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A THEORETICAL STUDY OF TEMPERATURE DEPENDENCE OF THERMAL DIFFUSIVITY OF LINEAR AMORPHOUS AND SEMICRYSTALLINE POLYMERS

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ABSTRACT

The On the basis of Spring Dashpot Model it is shown that the temperature dependence of the thermal diffusivity (α) of linear amorphous and semicrystalline polymers can be expressed as $\alpha = \alpha_0 \exp(kT_c / kT)$, where α_0 and kT_c are the measure of elasticity and flexibility of the polymeric chains, respectively. α_0 and $\exp(kT_c / kT)$ are the contribution of the recoverable and irrecoverable movements of polymeric chains to thermal diffusivity, respectively. Calculated values of α of twenty-two polymers are in excellent agreement with the observed values, over a wide range of temperature including glassy, leathery and rubbery regions, maximum deviation being 6%. Further the evaluated glass transition temperatures T_g are also in close agreement with the reported values, maximum deviation being less than 4% for all the polymeric samples except P4MP1.

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INTRODUCTION

The thermal diffusivity (α) is an important thermo-physical property when temperature changes are rapid. Precise values of thermal diffusivity are needed for heat flow calculations and for material selection and comparison. Therefore, the thermal diffusivity of polymers is of great practical importance to the designers of processing equipments such as extruding and injection-moulding machines. It provides insight to structure-property relationships for the material considered.

Although several attempts (Choy *et al.*, 1981; Chen *et al.*, 1977; Zhang and Fujii, 2003; Hattori, 1964; Steere, 1966; Santos *et al.*, 2005; Morikawa *et al.*, 1995; Agari *et al.*, 1995) have been made to measure the thermal diffusivity of polymeric materials, yet a few efforts have been made to explain the observed thermal diffusivities theoretically. Any theoretical development of thermal diffusivity of polymers is a challenging task as it depends on many factors such as the strength of primary and secondary bonding, presence of polar side pendants, length of side groups, constituents of main chain, crystallinity, pressure, etc. Usually, information about these factors is not available. Generally, it is not possible to calculate α from relation $\lambda = \alpha \cdot \rho C_p$ as it is very difficult to obtain literature value of the thermal conductivity (λ), density (ρ) and specific heat (C_p) for the same polymeric sample. The most intriguing feature of the thermal properties of linear amorphous and semicrystalline polymers is that these materials show considerable diversities in trends of λ with temperature

whereas there is a common trend concerning the dependence of α on temperature. Regarding trends of λ , broadly these polymers 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 negative or positive slope (iii) those that show an almost linear increase in glassy and rubbery regions, with a change in slope at T_g . In contrast, for thermal diffusivity, these materials show a common trend of exponential decrease with rise in temperature, in both glassy and rubbery state with a marked change in pre-exponent and exponent factor at T_g . The specific heat shows complex temperature dependence although it increases with temperature in both the regions below and above T_g . The varying trends of λ with temperature have been explained successfully through a formalism developed recently by Dashora and Gupta (Dashora and Gupta, 1996), considering structural features and the effect of temperature on the structural units in a phenomenological manner. Motivated by this, in the present work, a simple relation for variation of thermal diffusivity α with temperature based on Spring-Dashpot model (Hayden *et al.*, 1968; Cowie, 2004; Young and Lovell, 2004) has been proposed. It is fascinating to see that the so obtained simple mathematical relation explains successfully the observed temperature dependence of thermal diffusivity of twenty-two samples of fourteen different polymers viz. Polypropylene (PP), Polyvinylidene fluoride (PVDF), Polychlorotrifluoroethylene (PCTFE), PolyButene1 (PB-1),

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Poly4methylpentane1 (P4MP1), Polyvinylchloride (PVC), Polymethylmethacrylate (PMMA), Polystyrene (PS), Polyethyleneoxide (PEO), Polyoxymethylene (POM), Nylon, Polyethyleneterephthalate (PET), Polybutyleneterephthalate (PBT) and Polycarbonate (PC). It is quite encouraging that for all linear polymers, theoretically evaluated T_g are also quite close to the reported ones.

Development of formalism

Theoretical considerations

In case of linear polymers there are strong covalent bonds along the chain axis whereas the inter-chain interactions are weak van der Waals type or are strong polar, depending on chemical composition of the material. Depending on the structure type, different types of movements of structural units become allowed in different temperature regions. So the crucial aspect of the present approach is the correct identification of the dominant movements of the structural units in different temperature regions, which has been done here using the Spring Dashpot model (Hayden *et al.*, 1968; Cowie, 2004; Young and Lovell, 2004). According to this model, in the glassy state at relatively low temperatures, the small atomic vibrations and small angle rotations i.e. recoverable movements are dominant. The polymer in this state behaves like a stiff spring with high modulus. At high temperature, in the melt state, the irrecoverable motions like large angle rotations; skeletal vibrations of chains as whole and co-operative movements of small chains become dominant rendering the system dashpot like behaviour. At intermediate temperatures, as the transition from the glassy to rubbery through leathery state takes place, the system exhibits a mixture of both spring like and dashpot like behaviours. Initially the system is more spring like and as irrecoverable motions start picking up gradually, with increase in temperature, it becomes more dashpot like. The transition from glassy state to rubbery state can be viewed as the transformation of a stiff spring to a weak spring. For glassy, leathery and rubbery regions the major structural change occurs in glass transition region, therefore in the proposed approach the temperature range has been divided into two distinct regions: below T_g and above T_g .

Temperature dependence of thermal diffusivity

The thermal diffusivity is defined as the flux of energy, across any section, per unit enthalpy gradient, under unsteady state heat transfer condition. It may be defined through the Fourier's law for heat conduction through a medium, for unsteady state, i.e.

$$J_q = -\alpha \frac{d}{dx} (\rho C_p T) \quad (1)$$

Where J_q is flux of heat and $\rho C_p T$ represents enthalpy per unit volume. Equation (1) reveals that the state of the system, which governs allowed movements of the constituent units as well as the enthalpy per unit volume are the predominant factors in deciding the flux of energy

through a section. As the system passes from the glassy to rubbery through leathery state, heat transfer by both recoverable and irrecoverable movements contribute to thermal diffusivity.

Contribution of recoverable movements to the thermal diffusivity

According to Spring Dashpot model, for all linear amorphous and semi-crystalline polymers, in the glassy state recoverable movements i.e. the small atomic vibrations and small angle rotations are dominant. So the major portion of heat transfer takes place through the coupling of the recoverable movements. Besides the allowed small angle rotations, allowed conformations and the inter chain separations etc., the recoverable movements primarily depend on chemical composition of the polymeric chains through the primary and secondary bond strengths. Consequently the contribution of recoverable movements or chain elasticity in a given physical state is almost independent of temperature and changes only at change of state. Here it is represented by α_0 . Since below T_g these polymers behave as a stiff spring a high value of α_0 is expected below T_g and decrease in α_0 across the glass transition is representative of transition of the system from the stiff spring like to weak spring like region. According to the proposed model polymers which have symmetrical chains or relatively strong bonding, polar bonding through the side pendants, and which have greater probability of chain entanglement should have high value of α_0 below T_g . Similarly higher crystallinity (X) should also lead to the higher value of α_0 .

Contribution of irrecoverable movements to the thermal diffusivity

The heat transfer through irrecoverable movements depends on both the chain flexibility as well as the thermal state of the system. The irrecoverable movements like the large angle rotations, skeletal vibrations of chain as a whole, sliding of chain segments, chain straightening etc. depend on chain flexibility. It is proposed here that a quantitative measure of the chain flexibility can be written as the characteristic energy kT_c . Where k is the Boltzmann constant and T_c is the characteristics temperature. kT_c is a constant in a given physical state which besides inter and intra chain interactions, primarily depends on the available free volume and degree of polymerization. It also represents the energy transfer capability through irrecoverable movements in a particular system or the dashpot like character of the system. Therefore, as per proposed model its value must increase across glass transition for all linear amorphous and semicrystalline polymers. Presence of a longer sequence of aliphatic group in the backbone chain reduces the chain flexibility resulting in decrease in the value of T_c for such polymers. As the polymer crosses its glass transition region, the available free volume increases and chain straightening takes place. This process may considerably decrease the inter-chain interactions and also the chain entanglements present below T_g , resulting in an increase in the value of T_c above T_g . Moreover the thermal state of the system

represented by kT is a measure of enthalpy of the constituent units. Hence it is the ratio (T_c / T) , which governs the temperature dependence of the thermal diffusivity. Further it is proposed here that the approach from an ideal spring like to ideal dashpot like behaviour

RESULTS AND DISCUSSION

In the present study calculation have been done for the thermal diffusivity of twenty-two samples of fourteen different linear polymers over a wide range of temperature including glassy, leathery and rubbery

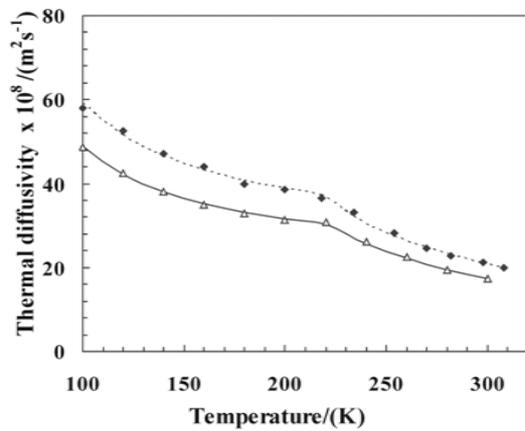


Fig 1. Variation of thermal diffusivity (α) with temperature (T). (.....) Calcd. and (\diamond) exptl. data of POM; (—) Calcd. and (Δ) exptl. data of PEO.

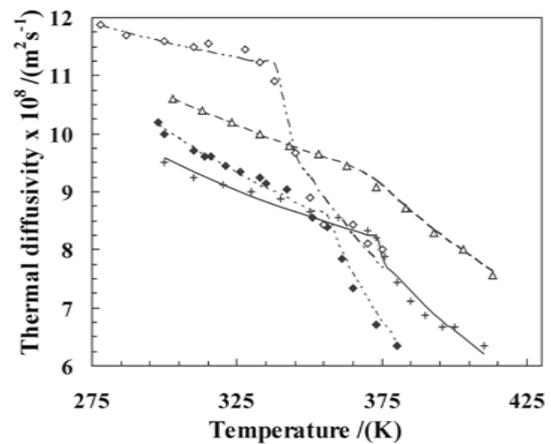


Fig 2. Variation of thermal diffusivity (α) with temperature (T). (---) Calcd. And (\diamond) exptl. data of PVC; (.....) Calcd. and (Δ) exptl. data of PMMA; (.....) Calcd. and (\diamond) exptl. data of PS^d; (—) Calcd. and (+) exptl. data of PS^b.

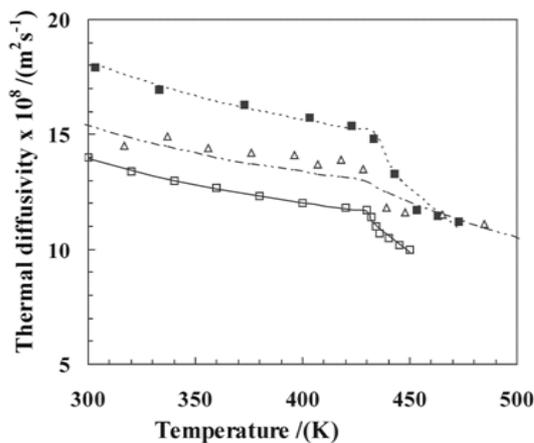


Fig 3. Variation of thermal diffusivity (α) with temperature (T). (.....) Calcd. and (\square) exptl. data of PC^e; (---) Calcd. and (Δ) exptl. data of PC^c; (—) Calcd. and (\square) exptl. data of PC^h

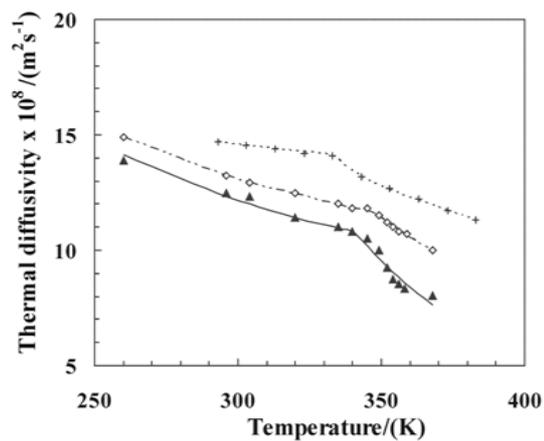


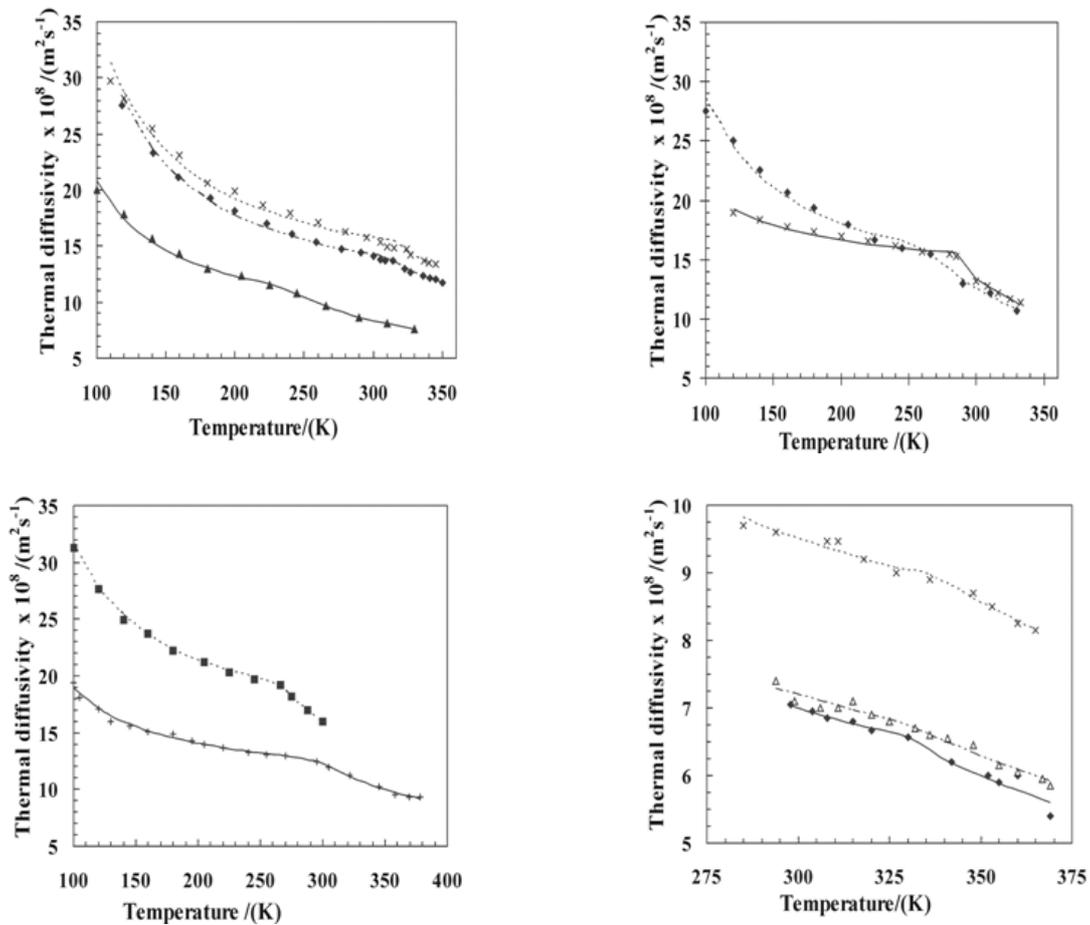
Fig 4. Variation of thermal diffusivity (α) with temperature (T). (.....) Calcd. and (+) exptl. data of Nylon; (---) Calcd. and (\diamond) exptl. data of PET($X=0.3$); (—) Calcd. and (\blacktriangle) exptl. data of PET ($X=0$).

would follow an exponential path i.e. the irrecoverable movements are expected to pick up exponentially with rise in temperature. Consequently, an exponential dependence on (T_c / T) is expected for the contribution of irrecoverable movements to the thermal diffusivity. Combining both the contributions, the variation of the thermal diffusivity with temperature for linear amorphous and semi-crystalline polymers may be expressed as

$$\alpha = \alpha_0 \exp(T_c / T) \quad (2)$$

According to spring dashpot model, the contribution of the recoverable movements in the region below glass transition must be higher than the contribution of the irrecoverable movements and vice versa in the region above T_g .

The calculated and reported experimental (Choy *et al.*, 1981; Chen *et al.*, 1977; Zhang and Fujii, 2003; Hattori, 1964; Steere, 1966; Santos *et al.*, 2005; Morikawa *et al.*, 1995; Agari *et al.*, 1995) values of α of these twenty-two polymeric samples are shown in Figures (1-8). The maximum deviation in values of calculated thermal diffusivities and the reported ones is less than 6% which is well within the experimental uncertainties. The maximum percentage



deviations for these polymers are: POM^a(2.28%), PEO^a (1.4%), Nylon^a (0.39%), P4MP1^a (2.01%), PB-1^a (4.25%), PP^e (3.1%), PP^a (1.4%), PVC^d (5.3%), PMMA^f (1.2%), PS^h (2.4%), PS^d (3.4%), PC^h (1.4%), PC^g(5.9%), PC^c (5.85%), PET(Amorphous)^b (4.87%), PET(X=0.3)^b (0.76%), PBT(X = 0.12)^a (2.53%), PBT(X=0.34)^a (5.76%), PVDF^a (3.9%), PCTFE^d (3.7%), PCTFE^d (1.9%) and PCTFE^d (1.7%). A careful analysis of Figures (1-8) reveals that in glassy, leathery and rubbery region with the rise in temperature thermal diffusivity of all linear amorphous and semi-crystalline polymers exhibit a common trend of exponential decrease. As expected according to the proposed description there is a marked change in both pre exponent and exponent factors at the glass transition. The calculated values of characteristic constants α_0 and T_c giving the best fit with the reported experimental values of diffusivity [1-8], both in the region below and above T_g , have been given in Table 1. This table also includes the reported crystallinity (X) of the polymeric samples. For all the polymers considered here the value of pre exponent factor α_0 decreases on glass transition representing the marked decrease in spring like behaviour while T_c increases on glass transition representing the increase in the dashpot like behaviour. For all polymers in the region below glass transition the value of α_0 is higher than $\exp(T_c/T)$ and vice versa in the region above T_g which clearly indicates that below T_g most of the heat is diffused through the recoverable

movements while above T_g irrecoverable movements play dominant role. It is quite fascinating to see that the values of constants α_0 and T_c for these polymers correlate well with their structural features.

Following are some of the interesting observations: the strictly linear polymers POM and PEO have symmetrical chains possessing polar backbone bonds that encourage strong intermolecular attraction; both these polymers have highly stiff chains and therefore much higher α_0 in the region below and above T_g . The carbonate molecule also has a symmetrical structure and is more polar than the ester group thus for amorphous PC the value of α_0 is higher and the value of T_c is lower than those of amorphous PET. Comparison of the semi crystalline samples of PBT and PET of same crystallinity shows that α_0 is more and T_c is less for PBT because the presence of longer sequence of methyl groups in the repeating units of PBT renders the chains lesser flexibility and makes PBT more polar than PET. A careful inspection for PP^e, PB-1 and P4MP1 shows that increase in side chain length, in the region below T_g will stiffen the chain so that α_0 increases as side chain length increases. The T_c value below T_g for P4MP1 is the least among these three suggesting that the chains in this polymer below T_g may be highly entangled reducing the chain flexibility in the region below T_g . It seems that above T_g chain straightening occurs and there is increase in the

Table 1 Values of crystallinity (X), the glass transition temperature (T_g) and constants for different polymers

| Polymer | X | T_g (K) | | | $\alpha_0 \times 10^8$ ($m^2 s^{-1}$) | | T_c (K) | |
|--------------------|-------------|--------------|--------|-------|--|-------------|--------------|-------------|
| | | exptl. | Calcd. | % dev | below T_g | above T_g | below T_g | above T_g |
| POM ^a | 0.63 | 202 | 210 | 3.96 | 25 | 4.46 | 84 | 462 |
| PEO ^a | 0.8 | 210 | 218 | 3.81 | 20 | 3.59 | 88 | 472 |
| NYLON ^f | Crystalline | 328 | 327 | 0.30 | 10.22 | 3.06 | 107 | 501 |
| P4MP1 ^a | 0.23 | 300 | 278 | 7.33 | 13.36 | 2.25 | 44 | 536 |
| PB-1 ^a | 0.55 | 256 | 259 | 1.17 | 11.31 | 2.47 | 93 | 487 |
| PP ^e | Amorphous | 283 | 290 | 2.47 | 10.43 | 2.91 | 59 | 431 |
| PP ^a | 0.6 | 263 | 264 | 0.38 | 14.39 | 3.97 | 79 | 418 |
| PVC ^d | Amorphous | 333 | 332 | 0.30 | 8.53 | 0.6 | 94 | 963 |
| PMMA ^f | Amorphous | 370 | 372 | 0.54 | 5.3 | 1.33 | 211 | 721 |
| PS ^h | Amorphous | 373 | 368 | 1.34 | 4.39 | 0.53 | 234 | 1009 |
| PS ^d | Amorphous | 356 | 355 | 0.28 | 3.6 | 0.098 | 309 | 1580 |
| PC ^h | Amorphous | 426 | 427 | 0.23 | 7.68 | 0.45 | 179 | 1390 |
| PC ^g | Amorphous | 432 | 425 | 1.62 | 9.96 | 0.589 | 180 | 1380 |
| PC ^c | Amorphous | 430 | 420 | 2.33 | 8.81 | 2.97 | 167 | 630 |
| PET ^b | Amorphous | 342 | 340 | 0.58 | 4.56 | 0.095 | 294 | 1614 |
| PET ^b | 0.3 | 346 | 346 | 0.00 | 5.58 | 0.8 | 256 | 929 |
| PBT ^a | 0.12 | 312 | 306 | 1.92 | 9.11 | 3.05 | 133 | 468 |
| PBT ^a | 0.34 | 320 | 308 | 3.75 | 10.55 | 3.62 | 120 | 450 |
| PVDF ^a | 0.46 | 230 | 232 | 0.87 | 7.11 | 2.75 | 109 | 333 |
| PCTFE ^d | 0.77 | 322 | 324 | 0.62 | 3.47 | 1.62 | 209 | 456 |
| PCTFE ^d | 0.82 | 325 | 328 | 0.92 | 3.73 | 1.9 | 196 | 417 |
| PCTFE ^d | 0.84 | 332 | 330 | 0.60 | 5.26 | 2.79 | 176 | 392 |

Note:-The experimental data for thermal diffusivity of the polymer has been taken from ^aRef.1, ^bRef.2, ^cRef.3, ^dRef.4, ^eRef.5, ^fRef.6, ^gRef.7, ^hRef.8.

intermolecular distance so that T_c increases and α_0 decreases with the increase in side chain length representing the increased chain flexibility. Inspecting the fluoro polymers PVDF and PCTFE one finds that the introduction of chlorine atom in PCTFE, which is larger than the fluorine atom, reduces the close chain packing. This increase in the chain flexibility is clearly reflected in the values of T_c of PCTFE and PVDF.

The study reveals that the semi-crystalline polymers have higher values of α than the amorphous polymers and the latter shows more drop in value as it crosses the glass transition region. PMMA being helical do not show much variation in constants across glass transition as the other amorphous polymers are showing. Helical polymers like PMMA, PCTFE and Nylon show a smoother variation across the glass transition. As expected the value of α_0 is more and T_c is less, in regions both below and above T_g , for the samples having higher crystallinity in case of samples of PCTFE, PBT, PET and PP. The glass transition temperatures T_g computed through the intersection of trends below T_g and that above T_g , are also in close agreement with reported experimental values of T_g as shown in Table1. The maximum deviation in values of calculated glass transition temperature and the reported (experimental) one is less than 4 % except for P4MP1 which is 7.3%.

CONCLUSIONS

In this paper, a simple relation for variation of thermal diffusivity α with temperature based on the Spring Dashpot model has been proposed. According to this model, in the glassy state the recoverable movements and in the rubbery state the irrecoverable movements of the

polymeric chains are dominant. The study proposes that the irrecoverable movements are expected to pick up exponentially with rise in temperature. The allowed movements of the constituent units of the polymeric chain as well as the enthalpy per unit volume are the predominant factors in governing the thermal diffusivity of the polymer. It is interesting that the so obtained simple mathematical relation explains successfully the observed temperature dependence of thermal diffusivity of twenty-two samples of fourteen different polymers. The proposed constants correlate the trends of diffusivity with the structural features of the polymers besides providing the values of thermal diffusivities as a function of temperature for linear amorphous and semi crystalline polymers which can be used in absence of available experimental data.

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