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Thermochimica Acta 425 (2005) 39–46

thermochimica acta

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Thermodynamics of phenylated polyphenylene in the range from $T \to 0$ to 640 K at standard pressure

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Received 30 April 2004; received in revised form 21 May 2004; accepted 23 May 2004

Abstract

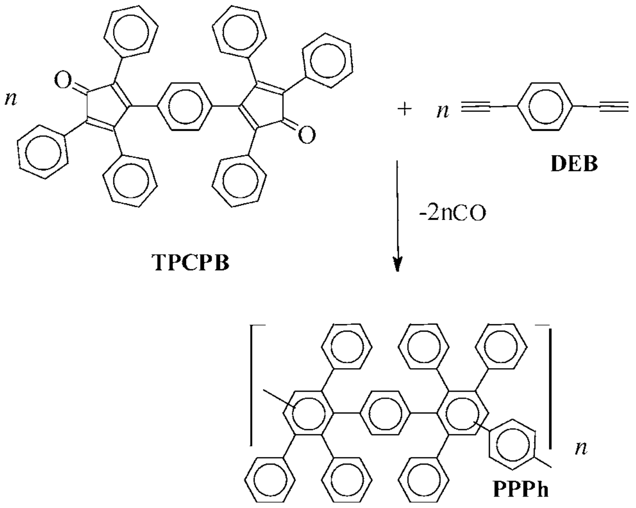
By dynamic calorimetry the temperature dependences of heat capacity of phenylated polyphenylene (PPPh) and 1,4-bis-(2,4,5-triphenylcyclopentadienone-3-yl)benzene (TPCPB) in the range 300–640 K at standard pressure have been determined within ±1.5%. The thermodynamic characteristics of fusion of TPCPB, namely temperature, enthalpy and entropy, as well as the parameters of glass transition and glassy state for PPPh such as temperature, zero entropy of glassy state, the difference in zero enthalpies of glassy and crystalline states have been estimated. The experimental data obtained in the present work and literature findings were used to calculate their thermodynamic functions: the heat capacity C_p^o (T), enthalpy $H^o(T) - H^o(0)$, entropy $S^o(T)$ and Gibbs function $G^o(T) - H^o(0)$ over the range from $T \to 0$ to 640 K. The thermodynamic characteristics of synthesis reaction of phenylated polyphenylene have been evaluated between 0 and 600 K.

Keywords: 1,4-Bis-(2,4,5-triphenylcyclopentanone-3-yl)benzene; Phenylated polyphenylene; Calorimeter; Heat capacity; Thermodynamic functions

1. Introduction

Phenylated polyphenylene is a promising representative of the class of polymer compounds and its most significant characteristics are found to be the thermal stability and low dielectric permeability [1,2].

The reaction of PPPh synthesis is represented by the following scheme.



The thermodynamic properties of PPPh and TPCPB were examined by us earlier over the range from $T \to 0$ to 350 K [3]. It is obvious, however, that the temperature range of the study of the thermodynamic properties of PPPh and TPCPB should be extended in order to detect possible physical transformations of the compounds and to evaluate the thermodynamic characteristics of PPPh synthesis in the interval 330–640 K.

The present work is concerned the calorimetric study of the thermodynamic properties of PPPh prepared by the Diels–Alder reaction of isomerization copolymerization of TPCPB with *p*-diethynylbenzene (DEB), accompanied with the isolation of carbon monoxide [4], and those of TPCPB. The aim of this work is to measure the heat capacity C_p^o between 300 and 640 K with an uncertainty of 1.5%, tempera-

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doi:10.1016/j.tca.2004.05.023

tures and enthalpies of physical transformations, to calculate the thermodynamic functions $C_p^o(T)$, $H^o(T) - H^o(0)$, $S^o(T)$ and $G^o(T) - H^o(0)$ of PPPh and TPCPB from 300 to 640 K and the thermodynamic parameters of the synthesis reaction (enthalpy $\Delta_r H^\circ$ (T), entropy $\Delta_r S^\circ$ (T) and Gibbs function $\Delta_r G^\circ$ (T)) of PPPh in the range from $T \rightarrow 0$ to 640 K on the base of the data obtained by us and given elsewhere for DEB [5] and carbon monoxide [6,7].

2. Experimental

2.1. Sample

1,4-Bis(triphenylcyclopentadienone-3-yl)benzene was prepared by the procedure published elsewhere [8] and phenylated polyphenylene was synthesized by the procedure described in detail previously [4]. The characterization of both objects was performed by ^{1}H and ^{13}C NMR spectroscopy (a Bruker AMX 500 instrument), mass spectrometry (a VG Trio 2000 (EI, 70 eV) device) and size-exclusion chromatography (SEC). It was found that $M_w = 17.4 \times 10^3$ g/mol, $M_w/M_n = 2.0$. The elemental analysis results showed the coincidence of the CO_2 amount found in the combustion products with that calculated by the chemical formula of the compound within ±0.2 mass% for TPCPB and ±0.7 mass% for PPPh. Obviously, the polymer is amorphous [4].

2.2. Apparatus and measurement procedure

To measure the heat capacity, temperatures and enthalpies of physical transitions of the substances in the range 300–650 K, an automated thermophysical device operating by the principle of triple thermal bridge [9,10]—a high-precision dynamic calorimeter intended to study the thermodynamic properties of substances at elevated temperatures—was employed. The calorimeter design and the measurement procedure of the heat capacity, temperatures and enthalpies of physical transitions are described in detail elsewhere [9,10]. The reliability of the calorimeter operation was tested by measuring the heat capacity of a standard sample of synthetic corundum as well as the thermodynamic characteristics of fusion of indium, tin and lead. It was found that the calorimeter and the measurement procedure allow one to obtain the data on the heat capacity of substances in solid and liquid states with an uncertainty ±1.5% and the temperatures of physical transitions within about ±0.3 K.

The heat capacities of the same samples were determined earlier between 6 and 340 K [3]. For the measurement of the heat capacity in this interval a BCT-3 automated adiabatic vacuum calorimeter with discrete heating was used. The reliability of the calorimeter operation was tested by measuring the heat capacity of a special purity copper, standard synthetic corundum and K-2 benzoic acid prepared at metrological institutions of the State Standard of the Russian Federation. As the analysis results show, the uncertainty of C_p^o measurements at helium temperatures was within ±2%. With rising temperature up to 40 K, it decreased till ±0.5% and at $T > 80$ K it was ±0.2%.

3. Results and discussion

3.1. Heat capacity

The heat capacity C_p^o of TPCPB was measured between 330 and 620 K and of PPPh in the 330–640 K range. All measurement results are summarized in Tables 1 and 2. The masses of TPCPB and PPPh located in a calorimetric ampoule were 0.2593 and 0.2161 g, respectively. The heat capacity values for the TPCPB sample were obtained at three different rates of heating of the calorimeter and the substance (Table 3) and for the PPPh sample C_p^o was measured at an average rate of heating 0.02 K/s. The heat capacity of TPCPB and PPPh was between 30 and 40% and from 40 to 50%, respectively, of the total heat capacity (calorimetric ampoule and sample). Averaging of the experimental C_p^o values was made on a computer by means of degree and semilogarithmic polynomials so that the root mean square deviation of C_p^o from the corresponding smoothed curve $C_p^o = f(T)$ did not exceed an uncertainty of measurements.

Table 1
Experimental values[a] of heat capacity of 1,4-bis-(2,4,5-triphenylcyclopentadienone-3-yl)benzene

T (K)	C_p^o(J/(K mol))
Series 1	
328.7	856
331.0	864
334.0	871
337.5	880
340.9	890
344.7	899
348.2	910
352.3	923
356.2	936
359.8	948
363.3	960
366.6	973
370.5	987
374.3	1002
378.1	1018
381.8	1032
383.6	1037
387.2	1040
390.8	1046
394.3	1050
397.8	1056
401.3	1067
404.9	1078
408.4	1082
412.0	1092
415.7	1110
419.3	1125

Table 1 (*Continued*)

T (K)	C_p^o(J/(K mol))
423.0	1140
333.4	874
336.9	883
340.1	892
343.4	901
347.0	911
350.5	921
354.0	932
357.4	942
361.0	953
364.4	964
368.1	977
371.3	988
375.0	988
378.5	1003
381.8	1019
385.0	1029
388.4	1041
393.4	1051
396.9	1058
400.3	1053
403.8	1062
407.4	1069
411.0	1079
414.7	1085
418.5	1104
422.2	1136
426.0	1141
431.7	1149
435.5	1158
439.2	1174
444.7	1187
426.6	1146
430.1	1148
435.0	1155
440.8	1182
444.6	1191
448.3	1217
452.4	1218
456.3	1227
460.2	1232
464.1	1243
468.0	1270
472.0	1275
475.9	1279
479.8	1285
483.5	1305
487.6	1321
491.7	1337
495.9	1330
500.0	1351
504.1	1371
508.2	1389
512.1	1398
516.2	1425
520.4	1433
524.5	1458
528.5	1462
532.6	1481
536.4	1495
540.2	1520
448.3	1206
451.9	1212
455.5	1222
459.1	1237
464.4	1256
468.0	1262
473.3	1269
476.9	1280
480.6	1282
484.2	1294
487.9	1300
491.5	1326
495.2	1332
498.8	1345
502.5	1364
506.1	1371
509.7	1380
513.4	1390
517.0	1400
520.6	1421
524.3	1437
527.9	1428
531.5	1450
535.2	1466
538.9	1491
542.6	1510
546.3	1528
550.1	1535
553.8	1536
557.4	1561
561.0	1593
543.9	1545
547.5	1567
551.1	1614
554.6	1636
558.1	1655
561.5	1697
565.2	1752
568.8	1794
572.4	1844
576.1	2007
580.2	2186
583.5	2431
587.1	3107
590.6	4312
594.0	7100
595.0	9347
595.9	15175
596.4	13805
596.9	9314
598.4	2500
600.4	1860
603.1	1730
604.4	1621
605.0	1628
Series 2	
321.4	842
324.7	850
328.2	856
331.8	869
564.6	1618
568.1	1656
571.6	1707
575.2	1796
579.5	1894
582.2	2012
586.1	2250
589.3	2741
593.4	4216
595.3	6753
597.0	13750
598.0	11260
602.3	1885

Table 1 (*Continued*)

T (K)	$C_p^{\rm o}$(J/(K mol))
604.6	1624
606.9	1790
609.0	1631
611.0	1632
614.9	1639
618.7	1640
Series 3	
321.6	845
324.9	853
328.4	863
332.0	872
335.4	881
338.9	891
341.9	899
345.5	909
348.8	919
352.5	932
355.9	942
359.5	953
363.0	964
366.5	975
370.1	988
374.0	995
377.5	1003
381.1	1010
384.4	1024
387.5	1040
390.9	1049
394.2	1056
397.7	1068
401.1	1078
404.6	1080
408.2	1083
411.8	1094
415.5	1100
419.3	1119
423.1	1140
426.9	1146
430.7	1151
434.4	1157
439.2	1177
443.2	1189
447.3	1220
451.0	1226
454.5	1232
458.1	1248
463.4	1267
467.0	1273
470.6	1280
474.1	1286
477.8	1286
481.4	1299
485.0	1311
488.7	1317
492.3	1335
496.0	1349
499.6	1352
503.3	1363
506.9	1388
510.5	1394
514.2	1407
517.8	1417
521.5	1430
525.1	1445
528.7	1445
532.3	1457
536.0	1483
539.7	1508
543.4	1527
546.3	1533
550.1	1540
553.8	1553
557.4	1578
561.0	1610
564.6	1635
569.9	1686
573.4	1768
577.1	2150
581.3	2741
583.5	3123
587.5	4140
590.0	4950
593.3	6860
597.4	11640
599.1	9330
600.6	5530
603.9	2690
606.9	2090
609.0	2000
613.0	1625
616.8	1635
618.7	1640

$M = 690.84$ g/mol, $p = 101.325$ kPa.

[a] Each third value is given in the table.

Table 2

Experimental values of heat capacity of phenylated polyphenylene

T (K)	$C_p^{\rm o}$ (J/(K mol))	T (K)	$C_p^{\rm o}$ (J/(K mol))	T (K)	$C_p^{\rm o}$ (J/(K mol))
330.4	1035	428.5	1962	540.9	2467
334.4	1049	433.3	2012	543.2	2485
337.0	1058	438.1	2036	548.0	2500
339.5	1080	443.0	2052	552.8	2520
342.0	1089	447.9	2078	555.2	2530
345.5	1112	450.3	2085	560.1	2565
349.0	1138	452.7	2091	565.0	2601
352.4	1169	455.1	2101	569.9	2620
355.8	1203	457.6	2115	572.4	2636
359.4	1249	460.0	2129	577.0	2681
364.1	1302	462.4	2134	579.6	2690
368.9	1363	466.1	2155	582.0	2695
371.4	1400	471.0	2167	589.2	2716
373.8	1430	475.9	2182	593.9	2761
376.3	1458	480.7	2185	596.3	2770
380.1	1506	485.4	2197	601.1	2800
382.6	1530	490.1	2200	605.9	2828
385.0	1566	494.8	2235	608.3	2830
388.7	1606	499.6	2261	613.1	2859
393.2	1668	502.1	2278	617.9	2885
397.3	1729	507.0	2301	620.4	2895
402.2	1800	511.8	2327	622.8	2921
405.8	1843	514.2	2333	627.6	2957
409.4	1872	519.1	2360	630.0	2957
414.1	1901	523.9	2403	632.4	2992
418.8	1925	526.3	2420	634.8	3010
421.2	1944	531.2	2431	637.5	3028
423.6	1954	536.0	2460	640.6	3039

$M = 760.976$ g/mol, $p = 101.325$ kPa.

Table 3
Experimental and mean values of thermodynamic characteristics[a] of fusion of 1,4-bis-(2,4,5-triphenylcyclopentadienone-3-yl)benzene

Experiment	V (K/s)	$T^{\circ}_{\mathrm{fus},i} - T^{\circ}_{\mathrm{fus},f}$ (K)	$T^{o}_{\mathrm{fus},v}$ (±0.5) (K)	$C^{\circ}_{p,\max}$ (J/(K mol))	$\Delta_{\mathrm{fus}}H^{\circ}$ (kJ/mol)
1	0.033	540–615	597.4	11640	67.60
2	0.025	535–610	597.0	13750	68.52
3	0.008	535–603	595.9	15175	69.63
Mean			594.4 ± 0.5		68.6 ± 0.7

$M = 690.84$ g/mol, $p = 101.325$ kPa.

[a] V is the average rate of heating of calorimeter and substance; $T^{\circ}_{\mathrm{fus},i}$ and $T^{\circ}_{\mathrm{fus},f}$ the temperatures of the onset and end of fusion; $T^{\circ}_{\mathrm{fus},v}$ the temperatures at which the apparent heat capacity in the melting interval are maximum at the appropriate rate of heating; $\Delta_{\mathrm{fus}}H^{\circ}$ the molar enthalpy of fusion.

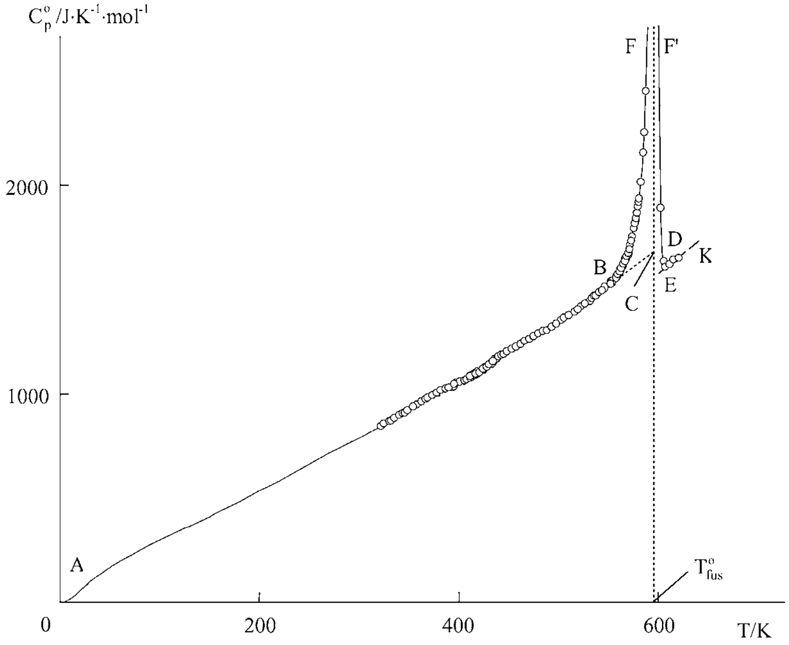

Fig. 1. Temperature dependence of heat capacity of 1,4-bis-(2,4,5-triphenylcyclopentadienone-3-yl)benzene: ABC: crystal; BFF′D: the apparent heat capacity in the melting interval; EDK: liquid.

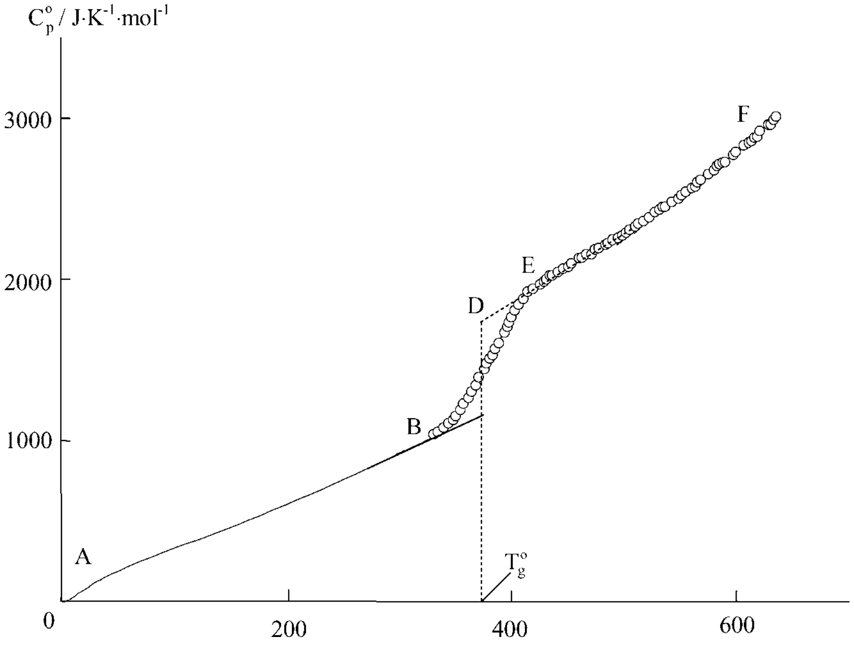

Fig. 2. Temperature dependence of heat capacity of phenylated polyphenylene: AC: glassy state; EF: high elasticity; CD: the increase in heat capacity on devitrification.

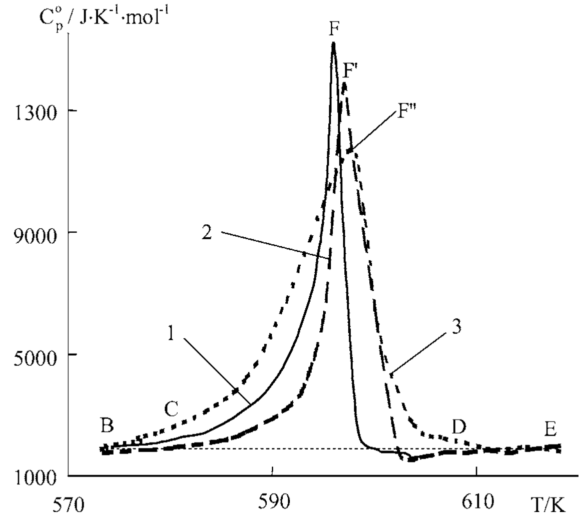

Fig. 3. Temperature dependence of heat capacity of 1,4-bis-(2,4,5-triphenylcyclopentadienone-3-yl)benzene in the melting interval at three different rates of heating of the calorimeter and substance : (1) 0.008 K/s; (2) 0.017 K/s and (3) 0.033 K/s; BC: crystal; DE: liquid; CFD, CF'D, CF''D: apparent heat capacities in the melting interval.

The temperature dependences of the heat capacity $C_p^o = f(T)$ for TPCPB are illustrated in Fig. 1 and for PPPh in Fig. 2, the C_p^o values in the range from 330 to (615–630) K were measured (circles) in this work, the data between 6 and 340 K were taken from [3].

Table 4
Characteristics of devitrification and glassy state[a] of phenylated polyphenylene

$T_{g,i}^o - T_{g,f}^o$ (K)	T_g^o (K)	$\Delta C_p^o(T_g^o)$ (J/(K mol))	S_{conf}^o (J/(K mol))
330–415	376 ± 1	517	132

$M = 760.976$ g/mol; $p = 101.325$ kPa.

[a] $T_{g,i}^o - T_{g,f}^o$ is the temperatures of onset and end of devitrification; T_g^o the temperature of devitrification; $\Delta C_p^o(T_g^o)$ the increase of heat capacity on devitrification; S_{conf}^o the configuration entropy.

As Fig. 1 shows, the heat capacity of crystalline TPCPB in 6–520 K range gradually increases with rising temperature. A sharp increase of C_p^o and the following break of the plot $C_p^o = f(T)$ between 520 and 607 K (Fig. 1) are caused with the fusion of crystals while C_p^o of liquid TPCPB does not display any special features in the range from 607 to 615 K and also smoothly increases as temperature rises. The experimental values of apparent heat capacity of TPCPB in the interval of its fusion (Fig. 3) depend on the heating rate of the calorimeter and the substance that is characteristic of first-order transitions,

The heat capacity of PPPh in a glassy (0–330 K) and high elasticity state (415–640 K) monotonously increases with rising temperature and its abrupt change between 330 and 415 K (BE section, Fig. 2) is related to its devitrification.

Table 5
Thermodynamics functions of 1,4-bis-(2,4,5-triphenylcyclopentadienone-3-yl)benzene

T (K)	C_p^o (J/(K mol))	$H^o(T) - H^o(0)$ (kJ/mol)	$S^o(T)$ (J/(K mol))	$-[G^o(T) - H^o(0)]$ (kJ/mol)
Crystalline state				
0	0	0	0	0
5	2.568	0.0032	0.8604	0.001077
10	15.31	0.0446	6.088	0.01625
15	33.79	0.1662	15.69	0.06908
20	55.28	0.3891	28.28	0.1765
25	76.31	0.7184	42.95	0.3553
30	96.76	1.152	58.71	0.6098
40	133.7	2.308	91.72	1.361
50	166.2	3.810	125.1	2.445
100	297.9	15.61	283.4	12.73
150	410.8	33.32	425.5	30.50
200	532.2	56.84	560.0	55.16
250	663.2	86.72	692.8	86.48
298.15	784.9	121.6	820.1	122.9
300	789.4	123.1	825.0	124.4
350	920.0	165.7	956.2	169.0
400	1061	215.5	1089	220.1
450	1213	272.2	1222	277.9
500	1338	336.1	1357	342.3
550	1449	406.1	1490	413.5
594.4	1550	472.7	1606	482.3
Liquid state				
594.4	1620	541.3	1722	482.3
600	1622	550.3	1737	492.0
610	1630	566.6	1764	509.3
620	1638	582.9	1790	527.2

$M = 690.84$ g/mol, $p = 101.325$ kPa.

3.2. Thermodynamic characteristics of physical transformations

3.2.1. Fusion

The experimental temperatures and the enthalpies of fusion of the TPCPB sample are listed in Table 3. Temperatures of the beginning and the termination of its fusion were determined graphically (B and D points, Fig. 1). The enthalpies of fusion were calculated as areas between curves 1–2 of the apparent heat capacity in the melting range (Fig. 3) and a normal trend of the heat capacity, i.e. $C_p^{\rm o} = f(T)$, which occurs when no melting takes place. The measurement results (Table 3) were used to calculate the thermodynamic characteristics of fusion of TPCPB (Table 4). The thermodynamic equilibrium temperature of melting for TPCPB was graphically found by extrapolating the relation $T^{\rm o}_{{\rm fus},v}$ versus $V^{1/2}$ to the zero rate of the calorimeter heating $V^{1/2} = 0$, this dependence being the straight line. The procedure of the determination of $T^{\rm o}_{{\rm fus},v}$ we used is described in detail elsewhere [11]. The enthalpy of fusion $\Delta_{\rm fus}H^o$ of TPCPB was found as the average of three values of the enthalpy (Table 3). The entropy of fusion $\Delta_{\rm fus}S^o$was evaluated from the melting temperature $T^o_{\rm fus}$ and the $\Delta_{\rm fus}H^o$ values by the expression:

$$\Delta_{\rm fus}S^{\rm o} = \frac{\Delta_{\rm fus}H^{\rm o}}{T^{\rm o}_{\rm fus}} \qquad (1)$$

3.2.2. Characteristics of devitrification and glassy state

The devitrification of PPPh occurred in the 330–415 K range. Table 4 shows its thermodynamic characteristics. Temperatures of the onset and the end of devitrification ($T^{\rm o}_{{\rm g},i}$, $T^{\rm o}_{{\rm g},f}$) were found graphically (Fig. 2). Temperatures, when the character of the relation $C_p^{\rm o}$ versus T changes, were regarded as $T^{\rm o}_{{\rm g},i}$ and $T^{\rm o}_{{\rm g},f}$ (B and E points, Fig. 2). The devitrification temperature $T^{\rm o}_{\rm g}$ and the increase in the heat capacity on devitrification $\Delta C_p^{\rm o}(T^{\rm o}_{\rm g})$ (CD section, Fig. 2) was determined graphically as demonstrated in detail in reference [12]. The configurational entropy $S^{\rm o}_{\rm conf}$ was calculated by the procedure given in [13] using the formula:

$$S^{\rm o}_{\rm conf}(\alpha) = \Delta C_p^{\rm o}(T^{\rm o}_{\rm g})\ln 1.29 \qquad (2)$$

3.3. Thermodynamic functions

From the experimental data on the temperature dependence of the heat capacity, measured by us and cited in reference [3] as well as the temperatures and enthalpies of physical transitions, the thermodynamic functions of TPCPB in the range from $T \to 0$ to 620 K and PPPh between $T \to 0$ and 640 K were estimated (Tables 5 and 6). In the calculation of absolute values of entropies for PPPh according to [4], it was assumed that its $S^{\rm o}(0) = S^{\rm o}_{\rm conf}(0)$. The enthalpy $H^{\rm o}(T) - H^{\rm o}(0)$ and entropy $S^{\rm o}(T)$ were calculated

Table 6
Thermodynamics functions of phenylated polyphenylene

T (K)	$C_p^{\rm o}$ (J/(K mol))	$H^{\rm o}(T) - H^{\rm o}(0)$ (kJ/mol)	$S^{\rm o}(T)$ (J/(K mol))	$-[G^{\rm o}(T) - H^{\rm o}(0)]$ (kJ/mol)
Glassy state				
0	0	0	132	0
5	6	0.008	134.1	0.6627
10	23.9	0.0794	143.3	1.354
15	46.3	0.2512	157.0	2.103
20	70.1	0.5428	173.6	2.929
30	114.3	1.468	210.5	4.847
40	154.0	2.814	248.9	7.144
50	187.9	4.528	287.0	9.824
100	327.5	17.55	462.1	28.65
150	456.5	37.12	619.0	55.73
160	484.2	41.82	649.3	62.07
170	512.7	46.81	679.5	68.72
180	541.8	52.07	709.6	75.66
190	571.2	57.64	739.7	82.91
200	601.0	63.50	769.8	90.45
250	753.8	97.34	920.2	132.7
298.15	911.5	137.4	1066.2	180.5
300	917.8	139.1	1071.9	182.5
350	1094	189.3	1226.4	239.9
376	1186	218.9	1308.0	272.9
High elasticity state				
376	1703	218.9	1308	272.9
400	1832	261.4	1417	305.6
450	2082	359.5	1648	382.2
500	2273	468.2	1877	470.4
550	2515	587.7	2105	569.9
600	2809	720.6	2336	680.9
640	3024	837.7	2525	778.1

$M = 760.976$ g/mol, $p = 101.325$ kPa.

Table 7
Thermodynamic characteristics of synthesis reaction of phenylated polyphenylene $C_{52}H_{34}O_2 + C_{10}H_6 \rightarrow C_{60}H_{40} + 2CO$ ($p = 101.325$ kPa)

T (K)	Physical states of reagents[a]	$-\Delta_r H^o$ (kJ/mol)	$\Delta_r S^o$ (J/(K mol))	$-\Delta_r G^o$ (kJ/mol)
0	cr, cr; gl, crII	1006	132	1006
100	cr, cr; gl, crII	986	441	1030
200	cr, cr; gl, g	986	446	1075
298.15	cr, cr; gl, g	985	447	1118
350	cr, cr; gl, g	982	448	1139
500	cr,cr,h.e.,g	880	631	1196
600	l, cr, h.e., g	857	668	1251

[a] cr: Crystalline; gl: glassy; g: gaseous; h.e.: high-elasticity; l: liquid.

by numerical integration of the relations $C_p^o = f(T)$ and $C_p^o = f(\ln T)$, the Gibbs function $G^o(T) - H^o(0)$ was estimated from the enthalpy and entropy values at the corresponding temperatures.

3.4. Thermodynamic characteristics of synthesis reaction of phenylated polyphenylene

The enthalpy $\Delta_r H^o$ and the entropy $\Delta_r S^o$ of PPPh synthesis over the range from $T \rightarrow 0$ to 600 K are listed in Table 7. The enthalpy of polymerization at temperatures 0–350 K was calculated in reference [3] and at other temperatures $\Delta_r H^o$ was obtained by Kirchhoff's expression with using the temperature dependences of the heat capacity for PPPh, TPCPB, DEB and CO. The entropy of polymerization was evaluated from the absolute values of entropies of the reagents (Tables 5 and 6), DEB and CO, in addition, the zero entropy of glassy PPPh, as determined in the given work, (the $\Delta_r S^o$ values cited in [3] were made more accurate by us) was taken into consideration. The Gibbs function $\Delta_r G^o$ was calculated from the $\Delta_r H^o$ and $\Delta_r S^o$ values at the corresponding temperatures as described in detail earlier [14]. The reaction scheme is represented further.

It is seen that the values of the standard Gibbs function of reaction are everywhere negative and judging by its absolute magnitudes, one may arrive at a virtually total shift of the equilibrium towards the formation of the reaction products. The entropy of reaction is always positive that is, certainly, caused by the liberation of two moles of carbon monoxide. The entropy of their formation substantially exceeds the decrease in the entropy that accompanies the formation of PPPh from TPCPB and DEB. The enthalpy of reaction is negative, and it is obvious that it accounts for the main part of the Gibbs function. The contribution of the entropy factor to $\Delta_r G^o$ is relatively small. Since $\Delta_r H^o < 0$ and $\Delta_r S^o > 0$ it is clear that with rising temperature of the reaction the $\Delta_r G^o$ value decreases as well. This implies that the process of PPPh synthesis has neither upper nor lower limiting temperature and that PPPh is thermodynamically stable relative to depolycondensation.

References

[1] A.L. Rusanov, T.A. Stadnik, K. Myullen, Usp. Khim. 68 (1999) 760.
[2] J.K. Still, F.W. Harris, R.O. Rakutis, H.J. Mukamal, J. Polym. Sci. Polym. Chem. Ed. 4 (1966) 791.
[3] B.V. Lebedev, T.G. Kulagina, N.N. Smirnova, Z.B. Shifrina, M.S. Averina, A.L. Rusanov, J. Thermal Anal. Calorim. 74 (2003) 735.
[4] Z.B. Shifrina, M.S. Averina, A.L. Rusanov, Macromolecules 33 (2000) 3525.
[5] N.V. Karyakin, V.N. Sapozhnikov, I.B. Rabinovich, Trudy po Khimii i Khim, Tekhnologii, Gorky State University, Gorky, B2, 1972.
[6] D.D. Wagman, J.E. Kilpatrick, W.J. Taylor, K.S. Pizer, F.D. Rossins, J. Res. Nat. Bur. Stand. 34 (1945) 143.
[7] J.O. Clayton, W.F. Giauque, J. Am. Chem. Soc. 55 (1933) 5071.
[8] M.A. Ogliaruso, L.A. Shadoff, E.I. Beker, J. Org. Chem. 28 (1963) 2725.
[9] M.Sh. Yagfarov, Zh. Fiz. Khimii 43 (1969) 1620.
[10] A.G. Kabo, V.V. Diky, Thermochim. Acta 347 (2000) 79.
[11] V.A. Bershetein, V.M. Egorov, Differential Scanning Calorimetry in Physicochemistry of Polymers, Khimiya, Leningrad, 1990.
[12] S. Alford, M. Dole, J. Am. Chem. Soc. 77 (1955) 4774.
[13] A.B. Bestul, S.S. Chang, J. Chem. Phys. 40 (1964) 3731.
[14] B.V. Lebedev, N.N. Smirnova, Macromol. Chem. Phys. 195 (1994) 35.

Further reading

[15] B.V. Lebedev, I.B. Rabinovich, Dokl. Acad. Nauk SSSR 237 (1997) 641.