

# Glass Transitions of Organic Compounds. III. Cellulose Substrate Technique and Aliphatic Alcohols

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The cellulose blotter/torsion pendulum technique used for the determination of relaxations that occur in low molecular weight compounds, oligomeric materials, and amorphous polymers is discussed. The glass transition temperature of a number of aliphatic alcohols and hydrocarbons have been determined and correlated with a method proposed by Gorskii in 1934. The glass transition temperature and molecular weight of these compounds follow the relationship  $T_g = BM^a$  rather than  $T_g = T_g(\infty) - K/M$ . Although differences exist between the primary, secondary, and tertiary alcohols, they appear to follow a similar general pattern. In contrast, the hydrocarbons investigated have markedly different behavior.

## INTRODUCTION

The importance of the glass transition and other relaxation phenomena is well known to polymer chemists. In the temperature range where the glass transition occurs, a hard and usually brittle material is transformed into a material that exhibits rubber-like characteristics. Thus, the modulus of a material decreases by orders of magnitude; and its ability to absorb energy is markedly altered in this temperature range. Of course, above the glass transition temperature and in the rubbery and flow regions, the characteristics of a material under investigation depend on such factors as molecular weight, thermoplasticity, degree of crosslinking, etc.

The characteristic changes that occur in the glass-to-rubber transition range are pronounced in nature and can be measured by a variety of techniques. When mechanical techniques are employed to measure the changes, it is difficult to obtain complete information through this temperature range if low molecular weight compounds, oligomeric materials, and thermoplastic, amorphous polymers are investigated. The main difficulty in obtaining information is concerned with flow and high energy dissipation coupled with low energy storage. For example, it is a simple matter to vitrify toluene. Yet, if modulus measurements were to be made with this material in an Instron tester by measuring stiffness-temperature characteristics, flow would occur as the glass transition temperature was approached and data could not be obtained. Similar difficulties exist when a torsion pendulum is used for the study. Thus, a way to support a liquid material and to obtain meaningful data is required.

Various techniques for the torsion pendulum which involve a substrate have been devised for circumventing this difficulty. The most widely known technique is the torsion braid analysis which was devised by Gillham and Lewis (1,2). Illers (3) and others (4) have used a crosslinked, extracted polystyrene as a support substrate for low molecular weight compounds. Fava and Chaney (5) have encapsulated polymers in a rigid matrix of cured phenolic resin. Other examples of substrates include coated aluminum foil sandwiches, cellulose, glass cloth, polypropylene felt, and asbestos paper (6,7). Although various substrates can be used if their nature is understood, the inherent stiffness of the substrate is important to obtaining proper response. If the substrate is too flimsy in nature, the characteristics of most instruments is such that meaningful results will not be obtained.

## EXPERIMENTAL

To solve the problem of supporting liquids (low molecular weight, oligomeric or polymeric), a cellulose substrate technique for use in conjunction with a freely oscillating, recording torsion pendulum was devised in our laboratories in the early 1960's. The torsion pendulum used is similar in design to that described by Nielsen (8). The substrate or support was a bleached cellulose paper which was first described in 1964 (6) for the study of oligomeric oxetanes.

With this technique, small strips of the bleached cellulose with a thickness of 0.8 mm are cut to about 30 mm in length and 6.5 mm in width. These are then dried for several hours in an oven at 105°C and stored in a desiccator until needed. In the case of low molecular weight liquids, such as the alcohols, the experiments are begun by dipping a cellulose strip into the liquid alcohol. Then

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the impregnated strip is immersed into liquid nitrogen. This rapid cooling technique usually results in vitrified samples which are clear and glassy. The cellulose-supported, glassy sample is then mounted in the jaws of the torsion pendulum which are enclosed in an insulated chamber that has been precooled to  $-195^{\circ}\text{C}$ —i.e., essentially the temperature of liquid nitrogen. The mounting operation is done quickly and carefully to ensure minimal warming which could result in devitrification and crystallization in many materials. Temperature control was accomplished with a mixture of warm and cold, dry nitrogen that was in turbulent flow in the sample chamber.

Experiments are begun at the lowest temperature,  $-195^{\circ}\text{C}$ , and damping measurements are made at regular temperature intervals. The intervals varied from 2 to  $10^{\circ}\text{C}$ , and the temperature range and interval depends on the character of the sample. To ensure thermal equilibrium, the sample is maintained at any given temperature for about 10 min, since experimental evidence indicates that such a time interval was needed to ensure thermal equilibrium and reproducible results. Measurements were made until a temperature above the glass transition temperature ( $T_g$ ) was reached. In the case of crystalline compounds or compounds that crystallized above the  $T_g$ , measurements were continued until a temperature greater than the melting point was reached.

Typical mechanical loss data obtained in this manner are shown in Fig. 1 using 2,3, 4-trimethylpentane as a model compound. The  $T_g$  for this compound is  $-162^{\circ}\text{C}$  and a small secondary relaxation is apparent at  $-180^{\circ}\text{C}$ . Values for these relaxations from  $G''$  were 1 or 2 degrees lower than the mechanical loss results. Although little work was done at temperatures above  $T_g$  with amorphous materials, other investigators have found relaxations above  $T_g$ . Recently, Nielsen (9) has indicated that

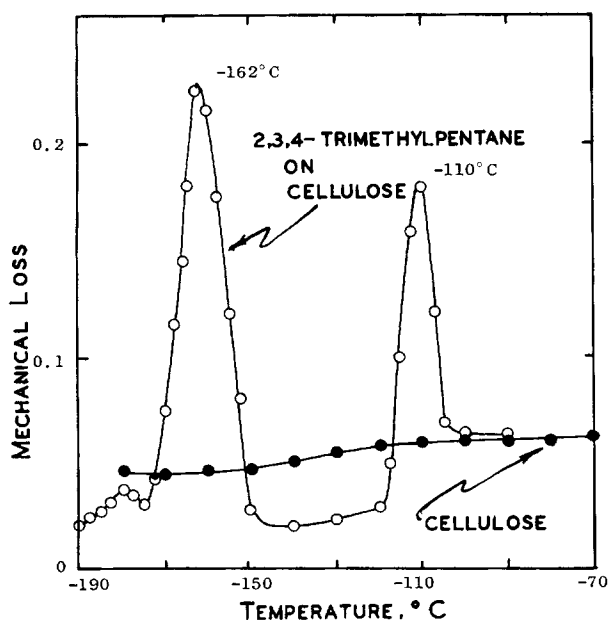


Fig. 1. Mechanical loss as a function of temperature for cellulose substrate and this substrate impregnated with 2,3,4-trimethylpentane.

relaxations above  $T_g$  may be an artifact of the technique when a substrate is employed.

In this substrate technique, the saturated blotter is a two-phase system. Below the glass transition region, the system is very rigid and characteristic of the impregnating compound. Above the glass transition, a low molecular weight compound will become liquid and flow off the blotter. The response will become typical of the blotter itself. In the particular case described in Fig. 1, the compound crystallized at a temperature somewhat above  $T_g$  and in the vicinity of  $-150$  to  $-140^{\circ}\text{C}$ . Thus, the typical blotter response was not obtained until the compound melted. The peak at  $-110^{\circ}\text{C}$  is related to the melting point. This same technique has been shown to be useful for measuring rotational or crystal-crystal transitions in neopentyl alcohol and neopentyl glycol (10). In this case, the information was found to be in agreement with wide-line nuclear magnetic resonance, dilatometric, and X-ray diffraction data.

In certain cases, low molecular weight organic compounds fail to vitrify regardless of the quenching method used and thus can only be obtained in a crystalline form. When a material fails to vitrify, it has been found that  $T_g$  of the compound can be determined with good accuracy by measuring the  $T_g$  of mixtures of the compound and a compatible second component of known  $T_g$ . The mixture data is then extrapolated to that of the pure unknown by the linear form (11) of the Gordon-Taylor (12) expression,

$$T_{g1,2} = T_{g1} + k [w_2(T_{g2} - T_{g1,2})/w_1] \quad (1)$$

In this expression,  $k$  is a constant,  $T_{g1,2}$  is the glass transition temperature of the mixture containing weight fractions  $w_1$  and  $w_2$  of the unknown (subscript 1) and the known (subscript 2) which have glass transitions  $T_{g1}$  and  $T_{g2}$ , respectively. In certain instances, it has been found that  $T_g$  is a linear function of weight fraction (7, 13); and the extrapolation can be made without resorting to Eq 1. Of course, in such instances, the Gordon-Taylor expressions can be used if desired. Since *n*-nonanol was a compound that could not be vitrified by the technique described above, the glass transition temperature of mixtures of it and *n*-pentanol were studied. The results are described in Fig. 2, and the intercept (Eq 1) indicates that the  $T_g$  of *n*-nonanol is  $153^{\circ}\text{K}$ .

In the case of oligomers or amorphous polymers, the cellulose substrate is saturated to form the two-phase system by immersion or by a molding technique. After the composite has been formed, it usually can be slow cooled or quenched from a melt state. The rate of cooling required depends on the propensity of the material to crystallize. Figure 3 is data obtained for molded, amorphous polystyrene alone and molded onto a cellulose substrate. When polystyrene alone was investigated,  $T_g$  could only be approached because at temperatures above  $90^{\circ}\text{C}$  the sample exhibited marked deformation and a meaningful response could not be obtained. In contrast, the molded cellulose/polystyrene composite could be investigated through the transition region, and the customary 1 Hz value of  $100^{\circ}\text{C}$  was obtained for the  $T_g$  of polystyrene.

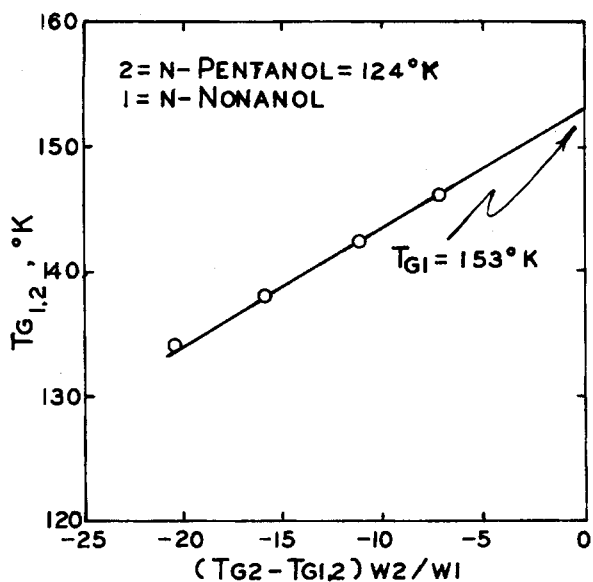


Fig. 2. Gordon-Taylor plot (Eq 1) for mixtures of *n*-pentanol and *n*-nonanol to obtain  $T_g$  of *n*-nonanol.

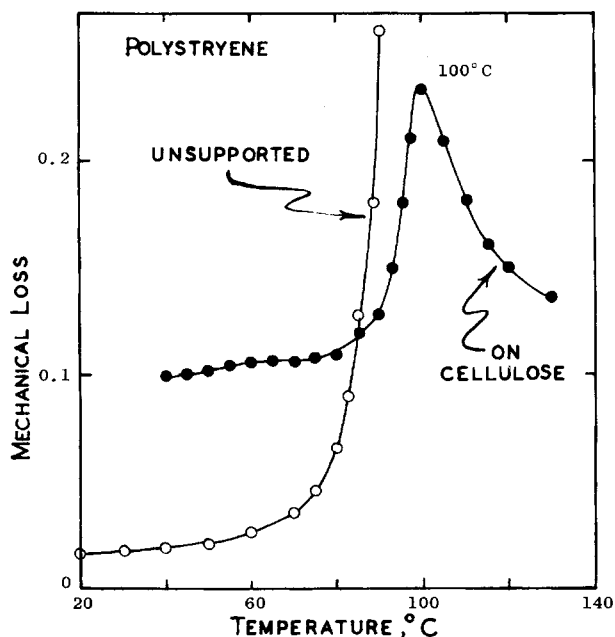


Fig. 3. Mechanical loss as a function of temperature for polystyrene. Data for polystyrene-cellulose composite has been shifted for clarity.

### DISCUSSION—ALCOHOLS AND HYDROCARBONS

The first systematic study of low molecular weight compounds carried out in our laboratories involved the glass transition temperature-molecular weight behavior of a series of polyhydroxyl compounds with the structure  $H-(CHOH)_x-H$  with  $x$  having a value of one to six (14). It is well known that the  $T_g$  increases with increasing molecular weight; and, for a given series, the  $T_g$  approaches a limiting value at infinite molecular weight (15). This behavior is customarily described by

$$T_g(M) = T_g(\infty) - K/M \quad (2)$$

However, for this series of low molecular weight com-

pounds, a curvilinear relationship resulted when the data was plotted in accord with Eq 2. It was found that the data were very closely fitted by the relationship

$$T_g = BM^n \quad (3)$$

that had been proposed by Gorskii (16) for correlation of glass temperature with molecular weight. For the series of polyhydroxy compounds (14) mentioned above, a value of  $B = 25.9$  and  $n = 0.47$  was determined.

When published data (7, 13) for the  $C_1$  and  $C_8$  normal alcohols along with the value of  $153^\circ K$  for *n*-nonanol obtained above are plotted in accord with the Gorskii expression, Fig. 4 is obtained. Only the data point for methanol is markedly different from the other members of the series, and it was disregarded when the best fit statistical line was calculated. For this family of compounds, which may be represented as  $CH_3-(CH_2)_x-OH$  with  $x$  ranging from one to eight,  $B = 22.21$  and  $n = 0.390$  with a correlation coefficient of 0.995. It should be pointed out that all  $T_g$  values used in this paper were obtained at essentially 1 Hz and were taken as the maximum in the loss component  $G''$  of the complex shear modulus unless differently indicated.

Since methanol is known to be strongly hydrogen bonded, its marked deviation from the other members in this series was somewhat expected. If the question as to what molecular weight linear alcohol methanol's  $T_g$  ( $110^\circ K$ ) corresponds, calculation indicates this molecular weight to be 60.5 or essentially twice that of methanol. This suggests that methanol may exist as a dimer in the glassy state.

In a sense, water might be considered to be the lowest molecular weight member of the series  $CH_3-(CH_2)_x-OH$  (i.e., let  $x = 0$  and remove a methylene group from the methyl group). An attempt to calculate the  $T_g$  of water was made by extrapolating the data for ethanol and methanol (dashed line in Fig. 4) to a

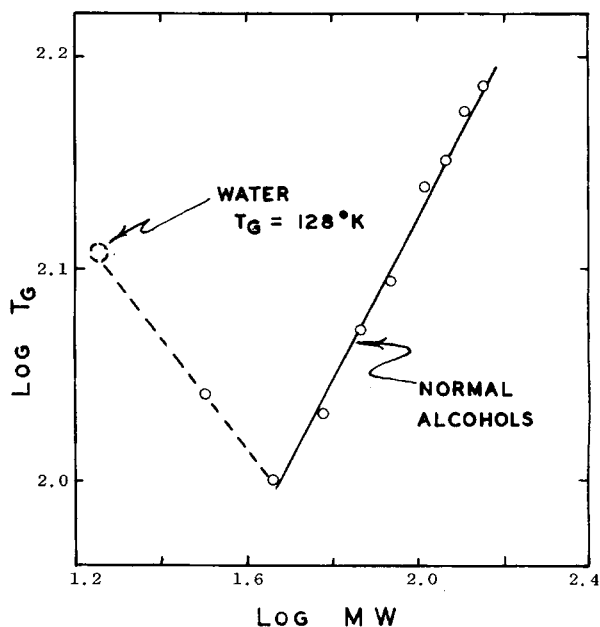


Fig. 4. Gorskii plot (Eq 3) for normal alcohols. Extrapolation to the  $T_g$  of water is shown.

molecular weight of 18. The Eq 2 constants for this line are  $B = 273.3$  and  $n = -0.26$  and the calculated  $T_g$  of water is  $128^\circ\text{K}$  which is in good agreement with the values obtained by Yannas (17) and Pryde and Jones (18). Of course, other values have been obtained for the  $T_g$  of water (19,20). If the question about the molecular weight of the glassy water is posed, assuming it is behaving as a linear alcohol, calculation indicates the molecular weight to be 89.2. This suggests that five molecules of water exist in a cluster at  $T_g$ .

In our studies of low molecular weight compounds, a large number of alcohols have been investigated. The glass transition temperature of selected alcohols has been correlated with molecular weight by means of the Gorskii expression. Primary, secondary, and tertiary alcohols and hydrocarbons will be described. Although the various ramifications of these data have not been fully considered, the data fit general patterns and it appears that other factors such as polarity, molar volume, etc., are needed to more fully elucidate the behavior. Table 1 contains a listing of composition and glass transition temperature for the compounds investigated.

Figure 5 contains correlations of the data obtained for the primary alcohols, and the normal alcohols are compared with the 2-methyl alcohols and 2,2-dimethyl alcohols. In each case, addition of a methyl group increases  $T_g$  from that of the nonbranched molecule. Geminal dimethyl substitution causes a further increase. Note that the first member of the series of 2,2-dimethyl alcohols, neopentyl alcohol or 2,2-dimethyl-1-propanol does not fit the relationship established for the other members. Thus, similar to the case of methanol, the first member shows abnormal behavior and has a higher  $T_g$  than is expected. Although it is not shown in Fig. 5 or Table 1, the first member of the 2-methyl alcohols might be considered to be 2-methyl-1-ethanol or normal propanol. However, it would not be expected to fit the relation, since it is a primary alcohol and belongs to a

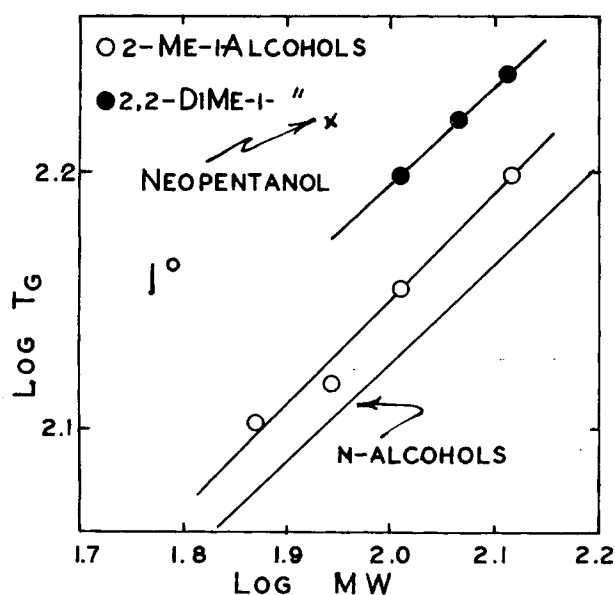


Fig. 5. Gorskii plot (Eq 3) for series of primary alcohols. Note deviation of neopentanol from other members of the dimethyl substituted series.

different series. As previously published (7), the  $T_g$  of n-propanol is  $-164^\circ\text{C}$ .

Figure 6 contains a comparison of the behavior of three series of secondary alcohols. Marked differences are readily apparent. The 4-alcohols have a noticeably lower slope and a larger intercept value. The next lower molecular weight member in the numbering scheme used for these series was of lower  $T_g$  than the relationship would predict. However, in each case the first member, if properly named, really is in a different series. That is, the next lower number after 2-propanol is 2-ethanol which really is not a member since it is a primary alcohol and belongs to the family of normal alcohols. The next lower members for the 4-alcohol and 3-alcohol series, when properly named, are seen to belong to the 3-alcohol and 2-alcohol families, respectively. That is, 4-hexanol is really 3-hexanol and 3-butanol is really 2-butanol.

The data in Fig. 7 describe the behavior of a series of methyl branched secondary alcohols. The data for these

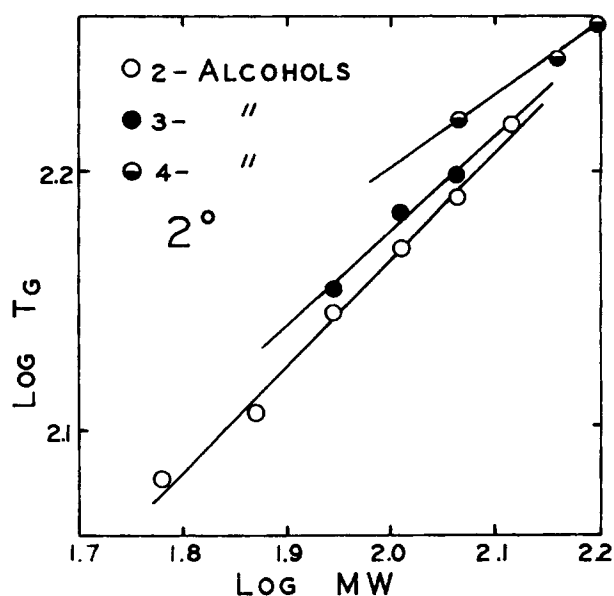


Fig. 6. Gorskii plot (Eq 3) for series of secondary alcohols.

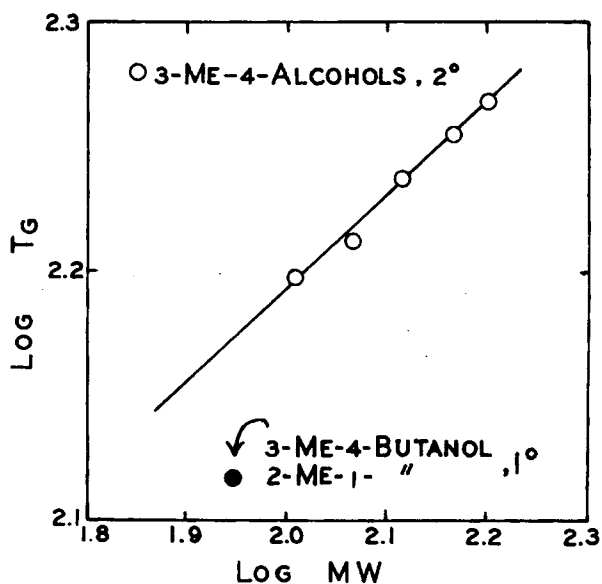


Fig. 7. Gorskii plot (Eq 3) for a series of 3-methyl-4-alcohols.

Table 1. Glass Transition Temperature for Series of Alcohols and Hydrocarbons

General name	General structure	T <sub>g</sub> , °K	Reference
Primary alcohols			
n-Alcohols*	CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>x</sub> -OH		
n-nonanol	x = 8	153	—
2-Methyl-1-alcohols	CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>x</sub> -CHCH <sub>3</sub> -CH <sub>2</sub> OH		
2-methyl-1-propanol	x = 0	127	(7)
2-methyl-1-butanol	x = 1	131	(7)
2-methyl-1-pentanol	x = 2	143	—
2-methyl-1-heptanol	x = 4	158	—
2,2-Dimethyl-1-alcohols	CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>x</sub> -C(CH <sub>3</sub> ) <sub>2</sub> -CH <sub>2</sub> OH		
2,2-dimethyl-1-propanol	x = 0	166	(7)
2,2-dimethyl-1-butanol	x = 1	158	—
2,2-dimethyl-1-pentanol	x = 2	166	—
2,2-dimethyl-1-hexanol	x = 3	173	—
Secondary alcohols			
2-Alcohols	CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>x</sub> -CHOH-CH <sub>3</sub>		
2-propanol	x = 0	121	—
2-butanol	x = 1	127	—
2-pentanol	x = 2	140	(7)
2-hexanol	x = 3	148	—
2-heptanol	x = 4	155	—
2-octanol	x = 5	166	—
3-Alcohols	CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>x</sub> -CHOH-CH <sub>2</sub> -CH <sub>3</sub>		
3-pentanol	x = 1	143	(7)
3-hexanol	x = 2	153	—
3-heptanol	x = 3	158	—
4-Alcohols	CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>x</sub> -CHOH-(CH <sub>2</sub> ) <sub>2</sub> -CH <sub>3</sub>		
4-heptanol	x = 2	166	—
4-nonanol	x = 4	175	—
4-decanol	x = 5	181	—
3-Methyl-4-alcohols	CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>x</sub> -CHOH-CHCH <sub>3</sub> -CH <sub>2</sub> -CH <sub>3</sub>		
3-methyl-4-pentanol	x = 0	158	—
3-methyl-4-hexanol	x = 1	163	—
3-methyl-4-heptanol	x = 2	173	—
3-methyl-4-octanol	x = 3	180	—
3-methyl-4-nonanol	x = 4	186	—
Tertiary alcohols			
2-Methyl-2-alcohols	CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>x</sub> -C(CH <sub>3</sub> ) <sub>2</sub> OH		
2-methyl-2-propanol	x = 0	180	—
2-methyl-2-butanol	x = 1	154	(7)
2-methyl-2-pentanol	x = 2	163	—
2-methyl-2-hexanol	x = 3	173	—
2-methyl-2-heptanol	x = 4	178	—
4-Methyl-4-alcohols	CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>x</sub> -CCH <sub>3</sub> OH-(CH <sub>2</sub> ) <sub>2</sub> -CH <sub>3</sub>		
4-methyl-4-heptanol	x = 2	170	—
4-methyl-4-octanol	x = 3	178	—
4-methyl-4-nonanol	x = 4	185	—
Hydrocarbons			
3-Methyl alkanes	CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>x</sub> -CHCH <sub>3</sub> -CH <sub>2</sub> -CH <sub>3</sub>		
3-methyl-pentane	x = 1	88	—
3-methyl-hexane	x = 2	99	—
3-methyl-heptane	x = 3	107	—
4-Methyl alkanes	CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>x</sub> -CHCH <sub>3</sub> -(CH <sub>2</sub> ) <sub>2</sub> -CH <sub>3</sub>		
4-methyl-nonane	x = 4	123	—
4-methyl-undecane	x = 6	135	—

\*See Ref. 7 and 13 for T<sub>g</sub> of the other n-alcohols.

3-methyl-4-alcohols correlate well when the Gorskii relationship is applied. As was found for the primary alcohols, the methyl branch causes an increase in T<sub>g</sub> at constant molecular weight. What might be termed the first member of this series, 3-methyl-4-butanol, is shown in Fig. 7. This alcohol does not fit the relationship since analysis of its structure or name indicates it is a primary alcohol.

The glass transition-molecular weight behavior for two series of tertiary alcohols is described in Fig. 8. Tertiary butanol or 2-methyl-2-propanol, a real first member in this case, again has a higher T<sub>g</sub> than other members of 2-methyl-2-alcohol series. Thus, it has a behavior comparable to that of methanol in the normal alcohol series and neopentyl alcohol in the 2-methyl-1-alcohol series. The next lower member of the

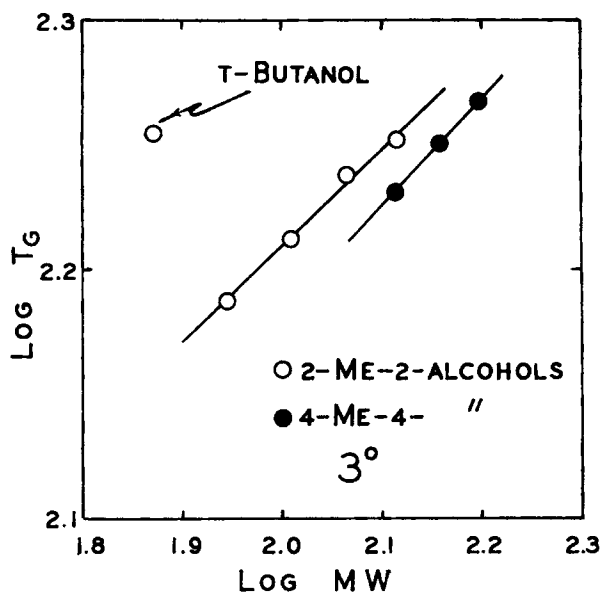


Fig. 8. Gorskii plot (Eq 3) for series of tertiary alcohols. Note deviation of *t*-butanol from other members of the 2-methyl-2-alcohol series.

4-methyl-4-alcohol series, 4-methyl-4-hexanol, is not shown; but it does deviate from the relationship since it belongs to the 3-methyl-3-alcohol series.

Figure 9 is a correlation of glass transitions for the 3- or 4-methyl alkanes and their behavior is compared to that of the normal alcohols. This series is mixed in the sense of the methyl group position, but it appears that the position of the methyl group has no effect on the correlation. As will be seen from the summary of slope and intercept values, the branched alkanes have a much greater slope and very low intercept relative to the alcohols. These factors suggest that correlation of information such as this with dipole moment, molar volume, and similar factors could provide further insight into the behavior of low molecular weight compounds.

Table 2 contains a compilation of the slope  $B$  and intercept  $n$  of the Gorskii relationship  $T_g = BM^n$  for the

Table 2. Constants for the Gorskii Relationship (16),  $T_g = BM^n$

Series	B	n	Correlation coefficient
Primary alcohols			
n-Alcohols	22.21	0.390	0.995
2-Methyl-1-alcohols	21.89	0.405	0.985
2,2-Dimethyl-1-alcohols	28.01	0.374	0.999
Secondary Alcohols			
2-Alcohols	21.74	0.415	0.993
3-Alcohols	28.22	0.363	0.987
4-Alcohols	45.14	0.274	0.995
3-Methyl-4-alcohols	27.41	0.378	0.991
Tertiary Alcohols			
2-Methyl-2-alcohols	27.84	0.382	0.995
4-Methyl-4-alcohols	22.51	0.416	0.994
Hydrocarbons			
3- or 4-Methyl alkanes	8.71	0.624	0.993

series of compounds discussed in this paper. The slope values obtained for the primary alcohols are quite similar in nature. Although the intercepts vary, no pattern is apparent from the data for these particular series. In the case of secondary alcohols, the constants are similar to those of the primary alcohols except for the 4-alcohols. However, there does appear to be a trend for the intercept to increase and the slope to decrease as the hydroxyl group moves from the 2-position to the 4-position on the unbranched secondary alcohols. The tertiary alcohols are similar to the others, but there is insufficient data to search for a trend. Although most of the constants are similar, the differences shown are significant and the constants for any given series cannot be used to calculate  $T_g$  values for another series. The series of 3- and 4-methyl alkanes are characterized by having constants that are markedly different from the alcohols. The intercept is markedly lower and the slope is higher than that of the alcohols.

## REFERENCES

1. A. F. Lewis and J. K. Gillham, *J. Appl. Polym. Sci.*, **6**, 422 (1962).
2. J. K. Gillham, *Crit. Rev. Macromol. Sci.*, **1**, 83 (1972).
3. K. H. Illers, *Rheol. Acta.*, **3**, 185 (1964).
4. T. Tsutsui, K. Furukawa, H. Imada, and M. Takayanagi, *Rpt. Prog. Polym. Phys.*, **11**, 299 (1968).
5. R. A. Fava and C. E. Chaney, *J. Appl. Polym. Sci.*, **21**, 791 (1977).
6. J. J. Stratta, F. P. Reding, and J. A. Faucher, *J. Polym. Sci.: Part A*, **2**, 5017 (1964).
7. J. A. Faucher and J. V. Koleske, *Phys. Chem. Glasses*, **7**, 202 (1966).
8. L. E. Nielsen, *Rev. Sci. Inst.*, **22**, 690 (1951).
9. L. E. Nielsen, *Polym. Eng. Sci.*, **17**, 713 (1977).
10. J. A. Faucher, J. D. Graham, J. V. Koleske, E. R. Santee, and E. R. Walter, *J. Phys. Chem.*, **70**, 3738 (1966).
11. J. V. Koleske and R. D. Lundberg, *J. Polym. Sci.: Part A-2*, **10**, 323 (1972).
12. M. Gordon and J. S. Taylor, *J. Appl. Chem.*, **2**, 493 (1952).
13. J. V. Koleske and J. A. Faucher, *Phys. Chem. Glasses*, **15**, 65 (1974).
14. J. A. Faucher and J. V. Koleske, *Zh. Fiz. Khim.*, **40**, 456 (1966).
15. T. G. Fox and S. Loshaek, *J. Polym. Sci.*, **15**, 371 (1955).
16. F. K. Gorskii, *Physik. Z. Sowjetunion*, **6**, 513 (1934).
17. I. Yannas, *Science*, **160**, 298 (1968).
18. J. A. Pryde and G. O. Jones, *Nature*, **170**, 685 (1952).
19. A. A. Miller, *Science*, **163**, 1325 (1969).
20. D. H. Rasmussen and A. P. MacKenzie, *J. Phys. Chem.*, **75**, 967 (1971).

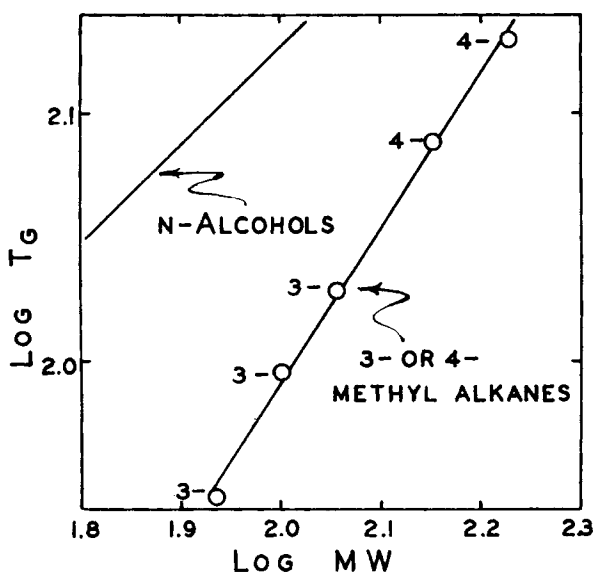


Fig. 9. Gorskii plot (Eq 3) for methyl substituted hydrocarbons and comparison with *n*-alcohols.