

STRUCTURE EFFECTS ON THE SOL FRACTION-DOSE RELATIONSHIP IN RADIATION CROSSLINKING OF POLYMERS*

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ABSTRACT

The structure effects of polymers on the relationship between sol fraction and radiation dose are discussed in detail. In consideration of the deviation of experimental results from Charlesby-Pinner's and Chen-Liu-Tang's expressions relating sol fraction to radiation dose, we introduced an exponent β concerned with the structure and property parameters of a polymer (glass transition temperature T_g and molecular internal rotating steric factor δ) and assumed that the fracture density is proportional to R^β (R is radiation dose). Thus, a general expression, formula (9), relating sol fraction to radiation dose is derived.

When $\beta = 1$ and $\beta = 0.5$, this expression is reduced to the above-said two expressions. Using this general expression, the experimental data of a number of polymers are treated. It is shown that the expression is in good agreement with the experimental results, β value is in the range of 0.5 to 1.0.

THEORETICAL ANALYSIS

In the late 50's, Charlesby-Pinner^[1] treated the random crosslinking of polymers using Flory's probability method^[2] on the basis of the following assumptions:

- 1) Radiation induced crosslinking is random and the molecular weight distribution of polymer is also random.
- 2) Crosslinking process within a molecule may be neglected.
- 3) Radiation induced scission occurs at random.
- 4) The reaction of crosslinking and scission is independent to each other.
- 5) The degree of crosslinking and fracture are both very small.
- 6) The degree of crosslinking and fracture are proportional to radiation dose respectively.

and obtained a simple expression relating sol fraction S to radiation dose R (Mr), i. e. Charlesby-Pinner expression (Charlesby's expression):

$$(S + \sqrt{S}) = \frac{p_0}{q_0} + \frac{1}{q_0 u_1 R} \quad (1)$$

where p_0 — fracture density, density of main chain scission per unit dose;
 q_0 — crosslinking density, portion of unit crosslinked per unit dose;
 u_1 — initial number-average degree of polymerization.

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According to this relation, a plot of $(S + \sqrt{S})$ against $1/R$ will give a straight line with a slope of $1/q_0 u_1$. However, many researchers' experimental results show that this expression is not in good agreement with sol data of radiation induced crosslinking of some polymers. Many researchers^[3,4] ascribed this deviation to that the initial molecular weight distribution does not fit the Flory's distribution. Using Saito's method^[4], Inokuti^[3] et al. treated the data of radiation induced polyethylene with initial molecular weight distribution obeying Schulz-Zimm distribution, but the agreement between theory and experimental results was not improved^[5]. According to Kotliar's analysis^[6], irrespective of initial molecular weight distribution, the radiolytic products of polymer will approach the Flory's distribution after the polymer is irradiated for certain period of time. Hence, the deviation of initial molecular weight distribution of polymer from the Flory's distribution is not the real reason for that this expression is not in agreement with experimental results.

In the late 70's, Chen-Liu-Tang^[7] studied the radiation induced crosslinking of polyethylene. On the basis of experimental results, they corrected Charlesby's assumption that fracture density is proportional to radiation dose and assumed that fracture density is proportional to the square root of radiation dose and obtained a new expression:

$$R(S + \sqrt{S}) = \frac{1}{q_0 u_1} + \frac{p'_0}{q_0} \sqrt{R} \quad (2)$$

where p'_0 —a constant; other symbols are similar to equation (1). This expression is in good agreement with the data of radiation induced crosslinking of polyethylene. According to their expression, portion of unit scission per unit dose is not constant and decreases with increasing radiation dose.

We treated the experimental results of our laboratory and from other researchers by Charlesby-Pinner and Chen-Liu-Tang expressions respectively and found that the radiation induced crosslinking of some polymers are in good agreement with Charlesby-Pinner expression but not in agreement with Chen-Liu-Tang expression, such as polyvinylchloride (Fig. 1), while the experimental results of radiation crosslinking of other polymers are in agreement with Chen-Liu-Tang expression but not in agreement with Charlesby-Pinner expression, such as polyethylene (Fig. 4). The experimental results of still other polymers are neither in

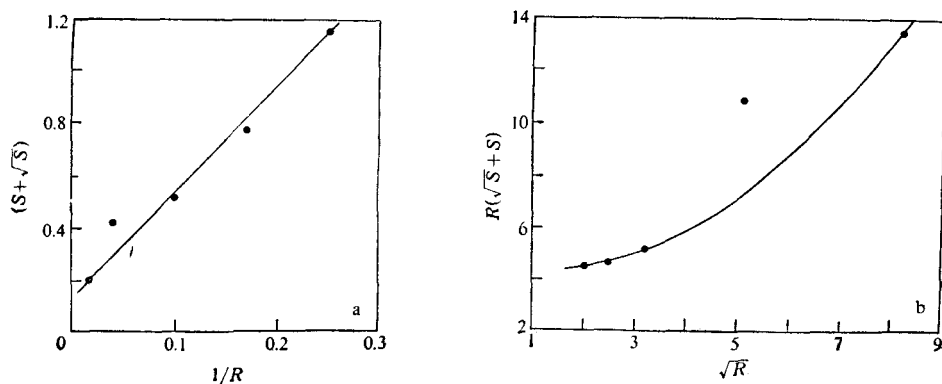


Fig. 1 Radiation crosslinking of polyvinylchloride

agreement with Charlesby-Pinner expression nor Chen-Liu-Tang one, such as polypropylene (Fig. 7). An analysis of available data shows that polymers with sol fraction in good agreement with Charlesby-Pinner expression possess the following structural features:

1) Stiff main-chain;

2) The polymers or copolymers are of the degrading type. On the other hand, the structural features of polymers whose sol data are in agreement with Chen-Liu-Tang expression are

1) Flexible main-chain;

2) Branched polymers.

It is obvious that the structural features of polymer have an important effect on its crosslinking behavior. In most cases, the crosslinking and scission reaction occur simultaneously, but the probability of these two reaction is different. The structure of polymer is an important factor that determines the probability of each reaction. Therefore, we suppose that the main reason why the above theoretical expressions are not well fit to experimental results lies in the assumption that fracture density is proportional to radiation dose or to its square root which are questionable or might be two special cases.

We suppose that the relationship between fracture density and radiation dose is dependent on the chain structure of polymers, i. e. connected with stiffness or flexibility of polymer chain⁽⁸⁾. However, how does the structure of polymer influence on the relationship between fracture density and radiation dose and how to define the influence quantitatively is a difficult problem.

When random crosslinking and random scission occur under radiation in a linear polymer simultaneously, the crosslinking and fracture density are denoted by q and p , and assume that the molecular weight distribution of polymer after irradiation approaches Flory's distribution, then sol fraction of the radiolytic product should obey the following equation:

$$(S + \sqrt{S}) = \frac{1}{r} = \frac{1}{q u_1'} \quad (3)$$

where r represents crosslinking index and u_1' is number-average degree of polymerization and let

$$\frac{1}{u_1'} = \frac{1}{u_1} + p \quad (4)$$

in which u_1 is initial number-average degree of polymerization. According to de Genne's scaling theory, it can be assumed that fracture density p is proportional to R^β :

$$p = p_0' R^\beta \quad (5)$$

where p_0' is a constant; β is an exponent dependent on the structure of polymer. Substituting eq. (5) into eq. (4), eq. (4) can be written in the form:

$$\frac{1}{u_1'} = \frac{1}{u_1} + p_0' R^\beta \quad (6)$$

Substituting eq. (6) into eq. (3), we obtain

$$(S + \sqrt{S}) = \frac{1/u_1 + p_0' R^\beta}{q} \quad (7)$$

On the basis of experimental data, we may take crosslinking density proportional to dose directly, i. e.

$$q = q_0 R \quad (8)$$

Thus, eq. (7) becomes:

$$R(S + \sqrt{S}) = \frac{1}{u_1 q_0} + \frac{p_0'}{q_0} R^\beta \quad (9)$$

When $\beta = 1$, $p = p_0' R$, hence $p_0' = p_0$, eq. (9) is reduced to the Charlesby-Pinner expression (1). When $\beta = 0.5$, eq. (9) is reduced to the Chen-Liu-Tang expression. Thus, Charlesby-Pinner and Chen-Liu-Tang expressions are two special cases of our general expression. In addition, eq. (9) is valid only within certain limits of dose as in the case of eq. (1) and eq. (2) because eq. (3) is only an approximate solve of the equation of sol-gel relation, assuming degree of crosslinking and fracture are very small. If the conditions that q is proportional to dose R and p is proportional to R^β at $R \rightarrow \infty$ are satisfied, the assumptions that p and q are very small are no longer satisfied.

The exponent β in eq. (9) is a parameter relative to the structure of polymer, intramolecule and intermolecule force, such as molecular internal rotating steric factor σ , the cross-section area of a single molecular chain A and the cohesive energy density between chains E_c so we may assume $\beta = f(\sigma, A, E_c)$. According to He Tianbai's results^[22], a plot of the product of E_c and A against T_g is a straight line, we may express β in function of T_g and σ . Up to now, we cannot derive a quantitative relationship between β and σ as well as T_g theoretically, but an empirical equation might be obtained with the help of sol data.

Put $\beta = a\sigma + b T_g$ (10) and substitute the value of σ and T_g for polystyrene with $\beta = 1$ and that for polyethylene with $\beta = 0.524$ (shown in Table 1) into eq. (10). We can determine the value of a and b in eq. (10):

$$a = 0.17; \quad b = 0.00167 \quad (10)$$

Then,

$$\beta = 0.17 \sigma + 0.00167 T_g \quad (11)$$

On the basis of the value of σ and T_g for polymers, values of β for some polymers are calculated from eq. (11) and listed in Table 1.

Table 1 β value and the relationship between sol fraction (S) and radiation dose (R) of some polymers

$$R(S + \sqrt{S}) = \frac{1}{q_0 u_1} + \frac{p_0'}{q_0} R^\beta$$

Name of polymer	σ^*	$T_g^*(K)$	β	Data source
Polystyrene	2.22	373	1	10
Polyacrylonitrile	2.20	370	1	
Poly(vinylchloride)	2.32	355	1	12
Poly(vinylalcohol)	2.04	358	0.95	13
Perfluoro-poly(ethylene-propylene)	1.81**	363	0.91	our lab.
Poly(vinylacetate)	2.14	318	0.90	11

(Continued)

Poly(ethylene terephthalate)	1.68	342	0.86	20
Polypropylene	1.85	265	0.76	our. lab. 21
Polyhexene	2.14	228	0.75	19
Polypentene	2.08	183	0.66	19
Natural rubber	1.67	210	0.64	17
Poly(ethylene oxide)	1.63	206	0.62	18
Poly(propylene oxide)	1.62	198	0.61	16
Polyethylene	1.63	148	0.52	14
Polydimethylsiloxane	1.37	150	0.48	15

* - σ and T_g values taken from "Polymer Hand-book" 2nd. Ed (Wiley-Interscience, 1975);

** - σ value calculated according to reference 9.

EXPERIMENTAL

Materials and irradiation

F-46 (copolymer of tetrafluoroethylene and hexafluoropropylene) samples in 1 mm thick sheet were evacuated and sealed under vacuum in glass tubes and irradiated in a 60,000-curie Co 60-source at 240°C.

The radiation crosslinking of polypropylene were carried out under vacuum at 100°C and 20°C respectively.

Determination of gel content

Accurately weighted 0.2 gm minced F-46 samples were extracted under reflux with a fluorochloro oil (telomer of trifluorochloroethylene) under N_2 for 24 hours. After cooling and washing with acetone, the samples were dried to constant weight.

The gel content of polypropylene is determined similarly with xylene as the extracting solvent.

RESULTS AND DISCUSSION

From the expression (9), polymers may be classified according to their β value into three groups, stiff chain polymers, flexible chain polymers, and polymers between the above two groups

(1) *Stiff chain polymers* ($\beta = 0.9-1.0$)

Polystyrene, polyvinylacetate, polyvinylchloride and F-46 belong to stiff chain polymers. Polyvinylalcohol is a stiff polymer with hydrogen bonds. In the crystal region, the mobility of polymer chain is blocked, so it is hard for crosslinking to take place. Thus, β values of these polymers are all very large. Figs. 2, 3 show the results obtained by treating experi-

mental data^[10-13] of these polymers. It is expected that the results obtained by treating experimental data with Charlesby's and with our expressions are almost the same because β values of these polymers equal to 1 or approach to 1.

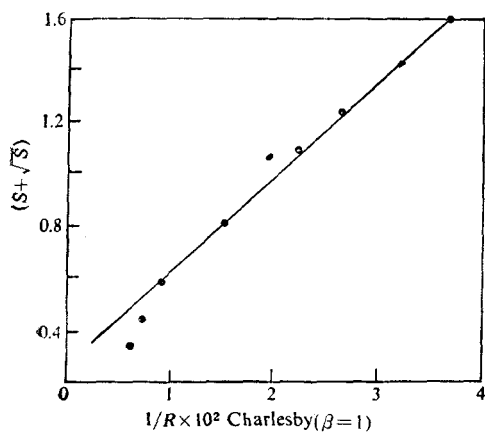


Fig. 2 Radiation crosslinking of polystyrene

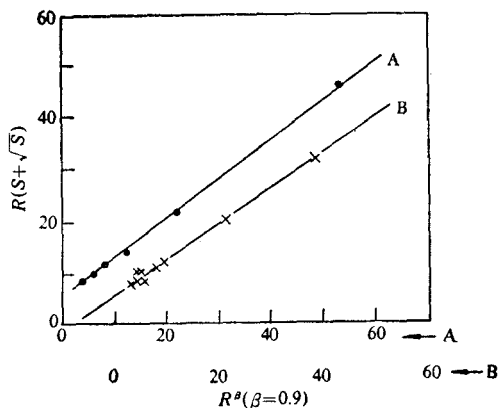


Fig. 3 Radiation crosslinking of poly(vinylacetate)

(2) Flexible chain polymers ($\beta = 0.5-0.65$)

Polyethylene, polydimethylsiloxane, polypropylene oxide, natural rubber and polyethylene oxide belong to the flexible chain polymers, their T_g and σ values are small. The free radicals produced by the main chain scission in these polymers can recombine easily because the mobility of the polymer molecule chain is much higher. Thus, their β values are smaller. In most cases, the values are within the range of 0.5 to 0.65. We treated the experimental data^[14-18] of these polymers. The results are given in Figs. 4, 5. It is shown that the experimental results are in good agreement with Chen-Liu-Tangs and with our expressions.

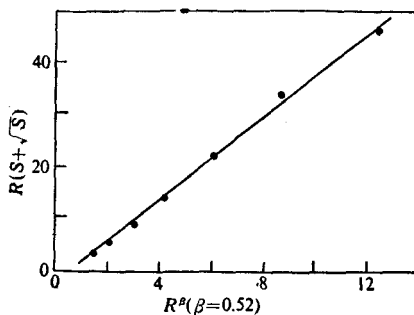


Fig. 4 Radiation crosslinking of polyethylene

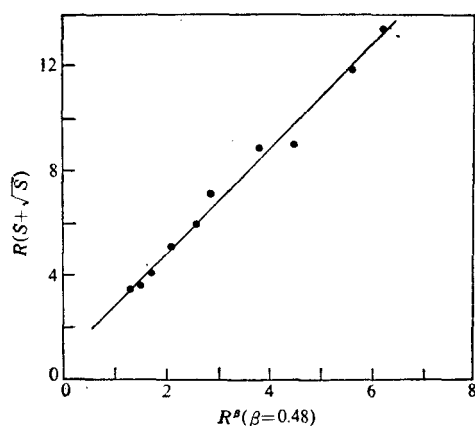


Fig. 5 Radiation crosslinking of polydimethylsiloxane

(3) Polymers between the above two groups ($\beta = 0.65$ — 0.9)

In the case of polyhexene, polypentene, PET and polypropylene, their β values are within the range of 0.65 to 0.9. The experimental data^[19-21] of these polymers are in good agreement with our expression, as shown in Figs. 6, 7 but not with the other two.

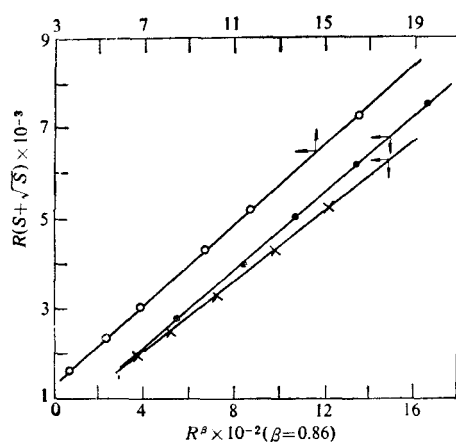


Fig. 6 Radiation crosslinking of poly(ethylene terephthalate)
●— N_2 ; ×— Vacuum; ○— Air.

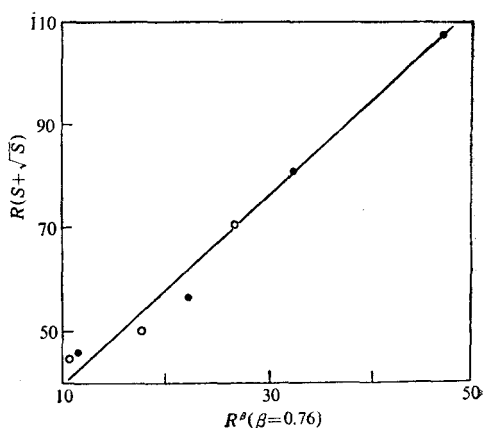


Fig. 7 Radiation crosslinking of polypropylene (our lab.)

The degree of branching can also influence on the β value, for example the T_g value of polyvinylacetate decreases with increasing degree of branching.

This problem can be explained also by Mittelhauser's experimental results with different degree of branching on five samples of polyvinylacetate (Table 2).

Table 2 The property of PVAc⁽¹¹⁾

Sample No.	Conversion (%)	Degree of branching	<i>R</i> gel (Mr)
A	13.5	0.13	4.63
B	25	0.27	4.16
C	41	0.54	3.12
D	55	0.92	2.42
E	71	1.74	1.79

Sample A and B have a lower degree of branching. They satisfy the crosslinking rule of unbranched polyvinylacetate, i.e. β value is 0.9, as shown in Fig. 3. Sample C, D and E have larger degree of branching. Their crosslinking process does not satisfy Charlesby-Pinner expression but Chen-Liu-Tang expression, i.e. β value equals to 0.5 or so, as shown in Fig. 8. This shows that the degree of branching is in favour of crosslinking but not scission.

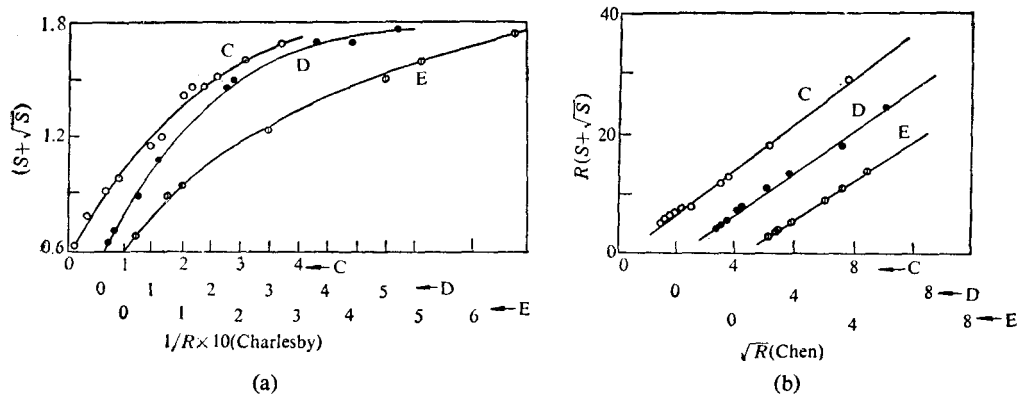


Fig. 8 Radiation crosslinking of polyvinylacetate

As stated above, both Charlesby-Pinner and Chen-Liu-Tang expressions can not be used for all classes of polymers. The experimental data of radiation-induced crosslinking of some polymers are not fit to one or other expression. The main reason of the deviation of experimental data from the expressions is due to the unperfectness in assumption. The structure of polymer, especially the chain stiffness may influence the relationship between the fracture density and radiation dose. The general expression relating sol fraction to radiation dose connected with the structure of polymers proposed by us can fit the experimental results of radiation crosslinking of different classes of polymer.

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