CALCULATION OF MOLECULAR INTERNAL ROTATING STERIC FACTOR OF FLUOROPOLYMERS BY RADIATION CROSSLINKING METHOD*

Zhang Wanxi (张万喜)

(Changchun Institute of Applied Chemistry, Academia Sinica, Changchun 130022, China)

(Received Feburary 1990)

ABSTRACT

In this paper, the relationship between radiation crosslinking parameter β and the molecular internal rotating steric factor (σ) for fluoropolymers were studied. An expression calculating the molecular internal rotating steric factor of fluoropolymers, $\sigma = 1.44 + (\beta - 0.206)/1.946$, was established. σ value obtained by this method is in agreement with that given in the literature.

Keywords: Radiation crosslinking parameter of fluoropolymers Molecular internal rotating steric factor Radiation crosslinking of polymer

I . INTRODUCTION

It was found that the flexibility of polymer chain is in close relationship with the many physical properties of polymer. In general, the molecular internal rotating steric factor is used to characterize the flexibility of polymer chain, whose value can be obtained from the properties of the dilute solution of polymer. However, the research on the relationship between the flexibility of the chain and physical properties of fluoropolymers was restricted because they are difficult to be solved on the general condition due to special aggregation state (high crystalline) of fluoropolymers.

It was shown in a number of experiments that the behavior of radiation crosslinking for polymers is in close relationship with their molecular chain flexibility[1]. In this work, it has been studied from the above conclusion that the relationship between the molecular internal rotating steric factor and crosslinking parameter β , thus it offers a new method for calculating σ value of fluoropolymers.

II . EXPERIMENTAL

1) Irradiation The glasstubes containing fluoropolymer samples were evacuated, and sealed under vacuum (0.133Pa) and irradiated in a ^{60}Co source.

* The project was supported by the research foundation of IAEA, Agency Research Contract No. 4316/RB.

2) Determination of gel content Accurately weighed 0.2 g of the minced crosslinked samples were extracted respectively with solvent for fluoropolymers under reflux. After cooling and washing with acetone, the samples were dried to constant weight, then gel contents were calculated.

Ⅲ. RESULTS AND DISCUSSION

We had introduced a parameter β concerned with the glass transition temperature (T_g) into the relationship between sol fraction and radiation dose, and derived a general expression[1]:

$$R(S+S^{1/2}) = 1/q_0U_1 + (\alpha_0/q_0)R^{\beta} \quad (1)$$

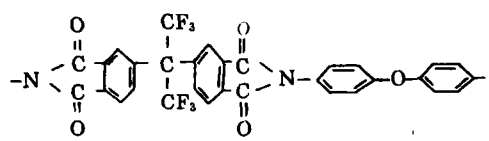
where S is the sol fraction; R, radiation dose; q_0, crosslinking density, portion of unit crosslinked per unit dose; U_1, initial number-average degree of polymerization; α_0, a constant, and β is a crosslinking parameter characterizing the relationship between the molecular chain flexibility and the behavior of radiation crosslinking for polymer. β value for fluoropolymers can also be expressed by the following equation[5]:

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

Clearly, there is a relationship between σ and the crosslinking parameter β, because σ is a structural parameter characterizing the chain flexibility.

Table 1

The structure and some parameters for fluoropolymers[4]

No.	Polymer	Structure	T_g (K)	A (nm^3)	σ
1	PVF_2	$-CH_2-CF_2-$	236	0.206	1.69
2	F-40	$-CH_2-CH_2-CF_2-CF_2-$	320	0.240	1.75
3	F-30	$-CH_2-CH_2-CF_2-CFCl-$	337	0.270	1.80
4	F-46	$-CF_2-CF_2-CF_2-CF(CF_3)-$	356	0.279	1.81
5	FPI		546	–	–
6	TFPP	$-CF_2-CF_2-CH(CH_3)-CH_2-$	–	–	–
7	F-406	$-CF(OCF_3)-CF_2-CF_2-CF_2-$	283	–	–
8	F-2406	$-CH_2-CF_2-CF_2-CF_2-CF_2-CF(OCF_3)-$	258	–	–

Considering that the glass transition temperature of a polymer reflects its molecular chain flexibility, a relationship between T_g and σ was given in reference [2] as follows:

$$T_g = E(\sigma - a) \tag{3}$$

Substituting Eq.(3) into Eq.(2) gives

$$\sigma = a + (\beta - 0.206)/0.002E \tag{4}$$

where E and a are constant, whose values vary with the structure of different polymers.

Taking account of that the cross- sectional area of a single molecular chain (A) has relation to the flexibility of molecular chain, that is the structure of molecular chain for polymer, polymers can be classified according to different relationship between T_g and A for them.

Table 1 shows that the structure and some parameters of fluoropolymers. T_g for some fluoropolymers listed in Table 1 were plotted against A in the double-logarithmic coordinates (Fig.1), and a straight line was obtained. This result shows that the fluoropolymers are a polymer series. Therefore, the relationship between T_g and σ for fluoropolymer will obey the similar law to that of the other polymers (Fig.2)[3].

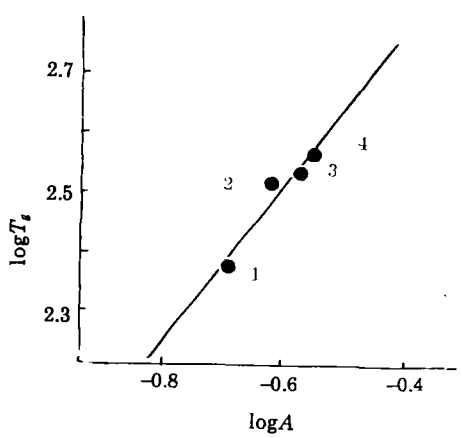


Fig.1 The relationship between log T_g and log A for fluoropolymers

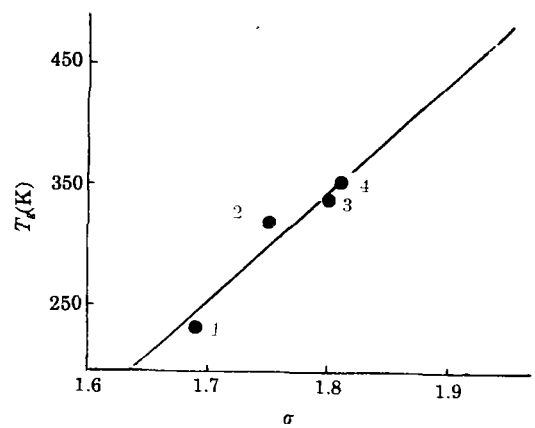


Fig.2 The relationship between T_g and σ for fluoropolymers

From Fig.2, we can obtain values of E and a for fluoropolymers, whose values are 973 and 1.44 respectively. Substituting these two values into Eq.(4), we obtain

$$\sigma = 1.44 + (\beta - 0.206)/1.946 \tag{5}$$

Substituting R and S experimental data for fluoropolymers into Eq.(1), we can obtain the experimental values of β and the correlation coefficient fitting Eq.(1) with the mathematical regression method, then substituting the β experimental value into Eq.(5), the values of σ for fluoropolymers are obtained and listed in Table 2.

From Table 2, it can be seen that calculated values of σ from Eq.(5) are in good agreement with those given in reference, showing that calculating σ values of fluoropolymers by the radiation crosslinking method is reasonable.

Table 2

σ value of fluoropolymers

Polymer	β exp.[5] (r)	σ cal. from Eq. (5)	σ from Ref. [4]
PVF_2	0.70 (0.995)	1.69	1.69
F-40	0.85 (0.994)	1.77	1.75
F-30	1 (1)	1.85	1.80
F-46	0.91 (0.980)	1.80	1.81
FPI	1 (0.980)	1.85	–
TFPP	1 (1)[6]	1.85	–
F-406	0.77 (1)	1.73	–
F-2406	0.68 (1)	1.68	–

r–correlation coefficient fitting Eq.(1)

REFERENCES

[1] Zhang Wanxi *et al.*, *Chinese Science Bulletin*, **3** (1986), 189.

[2] V.P.Privalko and Yu. S.Lipatov, *J. Macromol. Sci. Phys*, **B9** (1974), 3:551.

[3] He Tianbai, *Polymeric Letters (in Chinese)*, **6** (1983), 427.

[4]R.F.Boyer and R.L.Miller, *Rubber Chem. Technol.*, **50** (1977), 778.

[5] Zhang Wanxi *et al.*, *Journal of Radiation Research and Radiation Processing* (in Chinese), 4 (1986), 3:35.

[6] G.Kojima and Y.Tabata, *J. Macromol. Sci. – Chem.*, **A5** (1971), 6:1087.