Heat Capacity and Other Thermodynamic Properties of Linear Macromolecules.
IX. Final Group of Aromatic and Inorganic Polymers

Umesh Gaur, Suk-fai Lau, and Bernhard Wunderlich

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181

In this final review, a series of polymers which include aromatic rings and/or inorganic chain atoms are treated. Heat capacities of poly(4,4′-isopropylidenediphenylene carbonate), polyphenylenediamides, polyheteroarylenes, poly(dimethyl siloxane), poly(diethyl siloxane), poly(trimethylsilyl-ethylene), poly(dimethylphenylsilyl ethylene), poly(dimethylbenzylsilyl ethylene), poly(vinylene diphenylsilylene), poly(vinylene diphenylgermylene), poly(diethnyl diphenysilylene), poly(diethnyl diphenylgermylene), poly(2,3,4,5-tetraphenyl-1, 1-diethylgermocyclopentadiene), poly(phenylsilsesquioxane), poly[ethylene -N-(β-trimethylsilylethyl)imine] and polysulfones have been reviewed on the basis of measurements on 36 samples reported in the literature. All heat capacity data are compiled and a set of recommended data are derived. Enthalpy and entropy functions are calculated for poly(4,4′-isopropylidenediphenylene carbonate) and poly(dimethyl siloxane).

Key words: enthalpy; entropy; glass transition; germanium polymers; heat capacity; linear macromolecules; polycarbonate; poly(dimethyl siloxane); polyheteroarylene; polyphenylenediamide; polysulfone; silicon polymer.

Contents

List of Tables

Reprints available from ACS; see Reprint List at back of issue.

0047-2689/83/010091-18/$06.00

List of Tables Deposited in PAPS[a]

List of Figures

1. Introduction

This is the last paper in a series of discussions on the heat capacity of linear macromolecules. In the earlier papers,[1–8] the heat capacity of selenium, polyethylene, polypropylene, polystyrene and various types of polyoxides, polyesters, polyamides, acrylic polymers, and other carbon backbone polymers have been analyzed. This paper deals with acrylic polymers which contain aromatic[b] groups, and/or inorganic chain atoms.[c] These polymers are used as engineering thermoplastics and their use as heat resistant materials has increased in the recent past.

The aromatic polymers analyzed in this paper are:

poly(4,4′-isopropylidenediphenylene carbonate),
poly[carbonylimino(6-hydroxy-1, 3-phenylene) methylene-(4-hydroxy-1, 3-phenylene)iminocarbonyl-1, 3-phenylene,
poly(imino-1, 2-phenyleneiminoisophthaloyl),
poly(imino-1, 3-phenyleneiminoisophthaloyl),
poly(imino-1, 4-phenyleneiminoisophthaloyl),
poly(imino-1, 2-phenyleneiminoterephthaloyl),
poly(imino-1, 3-phenyleneiminoterephthaloyl),
poly(imino-3, 5-pyromellitolylimino-1, 4-phenyleneoxy-1, 4-phenylene),
poly(pyroazolino[3,4-C]quinazoline-3, 5-diyl-1, 3-phenylenepyroazoline[3,4-C]quinazoline-5, 3-diyl-1, 4-phenylene),
poly(imino-1, 2-phenylene-4H-1, 2, 4-triazole-3, 5-diyl-1, 3-phenylene-4H-1, 2, 4-triazole-3, 5-diyl-1, 2-phenyleneiminoterephthaloyl),

---

[a] See AIP document no. PAPS JPCRD-12-0091-7 for 7 pages of data tables. Order by PAPS number and journal reference from American Institute of Physics, Physics Auxiliary Publication Service, 335 East 45th Street, New York, N.Y. 10017. The price is \$1.50 for a microfiche or \$5.00 for photocopies. Airmail is additional. This material also appears in *Current Physics Microform*, the monthly microfilm edition of the complete set of journals published by AIP, on the frames following this journal article.

[b] Some other polymer containing phenyl group have been analyzed in previous publications: poly(oxy-1, 4-phenylene)s,[3] polystyrene,[5] poly(vinyl benzoate)s,[7] poly(ethylene terephthalate).[8]

[c] In our classification of polymers, an inorganic chain atom is any atom besides carbon and oxygen.

poly(2,5-benzoxazolediylmethylene-5, 2-benzoxazolediyl-1, 3-phenylene),
poly(5,7-dihydro-1, 3, 5, 7-tetraoxobenzo [1,2-c:4, 5-c′] diphyrrole-2, 6[1H,3H]-diyl-1, 4-phenyleneoxy-1, 4-phenylene),
poly[oxy(4-amino-1, 3-phenylene)iminocarbonyl-(4,9-dicarboxytricyclo[4.2.2.0^{2,5}]-7-decane-3, 10-diyl)carbonylimino-(6-amino-1, 3-phenylene)],
poly(hydrazocarbonyl-1, 4-phenylene-2, 1-benzo[c]furone-3, 3-diyl-1, 4-phenylenecarbonylhydrazoterephthaloyl),
poly(1,4-phenylene-1, 3, 4-oxadiazole-2, 5-diyl-1, 4-phenylene-2, 1-benzo[c]-furone-3, 3-diyl-1, 4-phenylene-1, 3, 4-oxadiazole-2, 5-diyl),
and poly[6,6′-bis[3,3′-diphenylquinoxaline)-2, 2′-diyl-1, 4-phenyleneoxy-1, 4-phenylene).

The polymers with inorganic main or side chain atoms analyzed in this paper are:

poly(dimethyl siloxane),
poly(diethyl siloxane),
poly(trimethylsilyl ethylene),
poly(dimethylphenylsilyl ethylene),
poly(dimethylbenzylsilyl ethylene),
poly(vinylene diphenylsilylene),
poly(vinylene diphenylgermylene),
poly(vinylene diphenylsilylene vinylene diphenylgermylene),
poly(diethnyl diphenylsilylene),
poly(diethnyl diphenylgermylene),
poly(2,3,4, 5-tetraphenyl-1, 1-diethnylgermocyclopentadiene),
polyphenylsilsesquioxane,
poly[ethylene-N-(β-trimethylsilyethyl)imine],
poly(propene sulfone),
poly(1-butene sulfone),
and poly(1-hexene sulfone).

This is the last paper in a series of discussions on heat capacities of linear macromolecules. In this series the available heat capacity data on all the linear macromolecules have been compiled and analyzed.

2. Recommended Data on Heat Capacity and Thermodynamic Properties of Aromatic Polymers

2.1. Poly(4,4′-isopropylidenediphenylene carbonate)

This industrially important polycarbonate is made by condensation of 4,4-dihydroxydiphenyl-2, 2-propane and phosgene in the presence of alkali. Its repeating unit is C_6H_4–$C(CH_3)_2$–C_6H_4–OCOO–with a formula weight of 254.29.

The crystal structure of poly(4,4′-isopropylidenediphenylene carbonate), thereafter referred to as polycarbonate, is monoclinic (space group Pc). The molecular chains which form a 16*2/1 helix along the crystallographic c-axis are 15%–20% shortened from the fully stretched form to achieve closer carboxyl alignment. The unit cell parameters have been determined by Bonart[9]

$$a = 1.23 \text{ nm}, \quad b = 1.01 \text{ nm}, \quad c = 2.08 \text{ nm}, \quad \gamma = 84.$$

The crystalline density is 1.314 Mg m^{-3} at 298 K which corresponds to a packing density of 0.72.[10] The equilibrium melting parameters have been summarized by Wunderlich[10,11] at $T_m^0 = 568$ K and $\Delta H_f^0 = 33.6$ kJ mol^{-1}.

The density of amorphous polycarbonate at room temperature is 1.196 Mg m^{-3}. This corresponds to a packing density of 0.66. The glass transition for amorphous polycarbonate is well established at 418 K.[12]

Thirteen investigations of the heat capacity of poly(4,4′-isopropylidenedipheylene carbonate) have been reported in the literature. Heat capacity of 16 samples of various crystallinities and molecular weight have been measured over a wide range of temperature.

All investigations were critically evaluated in terms of sample characterization, experimental technique, error limit, and accuracy of representation of data. It was found that only three of the thirteen investigations met our standards of acceptable data (discussed in Ref. 1). These investigations are listed in Table 1. They contain heat capacity data on five polycarbonate samples of low crystallinity ($w^c = 0 - 0.25$). Ten investigations which did not contain acceptable data were not included in further analysis. These are listed in Table 2, along with brief comments on the reasons for exclusion from this study.

The heat capacity data on various polycarbonate samples retrieved from the literature are given in Tables A1 to A4. These tables have been deposited with the Physics Auxiliary Publication Service of the American Institute of Physics. The low temperature data (below 5 K) are given in Table A1. Tables A2 and A3 contain data on various polycarbonates below and above the glass transition, respectively. Finally, Table A4 contains data on various molten samples of polycarbonate.

Heat capacity measurements on amorphous polycarbonate are available over the entire temperature range from 0 to 560 K. For semicrystalline samples, the measurements are restricted to samples of low crystallinity and cover a limited temperature range (above 120 K only). Moreover, O'Reilly *et al.*[14] have established that from 120 K to the glass transition, the heat capacity has limited or no dependence on the crystallinity. Thus, the crystallinity dependence of the heat capacity (which would be expected to be significant at lower temperatures) cannot be estimated at present over the whole temperature range. Thus, the recommended data have been derived for amorphous polycarbonate only.

From 0 to 4 K, the data of sample 6 are recommended and from 10 to 110 K, the data of sample 1 are recommended. From 120 K to the glass transition temperature (418 K), the recommended data were obtained by curve fitting the heat capacities of samples 1, 2, 3, and 4 into the equation

$$C_p = \exp[0.0436596(\ln T)^3 - 0.660333(\ln T)^2 + 4.2605(\ln T) - 5.19373] \text{ J mol}^{-1} \text{ K}^{-1}. \quad (1)$$

The rms deviation was 1.0%.

To obtain recommended heat capacity data on molten polycarbonate from 418 to 560 K, the heat capacities on

Table 1. Heat capacity measurements of poly(4,4'-isopropyledenediphenylene carbonate)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Dainton et. al. (1962) [13]	1. Lexan[a] $w^c \simeq 0$	20-310	Adiabatic (1%)	Table
O'Reilly et al. (1963) [14]	2. Lexan[a] $\bar{M}_v = 40{,}000$ Powder $\Delta H_f = 5.89$ kJ mol^{-1} $w^c = 0.18$	120-550	Adiabatic (0.4%)	Graph
	3. Lexan[a] $\bar{M}_v = 40{,}000$ Solution crystallized $\Delta H_f = 8.23$ kJ mol^{-1} $w^c = 0.25$	240-560	Adiabatic (0.4%)	Graph
	4. Lexan[a] $\bar{M}_v = 40{,}000$ Quenched $w^c \simeq 0$	380-550	Adiabatic (0.4%)	Graph
Cieloszyk et al. (1973) [15]	6. Lexan[a] $\rho = 1.19$ Mg m^{-3} $w^c \simeq 0$	0.4-4.25	Heat Pulse (10%)	Equation[b]

---

[a] Lexan is the trade name for poly(4,4'-isopropylidenediphenylene carbonate) manufactured by General Electric Company.

[b] The data given in tabular form were curve fitted into the equation $C_p = \exp[-0.30631(\ln T)^3 + 0.260113(\ln T)^2 + 3.19906(\ln T) - 9.8971]$ J mol^{-1}K^{-1} (RMS dev. = 2.1%).

Table 2. Investigations on heat capacity of poly(4,4'-isopropylidenediphenylene carbonate) not included in this study

Reference	Reason(s) for exclusion
Hellwege et al. (1962) [16]	Heat capacity data reported for Markolon (Farbenfabriken Bayer AG) from 300 to 450 K. Their data differ 5-8% from the data reported here.
Steere (1966) [17]	Heat capacities per unit volume have been reported. These values are not directly comparable to the data presented here.
Park and Uhlmann (1973) [18]	Heat capacity measurements reported from 360 to 460 K on a drawn sample (55.6% elongation) after annealing at 423 K.
Bashirov et al. (1975, 1976) [19, 20]	Sample characterization not reported. Data could not be read accurately from too small graphs.
Adam et al. (1976) [21]	Heat capacity data reported for an amorphous sample and a semi-crystalline sample. Their data is 5-30% lower than the recommended values reported here.
Zemlyanoi and Dushchenko (1976) [22]	Data could not be read accurately from too small graphs.
Dushchenko et al. (1977) [23]	Heat capacity data reported in the glass transition region as a function of heating rate.
Belostotskii et al. (1977) [24]	The pressure dependence of heat capacity was investigated from simultaneous measurements of thermal conductivity and diffusivity at 303 and 333 K in the pressure range 0-2.5 bar. Heat capacity increases by about 5% with pressure.
Gilmour et al. (1978) [25].	Data could not be read accurately from too small graphs.

samples 2, 3, and 4 were curve fitted into the equation

$$C_p = 0.579\,T + 237.08 \text{ J mol}^{-1}\text{ K}^{-1}. \quad (2)$$

The rms deviation was 0.6%.

The recommended heat capacity data on amorphous polycarbonate are listed in Table 3 and plotted in Fig. 1. These heat capacities were used to derive thermodynamic functions for amorphous polycarbonate. These are also listed in Table 3. H_0^a and S_0^a refer to zero point enthalpy and

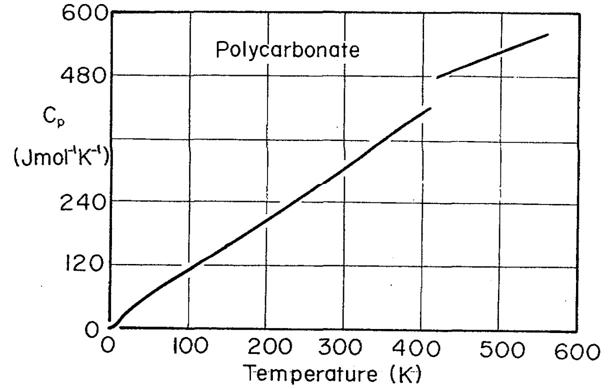


FIG. 1. Recommended heat capacity data for poly(4,4′-isopropylidenediphenylene carbonate).

Table 3. Recommended thermodynamic data for amorphous poly(4,4'-isopropylidenediphenylene carbonate)[a]

T(K)	C_p (J mol^{-1}K^{-1})	H^a_T-H^a_o (J mol^{-1})	S^a_T-S^a_o (J mol^{-1}K^{-1})
0.0	0.0	0.0	0.0
0.4	0.0000042	0.0000008	0.0000021
0.5	0.0000069	0.0000014	0.0000033
0.6	0.0000109	0.0000023	0.0000049
0.7	0.0000169	0.0000037	0.0000070
0.8	0.0000251	0.0000053	0.0000098
0.9	0.0000360	0.0000088	0.0000134
1.0	0.0000503	0.0000131	0.0000179
1.2	0.0000908	0.0000273	0.0000305
1.4	0.000150	0.0000513	0.0000488
1.6	0.000232	0.0000895	0.0000740
1.8	0.000339	0.0001466	0.0001073
2.0	0.004729	0.0006534	0.0003626
3.0	0.01542	0.01073	0.00411
4.0	0.03094	0.03391	0.01055
10.0	5.950	17.98	1.819
20.0	25.38	174.6	11.11
30.0	39.85	500.8	24.13
40.0	52.46	962.3	37.32
50.0	63.75	1543.	50.26
60.0	73.72	2230.	62.78
70.0	82.62	3012.	74.82
80.0	91.39	3882.	86.43
90.0	100.4	4841.	97.72
100.0	109.7	5891.	108.8
110.0	118.8	7034.	119.7
120.0	128.9	8272.	130.4
130.0	139.0	9612.	141.2
140.0	148.9	11051.	151.8
150.0	158.8	12590.	162.4
160.0	168.7	14227.	173.0
170.0	178.5	15963.	183.5
180.0	188.3	17797.	194.0
190.0	198.0	19729.	204.4
200.0	207.8	21758.	214.8
210.0	217.6	23885.	225.2
220.0	227.3	26109.	235.6
230.0	237.1	28431.	245.9
240.0	247.0	30852.	256.2
250.0	256.8	33371.	266.5
260.0	266.7	35988.	276.7
270.0	276.7	38705.	287.0
273.15	279.8	39596.	290.3
280.0	286.7	41522.	297.2
290.0	296.7	44439.	307.5
298.15	304.9	46906.	315.9
300.0	306.8	47456.	317.7
310.0	316.9	50575.	327.9
320.0	327.1	53795.	338.2
330.0	337.4	57117.	348.4
340.0	347.7	60543.	358.6
350.0	358.1	64072.	368.8
360.0	368.5	67705.	379.1
370.0	379.1	71443.	389.3
380.0	389.7	75287.	399.6
390.0	400.3	79237.	409.8
400.0	411.1	83294.	420.1
410.0	421.9	87459.	430.4
418.0(T_g)	430.6	90869.	438.6
418.0(T_g)	479.1	90869.	438.6
420.0	480.3	91828.	440.9
430.0	486.0	96659.	452.3
440.0	491.8	101548.	463.5
450.0	497.6	106495.	474.6
460.0	503.4	111500.	485.6
470.0	509.2	116563.	496.5
480.0	515.0	121684.	507.3
490.0	520.8	126863.	518.0
500.0	526.6	132100.	528.6
510.0	532.4	137395.	539.0
520.0	538.2	142748.	549.4
530.0	543.9	149159.	559.7
540.0	549.7	153627.	569.9
550.0	555.5	159153.	580.1
560.0	561.3	164737.	590.1

[a] The table may contain more significant figures than justified by both source of data and data treatment. The extra significant figures are included only for the purpose of smooth representation.

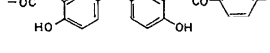
residual entropy of the polymer.

The heat capacity change at the glass transition is 48.5 J mol^{-1} K^{-1}.

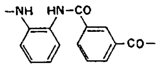
2.2. Polyphenylenediamides

Three investigations[26–28] have been reported in the literature on the heat capacity of polyphenylenediamides. The heat capacity of the following polyphenylenediamides have been measured:

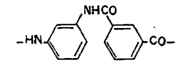
I. Poly[carbonylimino-(6-hydroxy-1, 3-phenylene)-methylene-(4-hydroxy-1, 3-phenylene)iminocarbonyl-1, 3-phenylene] (formula wt. = 360.37).



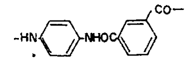
II. Poly(imino-1, 2-phenyleneiminoisophthaloyl) (formula wt. = 238.24).



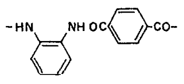
III. Poly(imino-1, 3-phenyleneiminoisophthaloyl) (formula wt. = 238.24).



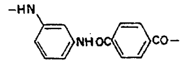
IV. Poly(imino-1, 4-phenyleneiminoisophthaloyl) (formula wt. = 238.24).



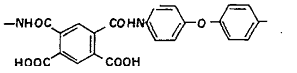
V. Poly(imino-1, 2-phenyleneiminoterephthaloyl) (formula wt. = 238.24).



VI. Poly(imino-1, 3-phenyleneiminoterephthaloyl) (formula wt. = 238.24).



VII. Poly(imino-3, 5-pyromellitolylimino-1, 4-phenyleneoxy-1, 4-phenylene) (formula wt. = 418.33).

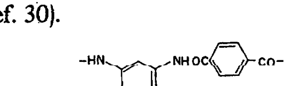


All measurements have been reported by Karayakin and co-workers and meet our standards of acceptable data (discussed in Ref. 1). Heat capacity measurements were made using an adiabatic calorimeter (claimed uncertainty 1%). Polymers I and VII were amorphous and polymers II–VI were semicrystalline (crystallinity not reported).

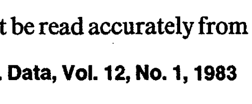
Recommended data on the heat capacity of all polyphenylenediamides were obtained by interpolating the author's tabulated data using the spline function technique to obtain the heat capacity values at every 10 deg intervals. These values are listed in Table 4. Heat capacity data above 400 K for all the polyphenylenediamides have also been reported. These data are associated with uncharacterized transitions and are not reported here.

Heat capacity data on two other polyphenylenediamides have been reported in the literature. These polymers are listed below.

Poly[oxy-(4-amino-1, 3-phenylene)iminocarbonyl (6-carboxy-1, 3-phenylene)oxy(4-carboxy-1, 3-phenylene)-carbonylimino(6-amino-1, 3-phenylene)] (Ref. 29).



Poly[imino-(4, 6-dianilyl-1, 3-phenylene) iminoterephthaloyl] (Ref. 30).



The data could not be read accurately from too small graphs.

Table 4. Recommended heat capacity data for polyphenylenediamides in J $mol^{-1}K^{-1}$

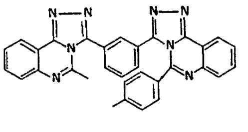
Temp (K)	I[a]	II[a]	III[a]	IV[a]	V[a]	VI[a]	VII[a]
50		57.3	56.1	55.6	57.3	53.1	
60		67.5	65.5	64.4	65.7	62.3	124
70		77.6	74.8	73.2	74.1	71.5	149
80		87.6	84.0	82.0	82.6	80.7	173
90		97.3	93.1	90.6	91.1	89.8	196
100	160	107	102	99.2	99.9	98.9	218
110	174	116	111	108	109	108	238
120	188	125	119	116	118	117	258
130	202	133	128	124	127	126	276
140	216	141	136	132	136	135	293
150	230	150	145	141	145	144	309
160	245	158	154	149	153	153	324
170	259	166	162	157	162	161	339
180	274	174	171	166	170	170	354
190	290	182	179	174	179	178	369
200	305	191	188	183	187	186	385
210	321	200	197	191	196	194	401
220	338	209	206	200	205	202	417
230	354	219	215	208	214	210	435
240	371	228	224	217	223	218	455
250	388	238	233	226	232	226	475
260	406	247	242	236	241	235	497
270	423	257	252	246	250	244	521
280	441	267	262	255	261	254	544
290	458	280	272	265	274	263	569
300	476	294	282	274	289	273	593
310		311	293	283	307	283	617
320		330	303	291	328	293	640
330		351	315	301	351	303	663
340		372	326	310	373	314	686
350		394	339	322	395	325	708
360		415	351	334	416	336	731
370		436	365	348	435	348	754
380		456	378	363	452	361	777
390		476	392	379	470	373	800
400		496	407	395	487	386	823

[a] The structural formulae of the polyphenylenediamides are given in the text (sec. 2.2).

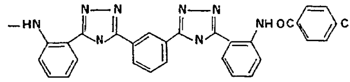
2.3. Polyheteroarylenes

Polyheteroarylenes, which combine good physical and chemical resistance with good solubility in organic solvents are widely used as heat resistance polymers. Six investigations[26,28,31–34] have been reported in the literature on the heat capacity of polyheteroarylenes. Heat capacity of the following polyheteroarylenes have been measured.

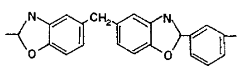
VIII. Poly(pyroazolino[3,4-c]quinazoline-3, 5-diyl-1, 3-phenylenepyroazoline[3, 4-c]quinazoline-5, 3-diyl-1, 4-phenylene) (formula wt. = 486.52).



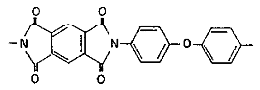
IX. Poly(imino-1, 2-phenylene-4H-1, 2, 4-triazole-3, 5-diyl-1, 3-phenylene-4H-1, 2, 4-triazole-3, 5-diyl-1, 2-phenyleneiminoterephthaloyl) (formula wt. = 522.53).



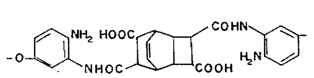
X. Poly(2, 5-benzoxazolediylmethylene-5, 2-benzoxazolediyl-1, 3-phenylene) (formula wt. = 326.36).



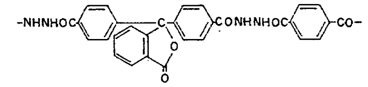
XI. Poly(5, 7-dihydro-1, 3, 5, 7-tetraoxobenzo[1, 2-c:4, 5-c′] diphyrrole-2, 6[1H,3H]-diyl-1, 4-phenyleneoxy-1, 4-phenylene) (formula wt. = 382.33).



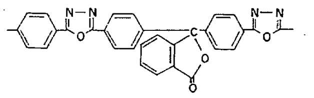
XII. Poly[oxy-(4-amino-1, 3-phenylene)iminocarbonyl(4, 9-dicarboxytricylo[4.2.2.$0^{2,5}$]-7-decane-3, 10-diyl)-carbonylimino-(6-amino-1, 3-phenylene)] (formula wt. = 504.50).



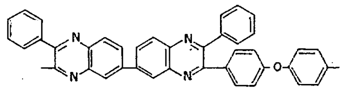
XIII. Poly(hydrazocarbonyl-1, 4-phenylene-2, 1-benzo[c]furone-3, 3-diyl-1, 4-phenylenecarbonylhydrazoterephthaloyl) (formula wt. = 528.53).



XIV. Poly(1, 4-phenylene-1, 3, 4-oxadiazole-2, 5-diyl-1, 4-phenylene-2, 1-benzo[c]furone-3, 3-diyl-1, 4-phenylene-1, 3, 4-oxadiazole-2, 5-diyl) (formula wt. = 496.49).



XV. Poly[6, 6′-bis(3, 3′-diphenylquinoxaline)-2, 2′-diyl-1, 4-phenyleneoxy-1, 4-phenylene] (formula wt. = 576.66).



Heat capacity measurements for VIII–XIV have been reported by Karyakin and co-workers using adiabatic calorimetry (claimed uncertainty 1%) and for XV by Wrasidlo using a differential scanning calorimeter (claimed uncertainty 2%). All measurements were made on amorphous samples and meet our standards of acceptable data (discussed in Ref. 1).

Recommended data on the heat capacity of all polyheteroarylenes were determined by interpolating the authors' tabulated data using the spline function technique to obtain the heat capacity values at every 10 deg intervals. These values are listed in Table 5. Heat capacity data through the transitions for polyheteroarylenes VIII, IX, X, XI, XIII, and XIV have also been reported by the authors. These data were not retrieved.

Table 5. Recommended heat capacity data for glassy, amorphous polyheteroarylenes in J $mol^{-1}K^{-1}$

Temp (K)	VIII[a]	IX[a]	X[a]	XI[a]	XII[a]	XIII[a]	XIV[a]	XV[a]
60				94.1		126	122	
70				112		153	146	
80				129		177	166	
90				145		196	183	
100	165	195	120	161	232	213	197	
110	181	212	130	175	252	230	211	
120	197	230	140	189	272	247	226	
130	213	248	149	202	292	265	241	
140	229	265	159	215	312	284	257	
150	245	283	169	228	332	302	273	
160	260	300	179	241	352	321	289	
170	276	318	189	254	373	340	305	
180	292	336	199	268	393	360	321	
190	308	353	209	281	415	379	337	
200	324	371	219	294	437	398	354	
210	340	388	230	307	460	417	371	
220	356	406	240	319	483	436	388	
230	372	424	250	332	507	455	406	
240	388	441	261	344	532	474	423	
250	404	459	271	357	557	493	440	
260	420	476	282	370	583	512	456	
270	436	494	293	383	609	531	472	
280	452	512	303	396	635	550	488	
290	467	529	314	410	661	568	503	686
300	483	547	325	423	687	587	519	719
310	499	564		436		606	534	739
320	515	582		449		625	550	755
330	531	600		462		644	566	776
340	547	617		475		663	583	791
350	563			487		682	602	806
360						702	622	823
370						722	643	842
380						744	666	857
390						768	689	875
400						795	713	895
410						824	737	913
420						855	760	927
430						885	781	944
440						912	801	961
450						935	817	977
460						952	830	995
470						964	840	1009
480						973	848	1024
490						979	854	1042
500						983	859	1058
510								1074
520								1090
530								1104
540								1119
550								1131
560								1145

[a] The structure formulae of the polyheteroarylenes are discussed in the text (sec. 2.3).

Table 6. Recommended heat capacity data for a molten polyheteroarylene in J $mol^{-1}K^{-1}$[a]

Temp (K)	XV[b]
590	1359
600	1373
610	1383
620	1393
630	1402
640	1413
650	1426
660	1436
670	1445
680	1457
690	1467
700	1479
710	1489
720	1500
730	1511
740	1520
750	1530
760	1540
770	1548

[a] The table may contain more significant figures than justified by both souce of data and data treatment. The extra significant figures are included only for the purpose of smooth representation.

[b] The structural formula of polyheteroarylene XV is given in the text (sec. 2.3).

Heat capacity in the molten state has only been reported for polyheteroarylene XV by Wrasidlo.[34] The recommended data for molten polyheteroarylene XV were determined by curve fitting the author's tabulated data onto the equation

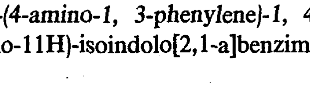
$$C_p = 1.071\ T + 728.3\ J\ mol^{-1}K^{-1}. \qquad (3)$$

The rms deviation was 0.1%. Recommended data obtained from Eq. (3) are listed in Table 6.

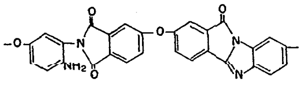
The heat capacity change at the glass transition for polyheteroarylene XV ($T_g = 573$ K) was determined by linearly extrapolating the glassy and the molten data and was found to be 177.4 J mol^{-1} K^{-1}.

Heat capacity data on three other polyheteroarylenes have been reported in the literature. These polymers are listed below.

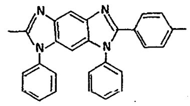
Poly[oxy-(4-amino-1, 3-phenylene)-1, 4-phthalimidediyloxy-4, 1-phthalimidediyl-(6-amino-1, 3-phenylene)] (Ref. 29).



Poly[oxy-(4-amino-1, 3-phenylene)-1, 4-phthalimide-diyloxy-(11-oxo-11H)-isoindolo[2,1-a]benzimidazole-2, 8-diyl] (Ref. 29).



Poly[(3,5 diphenyl-benzo[1,2-*d*:4,5-*d*′]diimidazol-2, 6-diyl)-1-4-phenylene] (Ref. 30).



These data could not be read accurately from too small graphs.

2.4 Other Aromatic Polymers

Heat capacity measurements have been reported on oligomeric poly[1,4-phenylene-(5-phenyl-1, 3-phenylene)] (degree of polymerization, $x = 6.5 \pm 0.5$) by Karyakin *et al.*[35,36] from 100 to 600 K. The data could not be read accurately from too small graphs.

Alpaugh and Morrow[37] have measured the heat capacity of poly(chloroparaxylylene) from 100 to 390 K using transient heating techniques. These data are associated with large error limits. Some differential scanning calorimetry data over limited temperature range on the same sample have a somewhat smaller error limits, however, these data could not be read accurately from too small graph.

Lebedev *et al.*[38,39] have reported the heat capacity of polymer made by polycyclotrimerization of 2, 2-bis(4-cyanatophenyl) propane. These data are on nonlinear polymers and are not of interest in this study.

A large number of commercial phenol-formaldehyde polymers have been subjected to heat capacity measurement. These investigations: Warfield *et al.*,[40] Era *et al.*,[41,42] and Harwood *et al.*[43] on crosslinked polymeric systems are not within the scope of this study.

3. Recommended Data on Heat Capacity and Thermodynamic Properties of Inorganic Polymers

3.1. Poly(dimethyl siloxane)

Poly(dimethyl siloxane) is the most widely used inorganic polymer. Its repeating unit and formula weight are: $Si(CH_3)_2$–O–,74.15. Three investigations[44,45,63] have been reported in the literature on the heat capacity of poly(dimethyl siloxane). Turdakin *et al.*[44] and Lebedev *et al.*[45] have reported measurements on semicrystalline samples of poly(dimethyl siloxane) over a wide range of temperature. Rastorguev and Nemzer[63] have reported heat capacities for poly(dimethyl siloxane) liquids ($\overline{M}_n = 110$–74 000). The heat capacity data of Rastorguev and Nemzer decrease with increasing molecular weight by about 15%. Their data for the highest molecular weight poly(dimethyl siloxane) is about 15% lower than the data of Turdakin *et al.*[44] and Lebedev *et al.*[45] on molten poly(dimethyl siloxane). Thus the data of Rastorguev *et al.* was not used in this discussion.

Details of the heat *capacity measurements by Turdakin et al.* and Lebedev *et al.* are given in Table 7. The data which span a wide temperature range are given in Tables A5 and A6. These tables have been deposited with the Physics Auxiliary Publication Service. Table A5 lists the heat capacity data on the poly(dimethyl siloxane)s below the glass transition temperature, and Table A6 contains data on molten

Table 7. Heat capacity measurements of poly(dimethyl siloxane)

Investigator	Sample characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Turdakin et al. (1976) [1197]	1. Semicrystalline $\bar{M}_w$ = 600,000	55-300	Adiabatic (4%)	Table
Lebedev et al. (1978) [1253]	2. Semicrystalline w^c = 0.68	8-332	Adiabatic (0.2%)	10-150 K: Table[a] 220-340 K: Equation[b]

[a] Authors tabulated data were interpolated using the spline function technique to obtain heat capacities at every ten degree interval .

[b] Authors tabulated data were curve fitted into the equation

C_p = 0.1214T + 81.77 J $mol^{-1}K^{-1}$ (RMS dev. = 0.2%)

Table 8. Recommended thermodynamic data for semicrystalline poly(dimethyl siloxane) (w^c = 0.68 ± 0.05)[a]

T(K)	C_p (J $mol^{-1}K^{-1}$)	H_T-H_o (J mol^{-1})	S_T-S_o (J $mol^{-1}K^{-1}$)
0.0	0.0	0.0	0.0
5.0	0.7023	1.035	0.2842
10.0	2.804	9.399	1.361
15.0	5.572	30.16	3.007
20.0	8.627	65.59	5.024
25.0	11.79	116.6	7.288
30.0	14.98	183.5	9.719
40.0	21.23	364.8	14.89
50.0	27.23	607.3	20.28
60.0	32.92	908.3	25.75
70.0	38.31	1264	31.23
80.0	43.42	1673	36.69
90.0	48.27	2132	42.08
100.0	52.88	2638	47.41
110.0	57.28	3189	52.66
120.0	61.48	3783	57.82
130.0	65.49	4418	62.90
140.0	69.35	5092	67.90
146.0(T_g)	71.59	5515	70.85
146.0(T_g)	99.30	5515	70.85
150.0	99.78	5913	73.55
160.0	101.0	6917	80.02
170.0	102.2	7933	86.18
180.0	103.4	8961	92.06
190.0	104.6	10001	97.68
200.0	105.9	11054	103.1
210.0	107.1	12119	108.3
220.0	108.3	13195	113.3
230.0	109.5	14284	118.1
240.0	110.7	15385	122.8
250.0	111.9	16499	127.4
260.0	113.1	17624	131.8
270.0	114.4	18762	136.1
273.15	114.7	19124	137.4
280.0	115.6	19911	140.2
290.0	116.8	21073	144.3
298.15	117.8	22030	147.6
300.0	118.0	22247	148.3
310.0	119.2	23433	152.2
320.0	120.4	24632	156.0
330.0	121.7	25842	159.7
340.0	122.9	27065	163.4

[a] The table may contain more significant figures than justified by both source of data and data treatment. The extra significant figures are included only for the purpose of smooth representation.

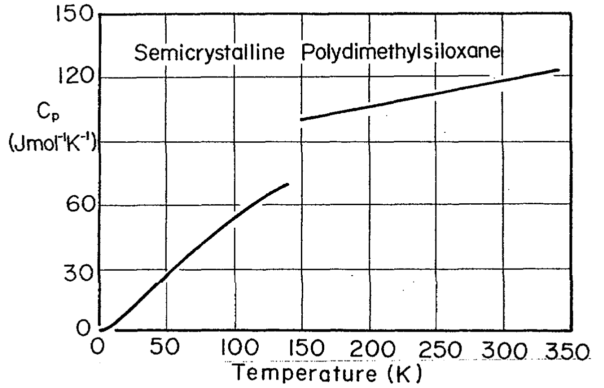


FIG. 2. Recommended heat capacity data for semicrystalline poly(dimethyl siloxane) ($w^c = 0.68 \pm 0.05$).

poly(dimethyl siloxane)s. The glass transition and the melting regions for both samples extended from 150 to 220 K. The heat capacity associated with these transitions show large deviations and were not retrieved. Yagfarov *et al.*[46,47] have also reported heat capacity data in the glass transition and melting regions (140 to 280 K).

The data on samples 1 and 2 are in good agreement, both are below the glass transition and in the molten state. The changes in the heat capacity at the glass transition (which are due to amorphous regions only) are also in good agreement (10 ± 1 J mol^{-1} K^{-1}). This seems to indicate that crystallinities for both samples would be about the same ($w^c = 0.68 \pm 0.05$). Thus, recommended data have been derived for semicrystalline poly(dimethyl siloxane) of crystallinity 0.68 ± 0.05.

To determine the recommended data for semicrystalline poly(dimethyl siloxane) below the glass transition, the data on both the samples up to 140 K were curve fitted into the equation

$$C_p = \exp[0.0189189(\ln T)^3 - 0.402175(\ln T)^2 + 3.35144(\ln T) - 4.78444] \text{ J mol}^{-1} \text{ K}^{-1}. \quad (4)$$

The rms deviation was 1.4%.

The recommended data for molten poly(dimethyl siloxane) were obtained by curve fitting the molten data into the equation

$$C_p = 0.1215T + 81.55 \text{ J mol}^{-1} \text{ K}^{-1}. \quad (5)$$

The rms deviation was 0.3%.

Recommended heat capacity data obtained from Eq. (4), up to 146 K (T_g) and from 146 to 340 K from Eq. (5) are given in Table 8 and plotted in Fig. 2. The heat capacity values were further integrated to obtain the thermodynamic data for semicrystalline poly(dimethyl siloxane). These data are also listed in Table 8.

Heat capacity change at the glass transition for poly(dimethyl siloxane) is 27.71 J mole^{-1}K^{-1}.

3.2. Poly(diethyl siloxane)

Two investigations[44,48] have been reported in the literature on the heat capacity of poly(diethyl siloxane) [repeating unit $Si(CH_2CH_3)_2$–O–, formula wt. = 102.2]. The details of these investigations are given in Table 9. The heat capacity data from 60 to 300 K are listed in Table 10. The heat capacity data are associated with a number of transitions, and the nature of these transitions is not well established.[48,64] Moreover, the heat capacity data on both the samples differ by 2%–9%. Thus, no recommendations for the heat capacity of poly(diethyl siloxane) are possible at present.

A rough estimate for ΔC_p (at T_g) was made by extrapolating the average data on glassy and molten samples. ΔC_p (at $T_g = 131$ K) was found to be 15.6 J mol^{-1} K^{-1}.

Table 9. Heat capacity measurements of poly(diethyl siloxane)

Investigator	Sample no., characterization	Temperature range (K)	Experimental technique (claimed uncertainty)	Source of data
Beatty and Karasz (1975) [48]	1. $\bar{M}_w = 112{,}000$	50-300	Adiabatic (Unreported)	Equation[a]
Turdakin et al. (1976) [44]	2. $\bar{M}_w = 1{,}530$	55-300	Adiabatic (0.4%)	Table

[a] Authors; tabulated data were curve fitted into the following equations

60-140K: $1.0987 \cdot 10^{-4} T^2 - 0.016778\, T + 1.297$ J g^{-1}K^{-1} (RMS dev. = 2.3%)
150-190K: $1.1864 \cdot 10^{-4} T^2 - 0.033338\, T + 3.505$ J g^{-1}K^{-1} (RMS dev. = 2.4%)
200-230K: $3.2433 \cdot 10^{-4} T^2 - 0.1382\, T + 16.17$ J g^{-1}K^{-1} (RMS dev. = 1.6%)
270-300K: $2.8756 \cdot 10^{-3} T + 0.7695$ J g^{-1}K^{-1} (RMS dev. = 2.1%)

Table 10. Heat capacity of various poly(diethyl siloxane)s[a] in J $mol^{-1}K^{-1}$

T(K)	1	2
60	b	47.30
70	60.71	55.20
80	65.87	62.57
90	71.03	69.39
100	76.19	75.85
110	81.34	82.59
120	86.50	89.53
130	c	96.39
140	115.1	f
150	119.7	f
160	124.3	f
170	128.9	f
180	d	f
190	d	f
200	d	f
210	147.5	150.3
220	149.8	153.2
230	152.3	155.6
240	e	157.8
250	e	160.2
260	e	162.4
270	158.0	164.7
280	161.0	167.6
290	163.8	170.7
300	166.8	173.6

[a] Sample numbers correspond to the samples described in table 9.

[b] Sub-glass transition

[c] Glass transition

[d] Crystal-crystal transition

[e] Melting

[f] Heat capacity data associated with large endothermic effects.

Table 11. Recommended heat capacity data for glassy poly-(trimethylsilyl ethylene), poly(dimethylphenylsilyl ethylene) and poly(dimethylbenzylsilyl ethylene)[a] in J $mol^{-1}K^{-1}$

T(K)	PTMSE	PDMPSE	PDMBSE
10			8.290
20			21.80
30			30.05
40			45.31
50		48.74	56.15
60	54.85	58.08	65.68
70	63.22	67.15	75.58
80	70.66	75.86	85.57
90	77.58	84.23	95.33
100	84.58	92.38	104.6
110	92.05	99.79	113.2
120	99.53	106.8	121.1
130	106.4	113.9	128.5
140	112.1	120.6	135.7
150	117.2	127.1	142.8
160	122.2	133.6	149.9
170	126.4	140.1	157.1
180	130.1	145.2	164.5
190	133.4	152.9	172.1
200	136.5	159.6	179.7
210	139.7	166.6	188.0
220	143.1	173.7	196.4
230	~~147.0~~	~~180.9~~	~~205.0~~
240	151.5	188.1	213.6
250	156.2	195.3	(220.0)[b]
260	160.8	202.5	(230.4)[b]
270	165.5	209.9	(238.9)[b]
280	170.3	217.3	
290	175.1	224.9	
300	180.0	232.4	

[a] The table may contain more significant figures than justified by both source of data and data treatment. The extra significant figures are included only for the purpose of smooth representation.

[b] Authors' data below 240 K, linearly extrapolated to the glass transition.

3.3 Poly(trimethylsilyl ethylene), Poly(dimethylphenylsilyl ethylene), and Poly(dimethylbenzylsilyl ethylene)

Heat capacity measurements for poly(trimethylsilyl ethylene) (repeating unit $-CH_2-CH[Si(CH_3)_3]-$; formula wt. = 100.24), poly(dimethylphenylsilyl ethylene) (repeating unit $-CH_2-CH[Si(CH_3)_2C_6H_5]-$; formula wt. = 162.31) and poly(dimethylbenzylsilyl ethylene) (repeating unit $-CH_2-CH[Si(CH_3)_2\ CH_2C_6C_5]-$; formula wt. = 176.37) thereafter referred to as PTMSE, PDMPSE, and PDMBSE, respectively, have been reported by Lebedev *et al.*[49–53] All the measurements were made on amorphous samples (Molecular weight: PTMSE—775 000; PDMPSE—20 000; PDMBSE—450 000) using adiabatic calorimetry (claimed uncertainty, 0.2%) and meet our standards of acceptable data (discussed in Ref. 1).

The heat capacity measurements for PTMSE were made over the temperature interval from 60 to 300 K. To determine the recommended data, the authors' data were interpolated using the spline function technique to obtain heat capacity values at every 10 deg interval. These recommended data are listed in Table 11 and plotted in Fig. 3. The authors have also estimated heat capacities below 60 K. These estimated values are considered unacceptable (method of estimation not reported).

Heat capacity measurement for PDMPSE spans the temperature range from 50 to 300 K. Below 50 K the authors have estimated heat capacity by curve fitting the data above 50 K into a one-dimensional Debye equation. These estimated values are considered unacceptable since there is no justification to represent heat capacity data at low temperatures (below 50 K) using a one-dimensional Debye function. Recommended heat capacity data from 50 to 300 K were obtained by interpolating the authors' heat capacity data using

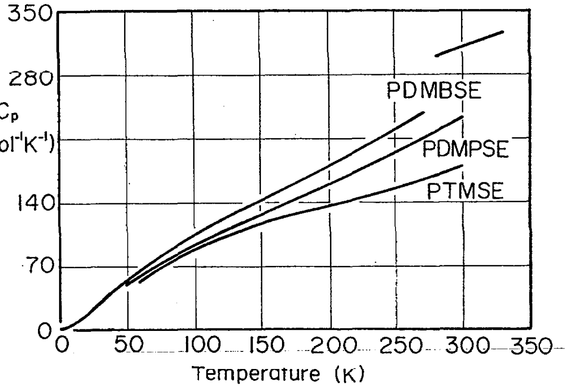


FIG. 3. Recommended heat capacity data for poly(trimethylsilyl ethylene) (PTMSE), poly(dimethylphenylsilyl ethylene) (PDMPSE), and poly(dimethylbenzylsilyl ethylene) (PDMBSE).

the spline function technique to determine the heat capacity values at every 10 deg interval. These recommended data are listed in Table 11 and plotted in Fig. 3.

Heat capacity measurement on PDMBSE from 10 to 330 K have been reported. The heat capacity data from 250 to 290 K are associated with the glass transition effects (T_g = 279 K). From 10 to 240 K, the recommended data were obtained by interpolating the author's tabulated data using the spline function technique to obtain the heat capacity values at every 10 deg interval. Heat capacity values from 250 K to the glass transition temperature were obtained by linearly extrapolating the data below 240 K. The heat capacity values from 200 to 240 K were curve fitted into the equation.

$$C_p = 0.846 + 10.48 \text{ J mol}^{-1} \text{ K}^{-1}. \quad (6)$$

The rms deviation was 0.1%. The recommended data for the heat capacity of PDMBSE from 10 to 240 K were obtained by interpolation and from 250 to 270 K calculated from Eq. (6) are listed in Table 11 and plotted in Fig. 3.

The recommended data for molten PDMBSE were obtained by curve fitting the author's data points at 298.15 and 330 K into the equation

$$C_p = 0.5118\ T + 157.92 \text{ J mol}^{-1} \text{ K}^{-1}. \quad (7)$$

Recommended data for molten PDMSBE from Eq. (7) are listed in Table 12 and plotted in Fig. 3.

Table 12. Recommended heat capacity data for molten poly(dimethylbenzylsilyl ethylene)[a]

T(K)	Heat capacity ($J\ mol^{-1}K^{-1}$)
280	301.2
290	306.3
300	311.4
310	316.6
320	321.7
330	326.8

[a] The table may contain more significant figures than justified by both source of data and data treatment. The extra significant figures are included only for the purpose of smooth representation.

The heat capacity change at the glass transition for PDMSBE was found to be 54.2 J mol^{-1} K^{-1}.

3.4. Poly(vinylene diphenylsilylene) and Poly(vinylene diphenylgermylene)

Heat capacity measurements for poly(vinylene diphenylsilylene) (repeating unit $-CH = CH-Si(C_6H_5)_2-$, formula weight = 208.34), poly(vinylene diphenylgermylene) (repeating unit $-CH = CH-Ge(C_6H_5)_2-$, formula wt. = 252.84) and their alternating copolymer (repeating unit $-CH = CH - Si(C_6H_5)_2-CH = CH-Ge(C_6H_5)_2-$ formula wt. = 461.18), thereafter referred to as PVDS, PVDG, and PVDSVDG, have been reported by Lebedev *et al.*[54,55] All measurements span the temperature range from 10 to 320 K and were made on amorphous samples (Molecular weight: PVDS—1200; PVDG—1400; PVDSVDG—10 000) using adiabatic calorimetry (claimed uncertainty 0.2%). All the measurements meet our standards of acceptable data (discussed in Ref. 1).

The recommended data for amorphous PVDS from 10 to 200 K were determined by interpolating the authors' tabulated data using the spline function technique to determine the heat capacity values at every 10 deg interval. The authors' data above 200 K are somewhat higher because they are associated with the beginning of the glass transition. The recommended data from 210 to the glass transition (T_g = 237) were determined by linearly extrapolating the data below 200 K. The heat capacity values from 180 to 230 K were curve fitted into the equation

$$C_p = 0.7841\ T + 25.30 \text{ J mol}^{-1} \text{ K}^{-1}. \quad (7)$$

The rms deviation was 0.2%. The recommended values of the heat capacity of amorphous PVDS obtained by interpolation from 10 to 200 K and from Eq. (7) from 210 to 260 K are listed in Table 13.

The recommended data on the heat capacity of molten PVDS were obtained by curve fitting the authors' tabulated data from 300 to 320 K into the equation

$$C_p = 0.800\ T + 91.90 \text{ J mol}^{-1} \text{ K}^{-1}. \quad (8)$$

The rms deviation was 0.1%. Recommended heat capacity data from Eq. (8) from 270–320 K are listed in Table 14.

The recommended data for amorphous PVDS from 10 to 200 K were determined by interpolating the authors' tabulated data using the spline function technique to determine the heat capacity values at every 10 deg interval. The authors' data above 200 K are somewhat higher because they are associated with the beginning of the glass transition. The recommended data from 210 to the glass transition (T_g = 264 K) were determined by linearly extrapolating the data below 200 K. The heat capacity values from 150 to 200 K were curve fitted into the equation

$$C_p = 0.7908\ T + 29.20 \text{ J mol}^{-1} \text{ K}^{-1}. \quad (9)$$

The rms deviation was 0.1%. The recommended values of the heat capacity of amorphous PVDG obtained by interpolation from 10 to 200 K and from Eq. (9) from 210 to 230 K are listed in Table 13.

The recommended data on the heat capacity of molten PVDG were determined by curve fitting the authors' tabu-

Table 13. Recommended heat capacity data for glassy poly(vinylene diphenylsilylene), poly(vinylene diphenylgermylene) and poly(vinylene diphenylsilylene vinylene diphenylgermylene) in J $mol^{-1} K^{-1}$ [a]

T(K)	PVDS	PVDG	PVDSVDG
10	6.250	8.452	17.30
20	21.69	24.77	48.35
30	36.53	41.00	70.01
40	49.30	54.39	95.22
50	60.56	66.03	120.7
60	70.85	76.57	143.2
70	80.38	85.77	162.6
80	89.28	94.27	179.8
90	97.68	102.7	195.5
100	105.7	110.7	210.6
110	113.5	118.4	225.7
120	121.1	125.7	240.8
130	128.5	133.1	256.0
140	135.9	140.4	271.1
150	143.3	148.0	286.2
160	150.8	155.4	301.2
170	158.3	163.2	316.1
180	166.1	171.0	331.3
190	174.2	179.1	346.8
200	182.6	187.5	362.8
210	(190.0)[b]	(197.8)[b]	379.4
~~220~~	~~(197.8)[b]~~	~~(207.1)[b]~~	~~396.5~~
230	(205.7)[b]	(216.4)[b]	414.0
240	(213.5)[b]		431.8
250	(221.4)[b]		449.8
260	(229.2)[b]		(466.8)[c]
270			(484.3)[c]
280			(501.7)[c]
290			(519.2)[c]
300			(536.6)[c]

[a] The table may contain more significant figures than justified by both source of data and data treatment. The extra significant figures are included only for the purpose of smooth representation.

[b] Authors' tabulated data below 200 K, linearly extrapolated to the glass transition.

[c] Authors' tabulated data below 250 K, linearly extrapolated to the glass transition

lated data from 250 to 325 K into the equation

$$C_p = 0.5406\,T + 174.24 \text{ J mol}^{-1}\text{ K}^{-1}. \qquad (10)$$

The rms deviation was 0.2%. Recommended heat capacity data from Eq. (10) are listed in Table 14.

The recommended data for amorphous PVDSVDG from 10 to 250 K were determined by interpolating the authors' tabulated data using the spline function technique to obtain the heat capacity values at every 10 deg interval. The authors' data above 250 K are somewhat higher because they are associated with the beginning of the glass transition. The recommended data from 260 to the glass transition (T_g = 301 K) were determined by linearly extrapolating the

Table 14. Recommended heat capacity data for molten poly(vinylene diphenylsilylene), poly(vinylene diphenylgermylene) and poly(vinylene diphenylsilylene vinylene diphenylgermylene)[a] in J $mol^{-1} K^{-1}$

T(K)	PVDS	PVDG	PVDSVDG
240		304.0	
250		309.4	
260		314.8	
270	307.9	320.2	
280	315.9	325.6	
290	323.9	331.0	
~~300~~	~~331.9~~	~~336.4~~	
310	339.9	341.8	671.7
320	347.9	347.2	691.0

[a] The table may contain more significant figures than justified by both source of data and data treatment. The extra significant figures are included only for the purpose of smooth representation.

data below 250 K. The heat capacity values from 200 to 240 K were curve fitted into the equation

$$C_p = 1.744\,T + 13.48 \text{ J mol}^{-1}\text{ K}^{-1}. \qquad (11)$$

The rms deviation was 0.1%. The recommended values of the heat capacity of amorphous PVDSVDG obtained by interpolation from 10 to 250 K and from Eq. (11) from 260 to 300 K are listed in Table 13.

The recommended data on the heat capacity of molten PVDSVDG were determined by curve fitting the authors' tabulated data 301 and 320 K into the equation

$$C_p = 1.926\,T + 74.58 \text{ J mol}^{-1}\text{ K}^{-1}. \qquad (12)$$

The recommended heat capacity data from Eq. (12) are listed in Table 14.

The heat capacity change at the glass transition for PVDS, PVDG, and PVDSVDG are 70.7, 79.5, and 116.0 J mol^{-1} K^{-1}, respectively. Assuming additivity of ΔC_p (at T_g), the estimated ΔC_p for the alternating copolymer PVDSVDG is 150.2 J mol^{-1} K^{-1}. This is significantly higher than the recommended ΔC_p of 116.0 J mol^{-1} K^{-1}.

Recommended heat capacity data for PVDS, PVDG, and PVDSVDG are plotted in Fig. 4.

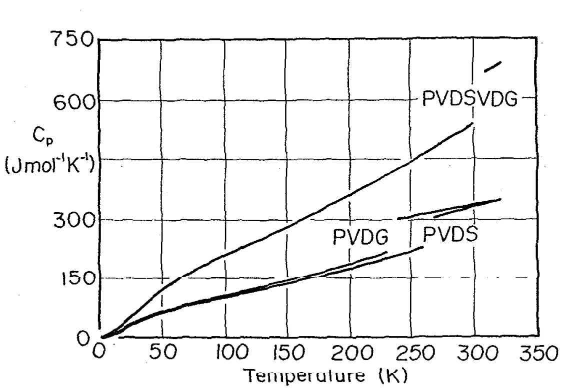


FIG. 4. Recommended heat capacity data for poly(vinylene diphenylsilylene) (PVDS), poly(vinylene diphenylgermylene) (PVDG), and their alternating copolymer (PVDSVDG).

3.5. Poly(diethnyl diphenylsilylene) and Poly(diethnyl diphenylgermylene)

Heat capacity measurements for poly(diethnyl diphenylsilylene) [repeating unit $-C{\equiv}C-Si(C_6H_5)_2-C{\equiv}C-$; formula wt. = 230.34] and poly(diethnyl diphenylgermylene) [repeating unit $-C{\equiv}C-Ge(C_6H_5)_2-C{\equiv}C-$; formula wt. = 274.85] thereafter referred to as PEPS and PEPG, have been measured by Lebedev *et al.*[56–58] The measurements were made using adiabatic calorimetry (claimed uncertainty 0.5%) on amorphous samples of somewhat low molecular weight ($\bar{M}_n = 3000$ for PEPS and 4500 for PEPG). All the measurements meet our standards of acceptable data (discussed in Ref. 1).

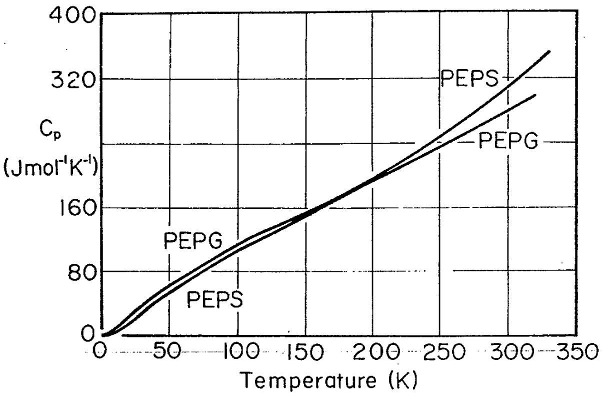


FIG. 5. Recommended heat capacity data for poly(diethnyl dipeheneylsilylene) (PEPS) and poly(diethnyl diphenylgermylene) (PEPG).

The heat capacity measurements on PEPS span the temperature range from 70 to 330 K. The authors' data were interpolated using the spline function to obtain the recommended heat capacity values from 70 to 330 K in every 10 deg interval. Below 70 K, the preliminary recommended data were obtained using the authors' fitted Tarasov equation

$$C_p = 6.263\{D_1(416.0/T) - 0.3[D_1(124.8/T) - D_3(124.8/T)]\}. \tag{13}$$

These recommended data on the heat capacity of amorphous PEPS are listed in Table 15 and plotted in Fig. 5.

Table 15. Recommended heat capacity data for glassy poly(diethnyl diphenylsilylene) and poly(diethnyl diphenylgermylene)[a] in J $mol^{-1}K^{-1}$

T(K)	PEPS	PEPG
10	(0.4187)	(6.870)
20	(10.89)	(24.80)
30	(27.05)	(39.70)
40	(42.71)	(51.98)
50	(56.99)	(62.91)
60	(69.09)	(73.53)
70	80.39	83.97
80	90.44	94.13
90	98.40	103.9
100	106.4	113.2
110	113.9	122.0
120	121.4	130.3
130	131.9	138.2
140	139.4	146.0
150	146.6	153.8
160	155.8	161.6
170	162.9	169.5
180	172.1	177.6
190	183.8	185.8
200	192.2	194.1
210	204.7	202.6
220	215.6	211.2
230	226.1	219.9
240	237.0	228.7
250	248.7	237.5
260	260.0	246.3
270	271.7	255.0
280	284.7	263.7
290	296.9	272.4
300	309.2	281.0
310	325.1	289.6
320	337.7	298.1
330	349.4	

[a] The table may contain more significant figures than justified by both source of data and data treatment. The extra significant figures are included only for the purpose of smooth representation.

Heat capacity measurement on PEPG extend from 12 to 320 K. The authors' graphical data from 20 to 50 K and tabulated data above 50 K were interpolated to obtain the recommended heat capacity values at every 10 deg interval. The data point at 10 K was calculated from the authors' fitted Debye equation

$$C_p = 3D_3(81/T). \tag{14}$$

These recommended data on the heat capacity of amorphous PEPG are listed in Table 15 and plotted in Fig. 5.

3.6. Polysulfones

Heat capacity measurements for poly(propene sulfone) (repeating unit $CH_2-CHCH_3-SO_2-$; formula wt. = 106.14), poly(1-butene sulfone) [repeating unit $CH_2-CH(C_2H_5)-SO_2$, formula weight = 120.17] and poly(1-hexene sulfone) [re-

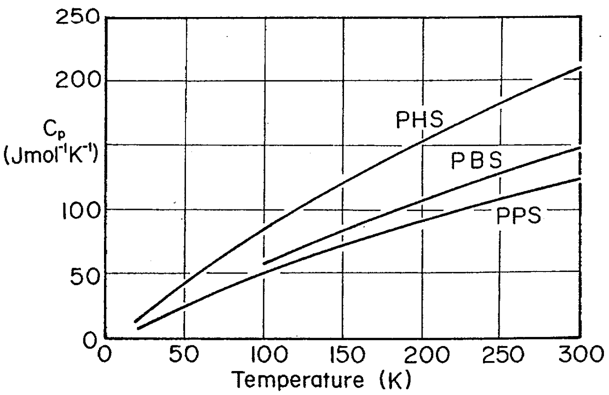


FIG. 6. Recommended heat capacity data for poly(propene sulfone) (PPS), poly(1-butene sulfone) (PBS), and poly(1-hexene sulfone) (PHS).

Table 16. Recommended heat capacity data for poly(propene sulfone), poly(1-butene sulfone) and poly(1-hexene sulfone)[a] in J $mol^{-1}K^{-1}$

T(K)	PPS	PBS	PHS
20	8.165		13.40
30	14.03		22.99
40	20.10		32.99
50	26.13		42.67
60	31.65		51.25
70	36.94		59.40
80	42.08		67.37
90	47.04		75.22
100	51.71	59.08	82.94
110	56.04	64.51	90.52
120	60.17	69.88	97.82
130	64.24	75.15	105.0
140	68.21	80.31	111.8
150	71.98	85.32	118.4
160	75.62	90.10	124.7
170	79.23	94.57	130.7
180	82.90	98.81	136.5
190	86.68	103.0	142.3
200	90.44	107.2	148.2
210	94.06	111.6	151.2
220	97.56	116.0	160.4
230	101.0	120.3	166.6
240	104.3	124.4	172.9
250	107.4	128.3	179.2
260	110.5	132.3	185.5
270	113.6	136.3	191.8
280	116.8	140.3	198.1
290	120.3	143.9	204.3
300	124.0	147.4	210.7

[a] The table may contain more significant figures than justified by both source of data and data treatment. The extra significant figures are included only for the purpose of smooth representation.

Table 17. Recommended heat capacity data for glassy poly(2,3,4,5-tetraphenyl-1,1-diethnyl-1-germocyclopentadiene)[a]

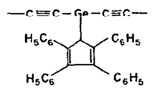
T(K)	Heat Capacity ($J\ mol^{-1}K^{-1}$)
10	8.631
20	42.11
30	63.47
40	84.18
50	105.5
60	124.6
70	141.4
80	156.6
90	170.6
100	184.3
110	198.1
120	212.0
130	226.2
140	240.6
150	255.1
160	269.8
170	284.8
180	299.9
190	315.1
200	330.6
210	346.3
220	362.1
230	378.0
240	394.2
250	410.4
260	426.8
270	443.2
280	459.7
290	476.3
300	492.9

[a] The table may contain more significant figures than justified by both source of data and data treatment. The extra significant figures are included only for the purpose of smooth representation.

peating unit CH_2–$CH(C_4H_9)$–SO_2– formula wt. = 148.23] thereafter referred to as PPS, PBS, and PHS have been reported by Dainton *et al.*[65] The measurements were made using adiabatic calorimetry (claimed uncertainty 1%). The measurements meet our standards of acceptable data (discussed in Ref. 1). The authors' tabulated values are listed in Table 16 and plotted in Fig. 6.

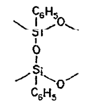
3.7. Other Inorganic Polymers

Heat capacity measurements for poly(2,3,4,5-tetraphenyl-1, 1-diethnyl-1-germocyclopentadiene) have been reported by Kiparisova *et al.*[59] The chemical structure of the repeating unit is (formula wt. = 490.13)



The heat capacity was measured from 10 to 300 K using an adiabatic calorimeter (claimed uncertainty 0.2%) on an amorphous sample. The measurement meets our standards of acceptable data. The recommended data were determined by interpolating the authors' tabulated data using the spline function technique to obtain heat capacities at every 10 deg interval. These recommended data are listed in Table 17 and plotted in Fig. 7.

Heat capacity measurements for polyphenylsilsesquioxane have been reported by Tikhomova *et al.*[60] The chemical structure of the repeat unit is (formula wt. = 258.28)



The heat capacity was measured from 68 to 300 K using

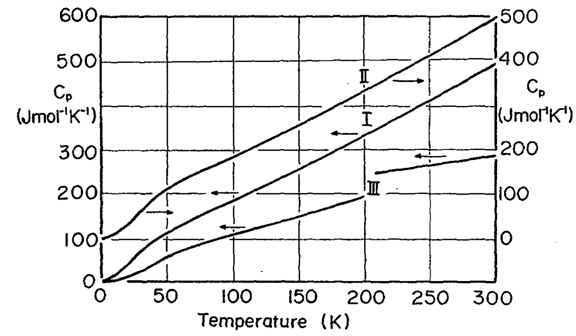


FIG. 7. Recommended heat capacity data for poly(2,3,4,5-tetraphenyl-1, 1-diethnyl-1-germocyclopentadiene) (I), polyphenylsilsesquioxane (II), and Poly[ethylene-N-(β-trimethylsilylethyl)imine] (III). The data for polyphenylsilsesquioxane have been moved upwards by 100 J mol^{-1} K^{-1}.

an adiabatic calorimeter (claimed uncertainty 0.3%) on an amorphous sample. The measurement meets our standards of acceptable data. The authors have extrapolated their heat capacity data to 0 K using a Tarasov equation (θ-temperatures not reported). The authors' data (extrapolated data below 68 K and smoothed experimental data above 68 K) were interpolated using the spline function technique to obtain recommended heat capacities at every 10 deg interval. These recommended data are listed in Table 18 and plotted in Fig. 7. The values in parenthesis are preliminary data from the Tarasov extrapolation.

Heat capacity measurements for poly[ethylene-N-(β-trimethyl silylethyl)imine] (repeating unit $-CH_2CH_2N(CH_2CH_2Si(CH_3)_3)$, formula wt. = 143.31) have been reported by Lebedev and co-workers.[61,62] The measurements which span the temperature range from 60 to 304 K were made on an amorphous sample using an adiabatic calori-

Table 18. Recommended heat capacity data for glassy polyphenylsilsesquioxane[a]

T(K)	Heat capacity ($J\ mol^{-1}K^{-1}$)
10	(3.936)
20	(33.29)
30	(61.56)
40	(87.67)
50	(110.5)
60	(129.4)
70	145.1
80	158.7
90	171.2
100	183.8
110	197.4
120	211.8
130	226.9
140	242.4
150	257.9
160	273.3
170	288.6
180	303.7
190	318.9
200	334.1
210	349.5
220	364.9
230	380.6
240	396.4
250	412.4
260	428.7
270	445.1
280	461.6
290	478.2
300	494.9

---

[a] The table may contain more significant figures than justified by both source of data and data treatment. The extra significant figures are included only for the purpose of smooth representation.

Table 19. Recommended heat capacity data for amorphous poly[ethylene N-(β-trimethylsilylethyl)imine][a]

T(K)	Heat capacity ($J\ mol^{-1}K^{-1}$)
10	(2.595)
20	(12.40)
30	(28.36)
40	(42.59)
50	(54.04)
60	66.32
70	77.54
80	87.80
90	97.31
100	106.3
110	114.9
120	123.3
130	131.6
140	139.8
150	148.0
160	156.3
170	164.8
180	173.3
190	182.1
200	191.1
209(T_g)	199.3
209(T_g)	246.2
210	246.8
220	251.3
230	255.8
240	260.3
250	264.7
260	269.2
270	273.7
280	278.2
290	282.7
300	287.2

---

[a] The table may contain more significant figures than justified by both source of data and data treatment. The extra significant figures are included only for the purpose of smooth representation.

meter (claimed uncertainty 0.5%). The measurement meets our standards of acceptable data (discussed in Ref. 1). To determine the recommended heat capacity data below the glass transition, the authors' tabulated data on glassy polymer from 60.6 to 200.9 K was curve fitted into the equation

$$C_p = \exp[0.182552(\ln T)^3 - 2.61942(\ln T)^2 + 13.3373(\ln T) - 20.4634] \text{ cal mol}^{-1}\text{ K}^{-1}. \tag{15}$$

The rms deviation was 0.3%. To determine the recommended data above the glass transition, the authors' tabulated data on molten polymer from 213.2 to 304.6 K were curve fitted into the equation

$$C_p = 0.1072\,T + 36.42 \text{ cal mol}^{-1}\text{ K}^{-1}. \tag{16}$$

The rms deviation was 0.2%. The preliminary recommended data below 60 K were obtained from authors' Tarasov curve fitted equation

$$C_p = 7\{D_1(505.5/T) - 0.2[D_1(101.1/T) - D_3(101.1/T)]\}. \tag{17}$$

The preliminary data from 10 to 50 K obtained from Eq. (17), from 60 to 209 K obtained from Eq. (15), and from 209 to 30 K obtained from Eq. (16) are listed in the Table 19 and plotted in Fig. 7. The heat capacity change at the glass transition $T_g = 209$ K is 46.9 J mol^{-1} K^{-1}.

Table 20. Heat capacity change at the glass transition

Polymer	T_g(K)	$\Delta C_p(T_g)$ (J mol^{-1}K^{-1})
Poly(4,4'-isopropylidenediphenyl carbonate)	418	48.5
Poly[6,6'-bis(3,3'-biphenylquinoxaline)-2,2'-diyl-1,4-phenyleneoxy-1,4 phenylene]	573	177.4
Poly(dimethyl siloxane)	146	27.7
Poly(diethyl siloxane)	131[a]	15.6[b]
Poly(dimethylbenzylsilyl ethylene)	279	54.2
Poly(vinylene diphenylsilylene)	264	70.7
Poly(vinylene diphenylgermylene)	237	79.5
Poly(vinylene diphenylsilylene vinylene diphenylgermylene)	301	116.0
Poly[ethylene-N-(β-trimethylsilylethyl)imine]	209	46.9

[a] Glass transition temperature not well established.

[b] Estimated value.

4. Conclusions

The heat capacities of the following polymers are reviewed on the basis of 36 measurements reported in the literature:

poly(4,4'-isopropylidenediphenylene carbonate
poly[carbonylimino(6-hydroxy-1, 3-phenylene)methylene-(4-hydroxyl-1, 3-phenylene)iminocarbonyl-1, 3-phenylene],
poly(imino-1, 2-phenyleneiminoisophthaloyl),
poly(imino-1, 3-phenyleneiminoisophthaloyl),
poly(imino-1, 4-phenyleneiminoisophthaloyl),
poly(imino-1, 2-phenyleneiminoterephthaloyl),
poly(imino-1, 3-phenyleneiminoterephthaloyl),
poly(imino-3, 5-pyromellitolylimino-1, 4-phenyleneoxy-1, 4-phenylene),
poly(pyroazolino[3,4-C]quinazoline-3, 5-diyl-1, 3-phenylenepyroazoline[3,4-C]quinazoline-5, 3-diyl-1, 4-phenylene),
poly(imino-1, 2-phenylene-4H-1,2,4-triazole-3, 5-diyl-1, 3-phenylene-4H-1, 2, 4-triazole-3, 5-diyl-1, 2-phenyleneiminoterephthaloyl),
poly(2, 5-benzoxazolediylmethylene-5, 2-benzoxazolediyl-1, 3-phenylene),
poly(5, 7-dihydro-1, 3, 5, 7-tetraoxobenzo[1,2-c:4,5-c']diphyrrole-2, 6[1H,3H]-diyl-1, 4-phenyleneoxy-1, 4-phenylene),
poly[oxy(4-amino-1, 3-phenylene)iminocarbonyl-(4,9-dicarboxytricyclo[4.2.2.0^{2,5}]-7-decane-3, 10-diyl)carbonylimino-(6-amino-1, 3-phenylene)],
poly(hydrazocarbonyl-1, 4-phenylene-2, 1-benzo[c]furone-3, 3-diyl-1, 4-phenylenecarbonylhydrazoterephthaloyl),
poly(1, 4-phenylene-1, 3, 4-oxadiazole-2, 5-diyl-1, 4-phenylene-2, 1-benzo[c]-furone-3, 3-diyl-1, 4-phenylene-1, 3, 4-oxadiazole-2, 5-diyl),
poly[6,6'-bis(3,3'-diphenylquinoxaline)-2, 2'-diyl-1, 4-phenyleneoxy-1, 4-phenylene),
poly(dimethyl siloxane),
poly(diethyl siloxane),
poly(trimethylsilyl ethylene),
poly(dimethylbenzylsilyl ethylene),
poly(vinylene diphenylsilylene),
poly(vinylene diphenylgermylene),
poly(vinylene diphenylsilylene vinylene diphenylgermylene).
poly(diethnyl diphenylsilylene),
poly(diethnyl diphenylgermylene),
poly(2,3,4,5-tetraphenyl-1, 1,-diethnylgermocyclopentadiene),
polyphenylsilisesquioxane,
poly[ethylene-N-(β-trimethylsilyethyl)-imine],
poly(propene sulfone),
poly(1-butene sulfone),
and poly(1-hexene sulfone).

A set of recommended data is dervied for each polymer. Entropy and enthalpy functions have been derived for poly(4,4'-isopropylidenediphenylene carbonate) and poly(dimethyl siloxene) only.

Recommended heat capacity data on these polymers are being analyzed in terms of their chemical structure to derive heat capacities for various structural units and updated heat capacity addition scheme.[66–68] The results of this analysis will be reported at a later date

Heat capacity change at the glass transition, for polymers discussed in this paper, for which recommended heat capacity data are available in their glassy and molten states are listed in Table 20. These $\Delta C_p(T_g)$ data are being analyzed, along with other $\Delta C_p(T_g)$ data for other linear macromolecules in terms of the hole theory of the glass transition.[67,69] The results of this analysis will also be reported at a later date.

Acknowledgments

This work has been supported by the National Science Foundation Grant #DMR78-15279 (Polymers Program). The assistance of B. B. Wunderlich is greatly appreciated.

5. References

[1] U. Gaur, H.-C. Shu, A. Mehta, and B. Wunderlich, J. Phys. Chem. Ref. Data **10**, 89 (1981).

[2] U. Gaur and B. Wunderlich, J. Phys. Chem. Ref. Data **10**, 119 (1981).

[3] U. Gaur and B. Wunderlich, J. Phys. Chem. Ref. Data **10**, 1001 (1981).

[4] U. Gaur and B. Wunderlich, J. Phys. Chem. Ref. Data **10**, 1051 (1981).

[5] U. Gaur and B. Wunderlich, J. Phys. Chem. Ref. Data **11**, 313 (1982).

[6] U. Gaur, S.-F. Lau, B. B. Wunderlich, and B. Wunderlich, J. Phys. Chem. Ref. Data. **11**, 1065 (1982).

[7] U. Gaur, B. B. Wunderlich, and B. Wunderlich, "Heat capacity and other thermodynamic properties of linear macromolecules. VII. Other carbon backbone polymers" (to be published).

[8] U. Gaur, S.-F. Lau, B. B. Wunderlich, and B. Wunderlich, "Heat capacity and other thermodynamic properties of linear macromolecules. VIII. Polyesters and polyamides" (to be published).

[9] R. Bonart, Makromol. Chemie **92**, 149 (1966).

[10] B. Wunderlich, *Macromolecular Physics* (Academic, New York, 1973, 1976, 1980), Vols. 1, 2, and 3.

[11] B. Wunderlich, Polym. Eng. Sci. **18**, 431 (1978).

[12] J. Brandrup and E. H. Immergut, *Polymer Handbook*, 2nd ed. (Wiley, New York, 1975).

[13] F. S. Dainton, D. M. Evans, F. E. Hoare, and T. P. Melia, Polymer **3**, 316 (1962).

[14] J. M. O'Reilly, F. E. Karasz, and H. E. Bair, J. Polymer Sci. **C6**, 109 (1963).

[15] G. S. Cieloszyk, M. T. Cruz, and G. L. Salinger, Cryogenics **13**, 718 (1973).

[16] K. H. Hellwege, W. Knappe, and W. Wetzel, Kolloid-Z. **180**, 126 (1962).

[17] R. C. Steere, J. Appl. Polymer Sci. **10**, 1673 (1966).

[18] J. B. Park and D. H. Uhlmann, J. Appl. Phys. **44**, 201 (1973).

[19] A. B. Bashirov, K. Akhundov, and Yu. V. Selenev, Plaste Kautschuk **23**, 31 (1976).

[20] A. B. Bashinov and A. N. Manukyan, Mekh. Polim. **1975**, 555 (1975).

[21] G. A. Adam, J. N. Hay, I.W. Parsons, and R. N. Haward, Polymer **17**, 51 (1976).

[22] G. Y. Zemlyanoi and V. P. Dushchenko, Vysokomol. Soedin. Ser. **B18**, 752 (1976).

[23] P. Dushchenko, Y. I. Gannichenko, V. S. Tytyuchenko, G. Y. Zemlyana, and V. N. Smola, Teplofiz. Teplotekh. **32**, 62 (1977).

[24] M. V. Belostotskii, B. A. Arvtyunov, V. S. Bil, and R. D. Stepanov, Mekh. Polim. **1977**, 163 (1977).

[25] I. W. Gilmour, A. Trainor, and R. N. Haward, J. Polym. Sci. Polym. Phys. Ed. **16**, 1277 (1978).

[26] N. V. Karyakin, A. N. Mochalov, G. P. Kamelova, E. G. Kiparisova, G. M. Iseitlin, V. N. Kulagin, I. B. Rabinovich, and V. V. Korshak, Tr. Khim. Khim. Tekhnol. **1973**, 67 (1973).

[27] N. V. Karyakin, S. G. Kunyavskaya, V. N. Sapozhnikov, L. B. Sokolov, G. A. Kuznetsov, and I. B. Rabinovich, Tr. Khim. Khim. Tekhnol. **1974**, 134 (1974).

[28] N. V. Karyakin, N. G. Buzhan, V. N. Sapozhikov, K. G. Shvetsova, G. L. Berestneva, A. N. Lomteva, Y. B. Zimin, and V. V. Korshak, Vysokomol. Soedin. Ser. A **19**, 1541 (1977).

[29] I. B. Rabinovich, A. N. Mochalov, L. I. Pavtinov, V. V. Kovshak, A. L. Rusanov, and R. D. Katsarava, Dokl. Akad. Nauk SSSR **198**, 597 (1971).

[30] V. V. Karshak, G. L. Berestneve, T. S. Astaf'eva, A. L. Rusano, and D. S. Tugushi, Vysokomol. Soedin. Ser. B. **16**, 681 (1974).

[31] N. V. Karyakin, V. N. Sapozhnikov, A. L. Rusanov, T. G. Iremashvik, I. B. Rabonovich, and V. V. Korshak, Tr. Khim. Khim. Tekhnol. **1973**, 62 (1973).

[32] B. A. Zhubanov, N. V. Karyakin, P. E. Messerle, V. A. Solomin, and N. P. Lyubchenko, Vysokomol. Soedin. Ser. B. **20**, 666 (1978).

[33] N. V. Karyakin, V. N. Sapozhnikov, G. P. Kamelova, V. V. Korshak, G. L. Berestneva, and D. R. Tur, Vysokomol. Soedin. Ser. A. **21**, 18 (1979).

[34] W. Wrasidlo, J. Polymer Sci. Part 2 **9**, 1603 (1971).

[35] N. V. Karyakin, V. N. Sapozhikov, M. M. Teplyakov, and V. P. Chebotarev, Dokl. Akad. Nauk. SSSR **237**, 367 (1977).

[36] N. V. Karyakin, V. N. Sapozhrikov, M. M. Teplyakov, and V. P. Cheboturev, Vysokomol. Soedin. Ser. **A20**, 1950 (1978).

[37] W. A. Alpaugh and D. R. Morrow, Thermochimica Acta **9**, 171 (1974).

[38] B. V. Lebedev, B. M. Aron, E. G. Kiparisova, I. B. Rabinovich, V. A. Pankratov, S. V. Vinogradova, and V. V. Korshak, Vysokomol. Soedin. Ser. A **17**, 2694 (1975).

[39] V. Lebedev, I. B. Rabinovich, E. G. Kiparlsova, A. A. Estropov, V. V. Korshak, V. A. Pankratov, and L. F. Larina, Dokl. Akad. Nauk. SSSR **237**, 383 (1977).

[40] R. W. Warfield and E. G. Kayser, J. Macromol. Sci. Phys. **B11**, 325 (1975).

[41] V. A. Era, A. Mattila, and J. J. Lindberg, Makromol. Chem. **64**, 235 (1977).

[42] V. A. Era and A. Mattila, Tutkimus Tek. **1977**, 28 (1977).

[43] C. Harwood, G. H. Wostenholm, B. Yates, and D. V. Badami, J. Polym. Sci. Polym. Phys. Ed. **16**, 759 (1978).

[44] V. A. Turdakin, V. V. Tarasov, and A. K. Mal'tsev, Zh. Fiz. Khim. **50**, 1980 (1976).

[45] B. V. Lebedev, N. N. Mukhina, and T. G. Kulagina, K. Vysokomol. Soedin. Ser. A **20**, 1297 (1978).

[46] M. Sh. Yagfarov and V. S. Ionkin, Vysokomol. Soedin. Ser. A **10**, 1613 (1968).

[47] M. Sh. Yagfarov, V. S. Ionkin, and Z. G. Gizatullina, Vysokomol. Soedin. Ser. A **11**, 2306 (1969).

[48] C. L. Beatty and F. F. Karasz, J. Polym. Sci. Phys. Ed. **13**, 921 (1975).

[49] B. V. Lebedev, L. Y. Tsvetkova, and I. B. Rabinovich, Tr. Khim. Khim. Tekhnol. **1973**, 17 (1973).

[50] I. B. Rabinovich, B. V. Lebedev, L. Y. Tsvetkova, N. S. Nametkin, S. G. Durgar'yan, V. S. Khotimskii, and E. G. Kipanisova, Vysokomol. Soedin. Ser. A **17**, 1421 (1975).

[51] B. V. Lebedev, B. M. Aron, and V. I. Milov, Tr. Khim. Khim. Tekhnol. **1975**, 26 (1975).

[52] B. V. Lebedev, I. B. Rabinovich, N. K. Lebedev, V. G. Tsvetka, S. C. Durgar'yan, and V. S. Khotimskii, Vysokomol. Soedin. Ser. A **19**, 513 (1977).

[53] N. K. Lebedev, B. V. Lebedev, V. S. Khotimskii, and S. G. Durgar'yan, Vysokomol. Soedin. Ser. A **21**, 1031 (1979).

[54] B. Lebedev, I. B. Rabinovich, N. K. Lebedev, A. M. Sladkov, and N. A. Vasneva, Vysokomol. Soedin. Ser. A **20**, 338 (1978).

[55] B. V. Lebedev, V. I. Milov, V. Y. Lityasov, A. M. Sladkov, and L. K. Luneva, Tr. Khim. Khim. Tekhnol. **1975**, 46 (1975).

[56] R. V. Lebedev, I. B. Rabinovich, V. I. Milov, A. M. Sladkov, and N. A. Vasneva, Izv. Akad. SSSR, Ser. Khim. **1977**, 1979 (1977).

[57] B. V. Lebedev, L. Y. Tsvetkova, V. I. Milov, L. K. Luneva, A. M. Sladkov, and I. B. Rabinovich, Tr. Khim. Khim. Tekhnol. **1973**, 23 (1973).

[58] V. I. Milov, B. V. Lebedev, L. Y. Tsvetkova, A. M. Sladkova, L. K. Luneva, N. K. Lebedev, and A. A. Evstropov, Tr. Khim. Khim. Tekhnol. **1974**, 140 (1974).

[59] E. G. Kiparisova, B. V. Lebedev, T. A. Bykova, A. M. Sladkova, and N. A. Vasheva, Izv. Akad. Nauk SSST, Ser. Khim. **1978**, 1459 (1978).

[60] O. A. Tikhonova, L. Y. Tsvetkova, B. V. Lebedev, and I. B. Rabinovich, Tr. Khim. Khim. Tekhnol. **1973**, 21 (1973).

[61] B. V. Lebedev, L. Y. Tsvetkova, E. G. Kiparisova, V. N. Perchenko, G. A. Symov, and I. B. Rabinovich, Vysokomol. Soedin. Ser. A **17**, 626 (1975).

[62] L. Y. Tsvetkova, B. V. Lebedev, and V. I. Milov, Tr. Khim. Khim. Tekhnol. **1974**, 97 (1974).

[63] Y. L. Rastorguev and V. G. Nemzer, Teploenergetika **17**, 80 (1970).

[64] C. L. Lee, O. K. Johannson, O. L. Flaningan, and P. Hahn, "Calorimetric studies on the phase transitions of crystalline polysiloxanes," Polymer Preprints **10**, 1319 (1969).

[65] F. S. Dainton, D. M. Evans, F. E. Hoare, and T. P. Melia, Polymer **3**, 310 (1962).

[66] B. Wunderlich and L. D. Jones, J. Macromol. Sci. Phys. **B3**, 67 (1969).

[67] U. Gaur and B. Wunderlich, "Additivity of the heat capacities of linear macromolecules in the molten state," Polymer Div., Am. Chem. Soc. Preprints **20**, 429 (1979).

[68] B. Wunderlich and U. Gaur, "Addition scheme for heat capacities of linear macromolecules," *Thermal Analysis*, edited by W. Hemminger (Birkhaeuser, Basel, 1980).

[69] B. Wunderlich, J. Phys. Chem. **64**, 1052 (1960).