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Multiple Transitions in Polyvinyl Alkyl Ethers at Low Temperatures

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Multiple Transitions in Polyvinyl Alkyl Ethers at Low Temperatures

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SUMMARY

A series of polyvinyl alkyl ethers, with the ether side chain ranging in length from methyl to n-decyl, has been studied from $\sim 60^\circ\text{K}$ to above the glass transition. A linear variable differential transformer was used to measure the linear expansion coefficient, α' , complemented by mechanical loss measurements with a freely oscillating torsion pendulum and dielectric loss measurements. In addition to the glass transition, two low-temperature transitions have been observed in these systems. The first below T_g , $T_{gg}(1)$, follows the same trend as the glass transition, i.e., as the side chain length increases the temperature at which the transition occurs decreases, until n-octyl, where side chain crystallization is manifested. The second transition below T_g , $T_{gg}(2)$, occurs at $\sim 100^\circ\text{K}$ irrespective of side chain length. Because of their analogous dependence on side chain length, $T_{gg}(1)$ is thought to be similar to the glass transition, i.e., due to main chain motion.

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$\Delta\alpha'$ at $T_{gg}(2)$ is of greater magnitude than $\Delta\alpha'$ at $T_{gg}(1)$ and is thought to be a result of reorientation of the side chain.

The value of the Simha-Boyer free volume product, $(\alpha_l - \alpha_g)$, T_g , decreases with increasing side chain length, suggesting retention of excess free volume by the flexible pendant group. A generalization of this quantity is considered which takes into account the locations and magnitudes of the g-g transitions and results in a more nearly constant value of a free-volume fraction.

INTRODUCTION

The relaxation* behavior of polymers at low temperatures has been studied in recent years by a variety of dynamic methods in order to elucidate the molecular origins of the losses observed. Dilatometry, which has been a traditional tool to investigate the glass transition, has recently been employed by us [1-4] in a wide temperature range below T_g , extending in this manner the frequency range covered by dynamic procedures and the resolution of the loss spectrum. Among others, two particular homologous series, namely, the polyalkyl methacrylates between T_g and the liquid He range of temperatures [2, 4] and the polyvinyl alkyl ethers [3], have been the object of our attention. The general observation has been the existence of several g-g transitions, some in general accord with dynamic measurements, but differing in detail, due to improved resolution, as compared with torsion pendulum data [2, 3]. The purpose of the present paper is to extend some of the earlier results on the polyvinyl alkyl ethers to lower temperatures and to compare dilatometric, dielectric, and low-frequency mechanical observations, where feasible. The absence of crystallinity in the main chain and the relatively simple structure make these polar polymers a desirable object of investigation. Finally, the information about the expansion coefficients over a wide range of temperatures in the two series mentioned permits certain free-volume estimates.

*The terms relaxation and transition are used interchangeably here.

EXPERIMENTAL

The samples and their preparation have been described elsewhere [3, 5]. The basic structure of the polyvinyl alkyl ethers (PVAE) is $-\text{CH}_2-\text{CH}[\text{OR}]-$, where the OR group includes here methyl (M), ethyl (E), n-butyl (nB), i-butyl (iB), n-hexyl (nH), n-octyl (nO), and n-decyl (nD). The polymers are rubbery at room temperature and easily shaped.

The length-dilatometric apparatus and data analysis have also been described previously [2, 4]. Essentially, the length-temperature data are directly differentiated by a least-square technique based on moving arcs, to yield directly the coefficient of linear expansion, α' , as a function of temperature. A transition temperature is obtained by drawing tangents on either side of the step and choosing the midpoint of the step on the temperature axis.

Dielectric loss data on two of the samples, PVME and PVnBE, were obtained with a General Radio Bridge, Model 716-C by Dr. Thomas F. Schatzki of Shell Development Co., Emeryville, Calif. The measurements were made at several frequencies in order to obtain apparent activation energies for the sub- T_g transitions.

Low-temperature mechanical observations were made on the freely oscillating torsion pendulum used previously [2]. The results are expressed in terms of the logarithmic decrement, Δ , as a function of temperature.

RESULTS

Dilatometry

Some of the plots of linear expansion coefficient versus temperature are shown in Figs. 1-5 (see also Figs. 1-3 of Ref. [3]). The overlap between data taken below and above liquid nitrogen is acceptable with the α' 's differing by 15% at most. Table 1 lists the transition temperatures and expansion coefficients. α'_g was not obtainable by our procedures for PVnOE and PVnDE, due to the softness of the polymers above T_g . Previous measurements of PViBE [3] suggested the presence of two T_{gg} transitions in the liquid N_2 temperature range. However, repeated runs indicate no distinct transitions but instead a gradual decline in α' from 1.26×10^{-4} to $1.12 \times 10^{-4}/^\circ\text{C}$.

The main glass temperature for the series decreases with increasing side chain length until the n-octyl ether, where it begins to rise again.

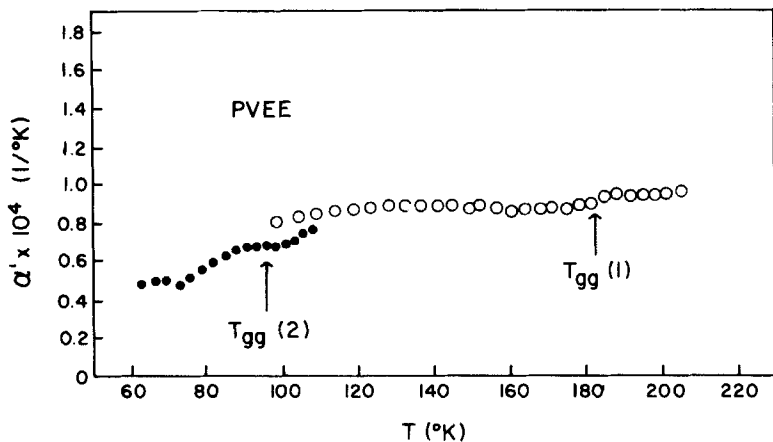


Fig. 1. Linear expansion coefficient as a function of temperature for polyvinyl ethyl ether. ○, Ref. [3]; ●, this work.

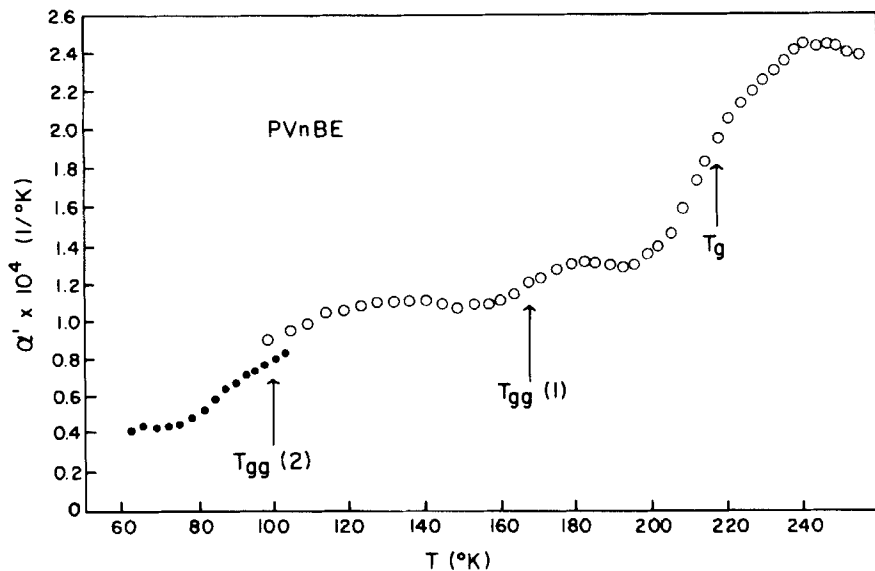


Fig. 2. Linear expansion coefficient as a function of temperature for polyvinyl n-butyl ether. ○, Ref. [3]; ●, this work.

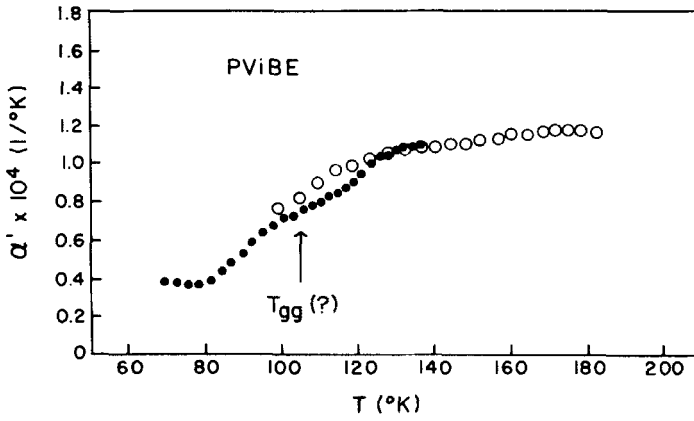


Fig. 3. Linear expansion coefficient as a function of temperature for polyvinyl i-butyl ether. \circ , liquid nitrogen measurements; \bullet , helium measurements.

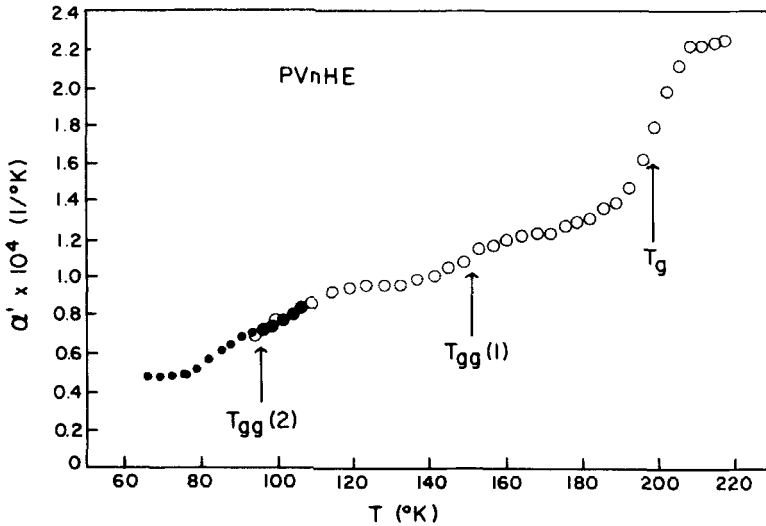


Fig. 4. Linear expansion coefficient as a function of temperature for polyvinyl n-hexyl ether. \circ , Ref. [3]; \bullet , this work.

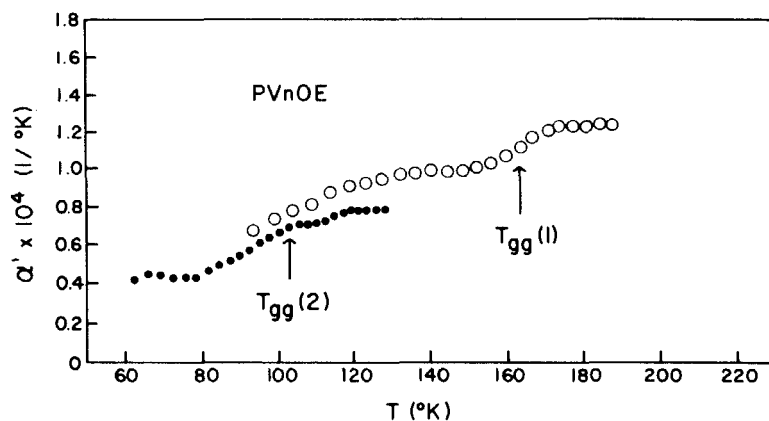


Fig. 5. Linear expansion coefficient as a function of temperature for polyvinyl n-octyl ether. \circ , Ref. [3]; \bullet , this work.

Table 1. Transition Temperatures and Thermal Expansivities

Polymer	T_g	($^{\circ}\text{K}$)			($\times 10^4, 1/^{\circ}\text{C}$)			
		$T_{gg}(1)$	$T_{gg}(2)$	$T_{gg}(1)/T_g$	α'_{ℓ}	α'_g	$\alpha'_{gg}(1)^a$	$\alpha'_{gg}(2)^a$
PVEE	240	183	95	0.76	2.42	1.01	0.89	0.49
PVnBE	217	168	97	0.77	2.42	1.30	1.10	0.43
PViBE	251	—	105	—	2.26	1.26	1.12	0.39
PVnHE	199	151	96	0.78	2.22	1.25	0.97	0.48
PVnOE	193	163	103	0.84	—	1.23	0.99	0.44
PVnDE ^b	211	183	—	0.87	—	~ 1.5	1.16	—

^aReplacing the previous notation α'_g , etc. [2].

^bTaken from Ref. [3].

Using a differential scanning calorimeter, a first-order crystalline melting point at about -41°C was actually observed in PVnDE resulting from crystallization in the side chains. The magnitude of the transition, $\Delta\alpha'_{\ell} = 1 - \alpha_g\alpha_{\ell}$ at T_g , decreases with increasing side chain length, at least up to n-hexyl, as may be seen in Table 1.

All of the polymers exhibit a $T_{gg}(1)$ transition at a ratio of $T_{gg}(1)/T_g \cong 0.8$ (see Table 1). $T_{gg}(1)$ in PVnDE is not as obvious as in the others, but the breadth of the T_g -relaxation region suggests the presence of two transitions.

The second glass-glass transition, $T_{gg}(2)$, occurs around 100°K, irrespective of the side chain length. The change $\Delta\alpha'$ at $T_{gg}(2)$ is much greater than at $T_{gg}(1)$. PVnDE is very difficult to handle, and measurements below 77°K are still in progress. There is, however, again a suggestion of a $T_{gg}(2)$ around 100°K, because α' is noted to decrease sharply. Preliminary measurements on PVME below the liquid nitrogen range also indicate a relaxation at approximately 98°K with an α' below $T_{gg}(2)$ of approximately $0.36 \times 10^{-4}/^{\circ}\text{C}$.

Our results are not inconsistent with the possible presence of two relaxations in the $T_{gg}(2)$ transition; however, being unable to clearly resolve this region, we assume the presence of only one rather broad relaxation.

Dielectric Loss

Some preliminary dielectric loss data for PVME and PVnBE are shown in Figs. 6 and 7. The main glass transition is observed in PVME at $\sim 262^{\circ}\text{K}$ at a frequency of 100 Hz, compared with 251°K by dilatometry [3]. Dielectric loss data of Thurn and Wolf [6] show the glass transition at 308°K and 2×10^6 Hz to be in good agreement with these results. T_g for PVnBE is found at 242°K and 100 Hz.

$T_{gg}(1)$ for PVME is seen at 193°K and 100 Hz. The apparent activation energy for this process, derived from measurements at three different frequencies, is 10.7 kcal/mole (see Fig. 9). Thurn and Wolf's measurements also show a $T_{gg}(1)$ transition, but at $\sim 188^{\circ}\text{K}$ (2×10^6 Hz). No further dielectric transition is observed down to 110°K , in agreement with Thurn and Wolf. Dielectric loss for PVnBE shows a T_{gg} transition at 132°K and 100 Hz in apparent agreement with the $T_{gg}(2)$ observed dilatometrically.

Dynamic Mechanical Loss

The dynamic loss curve for PVnBE is exhibited in Fig. 8. Two secondary transitions are observed in addition to the main glass temperature. T_g occurs at 223°K at a frequency of 0.10 Hz in qualitative agreement with the dilatometric results.

The first g-g transition is seen to be of low magnitude, as was also observed by dilatometry. This transition occurs at 180°K and 0.14 Hz. The ratio of $T_{gg}(1)/T_g$ is found to be 0.81, compared with the dilatometric value of 0.78 for PVnBE. A loss peak was noted at approximately 200°K and 8 Hz by Schmieder and Wolf [7] but was not seen in PVEE by Saba et al. [8].

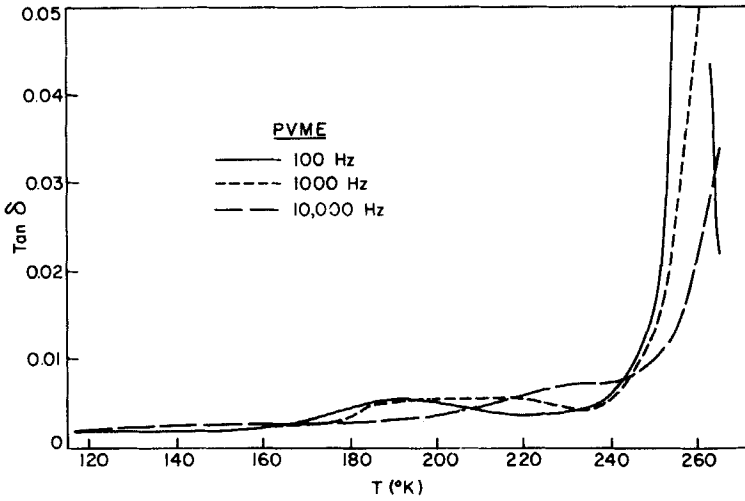


Fig. 6. Dielectric loss as a function of temperature at various frequencies for polyvinyl methyl ether.

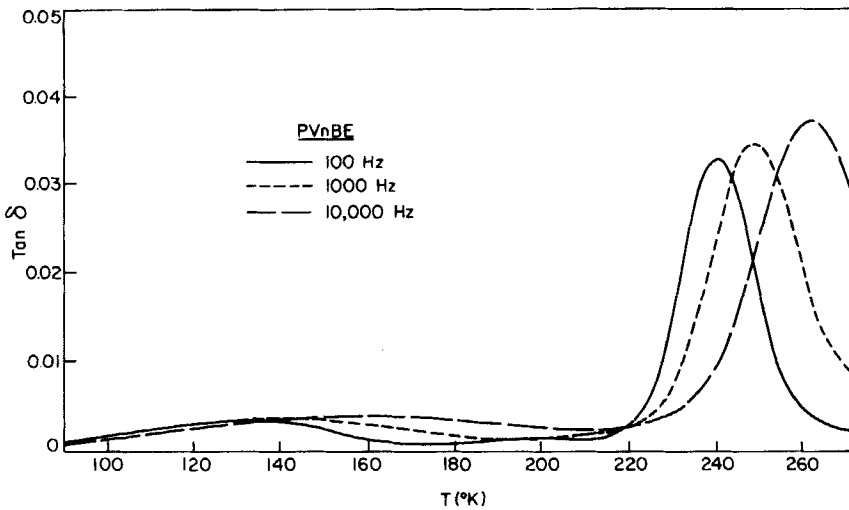


Fig. 7. Dielectric loss as a function of temperature at various frequencies for polyvinyl n-butyl ether.

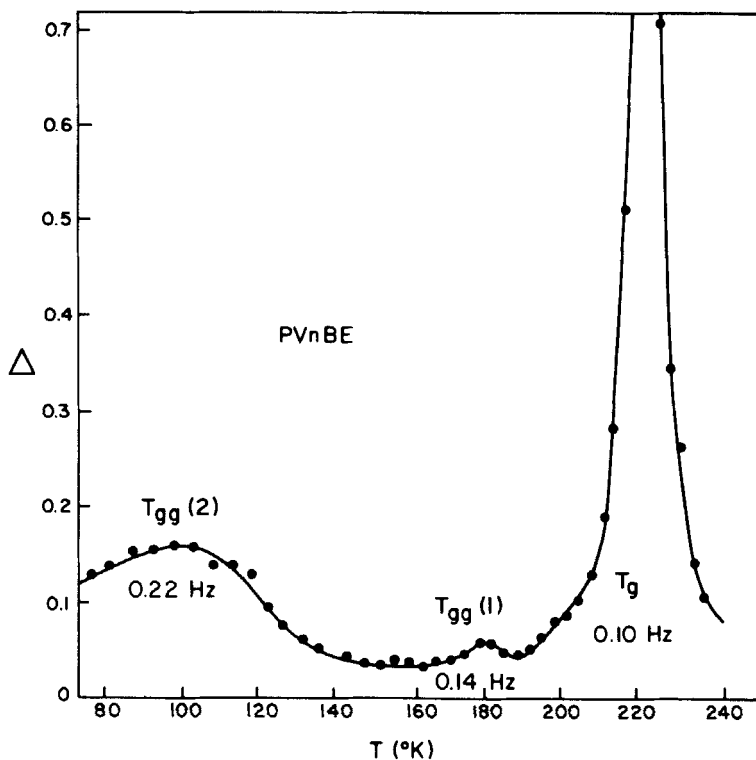


Fig. 8. Mechanical loss as a function of temperature for polyvinyl n-butyl ether.

There is a second broad relaxation region below T_g , which peaks at approximately 103°K , corresponding to a frequency of 0.22 Hz. Here the magnitude of the loss peak is larger than at $T_{gg}(1)$, consistent with the dilatometric results. The temperature shift resulting from the change in frequency is not as great as one might expect, but it was difficult to measure accurately because of the breadth of the transition and temperature limits of our apparatus. The occurrence of this transition is in agreement with the loss data of Schmieder and Wolf [7] and Saba et al. [8]. The former observed a $T_{gg}(2)$ in PVnBE at 123°K and a frequency of 10.4 Hz. In PVEE, Saba et al. found a relaxation at 100°K and 0.9 Hz.

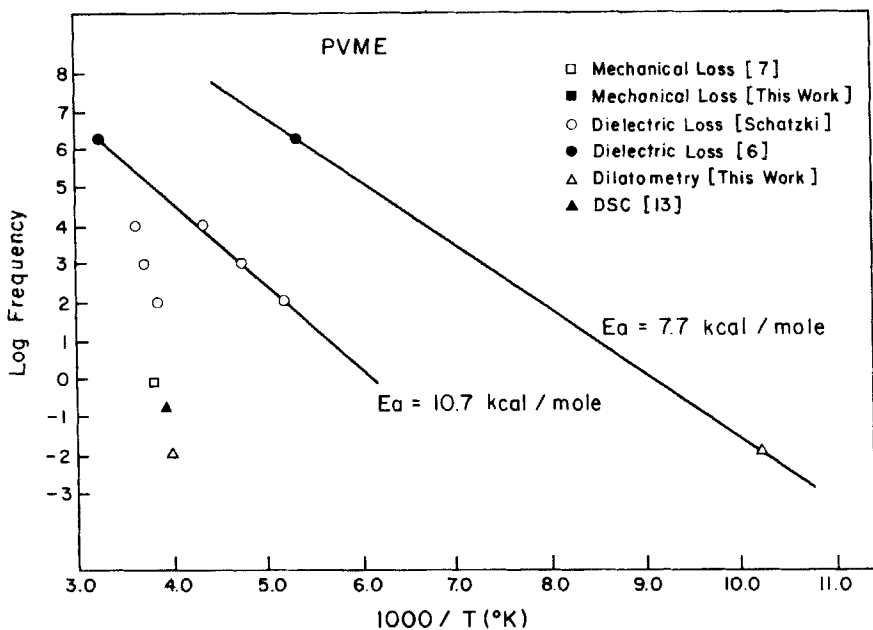


Fig. 9. Arrhenius plots for relaxations in polyvinyl methyl ether.

Frequency Dependence of Transitions

Figures 9 and 10 show logarithmic plots of frequency as a function of temperature for PVME and PVnBE. A frequency of 0.01 Hz was chosen for dilatometry, which is somewhat arbitrary but of reasonable magnitude based on the rate of temperature change. In both polymers three distinct transitions are seen. However, $T_{gg}(1)$ is dielectrically active in PVME but not in PVnBE, whereas $T_{gg}(2)$ is dielectrically active in PVnBE but not in PVME according to our assignment. The apparent activation energies for the low-temperature processes are also shown and are seen to be of the expected order of magnitude.

DISCUSSION

The dilatometric transition temperatures T_g and $T_{gg}(i)$ as a function of side chain length are exhibited in Fig. 11. We note that the main glass

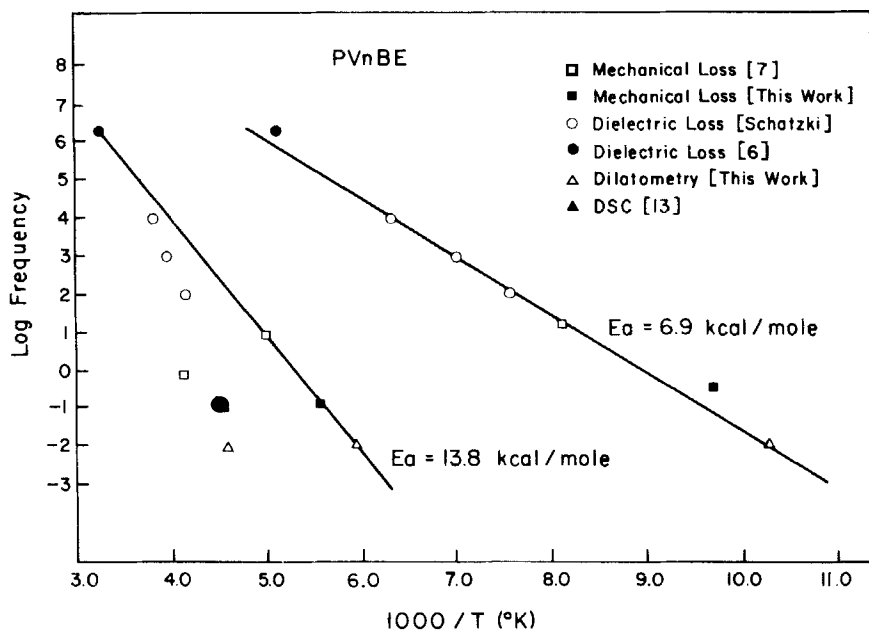


Fig. 10. Arrhenius plots for relaxations in polyvinyl n-butyl ether.

temperature decreases with increasing side chain length. Similar behavior has also been found in a series of poly- n - α -olefins [9] and polyalkyl methacrylates [2, 5] and has been ascribed to increased mobility of the main chain as a result of the presence of flexible side chains. The density of the polymers decreases with increasing side chain length [5], also indicating a loosening of the structure. As the side chain length reaches n -octyl ether, however, the glass transition temperature increases, with side chain crystallization occurring in PVnDE, as evidenced by DSC. Side chain crystallization will act as a physical cross-link and raise T_g .

Although there is no first-order crystalline melting point in PVnOE, the side chains are probably ordered to some extent; this regular structure may also act as physical cross-links and account for the increase in T_g .

$T_{gg}(1)$ is seen to show the same trend as T_g , i.e., a decrease with increasing side chain length until n -octyl. This fact, coupled with the low magnitude and relatively high temperature of the transition, suggests a motion associated or in cooperation with the main chain. This might be some type of partial rotation involving a few segments in the backbone and

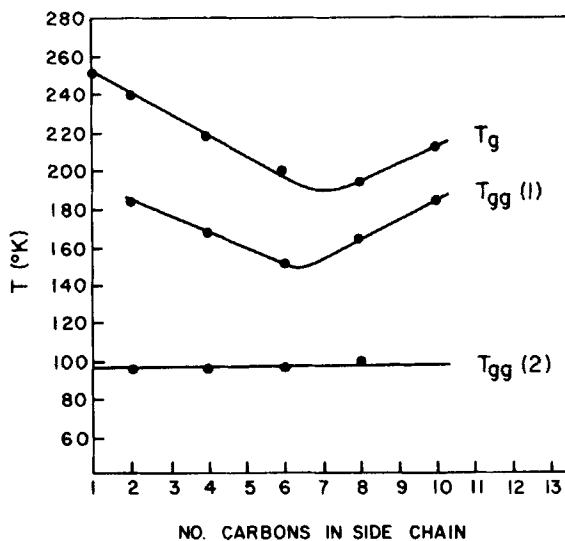


Fig. 11. Dilatometric transition temperatures as a function of side chain length for polyvinyl n-alkyl ethers.

requiring two colinear carbon bonds. Such a requirement would statistically reduce the number of groups available for movement and thereby lower the magnitude of the transition. Nevertheless, any major motion of the main chain would involve the permanent dipole of the ether linkage and should result in a dielectric loss peak, although it might possibly be small. We see indeed a secondary transition in the dielectric loss data for PVME, but at a lower temperature than would be expected. There is no dielectric loss peak in PVnBE that could correspond to $T_{gg}(1)$, but, as can be seen from the $\log f$ vs. $1/T$ plot, there is a strong indication that $T_{gg}(1)$ is merging with T_g at these higher frequencies. The mechanical loss data for PVnBE also show a $T_{gg}(1)$ transition at the temperature which is consistent with the dilatometric results, tending to confirm its existence. Polymers without side chains show a T_{gg} transition at approximately a ratio of 0.7 for T_{gg}/T_g [10], indicating a general type of secondary transition in the main chain.

The second g-g transition has been widely observed and ascribed to relaxation processes in the side chain [7, 8, 11]. We note that its location is practically independent of side chain length and the magnitude is relatively large and comparable on a fractional basis with the ℓ -g transition. Since

the fraction of the polymer contained in the side chains is relatively high, we would expect a large change in α' . The dielectric loss results show no apparent $T_{gg}(2)$ transition in this region for PVME. However, in PVnBE we find a $T_{gg}(2)$ that fits very satisfactorily with mechanical loss and dilatometric data (see Fig. 10). An appropriate side chain motion would involve the rotation of the oxygen dipole about the ether linkage to the main chain carbon and could thus account for the dielectric loss. The mechanical loss data clearly indicate a $T_{gg}(2)$ transition in PVnBE, although it occurs at a somewhat lower temperature than expected for the frequency employed. Again, the greater mechanical loss peak at $T_{gg}(2)$ than at $T_{gg}(1)$ is expected for the same reasons mentioned previously. All in all, our results tend to confirm the assignment of side chain reorientation to the $T_{gg}(2)$ transition.

There is no apparent explanation for the discrepancy between the dielectric results for PVME and PVnBE, but work in progress on the mechanical and dielectric loss measurements of the other polymers in the series should help to clear up the issue. Further transitions below 60°K are also expected, e.g., methyl and ethyl rotation, and continuation of this investigation is planned on that aspect as in the polyalkyl methacrylates [4].

Free-Volume Considerations

Simha and Boyer [12] rationalized their observation that $(\alpha_l - \alpha_g)T_g \approx$ constant for a variety of polymers by considering a linear extrapolation of the volume-temperature curve above and below T_g to $T = 0$, which yields volumes $V_{0,g}$ and $V_{0,l}$, postulating a constant value of the free-volume quantity $(V_{0,g} - V_{0,l})/V_{0,g} \approx (V_{0,g} - V_{0,l})/V_{0,l}$, neglecting terms $O(\alpha^2 + \beta^2)$. However, in the polyalkyl methacrylate series [2, 4], the magnitude of this product decreases monotonically with increasing length of the side chain except for chains with bulky side groups such as t-butyl. Similar behavior is noted for the polyvinyl alkyl ether series, resulting from relatively large values of α_g in these polymers. In order to correct for this, it was suggested [12] that α_g be replaced by an expansion coefficient below $T_{gg}(1)$. A substitution of $\alpha_{gg}(2)$ for polyalkyl methacrylates [2] actually restores approximate constancy to the free-volume ratio.

On the other hand, a consistent generalization of the free-volume ratio $(\alpha_l - \alpha_g)T_g$ at $T = T_g$ may be considered that takes into account g-g processes. The expansion of the (extrapolated) volume of the liquid, $V_{0,l}$, between $T = 0$ and T_g is now given by a product encompassing all transition regions, viz.:

$$V_{0,q} \prod_{i=0}^n \left\{ 1 + \alpha_{gg}(i) [T_{gg}(i) - T_{gg}(i+1)] \right\}$$

with the conventions: $T_{gg}(0) \equiv T_g$, $\alpha_{gg}(0) \equiv \alpha_g$, $T_{gg}(n+1) \equiv 0$. This equation disregards variations in α between two relaxation regions and replaces the actual change of α in the transition region by a step function. In the subsequent numerical computations we have used an average value of the expansion coefficient when a significant decrease with decreasing temperature occurs between two measurable relaxation regions. Again, neglecting second powers in products $\alpha\Delta T$, we arrive at the replacement:

$$(\alpha_q - \alpha_g)T_g \rightarrow \alpha_q T_g - \sum_{i=0}^n \alpha_{gg}(i) [T_{gg}(i) - T_{gg}(i+1)]$$

When $\alpha_{gg}(i) = \alpha_{gg}(0) = \alpha_g = \text{constant}$, the two expressions become identical. Each of these expressions also represents the intercept ratio $(V_{0,g} - V_{0,q})/V_{0,q}$ to $0(\alpha^2 T^2)$.

Table 2 lists the results of our estimates for the polyalkyl methacrylates. Here, four terms in the sum above are available for PMMA and PsBMA and five for the other members [2, 4]. Except for PtBMA, the fluctuations in the free-volume ratio are reasonably small. The same, however, may be said in respect to the quantity $\alpha_q T_g$, which fluctuates even less here, although considerably more in polymers without long, flexible side chains [12]. The last column contains the estimated contribution of the g-g relaxations to the free-volume ratio. A reference level with deviations at both ends of the series is evident. It should be noted that PtBMA shows significant deviations also in respect to the product $[\alpha_q - \alpha_{gg}(2)] T_g$, which equals 0.15 compared with the range of 0.10 to 0.12 for the other members of the series investigated [2]. In the polyvinyl alkyl ether series, the values in the third column are similar to those for the preceding series.

The numerical values of the free-volume ratio obtained here are similar to those derived earlier for "normal" polymers based on the product $(\alpha_q - \alpha_g)T_g$. Obviously, however, all of these polymers should exhibit relaxations in the glassy state, which are manifested in the thermal expansivities, although only a few systems have been explored in this manner sufficiently far below T_g [1-4]. Our application of the revised relations to these polymers necessarily raises the value of the "constant," as can readily be seen for PMMA where we have 0.132 in Table 2 compared with 0.096. It

Table 2. Summary of Free-Volume Calculations

Polymer	$3(\alpha'_g - \alpha'_g)T_g^a$	$(V_{0,g} - V_{0,g})/V_{0,g}$	$\alpha'_g T_g$	$\sum_{i=0}^n \alpha'_{gg(i)} [T_{gg(i)} - T_{gg(i+1)}]$
PMMA	0.096	0.132	0.180	0.048
PEMA	0.067	0.113	0.181	0.068
PnPMA	0.049	0.111	0.175	0.065
PnBMA	0.045	0.106	0.175	0.069
PtBMA	0.060	0.124	0.191	0.067
PsBMA	0.049	0.116	0.183	0.067
PtBMA	0.117	0.156	0.223	0.067
PnHMA	—	—	—	0.074
PnOMA	—	—	—	0.064
PnDMA	—	—	—	0.040
PVME	0.108	0.121	0.162	0.041
PVEE	0.102	0.120	0.174	0.055
PVnBE	0.073	0.103	0.158	0.055
PViBE	0.075	0.106	0.170	0.064
PvsBE	0.065	—	0.153	—
PVnHE	0.058	0.085	0.133	0.048
PVnOE	—	—	—	0.044

^a Taken from Refs. [2] and [3].

remains to be seen whether an exploration of the whole temperature scale below T_g will place "normal" polymers and those containing flexible side chains on an equal numerical basis. This would require significant contributions $\alpha_{gg}(i)[T_{gg}(i) - T_{gg}(i + 1)]$, i.e., relatively large expansivities and/or widely separated relaxation intervals at cryogenic temperatures for the former and the opposite for systems with flexible side chains.

ACKNOWLEDGMENTS

This work was supported in part by the National Aeronautics and Space Administration under Grant NsG-343 to the University of Southern California. We are indebted to Dr. Thomas F. Schatzki for the results of his dielectric measurements. The services of the University of Southern California Computer Sciences Laboratory are also acknowledged.

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Note Added in Proof

The temperature range for the ether series discussed has been extended to a lower limit of about 20°K (W. J. Schell, Ph.D. thesis, University of Southern California, June 1969). Similarly as in the polymethacrylate series [4], a monotonic decrease of the thermal expansivity is observed below about 60°K.

The two free volume ratios $(V_{0,g} - V_{0,l})/V_{0,g}$ and $(V - V_{0,l})/V$ [12] have been recomputed for the two series shown in Table 2 (R. Simha and C. E. Weil, *J. Macromol. Sci.*, B, to be published). For this purpose the experimental $\alpha_g - T$ function is integrated over the interval $0 \leq T \leq T_g$, requiring at present an extrapolation over about 20°. The corresponding integration over α_l is performed by making use of earlier corresponding states results on oligomer and polymer liquids.

Discussion of Paper by W. J. Schell, R. Simha, and J. J. Aklonis**Multiple Transitions in Polyvinyl Alkyl Ethers at Low Temperatures**

E. Scalco: Are you implying that the free volume fraction should be constant at 0°K rather than at T_g ? Do you think that this may also be true for other common polymers?

W. J. Schell: The ratio $(V_{0,g} - V_{0,l})/V_{0,g}$ represents the free volume quantity considered by Simha and Boyer [12] between 0°K and T_g . It is, to a first approximation, represented by the product $(\alpha_l - \alpha_g)T_g$, if the temperature dependence of the α 's is neglected. In polymers with significant side-chain contributions, the ratio as calculated here by taking into account sub- T_g -relaxations, exhibits considerably lesser variations with side-chain length than $(\alpha_l - \alpha_g)T_g$. See also Note Added in Proof.