Heat capacities of aliphatic and aromatic polysulphones

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Heat capacities were measured for three aromatic polysulphones: poly(1,4-phenylene sulphonyl), PAS; poly(oxy-1,4-phenylene-sulphonyl-1,4-phenylene), PPES; and poly[oxy-1,4-phenylene-sulphonyl-1,4-phenylene-oxy-1,4-phenylene-(1-methylidene)-1,4-phenylene], PBISP; from 150 to 620 K using differential scanning calorimetry. These new data, along with the prior ATHAS (Laboratory for Advanced Thermal Analysis, University of Tennessee) recommended experimental heat capacities for three aliphatic polysulphones: poly(1-propene sulphone), P1PS (20–300 K); poly(1-butene sulphone), P1BS (100–300 K); poly(1-hexene sulphone), P1HS (20–300 K), were fitted to an approximate frequency spectrum below their respective glass transition temperatures. The ATHAS computation scheme was used to compute the heat capacities that arise from these vibrations from 0.1 to 1000 K. The θ_1-temperature changed from 685 K for P1PS to 587 K for P1HS while for PPES and PBISP much higher values (799.5 K and 777.8 K) than the other phenylene polymers analysed at ATHAS, were obtained. Using these data and the smoothed experimental liquid heat capacities, the glass transition temperatures for PAS, PPES and PBISP were obtained at 492.6, 497.4 and 458.2 K. The corresponding values for ΔC_p were 18.1, 37.7 and 126.6 J K^{-1} mol^{-1}, respectively.

(Keywords: polysulphones; heat capacity; crystalline; vibrational spectrum; glass transition)

INTRODUCTION

Polysulphones containing a sulphone group (SO_2) along with an aromatic group in the backbone possess good thermal stability and are resistant to oxidation[1,2]. They are therefore widely used as engineering plastics. The presence of the electron-withdrawing sulphone group strongly influences the properties of the polymer. A polysulphone containing only the sulphone and phenylene groups, i.e. poly(1,4-phenylene sulphonyl) also known as poly(aryl sulphone) or PAS, is difficult to process due to the relatively inflexible and immobile phenylene and SO_2 groups. Hence, polysulphones containing the flexible O and $C(CH_3)_2$ groups besides the SO_2 and phenylene groups in the backbone have gained more commercial importance.

There is, however, little information on the thermal analysis of this interesting class of polymers. Heat capacities were reported from 14 to 480 K and from 380 to 540 K for the poly[oxy-1,4-phenylene-sulphonyl-1,4-phenylene-oxy-1,4-phenylene-(1-methylidene)-1,4-phenylene], PBISP[3,4]. Its glass transition temperature was found to be between 450 and 460 K. In addition, glass transition temperatures were measured for a series of poly(arylene ether sulphones) and were found to vary between 438 and 520 K, depending on the position of the ether linkage[5]. The poly(oxy-1,4-phenylene-sulphonyl-1,4-phenylene), PPES, had a glass transition[5] between 501 and 513 K. For aliphatic polysulphones, three sets of heat capacities were reported some time ago[6]: for poly(1-propene sulphone) (P1PS) and poly(1-hexene sulphone) (P1HS) from 20 to 300 K, and for poly(1-butene sulphone) (P1BS) from 100 to 300 K. These data are already included in our ATHAS (Laboratory for Advanced Thermal Analysis, University of Tennessee) data bank of recommended experimental heat capacities[7].

In this paper, heat capacities were measured for three aromatic polysulphones: poly(1,4-phenylene sulphonyl), PAS; poly(oxy-1,4-phenylene-sulphonyl-1,4-phenylene), PPES; and poly[oxy-1,4-phenylene-sulphonyl-1,4-phenylene-oxy-1,4-phenylene-(1-methylidene)-1,4-phenylene], PBISP. For PBISP, the new data were combined with the prior measurements to arrive at a set of recommended experimental heat capacities, both for the solid and the liquid states.

At ATHAS, heat capacities are measured and collected for inclusion in the critically assessed data bank and, in addition, the heat capacities are analysed in terms of molecular motion and disorder. The heat capacities of about 100 solid polymers have been studied to date, based on approximate vibrational spectra[8–23]. The discrepancy between the experimental and computed heat capacity in the temperature region of exclusively vibrational motion (solid) is in most cases less than $\pm 3\%$. In this paper this analysis is extended to the series of polysulphones.

The ATHAS computation scheme (described elsewhere in detail[24–26]) is used to compute heat capacity for the solid state for the aliphatic and aromatic polysulphones, from 0.1 to 1000 K, by fitting the limited experimental heat capacities for the solids below their glass transitions

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(T_g) with the two parameters θ_1 and θ_3 of the Tarasov equation to obtain an approximate skeletal vibrational spectrum. The total vibrational spectrum is arbitrarily separated into group and skeletal vibrations. The strongly coupled skeletal vibrations are usually well approximated by the Tarasov equation in which the parameters θ_3 and θ_1 represent the upper limits of the intermolecular and the intramolecular frequencies, respectively [$\theta = h\nu/k$, where ν is the frequency (Hz) and h and k are Planck's and Boltzmann's constants, respectively. The frequency θ is expressed in K ($1\ cm^{-1} = 1.4388\ K$)]. The group frequencies are coupled only to a limited degree. They are derived from i.r. and Raman data and their normal mode distribution can be approximated by a series of Einstein functions (single frequencies) and box distributions (wider range frequencies). Having thus established an approximate overall vibrational spectrum, it is inverted to C_v. The C_p to C_v conversion is made using the empirical Nernst–Lindemann equation[27,28]:

$$C_p - C_v = 3RA_0(\text{new})C_p^2T/(C_vT_m^0) \qquad (1)$$

where A_0(new) is the Nernst–Lindemann constant, R is the gas constant and T_m^0 is the equilibrium melting temperature.

Based on experimental expansivity (α) and compressibility (β) for a larger number of polymers, a universal value of 3.9×10^{-3} K mol J^{-1} was obtained for the A_0(new) in the ATHAS data bank. This value is used when no experimental information is available on α and β for a particular polymer.

The liquid heat capacity can usually be represented over a wide temperature range by a linear equation, which, in addition, is additive with respect to contributions from the various groups that make up the macromolecule. After establishing the solid (calculated) and liquid (smoothed experimental) heat capacities as base lines, it was possible to determine the heat capacity increase, ΔC_p, at the glass transition temperature for the aromatic polysulphones. For aliphatic polysulphones, the solid heat capacity was used along with that of the liquid derived from an empirical addition scheme, to find a probable glass transition temperature.

EXPERIMENTAL

Samples

The samples of PAS were obtained from Amoco Performance Products Inc (Ridgefield, CT, USA). Two samples were analysed. These had the trade names Radel A100 and Radel A200. The molecular masses of these ranged between 20 000 and 30 000 with Radel A200 having a lower molecular mass than Radel A100. Both were in pellet form. PPES and PBISP were obtained as pellets from Scientific Polymers Products Inc (Ontario, NY, USA). This PBISP will be referred to as PBISP-S throughout the text. No information was available for the molecular mass of PPES. For PBISP-S a weight average molecular mass between 30 000 and 76 000 was suggested. An additional polysulphone, Udel (trade name of Amoco Performance Products), with the same chemical structure as PBISP-S was supplied by Amoco in powder form. This polymer was also analysed and will be referred to as PBISP. No information was available on its molecular mass. All samples were used as supplied. The rather incomplete molecular characterization does not affect heat capacities outside the transition region.

Instruments and experiments

Transition analysis. The analysis of the glass transition temperature was carried out with the Thermal Analyst 2100 system from TA Instruments Inc. (formerly DuPont Co., Instrument Systems Division). All measurements for transitions were carried out from 320 to 570 K at a heating rate of 10 K min^{-1} after cooling the samples at 20, 10, 5 and 1 K min^{-1}. The glass transition temperature T_g was fixed at the mid-point of the heat capacity increase using the software supplied by TA Instruments. Temperature calibration was carried out with indium, naphthalene and benzoic acid with the onset of melting being 429.75, 353.42 and 395.5 K, respectively. The sample masses ranged between 15 and 20 mg.

Calorimetry. Heat capacity measurements were carried out for all aromatic polysulphones from 150 to 620 K using the TA Instruments system equipped with a 912 Dual Sample differential scanning calorimeter and an auto sampler. The calorimeter was modified to carry out low temperature measurements[29]. Measurements were carried out in two different ranges: 150–370 K and 320–620 K. In each case the sample was cooled with liquid nitrogen at an uncontrolled cooling rate and sufficient time was given for thermal equilibrium to be established before initiating the measurement on heating. From 150 to 370 K the outside of the calorimeter was surrounded by liquid nitrogen to maintain a constant temperature environment. For the measurements from 320 to 620 K the constant environment was provided by the heater jacket of the calorimeter which was maintained at 320 K. The temperature calibration was carried out using the onset of the transition peaks of cyclohexane (186.1, 279.7 K), cycloheptane (134.75, 265.13 K), 1-chlorobutane (150.05 K), naphthalene (353.42 K), and indium (429.75 K) from 150 to 370 K, and benzoic acid (395.5 K), naphthalene, tin (505.05 K), potassium nitrate (607.15 K), and indium from 320 to 620 K. In addition, the heat capacity data were corrected for temperature lag, asymmetry of the three measuring positions and heating rate, using the computer program developed in our laboratory (details of the program are given in ref. 30). The error was $<1\%$ for the high-temperature data (320–620 K) and $<3\%$ for the low-temperature data (150–370 K). All heat capacities were measured at a heating rate of 10 K min^{-1} using nitrogen as a purge gas. The typical sample masses were 20–30 mg. All data were corrected at every measured temperature with results from the measurements of sapphire heat capacities[31].

In addition to the heat capacity measurements with the TA Instruments system, heat capacities were also measured with a Perkin-Elmer DSC 7 from 230 to 420 K. A mechanical refrigerator was used to cool the calorimeter to 230 K, and both the temperature and heat of fusion were calibrated using the standard materials tin (505.05 K, 60.46 J g^{-1}), indium (429.75 K, 28.45 J g^{-1}) and cyclohexane (186.1 K, 79.58 J g^{-1} and 279.1 K, 31.25 J g^{-1}). The calculations of heat capacity were carried out with the commercial software supplied by Perkin-Elmer and corrected with separately measured sapphire heat capacities[31].

Table 1 Experimental heat capacities of aromatic polysulphones

Temperature (K)	Heat capacity (J K^{-1} mol^{-1})				
	PAS[a]	PPES[b]	PBISP-S[c]	PBISP[d]	PBISP-R[e]
150	83.7	105.7	275.8	300.2	256.8
160	87.7	117.7	296.5	310.0	272.6
170	91.7	128.8	315.4	320.2	288.4
180	95.7	139.1	332.8	330.7	304.2
190	99.7	148.7	349.0	341.7	319.9
200	103.7	157.5	364.3	353.1	335.6
210	107.6	165.9	378.8	365.1	351.1
220	111.5	173.8	392.9	377.6	366.6
230	115.4	181.4	406.6	390.7	381.9
240	119.2	188.9	420.2	404.5	397.1
250	123.0	196.2	433.8	418.8	412.2
260	126.8	203.5	447.6	433.9	427.1
270	130.5	210.9	461.7	449.6	441.8
280	134.2	217.8	476.1	466.1	456.3
290	137.8	223.1	491.0	483.4	470.6
300	141.4	228.9	506.4	501.4	484.6
310	144.9	235.0	522.5	520.3	498.4
320	148.4	241.6	539.4	540.0	523.0
330	151.8	248.4	557.0	560.6	536.8
340	155.2	255.4	575.5	582.1	550.1
350	158.5	262.5	594.9	604.6	562.8
360	161.8	269.8	615.4	628.0	574.4
370	165.0	277.1	n.a.	n.a.	586.5
380	168.2	284.4	n.a.	n.a.	608.4
390	171.3	291.7	n.a.	n.a.	628.2
400	174.4	298.9	n.a.	n.a.	645.7
410	177.4	305.9	n.a.	n.a.	661.0
420	180.4	312.8	n.a.	n.a.	674.2
430	183.3	319.5	n.a.	n.a.	685.2
440	186.2	326.0	n.a.	n.a.	696.7
450	189.0	332.2	n.a.	n.a.	727.2
460	191.7	338.1	n.a.	n.a.	779.4
470	194.4	343.7	n.a.	n.a.	851.8
480	197.1	348.9	n.a.	n.a.	866.5
490	199.7	353.8	n.a.	n.a.	872.2
500	220.2	382.9	n.a.	877.9	877.9
510	221.0	389.5	n.a.	883.7	883.7
520	221.8	390.2	n.a.	889.4	889.4
530	222.7	395.2	n.a.	895.1	895.1
540	223.5	395.9	n.a.	900.8	900.8
550	224.3	396.6	n.a.	906.5	906.5
560	225.1	397.4	n.a.	912.3	912.3
570	226.0	398.1	n.a.	918.0	918.0
580	226.8	398.8	n.a.	923.7	923.7
590	227.6	399.6	n.a.	929.4	929.4
600	228.4	400.3	n.a.	935.2	935.2
610	229.3	401.1	n.a.	940.9	940.9
620	230.1	401.8	n.a.	946.6	946.6

n.a. = data not available

[a]From 150 to 470 K the data from TA Instruments System and Perkin-Elmer DSC 7 were averaged to represent the solid

$$C_p = \exp[14.03310 - 6.633458(\ln T) + 1.356265(\ln T)^2 - 0.08282718(\ln T)^3] \ (\pm 1.4\%)$$

From 480 to 500 K the data were smoothed by a spline function and are affected by cooling and heating rates (glass transition region)
From 510 to 620 K

$$C_p = 179.007985 + 0.082375T \ (\pm 0.4\%)$$

for the liquid state

RESULTS

D.s.c. of the transitions

All aromatic polysulphones analysed showed a sharp glass transition accompanied by an endothermic hysteresis peak. No other transitions were observed, thereby indicating that all the samples analysed were amorphous. The glass transition temperature obtained from these transition measurements showed no significant change for the samples cooled at the different cooling rates. For the samples cooled at 10 K min^{-1} and heated at 10 K min^{-1} it was 492.2 K for PAS (higher molecular mass sample), 497.6 K for PPES, 459.5 K for PBISP and 462.6 K for PBISP-S.

Heat capacities in the solid and liquid states by d.s.c.

For all samples, three to five measurements were made. The data of two to four of the sets were averaged and smoothed. For each polysulphone these data are listed in *Table 1* along with the equations used to smooth the data and the average and root mean square errors.

PAS. The polysulphone with higher molecular mass was analysed from 150 to 360 K using the TA Instruments system and from 230 to 480 K with the Perkin-Elmer DSC 7. The average and root mean square deviations between the two sets of data over the range of overlap were, as expected, small ($0.25 \pm 1.3\%$). The TA Instruments data from 150 to 360 K and the DSC 7 data from 370 to 470 K were further smoothed and are listed in *Table 1*. They represent the recommended experimental heat capacity for the solid. The heat capacities in the glass transition region (480–500 K) depend on the thermal history of the sample. The heat capacity of the liquid, measured with the TA Instruments system, could, as usual, be represented with a linear temperature dependence. Heat capacity was also measured for the lower molecular mass PAS from 230 to 420 K with the Perkin-Elmer DSC 7. The agreement with the data of the higher molecular mass sample was better than 1%. The recommended experimental data for the solid and the melt are those for the higher molecular mass as given in *Table 1*.

PPES. The heat capacity of PPES below the glass transition, in the glass transition region, and for the isotropic melt are also listed in *Table 1*. Recommended experimental data for the solid state were obtained from d.s.c. data measured using the TA Instruments system and the Perkin-Elmer DSC 7 while the melt heat capacities were obtained using the TA Instruments system. Since the heat capacities in the glass transition region show a dependence on the thermal history, these vary from sample to sample. The recommended experimental heat capacities up to the glass transition temperature must thus be obtained by extrapolating the solid and the liquid data to the glass transition temperature.

PBISP. Heat capacities were measured for both the powdered sample, PBISP, and the pellets, PBISP-S. The C_p for both samples, measured with the TA Instruments system, agreed to $\pm 2\%$ from 170 to 360 K. The data, along with the equations representing the smoothed heat capacities, are listed in *Table 1*. New data were also obtained for the melt and are given in *Table 1*. The present data for the solid and the melt were compared to the prior measurements. A set of recommended heat capacities in the ATHAS data bank (1990)[32] were derived earlier from the data reported in the literature[3,4]. The new data of this research are more extensive. Below the glass transition the heat capacities for the solid PBISP measured earlier using adiabatic calorimetry on samples from Union Carbide[3] agree with the present data to better than $\pm 1\%$. From 330 to 480 K, the earlier reported data[3] measured with a differential scanning microcalorimeter, DSM-4, showed an error of $\approx 5\%$. On comparison with our new data obtained with the Perkin-Elmer DSC 7, it was found that the C_p obtained by adiabatic calorimetry[3] between 330 and 360 K agreed to within 1–2%. Therefore, earlier recommended data based on ref. 3 were retained from 10 to 360 K.

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[b] From 150 to 270 K

$$C_p = \exp[-183.0187 + 100.4943(\ln T) - 18.0408(\ln T)^2 + 1.08967(\ln T)^3] \ (\pm 0.8\%)$$

From 280 to 490 K the data are the average of data from TA Instruments System and Perkin-Elmer DSC 7

$$C_p = \exp[292.7648 - 147.5393(\ln T) + 25.10034(\ln T)^2 - 1.4140(\ln T)^3] \ (\pm 0.9\%)$$

From 500 to 520 K the data were smoothed by a spline function and are affected by cooling and heating rates (glass transition region)
From 530 to 620 K

$$C_p = 356.3796 + 0.07318T \ (\pm 0.5\%)$$

[c] From 150 to 360 K the data are from TA Instruments system

$$C_p = \exp[-119.219 + 67.5573(\ln T) - 12.28442(\ln T)^2 + 0.753198(\ln T)^3] \ (\pm 0.8\%)$$

[d] From 150 to 360 K the data are from TA Instruments system

$$C_p = \exp[-19.7795 + 15.3476(\ln T) - 3.17773(\ln T)^2 + 0.225473(\ln T)^3] \ (\pm 0.7\%)$$

From 500 to 620 K

$$C_p = 591.81 + 0.57224T \ (\pm 0.3\%)$$

[e] ATHAS recommended experimental data (1991) as described in the text
For data from 10 to 360 K see ref. 32
From 370 to 430 K

$$C_p = -1764.871 + 10.40851T - 0.01096T^2 \ (\pm 0.3\%)$$

From 440 to 470 K the data were smoothed by a spline function and are affected by cooling and heating rates (glass transition region)
From 480 to 620 K

$$C_p = 591.81 + 0.57224T \ (\pm 0.3\%)$$

From 370 to 430 K the present data and those measured by Richardson and Savill[4] were available. These agreed in this temperature range with a precision of $\pm 1\%$ and were, therefore, averaged over the range of measurements and smoothed further. These new data are used instead of the previously recommended heat capacities[32]. The melt data are based entirely on the new experimental data measured in this research. The earlier available data from ref. 4 (480–540 K) showed deviations of 1–3%, and only two data points were given by Novoselova *et al.*[3]. The new set of recommended data for PBISP (1991) is shown in the last column of *Table 1* (PBISP-R).

Computation of the heat capacities of the solids

The recommended experimental heat capacities available in the ATHAS data bank (1990) for solid aliphatic polysulphones – P1PS (20–300 K), P1BS (100–300 K) and P1HS (20–300 K) – and for the newly analysed aromatic polysulphones (*Table 1*) – PAS and PPES (150–360 K) and PBISP (10–350 K) – were used to fit to an approximate vibrational spectrum. For this purpose the vibrational spectrum was separated into group and skeletal vibrations as listed in *Tables 2* and *3*. The group vibrations for the aliphatic polysulphones consisted of group contributions from CH_3, CH_2, CH and SO_2 groups. For the CH_3, CH_2 and CH groups, the frequencies were obtained from the normal-mode calculations of polypropylene[8]. The group frequencies for SO_2 groups were retrieved from the vibrational spectrum analysis of dimethyl sulphone, as described in ref. 33. The frequencies corresponding to the various modes were given as follows: SO_2 asymmetric and symmetric stretch at 1867 and 1641 K, C–S–C asymmetric and symmetric stretch at 1009–1108 K and SO_2 bending, wagging, twisting and rocking at 724 K, 665 K, 551 K and 460 K, respectively. For the aromatic polysulphones, the 27 group frequencies for the phenylene group were taken from the normal-mode calculations of poly(*p*-phenylene), as described in ref. 14, while the 18 frequencies for the $C(CH_3)_2$ group were chosen as described for the case of polyisobutylene[16] and also found to be applicable for polycarbonate[14]. For the various polysulphones, the computation steps and parameters are described next. A full description of the ATHAS scheme of calculation can be found, for example, in refs 24–26.

Table 2 Number of vibrational modes used as group frequencies of aliphatic polysulphones

Approximate mode	P1PS	P1BS	P1HS
CH_3 group[a]			
CH_3 asymmetric stretch	2	2	2
CH_3 symmetric stretch	1	1	1
CH_3 asymmetric bend	2	2	2
CH_3 symmetric bend	1	1	1
CH_3 rock	2	2	2
CH_3–C stretch	1	1	1
CH_2 group[a]			
CH_2 asymmetric stretch	1	2	4
CH_2 symmetric stretch	1	2	4
CH_2 bend	1	2	4
CH_2 wag	1	2	4
CH_2 twist	1	2	4
CH_2 rock	1	2	4
C–C chain stretch	1	2	4
CH group[a]			
CH stretch	1	1	1
CH bend	2	2	2
SO_2 group[b]			
SO_2 asymmetric stretch	1	1	1
SO_2 symmetric stretch	1	1	1
C–S–C chain stretch	2	2	2
Total group vibrational modes	23	30	44
Skeletal vibrational modes	13	15	19
Total vibrational modes	36	45	63

[a]Group frequencies were obtained from the normal-mode calculations of polypropylene[8]
[b]Group frequencies were retrieved from the vibrational spectra analysis of dimethyl sulphone[33]

Table 3 Number of vibrational modes used as group frequencies of aromatic polysulphones

Approximate mode	PAS	PPES	PBISP
Phenylene group[a]	27	52	106
SO_2 group[b]			
SO_2 asymmetric stretch	1	1	1
SO_2 symmetric stretch	1	1	1
C–S–C chain stretch	1	2	2
O group[a]			
C–O stretch	–	2	4
$C(CH_3)_2$ group[c]			
CH_3 asymmetric stretch	–	–	4
CH_3 symmetric stretch	–	–	2
CH_3 asymmetric bend	–	–	4
CH_3 symmetric bend	–	–	2
CH_3 rock	–	–	4
CH_3–C stretch	–	–	2
Total group vibrational modes	30	58	132
Skeletal vibrational modes	9	14	30
Total vibrational modes	39	72	162

[a]Group frequencies were obtained from the normal-mode calculations of poly(*p*-phenylene)[14]
[b]Group frequencies were retrieved from the vibrational spectra analysis of dimethyl sulphone[33]
[c]Group frequencies were as in ref. 16

P1PS. For P1PS, low temperature heat capacities from 20 to 50 K in the ATHAS data bank[7] were fitted to a Debye function. The θ_D varied from 200.6 K at 20 K to 316 K at 50 K (13 skeletal modes: two for each CH_2 group, three for the CH_3 group and six for the SO_2 group). Since the θ_D values changed linearly with temperature, they were initially extrapolated to 0 K to give a trial θ_D of 128.2 K. Using this value of θ_D, the skeletal heat capacities at constant volume (obtained by subtracting the group vibration contributions from the experimental C_v), were fitted to a Tarasov equation to yield a θ_1 of 689.8 ± 7.7 K and a θ_3 of 55.3 ± 0.31 K from 50 to 200 K. Using these values of θ_1 and θ_3 to represent the skeletal part of the frequency spectrum together with the 23 group vibrations, heat capacities C_v were computed from 0.1 to 1000 K. The C_v–C_p conversion was made using the universal A_0 of 0.0039 K mol J^{-1} in the modified Nernst–Lindemann equation described earlier. The T_m° value was taken to be 550 K.

The average and root mean square errors of the calculated heat capacities from the experimental data were $-0.5 \pm 1.7\%$ from 30 to 300 K. The errors at 20 and 30 K were much larger (13% and 7.6%, respectively). If a slightly higher value of θ_D of 175.4 K

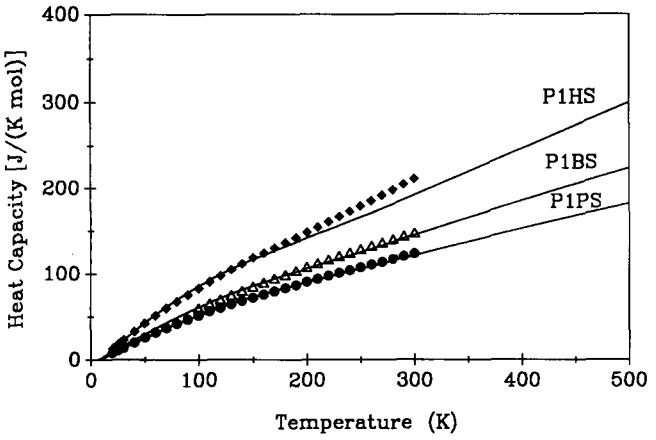

Figure 1 Heat capacities of the aliphatic polysulphones: ◆, △, ●, experimental values; ——, calculated values

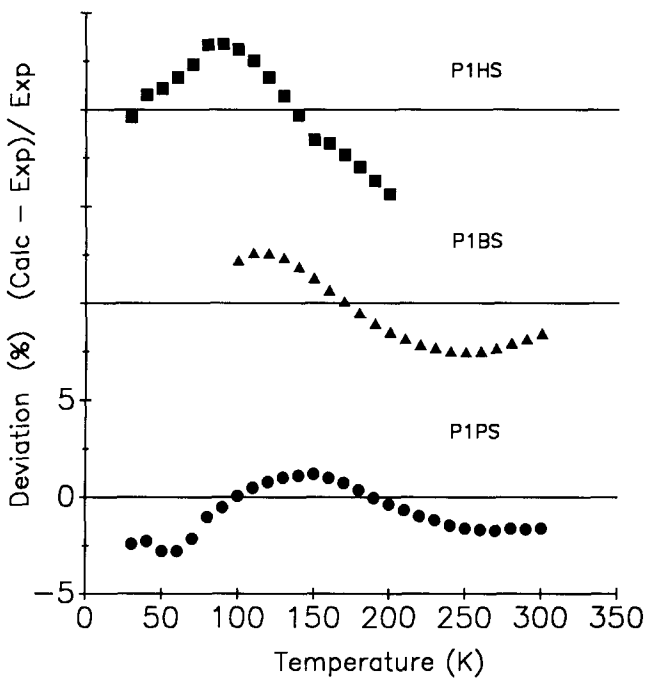

Figure 2 Deviation of the computed heat capacities from the experimental data for the aliphatic polysulphones

(corresponding to a temperature of about 10 K) was used, the θ_1 showed no significant change (685.2 ± 11.4 K, 40–200 K) while θ_3 changed to 88.8 ± 0.7 K. Recalculating the heat capacities for P1PS using a θ_3 of 88.8 K resulted in an improvement in the low temperature data (errors at 20 and 30 K were 10% and 4%, respectively). The root mean square error from 30 to 300 K improved to ±1.2% from ±1.7%. The computed heat capacity is plotted in *Figure 1* and the error plot is shown in *Figure 2*. Both sets of data were within the customary error limit of ±3% of the ATHAS computed heat capacities. The heat capacities calculated with a θ_3 of 88.8 K and a θ_1 of 685.2 K are taken as the recommended data. The recommended parameters are shown in *Table 4*.

P1BS. Heat capacities were available in the ATHAS data bank[7] from 100 to 300 K. Since no low temperature data were measured, the θ_D of 175.4 K of P1PS was used for the 15 skeletal modes. Similarities of θ_D in homologous series are common and this choice of θ_D is also supported by the results on P1HS (described below). The four bending modes for the sulphone group were taken as a part of the skeletal backbone in addition to the two low frequency C–S–C bending modes as in P1PS. The θ_1 and θ_3 obtained by fitting the skeletal heat capacities were 668.9 ± 9.3 K and 89.3 ± 0.6 K, respectively (100–140 K). Using the universal A_0 of 0.0039 K mol J^{-1} and an estimated T_m^o of 480 K, heat capacities were computed from 0.1 to 1000 K. The agreement between calculated and experimental C_p was −0.6 ± 1.9% (100–300 K). The data are plotted in *Figure 1* and the error plot is shown in *Figure 2*; the recommended parameters are given in *Table 4*.

P1HS. Experimental heat capacities were available[7] from 20 to 300 K. The low temperature heat capacities from 20 to 50 K were fit to a Debye function and resulted in a θ_D of 192.8 K at 20 K and 300.0 K at 50 K when 19 skeletal modes and 44 group vibrational modes were used. These θ_D values were close to those obtained for P1PS (described above). Therefore, similar to the case of P1PS, an estimated θ_D of ≈175 K was used to calculate θ_1 to be 587.3 ± 27.8 K and θ_3 to be 95.6 ± 2.3 K

Table 4 Various parameters for polysulphone heat capacities

Polymer	Experimental C_p data range (K)	Number of skeletal modes	θ_1(K)[a]	θ_3(K)[a]	Average r.m.s. error (%)[b]
P1PS	20–300	13	685.2 ± 11.4 (40–200)	88.8 ± 0.7 (40–200)	−0.8 ± 1.2 (30–300)
P1BS	100–300	15	668.9 ± 9.3 (100–140)	89.3 ± 0.6 (100–140)	−0.6 ± 1.9 (100–300)
P1HS	30–300	19	587.3 ± 27.8 (50–200)	95.0 ± 2.3 (25–200)	0.5 ± 2.6 (30–200)
PAS	150–492.6 (T_g)	9	495.0 ± 39 (150–350)	46.0 (from PBISP)	−0.2 ± 0.6 (150–470)
PPES	150–497.4 (T_g)	14	799.5 ± 7.3 (170–300)	46.0 (from PBISP)	0.3 ± 1.0 (180–420)
PBISP	10–458.2 (T_g)	30	777.8 ± 13 (90–300)	46.0 ± 0.4 (90–300)	0.6 ± 1.0 (100–410)

[a] Values in parentheses represent the temperature range used for fitting the θ temperature

[b] Values in parentheses represent the temperature range over which the experimental heat capacity agrees with the computed heat capacity:

[(calculated − experimental)/(experimental at 10 K intervals)

(averages from 25 to 200 K). Using the universal A_0 of 0.0039 K mol J^{-1} and an estimated melting temperature (T_m°) of 500 K, the heat capacities were calculated from 0.1 to 1000 K. The average and root mean square error from 30 to 200 K was $0.5 \pm 2.6\%$. Beyond 200 K, the experimental heat capacities showed an increasingly positive deviation from the calculated data and at a temperature of 300 K, the errors were as high as ~9%. The calculated C_p is plotted in *Figure 1* and the error is plotted in *Figure 2*. *Table 4* gives the recommended parameters for the computed heat capacities.

PAS. The separation of the vibrational spectrum into skeletal and group contributions is shown in *Table 3*. The phenylene group contributes a total of 30 vibrational modes; 27 of these were taken as group vibrations and the remaining three low frequency modes were assigned to the skeletal part. Two modes, corresponding to a box distribution in the low frequency range of 60–90 K were taken as the group vibrations, as had been done for several of the previously analysed phenylene-containing polymers[14]. For the SO_2 group (similar to the treatment in aliphatic polysulphones), six vibrations were assigned to the skeletal part, while the remaining were included as group vibrations. Hence a total of nine skeletal and 30 group vibrations were used for the computation. The skeletal heat capacity obtained by subtracting the group contribution from the total C_v were then fitted to a Tarasov equation. A $\theta_1 = 495 \pm 39$ K was obtained from 150 to 350 K. The value of θ_3 was estimated to be 46 K based on the result obtained for PBISP (described below, and close to 40 K found for many other phenylene-containing polymers)[14]. The universal A_0 of 0.0039 K mol J^{-1} was used along with a T_m° of 739 K ($3/2T_g$) to compute heat capacity for the solid from 0.1 to 1000 K.

The computed data were somewhat higher than the experimental heat capacities from 150 to 470 K (for example at 370 K the error was 2% and at 470 K it was about 3%). The average and root mean square error over the range 150–470 K was $1.4 \pm 0.9\%$. This systematically increasing error of the calculated heat capacities may well be caused by the estimated values of A_0 being too large for the C_p–C_v conversion. Hence a 36% lower value of A_0 of 0.0025 K mol J^{-1}, was used to improve the calculated data. The average and root mean square errors were now $-0.2 \pm 0.6\%$ from 150 to 470 K. The recommended parameters for the computation are listed in *Table 4*. The data are plotted in *Figure 3* along with the experimental solid and liquid heat capacities. *Figure 4* shows the deviation of the calculated data from the experimental C_p.

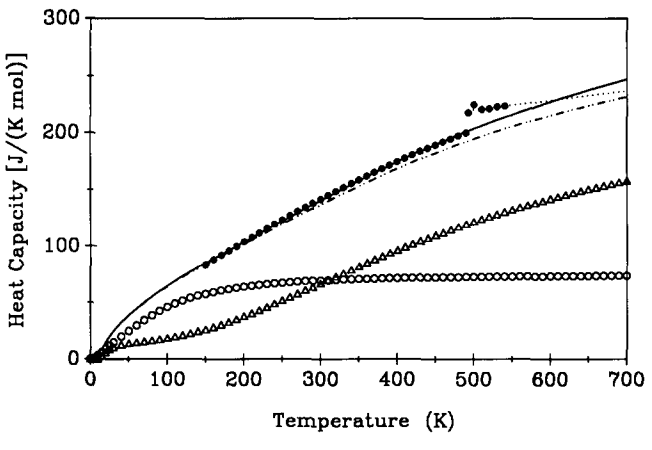

Figure 3 ATHAS computed and experimental heat capacities of PAS: ···, experimental liquid C_p; ●, experimental C_p; ——, calculated solid C_p; –·–·–, C_v; △, group vibrations; ○, skeletal vibrations

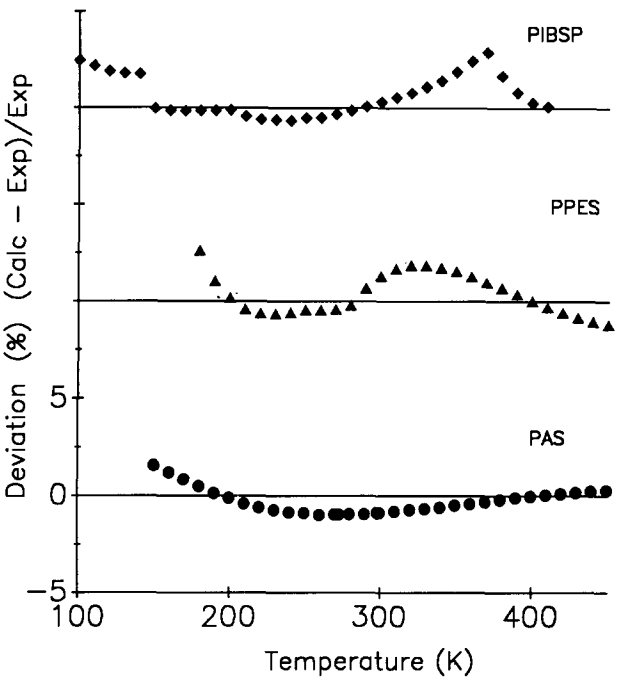

Figure 4 Deviation of the computed heat capacities from the experimental data for aromatic polysulphones

PPES. The recommended experimental heat capacities of *Table 1* from 150 to 360 K were fitted to a vibrational spectrum approximated by 14 skeletal (six for two C_6H_4 groups, two for the O groups and six for the SO_2 group) and 59 group vibrations (*Table 3*). The θ_1 obtained was 799.5 ± 35.2 K (170–300 K). An estimated θ_3 value at 46 K (same as for PBISP, described below and also used for PAS, described above) was used since heat capacities below 150 K were not available. Using the universal value of $A_0 = 0.0039$ K mol J^{-1} and a $T_m^\circ = 746$ K ($3/2T_g$), the average and root mean square error of the calculated C_p from the experimental data was $2.6 \pm 1.0\%$ (190–490 K). Again, a 49% decrease in A_0 to 0.002 K mol J^{-1} resulted in a better agreement between the experimental and the calculated data, and the average and root mean square error decreased to $0.3 \pm 1.1\%$ from 180 to 460 K. The final recommended parameters are included in *Table 4*. *Figure 5* shows the heat capacities of PPES (experimental and calculated), and *Figure 4* the deviation of the calculated C_p from the experimental C_p.

PBISP. The recommended experimental heat capacities from 10 to 300 K derived in this paper (*Table 1*) were used to fit to a vibrational spectrum, separated into 30 skeletal and 132 group vibrational modes (*Table 3*). The θ_1 and θ_3 values calculated from 90 to 300 K were 777.8 ± 13 K and 46.1 ± 0.4 K, respectively. The θ_D used in the expression $\theta_D = (\theta_1\theta_3^2)^{1/3}$ was chosen to be 118.3 K. This value was obtained by linear extrapolation to 0 K of the Debye temperature that changed from 132.3 to 217.5 K for a temperature range from 10 to 50 K. Using the above derived values of θ_1 and θ_3 together

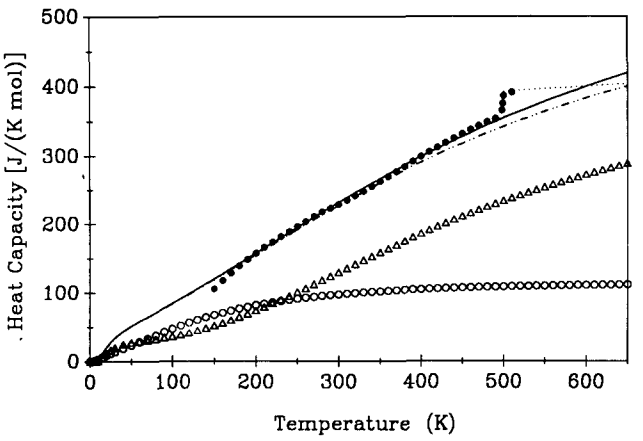

Figure 5 ATHAS computed and experimental heat capacities of PPES: ···, experimental liquid C_p; ●, experimental C_p; ——, calculated solid C_p; –·–·–, C_v; △, group vibrations; ○, skeletal vibrations

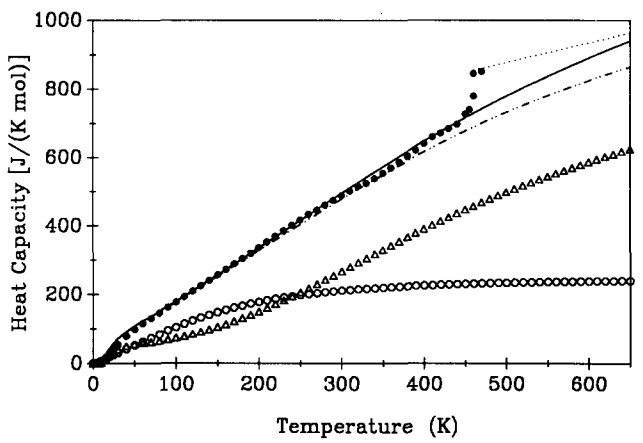

Figure 6 ATHAS computed and experimental heat capacities of PBISP: ···, experimental liquid C_p; ●, experimental C_p; ——, calculated solid C_p; –·–·–, C_v; △, group vibrations; ○, skeletal vibrations

with the 132 group vibrations, heat capacities were calculated from 0.1 to 1000 K. For the C_p–C_v conversion, an experimental value for $A_0 = 0.00315$ K mol J^{-1} obtained from expansivity and compressibility[28] was used and T_m^o was taken to be 687 K ($3/2T_g$).

Although the C_p from 100 to 410 K agreed reasonably well with the experimental data (the average and root mean square was 0.6 ± 1.0%), the errors were rather high below 50 K. At 10 K it was ~30% and this increased to ~50% at 20 K and then showed a decrease with increase in temperature (the error at 50 K being about 11%). These large errors could either be due to experimental uncertainty or due to selection of too many low frequency (skeletal) vibrators. The second possibility was checked by recalculating the heat capacities using 26 skeletal modes and considering the four bending modes of SO_2 group at 724, 665, 551 and 460 K as group vibrations (total group vibrations considered were 136). The θ_1 and θ_3 obtained in this fashion were 705.9 ± 6.3 K and 48.4 ± 0.2 K from the temperature range 90–280 K. The errors below 50 K improved only very slightly as the θ_3 changed only slightly by changing N from 30 to 26. If a higher value of $\theta_D = 152$ K, corresponding to a temperature of 15 K, was used, θ_3 changed to 70 K. Using this θ_3 and the θ_1 of ≈706 K did not bring about any significant improvement in the data (the error at 20 K was ≈40% and at 50 K was ≈8%) indicating that either the data below 50 K have an associated experimental error or the low frequency vibrations at 60–90 K do not correspond to the polyphenylene analysis. More low temperature data on polymers with *p*-phenylene groups in the main chain are needed to resolve this question. For the present, the first set of data calculated with the number of skeletal vibrations $N = 30$, $\theta_1 = 777.8$ K and $\theta_3 = 46$ K was taken as the recommended set of heat capacities in order to be consistent with the previously analysed polysulphones. The recommended parameters are given in *Table 4* and the calculated heat capacities are plotted in *Figure 6*. The error plot is shown in *Figure 4*.

Enthalpies, entropies and Gibbs functions

The enthalpies, H, entropies, S and Gibbs functions, G, of all polysulphones analysed in this paper have been computed by integrating the approximate heat capacity from 0 K using the computed solid and experimental liquid heat capacities where available. Data tables are available on request from the authors.

DISCUSSION

Computed heat capacities

Aliphatic polysulphones. For the three aliphatic polysulphones analysed, P1PS, P1BS and P1HS, the Tarasov equation represents the skeletal heat capacities well. Our prior experience of ATHAS had shown that this equation was indeed applicable to all linear macromolecules where the mass distribution and force constants do not vary significantly along the chain. The equation worked well for polypropylene[8] as well as for the most recently analysed polysilylenes[22]. In polysilylenes with long side chains, backbone and side chains had to be included in the Tarasov fit to obtain good agreement between the calculated and the experimental data. For cases where there was an uneven distribution in mass along the chain, it had been observed earlier that the deviations were larger than the experimental uncertainty[8,10,11]. In the present analysis of the aliphatic and aromatic polysulphones, considering the entire bulky sulphone group as part of the skeletal worked well.

For the polymers[14] where the backbone contains the bulky C_6H_4 group, a correction was used that was derived for polyphenylene and consisted of the inclusion of a box distribution of two modes of vibrations with frequencies from 60 to 90 K. This correction worked well to represent the low temperature skeletal heat capacities for a large number of phenylene-containing polymers[14] and also seemed appropriate for PAS and PPES. In the case of PBISP, the errors at temperatures below 50 K could be due to experimental uncertainty, but it must be repeated that these errors could also be associated with the inclusion of eight 60–90 K box terms for the four phenylene groups, resulting in a higher calculated C_p in this temperature region most affected by this choice [(0.1–0.8) θ_3].

The choice of the θ_1 temperatures for the three aliphatic polysulphones indicates that, as observed in the other polymers analysed in ATHAS, the group vibrations derived from normal-mode calculations or from i.r. and Raman data can well represent the heat capacity contribution of the intramolecular

vibrations. From P1PS to P1HS θ_1 decreases from 685 to 587 K and approaches, as expected, the value for polyethylene (519 K)[9]. Assuming that the intramolecular force constants do not change significantly between these polymers, the θ_1 value can be calculated [$\theta_1 \propto (1/\text{molecular mass})^{1/2}$] to be $\approx$645 K for P1BS and $\approx$580 K for P1HS if the value of $\approx$685 K derived experimentally for P1PS is used for estimation. The θ_1 for P1PS ($\approx$685 K) can also be compared to that of polypropylene, PP (714 K for crystalline and 633 K for amorphous). The θ-temperature of P1BS can be compared with that of poly(1-butene), PB, and that of P1HS with poly(1-hexene), PHEX (for PB θ_1 = 618 K and for PHEX θ_1 = 563 K). In all cases similar trends are observed.

Aromatic polysulphones. The θ temperatures derived for the three aromatic polysulphones can be compared to those of other phenylene-containing polymers in the ATHAS data bank. The θ_1 of 495 K for PAS is, indeed, not much different from the other phenylene-containing polymers in which θ_1-temperature varied between 544 K for poly(*p*-phenylene), PPP, to 586 K for poly(ethylene terephthalate), PET. This suggests that in these polymers the θ_1-temperature does not depend much on the nature of the backbone. One should assume that PPES could be compared to poly(oxy-1,4-phenylene) POP (θ_1 = 555 K) and poly(thio-1,4-phenylene), PTP (θ_1 = 566 K). The observed value of θ_1 = 800 K for PPES is thus quite surprising. Similarly the θ_1 value of PBISP is surprisingly high.

Glass transition

The glass transition temperature in all three aliphatic polysulphones could not be analysed due to the lack of experimental heat capacities beyond 300 K. There were, however, indications of the approaching glass transition temperature in all these aliphatic polysulphones in the error plot (*Figure 2*) and to some extent in *Figure 1* where the experimental C_p data is tending higher than the computed solid heat capacities. The ATHAS recommended glass transition temperature for polyethylene and PP are 237 and 270 K, respectively. Because of the rigidity introduced by the SO_2 group, one would expect the glass transition temperature to be higher in these aliphatic polysulphones. Going from P1PS to P1HS the number of CH_2 groups increases from one to four and the glass transition is lowered. Its beginning can therefore be more clearly seen in P1HS (*Figures 1* and *2*).

No information is available in the literature on the heat capacities of the liquids of the three aliphatic polysulphones. Hence, the ATHAS empirical addition scheme for the heat capacity was used to obtain the C_p for the liquid. The heat capacity contribution of the liquid SO_2 group had to be derived from the aromatic polysulphones. For this purpose the C_6H_4 group contribution was derived from the phenylene-containing polymers: poly(butylene terephthalate), PET and poly(oxybenzoate). The averaged smoothed data for the phenylene heat capacity could be represented by equation (2), which is based on an improved set of melt heat capacities over those used earlier[34]:

$$C_p = 64.1837 + 0.13764T \ (\pm 0.5\%) \qquad (2)$$

Subtracting the contribution of the phenylene group from the heat capacity of POP gave the O group contribution. For the isopropylidene group, the heat capacity contribution in the liquid state had been derived earlier[35]. Subtracting the contribution of these groups from the aromatic polysulphone melt heat capacities gave the contribution for the SO_2 group. The heat capacity of the SO_2 group from 500 to 550 K agreed for PAS and PES, with a root mean square error of $\pm$2.6%. The data were then averaged and the smoothed heat capacity for the sulphone group can be represented by:

$$C_p = 154.0051 - 0.1311T \qquad (3)$$

Heat capacity for the P1HS could then be generated by adding the sulphone group contribution of equation (3) to the heat capacity of the CH_2 group (from polyethylene)[36] and the CH_2–$CH(CH_3)$ group from PP[37]. The ΔC_p obtained by subtracting the computed solid heat capacity from the addition scheme liquid value at 300 K is 103.6 J K^{-1} mol^{-1}, much too high for any estimate of ΔC_p. The heat capacity increase at T_g per 'small bead' of the backbone chain has been established for a large number of macromolecules in the ATHAS data bank. Each small bead contributes a value of about 11.5 J K^{-1} mol^{-1} to ΔC_p. Based on this and the low ΔC_p of PHEX of only 25.1 J K^{-1} mol^{-1} one would not expect more than 50 J K^{-1} mol^{-1} for P1HS. This value is reached only at a temperature of about 375–425 K, which at this stage could be taken as an estimate of the glass transition temperature.

For the aromatic polysulphones the calculated 'vibration only' C_p and the linearly extrapolated C_p of the liquid could be used as baselines to analyse the increase in heat capacity in the glass transition regions. From the heat capacity plots, the values of T_g were determined graphically at the mid-point of the heat capacity increase and are listed in *Table 5*. These are close to the values determined directly from the d.s.c. scans, described earlier in the Results section. The values of ΔC_p were calculated from the difference of the experimental C_p of the liquid and the computed C_p of the solid and are given in *Table 5*. The ΔC_p of 18.1 J K^{-1} mol^{-1} for PAS can be compared to that of POP[34] where the ΔC_p obtained was 25.7 J K^{-1} mol^{-1} and the case of PTP, PPS[34], where the ΔC_p was about 29 J K^{-1} mol^{-1}. In both these polymers the value of ΔC_p (almost double that of the 'small bead') was attributed to 'large beads' like C_6H_4–O and C_6H_4–S. In case of PAS the ΔC_p corresponds to a similarly 'large bead' C_6H_4–SO_2. For PPES the value of ΔC_p can be better understood if one considers this as an alternating copolymer of POP and PAS. The value of ΔC_p listed in *Table 5* is about the same as would be expected by combining the data for POP and PAS. Similarly, ΔC_p

Table 5 Heat capacity increase at the glass transition (T_g)

Polymer	T_g (K)[a]	ΔC_p	Number of beads[b]
PAS	492.6	18.10	0 + 1
PPES	497.4	37.72	0 + 2
PBISP[c]	458.2	126.56	0 + 5

[a]Recommended value of T_g

[b]The first number refers to 'small beads' such as CH_2, O, $C(CH_3)_2$, etc. Their ΔC_p is about 11.5 J K^{-1} mol^{-1}. The second number refers to 'large beads' such as C_6H_4, $C_6H_4SO_2$, C_6H_4O, etc. Their ΔC_p is double that of a small bead

[c]Polysulphone is from Amoco Chemical Company

for PBISP could account for five large beads gaining mobility at the glass transition temperature.

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