Plasma-Induced Polymerization
6. "Living" Macroradicals as Macromolecular Initiators

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Dedicated to Prof. Dr. Dragutin Fleš at the Occasion of his 60th Anniversary

SUMMARY

Investigations carried out in plasma-induced polymeri-
zation (copolymerization) led to the idea of the exis-
tence of "living" macroradicals. Their presence in
both homogeneous and heterogeneous media was experi-
mentally proved and theoretically explained and their
use as macromolecular initiators in polymerization
processes is exemplified.

INTRODUCTION

In some previously published papers, plasma-induced
homopolymerizations (SIMIONESCU et al., 1980a, 1981)
and copolymerizations (SIMIONESCU et al., 1980b,
1980c) were reported. Experimental data showed that
very high molecular weight compounds were yielded in
such reactions and proved the radicalic nature of the
plasma-induced polymerization process.
This new approach to polymer synthesis presents some
specific features. So, in all cases, no matter if po-
lymerizations or copolymerizations are taken into ac-
count, the bulk processes were characterized by gra-
dual increase of the viscosity of the reaction milieu,
and the molecular weight of the resulting polymers
was observed to grow during days and even weeks after
the initiation took place. In the concrete case of
low conversion plasma-induced bulk homopolymerization
of styrene, for instance, the relative viscosity of
the system increased 200 times in about 400 hours
(post - polymerization period), the molecular weight
(M_w) increased to $2.0 \cdot 10^7$ in the same number of hours,
while the conversion remained under 3% (SIMIONESCU et
al., 1981).
These observations led to the idea of the possible
existence of very long-lived ("living") macroradicals
in such systems; their presence could explain the
very long post - polymerization reactions, observed
not only in our studies, but also in photochemical or

radiation polymerization (e.g., in radiation polymeri-
zation, at 20°C, post - polymerization of acrylic acid
continues for a few days, and of acrylonitrile for se-
veral months (CHAPIRO, 1981)). Considering, in addi-
tion, the possible "capture" or "immobilization" of
these "living" macroradicals and their use as macro-
molecular initiators in polymerization reactions, it
seems interesting to try to prove their existence and
to obtain some data on the characteristics they possess.
The paper presents some experimental results in this
direction and some theoretical considerations explai-
ning their presence and unusually high activity.

EXPERIMENTAL AND RESULTS

The general technique of plasma-induced polymerization
was previously described.
Acrylic acid (AA) and styrene (S) were purified and
dried by the usual methods. Acrylamide (AAm) was twice
recrystallized before use.
The monomers (or their solutions) were evacuated to
$10^{-3} - 10^{-4}$ Torr. The electrical discharges were ope-
rated during 180 or 60 seconds.
The molecular weights of the obtained polymers were
determined by light scattering.
Three experiments were performed to prove the existence
of "living" macroradicals (see also the schematic re-
presentation):

1/ 5 ml of a 3 M/l solution of acrylamide (1.066 g) in
water were degassed, submitted during 180 seconds to
the discharge, and kept in dark, at 22°C, in a closed
reaction tube. Ten hours later, a solid, perfectly
transparent block was obtained. The sample was further
maintained at 22°C, in dark, for 72 hours, and then a
3 M/l solution (30 ml) of AAm (6.397 g monomer), fres-
hly prepared and degassed, was introduced in the reac-
tion tube. A control experiment, carried out simulta-
neously and in identic conditions, was opened a few
moments before the addition of the new amount of mono-
mer, and 0.462 g PAAm (43.33% from the monomer) with
$Mw = 8.600 \cdot 10^5$ were obtained. The reaction tube con-
taining the solid block and the added solution was kept
in dark, at 22°C, for 5 days, then opened, and the re-
action mixture was dissolved under moderate stirring
in water and precipitated in methanol. The sample yiel-
ded 0.800 g PAAm (0.462 g from the initial stage of
the reaction and 0.338 g (10.71% yield) from the added
monomer) with $Mw = 1.834 \cdot 10^7$.

2/ 10 ml (10.5 g, 0.146 mole) acrylic acid were degas-
sed, submitted to a 180 seconds discharge and kept in
dark, at 22°C; the appearance of the white polymer was
observed immediately after the discharge. The conver-

sion reached 100% after 5 hours (Mw = $6.120 \cdot 10^6$, accor-
ding to the control experiment). A freshly distilled
and degassed quantity of 30 ml (31.5 g, 0.438 mole)
AA was introduced after 30 days, and 5 days later the
sample was opened, dissolved in methanol and precipi-
tated in toluene. The reaction yielded 14.802 g PAA
(13.65% from the added monomer was transformed in poly-
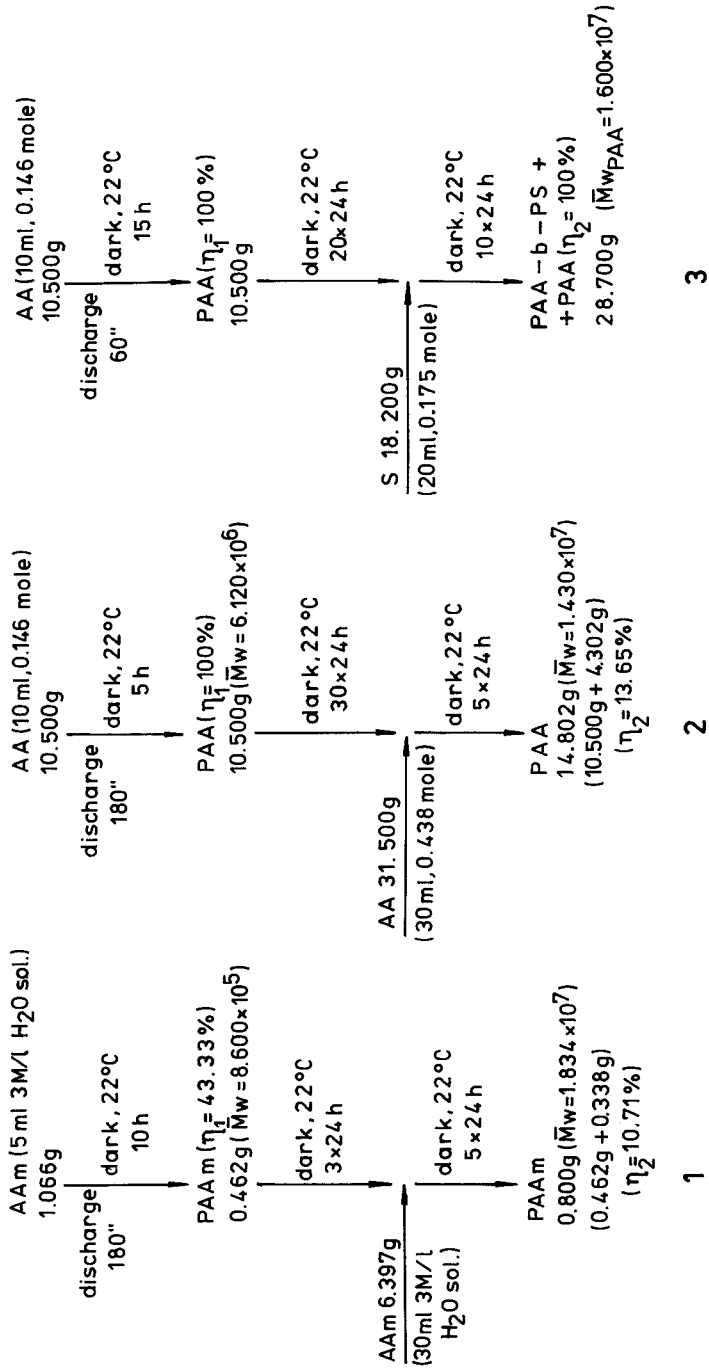mer) with Mw = $1.430 \cdot 10^7$.

3/ 10 ml (10.5 g, 0.146 mole) AA were degassed and
submitted to a 60 seconds discharge; the sample was
kept in dark, at $22^{\circ}C$. A compact, white block obtained
in about 15 hours (conversion 100%). 20 ml (18.2 g,
0.175 mole) of freshly distilled and degassed S was
added after 20 days; the sample was opened after 10
days. The result of the whole process was a very elas-
tic, rubbery compact block (28.7 g, yield 100%). The
material was then stirred in hot toluene, during 3
days, but no PS was precipitated from toluene. (In
fact, this is no surprising – the PS appearance should
signify the existence of transfer reactions to S, or
these reactions are highly improbable at room tempera-
ture). The block was then kept, under stirring, in hot
methanol, for 3 days, and free PAA was precipitated in
toluene (Mw = $1.600 \cdot 10^7$). The material proved to be
completely soluble, in time, even at room temperature,
in dioxane.
More data on this block copolymer will be published in
the next future.

DISCUSSION

The classical kinetic model of free radical polymeri-
zation assumes that the reactivities of the growing
chains are independent of their lengths, and that the
termination rate constant k_t is also independent of
chain length. However, theoretical and experimental
work has shown, last years, that, in diffusion con-
trolled reactions, k_t is function of chain length
(YASUKAWA and MURAKAMI, 1980; O'DRISCOLL, 1981). The
following data argue for this dependence:
i) experimental observations have shown that k_t of two
macroradicals is several orders of magnitude smaller
than that for the recombination of small radicals;
ii) the rate constant of termination reaction between
two macroradicals in solution is inversely proportio-
nal to solvent viscosity, which is directly proportio-
nal to chain length;
iii) in order to react to form "dead" (unactive) poly-
mer, two growing chains must first undergo translatio-
nal diffusion to collide, and then segmental diffusion
to bring the active chain ends into a very small vo-
lume element, where combination or disproportionation
takes place (MAHABADI and O'DRISCOLL, 1977). Both men-

AAm (5ml 3M/l H_2O sol.) 1.066g

discharge 180"

| dark, 22°C
10h

PAAm (η_1= 43.33%) 0.462g (Mw=8.600×10^5)

dark, 22°C 3×24h

AAm 6.397g (30ml 3M/l H_2O sol.)

| dark, 22°C 5×24h

PAAm 0.800g (Mw=1.834×10^7) (0.462g+0.338g) (η_2=10.71%)

1

AA (10ml, 0.146 mole) 10.500g

discharge 180"

| dark, 22°C 5h

PAA (η_1=100%) 10.500g (Mw=6.120×10^6)

dark,22°C 30×24h

AA 31.500g (30ml, 0.438 mole)

| dark,22°C 5×24h

PAA 14.802g (Mw=1.430×10^7) (10.500g+4.302g) (η_2=13.65%)

2

AA(10ml, 0.146 mole) 10.500g

discharge 60"

| dark, 22°C 15h

PAA (η_1= 100%) 10.500g

dark, 22°C 20×24h

S 18.200g (20ml, 0.175 mole)

| dark, 22°C 10×24h

PAA-b-PS + +PAA (η_2=100%) 28.700g (Mw$_{PAA}$=1.600×10^7)

3

tioned processes are viscosity and molecular weight
dependent, the last one being the rate-determining
step for radical termination reactions.
Considering two flexible macroradicals, MAHABADI and
O'DRISCOLL (1977) compared the experimental and theo-
retical termination rate constants for three polymeric
systems, at 298°K (polystyrene - toluene, poly(methyl
methacrylate) - methyl methacrylate, polyoxyethylene -
- water). Both experimental and theoretical data
showed that k_t is decreasing with the increase of the
molecular weight.

Two different cases can be considered in radical poly-
merization processes:
i) when the resulting polymer is not soluble in the
reaction medium, the growing macroradicals, after ha-
ving reached a certain length, precipitate and form a
second phase together with the "dead" polymer. The in-
teraction of two growing chains may be very slow,
these being coiled and occluded in dead polymer parti-
cles (CHAPIRO, 1981).
ii) when the resulting polymer is soluble in the reac-
tion medium, the milieu may become very viscous due to
conversion to polymer and to the increase of the mole-
cular weight. At small initiator concentration, the
macroradicals may reach important lengths and they are
practically isolated one from each other. The system
may immobilize the growing chains in the viscous me-
dium, so that the termination step (diffusion con-
trolled) is hindered.
Both situations lead to long-lived macroradicals in
the systems, macroradicals which are responsable for
post - polymerization processes.

In the particular case of plasma-induced polymeriza-
tion (copolymerization) the initiation takes place at
the very beginning of the reaction. The initiation
efficiency is probably small, so that a small number of
radicals become growing macroradicals by adding mono-
mer molecules. Transfer reactions are highly improba-
ble at room temperature and, in time, part of the
macroradicals are immobilized in the reaction system
so that recombination or disproportionation reac-
tions become practically impossible. In this context,
the ultralong growing chains remain active in time,
becoming "living" macroradicals.
As concerns the reported results, some observations
must be underlined. First, it seems that the hetero-
geneous media are more adequate for the "capture" of
the "living" macroradicals. Secondly, it has to be
mentioned that in the third experiment the contact
between the added styrene and the existent PAA was far
from being perfect, so that an estimation of the
"dead" PAA is difficult to be given. Thirdly, the dif-

ferences noted between the efficiency of the "living" macroradicals from one experiment to another have to be explained by differences in experimental conditions (e.g., the vacuum in the reaction tube). Each experiment can be compared only with its control experiment, performed in identic conditions.

CONCLUSIONS

The experimental data, theoretically justified, prove the existence of ultralong macromolecular chains, able to keep their activity in time ("living" macroradicals). These chains appear in plasma-induced polymerization conditions, both in homogeneous and heterogeneous media. Due to its specific characteristics (the development of the propagation reaction at room temperature and the formation of very high molecular weight polymers), this new method of polymer synthesis proves to be very adequate for the study of these macromolecular initiators.

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