On the temperature dependence of the thermal conductivity of linear amorphous polymers

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The present study reveals that the observed variation of thermal conductivity λ with temperature, for any non-conducting linear amorphous polymer can be explained by considering phonons as chief heat carriers. It is proposed that in the temperature region below the glass transition temperature, T_g, structure scattering and chain-defect scattering are the predominant phonon scattering processes, while above T_g, vacant-site scatterings also play a significant role. Owing to the effect of temperature on the movement of structural units, the thermal resistances corresponding to these scattering processes have temperature dependence. Accordingly, relations for λ can be deduced using Matthiessen's rule. Calculated values of poly(vinyl chloride) with 0%, 10%, 20% and 40% plasticizers and several different styrene polymers are in excellent agreement with the reported experimental data, over a wide range of temperatures around T_g, maximum deviations being ~ 3%.

(Keywords: thermal conductivity; phonon scattering; linear amorphous polymers)

INTRODUCTION

A careful survey of existing literature on polymers[1,2] reveals that in spite of the very large polymer industry that exists today, and the large amount of work that has been done in polymer chemistry, synthesis and structure determination, there has been little work on correlating structure and physical properties. Among the various properties that have been studied, thermal conductivity has been studied the least, probably for the following reasons. (i) The thermal conductivity of these materials is generally very small, and its measurement is difficult and often time-consuming. (ii) As the temperature ranges for different phases of polymers, namely glassy, leathery, rubbery, viscous–rubbery and liquid, are relatively narrow, the same experimental method may not remain suitable over the entire range of interest.

Any theoretical development also faces several other problems. (i) The thermal conductivity of amorphous polymers depends on many factors, such as chemical constituents, strength of bonding, structure type, molecular weight of side groups, molecular density distribution, type and strength of defects or structural faults, size of intermediate range order, processing conditions and temperature, etc. Usually, information about these factors is not available. This makes the development of any rigorous theory a complex problem which has, so far, not been studied extensively. (ii) There are very few measurements covering all five regions, so comparison with experimental data to assess the applicability of a formalism is not always possible. (iii) There is a large scatter in the reported experimental data — the

discrepancies are found not only in the values, but varying dependence on temperature has also been reported for the same polymer[1,3,4]. Hardly any effort has been made to explain these through the structural features of these materials.

This paper considers the effect of temperature on the thermal conductivity of non-conducting linear amorphous polymers. Apparently these materials show considerable diversities in variation of λ with T. Broadly, these can be placed in three groups: (i) those that show a marked conductivity maximum in the region of the glass transition temperature T_g; (ii) those that show a broad plateau around T_g with very small positive or negative slope; (iii) those that show an almost linear increase in glassy and rubbery regions, with a change in slope at T_g. It is fascinating to see that all of these trends can be explained successfully through a common formalism developed recently by Dashora[5,6], considering structural features and the effect of temperature on the structural units in a phenomenological manner.

THEORETICAL CONSIDERATIONS

Our earlier work[5,6] and the present formalism are based on the following observations. (i) Values of various physical properties of polymers depend on a large number of factors, as mentioned in the Introduction, but the variation of properties with any physical parameter depends on the structure type and strength, and type of structural defects only. (ii) For non-conducting polymers phonons can be considered as the chief heat carriers. (iii) Since the motion of the structural units (side pendents, chain segments or molecules as a

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whole) of polymers is dependent on temperature, the most crucial aspect in this type of approach is the correct identification of the predominant scattering processes separately for different temperature regions. If the formalism is for glassy, leathery and rubbery regions only, as in the present work, the major structural change occurs in the region of the glass transition. The temperature range for such studies can be divided into two distinct regions: the region below T_g and the region above T_g.

Thermal conductivity in the region below the glass transition temperature T_g

The temperature region considered here is not very low, but is well below T_g. In this region the temperature dependence of λ is controlled by variation of phonon mean free path. The existence of some local order, even in amorphous polymers, is well established[1,7,8] and it is generally termed as intermediate-range order (IRO). Primarily, this IRO limits the phonon mean-free path. Besides, during cooling certain chain defects are also created in the system, such as bends in chains, gaps between two chains in line, chains of smaller lengths than the others, etc. Hence below T_g the following become the predominant phonon scattering processes.

1. Structure scattering. Lattice waves propagate uniformly inside each small domain with dimensions equal to the size of the IRO region and then are abruptly scattered by a sudden change of refractive index at the boundary[9,10].

The dimensions of IRO at T_g depend mainly on the processing conditions and degree of polymerization, hence it does not vary with temperature. Therefore, the contribution to thermal resistance corresponding to these processes is temperature-independent. Similar concepts have been used in the case of glasses and polycrystalline materials[7,8].

2. Chain-defect scattering. Defects introduced by bends and relatively smaller lengths of chain segments also scatter phonons, i.e. the elastic wave propagating along the chain finds itself at a point beyond which it can no longer proceed in the same direction with the same velocity. Therefore, it is reflected along the same chain or is refracted along some other permitted direction. In the temperature region below T_g, with a rise in temperature the polymeric chains straighten out more and more, increasing the corresponding mean-free path. So, the contribution to the corresponding thermal resistance decreases linearly with the rise in temperature. The chain defects are effectively identical to stacking faults[7,8] and hence are expected to show similar temperature dependence for thermal resistance.

With the above-mentioned considerations, the relation for thermal conductivity in this region, using Matthiessen's rule[6,7] can be expressed as:

$$\frac{1}{\lambda} = A + \frac{D}{T} \qquad (1)$$

The first term in this expression is the contribution to thermal resistance of structure scattering and the second is that of the chain-defect scattering. A and D are polymer-dependent parameters; their values depend on the extent of IRO in the polymer at T_g, the lengths of the

backbone chain and branch chains, the strength of the primary bonds and the molecular weight of the side groups.

Thermal conductivity in the region above the glass transition temperature T_g

In the glassy state, at relatively lower temperatures the vibrational motion of molecules is dominant, so it governs the variation of properties, although limited molecular mobilities or large torsional rotations are also possible. As temperature increases and the polymer passes to the rubbery through the leathery state, gradually individual units, atomic groups and small chain segments undergo intensive thermal motion and large torsional rotations, and the sliding of chain segments starts to play a dominant role in governing the variation of properties with temperature. This has a two-fold effect on the structure of the system. (i) Initially the dominant chain moments create some vacant sites or microvoids which scatter phonons like point defects[9,10]. With the rise in temperature, the number and size of these microvoids increases. Consequently, the contribution of vacant-site scattering to thermal resistance would increase linearly with temperature[5,6,9,10]. (ii) At the same time the dominant chain moments may also increase the IRO by increasing the chain alignments and bringing chain arrays closer. Thus chain mobilities may cause a linear decrease in the thermal resistance of the system also. Because of these two opposing effects, linear amorphous polymers apparently show different dependencies for variation trends in the thermal conductivity above T_g. Broadly these can be classified in three groups.

(A) Polymers which have relatively strong bonding, heavier chain segments and long branches, i.e. which have greater probability of chain entanglement, or polymers which have a high level of residual monomer or dimer and a low degree of polymerization. It is quite obvious that for these polymers, over a certain range of temperature above T_g, effects of type (i) mentioned above would be dominant. Thus structure scattering and vacant-site scattering become the predominant scattering processes resulting in a decrease in the thermal conductivity with a rise in temperature. It is obvious that for such systems above T_g using Mathiessen's rule, the thermal conductivity can be expressed as[6]:

$$\frac{1}{\lambda} = A + CT \qquad (2)$$

The first term in this expression is the contribution to thermal resistance of structure scattering and the second term is that of the vacant-site scattering. C is also a polymer-dependent parameter. Examples of this type of system are natural and a number of synthetic rubbers, which have been studied in our earlier work[5], and poly(vinyl chloride) (PVC) with different amounts of plasticizers, and polystrol P-33 studied in the present work.

(B) Polymers for which above T_g the effects of type (i) and type (ii) mentioned above are comparable. Thus with rise in temperature, the decrease in thermal conductivity due to vacant-site scattering is almost compensated by the increase in thermal conductivity due to increased chain mobilities, resulting in a thermal conductivity plateau over a considerable range. Accordingly, thermal conductivity of this class of polymers is given by

Table 1 Values of the characteristic constants for PVC and styrene polymers

| Polymer and specification	T_g	$A \times 10^3$ (cm k mW^{-1})	D (cm k^2 mW^{-1})	$C \times 10^4$ (cm mW^{-1})
PVC without plasticizer	363	534	26.1	
PVC with 10% plasticizer	319	547	22.6	2.29
PVC with 20% plasticizer	280	556	18.1	2.34
PVC with 40% plasticizer	260	568	12.1	2.55
Polystyrol p-33, low degree of polymerization, medium molecular weight	345[a]	130	169	13.9
Rubber-modified Polystyrene Monsanto HT-88-1000. Natural 'high impact' material with no pigment or dye	–	236	98.7	–
Polystyrene Monsanto HH-99-L2020. High molecular weight, low residual monomer, high heat distortion, unpigmented and untinted	325[a]	(for $T < T_g$) 487 (for $T > T_g$) 309	45.5 101	–

[a] Theoretically estimated value
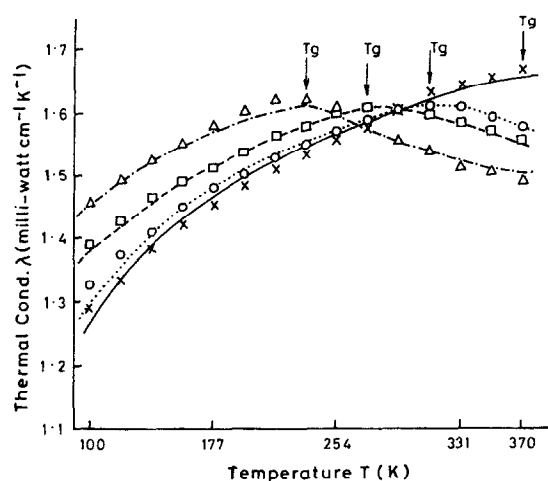
Figure 1 Variation of thermal conductivity (λ) with temperature of PVC. (—) Calculated and ($\times$) experimental data with 0% plasticizer; ($\cdots$) calculated and (O) experimental data with 10% plasticizer; (– – –) calculated and ($\square$) experimental data with 20% plasticizer; and (----) calculated and ($\triangle$) experimental data with 40% plasticizer
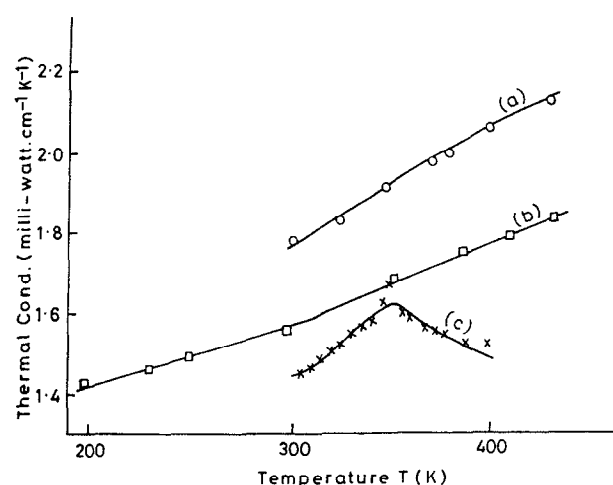

Figure 2 Variation of thermal conductivity (λ) with temperature of styrene polymers. (a) (——) Calculated and (O) experimental data of rubber-modified polystyrene Monsanto HT 88-1000; (b) (——) calculated and ($\square$) experimental data of polystyrene Monsanto HH-99-L2020; (c) (——) calculated and ($\times$) experimental data of polystyrol P-33

equation (1) in both regions, i.e. above and below T_g. Some amorphous styrene polymers show this type of variation[6].

(C) Polymers which have feeble interchain interactions and relatively lighter chain segments, and short and fewer branch chains. Obviously for these systems, above T_g the effects of type (ii) are dominant, i.e. the increase in the thermal conductivity due to increased chain mobilities completely masks the vacant-site scattering effect, again resulting in a linear increase in the thermal conductivity with rise in temperature. Therefore, for these polymers the functional form for the variation of thermal conductivity with temperature can be represented by equation (1) both above and below T_g. However, due to the chain mobilities and vacant-site scattering contributions the values of constants A and D may be different in the two regions. Styrene–acrylonitrile and acrylonitrile–butadiene–styrene studied in our earlier work[6] and some other styrene polymers studied in this work are examples of this type of polymer.

RESULTS AND DISCUSSION

Calculations have been made for the thermal conductivity of seven different polymers. Available information about the characteristic features of these polymers, as reported in the respective source of experimental thermal conductivity data (polystyrene I, polystyrene II, ref. 11; polystyrol P-33, ref. 12; PVC with 0%, 10%, 20% and 40% plasticizers, ref. 13), are listed in *Table 1*. Constants A, D, and C have been evaluated empirically for the best fit with the experimental data and these are also listed in *Table 1*. Calculated and experimental values of thermal conductivity λ, plotted in *Figures 1* and *2*, show an excellent agreement over the entire range, with maximum deviation being just 3%.

The present study offers not only a simple explanation of the varying dependencies of thermal conductivity on temperature for linear amorphous polymers, but can also be considered as a step towards understanding the complex interrelationship in the structure and bulk

physical properties of polymeric systems. However, so far, we have not been able to deduce exact relationships for the dependencies of constants A, C and D on various structural features. Qualitative inferences about these can be drawn, however, through a careful comparison of values of constants obtained through the present formalism. The following can be considered as illustrative examples.

For polymers having the same chemical constituents, values of A are inversely proportional to the dimension of the IRO region. It is well known that addition of plasticizer does not affect the structure type but it decreases the interchain interactions, consequently, IRO is expected to decrease with the addition of plasticizers. It also facilitates the motion of atomic units and sliding of small chain segments. Accordingly, an increase in the plasticizer content should result in an increase in the thermal resistance contribution of structure scattering and a decrease in the contribution to thermal resistance of chain scattering below T_g. Moreover, above T_g this should cause an increase in the vacant-site scattering contribution to thermal resistance. It is amazing to see that all these aspects are very clearly reflected in the values of constants A, D and C: values of A and C increase whereas that of D decreases with an increase in plasticizer content. The extent of IRO is also strongly dependent on the processing conditions, degree of polymerization, residual monomer content, etc. This is obvious from comparison of the value of A for the three styrene polymers, which essentially differs in these features, consequently, they show a significant difference in conductivity values and diversities in variation. Their behaviour can be easily understood through the theoretical explanation proposed here.

The present work also illustrates the following points. (i) Owing to various temperature regions, namely glassy, leathery, rubbery, viscous–rubbery and liquid, in which the thermal conductivity of polymers shows different temperature dependencies, the measured values cannot be extrapolated with confidence. (ii) Characteristic features of polymeric materials should also be reported along with the measured values of any physical quantity; only then can any meaningful comparison be made or efforts be made to develop a theoretical formalism correlating the structure and physical properties. (iii) Sometimes temperature regions for different phases of polymeric materials are quite narrow; measurements made with larger temperature intervals may not even be able to detect several interesting maxima. For example, with an interval of 70°C, i.e. from 50 to 120°C, in the case of polystyrol P-33 one would have completely overlooked the conductivity maximum or an inference of linear increase would have been drawn from the values measured at 30°C and 100°C only.

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