

## Temperature invariance of $S_0$ -parameter of polymers

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**Abstract.** The parameter  $S_0$  which is characteristic of molten alkali halides and liquids has also been shown to be characteristic of a wide variety of polymers. Calculated data using the volume expansivity of the polymer establish the temperature invariance and constancy of the  $S_0$ -parameter which retains, on an average, a constant value of 1.11 for polymers. Further understanding of the significance of fractional free volume and  $S_0$ -parameter in describing various thermoacoustic properties and the anharmonic behaviour in polymers, has been developed.

**Keywords.** Polymer;  $S_0$ -parameter; volume expansivity; heat capacity; Grüneisen parameter; fractional free volume.

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### 1. Introduction

The Grüneisen parameter has been shown to be an important quantity of current interest and useful as a measure of anharmonicity of molecular vibrations in studying the internal structure, molecular order and other thermoacoustic properties of polymers (Gibbons 1974; Sharma 1982a, b, 1983a, b). Recently Sharma (1983a) has shown that three dimensionless anharmonic parameters, the isobaric  $\Gamma$ , isochoric  $\Gamma''$  and isothermal  $\Gamma'$  microscopic (lattice) Grüneisen parameters for polymers are related to each other. Following a model-dependent approximation by Dugdale and MacDonald (1953), which is valid at all pressures,  $\Gamma$  and  $\Gamma''$  can be determined by using the isobaric and isochoric temperature dependence of bulk modulus respectively and  $\Gamma'$  from the isothermal pressure dependence of the bulk modulus for polymers (Sharma 1982a, b, 1983a, b). In this paper, an attempt has been made to relate  $\Gamma'$  (as a measure of anharmonicity of molecular vibration) with fractional free volume  $f$  (as a measure of disorder due to increased mobility of the molecules) and also the  $S_0$ -parameter and evaluate them for a wide variety of polymers from the volume expansivity data at various temperatures. The  $S_0$ -parameter which is characteristic of molten alkali halides, polyatomic ionic liquids, quasi-spherical molecular liquids and fluid hydrogen isotopes, has, on the average, a constant value of  $1.11 \pm 0.01$  in a wide variety of substances (Sharma 1983d, 1985, 1986a, b). It is shown that the  $S_0$ -parameter retains its constant

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value even in polymers at various temperatures and describes the temperature and volume or pressure dependence of several thermoacoustic and anharmonic parameters of polymers.

## 2. $S_0$ -parameter and Grüneisen parameter

The parameter  $S_0$  may be expressed as (Sharma 1985, 1986a; Sharma and Reddy 1985)

$$S_0 = -(x/2)(3 + 4\alpha T) = \tilde{B}(1 + 2\alpha T)(3 + 4\alpha T) \quad (1)$$

where  $x = (d \ln p_i / d \ln T)_v$  is the isochoric temperature coefficient of internal pressure,  $\tilde{B} = (B/B^*) = (\tilde{V})^{C_1}$  the reduced isothermal bulk modulus,  $\tilde{V} = (V/V^*)$  is the reduced specific volume,  $V^*$ ,  $B^*$  are respectively the hard core specific volume and bulk modulus at absolute zero temperature,  $C_1 = (dB/dp)_T$  the Moelwyn-Hughes parameter,  $p_i = (\alpha TB)$  the internal pressure which is identical to kinetic pressure in the zero pressure limit (at normal atmospheric pressure),  $\alpha$ ,  $B$  are respectively the volume expansivity and bulk modulus of the polymer at absolute temperature  $T$  and pressure  $p$ .

Using equation (1) the Huggins parameter,  $F$  for a polymer (Sharma 1983a) can be shown to be related to  $S_0$  as

$$\begin{aligned} F &= 1 + (2/3)\alpha T - (d \ln B / d \ln T)_v \\ &= 2[1 + S_0 / (3 + 4\alpha T)] - (3 + 4\alpha T) / 3. \end{aligned} \quad (2)$$

The isochoric and isothermal lattice Grüneisen parameters for a polymer (Sharma 1982a, 1983a) and  $S_0$ , using (1) and (2), as

$$\Gamma'' = (d \ln B / d \ln T)_v / 2\alpha T = 1 - S_0 [\alpha T (3 + 4\alpha T)]^{-1}, \quad (3)$$

$$\begin{aligned} \Gamma'' &= (1/2) [(dB/dp)_T - 1] = \Gamma + \Gamma'' \\ &= (2/3)(4 + \alpha T) + (2\alpha T)^{-1} - S_0 [\alpha T (3 + 4\alpha T)]^{-1} \\ &= (2/3)\alpha T + (2 - F + 4\alpha T)(2\alpha T)^{-1}. \end{aligned} \quad (4)$$

Equation (3) shows that  $\Gamma''$  is a negative quantity for a polymer, unlike quasi-spherical molecular liquids and fluorocarbon fluids (Sharma 1983c, d). Theoretical justification of this proposal has also been reported by Sharma (1983a) using the experimental data available on the temperature and pressure derivatives of the bulk modulus for the polymer. Equations (2)–(4) show that the parameters,  $F$ ,  $\Gamma'$  and  $\Gamma''$  are related to  $S_0$  and can be expressed in terms of only the volume expansivity of the polymer. The present proposal of relating  $\Gamma'$  to  $\alpha$  agree closely with the suggestion of Hartmann (1979) and Curro (1973) that the anharmonicity of intermolecular energy or potential is also governed by thermal expansion and a number of internal degrees of freedom. During the volume expansion of the polymer, more and more disorder is introduced which results in the changes in molecular vibration frequency, molecular order and structure, making the polymer less anharmonic at higher temperature than at lower temperature (Gibbons 1974; Warfield 1974; Gilmour *et al* 1978).

The fractional free volume as a measure of disorder due to increased mobility of

molecules in a polymer can be expressed in terms of  $\Gamma'$  as (Sharma 1983d)

$$f = (V_a/V) = (\Gamma' + 1)^{-1}, \tag{5}$$

where  $V_a = (V - V^*)$  is the free (available) volume of the molecules of the polymer. Equation (5) may be rearranged to give the dimensionless parameter  $A^*$  in terms of  $f$  and  $\Gamma'$  as

$$A^* = 1 + (f/\Gamma') = 1 + f^2/(1 - f). \tag{6}$$

Equation (6) shows that at low temperatures, close to absolute zero, the polymeric system would tend to be ordered, exhibiting little thermal expansion and fractional free volume, thereby making the parameter  $A^*$  a constant equal to unity.

Equations (1)–(6) demonstrate the significance of  $f$  and  $S_0$  in describing thermoacoustic properties and the anharmonic behaviour in polymers. Using these equations the parameters  $X$ ,  $\Gamma''$ ,  $\Gamma'$ ,  $f$ ,  $F$ ,  $A^*$  and  $S_0$  have been evaluated for 27 polymers. The necessary experimental data on  $\alpha$  are taken from literature (Allen *et al* 1960; Sharma 1982a, b, 1983a, b; Orwoll and Flory 1967; Eichinger and Flory 1968; Barker and Chen 1967). The results are presented in table 1. The parameter  $S_0$  for polystyrene, nylon 6 and teflon at various temperatures from 173 K to 383 K has been calculated using experimental data on  $\alpha$  from literature (Urzendowski and Guenther 1970). A plot of  $S_0$  as a function of temperature for these polymers is shown in figure 1.

### 3. Isochoric temperature coefficient of heat capacity and bulk modulus

Treating the fluctuation of intermolecular energy as the perturbation due to localized ordering of molecules, arising out of the effect of order in the random or disordered state in a polymer (Sharma 1980), the internal energy  $E$  may be expressed as

$$E = p_i V + TC_v = \Phi[1 + (\bar{\Gamma})^{-1}] \tag{7}$$

in which the thermodynamic Grüneisen parameter,  $\bar{\Gamma}$  treated as a measure of thermal stress for a polymer may be expressed as (Gilmour *et al* 1978; Sharma 1983d)

$$\bar{\Gamma} = V(dp/dE)_v = p_i V/TC_v, \tag{8}$$

where  $C_v = (dE/dT)_v$  is the isochoric heat capacity and  $\Phi = p_i V$  the intermolecular energy of the polymer. From thermodynamic considerations, using (1), (3), (7) and (9),

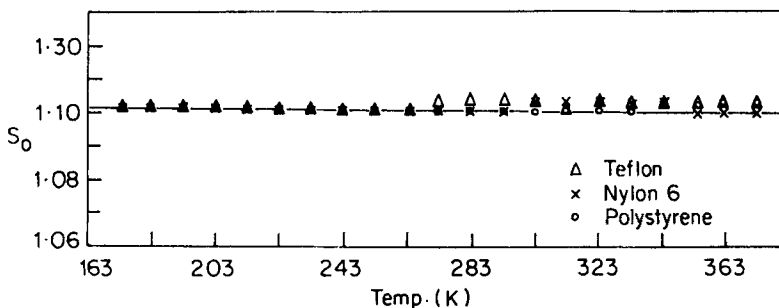


Figure 1. A plot of  $S_0$  vs temperature of polystyrene, nylon 6 and teflon.

**Table 1.** Calculated values of the  $S_0$  constant and other related anharmonic and thermoacoustic parameters of polymers.

Polymer	$T$ (K)	$\alpha \times 10^4$ <sup>a-c</sup> (K <sup>-1</sup> )	$X$	$\Gamma''$	$\Gamma'$	$F$	$f$	$A^*$	$S_0$
1	2	3	4	5	6	7	8	9	10
<i>n</i> -Tetradecane	293	9.0	-0.552	-0.048	3.691	1.201	0.213	1.057	1.120
Squalane	293	8.1	-0.568	-0.196	3.736	1.251	0.211	1.054	1.121
Polystyrene	293	6.8	-0.590	-0.482	3.827	1.325	0.207	1.048	1.121
Poly(ethyl acrylate)	293	6.8	-0.590	-0.482	3.827	1.325	0.207	1.048	1.121
Squalene	293	7.6	-0.576	-0.294	3.767	1.279	0.210	1.052	1.121
Natural rubber	293	6.7	-0.592	-0.509	3.836	1.331	0.207	1.048	1.121
Poly(ethylene oxide dimethyl ether)	293	7.8	-0.573	-0.253	3.754	1.268	0.210	1.052	1.121
Poly(propylene oxide dimethyl ether)	293	7.8	-0.573	-0.253	3.754	1.268	0.210	1.052	1.121
Poly(dimethyl siloxane)	293	9.0	-0.552	-0.048	3.691	1.201	0.213	1.057	1.120
Poly(methyl phenyl siloxane)	293	7.6	-0.576	-0.294	3.767	1.279	0.210	1.052	1.121
Poly(trifluoro-chloroethylene)	293	8.1	-0.568	-0.196	3.736	1.251	0.211	1.054	1.121
Phenolic polymer	303	3.1	-0.661	-2.520	4.532	1.536	0.181	1.026	1.116
Polyphenyl quinoxaline	303	2.6	-0.673	-3.269	4.797	1.568	0.172	1.021	1.115
Polymethyl Methacrylate	298	2.1	-0.685	-4.472	5.226	1.601	0.161	1.017	1.113
	303	2.70	-0.670	-3.097	4.736	1.561	0.174	1.022	1.115
Polyethylene oxide	298	3.30	-0.658	-2.346	4.470	1.527	0.183	1.027	1.117
	358	14.0	-0.437	-0.564	3.562	0.769	0.219	1.073	1.094
Poly(acrylonitrile butadiene styrene)	293	3.0	-0.666	-2.787	4.626	1.549	0.178	1.024	1.116
Polyethylene terephthalate	298	1.6	-0.696	-6.304	5.881	1.633	0.145	1.012	1.111
SBR rubber	298	6.6	-0.592	-0.505	3.835	1.330	0.207	1.048	1.121
Buty IIR	298	5.7	-0.609	-0.793	3.930	1.383	0.203	1.043	1.121
Polyisobutylene	273	5.51	-0.622	-1.067	4.024	1.421	0.199	1.039	1.120
	298	5.55	-0.612	-0.850	3.950	1.392	0.202	1.042	1.120
	323	5.60	-0.602	-0.664	3.887	1.361	0.205	1.045	1.121
	373	5.68	-0.583	-0.375	3.792	1.300	0.209	1.050	1.121
	423	5.77	-0.564	-0.155	3.723	1.238	0.212	1.055	1.121
Polymethylene	298	6.92	-0.586	-0.421	3.807	1.311	0.208	1.049	1.121
	373	7.12	-0.551	-0.038	3.688	1.197	0.213	1.057	1.120
	413	7.20	-0.534	+0.102	3.649	1.137	0.215	1.061	1.118
	453	7.37	-0.515	+0.229	3.616	1.070	0.217	1.064	1.116
Teflon	295	1.35	-0.703	-7.823	6.425	1.650	0.135	1.010	1.110
	303	2.70	-0.670	-3.097	4.736	1.561	0.174	1.022	1.115
Nylon 6	303	2.40	-0.677	-3.656	4.935	1.580	0.168	1.020	1.114
Lexan PC	303	2.00	-0.686	-4.663	5.294	1.606	0.159	1.016	1.113
Polyethylene Hexamethyl disiloxane	303	4.60	-0.629	-1.258	4.089	1.444	0.196	1.037	1.120
Octamethyl trisiloxane	293	13.8	-0.480	-0.406	3.579	0.941	0.218	1.069	1.108
	293	12.4	-0.500	-0.312	3.597	1.015	0.218	1.066	1.113

<sup>a</sup> Allen *et al* (1960); <sup>b</sup> Sharma (1982a, b, 1983a, b); <sup>c</sup> Eichinger and Flory (1968); <sup>d</sup> Barker and Chen (1967); <sup>e</sup> Orwoll and Flory (1967).

together with the expressions of isothermal volume derivatives of  $C_v$  and  $\bar{\Gamma}$  obtained earlier (Sharma 1986a), the first order isochoric and isobaric temperature coefficients of  $C_v$  and  $\bar{\Gamma}$  for a polymer can be shown to be related to  $S_0$  as

$$Y = (d \ln C_v / d \ln T)_v = 2 S_0 \bar{\Gamma} (3 + 4\alpha T)^{-1}, \quad (9)$$

$$Y' = (d \ln C_v / d \ln T)_p = S_0 \bar{\Gamma} (3 + 4\alpha T)^{-1} (2 - \alpha T), \quad (10)$$

$$Z = (d \ln \bar{\Gamma} / d \ln T)_v = -[1 + 2 S_0 (\bar{\Gamma} + 1) (3 + 4\alpha T)^{-1}], \quad (11)$$

$$Z' = (d \ln \bar{\Gamma} / d \ln T)_p = Z + \lambda \alpha T = -[1 + \alpha T (2 \Gamma'' - 1) + 2 S_0 (3 + 4\alpha T)^{-1} + S_0 \bar{\Gamma} (3 + 4\alpha T)^{-1} (2 - \alpha T)], \quad (12)$$

in which  $\lambda = (d \ln \bar{\Gamma} / d \ln V)_T$  expresses the isothermal volume derivative of  $\bar{\Gamma}$  for the polymer. Equations (11) and (12) show that  $\bar{\Gamma}$  decreases with rise of temperature at constant volume and at constant pressure for the polymer. This proposal agrees closely with the suggestion of Gibbons (1974) that the thermal stress developed within the polymer chains due to large number of internal degrees of freedom is reduced, resulting in the drop of  $\bar{\Gamma}$  in polymers at high temperatures.

The relationship between the adiabatic bulk modulus,  $B_s$  and isothermal bulk modulus,  $B$  can be expressed as (Swenson 1968; Roberts and Smith 1970)

$$B_s - B = T C_v (\bar{\Gamma})^2 / V. \quad (13)$$

Equations (8)–(13) lead to the general relations between the isochoric temperature and isothermal pressure coefficients of  $B_s$  and  $B$  as

$$(B_s/B) (d \ln B_s / d \ln T)_v - (d \ln B / d \ln T)_v = \bar{\Gamma} \alpha T [1 + 2 S_0 \bar{\Gamma} (3 + 4\alpha T)^{-1} + (2Z/\bar{\Gamma})], \quad (14)$$

$$(dB/dp)_T - (dB_s/dp)_T = \bar{\Gamma} \alpha T [1 - 4\Gamma'' + S_0 \bar{\Gamma} (3 + 4\alpha T)^{-1}]. \quad (15)$$

By assuming that  $\bar{\Gamma}$  has no intrinsic (constant volume) temperature dependence, equations (14) and (15) reduce to the approximate relations obtained by Swenson (1968) and Roberts and Smith (1970). The present result presents an improvement over the work of these workers and expresses the correct isothermal volume and isochoric temperature dependence of  $C_v$  and  $\bar{\Gamma}$  for the polymer. Equations (9)–(12), (14) and (15) demonstrate further the significance of  $S_0$  in describing temperature, volume or pressure dependence of  $C_v$ ,  $\bar{\Gamma}$ ,  $B_s$  and  $B$  for a polymer and evaluating them from the knowledge of  $\bar{\Gamma}$  and  $\alpha$  for the polymer. Using (1), (8), (9)–(12) the parameters  $\bar{\Gamma}$ ,  $S_0$ ,  $Y$ ,  $Y'$ ,  $\lambda$  and  $(Z' - Z)$  have been evaluated for 23 polymers. The necessary experimental data on thermoacoustic parameters are taken from literature (Warfield 1974; Eichinger and Flory 1968; Sharma 1982a, b, 1983a, b; Urzendowski and Guenther 1970). The results are presented in table 2.

#### 4. Results and discussion

The calculated values of the isochoric temperature coefficient of both the internal pressure and bulk modulus in table 1 are negative. The absolute values of  $X$  range from

**Table 2.** Calculated values of temperature and volume derivatives of the isochoric heat capacity and thermodynamic Grüneisen parameter of polymers.

Polymer	$T$ (K)	$\alpha \times 10^4$ <sup>a-d</sup> (K <sup>-1</sup> )	$\bar{\Gamma}^{a,b}$	$S_0$	$Y$	$Y'$	$\lambda$	$(Z' - Z)$
Phenolic polymer	303	3.1	1.3	1.116	0.859	0.819	6.470	0.608
Polyphenyl quinoxaline	303	2.6	1.0	1.115	0.673	0.646	7.874	0.622
Polystyrene	293	2.11	0.79	1.113	0.541	0.524	11.170	0.690
Polymethyl methacrylate	298	2.1	0.82	1.113	0.562	0.544	10.225	0.640
Polyethylene	298	5.0	0.52	1.120	0.322	0.297	3.155	0.489
Polypropylene	298	4.8	0.96	1.119	0.602	0.559	3.687	0.527
Polymethylene oxide	298	2.43	0.51	1.114	0.345	0.333	8.525	0.617
Poly(4-methyl pentene-1)	298	3.80	1.07	1.118	0.692	0.653	5.060	0.573
Polyethylene oxide (Solid)	298	3.3	1.02	1.117	0.671	0.638	6.020	0.593
Polyethylene oxide (melt)	358	14.0	1.02	1.094	0.446	0.334	2.351	1.178
Polybutene-1	298	4.5	0.66	1.119	0.418	0.390	3.929	0.527
Polychlorotri- fluoroethylene	293	8.1	0.36	1.121	0.204	0.180	1.494	0.354
Polytetrafluoroethylene	295	1.35	0.40	1.110	0.281	0.275	16.787	0.668
Polyisobutylene	298	5.55	1.09	1.120	0.667	0.612	3.034	0.502
Polychloroprene	298	6.0	0.60	1.121	0.362	0.330	2.553	0.456
Polyepoxide + D	298	2.7	0.54	1.114	0.362	0.347	7.521	0.605
Polyvinyl chloride	298	2.5	0.61	1.114	0.412	0.397	8.280	0.617
Polyvinyl acetate	298	2.07	1.12	1.113	0.768	0.744	10.502	0.648
Polycarbonate	298	1.5	0.27	1.111	0.189	0.185	14.734	0.659
Transpolybutadiene	298	7.8	0.16	1.121	0.091	0.080	1.500	0.348
Polyethylene terephthalate	298	1.6	0.42	1.111	0.292	0.285	13.754	0.656
Polyisoprene	298	5.1	0.68	1.120	0.422	0.390	3.297	0.501
SBR rubber	298	6.6	0.74	1.121	0.438	0.395	2.229	0.438
Butyl IIR	298	5.7	0.68	1.121	0.414	0.379	2.793	0.474

<sup>a</sup> Warfield (1974); <sup>b</sup> Sharma (1982a, b, 1983a b); <sup>c</sup> Eichinger and Flory (1968); <sup>d</sup> Urzendowski and Guenther (1970).

about 0.44 to 0.77 and those of  $F$  from about 1.0 to 1.7 which are of the same order as observed for crystalline and molten alkali halides, liquid alkali metals, ionic and quasi-spherical molecular liquids (Sharma 1983d, 1986a, b). Large volume expansivity for a polymer at the same temperature corresponds to a small absolute value of  $X$ ,  $\Gamma'$  and  $F$  which decreases with rise of temperature for the polymer. The decrease in  $\Gamma'$  with temperature, arising due to large number of internal degrees of freedom and the nature of anharmonic interactions in a polymer may be indicative of some kind of molecular ordering effect. This suggests that the structural ordering process continues in the polymer due to the increasing storage of energy in high frequency vibrations as the temperature is raised in the glassy region, and  $\Gamma'$  and  $f$  become constant at the glass temperature of the polymer (Curro 1973; Warfield 1974; Gilmour *et al* 1978; Simha and Boyer 1962).

The values of  $f$  increase with temperature thereby introducing greater additional disorder in a polymer. For most of the polymers, the values of  $f$  are around 0.20, which are of the same order as observed for saturated hydrocarbons (Soczkiewicz 1977) and polycrystalline alkali halides, rare earth metals, liquid alkali metals, alkali halides and polyatomic ionic liquids (Sharma and Reddy 1985). The quasi-constancy of the quantity  $f$  at 293 K for a wide variety of polymers and liquids has echoes in the universal value of the fractional free volume at the glass temperature in the WLF theory (Williams *et al* 1955). The parameters  $S_0$  and  $A^*$  have, on the average, constant values of  $1.11 \pm 0.01$  and  $1.05 \pm 0.01$  respectively, for all the polymers examined presently. This implies that, on the average, the approximate relationships  $S_0 = 5.55f$  and  $A^* = 5.25f$  hold true for the polymers.

The plot of  $S_0$  as a function of temperature shown in figure 1 confirms the constancy and the temperature invariance of  $S_0$  for the polymers over the whole temperature range of 173 K to 383 K.

Equation (1) shows that  $S_0$  is proportional to the product of  $X$  and  $(3 + 4\alpha T)$ . It is interesting to note that a large  $\alpha$  corresponds to a small absolute value of  $X$  for a polymer. However, the value of the term  $(3 + 4\alpha T)$  increases with rise of temperature in such a way that  $S_0$  tends to be independent of the value of  $\alpha$  for the polymer. The temperature dependence of the sound speed of polymers in the glassy state is linear and is governed by the bulk modulus and not the density (Hartmann 1980). The logarithmic temperature derivative of the bulk modulus in a polymer is twice that of the sound speed in the polymer (Hartmann 1975, 1980). This shows that  $S_0$  in equation (3) is useful for imparting a negative isochoric temperature coefficient of sound speed indicating a decrease in the sound speed with temperature, in accordance with the earlier work (Sharma 1983a) for a polymer. This implies that volume changes caused by temperature have a greater effect on the bulk modulus or sound speed than equal volume changes caused by pressure for the polymer.

It has also been established (Sharma 1985, 1986b) that  $S_0$  may be termed as a molecular constant which retains its constancy for a wide variety of substances in polycrystalline, molten and liquid state. Due to the additive property implied in  $S_0$ , the possibility of computing the isochoric temperature coefficient of sound speed and bulk modulus for liquid mixtures and polymer solutions from equations (1) and (3) is extremely useful.

At the melting point  $T_m$ , the relationship  $0.31 \leq \alpha T_m \leq 0.33$  has been obtained for polymer melts (Simha and Jain 1978). Taking the average value of  $\alpha T_m = 0.32$ ,  $S_0 = 1.11$  for polymer melts, using equation (1) and the earlier expression (Sharma 1985) for  $C_1$ , the calculated values so obtained for  $C_1$ ,  $\dot{B}$  and  $\dot{V}$  are 7.885, 0.158 and 1.264 respectively. This value of  $\dot{V}$  is of the same order as observed for polymer melts (Simha and Jain 1978). Since  $B^*$  and  $V^*$  are constant for a polymer, these values render a relationship  $\dot{V}B^{(1/7.885)} = \text{constant}$  for polymers. An analogous relationship  $\dot{V}B_s^{(1/7)} = \text{constant}$  has been obtained by Wada for liquids (Jain and Pandey 1975) which is widely used for investigating the physico-chemical behaviour of fluids and fluid mixtures. This shows that  $S_0$  is useful in interpreting the bulk modulus in molecular terms for a polymer, leading to the relation  $B \propto V^{-7.885}$ , analogous to that of Wada for a liquid.

At the glass transition temperature  $T_g$ , the average value of  $\alpha T_g = 0.17$  has been obtained for polymer glasses (Simha and Boyer 1962). Using equation (1) and taking  $S_0 = 1.11$  for polymer glasses, the calculated values for  $C_1$ ,  $B$  and  $\dot{V}$  are 10.442, 0.225

and 1.153 respectively. This value of the reduced specific volume at  $T_g$ , based on the constancy and temperature invariance of  $S_0$ , renders the value of  $(V^*/V)$  as 0.87 which is identical to that obtained for polymers in the glassy state (Breuer *et al* 1966). This shows that equation (1) for  $S_0$  can be employed for estimating the molecular bulk modulus,  $B^*$  from the experimental data on  $\alpha$  and  $B$  at  $T_g$  for polymer glasses. The anharmonicity of molecular vibrations and the bulk modulus of a polymeric material are determined primarily by the inter-chain forces and are not dependent on the bonding along the macromolecule (Sharma 1983b). Thus  $S_0$  is useful for a wide variety of polymers and is significant for investigating various physicochemical, thermoacoustic and anharmonic properties.

The calculated values of the quantity  $Y$  and  $Y'$  as given in table 2 are positive and range from 0.09 to 0.86 and about 0.08 to 0.82 respectively for the polymers presently examined, indicating an increase in the isochoric heat capacity with temperature. This shows that the values of the isochoric and isobaric temperature coefficients of  $C_v$  are of the same order and differ by a factor less than 0.1, within 10% of  $Y$ , similar to that observed for cubic solids (Swenson 1968). The calculated values of  $\lambda$  are positive and range from about 2 to 17 for polymers as compared to 3 to 5 for fluorocarbon fluids and liquefied gases, and around 1 to 2 for alkali halides (Sharma 1983d). However, the values of the quantity  $(Z' - Z)$  expressing the difference between the isobaric and isochoric temperature coefficients of  $\bar{\Gamma}$  are low ( $< 0.7$ ) which is within 20% of  $\lambda$  for these polymers. This shows that  $\bar{\Gamma}$  increases with volume at constant temperature for polymer. A similar pattern has also been observed for cubic solids and alkali halides (Swenson 1968; Sharma 1983d).

The present treatment offers a convenient means for establishing the constancy and temperature invariance of  $S_0$  and for investigating several thermoacoustic properties by relating it to the isothermal lattice Grüneisen parameter, fractional free volume, and isobaric and isochoric temperature coefficients of thermodynamic Grüneisen parameter and isochoric heat capacity of polymers. This allows further understanding of the significance of  $S_0$  in describing anharmonic behaviour with regard to molecular order and interchain forces in glassy polymers and polymer melts.

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