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THE GLASS TRANSITION TEMPERATURE OF POLYTETRAFLUOROETHYLENE

The glass transition temperature, T_g, of polytetrafluoroethylene, hereafter referred to as PTFE, has long been a subject of controversy. A value of somewhere above 110°C. (1) was selected by Tobolsky from among several experimentally reported values (2–6) which varied from −112 to 130°. If this value were correct then it would not be expected that elastomers could result from compositions containing large proportions of tetrafluoroethylene, as for example in a copolymer. This is a consequence of the relationship, which Wood (7) demonstrated to be of general applicability in vinyl copolymer systems, between T_g and copolymer composition. This relationship can often be simplified to the form given by Fox (8) as follows:

$$1/T_{g1,2} = w_1/T_{g1} + w_2/T_{g2}$$

where $T_{g1,2}$ refers to the copolymer T_{g1} and T_{g2} refer to the homopolymers, and w_1 and w_2 are the weight fractions of the monomers incorporated into the copolymer. Therefore, a copolymer of tetrafluoroethylene with a monomer, the homopolymer of which has a T_g above room temperature, would not be expected to be normally elastomeric. However as will be shown subsequently, this was actually observed in the course of our work. This observation, and other data gathered, show that the T_g of PTFE is in reality in the vicinity of −50°C. rather than −110 or +130°C.

The comprehensive survey by Boyer (9) of transition temperatures has subsequently provided other arguments for the placement of T_g of PTFE at about this temperature. While a full discussion is beyond the scope of this communication, these same arguments seem to apply equally well to the earlier work cited by Boyer as well as to more recent results with contrary conclusions (10). Reports other than those used by Boyer are available which bolster our viewpoint. For example the solid state irradiation of tetrafluoroethylene, the formation of free radicals therein, and their subsequent destruction upon warming was followed by ESR (11). The signal attributed to radical sites on the polymer chain disappeared as the temperature was raised from −80 to −50°C. This corresponded well to the temperature noted for the relaxation of hindrance to rotation by NMR studies, −65 to −45°C. (12,13).

The lack of agreement in the various data is a consequence of the high level of crystallinity of PTFE which renders the direct methods of measurement of T_g largely useless, because of the masking and/or repression of transitions in the amorphous phase. Because of the lack of success in deducing T_g using partially crystalline polymers, we obtained values of T_g for copolymers of TFE which were completely noncrystalline, at least in the relaxed, unstretched state.

The polymers used in this work are described in Table I.

TABLE I

Copolymers of Tetrafluoroethylene

Comonomer	Wt.-% CF_2CF_2 incorporated	Physical appearance	[η] inh	T_g[a], °C.
Trifluorovinyl Trifluoroethyl ether	36	Tough elastomer	–	– 1
n-Butyl vinyl ether	65	Soft gum	0.15	–45
n-Butyl acrylate	50	Soft gum	0.25	–60

[a] Determined on a Du Pont Model 900 differential thermal analyzer.

Values of T_g for PTFE homopolymer were calculated from the Fox equation and data on the copolymers with trifluorovinyl trifluoroethyl ether, n-butyl vinyl ether, and n-butyl acrylate. Values of –48, –38, and –65°C. were obtained respectively. The average of these values, probably somewhat fortuitously, is –50°, the value selected by Boyer. The T_g of poly(trifluorovinyl trifluoroethyl ether), 35°C., was determined in the course of this work and values of –56°C. (14) for poly(n-butyl acrylate) and –55°C. (15) for poly(n-butyl vinyl ether) were used.

Thus evidence is presented to show that the T_g of PTFE is well below room temperature, rather than above, and tetrafluoroethylene can be a useful building block for specialty elastomers, providing means can be found to suitably reduce the high inherent crystallinity of these systems. At the present time our work is continuing towards these goals.

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References

(1) Tobolsky, A. V., J. Polymer Sci., 35, 555 (1959).

(2) Baccareda, M., and E. Butta, J. Polymer Sci., 31, 189 (1958).

(3) Ohzawa, Y., and Y. Wada, Rept. Prog. Polymer Phys. Japan, 6, 147 (1963).

(4) Kuroda, T., Nagoya Kogyo Gijutso Shikensho Hokoku, 5, 257 (1956); CA, 54, 19016c.

(5) Tobolsky, A. V., J. Polymer Sci., A1, 483 (1963).

(6) Satokawa, T., and S. Koisumi, Kogyo Kagaku Zasshi, 65, 1211 (1962); CA, 58, 1544h.

(7) Wood, L. A., J. Polymer Sci., 28, 319 (1958).

(8) Fox, T. G., Bull. Am. Phys. Soc., 1, 123 (1956).

(9) Boyer, R. F., Rubber Chem. Tech., 36, 1303 (1963).

(10) Araki, Y., J. Appl. Polymer Sci., 9, 421 (1965).

(11) Bruk, M. A., A. D. Abkin, and P. M. Khomikouski, Doklady Akad. Nauk SSSR, 149, 1322 (1963); Translated in Doklady (Chemistry), 149, 346 (1963).

(12) Smith, J. A. S., Discussions Faraday Soc., 19, 207 (1955).

(13) Powles, J. G., and J. A. E. Kail, J. Polymer Sci., 31, 183 (1958).

(14) Unpublished results of S. Loshaek, quoted in reference 7.

(15) Lal, L., and G. S. Trick, J. Polymer Sci., A2, 4559 (1964).

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