MASTER

Thermal Conductivity and Specific Heat of Non-Crystalline

Solids: Polystyrene and Polymethyl Methacrylate*

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ABSTRACT

Below 1 K, the specific heat of amorphous polystyrene and polymethyl methacrylate varies as $AT + BT^3$ and the thermal conductivity varies as $T^{1.8}$ in agreement with measurements on inorganic glasses, demonstrating that this phenomenon is not sensitive to details of morphology.

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It has recently been found by Zeller and Pohl¹ that the specific heat of amorphous SiO_2 , GeO_2 , and Se varies below 1 K as the first power of the temperature, rather than as the third power expected for a dielectric solid. In addition, it was found that the thermal conductivity of amorphous SiO_2 , Se, and Pyrex varies as $T^{1.8}$ below 1 K, quite different from the temperature dependences usually found in dielectric crystals. Earlier work² on polystyrene (PS) and polymethyl methacrylate (PMMA), and on glycerol³ above 1 K had shown indications of the same behavior. The present work on PS and PMMA below 1 K confirms this, and thus demonstrates that one is dealing with a surprisingly general phenomenon.

The apparatus and the experimental techniques were the same as reported in Ref. 1. The specific heat samples were cylinders 2 cm in diameter and 5 cm long machined from commercial extruded stock. Aside from cleaning the samples with soap and water, the samples were measured as received. Sample mass and mass of addenda was 21.66 gm and 0.2 gm for the PS and 19.82 gm and 0.14 gm for the PMMA. The thermal conductivity samples were sawed from the same material.

The experimental results together with the results for SiO_2 ¹ are shown on Figs. 1 and 2. In the region of overlap the data agree well with earlier measurements^{2,4} on different samples, which indicates that the results are not sample dependent. The specific heat, c , can be represented by $c = AT + BT^3$, plus higher order terms whose contributions are negligible below 0.8 K. The thermal conductivity below 0.5 K can be described with $\kappa(T) = C(T/K)^D$. The quantities A, B, C and D found to fit

our data best are listed in Table I together with those determined previously.

Various possible origins of the specific heat anomaly and of the thermal conductivity have been discussed.⁵ Most of them involve low frequency motional states of atoms or molecules. We wish to explore some of these possibilities specifically for polymeric structures. Our polymers contain a backbone made up of carbon atoms which structurally approximates a bowl of cooked spaghetti. To every other carbon atom in PS is attached a phenyl group ($-C_6H_5$), in PMMA, an ester ($-COOCH_3$) and a methyl ($-CH_3$) group, see Fig. 2. All other bonds are to hydrogen atoms. One-dimensional motion of free chain segments in voids could provide the mechanism to explain the low temperature thermal properties. It would require void sizes of 100 to 1000 Å, which are not known to exist in these polymers. The ends of chains are chemically different from repeat units along the chains and could conceivably have low energy motional states. Their number density, however, would depend upon the degree of polymerisation and would be sample dependent. Furthermore, the chain ends are known to have at best little effect upon the thermal properties above 0.4 K². One-dimensional motion of the chains between physical entanglement points could be a third mechanism. Such a motion, however, would appear to be restricted to polymers and hence we would have to invent a different model to explain the same observation in the other non-crystalline solids. This seems unnatural.

Hindered rotation of the phenyl and ester groups has been used to explain motions which occur between 4.0 and 150 K^{2,6,7}. It is possible

that a small fraction of these groups has motional (tunneling) states with energies small enough to become noticed below 1 K. Tunneling of the methyl group in the ester of PMMA is known to occur.⁸ A similar motion, however, does not exist for the stiff phenyl group of PS.⁸ Furthermore, the thermal conductivity of polystyrene below .5 K does not change with increased cross-linking with divinyl benzene (Berman et al., Ref. 4). Since the thermal conductivity and specific heat appear to be closely related it is doubtful that the specific heat in this temperature range will change with cross linking. Thus it is unlikely that the motion of the pendant groups can explain the low temperature thermal properties of our polymers. It should also be noted that the specific heat anomaly in GeO_2 ⁹ is independent of a Ge deficiency, and neither is it influenced in silica¹⁰ by neutron radiation damage.

The results presented here show that the low temperature thermal properties of amorphous materials are not dependent upon details of structure; we, however, have not come closer to an interpretation.

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FIGURE CAPTIONS

Figure 1. Specific heat plotted as c/T vs T^2 . Also shown are the repeat units of PS and PMMA.

Figure 2. Thermal conductivity. The squares are data taken from reference 2.

Table 1
Parameters Extracted from Data
(See text for explanation of symbols)

Material	A 10^{-7} J/gm K^2	B 10^{-7} J/gm K^4	B_{el}^* 10^{-7} J/gm K^4	C $10^{-4} \frac{\text{watts}}{\text{cm K}}$	D
PMMA	44	330	182	2.9	1.77
PS	52	460	255	1.56	1.78
SiO ₂	10	230	81	1.85	1.75
Se	7		70	7.5	1.8

* B_{el} , computed in the Debye approximation from elastic data, does not agree with B determined from c. This fact is well known for non-crystalline solids and has been discussed before, G. L. Salinger in Amorphous Materials, R. W. Douglas and B. Ellis, Eds., Wiley, London, to be published.

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