

The Relationship Between Glass Temperature, Molar Cohesion, and Polymer Structure*

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Numerous attempts have been made to find relationships which permit the estimation of glass temperatures from polymer structure. Edgar¹ has shown that the glass temperatures of polyesters containing various amounts of *p*-phenylene units can be adequately estimated by applying a "stiffness factor." The estimation of glass temperatures of copolymers when the values for the individual homopolymers are known can be made by using the relationship developed by Fox.² More recently, DiMarzio and Gibbs³ developed a system which can be used to calculate the glass temperatures of a series of alkyl methacrylates. It is the purpose of this paper to present a simple relationship between polymer structure, molar cohesion, and glass temperature which is generally applicable to all polymers.

Glass temperatures are known to vary with polymer molecular weight, plasticizer content, and with method of measurement. Thus it is obvious that any data used in obtaining the desired relationship must have been obtained on polymers of sufficiently high molecular weight, in the absence of plasticizers or excess monomer, and by either the same or at least very similar methods of measurement so that these effects may be lumped into a single constant. Fortunately, a large amount of data on a variety of polymers exists which fulfills these conditions. The major portion of the data used was obtained dilatometrically.

It is generally agreed that as a polymer is cooled the rotation of its various atoms and groups becomes less and less until at T_g such rotation is essentially inhibited. It is reasonable to assume that the basic reason for this restriction of rotation is the lack of sufficient rotational energy at T_g to overcome the forces which are holding the molecules together and thus prevent rotation. Thus at

T_g the equation $H_c = H_R + C$ can be used to express this assumption, where H_c is the molar cohesive energy, H_R is the molar rotational energy, and C is a constant which includes any molecular weight and rate effects.

There are several methods by which the cohesive energy H_c of a polymer may be obtained. Dunkel⁴ has compiled a list of cohesive energies for a few groups which can be added to yield the cohesive energy of a polymer. Cohesive energy densities of a few polymers are available in the literature.⁵ These are easily converted into molar cohesive energy by multiplying by the molar volume.

Rotational energy can be expressed by the term $0.5nRT_g$ where n is a number analogous to the degrees of freedom in expressions of kinetic energy. If from polymer structure values of n can be obtained which, in conjunction with the molar cohesive energy, consistently agree with the measured glass temperatures for a variety of polymers, then the relationship

$$H_c = 0.5nRT_g + C$$

becomes useful in the calculation of T_g for unknown polymers. The following rules for the determination of n , all of which are concerned with the ability of atoms or groups to rotate and the consequences of that rotation, have been established:

(1) The value of 1 is assigned for each atom or group in the polymer which can rotate without causing any chain motion.

(2) The value of 6 is assigned for each atom or group which causes chain motion when it rotates. This occurs with any chain atom or group whose valence angle is not 180°.

(3) An additional value of 2 is assigned whenever any branch group because of its size cannot rotate without bumping into the polymer chain. The phenyl group in polystyrene is an example of this.

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(4) Whenever a double bond or phenyl group prevents the rotation of a particular atom or group of atoms, the group so restricted is counted as one atom.

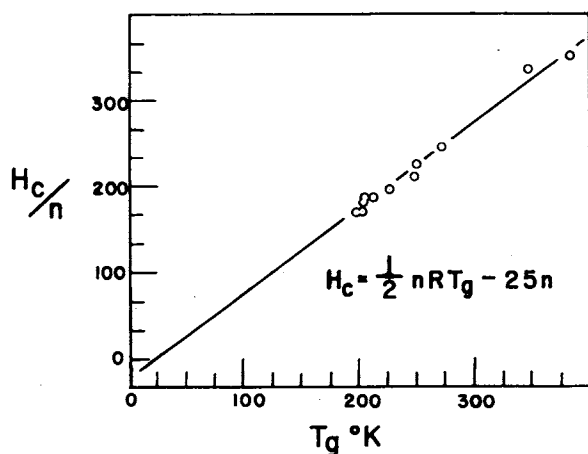


Fig. 1. Cohesive energy vs. glass temperature.

If these rules are correct, a plot of H_c/n versus T_g will be linear with a slope of $0.5R$. Such a plot is shown in Figure 1; evidently, it is linear and the slope is $0.5R$. Table I shows the variety of polymers, the values of T_g , and the molar cohesions which were used to construct the graph. The intercept at -25 shows the existence of other factors such as molecular weight and rate effects which are

TABLE I
Molar Cohesions and Glass Temperature of Polymers

Polymer	T_g , °K.	H_c , cal.	n
Natural rubber	200 ^a	4620 ^e	27
Polyisobutylene	199 ^a	3750 ^e	22
Polystyrene	381 ^b	8090 ^e	23
Polyvinyl chloride	348 ^a	5380 ^f	16
Butadiene-acrylonitrile (35 mole-% AN)	250 ^a	4610 ^e	20.6 ^g
Butadiene-styrene (15 mole-% St)	212 ^a	4290 ^e	23.1 ^g
Polymethyl acrylate	273 ^c	7580 ^f	31
Polyethyl acrylate	248 ^c	8210 ^f	39
Polypropyl acrylate	225 ^c	9200 ^f	47
Polybutyl acrylate	203 ^c	10,190 ^f	55
Polyethylene adipate	202 ^d	12,940	72

^a Data of Reference 6.

^b Data of Reference 7.

^c Data of Reference 8.

^d Data of Reference 1.

^e Calculated from cohesive energy density.⁵

^f Calculated from Dunkel's table of group cohesions.⁴

^g 18% of the butadiene is assumed to have polymerized in the 1,2 positions.

made constant by the proper selection of data. Thus it appears that

$$H_c = 0.5nRT_g - 25n$$

expresses the relationship between glass temperature, molar cohesion, and polymer structure quite well.

The usefulness of such an equation in the calculation of T_g for proposed polymer structures obviously depends upon the development of a suitable list of group values of molar cohesions. The necessary data for calculation of these molar cohesions are not always available from the methods described previously. Table II shows a list of such values which are obtained by use of our equation and literature values of T_g for a wide variety of polymers. These values were obtained by calculation of the molar cohesion of the whole polymer from T_g and then calculation of the individual group values with Dunkel's value for $-\text{CH}_2-$ used as the starting point.

Table III shows the results obtained for a number of polymers containing some of the groups listed in Table II. The agreement of these calculated values with the observed is quite good.

Considerable caution should be exercised in using any additive method for obtaining molar cohesion of polymers, since any interaction between groups will obviously result in considerable errors. Some evidence of this can be seen in the fluorocarbon polymers. The value for $-\text{CF}_2-$ calculated from $-\text{CF}_2\text{CH}_2-$ is roughly twice as large, 2400 cal., as the 1150 cal. estimated from the cohesive energy density of low molecular weight perfluorocarbons. This enhancement may be due to hydrogen bonding between the CH_2 and CF_2 groups.

The only known instance where the equation is unsatisfactory in predicting glass temperatures is that of the various stereoisomers of polymethyl methacrylate, there being a significant difference in T_g for the atactic and isotactic varieties. The equation as constituted allows for no such differences as it is difficult to believe that the molar cohesions of such polymers would be different, and our method of determining n would give the same values. The only reasonable explanation of this phenomenon is that some form of steric hindrance is present in one of the isomers that is not present in the other. At the present time there is insufficient data on other stereoregular polymers to check the validity of this point. It may be significant to note that the glass temperatures of

cis-polyisoprene (natural rubber) and *trans*-polyisoprene (balata) are identical.

The equation as developed is empirical and as such is open to some objections. It would be

highly desirable if some theoretical significance could be attached to the value of n . However, the remarkable agreement of the relationship with the experimental data does indicate that this

TABLE II
Molar Cohesions and n for Various Groups

Group	b	H_c	Polymer and data source
—CH ₂ —	8	990	Reference ⁴ (cohesive energy)
—CH(CH ₃)—	11	3060 ^a	Polypropylene ⁹
—CH(CH ₃)—	11	1700 ^a	Polypropylene terephthalate ¹
—C(CH ₃) ₂ —	14	2840	Polyisobutylene ⁶
—CH(COOCH ₃)—	23	6720	Polymethyl acrylate ⁸
—C(CH ₃)(COOCH ₃)—	26	11,000	Polymethyl methacrylate ⁸
—CHC ₆ H ₅ —	15	7190	Polystyrene ⁷
—CHCl—	8	4180	Polyvinyl chloride ¹¹
—COO—	12	3380	Polyethylene adipate ¹
<i>p</i> -Phenylene	5 ^b	5700	Polyethylene terephthalate ¹
<i>m</i> -Phenylene	10	6170	Polyethylene isophthalate ¹⁰
—C(CH ₃)=CH—	11	2740	Natural rubber ⁶
—CH=CH—	8	1790	Polybutadiene ¹²
—CH(CH=CH ₂)—	11	3080	Polybutadiene ¹²
—CCl=CH—	8	3010	Neoprene ⁶
—CHCN—	8	5760	N-rubber ⁶
—CCl ₂ —	8	2700	Polyvinylidene chloride ⁶
—NHCO—	13	10,680	Nylon 66 ¹¹
—CH(OCOCH ₃)—	23	7580	Polyvinyl acetate ⁶
—NHCOO—	19	6280	Urethane of butanediol and hexamethylene diisocyanate ¹¹
—CF ₂ —	8	1150	Reference 5, cohesive energy density of low molecular weight carbons
—CH ₂ CF ₂ —	16	3350	Polyvinylidene fluoride ¹⁴
—CF(CF ₃)—	13	4400	Copolymer of vinylidene fluoride and perfluoropropylene ¹³
—O—	6	1630	Reference 4 (cohesive energy)

^a Two values are given for —CH(CH₃)— to account for presumed differences between attachment of the group to oxygen and attachment to carbon.

^b The valence angle between *p*-phenylene and the polymer chain is 180°, and so rule 1 and not rule 2 applied.

TABLE III
Calculated vs. Observed Glass Temperatures for a Variety of Copolymers

Polymer	T_g , °K.	
	Calc.	Obs.
Polyethylene terephthalate-ethylene sebacate (50 mole-% sebacate)	233	250 ^a
Polyethylene terephthalate-ethylene oxalate (20 mole-% oxalate)	327	331 ^a
Polyethylene terephthalate-ethylene succinate (30 mole-% succinate)	302	293 ^a
Polyethylene terephthalate-ethylene adipate (40 mole-% adipate)	271	270 ^a
Polymer of diethylene glycol and bibenzoic acid	355	353 ^b
Polyethylene-bis- <i>p</i> -carboxyphenoxybutane	316	326 ^b
Styrene-methyl methacrylate (50 mole-% styrene)	319	306 ^c
Urethane of butenediol and hexamethylene diisocyanate	227	229 ^d

^a Data of Reference 1.

^b Data of Reference 10.

^c Data of Reference 15.

^d Data of Reference 11.

approach is a valid and useful one. It is hoped that expansion of the approach may lead to the estimation of other properties and thus be another step in the correlation of polymer structure with polymer properties.

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Synopsis

An empirical equation relating glass temperature, molar cohesion, and polymer structure has been developed from data found in the literature. A fairly extensive list of group cohesion values has been obtained from this relationship and glass temperatures which are in good agreement with reported values have been calculated. The equation is

$$H_c = 0.5nRT_g - 25n$$

where H_c is the molar cohesion and n is an empirical number obtained from the polymer structure.

Résumé

Une équation empirique se rapportant à la température vitreuse, à la cohésion molaire et à la structure des polymères a été établi à partir des résultats trouvés dans la littérature. Une liste assez étendue des valeurs des cohésions de groupes a été obtenue à partir de cette relation et les températures vitreuses sont en accord avec les chaleurs qui ont été calculées. Cette équation est $H_c = 0.5nRT_g - 25n$ ou H_c est la cohésion molaire et n un nombre empirique obtenu à partir de la structure du polymère.

Zusammenfassung

Aus Literaturdaten wurde eine empirische Beziehung zwischen Glastemperatur, Molkohäsion und Polymerstruktur entwickelt. Mit Hilfe dieser Beziehung wurde eine ziemlich umfangreiche Liste von Gruppenkohäsionswerten erhalten und Glastemperaturen in guter Übereinstimmung mit dekannten Werten berechnet. Die Beziehung lautet $H_c = 0,5nRT_g - 25n$, wo H_c die Molkohäsion und n eine empirische, aus der Polymerstruktur erhaltene Zahl ist.

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