Thermodynamic properties of carbosilane dendrimers of the seventh and ninth generations with terminal butyl groups in the temperature range from $T \to 0$ to 600 K

N. N. Smirnova,[a]★ O. V. Stepanova,[a] T. A. Bykova,[a] A. V. Markin,[a] E. A. Tatarinova,[b] and A. M. Muzafarov[b]

[a]*Research Institute of Chemistry,*
N. I. Lobachevsky Nizhnii Novgorod State University,
Building 5, 23 prosp. Gagarina, 603950 Nizhnii Novgorod, Russian Federation.
Fax: +7 (831) 465 6450. E-mail: smirnova@ichem.unn.ru
[b]*N. S. Enikolopov Institute of Synthetic Polymer Materials, Russian Academy of Sciences,*
70 ul. Profsoyuznaya, 117999 Moscow, Russian Federation

Temperature dependences of the heat capacity of carbosilane dendrimers with butyl terminal groups of the seventh and ninth generations were determined in the temperature range from 6 to 600 K by precision adiabatic vacuum calorimetry and differential scanning (dynamic) calorimetry. The physical transitions were revealed and their thermodynamic characteristics were analyzed. The experimental data obtained were used to calculate the standard thermodynamic functions $C_p(T)$, $H°(T) - H°(0)$, $S°(T)$, and $G°(T) - H°(0)$ for the temperature range from $T \to 0$ to 600 K. The thermodynamic function—molar weight isotherms for the dendrimers of the third—ninth generations with terminal butyl groups in the glassy and highly elastic state are linear.

Key words: carbosilane dendrimers, chemical thermodynamics, heat capacity, glass transition, thermodynamic functions.

Investigation of the synthesis and physicochemical properties of dendrimers, being monodispersed, nanosized, regularly branched macromolecular particles, is a promising direction of the modern chemistry of high-molecular-weight compounds.[1—11] Since the first reports on the synthesis of carbosilane dendrimers have been published,[6,7] they were used, along with other compounds with dendrite organization of the molecular structure, as objects for the determination of the thermodynamic characteristics.[12—19] In particular, methods of precision calorimetry were used to study the low-temperature dependence of the heat capacity in a wide temperature range, and the experimental values were used in calculating the thermodynamic functions in the temperature range from $T \to 0$ to 340—600 K.

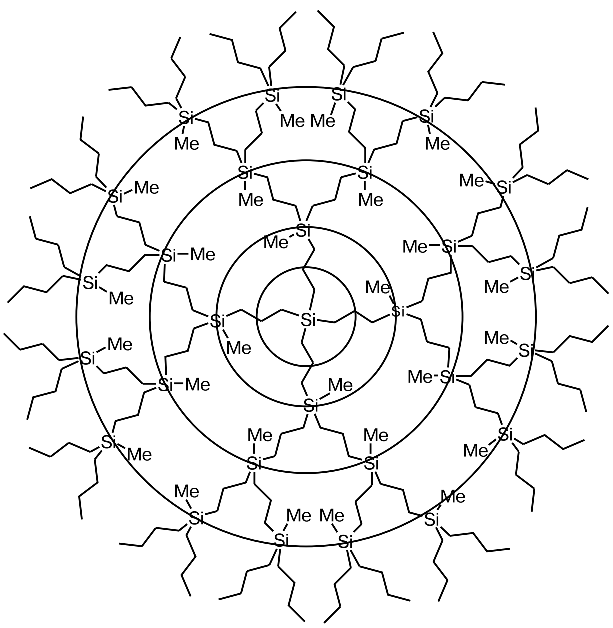
We have earlier[19] obtained the standard thermodynamic functions of the carbosilane dendrimers of the third—sixth generations with the terminal butyl groups in the range from $T \to 0$ to 340—600 K and determined and analyzed changes in these functions depending on the composition and structure of compounds. The systematic studies of the temperature dependence of the heat capacity of the dendrimers revealed the second relaxation transition, which is an important principal result. The appearance of the transition is consistent with a change in the physical state of the dendrimers. It was of interest to elucidate whether this transition is characteristic of dendrimer samples of higher generations from the same homological series. The presence of the transition would mean that we deal with a general phenomenon for dendrimers of high generations.

The purpose of this work is the calorimetric study of the temperature dependence of the heat capacity $C_p° = f(T)$ of the carbosilane dendrimers of the seventh and ninth generations in the temperature range from 6 to 550—600 K and elucidation and physicochemical interpretation of possible physical transitions on heating and cooling. We also intended to calculate the standard thermodynamic functions $C_p(T)$, $H°(T) - H°(0)$, $S°(T)$, and $G°(T) - H°(0)$ from the experimental data for the range from $T \to 0$ to 550—600 K and to approximate the calculated thermodynamic functions to the corresponding isotherms thermodynamic function—molar weight, which have been determined by us earlier.[19]

Experimental

The structure of the carbosilane dendrimer of the third generation with terminal butyl groups is presented below as an example.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 1924—1928, October, 2007.



G-3(Bu)$_{32}$

It is customary to assign the designation G-*n*(Bu)$_m$ to a dendrimer of the *n*th generation with terminal butyl groups, where G is the generation; $n = 1, 2, 3, ...$ is the number of generations; *m* is the number of butyl groups on the external sphere of dendrimer molecules.[17] For the dendrimers of the seventh and ninth generations, the designations take the form G-7(Bu)$_{512}$ and G-9(Bu)$_{2048}$.

Samples of the carbosilane dendrimers G-7(Bu)$_{512}$ and G-9(Bu)$_{2048}$ (with the molecular formulas $C_{4080}H_{9180}Si_{509}$ and $C_{16368}H_{36828}Si_{2045}$, respectively, M = 72 553.3 and 291 151.3 g mol^{-1}) were synthesized by a known procedure[20] at the N. S. Enikolopov Institute of Synthetic Polymer Materials (Russian Academy of Sciences).

Under standard conditions, the dendrimer samples under study were colorless transparent gel-like substances. Their composition and structure were identified by gel permeation chromatography, dynamic light scattering, ^{1}H NMR spectroscopy, FTIR spectroscopy, and elemental analysis.[19]

A BKT-3 precision automated adiabatic vacuum calorimeter with discrete heating was used to measure the heat capacity C_p° in a range of 6—340 K. The design of the calorimeter and procedure of its operation have been described earlier.[21,22] The calorimeter was checked by measuring the heat capacity of copper (special-purity grade), reference substance of synthetic corundum, and benzoic acid (K-2 trade mark). The analysis of the results obtained show that the error of measurement of the heat capacity of substances at helium temperatures does not exceed ±2%, whereas with the temperature increase to 40 K the error decreases to ±0.5% and achieves ±0.2% at $T > 40$ K. The error of measurement of temperatures of physical transitions is ±0.02 K.

To study the heat capacity of substances in the 320—600 K temperature range, we used the automated thermoanalytical complex, *viz*., differential scanning calorimeter operating according to the principle of triple thermal bridge.[23,24] Reliability of the operation of the calorimeter was checked by measurements of the heat capacity of an authentic samples of synthetic corundum and the thermodynamic characteristics of melting of indium, tin, and lead. As a result, it was revealed that the calorimeter used and measurement procedure provide data on heat capacities of substances in the condensed state with an error of ±2%, and the temperatures of physical transitions can be determined with an error of ±0.5 K.

Heat capacities of substances in an interval of 320—340 K were also measured with an adiabatic vacuum calorimeter (error ±0.2%). Conditions of measurements in the dynamic calorimeter were selected in such a way that the C_p° heat capacity values measured on the both calorimeters coincided at 320—340 K. This suggests that at $T > 340$ K the C_p° value was determined with the error ±(0.5—1.5)%. The heat capacity at 320—600 K was measured at an average heating rate of the calorimeter with the sample of 0.0133 K s^{-1}.

Results and Discussion

Heat capacity. Samples of G-7(Bu)$_{512}$ (0.1449 g) and G-9(Bu)$_{2048}$ (0.2392 g) were placed in the calorimetric ampule of the adiabatic vacuum calorimeter, and the samples 0.2231 and 0.2200 g in weight, respectively, were placed in the ampule of the dynamic calorimeter. Seven series of measurements of the heat capacities of G-7(Bu)$_{512}$ and G-9(Bu)$_{2048}$ gave 451 and 424 experimental C_p° values, respectively. The experimental C_p° values and averaging curves of the temperature dependence of C_p° are presented in Fig. 1.

The samples under study were cooled from room temperature to the temperature of measurement onset (~6 K) with a rate of 0.01 K s^{-1} under the conditions of the BKT-3 calorimeter. Upon subsequent heating, the

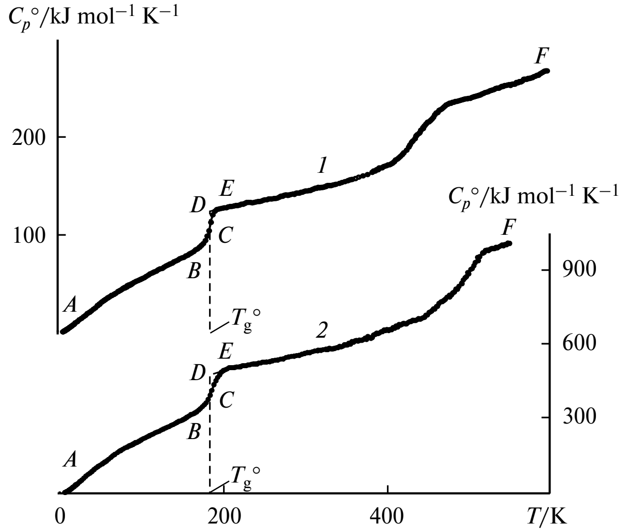


Fig. 1. Temperature plots of the heat capacity of the carbosilane dendrimers of the seventh generation G-7(Bu)$_{512}$ (*1*) and ninth generation G-9(Bu)$_{2048}$ (*2*): *AC* is the glassy state, *DF* is the highly elastic state, *BE* is the heat capacity in the glass transition interval, *CD* is the heat capacity increase upon the glass transition, and T_g° is the glass transition temperature.

Table 1. Parameters of the glass transition and glassy state for the carbosilane dendrimers G-7(Bu)$_{512}$ and G-9(Bu)$_{2048}$

Dendrimer	Molecular formula	M/g mol^{-1}	$T_g°$±0.5/K	$G_p°$	$S°_{conf}$
				kJ mol^{-1} K^{-1}	
G-7(Bu)$_{512}$	$C_{4080}H_{9180}Si_{509}$	72553.3	186.6	30.8	7.84
G-9(Bu)$_{2048}$	$C_{16368}H_{36828}Si_{2045}$	291151.3	187.2	126.4	32.2

dendrimers underwent the glass transition in a range of 165—210 K. The thermodynamic characteristics of the transition are given in Table 1.

The data presented in Fig. 1 show that the behavior of G-7(Bu)$_{512}$ in the low-temperature region is virtually the same as that of the earlier studied[18] G-7(All)$_{512}$ system with the allyl framing at the silicon atoms. The dependences of $C_p°$ on T for the dendrimer samples of the seventh and ninth generations were reproduced every time upon cooling to the temperature below $T_g°$ and subsequent heating upon the repeated measurement of $C_p°$. In this case, the characteristics of the process remained unchanged if the measurement cycle was carried out for the samples cooled with different rates from the highly elastic state. Thus, no crystallization of the studied dendrimer samples occurs under the conditions of our experiment. In the studied temperature region, these samples existed in the glassy and highly elastic states.

The heat capacity of the dendrimers increases smoothly with the temperature increase in the region of the glassy and highly elastic states. At elevated temperatures the $C_p° = f(T)$ curves exhibit the second transition at 390—490 K, whose shape resembles the glass transition (see Fig. 1). Since an analogous heat capacity jump has been observed previously[19] for the G-6(Bu)$_{256}$ carbosilane dendrimer of the sixth generation, we can assume that this jump is regular and can be attributed to rearrangements in the block organization of dendrimers of high generations. As already mentioned, the appearance of the second transition coincides with the change in the dendrimer state from the liquid (first—fifth generation) to gel state (sixth—ninth generation). When the generation number increases, the interval of the second generation shifts successively to the higher-temperature region: from 370—470 K for the sixth generation to 390—490 K for the seventh and ninth generations.

The appearance of the second transition has earlier been ascribed to differences in mobility of the internal and external spheres of the molecular structure[25] affecting the general mobility of a dendrimer molecule. The values of the glass transition temperature have been observed recently for the dendrimers with fluoro-containing substituents at the silicon atoms of the external layer.[26]

These data obtained for the sample with high differences in the chemical nature of the core and shell indicate that the core exerts no decisive effect on the dynamics of a dendrimer molecule up to the glass transition temperature. Since the chemical nature of the external layer of the molecular structure remains unchanged along the whole homological series, the appearance of the second transition for the dendrimers of the sixth and higher generations possibly indicates a change in the character of intermolecular contacts between the dendrimers.

Thermodynamic characteristics of the glass transition temperature and glassy state. The characteristics of the glass transition and glassy state of the compounds under study are listed in Table 1. The glass transition temperature $T_g°$ was determined from the point of inflection on the temperature plot of the entropy of heating.[27] The glass transition intervals and an increase in the heat capacity upon the glass transition $\Delta C_p°(T_g°)$ was determined graphically.[28] The configurational entropy $S°_{conf}$ was calculated using the known equation[29]

$$S°_{conf} = \Delta C_p°(T_g°)\ln T_g°/T_2°, \qquad (1)$$

where $T_2°$ is Kauzmann´s temperature,[30] and the $T_g°/T_2°$ ratio is equal to 1.29±0.14.[29,31] This ratio is evidently valid for the dendrimers under study as well. The $S°_{conf}$ value is close to $S°(0)$.[28,29] Taking into account this value for the estimation of the absolute value of entropy, we can accept that $S°(0) = S°_{conf}$.

Standard thermodynamic functions. To study the standard thermodynamic functions of the dendrimers under study (Tables 2 and 3), we extrapolated their heat capacity values $C_p°$ from the temperature of the measurement onset to 0K using the heat capacity Debye function

$$C_p° = nD(\theta_D/T), \qquad (2)$$

where D is the Debye function; n and θ_D are the specially selected parameters, being 1754 and 78 K, respectively, for the dendrimers of the seventh generation in an interval of 7—13 K, whereas for the dendrimers of the ninth generation they are 5755 and 70 K, respectively. Equation (2) with these parameters describes the experimental $C_p°$ values of the dendrimers under study in the 7—13 K interval with an error of ±1%. When calculating the functions, we accepted that Eq. (2) reproduces the $C_p°$ values at $T < 7$ K with the same error. The enthalpy $H°(T) - H°(0)$ and entropy $S°(T) - S°(0)$ were deter-

Table 2. Standard thermodynamic functions of the carbosilane dendrimer G-7(Bu)$_{512}$ (M = 72553.3 g mol^{-1})

T/K	$C_p(T)$	$S°(T)$	$H°(T) - H°(0)$	$-[G°(T) - H°(0)]$
	kJ mol^{-1} K^{-1}		kJ mol^{-1}	
		Glassy state		
5	0.298	7.94	0.400	0.124
10	2.16	8.57	5.40	1.81
20	8.300	11.88	56.80	23.96
50	27.95	27.02	595.9	363.1
100	53.56	54.90	2680	2026
150	74.85	80.73	5901	5032
186.6	93.10	98.96	8969	8030
		Highly elastic state		
186.6	123.9	98.96	8969	8030
200	126.6	107.6	10650	9310
250	134.7	136.8	17190	15050
298.15	143.5	161.3	23880	21860
350	153.8	185.0	31580	30440
400	169	207	39660	39850
450	211	229	48990	50320
500	239	253	60450	61960
550	253	276	72740	74790
600	270	299	85730	88770

Table 3. Standard thermodynamic functions of the carbosilane dendrimer G-9(Bu)$_{2048}$ (M = 291 151.3 g mol^{-1})

T/K	$C_p(T)$	$S°(T)$	$H°(T) - H°(0)$	$-[G°(T) - H°(0)]$
	kJ mol^{-1} K^{-1}		kJ mol^{-1}	
		Glassy state		
5	1.35	32.6	1.70	0.561
10	8.92	35.6	25.0	8.77
20	35.10	49.32	238.5	104.1
50	116.2	111.6	2470	1499
100	218.2	226.5	11060	8373
150	300.5	330.4	24010	20725
187.2	375.6	404.7	36540	33200
		Highly elastic state		
187.2	502.0	404.7	36540	33200
200	506.8	438.1	43000	38190
250	534.0	553.9	68980	61460
298.15	569.1	650.8	95490	88960
350	607.9	744.9	125920	123510
400	665.4	830	157740	161280
450	722.5	912	192460	203220
500	905.9	997	232970	249260
550	1021	1090	281940	299810

mined by the numerical integration with respect to T of the $C_p° = f(T)$ and $C_p° = f(\ln T)$ curves, respectively. The Gibbs functions $G°(T) - H°(0)$ were calculated from the enthalpy and entropy values at the corresponding temperatures. The calculation procedure has been published earlier.[28] The error of the calculated values of the function at $T < 30$ K was assumed to be ±1%, and at 30—80, 80—350, and 350—600 K it was ±0.5, ±0.2, and ±1.5%, respectively.

The standard entropies of formation ($\Delta_f S°$) of G-7(Bu)$_{512}$ and G-9(Bu)$_{2048}$ in the highly elastic state were calculated from the absolute entropies of the carbosilane dendrimers (see Tables 1—3) and the corresponding simple substances (C (gr), H_2 (g), Si (cr), where gr is graphite, g is gas, and cr is crystal)[32,33] at 298.15 K. The calculated $\Delta_f S°$ values were -470.8 ± 0.1 and -1885.0 ± 0.1 kJ mol^{-1} K^{-1}, respectively.

Dependence of the thermodynamic functions of the dendrimers on their composition and structure. We have earlier[19] obtained equations for the dependences of the thermodynamic functions (C_p, $H°(T) - H°(0)$, $S°(T) - S°(T)$, $G°(T) - H°(0)$, $\Delta_f S°(T)$) for the carbosilane dendrimers of the third—sixth generation on the molecular weight at four different temperatures (100, 200, 298.15, and 340 K). The selected isotherms are linear. The isotherms (T = 200 K) of the $C_p° = f$(M) and $H°(T) - H°(0) = f$(M) dependences are presented in Fig. 2 as examples.

The comparison of the values of the thermodynamic functions obtained in this work for the G-7(Bu)$_{512}$ and G-9(Bu)$_{2048}$ dendrimers (see Tables 2 and 3) calculated by the corresponding equations[19] showed that the former

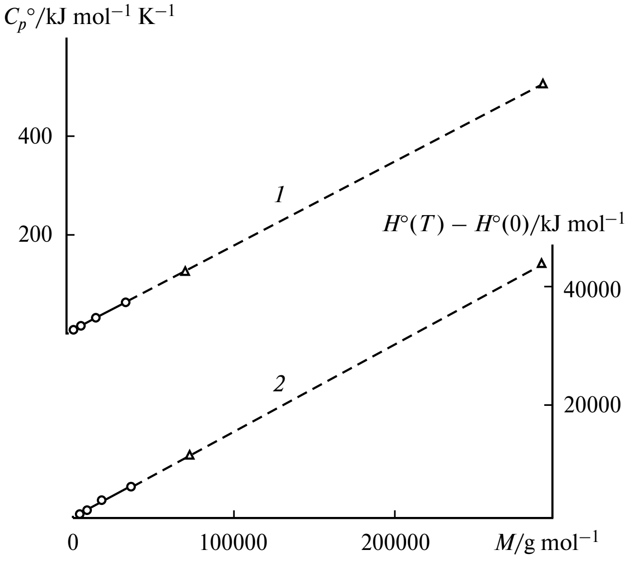


Fig. 2. Isotherms (T = 200 K) of the dependences of the heat capacity (*1*) and heating enthalpy (*2*) of the carbosilane dendrimers of the third—ninth generations with terminal butyl groups on their molecular weight. The data for the third—six generations were obtained in Ref. 19 and those for the seventh—ninth generations are the results of this work, and the approximation of the earlier[19] selected linear dependence is given by dashed line.

are described by the earlier derived equations[19] with an acceptable error (C_p°, 1.5—4%; $H^\circ(T) - H^\circ(0)$, 0.2%; $S^\circ(T) - S^\circ(0)$, 0.3—1.0%; $G^\circ(T) - H^\circ(0)$, 0.3—1.4%; $\Delta_f S^\circ(T)$, 2.5%). This confirms that the earlier obtained[19] thermodynamic function—molar weight isotherms are reliable and the conclusions are substantiated.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 05-03-32363), the Federal Agency on Science and Innovations of the Russian Federation (Program "Research Performed by Young Scientists," State Contract No. 02.442.11.7486), the Council on Grants at the President of the Russian Federation (Program for Support of the Leading Scientific Schools of the Russian Federation, Grant NSh-4439.2006.3), and the National Project "Education" of the innovation educational program of the N. I. Lobachevsky Nizhnii Novgorod State University.

References

1. D. A. Tomalia and J. M. J. Frechet, *J. Polym. Sci.: Part A*, 2002, **40**, 2719.
2. V. V. Narayanan and G. R. Newkome, *Top. Curr. Chem.*, 1998, **197**, 19.
3. J.-P. Majoral and A.-M. Caminade, *Chem. Rev.*, 1999, **99**, 845.
4. A. M. Muzafarov, E. A. Rebrov, and V. S. Papkov, *Usp. Khim.*, 1991, **60**, 1596 [*Russ. Chem. Rev.*, 1991, **60**, 807 (Engl. Transl.)].
5. M. N. Bochkarev and M. A. Katkova, *Usp. Khim.*, 1995, **64**, 1106 [*Russ. Chem. Rev.*, 1995, **64**, 1035 (Engl. Transl.)].
6. I. P. Beletskaya and A. V. Chuchuryukin, *Usp. Khim.*, 2000, **69**, 699 [*Russ. Chem. Rev.*, 2000, **69**, 639 (Engl. Transl.)].
7. F. Zeng and S. C. Zimmerman, *Chem. Rev.*, 1997, **97**, 1681.
8. A. M. Muzafarov and E. A. Rebrov, *Vysokomol. Soedin.*, *Ser. C*, 2000, **42**, 2015 [*Polym. Sci.*, *Ser. C*, 2000, **42**, 55 (Engl. Transl.)].
9. L. L. Zhou and J. Roovers, *Macromolecules*, 1993, **26**, 963.
10. A. M. Muzafarov, O. B. Gorbatsevich, E. A. Rebrov, G. M. Ignat´eva, T. B. Chenskaya, V. D. Myakushev, A. F. Bulkin, and V. S. Papkov, *Vysokomol. Soedin.*, *Ser. A*, 1993, **35**, 1867 [*Polym. Sci.*, *Ser. A*, 1993, **35**, 1575 (Engl. Transl.)].
11. S. A. Ponomarenko, E. A. Rebrov, A. Yu. Bobrovsky, N. I. Boiko, A. M. Muzafarov, and V. P. Shibaev, *Liq. Cryst.*, 1996, **21**, 1.
12. B. V. Lebedev, N. N. Smirnova, M. V. Ryabkov, S. A. Ponomarenko, E. A. Makeev, N. I. Boiko, and V. P. Shibaev, *Vysokomol. Soedin.*, *Ser. A*, 2001, **43**, 315 [*Polym. Sci.*, *Ser. A*, 2001, **43**, 323 (Engl. Transl.)].
13. M. V. Ryabkov, T. G. Kulagina, and B. V. Lebedev, *Zh. Fiz. Khim.*, 2001, **75**, 2165 [*Russ. J. Phys. Chem.*, 2001, **75**, 1988 (Engl. Transl.)].
14. B. V. Lebedev, N. N. Smirnova, M. N. Vasil´ev, and M. N. Bochkarev, *Vysokomol. Soedin.*, *Ser. A*, 1996, **38**, 999 [*Polym. Sci.*, *Ser. A*, 1996, **38**, 644 (Engl. Transl.)].
15. K. V. Kir´yanov, B. V. Lebedev, and M. N. Bochkarev, *Vysokomol. Soedin.*, *Ser. A*, 1999, **41**, 1739 [*Polym. Sci.*, *Ser. A*, 1999, **41**, 1097 (Engl. Transl.)].
16. B. V. Lebedev, M. V. Ryabkov, E. A. Tatarinova, E. A. Rebrov, and A. M. Muzafarov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2003, 523 [*Russ. Chem. Bull.*, *Int. Ed.*, 2003, **52**, 545].
17. S. A. Ponomarenko, E. A. Rebrov, N. I. Boiko, A. M. Muzafarov, and V. P. Shibaev, *Vysokomol. Soedin.*, *Ser. A*, 1998, **40**, 1253 [*Polym. Sci.*, *Ser. A*, 1998, **40**, 763 (Engl. Transl.)].
18. N. N. Smirnova, B. V. Lebedev, N. M. Khramova, L. Ya. Tsvetkova, E. A. Tatarinova, V. D. Myakushev, and A. M. Muzafarov, *Zh. Fiz. Khim.*, 2004, **78**, 1196 [*J. Phys. Chem.*, 2004, **78** (Engl. Transl.)].
19. N. N. Smirnova, O. V. Stepanova, T. A. Bykova, A. V. Markin, A. M. Muzafarov, E. A. Tatarinova, and V. D. Myakushev, *Thermochim. Acta*, 2006, **440**, 188.
20. E. A. Tatarinova, E. A. Rebrov, V. D. Myakushev, I. B. Meshkov, N. V. Demchenko, A. V. Bystrova, O. V. Lebedeva, and A. M. Muzafarov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2004, 2484 [*Russ. Chem. Bull.*, *Int. Ed.*, 2004, **53**, 2591].
21. R. M. Varushchenko, A. I. Druzhinina, and E. L. Sorkin, *J. Chem. Thermodyn.*, 1997, **29**, 623.
22. V. M. Malyshev, G. A. Mil´ner, E. L. Sorkin, and V. F. Shibakin, *Pribory i tekhnika eksperimenta* [*Experimental Equipment and Technique*], 1985, **6**, 195 (in Russian).
23. M. Sh. Yagfarov, *Zh. Fiz. Khim.*, 1969, **43**, 1620 [*J. Phys. Chem. USSR*, 1969, **43** (Engl. Transl.)].
24. A. G. Kabo and V. V. Diky, *Thermochim. Acta*, 2000, **347**, 79.
25. G. M. Ignat´eva, E. A. Rebrov, V. D. Myakushev, A. M. Muzafarov, M. N. Il´ina, I. I. Dubovik, and V. S. Papkov, *Vysokomol. Soedin.*, *Ser. A*, 1997, **39**, 1302 [*Polym. Sci.*, *Ser. A*, 1997, **39**, 874 (Engl. Transl.)].
26. N. A. Shumilkina, V. D. Myakushev, E. A. Tatarinova, M. I. Buzin, N. V. Voronina, T. V. Laptinskaya, M. O. Galyamov, A. R. Khokhlov, and A. M. Muzafarov, *Vysokomol. Soedin.*, *Ser. A*, 2006, **48**, 2102 [*Polym. Sci.*, *Ser. A*, 2006, **48** (Engl. Transl.)].
27. S. Alford and M. Dole, *J. Am. Chem. Soc.*, 1955, **77**, 4774.
28. B. V. Lebedev, *Thermochim. Acta*, 1997, **297**, 143.
29. G. Adam and J. U. Gibbs, *J. Chem. Phys.*, 1965, **43**, 139.
30. W. Kauzmann, *Chem. Rev.*, 1948, **43**, 218.
31. A. Bestul and S. S. Chang, *J. Chem. Phys.*, 1964, **40**, 3731.
32. J. D. Cox, D. D. Wagman, and V. A. Medvedev, *Codata Key Values for Thermodynamics*, New York, 1984.
33. M. W. Chase, Jr., *J. Phys. Chem. Ref. Data*, Monograph 9, 1998, 1951.

Received June 25, 2007;
in revised form August 31, 2007