Dilatometric Study on Transition Phenomena of Various Polyethylenes with Different Degree of Chain Branching

By Kōji TANAKA

(Received January 26, 1960)

Much interesting work has been done about the effect of chain branching of polyethylene on its physical and chemical properties. It is well known that branches in ordinary high-pressure polyethylene are of two types, short chain and long chain branchings. According to Roedel[1] short chain branching has the most marked effect on such properties as melting point, yield point, bending modulus, hardness, and vapour permeability, while long chain branching has a marked effect on melt flow and viscoelastic properties. Richards[2] presented data on the relation between the degree of crystallinity and the degree of short chain branching in a series of polyethylenes, and Sperati et al.[3] gave quantitative relations between density, degree of chain branching, and degree of crystallinity, and also between density and many other physical properties.

An early study of polyethylene by volume dilatometry was carried out by Boyer and Spencer[4]. They found melting points at 103°C and in the neighborhood of 115°C for different polyethylenes. Hunter and Oakes[5] reported from the volume measurement of a number of polyethylenes in the range from 0° to 170°C that the percentage of crystalline part did not change up to about 70°C, but thereafter fell more and more rapidly until the substances became wholly amorphous at a temperature depending on the nature of the specimen and that density of molten polyethylene showed little dependence on average molecular weight, but the temperature at which crystalline material first appeared on cooling was raised by increase in molecular weight. Mandelkern and his coworkers[6] presented the results of a study of volume-temperature behavior and melting temperatures of linear polymethylene and highly branched polyethylene. For polymethylene a well defined first order transition or melting temperature was found at 136.5±0.5°C and 70% of melting occurred in only a three to four degree interval, while for branched polyethylene the melting temperature was 115°C and the melting range considerably extended in comparison with the linear polymethylene. Similar results were reported by Nielsen[7] and recently by Marker[8] as for the melting of polyethylene. Grams and Gaube[9] showed that melting temperature existed between 124° and 133°C for low-pressure polyethylene and between 104° and 111°C for high-pressure polyethylene. According to the results by Hunter and Oakes, and by Nielsen, specific volumes above melting point were equal for various polyethylenes at the same temperature, but according to Grams and Gaube high-pressure polyethylene had higher specific volume than low-pressure polyethylene. Gubler and Kovacs[10] determined the specific volume of three samples (high-pressure, Ziegler and Marlex) dilatometrically between −38.8° and 170°C after various heat treatments, and showed the variation of the degree of crystallinity with temperature, the size of the polyethylene crystal and the state of the distribution of the crystal. About the specific volume above melting point they also showed that all the polyethylenes had the equal specific volumes at the same temperature regardless of the properties of polyethylenes. Moreover they showed that the cubic expansion coefficient changed at the temperature between −20° and −25°C for high-pressure polyethylene and Ziegler polyethylene, which was well consistent with the result presented by Danusso et al.[11]

Now, according to Hunter and Oakes as is mentioned already, molecular weight is given as a factor affecting the properties such as melting point, crystallizing temperature, that is, the temperature at which crystalline material first appears on cooling, and premelting phenomenon. However, by the appearance of polyethylene made by the low-pressure process and from the

---

[1] M. J. Roedel, *J. Am. Chem. Soc.*, **75**, 6110 (1953).
[2] R. B. Richards, *J. Appl. Chem.*, **1**, 370 (1951).
[3] C. A. Sperati, W. A. Franta and H. W. Starkweather, Jr., *J. Am. Chem. Soc.*, **75**, 6127 (1953).
[4] R. F. Boyer and R. S. Spencer, *J. Appl. Phys.*, **15**, 398 (1944).
[5] E. Hunter and W. G. Oakes, *Trans. Faraday Soc.*, **41**, 49 (1945).
[6] L. Mandelkern et al., *J. Am. Chem. Soc.*, **75**, 4093 (1953).
[7] L. E. Nielsen, *J. Appl. Phys.*, **25**, 1209 (1954).
[8] L. Marker, R. Early and S. L. Aggarwal, *J. Polymer Sci.*, **38**, 369 (1959).
[9] E. Grams and E. Gaube, *Angew. Chem.*, 67, 548 (1955).
[10] M. G. Gubler and A. J. Kovacs, *J. Polymer Sci.*, **34**, 551 (1959).
[11] F. Danusso, G. Moraglio and G. Talamini, ibid., **21**, 139 (1956).

several reports above quoted, it seems that chain branching must be regarded as a more significant factor affecting those properties. But at present detailed data about this point are not yet available.

Therefore a series of measurements were performed in the present paper about melting point, crystallizing temperature, premelting phenomenon, glass transition temperature, and degree of crystallinity at 25°C for various polyethylenes with different degrees of short chain and of long chain branchings. The results obtained showed that the temperature and degree crystallinity were raised with the increase of short chain branching. About the effect of long chain branching, no remarkable result could be found, since the amount of long chain branching contained in the sample used was very small.

Sample.—Samples used in this investigation were Marlex 50-9, Ziegler polyethylenes, and eight kinds of high-pressure polyethylenes. These high-pressure samples were provided by the courtesy of Dr. Hammer of E. I. du Pont de Nemours and Company. These samples, the molecular parameters of which are listed in Table I, were different in molecular weight, melt index, degree of short chain branching and that of long chain branching. Marlex 50-9 and Ziegler polyethylene were commercially available polymers made by Phillips Petroleum Company and The Dow Chemical Company, respectively. As the molecular parameters for these samples were not available, the degree of short chain branching was determined by the infrared method by using the 1370 and 1378 cm^{-1} bands according to Slowinski[12]. It was found to be 0.25 for Marlex 50-9 and 0.4 for Ziegler polyethylene.

TABLE I. THE MOLECULAR PARAMETERS[a] FOR POLYETHYLENE SAMPLES

Sample	Melt index	$M_n \times 10^{-3}$	N_c[b]	N_w[c]
A[d]	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[e]	
Ziegler			0.4[e]	

a) These were determined in E. I. du Pont de Nemours and Company by the methods described in J. Am. Chem. Soc., **75**, 6110 (1953).

b) Short chain branching index in CH_3 groups per 100 CH_2 groups.

c) Long chain weight average number of branch points per molecule. According to Bunn*, polyethylene has generally a relatively small number of long chain branches, 8-10 per molecule on a weight average basis and this is equivalent to less than one per molecule on a number average basis.

* C. W. Bunn, Polythene, A. Renfrew and P. Morgan, eds., Iliffe, London, Interscience, New York, 1957, Ch. 7.

d) These (A to H) are high-pressure polyethylenes.

e) This was determined here by the infrared method.

Experimental

An experiment was carried out by volume dilatometry on which there was detailed description by Bekkedahl[13].

The dilatometer used in this experiment was made of Pyrex glass (as the volume expansion coefficient 0.00001/deg. was used) and consisted of three parts (Fig. 1, a). They were connected together tightly with springs and in the case of measurement the dilatometer was immersed into the bath up to the height a little below the ground joint connecting the parts A and B. Prior to the experiment the capillary of part A was calibrated. After the dried and weighed sample was put in part C and this part was combined with part B, they were weighed, and then they were connected to the apparatus shown in

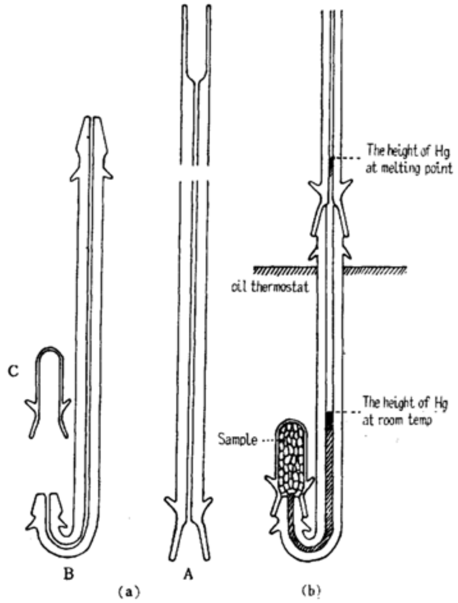

Fig. 1. Dilatometers: (a) for the measurements from about −40° to 150°C. (b) for the measurements above melting point.

---

12) E. J. Slowinski, Jr., H. Walter and R. L. Miller, ibid., **19**, 353 (1956).

13) N. Bekkedahl, *J. Research Natl. Bur. Standards*, **42**, 145 (1949).

Fig. 2 and all the ground parts greased with silicone grease. Mercury as the confining liquid was inserted by distillation under vacuum of 10^{-3} mmHg and finally the total weight was weighed again in order to known the amount of mercury. As this amount of mercury was insufficient for the measurement, the adequate amount of mercury was weighed and added after parts A and B were combined together. The specific volume of the sample at the fixed temperature was calculated from the weights of the sample and of mercury and the total volume of parts B and C of the dilatometer which had been determined by using mercury in advance. In the case of calculation, corrections for the emergent stem and the expansion or contraction of the glass of the dilatometer were made according to Bekkedahl.

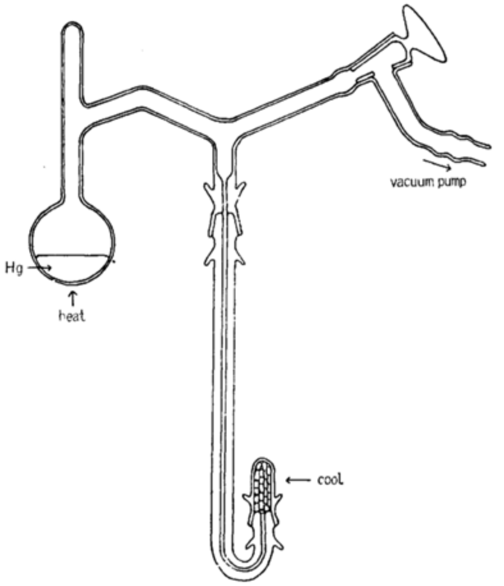

Fig. 2. The apparatus for insertion of Hg by vacuum distillation.

As is well known, the specific volume of polyethylene is dependent on temperature, as well as on its crystallinity and the amorphous region may have the possibility of further crystallization at temperature above its glass transition temperature, if the sample is not sufficiently crystallized. Therefore it is naturally expected that the volume-temperature curve above the glass transition temperature obtained by heating such a specimen contains both effects of the increase of volume by thermal expansion and the decrease of volume by further crystallization, which will obstruct the reproducibility of the curve and complicate the analysis of it. In order to eliminate such disadvantages, volume-temperature curves were taken for sufficiently crystallized samples. Sufficient crystallization of samples was carried out as follows. (1) The height of mercury in the capillary of the dilatometer containing the untreated polyethylene and mercury was recorded at 25°C exactly to 0.001 cm. (2) The dilatometer was gradually heated in the oil thermostat up to 150°C and kept at that temperature for about three hours to melt the sample in the dilatometer. (3) It was then cooled down slowly at the rate of 1/5°C per min. to 25°C. (4) The height of the mercury column was again recorded at 25°C. In this case the height was lower than that in the former case, which showed that the volume of the sample decreased by further crystallization by this treatment. Similar operations were performed, the time of melting being lengthened or shortened and the cooling rate being slower or faster, and also the dilatometer being kept for several hours at the temperature where crystallization occurred, on the way back to 25°C from 150°C at the rate of 1/5°C per min. The height of the mercury column thus obtained at 25° was equal to or higher than that obtained by the already mentioned way. As the result it is considered that the polyethylene sample can be crystallized to the highest degree by this procedure, and all the most highly crystallized specimens of polyethylene used for this investigation were obtained in this way. Volume temperature measurements were repeatedly performed in two temperature ranges, from 40°C to around freezing point of mercury and from 20° to 150°C. For measurements below 40°C a Dewar vessel containing toluene was used as a bath. The bath temperature was lowered about 5°C at a time by throwing pieces of dry-ice into the bath and it was kept at constant temperature for 15 min. by controlling the fluctuation of temperature ± 0.05°C. After that the bath temperature and the height of mercury column which corresponded to the volume change by cooling of the dilatometer contents, polyethylene and mercury, were recorded. It was confirmed that 15 min. was sufficient for polyethylene to attain the equilibrium temperature within the experimental error. Similar operations were taken down to the melting point of mercury. After the measurement at the lowest temperature was finished, the bath temperature was raised by inserting nichrom wire into the bath and measurements were performed in quite the same way up to 40°C. The temperature control of the bath was carried out by letting toluene chilled below the bath temperature run through the cooling pipe immersed in the bath. The current of chilled toluene was regulated so that it might be turned off or on automatically according to the change of the bath temperature.

The measurements from 20° to 150°C were performed in the oil thermostat which was used for thermal treatment of the sample and carried out in the same way as the measurements below 40°C except in the case of the temperature range around melting point of polyethylene. In the vicinity of the melting point of the specimen the height of mercury column abruptly increased owing to the expansion of the sample by premelting or melting, so the bath temperature was raised 1°C at a time and a sufficiently long time was taken until the sample ceased to expand. When the measurement was finished at 150°C, the dilatometer was kept at the temperature for three hours, and then cooled slowly down to 25°C at the rate of 1/5°C per min. to crystallize sufficiently the sample again, and the experiment was repeated. In this case the measurements were carried out around the melting point of the sample at a one degree intervals, in order to know exactly the crystallizing temperature. Experiments of these kinds were repeated two or three times for each sample.

Result and Discussion

The specific volume-temperature curves from around −40° to 150°C for the most highly crystallized polyethylenes are shown in Fig. 3.

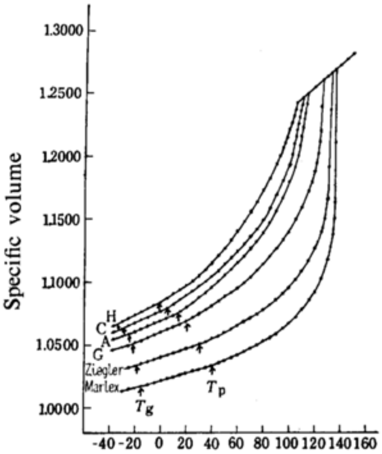

Fig. 3. Specific volume-temperature curves of the most highly crystallized polyethylenes from about −40° to 150°C. Those of samples B, D, E and F are omitted to avoid confusion.

As was mentioned already, the volume-temperature measurements were performed separately, covering two temperature ranges, below 40°C and above 20°C. The two curves obtained in these temperature ranges coincided perfectly between 20° and 40°C.

As is shown in the figure, the sample having the higher degree of short chain branching has the higher specific volume in the temperature range below melting point. Samples A, B and E which are equal in degree of short chain branching have almost equal values of specific volume at each measured temperature. This results shows that the highest degree of crystallinity of polyethylene is dependent upon the degree of short chain branching as was reported already by Richards. By inferring from the fact that when they are annealed, the unbranched linear polymethylene gets a considerably high degree of crystallinity and the more or less branched polyethylene has a lower one, it is considered that most of the amorphous regions of the most highly crytsallized polyethylene arises from the existence of short chain branching and branch point of long chain branching which disturb the regularity of molecules and keep the molecules from being arranged in good order in proportion to their number. Therefore polyethylene containing the larger amount of chain branching is considered to have the poorer degree of crystallinity, even if it has the highest degree of crytallinity.

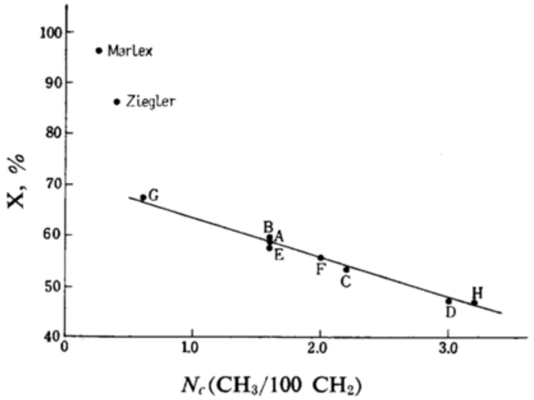

Fig. 4. The relation between degree of short chain branching and degree of crystallinity.

The highest degree of crystallinity of polyethylene samples at 25°C are illustrated in Fig. 4 as a function of short chain branching. They were obtained transforming the following equation, as was done by Kuroda et al.[14],

$$X=\frac{V-V_l}{V_c-V_l} \tag{1}$$

where V was the specific volume of the sample directly obtained from the volume-temperature measurement, V_l the specific volume of purely amorphous region, and V_c that of the entirely crystalline region. According to Gubler and Kovacs, V_l and V_c are expressed as follows;

$$V_l=1.170+9\times10^{-4}(T-25) \tag{2}$$

and

$$V_c=1.0255+3\times10^{-4}(T-25) \tag{3}$$

where T shows temperature in °C. The relation between V and T at any degree of crystallinity is shown by a straight line by putting V_l, V_c above presented and optional value for X into the equation (1). For the values 0.0, 0.1, 0.2, ... 0.9 and 1.0 of X, a series of $V-T$ line was obtained (Fig. 5) and from these straight lines and specific volume-temperature curve of polyethylene the degree of crystallinity was estimated.

A curve similar to that shown by Richards was obtained as a whole between the degree of crystallinity and the degree of short chain branching. According to the equations presented by Sperati et al. which showed the relation

---

[14] T. Kuroda et al., given out in the symposium on polyethylene in Tokyo, November 1959.

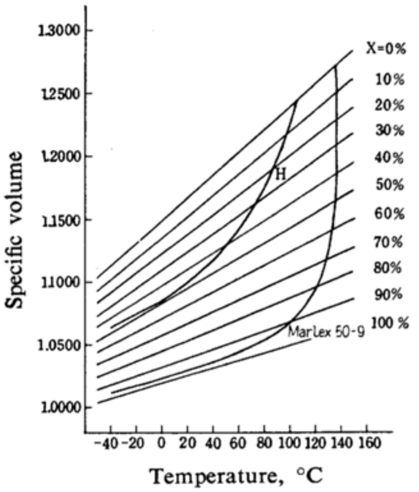

Fig. 5. The relationship between specific volume and temperature in various degree of crystallinity from which the degree of crystallinity of polyethylene was estimated.

between the density and the degree of crystallinity and that between the density and short chain branching, the linear relation is formed between the degree of crystallinity and the degree of short chain branching in the range of $CH_3/100C$ from 0.4 to 5.0 and within the accuracy of ±1.0%. In this experiment the linear relation was also obtained in the range of degree of short chain branching within the same accuracy shown by Sperati et al., though the slope of the straight line differed from that obtained by them. Marlex and Ziegler polyethylenes have a remarkably high degree of crystallinity in comparison with high-pressure polyethylene, which is probably due to the difference in the nature of their short chain branching reported by Willbourn[15]; that is, according to him 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, which are shorter than butyl. Therefore these low-pressure polyethylenes are considered to have a higher degree of crystallinity. As is mentioned already it is expected that the increasing amount of branch point of long chain branching lowers the degree of crystallinity. In this experiment, however, no appreciable result was obtained in this respect. This is probably due to the very small amount of long chain branching.

Above the melting point the values of specific volume of all samples at each temperature were equal within the experimental error. The calculation of specific volume by volume dilatometry is accompanied by a larger error as the difference between bath temperature and room temperature becomes larger. In order to reduce the error, volume-temperature measurements were performed in the temperature range from the melting point to 150°C by using a larger amount of the sample than that previously used. For this experiment the bulb (part C in Fig. 1, a) and the inside diameter of the capillary in part B were made large. As part A, the capillary of the equal diameter as previous was used, so as not to reduce the accuracy of the measurement. The amount of mercury inserted was adjusted so that its top might be at the middle part of part B at room temperature, and measurements were started after the bath temperature was raised and the top of the mercury column reached a height a little above the joint connecting parts A and B at around the melting point of the sample (Fig. 1, b). The total volume up to a height a little above the joint was measured by using mercury in advance and in the case of calculation, corrections were made in quite the same way as previously. Results thus obtained for low-pressure and high-pressure polyethylenes were almost equal and well consistent with the result shown by Gubler and Kovacs in specific volume and the degree of cubic expansion, and also with those by Danusso et al.[16] for a polyethylene and a polypropylene which has methyl branch every second carbon. From these results it was confirmed that the volume-temperature relation above melting point was equal regardless of the kind of polyethylene. These results

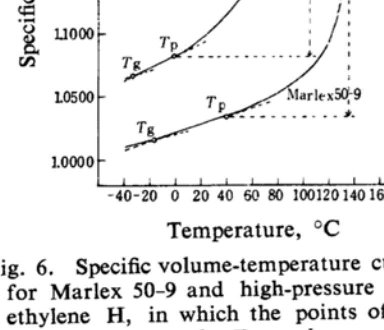

Fig. 6. Specific volume-temperature curves for Marlex 50-9 and high-pressure polyethylene H, in which the points of T_m, T_c, T_p and T_g and ΔT are shown.

---

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

[16] F. Danusso, G. Moraglio and G. Natta, *Ind. Plastiques Mod.* (*Paris*), **10**, 40 (1958).

TABLE II. TEMPERATURES OF VARIOUS TRANSITIONS OF POLYETHYLENES IN °C

Sample	N_c	T_m	T_c	T_p	T_g	ΔT
Marlex 50-9	0.25	135.5	125.0	40.5	−16.0	2.5
Ziegler	0.4	132.1	122.0	30.8	−19.0	6.1
G	0.6	122.8	113.7	21.5	−22.2	11.8
A	1.6	113.2	106.8	13.3	−25.2	19.3
B	1.6	113.5	108.5	10.9	−25.8	21.0
E	1.6	113.5	105.6	11.7	−26.3	19.8
F	2.0	111.6	102.9	4.5	−27.3	22.1
C	2.2	109.8	103.2	5.5	−28.8	22.8
D	3.0	108.1	100.8	−1.8	−32.5	30.7
H	3.2	105.1	94.1	−2.0	−34.0	32.1

led to the following equation by using the method of least square;

$$V_{sp}=9\times10^{-4}T+1.1480$$

As is shown in Fig. 6 for Marlex 50-9 and high-pressure polyethylene H as examples, the specific volume-temperature curve of polyethylene has several transition points peculiar to the kind of polyethylene, that is, a melting point T_m, a crystallizing point T_c, a glass transition temperature T_g, and a premelting point T_p, at which the volume-temperature relation above T_g deviates from the straight line and polyethylene crystals are considered to begin to melt. Their temperatures became higher with the decrease of degree of short chain branching. They are listed in Table II in the order of degree of short chain branching. The curvature of the curve between premelting point and melting point which showed the premelting process grew larger and the curve came to show almost typical first order transition as the amount of short chain branching became smaller. The premelting phenomenon is considered to be due to the variety of the size of crystalline regions in polyethylene which have different melting points according to their size. According to Gubler and Kovacs the crystalline region of low-pressure polyethylene is on the whole considerably larger than that of high-pressure polyethylene. Therefore it is considered that low-pressure polyethylene begins and finishes melting at the higher temperature and sharply at that. In order to show quantitatively the difference of curvature of these curves, ΔT was given in Table II for each sample. Here, ΔT represents the temperature difference beween the melting point and the point at which half of the difference between specific volume at the premelting point and that at the melting point is shown (Fig. 6). The values of ΔT were plotted as a function of short chain branching in Fig. 7. Among high-pressure polyethylenes it seems that these values increase with the increasing amount of short chain branching and between these two quantities the following linear relationship is obtained approximately;

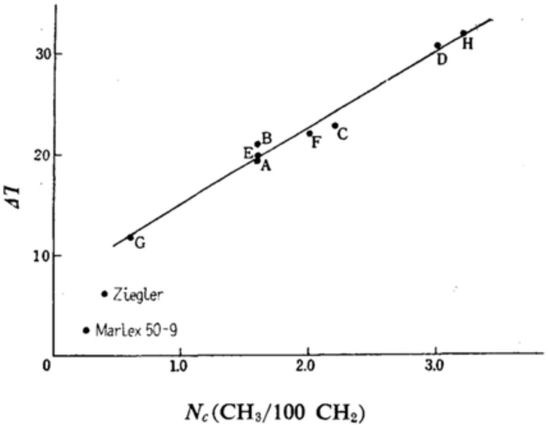

Fig. 7. The relation between short chain branching and the temperature difference between T_m and the point where half of the difference in specific volumes at T_p and T_m are shown.

$$\Delta T=7.7N_c+7.3$$

According to Hunter and Oakes, melting point, crystallizing temperature and premelting phenomenon were dependent upon the molecular weight of the sample. In this experiment the values of T_m, T_c, T_p and T_g apparently rose with the increase of molecular weight on the whole. But sample E showed almost equal values of these temperatures to those of samples A and B, though it had lower molecular weight by about 10,000 than samples A and B, and it was the same with samples C and F, that is, sample F which is almost equal in the amount of short chain branching to sample C and in molecular weight more than double that of sample C, showed almost equal values of these temperatures to those of sample C. Therefore it seems that molecular weight has almost no or a very small effect on these temperatures in comparison with short chain branching.

The glass transition temperature appears at present to be considered $-21°C$ regardless of molecular weight, degree of crystallinity and degree of chain branching from the experimental results by Danusso et al., though there had been presented different values by other researchers previously. The results obtained in this experiment, however, showed that the glass transition temperature of polyethylene was dependent upon the degree of short chain branching. The details about this will be presented later.

As quenched polyethylene has a very low degree of crystallinity and crystalline regions of rather small size are considered to be distributed in it, it is expected that quenched low-branched polyethylene melts in the process similar to that of highly-branched polyethylene. Therefore volume temperature measurements were carried out by using quenched Marlex 50-9. Quenching of the sample was performed by immersing the dilatometer containing the sample and mercury into the toluene-bath cooled at $-40°C$ after it was kept at 150°C for about three hours. The volume-temperature curve for Marlex 50-9 treated in this way is shown in Fig. 8 with the curve for the most highly crystallized Marlex 50-9. This quenched sample had a low degree of crystallinity of 38.6% at 25°C. The result as expected, however, was not obtained, but the curve showing sharp melting phenomenon was obtained, which is probably due to further crystallization which is occurring slowly on raising temperature. Similar measurements were performed by using sample H quenched in the same way. The volume-temperature curve was also illustrated in Fig. 8 with the curve for the most highly crystallized sample H. The degree of crystallinity of this quenched sample was 40.0% at 25°C. The curve for quenched and the most highly crystallized Marlex 50-9 do not overlap with each other up to just below melting point, while the curve for quenched sample H falls on the curve for the most highly crystallized sample at around 50°C. From these results it is considered that further crystallization of the quenched sample occurs at a lower temperature and more easily in highly-branched polyethylene than in low-branched polyethylene. Probably short chain branchings of polyethylene expand the average intermolecular distances in the amorphous regions and weaken the intermolecular interaction, and as a result the molecules can begin to move easily at low temperature.

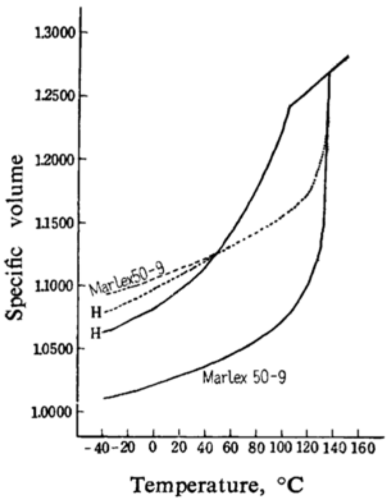

Fig. 8. Volume-temperature curves of Marlex 50-9 and high-pressure polyethylene H obtained for the most highly crystallized and quenched samples.

Summary

The specific volumes of various kinds of polyethylenes with the different degrees of short chain and long chain branchings were measured by volume dilatometry in the temperature range from $-40°$ to 150°C, and volume-temperature curves were determined. Polyethylene having the higher degree of short chain branching had the higher specific volume at any temperature below the melting point. Above the melting point specific volumes of all the polyethylenes were equal at the same temperature. Melting point, crystallizing temperature, premelting point, and glass transition temperature were raised with the decrease of degree of short chain branching. The curvature of the curve showing premelting process grew large as the amount of short chain branching contained in the sample became small, and came to show the typical first order transition phenomenon.

The author is indebted to Professor Masatami Takeda for his helpful suggestions and discussion. He also thanks Dr. C. F. Hammer of E. I. du Pont de Nemours and Company for providing the samples of polyethylene. It is also a pleasure to aknowledge the assistance in experimental work given by Miss Masako Yoshida.

Department of Chemistry
Faculty of Science
Tokyo College of Science
Kagurazaka, Shinjuku-ku
Tokyo