Macromolecules 1980, *13*, 445–446

Notes

The Glass Transition Temperature of Polyethylene

UMESH GAUR and BERNHARD WUNDERLICH*

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181. *Received September 10, 1979*

Much has been written about the glass transition temperature of polyethylene. Recently, this topic has been brought to renewed timeliness through the review of Beatty and Karasz,[1] who strongly favor a glass transition temperature of 145 K. Their argument for such a low glass transition temperature in the vicinity of the dynamic mechanical γ region is mainly based on a qualitative interpretation of high precision heat capacity measurements on ultra high molecular weight polyethylene of low crystallinity. Earlier suggestions of such low glass transition temperatures by Stehling and Mandelkern[2] (based on qualitative heat capacity measurements, linear expansion coefficient measurements, and dynamic mechanical measurements) and Fischer and Kloos[3] (based on low-angle X-ray intensity) were refuted in detail by Illers[4] and Boyer[5] and will not be addressed here. A histogram showing the distribution of the glass transition temperatures of 50 reports on polyethylene with references is shown by Davis and Eby.[6] This histogram has clear maxima between 140 and 160, 185 and 200, and 230 and 260 K.

In this note we would like to reaffirm our earlier[7] interpretation of the glass transition interval which was based on quantitative discussion of the difference in heat capacity between a completely crystalline and an amorphous polyethylene. At that time the discussion was based on the extrapolation of literature data of seven semicrystalline samples[8] to 0 and 100% crystallinity. The heat capacity of the amorphous polyethylene showed a clear step at 237 K. The difference in heat capacity between the two limiting states was of the proper order of magnitude for a glass transition.[9] In addition, it was found that only the large scale motion signified by the hole equilibrium[10] stops at 237 K. The trans-gauche equilibrium was found to freeze slowly over the temperature range 220–120 K.[7]

In the meantime, we have established a data bank of heat capacities of linear macromolecules.[11] For polyethylene, data on more than 100 samples have presently been collected.[12] In addition, there are quantitative data on amorphous copolymers of ethylene and propylene.[13]

In this note we would like to update our earlier conclusions of the glass transition making use of information of the data bank[12] and other supporting information.[6,14] This will be followed by a discussion of the argument of Beatty and Karasz.[1] Last, new experiments by Hendra et al.[15] and Breedon Jones et al.[16] on completely amorphous polyethylene, which crystallizes between 145 and 170 K, will be shown to yield more insight into the motion in polyethylene.

In the temperature range of interest (100 to 300 K), 21 measurements on well-characterized polyethylene of crystallinity between 25 and 97% are available.[12] Except for samples on ultra high molecular weight polyethylenes (four samples) all heat capacities of branched and linear polyethylenes were linearly dependent on crystallinity. The root mean square deviations from linear functions between 25 and 250 K are 2% or less at any one temperature. Table I contains the "best data" of amorphous and crystalline polyethylene (C_{p_a} and C_{p_c}). The temperature of half-freezing is still about 237 K, as before.[8] The difference between the heat capacity of crystalline polyethylene and the extrapolated heat capacity of the melt is 10.48 J K^{-1} mol^{-1} at 237 K. This ΔC_p agrees well with the average of 11.3 ± 2.1 J K^{-1} mol^{-1} of 40 linear macromolecules calculated per single small, rigid molecular backbone subunit (bead). The trans-gauche contribution to the heat capacity of linear polyethylene can be estimated as before, using a three-rotational isomer model.[7,17] The results for the frequently chosen energy values of 3.0 and 2.0 kJ mol^{-1} for the energy difference[18] are given in Table II. Indeed, a reasonable fit can be achieved. The percentage columns are an indication of the slow freezing of the trans-gauche equilibrium. The remaining hole contribution can be represented with a molar hole energy of 3.23 kJ and a molar hole volume of 10.95 cm^3 (which gives a ΔC_p at 237 K of 6.16 JK^{-1} mol^{-1}).

Table I
Best Extrapolated Data of Amorphous and Crystalline Polyethylene[a]

T, K	C_{p_a}, J K^{-1} mol^{-1}	C_{p_c}, J K^{-1} mol^{-1}	ΔC_p
100	9.75	9.45	0.30
120	11.39	10.92	0.47
140	13.16	12.25	0.91
160	14.98	13.45	1.53
180	16.83	14.53	2.30
200	18.92	15.57	3.35
220	21.71	16.66	5.05
240	25.74	17.88	7.86
260	29.16	19.23	9.93
280	30.03	20.58	9.45
300	30.89	21.81	9.08

[a] Excerpt from Tables 9 and 10 of ref 12.

These values are in good accord with the discussion of the glass transition region of Illers,[4] the two-glass transition concept of Boyer,[5] and the interpretation of β and γ processes measured by dynamic mechanical measurements by Matsuoka.[19] Also, the observations of volume relaxation on quick cooling into the 240 K region observed by Davis and Eby[6] and the similar enthalpy relaxation observed by Chang[20] are easily explained as being caused by the major "hole relaxation".

A long-standing qualitative argument that in the here presented extrapolation of the heat capacities samples with higher amorphous content have increasingly higher branch content and thus lead to the heat capacity of amorphous, highly branched polyethylene can now be discussed more quantitatively. Figure 1 illustrates the increase in heat capacity at the glass transition temperature for amorphous poly(ethylene-*co*-propylene)s. A continuous decrease in ΔC_p is observed in going from atactic polypropylene to higher ethylene contents, finally reaching values close to the here estimated heat capacity increase due to intermolecular long-range motion only (12.32 J K^{-1} mol^{-1}). We interpret this as an increasing separation of the freezing of the trans-gauche equilibrium from the hole equilibrium.

0024-9297/80/2213-0445$01.00/0

Table II
Heat Capacity Difference between Amorphous and Crystalline Polyethylene below the Main Glass Transition Temperature and the Calculated Trans-Gauche Contribution Assuming a 2.0 and 3.0 kJ mol^{-1} Energy Difference between the Rotational Isomers

		calcd (2.0 kJ mol^{-1})		calcd (3.0 kJ mol^{-1})	
T, K	ΔC_p, J K^{-1} mol^{-1}	ΔC_p	%	ΔC_p	%
120	0.47	5.59	8	6.16	8
140	0.91	4.77	19	6.32	14
160	1.53	4.00	38	6.06	25
180	2.30	3.35	69	5.59	41
200	3.08^a	2.82	100	5.04	61
220	3.81^a	2.39		4.50	85
230	4.13^a	2.20		4.25	97
237	4.33^a	2.09		4.08	

[a] Values diminished by the hole contribution of the glass transition through linear extrapolation of the amorphous heat capacity from 110-190 K to higher temperatures. For full values, see Table I.

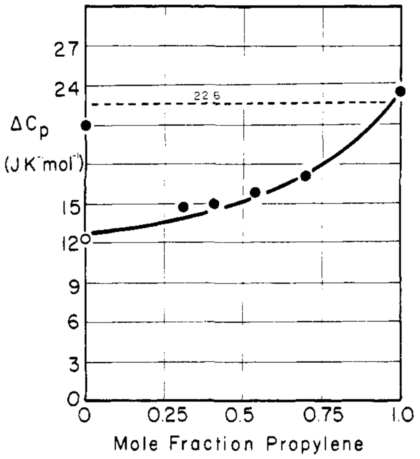

Figure 1. Heat capacity increase at the glass transition temperature for amorphous poly(ethylene-co-proylene)s. The dashed line corresponds to the expected ΔC_p of 22.6 J K^{-1} mol^{-1} for a two-bead repeating unit. The open circle for polyethylene corresponds to the estimated heat capacity increase due to intermolecular long-range motion only. Heat capacities calculated per two-atom repeat unit. Polyethylene and atactic polypropylene data are from ref 12, and amorphous copolymer data are from ref 13.

For atactic polypropylene (and most other linear macromolecules), the hole equilibrium which governs the long-range intermolecular motion and the trans-gauche equilibrium which governs the short-range intermolecular motion freeze practically simultaneously at the glass transition temperature. For polyethylene, a large separation of the two processes exists. Once observed, we find that such separation of processes at the glass transition seems to occur, although to a much smaller degree, in other linear macromolecules as, for example, in selenium, poly(oxytrimethylene), and even polypropylene. This topic will be discussed in more detail at a later date. The initial drop in ΔC_p in Figure 1 with ethylene concentration, and thus the separation of the two processes, is large enough so that the minor amount of branching which is needed to reduce the crystallinity is not expected to affect the heat capacities. Indeed, no systematic deviations of the heat capacities of branched and linear polyethylene can be observed in the crystallinity region of overlap in crystallinity vs. heat capacity plots.[12]

The glass transition argument for 145 K of Beatty and Karasz[1] rests largely with an observed sigmoidal increase in heat capacity between 130 and 190 K of about 1.5 J K^{-1} mol^{-1} for an ultra high molecular weight sample of polyethylene of 35% crystallinity. Correcting this ΔC_p to completely amorphous polymer leads to no more than 2.3 J K^{-1} mol^{-1}. This can under no circumstances be a full glass transition. In fact, it is of the order of magnitude expected for the freezing of the residual trans-gauche equilibrium (see column 2 of Table II). Other data on the ultra high molecular weight of polyethylene[20] were found to also have nonsystematic deviations in their heat capacities of similar magnitude, which are not related to a simple one-parameter crystallinity description. We concluded thus that for ultra high molecular weight polyethylene a more detailed structure determination is needed.[12] Perhaps it will be possible in the future to combine the present arguments with a study of the crystalline and amorphous structure for a full description, using more than a single parameter.

By using drastic quenching techniques, Hendra et al.[15] and Breedon Jones et al.[16] were able to produce small amounts of thin films of amorphous polyethylene. Infrared and Raman spectra indicated crystallization on warming below 190 K.[15] Scanning calorimetry revealed on heating a crystallization exotherm between 145 and 170 K with a broad maximum at about 160 K.[16] These direct experiments on amorphous polyethylene indicate that in the case of a separation of large scale intermolecular motion and remaining intramolecular motion, the latter can support crystallization of linear macromolecules. This type of crystallization and the resulting crystal morphology should be able to shed new light on the details of molecular motion in polyethylene.

Acknowledgment. This work was supported by the Polymers Program of the National Science Foundation, Grant No. DMR-7815297 (Polymers Program).

References and Notes

(1) C. L. Beatty and F. E. Karasz, *J. Macromol. Sci., Rev. Macromol. Chem.*, **17**, 37 (1979).
(2) F. C. Stehling and L. Mandelkern, *Macromolecules*, **3**, 242 (1970).
(3) E. W. Fischer and F. Kloos, *J. Polym. Sci., Polym. Lett. Ed.*, **8**, 685 (1970).
(4) K. H. Illers, *Kolloid Z. Z. Polym.*, **250**, 426 (1972).
(5) R. F. Boyer, *Macromolecules*, **6**, 288 (1973).
(6) G. T. Davis and R. K. Eby, *J. Appl. Phys.*, **44**, 4274 (1973).
(7) B. Wunderlich, *J. Chem. Phys.*, **37**, 2429 (1962); see also *J. Polym. Sci., Part C*, **1**, 41 (1963).
(8) B. Wunderlich, *J. Chem. Phys.*, **37**, 1203 (1962).
(9) B. Wunderlich, *J. Phys. Chem.*, **64**, 1052 (1960).
(10) N. Hirai and H. Eyring, *J. Appl. Phys.*, **29**, 810 (1958); *J. Polym. Sci.*, **37**, 51 (1959).
(11) U. Gaur and B. Wunderlich, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **20**, 429 (1979).
(12) U. Gaur and B. Wunderlich, *J. Phys. Chem. Ref. Data*, submitted for publication.
(13) C. A. Clegg, D. R. Gee, and T. P. Melia, *Makromol. Chem.*, **116**, 130 (1968).
(14) S. S. Chang, *J. Res. Natl. Bur. Stand., Sect. A*, **78**, 387 (1974).
(15) P. J. Hendra, H. P. Jobic, and K. Holland-Moritz, *J. Polym. Sci., Polym. Lett. Ed.*, **13**, 365 (1975).
(16) J. Breedon Jones, S. Barenberg, and P. H. Geil, *J. Macromol. Sci., Phys.*, **15**, 329 (1978).
(17) B. Wunderlich and H. Baur, *Adv. Polym. Sci.*, **7**, 151 (1970).
(18) See, for example: P. J. Flory, "Statistical Mechanics of Chain Molecules", Interscience, New York, 1969; R. P. Smith, *J. Polym. Sci., Part A-2*, **4**, 869 (1966); A. E. Tonelli, *J. Chem. Phys.*, **52**, 4749 (1970).
(19) S. Matsuoka, *Polym. Eng. Sci.*, **5**, 142 (1965).
(20) S. S. Chang, *J. Res. Natl. Bur. Stand., Sect. A*, **80**, 51 (1976).