

RELATIONSHIPS BETWEEN GLASS TRANSITION AND MELTING TEMPERATURES AND CHEMICAL STRUCTURES OF POLYPYROMELLITIMIDES

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At temperatures above 350° polypyromellitimides exhibit continuously increasing deformations. The temperatures of glass transition and melting were determined in their homologous series.

For the determinations, thermomechanical and combined thermogravimetric mass-spectrometric measurements were performed. Glass transition temperatures were also calculated on the basis of the structure of the repeating unit. Conclusions could be drawn on the structures and rigidities of the molecules. The roles of groups introduced into the diamine fragment could be determined.

The considerable interest aroused by polyimides in recent years is quite understandable, since this class of thermally stable polyheteroarylenes provides great possibilities for obtaining the required ratio cyclic to linear fragments of the chain-repeating unit in a controllable synthesis. The synthesis and subsequent processing lead to different wares, such as fibres, coverings, plastics, etc. with a required combination of properties [1-3].

One of the methods for regulation of relaxational and mechanical properties of polyimides consists in changing both the thermodynamic and the kinetic flexibilities of macromolecules by introduction of "pin-joint" groups (-O-, -CO-, -S-, -COO-, -NHCO-, -CH₂-, etc.) or bulky lateral groups into the polymer chain [1, 4].

It should be noted that little or no information is available in the literature on the glass transition and melting temperatures of polyimides with the exception of ref. [1, 5] where it has been shown that polyimides containing "pin-joint" groups in both the dianhydride and the diamine fragment of the repeating unit, or bearing bulky (polar) groups, exhibit a distinct first-order transition. According to the data presented in these papers, at temperatures above 350° polypyromellitimides exhibit continuously increasing deformations. Several authors indicate that glass transition temperatures exist for the best-known polypyromellitimide PM, however, as pointed out in [4], these data are very contradictory and require further confirmation. (Thus, for polypyromellitimide diphenyloxide) (polymer 8 in Table 1) the glass transition temperature is 250, 380 and 500° according to different sources.)

The use of polymers as plastic materials in machinery or engineering etc. is

often determined by the distance of their glass transition and melting temperatures from the required operating temperatures of the corresponding article or ware. Consequently, our main attention was directed to the determination of these temperatures in a given homologous series of polypyromellitimides.

In addition, it is necessary to know the glass transition and melting temperatures of polypyromellitimides in order to select the most favourable conditions for their crystallization and ultimate condensation during thermal treatment and hot draw. This makes possible to obtain polymer chains statistically homogeneous in composition and exhibiting a more perfect supermolecular organization in the corresponding wares, since the mobility of polymer chains appearing as a result of thermomechanical treatment above the glass transition temperature facilitates any structural changes in these polymers.

Experimental

In order to estimate the glass transition and melting temperatures, a thermo-mechanical method was used in combination with mass spectrometry-thermal analysis, thermogravimetry and some additional data on the temperature-dependence of the dynamic elastic modulus [6]. For completeness of the picture, glass transition temperatures of polypyromellitimides were also determined by calculations based on the chemical structure of the repeating unit, following the procedure proposed in [4].

Table 1
Glass transition and melting temperatures

Configuration of the diamine fragment of the polypyromellitimides	Glass transition temperature			Softening*
	from dependence $\varepsilon = f(T)$	from dependence $Eg = f(T)$	Calculated	from dependence $\varepsilon = f(T)$
1.	—	—	553	—
2.	460–480	470	475	490–500
3.	430–440	430–440	432	—
4.	400–430	420–430	422	400–430
5.	380–440	380–390	419	380–440
6.	410–445	410–420	425	410–445
7.	390–420	390–410	—	390–420
8.	380–426	380–420	403	465
9.	305–340	300–360	328	455
10.	250–310	260–300	283	360–445
11.	270–290	270–280	270	370–440
12.	220–300	250–255	253	360–390

* Softening is meant as: first-order transition (melting) for crystallizable polymers 1–3 and 8–12; process reverse to glass transition for non-crystallizable polymers 4–7.

Synthesis of polypyromellitimides and preparation of fibres from them were carried out according to standard methods described previously [1, 7]. The chemical structure of the elementary unit of the polypyromellitimides was varied by the use of different diamines; their formulae and designations are given in Table 1.

Thermomechanical characteristics were determined as described in ref. [8]. The heating rate was 6°/min, and the load for all samples investigated was 1 kg/mm². The maximum error in measurements of ϵ and T values did not exceed one per cent. The thermomechanical curve for polymer N 8 (Fig. 1) illustrates the

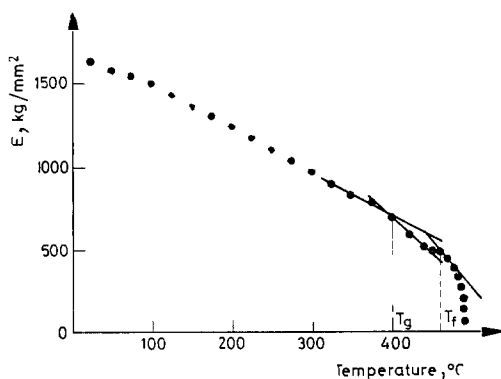


Fig. 1. Determination of glass transition and melting temperatures from the thermomechanical curve

of polypyromellitimides

temperature		T5%°	Structure	1 - f	T _g /T _m , K
from dependence $Eg = f(T)$	Acc. to MTA data				
—	—	550	C	1	—
490—500	490	510	C	1	0.99—0.95
—	—	—	C	1	—
420—430	420	435	A	0.5	—
380—390	380	460	A	0.67	—
410—420	415	465	A	0.67	—
390—410	—	515	A	0.67	—
460	465	490	C	0.67	0.94—0.88
465	—	505	C	0.5	0.84—0.78
400—420	410	445	C	0.4	0.92—0.74
420	420	500	C	0.5	0.84—0.76
370—380	—	455	C	0.34	0.89—0.76

C — Crystallizable, A — Amorphous.

use of the thermomechanical method for determination of the glass transition and softening temperatures of the investigated polypyromellitimides.

Investigations of the temperature-dependence of the dynamic elastic modulus $\varepsilon_{\text{dyn}} = f(T)$ were carried out with a device for the determination of the complex dynamic Young modulus under the force vibration conditions described in ref. [9]. Operating temperatures ranged from 20 to 500°; the frequency was 72 Hz.

The heating rate was 5°/min and the span of the sample was 15 mm. Absolute values of the complex dynamic Young modulus (Σ) vs. temperature for fibres 4, 8 are shown in Fig. 2.

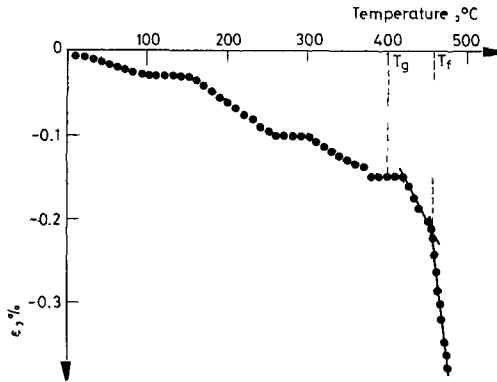


Fig. 2. Determination of glass transition and softening temperatures from the temperature-dependence of the elastic modulus

The procedure for calculation of glass transition temperatures was based on the chemical structures of the polypyromellitimides [4]. The glass transition temperature was determined from the equation:

$$\log T_g = \frac{\sum_i K_i^*}{N_A \sum_i \Delta V_i} + A$$

K_i^* being a parameter related to the packing coefficient and the volume expansion coefficient. Values of K_i^* in the sum $\sum K_i^*$ are adopted from ref. [4]. $\sum V_i$ designates the Van der Waals volume of the repeating unit, being the sum ΔV_i of the volumes of all atoms in this unit. Increments of volumes ΔV_i of atoms and atomic groups in the repeating unit of the polymer reported in ref. [10, 11] were used to calculate $\sum \Delta V_i$. The N_A in the preceding formulae is Avogadro's number, and A is a constant parameter equal to 1.435 for all linear polymers, irrespective of their chemical structure.

Thus, for polyimide 8 the value of $\sum K_i^*$ represents the sum of the increments K_i^* of twenty-two carbon atoms and two nitrogen atoms in the main chain, four

oxygen atoms in the side groups, one oxygen atom in the main chain and ten hydrogen atoms, and numbers relating to two dipole-dipole interactions and the symmetry coefficient, since all benzene rings in the main chain are substituted in the para position.

$$\Sigma K_i^* = 22 \times 10.74 + 2 \times 2.185 + 4 \times 3.925 + 1(-5.244) + 10(-1.248) + 2 \times 7.33 + 10.50 = 263.8$$

The volume of the repeating unit of this polymer is therefore the sum of increments for ten aromatic CH groups, eight aromatic carbon atoms, one oxygen atom bonded to aromatic carbon atoms, four carbonyl groups and two atoms of nitrogen in the imide ring:

$$\Sigma \Delta V_i = 10 \times 14.7 + 8 \times 8.4 + 1 \times 3.4 + 4(17.8 + 5.85) + 2 \times 0.9 = 314 \text{ \AA}^3$$

$$N_A \Sigma \Delta V_i \sim 6.02 \times 10^{23} \text{ mole}^{-1} \times 3.14 \times 10^{-24} \text{ cm}^3 = 189 \text{ cm}^3/\text{mole}$$

$$\log T_g = \frac{263.8}{189} + 1.435 = 1.395 + 1.435 = 2.83$$

$T_g = 676 \text{ K}$.

The effective flexibility of the polymer chains was estimated in terms of the Flory flexibility parameter:*

$$f = \frac{\text{number of "flexible" bonds}}{\text{number of "flexible" bonds} + \text{number of "rigid" bonds}}$$

In our case all bonds about which even a restricted rotation of the adjoining part of the chain is possible are considered as "flexible" or "pin-joint" bonds. "Rigid" bonds are those about which only torsional vibrations of single fragments of the macromolecule involving no changes in its conformation are possible, or bonds about which no rotations or vibrations are possible at all.

Thermal analysis of polypyromellitimides was carried out by thermogravimetric analysis (TG) and mass-spectrometric thermal analysis (MTA). Experiments were made in an air flow (flow rate 50 cm³/min) with a Du Pont 951 thermo-analyzer, and in vacuum with a Mettler thermobalance connected with a Balzers Quadrupole mass-spectrometer. The sample weight was 3–5 mg, and the heating rate was 5°/min.

It is known that the thermal stability of a polymer according to TG data is determined by the temperature of onset of weight loss (T_0) or by temperatures of 5 or 10 per cent weight loss (T_5 and T_{10}) [12]. Investigations of the thermal stabilities of various polyimides [13] have shown that in many cases the values of T_0 depend on the presence of low molecular weight impurities. Their separation may

* Determination of the conformational parameter of the flexibility of polypyromellitimide macromolecules from the ratio $\delta = \frac{\langle h^2 \rangle \phi^{1/2}}{\langle h^2 \rangle_0^{1/2}}$, where $\langle h^2 \rangle \phi^{1/2}$ are the unperturbed dimensions of coils in the solvent θ and $\langle h^2 \rangle_0^{1/2}$ are the dimensions corresponding to free rotations, is impossible because these polymers are insoluble.

change the T_0 value greatly, irrespective of the chemical structure of the polyimide.

The value of T_5 reflects the relationship between the thermal stability of the polyimide and its chemical structure more reliably, because up to this temperature low molecular weight products are removed, and the rate of weight loss attains the value of 0.1 per cent and subsequently starts to increase exponentially. Hence the value of T_5 may be adopted as the temperature of thermal degradation of a polyimide.

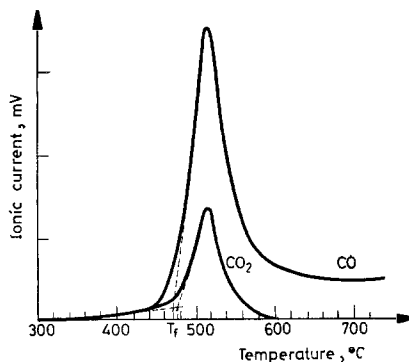


Fig. 3. Determination of melting temperatures from mass-spectrometric thermal analysis data. Curve 1 — evolution of CO; curve 2 — evolution of CO₂ during thermal degradation of a sample of polyimide fibre

TG data indicate the limit of thermal stability of a polyimide, whereas the MTA method, which is more sensitive to changes occurring in the polymer in the early stage of thermal degradation, permits estimation of the softening temperature range of the polymer from the beginning of gas evolution. The appearance of traces of gaseous products of thermal degradation indicates that macromolecules become more mobile and as a result low molecular weight products which were “locked” in a rigid polymer structure at lower temperatures are “liberated”. As the temperature is raised, gas evolution increases, leading to a sharp weight loss indicating degradation of the main structure (Fig. 3). The point of transition from the slow initial process to a rapid reaction, determined from the intersection of the gas evolution curve tangents according to MTA data, relatively accurately characterizes the softening temperature T_f , which is in good agreement with the data determined from the dependences $\Sigma = f(T)$ and $\varepsilon = f(T)$ (Table 1).

Results and discussion

The following points should be noted concerning the results shown in Table 1:

The chains of polymers 1–3, which have no “pin-joint” in the diamine fragment, are very rigid and therefore the number of possible conformations for each part of the chain is very restricted.

Due to this, their melting temperatures are located near or somewhat above the temperatures of thermal degradation and the glass transition temperatures and also turn out to be close to the temperatures of their intense thermal decomposition. A slight decrease in the glass transition temperature in the order $1 > 2 > 3$ when the number of para-phenylene groups in the diamine fragment increases is probably due mainly to increasing possibilities of rotation of chain fragments about the C–C bonds and a decreasing concentration of strongly polar CO groups responsible for the intermolecular interactions of neighbouring chains.

The introduction into the diamine fragment of $-\text{O}-$, $-\text{CH}_2-$, $-\text{S}-$, or $-\text{CO}-$ groups, or of the benzene ring in the meta-configuration (polymers 4–8) leads not only to an increase in the chain flexibility and to a certain general decrease in the thermal stability, but also to the appearance of a distinct range of a high elasticity state (cf. polymers 1–3).

Moreover, as was to be expected, for polymers 4–7 with an amorphous structure the values of the glass transition and softening temperatures coincide.

On the other hand, the glass transition temperature of polymer 8 was at least 50° lower than its melting temperature and 70° lower than the temperature of thermal degradation.

Quite a different situation is observed when various numbers of oxyphenylene groups are introduced into the diamine fragment (polymers 9–12). The increasing thermodynamic flexibility of the chains of these polymers leads to a certain widening of the temperature range within which polypyromellitimides are characterized by a considerable increase of deformability.

It is important that, irrespective of the number of “pin-joint” groups introduced into the diamine fragment, polymers 9–12 retain high values of thermal stability as estimated from the 5 per cent weight loss, whereas the glass transition temperatures of these polymers are approximately 100° lower than their melting temperatures and 200° lower than the temperatures of their sharp thermal degradation. By varying the nature and number of “pin-joint” groups introduced into the diamine fragment of the chain, it is possible not only to regulate the structure and thermomechanical properties of these polymers, but also to change the temperature range of their high elasticity state. This possibility in turn makes polymers 10–12 promising with regard to the possibility of direct melt processing.

The unusually high T_g/T_m ratios for polypyromellitimides with an ordered structure deserve special consideration. For a rigid-chain polypyromellitimide (polymer 2) without bending distortions, T_g/T_m is approximately 0.97, whereas the increase in the thermodynamic and kinetic flexibilities of the chains of polymers 8–12 due to the introduction of a certain number of oxyphenylene groups into the diamine fragment leads to a decrease in this ratio to 0.94–0.74. The obtained T_g/T_m ratios for the polypyromellitimides show that the empirical rule assumed for flexible-chain polymers: $T_g/T_m \approx 0.67$ [14] is no longer valid in our case. Possible reasons for the strong deviation from the “rule of two-thirds” have been discussed by Lee and Knight [15], who report values of $T_g/T_m = 0.97-0.25$ for a very wide variety of polymers of substantially different chemical structures.

Our data for the glass transition and melting temperatures of polypyromellitimides also clearly indicate that the T_g/T_m ratio depends strongly on definite peculiarities of the chemical structures of the polymers. However, abnormally high T_g/T_m ratios may be explained qualitatively in a more direct manner in terms of the model of Rudakov [9], according to which at least pairs of adjacent chains may exhibit only concordant mobility due to strong carbonyl-carbonyl interactions; in other words, a single-chain polymer in the condensed state (and for the polyimides investigated this is the only state) exhibits "pseudoledder" properties up to T_g .

Our data for the softening temperatures of polypyromellitimides obtained by using the MTA method are in good agreement with the softening temperature values found from the dependences $\varepsilon_{\text{dyn}} = f(T)$ and $\varepsilon = f(T)$. This suggests that the MTA method may be extended not only to the determination of the dynamics of polymer degradation and to the characterization of their thermal stabilities, but also to the determination of the temperature range of polymer softening.

References

1. N. A. ADROVA, M. J. BESSONOV, L. A. LAIUS and A. P. RUDAKOV, *Poliimidy — novy klass termostoikikh polimerov*, Nauka, Leningrad, 1968, p. 280.
2. V. V. KORSHAK, *Termostoikie polimery*, Nauka, Moscow, 1969, p. 410.
3. A. P. RUDAKOV, M. J. BESSONOV, SH. TUICHIEV, F. S. FLORINSKY, B. M. GINZBURG and S. YA. FRENKEL, *Vysokomolekul. Soedin.*, A12, N3 (1970) 641.
4. A. A. ASKADSKY and G. L. SLONIMSKY, *Uspek. Khim.*, N 9 (1975) 1688—1721.
5. *Sintez, struktura i svoystva polimerov*, Nauka, Leningrad, 1970, p. 314.
6. N. R. PROKOPCHUK, M. J. BESSONOV, L. N. KORZHAVIN, J. G. BAKLAGINA, N. P. KUZNETSOV and S. JA. FRENKEL, *Khimich. volokno*, N 4 (1976).
7. L. N. KORZHAVIN, *Tesis*, Leningrad, 1970.
8. A. P. RUDAKOV and N. A. SEMENOV, *Mekhanika polimerov*, N 3 (1965) 155.
9. A. P. RUDAKOV, *Thesis*, Leningrad, 1969.
10. G. L. SLONIMSKY and A. A. ASKADSKY, *Vysokomolekul. Soedin.*, A. 13 (1971) 1917.
11. A. A. ASKADSKY, *Deformatsiya polimerov*, Khimiya, Moscow, 1973, p. 43.
12. V. V. KORSHAK, *Khimicheskoe Stroenie i temperaturnye kharakteristiki polimerov*, Nauka, Moscow, 1970, p. 419.

RÉSUMÉ — Les polypyromellitimides montrent des déformations qui augmentent de manière continue aux températures supérieures à 350°. On a déterminé dans leurs séries homologues les températures de transition vitreuse et de fusion.

Ces déterminations ont été complétées par des essais thermomécaniques ainsi que par des mesures combinées en thermogravimétrie et en spectrométrie de masse. Les températures de transition vitreuse ont également été calculées sur la base de la structure unitaire. On en déduit des conclusions sur la structure et la rigidité des molécules. Le rôle des groupes introduits dans le fragment diamine a pu être déterminé.

ZUSAMMENFASSUNG — Polypyromellitimide weisen bei Temperaturen oberhalb von 350 °C ständig zunehmende Deformationen auf. Die Temperaturen des Glas-Überganges und des Schmelzens wurden in ihren homologen Reihen bestimmt.

Zur Bestimmung wurden thermomechanische und kombinierte thermogravimetrisch-massenspektrometrische Messungen durchgeführt. Die Glas-Übergangstemperaturen wurden auch auf Grund der Struktur der sich wiederholenden Einheit errechnet. Schlüsse über die Struktur und Rigidität der Moleküle konnten gezogen werden. Die Rolle der in das Diamin-Fragment eingeführten Gruppen konnte bestimmt werden.

Резюме — Полипиромеллитимиды при температурах выше 350° проявляют непрерывно увеличивающиеся деформации. Были определены в их гомологических сериях температуры стеклования и плавления. Для этих определений были использованы термомеханические и комбинированные термогравиметрические-масс-спектрометрические измерения. Температуры стеклования были также вычислены на основании структуры повторяющейся единицы. Выведены заключения о структуре и жесткости этих молекул. Определена роль групп, введенных в диаминовую часть молекул.