Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Kennedy, Joseph P. , Kelen, Tibor and Tüdös, Ferenc(1982) 'Quasiliving Carbocationic Polymerization. I. Classification of Living Polymerizations in Carbocationic Systems', Journal of Macromolecular Science, Part A, 18: 9, 1189 — 1207

To link to this Article: DOI: 10.1080/00222338208077218

URL: http://dx.doi.org/10.1080/00222338208077218

J. MACROMOL. SCI.–CHEM., A18(9), pp. 1189-1207 (1982-83)

Quasiliving Carbocationic Polymerization. I. Classification of Living Polymerizations in Carbocationic Systems*

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ABSTRACT

It has been shown that in addition to classical living polymerizations, several other polymerization systems exist that may exhibit partially living so-called quasiliving character. The single requirement for quasiliving polymerization is the absence of irreversible termination. The various possible living systems have been classified by taking into consideration the absence or reversibility of termination and the absence, reversibility, or irreversibility of chain transfer. In regard to chain transfer,

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*Dedicated to Professor Michael Szwarc on the 25th anniversary of his discovery of living anionic polymerization.

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both unimolecular and/or bimolecular processes have been considered. A comprehensive examination of all possibilities yielded, in addition to the classical terminationless-transferless living system, five quasiliving systems. Kinetic analysis led to equations defining these systems and to diagnostic techniques useful for the classification and characterization of the mechanism of living carbocationic polymerizations.

INTRODUCTION

Unquestionably, one of the truly pioneering breakthroughs in contemporary polymer science was the discovery of living anionic polymerizations by Professor Michael Szwarc about 25 years ago [1, 2]. By the use of the living polymerization concept the synthesis of new families of polymeric materials became realities, e.g., block copolymers, terminally functional polymers, several of which gave rise to important commercial commodities (for example, the thermoplastic elastomers Kraton by Shell and Solprene by Phillips) that have significantly contributed to the health, safety, comfort, and prosperity of mankind. It is our conviction that, as is so often the case, this discovery was not the result of serendipity coupled with astute observation (witness the discovery of low pressure ethylene polymerization by Ziegler et al. [3] which culminated in the discovery of stereoregular polymerizations, i.e., terminationless-transferless anionic polymerization of styrene and isoprene [1, 2]) but was due to an inspired assessment of basic chemical facts followed by ingenious experimentation.

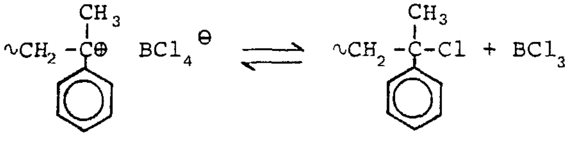
Since the time of demonstration of anionic living systems, efforts have also been made in the field of carbocationic polymerizations to find conditions under which living polymerizations could be obtained. Kennedy et al.'s early attempts [5] to adapt super-acid chemistry remained fruitless, and Higashimura et al.'s systems with iodine and very reactive monomers, i.e., N-vinyl carbazole [6] and p-methoxy styrene [7, 8], were also less than satisfactory. Stannett et al.'s trials to block poly(N-vinyl carbazole) from alkyl vinyl ether carbenium ions were also hampered by extensive chain transfer [9]. In a similar vein, Goethals et al. [10] used "dormant" polystyryl perchlorate esters to block aziridines. A detailed examination of these and similar data indicates that completely terminationless-transferless polymerization could not be achieved in carbocationic systems, and a truly living carbocationic polymerization has as yet not been obtained. According to Pepper [11], it is "unlikely that any cationic polymerization will display living characteristics in their full perfection, i.e., satisfy the molecular weights as well as rate criteria."

A thorough analysis of options (see below) leads to the conclusion that the situation is not as hopeless as that painted by Pepper [11], and while a completely and irreversibly terminationless-transferless carbocationic polymerization has not yet been assembled, systems have been defined which to the outside observer behave as characteristic typical living systems, i.e., exhibit linear molecular weight growth with time and lead to relatively narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n < 2.0$).

A systematic search for living carbocationic polymerizations has started in Akron in the framework of efforts directed toward macromolecular engineering. The discovery of new initiator/coinitiator systems, mainly alkylaluminum and boron trichloride based systems [12], was a milestone toward this goal and led to polymerizations with "controlled terminations" [13], i.e., to polymerizations where $R_t > R_{tr,M}$ (the rate of termination was higher than that of chain transfer to monomer). While controlled termination led to endgroup control (i.e., to terminally functionalized polymers) and gave rise to a series of new block copolymers, the desirable synthetic capabilities offered by living polymerizations remained elusive.

A large variety of carbocationic polymerizations have been found that gave molecular weight dispersities significantly below 2.0 [14] and these unexpected observations prompted us to derive a series of mechanisms which in turn led us to the conclusion that these results may be either due to a coupling between dead olefinic polymer formed by proton elimination and active propagating carbenium ions or to the absence or suppression of termination, i.e., at least partly living character [15]. Morawetz, who also examined this information [16], explained the observations by assuming a system containing partly living and partly terminated chains.

Another important step on the road toward quasiliving carbocationic polymerizations was the recognition that termination is reversible in many carbocationic systems, e.g., in $C_6H_5C(CH_3)_2Cl$/BCl_3/α-methylstyrene, because of rapid reionization [17]:



In the course of these studies, Faust et al. [17] assumed that in such a terminationless and/or "dormant" system, i.e., when termination is reversible, chain transfer could be suppressed by working in the virtual absence of monomer by continuous slow addition of a dilute monomer feed to a charge containing the initiator, and that by this technique a system could be assembled that behaved in many respects as a living one (quasiliving system). With the $C_6H_5C(CH_3)_2Cl$/BCl_3/α-methylstyrene system these authors were able to demonstrate molecular weight growth with time and a significant narrowing of the molecular weight distribution. Further exploration of other carbocationic polymerizations by the use of the dilute continuous monomer addition technique demonstrated the general nature of this finding and the existence of many systems that exhibit behavior quite similar to those of living polymerizations.

A purpose of this issue is to collect and discuss in one readily available volume the field of living carbocationic polymerizations, and the purpose of this article is to introduce and comprehensively classify this field.

CLASSIFICATION OF LIVING POLYMERIZATIONS IN CARBOCATIONIC SYSTEMS

A comprehensive systematization must start by definitions. A classical living polymerization is an addition (chain growth) polymerization in which $R_t = 0$ and $R_{tr} = 0$ (where R_t and R_{tr} = rates of termination and chain transfer, respectively), i.e., a system in which termination and chain transfer are absent [11]. As a consequence of these conditions, the concentration of active sites remains rigorously constant during the polymerization (criterium No. 1):

$$[R^{\oplus}] = \text{const} \quad (1)$$

and the degree of polymerization increases linearly with the monomer consumed (criterium No. 2):

$$\overline{DP}_n = \Delta M/[R^{\oplus}] \quad (2)$$

where ΔM is the amount of monomer built into the polymer. Necessarily, in such a system the molecular weight dispersion must be very near unity:

$$\overline{M}_w/\overline{M}_n = 1 \quad (3)$$

According to some authors, e.g., Ref. 11, another criterium of living polymerizations is the inequality $R_i > R_p$ (i.e., that the rate of initiation must be higher than that of propagation). This "rate requirement," however, can be neglected by separating the initiation and propagation steps: for example, by preparing a quantity of active (propagating) centers and subsequently adding monomer to the "seed," or by the use of dynamic polymerization methods, i.e., continuous monomer addition, in place of the conventional static technique.

The initiation phase can be neglected if the time of continuous monomer addition is long. (Other advantages of the continuous monomer addition method will be discussed below.) Evidently, the relative rate of initiation is not a criterium of living polymerizations and can be controlled by experimental technique and methodology.

The only rigorous criterium of living polymerization is the validity of Eq. (1) (this is in line with Pepper's most recent position [18]). Systems exhibiting living (or quasiliving) character may exist under a wide variety of conditions. In quasiliving systems, Eqs. (2) or (3) are only partially or approximately valid, or may even be invalid.

As a result of a thorough examination of pertinent mechanisms, the classification shown in Table 1 has been developed. The various living and quasiliving systems theoretically possible in carbocationic polymerizations have been defined by the three parameters $[R^{\oplus}]$, $\overline{DP}_n$, and $\overline{M}_w/\overline{M}_n$. To facilitate the quantitative evaluation of Eq. (2) (criterium No. 2), the table has been developed for dynamic systems, i.e., for systems in which the polymerization was sustained by continuous steady monomer addition to active centers.

The first line in Table 1 defines living polymerizations (symbol L_{00}), i.e., polymerizations in which both termination and chain transfer processes are absent. The subsequent five lines define quasiliving systems (symbol QL), i.e., polymerizations in which termination is absent or reversible (criterium No. 1 satisfied), however, chain transfer is absent, reversible, or present. For completeness sake the last three lines in Table 1 also define "conventional" nonliving systems, i.e., polymerizations in which irreversible termination is present (hence the symbol T).

In the first column (Mechanism symbol) the first subscript refers to termination and the second to chain transfer. For example, QL_{0R} signifies a quasiliving system in which termination is absent and chain transfer is reversible. The second and third columns indicate the absence (θ), reversibility (R) or presence (1) of kinetic termination and chain transfer, respectively. For living or quasiliving systems the "Termination" column <u>must</u> show θ or R, whereas "Transfer" may be θ, R, or 1. As a consequence of the absence or reversibility of termination, the concentration of active centers is constant in living or quasiliving systems; this is indicated by "const" in the $[R^{\oplus}]$ column. In nonliving systems $[R^{\oplus}]$ decreases during polymerization. The $\overline{DP}_n$ versus ΔM column indicates the manner the particular system meets criterium No. 2. Rigorous linearity in the $\overline{DP}_n$ versus ΔM plot exists only in the L_{00} and QL_{R0} systems. In the QL_{0R} and QL_{RR} systems, $\overline{DP}_n$ increases toward infinity with ΔM; however, the growth curve follows a nonlinear (square root) function. Finally, in the QL_{01} and QL_{R1} systems, irreversible transfer limits the growth of $\overline{DP}_n$, i.e., the $\overline{DP}_n$ versus ΔM plot approaches a limit.

TABLE 1. Classification of Living and Quasiliving Polymerizations in Carbocationic Systems

Mechanism symbol	Decisive mechanistic step[a]		$[R^{\oplus}]$	$\overline{DP}_n$ vs ΔM	$\overline{M}_w/\overline{M}_n$
	Termination	Transfer			
L_{00}	θ	θ	Const	Linear increase	1
QL_{R0}	R	θ	Const	Linear increase	>1
QL_{0R}	θ	R	Const	Approaches square root increase	>1
QL_{RR}	R	R	Const	Approaches square root increase	>1
QL_{01}	θ	1	Const	Approaches a limit	>1
QL_{R1}	R	1	Const	Approaches a limit	>1
		Nonliving ("conventional") Systems			
T_{10}	1	θ	Decrease	Approaches a limit	2
T_{1R}	1	R	Decrease	Approaches a limit	>2
T_{11}	1	1	Decrease	Approaches a limit	>2

[a] θ = absent, R = reversible, 1 = present.

The last column in Table 1 refers to molecular weight dispersities and shows that $\overline{M}_w/\overline{M}_n$ increases (i.e., distributions broaden) by moving from the top toward the bottom of the table. Exact numerical values of molecular weight distributions can be developed only by detailed calculations.

The section below concerns a quantitative kinetic analysis of living carbocationic systems, in particular, the dependence of $\overline{DP}_n$ on ΔM (the $\overline{DP}_n$ vs ΔM column in Table 1 has been derived from this analysis). Among the conclusions, we wish to emphasize that in the QL_{0R} and QL_{RR} systems the $\overline{DP}_n$ versus ΔM relationship is described by a nonlinear function and that it approaches the classical L_{00} mechanism with decreasing monomer addition rate.

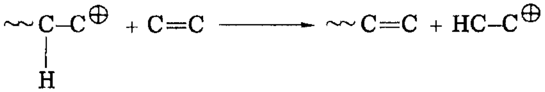
Ease and reliability of temperature control is another advantage of the slow continuous monomer addition technique. By the use of this technique, local overheating of the charge is avoided and disturbing temperature jumps often encountered during the mixing of ingredients in conventional static batch operations are largely eliminated. Reduced monomer addition rates greatly help to increase the reliability of $\overline{DP}_n$ data obtained with the QL_{01} and QL_{R1} systems also.

KINETIC TREATMENT

This kinetic analysis of living systems is of general validity. The individual limiting cases can be readily derived by suitable selection of constants. Only trends in $\overline{DP}_n$'s are considered so that a differentiation between the absence or reversibility of termination is unnecessary.

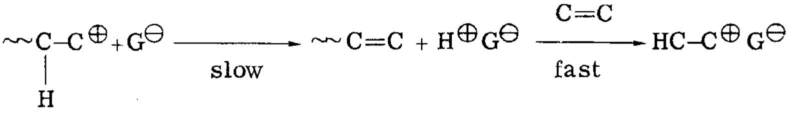
In contrast, two kinds of chain transfer processes will be considered [17]:

Bimolecular transfer to monomer:



$$\sim\!\sim \underset{\overset{|}{H}}{C}-C^{\oplus} + C{=}C \longrightarrow \sim\!\sim C{=}C + HC-C^{\oplus}$$

Pseudounimolecular transfer to counteranion:



$$\sim\!\sim \underset{\overset{|}{H}}{C}-C^{\oplus} + G^{\ominus} \xrightarrow[\text{slow}]{} \sim\!\sim C{=}C + H^{\oplus}G^{\ominus} \xrightarrow[\text{fast}]{C=C} HC-C^{\oplus}\,G^{\ominus}$$

The following five reactions and corresponding rate expressions provide the basis of subsequent calculations.

1. Chain transfer to monomer via unimolecular indirect proton transfer to the counteranion:

$$R^{\oplus}(+M) \longrightarrow M^{\oplus} + P^{=}, \qquad R_{tr,G^{\ominus}} = k_{tr,G^{\ominus}}[R^{\oplus}] \tag{4}$$

The M in parentheses serves to indicate that the rate-determining step is unimolecular deprotonation of the carbocation followed by rapid protonation of monomer. The second reaction (protonation) is usually so fast that the presence of free protons need not be taken into account.

2. Chain transfer to monomer via bimolecular direct proton-transfer to monomer:

$$R^{\oplus} + M \longrightarrow M^{\oplus} + P^{=}, \qquad R_{tr,M} = k_{tr,M}[R^{\oplus}][M] \tag{5}$$

3. Addition of protonated monomer (monomer carbocation) to olefin-terminated polymer, i.e., the reverse of Eq. (5):

$$M^{\oplus} + P^{=} \longrightarrow R^{\oplus} + M, \qquad R_{-tr,M} = k_{-tr,M}[M^{\oplus}][P^{=}] \tag{6}$$

4. Addition of monomer to protonated monomer:

$$M^{\oplus} + M \longrightarrow R^{\oplus}, \qquad R_p' = k_p[M^{\oplus}][M] \tag{7}$$

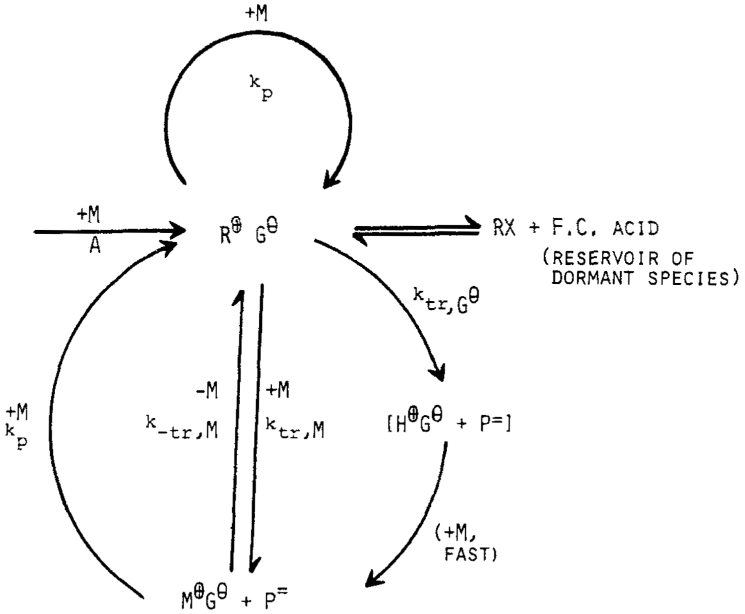
5. Addition of monomer to propagating carbocation (propagation):

$$R^{\oplus} + M \longrightarrow R^{\oplus}, \qquad R_p = k_p[R^{\oplus}][M] \tag{8}$$

where M = monomer, $M^{\oplus}$ = protonated monomer or monomer carbocation, $R^{\oplus}$ = growing active carbocation, $P^{=}$ = olefin-terminated polymer that arose by deprotonation during chain transfer. Thus

$$[R^{\oplus}] + [M^{\oplus}] = [I]_0 \tag{9}$$

where $[I]_0$ = effective active center concentration. The difference between the rate constants in Eqs. (7) and (8) is probably insignificant and can be neglected. Scheme 1 summarizes these events.



SCHEME 1.

The above set of reactions can be described by the following set of differential equations:

$$d[R^{\oplus}]/dt = R_p' + R_{-tr,M} - R_{tr,G^{\ominus}} - R_{tr,M} = -\, d[M^{\oplus}]/dt \qquad (10)$$

$$d[P^{=}]/dt = R_{tr,G^{\ominus}} + R_{tr,M} - R_{-tr,M} \qquad (11)$$

$$d[M]/dt = A + R_{-tr,M} - R_p' - R_p - R_{tr,G^{\ominus}} - R_{tr,M} \qquad (12)$$

where A = constant rate of monomer addition. Because of continuous monomer addition, the system rapidly reaches the stationary state so that

$$d[R^{\oplus}]/dt = -\, d[M^{\oplus}]/dt \cong 0 \qquad (13)$$

and

$$d[M]/dt \cong A - R_p \qquad (14)$$

The conversion of polymerization is defined as follows:

$$\xi = \frac{\Delta M}{At} = \frac{\int R_p\, dt}{At} \cong \frac{R_p}{A} \tag{15}$$

i.e.,

$$R_p = A\xi \qquad \text{and} \qquad \Delta M = At\xi \tag{16}$$

and, from (14) and (16):

$$d[M]/dt \cong A(1 - \xi) \tag{17}$$

For simplicity we assume complete conversion in the steady state, i.e., $\xi = 1$.

$$R_p = A, \qquad \Delta M = At \tag{18}$$

and

$$d[M]/dt \cong 0 \tag{19}$$

[In certain systems, e.g., p-t-butylstyrene (see Ref. 20) conversions are substantially lower than 1, monomer accumulates in the system, and instead of Eqs. (18) and (19), Eqs. (16) and (17) are applicable.]

From Eqs. (13) and (9) we obtain the following expressions:

$$[M^{\oplus}] = \frac{C_1 + C_2[M]}{[M] + \alpha[P^{=}] + C_1 + C_2[M]}[I]_0 \tag{20}$$

$$[R^{\oplus}] = \frac{[M] + \alpha[P^{=}]}{[M] + \alpha[P^{=}] + C_1 + C_2[M]}[I]_0 \tag{21}$$

where C_1 and C_2 are the unimolecular and bimolecular chain transfer constants, respectively:

$$C_1 = k_{tr,G^{\ominus}}/k_p \tag{22}$$

$$C_2 = k_{tr,M}/k_p \tag{23}$$

and α contains the rate constant of the backwards reaction (6) expressing reversibility of chain transfer:

$$\alpha = k_{-tr,M}/k_p \tag{24}$$

To calculate the number-average degree of polymerization, the number of polymer molecules produced by chain transfer, $[P^=]$, must be available. This quantity can be obtained from Eq. (11) by the use of Eqs. (20), (21), (12), and (14):

$$\frac{d[P^=]}{dt} = \frac{C_1 + C_2[M]}{[M] + \alpha[P^=] + 2(C_1 + C_2[M])} A \tag{25}$$

Since $[M] \approx$ const, Eq. (25) can be integrated by separating the variables and setting $t = 0$ and $[P^=] = 0$ as initial conditions. Thus a second-order equation is obtained:

$$\frac{C_1 + C_2}{C_1 + C_2[M]} \frac{C}{2(K_1 + K_2)} [P^=]^2 + [P^=] - CAt = 0 \tag{26}$$

which yields:

$$[P^=] = \frac{CAt}{\frac{1}{2} + (\frac{1}{4} + \frac{C_1 + C_2}{C_1 + C_2[M]} \frac{C^2}{2(K_1 + K_2)} At)^{1/2}} \tag{27}$$

where

$$K_1 = k_{tr,G\ominus}/k_{-tr,M} \tag{28}$$

$$K_2 = k_{tr,M}/k_{-tr,M} \tag{29}$$

$$C = \frac{C_1 + C_2[M]}{[M] + 2(C_1 + C_2[M])} \tag{30}$$

C is the overall chain transfer constant of the system. By the use of K_1 and K_2, α can also be expressed as follows:

$$\alpha = \frac{C_1 + C_2}{K_1 + K_2} \qquad (31)$$

Equations (26) and (27) contain [M], the steady-state concentration of monomer which can be obtained from (18):

$$[M] = A/k_p[I]_0 \qquad (32)$$

(If the polymerization is reversible, [M] can be calculated in this manner only when $[M]_{floor} < [M]$; otherwise [M] will be equal to $[M]_{floor}$.)

The number-average degree of polymerization is defined as follows ($\xi = 1$):

$$\overline{DP}_n = \frac{\Delta M}{[P]} = \frac{At}{[I]_0 + [P^=]} \qquad (33)$$

where [P] = total number of polymer molecules.

Depending on the particular polymerization mechanism shown in Table 1, $[P^=]$ will vary and as a consequence the $\overline{DP}_n$ equation (Eq. 33) will also be different.

A. The L_{00} and QL_{R0} System

In these systems chain transfer is absent so that $C = C_1 = C_2 = 0$ and the number of polymer molecules formed

$$[P^=] = 0 \qquad (34)$$

Thus criterium No. 1 is rigorously satisfied even in the QL_{R0} system:

$$\overline{DP}_n = At/[I]_0 \qquad (35)$$

Due to the reversible termination, however, $\overline{M}_w/\overline{M}_n > 1$ in QL_{R0} systems.

B. The QL_{0R} and Q_{RR} Systems

In these systems chain transfer is reversible. In case both uni- and bimolecular chain transfer processes operate, the number of molecules is given by Eq. (27). In case only the unimolecular (C_1) or bimolecular (C_2) chain transfer operates, Eq. (27) can be simplified:

In Case $C_1 = 0$

$$[P^{=}] = \frac{\dfrac{C_2}{1 + 2C_2} At}{\frac{1}{2} + \left\{\frac{1}{4} + \left(\dfrac{C_2}{1 + 2C_2}\right)^2 \dfrac{k_p[I]_0}{2K_2} t\right\}^{1/2}} \tag{36}$$

Depending on whether t is small or large $\overline{DP}_n$ will tend toward two limits:

when t = small: $$\overline{DP}_n = \frac{At}{[I]_0 + \dfrac{C_2}{1 + 2C_2} At} \tag{37}$$

when t = large: $$\overline{DP}_n = \left(\frac{k_p[I]_0}{2K_2A}\right)^{1/2} \sqrt{At} \tag{38}$$

As shown by Eq. (38), $\overline{DP}_n$, in line with the living character of the system, may grow toward infinity. The increase in $\overline{DP}_n$ as a function of At will not be linear and its growth rate will be determined by the monomer addition rate A. Evidently, $\overline{DP}_n$ will be higher at a lower A at a given monomer consumption.

In Case $C_2 = 0$

$$[P^{=}] = \frac{\dfrac{C_1}{[M] + 2C_1} At}{\frac{1}{2} + \left\{\frac{1}{4} + \dfrac{1}{2K_1}\left(\dfrac{C_1}{[M] + 2C_1}\right)^2 At\right\}^{1/2}} \tag{39}$$

Similarly to Eq. (36), depending on t, Eq. (39) also tends toward two asymptotic limits, i.e., two limiting $\overline{DP}_n$'s. (In this and later equations, [M] is expressed by the approximation of Eq. 32.)

$$\text{when } t = \text{small:} \qquad \overline{DP}_n = \frac{At}{[I]_0 + \dfrac{C_1}{[M] + 2C_1} At} \tag{40}$$

$$\text{when } t = \text{large:} \qquad \overline{DP}_n = \sqrt{At/2K_1} \tag{41}$$

As in the $C_1 = 0$ case, $\overline{DP}_n$ may grow toward infinity with growing t, i.e., the system exhibits living character.

C. The QL_{01} and QL_{R1} Systems

In these systems, chain transfer is irreversible, i.e., $K_1 \to \infty$ and $K_2 \to \infty$. Thus Eq. (27) can be significantly simplified:

$$[P^=] = CAt = \frac{C_1 + C_2[M]}{[M] + 2(C_1 + C_2[M])} At \tag{42}$$

The number of polymer molecules increases at a constant rate due to the irreversibility of chain transfer. Thus

$$\overline{DP}_n = \frac{At}{[I]_0 + CAt} \tag{43}$$

and $\overline{DP}_n$ will exhibit linear growth only at very short polymerization times, i.e., when $t \ll [I]_0/CA$. At large t, $\overline{DP}_n$ will grow toward a limit

$$\lim_{t\to\infty} \overline{DP}_n = \frac{1}{C} = \frac{[M] + 2(C_1 + C_2[M])}{C_1 + C_2[M]} \tag{44}$$

Evidently in these cases $\overline{DP}_n$ is entirely determined by chain transfer. In the presence of only unimolecular or only bimolecular chain

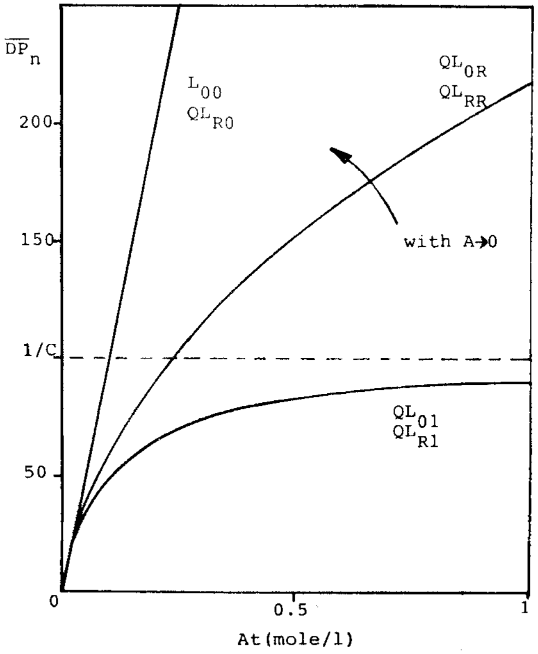


FIG. 1. Degree of polymerization vs amount of monomer consumed ($A = 10^{-2}$ mol/L·s, $C_2 = 10^{-2}$, $[I]_0 = 10^{-3}$ mol/L, $K_2 = 1$, $k_p = 10^6$ L·mol^{-1}s^{-1}).

transfer, Eqs. (42)-(44) can be further simplified. However, their character will not change.

DIAGNOSTIC TECHNIQUES: THE TREATMENT OF EXPERIMENTAL DATA

The classification of individual polymerization systems in terms of the mechanisms described in Table 1 can be readily effected by comparing the experimental data with the equations derived in the previous section. Specifically, three diagnostic techniques have been developed.

1. Representation of $\overline{DP}_n$ versus Monomer Consumed

According to this technique, $\overline{DP}_n$ versus At plots are prepared by the direct use of experimental data. Figure 1 illustrates characteristic trends of the systems identified in Table 1. This representation

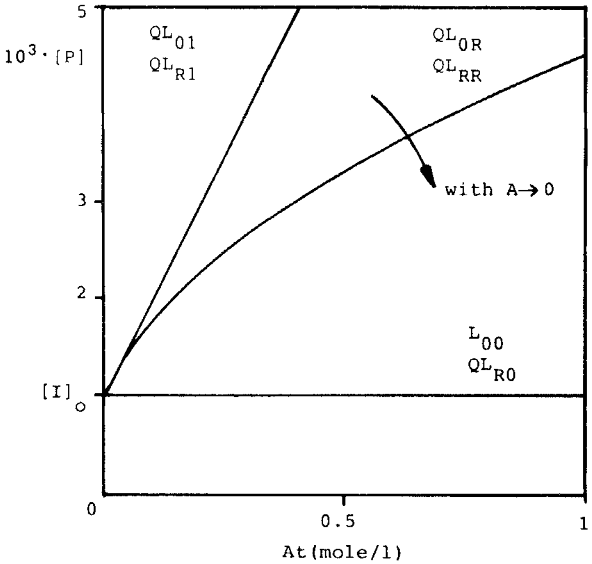


FIG. 2. Total number of polymer molecules as a function of the monomer consumed (constants as in Fig. 1).

emphasizes the (quasi)living nature of the systems at small At values; however, a reliable distinction between the individual mechanisms can only be obtained at relatively high At values. These plots do not give sufficiently accurate kinetic parameters. With decreasing monomer addition rate, the plots characteristic of the transfer-reversible QL_{0R} and QL_{RR} systems asymptotically move toward the straight line characteristic of the transferless L_{00} and L_{R0} systems. The curved arrow identified by A→0 in Fig. 1 serves to illustrate this tendency.

2. Representation of Number of Polymer Molecules versus Monomer Consumed

This diagnostic technique calls for a plot of the total number of polymer molecules formed [P] versus monomer consumption At. In this case P includes olefin-ended macromolecules $P^=$ plus any other polymeric species

$$[P] = [P^=] + [I]_0 = At/\overline{DP}_n \qquad (45)$$

Figure 2 shows characteristic shapes of [P] versus At plots for the systems in Table 1. The transferless systems L_{00} and QL_{R0} yield horizontal lines whereas systems with irreversible chain transfer give straight lines passing through $[I]_0$; the transfer-reversible systems QL_{0R} and QL_{RR} yield curves between these two limits.

In this representation $[I]_0$ is given by the intercept. This information is most welcome when the exact amount of initiator is unknown due to the presence of impurities, particularly moisture, or when initiator efficiency deviates from 100%. The irreversible chain transfer constant (i.e., the limit of $1/\overline{DP}_n$) can be determined with sufficient accuracy from the slope of the linear plot. With decreasing A the curves describing the transfer-reversible systems tend toward the horizontal line representing transferless systems (indicated by the curved arrow in Fig. 2).

3. Representation of At/[$P^=$] versus [$P^=$] Plots

At/[$P^=$] versus [$P^=$] plots are the best for diagnostic purposes because in such plots even transfer-reversible systems yield straight lines. The basis for these plots is provided by Eq. (46), obtainable by rearranging Eq. (26):

$$\frac{At}{[P^=]} = \frac{1}{C} + \frac{C_1 + C_2}{2(C_1 + C_2[M])(K_1 + K_2)}[P^=] \tag{46}$$

The necessary [$P^=$] values are available form Eq. (41):

$$[P^=] = \frac{At}{\overline{DP}_n} - [I]_0 \tag{47}$$

where At and $\overline{DP}_n$ are directly obtained from experimental data, and $[I]_0$ is given by the intercept of Fig. 2. Figure 3 illustrates characteristic plots of stystems described in Table 1. In this representation all the systems define straight lines: transferless systems fall on the vertical axis ([$P^=$] = 0), those with irreversible transfer give a horizontal line ($K_1 = K_2 = \infty$), whereas transfer-reversible systems yield straight lines between these two extremes. The slopes of plots associated with transfer-reversible systems increase with decreasing monomer addition rate i.e., they asymptotically approach

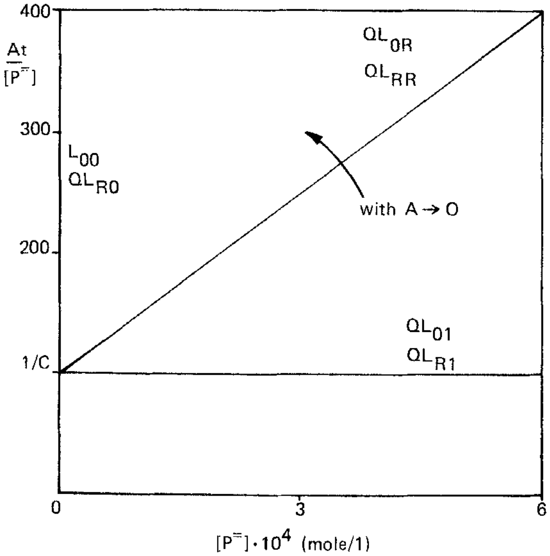


FIG. 3. At/[$P^=$] vs [$P^=$] representation (constants as in Fig. 1).

transferless systems and this tendency is indicated by the curved arrow in Fig. 3.

ACKNOWLEDGMENTS

Financial contributions by the NSF (INT-78-27245) and the Hungarian Academy of Sciences are gratefully acknowledged. We are most grateful to Professor M. Szwarc for his valuable comments.

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