

THE EFFECT OF CHAIN FLEXIBILITY OF FLUOROPOLYMERS ON THEIR RADIATION CROSSLINKING BEHAVIOR

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ABSTRACT

The effect of chain flexibility of fluoropolymers on their radiation crosslinking behavior is studied and the relationship between sol fraction and the radiation dose to the fluoropolymers given in our previous report^[1] is confirmed.

A number of fluoropolymers have many desirable properties, such as resistant to low and high temperature, chemical corrosion-resistant and high electrical insulation. The radiation crosslinked fluoropolymers have many new excellent properties, such as radiation-resistant. Experiments show that the radiation crosslinking behavior of a linear polymer is closely related to the flexibility of chain. Reference [1] suggested that the fracture density is proportional to R^a for polymers undergoing simultaneous crosslinking and scission, and the β value of a polymer depends on the chain flexibility.

In this paper, the relationship between the sol fraction and the radiation dose for the fluoropolymers is discussed, the crosslinking behavior of a polymer chain is associated with its structure, and the results in reference [1] are verified.

EXPERIMENTAL

Irradiation

The fluoropolymer samples were evacuated and sealed under vacuum in glass tubes and irradiated by a 60000-Curie Co^{60} -source.

Determination of gel content

Accurately weighed 0.2 g of the minced crosslinked sample was extracted by refluxing with solvent under N_2 . After cooling and washing with acetone, the sample was dried to constant weight.

The values of β are also calculated from eq. (2), which agree closely with the experimental

values (Table 1).

RESULTS AND DISCUSSION

In our previous paper [1], it assumed that the fracture density is proportional to R^{β} and obtained a general equation relating the sol fraction to the radiation dose:

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

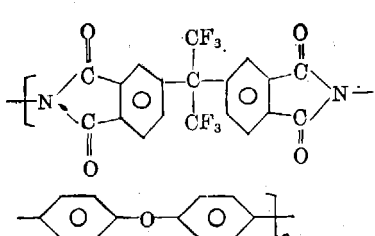
where β is a parameter related to the structure of the polymer, which reflects essentially the crosslinking probability of the polymer chain; q_0 —crosslinking density, caused by unit dose; p'_0 —constant; U_1 —initial number-average degree of polymerization; S —sol fraction; R —radiation dose.

Reference [2] suggested an equation for calculating β from the glass transition temperature T_g :

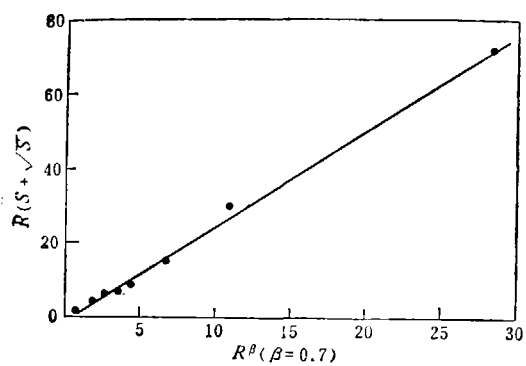
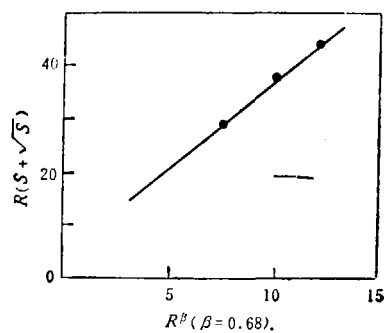
$$\beta = 0.002 T_g + 0.206 \quad (2)$$

Substituting the experimental value of R and S into eq. (1) then find out the values of β , which give the best linear relationship between $R(S + \sqrt{S})$ and R^{β} . The results are shown as Fig. 1 and listed in Table 1.

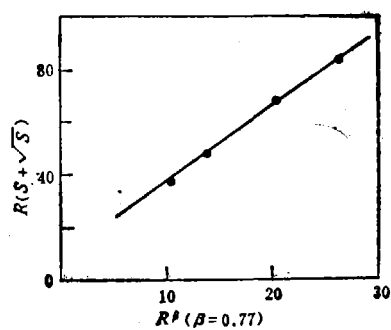
Table 1 β value for fluoropolymers

Polymer	Structure	T_g (K)	σ	$U^{[3]}$ (Kcal/Mol.)	$\beta_{exp.}$ (r)	$\beta_{cal.}$
PVF ₂	$-(CH_2-CF_2)_n-$	236	1.69	3.01	0.70 (0.995)	0.68
F-2406	$-(CH_2-CF_2)_m-(CF_2-CF_2)_n-$ $-(CF_2-CF)_x-$ OCF_3	258	—	—	0.68 (1)	0.72
F-406	$-(CF-CF_2)_m-(CF_2-CF_2)_n-$ OCF_3	283	—	—	0.77 (1)	0.77
F-30	$-(CH_2-CH_2-CF_2-CFCl)_n-$	337	1.80	3.20	1 ^[4] (1)	0.88
F-46	$-(CF_2-CF_2)_m-(CF_2-CF)_n-$ CF_3	356	1.81	3.22	0.91 (0.980)	0.92
FPI		546	—	—	1 (0.908)	1.30

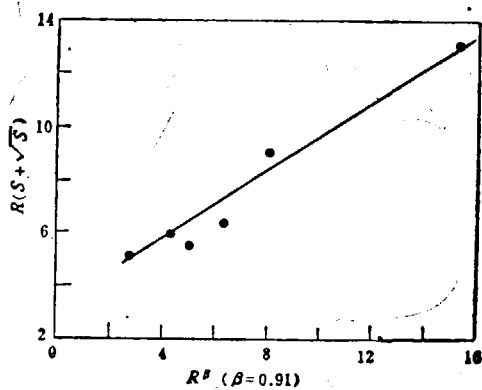
r —Correlation coefficient fitting eq. (1).

(a) PVF₂

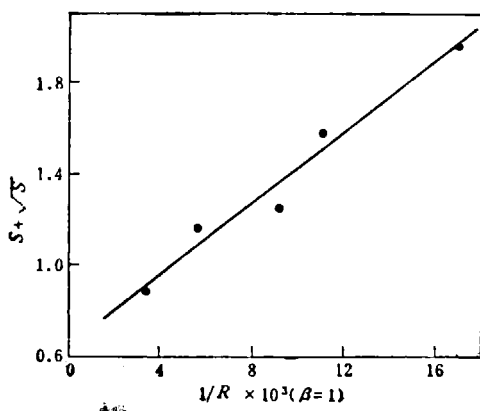
(b) F-2406



(c) F-406



(d) F-46



(e) FPI

Fig. 1 The relationship between $R(S+\sqrt{S})$ and R^β of fluoropolymers

Due to the specific aggregation, the molecular chain of fluoropolymers has greater accumulation density than other polymers, hence their T_g values are higher. Besides, the molecular internal rotating potential barrier (U) of the fluoropolymers, as given in the reference [3], is also higher than other polymers, thus the molecular internal rotating steric factor (σ) is also larger, and the molecular chain becomes stiffer. Therefore the β values of fluoropolymers are very large.

From the values of T_g and σ of the fluoropolymers, we can see that the chain flexibilities are in the following order:

$$\text{PVF}_2 > \text{F-2406} > \text{F-406} > \text{F-30} > \text{F-46} > \text{FPI}$$

It is known that the main chain of FPI has phenyl rings, which hinder the internal rotating movement of molecular chain, thus its chain is relatively stiffer, and the β value is relatively larger. But, it is easy for F-406 (the copolymer of perfluoro-methyl vinyl ether and tetrafluoroethylene) and F-2406 (the copolymer of vinylidene fluoride, tetrafluoroethylene and perfluoro-methyl vinyl ether) to form crosslinking because they are fluoro-rubber and their T_g and β values are much lower.

In summary, the radiation crosslinking of the fluoropolymers agrees closely with the eqs. (1) and (2), and the crosslinking behavior is related to the structure.

REFERENCES

- [1] 张万喜、孙家珍、钱保功, 辐射研究与辐射工艺学报 (*Journal of Radiation Research and Radiation Processing*), 1984, 2, 1.
- [2] 张万喜、何天白、孙家珍、钱保功, 科学通报 (*Science Bulletin*), 1986, 3, 189.
- [3] 何天白, 应用化学 (*Journal of Applied Chemistry*), 1985, 2, 1.
- [4] 罗云霞、庞福成、孙家珍, 高分子通讯 (*Polymer Communications*), 1982, 1, 19.