

CORRELATION BETWEEN GLASS TRANSITION OF POLYMERS AND ENERGY OF ROTATIONAL ISOMERIZATION OF MOLECULAR CHAINS*

HE Tianbai (何天白)

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

ABSTRACT

It has been shown that the free volume fraction at T_g is not a universal parameter for linear polymers of different molecular structure^[2]. The reason is that the volume expansion at T_g is partially contributed from the change of the numbers of conformations of isolated molecular chains due to internal rotation. In this paper, glassy transformation was connected with internal rotation of isolated molecular chains, and the relationship between free volume fraction of polymers at T_g and energy ϵ of rotational isomerization of isolated molecular chains was formulated, $\epsilon = -k \cdot T_g \cdot \ln (\Delta\alpha \cdot T_g / 1 - \Delta\alpha \cdot T_g)$. The values of calculated from the above formula are in good agreement with those published in the literatures. Thus, the method described in this paper can be used to estimate a parameter for the flexibility of isolated molecular chains.⁷

According to the free volume theory of glass transition, Simha and Boyer^[1] have suggested that the free volume fraction at glass temperature T_g , $f_g = \Delta\alpha \cdot T_g = (\alpha_1 - \alpha_g) \cdot T_g$, is nearly a constant for polymers with different structures. However, it has been shown^[2] experimentally that the parameter $\Delta\alpha \cdot T_g$ varies from 0.082 for natural rubber to 0.13 for polyurethane and the coefficient of volume expansion of polymers in the process of glass transformation depends on the flexibility of isolated molecular chains. Litt^[3] proposed that $\alpha_1 \simeq 0.16A$, with more flexible chains having lower values of A . Lipatov^[2] advanced the proposition that α_1 values of polymers are related to the conformational changes of macromolecular chains. In other words, the internal rotation of macromolecular chains plays a role in the volume change of polymers in the process of glassy transformation. Generally, the internal rotation is described in terms of a rotational potential function. Thus, the interrelation between internal rotation and the process of glassy transformation can be described by the energy change of isolated molecular chains in the process. Here, $\Delta\alpha \cdot T_g$ is used to express the probability that molecular chains are in a certain energy state at T_g .

The rotational bonds in the main chains are in higher energy state at a temperature T

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higher than T_g . As the temperature is lowered towards T_g , internal rotation becomes more difficult and the rotatable bonds are in lower energy states. In this paper, a flexible bond is defined as that rotatable bond which at temperature T is in an energy state higher than a certain critical energy state. If the energy at such a critical energy state is equal to the difference ϵ between energies conforming to *trans* and *gauche* conformations, i.e. the energy of rotational isomerization as defined by Gibbs and DiMarzio for flexible energy^[4], ϵ can be used for characterizing the flexibility of polymers. As the energy of rotational isomerization is distributed randomly, the flexible bond fraction, N , can be expressed by Boltzmann distribution, where $\epsilon/k \cdot T$ is the Boltzmann factor,

$$N = \frac{\exp(-\epsilon/k \cdot T)}{1 + \exp(-\epsilon/k \cdot T)} \quad (1a)$$

At the glass temperature T_g , the flexible bond fraction is

$$N_g = \frac{\exp(-\epsilon/k \cdot T_g)}{1 + \exp(-\epsilon/k \cdot T_g)} \quad (1b)$$

According to statistical mechanics, the probability that a molecular chain is in a certain energy state at temperature T is equal to the fraction of flexible bonds in the same state provided that the number of flexible bonds in the main chains is sufficiently large. Since the glass temperature of a polymer attains a constant value at molecular weights of polymeric range, it is assumed that molecular weight of polymers discussed here is large enough to satisfy the condition stipulated by statistical mechanics. Since $\Delta\alpha \cdot T_g$ has been used to express the probability that an isolated molecular chain is in a certain critical energy state at T_g , and the energy in this state is just the energy of rotational isomerization which is the same as that required for flexible bond, $\Delta\alpha \cdot T_g$ should be equal to N_g , the flexible bond fraction at T_g . Thus,

$$\Delta\alpha \cdot T_g = \frac{\exp(-\epsilon/k \cdot T_g)}{1 + \exp(\epsilon/k \cdot T_g)} \quad (2)$$

which can be transformed into

$$\epsilon = -k \cdot T_g \ln \left(\frac{\Delta\alpha \cdot T_g}{1 - \Delta\alpha \cdot T_g} \right) \quad (3)$$

The literature values of $\Delta\alpha$ and T_g for some polymers were substituted into eq. (3) for the calculation of ϵ . The calculated ϵ values are listed in Table 1 together with ϵ values found in the literature. In view of differences among values of ϵ published in the literature for the same polymers, the agreement between the calculated and published ϵ values is considered to be satisfactory.

It is believed^[5] that flexibility of polybutadienes with different 1,2-content depends upon the level of the latter, lower 1,2-content yielding more flexible chains. From values of $\Delta\alpha$ and T_g determined in this laboratory, the values of ϵ for polybutadienes with various 1,2-content were obtained from eq. (3) (Table 2). In Table 2 it is shown that polybutadienes with lower content of 1,2-structure give lower values of ϵ as expected. Moreover, the ϵ values of 1,2-polybutadienes fall reasonably between those of poly(*cis*-1,4-butadiene) and polystyrene (Table 2). Poly(*cis*-1,4-butadiene), having essentially no side groups, is known to be very flexible, whereas polystyrene suffers from more hindrance to rotation due to the bulky phenyl groups.

Table 1 Energy of rotational isomerization of polymers

Polymers	Glass temp. T_g (K)	Coeff. of expan. $\Delta\alpha \times 10^4 (1/K)$	$\Delta\alpha \cdot T_g$	Energy ϵ (kcal./mol.)	
				Calcd.	Published
Polyethylene	143 ^a	6.8 ^a	0.0972	0.63	0.66 ^a
	188 ^b	5.1 ^b	0.0959	0.84	0.45—0.8 ^c
Polypropylene	238 ^d	4.2 ^d	0.1000	1.04	0.8 —1.1 ^e
	256 ^b	4.18 ^b	0.107	1.08	
Polyisobutylene	199.4 ^a	4.7 ^a	0.0937	0.90	0.76 ^f
	202 ^g	4.22 ^g	0.0852	0.95	0.87 ^a
	205 ^g	3.75 ^g	0.0769	1.01	0.88 ^h
	199 ^g	4.39 ^g	0.0874	0.93	0.90 ⁱ
	200 ^b	4.175 ^b	0.0835	0.95	
Poly(<i>cis</i> -1,4-butadiene)	159 ^j	4.9 ^j	0.0779	0.78	0.76 ^h
	180 ^b	4.4 ^b	0.0792	0.88	0.84 ^a
Natural rubber	201 ^a	4.1 ^a	0.0824	0.96	0.85 ^h
	201 ^b	4.48 ^b	0.0900	0.92	0.87 ^a
	200 ^h	3.75 ^h	0.0750	1.00	0.92 ⁱ
	201 ^g	3.75 ^g	0.0753	1.00	
Poly(vinyl chloride)	355 ^a	3.1 ^a	0.110	1.47	1.18 ⁱ , 1.49 ^h
	355 ^g	2.93 ^g	0.104	1.52	1.58 ^a
	350 ^h	2.93 ^h	0.103	1.51	0.8—1.5 ^e
Poly(vinylidene chloride)	256 ^a	4.5 ^a	0.115	1.04	0.97 ^f , 1.14 ^a
Poly(vinyl acetate)	300 ^k	4.11 ^k	0.123	1.17	0.8—1.1 ^e
	302 ^g	4.63 ^g	0.140	1.09	1.06 ⁱ , 1.15 ^f
	302 ^g	4.25 ^g	0.128	1.15	1.36 ^a
	305 ^g	4.26 ^g	0.130	1.15	1.38 ^h
Polystyrene	360 ^d	3.00 ^d	0.108	1.51	1.0—1.5 ^e
	373 ^g	3.09 ^g	0.115	1.51	1.43 ^f , 1.67 ^a
	373 ^h	3.12 ^h	0.116	1.50	1.80 ^h
Poly(α -methyl styrene)	453 ^g	3.07 ^g	0.139	1.64	1.0—1.5 ^e
	445 ^h	3.98 ^h	0.177	1.36	1.2 ⁱ , 1.89 ⁱ
Poly(dimethyl siloxane)	150 ^a	5.4 ^a	0.0810	0.72	0.50 ⁱ , 0.64 ^h
	150 ^g	5.52 ^g	0.0828	0.72	0.65 ^h , 0.80 ^m
Poly(methyl methacrylate)	372 ^d	3.25 ^d	0.121	1.46	1.31 ⁱ
	388 ^h	3.1 ^h	0.120	1.53	1.44 ^g
	378 ^g	2.82 ^g	0.107	1.60	1.50 ^h
	378 ^g	3.65 ^g	0.138	1.38	1.69 ^a
	377 ^g	3.10 ^g	0.117	1.51	
	378 ^b	3.15 ^b	0.119	1.50	
Poly(ethyl methacrylate)	338 ^b	2.88 ^b	0.0973	1.50	1.05 ^h
	335 ^h	2.95 ^h	0.0988	1.47	1.46 ^a
Poly(ethylene terephthalate)	340 ^h	3.51 ^h	0.119	1.49	1.33 ⁱ
	337 ^g	3.51 ^g	0.118	1.35	1.53 ^h
	340 ^g	3.78 ^g	0.129	1.29	1.54 ^a
Poly(tetrafluoroethylene)	160 ^a	7.0 ^a	0.112	0.66	0.72 ^a

^aA. Eisenberg & S. Satio, *J. Chem. Phys.*, **45**, 1673 (1966). ^bS. M. Aharoni, *Polym. Prepr.*, **14** (1), 334 (1973). ^cR. H. Boyd & H. W. Starkweather, Jr., *J. Phys. Chem.*, **64**, 410 (1960). ^dSee ref. [2]. ^eV. G. Ros-tiashvili, *Vysokomol. Soedin.*, Ser. B, **20**, 837 (1978). ^fSee ref. [4]. ^gS. C. Sharma, L. Mandeikern & F. C. Stehling, *J. Polym. Sci.*, **B10**, 345 (1972). ^hI. Havlicek, V. Vojta, M. Ilavsky & J. Hrouz, *Macromolecules*, **13**, 357 (1980). ⁱJ. M. O'Reilly, *J. Appl. Phys.*, **48**, 404 (1977). ^jG. Karus, C. W. Childres & J. T. Gruver, *J. Appl. Polym. Sci.*, **11**, 1586 (1967). ^kP. Mearas, *J. Am. Chem. Soc.*, **76**, 3415 (1954). ^lJ. M. G. Cowie & P. M. Toporowski, *Eur. Polym. J.*, **4**, 621 (1968). ^mA. V. Tobolsky, "Properties and Structure of Polymers", John Wiley & Sons, New York, 1960, p. 70.

Table 2 Energy of rotational isomerization of polybutadienes

Polymers	Glass temp. T_g (K)	Coeff. of expan. $\Delta\alpha \times 10^4$ (1/K)	$\Delta\alpha \cdot T_g$	Energy ϵ (kcal. / mol.)	
				Calcd.	Published
Poly(<i>cis</i> -1,4-butadiene)	159 ^a	4.9 ^a	0.0779	0.78	0.76 ^a
Polybutadiene 30% 1,2-	188 ^b	4.77 ^b	0.0897	0.87	0.82 ^c
Polybutadiene 50% 1,2-	209 ^b	4.21 ^b	0.0880	0.97	0.91 ^c
Polybutadiene 66% 1,2-	221 ^b	3.73 ^b	0.0824	1.06	0.96 ^c
Polybutadiene 90% 1,2-	249 ^b	3.31 ^b	0.0824	1.19	1.08 ^c
Polystyrene	360 ^d	3.00 ^d	0.108	1.51	1.67 ^d

^aSee j in Table 1. ^bDetermined in this work. ^cCalculated with method by A. Eisenberg et al., see a in Table 1. ^dSee ref. [2].

Considering the difficulty in the determination of the energy of rotational isomerization of polymers and the discrepancies among the published values of the energy of rotational isomerization in the literature, the method discussed here might be simpler and reliable for calculating the energy of rotational isomerization and characterizing the flexibility of polymer chains.

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