Pure & Appl. Chem., Vol.52, pp.253-263.
Pergamon Press Ltd. 1980. Printed in Great Britain.

0033-4545/80/0201-0253 $02.00/0

NEW DEVELOPMENTS AND FUTURE OF SYNTHETIC POLYMER CHEMISTRY

Georges Smets

Laboratory of Macromolecular Chemistry,K.Universiteit,Leuven,
Belgium

Polymer chemistry is oriented towards improvement of existing materials through better understanding reaction mechanism and kinetics and towards the creation of specialty polymers,i.e. materials for special uses.This statement is illustrated by examples intentionally selected in different domains of basic research as chain initiation reaction, copolymerization of heterocyclic monomers,block polymerization and polymer transformation reactions.As specialty polymers special attention is given to polymers as organic reagent,as models for biopolymers and enzymes and as biological carriers.On the basis of the actual achievements future orientations of research are outlined.

INTRODUCTION

Since the last decade only a limited number of new polymers has been developed.It is mainly due to the poor economics of new polymer production if compared to that of the major ethylene based plastics ,namely low- and high density polyethylenes,polyvinyl chloride and polystyrene.Nevertheless polymer industry represents about the half of the organic chemical industry and notwithstanding the economic difficulties and the increasing legislation concerning environment and safety it is still expected to expand considerably.It may be stated that moving away from new materials for mass production polymer chemistry research was oriented towards the improvement of existing materials and processes and towards the development of new materials for special uses "specialty polymers" but of rather limited production (1)
Simultaneously very important progresses were obtained in polymer physics and engineering in establishing relations between the structure and the morphology of the materials and their final properties;the development of ultra-oriented high modulus polymers obtained by solid state extrusion is a typical example of such progress.(2,3,4)
The main purpose of the present paper is to illustrate these general trends of polymer chemistry on the basis of a few recent examples,and to infer on the basis of this analysis some lines for future research.It should however be stressed that polymer chemistry and physics benefit abundantly from the development of modern characterization methods.Most important is likely the ^{13}C-nuclear magnetic resonance for elucidating the microstructure of polymers (even recently in the solid state by spinning at magic angle) and for correlating chain segment motions with NMR-relaxation times.Major contributions come also from ESCA measurements for polymer surface analysis and surface phenomena,fluorescence spectroscopy for the determination of group interactions,energy trapping and even polymer compatibility,neutron scattering finally (if available) for the orientation and conformation of polymer chains in the solid state

REACTION MECHANISM AND POLYMERIZATION PROCESSES

In this first part we will consider successively new photochemical initiation processes,the polymerization and copolymerization of heterocyclic monomers, copolymerization with complexating agents,block-graft copolymerization and chemical transformation reactions of polymers.
Photoinitiated polymerization is normally a free radical polymerization;recently however photochemical initiators for cationic polymerization were developped using onium salts as aryldiazonium (5),diaryliodonium,triaryl sulfonium and selenonium (6,7,8) salts having complex metal halide anions MX_n^- such as BF_4^-,AsF_6^-,PF_6^-,SbF_6^-.Diaryliodonium and triarylsulfonium salts are highly

efficient photoinitiators;following reaction mechanism is proposed:

$$Ar_2I^+ MX_n^- \xrightarrow[\text{solv.RH}]{h\nu} ArI + ArH + Ar\text{-}Ar + HMX_n$$
$$Ar_3S^+ MX_n^- \qquad Ar_2S + ArH + Ar\text{-}Ar + HMX_n$$

In the first step the photolysis generates a strong protonic acid HMX_n which initiates a non-photochemical cationic polymerization of the cyclic ether, lactone or olefinic monomer present in the system.For cyclohexene oxide the order of the salts is SbF_6^- (nearly explosive)$\rangle AsF_6^- \rangle PF_6^- \rangle BF_4^-$
Noteworthy is that these photoinitiating systems can be photosensitized e.g. with perylene for triarylsulfonium salts,but are unsensitive to air oxygen and are not affected by classical triplet quenchers;likely the fragmentation occurs in the excited singlet state.An induced decomposition of these onium salts in the presence of electron donor radicals as produced by photolysis of butylbenzoin ether could produce with an adequate monomer,e.g. alkylvinyl ether, a chain reaction for carbocation formation and consequently afford a high quantum yield of photodecomposition (9,10).

$$\begin{array}{l} C_6H_5\text{-}\overset{\circ}{C}H\text{-}OC_4H_9 \\ \quad\text{or} \\ \text{-}CH_2\text{-}\overset{\circ}{C}H\text{-}OAlk \end{array} + Ar_2I^+PF_6^- \longrightarrow ArI + Ar^\circ + \begin{array}{l} C_6H_5\text{-}\overset{+}{C}H\text{-}O\text{-}C_4H_9\ PF_6^- \\ \\ \text{--}CH_2\text{-}\overset{+}{C}H\text{-}O\text{-}Alk\ PF_6^- \end{array}$$

This possibility is still controversial,and much has to be done in this domain of greattechnical importance,for photocuring of printing plates,surface coatings, inks etc.

Special mention deserves also the solid state thermal and photoinitiated polymerization of conjugated diacetylenes,which following Wegner is a unique example for homogeneous solid state reaction,i.e.where individual chains grow independently from each other from points randomly distributed in the lattice and without destroying it.The polymer chains grow via dicarbenes as active intermediate and the photopolymerization is a true chain reaction with quantum yield of 10 to 14 molecules/photon as determined on multilayer samples.(11)
The structure corresponds to a sequence of single,triple and double bonds with the substituents in trans-position with respect to the double bond:

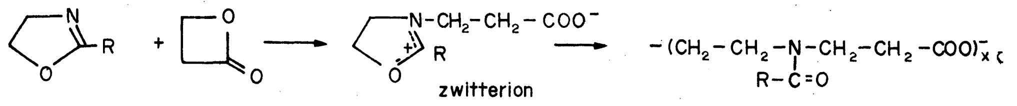
$$R\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}R \longrightarrow (\text{-}\underset{R}{C}{=}\overset{R}{C}\text{-}C{\equiv}C\text{-})_x \text{ where R is Ph-NH-CO-OCH}_2\text{-},\text{Tos-OCH}_2\text{-}$$

1,6 -Bis(N-carbazolyl)-2,4-hexadiyne seems the most attractive derivative. While the monomer is strongly phosphorescent and shows a broad fluorescence, both disappear as the polymer starts growing.Polyene-yn crystals show a pronounced thermochromism (from blue to red) which is linked to a phase transition;they present strong photoconductive properties.

Ring opening polymerization of heterocyclic monomers has received great interest during the last years and much has been learned about their mechanism and their kinetics (12). The polymerizability of the cyclic monomers depends on the ring size,on the angle strain for 3-4 membered rings and on hydrogen interactions for 7 membered and higher rings.Besides ring size,high reactivity may also result from ring unstability (iminoether structure) and,in the case of N-substituted oxazoline and oxazines,from resonance stabilization of the first adduct monomer-electrophile.

$$\text{-}N{=}\underset{R}{C}\text{-}O\text{-} \quad + \quad E^+ \quad \longrightarrow \quad \text{-}\overset{E}{N}\text{-}\overset{+}{\underset{R}{C}}\text{-}O\text{-} \qquad (13\text{-}17)$$

Polymerization occurs in the presence of excess monomer in the absence of a stronger nucleophile.If the electrophilic reagent is a comonomer M_E,e.g. propiolactone,propane sultone,acrylic derivatives, zwitterionic species are formed and propagate further into "no catalyst"alternating copolymers by addition of monomer pairs M_N-M_E,as demonstrated clearly by Saegusa and Kobayashi on an extensive range of interesting systems.(18);following equation shows the reaction of the oxazoline as the nucleophile with the beta-lactone as electrophile

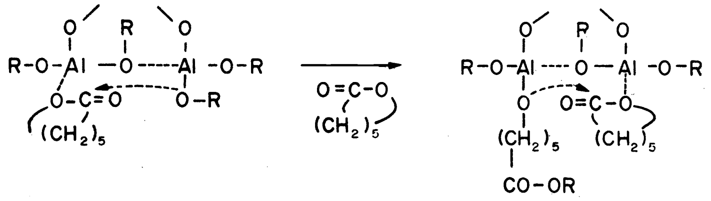


Attractive for the utilization of carbon dioxide are the alternating copolymers of carbon dioxide with oxiranes prepared in the presence of a catalyst based on diethylzinc and a compound with two active hydrogens (water,dihydroxybenzenes,primary amines);these catalysts have an oligomeric structure e.g. $C_2H_5(Zn\text{-}O\text{-})_xH$,$C_2H_5(Zn\text{-}O\text{-}C_6H_4\text{-}O)_xH$ (19-24). Supported catalysts on alumina were also recently described (25).

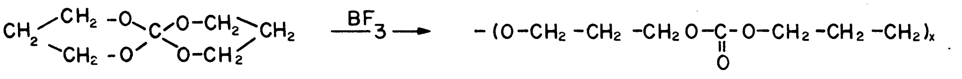
$$R\text{-}\underset{\diagdown O \diagup}{CH\text{-}CH}\text{-}R' + CO_2 \longrightarrow -(\underset{R}{CH}\text{-}\underset{R'}{CH}\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}O\text{-})_x$$

The glass-transition temperatures depend on the nature of R and R',and are equal to 33° and 135° for polypropylene- and polycyclohexene carbonate respectively. High molecular weights can be obtained;the reactions necessitate however relatively high catalyst/oxirane ratio (0.05) and long reaction times. Similar reactions were described with substituted aziridines (26) and aromatic diamines (27) with the formation of polyurethanes and polyureas respectively: $\text{-NH-CHR-CH}_2\text{-O-CO-NH-CHR-NH}_2\text{-O-CO--}$ and $\text{-CO-NH-CHAr-NH-CO-NH-CHAr-NH-}$

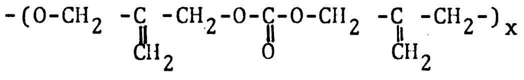
Between the types of initiators used for ring-opening polymerization of heterocyclic monomers undoubtedly coordination type initiators are particularly indicated not only for controlling the chain growth process but also in producing stereoregular polymers (28-30).A major advance in this field was obtained recently by Teyssié and coworkers in synthesizing well defined bimetallic μ-oxo-alkoxide catalysts of following general formula (31,32): $(RO)_xM_A\text{-}O\text{-}M_B\text{-}O\text{-}M_A(OR)_x$ e.g.$(nBuO)_2Al\text{-}O\text{-}Zn\text{-}O\text{-}Al(OBun)_2$.Such bimetallic μ-oxoalkoxides are associated in organic solution through the electron pairs of the alkoxide groups with the coordinatively unsaturated metal atoms.They are very efficient for the polymerization of oxiranes,lactones.With these lasts the polymerization proceeds with a typical living character,permitting the synthesis of polyester chains of well defined molecular weight and narrow molecular weight distribution.In agreement with the earlier suggestion of Vandenberg the reaction progresses through insertion of the monomer within the M_A-OR bond by a coordinative anionic propagation mechanism (28). It is best represented by a flip-flop reaction scheme on one or two aluminium atoms depending the degree of association of the catalyst and thus the polarity of the reaction medium.



In connection with ring-opening polymerization worthwhile to mention are the experiments of Bailey concerning the changes of volume occuring during these reactions.(33)It was stated that if monomers contain at least two rings to be opened for every new bond,no change of volume or even volume expansion during polymerization must be expected.Indeed several examples were developped,e.g. spiroorthocarbonates which polymerize to ether containing polycarbonates (34).



Introduction of unsaturation into such compounds affords substances which polymerize either with borontrifluoride either with di-tert-butylperoxide with ring opening and produces crosslinked polymers with increaseof volume (35).



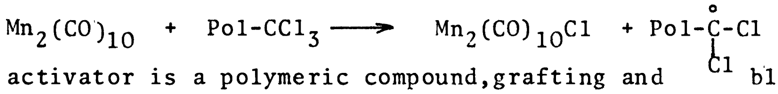
$$-(O-CH_2-\underset{\underset{CH_2}{\|}}{C}-CH_2-O-\underset{\underset{O}{\|}}{C}-O-CH_2-\underset{\underset{CH_2}{\|}}{C}-CH_2-)_x$$

Technical applications of no shrinkage polymerization or even volume expansion are multiple:strain-free composites,impression materials,high strength adhesives etc.Evidently a great variety of multiple ring compounds can be envisaged,also with other heteroatoms as nitrogen,sulfur.It is noteworthy that polymerization involving strained C-C single bonds proceeds only satisfactorily in bicyclic systems as bicyclobutane-carbonitrile by radical mechanism or anionically (36).

Synthesis of alternating copolymers of olefines or diolefines with acrylic monomers in the presence of alkyl aluminum halide as complexating agent is also an important problem. (37,38) Indeed butadiene-acrylonitrile alternate copolymers show oil resistance,,high flexibility and toughness superior to those of the conventional random copolymers of similar acrylonitrile content (39). In the same line high molecular weight alternate and acrylate-rich copolymers of propylene and ethyl acrylate have been prepared in the prepresence of free radical initiator (AIBN) by using boron fluoride as complexating agent of the acrylic component.(40)Their alternate composition is due either to a strong increase of the cross-propagation rate constants (r_1 and r_2 very small) or by complexation of the growing radical with unreacted monomer.It is rather unexpected that complexation of the acrylate ester permits to avoid the well-known free radical degradative chain transfer, characteristic for allyl compounds and thus propylene as well.

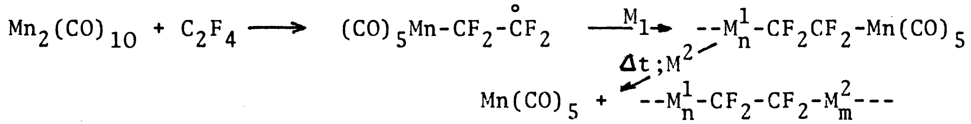
The need for new materials with appropriate performance/cost ratios has undoubtedly forced the polymer researchers to study more fundamentally the use of purely physical polymer blends.A main difficulty however resides in the fact that polymers are usually immiscible;the phase separation which occurs and the low attraction forces across the phase bondaries are responsible for poor mechanical properties.In order to improve adhesion between the phases and consequently mechanical properties as elongation,tensile strength,the first idea of connecting both phases by covalent bonds is obvious,and consists in the synthesis and use of block- and graft polymers.(41-43)
In earlier times these syntheses were carried out by free-radical polymerization,either direct grafting by chain transfer reaction (44) either by decomposition of labile groups attached at the end or as side-groups of a preformed polymer (45). Such graft/block polymers can be isolated but their characterization remains difficult.Nevertheless such materials remain interesting for their technological uses,e.g.in adhesives,rubbers,fibers and plastics in general,and also as dispersants for dispersion polymerization in organic media.Therefore the recent synthesis of graft/block polymers of vinyl chloride with styrene,methyl methacrylate and several acrylic esters should be mentioned (46);it is carried out in emulsion polymerization in

two steps using an heterofunctional polyperoxide.The vinyl chloride content could be varied on a large scale and interesting properties were obtained. Particularly interesting for its versatility is the method developed by Bamford (47,48) using metal carbonyl initiating systems in the presence of an activator,e.g. an alkyl halide.



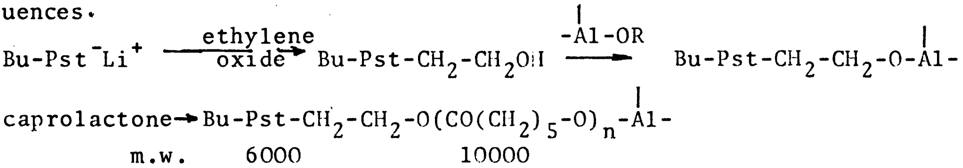
$$Mn_2(CO)_{10} + Pol\text{-}CCl_3 \longrightarrow Mn_2(CO)_{10}Cl + Pol\text{-}\overset{\circ}{\underset{Cl}{C}}\text{-}Cl$$

If the activator is a polymeric compound,grafting and block formation will occur in the presence of a monomer;crosslinking may proceed as well depending the reaction conditions.The same transition metal-carbonyls can also add to electron poor alkenes and on irradiation produce primary radicals that initiate the polymerization of monomer M_1.On heating, these endgroups decompose and yield blockpolymer with monomer M_2.



$$Mn_2(CO)_{10} + C_2F_4 \longrightarrow (CO)_5Mn\text{-}CF_2\text{-}\overset{\circ}{C}F_2 \xrightarrow{M_1} \text{--}M^1_n\text{-}CF_2CF_2\text{-}Mn(CO)_5 \xrightarrow{\Delta t;M^2} Mn(CO)_5 + \text{--}M^1_n\text{-}CF_2\text{-}CF_2\text{-}M^2_m\text{---}$$

It is nevertheless since the discovery of the living polymers by Szwarc that well defined block polymers with very low heterogeneity became available through anionic polymerization.The two general methods are well known: 1:sequential addition of monomers A and B in order of increasing electroaffinity;2:functionalization of the endgroup(s) of a living polymer,and use of these endgroups for the polymerization of second monomer or for coupling with preexisting blocks.(49-52)While the first method is well illustrated with the thermoplastic elastomer Pst-PBu-Pst in which the hard domains of polystyrene assure the physical crosslinking,the following example of Teyssié and Gallot (53) represents the second functionalization method.It makes use of the bimetallic μ-oxo-aluminum zinc alkoxide catalyst (mentioned above)for the synthesis of polystyrene-poly-ε-caprolactone blockpolymer with well defined sequences.



$$Bu\text{-}Pst^-Li^+ \xrightarrow[\text{oxide}]{\text{ethylene}} Bu\text{-}Pst\text{-}CH_2\text{-}CH_2OH \xrightarrow{\overset{|}{-Al}\text{-}OR} Bu\text{-}Pst\text{-}CH_2\text{-}CH_2\text{-}O\text{-}\overset{|}{Al}\text{-}$$

$$\xrightarrow{\text{caprolactone}} \underbrace{Bu\text{-}Pst}_{\text{m.w. }6000}\text{-}CH_2\text{-}CH_2\text{-}\underbrace{O(CO(CH_2)_5\text{-}O)_n}_{10000}\text{-}\overset{|}{Al}\text{-}$$

Thanks to the compatibility of polycaprolactone with many polymers(54),such polycaprolactone-b.styrene can be used as stabilizer of PVC/Pst (80/20)blends. For increasing the compatibility between polymers block polymers are more effective than graft copolymers (55) and their use as stabilizing agent for polymer dispersion is well known.The blends may contain one hard glassy phase and one rubbery phase (polystyrene-polyisoprene) or two soft phases (polybudiene-polyisoprene) (56,57).Mention should also be made of the use of amphiphilic blockpolymers as surfactants for microemulsions in the presence of a cosurfactant agent (58,59).

Another method for combining polymers without chemical bonding between partners is to form interpenetrating polymer networks (60,61).The conventional method of synthesis consists in swelling a crosslinked primary network with a solution of monomer and crosslinking agent,followed by polymerization "in situ" of the second network.The result is an extended primary network intermingled with a co-continuous secondary network to give a quasi-single phase

material.Ideal IPN's behave as miscible physical mixture i.e. with one T_g and a maximum tensile strength at intermediate composition;they differ considerably from phase separated mixtures.
Up to recently cationic polymerization was not considered as appropriate for making graft/block copolymers on account of chain transfer,isomerization and self termination reactions.It is the great merit of Kennedy and al.(62,63) to have studied the fundamentals of ion generation and initiation processes as well as termination with model compounds and to have extended these basic data to polymeric back-bone and polymer endgroups leading to new graft (even bigraft by selective initiation) and block polymers.

Polymer modification reactions are the last item to be considered;it is still a broad field of unlimited possibilities for producing new polymers.They give also informations about reactivity of functional groups and exhibit characteristic polymer effects as neighboring group effects,variation of chain conformation during the reaction,electrostatic effects between charges along the macromolecules etc.The kinetics and statistics of these reactions were fully considered by Morawetz (64) and Platé (65). The attachment of specific groups to a preformed polymer may produce polymers with controlled chemical and physical properties;for example photochemical crosslinking and free-radical grafting on one hand,energy transfer phenomena,fluorescent and photoconductive properties on the other hand.The photoconductive properties of polyvinylcarbazol and its charge transfer complex with 2,4,7-trinitrofluorenone are well known (66).
It must however be stressed that reactions may differ considerably if they are carried out in solution or in the solid state,especially below T_g;consequently the kinetics of model reactions in solution may be only a very rough approximation of thoses in the solid.On account of restricted segment mobility isomerization equilibrium involving rotation of bulky groups may be deeply affected,and the thermal reversibility may even become questionable.This effect was clearly taken in evidence with photochromic films containing indoleninospirobenzopyrane groups,especially if the groups are inserted in the polymer backbone (67,68). Similar effects are found with dissociation phenomena involving bisanthracene ,hexaphenylbisimidazole and benzpinacol units.In these cases cage effects become predominant due to restricted diffusion possibilities,and cage dimensions as well as diffusion constants have been evaluated (69).

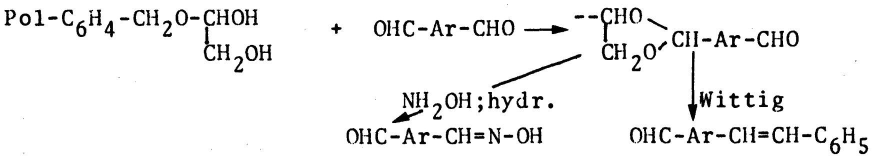
SPECIAL POLYMER APPLICATIONS

In this second part special attention will be devoted to polymers as organic reagent,as substrates and models for biopolymers and enzymes,and as biological carriers.
Since the pioneering work of Merrifield (70)in the use of crosslinked polystyrene resins for the repetitive sequential synthesis of polypeptides,the use of insoluble polymers as supports for organic reagents has steadily increased.Polymeric support must evidently be inert towards the reagents,be mechanically and thermally stable,be insoluble in the reaction medium but nevertheless compatible with solvent and reagent in order to keep free

accessibility of reagent and product near the catalytic site.When such conditions are met,monofunctional reactions afford similar yields as in solution, e.g.the preparation of N-blocked aminoalcohols and esters from insoluble 4-hydroxy-3nitro-benzylated polystyrene esters (71) :

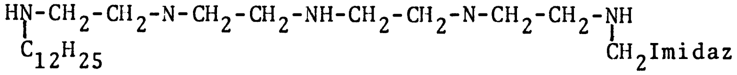
$$\mathrm{R\text{-}COOR'} \xleftarrow[\mathrm{R'OH}]{} \mathrm{Pol\text{-}C_6H_3(NO_2)\text{-}O\text{-}CO\text{-}R} \xrightarrow[\mathrm{NaBH_4}]{} \mathrm{R\text{-}CH_2OH}$$

The polymeric reagent can however be separated and reused,and allows easier recovery of high purity product.Sometimes the polymer anchored groups are very sophisticated e.g. macrocycles of two 1,1'-dinaphthyl units of identical R configuration linked together at their 2,2'-positions by two $-OCH_2-CH_2-OCH_2-CH_2-O-$ units.These macrocycles are host sites for the chromatographic resolution of enantiomers of aminoacids and esters salts (perchlorate,hexafluorophosphate),D guests being more firmly bounded by the R-R guests than L guests (72).An attractive aspect,although not extensively studied,is the use of polymers in organic synthesis as protecting groups of polyfunctional molecules.It is based on the assumption that functional groups attached to an insoluble polymer react only sluggishly with one another on account of restricted conformational motions of the polymer backbone and consequently a decrease of collision frequency between reactive groups. The polymer can thus protect one of the function of the substrate that can further be transformed on the remaining free function,e.g. the monofunctional protection of an aryldialdehyde for the synthesis of the monooxime:(73)



Sometimes protection may be very selective as in the use of crosslinked polystyrylboronic acid for the formation of selectively acylated glycosides (74). Catalysis by complexes of transition metals anchored on polymeric ligands deserves special mention for its broad spectrum of possible applications.Most important catalyzed reactions are the hydrogenation of alkenes and alkynes, hydroformylation of olefines-1,dimerization of ethylene/propylene,their polymerization and copolymerization (75). Taking account of the nature and structure of the catalysts,their recovery and recyclization may offer special interest;moreover it is said that the catalyst stability is often improved by anchoring on rigid support.

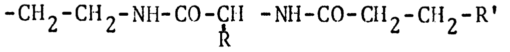
Polyelectrolytes can strongly influence the course of chemical reactions. Reactions between similarly charged ionic species are largely enhanced by addition of polyions of opposite charge,whereas those between oppositely charged ions are decelerated by both anionic and cationic polyions.Such phenomena were recently discussed by Ise (76).Most intensive researches concern however the catalytic properties of synthetic polyelectrolytes containing functional groups similar to those in enzyme molecules,for example imidazol rings. It is admitted that such synthetic polyelectrolytes could serve as simplified enzyme models,and consequently be useful for understanding more complicated enzymatic processes.As stated by Okubo and Ise enzymes require high efficiency,high specificity and regulative mechanism.So far main progress was only obtained with respect to hydrolytic efficiency (77) The reader should refer to excellent recent reviews by Overberger (78,79) and Kunitake(80). The increased activity of polyvinylimidazole and copolymers in esterolytic reactions compared to monomer imidazole catalysis is due to cooperative interactions between pendent imidazole groups,to electrostatic effects and to apolar hydrophobic binding effects.It seems to be in the catalytic hydrolysis of p-nitrophenyl esters with polyethyleneimine derivatives that the rate effect was most pronounced. .Klotz (81,82)studied the catalytic effect of polyethyleneimine carrying 10% dodecyl and 15% imidazolylmethyl N-substituents as well as analogous lauroylated products.



$$\underset{C_{12}H_{25}}{HN}-CH_2-CH_2-N-CH_2-CH_2-NH-CH_2-CH_2-N-CH_2-CH_2-\underset{CH_2Imidaz}{NH}$$

The hydrolysis was about 300 times faster than with imidazole itself.In the case of 4-nitrocatechol sulfate not only typical enzyme Michael-Menten kinetics were observed,but an acceleration of the rate by a factor of 10^{12} was found.Similarly Kabanov (83) studied the hydrolysis of p-nitrophenyl caproate with N-benzyl polyethyleneimin and found the polymer 10^5times more effective than its low molecular weight analog N,N-dimethylbenzylamine.As pointed out by Volkenstein (84)these synthetic polymers differ fundamentally from the biopolymers which are characterized by a well definite sequence of aminoacids and by the existence of interactions which stabilize a definite secondary, and very often a tertiary structure instead of a statistical coil.It is assumed that electronic conformational interactions are the basic mechanism of enzymatic activity.

Much polymer research was also devoted to nucleic acid chemistry, where one assumes the formation of base-base pairs (e.g. uracil-adenine) for replication and transcription of genetic codes in protein synthesis.Thus Takemoto and coworkers (85,86) studied the polymerization and copolymerization of N-vinylbases,as N-vinyladenine ,N-beta-methacroyloxyethyladenine ,as model compounds for nucleic acids.The rate of copolymerization of complementary uracyl and adenine methacroyl derivatives presents a maximum value at a monomer ratio 1:1 and the copolymerization parameters depend strongly on the solvent.Moreover the adenine derivative polymerized much faster when the complementary matrix is present.Such results suggest a template polymerization behavior due to interactions between complementary bases.Similarly graft copolymers of nucleic acid bases and L-alpha-aminoacids on polyethyleneimine were considered by Overberger and al.(87)



$$-CH_2-CH_2-NH-CO-\underset{R}{CH}-NH-CO-CH_2-CH_2-R'$$

where R is methyl,hydroxymethyl, CH_2COOH (aspartic) and $-CH_2$Imidaz.(histidine) and R' is adenine,thymine.Formation of complementary base-paired complexes and their stoichiometry were determined.It is function of the internal functional accessibility of the polymer,on the structure of the polymer backbone,the pH and temperature. The influence of such synthetic polymers on enzymes of nucleic acids was examined by Pitha (88).

Increased interest was also focused in recent years in the synthesis and the preparation of biodegradable materials for many applications such as gradual drug release i.e. prolongation of pharmacological activity and decrease of toxicity,surgical inplant materials,controlled release formulations of insecticide and pesticide carriers,degradable packaging etc.Biodegradability implies evidently the presence of enzyme sensitive bonds in the polymer chain,e.g. incorporation of aromatic side-groups adjacent to amide and ester groups (89);it may result as well from the degradability of natural polymers (dextrane,starch on which drugs are linked through amide or ester groups. Though this subject is out of scope of the present review,it has to be (90) mentioned on account of the important contribution of organic chemistry in this domain.The reader interested in pharmacologically active polymers and in related problems should refer to the excellent review of Ringsdorf (91) and later publications.

CONCLUSION

Present trends of polymer chemistry show that increased efforts in better understanding reaction mechanisms and processes make it possible to create new special materials and to improve the properties of many existing ones. Such efforts have to be pursued intensively in narrow cooperation with polymer physicists and technologists.In the domain of biopolymers the use of synthetic polymers with well definite structure as model substances must further contribute to elucidate the fundamentals of enzymes and nucleic acids activities.

Acknowledgement The author is indebted to the Ministry of Scientific Programmation and the National Science Research Foundation(NFWO,Belgium)for their continuing generous support.

REFERENCES.

(1) C.H.Bamford,A.Ledwith:Chem.Brit.15 19 (L979)
(2) C.R.Desper,J.H.Southern,R.D.Ulrich,R.S.Porter:J.Appl.Phys. 41 4284 (1970)
(3) A.Keller:J.Polym.Sci.Symposium 59 395 (1976)
(4) W.G.Perkins,R.S.Porter:Bull.Am.Phys.Soc. AJ 10 235 (1976)
(5) S.I.Schlesinger :Photog.Sci.Eng.18 387 (1974)
(6) J.V.Crivello,J.H.W.Lam: Macromolecules 10 1307 (1977)
(7) J.V.Crivello,J.H.W.Lam:J.Polym.Sci.Polym.Chem.Edit.16 2441(1978);17 977, 1059,1047 (1979)
(8) J.V.Crivello,J.H.W.Lam:Amer.Chem.Soc.Polym.Prepr.20 415 (1979)
(9) A.Ledwith:Polymer 19 1217 (1978)
(10) F.A.M.Abdul-Rasoul,A.Ledwith,Y.Yagci:Polymer 19 1219 (L978)
(11) G.Wegner:in Molecular Metals.Plenum Publ.Corp.1979 W.E.Hatfield edit. p209-42 and refer.therein
(11) Y.Yamashita :Adv.Polym.Sci. 8 1 (1978)
(13) D.A.Tomalia,D.P.Sheetz:J.Polym.Sci. A1 4 2253 (1966)
(14) W.Seeliger,W.Thier:Angew.Chem.Int.Ed.5 612 (1966)
(15) T.Kagiya,S.Narisawa,T.Maeda,K.Fukui:J.Polym.Sci. B 4-441(1966)
(16) T.Bassiri,A.Levy,M.Litt:J.Polym.Sci.B 5 612 (1966)
(17) T.Saegusa,H.Ikeda,H.Fujii: Polym.J. 3 35 (1972)
(18) T.Saegusa,S.Kobayashi:Pure Appl.Chem. 50 281(1978) and refers.Therein.

(19) S.Inoue ; Chem.Tech.1976 588

(20) S.Inoue,H.Koinuma,T.Tsuruta:Polym.J.2 220(1971);J.Polym.Sci.B 7 287 (1969);Makromol.Chem.130 210 (1969)

(21) S.Inoue,H.Kionuma,Y.Yokoo,T.Tsuruta:Makromol.Chem. 143 97 (1971)

(22) M.Kobayashi,S.Inoue,T.Tsuruta:J.Polym.Sci.Polym.Chem.Ed.11 2383 (1973)

(23) T.Hirano,S.Inoue,T.Tsuruta:Makromol.Chem. 176 1913 (1975)

(24) W.Kuran,S.Pasynkiewicz,J.Skupinska,A.Rokicki :Makromol.Chem.177 11(1976)

(25) K.Soga,K.Hyakkoku,K.Izumi,S.Ikeda:J.Polym.Sci.Polym.Chem.Ed.16 2383

(26) K.Soga,S.Hasoda,S.Ikeda:J.Polym.Sci.Polym.Chem.Ed.12 729 (1974) (1978) Makromol.Chem.175 3309 (1974)

(27) N.Yamazaki,F.Higashi,T.Iguchi:J.Polym.Sci.Polym.Chem.Ed.13 785 (1975)

(28) E.J.Vandenberg;J.Polym.Sci.47 486(1960);B 2 1085(1964);A-1 525(1969)

(29) C.C.Price,M.Osgan: J.Am.Chem.Soc.78 4787(L956)

(30) C.C.Price,R.Spector:J.Am.Chem.Soc.88 4171(1966)

(31) T.Ouhadi,A.Hamilton,R.Jerome,Ph.Teyssié:Macromolecules 9 927(1976) J.Polym.Sci.Polym.Chem.Ed.15 865(1977)

(32) Ph.Teyssié,J.P.Biuul,A.Hamilton,J.Heuschen,L.Occks,R.Jerome,T.Ouhadi: ACS Symposium Series 59 165(1977) Ring Opening Polymerization

(33) W.J.Bailey:Am.Chem.Soc.Polym.Prepr.18 (1) 17(1977)

(34) W.J.Bailey,H.Katsuki,T.Endo:Am.Chem.Soc.Polym.Prepr. 1976 (1973)

(35) T.Endo,W.J.Bailey:J.Polym.Sc.,Polym.Letters 13 193(1975);-Polym.Symp. 64 17(1978)

(36) H.K.Hall Jr,H.Tsuchiya,P.Ykman,J.Otton,V.Papanu,S.C.Snider,A.Deutschman Jr Am.Chem.Soc.Polym.Prepr.18 104 (1977)

(37) M.Hirooka,H.Yabuuchi,S.Morita,Skawasumi,K.Nakaguchi:J.Polym.Sci.B 5 47 (1967)

(38) M.Hirooka,H.Yabuuchi,J.Iseki,Y.Nakai:J.Polym.Sci.Polym.Chem.Ed. 6 1381(1968)

(39)J.Furukawa,Y.Iseda,K.Haga,N.Kataoka:J.Polym.Sci.Polym.Chem.Ed.8-1147(1970)

(40) A.L.Logothetis,J.M.Mc.Kenna:J.Polym.Sci.Polym.Chem.Ed.12 131(1974); 16 2797(1978)

(41) D.R.Paul,J.W.Barlow:Adv.in Chemistry SeriesACS 176(1979)Multiphase polymers.S.Cooper,G.M.Estes ed. 315

(42) B.R.M.Gallot:Adv.Polym.Sci.29 85(1978)

(43) B.J.Schmitt:Angew.Chem.91 286(1979)

(44) G.Smets,M.Claesen:J.Polym.Sci 8 289(1952)

(45) G.Smets,R.Hart:Adv.Polym.Sci.2 173(1960) and refers.therein.

(46) G.Weinand,G.Smets:J.Polym.Sci.Polym.Chem.Ed. 16 3091(1978),3077(with S. Deguchi),3107(with N.Overbergh)

(47) C.H.Bamford:J.Chem.Soc.Faraday I,72 2805(1976)

(48) C.H.Bamford,S.U.Mullik:J.Chem.Soc.Faraday I 73 1260(1977)

(49) M.Szwarc,M.Levy,R.Milkovich:J.Am.Chem.Soc.78 2656(1956)

(50) M.Szwarc:Carbanions,living polymers and electron transfer processes Wiley 1968 N.Y. and refers.therein.

(51) P.Rempp,E.Franta:Pure Appl.Chem.30 229 (1972)

(52) E.Franta,P.Rempp:Am.Chem.Soc.Polym.Prepr. 20 5 (1979)

(53) J.J.Herman,R.Jerome,P.Teyssié,M.Gervais,B.Gallot:Makromol.Chem. 179 1111(1978)

(54) J.V.Koleske:in Polymer Blends vol.2 Academ.Press N.Y.(1978) 369

(55)G.Riess,J.Kohler,C.Tournut,A.Banderet:Makromol.101 58(1967)
(56)T.Inoue,T.Soen,T.Hashimoto,H.Kawai:Macromolecules 3 87(1970)
(57)A.R.Ramos,R.E.Cohen:Am.Chem.Soc.Polym.Prepr.18 335(1977)
(58)G.Riess,J.Servo,D.Rogez:Am.Chem.Soc.Polym.Prepr.18 329(1977)
(99)P.Marie,Y.Gallot:Makromol.Chem.180 1611 (1979)
(60)S.C.Kim,D.Klempner,K.C.Frisch,W.Radiger,H.L.Frisch:Macromolecules 9 258
(61)D.A.Thomas,L.H.Sperling:Polymer Blends vol2.Academ.Press N.Y.1978 (1976)
(62)J.P.Kennedy ,S.Rengachary :Adv.Polym.Sci.14 1(1974)
(63)J.P.Kennedy:Am.Chem.Soc.Polym.Prepr.20 157(1979);J.Polym.Sci.Polymer Symposium 64 117(1978) and refers.therein.
(64)H.Morawetz:Pure Appl.Chem.38 267(1974)
(65)N.A.Platé,O.V.Noah:Adv.Polym.Sci.31 133(1979) and refrs.therein.
(66)H.Hoegl,O.Sus, Neugebauer:Germ.Patent 1.068115 Kalle A.G.(1957)
(67)G.Smets,G.Evens:Pure Appl.Chem.Macromol.Chem.8 357(1973)
(68)G.Smets,J.Thoen,A.Aerts:J.Polym.Sci.Sympos.51 119 (1975) and refrsthere
(69)G.Smets,G.Nijst,M.Schmits-Smets,A.Somers:J.Polym.Sci.Sympos. in press
(70)R.B.Merrifield:J.Am.Chem.Soc.85 2149 (1963);Biochemistry 3 1385(1964)
(71)R.Kalvi,A.Patchornik:J.Polym.Sci.Polymer Letters 16 35(1978)
(72)G.Dotsevi,Y.Sogah,D.J.Cram;J.Am.Chem.Soc.101 3035 (1979)
(73)C.C.Leznoff,T.Y.Wong:Can.J.Chem.51 3756(1973)
(74)J.M.J.Frêchet,L.J.Nuyens,E.Seymour:J.Am.Chem.Soc.101 432(1979)
(75)Y.Chauvin,D.Commereuc,F.Dawans:Prog.Polym.Sci 5 95 (1977)
(76)N.Ise:J.Polym.Sci.Symposium 62 205 (1978)
(77)T.Okubo,N.Ise:Adv.Polym.Sci. 25 136(1977)
(78)C.G.Overberger,A.C.Gutul jr.,Y.Kawakami,L.J.Mathias,A.Meenakshi,T.Tomono: Pure Appl.Chem.50 309(1978) and refers.therein.
(79)C.G.Overberger,S.Mitra:Pure Appl.Chem.51 1391 (1979)
(80)T.Kunitake,Y.Okibata:Adv.Polym.Sci.20 159 (1976)
(81)M.Klotz,G.P.Royer,I.A.Scarpa:Proc.Nat.Acad.Sci.USA 68 263 (1971)
(82)H.C.Kiefer,W.I.Corydoor,I.S.Scarpa,I.M.Klotz:ibid. 69 2155 (1972)
(83)V.S.Pshezhetskii,G.A.Murtazaeva,V.A.Kabanov:European Polymer J.10 571
(84)M.V.Volkenstein:Pure Appl.Chem. 51 801 (1979) (1974)
(85) K.Takemoto:Am.Chem.Soc.Polym.Prepr.18 547(1977);20 215(1979)
(86)M.Akashi,H.Takada,Y.Inaki,K.Takemoto:J.Polym.Sci.Chem.Ed.17 747(1979)
(87)C.G.Overberger,Y.Inaki:J.Polym.Sci.Chem.Ed.17 1739,1759 (1979)
(88)J.Pitha:Am.Chem.Soc.Polym.Prepr.20 326 (1979)
(89)S.J.Huang,D.A.Bansleben,J.R.Knox:J.Appl.Polym.Sci.23 429(1979)
(90)P.Ferruti,M.C.Tanzi,F.Vaccaroni:Makromol.Chem.180 375(1979)
(91)H.Ringsdorf: J.Polym.Sci.Sympos.51 135 (1975)and refers.therein.