

Optimal descriptors as a tool to predict the thermal decomposition of polymers

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Abstract Quantitative structure-property relationship for the thermal decomposition of polymers is suggested. The data on architecture of monomers is used to represent polymers. The structures of monomers are represented by simplified molecular input-line entry system. The average statistical quality of the suggested quantitative structure-property relationships for prediction of molar thermal decomposition function $Y_{d,1/2}$ is the following: $r^2 = 0.970 \pm 0.01$ and $RMSE = 4.71 \pm 1.01$ ($K \times kg \times mol^{-1}$).

Keywords QSPR · Monte Carlo method · Polymer · Thermal decomposition

1 Introduction

Polymers are among the species widely used in various commercial products. Their thermal stability is a key characteristic for many categories of their applications [1–5]. Thermal stability can be expressed by the temperature of half decomposition $T_{d,1/2}$,

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which is defined as the temperature at which the loss of weight during pyrolysis (at a constant rate of temperature rise) becomes reduced to 50 % of its initial values. The phenomenon of thermal mass reduction of polymer also can be described with the molar thermal decomposition function $Y_{d,1/2}$ that can be calculated with an equation: $Y_{d,1/2} = T_{d,1/2}/M$ (M is the molecular weight per repeating unit) [6].

The thermal decomposition ($T_{d,1/2}$) values are depended on molecular structures of polymers. The experimental determination of these characteristics involves considerable resources including time and equipment. As a cost efficient alternative, quantitative structure-property relationships (QSPR) approaches become an attractive way for the evaluation of the thermal decomposition properties of polymers. In fact, the QSPR analysis of physicochemical parameters for polymers [7–14] is similar to “classic” QSPR analysis, but as a rule the basic representation of polymers are their monomer units [15–18].

The aim of the present study is evaluation of optimal descriptors (calculated with features of monomer) as a tool for QSPR analysis of data on molar thermal decomposition function of polymers. Such approach, if proves to be feasible, promises development of fast and inexpensive alternative to costly experimental studies.

2 Method

2.1 Data

The numerical data on the molar decomposition function ($K \times kg \times mol^{-1}$) for 72 polymers (Table 1) are taken from the literature [6]. The first distribution of data into the training set and validation set is carried out following the scheme from previous studies [6]. However, in our work the training set is separated into the sub-training set and calibration set which are necessary to perform the QSPR analysis by the CORAL software [19,20]. There are two outliers in the model described in the previous work [6]. The first distribution ($n=70$) does not contain these polymers: these are poly(vinyl-trimethylsilane) and poly(pentachlorophenyl-methacrylate) [6]. Since a QSPR/Quantitative structure-activity relationship (QSAR) model is a “random event” [21], we have tested our approach with three additional random distributions into “visible” the sub-training and the calibration sets and “invisible”, the external validation set. No information about polymers from the validation set is involved in building up these models (distributions 2–4). These three splits contain the above mentioned two outliers ($n=72$).

2.2 Optimal descriptors

The optimal descriptors used as a representation of monomers for polymers are calculated as the following:

$$DCW(T, N) = \sum CW(S_k) \quad (1)$$

Table 1 Polymers and SMILES which are used for representation of the molecular structure of monomers

ID	Name of polymer	SMILES for representation of the monomer
1	Poly(vinyl-benzoate)	<chem>c1(C(OC=C)=O)ccccc1</chem>
2	Poly(vinyl-methyl-ether)	<chem>C(OC)=C</chem>
3	Poly(vinyl-ethyl-ether)	<chem>O(CC)C=C</chem>
4	Poly(vinyl-bromide)	<chem>C(=C)Br</chem>
5	Poly(vinylidene-chloride)	<chem>C(=C)(Cl)Cl</chem>
6	Poly(vinyl-sec-butyl-ether)	<chem>C(C(C)C)OC=C</chem>
7	Poly(vinylidene-bromide)	<chem>C(=C)(Br)Br</chem>
8	Poly(vinyl-n-butyl-ether)	<chem>C(CCC)OC=C</chem>
9	Poly(vinyl-cyclopentane)	<chem>C1CCC(C1)C=C</chem>
10	Poly(vinyl-propionate)	<chem>C(OC=C)(CC)=O</chem>
11	Poly(vinyl-pivalate)	<chem>C=COC(CCCC)=O</chem>
12	Poly(vinyl-sulfonic-acid)	<chem>C=CS(=O)(=O)O</chem>
13	Poly(vinylidene-fluoride)	<chem>C(=C)(F)F</chem>
14	Poly(p-methyl-styrene)	<chem>c1(ccc(cc1)C)C=C</chem>
15	Poly(o-methyl-styrene)	<chem>c1(c(cccc1)C)C=C</chem>
16	Poly(p-methoxy-styrene)	<chem>c1(ccc(OC)cc1)C=C</chem>
17	Poly(p-chloro-styrene)	<chem>c1(ccc(Cl)cc1)C=C</chem>
18	Poly(o-chloro-styrene)	<chem>c1(c(cccc1)Cl)C=C</chem>
19	Poly(p-bromo-styrene)	<chem>c1(ccc(Br)cc1)C=C</chem>
20	Poly(p-t-butyl-styrene)	<chem>c1(ccc(C=C)cc1)C(C)(C)C</chem>
21	Poly(ethyl-acrylate)	<chem>C(=O)(OCC)C=C</chem>
22	Poly(n-butyl-acrylate)	<chem>C(=O)(OCCCC)C=C</chem>
23	Poly(ethyl-methacrylate)	<chem>C(OCC)(C(C)=C)=O</chem>
24	Poly(t-butyl-methacrylate)	<chem>C(=O)(OCCCC)C(=C)C</chem>
25	Poly(sec-butyl-methacrylate)	<chem>C(C(=C)C)(O[C@@H](CC)C)=O</chem>
26	Poly(n-butyl-methacrylate)	<chem>C(=O)(OCCCC)C(=C)C</chem>
27	Poly(2-ethylbutyl-methacrylate)	<chem>O=C(OCC(CC)CC)C(=C)C</chem>
28	Poly(cyclohexyl-methacrylate)	<chem>C1(OC(=O)C(=C)C)CCCCC1</chem>
29	Poly(n-hexyl-methacrylate)	<chem>O(C(=O)C(=C)C)CCCCCC</chem>
30	Poly(benzyl-methacrylate)	<chem>c1(COC(C(C)=C)=O)ccccc1</chem>
31	Poly(n-octyl-methacrylate)	<chem>O(C(C(C)=C)=O)CCCCCCCC</chem>
32	Poly(2-hydroxyethyl-methacrylate)	<chem>C(=O)(C(=C)C)OCCO</chem>
33	Polyisobutylene	<chem>C(C)(C)=C</chem>
34	Poly(1,2-butadiene)	<chem>C(=C=C)C</chem>
35	Poly(1-butene)	<chem>C(C=C)C</chem>
36	Poly(acrylic-acid)	<chem>C(C=C)(O)=O</chem>
37	Polymethacrylonitrile	<chem>C(C#N)(C)=C</chem>
38	Poly(methacrylic-acid)	<chem>C(=C)(C(=O)O)C</chem>
39	Poly(methyl-ethacrylate)	<chem>C(C(C)=C)(OC)=O</chem>
40	Poly(methyl-a-chloroacrylate)	<chem>C(C(=C)Cl)(OC)=O</chem>

Table 1 continued

ID	Name of polymer	SMILES for representation of the monomer
41	Polyacrylamide	<chem>C(C=C)(N)=O</chem>
42	Poly(4-methyl-1-pentene)	<chem>C(C(C)C)C=C</chem>
43	Poly(vinyl-methyl-ketone)	<chem>C(C=C)(C)=O</chem>
44	Poly(1-pentene)	<chem>C(CC)C=C</chem>
45	Poly(1-hexene)	<chem>C(CC=C)CC</chem>
46	Poly(vinyl-methyl-sulfide)	<chem>C(=C)SC</chem>
47	Poly(methyl-a-cyanoacrylate)	<chem>C(C(OC)=O)(C#N)=C</chem>
48	Poly(2-vinyl-thiophene)	<chem>C=Cc1cccs1</chem>
49	Poly(vinyl-n-butyl-sulfide)	<chem>C(CC)CS</chem>
50	Poly(phenyl-methacrylate)	<chem>O=C(Oc1ccccc1)C(=C)C</chem>
51	Poly(N-vinyl-phthalimide)	<chem>O=C1N(C(=O)c2ccccc12)C=C</chem>
52	Poly(a-naphthyl-methacrylate)	<chem>C(C(=C)C)(Oc1cc2ccccc2cc1)=O</chem>
53	Poly(pentabromophenyl-methacrylate)	<chem>c1(c(c(Br)c(c(c1Br)Br)Br)Br)OC(C(=C)C)=O</chem>
54 ^a	Poly(vinyl-trimethylsilane)b	<chem>C([Si](C)(C)C)=C</chem>
55 ^a	Poly(pentachlorophenyl-methacrylate)b	<chem>Clc1c(OC(=O)C(=C)C)c(Cl)c(Cl)c(Cl)c1Cl</chem>
56	Poly(vinyl-chloride)	<chem>C(=C)Cl</chem>
57	Polyethylene	<chem>C=C</chem>
58	Poly(vinyl-acetate)	<chem>O(C(C)=O)C=C</chem>
59	Poly(vinyl-cyclohexane)	<chem>C1(CCCCC1)C=C</chem>
60	Poly(vinyl-alcohol)	<chem>C(=C)O</chem>
61	Poly(N-vinyl-pyrrolidone)	<chem>N1(C(=O)CCC1)C=C</chem>
62	Poly(a-vinyl-naphthalene)	<chem>c12c(C=C)cccc1cccc2</chem>
63	Poly(N-vinyl-carbazole)	<chem>c12c3c(cccc3)n(c1cccc2)C=C</chem>
64	Polystyrene	<chem>c1(ccccc1)C=C</chem>
65	Poly(a-methyl-styrene)	<chem>c1(ccccc1)C(C)=C</chem>
66	Poly(methyl-acrylate)	<chem>C(=O)(C=C)OC</chem>
67	Poly(methyl-methacrylate)	<chem>C(C(C)=C)(OC)=O</chem>
68	Polypropylene	<chem>C(C)=C</chem>
69	Poly(vinyl-fluoride)	<chem>C(=C)F</chem>
70	Polyacrylonitrile	<chem>C(C#N)=C</chem>
71	Poly(o-vinyl-pyridine)	<chem>c1(ccccn1)C=C</chem>
72	Poly(m-methyl-styrene)	<chem>c1(cc(ccc1)C)C=C</chem>

^a Polymers #54 and #55 are outliers in work [6]

where S_k is the simplified molecular input-line entry system (SMILES)-atom: it one or two characters from SMILES string, two characters are used only if their separately examination is impossible, e.g. 'Cl' (for chlorine atom), 'Br' (for bromine atom), but majority of SMILES-atoms are one symbol (e.g. 'C', '=', 'C', 'N', etc. [20]); $CW(S_k)$ represents the correlation weight of S_k ; the numerical data on the correlation weights are calculated by the Monte Carlo method [20]; the T is the threshold i.e. the minimal number of S_k in the training set, e.g. if $T=1$, all S_k which are absent in the training

set will be characterized by the correlation weight fixed as zero; N is the number of epochs of the Monte Carlo optimization [20].

The correlation coefficient between the optimal descriptor DCW(T,N) and molar decomposition $Y_{d,1/2}$ is a mathematical function of the threshold (T), the number of epochs of the Monte Carlo optimization (N), and the list of correlation weights $\{CW(S_k)\}$:

$$R^2 = F[T, N, \{CW(S_k)\}] \tag{2}$$

In order to define the model, it is necessary to select T^* and N^* together with $\{CW^*(S_k)\}$ which give maximum of correlation coefficient between DCW(T^*, N^*) and $Y_{d,1/2}$ for the calibration set:

$$R_{\text{calibration}}^{2*} = F[T^*, N^*, \{CW^*(S_k)\}] : R_{\text{calibration}}^{2*} = \text{Max } R_{\text{calibration}}^2 \tag{3}$$

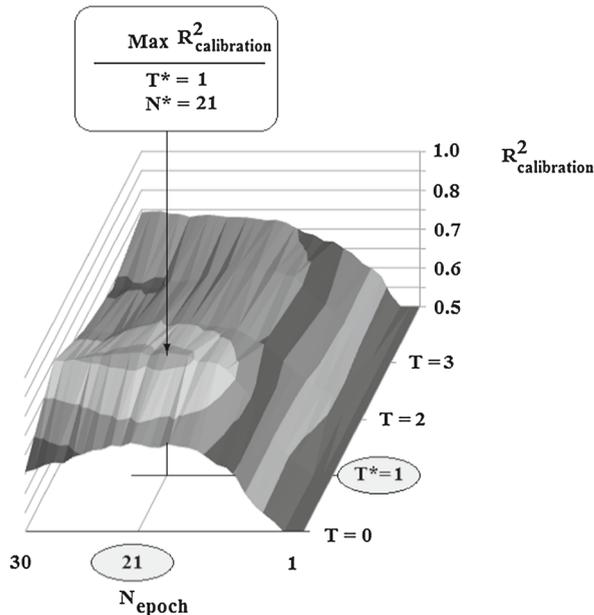
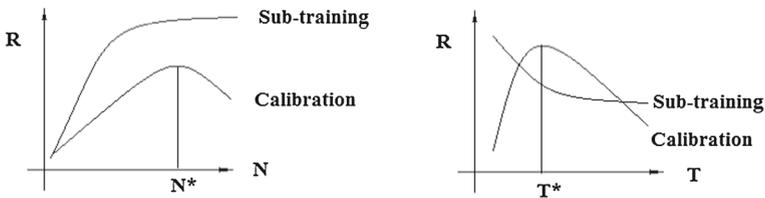


Fig. 1 The scheme of definition of preferable T^* (threshold) and N^* (number of epochs of the Monte Carlo optimization)

Figure 1 shows the essence of the Monte Carlo optimization with various T (1–5) and N (1–30). It is to be noted, correlation coefficients between descriptor and $Y_{d,1/2}$ for the sub-training and calibration sets do vary during the optimization by different ways (Fig. 1).

Having the numerical data on the T^* , N^* , and $\{CW * (S_k)\}$ one can calculate $DCW(T^*, N^*)$ for all polymers and calculate (using data on the sub-training set) by the Least squares method the model:

$$Y_{d,1/2} = C_0 + C_1 \times DCW(T^*, N^*) \quad (4)$$

The predictability of the model calculated with Eq. 4 should be validated with the external validation set.

3 Results and discussion

The approach described in the work [20] resulted in the following models for four distributions of the data into the sub-training, calibration, and validation sets:

Distribution 1

$$\begin{aligned} Y_{d,1/2} &= 5.7455 (\pm 0.2482) + 11.1978 (\pm 0.0418) * DCW(1, 21) \\ n &= 34, R^2 = 0.9974, q^2 = 0.9966, s = 2.24, F = 12319 \text{ (sub-training set)} \\ n &= 19, R^2 = 0.9272, s = 6.47, R_m^2 = 0.8936 \text{ (calibration set)} \\ n &= 17, R^2 = 0.9672, s = 5.42 \text{ (validation set)} \end{aligned} \quad (5)$$

Distribution 2

$$\begin{aligned} Y_{d,1/2} &= 8.5681 (\pm 0.1480) + 7.4133 (\pm 0.0109) * DCW(1, 17) \\ n &= 39, R^2 = 0.9934, q^2 = 0.9929, s = 3.33, F = 5546 \text{ (sub-training set)} \\ n &= 18, R^2 = 0.9606, s = 8.38, R_m^2 = 0.9359 \text{ (calibration set)} \\ n &= 15, R^2 = 0.9645, s = 5.67 \text{ (validation set)} \end{aligned} \quad (6)$$

Distribution 3

$$\begin{aligned} Y_{d,1/2} &= 7.7177 (\pm 0.3077) + 11.2679 (\pm 0.0460) * DCW(1, 7) \\ n &= 36, R^2 = 0.9924, q^2 = 0.9911, s = 3.97, F = 4448 \text{ (sub-training set)} \\ n &= 19, R^2 = 0.9512, s = 6.47, R_m^2 = 0.8739 \text{ (calibration set)} \\ n &= 17, R^2 = 0.9630, s = 4.68 \text{ (validation set)} \end{aligned} \quad (7)$$

Distribution 4

$$\begin{aligned} Y_{d,1/2} &= 3.2738 (\pm 0.1491) + 6.2741 (\pm 0.0063) * DCW(1, 17) \\ n &= 33, R^2 = 0.9962, q^2 = 0.9959, s = 2.99, F = 8093 \text{ (sub-training set)} \\ n &= 21, R^2 = 0.9183, s = 7.19, R_m^2 = 0.9165 \text{ (calibration set)} \\ n &= 18, R^2 = 0.9872, s = 3.08 \text{ (validation set)} \end{aligned} \quad (8)$$

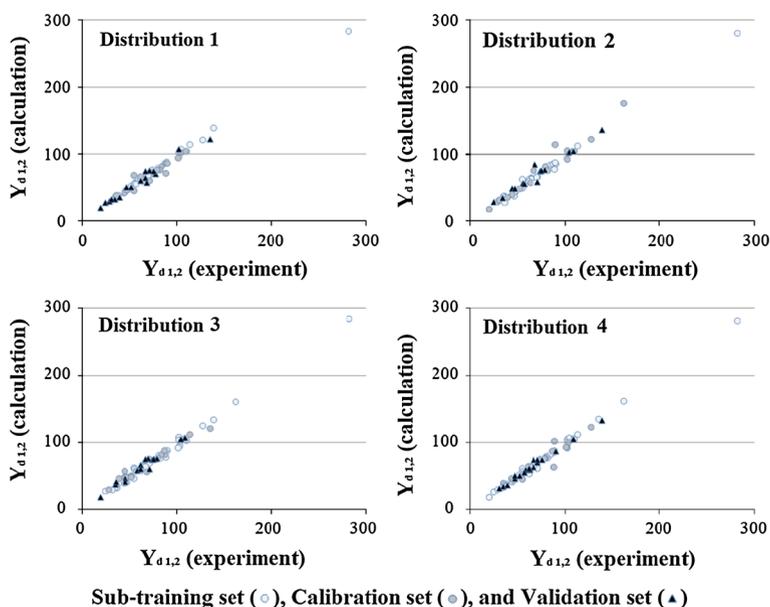


Fig. 2 Graphical representation of models calculated with Eqs. 5, 6, 7, and 8

In Eqs. 5–8: n is the number of polymers in a set (i.e. in sub-training, calibration, and external validation sets); R^2 is the correlation coefficient; q^2 is cross-validated R^2 ; s is the root-mean-square error; F is Fischer F-ratio; and R_m^2 is the metric of the predictability [22]: a model has predictive potential, if $R_m^2 > 0.5$ [22].

Figure 2 shows the graphical representation of models calculated with Eqs. 5, 6, 7, and 8.

Table 2 contains the correlation weights for calculation of optimal descriptors for models computed with Eqs. 5, 6, 7, and 8. One can see from Table 2, that there are three classes of the SMILES-atoms: (i) stable promoters of endpoint increase (all CWs > 0); (ii) stable promoters of endpoint decrease (all CWs < 0); and (iii) SMILES-atoms with unclear role, which have both positive and negative correlation weights for different distributions (Table 2). Thus, suggested model has mechanistic interpretation: the presence of double (=) and triple (#) covalent bonds is promoter of increase for $Y_{d,1/2}$; vice versa the presence of bromine ('Br'), sulphur ('S' and 's'), and nitrogen ('N' and 'n') is promoter of decrease for $Y_{d,1/2}$. It is to be noted that in the case of distribution 1, the list of SMILES-atoms which are involved in building up model is shorter than the lists of SMILES-atoms involved in building up model for the distributions 2, 3, and 4. It indicates that distribution into the "visible" sub-training and calibration sets and the "invisible" external validation set can modify the statistical quality of a QSPR model. Thus, a QSPR model represents a random event, but the statistical quality of a model is a mathematical function of the distribution into the "visible" and "invisible" sets. Table 3 contains experimental and calculated values of the molar thermal decomposition function and four distributions into the "visible" (sub-training and calibration) and "invisible" (validation) sets.

Table 2 The numerical data on the correlation weights for calculation with Eq. 1 which were obtained by the Monte Carlo method for distributions 1, 2, 3, and 4

Distribution 1		Distribution 2		Distribution 3		Distribution 4	
S _k	CW * (S) _k						
#	-0.00244	#	-1.45313	#	0.0	#	-0.76262
(0.04600	(0.07713	(0.09675	(0.17387
1	0.12856	1	-0.05850	1	-0.05088	1	0.08875
2	0.68525	2	0.63963	2	0.46475	2	0.68950
		3	-0.94250	3	0.0	3	0.60938
=	-0.24288	=	-1.14262	=	-0.60438	=	-0.35838
@@	-0.13863	@@	0.0	@@	-1.48438	@@	0.0
C	0.77431	C	1.23338	C	0.82613	C	1.40625
F	1.07431	F	1.72275	F	0.78425	F	1.89162
H	0.25125	H	0.0	H	-0.63563	H	0.0
Br	3.26763	Br	4.88000	Br	3.21475	Br	5.61037
Cl	1.08550	Cl	2.07313	Cl	1.06150	Cl	1.88663
N	0.56250	N	2.49600	N	1.46475	N	1.93450
O	0.65525	O	1.23738	O	0.62200	O	1.01163
S	2.74050	S	4.40625	S	2.80850	S	3.83875
		Si	1.63000	Si	1.03425	Si	3.92587
[-0.04531	[1.82613	[0.95512	[1.00100
c	0.61037	c	1.04787	c	0.65625	c	1.12500
		n	3.73038	n	0.0	n	1.60538
s	2.66675	s	4.22075	s	3.03125	s	5.02625

The statistical quality of the model suggested in work [6] calculated with quantum mechanics descriptors is the following: $n = 53$, $R^2 = 0.9814$, $s = 5.13$ (training set); and $n = 17$, $R^2 = 0.9685$, $s = 5.66$ (validation set). Thus the statistical quality of the models calculated with Eqs. 5, 6, 7, and 8 is very similar. However, the models calculated with Eqs. 3–6 are based on topology of monomers, without data on the quantum mechanics descriptors. The additional validation of the approach with three distributions into the “visible” sub-training and calibration sets together with the “invisible” external validation set has shown that statistical quality of the SMILES-based models remains quite good, even with two outliers (compounds #54 and #55 in Tables 1 and 3) which were removed from the consideration in the previous study [6].

4 Conclusions

The current study reports novel QSAR for the thermal decomposition of polymers. Here monomers' structures represented by simplified molecular input-line entry system are used to represent polymers. The suggested approach provides accurate descriptions of the investigated characteristics and can be useful alternative of the modeling

Table 3 The numerical data on the molar thermal decomposition for 72 polymers

ID	Distributions ^a				$Y_{d,1/2}, K \times \text{kg} \times \text{mol}^{-1}$				
	1	2	3	4	Experiment	Equation 3	Equation 4	Equation 5	Equation 6
1	C	S	C	S	87.5	86.9	85.4	83.6	85.8
2	C	S	V	V	34.5	37.4	37.8	38.0	36.0
3	C	S	V	S	44.9	46.1	47.0	47.3	44.8
4	S	C	S	C	55.6	58.0	55.7	57.9	56.1
5	C	S	S	C	54.1	46.7	51.4	47.8	46.7
6	C	S	S	S	63.1	64.4	66.4	68.1	64.7
7	S	C	S	C	101.9	95.6	93.0	96.3	93.4
8	S	S	S	C	63.8	63.4	65.3	65.9	62.5
9	S	S	V	C	61.0	67.6	64.4	67.1	66.1
10	S	S	V	V	57.6	60.4	58.0	59.0	59.9
11	S	V	V	S	73.5	76.7	75.1	75.5	75.4
12	C	S	S	S	54.3	69.7	63.9	62.9	61.7
13	S	S	C	S	46.6	46.5	46.2	41.6	46.8
14	S	S	V	V	75.6	75.0	75.6	76.4	75.3
15	S	S	S	C	75.7	75.0	75.6	76.4	75.3
16	S	S	C	S	83.2	82.3	84.7	83.4	81.7
17	S	S	C	C	79.2	78.5	81.8	79.1	78.3
18	S	C	S	C	79.3	78.5	81.8	79.1	78.3
19	C	V	S	C	103.1	103.0	102.6	103.3	101.7
20	S	S	S	S	101.5	103.0	105.3	108.7	106.2
21	S	C	S	V	62.4	60.4	58.0	59.0	59.9
22	C	C	S	S	81.4	77.7	76.3	77.6	77.6
23	S	S	S	V	70.4	70.1	68.3	70.5	71.0
24	S	S	C	C	86.5	87.4	86.6	89.1	88.6
25	S	C	S	C	88.7	88.7	114.8	88.9	103.3
26	C	S	S	V	89.4	87.4	86.6	89.1	88.6
27	S	C	V	S	107.6	104.8	104.8	107.7	106.2
28	S	V	V	S	103.9	107.6	104.0	106.6	107.4
29	S	V	S	V	108.3	104.8	104.8	107.7	106.2
30	S	C	S	S	109.4	105.3	104.9	104.4	105.6
31	S	C	S	C	127.2	122.1	123.1	126.4	123.9
32	C	V	V	C	78.0	77.4	77.4	77.5	77.3
33	C	S	V	C	35.0	39.8	39.0	42.5	40.7
34	S	S	S	C	35.5	36.0	29.3	33.5	36.3
35	S	S	S	S	37.2	38.7	37.8	40.3	38.5
36	C	C	C	S	43.7	43.0	39.7	40.4	42.3
37	S	S	C	C	44.2	46.0	46.7	59.0	48.0

Table 3 continued

ID	Distributions ^a				$Y_{d,1/2}, K \times \text{kg} \times \text{mol}^{-1}$				
	1	2	3	4	Experiment	Equation 3	Equation 4	Equation 5	Equation 6
38	S	S	C	S	51.7	52.7	50.0	51.9	53.3
39	C	V	V	S	70.2	61.4	59.1	61.2	62.1
40	S	S	S	C	63.7	64.9	65.3	63.9	65.1
41	S	V	C	C	43.4	42.0	49.0	49.9	48.1
42	S	V	S	S	54.7	57.1	57.2	61.1	58.3
43	S	S	V	C	45.3	44.4	39.7	42.7	44.8
44	C	S	C	V	46.7	47.4	47.0	49.6	47.3
45	S	V	C	V	56.1	56.1	56.1	58.9	56.1
46	S	S	S	S	61.1	60.7	61.3	62.7	53.8
47	S	S	V	S	69.3	67.7	66.9	77.7	69.5
48	S	S	S	S	80.0	80.4	79.9	82.1	79.6
49	C	S	S	C	88.0	72.1	78.9	78.8	64.8
50	C	S	S	C	100.6	95.6	94.6	92.9	94.6
51	S	S	C	S	112.8	114.5	114.1	113.1	113.1
52	S	V	S	V	138.6	139.3	136.3	135.2	133.7
53	S	S	S	S	281.6	283.7	281.2	285.0	281.5
54 ^b	–	S	S	S	88.3	–	88.4	87.2	88.9
55 ^b	–	C	S	S	162.0	–	176.0	161.5	162.5
56	V	V	S	S	33.9	33.5	34.9	33.7	32.7
57	V	C	V	S	19.2	20.4	18.4	19.5	18.7
58	V	V	C	V	46.6	51.7	48.8	49.7	51.1
59	V	S	C	V	70.6	76.3	73.5	76.4	74.9
60	V	V	S	S	24.1	28.7	8.7	28.7	27.2
61	V	S	S	S	76.9	70.9	75.6	76.7	75.7
62	V	C	S	S	101.3	108.0	105.8	105.0	101.2
63	V	S	C	S	135.1	122.7	136.2	121.9	135.2
64	V	S	S	V	66.3	65.2	65.3	64.9	64.3
65	V	C	V	V	66.1	5.0	75.6	76.4	75.3
66	V	C	C	V	51.7	51.7	48.8	49.7	51.1
67	V	S	V	V	61.0	61.4	59.1	61.2	62.1
68	V	C	C	S	27.8	30.1	28.7	31.0	29.7
69	V	C	S	V	30.5	33.4	32.3	30.5	32.7
70	V	C	C	V	38.4	36.3	36.4	47.5	37.0
71	V	V	C	S	67.7	58.4	85.2	57.5	67.3
72	V	V	V	S	74.6	75.0	75.6	76.4	75.3

^a S = sub-training set; C = calibration set; and V = validation set

^b Polymers #54 and #55 are outliers in work [6]

the thermal decomposition of polymers using the quantum mechanics descriptors suggested in the literature [6].

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