New Segment in New Theory of Polymer

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ABSTRACT: Melting temperature (T_m) can be divided in two steps of (T_m–T_g) and T_g in the glass transition temperature. There are respective segments in both steps. The difference of elongation, which causes a separation between two arrays in segment, is of two kinds: mechanical and thermal. T_g is given as disappearance of the segment, which would not be so if the kind of elongation were the same. A prefix of micro at Brown on T_g is meaningless, because the segment can be explained from a different point view the phenomena shown as a sign of melting at T_g. T_g between polymer and components of C—C bond in repeat unit is given as $T_g = \Sigma[1/n(1\%)/a_i] = \Sigma[(1/n)T_{gi}]$, where α is the linear coefficient of thermal expansion, n is the total number of components, T_{gi}, α_i is the value of component i. A magnitude of elongation of component C_i is given as α_i with the result, which the side chains have functioned like a weighting function. Strength of linear polymer is connected with the total number of segments. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 2859–2862, 2007

Key words: melting point; glass transition; strength; thermoplastics; resin

INTRODUCTION

A main chain in polymer is given like a meander. If it were not for segment in a main chain, polymer would not have any physical properties. A segment in main chain has been thought to happen spontaneously. A former work explains about a new segment, which has to do with the melting temperature (T_m), glass transition temperature (T_g), and strength.[1] A new segment is formed from a part of two arrays having the direction of main chain between two main chains. It is shown simply as a segment in this article. There is a fundamental difference *for* the segment between a cured resin and a linear polymer except a sort of chemical bond. T_g of cured resin changes with temperature of postcure. Therefore, it means that a segment grows to change the form by the given temperature. Whether the hardening is over or not, a higher T_g should not happen after a postcure at a higher temperature. But, a segment of linear polymer has T_g and T_m without any influence on the given temperature. The former work indicates that T_g causes when thermal elongation of C—C bond in a segment terminates. The limit of elongation is shown as $\alpha \cdot T_g = 1\%$ from 0°C, where $\alpha \, T_g$ is the elongation ratio. This work describes why a segment of polymer needs two arrays with connection between two main chains. When a connection happens between two main chains, it causes a segment within the direction to main chain. The segment is given a proper reason and a new information for additive equation of T_g. T_g has been thought to be on the way to T_m so that it gets started with agitation-free portions to rotate around the C—C bonds. This is called as micro-Brownnian motion. But, T_g is shown as the movement changing in the horizontal direction of C—C bond without a sign of T_m. T_m can be divided in two steps of (T_m–T_g) and T_g. Both steps mean to *be* different in existence independently. A difference of elongation for two steps is given in each segment. One elongation is mechanical and the other is thermal. If it were not for their difference, T_g would not exist. When the separation between two arrays in a segment is fulfilled at T_g, T_g can not leave because the following segment gets affected if the same mechanism for elongation is done. Strength of polymer can be explained only by the segment within the direction to main chain.

RESULTS AND DISCUSSION

A segment needs a part of two arrays between two main chains

A segment, which functions as a special unit group, does not form from a main chain without doing anything else. A connection between two main chains needs to form a segment with a part of two arrays. If a main chain was only a meander, the shape would not change when the temperature is high or low because there exists only expansion or shrink-

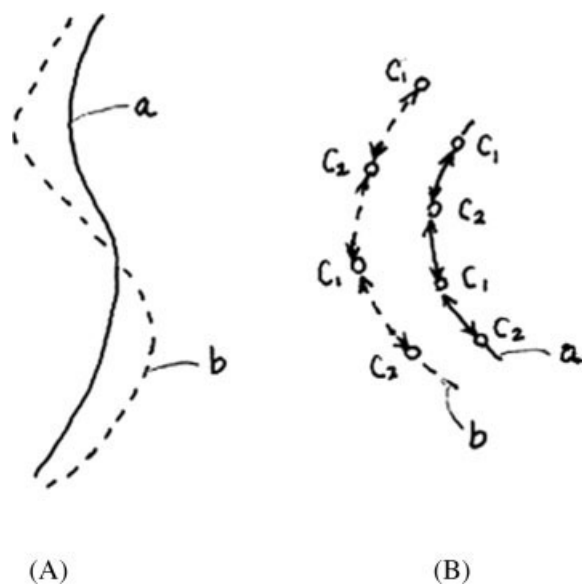(A)   (B)

Figure 1 (A) Main chain and (B) detail explanation (a) original (b) expansion; C_1, C_2 is an example of C atom.

age. Figure 1(A) shows the main chain before and after the expansion.

Figure 1(B) is a detailed explanation of (A), which changes according to the expansion of each C atom distance, e.g., between C_1 atom and C_2 atom in the main chain. An arrow in Figure 1(B) indicates the direction of expansion. Expansion and shrinkage in the main chain are reversible by an increase and a decrease of temperature. In case of shrinkage, (b) in Figure 1(A) is shown reversely as (a), under original temperature. A shrinkage of each C atom distance works like a folding door, where the direction is shown as an arrow in Figure 2(A). If a connection happens between two main chains, a folding-shrinking direction of C atom distance changes to face the connection point all at once for a drag as shown in Figure 2(B). A fixed shrinking direction generated is indispensable to form the segment.

A structure of segment formed with C—C bond and T_g

$T_g = \Sigma Q_i T_{gi}$ has been used as a base for the mathematic machinery of a method of additive properties, where T_{gi} is T_g for component i, Q_i is the weighting function for component i and has been chosen in different ways. The thought by segment agrees with Van Krevelen's choice, which expresses the number of component atoms in the main chain (f_i) divided by the total number of main chain atoms in the repeat unit (Σf_i):[2]

$$T_g = \sum f_i T_{gi} \Big/ \sum f_i \qquad (1)$$

A polymer chain is composed of side chain and main chain formed by mainly C—C bond. They are

expressed by an example of polypropirene as typical model to take easy understanding for the explanation. That is, $—H'C_1(CH_3)—H'C_2H—$ as repeat unit, where $—C_1—C_2—$ is the main chain and H, (CH_3) is the side chain of C_1, and H,H is the one of C_2. The weight function is given to make a difference for the elongation of each C atom, e.g., C_1,C_2. The elongation of C_2 is larger than C_1 since C_1 has a heavier side chain. T_{gi} of component atoms is handled in containing a magnitude of heavy by side chain. The elongation rate of each C is shown as α. If an elongation rate of C atom is large, α is also large. When reached T_g, the elongation rate of C atom per repeat unit and the polymer are given as 1%, where the share of C_1 and C_2 is divided by two of the total numbers to 1% equally. That is given as follows. The elongation rate of polymer (1%) = the elongation rate of C_1 (1/2%) + the elongation rate of C_2 (1/2%). From $\alpha \cdot T_g = 1\%$, $T_g = (1/2\%)/\alpha_{i1} + (1/2\%)/\alpha_{i2}$. If the number of C atoms per repeat unit is n, $f_i/\Sigma f_i$ in eq. (1) is expressed concisely as $1/n$. The equation of elongation rate by segment is expressed as follows:

$$T_g = \sum [1/n(1\%)/a_i] = \sum [(1/n)T_{gi}] \qquad (2)$$

The weighting function disappears to insert into α, so that the number only remains. The thought of segment with Van Krevelen's result indicates some importance. One is the existence of repeat unit. For example, a polymerization of propirene is done with a covalent bond. Therefore, the C—C bond is all the same. It should be shown as the highest T_{gi1} owing to the independent C_1 and C_2. In case of segment, T_g is shown as the separation by peeling two arrays composing of C pair off. Equation (2), shown as the mean value, means a relation that C_1 and C_2 are dependent. A peeling off of C_1 part happens easily under the influence of C_2 part separating already with a lower T_{gi2} from two arrays in a segment as shown in Figure 3. Then, the T_{gi}
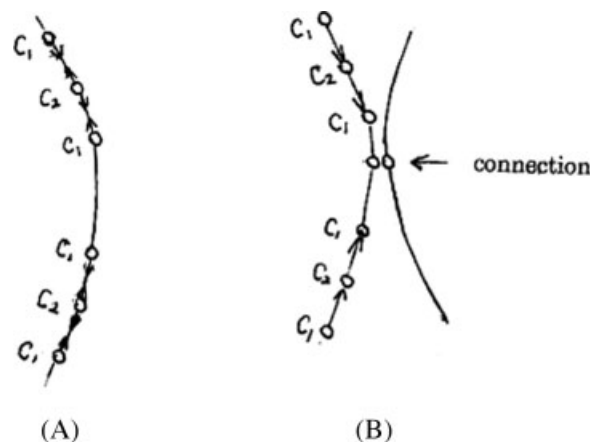

(A)   (B)

Figure 2 (A) Folding direction of C atom distance and (B) a fixed shrinking direction, C_1, C_2 is an example of C atom.
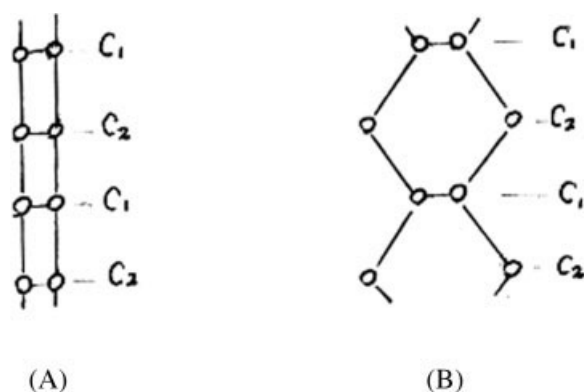
Figure 3 (A) two arrays in a segment composed of C_1, C_2 atom (B) the influence of C_2 atom pair to C_1 atom pair.

of C_1 falls up to the mean value. It means that the segment can make the existence of repeat unit clear. Another is a contribution to the molecular design for a prediction. An improvement of T_g has been done specially as to epoxy resin. Equation (2) might present an effective measure by number of C atom with the equal weighting function. If a repeat unit is composed of $C_A - C_B - C_B - C_C$, eq. (2) is shown as $T_g = 1/4T_{gA} + 1/4T_{gB} + 1/4T_{gB} + 1/4T_{gC}$. Suppose that a magnitude of T_g by each component is $T_{gB} < T_{gA} < T_{gC}$. A lower T_g is provided in aliphatic hydrocarbon, e.g., methylene group and a higher one is in aromatic group and a further high one is in naphthalene group. When it heightens T_g in the example, it might be applied a material of the highest T_{gC} among them. If a new C_C atom of the same material with an equal molecular weight is added, T_{gC} is a share of $2 \times 1/5$. The rising rate is 15% of up to 40% from 25%. When a substitute choice is given as reducing the number of C_B atom from the original number, T_{gC} can also rise about 8% of up to 33% from 25%. Since handling of material of higher T_g has various difficulties, e.g. viscosity, it might be given an effective measure.

T_m is divided into two steps between (T_m-T_g) and T_g

Relation between T_m and T_g is shown as next equation (K).[1]

$$T_g/T_m = \{T_g(^\circ C) + 273\,K\}/\{T_m(^\circ C) + 273\,K\} = k \quad (3)$$

where k is 1/2 (symmetrical structure) and 2/3 (unsymmetrical). In case of $k = 1/2$, eq. (1) is expressed as follows: if T_g is $x^\circ C$.

$$T_m(^\circ C) = 2x^\circ C + 273\,K \quad (4)$$

Equation (4) can be shared with two steps, i.e., $T_g = x^\circ C$ and $(T_m-T_g) = x^\circ C + 273$ K. A domain of (T_m-T_g) is considerably higher than T_g with addition to con-

stant 273°C owing to the transformation to Kelvin from degree Celsius. But a variable $x^\circ C$ of the point is common between them. The existence of two segments is approved in the common point. In case of $k = 2/3$, (T_m-T_g) is expressed as $(1/2) T_g$. It means that the symmetry of structure does not affect up to T_g, showing the difference of both structures after T_g.

Formation of first segment at (T_m-T_g) and second segment of up to T_g

After T_g, the elongation to an atom distance between C—C bond is not by thermal but mechanical cause, because thermal elongation terminates at T_g. The mechanical elongation is larger than thermal one (1%), so that a tensile elongation rate of polypropirene's fiber is given as 15–25%.[3] It means that their elongation is a different nature, which does not affect each other. When a connection happens between two main chains at T_m, the atom distance between bonding C becomes shorter owing to the bond. As a result, the resin volume decreases while forming solid from liquid. The contraction of solid works to shrink mechanically the atom distance between C—C bond in a main chain. Thereby, a concentrated shrinkage to a connection point causes the two main chains to come closer. The partner of reaction with the nearest distance is the neighbor C atom of a connection point. It may give the following connection when the partner comes closer by shrinkage.

The formation of first segment at (T_m-T_g), which is a part of two arrays, is done with some C pairs combined with themselves between two main chains by Van der Waal's force. The diagram of process is shown as follows. (A connection between two main chains happen → resin volume decreases → A shrinkage to a atom distance between C—C bond → A distance between two main chains comes closer → the following connection happens → continued on the following connection).

The formation of the second segment at (T_g-room temperature) is done with the same as the structure and mechanism of the first one. It is formed in succession from an end of the former segment, which happens closer between two main chains through shrinkage of atom distance by falling of temperature. The shrinkage is going while falling of temperature from T_g up to room temperature. There is a chance of formation with a moderate expanse of temperature. The direction of shrinkage to main chain coincides with the one of segment. The formation and the disappearance of segment are reversible. The disappearance of second segment means to happen for T_g and the one of first segment happens for T_m. Although a second segment is formed by mechanical operation like a stretch, it does not pay any attention to that.

A problem of Brownnian movement for macromolecule

A melting state of polymer is called as macro-Brownnian movement, and the other side T_g is micro-Brownnian motion. The former has been thought that a main chain moves freely in case of liquid like a water molecule in which Brown picks up. The latter has been handled as a sign of melting with agitation-free portions of the main chain. In case of melting state, the length of molecule is out of question. When it starts melting from solid state, the length of molecule has come up. It may be simple to explain by giving some examples. If a water molecule is considered as a small fish, a main chain is like a great fish, e.g., a whale. However, when they swim, it makes no difference. But the difference may happen when they go back to sea from running aground in the shore. Although a small fish can go back at once to the sea by surfing, a whale cannot go back except through jumping. The sea means the quantity of heat and the surf means the *additional one*. It is very difficult to move all C—C bonds composed of a long main chain, because it is wrong for the movement of subject even if a part in it keeps to stay. In other words, two main chains having some segments are to separate the original main chain perfect. The separation process consists of two parts at which one is a part of segment and the other is only main chain. The reason of separation in segment is important because the latter causes naturally from pulling when a separation of the former happens. The direction of separation at segment is horizontal for the vertical main chain. Two bonding C atoms composed of segment start to move horizontally when they reach T_g owing to the limit of vertical elongation. Then, all atom distance of C—C bond in main chain happen to stretch causing the resin swelled through a separation of between C atoms in segment. Their stretch helps to cause the following separation between C atoms. A prefix of micro at Brown is meaningless because the phenomena for a sign of T_m at T_g can be explained from movement to horizontal C atom. It should be called only as Brownnian movement.

Relation between segment and strength

A strength of linear polymer (σ) is shown as follows:

$$\sigma = a - (b/P) \tag{5}$$

where P is degree of polymerization and a and b are constants.[4] Since the total number of segment (N) is proportional to P, eq. (6) can be handled as strength versus N. That is expressed by:

$$\sigma = a - (c/N) \tag{6}$$

where c is a constant. A generation of strength can be explained only by the segment though P cannot. Stress on the main chain should be in the direction agreeable to both. If it is different like an elastomer, a stretch continues to come up in the same direction and strength appears. Strength of polymer can work at the start by segment with a necessary condition as mentioned earlier. Since all the segments in main chain stand in a straight line for a stress, they can catch it with equal share to reduce the load. P versus T_g is given by the Fox–Flory equation:

$$T_g = A - (B/P) \tag{7}$$

where A is equal to $T_{g\infty}$ and B is a constant.[5,6] T_g has been handled with a connection of the number of component atoms in repeat unit, but on the other hand, it should be considered to affect P. It seems that the separation between two arrays in a segment is related to P. In case of lower P, the separation becomes easily for a mono main chain connecting segment is easy to move, falling T_g. Although the elongation of $\alpha \cdot T_g$ is shown by 1% from 0°C, it means to change from inconstancy of T_g except α. The equation of T_g in component atoms stands up from the comparison to T_g of various polymers. It seems that an inconstancy of T_g cannot make it to fit a perfect form. A lot of equations given for them should be handled flexibly with tolerance level.

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