polymerization of sodium acrylate followed by ESR and DSC studies of the polymers were reported. Kishore and coworkers[22] have carried out thermochemical and kinetic studies on the oxidative degradation of polystyrene and DTA studies on thermal oxidations and crosslinking reactions of carboxyl-terminated poly(butadiene). The thermochemical investigations and solid state polymerizations would have relevance to space science and are to be pursued further.

Indian Institute of Technology, Bombay

Polymerization of methyl methacrylate induced by γ-rays in the presence of nematic and cholesteric liquid crystals (cholesteryl oleylcarbonate) was reported by Biswas *et al.*[23] and Deshpande and coworkers, Harriat mechanism was found to operate in the emulsion polymerization of vinyl acetate and Ziegler-Natta mechanism in polymerization of styrene catalyzed by Cu(II) + $AlEt_3$ (or $AlEt_2Cl$) in *n*-hexane. Minimum end-time policies in batch and chain addition polymerization were reported by Deshpande and coworkers. However, the utility of data to the industry is not indicated.

Indian Institute of Technology, Delhi

Bajaj and coworkers[25], and Babu and coworkers[26] have reported emulsion polymerization of styrene initiated by $S_2O_8^{2-}$ and copolymerization of styrene with vinyl methyl diacetoxyl silane. Polymerization of N-butyl vinyl ether with $SnCl_2$ as initiator, of iso-butyl vinyl ether with $ZnCl_2$ in CH_2Cl_2 as initiator and polymerization of acrylonitrile with Cr(VI)-glycerol as red-ox system were reported but the objective of these studies is not indicated. Solubility studies on poly(benzimidazoles) based on UV and visible spectra have been reported. A model for tubular reactors with diffusion on the walls was described by Nigam and coworkers[27], but the utility of the data to the industry is not indicated.

Indian Institute of Technology, Kanpur

Studies on the kinetics of polymerization of ethylene oxide and terephthalic acid catalyzed by tetraethylamine in butanol; step growth polymerization of monomer with unequal reactivities; effect of solvent and electrolytes on the polymerization of acrylonitrile initiated by Mn(III) were described by Bhatia *et al.*[28] and Gandhi and coworkers[29]. Kumar and coworkers[30] have described several types of reactors under diverse conditions of polymerization which are of great interest to polymer industry/technologist.

Indian Institute of Technology, Kharagpur

Studies on kinetics of Bz_2O_2-initiated polymerization of vinyl esters in bulk and in solution, evaluation of chain transfer constants, and the molecular weights of polymers were reported by Patra and coworkers[31] and Kurian and coworkers[32]. Polymerization of N-vinyl carbazole in C_6H_6 and of vinyl ethers, initiated by metal oxides of Group V, was studied by Mangaraj and coworkers[33] and Maiti and coworkers[34]. The mechanism of initiation by carbon black, $(C_2H_5)_2Zn$ Co(II)Cl, BuMgBr CrO_2Cl_2, V_2O_5, $SOCl_2$, and Ph.MgBr was found to be cationic and the cationic polymers were found to exchange with Cu(II) in the presence of zeolitic molecular sieve whose role was also explained by Biswas *et al.*[35]. Polymerization of α-methylstyrene, N-vinyl pyrrolidone with phosphonyl chloride and $CuCl_2$ as initiators and of butyl vinyl ether by $CrOCl_2$ as initiator was also explained through the cationic mechanism. The order of reactivity of metal oxides in the bulk polymerization of N-vinyl carbazole was: $V_2O_5 > MnO_2 > TiO_2 > Cr_2O_3 > NiO > ZnO > Cu_2O > CuO$. Work was also reported on electro-initiated cationic polymerization of styrene with Fe(III), of acrylonitrile with Mn(III)-mannitol and variations in $\bar{DP}$ (degree of polymerization) of poly(vinyl carbazole) with the initiators, PhMgBr and BuMgBr and sulphur vulcanization of SBR rubber. Work on polyvinyl carbazoles is the special metier of Biswas and coworkers and needs to be pursued further.

Indian Institute of Technology, Madras

Kinetics of vinyl polymerization initiated by various types of redox systems was the subject of investigations by Mahadevan and coworkers[36–38]. The oxidants used were Mn(III), Fe(III), Sn(IV) and Ce(IV) while the reductants were allyl alcohol, $POCl_3$, chloro-sulphonic acid, thiodiethanol and propane dinitrile. The mechanism suggested was that the complex formed (oxidant-reductant) decomposed, yielding initiating radicals and kinetics were followed though evaluation of rate and thermodynamic parameters, though the significance of the latter was not discussed. Other initiators used were AIBN in phosphorous oxychloride-trichloride and dichlorophenyl phosphine, tris(acac)Mn(III)-NH_2OH; phase transfer catalysis; V(IV)/V(III)-N-bromosuccinimide; V(II)-Bz_2O_2 in DMF red-ox systems and ammonium hexachlororhodate. Though a number of red-ox type of catalysts have been used, there is nothing significant either about the mechanism or the use of catalysts/initiators to the industry.

National Chemical Laboratory, Pune

Kapur and his associates have carried out a great deal of investigations in polymerizations initiated by Ziegler-Natta catalysts and red-ox systems to some extent. The mechanism of kinetics, evaluation of chain transfer constants, determination of microstructure of products; design of reactors, thermochemical properties were other interesting aspects studied. In the copolymerization of methyl methacrylate and acrylonitrile and methyl acrylate and allyl chloride, the effect of temperature on the reactivity ratios was studied. A new statistical procedure by Joshi[39] indicated the importance of Arrhenius activation energy rather than entropy of activation. Kapur and coworkers[40–42] used bifunctional peroxides, Cu(II)-hydrazine and other red-ox systems involving $S_2O_8^{2-}$ and Ziegler-Natta catalysts, [$ZrCl_4(ZrCl_3)$-$AlEt_3$; VCl_4-$AlEt_3$, etc] for the polymerization of isoprene and vinyl monomers.

Indian Petrochemicals Corporation Limited (IPCL), Baroda

Studies on kinetics of polymerization of acrylonitrile initiated by $Co(Acac)_3$-$AlEt_3$; cationic polymerization of α-methyl styrene and isobutyl vinyl ether by *t*-butyl chloride/diethyl aluminium chloride and copolymerization of acrylonitrile with styrene by Co(Acac)$_3$Et$_3$Al were reported by Sharma and coworkers[43] and Trivedi and coworkers[44]. The possible replacement of the conventional catalysts by those developed by IPCL with cost benefit analysis has not been indicated.

University of Bombay

Dharuwalla and coworkers have carried out investigations of applied nature and also studied the electrokinetic properties of polymers. Some other studies reported from this university include: Catalytic depolymerization of polyamide fibres during acid dyeing; variation of molecular weights of poly(vinyl acetate) in bulk and in glacial acetic acid[45]; acid hydrolysis of melamine-formaldehyde resin in the presence of MgCl$_2$ condensed on cotton fibres; polymerization kinetics and propeties of polyethylene terephthalate (PET); electro-kinetic properties (ζ-potential, surface charge density and conduction) of poly(oxymethylene) fibres in the presence of dyes[46,47]; and formation of acrylic esters initiated by monoalkyl sulphonic acids.

University of Calcutta

Extensive investigations were carried out by Ghosh, and coworkers[48–50] on red-ox, charge-transfer (C.T.) electro and conventional (Bz$_2$O$_2$ and AIBN) initiators for vinyl polymerizations and copolymerizations. Examples of thermal polymerization kinetics studied are: furfural by H$_3$PO$_4$; vinyl monomers by $S_2O_8^{2-}$ with sodium oleate; copolymerization of vinyl acetate and methyl methacrylate, polymerization of methyl methacrylate in DMF initiated by cetylpyridinium chloride-Bz$_2$O$_2$. Examples of photochemical initiators including charge-transfer agents used are: SO$_2$Cl$_2$, quinoline (picoline)-Br$_2$(Cl$_2$), Br$_2$(SO$_2$)-pyridine, benzophenone-allyl anilines, etc. In all the investigations, mechanisms of initiation were suggested and kinetic and thermodynamic properties were evaluated. However, the mechanisms suggested were not supported by other independent methods. Monochromaticity of light was not maintained and quantum yields were not evaluated.

University of Delhi

Nanda and Jain[51,52] and Malhotra *et al.*[53] have carried out theoretical and statistical investigations concerning condensation polymerization and such studies need to be pursued to cover the entire gamut of polymerization. The effect of impurities on various rates and variation of bimolecular rate constants with chain length following mono- and di-anionic mechanism was examined on statistical considerations for polycondensations. Kinetics of alkali-catalyzed condensation of *p*-cresol-formaldehyde and N-carboxy anhydrides were studied and mechanism elucidated.

Dibrugarh University

Many workers[54–56] have used charge-transfer complexes for initiation and have evaluated kinetic and thermodynamic parameters in the polymerization of methyl methacrylate, 2-vinyl pyridine. C.T. complexes, such as 2,4-dinitro phenylhydrazine-CCl$_4$; Fe(III)-urea; aliphatic amine-CCl$_4$; cyclopentylamine-CCl$_4$ were used. Retardation of AIBN initiated polymerization of styrene with (sulphosalicylate)-Fe(III); of methyl methacrylate with Me$_2$CH$_2$NH$_2$-CCl$_4$ in DMSO as well as with *n*-butyl aniline-CCl$_4$ in Me$_2$SO; of styrene with CuDMFCl$_2$ were discussed. Rate constants for poly(styryl) radicals with copper complexes of the type (CuDMF[illegible] and (Cu(DMF)$_3$N$_3$)$^+$ were reported. Catalytic effects and mechanism of complexes of DMSO + Rh(III) Ru(III) in the polymerization of acrylonitrile initiated by AIBN were explained. However, kinetic and thermodynamic parameters and mechanism of C.T. complexes has not been discussed.

Universities of Jabalpur and Jammu

Work on red-ox systems initiated vinyl polymerization explaining the nature and mechanism of initiation and termination and evaluation of kinetic and thermodynamic parameters has been done by Mishra and coworkers[57,58], although there is no raison d'etre or innovation about red-ox catalysts studied. The systems employed were: $S_2O_8^{2-}$-ascorbic acid-O$_2$; KMnO$_4$-tartaric acid (lactic, citric, glycolic, maleic and thiomaleic acids, mercaptosuccinic and -lactic acids, oxalic acid, pyruvic acid-glycine-cysteine); $S_2O_8^{2-}$-lactic acids (thiolactic, thiomaleic, citric); Ce(IV)-thiourea, (thiomaleic, thioglycolic acids, 1,4-butanediol, maleic acid, cysteine; citric, lactic acid and glycolic acids); Mn(III)-glycerol; Cu(II)-$S_2O_8^{2-}$; BrO$_3$-Fe(II).

University of Lucknow

Misra *et al.*[59] and Shukla *et al.*[60] elucidated the mechanism of kinetics of vinyl polymerization and chain transfer, using conventional catalysts and red-ox systems. However, red-ox systems chosen were routine and arbitrary and were not based on any particular objective.

University of Madras

Santappa and associates and many other workers have investigated kinetics of vinyl polymerization—photochemical and thermal. C.T. complexes[61] of the type Fe^{3+}X$^-$ (X = OH, Cl, N$_3$, citrate, oxalate) were used as photoinitiators and heavy metal ions, Co(III), Ce(IV) without any reductant[62,63] were used as thermal initiators. Red-ox systems involving Ce(IV) and Mn(III) were used to a limited extent. Chain transfer constants were evaluated in various solvents. Heavy metal ion thermal initiation showed interesting kinetic features that the initiating species were not OH radicals from water but radicals from monomers. Tl(III), Mn(III) and Mn(III)-oxime, lead tetraacetate were also used as initiators. It is found that Cr(VI) alone does not initiate but in the system Ce(IV) + Cr(VI), the former initiates and the latter terminates[64]. The following other systems have been used as thermal- and photoinitiators: red-ox systems V(V) + cyclohexanol (pindicol, lactic acid), $P_2O_8^{4-}$ + Ag(I) and Co(III) + butanol, $P_2O_8^{4-}$—VO (ascorbic acid) $S_2O_8^{2-}$ – Co(II) (thioacetic acid, cyclohexanol), Mn(III)-diglycolic acid (bisdiethanol amine, isobutyric acid); Ce(IV)-thiourea (benzyl alcohol); C.T. complex systems, dye + reducing agent: anthraquinone sulphonate + halide[65]; mono, diazido, chloro or nitro Co(III) amine complexes[66]. Other photosystems used are: uranyl ions; potassium trioxalate Co(III); Cu(II)-amino acid chelates, amino ethoxo Cu(II); dichloro-bis(acetophenacycline)-*p*[dimethyl amino) anilino] ferrate (II); (*o*-phenanthroline)$_3$-Fe. Condensation polymerization involving polyalkyl phenols + formaldehyde was studied. Characterization of alternating copolymers by IR and NMR; γ-ray induced polymerization kinetics and effect of metal laurates for polymerization of methyl methacrylate in C_6H_6 were reported. Other red-ox systems used were: bis(ethanolamine)-Co(III); N, N-dimethyl aniline-*p*-toluene sulphonyl chloride, lead tetracetate in acetic acid; $S_2O_8^{2-}$ + thioglycolic acid (thioacetamide); cyclohexanol + Ag (I). The chief merit of the work lies in the use of UO_2(II) and ion pairs, Fe(III)-X^-, as photoinitiators and heavy metal ions Co(III), Ce(IV), without any reductant as thermal initiators for the first time in the country. The importance of catalysts to the industry needs to be evaluated.

Ranchi University

Bhadani and coworkers[67] carried out electro-initiated vinyl polymerization and elucidated its mechanism. Electrolysis of isoprene in tetrahydrofuran with $ZnCl_2$ as supporting electrolyte and polymerization of the former by anionic mechanism involving living ends was reported. Other electro systems studied were: α-methylstyrene catalyzed by sodium tetraphenyl boron; acrylonitrile, trioxane and indene. Other investigations reported are: cathodic polymerization of acrylonitrile in DMF solution of tetra-*n*-butyl ammonium iodide at different electrodes; anodic polymerization of 1, 3, 5-trioxane in the presence of [$(CH_3)_4$, $NH_4(Cl)_6Sb$)]. In the polymerization of maleic anhydride, the order deduced was: γ-picoline > β-picoline > pyridine > α-picoline from rates and electrical conductivities. Other studies reported are simultaneous anodic and cathodic polymerization of acrylamide in $NaNO_3$/DMF, 'homogeneous' at the cathode by ionic route and heterogeneous at the anode by free radical mechanism and electro-polymerization of acrylamide in DMF initiated by NO_3 (free radical path). Polymerization of indene by anodic polymerization, of styrene by [$(C_2$-$H_5)_4$; $NH_4(Cl)_6Sb$], and of acrylamide in DMF, the initiating species in the former being styryl carbonium ion, was reported. Mathematical formulations correlating rate of initiation and chain length with electrolytic current were derived. Calculation of reactivity ratios r_1 and r_2 for copolymerization of acrylamide-methyl methacrylate; initiation by(i) NO_2 in DMSO-dioxane, (ii) triphenylphosphine, and (iii) $HClO_4$ in DMSO were the other reported studies. Electro-initiated polymerizations have currently only theoretical interest. The polymers have to be characterized for special features, if any, let alone for their commercial feasibility.

Utkal and Sambalpur Universities

Nayak, Samal, Lenka, Rout and their coworkers[68,69] have published extensive work on polymerization using various red-ox systems, C.T. complexes and dyes. In each case, mechanism has been suggested and rates and thermodynamic parameters have been evaluated. Effects of ionic miscelle'; organic solvents, neutral salts, complexing agents, added ions, Ag(I) and Cu(II), and inhibitors have been studied in many cases. The oxidants for the red-ox systems consisted of V(V), Ce(IV), BrO_3^-, Mn(III), $S_2O_8^{2-}$, $P_2O_8^{4-}$, Tl(III), $KHSO_5$, Fe(III), Cr(VI), MnO_4^-. The C.T. complexes used were: α-picoline (or γ-)-$Br_2(Cl_2)$; isoquinoline-$Cl_2(Br_2)$; lipidine-Br_x (histidine, quinidine, pyridine, quinaldine), fluorescein-ascorbic acid. A good contribution was made by Rout and his coworkers who calculated the substituent parameters for radical reactions in the polymerization of acrylonitrile initiated by Ce(IV)-acetophenone. The composite rate constant was correlated with a multi-parameter equation based on field and resonance (FAR) components and on positional weighting factors of the substituents (f and r). The effects of these substituents would lead to the understanding of reactions of polymer radicals with substituted phenols, etc. (retarders) and would also indicate whether the transition state is polar or non-polar. Work by Nayak's school has become voluminous because of indiscriminate choice of oxidants/reductants or C.T. complexes and also has no specific objectives.

Other Institutions

Jain[70] (Engineering College, Raipur) applied the kinetic rate theory pertaining to monomers to the analysis of microscopic crystal growth of polyethylene oxide. Jolly, Sashi and coworkers[71] (Forest Research Institute, Dehra Dun) found that the reaction of lignin + formaldehyde followed second order kinetics and was pH-dependent, but details about stoichiometry were missing. Bhattacharya[72] (Indian Lac Research Institute, Ranchi) studied the kinetics of polyesterification of 9, 10-dihydroxy-1, 16-hexadecane-dicarboxylic acid. The mechanism of pre- and post-gelation of shellac, polymerization of totally hydrolyzed lac and NO_2-initiated polymerization of acrylic acid and acryl amide in benzene and dimethyl sulphate are some other studies reported. But, the use of these studies to industry has not been mentioned. Oligomerization of styrene by molybdenum oxide supported on aluminium silicate catalyst was studied and cationic mechanism was suggested by Kumar, Rao and coworkers[73] (Vikram Sarabhai Space Centre, Trivandrum), but the use of the oligomers in space science was not indicated.

Kinetics of polymerization of methyl acrylate by γ-radiation in the presence of $Fe(OH)_3$ was carried out by Sharma, Tripathy, and coworkers[74] (Nuclear Research Institute, Srinagar); Mössbauer spectra were taken at regular intervals of polymerization but the detailed use of the technique in polymerization, in general, was not indicated. Activation energy for polymerization of 3, 3-(bis-chloromethyl)oxetane/butane catalyzed by $AlCl_3$ was evaluated by Prakash, Sushant and coworkers[75] (Shri Ram Institute for Industrial Research, New Delhi). The activity of the catalyst was found to increase with additives like thionyl chloride and epichlorohydrin, but no rational explanation was offered. Kinetics of thermal degradation of butyl rubber in decalin and p-xylene was studied and the degradation was found to follow random chain scission process for which kinetic and thermodynamic parameters were evaluated by Singh and Bhatnagar[76] (Regional Engineering Colleg, Kurukshetra), but the latter were not discussed. Kinetics of polyesterification of uncatalyzed ethylene (propylene)glycols with phthalic (maleic) anhydride were reported byMithal, Ramesh and coworkers[77] (Regional Engineering College, Rourkela). Studies by Chatterjee, Bandopadhyay and coworkers[78] (Regional Engineering College, Durgapur) of emulsion polymerization of methyl methacrylate by sodium metal and of styrene and ethyl methacrylate by $S_2O_8^{2-}$ indicated that rise and fall of molecular weights of polymers did not conform to Smith-Ewart-Gordon Theory, but the reasons for the failure have not been analysed. The relative merits of the initiators from kinetic point wer not indicated. Kulkarni and coworkers[79] studied th effect of various substituents (CH_3, Cl, Br) in the chai of undecyl acrylate and undecyl methacrylate on th rates of polymerization and found the substituent order as: H > OMe > Cl > Br > I > Ph. The kinetic of melt phase polyamidation of dimer fatty acids an ethylene diamine were studied by Kale, Vijay and co workers[80] without mentioning the relative merits o melt phase process over the conventional proce dures. Kinetics of aqueous polymerization of methac rylamide initiated by $S_2O_8^{2-}$-cysteine-HCl was reported by Behari and Gupta[81] (University of Allahabad), but no specific advantage of this red-ox system was advanced. Kinetics of polycondensation reactions of urea + formaldehyde and melamine + formaldehyde were studied by Nair and coworkes[8 (University of Cochin), which seems to have only theoretical interest. Kinetics of oxidative thermal degradation of the copolymer, bisphenol-A + POCl were studied by isothermal and non-isothermal (300-800°C) gravimetric analyses by Gupta and Srivastava[83] (University of Ghorakpur) and the reaction conformed to heterogeneous catalysis. Pramanick and coworkers[84] (University of Kalyani) have used Ce(IV)-benzilic acid (thiourea) systems to follow the kinetics of polymerization of styrene and acrylic monomers. The novel method of dye partition technique employed for determination of rates of initiation in the polymerization of methyl methacrylate needs to be applied for other monomers as well. Kinetics of vinyl polymerization initiated by $S_2O_8^{2-}$ and $P_2O_8^{4-}$ and the effect of addition of Ag(I) and Cu(II) to the former were studied by Venkata Rao and coworkers[85] (Madurai Kamaraj University). Red-ox systems such as Ce(IV)-thiourea; $KMnO_4$-oxalic acid (-ethyleneglycol; thioglycolic acid) etc. were used as initiators for the polymerization of N, N'-methylene bis acylamide and their mechanism was discussed. When 'per' salts by themselves are powerful initiators, why Ag(I) or Cu(II) was used is not clear.

Polymerization of methyl methacrylate in aqueous suspension of bentonite in the presence of aqueous alcohols was carried out and a radical mechanism was suggested by Talapatra and coworkers[86] (University of North Bengal), but no comparison of this catalyst with conventional catalysts has been made. Kinetics of polymerization of acrylonitrile by red-ox systems, Ce(IV)-maleic acid (-diacetone alcohol, -isopropyl alcohol, -methyl ethylketone) were investigated and mechanisms based on the decomposition of complexes between Ce(IV) + substrates yielding radicals, which initiated polymerization, was suggested by Murthy, Sethuram and coworkers[87] (Osmania University, Hyderabad). Polymerization of methyl methacrylate and methyl acrylate initiated by Cu(II)-cyclohexanone and termination of polymerization of acrylonitriles were other interesting aspects covered. High conversion of methyl methacrylate was achieved by utilizing gel-permeation and orthogonal chromatography by Balke and Patel[88] (Sardar Patel University, Vallabh Vidyanagar). Reddy, Venkatarao and coworkers[89] (Shri Krishna Devaraya University, Anantapur) studied kinetics of homopolymerization of ethyl methacrylate and ethyl acrylate initiated by Mn(III); suggested mechanisms and evaluated rate parameters.

Summary and State-of-the-Art

The era of polymer sciences in India is about four decades old. Early work was concerned with (i) the use of initiators such as Bz_2O_2, AIBN, etc. and (ii) study of the kinetics in bulk or solution to evaluate rates of initiation, R_i and the ratio of rate constant for propagation and termination, k_p/k_t, as well as degree of polymerization, DP. This was followed by evaluation of transfer constants to solvents, catalysts, etc. Later, a spurt of activity started with the use of red-ox system initiators, with all possible permutations and combinations as oxidants and reductants. Simultaneously, to a smaller extent Ziegler-Natta catalysts and various types of C.T. complexes were also used as photoinitiators. 'Dye-partition' and 'Reverse dye partition' techniques; statistical analysis of polymerizations; development of heavy metal ions, Co(III), Ce(IV) as thermal initiators; 'n-π' type C.T. complexes as photoinitiators; electrokinetic properties of fibres in the presence of dyes, electroinitiated polymerization; uses of Ziegler catalysts; and γ-ray initiation are some of the significant developments. Kinetic work on grafting has not been included here as it forms the subject-matter of a separate paper.

Suggestions for Further Work

This paper reviews critically and focuses on the state-of-the-art in the field of kinetics of polymerization in India and in which more than 1,000 publications in international and national journals have appeared and the full bibliography will appear elsewhere.

Taking into consideration the research in the field of kinetics of polymerization, the following suggestions are made for carrying out further work:

1. In red-ox polymerization, in spite of vast coverage, no attempt has been made to (i) characterize polymers and evolve procedures for scaling up; (ii) synthesize data in a unified manner; (iii) selecting red-ox combinations; (iv) develop novel catalytic systems like molecular sieves; and (v) transfer technology to the industry.
2. In the field of C.T. complexes and other photoinitiators, there is a need for working on (i) identification of the exact mechanism and species by other methods like flash photolysis, etc. to supplement and complement the kinetic data, (ii) extension of end group analysis by the dye partition techniques; and (iii) rationalization of exact nature of the photo-sensitizers initiating species.
3. In electro-initiated polymerization, future work may concentrate on elucidation of (i) the nature of the initiator species and the mechanism of their generation; (ii) effect of process variables like current density, electrolyte concentration; (iii) cost benefit ratio for scaling up; and (iv) any special properties of the polymers.
4. In copolymerization, emphasis may be on (i) extension regarding choice of novel and speciality monomers and initiators; (ii) evaluation of potential applications of the copolymers; and (iii) use of copolymers in the generation and design of new anchored catalysts.
5. The field of 'phase transfer catalysis' in solid state polymerization is fairly a virgin field and needs more attention to supplement the conventional 'suspension' or 'emulsion' polymerization.
6. Ziegler-Natta type catalysts have to be employed more extensively with an eye on their use in the industry.
7. It is surprising that except for only a few isolated kinetic studies on the use of γ-rays, no attempt has been made to evolve this method of polymerization into a viable commercial process in India.
8. Kinetics of condensation polymerization needs more attention.

The foregoing suggestions have been made so that work in this field in future will contribute both towards fundamental and applied aspects and at par with international standards.

Acknowledgements

The author wishes to thank Dr B Viswanathan of IIT, Madras for his suggestions and assistance and INSA, New Delhi for providing him the position of a Senior Scientist.

References

1 Panajkar M S & Rao K N, *J [illegible]*, 41 (2) (1975) [illegible]
2 Panajkar M S & Rao K N, *Proc, Natl Symp [illegible] Ind*, (1977) 253.
3 Sivarami Reddy B, Rajadurai S & Santappa M, *J Appl Polym Sci*, 24 (2) (1979) 339.
4 Reddy G Gangi, Nagabhushanam T, Venkata Rao K & Santappa M, *Angew Makromol Chem*, 115 (1983) 61.
5 Bajaj P, Kapoor S K & Chatterjee S R, *Defence Sci J*, 18 (2) (1968) 89.
6 Deb P C & Kapoor S K, *Eur Polym J*, 16 (8) (1980) 763.
7 Srivastava A K & Mathur G N, *Pop Plast*, 27 (8) (1982) 1.
8 Srivastava A K, *J Indian Chem Soc*, 62 (1985) 372.