

UNCONVENTIONAL RADICAL POLYMERIZATIONS

Cristofor I. Simionescu and Bogdan C. Simionescu

Department of Organic and Macromolecular Chemistry,
Polytechnic Institute of Jassy, 6600 Jassy, Romania

Abstract - The paper is dealing with unconventional radical polymerizations (copolymerizations) not described by the classical kinetic model. Plasma-induced polymerization is presented as an example of free radical polymerization with instantaneous initiation and without termination. This new approach to polymer synthesis is proved to proceed through a living radical mechanism and to yield ultrahigh molecular weight polymers with narrow polydispersity.

INTRODUCTION

Last years, numerous papers were concerned with radical polymerization processes. The interest in one of the most studied and known reactions in macromolecular chemistry is not surprising, considering that (a) about 60% of the now available polymers are obtained, on industrial scale, through radicalic techniques, and any improvement of an industrial process has important economic consequences, and (b) a thorough study of the published work on the kinetics of radical polymerization leads to the conclusion that many aspects are not as fully as reassuringly cleared. To exemplify only the last point, the existing models of radical polymerization kinetics, based on a number of assumptions, do not always describe realistically the polymerization processes. In particular, this is true in solution polymerization, at high initiator concentration and especially at high conversion of monomer to polymer (Ref. 1).

Two main directions could be noted in the recent literature concerned with radical polymerization, namely (a) a reconsideration of polymerization processes of the most common monomers, with emphasis on new initiating systems and on "uncatalyzed polymerizations", and (b) a search for more realistic kinetic schemes, able to describe in a greater extent the processes and having general applicability to different monomers, homopolymerization and copolymerization to complete conversion. However, in the second direction, the proposed kinetic models, with few exceptions, are only improvements of the simplest ("classical") kinetic model of free radical polymerization, and practically no studies were concerned with radical polymerizations which were proved to be unconventional from the kinetic point of view. This seems quite surprising considering that living anionic polymerization, discovered 25 years ago, and quasiliving carbocationic polymerization, quite recently proved (Ref. 2), have been fully accepted.

In this context, the present paper is aimed to present the existing experimental evidences on living radical polymerization, with an emphasis on plasma-induced polymerization (copolymerization) as technique of obtaining living macroradicals, and to propose a kinetic model of unterminated radical polymerization.

KINETIC ASPECTS OF RADICAL POLYMERIZATION

Using the main experimental results existing in the literature, one can synthesize a composite view of a simple radical polymerization. At the beginning of the process there is a short period when the rate of polymerization is increasing and then the reaction reaches a steady state; as it advances to about 10% conversion (depending on monomer and experimental conditions), both the rate and the degree of polymerization are passing through minima. This is considered as the onset of the "gel effect", reported for the first

time in 1939 by Norrish and Brookman (Ref. 3). The "gel effect" is characterized by auto-acceleration, the rate acceleration being accompanied by an increase in the cumulative molecular weight of the polymer and by a broadening of the molecular weight distribution. Ultimately, the rate of polymerization passes through a maximum and then it falls to nearly zero at conversions less than 100%.

As concerns the simplest ("classical") kinetic model of free radical polymerization kinetics (Ref. 1), it presumes the unimolecular decomposition of initiator, I, to produce two free radicals, R[•], a fraction of which, f, then add monomer (M) molecules to initiate the active polymer chain, P[•]. The active chain either propagates and grows by adding new monomer molecules, or stops its growth by chain transfer reactions with some species X (monomer, initiator, solvent, impurity, chain transfer agent) or by recombination or disproportionation with another active chain (Scheme 1).

	reaction	rate expression
initiation	$I \longrightarrow 2R^{\bullet}$	$k_d [I]$
	$R^{\bullet} + M \longrightarrow P_1^{\bullet}$	$k_i [R^{\bullet}][M]$
propagation	$P_n^{\bullet} + M \longrightarrow P_{n+1}^{\bullet}$	$k_p [P_n^{\bullet}][M]$
transfer	$P_n^{\bullet} + X \longrightarrow P_n + R^{\bullet}$	$k_{trX} [P_n^{\bullet}][X]$
termination	$P_n^{\bullet} + P_m^{\bullet} \longrightarrow P_{n+m}$	$k_{tc} [P_n^{\bullet}][P_m^{\bullet}]$
	$P_n^{\bullet} + P_m^{\bullet} \longrightarrow P_n + P_m$	$k_{td} [P_n^{\bullet}][P_m^{\bullet}]$

Scheme 1. The simplest ("classical") kinetic model of radical polymerization.

This model has three different stages - initiation, propagation and termination - and to solve it to obtain kinetic expressions it is assumed that

(a) the radical reactivity is independent of chain length (e.g., the termination rate constant is not function of chain length),

(b) the rate of chain initiation equals the rate of chain termination,

(c) the radicals formed in chain transfer reactions immediately reinitiate propagating chains, and

(d) the chains are very long so that the amount of monomer consumed during initiation and chain transfer reactions is small compared to that in propagation.

A classical living polymerization is an addition polymerization in which both transfer and termination are absent. As a consequence, (a) the concentration of active centres remains constant during the process, and (b) the degree of polymerization increases linearly with monomer consumption. In a living system, the molecular weight polydispersity has to be near unity. The living character of a radical polymerization has to be thus defined by three parameters: $[R^{\bullet}] = \text{const.}$, $DP_n \simeq \Delta M / [R^{\bullet}]$ (where ΔM is the amount of monomer built into the polymer), and $M_w / M_n = 1$.

Theoretically, to convert a radical polymerization into a living radical polymerization, the transfer and termination steps are to be eliminated or, at least, drastically diminished. This can be performed if

(a) the concentration of the initiator is strongly diminished, to produce only a very small number of growing chains (low probability of occurrence of recombination and disproportionation reactions),

(b) the process is carried out at as low as possible temperatures, to minimize transfer reactions and to increase the viscosity of the medium (the termination rate constant is inversely proportional to the viscosity of the polymerizing system),

(c) the medium is free of impurities and radical polymerization inhibitors, and

(d) the mobility of the growing macroradicals is strongly diminished e.g., by increasing the viscosity of the medium, by macroradical "trapping" or complexing.

Under these circumstances one should obtain living macroradicals. However, only few studies exist on living radical polymerization, even if the presence of living macroradicals has been observed in some cases. So, for some monomers, a prolonged post-polymerization period was noted during photo- and γ -ray initiated polymerization (both polymerization techniques require very pure media and low reaction temperatures).

A short review of the papers dealing with living macroradicals is following.

BRIEF REVIEW OF RESEARCH WORK ON LIVING RADICAL POLYMERIZATION

A possibility of living radical polymerization of styrene was pointed out in 1957 (Ref. 4) for emulsion polymerization under an intermittent irradiation of light. The same idea was applied for emulsion polymerizations using ozonized polypropylene and some reducing agents as initiators (Ref. 5&6). The polystyryl living macroradicals thus obtained were used as macromolecular initiators for block copolymerization with methyl methacrylate (Ref. 7). The molecular weight of the macromolecular initiator was shown to increase with conversion and its molecular weight distribution was determined to be very narrow ($M_w/M_n = 1.01 - 1.13$). The formation of living macroradicals was observed also when systems of some alkyl peroxides and amines were used as initiators (Ref. 8). Radical polymerization without termination was also reported to occur in other cases, e.g., in the case of monomers complexed with guest compounds (Ref. 9), of ethylene polymerization with the system triethylaluminum/ δ -butyrolactone/tert-butyl perisobutyrate (Ref. 10&11) and of methyl methacrylate in the presence of complexing agents (Ref. 12&13). The chain termination rate constant in radical polymerization was shown to decrease strongly with the introduction of a polyfunctional complexing agent into the system; an especially sharp decrease of the termination rate, up to the formation, under certain conditions, of living macroradicals, was reported for the methyl methacrylate - orthophosphoric acid system (Ref. 14). Solid state polymerization of acrylamide with γ -ray irradiation leads to polymer radicals stable for long periods of time at room temperature (Ref. 15), and its derivatives, such as N-methylacrylamide, methacrylamide, N-methylmethacrylamide produce long-lived macroradicals (Ref. 16-18) able to be used as macromolecular initiators in block copolymer synthesis. An interesting model for living radical polymerization was recently proposed (Ref. 19); the model was based on the use as initiators of organic sulfides acting as thermal or photo-iniferters (initiator-transfer agent-terminator) to synthesize mono- and α,ω -bifunctional oligomers and polymers (Ref. 20-22).

PLASMA-INDUCED POLYMERIZATION

Plasma-induced polymerization (copolymerization) is a new method of polymer synthesis. In this particular case, the initiation reaction takes place in the gaseous phase and the formation of low molecular active species is (practically) instantaneous, the molecular weight and polydispersity of the resulting polymers are directly related to the reaction conditions, and the activity of the propagating chains appears to be unusually high and very stable in time, even at room temperature. The polymerization reactions performed according to this technique yield very high or ultrahigh molecular weight polymers and occur at room temperature.

Experimental technique

The general experimental procedure was described in our papers related to this subject (see, e.g., Ref. 23&24) (see Note a). Typically, the monomers were purified with great care and then introduced in polymerization ampoules, frozen in liquid nitrogen after degassing, evacuated repeatedly to $10^{-3} - 10^{-4}$ Torr and sealed. An electrical discharge was then operated between two external electrodes, situated at about 2.5 cm and 7.0 cm, respectively, from the frozen sample. Both electrodes were coupled to a high frequency discharge generator (frequency - 2.5 MHz, power - 100 W). A third electrode, unconnected to the power source, was placed at about 1.0 cm from the sample, in order to restrict the discharge and to impede it to touch the frozen monomer. The discharges were operated during 20 - 300 seconds. The ampoules were kept in dark, at room temperature, for different periods of time, then opened to separate the polymer.

All polymers and copolymers synthesized through this technique were proved to be completely soluble in the specific solvents. No mechanical stirring was applied to polymer (copolymer) solutions at any stage, to prevent shear degradation.

Note a. All papers treating this subject were published under the general titles of "Plasma-Induced Polymerization" and "Solution Properties of Ultrahigh Molecular Weight Polymers".

Plasma-induced homo- and copolymerizations

Different homo- and copolymerization reactions initiated in this manner were studied. Table 1 presents some results obtained in solution and bulk homopolymerization of some usual monomers. As will be shown later, the determined molecular weights, generally very high, can be further increased by increasing the post-polymerization period and by selecting the initiation conditions.

TABLE 1. Plasma-induced solution and bulk homopolymerizations

Monomer and homopolymerization conditions	Polymer yield (%)	\bar{M}_w^*	Reference
solution homopolymerization			
N-vinyl carbazole/benzene (discharge 60 s., post-polym. period, 720 h)	3.78	$1.8 \cdot 10^4$	25
styrene/benzene (60 s., 240 h)	0.30	$5.0 \cdot 10^4$	25
acrylamide/H ₂ O (60 s., 240 h)	7.90	$1.4 \cdot 10^7$	25
bulk homopolymerization			
styrene (180 s., 1080 h)	18.00	$3.9 \cdot 10^7$	25
acrylic acid (60 s., 3 h)	100.00	$2.2 \cdot 10^6$	25
methacrylic acid (60 s., 240 h)	0.50	$1.4 \cdot 10^7$	25
methyl methacrylate (60 s., 330 h)	10.10	$1.2 \cdot 10^8$	26
ethyl acrylate (60 s., 220 h)	0.80	$1.5 \cdot 10^7$	25
butyl acrylate (60 s., 180 h)	9.10	$3.2 \cdot 10^7$	27
butyl methacrylate (60 s., 180 h)	7.20	$3.7 \cdot 10^7$	27

* determined by light scattering

The polymerization reaction proceeds by radical mechanism, as proved by inhibition experiments carried out in presence of radical polymerization inhibitors and by the results obtained from the study of different bulk copolymerization systems (Table 2).

TABLE 2. Plasma-induced bulk copolymerizations

M_1/M_2 system	r_1	r_2	Q^*	Reference
methyl methacrylate/styrene	0.41	0.57	0.48	28
methyl methacrylate/ α -methyl styrene	0.42	0.22	0.21	29
acrylonitrile/ α -methyl styrene	0.03	0.14		29
methacrylonitrile/styrene	0.21	0.34	1.00	30, 31
butyl methacrylate/styrene	0.59	0.74		32, 33

* probability of alternating coisotactic addition

As proved by the linearity of the Kelen-Tudös plots, all studied systems can be treated by the simple terminal copolymerization model. Weight-average molecular weights of the copolymers ranged in the $10^6 - 3 \cdot 10^7$ domain.

Table 2 shows that (a) the reactivity ratio values of the monomers copolymerized through this technique are very close to those resulting from the classical radical copolymerization of the same monomer pairs, and (b) the microstructure of the copolymers is similar to the microstructure of their radically obtained homologues.

In all cases, no matter if polymerizations or copolymerizations are taken into consideration, the processes were characterized by gradual increase of the viscosity of the reaction milieu, and both molecular weights and conversions were observed to grow during days and even weeks after initiation. 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 weight-average molecular weight increased to $2.0 \cdot 10^7$ during the same period, while the conversion remained under 3% (Fig. 1).

The same evolution of conversion and molecular weight with the post-polymerization period appear during the homopolymerization of methyl methacrylate (Fig. 2) or during the copolymerization of the mentioned monomer with styrene (Fig. 3).

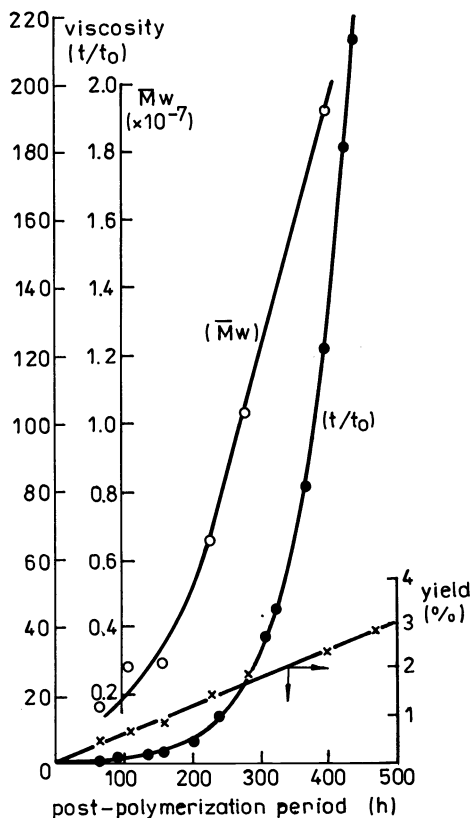


Fig. 1. Variation of the relative viscosity of the system, of the weight-average molecular weight and of the yield with post-polymerization period for plasma-induced bulk homopolymerization of styrene (Ref. 23).

As concerns the molecular weight polydispersity of the obtained polymers, the reactions can be directed towards the synthesis of low polydispersity macromolecular compounds. Under proper conditions (initiation), the molecular weight heterogeneity was found to decrease with post-polymerization period (Tables 3 and 4).

TABLE 3. Molecular weight and polydispersity data of poly(methyl methacrylate) samples obtained by plasma-induced polymerization[‡]

Sample	Post-polymerization period (h)	$\bar{M}_w \cdot 10^{-7}$	\bar{M}_w/\bar{M}_n	\bar{M}_w/\bar{M}_n
1	44.5	0.7497	0.5418	1.384
2	77.5	0.9996	0.7331	1.365
3	98.0	1.1735	0.8995	1.305
4	196.5	1.2268	0.9422	1.302
5	243.5	1.3495	1.0381	1.299
6	293.0	1.5876	1.2307	1.290
7	333.5	1.8726	1.4573	1.285

[‡] 20 s discharge initiation; ^{‡‡} calculated from light scattering data according to Miyaki et al. (Ref. 34); details on plasma-induced bulk homopolymerization of methyl methacrylate are given in Ref. 26. The polymerization rate value was determined to be about $3.3 \cdot 10^{-7} \text{ mol} \cdot \text{l}^{-1} \cdot \text{s}^{-1}$ (pure thermal polymerization, $3.9 \cdot 10^{-8} \text{ mol} \cdot \text{l}^{-1} \cdot \text{s}^{-1}$) and is in agreement with that calculated by Johnson et al. (Ref. 35).

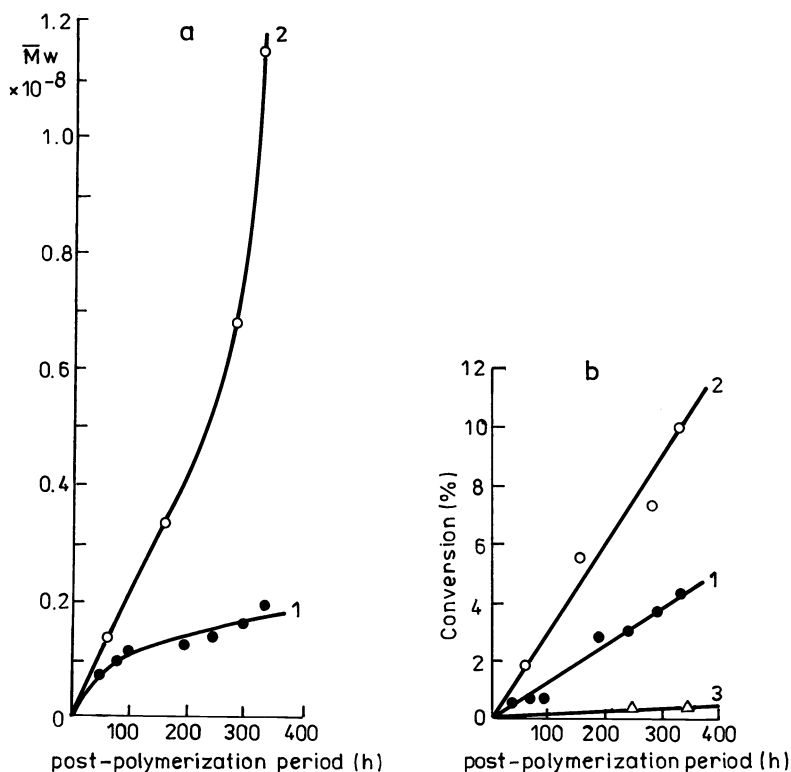


Fig. 2. Dependence of weight-average molecular weight (a) and conversion (b) on post-polymerization in the case of plasma-induced bulk homopolymerization of methyl methacrylate (Ref. 26&36). 1 - 20 sec. discharge initiation; 2 - 60 sec. discharge initiation; 3 - thermal polymerization. The data were obtained for two different portions of monomer.

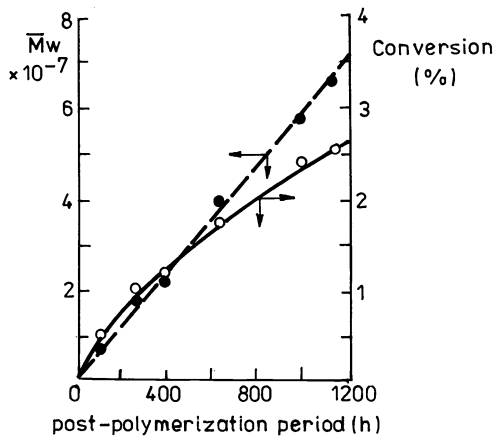


Fig. 3. Dependence of weight-average molecular weight and conversion on post-polymerization period for plasma-induced bulk copolymerization of methyl methacrylate and styrene (Ref. 28, 37&38). The initial mixture of the monomers was calculated to yield copolymers of 50:50 composition.

All copolymers obtained through plasma-induced copolymerization technique, no matter the composition, present a small compositional heterogeneity. Table 5 gives some data on methacrylonitrile - styrene copolymers (Ref. 39). The data presented in Table 4 on methyl methacrylate - styrene 50:50 random copolymers confirm this observation.

TABLE 4. Molecular weight and polydispersity data of methyl methacrylate - styrene 50:50 random copolymers obtained by plasma-induced bulk copolymerization [※]

Sample	Post-polymerization period (h)	$\bar{M}_w \cdot 10^{-7}$			$\bar{M}_n \cdot 10^{-7}$
		D ^{※※}	EMK ^{※※}	C ^{※※}	
1	120	0.73	0.73		
2	280	1.84	1.79	1.83	1.13
3	480	2.04	2.02		
4	640	3.68	3.95	3.73	2.49
5	1003	5.53	5.77		
6	1143	6.76	6.60		

※ Ref. 36. ^{※※} D, 1,4-dioxane; EMK, ethyl methyl ketone; C, cyclohexanol (theta solvent at 68.6°C).

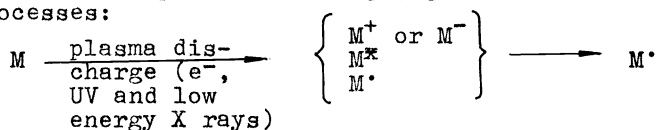
TABLE 5. Molecular weight data of methacrylonitrile - styrene copolymers obtained by plasma-induced bulk copolymerization [※]

Sample	Copolymer composition		$\bar{M}_{ap} \cdot 10^{-6}$ ^{※※}			
	MAN(%)	S(%)	EMK ^{※※※}	D ^{※※※}	DMF ^{※※※}	C ^{※※※}
1	70.33	29.67	1.00	1.00	1.01	1.01
2	54.75	45.25	1.51	1.54	1.55	1.59
3	47.65	52.35	1.50	1.53	1.54	1.58
4	40.83	59.17	1.63	1.65	1.66	1.68
5	32.43	67.57	1.18	1.20	1.21	1.23

※ Ref. 39. ^{※※} weight-average apparent molecular weight.
^{※※※} EMK, ethyl methyl ketone; D, 1,4-dioxane; DMF, dimethylformamide; C, chloroform.

Kinetic aspects of plasma-induced polymerization

When submitted to plasma discharge, gaseous monomer molecules suffer different processes:



The greatest part of the formed low molecular weight radicals are annihilated by mutual recombination and only part of them are directed towards the surface of the frozen monomer, being consumed by reacting with monomer molecules to produce macroradicals. Thus, the initiation takes place at the very beginning of the reaction (instantaneous initiation) and, under proper conditions, e.g., short discharge period, only a very small number of active species act as propagating centers a few moments after the discharge. An approximative calculation showed that the concentration of the formed radicals is about $10^5 - 10^7$ times less important than in a classical radical polymerization (Ref. 37). In these conditions, at least as long as the conversion is small, the only reaction to be considered is propagation. The absence of termination reactions explains the appearance of auto-acceleration processes for very small conversions, processes which are not yield-depending phenomena, as in classical radical polymerization, but molecular weight-depending phenomena. Such auto-acceleration processes appear, for instance, in Fig. 1 and Fig. 2 (for 60 sec. discharge initiation).

Both conversion and molecular weight have the same consequence - a dramatic increase of the viscosity of the reaction milieu, followed by a decrease of the mobility of the macromolecular chains and of the collisions between the growing chains. The reaction rate constant of termination decreases after the viscosity reaches a relatively high value, value appearing for very low conversions, but very high molecular weights in the case of plasma-induced polymerization.

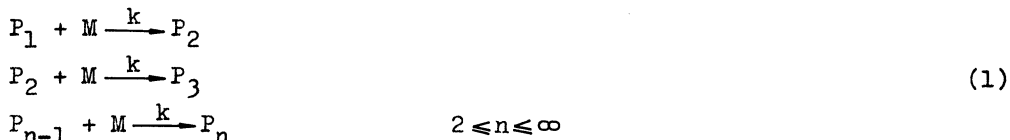
Due to the formation of very high molecular weight macromolecular compounds (and, as a consequence, to the enormous increase of the viscosity for very low conversions) one can exclude the termination reaction and consider the possible formation of living macroradicals. In fact, two growing polymer coils, to form a dead polymer, must first undergo translational diffusion

to collide and then a segmental diffusion to bring the active chain ends into a very small volume element where termination reaction takes place (Ref. 40). Both diffusion phenomena are function of medium viscosity and the termination rate constant in radical polymerization is inversely proportional to the viscosity of the polymerizing system (Ref. 41&42). At the same time, plasma-induced polymerizations take place at room temperature, so that transfer reactions have small importance.

These considerations also explain the slow but permanent decrease of the polydispersity of the polymers with the post-polymerization period.

All these experimental data and theoretical considerations justify the examination of a kinetic model able to describe a living radical process (polymerization with instantaneous initiation and without termination); the case illustrated by plasma-induced polymerization will be considered (Ref. 43).

The propagation process is represented by the equations



where M is the monomer, P_2, P_3, \dots, P_n represent active chains of 2, 3, \dots, n length and k is the propagation rate constant. The following simplifying hypothesis are introduced:

- (1) the propagation rate constant is independent of chain length,
- (2) some of the features specific to radical polymerization processes (e.g., the gel effect) do not influence the propagation,
- (3) each propagation step is first order with respect to monomer and to propagating chains.

The kinetic model of the process, represented by equations (1), will thus be given by the following infinite system of differential equations:

$$\begin{aligned} dM/dt &= -kM \sum_{n=1}^{\infty} P_n ; & M(0) &= M_0 \\ dP_1/dt &= -kMP_1 ; & P_1(0) &= P_{10} \\ dP_2/dt &= -kMP_2 + kMP_1 ; & P_2(0) &= 0 \\ dP_n/dt &= -kMP_n + kMP_{n-1} ; & P_n(0) &= 0 \quad \text{for } 2 \leq n \leq \infty \end{aligned} \quad (2)$$

Considering that the polymerization is without termination,

$$\sum_{n=1}^{\infty} P_n = P_{10}$$

so that the first equation of system (2) can be easily solved, and then the whole system can be solved step by step giving the system (3):

$$\begin{aligned} M &= M_0 e^{-kP_{10}t} \\ P_1 &= P_{10} \exp[-(M_0/P_{10})(1 - e^{-kP_{10}t})] \\ P_2 &= M_0(1 - e^{-kP_{10}t}) \exp[-(M_0^2/2P_{10})(1 - e^{-kP_{10}t})] \\ P_3 &= (M_0^2/2P_{10})(1 - e^{-kP_{10}t})^2 \exp[-(M_0/P_{10})(1 - e^{-kP_{10}t})] \\ P_n &= [P_{10}/(n-1)!] [(M_0/P_{10})(1 - e^{-kP_{10}t})]^{n-1} \exp[-(M_0/P_{10})(1 - e^{-kP_{10}t})] \end{aligned} \quad (3)$$

$$\text{If a new time variable, } \mathcal{Z}, \quad \mathcal{Z} = (M_0/P_{10})(1 - e^{-kP_{10}t}) \quad (4)$$

is introduced, system (3) turns into system (5):

$$M = M_0 - P_{10} \mathcal{Z}$$

$$\begin{aligned}
 P_1 &= P_{10}e^{-z} \\
 P_2 &= P_{10}ze^{-z} \\
 P_3 &= P_{10}(z^2/2)e^{-z} \\
 P_n &= P_{10}[(z^{n-1})/(n-1)!] e^{-z}
 \end{aligned}
 \tag{5}$$

The last system represents the well known Poisson distribution. The total amount of polymer is given by equation (6)

$$P_{n_t} = \int_0^\infty P_n dZ = [P_{10}/(n-1)!] \int_0^\infty z^{n-1} e^{-z} dz = [P_{10}/(n-1)!] \Gamma(n) = P_{10}$$

where $\Gamma(n)$ is the gamma function,

$$\Gamma(n) = \int_0^\infty z^{n-1} e^{-z} dz$$

The distribution, in time, of the dimensionless concentration of the living polymer of length n will thus be given by

$$(P_n/P_{10}) = P_n^* = [z^{n-1}/(n-1)!] e^{-z}
 \tag{7}$$

and will be represented as in Fig. 4.

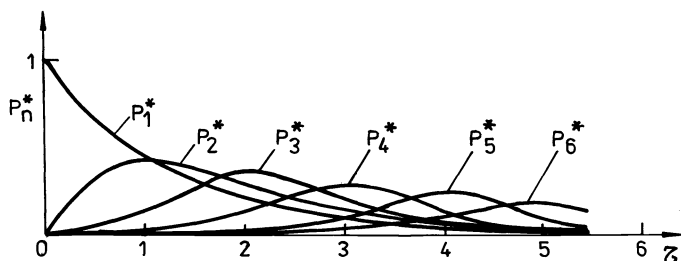


Fig. 4. Distribution of the dimensionless concentration of living polymer chains of $n = 1, 2, 3, \dots, n$ length (Ref. 43).

The maximum concentration of n length chains can be found from

$$(dP_n/dz) = (d/dz) [(P_{10}z^{n-1})/(n-1)!] e^{-z} = 0 ; z_{max} = n - 1
 \tag{8}$$

$$P_{n_{max}} = P_{10} [(n-1)^{n-1}/(n-1)!] e^{-(n-1)}
 \tag{9}$$

Thus, at a particular moment of the process, the amount of a certain species reaches a maximum value. The average life time of these species is given by

$$\begin{aligned}
 \bar{z} &= (\int_0^\infty z P_n dZ) / (\int_0^\infty P_n dZ) = (\int_0^\infty z^n e^{-z} dz) / (\int_0^\infty z^{n-1} e^{-z} dz) = \\
 &= \Gamma(n+1) / \Gamma(n) = n! / (n-1)! = n
 \end{aligned}
 \tag{10}$$

From equations (8) and (10) one can see that the symmetry of the distribution of chain concentration increases with the increase of chain length.

By using equation (5), one can calculate the molecular weight distribution of the living polymer, according to

$$\bar{M}_n = m(\int_0^\infty n P_n dn) / (\int_0^\infty P_n dn) = \dots = m(1 + z)
 \tag{11}$$

$$\bar{M}_w = m(\int_0^\infty n^2 P_n dn) / (\int_0^\infty n P_n dn) = \dots = m\{1 + z + [z/(1+z)]\}
 \tag{12}$$

The polydispersity index is given by

$$I = \overline{M}_w / \overline{M}_n = 1 + \zeta / (1 + \zeta)^2 \quad (13)$$

The maximum polydispersity is 1.25 for $\zeta = 1$. As can be seen from Fig. 4, for this ζ value the dimer and P_1 active species are in equal amounts, the former reaching its maximum value. Thus, for important periods of time, one should have theoretically a nearly monodisperse living polymer. This conclusion is verified in part by the experimental data presented in Table 3, the polydispersity index decreasing with the increase of the post-polymerization period of methyl methacrylate.

According to the definition of ζ (equation 4), for variation of t between 0 and ∞ , ζ varies between 0 and M_0/P_{10} , so that the process develops up to a limited molecular weight, given by

$$[\overline{M}_n]_{t=\infty} = m [1 + (M_0/P_{10})] \quad (14)$$

which increases continuously with the decrease of the concentration of active species produced by the instantaneous initiation.

The variation of monomer conversion with time, x , is given by

$$x = (1 - M/M_0) / [1 + \xi(M/M_0)] \quad (15)$$

where ξ is the expansion factor which can be determined from monomer and polymer densities (ρ_m and ρ_p , respectively):

$$\xi = [(1/\rho_p) - (1/\rho_m)] / (1/\rho_m) \quad (16)$$

From equations (3), (15) and (16) one can obtain

$$x = [1 - (M/M_0)] / [1 + \xi(M/M_0)] = (1 - e^{-kP_{10}t}) / (1 + \xi e^{-kP_{10}t}) \quad (17)$$

This equation shows that, for an infinite post-polymerization period, the total conversion is reached, the process going asymptotically to this value. Certainly, for high conversions the model could be erroneous.

Living macroradicals as macromolecular initiators

The best proof for the existence of living macroradicals in plasma-induced polymerization systems is their use as macromolecular initiators (e.g., for the synthesis of block copolymers). Three experiments were performed to prove the existence of living macroradicals (Fig. 5). These practical examples show that due to (a) the very small concentration of active species, (b) the very important length of the macroradicals and the high viscosity of the medium, and (c) the existence of insignificant transfer reactions (low temperature), in such media one can obtain living macroradicals able to be used as macromolecular initiators.

Two different cases can be considered:

(a) when the resulting polymer is not soluble in the reaction medium, the growing macroradicals, after having reached a certain length, precipitate and form a second phase together with the dead polymer. The interaction of two growing chains may be very slow, these being coiled and occluded in dead polymer particles (Ref. 44);

(b) when the resulting polymer is soluble in the reaction medium, the milieu becomes very viscous due to conversion to polymer and to the increase of the molecular weight. At small initiator concentration (or, for plasma-induced polymerization, for small discharge periods), the macroradicals reach important lengths and they are practically isolated one from each other. The system immobilizes the growing chains in the viscous medium, so that the termination step (diffusion controlled) is hindered. Both situations lead to living macroradicals in the system, macroradicals which are responsible for post-polymerization processes.

The experimental data presented in Fig. 5 prove the formation, in plasma-induced polymerization conditions, of living macroradicals, able to keep their activity for long periods of time. The living macroradicals appear both in homogeneous and heterogeneous media.

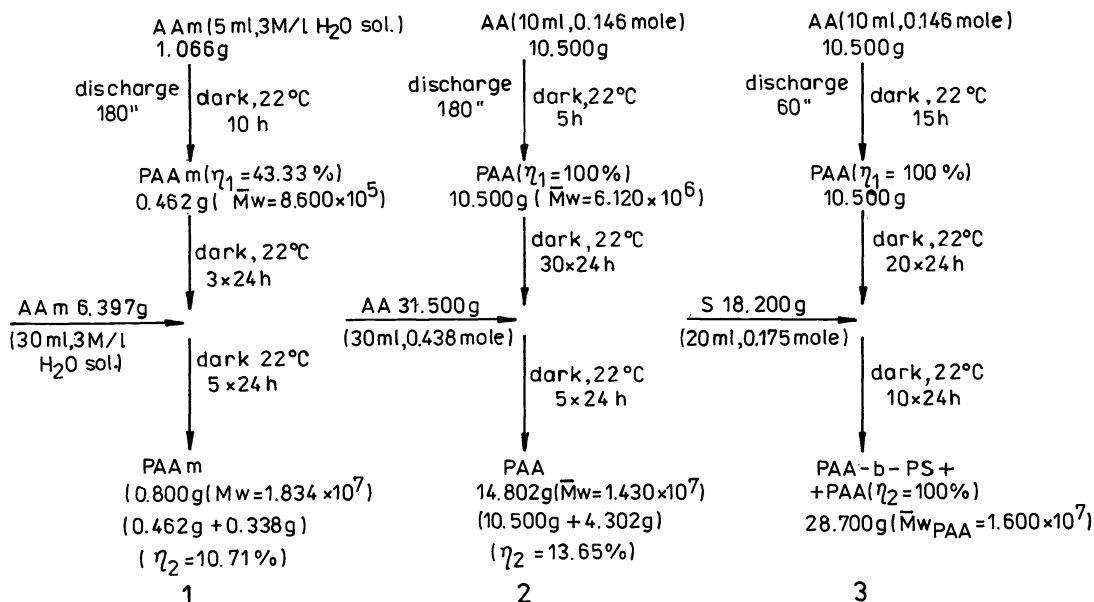


Fig. 5. Schematic representation of the experiments proving the formation of living macroradicals in plasma-induced polymerization media (Ref. 45, 46&47). AAm, acrylamide; AA, acrylic acid; S, styrene. The differences noted between the efficiency of the living macroradicals from one experiment to another have to be explained by differences in experimental conditions (e.g., in the third experiment, the contact between the added styrene and the existent poly(acrylic acid) was not perfect, so that an estimation of the dead polymer was difficult).

CONCLUSIONS

The data presented attest that, notwithstanding the relatively advanced state of radical polymerization processes, many aspects are still to be considered.

Both the experimental results and the theoretical considerations prove the existence of living macroradicals appearing in some radical polymerization processes. The particular case of plasma-induced polymerization seems to be very adequate for the study of these long living species, due to its characteristics.

These results open new prospects, part of them previously characteristic only to living anionic polymerization:

(a) the possibility of synthesizing, by radical mechanism, of homo-, copolymers and block copolymers with ultrahigh molecular weights (part of the molecular weights reported in this article are the greatest ever reported) and narrow polydispersity,

(b) these results offer the experimental material to be used for the reconsideration of some aspects of polymer physics (e.g., concerning polymer solutions) and of radical polymerization kinetics, and

(c) some very interesting practical applications could be envisaged (e.g., the easy synthesis of ultrahigh molecular weight polyacrylamide).

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