PROFESSOR BAMFORD's   CONTRIBUTION TO POLYMER SCIENCE AND

ITS SIGNIFICANCE.

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Abstract The contribution of C.H.Bamford to Polymer Science is
considered successively from following aspects:a the conforma-
tion and properties of poly-alpha-aminoacids and polypeptide
synthesis. b solid-phase addition polymerization.c free radical
polymerization kinetics d new initiating systems for free radi-
cal polymerization and their application to block- and graft
polymerization.Special attention is devoted to recent develop-
ments and their application possibilities.

INTRODUCTION

It is a challenge to present and discuss the contributions of a researcher
who is still engaged in the front of advanced research and progress.The
exceptional scientific activity of Professor Bamford for over 40 years,
coupled with his authoritative competence,has however strongly marked the
development of the physical chemitry and especially of the chemical kinetics
of high polymers during the last decennia.It is my great privilege and honour
to have been invited to present at this distinguished assembly Bamford's
contribution to Polymer Science,and by doing so to participate to the cele-
bration of an excellent scientist and a good colleague and friend.

C.H.Bamford started his career in Trinity College Cambridge where he recei-
ved his Ph.D. under the guidance of R.G.W.Norrish with researches on the
primary photochemical reactions and photodecomposition of aldehydes and
ketones (1) It is from these early days that the distinction became clear
between two types of reaction mechanisms of carbonyl compounds,type 1
characterized by decarbonylation and formation of saturated hydrocarbons
type 2 by formation of unsaturated hydrocarbons and simpler ketones,the
differences being due to the much shorter lifetime of the reaction interme-
diates in type 2 reactions,in which no radicals are produced.
Gas phase photochemistry researches were pursued by studies on the photolysis
of organic nitrogen compounds (e.g. dialkylnitrosoamines,methyl isocyanate)
(2) and much later,when he was already in Liverpool,on reactions of methyle-
ne (produced by photolysis of ketene) with organic halides (3) in which the
relative importance of the primary atom abstraction to the insertion reaction
was evaluated for several examples.Very likely these fundamental photochemistry
researches have originated and strongly stimulated Bamford's great interest
for the study of reaction mechanisms and kinetics,which is characteristic of
his entire further career.

PROPERTIES and SYNTHESIS of POLY-alpha-AMINOACIDS.

The work on the conformation and the properties of poly-alpha-aminoacids
(mainly with W.E.Hanby,F.Happey and I.F.Trotter) and the related polymeriza-
tion of N-carboxy-alpha-aminoacid anhydrides (with G.H.Ballard and H.Block)
is one of the most important achievements of Bamford (4).These researches
which extended over a period of nearly twelve years coincide practically
with his directorship of Courtauld Research laboratories.
Much attention was paid to the reversible alpha--beta transformation from the
folded configuration into the extended one for several synthetic polypepti-
des,as poly-L-alanine,poly-D,L-phenylalanine,poly-γ-methyl glutamate and co-
polypeptides.Changes of X-ray distances and remarkable modifications of infra
red spectra after treatment with carboxylic acids (formic,dichloroacetic)
were discussed in detail.

Concerning the mechanism of polypeptide synthesis from N-carboxyanhydrides the influences of primary and secondary bases,including preformed polymer, were examined as well as the catalytic effects of added metal salts (e.g.LiCl and alkali-metal salts of weak acids (sodium beta-phenylpropionate).They were interpreted assuming a partial displacement of mobile protons by the metal cation.Similarly with tertiary bases,as pyridine,alpha-picoline the initial attack on the monomer proceeds through removal of the proton from the endo-cyclic NH nitrogen,and the anion reacts further with a NCA-molecule without rupture of the -N-CO-bond (5)

Chain effect and heterogeneity effects which were observed deserve special attention.(6,7,8) The <u>chain</u> effect consists in a much higher rate increase in the presence of polysarcosine (optimum degree of polymerization 10) than with ordinary secondary bases;it is assumed that the polymerization takes place on the surface of the polysarcosine on account of the formation of H-bonded complexes,as shown afterwards by infrared analysis.The kinetics are comparable with thoses of enzymatic reactions. The <u>heterogeneity</u> effect is an increase of reaction velocity that coïncides with the appearance of hete-rogeneity;it is admitted that the NCA's are preferentially soluble in the precipitating swollen polypeptide than in the reaction medium.Precipitation therefore increases the effective concentration of both monomer and catalyst and consequently causes an increase of rate of polymerization.

Undoubtedly these scientific results and their critical interpretations illustrate clearly the high sagacity and experimental cleverness of their authors.

SOLID-PHASE ADDITION POLYMERIZATION

Solid-phase addition polymerization was studied by Bamford's group in the sixties mainly with the collaboration of Eastmond,Jenkins,Ward and Bibby. At that time much efforts were spent on similar problems in many internatio-nally reputed laboratories,e.g. in Kyoto by Okamura and Hayashi (especially on cyclic monomers as trioxane,beta-propiolacton),in Moscow Kargin and Kaba-nov,in Brooklyn by Morawetz.A very interesting and critical review of the field was written by Bamford and Eastmond ; the reader should refer to the original text (9) The main efforts of Bamford and colleagues were devoted to the polymerization of crystalline methacrylic acid,in which crystal dis-locations play the major role since they determine sites of local mobility which is necessary for chain propagation.On U.V.irradiation of monomer, excitons are formed which can migrate through the lattice until trapped in imperfections,where radical may be formed.Application of stress was shown to be capable to suppress completely the polymerization of acrylic and meth-acrylic acids on account of restrictions of molecular mobility;polymeriza-tion is however resumed on release of the stress.

Fundamental differences were pointed out between the polymerization of cyclic monomers in which the orientation in the lattice is favorable for propagation and requires only limited mobility of atoms,and the polymeriza-tion of vinyl monomers where the interatomic (sp^2 into sp^3) and inter-molecular distances have to change appreciably.

On looking to the more recent data on solid state polymerization of Hasegawa (10) on photocyclodimerization reactions and of Wegner on dyine polymeriza-tion (11) it may be said that Bamford's contribution was one of the major precursors of the actual development of this promising field of research.

KINETICS OF FREE RADICAL POLYMERIZATION

Free radical polymerization has been investigated by Bamford since 1946, with the collaboration first of Dr.Dewar later with A.D.Jenkins.From that period dates the so-called viscosity method (12)for determining the indivi-dual velocity coefficients in polymerization reactions.Besides the rotating sector technique the method of Dewar and Bamford was much used for its convenience and high sensitivity:indeed it needs only measurement of the viscosimetric rate with thermal initiation alone and at different rates of photoinitiation,one molecular weight determination and measurement of the viscosity after-effect.

Kinetics of vinyl polymerization in heterogeneous conditions were mostly studied in collaboration with A.D.Jenkins,particularly for the case of acry-lonitrile (13,14)Photochemical after-effects due to occluded radicals below 60° were shown and their consequence on the overall reaction kinetics dedu-ced.Elaborated study of chain transfer reactions with tertiary amines was at the basis of one of the first method for preparing block polymers by free

radical mechanism.It involves the polymerization of a second monomer (e.g.
acrylonitrile) in the presence of a preformed polymer of the first monomer
carrying tertiary amine endgroups.
The role of radical intermediates in polymerization processes has been re-
viewed recently by Bamford himself;in the present context it will be suffici-
ent to underline just a few points (15)It was shown that solvent effects can
affect in homopolymerization and copolymerization the values of the propaga-
tion and termination rate constants and may even influence the reactivity ra-
tios in copolymerization;these effects are however weak.Much stronger are
the effect of the addition of salts,particularly Lewis acids which form com-
plexes with monomers and their radicals if they carry polar groups.The resul-
ting changes of electron density cause significant modifications of the reac-
tivities of the monomer and derived radicals.Sometimes even the tacticities
of the resulting polymer may be modified.The most spectacular consequence of
this complex formation was the synthesis of alternating copolymers of propy-
lene and acrylonitrile in the presence of ethyldichloroaluminum by
Hirooka et al. (16) who extended the method to several other vinyl monomer-
Lewis acid combinations,all yielding alternating copolymers.Mechanistic con-
 siderations indicate that these regulated copolymerizations proceed likely
through an alternating addition mechanism (15)
Interesting also are the considerations about the reactivity of free radicals
as developed with Jenkins (17)A new interpretation of the O-e scheme was
propsed ona more experimental basis,evaluating the general reactivity by
transfer reaction with toluene and the polarity of the monomers on the basis
of Hammett's sigma values.

NEW INITIATING SYSTEMS FOR FREE RADICAL POLYMERIZATION

New initiating systems for free radical polymerization of vinyl monomers
became the focus of a very intensive and successful research of Bamford and
coworkers begin of the sixties (17,18)Different types of systems have been
studied throughout and will be considered here in their principles only.
The first systems are based on organometallic derivatives of a transition
metal in a low oxidation state (e.g.metal carbonyls) and a reactive additive.
If the additive is a reactive organic halide (CCl_4,CBr_4,chloroform,ethylchlo-
roacetate)reaction with molybdenum and manganese carbonyls proceeds through
electron transfer from the transition metal to halide.In this case the predo-
minant reaction scheme is $M^\circ + Cl-R \longrightarrow M^1Cl^- + R^\circ$
Organic radicals R° are produced and will initiate polymerization.The occu-
rence of the alternative reaction
$$M^\circ + Cl-R \longrightarrow M^1R^- + Cl^\circ$$
depends on the electron affinity of R,the nature of the metal and that of the
ligands (carbon oxide,arylisocyanide,triarylphosphine,trialkylphosphites etc)
solvation effects.
All these systems generate radicals thermally on mixing both components,which
are individually very stable.Some of them are also active photoinitiators,
e.g.manganese and rhenium carbonyls which absorb and are active at 460 and
380 nm.respectively.
The principle of photosensitization of reactive halide with metal carbonyl
can be nicely illustrated by a recent example of Bamford,Ledwith and cowor-
kers (19) Using N-bromo-acetyl-di(benz-bf-azepine)as reactive halide,polymers
were obtained with endgroup functionalization.Terminal dibenz(bf)azepine
groups permit chain extension by cyclodimerization.
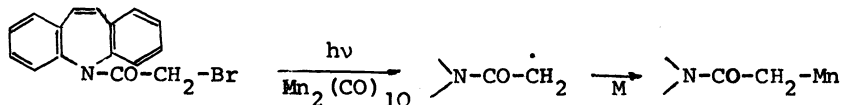
It was however discovered later that thermal initiation can result from the
reaction of organotransition metal complexes with compounds with no abstrac-
table halide or even halide free,e.g.tetrafluoroethylene,chlorotrifluoroethy-
lene,alkyl acetylene dicarboxylate,dimethyl fumarate,mostly olefines with
strong electronattracting groups (20,21).Initiating radicals result in these
cases from the addition at the olefinic bond, e.g.

$$(CO)_5Mn-CF_2CF_2^\circ \quad , \qquad (CO)_5Mn-\underset{\underset{CO_2Me}{|}}{C} = C^\circ CO_2Me$$

and the polymer will contain these fragments as end groups.On this principle
is based the photoinitiated polymerization of tetrafluoroethylene in acetic
acid at ambient temperature by transition metal carbonyls as $Mn_2(CO)_{10}$,
$Re_2(CO)_{10}$,$Os_3(CO)_{12}$ as well as that of common vinyl monomers containing low
concentrations of tetrafluoroethylene.
It is important to point out here the significance of these new methods of
thermal and/or photochemical initiation of polymerization.They permit to
functionalize polymers by introducing active groups at the polymer chain ends
and permit therefore the synthesis of block polymers.Indeed by introducing
one or two terminal CX_3 groups per chain block polymerization with a second
monomer becomes easy and will lead to a $(A_xB_y)_n$ multiblock polymer in which   n
may vary and depends on the chain termination processes of both A and B gro-
wing chains.

$$--A_x-CX_3 \xrightarrow{\ h\nu\ }{Mn_2(CO)_{10}} \quad --A_x-CX_2^\circ \xrightarrow{\ \ }{B} \quad --A_x-CX_2-B_y--$$

Similarly the presence of thermolabile $(CO)_5Mn-CF_2-CF_2-$ endgroups yields
on decomposition in the presence of a second monomer   block polymers:

$$--A_x-CF_2-CF_2-Mn(CO)_5 \xrightarrow{\ B\ }{\triangle t} Mn(CO)_5 + \quad --A_x-CF_2-CF_2-B_y-$$

Compared to the anionic living polymerization method,the resulting block po-
lymers have a much less defined structure;however this technique is much more
versatile since it is applicable to a much broader range of vinyl monomers.

The synthesis of graft copolymers is also possible by this method as far as
the polymer chains carry adequate side-groups,e.g.polymers or copolymers of
vinyltrichloro/tribromo acetate (22).Depending the chain termination process
of the second monomer grafting (chain branching) and/or network formation
will result following the reaction scheme:

Another example of grafting is based on the fact that $C_2F_4/Mn_2(CO)_{10}$
growing chains react rapidly with benzene by substitution and by addition
reaction:

substitution   addition

Applied to styrene-methyl methacrylate copolymers the method produces grafts
of short polytetrafluoroethylene chains with $Mn(CO)_5$ end groups.The functio-
nalized copolymer constitutes a polyfunctional macroinitiator which can be
grafted at 100°C by scission of the $-CF_2-Mn(CO)_5$ bonds in the presence of
second monomer,e.g. N-vinylpyrrolidone (23)

A last method of free radical initiation described by Bamford (24) is based
on the use of transition metal chelates,in which the metal is in a high oxi-
dation state,either alone or   together with an electrodonor additive.
Thus manganic acetylacetonate on heating around 110° initiates the polymeri-
zation of styrene,methyl methacrylate.

In the presence of a suitable electrondonor such as dimethylsulfoxide, active
and quasi-selective initiation of free radical polymerization occurs at 25°C
One assumes partial ligand displacement by the electrodonor additive,follo-
wed by insertion of monomer and electron transfer,producing Mn^2 and the
initiating radical (25) Contrarily to the metal carbonyls,it must be remarked
that photoinitiation with metal chelates has only a low quantum yield of
initiation (around 0.01-0.02)
Nevertheless vanadium chelate photosensitivity was used recently (26) for
photografting onto preformed polymers carrying pendant hydroxyl groups,e.g.
2-hydroxyethyl methacrylate-methyl methacrylate copolymers.The chelating
group is the oxo-bis(8 quinolyl-oxo)vanadium[5] (OVO_2OR) of following formula:

Irradiation of such copolymers,in methyl methacrylate solution gives rise
to extensive gelation,resulting from grafting and crosslinking through
the macroradicals,as represented in following scheme

$$-\!\!\left|\text{CO-O-CH}_2\text{-CH}_2\text{-O-VOQ}_2 \xrightarrow[\text{365 nm}]{h\nu} -\!\!\left|\text{COO-CH}_2\text{-CH}_2\text{-O}^\circ \rightarrow -\!\!\left|\text{CO-OCH}_2\text{CHOH}^\circ\right.\right.\right.$$
$$+\ \text{VOQ}_2 \quad\quad\quad \searrow_{\text{MMA}}$$

The method presents the advantage to operate at relatively long
wave length.Undoubtedly it is susceptible for further improvements.

CONCLUSION

The present review stresses the main contributions of C.H.Bamford in the
domain of free radical polymerization and free radical kinetics.They have
considerably influenced our fundamental understanding of polymerization
phenomena and the future development of Polymer Science in general.

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