

RADIATION CROSSLINKING OF BRANCHED POLY(VINYL ACETATE)*

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ABSTRACT

In the present work, radiation crosslinking of different branched poly (vinyl acetate) have been studied and the validity of the relationship^[4] between sol fraction and radiation dose:

$$R(S + \sqrt{S}) = \frac{1}{U_1 q_0} + \frac{\beta' q_0}{q_0} R^{\beta}$$

to branched poly(vinyl acetate) have been assured.

Two different relationships between sol fraction and radiation dose in radiation crosslinking of polymer have been reported in the references [1, 2].

On the basis of an analysis of available data, the reference [3] have shown that the relationship between sol fraction and radiation dose obeys Charlesby-Pinner relationship^[1] for the polymers with relative stiff chain and Chen-Liu-Tang relationship^[2] for the polymers with the relative flexible chain and branched polymer.

The reference [4] found that the relationship between fracture density and radiation dose depends on the structure of polymer, i.e., the stiffness or flexibility of polymer chain, and introduced a structure parameter β concerned with the structure parameters of polymer (glass transition temperature T_g and molecular internal rotating steric factor σ) in the sol-dose relationship.

Because the flexibility of branched polymer chain varies with the degree of branching of polymer, it is important to study the radiation crosslinking behavior of different branched polymer for verifying the result of the reference [4] and showing the crosslinking behavior of branched polymer.

EXPERIMENTAL

1. The preparation and the determination of degree of branching for the branched poly (vinyl acetate) (PVAc)

The degree of branching of poly (vinyl acetate) are regulated by controlling the conversion of monomer in emulsion polymerization. The polymerization reaction were carried out under N_2 .

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The poly (vinyl alcohol) is prepared by dissolving branched poly (vinyl acetate) in methanol at 50°C with the presence of NaOH.

The number-average molecular weight of poly (vinyl acetate) and poly (vinyl alcohol), $\bar{M}_{n(\text{PVAc})}$ and $\bar{M}_{n(\text{PVA})}$ are determined with inherent viscosity method:

$$[\eta] = 1.66 \times 10^{-2} \bar{M}_{n(\text{PVAc})}^{0.72} \quad (1)$$

$$[\eta] = 7.5 \times 10^{-4} \bar{P}_{n(\text{PVA})}^{0.64} \quad (2)$$

The degree of branching were characterized with Sakurada method^[7]:

$$K = \frac{\bar{P}_{n(\text{PVAc})} - \bar{P}_{n(\text{PVA})}}{\bar{P}_{n(\text{PVAc})}} \quad (3)$$

2. Irradiation

The branched PVAc samples in 1 mm thick sheet were evacuated and sealed under vacuum (3×10^{-2} Torr) in glass tubes and irradiated in a 60000-Curie Co⁶⁰-Source.

3. Determination of gel content

Accurately weighed 0.2 g minced samples were extracted under reflux with benzene for 48 hours. After cooling and washing with acetone, the samples were dried to constant weight.

4. Glass transition temperature

It was determined with the DSC method.

RESULTS AND DISCUSSION

We have assumed that the fracture density is proportional to R^{β} and obtained a general expression relating sol fraction to radiation dose in reference [4]:

$$R(S + \sqrt{S}) = \frac{1}{q_0 U_1} + \frac{p'_0}{q_0} R^{\beta} \quad (4)$$

where β is a parameter concerned with the structure of a polymer; q_0 —crosslinking density, portion of unit crosslinked per unit dose; p'_0 —a constant; U_1 —initial number-average degree of polymerization; S —sol fraction; R —radiation dose.

This expression associates the behavior of a polymer in radiation crosslinking with its structure. Because there is no σ value for branched polymer, calculating its β value from T_g and σ of them according to the reference [4] is impossible. An equation for calculating β value with T_g value

$$\beta = 0.002T_g + 0.206 \quad (5)$$

were proposed in reference [8].

It is well known that short chain branching can lead to the decrease of T_g value of polymer^[9]. Clearly, the higher degree of branching, the smaller the β' value of branched polymer. Now, substituting R and S experimental data of different branched poly(vinyl acetate) in radiation crosslinking into eq. (4) and assuming some different β values, then inspect the linear relationship between $R(S + \sqrt{S})$ and R^{β} . The β value with the best linear relationship (Fig. 1) is β value of the polymer fit into eq. (4) and listed in Table 1.

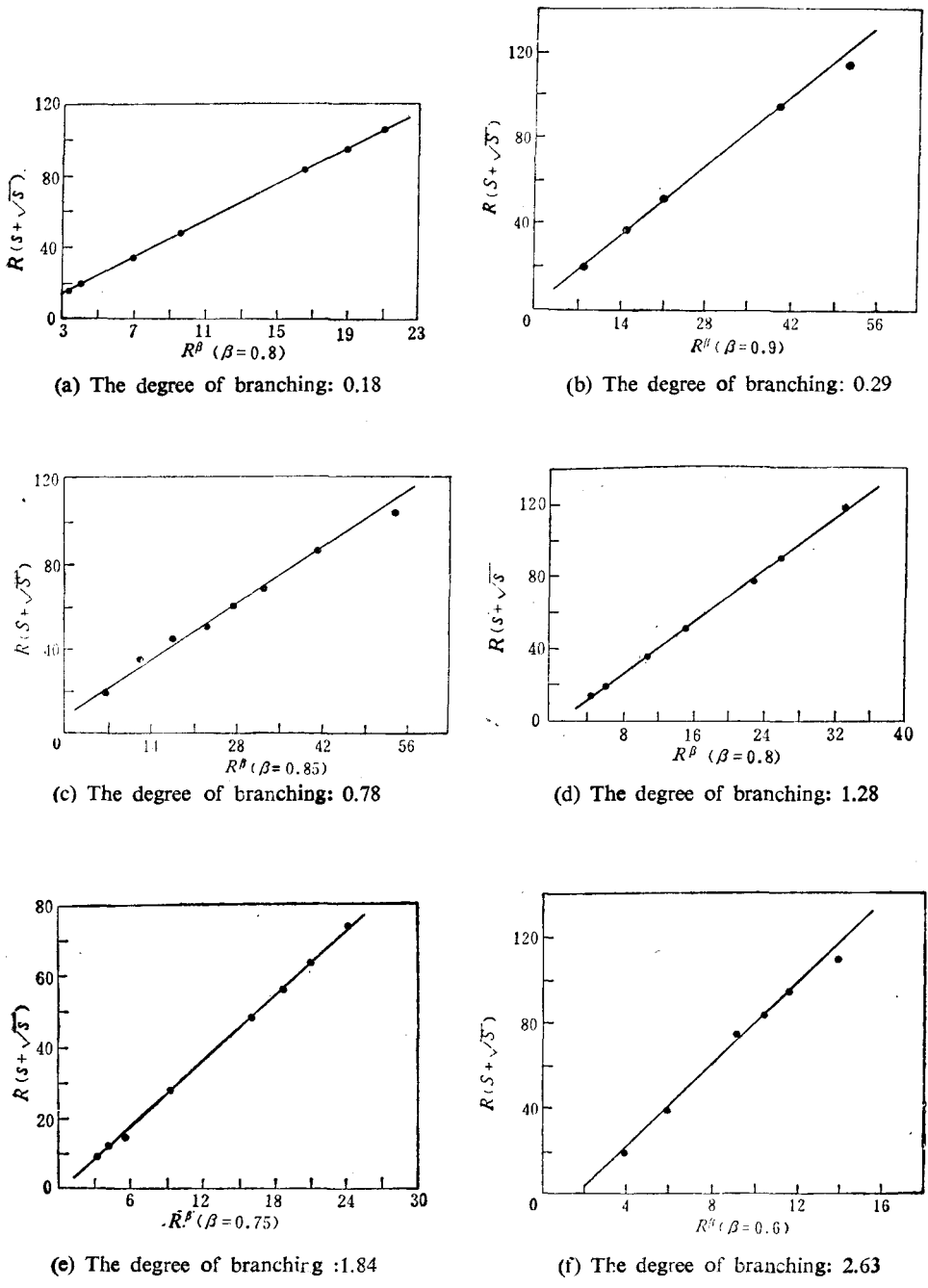


Fig. 1 The radiation crosslinking of branched PVAc

The values of β calculated from eq. (5) according to the experimental value of T_g for the polymer are in agreement with experimental values (Table 1) in the tendency of variation.

Table 1 The β value of the branched PVAc

Sample No.	The degree of branching	T_g (K)	$\beta_{\text{exp}(r)}$	β_{cal}
1	0.18	318	0.8 (0.999)	0.842
2	0.29	317	0.9 (0.998)	0.840
3	0.78	318	0.85(0.996)	0.842
4	1.28	316	0.80(0.999)	0.838
5	1.84	314	0.75(0.999)	0.834
6	2.63	306	0.60(0.995)	0.818

r —correlation coefficient fitting eq. (4).

With the above method, we treated the experimental data in reference [10] and the results were listed in Table 2. From Table 2, it is found that β value decreases with the increase of degree of branching. This assure that the relationship between fracture density and radiation dose is indeed in close relationship with the structure and the flexibility of polymer chain, thus eq. (4) and eq. (5) are reasonable.

In general, the higher the degree of branching, the larger the internal rotating steric factor of polymer main chain and the smaller the mobility of polymer main chain, while experimental results are that the higher the degree of branching, the smaller the β values. This may concern with the mechanism of radiation crosslinking of branched PVAc. We suppose that branching chain of PVAc take part in crosslinking reaction.

Table 2 The β value of the branched PVAc

Sample No.	The degree of branching	β_{exp}
A	0.13	0.9
B	0.27	0.9
C	0.54	0.6
D	0.92	0.5
E	1.74	0.5

Because the mobility of branching chain is relative larger, it may lead to increasing the probability of recombination of free radicals of branching chain on different molecular main chain, thus the β value decreases with the increase of degree of branching, since β value is a parameter concerned with the structure and mobility of polymer chain and reflects probability of recombination of polymer chain free radicals with different structures.

In summary, the radiation crosslinking of branched polymer fit to the expression (4) and the degree of branching is in favour of crosslinking.

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