SHORT COMMUNICATIONS

The Glass Transition Temperatures of Various Kinds of Polyethylenes

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It is well known that various physical properties of polyethylene are considerably affected by the chain branching. According to C. A. Sperati et al.[1], for instance, short chain branching controls crystallinity, and long chain branching the viscoelastic properties of the molten polymer and the ultimate strength of the solid.

The author performed an experiment in order to know whether chain branching affects the glass transition temperature or not.

Samples used in this investigation are Marlex 50, Ziegler type polyethylene, and eight kinds of high-pressure polyethylene which are different in their molecular weights, melt index and numbers of short and long chain branchings. These high-pressure samples were provided by courtesy of E. I. du Pont de Nemours and Company. Marlex 50 and Ziegler were commercial polymers. In Table I are shown molecular parameters for these high-pressure polyethylenes. For Marlex 50 and Ziegler these data were not available hitherto, but since the number of short chain branchings was found for

1) C. A. Sperati, W. A. Franta and H. W. Starkweather, Jr., *J. Am. Chem. Soc.*, 75, 6127 (1953).

the two materials in the paper by R. C. Rempel et al.[2], those were adopted for reference. These are 0.15 and 0.25 for Marlex 50 and Ziegler, respectively. Prior to a series of measurements these ten samples were sufficiently crystallized by thermal treatment.

TABLE I. MOLECULAR PARAMETERS[a] FOR HIGH-PRESSURE POLYETHYLENES

Sample	Melt index	$Mn\times10^{-3}$	Nc[b]	Nw[c]
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	1.6	12	3.2	29

a) These data were determined at E. I. du Pont de Nemours and Company according to the method 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[3].

Measurements were carried out by volume dilatometry[4]. As confining liquid mercury and absolute alcohol were used for the run above −40°C and for that from −70°C to room temperature, respectively. A Dewar vessel containing toluene was used as a bath. Cooling and heating of the bath were conducted at the rate of 0.3°C per min. by throwing dry ice and inserting nichrom wire into the bath.

Glass transition temperature, T_g, was determined from intersection of two straight lines on the volume-temperature curve and from discontinuity of the curve obtained by plotting the volume-temperature derivatives as a function of temperature.

Glass transition temperatures obtained from this experiment were plotted as a function of the short chain branching index (Fig. 1). From the figure it seems that the glass transition temperature of these samples lowers proportionally with the increase of the short chain branchings, though Marlex and Ziegler appear to deviate somewhat from this tendency. Then the relation between the glass

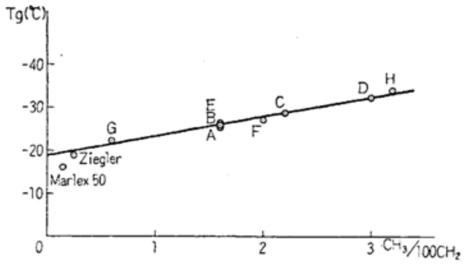

Fig. 1. Glass transition temperatures of various polyethylene samples different in their short chain branching index.

transition temperature and the short chain branching index of these high-pressure polyethylenes was led to the following equation:

$$T_g = -4.6\ \mathrm{Nc} - 18.7$$

On the other hand, long chain branching does not appear to affect the glass transition temperature so much as short chain branching does.

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2) R. C. Rempel, H. E. Weaver, R. H. Sands and R. L. Miller, *J. Appl. Phys.*, 28, 1082 (1957).

3) B. H. Zimm and W. H. Stockmayer, *J. Chem. Phys.*, **17**, 1301 (1949).

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