Organic Chemistry

Q1:Derive an equation describing the relationship between the G-value of polymer mean chain length and the dose-rate.

Q2: For radiation-induced polymerization (at high degree of polymerization and at steady state radiolysis), derive an equation by which you can demonstrate that the overall rate of polymerization depends on the monomer concentration [M], monomer radical concentration, and the radical concentration produced from the solvent.

Q3: In the pulse radiolysis of N_2O-saturated aqueous solutions of [0.9×10^{-2} M] poly vinyl pyrridon (with $M_{w,o}$ = 360,000 g/ mol), it was found that the concentration of the number of inter-molecular crosslinking bonds in a unit volume of sample is $2x\ 10^{-7}$ ML^{-1}. Determine the M_w of the poly vinyl pyrridon, and the G(crosslinking) assuming that the solution was received 5 kGy of dose.

Q4: A polymer with weight average degree of polymerization (M_w) (assuming random distribution) of 10^5 and the minimum required absorbed dose for gel formation (r_g) is 30 kGy. Calculate the values for corsslinks and crosslinks units in **SI** units (mole per joule) and what are the values of the weight average molecular weight after irradiation and γ?

Q5: During the radiolysis of polyethylene, the following results were generated:

D (MGy)	Sol fraction (s)
0.250	0.788
0.200	0.932
0.167	1.07
0.143	1.16
0.125	1.25

Calculate the G (scission), assuming the G (crosslink) = 1.16 per 100 eV.

Q6: How many crosslinks per weight average and number average polymer molecule are required to reach the gel point

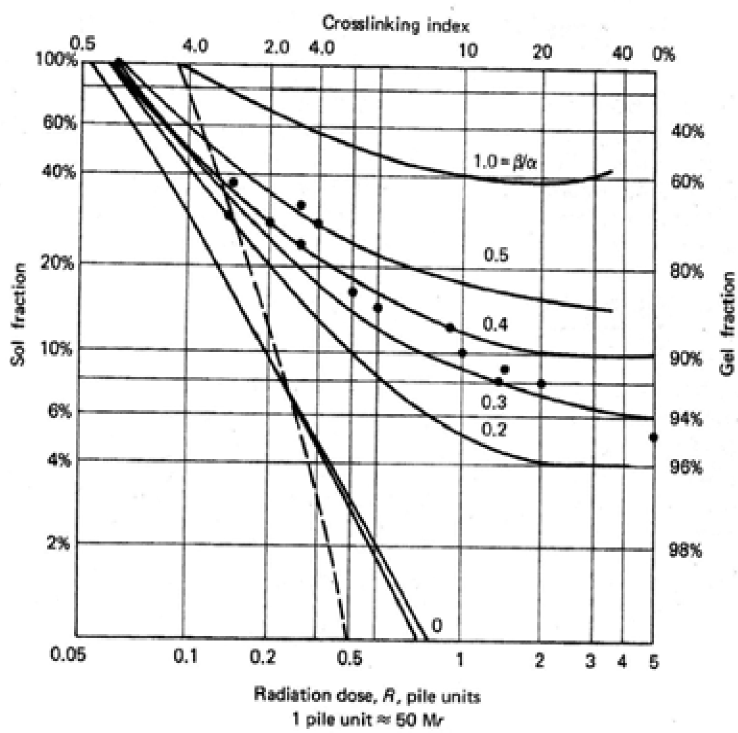
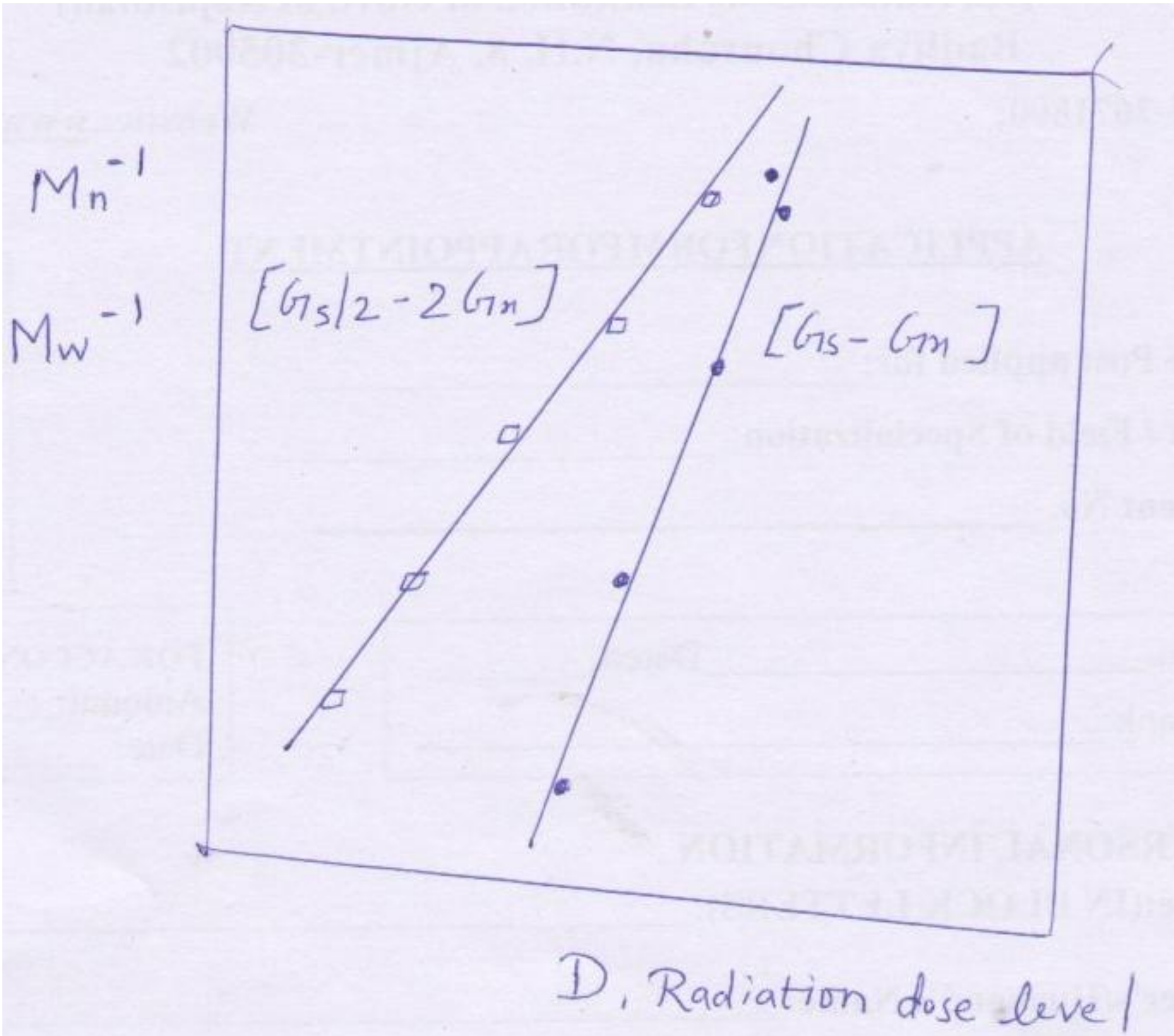


Fig. . Sol and gel fraction of irradiated polyethylene. The black dots indicate observed values, solid lines indicate theoretical curve assuming a random probability initially (numbers represent ratio of chain fracture to crosslinking), and broken lines indicate theoretical curve assuming uniform initial distribution (no chain fracture). (A. Charlesby, "Atomic Radiation and Polymers," Pergamon Press, London, 1960.)

Q7: Develop an equation for the degree of polymerization at high dose-rates.

Answer-1



Relation Between G-Value of Polymer Mean Chain length and dose Rate

$$M_n^{-1} = M_{n,0}^{-1} + [G_s - G_m] D/100 N_{av}$$

$$M_w^{-1} = M_{w0}^{-1} + [G_s/2 - 2G_m] D/100 N_{av}$$

G_s = G scission

D = Dose level

M_w = Molecular weight

G_m = Crosslinking

Answer-2

In polymerization, the reaction rate for initiation, propagation and termination is defined in following manner.

$$v_i = \mathrm{d}[M\cdot]/\mathrm{d}t = 2k_d f[I]$$

$$v_p = k_p[M][M\cdot]$$

$$v_t = -\mathrm{d}[M\cdot]/\mathrm{d}t = 2k_t[M\cdot]^2$$

In this, *f* is denoted as the efficiency of the initiator and k_d, k_p, and k_t are defined as the constants for three phases of polymerization those are initiator dissociation, chain propagation and termination. [I], [M] and [M\cdot] is the concentration of the initiator, monomer and the active growing chain. In the steady rate approximation, the concentration of the active growing chains remains constant, like, the rate of initiation and termination is identical. The concentration of active chain can be deduced and conveyed in some known species (Sorrell, 2006).

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

Under this case, the rate of chain propagation can be defined with the use of a function of the initiator and monomer concentration

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

The kinetic chain length v is a aspect of the standard item of monomer units those react with an active center in the period of its life time and is linked to the molecular weight with the termination mechanism (Sorrell, 2006). The dynamic chain length is the function of propagation rate and initiation rate, without chain transfer,

$$v = \frac{R_p}{R_d} = \frac{k_p[M][M\cdot]}{2fk_d[I]} = \frac{k_p[M]}{2(fk_dk_t[I])^{1/2}}$$

With lack of chain transfer effect occurs in the reaction, P_n, the number average degree of polymerization can be associated with the length of the kinetic chain. 1 polymer molecule is developed per every kinetic chain under the termination by disproportionation,

$$P_n = v$$

Termination by combination results in the production of one polymer molecsule per two kinetic chains:

$$P_n = 2v$$

Any mixture of these both mechanisms can be described by using the value *δ*, and the contribution of disproportionation to the overall termination process:

$$P_n = \frac{2}{1+\delta}v$$

If chain transfer is taken into consideration, then there are some other methods to conclude the growing chain. The equation for dynamic chain length will be modified as the following.

If chain transfer is taken into consideration, the kinetic chain length is not influenced by the transfer process, as the growing free-radical center produced by the initiation step stays energetic after any event of chain transfer, even though multiple polymer chains are produced. Nevertheless, the number average degree of polymerization reduces as the chain transfers, since the developing chains are finished by the events of chain transfer (Sorrell, 2006). By considering the chain transfer reaction towards solvent *S*, initiator *I*, polymer *P*, and added chain transfer agent *T*, the P_n equation can be enhanced:

$$\frac{1}{P_n} = \frac{2k_{t,d} + k_{t,c}}{{k_p}^2[M]^2} R_p + C_M + C_S\frac{[S]}{[M]} + C_I\frac{[I]}{[M]} + C_P\frac{[P]}{[M]} + C_T\frac{[T]}{[M]}$$

It is usual to define chain transfer constants C for the different molecules

$$C_M = \frac{k_{tr}^M}{k_p}, \; C_S = \frac{k_{tr}^S}{k_p}, \; C_I = \frac{k_{tr}^I}{k_p}, \; C_P = \frac{k_{tr}^P}{k_p}, \; C_T = \frac{k_{tr}^T}{k_p}$$

Answer 3 .$M_{w = 360,000 g/mol}$

cross linking bond $=2x10^{-7}$ mc^{-1}

D= 5kGy of dose

$M_w^{-1} = M_w^{-1}{}_0 + (Gs/2 - 2\ Gx)/\ D/100\ Nav$

$M_w^{-1} = 360000 + (\ 2x\ 10^{-7} - 2\ x\ 0.9\ x10^{-2}\ )\ 5/100\ Nav$

$M_w^{-1} = 360000 + (\ 2\ x\ 10^{-7} - 1.8\ x\ 10^{-2}\ )\ 1/20\ Nav$

$M_w^{-1} = 360000 + (\ 0.2\ x\ 10^{-5})\ 0.05$

$M_w^{-1} = 360000 + 0.01\ x\ 10^{-5}$

$M_w^{-1} = 360000.01\ x\ 10^{-5}$

$M_w = 360000.01\ x\ 10^{-4}$

Now calculate G

$D_{gel} = 0.5x\ 10^7 /\ G(x)\ Mw$

D =5 kGy

$Mw = 360000.01\ x\ 10^{-4}$

Now G=?

$5 = 0.5x\ 10^7 /G(x)\ x\ 360000.01\ x\ 10^{-4}$

$Gx = 0.5x\ 10^7 /\ 5\ x\ 360000.01\ x\ 10^{-4}$

$Gx = 0.5\ x10^7 /\ 1800000.05\ x10^{-4}$

$Gx = 36000001\ x\ 10^3$

Answer-4

Ans 4.calculate G (crosslink)

D_{gel} = 0.5x 10^7 / G(x) Mw

D =30kGy

Mw = 1x10^5

Now G = 0.5 x10^7 / D_{gel} xMw

G = 0.5 x10^7/ 30 x 1x10^5

G = 0.5 x10^7 / 30 x10^5

G = 0.0166 x10^2 mole per joule

In SI unit G = 0.0166 x10^2 $m^2 \cdot kg \cdot s^{-2} \cdot mol^{-1}$

Answer-5

Calculate $G_{scission}$

Mn^{-1} = Mn^{-1} 0 + (Gs –Gx) D/100 Nav

$G_{value\ =}$ no. of events (yield) per 100eV or radiation energy

100eV = 1.602 x 10^{-17}kGy.g

Mn^{-1} = Mn^{-1} 0 + (Gs –Gx) D/100 Nav

Mn^{-1} = no. of radiolysis=5

Gs = G scission = ?

Gx = G crosslink =1.16 per 100 eV.

100eV = 1.602 x 10^{-17}kGy.g

So Gx = 1.16 x 1.602 x 10^{-17} kgy.g

$= 1.85832\ x10^{-17}$ kGy.g

D (MGy)	Sol fraction (s)
0.250	0.788
0.200	0.932
0.167	1.07
0.143	1.16
0.125	1.25

D = 0.250+ 0.200+0.167+0.143+0.125 = 0.885/5 = 0.177

$Mn^{-1} = Mn^{-1}\ 0 + (Gs – Gx) D/100\ Nav$

$5= 5+ (Gs - 1.85832\ x10^{-17})\ 0.177/100$

$Gs = 5+ (- 1.85832\ x10^{-17}/5)\ 0.00177$

$Gs = 5 + (0.07433\ x\ 10^{-17})\ 0.00177$

$Gs = 5 + 0.000131\ x10^{-17} = Gs = 5.000131\ x10^{17}$

Answer-6

ANS.6 Pc = 1/ (R+Rp(F-2))0.5

R = RADIATION DOSE PILE UNIT 1 PILE UNIT = 50mr

In this graph gel point is 5 so r =5x50 = 250

P = 0.2

F = 96%

Pc = 1/ (250 + 250 x 0.2 (96/100 -2) 0.5

= 1/ 250+ 50 (0.96 -2) 0.5

= 1/300 (1.04) 0.5

$= 1/300 \times 0.52$

$= 1/156.00$

$= 0.00641 = 64 \times 10^{-4}\ m^2 \cdot kg \cdot s^{-2} \cdot mol^{-1}$ crosslinks are required

References

Sorrell, T.N. (2006). *Organic chemistry*. University Science Books.

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