Thermal Conductivity of Cross-linked Polymers

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ABSTRACT: Thermal conductivity of cross-linked polymers was studied theoretically. A theory derived from the network model, which consists of thermal conduction through van der Waals and primary bonds, predicts that the thermal conductivity increases with an increasing degree of cross-linking. Calculations for estimating the effect of cross-linking on the thermal conductivity were made for polystyrene and poly(methyl methacrylate). Thermal conduction through the van der Waals and primary bonds was also discussed using the Debye formula for the thermal conductivity of low molecular crystals.

KEY WORDS Thermal Conductivity / Cross-linking / Primary Bond / Van der Waals Bond / Specific Heat / Sound Velocity / Grueneisen's Number / Polymer /

From studies of thermal conductivity of linear amorphous polymers, it has become clear that this property is dependent on molecular weight[1,2] and molecular orientation.[3,4] These macroscopic parameters are essentially related to the energy transport through van der Waals and primary bonds. Eiermann and Hellwege, *et al.*,[3-5] pointed out that the thermal conductivity through the primary bonds is about ten times greater than that through the van der Waals bonds. The orientation effect, as a typical example, has been explained in terms of the "elementary" resistances of these bonds. By stretching the polymer chain, primary bonds are aligned in the direction of stretching and van der Waals bonds perpendicular to it, so that the thermal conductivity increases in the direction of stretching and decreases in the direction perpendicular to it.

When a polymer is cross-linked by chemical methods or irradiation, the effects of cross-linking are observed in some physical properties of the polymer such as the specific volume or the glass transition temperature.[6] These effects have been discussed from the standpoint of the change in the molecular weight of segments between cross-links. However, it is also possible to discuss these effects on the basis of the change in the relative number of the van der Waals bonds (or primary ones), because cross-linking replaces some van der Waals bonds with covalent ones. Recently, the thermal conductivity of some cross-linked polymers has been investigated and found to increase with increasing degrees of cross-linking.[7,8]

In this paper we will discuss theoretically the effect of cross-linking on the thermal conductivity, using the concept presented by Eiermann and Hellwege, *et al.*, in the interpretation of the thermal conductivity for linear amorphous polymers.

THEORETICAL CONSIDERATIONS

Theoretical Equation for the Thermal Conductivity for Cross-linked Polymers

An equation for estimating the effect of cross-linking on the thermal conductivity of polymers can be derived, using the network model presented by Eiermann and Hellwege, *et al.*,[3-5] for the thermal conduction of linear amorphous polymers. On the macroscopic basis, it is reasonable to assume that one-third of polymer segments are oriented in one direction, while the remaining two-thirds are oriented in a direction perpendicular to the first segments (see

Figure 8 in ref 8). When a thermal gradient exists in the polymer, the over-all thermal resistance of the polymer is believed to result from the separate contributions, R_1 and R_2, of the polymer segments vertical and parallel to the direction of the thermal gradient. Then R, the over-all thermal resistance, is given by

$$3R = 2R_1 + R_2 \qquad (1)$$

As has been discussed in a previous paper,[8] only R_1 will be altered by introducing cross-links into the polymer. However, in the direction of the thermal gradient one-half of the value of the cross-linking parameter $X = M_g/M_c$ should be accounted for, where M_g is the molecular weight of a chain unit and M_c is that of the chain segments between cross-links. The thermal resistances R_1 and R_2 are therefore described as follows

$$\frac{1}{R_1} = \frac{X/2}{R_e} + \frac{1-X/2}{R_w} \; ; \qquad R_2 = R_e \qquad (2)$$

R_w and R_e are the thermal resistances of the van der Waals and primary bonds. Inserting eq 2 in eq 1, we get the over-all thermal resistance of the cross-linked polymer:

$$3R = \frac{(2+X/2)R_e R_w + (1-X/2)R_e^2}{(X/2)R_w + (1-X/2)R_e} \qquad (3)$$

Since the thermal resistance is reciprocal to the thermal conductivity, eq 3 can be written as follows:

$$\lambda_c = \frac{(X/2)\lambda_e + (1-X/2)\lambda_w}{(2+X/2)\lambda_e + (1-X/2)\lambda_w}\lambda_e \qquad (4)$$

where λ_c is the thermal conductivity of the cross-linked polymer, λ_w and λ_e are the thermal conductivities through the van der Waals and primary bonds. If the parameter $X=0$, eq 4 becomes

$$\frac{3}{\lambda_0} = \frac{1}{\lambda_e} + \frac{2}{\lambda_w} \qquad (5)$$

This is identical to the equation presented by Eiermann[5] for linear amorphous polymers. To compare the thermal conductivities of cross-linked and uncross-linked polymers, the following calculation was carried out. From eq 4 and 5, the ratio of λ_c to λ_0 is

$$\frac{\lambda_c}{\lambda_0} = \frac{(X/2)P+(1-X/2)}{(2+X/2)P+(1-X/2)}(2P+1)$$
$$= \frac{1+(P-1)X/2}{1+\{(P-1)/(2P+1)\}X/2} \qquad (6)$$

The second term of the denominator is generally small, so that eq 6 can be expressed in the following form

$$\frac{\lambda_c}{\lambda_0} = \left\{1+(P-1)\frac{X}{2}\right\}\left\{1-\left(\frac{P-1}{2P+1}\right)\frac{X}{2}\right\}$$
$$= 1 - \frac{P^2-P}{2P-1}X \qquad (7)$$

Since the value $P=\lambda_e/\lambda_w$ is approximately 10, we get the simple equation:

$$\frac{\lambda_c}{\lambda_0} = 1 + 4.3X \qquad (8)$$

Thus, from eq 7 or eq 8 we can estimate theoretically the effect of cross-linking on thermal conductivity.

Theoretical Equation for Thermal Conductivity for Amorphous Copolymers

In this section we discuss the thermal conductivities, λ_e and λ_w. In the following way data on the thermal conductivity of copolymers permits an estimation of the magnitude of λ_e and λ_w. In discussing the thermal conductivity of copolymers, it is necessary to define parameters f_a and f_b ($f_a = 1-f_b$). They represent the fractions of monomer units A and B found in the copolymer chain:

$$f_a = \frac{N_a}{N_a + N_b}, \qquad f_b = \frac{N_b}{N_a + N_b} = 1 - f_a \qquad (9)$$
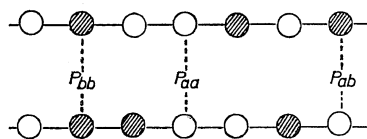
Number of Monomer Units A and B in the Copolymer Chain ---- N_a and N_b

$$f_a = \frac{N_a}{N_a + N_b} \; , \; f_b = \frac{N_b}{N_a + N_b} = 1 - f_a$$

$$P_{aa} = f_a^2 \; , \; P_{bb} = f_b^2 \; , \; P_{ab} = 2f_a f_b$$

Figure 1. Schematic representation of copolymer system.

where N_a and N_b are the number of monomer units A and B in the copolymer chain. The probabilities P_{aa} and P_{bb} that the same monomer pair will be found in the two different polymer chains can be expressed as

$$P_{aa}=f_a{}^2=\left(\frac{N_a}{N_a+N_b}\right)^2; \quad P_{bb}=f_b{}^2=\left(\frac{N_b}{N_a+N_b}\right)^2 \tag{10}$$

The probability P_{ab} for the different monomer pair is

$$P_{ab}=2f_af_b=\frac{2N_aN_b}{(N_a+N_b)^2} \tag{11}$$

As can be seen in Figure 1, the thermal resistance R_w of the van der Waals bond, similar to that for the cross-linked polymer, is expressed by

$$\frac{1}{R_w}=\frac{P_{aa}}{R_{aw}}+\frac{P_{bb}}{R_{bw}}+\frac{P_{ab}}{R_{abw}} \tag{12}$$

where R_{aw}, R_{bw}, and R_{abw} are the thermal resistances of the van der Waals bonds with the same monomer pair or a different one. Substituting eq 12 for R_1 in eq 1 and rewriting the equation of thermal conductivity, we obtain the following equation

$$\lambda_{cop}=\frac{3(P_{aa}\lambda_{aw}+P_{bb}\lambda_{bw}+P_{ab}\lambda_{abw})}{2+P_{aa}(\lambda_{aw}/\lambda_e)+P_{bb}(\lambda_{bw}/\lambda_e)+P_{ab}(\lambda_{abw}/\lambda_e)} \tag{13}$$

If λ_{abw} can be expressed as an arithmetic mean value of λ_{aw} and λ_{bw}, eq 13 is simplified as

$$\lambda_{cop}=\frac{3f_a\lambda_{aw}+3f_b\lambda_{bw}}{2+f_a(\lambda_{aw}/\lambda_e)+f_b(\lambda_{bw}/\lambda_e)} \tag{14}$$

Indeed, it was found that eq 14 holds for the case of styrene—methyl methacrylate copolymer (ST—MMA).

Thermal Conductivity Obtained for the Heat Currents through the van der Waals and Primary Bonds

Recently, Knappe, et al., measured the thermal conductivity for some copolymers in the temperature range between -180 and $140°C$. In this study the calculation for estimating the values of λ_e and λ_w was made using the values of ST—MMA copolymer whose composition is known. In Figure 2 the solid line is the calculated curve obtained as the best fit of eq 13 to
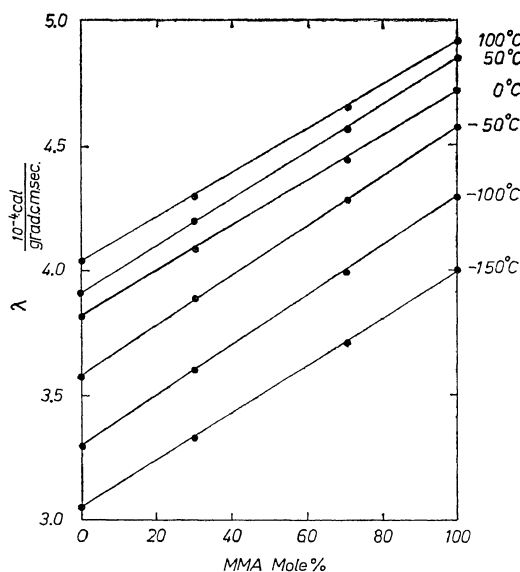

Figure 2. Thermal conductivity of styrene-methylmethacrylate copolymer: ●, measured (data of Knappe, et al.); —, calculated.
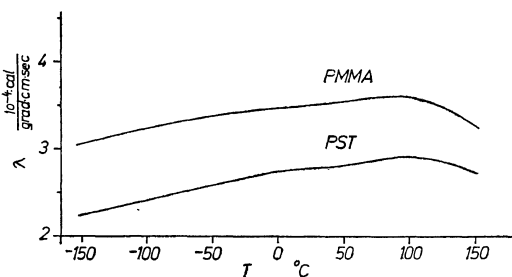

Figure 3. Temperature dependence of the thermal conductivity through the van der Waals bond.

the measured thermal conductivity. Figure 3 shows the temperature dependence of the calculated thermal conductivity for the van der Waals bond. In the temperature curve, a break was found at the glass transition temperature for both PMMA and PST. From this fact, the observed break for amorphous polymers at the glass transition temperature can be directly related to the state of the van der Waals forces. Figure 4 shows the temperature dependence of the thermal conductivity for the primary bond. For comparison, the thermal conductivity data of inorganic glasses are also plotted.[10] The value at room temperature is in the order of 10^{-3} cal/grad cm sec, as well as those for the inor-
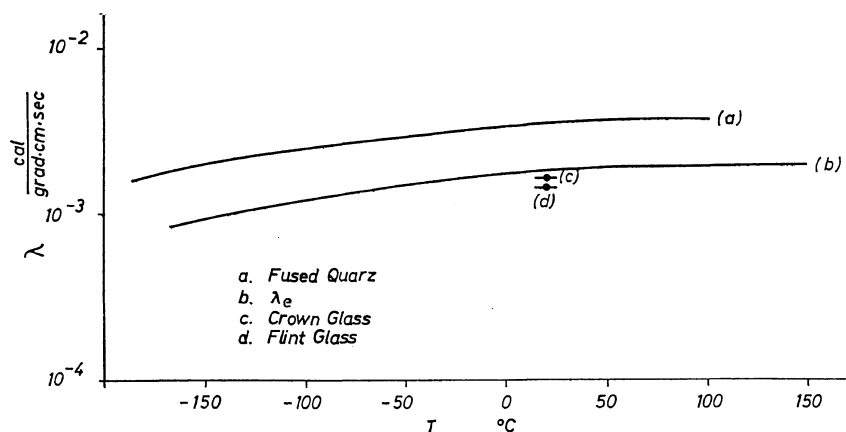
Figure 4. Temperature dependence of the thermal conductivity through the primary bond.

ganic glasses, which is about ten times greater than the thermal conductivity through the van der Waals bond. The thermal conductivity, unlike λ_w, was found to increase with increasing temperature without any change at the glass transition temperature.

Thermal Conduction through the van der Waals Bond

According to the theory of thermal conductivity for low-molecular substances,[10] λ is expressed as follows

$$\lambda = \tfrac{1}{3} C_v \rho u l \qquad (15)$$

In this equation C_v is the specific heat at constant volume, ρ is the density, u is the sound velocity and l is the average-mean free path of phonons. There are two primary factors restricting the mean free path,[11] namely, the interactions between the phonons themselves and the interactions between the phonons and defects, so that the mean free path depends on temperature and structure. For an amorphous substance at high temperature, the mean free path may be taken as a constant value independent of temperature.[10] Consequently, the behavior of the thermal conductivity at high temperatures is characterized by the factors C_v, u, and ρ. Using this expression, the thermal conductivity through the van der Waals bond will be discussed as follows.

Specific Heat. The specific heat at constant volume may be calculated by using the thermo-

Table I. A values of poly(methyl methacrylate) and polystyrene

Temp, °C	PMMA, g/cal	PST, g/cal
20	5.1×10^{-4}	6.9×10^{-4}
106.7	—	7.3×10^{-4}

dynamic relationship

$$C_p - C_v = \frac{\alpha^2 v T}{\beta} \qquad (16)$$

where α is the coefficient of thermal expansion, β is the isothermal compressibility and v is the specific volume. Specific heat at constant pressure C_p is determined by experiment. If insufficient data for the evaluation of eq 16 are available, the following equation may be used for the estimation of C_v from C_p:

$$C_p - C_v = C_p^2 A T \qquad (17)$$

A seems to be constant in the temperature range where no transition occurs. For PMMA and PST, we calculated A values at two temperatures below and above the glass transition temperature (see Table I). The data necessary for the evaluation of A values were taken from the literature.[12-15] Figures 5 and 6 show the temperature dependence of the specific heat for PMMA and PST. The values C_v were calculated with both eq 16 and eq 17. From Figures 5 and 6, it is seen that C_v contributed from lattice vibrations increases with increasing temperature without any increase
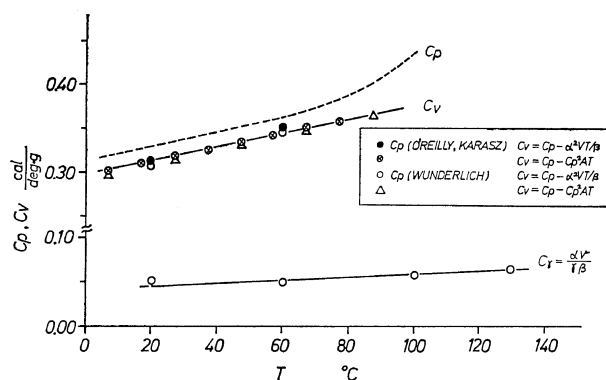
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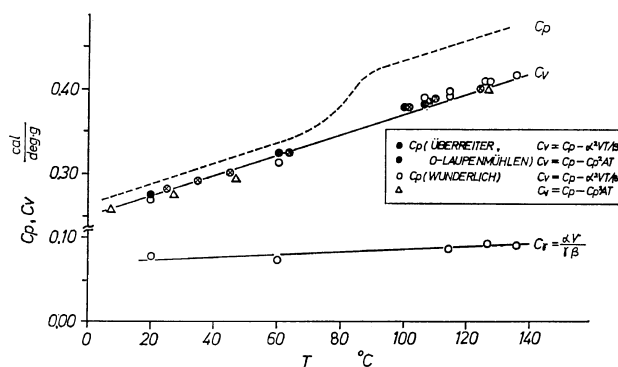**Figure 5.** Specific heat of poly(methyl methacrylate).

Figure 6. Specific heat of polystyrene.

at the glass transition temperature T_g, while C_p increases abruptly with hole formation at T_g. For chain structure as found in linear polymers, the anisotropy of the forces must be considered. The forces between chains are weaker than the forces along the chain. Taking into account weak interactions between the chains, the specific heat C_v can be divided into two elements, *i.e.*, the contributions from the intra- and inter-chain vibrations.[15,16] If we apply the specific heat at constant volume to the thermal conductivity through the van der Waals bond, we should have only the specific heat due to the inter-chain vibrations.[16] It is known that the specific heat C_γ obtained from Grueneisen's equation corresponds to that due to the inter-chain vibrations.[16] Grueneisen's equation is written as follows[17]

$$\gamma_G = -\left(\frac{\partial \ln \Theta}{\partial \ln V}\right)_T = \frac{\alpha v}{C_\gamma \beta} \qquad (18)$$

where Θ is the Debye temperature and γ_G is the Grueneisen number. According to Slater,[18] the Grueneisen number can be expressed as

$$\gamma_G = \frac{a_2}{a_1^2} - \frac{2}{3} \qquad (19)$$

In this expression a_1 and a_2 are the first and second compressibility coefficients in Bridgman's relation given by

$$\frac{\Delta V}{V} = -a_1 P + a_2 P^2 - \cdots \qquad (20)$$

where ΔV is the change in volume, V is the original volume and P is the pressure. The determinations of a_1 and a_2 for some typical polymers were made by using the compressibility data of Hellwege, *et al.*[12] Figure 7 shows the Grueneisen number calculated with eq 19 for PST, PMMA, and high-pressure polyethylene. The values at room temperature are 3.8 for PST and PMMA. Recently, Wada, *et al.*,[16] reported
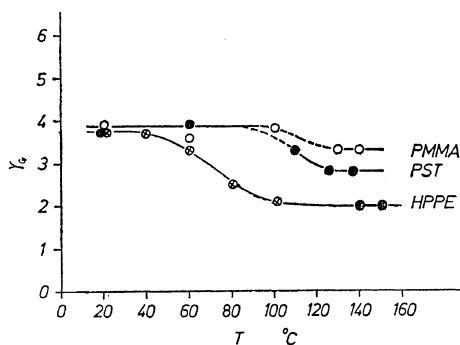
Figure 7. Grueneisen numbers for some polymers in the temperature range 20—150°C.

the Grueneisen number determined from the pressure dependence of the sound velocity. They showed that the values at room temperature are about 4 for PST and PMMA. The values obtained here seem to give the lower limit.[19] From Figure 7 it can be seen that the Grueneisen number is almost constant except for the change near the transition temperature. However, in any case, a remarkable decrease was found in the transition range. These results may be useful for a discussion of the temperature dependence of the sound velocity, which will be given later. From the γ_G values, the specific heat C_γ can be evaluated with eq 18. The results are also shown in Figures 5 and 6. The calculated C_γ, as pointed out by Wada, et al., is quite small. The general behavior of C_γ is similar to C_v, but the temperature dependence of C_γ is smaller than that of C_v. When we discuss the specific heat of polymers, Tarasov's expression[20] which consists of both one- and three-dimensional terms based on the anisotropic nature of the polymer chain, is applied to this property and is given by

$$\frac{C_v}{R} = D_1\left(\frac{\Theta_1}{T}\right) - \frac{\Theta_3}{\Theta_1}\left[D_1\left(\frac{\Theta_3}{T}\right) - D_3\left(\frac{\Theta_3}{T}\right)\right] \quad (21)$$

where D_n is the n-dimensional Debye function and Θ's are the Debye temperatures. At low temperatures, the inter-chain vibrations dominate and the specific heat of the polymer depends on the cube of the temperature, so that C_γ is closely approximated by the Debye function:[11]

$$C_\gamma = 9NK_b\left(\frac{T}{\Theta}\right)^3 \int_0^{\Theta/T} \frac{x^4 e^x}{(e^x-1)^2}\,dx; \quad \left(x = \frac{\hbar\omega}{K_b T}\right) (22)$$

where K_b is the Boltzmann constant, $\hbar$ is the Planck constant divided by 2π, N is the number of modes of vibrations and ω is the angular frequency.

Sound Velocity. From the Debye theory which predicts the cubic dependence of the specific heat on temperature at low temperatures, the Debye temperature is related to the sound velocity[11] as

$$\Theta = \left(\frac{\hbar u}{K_b}\right)\left(\frac{6\pi^2 N}{V}\right)^{1/3} \quad (23)$$

Combining eq 18 and eq 23, we get the following relations

$$u = \text{constant } V^{-\gamma+1/3} = K\rho^{\gamma-1/3} \quad (24)$$

where K is independent of temperature. The second equation is obtained by replacing $\rho = M/V$. Although K is not known, it is possible to discuss the relative change of the sound velocity with temperature (or with the change of density). Figure 8 shows the temperature dependence of the relative sound velocity for PMMA and PST. V_0 is the sound velocity at 20°C taken as reference. The relative sound velocity decreases slightly with increasing temperature and an abrupt decrease is found in the glass transition range. The data for the ultrasonic sound velocity show similar change[21,22] and the results

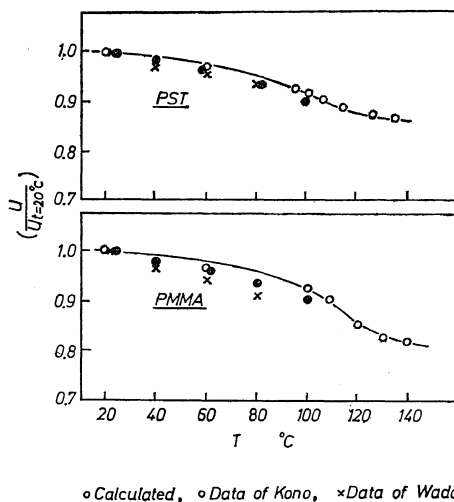o *Calculated,* ○ *Data of Kono,* ×*Data of Wada,*

Figure 8. Temperature dependence of the relative sound velocity for polystyrene and poly(methyl methacrylate).

obtained here seem to explain fairly well the measured sound velocity. As can be seen in Figure 3, the thermal conductivity through the van der Waals bond below T_g increases slightly with increasing temperature. A small increase of λ_w with temperature, based on the above discussion, can be attributed to that of the specific heat. On the other hand, in the glass transition range the sound velocity (or the density) decreases abruptly and hence causes a decrease in thermal conductivity. However, it may be expected from Figure 8 that the temperature dependence of λ_w at higher temperatures above T_g becomes smaller again. Sheldon and Lane[23] pointed out this probability from the thermal conductivity data of poly(vinyl chloride).

Thermal Conduction through the Primary Bond

The behavior of λ_e is quite similar to that of inorganic glasses. The thermal conductivity of these substances has been discussed by Kittel.[10] The results obtained by Kittel are also applied to the thermal conductivity through the primary bond. According to his discussion, the sound velocity was assumed to be independent of temperature, so that the increase of λ_e with temperature can be attributed to the increase in specific heat. However, for polymers, the specific heat calculated from the one-dimensional Debye function may contribute to the thermal conductivity. This implies that a large amount of the difference in C_v and C_γ may be incorporated into the thermal conduction through the primary bond.

Some Remarks on the Discussion in the Previous Section

When a factor affecting the thermal conductivity is introduced into a polymer, the resulting change arises only from the polymer segments vertical to the direction of the thermal gradient. We can then assume that the thermal conductivity of the polymer is approximately

$$\lambda = K\lambda_w \qquad (25)$$

where K is independent of temperature and relates to the number of the van der Waals bonds. This assumption was first made by Eiermann[5] to explain the thermal conductivity of polymers. For amorphous polymers at high temperatures, as discussed previously, we get the following equation from eq 15, 24, and 25

$$\lambda = \text{constant } C_\gamma \rho^{\gamma+2/3} \qquad (26)$$

If the thermal conductivity accompanied with the change of the density is represented by λ^*, the equation of λ^* may be given by

$$\lambda^* = \text{constant } C_\gamma (\rho + \varDelta\rho)^{\gamma+2/3} \qquad (27)$$

In this equation ρ is expressed as $(\rho + \varDelta\rho)$. It should be noted that eq 26 is valid only for the system where C_γ is not affected by the introduced factor. Then the ratio of λ^* to λ can be calculated and we obtain as the equation relating to the change of the density:

$$\frac{\lambda^*}{\lambda} = \left(\frac{\rho+\varDelta\rho}{\rho}\right)^{\gamma+2/3} = \left(1+\frac{\varDelta\rho}{\rho}\right)^{\gamma+2/3}$$
$$= 1 - \left(\gamma+\frac{2}{3}\right)\frac{\varDelta\rho}{\rho} = 1 + \varphi\frac{\varDelta\rho}{\rho} ; \quad \left(\varphi = \gamma + \frac{2}{3}\right)$$
$$(28)$$

By using a Grueneisen number below T_g for PST and PMMA, we obtain $\varphi = 4.2$—4.7. The value of φ seems to correspond to that of 4.3 in eq 8.

Recently, Lohe[5,24] investigated the pressure dependence on the thermal conductivity of polymers in the molten state. The results obtained by Lohe may support the above consideration. The equation describing the pressure dependence of the thermal conductivity can be derived from eq 26

$$\frac{1}{\lambda}\left(\frac{d\lambda}{dP}\right)_T = \frac{1}{C_\gamma}\left(\frac{dC_\gamma}{dP}\right)_T + \varphi\frac{1}{\rho}\left(\frac{d\rho}{dP}\right)_T \qquad (29)$$

The first term at the right-hand side of eq 29 is not known. However, Bridgman[25] found that $1/C_v(dC_v/dP)_T$ has an approximate value of -4×10^{-5} cm^2/kp for organic liquids. If we apply this value to the first term of eq 29, we get the experimentally determined φ value. In this case the second term of eq 29 is calculated from the literature in the pressure range from 0 to 400 kp/cm^2.[12] The theoretical φ value can be obtained from the Grueneisen number above the transition temperature. The results for PMMA, PST, and high-pressure polyethylene are listed in Table II. It appears that the experimentally determined values agree with those calculated.

Table II. Experimental and calculated φ values near 140°C for poly(methyl methacrylate), polystyrene and high-pressure polyethylene

Material	$\dfrac{1}{\lambda}\left(\dfrac{d\lambda}{dP}\right)_T$, $10^{-5}\ cm^2/kp$	$\dfrac{1}{\lambda}\left(\dfrac{d\lambda}{dP}\right)_T - \dfrac{1}{C_v}\left(\dfrac{dC_v}{dP}\right)_T$, $10^{-5}\ cm^2/kp$	$\dfrac{1}{\rho}\left(\dfrac{d\rho}{dP}\right)_T$, $10^{-5}\ cm^2/kp$	φ	
				Exptl	Calcd
PMMA	15	19	5.5	3.6	3.8—4.0
PST	14	18	6.0	3.0	3.3—3.5
HPPE	20	24	9.7	2.5	2.5—2.7

Theoretical Calculation of the Thermal Conductivity for Cross-linked Poly(methyl methacrylate) (PMMA) and Polystyrene(PST)
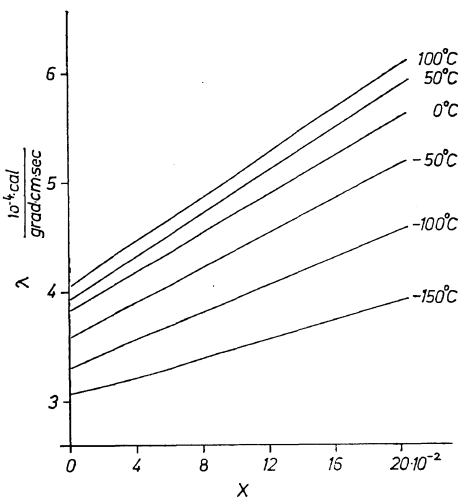
Turning to the first and second sections of this paper, we estimate the effect of cross-linking on the thermal conductivity of polymers. By using eq 7 with the values of λ_e and λ_w obtained previously, we calculated the effect of cross-linking on the thermal conductivities of PMMA and PST in the range $X=0$ to $X=0.2$. The results can be seen in Figures 9 and 10.
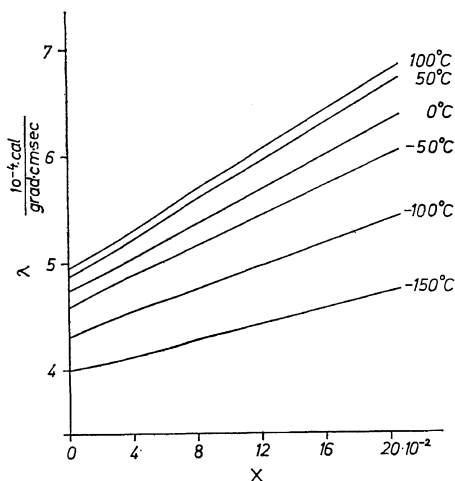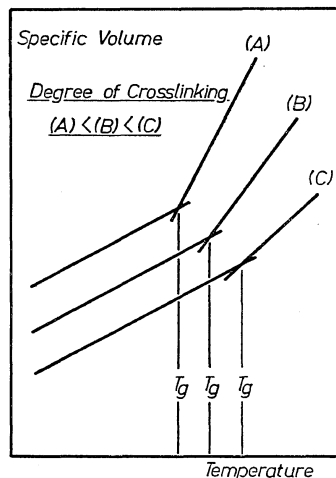

Figure 9. Theoretical calculation of the thermal conductivity for cross-linked poly(methyl methacrylate).

Figure 10. Theoretical calculation of the thermal conductivity for cross-linked polystyrene.

Figure 11. Temperature dependence of the specific volume for cross-linked polymer.

CONCLUSIONS

From the above discussion we arrive at the following conclusions. (1) Thermal conductivity increases with increasing degree of cross-linking. (2) The slope of the curves in Figures 9 and 10 becomes progressively greater as temperature increases. (3) The effect of cross-linking can be expected to be seen in the temperature curve of thermal conductivity. Cross-linking decreases considerably the thermal expansion above T_g, though the thermal expansion below T_g is not

greatly affected by cross-linking[6] (see Figure 11). This leads to the temperature coefficient above T_g becoming smaller with an increasing degree of cross-linking.

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