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## New theory on new segment in polymer

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### ABSTRACT

New segment, formed by a group of two arrays between two main chains, makes up their figure and physical properties. Segment gives two types by temperature, which belongs thermal (under  $T_g$ ) and mechanical domain ( $T_m - T_g$ ).  $T_g$  happens to reach elongation limit of  $\alpha \cdot T_g = 1\%$ . where  $T_m$  is melting point,  $T_g$  is transition temperature and  $\alpha$  is thermal expansion rate. Two domains have the same 1% elongation limit. Although symmetrical structure holding  $T_g = \sum T_{g_i}$  shows the same  $\alpha = \sum \alpha_i$  in both domains, asymmetry changes  $2\alpha = 2\sum \alpha_i$  in mechanical domain. Where  $\alpha_i$  is component molecule. The common  $\alpha$  in symmetrical domains supports existence of crystallization. The mechanical moving of horizontal direction happens displacement of C-C bond less than  $8^\circ$  at 1% limit, which all elongation of composite molecules forms a line. Segment having a sturdy structure due to fine stroke by thermal elongation is in charge of Young's modulus in the equation of strength and elongation happens in single main chain.  $\alpha$  can use to replace entropy with traditional ways of thinking for polymer.

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### KEYWORDS

Melting point;  
Glass transition temperature;  
Thermal expansion rate;  
Strength;  
Thermal properties;  
Thermo plastics.

### INTRODUCTION

The physical properties of polymer have been thought to cause by the segment defined as a special unit group of 20~40 molecules in a main chain. But it cannot explain what  $T_g$  and  $T_m$  has each constant value or the both ratio gives the constant one. Where  $T_g$  is the glass transition temperature. It is not obvious what the segment functions and numbers of happening segment can not estimate to may be a lot or a few. Strength theory affected their numbers brings a fatal fault because of without expectation of fixed happening. The new segment, showed as segment simply as follows, is formed by a group of two arrays having the direction of main chain, which each atom between two main chains

in a segment combines by Van der Waals force<sup>[1,2]</sup>. In this case, the forming of segment can explain reasonable<sup>[2]</sup>. The segment gives compact structure but changes loose one after  $T_g$  and both of them is reversible in temperature. These can give a basis that  $T_g$  of polymer is shown by changing from rigid to soft. New thought of segment gives important fact from ratio of  $T_g$  and  $T_m$ , which the 1% limit exists elongation between atoms and gives the same limit in thermal and mechanical elongation. Here is shown the fact and theoretical mechanism and background of the latter. It has been published that  $T_g$  happens when thermal elongation of C-C bond terminates<sup>[1,2]</sup>. The limit of elongation is shown as,

$$\alpha \cdot T_g = 1\% \text{ from } 0^\circ\text{C} \quad (1)$$

where  $\alpha$  is the linear coefficient of thermal expansion

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and  $\alpha \cdot T_g$  is the elongation ratio. After  $T_g$ , a movement of C atom in C-C bond changes in the horizontal direction from vertical line of thermal expansion. The horizontal movement of C atom make a single main chain return at  $T_m$  and happens liquid by Brownian movement. Those are shown to divide into two elongation in thermal domain of under  $T_g$  and mechanical one of ( $T_m - T_g$ ). Because all atoms of element has the 1% limit including C atom, it may deal with in general field<sup>[3]</sup>.  $\alpha$  given as thermal expansion makes a new understanding of, specific heat, heat conduction in a metal and strength. Entropy has been used to explain a change of  $T_g$  for a difference of molecular structure<sup>[4]</sup>. Because  $\alpha$  is replaced to entropy essentially, it means a substance of entropy, making easy a imagination due to embodiment. A elongation deals with to include a shrinkage because the relation of both is reversible except a special case. The magnitude of thermal properties are made by the symmetry of arrangement, which causes a crystals of element.

## RESULT

### Basic two elongation and their elongation rate ( $\alpha$ )

The happening elongation by a heat quantity are classified in two sort from the different working. One is in case of happening by thermal and the other is by mechanical stress. A stress has been originally used to work from the outside like the tensile test. But the stress happening in elements itself gives as the inside. A elongation in the direction of main chain stops and a mechanical stress of tangential one happens. A stress ( $\sigma$ ) by the movement is related to elongation through next equation (2).

$$\sigma = ER \quad (2)$$

where E is Young's modulus and R is elongation rate. On the other hand, the equation of thermal elongation is given as follows

$$\alpha = (\text{elongation rate})/t = (\Delta l/l)/t \quad (3)$$

where t is temperature ( $^{\circ}\text{C}$ ) and elongation rate is the ratio of the expanded length ( $\Delta l$ ) to length of element (l).  $\alpha$  is a important elongation rate showing thermal properties of material, a molecule and a component molecule. It can use in a wide fields including application of comparison through the addition of them is pos-

sible<sup>[6]</sup>. The relation between  $T_g$  and  $\alpha$  gives two different equations from  $0^{\circ}\text{C}$  limits. The equation below  $0^{\circ}\text{C}$  is given as<sup>[3]</sup>;

$$\alpha = 1\% \cdot T_g \quad (4)$$

From equation (1) and (4), figure 1 shows  $\alpha$  vs.  $T_g$  of up to  $200^{\circ}\text{C}$  from  $-200^{\circ}\text{C}$  except  $0^{\circ}\text{C} \sim 1^{\circ}\text{C}$ .

### Thermal and mechanical elongation

A polymer chain is composed of side chain and main chain formed by mainly C-C bond, though the others are N atom, O atom and so on, which shows as figure 3(a) inset.

### Thermal (under $T_g$ ) and mechanical ( $T_m - T_g$ ) domain

In case of a linear polymer, after  $T_g$  changes a mechanical elongation up to  $T_m$ . Next equation (5) is well known as empirical law (K).

$$\frac{T_g}{T_m} = \frac{T_g(^{\circ}\text{C}) + 273\text{K}}{T_m(^{\circ}\text{C}) + 273\text{K}} = k \quad (5)$$

where k is 1/2 (symmetrical structure) and 2/3 (asymmetry). In case of  $k = 1/2$ , equation (5) is expressed as follows,

$$\text{if, } T_g \text{ is } x^{\circ}\text{C} \cdot T_m(^{\circ}\text{C}) = 2x^{\circ}\text{C} + 273\text{K} \quad (6)$$

It can be shared with two domain, which are,

$$T_g = x^{\circ}\text{C} \text{ and } (T_m - T_g) = x^{\circ}\text{C} + 273\text{K} \quad (7)$$

The latter is a temperature of mechanical domain. Suppose  $T_g = 100^{\circ}\text{C}$  were,  $T_m$  would be  $473^{\circ}\text{C}$ .  $T_m$  is a rather high value in comparison with  $T_g$ , because absolute temperature of 273K is included newly. That is, two domains have a peculiar of composing from the same absolute temperature (k). It indicates a important contents for after  $T_g$  that starting from absolute zero suggests a new movement of elongation between atoms, having a different content from under  $T_g$  though it shows the same 1% elongation limit.

### Mechanical domain

#### Two domains of symmetrical structure ( $k = 1/2$ )

Polymer of asymmetry structure with low  $T_g$  is intended for aliphatic hydrocarbon, e.g. methylene group but symmetrical structure with high  $T_g$  is mainly aromatic group. Elongation ( $\alpha$ ) of the former is higher and the latter is lower, which is given from equation (1) shown as  $\alpha \cdot T_g = 1\%$ . After  $T_g$  brings to soft from rigid by

increasing  $\alpha$ . In this case, it does not affect  $\alpha$  by next reason. Because a crystal in polymer which symmetrical structure makes, disappear to shift amorphous body<sup>[5]</sup>. This supports existence of crystallization, applying to asymmetry structure.

### Relation between apparent $\alpha$ and Tg

When a crystal disappeared, its volume increases a little ( $\Delta V$ ). From  $\Delta V \approx 3\alpha'$ ,  $\alpha$  of after Tg increases to  $\alpha_0 + \alpha'$ . Where  $\Delta V$  is increasing volume and  $\alpha_0$  is  $\alpha$  of polymer,  $\alpha'$  is  $\alpha$  of increasing volume.

Since apparent  $\alpha$  makes a turning point, it shows Tg at measurement. It indicates that  $\alpha$  keeps to have a good reason for Tg even if it doesn't change before and after Tg.

### The difference of two domains

A characteristic of thermal domain is able to add each Tg of component molecular. Up to Tg, the relation between Tg of polymer and Tg<sub>i</sub> of component molecular is given as<sup>[2]</sup>,

$$T_g = \sum 1\% \cdot 1/\alpha_i = \sum T_{g_i}$$

From the adding property of  $\alpha$ ,  $\alpha$  of polymer is obtained as<sup>[6]</sup>,

$$\alpha = \sum \alpha_i \quad (8)$$

An example of polypropylene is given an explanation of this equation. A polymer chain is composed of side chain and main chain. That is shown as  $-H \cdot C_1 \cdot (CH_3) \cdot H \cdot C_2 \cdot H$  in repeat unit. Where  $-C_1 - C_2 -$  is main chain and  $\cdot H, (CH_3) \cdot$  is the side chain of  $C_1 \cdot H, H \cdot$  is the one of  $C_2$ . The elongation ( $\alpha$ ) of  $C_2$  is larger than  $C_1$  because  $C_1$  have a heavier side chain. The addition of Tg<sub>i</sub> in mechanical domain continues to exist.

### Two domains of asymmetrical structure (k=2/3)

In case of  $k = 2/3$ , equation (9) is given as;

$$T_g = x^\circ C \text{ and } (T_m - T_g) = x^\circ C / 2 + 273 K \quad (9)$$

It is the same as symmetrical structure up to Tg. But  $\alpha$  in mechanical domain increases twice uniformly as given from equation (1). It means that dynamic action works them to give a mechanical evidence.

### Mechanical elongation

Mechanical elongation is proportional to temperature like thermal one. It needs to know the reason what and why because of a different elongation. The force of

separation happens by changing tangent direction when the elongation stops at Tg. If a movement of C atom up to Tg are in the direction of Y-axis, one of (Tm-Tg) will be in the direction of X-axis. Because the elongation of vertical motion stops at Tg, each C atoms in C-C bond are forced to move to horizontal direction by additive heat energy. When a temperature becomes Tg, a C atom couple in the segment of under Tg seems to be making a form to separate by repelling each other against interference of movement. Figure 2 shows what a C atom in one side of two array move after Tg. A length between C-C bond at Tg is given as  $C_1$  and  $C_2$ , which is an example given for an explanation mentioned above. When  $C_2$  atom with lower Tg reaches Tg<sub>2</sub> first, it does not start a movement to X-axis yet, because additive heat energy is used for elongation of  $C_1$  side. When it reaches the highest Tg in component molecule, here is Tg<sub>1</sub>, begins the movement.

### Calculating elongation of $C_2$

If the elongation of after Tg deals with the tracks by  $C_2$  atom from starting point of  $C_2$ , a position of transference of  $C_2$  atom by horizontal movement is given as  $C_3$  or  $C_4$ . The  $C_3$  is a calculating model and the  $C_4$  means a practical model with a slight gradient to horizontal direction. When the elongation shown as  $C_1 - C_3$  has reached the 1% elongation limit, the angle of  $C_1$  provides about 8 degrees from next equation (10),

$$\frac{h + \beta h}{\sin 90^\circ} = \frac{h}{\sin(90^\circ - \theta^\circ)} \quad (10)$$

therefore,  $\theta = 8^\circ$  is obtained from  $\cos \theta^\circ = \frac{1}{1.01} = 0.9900$ , where  $h$  is a length between  $C_1$  and  $C_2$ ,  $\beta$  is the 1% elongation rate and  $\theta^\circ$  is the angle of  $C_1$ .

### Practical elongation of $C_2$

When  $C_2$  atom with high elongation get started to move,  $C_1$  atom bound the movement of  $C_2$  is not to move yet.  $C_2$  atom becomes a difficult movement in the direction of X-axis but it means to happen in the diagonal direction with easy movement to pull at the axis of  $C_1 - C_2$ . The angle of main axis shown as  $\theta^\circ$  brings a rather lower value than 8. The relation between a distance  $x$  of a diagonal movement of  $C_2$  atom and a expanded elongation  $y$  of  $C_1 - C_2$  bond, is given as equation (11). Because  $\theta^\circ$  is a rather lower value, equation

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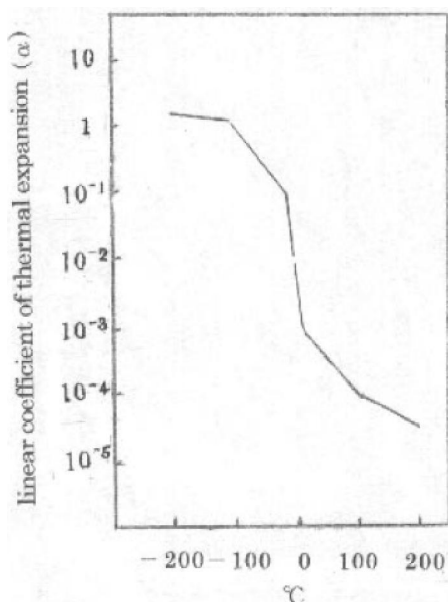


Figure 1 : A diagram of  $\alpha$  vs.  $T_g$  ( $^{\circ}\text{C}$ ). A diagram shows a transformation compressing the upper value due to a wide extent. The equation over  $0^{\circ}\text{C}$  provides  $\alpha \cdot T_g(^{\circ}\text{C}) = 1\%$ . As  $1^{\circ}\text{C}$  is an inflection point, it cannot use from  $1\text{C}$  to  $0^{\circ}\text{C}$  with indefiniteness. The equation below  $0^{\circ}\text{C}$ , which shows  $\alpha = 1\% \cdot T_g(^{\circ}\text{C})$

(12) is obtained from equation (11)

$$\therefore y = \cos \varepsilon^{\circ} \left\{ \frac{x}{\sin \theta^{\circ}} \right\} \rightarrow$$

$$\therefore y = \cos \varepsilon^{\circ} \left\{ \frac{x}{\sin \theta^{\circ}} \right\} \doteq \cos \varepsilon^{\circ} \left\{ \frac{x}{\theta(\text{radian})} \right\}$$

$$\cos \varepsilon^{\circ} \left\{ \frac{x}{\theta(\text{radian})} \right\} \quad (11)$$

$$Y = \cos \varepsilon^{\circ} \cdot X \quad (12)$$

where  $x$  is a length between  $C_2$  and  $C_4$ ,  $y$  is a length between  $C_1$  and  $C_4$  and  $X$  is  $x$  per radian. Elongation  $y$  is introduced to be a proportional relation to  $X$  at constant  $\cos \varepsilon^{\circ}$ , which  $X$  is given as increasing temperature. This shows a proportional relation between mechanical elongation and increasing temperature.

### Practical mechanical elongation

A mechanical elongation by all  $C$  of composite molecule finishes when a  $C$  atom of the lowest elongation, here is  $C_1$ , has reached at the 1% elongation limit. If  $C_0$  is put a starting point of  $C_1$ , a elongation between  $C_1$  and  $C_0$  adds to a length between  $C_1$  and  $C_4$  ( $y$ ) shown on figure 2. In case of a composite molecular starts from  $C_0$  of a basic point and adds elongations of each  $C$

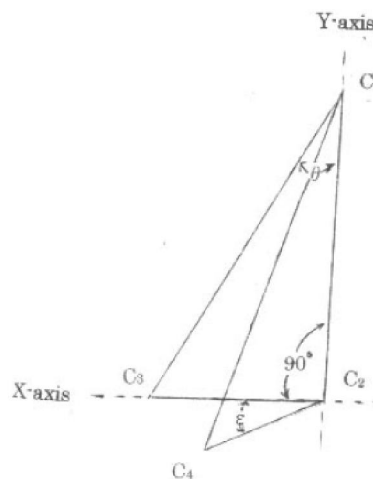


Figure 2 : A movement of  $C_2$  atom by the mechanical elongation.  $C_2$  atom is lower  $T_g$  than  $C_1$  one.  $C_3$  is a position of transference of  $C_2$  atom by horizontal movement. The expanded length is shown as  $C_1$ - $C_3$ , which  $\theta$  is a angle given from horizontal transference. When a movement of  $C_3$  reached at the 1% elongation limit,  $\theta$  is given about 8 degrees.  $C_4$  is the practical movement of  $C_2$  with a slight gradient shown an angle of  $\varepsilon$ . A movement of  $C_2$  on a line at constant  $\varepsilon$  can be shown as a function of  $\theta$  radian, which is proportional to temperature

reaching the 1% elongation limit. From equation (3) and (8), total practical elongation of symmetrical structure is given as;

$\sum \alpha_n$  (original distance between atoms) ( $T_m - T_g$ ) and a asymmetry one is;

$\sum 2\alpha_n$  (the same as symmetrical one) ( $T_m - T_g$ ).

The two practical elongations means to be in proportion to total  $\alpha$ , because the each value in parentheses is constant. It means to be reasonable as practical movement that all elongation of composite molecules forms a line, which is shown from  $C_0$  (equivalent to the point of  $C_1$  on Figure 2) to  $C_4$ .

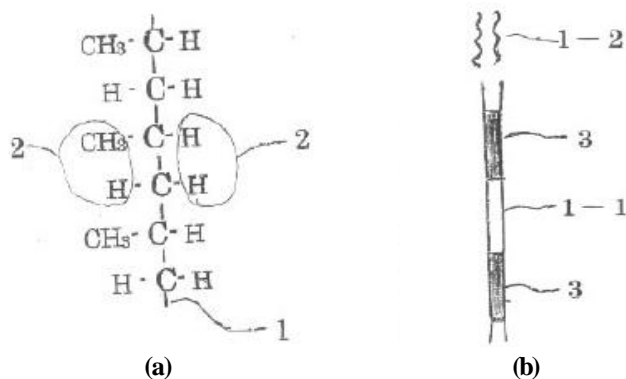
### Function of elongation to strength

If a stress works to a polymer, all segments in any main chain catch them with equal share to reduce the load. Because in the direction of segments agree with one of the stress, those can stand on the same straight line. First, stress functions to make a straight line (Figure 3b) to stretch a slack parts in a single main chain (Figure 3b) and gets rupture point by breaking  $C$ - $C$  bond. Equation of the strength provides,

$$\sigma = ER$$

The thermal segment is rigid due to a compact structure which is made up of fine stroke by thermal elonga-





**Figure 3 : An explanatory diagram for new segments. (a) A main chain composed of C-C bond 1 and side chain 2 is shown an example of polypropylene which repeat unit is propylene. (b) new segment 3 is composed of two arrays between main chains and single main chain (1-1 or 1-2). Here 1-1 shows under stretch and is usually sagging without stretch like 1-2**

tion to form a sturdy structure at room temperature. So segment assigns to  $E$  and breaking elongation of single main chain is  $R$ . The magnitude of  $E$  is clear to has the relation with the compact degree which the thermal elongation participate so that  $E$  in flexure vs.  $\alpha$  of cured epoxy resin was reported as a linear type<sup>[7]</sup>. If  $\alpha$  is a large value like aliphatic hydrocarbon, the elongation becomes larger, giving a large  $R$ . A toughness, which is impact strength, is shown as;

$$1/2\sigma \cdot R = 1/2 E \cdot R^2 \quad (12)$$

In this case, it means that a large value  $\alpha$  gives a effective result. As equation (2) has general use, it means that those elements have already similar  $E$  to that of polymer because those were formed through condensation from a melting state. For example, strength of metal may be also applied as segment using a line of single bond from compact atomic structure and lower  $\alpha$ . The elongation, that is,  $\alpha$  has to do with the structure of substance. Although a chemical structure serves to make a magnitude of  $\alpha$ , it doesn't mean to make the cause. The arrangement of atoms, which is either the symmetrical structure or the asymmetry one, is concerned a crystallization. It seems that a crystallization of element is also to have to do with the symmetrical structure. Thermal conductivity applies in metal with small  $\alpha$ . It can think that a happening elongation by a heat discharges it after traveling in a metal, going back its original state.

### Relation between entropy and elongation ( $\alpha$ )

$T_m$  has been handled by entropy from equation

(13).  $T_g$  connected with equation (5) also may be done the same handling.

$$T_m = T_g/k = \Delta H/\Delta S \quad (13)$$

where  $k$  is constant,  $H$  is enthalpy and  $S$  is entropy. The magnitude of  $T_m$  has been given in inverse proportion to  $S$  at equation (13). For example,  $T_m$  of aromatic group is high because  $S$  is low and aliphatic hydrocarbon is low from the contrary reason. But this is able to express by  $\alpha$  from the relation of  $\alpha \cdot T_g = 1\%$ . Both sides means the same as content. The difference between  $\alpha$  and  $S$  is given as enthalpy and elongation rate. Enthalpy for  $S$  means to function for elongation ( $\alpha$ ) of a distance between atoms and is stored in them, which elongation is the substance of entropy so that one of potential energy is height. There is a important point of agreement that  $T_g$  shown as  $\alpha$  starts from 0K and  $S$  is also zero at 0K as the third law of thermodynamics shows<sup>[8]</sup>.

## DISCUSSION

A change of elongation between atoms can explain a phenomena happening by rotation and vibration of molecule in polymer at  $T_g$ , which thought of micro Brownian movement makes no sense from a idealistic treatment as if a living thing. High temperature from  $T_g$  up to  $T_m$  means to happen mechanical elongation, because it is obvious to add 273K newly. It supports existence of crystallization that  $\alpha$  does not change before and after  $T_g$ . It means to be able to apply asymmetry structure of the same property on  $T_g$ . Kinetic movement of elongation after  $T_g$  appears increasing  $\alpha$  in asymmetry mechanical domain. It supports a different movement of elongation. A sturdy structure of segment is in charge of Young's modulus, which is formed from fine stroke by thermal elongation. The relation between degree of polymerization which is proportion to number of segments and strength can explain at most reasonable.  $\alpha$  replaced entropy gives concreteness so that potential energy is height. Although the interpretation of entropy used to take up a random arrangement, the example is not in thermal field.  $\alpha$  in a elongation between atoms causes heat, which is suitable for the substance at the stand of interpretation. A random arrangement can explains through thermal and mechanical  $\alpha$ .

**CONCLUSION**

Segment gives two types by temperature, which belongs to thermal (under  $T_g$ ) and mechanical domain ( $T_m - T_g$ ). Two domains have the same 1% elongation limit. Although symmetrical structure holding  $T_g = \Sigma T_{g_i}$ , shows the same  $\alpha = \Sigma \alpha_i$  in both domains, asymmetry changes  $2\alpha = 2\Sigma \alpha_i$  in mechanical domain. The common  $\alpha$  in symmetrical domains supports existence of crystallization. The mechanical moving of horizontal direction happens displacement of C-C bond less than  $8^\circ$  at 1% limit, which all elongation of composite molecules forms a line. Segment having a sturdy structure due to fine stroke by thermal elongation is in charge of Young's modulus in the equation of strength and elongation happens in single main chain.  $\alpha$  can use to replace entropy with traditional ways of thinking for polymer.

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