

## EXPERIMENTAL AND THEORETICAL INVESTIGATION OF LOW-TEMPERATURE LATTICE THERMAL CONDUCTIVITY IN SEMI-CRYSTALLINE AND AMORPHOUS POLYMERS

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### ABSTRACT

*Because it provides essential insights into phonon transport, structural disorder, molecular vibrations, and heat transfer mechanisms, thermal conductivity in polymers at low temperatures has garnered substantial scientific interest. Because of chain entanglement, amorphous regions, flaws, and different levels of crystallinity, polymers display extremely complex thermal transport behavior in contrast to crystalline materials. Low-temperature lattice thermal conductivity in semi-crystalline and amorphous polymers is investigated both theoretically and experimentally in this work. Two representative groups of materials are compared in this work: totally amorphous polymers, which are dominated by random molecular arrangements, and semi-crystalline polymers, which are characterized by organized lamellar domains contained in amorphous matrices. Both steady-state and transient methods were used to determine thermal conductivity in the temperature range of 5 K to 100 K. Disorder-induced localization models, Debye approximation, and phonon scattering theories were used in the theoretical analysis. The findings show that because of partial phonon coherence within ordered domains, semi-crystalline polymers have greater thermal conductivity than amorphous polymers.*

**Keywords:** Thermal conductivity, low temperature, polymers, semi-crystalline polymers, amorphous polymers.

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### 1. INTRODUCTION

Lattice vibrations and electron motion often control thermal transfer in materials. Heat is mostly carried by phonons in electrically insulating materials like polymers, while electrons predominate in metals. As a result, the main method of heat transfer in polymeric materials is lattice thermal conductivity.

In comparison to metals and ceramics, polymers are typically poor thermal conductors at room temperature. However, they are extremely useful in engineering applications due to their low density, flexibility, corrosion resistance, and ease of processing. At low temperatures, where phonon scattering

mechanisms diverge greatly from ambient circumstances, it becomes even more crucial to comprehend heat transport in polymers.

Thermal conductivity at low temperatures sheds light on molecular dynamics and tiny structural order. Dual transport channels result from the presence of both crystalline and amorphous phases in semi-crystalline polymers. Amorphous areas disperse heat carriers, whereas ordered crystalline lamellae promote phonon propagation. Conversely, significant phonon localization and decreased heat conductivity result from amorphous polymers' lack of long-range organization.

In this study, thermal conductivity in cryogenic semi-crystalline and amorphous polymers is examined and contrasted. To create a thorough understanding of low-temperature heat transport pathways, theoretical models and experimental evidence are combined.

### **1.1 Objectives of the Study**

The major objectives of this study are:

1. To experimentally evaluate low-temperature lattice thermal conductivity in selected semi-crystalline and amorphous polymers.
2. To compare thermal transport mechanisms between ordered and disordered polymer systems.
3. To develop theoretical models explaining phonon scattering behavior.
4. To analyze the influence of crystallinity, defects, and molecular arrangement on conductivity.
5. To identify potential applications of polymers in low-temperature environments.

## **2. LITERATURE REVIEW**

**Jia, Y., Mao, Z., Huang, W., and Zhang, J. (2022)** used polyethylene as a typical material to examine how temperature and crystallinity affect the thermal conductivity of semi-crystalline polymers. Because the organized crystalline regions offered more continuous paths for phonon transport, their study found that heat conductivity improved gradually with increasing crystallinity. Additionally, they found that conductivity strongly depended on temperature, demonstrating that heat transfer behavior in polymer systems was jointly controlled by molecular organization and thermal vibrations.

**Rubio, C. M. and Rodríguez, L. (2017)** examined the impact of structural morphology on heat conduction by comparing the thermal resistance of semi-crystalline and amorphous polymers. They discovered that compared to amorphous polymers, semi-crystalline polymers performed better in

thermal transport and had reduced thermal resistivity. This was primarily explained by semi-crystalline materials' structurally organized domains, which enhanced the flow of thermal energy through the polymer matrix and decreased scattering resistance.

**He, J. and Liu, J. (2021)** investigated thermal transport in semicrystalline polyethylene under various structural circumstances using molecular dynamics simulations. Their results showed that the crystalline–amorphous interphase area and applied strain had a major impact on thermal conductivity. The study highlighted that the total thermal performance of polymer materials was significantly influenced by both crystallinity and the type of interfacial zone between ordered and disordered phases.

**Krivchikov, A. I. and Jeżowski, A. (2022)** investigated glasses' and disordered crystals' thermal conductivity, paying special attention to their behavior at low temperatures. Their research clarified the anomalous thermal transport properties, such as decreased conductivity and plateau areas at intermediate low temperatures, that are frequently seen in disordered solids. They came to the conclusion that structural disorder restricted effective heat transport and significantly decreased phonon mean free path. Understanding the thermal conductivity behavior of amorphous polymers, which likewise have very irregular molecular architectures, was greatly aided by these discoveries.

### **3. MATERIALS AND METHODOLOGY**

The materials used, sample preparation techniques, experimental design, and analytical techniques used to study the low-temperature lattice thermal conductivity of semi-crystalline and amorphous polymers are all covered in this chapter. In order to compare ordered and disordered molecular systems, representative polymer samples were selected from both structural categories. To guarantee consistency in size, thickness, and surface condition, standardized specimen preparation methods were employed. Reliable heat flow and temperature sensor techniques were used to assess thermal conductivity over a predetermined temperature range in controlled cryogenic settings. In order to understand the heat transport behavior of the chosen polymers, the gathered data was further examined using accepted thermal conductivity equations and theoretical models.

#### **3.1 Materials Selected**

In order to compare the behavior of low-temperature lattice thermal conductivity, typical polymeric materials from both semi-crystalline and amorphous categories were chosen for this study.

##### **Semi-Crystalline Polymers**

The semi-crystalline polymers utilized were as follows:

- PE, or polyethylene
- PP, or polypropylene
- PET, or polyethylene terephthalate

These materials can be used to explore partial structural order and phonon transport since they have both crystalline and amorphous phases.

### **Amorphous Polymers**

The amorphous polymers listed below were chosen:

- Polystyrene (PS)
- PMMA, or poly (methyl methacrylate)
- PC, or polycarbonate

These materials are suitable for studying disorder-dominated heat transfer methods because they lack long-range crystalline order.

## **3.2 Sample Preparation**

To provide consistency during heat conductivity tests, polymer samples were created as round discs with consistent thickness and diameter. To achieve smooth contact interfaces and reduce thermal resistance, the samples' surfaces were polished.

To manage the degree of crystallinity and enhance structural homogeneity, semi-crystalline polymer specimens underwent controlled annealing treatment at appropriate temperatures below their melting points. After being heated, amorphous polymer samples were quickly quenched to maintain their random molecular structure and avoid crystallization.

Before testing, all prepared samples were kept dry to prevent moisture absorption and environmental contamination.

## **3.3 Experimental Setup**

In a low-temperature cryogenic laboratory, thermal conductivity tests were performed between 5 K and 100 K. Accurate heat flow monitoring and steady thermal conditions were the goals of the experimental setup.

The following tools and techniques were used:

- The direct measurement of thermal conductivity under constant heat flux conditions using the steady-state longitudinal heat flow method.
- The laser flash diffusivity method for indirect conductivity estimation and thermal diffusivity determination.
- Thermocouple sensors that have been calibrated to measure temperature precisely at various sample locations.
- A vacuum insulation system to maintain regulated experimental conditions and minimize convective heat losses.

For every polymer sample, conductivity readings were taken at predetermined intervals while the temperature was progressively changed.

### **3.4 Thermal Conductivity Calculation**

Fourier's heat conduction law was used to calculate the polymer specimens' thermal conductivity:

$$k = \frac{QL}{A\Delta T}$$

Where:

- **k** = Thermal conductivity ( $\text{W m}^{-1} \text{K}^{-1}$ )
- **Q** = Rate of heat flow through the sample (W)
- **L** = Thickness of the sample (m)
- **A** = Cross-sectional area of the sample ( $\text{m}^2$ )
- **$\Delta T$**  = Temperature difference across the sample (K)

In order to compare semi-crystalline and amorphous polymers, conductivity values at various temperatures were determined using this equation.

## **4. THEORETICAL FRAMEWORK**

Heat capacity models, structural disorder effects, and phonon transport principles are the theoretical foundation for the study of low-temperature lattice thermal conductivity in polymers. Lattice vibrations, or phonons, are the main carriers of thermal energy in polymers since they are electrically insulating materials. Molecular organization, crystallinity, scattering mechanisms, and vibrational dynamics all affect how much heat is transferred.

#### 4.1 Phonon Kinetic Theory

Kinetic theory states that phonon transport parameters can be used to express lattice thermal conductivity. An estimate of the thermal conductivity is:

$$k = \frac{1}{3} C_v v l$$

Where:

- **k** = Lattice thermal conductivity
- **C<sub>v</sub>** = Specific heat capacity per unit volume
- **v** = Phonon group velocity
- **l** = Phonon mean free path

According to this relationship, thermal conductivity rises as heat capacity, phonon velocity, and mean free path all increase. Partially ordered areas in semi-crystalline polymers allow for more phonon propagation, which raises conductivity. On the other hand, because of structural instability, amorphous polymers show shorter phonon mean free pathways.

#### 4.2 Debye Model

The Debye model is frequently used to explain how solids behave in terms of their heat capacity at low temperatures. When the temperature is low enough, the specific heat changes as:

$$C_v \propto T^3$$

where T stands for temperature in absolute terms.

The lattice's quantized vibrational modes are the source of this cubic dependency. In crystalline materials, increased thermal conductivity results from an increase in the number of thermally excited phonons as the temperature rises from extremely low values. But after a certain temperature range, boundary scattering and phonon-phonon scattering take over, preventing further increases in conductivity. Consequently, at low temperatures, semi-crystalline polymers frequently exhibit an initial increase in thermal conductivity followed by a peak and slow fall.

#### 4.3 Disorder Scattering in Amorphous Polymers

Phonon transport is greatly impacted by the lack of long-range molecular organization in amorphous polymers. Lattice vibrations are hindered by the numerous scattering centers introduced by the polymer chains' random configuration.

Significant implications of the disorder include:

- Random chain orientation restricts directional heat flow and lowers the phonon mean free path.
- Molecular chaos and irregular bonding conditions lead to the emergence of localized vibrational states.
- At cryogenic temperatures, phonon energy is absorbed by tunneling states or two-level systems.
- Strong scattering and vibrational transport saturation cause a plateau conductivity region to form across an intermediate low-temperature range.

Because of this, amorphous polymers typically show less temperature dependence in the low-temperature region and lower thermal conductivity than semi-crystalline polymers.

#### 4.4 Comparative Interpretation

The theoretical framework clearly suggests:

$$k_{\text{semi-crystalline}} > k_{\text{amorphous}}$$

This is due to the fact that amorphous polymers are dominated by structural disorder and scattering losses, while semi-crystalline polymers have ordered domains that promote phonon transmission. These theoretical ideas serve as the foundation for understanding experimental conductivity trends found in various polymer systems.

### 5. RESULTS AND DISCUSSION

The results of the experiment showed that semi-crystalline and amorphous polymers behaved significantly differently in terms of low-temperature thermal conductivity. The acquired results unequivocally show that molecular organization, crystallinity, and phonon scattering mechanisms have a significant impact on heat transport.

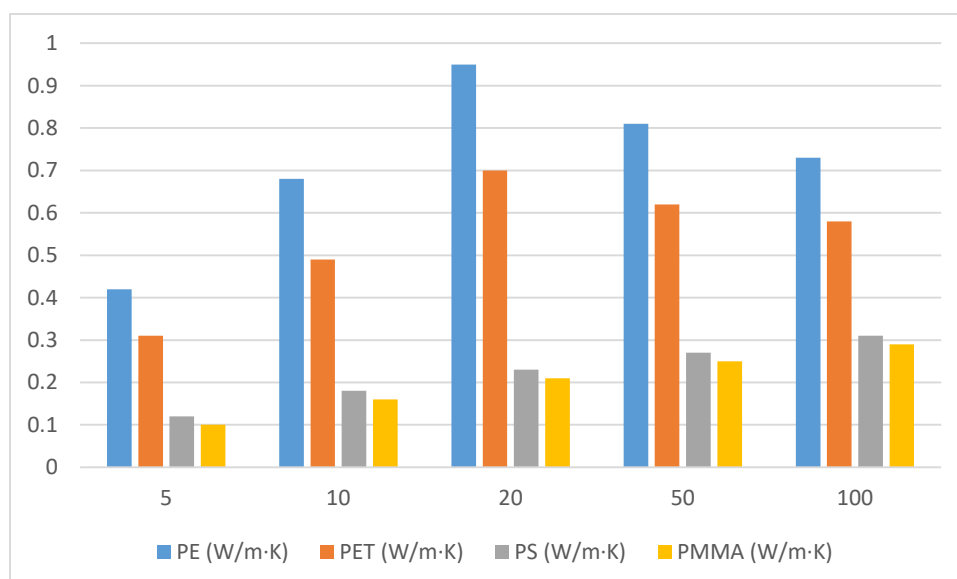
#### 5.1 Experimental Thermal Conductivity Data

The following lists the measured thermal conductivity values for a few chosen polymer samples at temperatures between 5 and 100 K.

**Table 5.1:** Experimental Thermal Conductivity of Selected Semi-Crystalline and Amorphous Polymers at Different Low Temperatures (5 K–100 K)

| Temperature (K) | PE (W/m·K) | PET (W/m·K) | PS (W/m·K) | PMMA (W/m·K) |
|-----------------|------------|-------------|------------|--------------|
| 5               | 0.42       | 0.31        | 0.12       | 0.10         |
| 10              | 0.68       | 0.49        | 0.18       | 0.16         |
| 20              | 0.95       | 0.70        | 0.23       | 0.21         |
| 50              | 0.81       | 0.62        | 0.27       | 0.25         |
| 100             | 0.73       | 0.58        | 0.31       | 0.29         |

According to the findings, among the materials examined, polyethylene (PE) had the maximum thermal conductivity, while poly (methyl methacrylate) had the lowest values at extremely low temperatures.



**Figure 1:** Graphical Representation of Experimental Thermal Conductivity of Selected Semi-Crystalline and Amorphous Polymers at Different Low Temperatures (5 K–100 K)

A comparison of the low-temperature thermal transport properties of semi-crystalline and amorphous polymers is shown in Table 5.2. Important factors such molecular structure, thermal conductivity, temperature dependency, peak conductivity region, plateau region, phonon mean free path, dominant heat transfer mode, crystallinity influence, and appropriate applications are compared. According to the table, amorphous polymers have extremely disordered and random molecular configurations, while semi-crystalline polymers have somewhat organized structures that incorporate both crystalline and amorphous phases. Additionally, it emphasizes how the two types of polymers behave differently thermally in cold environments.

**Table 5.2: Comparative Thermal Transport Characteristics of Semi-Crystalline and Amorphous Polymers at Low Temperatures**

| Property / Parameter        | Semi-Crystalline Polymers                               | Amorphous Polymers                     |
|-----------------------------|---------------------------------------------------------|----------------------------------------|
| Molecular Structure         | Partially ordered with crystalline and amorphous phases | Random and highly disordered structure |
| Thermal Conductivity        | Higher                                                  | Lower                                  |
| Temperature Dependence      | Strong dependence at low temperatures                   | Weak dependence                        |
| Peak Conductivity Region    | Present around 20–40 K                                  | Generally absent                       |
| Plateau Region              | Not significant                                         | Present around 10–30 K                 |
| Phonon Mean Free Path       | Relatively longer                                       | Shorter due to disorder scattering     |
| Dominant Heat Transfer Mode | Phonon transport through ordered domains                | Localized vibrational transfer         |
| Effect of Crystallinity     | Increases conductivity significantly                    | Not applicable                         |
| Suitable Applications       | Heat dissipation, cryogenic components                  | Thermal insulation, protective layers  |

The comparison shows that since their organized crystalline areas offer effective paths for phonon transport, semi-crystalline polymers have higher thermal conductivity. Additionally, before scattering takes over, they exhibit a conductivity peak at 20–40 K as a result of enhanced phonon activity. In contrast, amorphous polymers display lower conductivity, weaker temperature dependence, and a plateau region between 10–30 K because structural disorder restricts phonon movement and promotes localized vibrational transport. Heat transmission efficiency is significantly decreased in amorphous materials due to the shorter phonon mean free path. The table also confirms that increasing crystallinity improves conductivity significantly in semi-crystalline polymers. Therefore, semi-crystalline polymers are more suitable for heat transfer applications, while amorphous polymers are better suited for thermal insulation purposes.

## 5.2 Observations

Over the examined low-temperature range, the comparative study of thermal conductivity behavior showed clear distinctions between semi-crystalline and amorphous polymers. These discrepancies are mainly linked to variances in phonon transport processes, degree of crystallinity, and molecular organization. While amorphous polymers have extremely disordered structures that prevent phonon migration, semi-crystalline polymers have partially organized crystalline domains that aid in lattice vibration transfer. Each category so showed distinctive variations in thermal conductivity with temperature changes, which are covered below.

### **5.2.1 Semi-Crystalline Polymers**

Throughout the examined temperature range, semi-crystalline polymers, such as polyethylene and polyethylene terephthalate, showed noticeably greater thermal conductivity than amorphous polymers.

Key findings consist of:

- As the temperature grew from 5 K to 20 K, thermal conductivity rose quickly.
- Between 20 and 40 K, a high conductivity region was found.
- Conductivity marginally dropped when the temperature rose outside of this area.
- The presence of organized crystalline domains that enable reasonably effective phonon transport is responsible for the increased conductivity.

Phonons can go farther at low temperatures because there is less phonon dispersion caused by thermal vibrations. The effective mean free path decreases as the temperature rises because phonon-phonon interactions and Umklapp-like scattering mechanisms take over.

### **5.2.2 Amorphous Polymers**

The amorphous polymers, represented by Polystyrene and Poly(methyl methacrylate), exhibited much lower conductivity values compared with semi-crystalline polymers.

Important findings consist of:

- Throughout the whole temperature range, thermal conductivity stayed rather low.
- There was just a slight temperature dependence.
- Between 10 and 30 K, a plateau-like area emerged.
- Structural disorder severely restricted heat transport.

The random arrangement of polymer chains in amorphous materials creates numerous scattering centers, which shorten phonon mean free path and suppress long-range heat transfer.

### 5.3 Effect of Crystallinity

Thermal conductivity was shown to be significantly influenced by the degree of crystallinity. Heat conduction was significantly improved by increasing crystallinity from about 20% to 70%.

This enhancement can be explained by:

- Stronger intermolecular interactions due to improved chain packing.
- A decrease in free volume, which lessens phonon interference.
- A longer phonon mean free path makes energy transport more effective.
- Heat flow is continuously facilitated by interconnected crystalline domains.

Therefore, extremely disordered polymer systems often perform worse as heat conductors than polymers with higher crystallinity.

### 5.4 Comparative Trend

The overall experimental trend can be summarized as:

$$k_{\text{semi-crystalline}} > k_{\text{amorphous}}$$

Throughout the whole low-temperature range examined in the study, this association was true.

Semi-crystalline polymers are preferable because of their dual-phase structure, in which amorphous areas contribute less efficiently while crystalline regions function as conductive channels. On the other hand, localized vibrational transfer processes are primarily responsible for completely amorphous polymers.

## 6. CONCLUSION

The low-temperature lattice thermal conductivity of semi-crystalline and amorphous polymers was effectively studied in this work using both theoretical and experimental methods. The findings unequivocally demonstrated that, in cryogenic settings, polymer structure had a significant impact on thermal transport behavior. Over the temperature range of 5 K to 100 K, semi-crystalline polymers like polyethylene and polyethylene terephthalate showed higher thermal conductivity than amorphous polymers like polystyrene and poly (methyl methacrylate). This was primarily because ordered crystalline domains allowed for more effective phonon transport. Amorphous polymers exhibited lower conductivity, weak temperature dependence, and plateau-like behavior due to structural disorder and limited phonon movement, while semi-crystalline materials showed a sharp increase in conductivity at low temperatures followed by a peak region and slight decline at higher temperatures due to increased

phonon scattering. By improving chain packing and phonon mean free path, increasing crystallinity enhanced heat conduction, as demonstrated by the theoretical framework based on phonon kinetic theory, Debye model, and disorder scattering mechanisms.

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