The Effect of Chain Branching and Molecular Weight of Polyethylene on its Glass Transition Temperature

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In the previous paper[1] the effects of chain branching, mainly short chain branching, on such properties as the melting point, the crystallizing temperature and the premelting phenomenon were reported and discussed. In this paper the effect of chain branching on the glass transition temperature and the degree of cubic expansion above and below the glass transition temperature are described.

Regarding the glass transition temperature, a sort of second-order transition temperature, of polyethylene, a number of reports have been presented. Hunter and Oakes[2] showed from the measurement of linear expansion that there was a sign of transition occurring at about −45°C. Later Danusso et al.[3] reported from the volume expansion measurement that the second-order transition temperature of polyethylene existed arround −20°C regardless of molecular weight, degree of chain branching or degree of crystallinity. According to the paper of Gubler and Kovacs[4] the cubic expansion coefficient changes between −20 and −25°C for both a high-pressure and a Ziegler polyethylene. It has also been confirmed by some other methods that a transition occurs at about −20°C or at a still lower temperature[5-10]. By considering the change of mechanical properties of polyethylene at about −50°C, reported by Carey et al.[11], and the brittle point of −68°C reported by Boyer and Spencer[12], this second-order transition at arround −20°C seems to be the glass transition, though the existence of another transition at the temperature below −100°C was reported by Schmieder and Wolf[13], Oakes and Robinson[14] and Dannis[15]. As for the effect of the degree of chain branchig on the glass transition temperature, it may be inferred from the results reported hitherto that the degree of chain branching has no effect on the glass transition temperature. Such a conclusion, however, can not be reached so hastily, as only a few kinds of samples were used in each experiment.

The glass transition temperature is generally defined as the point at which the main chain in an amorphous region of a polymer acquires large scale mobility. It is therefore expected that short chain branching and the branch point of long chain branching, which are contained in the amorphous region, disturb the regularity of molecules and keep the molecules from arranging themselves in good order in proportion to the number of them, and consequently the molecular mobility of the amorphous region is affected not a little by them; that is, the more branches the amorphous region contains, the more easily it initiates the large scale molecular motion and as a result the glass transition of polyethylene having the higher degree of chain branching occurs at the lower temperature.

From this point of view, a series of measurements have been taken by using various polyethylenes. From the results obtained it appears that short chain branching has a large effect on the glass transition temperature, independent of the degree of crystallinity. Long chain branching scarcely exists in low-pressure polyethylene, and in high-pressure polyethylene only a few long chain branching are contained in comparison with short one. It is therefore considered that its effect is not noticeable, even if each branch point has some effect on the glass transition temperature.

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[1] K. Tanaka, This Bulletin, **33**, 1060 (1960).

[2] E. Hunter and W. G. Oakes, *Trans. Faraday Soc.*, **41**, 49 (1945).

[3] F. Danusso, G. Moraglio and G. Talamini, *J. Polymer Sci.*, **21**, 139 (1956).

[4] M. G. Gubler and A. J. Kovacs, *J. Polymer Sci.*, **34**, 551 (1959).

[5] E. Butta and A. Charlesby, *J. Polymer Sci.*, **33**, 119 (1958).

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Samples

Samples used were Marlex 50-9, Ziegler polyethylene, and eight kinds of high-pressure polyethylenes with the different molecular parameters which were provided by courtesy of Dr. Hammer of E. I. du Pont de Nemours and Company. The molecular parameters are shown in Table I. Marlex 50-9 and Ziegler polyethylene were commercially available polymers made by Phillips Petroleum Company and Dow Chemical Company, respectively. As the molecular parameters for these two samples were not available, the degree of short chain branching was determined by the infra-red method according to Slowinski[16]. It was found to be 0.25 for Marlex 50-9 and 0.4 for Ziegler polyethylene.

TABLE I. THE MOLECULAR PARAMETERS FOR POLYETHYLENE SAMPLES

Sample	Melt index	$M_n \times 10^{-3}$	N_c*	N_w**
A***	0.2	34	1.6	20
B	2.1	32	1.6	18
C	2.1	21	2.2	27
D	2.1	18	3.0	34
E	3.8	20	1.6	13
F	2.0	50	2.0	18
G	1.8	27	0.6	10
H	16.0	12	3.2	29
Marlex 50-9			0.25	
Ziegler			0.4	

* Short chain branching index in CH_3 groups per 100 CH_2 groups.

** Long chain weight average number of branch points per molecule.

*** These (A to H) are high-pressure samples.

Experimental

Dilatometric measurements were at first taken in the temperature range from −40 to 150°C by using mercury as the confining liquid. However, it seemed to be undesirable to determine the glass transition point merely from the measurements in which mercury was used as the confining liquid, as the temperature range below the glass transition temperature was small. Therefore 99.5% ethanol being used as the confining liquid, measurements were carried out over the temperature range from room temperature to −70°C. In this measurement Bekkedahl's straight type dilatometer[17] was used and the preparation of the most highly crystallized sample was performed by following the way mentioned in the previous paper in the sufficiently evaluated glass tube in order to protect the sample from oxidation before it was enclosed in the dilatometer. A Dewar vessel containing toluene was used as a bath. The details about the experimental procedure were omitted in this paper, as they were described in the previous paper.

The glass transition temperature, T_g, was determined by extrapolation of two straight lines connected by a curved section, consisting of the volume-temperature curve of high polymer. As polyethylene is a semi-crystalline polymer and the difference between cubic expansion coefficients above and below T_g is small, an error is apt to be made. In order to eliminate such an error T_g was also determined from the discontinuity of the curve obtained by plotting the volume temperature derivatives, $\Delta V/\Delta t$, as a function of temperature as was done by Hoffmann and Weeks[18].

Results and Discussion

The specific volume-temperature curves of the most highly crystallized polyethylenes ranging from above to below the glass transition temperature are shown in Fig. 1. The volume temperature derivatives are plotted as a function of temperature in Fig. 2. In these two figures only a few curves were shown to avoid confusion.

The average value of the glass transition temperature obtained for each sample is given in Table II. These values are plotted in Fig. 3 as a function of the degree of short chain branching. As is shown in the figure, the glass transition temperature lowered with the increasing amount of short chain branching

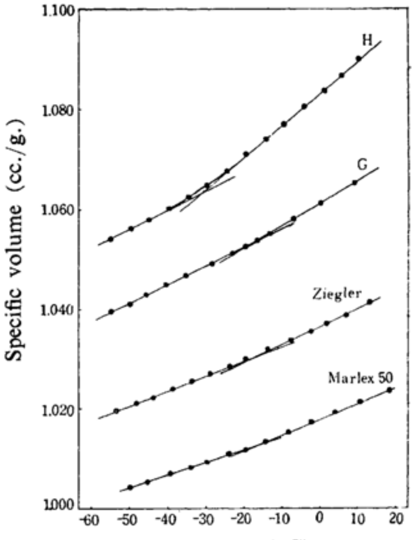

Fig. 1. Specific volume-temperature curves of the most highly crystallized polyethylene ranging from above to below T_g.

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[16] E. J. Slowinski, Jr., H. Walter and R. L. Miller, *J. Polymer Sci.*, **19**, 353 (1956).

[17] N. Bekkedahl, *J. Research Natl. Bur. Standards*, **42**, 145 (1949).

[18] J. D. Hoffmann and J. J. Weeks, *J. Research Natl. Bur. Standards*, **61**, 465 (1958).

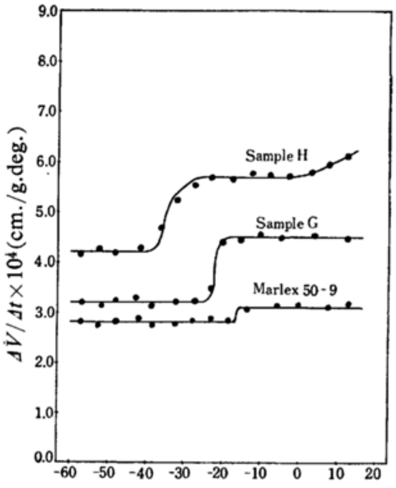

Fig. 2. Volume-temperature derivatives of some of the most highly crystallized samples as a function of temperature.

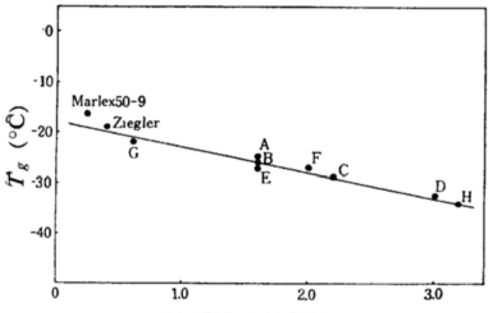

Fig. 3. T_g as a function of degree of short chain branching

TABLE II. THE GLASS TRANSITION TEMPERATURES AND DEGREES OF CUBIC EXPANSION ABOVE AND BELOW THAT TEMPERATURE

Sample	N_c	T_g	$\alpha_1{}^{*} \times 10^4$	$\alpha_2{}^{**} \times 10^4$
Marlex 50-9	0.25	−16.0	2.8	3.1
Ziegler	0.4	−19.1	2.8	3.4
G	0.6	−22.2	3.2	4.5
A	1.6	−25.2	3.9	5.1
B	1.6	−25.8	3.5	5.0
E	1.6	−26.3	3.7	5.3
F	2.0	−27.3	4.0	5.3
C	2.2	−28.8	3.9	5.2
D	3.0	−32.5	4.1	5.9
H	3.2	−34.0	4.2	5.7

* Degree of expansion below T_g.
** Degree of expansion above T_g.

and there seems to be a linear relation between the glass transition temperature and the degree of short chain branching.

The degree of cubic expansion above and below the glass transition temperature, which are presented by the gradients of the straight lines above and below the temperature, are also listed in Table II. These values generally increased as the amount of short chain branching became larger and those above the glass transition point increased in a greater extent than did those below the point, which fact is probably because the large-scale segmental motion in the amorphous region is excited at the temperature above the glass transition point and the more the sample of polyethylene branched, the greater is the scale of the motion. As regards the degree of cubic expansion below the glass transition point there is a view by Price[19] and Danusso et al.[20] that it is considered to be equal for all the polyethylene, but in this experiment the result as above was obtained, that is, the degree of cubic expansion below the glass transition point increased as a whole with the increase of the degree of short chain branching.

Since short chain branching affects the degree of crystallinity of polyethylene as was mentioned in the previous paper, it is expected that the lowering of the transition temperature by the increase of short chain branching shown in Fig. 3 is attributable to the decrease of the degree of crystallinity. However, glass transition temperatures of the quenched samples of these polyethylenes, which showed a low degree of crystallinity about 40% at 25°C, were found at nearly equal temperatures to those of crystallized samples. Therefore the lowering of the glass transition temperature is probably due to the direct effect of short chain branching itself and not to the decrease of the degree of crystallinity. According to the recent result of linear expansion measurements by Saito[21], a transition was found at around −32°C for a low-branched polyethylene and at about −45°C for a highly-branched polyethylene. The difference between these temperatures was almost equal to that found by the author, though each temperature was lower by about 10 degrees than that obtained here.

Considering the results mentioned above, short chain branching of polyethylene appears to affect the glass transition temperature independent of such factors as degree of crystallinity and molecular weight. Moreover, according to Gubler and Kovacs[4] the number of CH_2 groups constituting the main chain in amorphous regions of polyethylene thermally

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[19] F. P. Price, *J. Chem. Phys.*, **19**, 973 (1951).
[20] F. Danusso, G. Moraglio and G. Natta, *Ind. Plastiques Mod.* (*Paris*), **10**, 40 (1958).
[21] S. Saito, private communication.

treated in the same way are almost equal regardless of its kind. Therefore the polyethylene having the higher degree of short chain branching will contain more branches in one amorphous region, provided that short chain branching is distributed equally in all the amorphous regions. It is considered that the shorter the branches which are contained in the amorphous regions equal in size, the smaller is the intermolecular interaction between the segments in those regions in the temperature range below the glass transition temperature, and as a result the Macro-Brownian motion in amorphous regions starts at the lower temperature, that is, the glass transition occurs at the lower temperature.

The relation between the glass transition temperature and degree of short chain branching in high pressure polyethylene shown in Fig. 3 is led to the following expression by using the method of least square,

$$T_g = -4.6N_c - 18.7$$

Marlex 50-9 and Ziegler polyethylene deviate somewhat from this expression. According to Willbourn[22] short chain branches of high-pressure polyethylene are ethyl and butyl branches and those of Marlex and Ziegler polyethylene are methyl, and methyl and ethyl, respectively. Therefore in the amorphous region of Marlex 50-9 and Ziegler polyethylene molecules possess a greater intermolecular interaction than expected from the case of high-pressure polyethylene.

As in short chain branching, so in long chain branching, it is expected that the increasing amount of long chain branching lowers the glass transition temperature. In this experiment, however, no appreciable result was produced. This is probably attributable to the very small amount of long chain branching, that is, the effect of long chain branching on the glass transition temperature is covered by the effect of short chain branching and of molecular weight. For example, as to the samples A, B and E which were equal in degree of short chain branching but different in degree of long chain branching, even the reverse phenomenon was observed that the sample having the larger amount of long chain branching showed a higher glass transition temperature. It is perhaps due to the effect of molecular weight of the sample as is discussed below.

It is generally said that the glass transition temperature is affected by molecular weight. Molecular weights of the samples used cover a wide range, so transition temperaturs are illustrated in Fig. 4 as a function of molecular weight. In the figure the glass transition temperature apparently rises with the increase of molecular weight, but short chain branching considerably affects the glass transition temperature as was stated above. A definite conclusion cannot be deduced without eliminating the effect of short chain branching. In order to remove this effect, the difference between the glass transition temperature obtained from practical measurement and that from the expression already presented is illustrated in Fig. 5 as a function of molecular weight. As is shown in the figure the rise of the glass transition temperature is only less than 2°C as molecular weights increase from 10,000 to 50,000. Therefore it will be evident that molecular weight has a smaller effect on this transition temperature compared with that of short chain branching. According to Fox and Flory[23], however, the glass transition temperature of atactic polystyrene rose by 14°C as the molecular weight increases from 10,000 to 50,000 as is shown in Fig. 5. This difference in polyethylene and polystyrene is probably due to the fact that the former is a crystalline polymer and the latter an amorphous polymer.

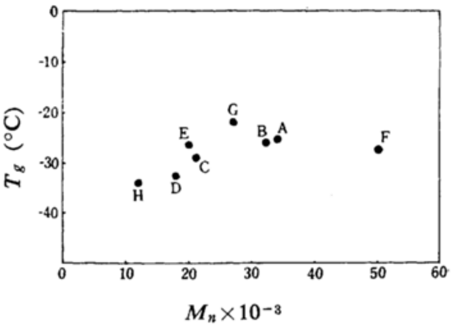

Fig. 4. T_g as a function of molecular weight.

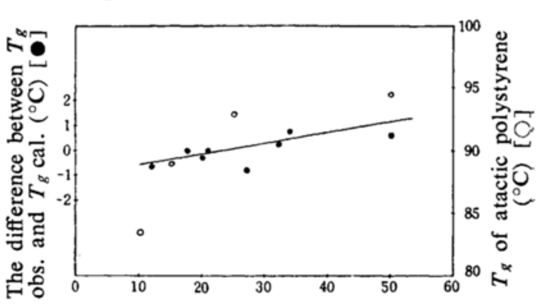

Fig. 5. The difference between T_g from the practical measurement and that from the expression presented in this paper, and T_g of atactic polystyrene are illustrated as a function of molecular weight.

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[22] A. H. Willbourn, *J. Polymer Sci.*, **34**, 569 (1959).

[23] T. G. Fox, Jr. and P. J. Flory, *J. Appl. Phys.*, **21**, 581 (1950).

that is, this contains very large amorphous regions, whose size is greatly affected by molecular weight, while that includes alternately crystalline and amorphous regions. According to Gubler and Kovacs the size of the individual amorphous region in the samples thermally treated in the same way is almost equal regardless of the kind of polyethylene, as was mentioned already. From this point of view, it is considered that the effect of molecular weight on the glass transition temperature is essentially very small in polyethylene.

In addition it is reported by Smith[24] that polyethylene contains double bonds in it and most of them belong to the terminal of the main chain for Marlex and to the side chain for high-pressure polyethylene. But, as the amount of double bonds is very small, the effect on the glass transition temperature and degree of crystallinity will not be worth discussing in this paper.

Summary

A series of measurements by volume dilatometry were performed in order to know whether short chain and long chain branchings, and molecular weight of polyethylene affected the glass transition temperature or not. The glass transition temperature, T_g, was obtained from the intersection of two straight lines of volume-temperature curve and from the discontinuity of the curve obtained by plotting the volume temperature derivatives as a function of temperature. T_g lowered with the increasing amount of short chain branching and there seems to be a linear relationship between T_g and the degree of short chain branching. No appreciable effect of long chain branching on T_g was observed. T_g rose apparently with the increase of molecular weight, but the true rise of T_g was only less than 2°C as molecular weight increased from 10,000 to 50,000. The degree of cubic expansion above and below T_g increased generally as the amount of short chain branching increased.

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[24] D. C. Smith, *Ind. Eng. Chem.*, **48**, 1161 (1956).