

CALCULATING THE MOLECULAR INTERNAL ROTATING STERIC FACTOR OF POLYMERS BY THE RADIATION CROSSLINKING METHOD

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ABSTRACT

In this paper, calculating the molecular internal rotating steric factor of polymers by the radiation crosslinking method is studied and a relationship between the molecular internal rotating steric factor (σ) and crosslinking parameter β is established^[1] by taking account of the effect of polymer chain flexibility on β value. σ value of polymer obtained by this method is in agreement with that given with other method.

It is found that the molecular internal rotating steric factor (σ) as a structure parameter, which characterizes the flexibility of polymers, relates to many physical properties of polymer. It was shown in a number of experiments that the behavior of radiation crosslinking of polymers is in close relationship with their molecular chain flexibility^[1]. In this work, the relationship between the molecular internal rotating steric factor and crosslinking parameter β has been studied and, therefore, it offers a new method for calculating σ value of polymer.

EXPERIMENTAL

Irradiation

The glasstubes containing polymer samples were evacuated, and sealed under vacuum and irradiated in a 60,000-curie ^{60}Co source.

Determination of gel content

Accurately weighed minced samples of 0.2 gm were extracted respectively with the solvent for polymers under N_2 . After cooling and washing with acetone, the samples were dried to constant weight.

RESULTS AND DISCUSSION

A parameter β concerned with the glass transition temperature (T_g) is introduced into the relationship between sol fraction and radiation dose, and a general expression is derived in reference [1] as follows:

$$R(S + \sqrt{S}) = \frac{1}{q_0 U_1} + \frac{\alpha_0}{q_0} R^\beta \quad (1)$$

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 as

follows:

$$\beta = 0.002 T_g + 0.206 \tag{2}$$

Since the glass transition temperature (T_g) of a polymer reflects its molecular chain flexibility and intermolecular force, a relationship between T_g and σ is given in reference [2]

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

where B and a are constant, whose value varies with the structure of different polymers.

Taking account of that the cross-sectional area of a single molecular chain A has some relationship with the flexibility of molecular chain, that is the structure of molecular chain, we can classify the polymers according to their T_g and A values. The values of T_g for a large number of polymers listed in Table 1 are plotted against A in the double-logarithmic coordinates, shown in Fig. 1, and the resulting plots split into three straight lines for polymer series differing in their

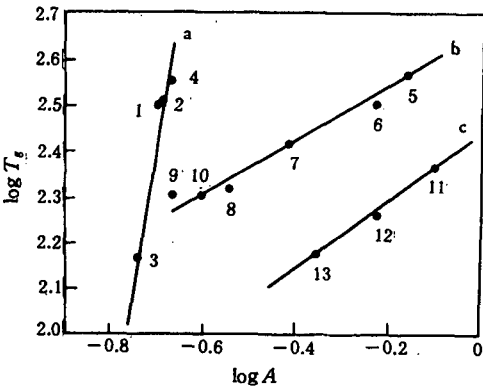


Fig. 1 The relationship of $\log T_g$ and $\log A$ of polymers.

Table 1 Glass transition temperatures and the cross-sectional area of a single molecular chain for polymer

No.	Polymer	$A^{(4)}$ (nm ²)	$T_g^{(5)}$ (K)	Helix ⁽⁴⁾
(a)				
1	Poly(hexamethylene-adipamide)	0.199	317	1/1
2	Poly(iminohexamethyleneiminosebacoyl)	0.203	323	1/1
3	Polyethylene	0.182	148	1/1
4	Poly(vinyl alcohol)	0.216	358	1/1
(b)				
5	Polystyrene	0.698	373	3/1
6	Poly(vinyl acetate)	0.593	318	—
7	Polypropylene	0.378	265	3/1
8	Natural rubber	0.280	210	—
9	Poly(ethylene oxide)	0.215	206	7/2
10	Poly(propylene oxide)	0.245	198	2/1
(c)				
11	Polyhexene	0.780	228	7/2
12	Polypentene	0.587	183	4/1
13	Polydimethylsiloxane	0.436	150	—

crystalline conformations. We observe that line(a) corresponds to polymers with extended chain conformation in crystalline state, whose molecular chain has the greater accumulation density, thus intermolecular force is also relatively larger, it reflects that line(a) has the largest slope in Fig. 1. We note, further, that lines (b) and (c) correspond to polymers with the looser helical conformations of chain repeating units in the crystalline state, which have the greater accumulation density of molecular chain and whose intermolecular force is smaller than that of polymers on line (a).

Values of B and a for the three different polymer series are obtained from the reference [2]

Table 2 Values of parameter B , a and σ for polymer

Polymer	$\beta_{exp.}^{(1)}$ (r)	$\sigma_{cal.}$ from Eq.(4)	σ from Ref.[5]	B (K)	a
(a)					
Poly(hexamethylene adipamide)	1 ^[6] (0.999)	1.98	1.85	630	1.35
Poly(iminohexamethylene iminosebacoyl)	1 ^[7] (0.996)	1.98	—		
Polyethylene	0.52 (0.998)	1.60	1.63		
Poly(vinyl alcohol)	1 (0.978)	1.98	2.04		
(b)					
Polystyrene	1 (0.988)	2.15	2.22	360	1.05
Poly(vinyl acetate)	0.91 (0.999)	2.03	2.14		
Polypropylene	0.76 (1)	1.82	1.85		
Natural rubber	0.64 (0.997)	1.65	1.67		
Poly(ethylene oxide)	0.62 (0.939)	1.63	1.63		
Poly(propylene oxide)	0.61 (0.990)	1.61	1.62		
(c)					
Polyhexene	0.75 (1)	2.08	2.14	225	0.87
Polypentene	0.66 (0.997)	1.88	2.08		
Polydimethylsiloxane	0.48 (0.999)	1.48	1.37		

r—correlation coefficient fitting Eq.(1).

and listed in Table 2. Now, substituting Eq.(3) into Eq.(2) we get Eq.(4)

$$\sigma = a + \frac{\beta - 0.206}{0.002 B} \quad (4)$$

Substituting R and S experimental data into Eq.(1), we can obtain the experimental values of β and the correlation coefficient fitting Eq.(1) with the mathematical regression method (Table 2), then substituting the β value into Eq.(4), the values of σ for polymers are obtained and listed in Table 2.

As demonstrated above, there is a relationship between σ and the crosslinking parameter β because parameter β relates to the flexibility of polymer molecular chain and σ is a structural parameter characterizing the chain flexibility. Thus calculated values of σ are in good agreement with those given in references, showing that calculating σ values of polymer with the radiation crosslinking method is reasonable.

Keywords:

Molecular internal rotating steric factor; Radiation crosslinking; Chain flexibility; Crosslinking parameter

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