

## Modeling of the Heat Capacity of Polymers with the Variable Connectivity Index

Dahuan LIU and Chongli ZHONG<sup>†</sup>

*Department of Chemical Engineering, PO Box 100, Beijing University of Chemical Technology, Beijing 100029, China*

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**ABSTRACT:** Correlations for the heat capacity at constant pressure of solid and liquid polymers at room temperature were proposed based on the variable connectivity index in this work. The experimental heat capacity data of 81 solid polymers and 79 liquid polymers were used to establish the correlations, and the average absolute deviations of the heat capacity are 4.8% and 3.8%, respectively. The correlations proposed are simple, which can be used to predict the heat capacity of polymers at room temperature as long as the chemical structure of the polymer concerned is known.

**KEY WORDS** Modeling / Heat Capacity / Polymer / Connectivity Index /

The heat capacity is a macroscopic, thermodynamic quantity that is based on the molecular motion, which is one of the most important thermophysical properties of materials. It can be used to calculate other calorimetric properties, such as the enthalpy, entropy, and Gibbs free energy, which is also useful in estimating the thermal conductivity. Since most polymer manufacture and processing involve heat transfer, the knowledge of the heat capacity is very important in polymer processing operations.

A lot of experimental heat capacity data have been measured, but its accurate measurement is still difficult, and the data may show large discrepancy even for some well-characterized polymers. Wunderlich *et al.* analyzed all available data for molar heat capacity at constant pressure,  $C_p(T)$ , and determined and listed extensive tables of smoothed values of  $C_p(T)$ , which contributed greatly to progress in this area.<sup>1</sup>

Theoretical models have also been proposed,<sup>1–5</sup> and one of the commonly used methods for the estimation of the heat capacity at constant pressure at room temperature ( $C_p(298\text{ K})$ ) is the group contribution methods proposed by Satoh and Shaw.<sup>2</sup> Recently, connectivity indices, the widely used structure descriptors for normal molecules, have been applied to establish predictive models for the properties of polymers, and correlations have been proposed successfully for a wide variety of properties.<sup>1</sup> More recently, an approach was proposed in our previous work<sup>6</sup> to calculate high order connectivity indices for polymers in a consistent manner.

The previous investigations<sup>1, 6, 7</sup> show that connectivity indices are quite useful in developing simple correlations for the prediction of the properties of polymer and polymer solutions from molecular structure infor-

mation. In this work, the variable connectivity index proposed by Randić<sup>8</sup> is used to establish correlations for the  $C_p(298\text{ K})$  of polymers and compared with those correlations based on the traditional connectivity index.

### THEORY

#### *The Connectivity Index*

Connectivity indices have been widely used as structure descriptors, which contain a large amount of information about the molecule, including the numbers of hydrogen and non-hydrogen atoms bonded to each non-hydrogen atom, the details of the electronic structure of each atom, and the molecular structural features (paths, branches, clusters, and rings).<sup>1, 9, 10</sup> Details of their definition and the calculation method can be found elsewhere,<sup>9, 10</sup> and a review on the development of the connectivity index was recently published by Randić.<sup>11</sup>

The general expression for the  $m$ th-order connectivity index is as follows:

$${}^m\chi_t = \sum_{j=1}^{n_m} \prod_{i=1}^{m+1} (\delta_i)_j^{-0.5} \quad (1)$$

where  $m$  is the order of the connectivity index,  $t$  denotes a contiguous path type of fragment, which is divided into paths (P), clusters (C), path/clusters (PC), and chains (cycles) (CH).  $n_m$  is the number of the relevant paths, and  $\delta_i$  is the simple connectivity index, equal to the number of non-hydrogen atoms to which the  $i$ th non-hydrogen atom is bonded.

If  $\delta_i$  is replaced by  $\delta_i^v$ , the valence connectivity index, we can obtain the expression for the  $m$ th-order valence connectivity index,  ${}^m\chi_t^v$  as follows:

<sup>†</sup>To whom correspondence should be addressed (Tel: +86-10-64419862; Fax: +86-10-64436781; E-mail: zhongcl@mail.buct.edu.cn).

$${}^m\chi_i^v = \sum_{j=1}^{n_m} \prod_{i=1}^{m+1} (\delta_i^v)^{-0.5} \quad (2)$$

Recently, a new kind of connectivity index has been introduced,<sup>8</sup> that is the so-called variable connectivity index, which can be calculated by the following expression:

$${}^m\chi_i^f = \sum_{j=1}^{n_m} \prod_{i=1}^{m+1} (\delta_i^f)^{-0.5} \quad (3)$$

where the variable connectivity index,  $\delta_i^f$ , is related to the simple connectivity index,  $\delta_i$ , by

$$\delta_i^f = \delta_i + x_i$$

where  $x_i$  is a variable for a non-hydrogen atom, and the numerical value for the variable needs to be selected so to minimize the standard error for a regression. Therefore,  $x_i$  is a weight variable, which can increase or decrease the contribution of the atom to the property concerned. As a result, the numerical value of  $x_i$  for an atom may vary largely for different properties, and its value for the same atom in cyclic structure and acyclic structure may be different.<sup>12</sup> The main advantage of the variable connectivity index is that it gives flexibility to connectivity index as structure descriptor, and therefore can increase correlative accuracy with a simpler expression. However, the numerical values of  $x_i$  should be regressed by fitting experimental data, and they may change largely when another property is concerned. On the other hand, for a certain property once the numerical values of the weights are determined, the variable connectivity indices can be calculated as simple as the traditional connectivity indices. Therefore, the correlations based on the variable connectivity index have the same predictive capability as those based the traditional connectivity index.

#### *The Existing Correlations for $C_p$ (298 K) of Polymers Based on the Traditional Connectivity Index*

Based on connectivity index, Bicerano<sup>1</sup> has proposed two correlations for  $C_p$ (298 K) of solid and liquid polymers separately as follows:

$$C_p^S(298 \text{ K}) = 8.985304 {}^0\chi + 20.920972 {}^1\chi^v + 7.304602(N_{\text{rot}} + 5N_{\text{Si}}) \quad (4)$$

$$C_p^L(298 \text{ K}) = 8.162601 {}^0\chi + 23.215188 {}^0\chi^v + 8.477370N_{\text{BBrot}} + 5.350331N_{\text{SGrot}} \quad (5)$$

where  $C_p^S(298 \text{ K})$  and  $C_p^L(298 \text{ K})$  are the heat capacity at constant pressure at room temperature for solid and liquid polymers, respectively.  $N_{\text{BBrot}}$  and  $N_{\text{SGrot}}$  are the

rotational degrees of freedom of the backbone and side group portions of the repeat units of polymers, respectively.  $N_{\text{rot}}$  is the total number of rotational degrees of freedom, and  $N_{\text{Si}}$  is the number of silicon atoms.

The heat capacity of polymers at a certain temperature can be estimated by the following two expressions:<sup>1</sup>

$$C_p^S(T) = C_p^S(298 \text{ K})(0.106 + 0.003T) \quad (6)$$

and

$$C_p^L(T) = C_p^L(298 \text{ K})(0.613 + 0.0013T) \quad (7)$$

As a result, as long as the  $C_p(298 \text{ K})$  is known, the  $C_p(T)$  at the temperature interest can be estimated using eqs 6 and 7.

Another important heat capacity value is the change in the heat capacity at the glass transition,  $\Delta C_p(T_g)$ . Obviously, it can be calculated readily using eqs 6 and 7, supposed the required  $T_g$  is known for a polymer.

#### *Development of New Correlations Based on the Variable Connectivity Index*

The variable connectivity index is more flexible in describing the chemical structure of molecules, which has been successfully applied to a variety of properties of normal molecules.<sup>10</sup> In this work, we will adopt it to model the physical properties of polymers, and correlations based on the variable connectivity index will be developed for  $C_p^S(298 \text{ K})$  and  $C_p^L(298 \text{ K})$  in the following section.

It should be pointed out that Bicerano<sup>1</sup> has tried to optimize the value of  $\delta^V$  for each distinct electronic configuration of each atom, for each property, and thus to establish simpler correlations, and applied this method to the correlation of the van der Waals volume of polymers as an example. The basic idea of Bicerano's method is the same as that the variable connectivity index method proposed by Randić.<sup>8</sup>

## RESULTS AND DISCUSSION

#### *Correlation of $C_p^S$ (298K) for Solid Polymers*

The experimental data of  $C_p^S(298 \text{ K})$  for solid polymers collected by Bicerano<sup>1</sup> from the literature were used as the database to establish the new correlation for  $C_p^S(298 \text{ K})$ . The experimental data and the variable connectivity index used are shown in Table I. Based on these data, the following correlation was obtained:

$$C_p^S(298 \text{ K}) = 52.287 {}^0\chi^f - 3.9356 \quad (8)$$

The optimal weights for the non-hydrogen atoms in the calculation of  ${}^0\chi^f$  were obtained by fitting the data,

**Table I.** Calculated results for  $C_p^S$  (298 K) of solid polymers and the variable connectivity indices used

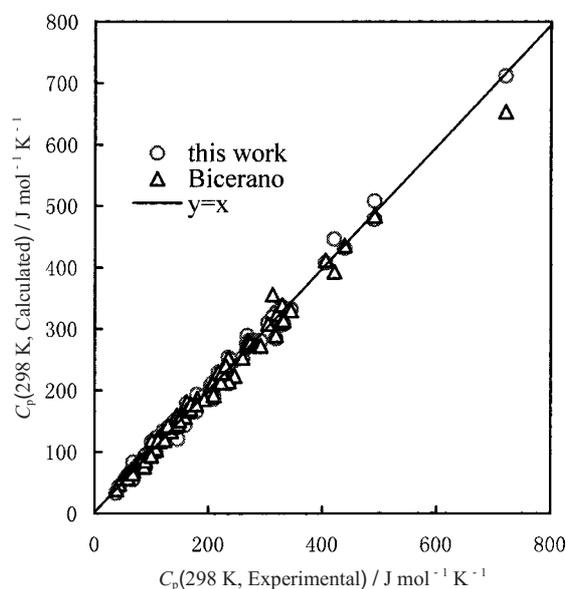
Polymer	${}^0\chi^f$	$C_p^S$ (298 K) (J mol <sup>-1</sup> K <sup>-1</sup> )		
		exp.	this work	Bicerano
Poly( <i>p</i> -phenylene)	1.7171	84.5	85.8	86.4
Poly(oxy( <i>p</i> -phenylene))	1.9691	108.5	99.0	103.4
Poly(thio( <i>p</i> -phenylene))	2.4314	110.2	123.2	120.5
Poly( <i>p</i> -hydroxybenzoate)	2.6404	121.8	134.1	134.4
Polystyrene	2.5904	126.5	131.5	133.5
Poly( <i>p</i> -xylylene)	2.6188	134.7	133.0	133.8
Poly( <i>p</i> -chloro styrene)	2.9673	141.1	151.2	151.3
Poly( <i>p</i> -bromo styrene)	2.8936	144.9	147.4	160
Poly( $\alpha$ -methyl styrene)	3.0646	149.8	156.3	156.5
Poly( <i>p</i> -methyl styrene)	3.084	150.0	157.3	157.2
Poly( <i>N</i> -vinyl pyrrolidone)	2.8099	158.9	143.0	156.5
Poly(vinyl benzoate)	3.5138	162.4	179.8	181.3
Polyoxynaphthoate	3.7775	180.6	193.6	186.8
poly( $\alpha$ -vinyl naphthalene)	3.7275	192.9	191.0	186.1
Poly(vinyl butyral)	4.0522	204.6	207.9	208.8
Poly(vinyl <i>p</i> -ethylbenzoate)	4.4582	217.6	229.2	230.4
Poly(vinyl <i>p</i> -isopropylbenzoate)	4.9234	235.4	253.5	253.5
Poly( <i>N</i> -vinyl carbazole)	4.8352	245.8	248.9	223.8
Bisphenol-A polycarbonate	5.9998	304.9	309.8	308.3
Poly(ether ether ketone) (PEEK)	6.3266	319.7	326.9	324.2
Poly( <i>N,N'</i> -( <i>p,p'</i> -oxydiphenylene)pyromellitimide)	8.6143	420.6	446.5	393.1
Udel	9.7859	491.2	507.7	498.0
Ultem	13.691	720.5	711.9	653.5
Polyethylene	0.9017	43.4	43.2	48.2
Polypropylene	1.3669	67.8	67.5	71.6
Poly(1,4-butadiene)	1.8033	88.0	90.4	81.8
Polyisobutylene	1.8411	94.0	92.3	93.7
Polyisoprene	2.2686	108.0	114.7	105.4
Poly(4-methyl-1-pentene)	2.7338	144.5	139.0	143.2
Polyoxymethylene	0.7028	38.3	32.8	39.4
Polyoxyethylene	1.1536	55.1	56.4	63.5
Poly(vinyl chloride)	1.2502	59.0	61.4	65.9
Poly(vinyl fluoride)	1.1411	59.5	55.7	56.8
Poly(glycolic acid)	1.3742	65.1	67.9	70.8
Polyacrylonitrile	1.6645	68.4	83.1	69.3
Polyoxytrimethylene	1.6045	79.3	80.0	87.6
Poly(vinylidene chloride)	1.6077	80.9	80.1	81.9
Polytrifluoroethylene	1.629	87.7	81.2	75.8
Polytetrafluoroethylene	1.8774	89.8	94.2	85.8
Polychlorotrifluoroethylene	1.9865	99.6	99.9	93.7
Poly(vinyl acetate)	2.2903	101.2	115.8	118.6
Poly(methylacrylate)	2.2903	115.0	115.8	117.8
Poly( $\alpha$ -methyl acrylamide)	2.3592	118.1	119.4	120.3
Poly(menthyl methacrylate)	2.7645	137.0	140.6	140.7
Poly( $\epsilon$ -caprolactone)	3.1775	161.6	162.2	167.2
Poly(ethyl methacrylate)	3.2153	166.5	164.2	166.7
Poly( $\epsilon$ -caprolactam)	3.2574	168.9	166.4	169.6
Poly( <i>n</i> -butyl acrylate)	3.6428	210.0	186.5	192
Poly( <i>n</i> -butyl methacrylate)	4.117	235.9	211.3	214.9
Poly(vinyl alcohol)	1.1222	67.4	54.7	64.9
Poly(methacrylic acid)	2.2678	111.9	114.6	118.9
Poly(propylene sulfone)	2.3902	123.3	121.0	119.7
Poly(ethylene oxalate)	2.7484	129.1	139.8	142.4
Poly(1-butene sulfone)	2.3869	146.8	120.9	144.7

Poly(oxy(2,6-dimethyl-1,4-phenylene))	2.9563	149.0	150.6	151.1
Poly(oxy(2,6-dimethyl-5-bromo-1,4-phenylene))	3.2594	169.0	166.5	177.8
Poly(vinyl trimethylsilane)	3.2409	179.1	165.5	177.8
Poly(dimethyl itaconate)	4.1387	207.6	212.5	210.9
Poly(1-hexene sulfone)	3.7427	209.5	191.8	192.9
Poly(isobutyl methacrylate)	4.1314	222.1	212.1	213.4
Poly(ethylene terephthalate)	4.4655	223.9	229.6	228.9
Poly(vinyl dimethylphenylsilane)	4.4644	231.0	229.5	240.6
Poly( <i>p</i> -methacryloxy benzoic acid)	4.9083	260.2	252.7	253.3
Poly(tetramethylene terephthalate)	5.3671	267.9	276.7	277.1
Poly(ethylene-2,6-naphthalenedicarboxylate)	5.6025	268.5	289.0	281.3
Poly( <i>m</i> -phenylene terephthalamide)	5.4407	271.2	280.5	272.6
Poly(vinyl <i>p</i> - <i>t</i> -butylbenzoate)	5.3976	271.6	278.3	275.5
Poly( <i>p</i> -phenylene isophthalamide)	5.4407	272.3	280.5	272.6
Poly(oxy(2,6-diphenyl-1,4-phenylene))	5.4033	272.8	278.6	276.5
Poly( <i>m</i> -phenylene isophthalamide)	5.4407	280.2	280.5	272.6
Poly( <i>o</i> -phenylene terephthalamide)	5.4407	286.2	280.5	272.7
Poly( <i>o</i> -phenylene isophthalamide)	5.4407	291.4	280.5	272.7
Poly(1,4-cyclohexylidene dimethylene terephthalate)	6.1826	312.3	319.3	355.6
Poly(11-aminoundecanoic acid)	5.5116	318.3	284.3	290.2
Poly(di( <i>n</i> -propyl) itaconate)	5.942	328.1	306.8	311.1
Poly(hexamethylene adipamide)	6.5148	329.2	336.7	339.1
Poly(12-aminododecanoic acid)	5.9624	331.5	307.8	314.3
Poly(hexamethylene isophthalamide)	6.4286	344.6	332.2	330
Poly(hexamethylene azelamide)	7.8673	405.7	407.4	411.5
Poly(hexamethylene sebacamide)	8.3182	439.0	431.0	435.6
Nylon-6,12	9.2198	491.0	478.1	483.8
overall error*			4.8	5.0

$$* \frac{1}{N} \sum \left| \frac{C_{pi}^{\text{exp.}} - C_{pi}^{\text{cal.}}}{C_{pi}^{\text{exp.}}} \right| \times 100.$$

which are  $x_C = 2.92$ ,  $x_N = 7.08$ ,  $x_S = -0.04$ ,  $x_O = 13.75$ ,  $x_{Cl} = 5.63$ ,  $x_{Br} = 9.10$ ,  $x_F = 11.82$ , and  $x_{Si} = -2.66$  for the atoms of carbon, nitrogen, sulphur, oxygen, chlorine, bromine, fluorine, and silicon in acyclic structure, respectively. And the optimal weights for the atoms of carbon, nitrogen, and oxygen in cyclic structure are  $x_{CC} = 9.89$ ,  $x_{CN} = 0.44$ , and  $x_{CO} = 1.50$ , respectively.

The calculated results with eq 8 and the optimal weights obtained are listed in Table I and depicted in Figure 1. The calculated results of Bicerano are also shown in Table I for comparison. Obviously, the new model shows comparable accuracy with eq 4, however, the new correlation is more simple, which does not require atomic correction term as well as the  $N_{\text{rot}}$  term. By introducing variable weights into the non-hydrogen atoms, the contribution of a certain atom to a property can be increased or decreased, which makes the traditional "fixed-value" connectivity index more flexible, and leads to better relative accuracy and simpler expression. Once the weights are obtained, the correlations based on the variable connectivity index have the same predictive capability as those based on the traditional connectivity index.



**Figure 1.** Calculated vs. experimental heat capacity at constant pressure at room temperature for solid polymers.

#### Correlation of $C_p^l$ (298 K) for Liquid Polymers

Based on the experimental  $C_p^l$  (298 K) data<sup>1</sup> of liquid polymers shown in Table II, the following correlation was proposed:

$$C_p^l(298 \text{ K}) = 52.981 {}^1\chi^f + 5.1689 \quad (9)$$

**Table II.** Calculated results for  $C_p^l(298\text{ K})$  of liquid polymers and the variable connectivity indices used

Polymer	${}^1\chi^f$	$C_p^l(298\text{ K})$ ( $\text{J mol}^{-1}\text{K}^{-1}$ )		
		exp.	this work	Bicerano
Polyoxymethylene	0.9891	57.6	57.6	54.4
Polyethylene	1.0811	61.6	62.4	61.3
Poly(vinyl fluoride)	1.2591	72.7	71.9	74.2
Poly(vinylidene fluoride)	1.4172	82.9	80.3	88.7
Polyoxyethylene	1.5297	87.8	86.2	85.1
Polypropylene	1.5135	88.1	85.4	94.0
Polytrifluoroethylene	1.6596	93.1	93.1	101.6
Polytetrafluoroethylene	1.8550	102.6	103.4	116.1
Poly(1,4-butadiene)	2.1622	105.7	119.7	108.2
Polyisobutylene	1.8550	109.6	103.4	128.3
Poly(propylene oxide)	1.9710	110.9	109.6	117.7
Poly(glycolic acid)	1.8670	112.2	104.1	96.8
Poly(1-butene)	2.1040	116.7	116.6	121.5
Poly(dimethyl siloxane)	2.1272	117.8	117.9	121.3
Polyoxytrimethylene	2.0702	119.2	114.9	115.7
Polyisoprene	2.5946	129.8	142.6	142.0
Poly(vinylidene chloride)	2.3610	130.0	130.3	123.8
Poly( $\beta$ -propiolactone)	2.0091	135.1	111.6	127.5
Poly(oxymethyleneoxyethylene)	2.5188	135.9	138.6	139.4
Poly(oxy( <i>p</i> -phenylene))	2.6020	141.6	143.0	141.5
Polyoxytetramethylene	2.6107	142.8	143.5	146.4
Poly(1-pentene)	2.6445	143.8	145.3	149.1
Poly(methyl acrylate)	2.8885	151.7	158.2	153.9
Poly( $\gamma$ -butyrolactone)	2.9481	155.7	161.4	158.2
Poly(vinyl acetate)	2.8489	156.3	156.1	153.9
Poly(thio( <i>p</i> -phenylene))	2.8714	157.2	157.3	160.5
Poly(2-methyl-1,4-pentadiene)	3.1351	157.5	171.3	172.7
Poly(oxy(diethylsilylene))	3.2991	165.0	180.0	176.4
Polystyrene	3.1874	174.2	174.0	174.8
Poly(1-hexene)	3.1850	178.0	173.9	176.6
Poly(ethyl acrylate)	3.4509	178.5	188.0	181.4
Poly( $\delta$ -valerolactone)	3.4886	183.2	190.0	188.8
Poly(methyl methacrylate)	3.2707	183.7	178.5	188.2
Poly(oxymethyleneoxytetramethylene)	3.5999	194.2	195.9	200.8
Poly( <i>p</i> -chloro styrene)	3.8956	195.3	211.6	206.4
Poly( <i>p</i> -methyl styrene)	3.6423	197.1	198.1	208.7
Poly( <i>p</i> -bromo styrene)	3.6297	197.5	197.5	225.7
Poly(ethyl methacrylate)	3.5761	203.3	194.6	215.7
Poly( $\epsilon$ -caprolactone)	4.0292	206.5	218.6	219.5
Poly(oxy(2,6-dimethyl-1,4-phenylene))	3.5256	208.7	192.0	209.3
Poly(isobutyl acrylate)	4.2338	231.5	229.5	241.6
Poly( <i>n</i> -butyl acrylate)	4.5319	232.7	245.3	236.5
Polyoxynaphthoate	4.9697	239.8	268.5	255.0
Poly(vinyl benzoate)	4.5228	243.1	244.8	234.7
Poly( <i>n</i> -butyl methacrylate)	4.6572	262.5	251.9	270.8
Poly( $\epsilon$ -caprolactam)	4.3284	269.5	234.5	221.6
Poly(isobutyl methacrylate)	4.7561	273.5	257.2	275.9
Poly(vinyl <i>p</i> -ethylbenzoate)	5.5968	281.1	301.7	296.1
Poly(dimethyl itaconate)	5.1946	281.6	280.4	275.6
Poly(ethylene- <i>n</i> -( $\beta$ -trimethylsilyl ethyl)imine)	5.0831	286.4	274.5	271.2
Poly(trimethylene succinate)	5.3557	288.0	288.9	285.6
Poly(vinyl <i>p</i> -isopropylbenzoate)	6.0114	309.4	323.7	328.8
Poly(ethylene terephthalate)	5.9236	321.2	319.0	311.5
Poly( <i>n</i> -hexyl methacrylate)	5.1978	324.0	280.6	325.9

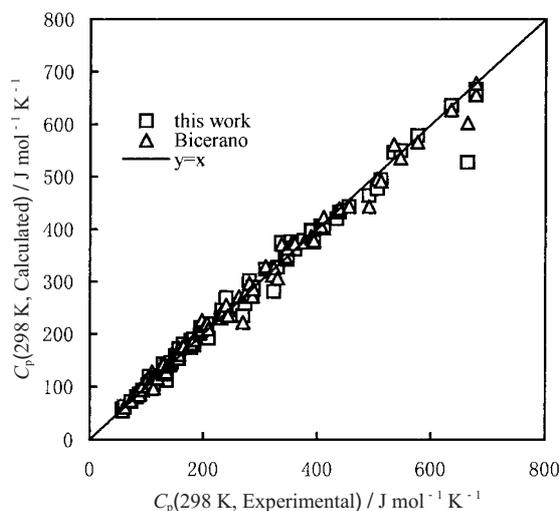
Poly(vinylene diphenylsilylene)	6.0763	330.4	327.1	306.1
Poly(oxy(2,6-diphenyl-1,4-phenylene)	6.9676	337.2	374.3	370.9
Poly(trimethylene adipate)	6.4367	343.7	346.2	347.0
Poly(vinyl <i>p</i> - <i>t</i> -butylbenzoate)	6.3426	347.4	341.2	363.1
Poly(tetramethylene terephthalate)	7.0047	354.5	376.3	372.8
Polyundecanolactone	6.7319	360.7	361.8	372.8
Poly(11-aminoundecanoic acid)	7.0311	376.7	377.7	374.9
Poly(di( <i>n</i> -propyl) itaconate)	7.4005	388.8	397.3	385.8
Poly(ethylene-2,6-naphthalenedicarboxylate)	7.3953	390.4	397.0	382.5
Poly(tetramethylene adipate)	6.9773	394.0	374.8	377.6
Poly(12-aminododecanoic acid)	7.5716	406.4	406.3	405.6
Bisphenol-A polycarbonate	7.4787	410.8	401.4	423.1
Polytridecanolactone	7.8130	433.9	419.1	434.1
Poly(ethylene sebacate)	8.0584	438.3	432.1	439.0
Poly(ether ether ketone)	8.2626	455.9	442.9	443.3
Poly(hexamethylene adipamide)	8.6567	490.7	463.8	443.2
Polypentadecanolactone	8.8940	505.1	476.4	495.5
Poly(dodecyl methacrylate)	9.2385	511.5	494.6	491.1
Poly(hexamethylene sebacate)	10.2205	534.3	546.7	561.6
Poly(hexamethylene azelamide)	10.2783	545.8	549.7	535.2
Poly(hexamethylene sebacamide)	10.8189	575.5	578.4	565.9
Nylon-6,12	11.8999	634.8	635.6	627.2
Poly(dicyclooctyl itaconate)	9.8586	663.6	527.5	602.5
Poly(octadecyl methacrylate)	12.4817	677.8	666.5	656.3
Udel	12.2628	678.1	654.9	678.4
Overall error			3.8	4.3

The optimal weights for the non-hydrogen atoms in the calculation of  ${}^1\chi^f$  were obtained by fitting the data, which are  $x_C = -0.15$ ,  $x_N = -0.76$ ,  $x_S = -0.86$ ,  $x_O = 0.21$ ,  $x_{Cl} = -0.60$ ,  $x_{Br} = -0.11$ ,  $x_F = 1.33$ , and  $x_{Si} = -1.27$  for the atoms of carbon, nitrogen, sulphur, oxygen, chlorine, bromine, fluorine, and silicon in acyclic structure, respectively. And the optimal weight for carbon atom in cyclic structure is  $x_{CC} = 0.84$ .

The calculated results and those from eq 5 are shown in Table II and depicted in Figure 2. Similar to that for solid polymers, the new correlation gives comparable accuracy with eq 5 based on the traditional connectivity index, which again illustrates that the utilization of the variable connectivity index can improve correlations either by giving higher accuracy or a simpler expression.

#### Prediction of the Change in the Heat Capacity at the Glass Transition

The change in the heat capacity at the glass transition,  $\Delta C_p(T_g)$ , is an important property, it can be calculated readily using eqs 6 and 7 combined with the correlations for  $C_p^S(298\text{ K})$  and  $C_p^L(298\text{ K})$  proposed. However, the calculation requires the glass transition temperature values. The experimental  $\Delta C_p(T_g)$  and the corresponding  $T_g$  data, as shown in Table III, were taken from the book of Bicerano,<sup>1</sup> they were employed to test the predictive accuracy of the proposed correlations combined with eqs 6 and 7 for  $\Delta C_p(T_g)$ . The

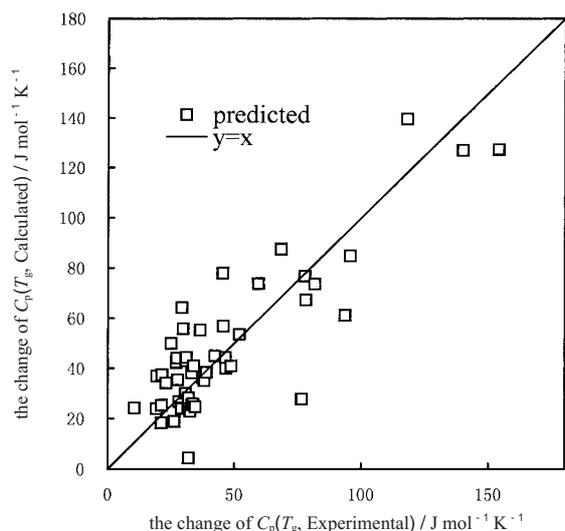


**Figure 2.** Calculated vs. experimental heat capacity at constant pressure at room temperature for liquid polymers.

predictive results are shown in Table III and depicted in Figure 3. Obviously, the deviation is large, this is expected because the extrapolation of eqs 6 and 7 to  $T_g$  may introduce large error, and the  $T_g$  value is not only polymer-dependent but also depends largely on the detailed structure of the polymer concerned. In addition, the experimental data of  $\Delta C_p(T_g)$  may also have large uncertainty.

**Table III.** Predicted results for  $\Delta C_p(T_g)$  of polymers

Polymer	$T_g$ (K)	$\Delta C_p(T_g)$ (J mol <sup>-1</sup> K <sup>-1</sup> )	
		exp.	predicted
Polyethylene	195	10.5	24.2
Polypropylene	233	19.2	23.9
Poly(vinyl chloride)	348	19.4	36.9
Poly(vinylidene fluoride)	233	21.2	18.2
Polyisobutylene	199	21.3	25.2
Poly(oxy( <i>p</i> -phenylene))	358	21.4	37.4
Poly(1-butene)	228	23.1	34.1
Poly(1-hexene)	223	25.1	49.9
Poly( $\alpha$ -methyl styrene)	409	26.3	18.9
Poly(1-pentene)	223	27.0	42.3
Poly(1,4-butadiene)	171	27.2	44.0
Poly(dimethyl siloxane)	152	27.7	35.3
Polyoxymethylene	218	28.2	26.7
Poly(oxy(diethylsilylene))	130	29.2	64.2
Poly(thio( <i>p</i> -phenylene))	360	29.2	23.9
Poly( <i>n</i> -butyl methacrylate)	293	29.7	55.7
Polystyrene	373	30.8	29.9
Polyisoprene	203	30.9	43.0
Poly( <i>p</i> -chloro styrene)	389	31.1	44.2
Poly(ethyl methacrylate)	324	31.7	24.2
Poly(oxy(2,6-dimethyl-1,4-phenylene))	482	31.9	25.7
Poly( <i>p</i> -bromo styrene)	417	31.9	28.1
Poly(methyl methacrylate)	378	32.7	22.8
Poly(propylene oxide)	206	33.2	38.1
Poly( <i>p</i> -fluoro styrene)	379	33.3	25.4
Poly(4-methyl-1-pentene)	302	33.7	25.8
Poly( <i>p</i> -hydroxybenzoate)	420	34.0	41.0
Poly( <i>p</i> -methyl styrene)	374	34.6	24.6
Poly(isobutyl acrylate)	249	36.6	55.2
Poly( <i>p</i> -xylylene)	333	37.6	36.1
Polyoxyethylene	206	38.2	35.1
Poly(isobutyl methacrylate)	321	39.0	38.3
Poly(methyl acrylate)	281	42.3	44.9
Poly( <i>n</i> -butyl acrylate)	219	45.4	77.9
Poly(ethyl acrylate)	251	45.6	56.8
Polyoxytrimethylene	195	46.6	44.3
Poly(vinyl acetate)	301	46.7	39.9
Bisphenol-A polycarbonate	423	48.8	40.8
Polyoxytetramethylene	190	52.0	53.4
Poly( $\epsilon$ -caprolactone)	213	59.5	73.7
Poly(12-aminododecanoic acid)	310	74.3	93.9
Poly(11-aminoundecanoic acid)	315	68.4	87.5
Poly(oxy(2,6-diphenyl-1,4-phenylene))	493	76.6	27.8
Poly(ethylene terephthalate)	345	77.8	76.8
Poly(oxy-1,4-phenylene-oxy-1,4-phenylene-carbonyl-1,4-phenylene)	419	78.1	67.2
Poly(ethylene-2,6-naphthalenedicarboxylate)	397	81.6	73.4
Poly( $\epsilon$ -caprolactam)	335	93.6	61.0
Polyoxyoctamethylene	203	95.7	84.8
Poly(hexamethylene sebacamide)	313	118.0	139.5
Poly(tetramethylene adipate)	205	140.0	126.9
Poly(hexamethylene adipamide)	330	145.0	114.3
Poly(ethylene sebacate)	243	154.0	127.2
Overall error			32.2



**Figure 3.** Predicted vs. experimental the change in the heat capacity at the glass transition.

## CONCLUSION

Two correlations based on the variable connectivity index were proposed for the heat capacity at constant pressure for solid and liquid polymers, respectively. The correlations are simple with comparable relative accuracy to the existing ones. The present work shows that the variable connectivity index has more flexibility in characterizing polymers, which can lead to simpler correlations with better relative accuracy.

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## LIST OF SYMBOLS

$C_p(T)$ ,	Heat capacity at constant pressure [J mol <sup>-1</sup> K <sup>-1</sup> ]
$C_p(298\text{ K})$ ,	Heat capacity at constant pressure at room temperature [J mol <sup>-1</sup> K <sup>-1</sup> ]
$\Delta C_p(T_g)$ ,	The change in the heat capacity at the glass transition [J mol <sup>-1</sup> K <sup>-1</sup> ]
$N$ ,	The number of data points
$N_{\text{BBrot}}$ ,	The rotational degrees of freedom of the backbone portion of the repeat units of polymer
$N_{\text{rot}}$ ,	The total number of rotational degrees of freedom

$N_{\text{SGrot}}$ ,	The rotational degrees of freedom of the side group portion of the repeat units of polymer
$n_m$ ,	The number of the relevant paths
$N_{\text{Si}}$ ,	The number of silicon atoms
$T$ ,	Temperature [K]
$T_g$ ,	Glass transition temperature of polymers [K]
$x_i$ ,	The weight to a non-hydrogen atom

## Greek letters

${}^m\chi_t$ ,	mth-order connectivity index
${}^m\chi_t^f$ ,	mth-order variable connectivity index
${}^m\chi_t^v$ ,	mth-order valence connectivity index
$\delta$ ,	The simple connectivity index
$\delta^v$ ,	The valence connectivity index
$\delta^f$ ,	The variable connectivity index

## Subscripts

$i$ ,	Atom $i$
$t$ ,	A contiguous path type of fragment

## Superscripts

cal.,	Calculated value
exp.,	Experimental value
l,	Liquid
S,	Solid

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