AUTO-ACCELERATION IN FREE RADICAL POLYMERIZATIONS CAUSED BY ORIENTED MONOMER-POLYMER ASSOCIATION COMPLEXES

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Abstract - Auto-accelerated polymerizations are known to occur
in viscous reaction media ("gel-effect") and also when the
polymer precipitates as it forms. It is generally assumed that
the cause of auto-acceleration is the arising of non-steady-
state kinetics created by a diffusion controlled termination
step. Recent work has shown that the polymerization of acrylic
acid in bulk and in solution proceeds under steady or auto-
accelerated conditions irrespective of the precipitation of
the polymer. On the other hand, a close correlation is esta-
blished between auto-acceleration and the type of H-bonded
molecular association involving acrylic acid in the system.
On the basis of numerous data it is concluded that auto-acce-
leration is determined by the formation of an oriented mono-
mer-polymer association complex which favors an ultra-fast
propagation process. Similar conclusions are derived for the
polymerization of methacrylic acid and acrylonitrile based on
studies of polymerization kinetics in bulk and in solution and
on evidence of molecular associations. In the case of acrylo-
nitrile a dipole-dipole complex involving the nitrile groups
is assumed to be responsible for the observed auto-accelera-
tion.

INTRODUCTION

The polymerization of a monomer under "normal" conditions follows the rules of
stationary state and the rate, which then remains constant over a fairly broad
range of conversions, is expressed in terms of the classical equations of
chain reactions. It is well known, however, from the study of numerous systems
that after a certain conversion to polymer is reached, the reaction medium
turns very viscous and the rate may then increase gradually leading to kinetic
anomalies referred to as the "gel-effect". This effect, which was reported for
the first time in 1939 by NORRISH and BROOKMAN (1) to occur in the bulk poly-
merization of methyl methacrylate, is sometimes wrongly called "TROMMSDORFF
effect" on the basis of a report on German science during world war II, pu-
blished by the Allied Forces in 1945. The "gel-effect" is characterized by
auto-acceleration and, under extreme conditions, when the heat of the reac-
tion is not dissipated fast enough, it may result in thermal explosions.

Deviations from "normal" kinetic behaviour are also known to occur in polymerizing systems when the resulting polymer is not soluble in the reaction medium. In such an event, the growing chains precipitate after having reached a certain length and form a second phase together with the "dead" polymer. The physical state of the precipitated polymer determines the type and the extent of kinetic anomalies observed in such cases. In systems where the polymer is highly swollen by the reaction medium and forms a fluid and transparent coacervate the growing chains separate as tiny droplets which coalesce and thereby favour bimolecular chain termination. Precipitation under such conditions leads to a reduction of over-all rates and of molecular weights. In an other extreme case, when the polymer swells very little in the system, the tightly coiled chains show little tendency to associate and the polymer then precipitates as a fine powder in which each particle comprises one or a small number of chains. In such an event, the termination step, which requires the interaction of two growing chains, may become very slow and one observes kinetic anomalies similar to those occuring in the gel-effect. The conversion curves exhibit auto-acceleration and the order of the reaction with respect to the rate of chain initiation is higher than one half, and usually lies between one half and one. Other anomalies may appear in such systems as will be pointed out below.

It is most generally accepted that the auto-accelerated character of these reactions directly follows from the non-stationary conditions created in the system as a result of the sterically hindered termination step. The growing chains are assumed to be immobilized in the viscous medium ("gel-effect") or tightly coiled and occluded in dead polymer particles (under precipitating conditions). This leads to two consequences : on the one hand a gradual increase in the number of growing chains (non steady-state conditions) which is assumed to be the actual cause of auto-acceleration and on the other hand long-lived radicals build up in the system which are responsible for long-lasting ESR signals and for a "post-polymerization", a process which goes on for a considerable length of time once the sample has been removed from the light source or from the radiation field in the case of photochemical or radiation chemical initiation. It was further noticed in several systems that the molecular weight of the polymer rises at the point when auto-acceleration sets in.

It is clear, however, that a simultaneous increase in polymerization rate and molecular weight could either follow from a reduction in the rate of termination or from an increase in the rate of propagation. This last possibility has seldom been considered, except in some of the very early studies such as in the work of Bengough and Norrish (2) on the bulk polymerization of vinyl chloride where a "catalytic" action was attributed to the precipitated polymer.

The purpose of the present communication is to demonstrate that in the case of some polar monomers, auto-acceleration under precipitating conditions is at least in part caused by accelerated propagation in monomer-polymer association complexes. This conclusion is reached on both kinetic evidence and the investigation of molecular associations.

POLYMERIZATION OF ACRYLIC ACID

Poly(acrylic acid) is not soluble in its monomer and in the course of the bulk polymerization of acrylic acid the polymer separates as a fine powder. The conversion curves exhibit an initial auto-acceleration followed by a long pseudo-stationary process (Ref. 3). This behaviour is very similar to that observed earlier in the bulk polymerization of acrylonitrile. The non-ideal kinetic relationships determined experimentally in the polymerization of these two monomers are summarized in Table 1.

It clearly appears that the kinetic features observed in both systems are strikingly similar. In addition, the poly(acrylic acid) formed in bulk over a fairly broad range of temperatures (20 to 76°C) exhibits a high degree of syndiotacticity and can be crystallized readily (Ref. 3).

A detailed investigation of the polymerization of this monomer in a series of solvents has shown, however, that the auto-accelerated character of the reaction is not related to the precipitation of the polymer.

TABLE 1. Comparison of the kinetic features observed in the bulk
polymerization of acrylic acid and acrylonitrile

	Acrylonitrile	Acrylic acid
Polymer phase	Precipitates as a fine powder	Precipitates as a fine powder
Conversion curves	Auto-accelerated until 2-3 per cent conversion ; thereafter linear ("Auto-acceleration index" "β" = 1.3 at 20°C)	Auto-accelerated until 1-2 per cent conversion ; thereafter linear ("β" = 1.8 - 2.0 at 20°C)
Order with respect to initiation (at 20°C)	0.8	0.8
Post-polymerization (at 20°C)	Continues for several months	Continues for a few days
Over-all activation energy	45 KJ/mole between 10 and 60°C. 12.5 KJ/mole above 60°C.	11.3 KJ/mole between 20 and 76°C

Thus, linear conversion curves and atactic polymers are obtained if the mono-
mer is diluted in such non-associating solvents as toluene, n-hexane, carbon
tetrachloride and chloroform, in spite of the precipitation of the polymer,
whereas, both auto-acceleration and syndiotacticity persist for fairly high
dilutions in water, methanol and dioxane even under conditions where the reac-
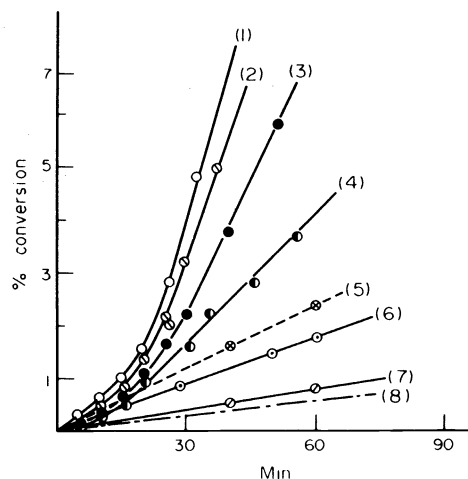tion medium turns homogeneous (Ref. 4).

Fig. 1. Conversion curves for
the polymerization of acry-
lic acid in toluene solutions
(Ref. 4). Monomer concentra-
tions : (volume per cent)
1:100 ; 2:95 ; 3:90 ; 4:85 ;
5:80 ; 6:65 ; 7:50 ; 8:27.
The polymer precipitates as
a fine powder at all concen-
trations. Initiation by gamma-
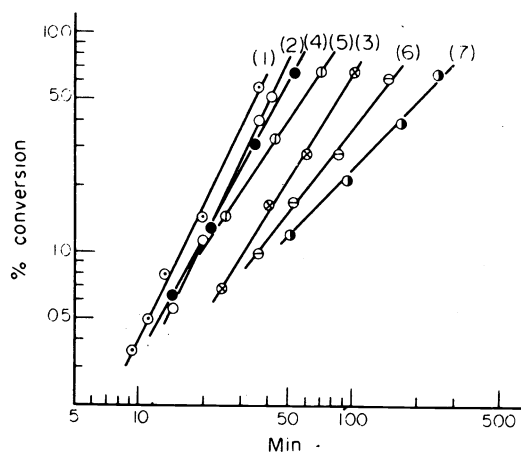rays at 20°C and 12 rad/min.

Fig. 2. Log-log plots of the conver-
sion curves for acrylic acid in metha-
nol solutions (Ref. 4). Monomer con-
centrations : (volume per cent) 1:100 ;
2:80 ; 3:75 ; 4:60 ; 5:50 ; 6:25 ;
7:15.
The polymer precipitates as a fine
powder for monomer concentrations of
100 to 75 per cent ; it forms a swol-
len gel for 75 to 50 per cent monomer ;
the reaction medium is homogeneous
for less than 50 per cent monomer

Figures 1 and 2 show the corresponding conversion curves in toluene and in methanol solutions respectively. In the latter case log-log coordinates are used to represent the data. The conversion curves are then linear and their slope β, which is the exponent of time in the relation : per cent conversion = Kt^{β}, measures the extent of auto-acceleration. β is referred to as the "auto-acceleration index". For pure acrylic acid β = 1.8 - 2.0 ; in non polar solvents β tends towards unity.

On the other hand, a good correlation was established between auto-acceleration and the type of molecular association involving the monomer in the system. Pure acrylic acid associates to "cyclic dimers" and "linear oligomers" by hydrogen bonding. The two species are in equilibrium.

(I)   (II)

Cyclic dimers   Linear oligmers
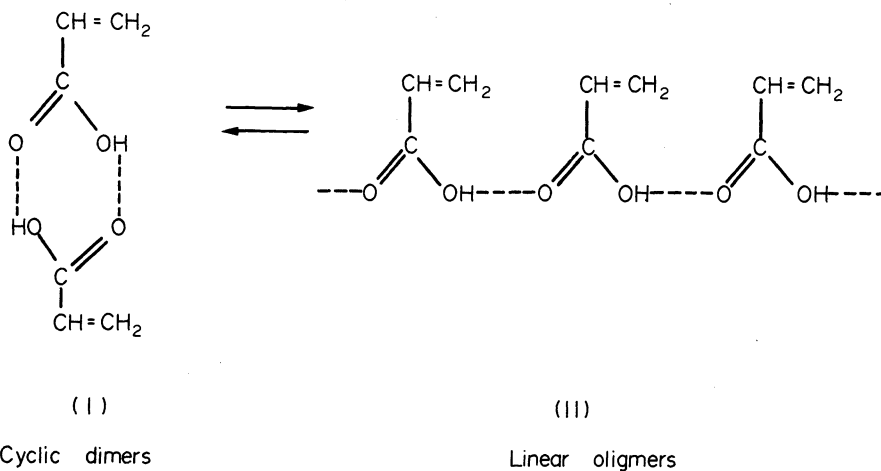
The relative abundance of each of these species can be followed for instance by infrared analysis (Ref. 4 & 5). Figure 3 shows the I.R. spectrum of acrylic acid in the 1700 cm^{-1} region. The main peak at 1705 cm^{-1} is due to the vibration of the carbonyl group in the cyclodimeric form, whereas the shoulders at 1730 and 1740 cm^{-1} correspond to "open dimers" and "linear oligomers".
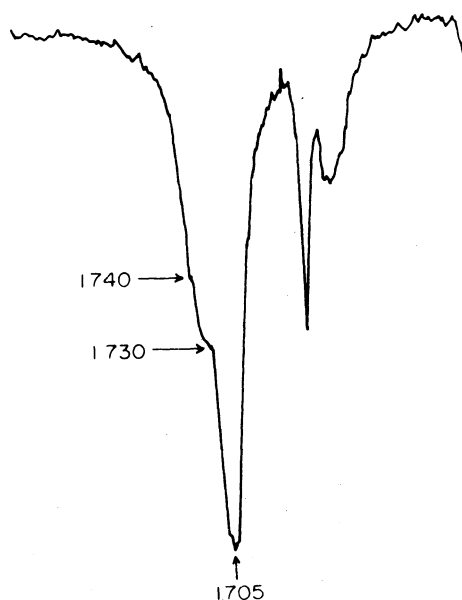

Fig. 3. Infra-red spectrum of acrylic acid in the 1700 cm^{-1} region.

Dilution in non-polar solvents shifts the equilibrium to the dimeric form (Fig. 4) while an increase in temperature favors the linear oligomers (Fig. 5).
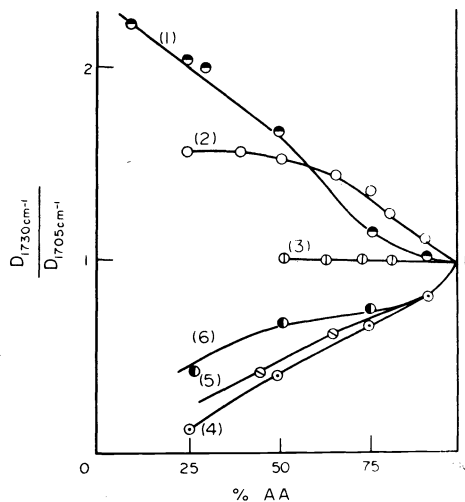

Fig. 4. Ratios of optical densities at 1730 cm^{-1} (linear oligomers)/1705 cm^{-1} (cyclic dimers) as a function of mole fraction of acrylic acid in various solvents : 1:dioxane ; 2:methanol ; 3:acetic acid ; 4:chloroform ; 5:toluene ; 6:CCl$_4$ (Ref. 4).
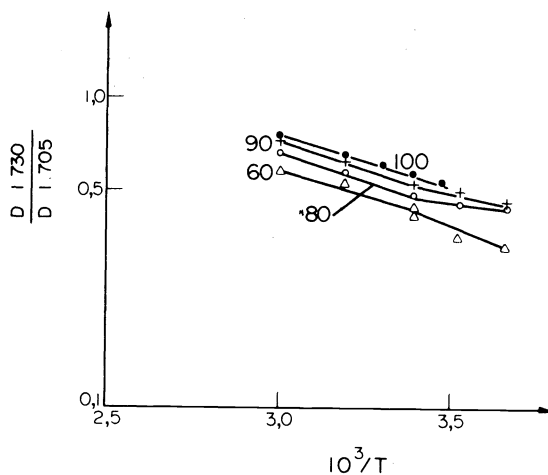
Fig. 5. Ratios of optical densities at 1730 cm^{-1}/1705 cm^{-1} plotted in Arrhenius coordinates for pure acrylic acid (100) and acrylic acid solutions in toluene at 90, 80 and 60 volume per cent of monomer (Ref. 5).

Experiments conclusively demonstrated that auto-acceleration vanishes upon dilution when the oligomers are replaced by cyclodimers (Ref. 4) while an increase in temperature, which restores oligomers again brings about auto-acceleration and syndiotacticity (Ref. 5). This good correlation between the presence of oligomers and auto-acceleration does not, however, explain why auto-acceleration occurs. Since dimers and oligomers are present in the system right from the beginning the mere presence of oligomers cannot be taken as the cause of auto-acceleration. It was therefore assumed that such oligomers may associate with the polymer arising in the initial stages of the reaction to form a structure III in which the monomer is aligned in a regular
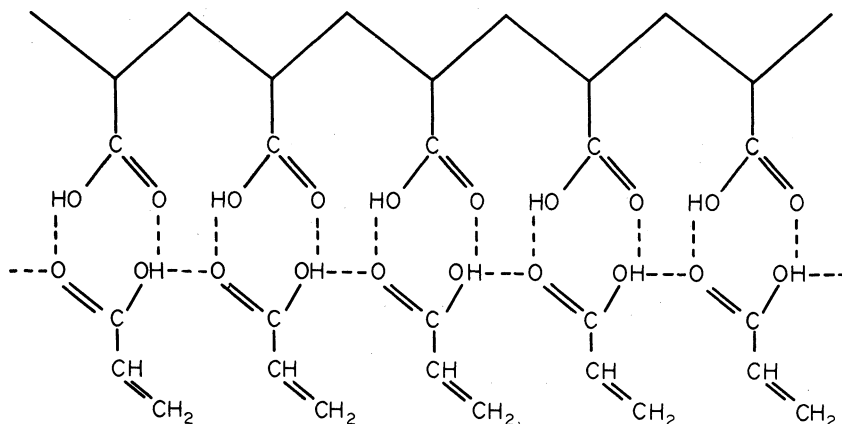
(Structure III)

manner on the polymeric matrix. In this ordered, "pre-oriented" structure an ultra-fast propagation is assumed to occur.

The gradual accumulation of structures III in the initial stages of the reaction could account for its auto-catalytic character until a "stationary-state" is reached in which the surface of the precipitated polymer available for such association with monomer remains practically constant. A structure such as III could also be responsible for the stereo-control of the propagation step. Indeed, the polymer formed at conversions below 2 per cent exhibited much lower stereoregularity than at higher conversions (see Fig. 6).
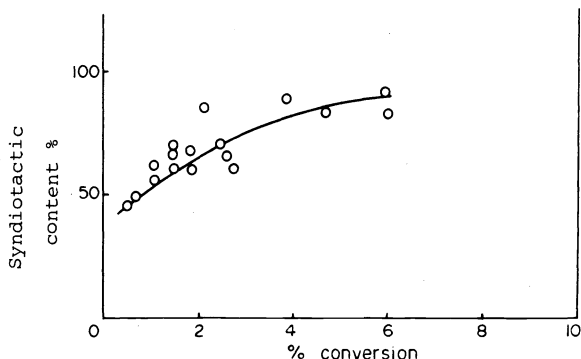

Fig. 6. Percentage of syndiotactic polymer formed at very low conversions in the bulk polymerization of acrylic acid (Ref. 4).

These various peculiar consequences connected with the arising of structure III will be referred to as "matrix effect".

It should be noted that the absence of a matrix effect when the monomer is only associated in the cyclodimeric form suggests that structure I is more stable than the association of the monomer with the polymer and that therefore long ordered structures of type III do not arise. In very dilute acrylic acid solutions in hydrocarbons or chlorinated compounds a matrix effect (auto-acceleration) is again observed. This is believed to arise as a result of a structure III formed by the association of the polymer with "free" monomer (Ref. 4).

On dilution in solvents which may associate via hydrogen bonds (water, methanol, dioxane) the situation is more complex. I.R. and Raman spectroscopy indicate the formation of various monomer-solvent complexes (Ref. 4 & 6). The corresponding absorption bands are in the same range as the characteristic bands for open dimers and oligomers and the latter cannot therefore be determined quantitatively. However, the viscosity of carboxylic acids was found to rise on addition of water or methanol (Ref. 4 & 7) suggesting that these solvents bind together "oligomers". The persistence of auto-acceleration and syndiotacticity down to fairly high dilution further indicates that the oligomeric structure is maintained. One could also assume that monomer-solvent association complexes are formed which generate more easily an ordered structure such as III. Under very special conditions an "exaltation" of the matrix effect was observed leading to auto-acceleration indexes as high as 10 or even 15. The species responsible for this exaltation was assumed to be the complex (acrylic acid)$_2$-methanol which was characterized in such solutions (Ref. 6).

POLYMERIZATION OF METHACRYLIC ACID

Methacrylic acid also polymerizes in bulk under precipitating conditions. It forms molecular associations very similar to those of acrylic acid. However, the conversion curves were found to be linear under a variety of experimental conditions : temperatures of 16.5 to 60°C and broad ranges of initiation rates and monomer concentration in numerous solvents (Ref. 7). It was assumed that structures of type III do arise but, owing to steric hindrance and to the rigidity of the poly(methacrylic acid) molecule, the monomer cannot align to

form a "pre-oriented" complex as in the case of acrylic acid and propagation
is not favored.

Investigation of the copolymerization in bulk of acrylic and metha-
crylic acids showed that auto-acceleration vanishes in the monomer mixture
which generates a copolymer containing on the average one methacrylic for
each acrylic unit (Ref. 8). Figure 7 is a plot of various conversions curves
in log-log coordinates. This result conclusively demonstrates that sequences
of acrylic acid units of a certain length are required for auto-acceleration
to set in, due to the regular alignment of monomers along the polymeric
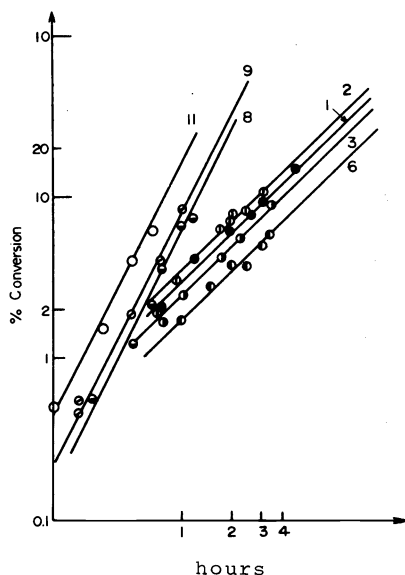matrix.

Fig. 7. Log-log plots of the conversion curves of the copolymeriza-
tion of acrylic acid with methacrylic acid (Ref. 8). Mole % acrylic
acid in the mixture : 1:0 ; 2:23.5 ; 3:45.5 ; 6:71 ; 8:83.2 ;
9:86 ; 11:100.
The copolymer formed in a mixture of 75 mole per cent acrylic acid
contains 50 per cent acrylic acid and 50 per cent methacrylic acid
units.

Auto-acceleration was observed in the homopolymerization of methacry-
lic acid over limited concentration ranges in methanol and in water. Perhaps
under such conditions swelling of the polymer favors monomer diffusion lea-
ding to a larger amount of pre-oriented structures III. Alternatively, a
monomer-solvent complex may arise which favors a pre-oriented structure and,
thus, may be responsible for the onset of a matrix effect (Ref. 9).

POLYMERIZATION OF ACRYLONITRILE

The bulk polymerization of acrylonitrile has been studied by numerous workers
(for a literature survey on the problem see ref. 10 & 11). The kinetic fea-
tures of this reaction at room temperature are summarized in Table 1. It is
one of the typical examples of polymerization under heterogeneous conditions
in which the anomalies are generally assumed to arise as a result of non-
stationary conditions caused by the "occlusion" of growing chains in the pre-
cipitated polymer (Ref. 10). The presence of occluded radicals was indeed
demonstrated by ESR measurements (Ref. 12) and by reaction with DPPH (Ref.13).
These long-lived species are also responsible for the post-polymerization
observed in the photo-or radiation-initiated reaction after the radiation
has been switched off.

On the other hand, it should be noted that organic nitriles
are known to associate to form dipole-dipole complexes (Ref. 14). The bond

dissociation energy of such associated dimers is ca. 20 Kj.mole^{-1} (Ref. 15)
a value of the same order of magnitude as that of hydrogen bonds. The lack
of solubility of polyacrylonitrile in its monomer is at least in part due to
the formation of -CN---CN- bridges which link polymer chains together. This
structure is also responsible for the high melting temperature of the poly-
mer (Ref. 15).

        The data presented in Table 1 snow that the kinetic features of the
bulk polymerization of acrylonitrile are very similar to those observed with
acrylic acid. It therefore seems pertinent to query whether a matrix effect
could not arise in the polymerization of acrylonitrile through a regular
orientation of monomer molecules along the polymeric matrix involving dipole
interaction of the -C≡N groups (structure IV). Several recent studies carried
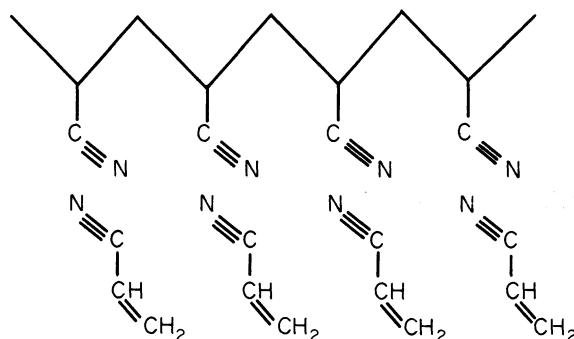
out in these laboratories did provide evidence for a matrix effect operating
in the polymerization of acrylonitrile. These include :

        Bulk polymerization of acrylonitrile at various temperatures.

        Polymerization of acrylonitrile adsorbed on polyacrylonitrile.

        Swelling of polyacrylonitrile in nitriles.

        Polymerization in polar solvents.

Bulk polymerization of acrylonitrile at various temperatures
The bulk polymerization of acrylonitrile was recently reinvestigated at tem-
peratures ranging from -9 to 85°C, using gamma-rays for initiation (Ref. 16).
In order to evaluate semi-quantitatively the extent of auto-acceleration all
conversion curves were plotted in log-log coordinates. The slope "β" of the
resulting straight lines, defined as the "auto-acceleration index", was found
to be essentially constant at all temperatures from 20 to 85°C and was 1.25
to 1.30. Below 20°C, the value of β dropped to 1.15. The Arrhenius diagrams
based on the "initial" and "pseudo-stationary" rates are shown in fig. 8.
These diagrams exhibit two breaks at ca.10 and 60°C respectively, the acti-
vation energies are 12.5 KJ.mole^{-1} above 60°C, 44-46 KJ.mole^{-1} between 10 and
60°C and are poorly defined below 10°C. The shape of the diagrams suggests
the existence of three temperature zones for the reaction. Studies of the
"post-polymerization" further showed that this process which is very marked
at 20 and 25°C (see also Ref. 17) is very slow at 0°C and strongly reduced
above 60°C. Figure 9 shows some of these results. Finally, the order of the
reaction with respect to rate of initiation (dose-rate of gamma-rays) is
0.8 at 0, 20 and 50°C but drops to 0.6 at 75°C (Ref. 16).

        From these observations it was concluded that the bulk polymerization
of acrylonitrile proceeds by different mechanisms depending on the tempera-
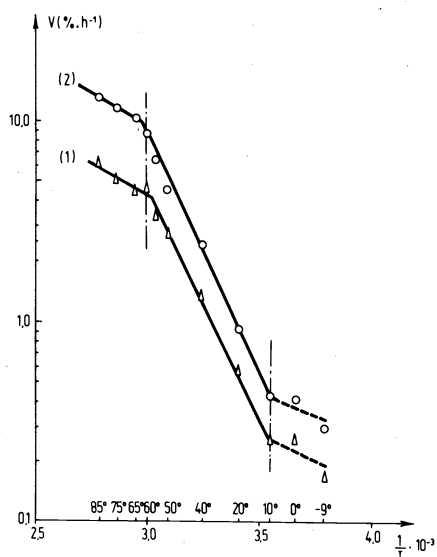ture at which the reaction is carried out.

Fig. 8. Arrhenius diagram of
the gamma-ray initiated poly-
merization of acrylonitrile
in bulk (Ref. 16).
Curve 1 : "Initial rates" ;
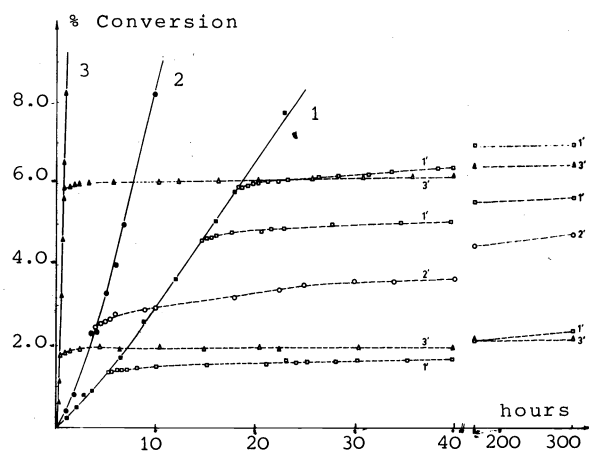curve 2 : "Pseudo-stationary
rates".

Fig. 9. Post-polymerization of acry-
lonitrile following the gamma-ray
initiated reaction (shown by the
steep curves) at 0° (curve 1),
20° (curve 2) and 75°C (curve 3)
(Ref. 18).

The reaction above 60°C.   Bamford and Jenkins (12) have shown earlier that
the radicals trapped in the precipitated polymer disappear rapidly above
60°C suggesting a significant bimolecular interaction of growing chains-ends.
This conclusion is supported by the drop to 0.6 of the dose-rate exponent in
the gamma-ray initiated reaction at 75°C and by the reduction of the post-
polymerization above 60°C (Fig. 9). Popov et al. (19) further found that the
swelling of polyacrylonitrile by its monomer suddenly increases above 70°C
which corresponds to a transition temperature of the system.

      The bulk polymerization of acrylonitrile in this range of temperatu-
res exhibits kinetic features very similar to those observed with acrylic
acid (cf. Table 1). The very low over-all activation energies (11.3 and
12.5 KJ.mole^{-1}) found in both systems suggest a high temperature coefficient
for the termination step such as would be expected for a diffusion controlled
bimolecular reaction involving two polymeric radicals. It follows that for
these systems, in which radicals disappear rapidly and where the post-polyme-
rization is strongly reduced, the concepts of non-steady-state and of occlu-
ded polymer chains can hardly explain the observed auto-acceleration. Hence
the auto-acceleration of acrylonitrile which persists above 60°C and exhibits
the same "auto-acceleration index" as at lower temperatures has to be accoun-
ted for by another cause.

      In view of the striking similarities between the kinetic parameters
found for acrylonitrile in this temperature range and for acrylic acid it is
suggested that in both systems the auto-acceleration originates from the same
cause, namely the ability of the polymer formed in the very early stages of
the reaction to act as a matrix onto which the monomer associates to form
regularly oriented structures such as III and IV in which propagation is
assisted by the pre-orientation of the monomer molecules.

The reaction below 10°C.   In this temperature range the "occlusion effect"
is operating. Numerous growing chains become occluded in the dead polymer as
demonstrated by long lasting ESR signals. The very small post-polymerization
observed in this systems indicates that the monomer diffusion towards the
active chain-ends is very slow. This is presumably related to the very low
degree of swelling of the polymer. The kinetics are dominated by this "occlu-
sion effect". The over-all activation energy is poorly defined and is presu-
mably determined by a complex ratio of propagation to monomolecular (?) ter-

mination which strongly depends on external parameters.

The auto-acceleration observed under such conditions is reduced
(β = 1.15) and could partially result from non-steady-conditions but also
from a "matrix effect" operating on the surface of unswollen polymer parti-
cles. It should be noted in this respect that the post-polymerization which
is induced by the growing chains occluded in the precipitated polymer exhi-
bits an initial rate very much lower than the rate observed during irradia-
tion (Fig. 9) which suggest that the contribution of the growth of occluded
chains to the over-all rate is small.

The reaction between 10 and 60°C.   In this range of temperatures the activa-
tion energy is very high (44-46 Kj.mole^{-1}). Since the polymer gradually swells
in its monomer as the temperature rises the corresponding increase in rate
cannot result from a reduction in chain termination. It seems much more likely
to assume that the gradual swelling of the polymer favors chain propagation
which introduces an additional term to the activation energy. This term, which
amounts to ca. 30 KJ.mole^{-1}, presumably corresponds to the increasing concen-
tration of monomer around the growing chains as the temperature rises and
perhaps also to an increased contribution of propagation in oriented monomer
aggregates ("matrix effect").

Polymerization of acrylonitrile adsorbed on polyacrylonitrile
An intimate mixture of polyacrylonitrile solvated by its monomer is obtained
if one melts acrylonitrile crystals which have been subjected to high energy
radiation at low temperatures. The polymer forms under irradiation within
the crystal lattice and upon melting, a gel-like phase is obtained in which
the individual polymer molecules do not aggregate, presumably because most
of the CN groups are associated in pairs with the -CN groups of the monomer.
Such a polyacrylonitrile solvated by its monomer should indeed be an ideal
medium for the matrix effect to operate.

Experiments were therefore performed in which crystalline acryloni-
trile was preirradiated to a certain dose at -196 and at -95°C. The reaction
mixture was then warmed to room temperature and the excess monomer separated
by gravity (by keeping the irradiated ampoule up-side down for 16 hours).
The gel-like mixture of acrylonitrile and polyacrylonitrile was then irradia-
ted at 20°C and the rate of conversion of monomer determined gravimetrically
(Ref. 20). Figure 10 shows some of the conversion curves obtained under such
conditions. It appears that the rate of polymerization of acrylonitrile can
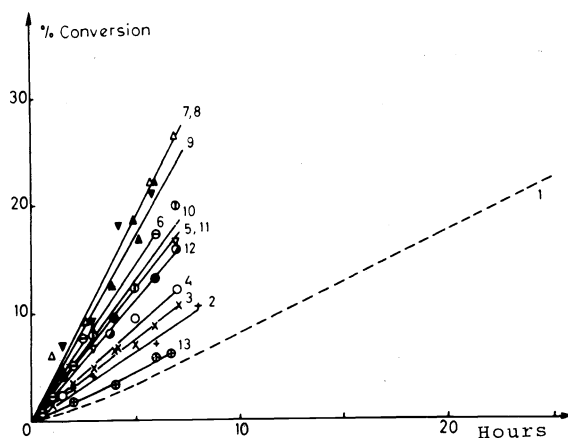be increased tenfold in the presence of highly divided polyacrylonitrile.

Fig.10. Polymerization of acrylonitrile at 20°C in an intimate mix-
ture with a highly divided polyacrylonitrile obtained by pre-irradia-
tion of the crystalline monomer at -95°C (Ref. 20). Doses of pre-
irradiation of 0.11 Mrad (curve 2) to 3.14 Mrad (curve 12). The bro-
ken curve 1 pertains to the polymerization of pure acrylonitrile ;
curve 13 is obtained in the presence of polyacrylonitrile pre-poly-
merized at 20°C.

To ensure that no "catalyst" was created during the irradiation of crystal-
line acrylonitrile, the monomer separated from the "gel" was also irradiated.
Its rate of polymerization at 20°C was found to be the same as that of pure
acrylonitrile. Moreover, irradiation of acrylonitrile in the presence of
polymer formed at 20°C did not exhibit any significant acceleration over the
reaction in bulk (curve 13 in Fig. 10).

Swelling of polyacrylonitrile in nitriles
If acrylonitrile associates with its polymer to form oriented structures of
type IV one should be able to detect a certain amount of swelling of the
polymer in its monomer even at room temperature. Experiments along these
lines were carried out using a film of polyacrylonitrile cast from DMF solu-
tion and carefully dried. It was indeed found that the film slowly absorbs
monomer. The limiting swelling ratio was reached within ca. 60 hours and was
16 per cent at 25°C (curve 2 in Fig. 11) and 18 per cent at 75°C (curve 3
in Fig. 11). These correspond on the average to one monomer molecule per
6-7 monomer units in the polymer. More pronounced swelling was observed in
50-50 per cent mixtures of acrylonitrile with acetonitrile. The swelling
ratio was 28 per cent after 100 hours which corresponds to 1 monomer per
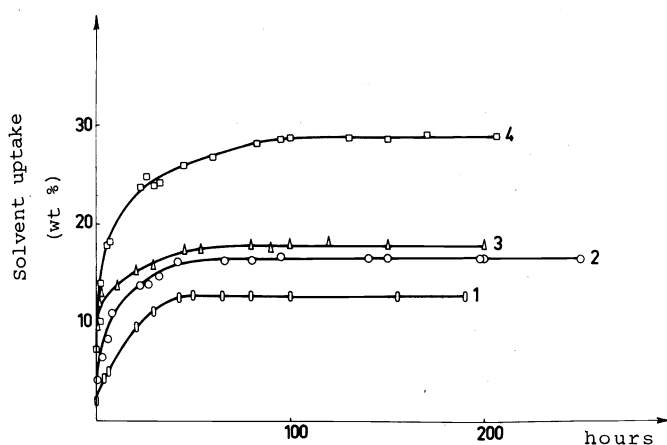4-5 units (curve 4 in Fig. 11).

Fig. 11. Kinetics of the swelling of a polyacrylonitrile film in
1 a 50-50 per cent mixture of acrylonitrile with toluene at 25°C.
2 pure acrylonitrile at 25°C. 3 pure acrylonitrile at 75°C.
4 a 50-50 per cent mixture of acrylonitrile with acetonitrile at
25°C. (Data of Ref. 18).

The very low rate of swelling suggests a complex process which could be the
gradual (and slow) exchange of polymer-polymer to polymer-monomer associa-
tion via dipole-dipole interactions of CN groups. A similar effect was obser-
ved earlier in the swelling of PTFE membranes grafted with acrylic and metha-
crylic acid (Ref. 21). Such membranes reached their limiting swelling
within 10-15 minutes in water. Whereas, 100 to 500 hours were required to
swell the same membranes in carboxylic acids. The limiting swelling reached
in these experiments corresponded to a "molar solvation" of 0.6 to 0.9 car-
boxylic monomers per carboxylic unit in the polymer (Ref. 21). Taking advan-
tage of the swelling of polyacrylonitrile in its monomer, experiments were
recently performed in which acrylonitrile was grafted in the bulk of PTFE
films using gamma-ray initiation. In this process the grafted front moves
inwards in the bulk of the film by a progressive swelling of the grafted
zones. 50 μm thick PTFE films were successfully grafted in the bulk by irra-
diation at 20°C in pure acrylonitrile to a grafting ratio of 30 per cent.
Such a process can only occur if the grafted zones actually swell in the
reacting monomer.

        The above results demonstrate that polyacrylonitrile is solvated by
its monomer and that the process involves molecular association presumably
via dipole-dipole interaction of the CN groups.

Polymerization of acrylonitrile in polar solvents
Polar solvents are expected to interfere with the association of nitrile
groups in pairs and to replace the nitrile-nitrile association complex by a
nitrile-solvent association. Under such conditions structures such as IV
should no longer arise and the "matrix effect" should disappear.

Experiments conducted with dimethylformamide solutions at 20°C have
shown that the "auto-acceleration index" β indeed decreases upon dilution and
becomes 1.0 in a 40 per cent monomer solution where the polymer still preci-
pitates (Ref. 18). The data are summarized in Table 2.

Table 2. Influence of diluting acrylonitrile in DMF on the value of
the "auto-acceleration index" β (Ref. 18).

Acrylonitrile (volume per cent)	100	90	80	70	60	50	40	30	20	15	10
			Precipitating					Homogeneous			
β	1.30	1.30	1.25	1.15	1.10	1.10	1.0	1.0	1.0	1.0	1.0

However, DMF is a solvent for polyacrylonitrile and the polymeriza-
tion occurs in a homogeneous medium for solutions containing 30 per cent mono-
mer or less. This reduces the value of these experiments as an argument to
show the influence of a matrix effect. Indeed the fact that auto-acceleration
disappears when DMF is added to acrylonitrile was considered as a proof for
the fact that precipitation of the polymer was the cause of auto-acceleration.

Further experiments were therefore carried out with polar sol-
vents which do not dissolve the polymer. Most striking results were obtained
with trichloroacetic acid. The polymerization of acrylonitrile in this sol-
vent was found to proceed under precipitating conditions at all concentra-
tions. In spite of this, the conversion curves were perfectly linear in solu-
tions containing 60 volume per cent monomer or less (Ref. 18). Moreover,
these systems exhibit marked post-polymerization showing the presence of
long-lived radicals.

These results conclusively demonstrate that precipitation of poly-
acrylonitrile as a fine powder and occlusion of growing chains resulting in
post-polymerization do not bring about auto-acceleration if a highly polar
solvent is present in the system. This solvent prevents the dipole-dipole
interaction of the -CN groups and thus, prevents the formation of the pre-
oriented association complex which favours propagation and is thus responsi-
ble for auto-acceleration.

CONCLUSION

From the results presented above it can be concluded that the auto-accelera-
ted conversion curves observed in the polymerization of acrylic acid, metha-
crylic acid and acrylonitrile are not caused by non-steady conditions arising
as a result of the occlusion of growing chains in the precipitated polymer.
This occlusion which is responsible for the post-polymerization observed in
these systems only contributes to a limited extent to the over-all rates.

Auto-acceleration is determined by a "catalytic" action of the poly-
mer formed in the early stages of the reaction. The monomer selectively "sol-
vates" the polymer to form a pre-oriented monomer-polymer complex in which
propagation occurs at a much higher rate. At this point it seems difficult to
determine to what extent the conclusions reached above can be generalized to
other systems. Experiments along these lines are in progress.

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