FREE-RADICAL POLYMERIZATION

At the end of this lecture, you should be able to:

- Understand the kinetic of free-radical polymerization.
- Learn what is meant by kinetic-chain length.
- Understand the calculation of kinetic-chain length.
- Understand the chain-transfer reactions
- Solving problems including chain-transfer reactions
- Effect of temperature on the polymerization

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Kinetics of Free Radical Polymerization

1. Initiation

$$I \xrightarrow{k_d} 2\,R\cdot$$ *Radical Generation*

$$R\cdot + M \xrightarrow{k_i} M_1\cdot$$ *Initiation*

Assuming that $k_i >> k_d$ *and accounting for the fact that two Radicals are formed during every initiator decomposition,*

The rate of initiation, R_i *is given by:*

$$R_i = \frac{d[M_i]}{dt} = 2fk_d[I]$$

f *= efficiency of the initiator and is usually* $0.3 < f > 0.8$

2. Propagation

$$M_1\cdot \; + \; M \xrightarrow{k_p} M_2\cdot$$

$$M_2\cdot \; + \; M \xrightarrow{k_p} M_3\cdot$$

$$M_3\cdot \; + \; M \xrightarrow{k_p} M_4\cdot$$

$$\vdots$$

$$M_x\cdot \; + \; M \xrightarrow{k_p} M_{x+1}\cdot$$

$$R_p = -\frac{d[M]}{dt} = k_p[M\cdot][M]$$

3. Termination

$$M_x\cdot \; + \; \cdot M_y \xrightarrow[c]{k_t} M_x\text{-}M_y \; \textit{(Combination)}$$

$$M_x\cdot \; + \; \cdot M_y \xrightarrow{k_{td}} M_x \; + \; M_y \; \textit{(Disproportionation)}$$

Since two radicals are consumed in every termination, then:

$$R_t = 2k_t[M\cdot]^2$$

4. Steady-state Assumption

Very early in the polymerization, the concentration of radicals becomes constant because $R_i = R_t$

$$\therefore \; 2fk_d[I] = 2k_t[M\cdot]^2$$

$$2fk_d[I] = 2k_t[M\cdot]^2$$

Solve this equation for $[M\cdot]$:

$$[M\cdot] = (fk_d[I]/k_t)^{1/2}$$

Substituting this into the propagation expression:

$$\boxed{R_p = k_p[M\cdot][M] = k_p[M](fk_d[I]/k_t)^{1/2}}$$

Since the rate of propagation, R_p, *is essentially the rate of polymerization, the rate of polymerization is proportional to* $[I]^{1/2}$ *and* $[M]$.

5. KINETIC CHAIN LENGTH

The kinetic chain length, **ν**, is defined as the average number of monomers consumed by each primary radical. Obviously from this definition, the magnitude of the kinetic chain length will depend on the rate of the propagation relative to the termination rate, i.e.,:

$$\nu = \frac{R_p}{R_t} \qquad \boxed{1}$$

At Steady – State:

$$\nu = \frac{R_p}{R_t} = \frac{R_p}{R_i} \qquad \boxed{2}$$

We know that :

$$\mathbf{R_p = -\frac{d[M]}{dt} = k_p[M\cdot][M]} \qquad \boxed{3} \qquad\qquad R_t = \frac{-d[M\cdot]}{dt} = 2k_t[M\cdot]^2 \qquad \boxed{4}$$

It follows on substitution for Rp and Rt in equation (2):

$$\nu = \left(\frac{k_p}{2k_t}\right)\frac{[M]}{[M\cdot]} \qquad \boxed{5}$$

Substituting for **[M·]** from Equation(3) yields:

$$\nu = \left(\frac{k_p^{\,2}}{2k_t}\right)\frac{[M]^2}{R_p} \qquad \boxed{6}$$

Equations (5) and (6) are quite general and do not depend on the nature of initiation. Notice the inverse relation between the kinetic chain length and the radical concentration. For reactions initiated by the decomposition of an initiator,

$$[M\cdot] = \left(\frac{fk_d}{k_t}\right)^{1/2} [I]^{1/2}$$

Thus,

$$\nu = \frac{k_p}{2(fk_d\, k_t)^{1/2}} \frac{[M]}{[I]^{1/2}}$$

Now, the number-average degree of polymerization can be calculated as follows::

X_n (or DP_n) $= 2R_p / R_t = 2\, R_p/R_i$ **for termination by combination**

X_n (or DP_n) $= R_p / R_t = R_p/R_i$ **for termination by disproportionation**

So,

$X_n = 2\,\nu$ **for termination by combination**

$X_n = \nu$ **for termination by disproportionation**

Example (1): For pure styrene polymerized at 60°C, the value of the ratio k_p^2/k_t is 0.0012 1/mol-s. The corresponding value for pure vinyl acetate polymerized at 60°C is 0.125 l/mol-s.

a. Estimate their relative kinetic length chain lengths.
b. Calculate the kinetic chain length for polystyrene if the rate of polymerization is 10^{-4} mol/l-s and monomer concentration is 8.35 mol/l.

Solution:

$$\nu = \left(\frac{k_p^2}{2k_t}\right)\frac{[M]^2}{R_p}$$

Assume the rates of polymerization and monomer concentrations are the same for styrene(s), and vinyl acetate (VA).

a) $\nu_{VA}/\nu_s = \left(k_p^2/k_t\right)_{VA} / \left(k_p^2/k_t\right)_s = 0.125/0.0012 = 104$

b) $\nu_s = (0.0012/2)\,(8.35)^2/10^{-4} = 400$

CHAIN-TRANSFER REACTIONS

The number of polymer molecules is generally found to be less than would be expected to be produced by the primary radicals (i.e., Xn is always less than either 2ν or ν). Obviously, other components of the reaction medium initiate chain growth. The existence of such polymer-producing extraneous reactions is attributable to chain-transfer reactions that consist essentially of the following sequence of steps:

$$M_{x\cdot} + TL \rightarrow M_xL + T\cdot$$

$$T\cdot + M \rightarrow TM\cdot, \text{etc.}$$

where TL = transfer agent, which may be a solvent, monomer, initiator, or polymer

L = a labile group such as hydrogen or chlorine atoms, etc.

Transfer to a polymer does not alter the number of polymer molecules produced, therefore we neglect this type of transfer reaction in the subsequent discussion.

In the presence of transfer reactions, the expression of the kinetic chain length has to be modified to include all possible sources of polymer molecules. Thus

$$\nu = \frac{R_p}{\text{Rate of All Reactions Leading to Polymer Molecule Production}}$$

$$\nu = \frac{R_p}{fk_d[I] + k_{tr,M}[M][M\cdot] + k_{tr,s}[S][M\cdot] + k_{tr,I}[I][M\cdot]}$$

where $k_{tr,M}$ $k_{tr,S}$ and $k_{tr,I}$ are velocity constants for chain transfer to monomer M, solvent S, and initiator I, respectively. To estimate the tendency for transfer quantitatively, we define transfer constants:

$$\frac{1}{\overline{X}_n} = \frac{k_t}{k_p^2}\frac{R_p}{[M]^2} + C_M + C_s\frac{[S]}{[M]} + C_I\left(\frac{k_t}{k_p^2 fk_d}\right)\frac{R_p^2}{[M]^3}$$

Since $Xn = \nu$ and substituting for [I] and [M·] in the above Equation becomes:

$$C_M = \frac{k_{tr,M}}{k_p};\ C_S = \frac{k_{tr,S}}{k_p};\ C_I = \frac{k_{tr,I}}{k_p}$$

Example(2): For the polymerization of pure (undiluted) styrene with benzoyl peroxide at 60°C, the number-average degree of polymerization, Xn, is given by the expression:

$$\frac{1}{X_n} = 0.6 \times 10^{-4} + 12.0\ R_p + 4.2 \times 10^{4}\ R_p^{2}$$

where Rp = rate of polymerization (mol/l-s).

a. What is the transfer constant to the monomer, CM?

b. Calculate the transfer constant to the initiator if the monomer concentration [M] is 10 mol/l and fkd kp2/kt = 2.29×10^{-9}.

Solution:

CM = 0.6×10^{-4}

$$C_I \left(\frac{k_t}{k_p^{2}\, f k_d} \right) \frac{R_p^{2}}{[M]^{3}} = 4.2 \times 10^{4}\ R_p^{2}$$

$$C_I = 4.2 \times 10^{4}\ [M]^{3} \times 2.29 \times 10^{-9}$$

$$= 0.0962$$

A. TRANSFER TO UNDILUTED MONOMER:

For bulk polymerization (i.e., polymerization in the absence of a solvent) the general Equation reduces to:

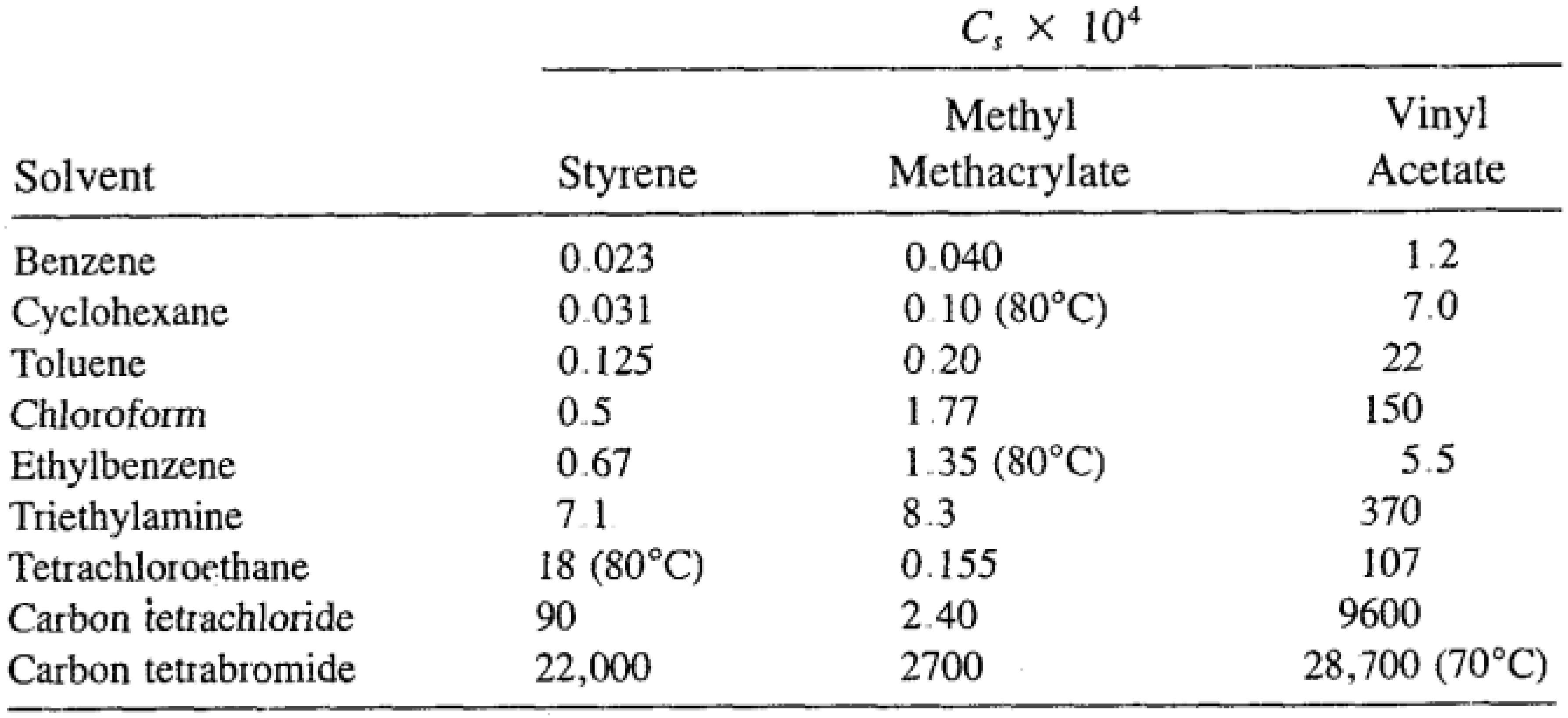
$$\frac{1}{\overline{X}_n} = C_M + \left(\frac{k_t}{k_p^2}\right)\frac{R_p}{[M]^2} + C_I\left(\frac{k_t}{k_p^2 f k_d}\right)\frac{R_p^2}{[M]^3}$$

B. TRANSFER TO SOLVENT

In the presence of a solvent and with a proper choice of reaction conditions so as to minimize other types of transfer, the general expression for transfer (i.e., the general Equation) becomes

$$1/X_n = 1/X_{no} + C_S\,[S]/[M]$$

Chain Transfer Constants for Various Solvents and Radicals at 60°C Except as Noted



	$C_s \times 10^4$		
Solvent	Styrene	Methyl Methacrylate	Vinyl Acetate
Benzene	0.023	0.040	1.2
Cyclohexane	0.031	0.10 (80°C)	7.0
Toluene	0.125	0.20	22
Chloroform	0.5	1.77	150
Ethylbenzene	0.67	1.35 (80°C)	5.5
Triethylamine	7.1	8.3	370
Tetrachloroethane	18 (80°C)	0.155	107
Carbon tetrachloride	90	2.40	9600
Carbon tetrabromide	22,000	2700	28,700 (70°C)

Example(3): The transfer constant to the solvent for the polymerization of styrene in benzene at 100°C is 0.184 X 10^{-4}. How much dilution is required to halve the molecular weight given that $1/X_{no} = 2.5 \text{ X } 10^{-4}$?

Solution:

$$1/X_n = 1/X_{no} + C_S\,[S]/[M]$$

$$\left(\frac{2}{\overline{X}_{no}}\right) - \frac{1}{X_{no}} = 0.184 \times 10^{-4}\,[S]/[M]$$

$$\left(\frac{1}{\overline{X}_{no}}\right)\frac{10^4}{0.184} = \frac{[S]}{[M]}$$

$$[S] = 13.6\,[M]$$

Therefore , the dilution factor is about 13.6

Control of Molecular Weight by Transfer

Chain-transfer agents with transfer constants near unity are quite useful in depressing molecular weight in polymerization reactions. This is often of great commercial importance, for example, in the polymerization of dienes to synthetic rubbers, where chain length must be controlled for ease of processing. The choice of transfer constant near unity ensues that the transfer agent, or regulator, is consumed at the same rate as the monomer. So that [S]/[M] remains constant throughout the reaction. Too large quantities are needed of chain-transfer agents with constants much lower than unity, and agents with transfer constants greater than about 5 are used up too early in th suitable transfer agents for several comm

$$C_M = \frac{k_{tr,M}}{k_p};\ C_S = \frac{k_{tr,S}}{k_p};\ C_I = \frac{k_{tr,I}}{k_p}$$

TEMPERATURE DEPENDENCE OF DEGREE OF POLYMERIZATION

The dependence of the polymerization rate and the number-average degree of polymerization on temperature can be demonstrated if the respective relation is expressed in the form of the Arrhenius equation.

$$\boxed{k_b = A \exp\left(\frac{-E_b}{RT}\right)}$$

$$\boxed{\frac{d \ln R_p}{dT} = \frac{\left(E_p - \frac{E_t}{2}\right) + \frac{E_d}{2}}{RT^2}}$$

$$\boxed{\frac{d \ln \overline{X}_n}{dT} = \frac{\left(E_p - \frac{E_t}{2}\right) - \frac{E_d}{2}}{RT^2}}$$

NOTE: For radical polymerizations the activation energy of decomposition is of the order of 30 kcal/mol while (Ep – Et/2) is about 4 to 7 kcal/mol. Thus the temperature coefficients are, respectively,

$$\boxed{\begin{aligned} dR_p/dT &> 0 \\ dX_n/dT &< 0 \end{aligned}}$$

These results predict that the rate of polymerization increases with increasing temperature while the molecular weight decreases. The same conclusion can be drawn for thermal polymerizations since (Ep – Et/2) – Ed /2 is a negative quantity.

Example (4): The energies of activation for the polymerization of styrene with di-tertiary-butyl peroxide as initiator are
Ed = 33.5 kcal/mol
Ep = 7.0 kcal/mol
Et = 3.0 kcal/mol

Calculate the relative (a) rates of propagation and (b) degree of polymerization (X**η)** if the polymerization temperature is changed from 50°C to 60°C.

a. $$\frac{d\ \ln R_p}{dT} = \frac{E}{RT^2}$$

where $E = E_p - \frac{E_t}{2} + \frac{E_d}{2}$.

$$\int_{R_{p/T_o}}^{R_{p/T}} d\ \ln R_p = \int_{T_o}^{T} \frac{E}{RT^2}\, dT$$

$$\ln \frac{R_{pT}}{R_{pT_o}} = \frac{E}{R}\left[\frac{1}{T_o} - \frac{1}{T}\right]$$

$$T_o = 50°C = 323\ K;\ \ T = 333\ K$$

$$E = 7 - \frac{3}{2} + \frac{33.5}{2} = 22.25\ kcal/mol$$

$$\frac{E}{R} = \frac{22.25 \times 10^3\ cal/mol}{1.99\ cal/mol - K}$$

$$\frac{1}{T} - \frac{1}{T_o} = 0.0001\ K^{-1}$$

$$\ln \frac{R_{p60}}{R_{p50}} = 1.12$$

$$R_{p60}/R_{p50} = 1^{1.12} = 3.06$$

$$\ln \overline{X}_{n60}/\overline{X}_{n50} = \frac{E}{RT}\left[\frac{1}{T_o} - \frac{1}{T}\right];\ \ E - E_p - \frac{E_t}{2} - \frac{E_d}{2}$$

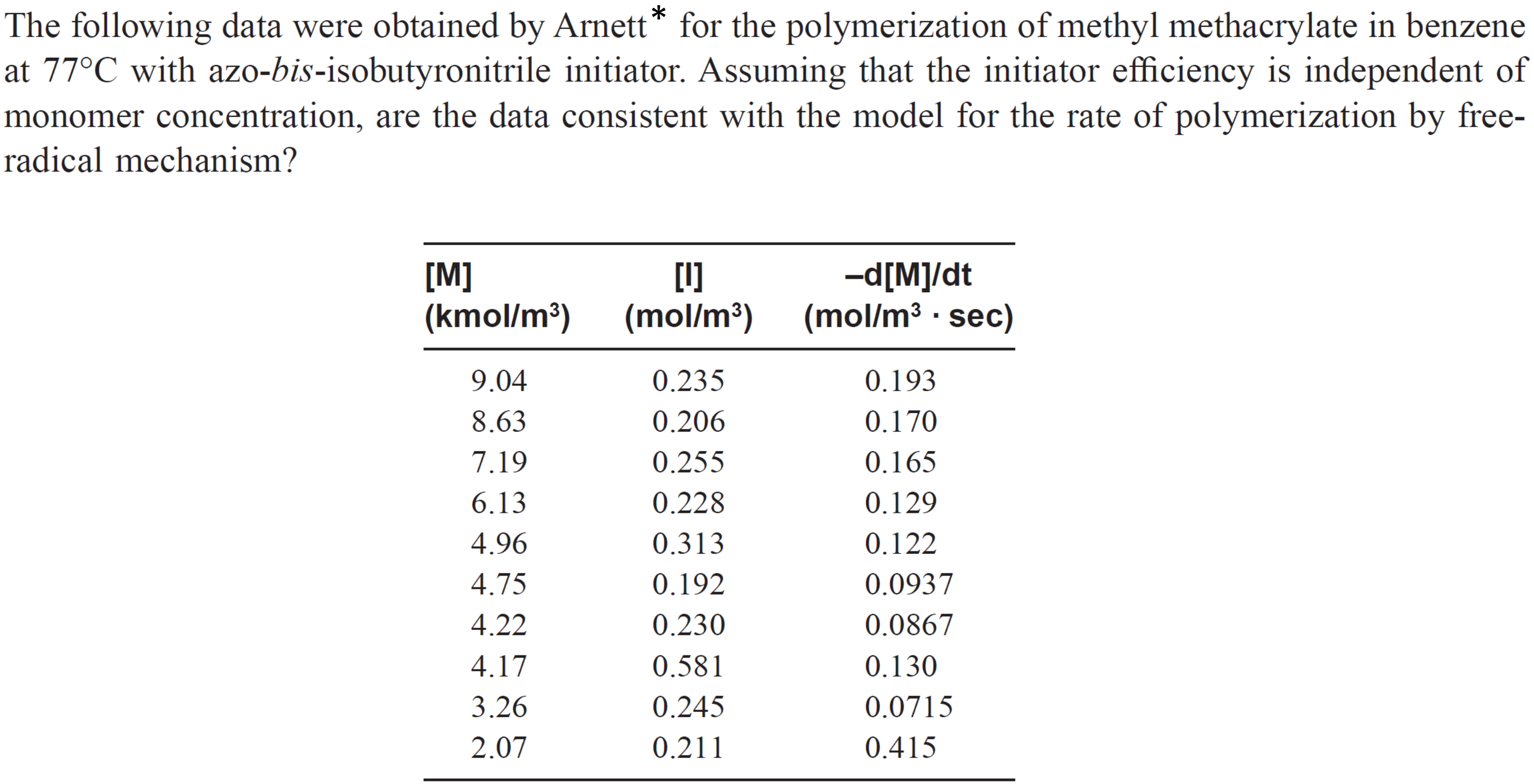
$$= -11.25\ kcal/mol$$

$$E/RT = \left(-\frac{11.25 \times 10^3\ cal/mol}{1.99\ cal/mol - K}\right)\left(0.001\ K^{-1}\right)$$

$$= -0.57$$

$$\frac{\overline{X}_{\eta 60}}{\overline{X}_{\eta 50}} = 1^{-0.57} = 0.57$$

Extra – Problems



Q1 The following data were obtained by Arnett* for the polymerization of methyl methacrylate in benzene at 77°C with azo-*bis*-isobutyronitrile initiator. Assuming that the initiator efficiency is independent of monomer concentration, are the data consistent with the model for the rate of polymerization by free-radical mechanism?

[M] (kmol/m³)	**[I] (mol/m³)**	**–d[M]/dt (mol/m³ · sec)**
9.04	0.235	0.193
8.63	0.206	0.170
7.19	0.255	0.165
6.13	0.228	0.129
4.96	0.313	0.122
4.75	0.192	0.0937
4.22	0.230	0.0867
4.17	0.581	0.130
3.26	0.245	0.0715
2.07	0.211	0.415

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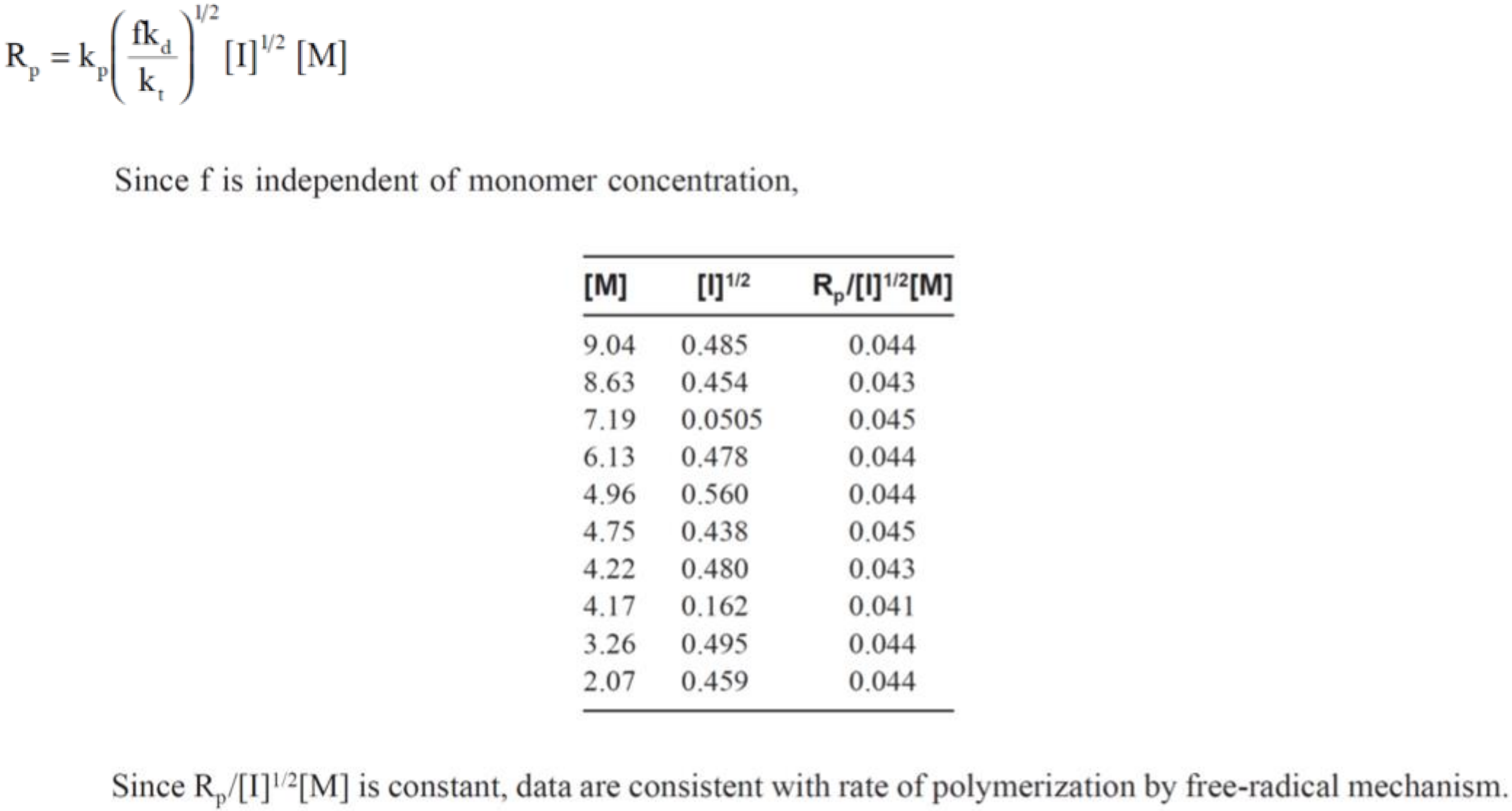
* J. Am. Chem. Soc. 74, 2027 (1952)

Sol



$$R_p = k_p\left(\frac{fk_d}{k_t}\right)^{1/2}[I]^{1/2}[M]$$

Since f is independent of monomer concentration,

[M]	$[I]^{1/2}$	$R_p/[I]^{1/2}[M]$
9.04	0.485	0.044
8.63	0.454	0.043
7.19	0.0505	0.045
6.13	0.478	0.044
4.96	0.560	0.044
4.75	0.438	0.045
4.22	0.480	0.043
4.17	0.162	0.041
3.26	0.495	0.044
2.07	0.459	0.044

Since $R_p/[I]^{1/2}[M]$ is constant, data are consistent with rate of polymerization by free-radical mechanism.

Q2A steady-state free-radical styrene polymerization process is being controlled such that the rate of polymerization is constant at 1.79 g of monomer/ml-min. The initiator concentration is 6.6×10^{-6} mol/ml.

a. What must be done to maintain the constant rate of polymerization?
b. If the rate constant for the first-order decomposition of the initiator, k_d, is 3.25×10^{-4} min^{-1}, what is the rate of free radical generation per second per milliliter? What is X_n?
c. What percentage of the original initiator concentration remains after a reaction time of 3 h?

Sol:

a.

$$R_p = k_p\left(\frac{fk_d}{k_t}\right)^{1/2}[I]^{1/2}[M]$$

Assuming f is independent of [M] to keep R_p constant, [I] and [M] must be kept constant.

b. If the rate constant for the first-order decomposition of the initiator, k_d, is 3.25×10^{-4} min^{-1}, what is the rate of free radical generation per second per milliliter? What is X_n?

Sol:

$$\frac{d[M\cdot]}{dt} = 2f\,k_d[I]$$

$$= 2k_d[I] \text{ assume } f = 1$$

$$k_d = 3.25 \times 10^{-4}\,\text{min}^{-1}$$

$$= 5.42 \times 10^{-6}\,\text{s}^{-1}$$

$$I = 6.6 \times 10^{-6}\,\text{mol/ml}$$

$$R_i = \frac{d[M\cdot]}{dt} = 2\left(5.42 \times 10^{-6}\,\text{s}^{-1}\right)\left(6.6 \times 10^{-6}\,\text{mol/ml}\right)$$

$$= 7.5 \times 10^{-11}\,\text{mol/ml} - \text{s}$$

$$\overline{X}_n = \frac{R_p}{R_i}$$

$$R_p = 1.79 \times 10^{-3}\,\text{g/ml} - \text{min}$$

$$= \frac{1.79}{104} \times 10^{-3}\,\text{mol/ml} - \text{min}$$

$$= 1.72 \times 10^{-5}\,\text{mol/ml} - \text{min}$$

$$\overline{X}_n = \frac{1.72 \times 10^{-5}\,\text{mol/ml} - \text{min}}{4.29 \times 10^{-9}\,\text{mol/ml} - \text{min}}$$

$$= 4.01 \times 10^{3}$$

c. What percentage of the original initiator concentration remains after a reaction time of 3 h?

Sol:

$$\frac{-d[I]}{dt} = f\,k_d[I]$$

$$\frac{-d[I]}{[I]} = k_d\,dt;\ f = 1$$

$$[I] = e^{-k_d t}$$

$$= e^{-\left(3.25 \times 10^{-4} \times 60 \times 3\right)}$$

$$= 94.3\%$$