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Thermodynamic characterization of segmented polyurethanes

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Abstract

Segmented polyurethanes (SPU), with oligomeric propylene glycole as a soft-chain component, and 4,4′-diphenylmethane diisocyanate extended with ethylene glycole as a stiff-chain component, were characterized by precise heat capacity measurements in the temperature interval 4.2–420 K. Based on the values of the basic thermodynamic quantities derived from the experimental data, it was concluded that incomplete phase separation resulting in formation of a boundary interphase should be regarded as the main source of intrinsic instability of the three-microphase-type morphology of SPU.

Keywords: Boundary interphase; Heat capacity; Segmented polyurethanes; Thermodynamic stability

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1. Introduction

Incomplete phase separation resulting in an apparently three-phase-type morphology, i.e. essentially pure microphases of individual components 1 and 2, and the boundary interphase, BI, of intermediate composition, is now recognized as a characteristic structural feature of multiblock copolymers like segmented polyurethanes (SPU), especially those with both soft- and stiff-chain polar fragments (see, for example, Refs. [1–3]). The apparent failure of the Gibbs phase rule to apply for microphase-separated block copolymers [4] suggests that morphology of this type is in thermodynamic non-equilibrium, i.e. the relative amount of each microphase depends more on the kinetic conditions of sample preparation than on temperature and/or

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pressure. Another example of a conceptually similar violation of the Gibbs phase rule is the case of semi-crystalline polymers in which the fractions of metastable "amorphous" and "crystalline" microphases coexisting below the crystal melting point may also be varied depending on crystallization conditions. In this latter case, "partial" properties of each microphase may be derived from relevant experimental data for a series of samples with different crystallinities [5–7]; moreover, there is even evidence suggesting the possibility of experimental determination of dynamically different, i.e. "rigid" and "mobile", fractions of the amorphous microphase [8].

As already stated above, the relative content of each microphase in microphase-separated SPU also strongly depends on the kinetic conditions of sample preparation. The kinetic stability, i.e. the thermodynamic metastability, of such three-phase-type morphology at sufficiently low temperature (with respect to the temperature of transition into a homogeneous, single-phase state) permits, however, quantitative determination of the structural parameters of the SPU, e.g. the degree of microphase separation, the dimensions of the stiff-chain domains, the thickness of BI, etc., from an appropriate analysis of experimental small-angle X-ray scattering data [9–11]. In our previous communications [12,13], such structural information was combined with the results of the measurements of density and heats of dissolution to estimate the corresponding "partial" properties of BI in a systematic series of SPU. In the present paper, the same approach was used to characterize the thermodynamic state of BI from precise heat capacity measurements.

2. Experimental

Samples of the SPU series, with propylene glycole oligomer (OPG-2000) as a soft-chain component, and 4,4′-diphenylmethane diisocyanate (MDI) extended with ethylene glycole (EG) as a stiff-chain component, cast from 2–5% solutions in dimethyl formamide (DMFA) onto glass slides and subsequently dried to a constant weight in vacuo at 373 K, served as the test specimens. Sample compositions, as well as the values of the volume fraction of the stiff-chain component φ, the density ρ, and the fraction of BI ν [9,10] are shown in Table 1.

The heat capacity C_p in the temperature interval 4.2–300 K was measured in steps of 0.2–0.6 K (in the interval 4.2–50 K), 0.6–1.5 K (in the interval 50–150 K) and 1.5–5 K (at higher temperatures) with the aid of an automated adiabatic calorimeter [14]; the

Table 1
Selected physical properties of SPU

N	Sample code	Molar ratio OPG/EG/MDI	φ	ρ/g cm^{-3}	ν
1	OPG	1/0/0	0	1.006	–
2	SPU-13	1/0.35/1.35	0.13	1.113	0.32
3	SPU-55	1/7/8	0.55	1.188	0.21
4	SPU-82	1/24/25	0.82	1.285	0.10
5	SPU-100	0/1/1	1.0	1.325	–

estimated maximum errors in the indicated temperature intervals did not exceed 2%, 1% and 0.5%, respectively. In addition, C_p was measured (relative error of a single run about 3%) with a home-made differential calorimeter with diathermal shells (DCDS) [15,16] in the temperature interval 150–420 K at a constant heating rate of 2 K min^{-1}. The values of C_p from three to five independent DCDS runs for each sample were reproducible to within 2%. In the overlapping temperature intervals, the experimental data from both instruments agreed to 3–5%.

3. Results and discussion

In essential agreement with other data [17–19], after an initial smooth increase the heat capacity of the soft-fragment homopolymer, OPG-2000, exhibits a sudden jump of $\Delta C_p = 0.70\ \text{J g}^{-1}\ \text{K}^{-1}$ at the glass transition temperature $T_g = 200 \pm 1$ K, and then increases at a lower rate again (Fig. 1). Concomitant with a soft-chain T_g shift of the sample SPU-13 with the lowest stiff-chain content of about 40 K to higher temperatures and a decrease of the corresponding ΔC_p to 0.55 $\text{J g}^{-1}\ \text{K}^{-1}$, one observes the appearance of an endothermic enthalpy relaxation at around 400 K which may be attributed to the softening of the stiff-chain microphase [12]. As φ increases, the intensities of the low-temperature (soft-chain) and high-temperature (stiff-chain) relaxations become weaker and stronger, respectively, until the former completely disappears at $\varphi \to 1$ (Fig. 1).

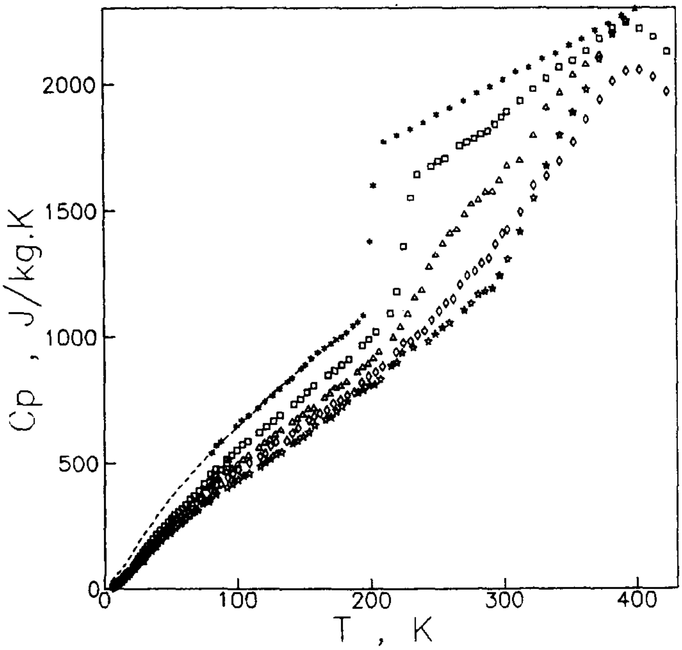

Fig. 1. Heat capacities of OPG-2000 (*), SPU-13 (□), SPU-55 (Δ), SPU-82 (◇) and SPU-100 (☆).

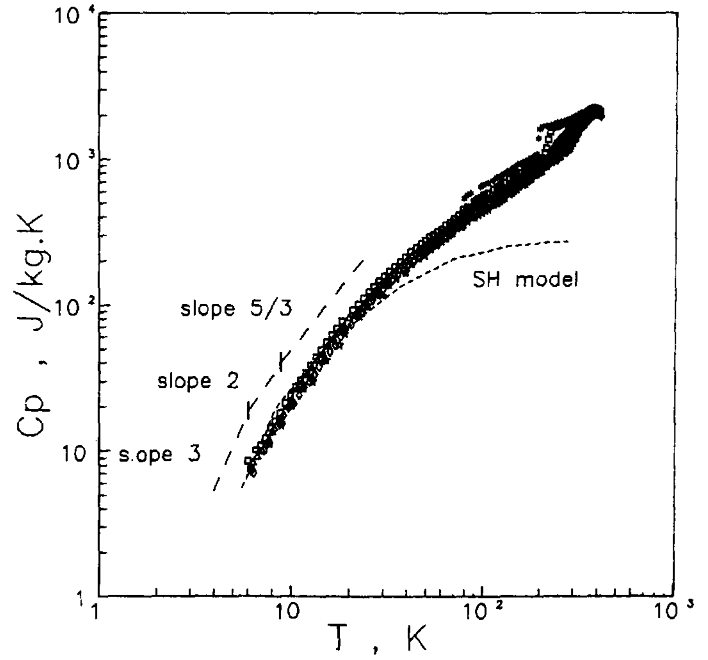

Fig. 2. Double-log plot of the data in Fig. 1.

As can be seen from log C_p vs. log T plots (Fig. 2), the heat capacity of all the studied SPUs below 20 K may be reasonably well fitted to the Stockmayer–Hecht (SH) model [20] assuming $T^* = 280$ K for the characteristic temperature, $\nu^* = 195\ \mathrm{cm}^{-1}$ for the characteristic frequency of vibrations, and $m^* = 65\ \mathrm{g\,mol}^{-1}$ for the effective mass of the chain vibrating unit (disregarding the variation of these parameters with composition). However, because the SH model was developed for polymer crystals [20], a different approach accounting explicitly for the disordered structure of the studied SPUs would be more appropriate. In fact, on closer scrutiny of the same data, one can distinguish two temperature intervals (roughly 8–10 K and 10–30 K), in which the raw values of C_p apparently obey the scaling relationship, $C_p \sim T^\alpha$, with the exponents $\alpha = 2$ and 5/3, respectively (Fig. 2) as predicted [21] for the onset of a fracton-like vibration regime, i.e. localized vibrations on fractals, in polymer glasses.

Pragmatically, within the limits of experimental uncertainty the raw values of C_p for all studied SPUs in the solid (glassy) state below 200 K could be fitted to the 4- or 6-power polynomials of temperature (Table 2). These polynomials were subsequently used to derive the smoothed values of C_p in the temperature interval 0–200 K; at higher temperatures, the raw data were smoothed graphically. The smoothed values of C_p for OPG-2000 below 80 K (dotted line in Fig. 1) were calculated from the 6-power polynomial fitted to the experimental data in the temperature interval 80–200 K.

Table 2

Coefficients of the equation C_p (J kg^{-1} K^{-1}) $= A + BT + CT^2 + DT^3 + ET^4 + FT^5 + GT^6$

Sample	$A \times 10^2$	B	$C \times 10^2$	$D \times 10^3$	$E \times 10^6$	$F \times 10^8$	$G \times 10^{11}$
OPG	−1.31	6.85	3.87	−1.02	9.12	−3.81	6.13
SPU-13	−2066	4.15	8.62	−1.54	12.0	−5.15	8.35
SPU-55	−450	2.27	13.0	−1.89	12.3	3.69	4.13
SPU-82	−485	3.07	4.79	−0.41	1.01	0	0
SPU-100	21	−0.19	25.5	−4.42	43.2	−18.0	28.6

The smoothed values of C_p were used to calculate absolute enthalpy, $H - H_0 = \int C_p \mathrm{d}T$, absolute entropy, $S - S_0 = \int C_p \mathrm{d}\ln T$, and absolute Gibbs free energy, $G = (H - H_0) - T(S - S_0)$, where H_0 and S_0 are the zero-point enthalpy and entropy (Tables 3–7). As a general trend, the plots of composition dependences of all

Table 3

Thermodynamic functions of OPG-2000

T/K	C_p/J kg^{-1} K^{-1}	$H - H_0$/J kg^{-1}	$S - S_0$/J kg^{-1} K^{-1}	$-G$/J kg^{-1}
2	13.8	13.8	6.9	0
5	35.1	87.12	27.77	51.75
10	71.5	353.4	63.18	278.3
20	145.8	1440	135.4	1267
30	219.4	3266	208.4	2985
40	290.5	5815	281.2	5435
50	358.6	9061	353.4	8610
60	421.9	12960	424.4	12500
70	483.5	17490	494.1	17100
80	539.5	22605	562.4	22385
90	593.1	28270	629.0	28350
100	646.8	34470	694.3	34970
110	696.5	41185	758.3	42235
120	747.0	48400	821.1	50135
130	796.4	56120	882.9	58655
140	844.1	64320	943.7	67790
150	887.9	72980	1003	77530
160	932.6	82085	1062	87860
170	973.7	91615	1120	98770
180	1015	101560	1177	110260
190	1062	111945	1233	122310
200	1580	125150	1300	134920
210	1770	141900	1382	148315
220	1800	159740	1465	162555
230	1822	177840	1545	177615
240	1846	196180	1623	193465
250	1877	214795	1700	210085
260	1905	233705	1774	227455
270	1933	252895	1846	245560
280	1964	272380	1917	264380
290	1987	292135	1986	283900
300	2018	312160	2054	304105

Table 4
Thermodynamic functions of SPU-13

T/K	C_p/J kg^{-1} K^{-1}	$H-H_0$/J kg^{-1}	$S-S_0$/J kg^{-1} K^{-1}	$-G$/J kg^{-1}
2	0.8	0.8	0.4	0
5	2.1	5.15	1.63	3.0
10	28.0	80.4	9.68	16.4
20	86.4	652.4	45.3	253.2
30	148.8	1829	91.7	922.0
40	212.0	3633	143.0	2087
50	273.8	6062	196.9	3782
60	333.1	9097	252.0	6025
70	389.8	12710	307.6	8823
80	444.0	16880	363.2	12180
90	495.9	21580	418.5	16090
100	546.0	26790	473.4	20550
110	594.6	32490	527.7	25555
120	641.7	38675	581.4	31100
130	687.7	45320	634.7	37185
140	731.6	52420	687.2	43795
150	774.6	59950	739.2	50930
160	816.1	67900	790.5	58580
170	858.3	76275	841.3	66740
180	902.4	85080	891.6	75405
190	950.8	94345	941.7	84570
200	1020	104500	995.1	94500
210	1080	114650	1043	104405
220	1190	126000	1096	115090
230	1555	139730	1157	126320
240	1650	155750	1225	138230
250	1690	172450	1293	150820
260	1720	189500	1360	164090
270	1760	206900	1426	178020
280	1790	224650	1490	192600
290	1825	242730	1554	207825
300	1870	261200	1616	223675

thermodynamic quantities are markedly non-additive, the deviations from additivity increasing with decreasing φ (Fig. 3). The corresponding "partial" properties of BI, P_{BI}, were derived from the treatment of these data according to the relationship [13]

$$P=(1-\nu)[(1-\varphi)P_{\mathrm{SF}}+\varphi P_{\mathrm{ST}}]+\nu P_{\mathrm{BI}}$$

where P, P_{SF} and P_{ST} are the properties of SPU and of pure soft-chain (OPG-2000) and stiff-chain (SPU-100) components, respectively. As can be judged from the values of P_{BI} derived in this manner, i.e. $H_{\mathrm{BI}} = 180$ J g^{-1}, $S_{\mathrm{BI}} = 1.21$ J g^{-1} K^{-1} and $G_{\mathrm{BI}} = -105$

Table 5
Thermodynamic functions of SPU-55

T/K	C_p/J kg^{-1} K^{-1}	$H-H_0$/J kg^{-1}	$S-S_0$/J kg^{-1} K^{-1}	$-G$/J kg^{-1}
2	0.6	0.6	0.3	0
5	9.8	16.2	3.69	2.25
10	29.1	113.5	15.87	45.2
20	78.4	651.0	50.02	349.4
30	135.8	1722	92.25	1046
40	196.2	3382	139.4	2194
50	255.9	5642	189.5	3834
60	312.5	8484	241.2	5985
70	366.1	11880	293.3	8657
80	415.5	15785	345.5	11850
90	461.1	20170	397.0	15565
100	502.9	24990	447.8	19790
110	543.8	30220	497.7	24520
120	583.0	35855	546.7	29750
130	622.1	41880	594.9	35455
140	661.8	48300	642.5	41645
150	703.1	55125	689.5	48305
160	744.3	62365	736.2	55435
170	786.7	70020	782.6	63030
180	828.6	78095	828.8	71090
190	868.3	86580	874.7	79605
200	910.0	95470	920.3	88580
210	975.0	104895	966.2	98010
220	1030	114920	1013	107905
230	1140	125770	1061	118270
240	1200	137470	1111	129125
250	1345	150195	1163	140485
260	1420	164020	1217	152380
270	1485	178545	1272	164820
280	1545	193695	1327	177815
290	1575	209295	1382	191360
300	1670	225520	1437	205445

J g^{-1}, "specific" (albeit so far unspecified) interactions between soft-chain and stiff-chain fragments within BI lower the thermodynamic stability of the latter with respect to either of the pure components.

A further insight into the problem of the thermodynamic state of BI may be gained from the analysis of the excess properties P_{ex} derived from the standard relationship

$$P = (1 - \varphi)P_{SF} + \varphi P_{ST} + P_{ex}$$

As can easily be verified, the values of all P_{ex} increase approximately linearly with BI content, v; thus, estimation of the relevant properties of BI by a linear extrapolation to

Table 6
Thermodynamic functions of SPU-82

T/K	C_p/J kg^{-1} K^{-1}	$H-H_0$/J kg^{-1}	$S-S_0$/J kg^{-1} K^{-1}	$-G$/J kg^{-1}
2	1.5	1.5	0.75	0
5	11.6	21.15	5.36	5.63
10	21.1	102.9	16.43	61.4
20	72.5	570.9	45.11	331.2
30	120.0	1533	83.23	963.5
40	170.8	2987	124.6	1996
50	223.2	4957	168.2	3455
60	275.9	7453	213.6	5361
70	327.8	10470	260.0	7726
80	377.9	14000	307.0	10560
90	425.7	18020	354.2	13870
100	470.7	22500	401.5	17645
110	512.8	27420	448.3	21895
120	551.9	32740	494.6	26610
130	588.6	38445	540.2	31790
140	623.3	44500	585.1	37420
150	656.8	50900	629.3	43490
160	690.2	57640	672.8	50000
170	724.8	64715	715.6	56945
180	762.2	72150	758.1	64315
190	803.9	79980	800.5	72110
200	850.0	88250	842.9	80325
210	890.0	96950	885.3	88965
220	955.0	106175	928.2	98030
230	985.0	115875	971.3	107530
240	1025	125925	1014	117460
250	1100	136550	1057	127810
260	1150	147800	1101	138605
270	1230	159700	1146	149840
280	1280	172250	1192	161535
290	1325	185275	1238	173685
300	1415	198975	1284	186290

$v = 1$ becomes meaningful (this implies, of course, that the specific interactions responsible for the occurrence of P_{ex} are localized within BI). Once again, very high (by magnitude) values of P_{ex} for BI (Fig. 4) confirm its intrinsic thermodynamic instability.

4. Conclusions

According to the experimental evidence obtained in the present work, the thermodynamic stability of SPU decreases with increasing relative amount of BI. The structural implications of this purely phenomenological result are uncertain; it may be

Table 7
Thermodynamic functions of SPU-100

T/K	C_p/J kg^{-1} K^{-1}	$H-H_0$/J kg^{-1}	$S-S_0$/J kg^{-1} K^{-1}	$-G$/J kg^{-1}
2	0.8	0.8	0.4	0
5	5.2	9.80	2.56	3.0
10	19.3	71.05	9.98	28.8
20	65.5	495.1	36.01	225.2
30	122.1	1433	72.74	749.0
40	179.3	2940	115.5	1680
50	232.0	4997	161.1	3059
60	278.5	7549	207.5	4902
70	319.5	10540	253.5	7209
80	356.5	13920	298.6	9973
90	391.8	17660	342.7	13180
100	427.2	21755	385.8	16825
110	463.9	26210	428.3	20900
120	502.3	31045	470.3	25390
130	542.0	36265	512.0	30305
140	581.9	41885	553.7	35635
150	620.5	47895	595.2	41380
160	657.2	54285	636.4	47540
170	692.1	61030	677.3	54105
180	728.0	68130	717.8	61080
190	770.9	75626	758.4	68460
200	832.2	83640	799.4	76250
210	855.0	92080	840.6	84450
220	910.0	100900	881.7	93060
230	960.0	110250	923.2	102085
240	970.0	119900	964.3	111525
250	1020	129850	1004	121370
260	1065	140280	1046	131625
270	1110	151150	1087	142285
280	1170	162550	1128	153360
290	1190	174350	1170	164850
300	1295	186780	1212	176750

speculated, however, that soft-chain and/or stiff-chain fragments within BI adopt somewhat extended conformations (compared to those in the corresponding pure phases), favouring stronger interchain interactions (hence, $H_{ex} < 0$); however, the concomitant entropy losses are so severe ($S_{ex} < 0$) that the thermodynamic stability of SPU is decreased ($G_{ex} > 0$). In other words, incomplete microphase separation resulting in formation of BI should be considered as the main source of intrinsic instability of the three-microphase-type morphology of SPU.

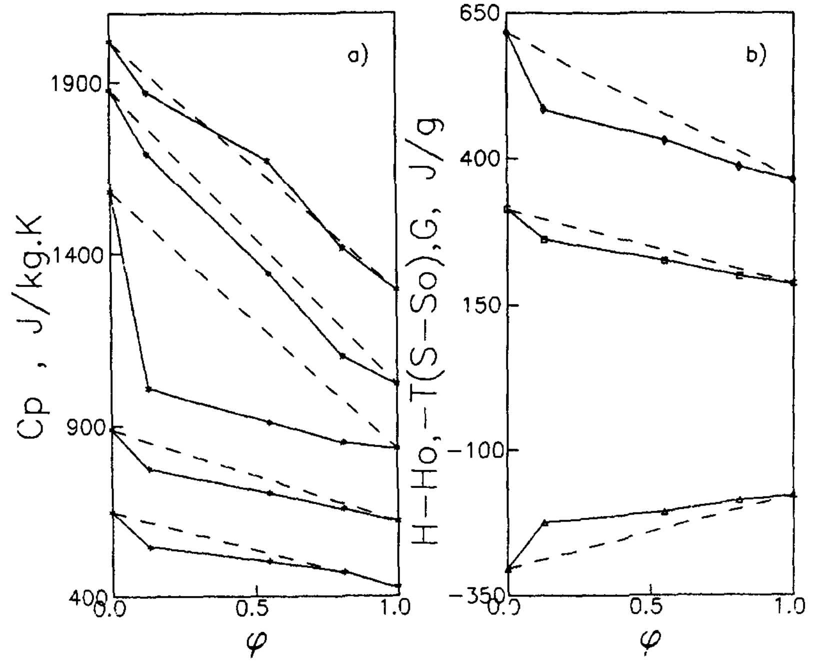

Fig. 3. Composition dependences of C_p (from top down) at 300, 250, 200, 150, 100 and 50 K (a), and of $H - H_0$ (□), $T(S - S_0)$ (◇) and G (Δ) at 300 K (b).

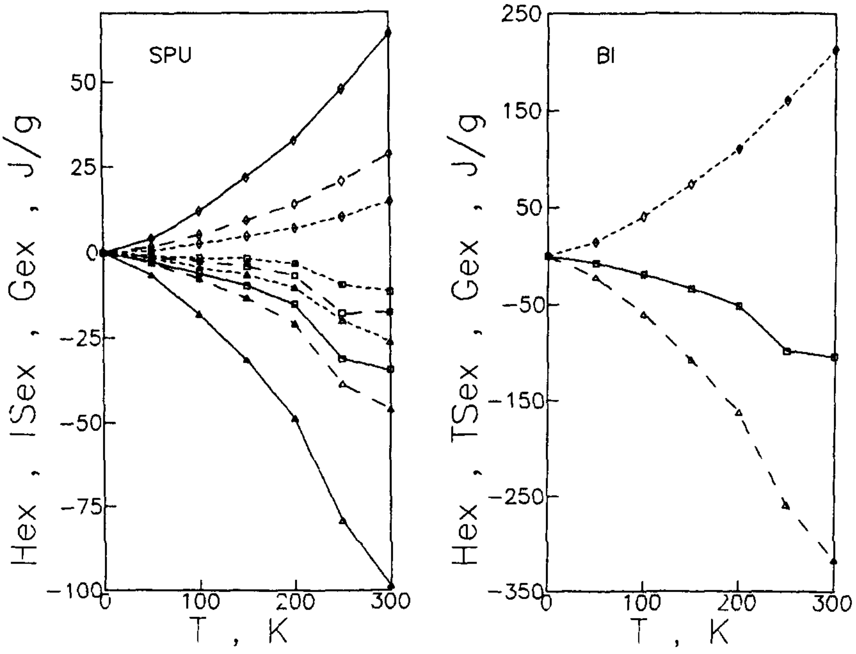

Fig. 4. Temperature dependences of H_{ex} (□), TS_{ex} (Δ) and G_{ex} (◇) for SPU (left): SPU-13 (solid lines), SPU-55 (broken lines) and SPU-82 (dotted lines); and for BI (right).

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