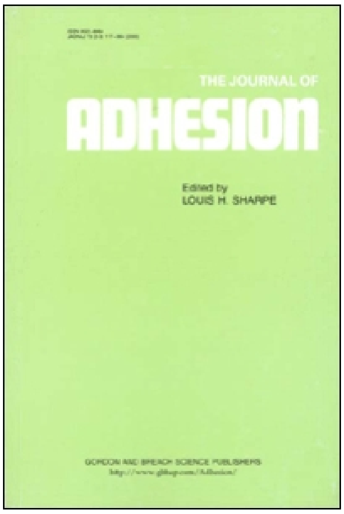

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The Glass Transition of Oligomers Confined to Small Pores of a Controlled Pore Glass*

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The glass-transition temperatures, T_g, of oligopropylene glycol (OPG) and oligoethylene glycol (OEG) of molecular weights $M_w = 1000$ g/mol confined to the small pores of a controlled pore glass with pore diameter ~ 102 Å were studied by differential scanning calorimetry. In several cases the surface of the porous glass was modified with trimethylchlorosilane to make it more hydrophobic. We find that the T_gs of both oligomers in the pores are lower than those in the bulk, the depression of T_g increasing with surface treatment. For example, the depression of the glass-transition temperature, ΔT_g, in the unmodified glass was 1.5 K for OEG and 2.0 for OPG, whereas in the silanized glass ΔT_gs were 11.0 K and 8.3 K, respectively. The last effect can be explained by increasing spatial limitations as the surface of the pores becomes more hydrophobic.

Keywords: Glass transition; controlled pore glass; oligoethylene glycol; oligopropylene glycol; differential scanning calorimetry; confinement effect; silanization; boundary layer; melting temperature

INTRODUCTION

It is well known that the behaviour of macromolecules at the solid–polymer interface is determined by many properties of polymers such as, *e.g.*, their adhesion [1, 2]. As was shown at first in the general case by theoreticians [3] and then, more recently, by experimentalists

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[4–6], the peculiarities of such behaviour should be attributed to both the special structure of polymers in thin (thickness up to several nanometres) layers of the polymers at the interface, and to their different physical-chemical properties in surface layers and in the bulk, respectively.

On the other hand, theoretical [7–9] and computer simulation [10–13] data show that different static and dynamic properties of amorphous polymers such as the glass transition have essentially to change at solid surface; but the influence of the pore surface does not exceed several molecular or segmental (in the case of chain molecules) diameters. However, up to now there has been a very limited amount of information on the peculiarities of the glass transition of macromolecules in boundary layers with two-dimensional spatial limitations (cylindrical pores of synthetic porous glass, for example) [14, 15]. The latter is connected with the difficulties of measurements of the corresponding parameters in boundary layers of thickness ~ 1–5 nm. It is evident that to distinguish the contribution of boundary layers from the properties of the whole system the greater part of a material has to be in the boundary layer state. Recently, this was achieved for small molecule liquids in synthetic porous glasses with pore sizes in the range 3–70 nm [16–18] and for thin polymer films [19–21] where spatial limitations in one direction are observed. Similar experimental studies for polymer molecules in porous systems with two-dimensional confinements are practically absent [14, 15].

This work presents the experimental results of calorimetric measurements of glass-transition temperatures, T_g, of oligopropylene glycol (OPG) and oligoethylene glycol (OEG) of molecular weights $M_w = 1000$ g/mol confined to small pores of a controlled porous glass with mean pore diameter ~ 102 Å. The decrease of glass-transition temperatures in the pores was observed for both oligomers.

EXPERIMENTAL

In our study, liquid oligopropylene glycol (OPG) and oligoethylene glycol (OEG), both of molecular weights $M_w = 1000$ g/mol, $M_w/M_n \leqslant 1.2$, purchased from Aldrich Chemical Company, were used. The controlled pore glass (CPG) Bioran (Schoot Company, Germany) used in this study was made by acid leaching of the boron-rich phase of a spinodally decomposed borosilicate glass. The CPG is a white free-flowing powder consisting of 30–60 mm particles with an inner surface area of 225 m^2 per g of glass, a pore volume of 0.8 cm^3 per g of glass, and a mean pore diameter of 102 Å with a narrow distribution of pore sizes (5%) [22]. The native CPG contains a large number of silanol groups on the surface.

To remove the water adsorbed by SiOH groups, the glass was thoroughly cleansed by washing in acetone and drying under vacuum for 24 h at a temperature up to 650 K. Thereafter, the glasses were mixed with the oligomers and gently stirred for 24 h so that the pores were filled by capillary wetting. To remove OPG molecules off the outer surface of the glass the latter was immersed into ethyl acetate for 10 s. The degree of filling of the glass was determined from the coke residue of CPG filled by oligomer after burning in a kiln. CPG samples were treated with trimethyl-chlorosilane to convert the surface hydroxyl groups to trimethyl-silyl groups. This procedure makes the glass more hydrophobic and promotes wetting by organic liquids. The silanization procedure is described elsewhere [23].

The experiments were run on the differential scanning calorimeter (DSM-2M), the lowest starting temperature being 150 K. The CPG and oligomers were weighed into the pre-weighed sample pan so that quantitative measurements could be made. For OEG, the quenched glass was prepared by heating above the melting point (~ 298 K) to 320 K and then cooling at 64 K/min to 170 K. The T_gs were then measured in heating scans at 16 K/min. For OPG, which is a liquid at rook temperature, the glass was also prepared by cooling at 64 K/min to 170 K and then by reheating at 16 K/min.

RESULTS AND DISCUSSION

The experimental data obtained from DSC scans for oligoethylene glycol confined in the pores of initial and silanized CPG (sCPG), as well as for bulk samples, are shown in Figure 1. Similar data for oligopropylene glycol are shown in Figure 2. In these curves the midpoints of the glass transition regions were interpreted as T_g. The values of T_g and ΔT_g, where ΔT_g is the difference between bulk T_g and T_g in

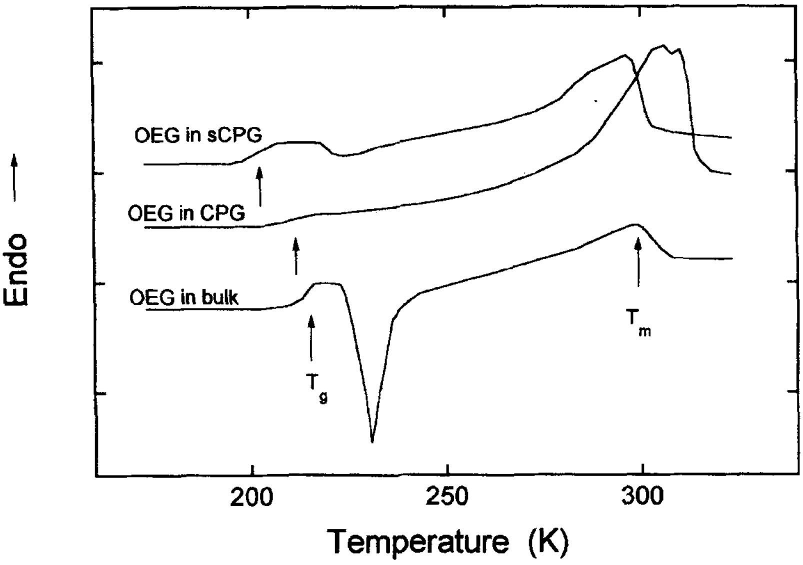

FIGURE 1 Differential scanning calorimetry data for oligoethylene glycol (OEG) of $M_w = 1000$ g/mol confined in controlled pore glass of pore diameter ~ 102 Å, both surface modified with trimethylchlorosilane (sCPG) and non-modified surface (CPG). In the bottom scan are shown the data for OEG in the bulk.

the pore, for both OEG and OPG are given in Table I. As is seen in this table, a negative shift of T_g for both oligomers in the pores of the porous glasses (CPG and sCPG) is observed. The temperature region of glass-transition for OEG in the bulk is more narrow then those for OEG in CPG and OEG in sCPG.

The analysis of the data obtained shows that for OEG in bulk at $T = 170$ K most of the oligomer is in the amorphous state, whereas for OEG in CPG and in sCPG the greater part of the molecules are crystalline. That is why we have not observed crystallization of OEG in CPG; moreover, this effect was very small for OEG in sCPG. ΔT_m values for the shift of the crystal melting transition temperature, T_m, are also included in Table I. As is seen from this table, the data for melting temperature are not regular and in the case of OEG in CPG we have observed even two different melting temperatures.

The depression of the glass-transition temperature observed for both OEG and OPG confined in restricted geometry of the unmodified

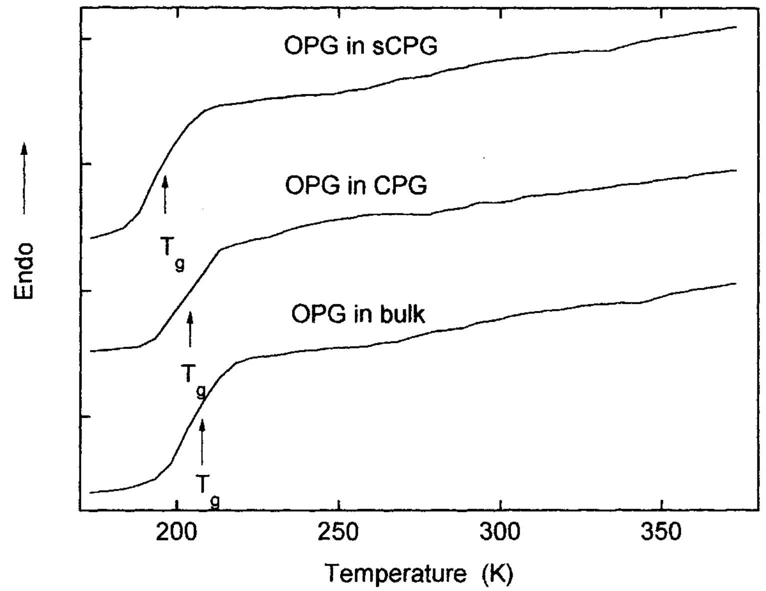

FIGURE 2 Differential scanning calorimetry data for oligopropylene glycol (OPG) of the same M_w again in Figure 1 confined in sCPG, in CPG and in the bulk.

TABLE I Glass-transition and melting temperature for oligoethylene glycol and oligopropylene glycol in non-modified (CPG) and silanized (sCPG) controlled pore glasses as well as in the bulk.

	$T_g(K)$	$\Delta T_g(K)$	$T_m(K)$	$\Delta T_m(K)$
	Oligoethylene glycol			
Bulk	212.2		298.2	
CPG	210.7	−1.5	305.9 310.2	+7.7 +12.0
sCPG	201.2	−11.0	296.2	−2.0
	Oligopropylene glycol			
Bulk	204.2			
CPG	202.2	−2.0		
sCPG	195.9	−8.3		

porous glass (CPG) ($\Delta T_g = 1.5$ K for OEG and 2.0 K for OPG) is similar in direction, but smaller in magnitude, than that of T_g for oligomers in silanized sCPG ($\Delta T_g = 11.0$ K and 8.3 K, respectively). Similar negative shifts of glass-transition temperatures were also observed by

Jackson and McKenna [16], Zhang, Liu, and Jonas [17], and Pissis *et al.* [18] for different confined, small molecule, hydrogen-bonded liquids. Jackson and McKenna [16] have also observed an increase of ΔT_g with decreasing pore size. Their data can be expressed as

$$T_g(d) = T_g(d \to \infty) - k/d, \tag{1}$$

where $T_g(d \to \infty)$ is T_g in bulk; d is pore diameter and k is a constant. The latter dependence suggests that the process of surface silanization leads to decrease of effective pore volume (size) and to increase of spatial limitation of oligomer molecules.

Computer simulation data for oligomers and short chain polymer liquids [10–13] at different surfaces show that the influence of the pore surface does not exceed several segmental diameters, a. For OEG, $a = 11.7$ Å [24]. Thus, in the unmodified CPG the pore diameter is much larger than the segmental diameter, $d(= 102\ \text{Å}) \gg a$. In this case, the greater part of the oligomer ($\sim 80\%$) is in the inner pore volume; therefore, the influence of the surface on the glass-transition is small ($\Delta T_g = 1.5$ K for OEG and 2.0 K for OPG). Using Eq. (1) we calculated the effective size of pores in the porous glass after silanization (sCPG), d^*. We obtained $d^* \sim 14$ Å for OEG and ~ 25 Å for OPG. These values of d^* are very close to the segmental diameter, a, for OEG molecules. It indicates that practically the whole oligomer in sCPG in in boundary layers, are liquid molecules experience in this case (in sCPG) much larger spatial limitation compared with the unmodified porous glass (CPG).

Finally, we would like to note that data on the negative shift of T_g observed for liquid OPG and OEG are in contrast to theoretical predictions of the glass trnansition based on both entropy models [25, 26] and free volume concepts [27, 28]. To predict the observed negative shift in T_g, the entropy and free volume at any given temperature must increase. An increase in either entropy or in free volume could be explained if the bulk density of the liquid in the pores is reduced, perhaps as a results of difficulty in the packing of molecules. A depression of bulk density might also occur if a glass is formed under a negative pressure [29]. For example, the cavitation pressure for *o*-terphenyl is -70 bar [29]. On the other hand, as was shown in [3], the decrease of T_g may be connected with plasticization of the organic glass by trimethylsilyl groups on the surface of the CPG;

however, we observed negative shifts of T_g for oligomers both in silanized sCPG and in non-modified CPG. A more correct and complete explanation of the contradiction between our data and theoretical predictions, as well as other experimental data on positive shifts of T_g for different liquids in confined media [14,31,32], would require further systematic theoretical and experimental studies of the properties of polymer molecule in confined systems.

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