Effect of conformational rigidity on the glass transition and initial decomposition temperatures of polyimides

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The dependence of the glass transition and initial decomposition temperatures of polyperyleneimide and polynaphthylimide on the conformational rigidity was studied by the Monte Carlo, Kuhn segment, and quantum chemical AM1 methods. The corresponding linear plots can be used for estimation of the glass transition and initial decomposition temperatures when experimental determination is difficult.

Key words: polyperyleneimides, polynaphthylimides, conformational analysis, quantum-chemical calculations, Monte Carlo method, Kuhn segment, glass transition temperature, initial decomposition temperature.

Among thermally stable heterocyclic polymers, polyimides with six-membered imide rings, in particular, polynaphthylimides (PNI)[1—3] and polyperyleneimides (PPI)[3,4] have aroused substantial interest in recent years. These polyimides are prepared by a one-step procedure, namely, by high-temperature catalytic polycyclocondensation of the corresponding aromatic dianhydrides and diamines.[1—6] Thermally stable polyimides are of special interest. These materials can be processed both from solutions and from melts,[2] which extends the scope of their practical application (for example, as gas separating membranes).[7]

Study of the thermal characteristics of these polymers, in particular, the glass transition temperature (T_g) and the initial decomposition temperature (T_d), is complicated in some cases by the closeness of the T_g and T_d values. The purpose of this study is theoretical estimation of the glass transition and initial decomposition temperatures in those cases where these values are difficult to determine experimentally.

Results and Discussion

Previously,[8] it was shown using a number of examples that the conformational rigidity of polyheteroarylenes correlates with the physical properties of polymers such as glass transition temperature, modulus of elasticity, tensile strength, *etc*. This led to the suggestion that the initial decomposition temperatures are also correlated with the conformational rigidity of the polymer.

The conformational rigidity of a polymer can be estimated using the Kuhn segment

$$A_{fr} = \lim_{n\to\infty} [<R^2>/(nl_0)],$$

where A_{fr} is the Kuhn segment calculated with the assumption of free rotation, $<R^2>/(nl_0)$ is the ratio of the root-mean-square distance between the chain ends to its contour length, n is the number of units, and l_0 is the contour length of one unit. In the case of polyheteroarylenes in which the macromolecular unit contains virtual bonds with different lengths and different angles between them, the length of the zigzag line connecting the midpoints of the virtual bonds is taken as the contour length. In this case, l_0 does not depend on the chain conformation and can serve as a measure for the length of the macromolecule.

The conformational rigidity of the polyheteroarylene chain varies over a broad range as a function of the structure of the repeating unit containing virtual bonds of different lengths with different angles between them. The total hindrance to rotation is virtually missing, the calculated conformational rigidity parameters being close to experimental values.[9—11]

The introduction of bulky substituents should result in an increase in the polymer rigidity because the rotation becomes hindered. Thus, the assumption of free rotation is no longer legitimate and the effect of substituents on the hindrance to rotation should be taken into account. Let us designate the Kuhn segment calculated taking account of hindrance by A_h.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 757—761, May, 2002.

The known Kuhn segment can be used to calculate some other conformational parameters, namely, the hindrance parameter

$$\sigma = \sqrt{A_h/A_{fr}}\ ,$$

which characterizes the influence of substituents on the conditions of rotation about the virtual bonds; the characteristic ratio

$$C_\infty = A/l_0,$$

which shows how many polymer units can be accommodated in the Kuhn segment; and the number of aromatic rings in the Kuhn segment

$$p = (A/l_0)k = C_\infty k,$$

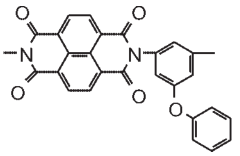
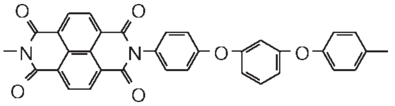
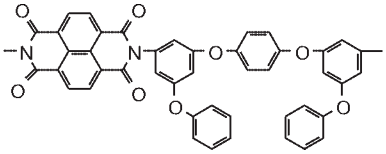
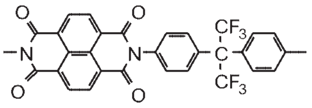
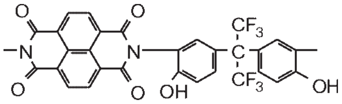
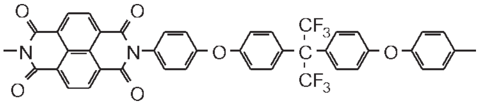
where k is the number of aromatic rings in the structural unit of the polymer. Since many physical properties (for example, glass transition temperature) of polyheteroarylenes are determined by the presence of aromatic rings or heterocycles in the polymer backbone, the introduction of this parameter is very useful for comparison of polymers with different structures but containing the same heterocycles.

Previously, we developed procedures for calculation of the conformational parameters of polyheteroarylenes both with the assumption of free rotation[8] and with allowance for the hindered rotation.[11,12]

The geometric structure of the polymer structural unit is designed on the basis of the structures of simple organic compounds incorporated in the macromolecule unit as fragments. It is assumed that the geometric structure of the chain units does not change significantly upon entering the polymer. The structural unit thus designed is refined using the AM1 quantum-chemical method.[13]

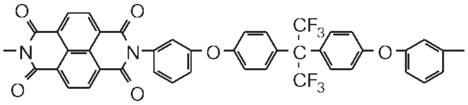
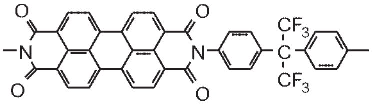
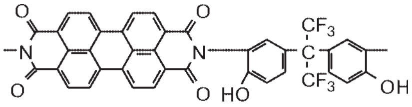
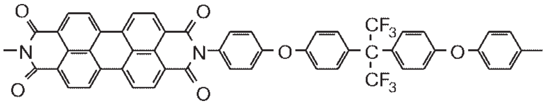
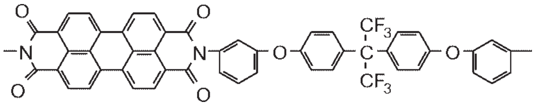
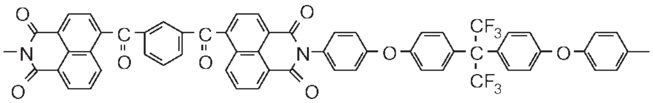
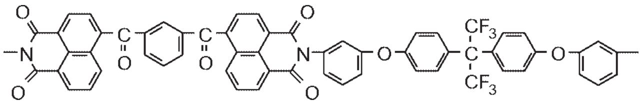
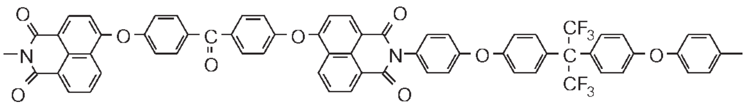
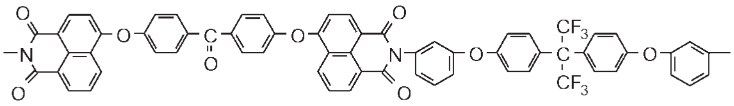
Table 1 presents the calculated values of the conformational parameters of PNI and PPI, together with their

Table 1. Calculated conformational parameters and glass transition and initial decomposition temperatures for PNI **1—7**, **12—15**, and PPI **8—11**

Structural unit	l_0	A_{fr}	A_h	C_∞	p	T_g	T_d
		Å				°C	
 (**1**)	12.21	39.96	—	3.27	6.55	440,[a] 424[b]	460
 (**2**)	22.85	34.41	—	1.05	6.02	410	500
 (**3**)	22.94	22.34	—	0.974	3.90	260	480
 (**4**)	15.40	49.99	54.99	3.57	10.71	500	500
 (**5**)	17.26	19.96	21.96	1.27	3.81	380	460
 (**6**)	26.79	36.43	38.98	1.46	7.27	350	520

(*to be continued*)

Table 1 (continued)

Structural unit	l_0	A_{fr}	A_{h}	C_∞	p	T_{g}	T_{d}
	Å					°C	
 **(7)**	27.09	20.47	21.08	0.778	3.89	270	440
 **(8)**	19.04	61.76	64.86	3.40	13.62	526,[c] 530[d]	460
 **(9)**	21.60	25.02	26.27	1.216	4.86	303,[c] 310[d]	470
 **(10)**	31.09	42.12	43.38	1.395	8.37	405	470
 **(11)**	31.45	24.12	24.84	0.790	4.74	300	450, 472,[e] 472[f]
 **(12)**	39.08	27.20	28.01	0.717	5.05	270	500
 **(13)**	38.84	19.65	20.24	0.521	3.65	260, 236,[g] 239[h]	490
 **(14)**	44.06	30.35	30.65	0.695	5.57	280	470, 492[i]
 **(15)**	43.82	23.34	23.57	0.538	4.30	250	500

[a] From the dependence $T_{\mathrm{g}} = 292.38 + 3.70A_{\mathrm{fr}}$.
[b] From the dependence $T_{\mathrm{g}} = 309.00 + 17.67p$.
[c] From the dependence $T_{\mathrm{g}} = 159.32 + 5.66A_{\mathrm{h}}$.
[d] From the dependence $T_{\mathrm{g}} = 176.81 + 25.99p$.
[e] From the dependence $T_{\mathrm{d}} = 478.67 - 0.27A_{\mathrm{h}}$.
[f] From the dependence $T_{\mathrm{d}} = 77.36 - 1.18p$.
[g] From the dependence $T_{\mathrm{g}} = 149.76 + 4.26A_{\mathrm{h}}$.
[h] From the dependence $T_{\mathrm{g}} = 148.11 + 23.84p$.
[i] From the dependence $T_{\mathrm{d}} = 466.5 + 6.9p$.

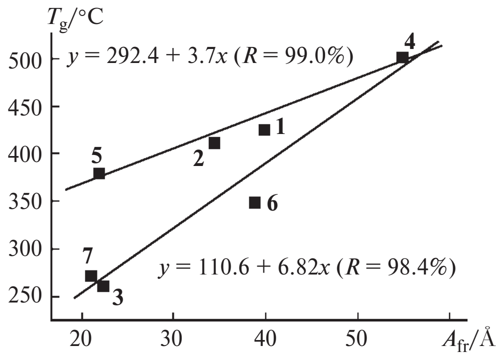


Fig. 1. Glass transition temperature (T_g) *vs.* Kuhn segment (A_{fr}) for polymers PNI **1—7**.

glass transition and initial decomposition temperatures. The polymers under consideration can be divided conventionally into three groups, namely, polymers **1—7** prepared from naphthalene-1,4,5,8-tetracarboxylic acid dianhydride; polymers **8—11** based on perylene-3,4,9,10-tetracarboxylic acid dianhydride; and polymers **12—15** synthesized using bis-naphthalic anhydrides with bridging groups.

We studied the dependences of glass transition and initial decomposition temperatures on the Kuhn segment and on the number of aromatic rings in the Kuhn segment (Figs. 1—3).

The dependences of the glass transition temperature of PNI **1—7** on the Kuhn segment calculated under the assumption of free rotation and on the number of rings in the Kuhn segment are shown in Figs. 1 and 2, *a*, respectively. The points break apart to form two linear dependences, which originate from the same point for polymer **4**. Using the least-squares method, each dependence can be described by a linear equation with a good convergence factor. The glass transition temperature of polymer **1** found from the plots shown in Figs. 1 and 2, *a* is lower than the initial decomposition temperature by ~20—35 °C. This difference between the glass transition and initial decomposition temperatures is too small to be determined accurately. Since the p value takes into account both factors affecting the conformational mobility of units of the polymer chain (aromaticity and rigidity), subsequently, we consider correlations only with this value.

The variation of the initial decomposition temperature of PNI **1—7** *vs.* the number of aromatic rings in the Kuhn segment is shown in Fig. 2, *b*. In this case, the points also break apart to give two linear dependences with a good convergence factor. This confirms our hypothesis of the linear dependence of the initial decom-

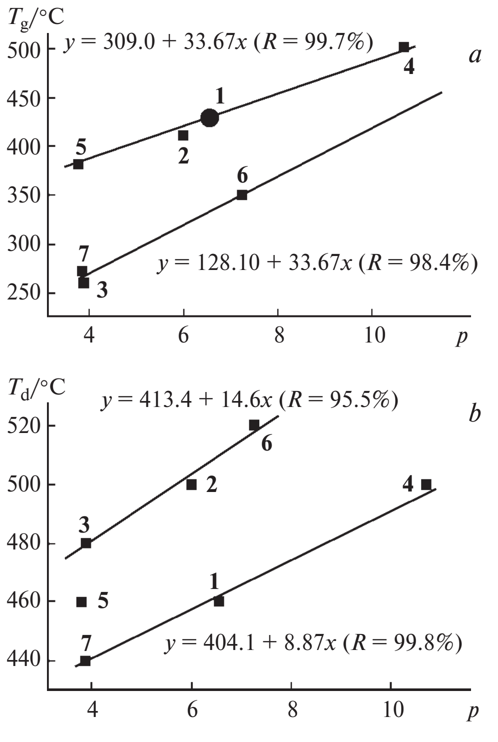


Fig. 2. Glass transition temperature (*a*) and initial decomposition temperature (*b*) *vs.* the number of aromatic rings in the Kuhn segment (p) for polymers PNI **1—7**. The circle marks the glass transition temperature of polymer **1** calculated from the dependence presented in Fig. 1, *a*.

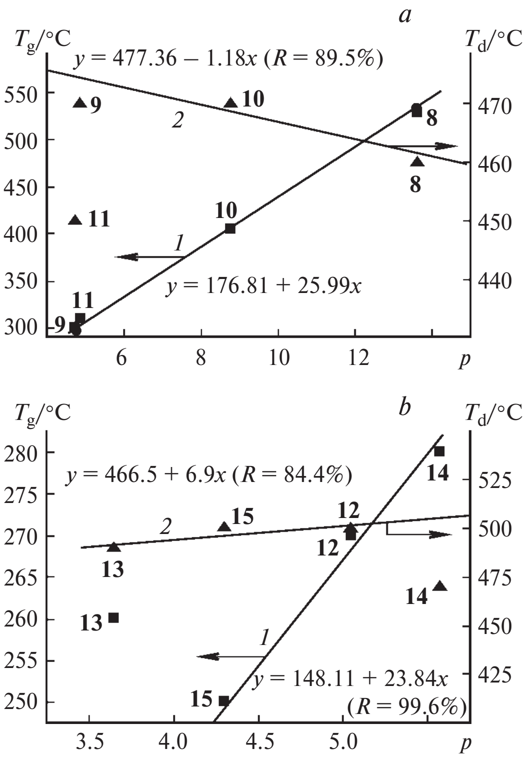


Fig. 3. Glass transition temperature (*1*) and initial decomposition temperature (*2*) *vs.* the number of rings in the Kuhn segment for polymers PPI **8—11** (*a*) and PNI **12—15** (*b*).

position temperature on the conformational rigidity of the polymer.

The dependences of the glass transition and initial decomposition temperatures of PPI **8—11** on the number of rings in the Kuhn segment are shown in Fig. 3, *a*. For this group of polymers, the Kuhn segment was calculated with allowance for hindered rotation. This is due to the presence of trifluoromethyl groups at the central carbon atoms in the backbone. Since the glass transition temperatures have been determined only for two of the second-group polymers (**10** and **11**), our estimates of the glass transition temperature for polymers **8** and **9** are rather arbitrary. However, for polymer **8**, this value is 526—530 °C, which is much higher than the initial decomposition temperature, and hence, it really cannot be determined experimentally. For polymer **9**, the glass transition temperature was found to be 303—310 °C, which is much lower than the initial decomposition temperature.

The variation of the initial decomposition temperature is also linear but the point corresponding to polymer **11** falls out of the dependence (see Fig. 3, *a*, straight line *2*). The initial decomposition temperature for polymer **11** found by calculations based on this dependence is 22 °C higher than the value determined experimentally.

The dependences for the glass transition and initial decomposition temperatures on the number of aromatic rings in the Kuhn segment calculated with allowance for hindered rotation for PNI **12—15** are shown in Fig. 3, *b*. The point corresponding to polymer **13** falls out of both dependences. The variation of the glass transition temperature *vs.* the number of aromatic rings in the Kuhn segment (see Fig. 3, *b*, straight line *1*) is linear, and the glass transition temperature calculated from it proved to be ~21—25 °C lower than the value determined experimentally.

The variation of T_d *vs.* p given in Fig. 3, *b* is also linear but the convergence factor is somewhat lower than that for the dependence of T_g on the same conformational parameter. The T_d value for polymer **13** found from this dependence is 490 °C, *i.e.*, it is 20 °C higher than the experimental value.

Polymers **11** and **13** whose T_g and T_d values fall out of the general trend are close in the chemical composition of the diamine component.

Thus, based on calculations of the conformational parameters of PNI and PPI (see Table 1), we demonstrated that the glass transition temperatures (or the initial decomposition temperatures) of polymers of one group containing identical imide rings are correlated with the conformational rigidity of these polymers.

The use of correlations established here made it possible to correct some values for glass transition or initial decomposition temperature for those polymers where the experimental determination of these values was difficult.

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Received February 9, 2001;
in revised form October 10, 2001