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THERMAL AND THERMO-OXIDATIVE STABILITIES OF SOME POLY(SILOXANE-AZOMETHINE)S

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Thermal and thermo-oxidative stability of some poly(siloxane-azomethine)s obtaining starting from *bis*(formyl-*p*-phenoxymethyl)tetramethyldisiloxane and different organic diamines have been investigated by TG+DTG+DSC simultaneous analyses performed in argon flow and air static atmosphere, respectively. TG, DTG and DSC curves of each polymer showed three or four successive degradation steps at different temperatures according to the composition of the sample and the gaseous atmosphere in which the thermal analysis was performed. For each process, the following parameters were evaluated: total mass loss, temperature corresponding to the maximum reaction rate, maximum reaction rate, temperature corresponding to certain mass loss. In order to determine the thermal and thermo-oxidative stabilities of investigated polymers, the following values were determined: $T_{x\%}$ – temperature corresponding to x% mass loss, and $\%\Delta m_T$ – mass loss at a given temperature T. The obtained orders of stability were correlated with the structure of investigated polymers.

Keywords: *polyazomethines, siloxane, thermal analysis, thermal and thermo-oxidative stabilities*

Introduction

In a previous paper [1] the synthesis of some poly(siloxane-azomethine)s obtained starting from *bis*(formyl-*p*-phenoxymethyl) tetramethyldisiloxane and different organic diamines was presented. Elemental analysis, IR, NMR, solubility measurements and DSC analysis were performed [1] for the characterization of these polymers. Generally, polyazomethines distinguish by many attractive properties like relative high heat stability [2], hole transport properties [2], liquid crystalline behaviour [3], and many technical applications (e.g., battery anodes and cathodes, semiconductors, energy storage, conversion devices, integrated electro-optics for switching display [4]).

The aim of this work is to complete the characterization of poly(siloxane-azomethine)s with the determination of their thermal and thermo-oxidative behaviours. For this purpose, the simultaneous TG+DTG+DSC analyses in inert atmosphere (Ar) and in oxidative atmosphere (static air) have been performed. The differences among the thermal parameters will be discussed in relation with the polymers structures and the orders of thermal and thermo-oxidative stabilities will be established.

Experimental

Materials

Scheme 1 shows schematically the synthesis of poly(siloxane-azomethine)s PAM1 – PAM9.

The samples were prepared by means of two-step reaction. In the first step, a disiloxane- (and polysiloxane-) dialdehyde precursors were obtained from bis(chloromethyl)disiloxane and *p*-hydroxybenzaldehyde. In the second step, poly(siloxane-azomethine)s were obtained by solution polycondensation, starting from *bis*(formyl-*p*-phenoxymethyl) tetramethyldisiloxane (or polysiloxane) and different organic diamines, having an aromatic, aliphatic chain with the presence, or not, of ether linkages. Some details concerning preparation, as well as an exhaustive characterization by various techniques (IR, ^{1}H NMR spectroscopy, elemental analysis, DSC, X-ray diffraction, etc.) of these polymers were given in our previous paper [1].

Methods

Thermal analysis

The heating curves (TG, DTG and DSC) of samples were simultaneously recorded with STA 490C apparatus produced by Netzsch-Germany using alumina crucible, in argon flow (purity 99.999%; 30 mL min^{-1}) and in static air atmosphere, in the temperature range 25–900°C, and a heating rate of 10 K min^{-1}. The mass of the analysed-sample was in the range 4.1–5.7 mg. The drift corrections were performed by an initial recorder of TG and DSC curves with empty crucible and in conditions of thermal analysis of the samples.

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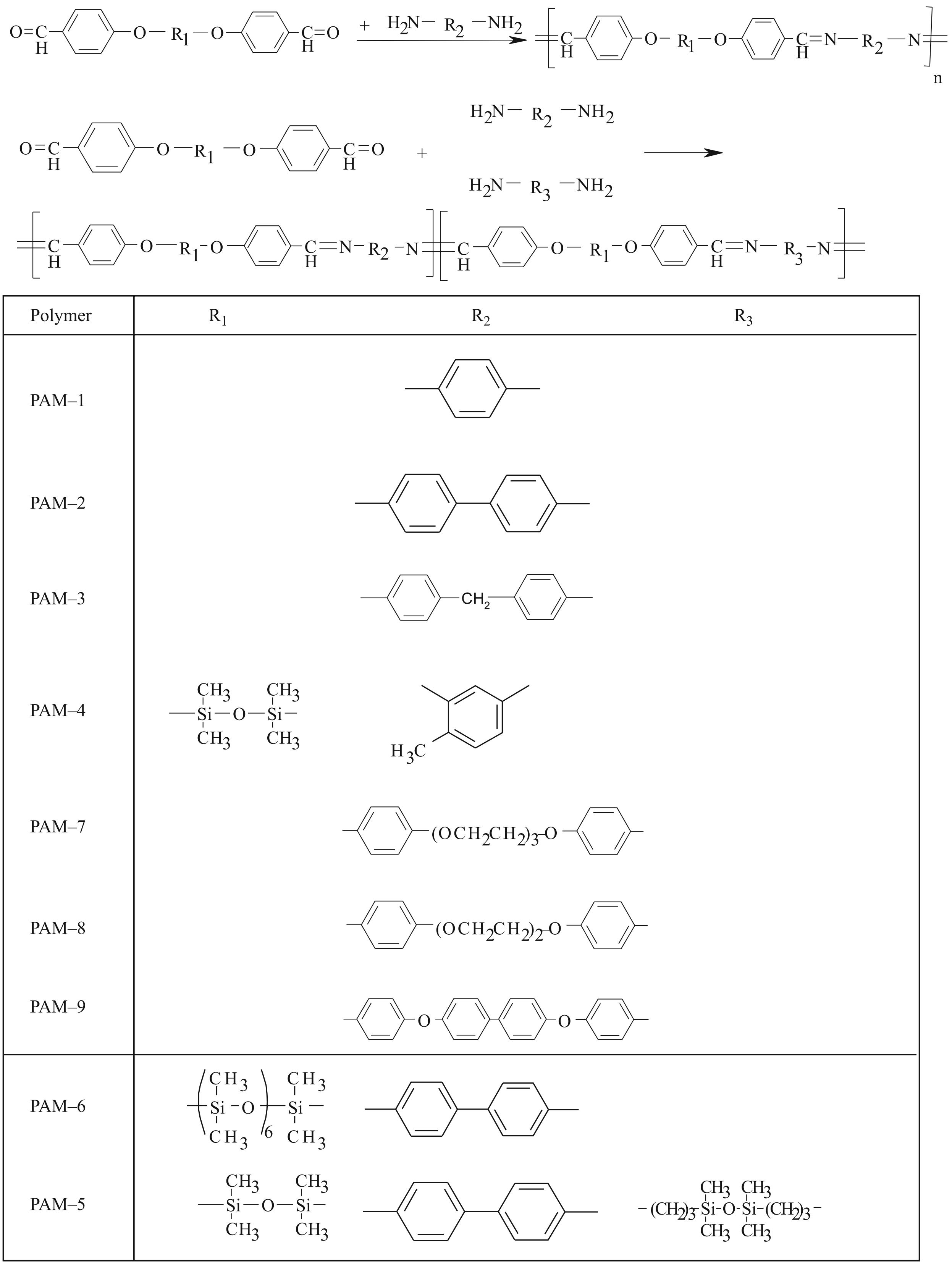

Scheme 1 Synthesis of poly(siloxane-azomethine)s

Results and discussion

Thermal degradation

Figure 1 shows the TG, DTG and DSC curves for PAM1 recorded in argon flow. The decomposition of the sample occurs by three successive processes with formation of volatile compounds. Similar plots have been obtained for PAM1-PAM4 poly(siloxane-azomethine)s, which do not contain O atoms in the organic segment (R_2). For PAM5 and PAM6 that have more complex structures than PAM1-PAM4, as well as for PAM7-PAM9, which have ether bonds in the organic part, the process III is very slow and therefore a peak III is not put in evidence in DTG and DSC curves. The process II occurs in closed temperature range for all polymers (maximum of DTG curve in the temperature range 402–442°C). Although the degradation occurs in inert atmosphere, this process is an exothermic one. This could be explained by oxidation of polymers with the oxygen contained in macromolecules.

Table 1 lists the main characteristic parameters evaluated from TG, DTG and DSC curves.

In order to determine the thermal stability of the investigated polymers, the following values were determined: $T_{x\%}$ – temperature corresponding to $x\%$ mass loss ($x\%$=10 and 15%), and $\%\Delta m_T$ – mass loss at a given temperature T (T=390 and 400°C). The decreasing order of $T_{x\%}$ or increasing order of $\%\Delta m_T$ is the order of decreasing of thermal stability [5–7].

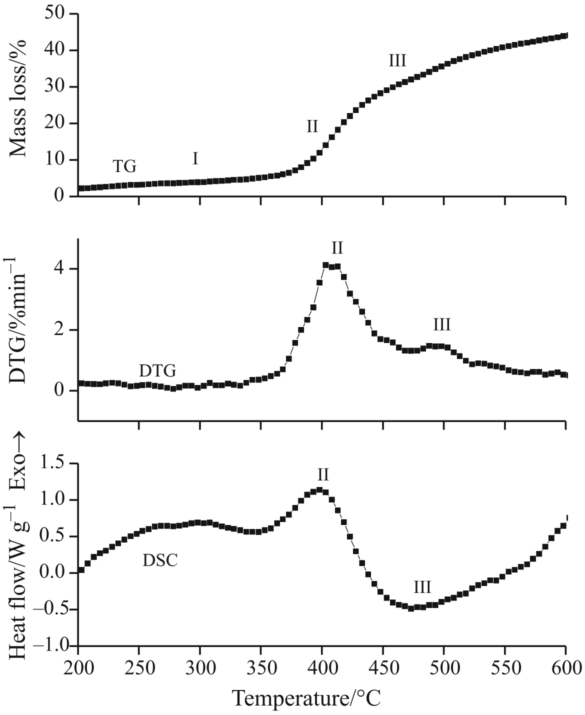

Fig. 1 TG, DTG and DSC curves for PAM 1 heated in argon flow

These criteria could be applied to series of similar compounds. Therefore, the investigated polymers were divided in two groups, namely: polymers for which R_2 do not contain ether functions (PAM1-PAM6) and polymers containing ether functions (PAM7-PAM9). The analysis of data listed in Table 1 leads to the following orders of thermal stability:

- for PAM1-PAM6 and $T_{10\%}$ criterion: PAM6>PAM1>PAM4≈PAM5>PAM2≈PAM3;
- for PAM1-PAM6, and $T_{15\%}$ and $\%\Delta m_T$ criteria: PAM6>PAM1>PAM4>PAM2≈PAM3>PAM5;
- for PAM7-PAM9 and all criteria: PAM9>PAM7>PAM8.

For the first group of polymers (PAM1-PAM6), the following observations can be made:

- PAM6, which is the single polymer containing in the macromolecular chain $(Si(CH_3)_2–O)_6$ groups (the rest of polymers contain the $(Si(CH_3)_2–O)$ groups), exhibits the highest thermal stability;
- PAM1 and PAM4 that have in R_2 a single aromatic nucleus have a higher thermal stability than PAM2, PAM3 and PAM5, which have R_2 with two aromatic nucleuses.

For the second group of polymers (PAM7-PAM9) one notes that the existence in R_2 of the –O– function bonded on two aromatic nucleuses determines a higher thermal stability for PAM9. PAM7 and PAM8, which contain in R_2 aliphatic–O–aliphatic and aliphatic–O–aromatic groups have a smaller thermal stability than PAM9.

Thermo-oxidative degradation

The TG, DTG and DSC curves recorded for samples heated in air static atmosphere show that PAM1, PAM2, PAM5 and PAM6 exhibit three successive exothermic processes with formation of volatile compounds (Fig. 2a – processes denoted by I, II and III), while PAM3, PAM4, PAM7, PAM8 and PAM9 exhibit four such processes (Fig. 2b – processes denoted by I, II, II' and III). Unlike PAM3 and PAM4, PAM7-PAM9 present DTG and DSC curves in which the process II' is very well put in evidence. It appears that the existence of process II' for PAM7-PAM9 could be associated with the ether bonds from the macromolecular chains of these polymers.

Table 2 lists the main characteristic parameters evaluated from TG, DTG and DSC curves.

The inspection of this table shows that the values of the characteristic parameters depend on the structures of the investigated polymers, but some of these parameters have values in relative narrow ranges (for process II: $330.5°C\le T^{\mathrm{DTG}}_{\max}\le 369.5°C$ and

Table 1 The parameters of non-isothermal degradation in Ar of PAM1–PAM9

Polymer	Process I	Process II				Process III							
	Δm/ %	Δm/ %	T_{max}^{DTG}/ °C	T_{max}^{DSC}/ °C	$v_{T_{max}^{DTG}}$/ min^{-1}	Δm/ %	T_{max}^{DTG}/ °C	$v_{T_{max}^{DTG}}$/ min^{-1}	Δm_t/ %	$T_{10\%}$/ °C	$T_{15\%}$/ °C	Δm_T/% T'=390°C	Δm_T/% T'=400°C
PAM 1	4.1	27.9	413.0	398.8	4.088	15.5	488.0	1.473	47.5	391.3	405.2	9.7	12.8
PAM 2	8.3	29.9	417.4	≈414	3.706	14.6	482.4	1.742	52.8	352.3	387.1	15.7	18.3
PAM 3	8.0	36.1	414.0	≈412	3.674	7.4	579.0 619.0	0.790 0.621	51.5	352.1	384.3	16.3	19.2
PAM 4	7.8	24.1	412.0	≈409	2.683	7.2	592.0 617.0	0.547 0.559	39.1	369.9	397.4	13.2	15.7
PAM 5	5.6	42.7	407.0	≈405	3.978	5.8	–	–	54.1	361.3	382.2	17.6	21.5
PAM 6	1.3	56.3	438.0	≈434	6.064	6.9	–	–	64.8	404.5	417.1	6.4	8.7
PAM 7	4.1	49.5	415.0	–	10.160	9.0	–	–	60.9	392.7	402.1	9.0	13.7
PAM 8	10.9	38.4	402.0	–	4.419	23.5	–	–	61.9	277.9	354.9	25.5	29.8
PAM 9	2.8	43.3	441.5	≈425	5.160	8.6	–	–	54.7	416.9	428.7	4.5	5.6

%Δm=mass loss; %Δm_t=total mass loss; T_{max}^{DTG}=temperature corresponding to maximum rate; T_{max}^{DSC}=temperature corresponding to maximum of DSC curve; $v_{T_{max}^{DTG}}$= rate at T_{max}^{DTG}; $T_{x\%}$ – temperature corresponding to *x%* mass loss; %Δm_T=mass loss at the temperature T

Table 2 The parameters of non-isothermal degradation in static air atmosphere of PAM1–PAM9

	Process I	Process II				Process II’			Process III								
Polymer	Δm/ %	Δm/ %	T_{max}^{DTG}/ °C	T_{max}^{DSC}/ °C	$\nu_{T_{max}^{DTG}}$/ min^{-1}	Δm/ %	T_{max}^{DTG}/ °C	T_{max}^{DSC}/ °C	Δm/ %	T_{max}^{DTG}/ °C	T_{max}^{DSC}/ °C	$\nu_{T_{max}^{DTG}}$/ min^{-1}	Δm_t/ %	$T_{10\%}$/ °C	$T_{15\%}$/ °C	Δm_T/% T’= 390°C	Δm_T/% T’= 400°C
PAM 1	2.5	6.7	330.5	392.2	1.116	–	–	–	63.6	645.5	635.1	4.060	72.8	396.0	471.1	9.7	10.2
PAM 2	5.0	12.8	334.9	341.4	1.963	–	–	–	68.0	635.2	610.4	3.562	85.8	329.6	357.4	17.4	17.8
PAM 3	2.7	9.9	369.5	359.9	1.499	14.0	417.0	–	58.9	637.0	611.0	4.133	85.6	364.5	398.8	13.6	15.2
PAM 4	1.5	6.8	369.5	–	0.689	6.6	371.5	370.0	70.2	626.5	619.0	3.086	78.6	326.8	383.5	15.6	16.6
PAM 5	7.1	19.0	341.2	350.0	2.180	–	–	–	53.3	603.7	585.6	3.095	79.4	316.4	341.9	22.4	23.4
PAM 6	3.0	21.0	364.3	386.5	3.710				38.1	636.0	554.4 605.1	2.410	62.1	404.3	417.8	6.3	8.7
PAM 7	1.8	9.0	341.7	344.8	2.211	28.9	386.7	393.0	40.4	596.7	564.5	3.160	80.1	369.7	384.1	23.3	28.2
PAM 8	4.3	14.7	347.0	346.0	3.148	25.2	397.0	403.8	42.8	582.0	564.0	2.854	87.0	343.4	362.7	19.6	34.7
PAM 9	3.2	4.7	351.0	–	0.739	13.5	421.0	420.0	67.0	558.9 644.8	580.0 633.3	4.230	88.4	417.0	422.7	7.4	7.8

%Δm=mass loss; %Δm_t=total mass loss; T_{max}^{DTG}=temperature corresponding to maximum rate; T_{max}^{DSC}=temperature corresponding to maximum of DSC curve; $\nu_{T_{max}^{DTG}}$= rate at T_{max}^{DTG}; $T_{x\%}$ – temperature corresponding to $x\%$ mass loss; %Δm_T=mass loss at the temperature T

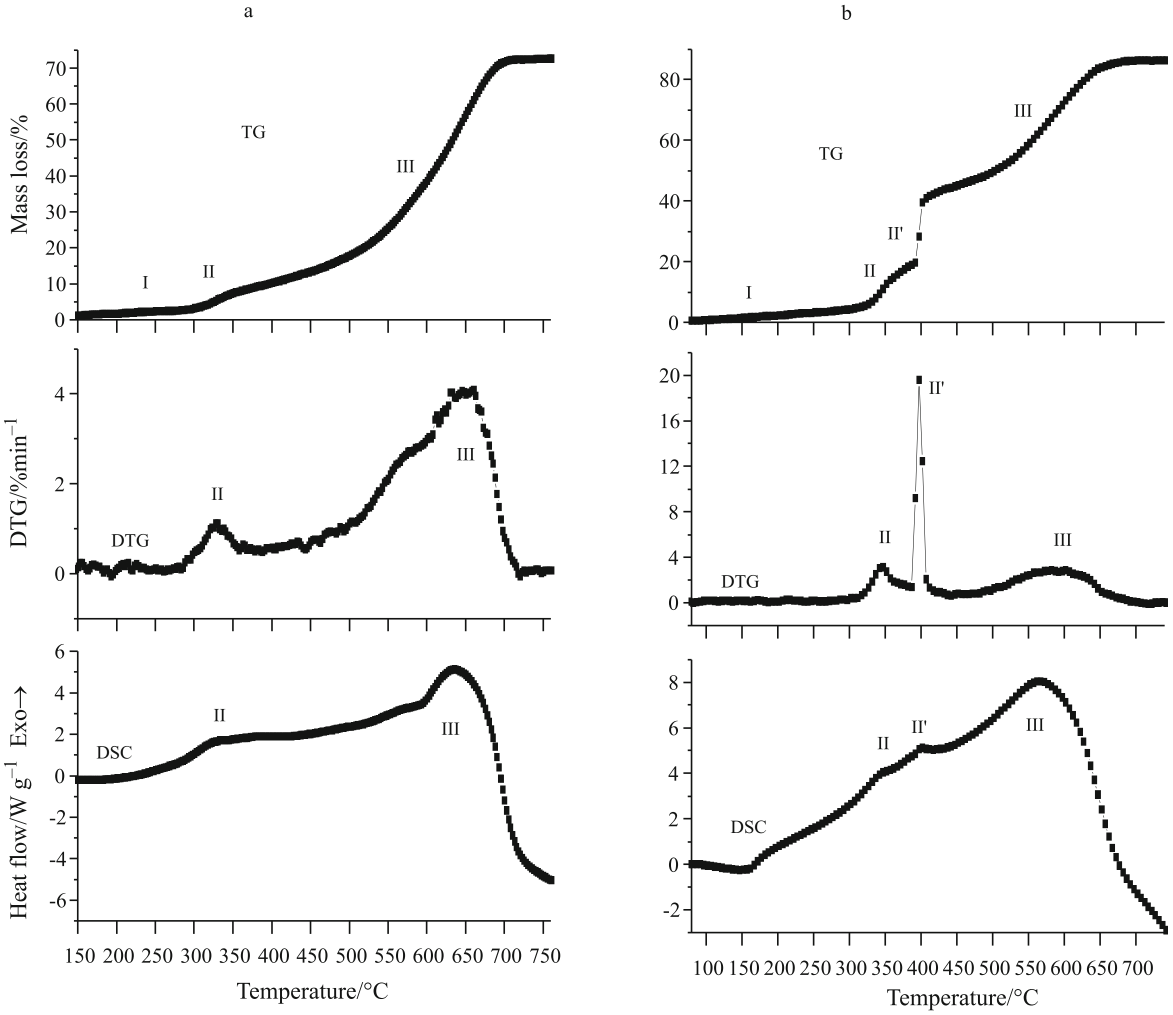

Fig. 2 TG, DTG and DSC curves obtained by heating in air static atmosphere of a – PAM1 and b – PAM8. PAM2, PAM5 and PAM6 have similar TG, DTG and DSC curves with PAM1. PAM3, PAM4, PAM7 and PAM9 have similar TG, DTG and DSC curves with PAM8

$341.5°C \le T_{max}^{DSC} \le 386.5°C$; for process III: $596.7°C \le T_{max}^{DTG} \le 645.5°C$ and $585.5°C \le T_{max}^{DTG} \le 635.1°C$).

It is plausible that SiO_2 to be the final product of the thermo-oxidative degradation of all investigated polymers. The check of this assumption was performed by comparing of calculated and experimental values of total mass losses. The results listed in Table 3 support this hypothesis. Some differences between calculated and experimental values could be due to the heterogeneity of each polymer and the inherent experimental errors.

For the reasons above mentioned, the thermo-oxidative stability will be also discussed for two groups of polymers, namely: PAM1-PAM6 (polymers with R_2 without ether functions) and PAM7-PAM9 (polymers with R_2 containing ether functions). The criteria of thermo-oxidative stability are the same with those used for establishing of thermal stability. The analysis of the data listed in Table 2 leads to the following orders of thermo-oxidative stability:

- for PAM1-PAM6 and $T_{10\%}$ criterion: PAM6>PAM1>PAM3>PAM2>PAM4>PAM5;
- for PAM1-PAM6 and $T_{15\%}$ criterion: PAM1>PAM6>PAM3>PAM4>PAM2>PAM5;
- for PAM1-PAM6, and $\%\Delta m_T$ criteria: PAM6>PAM1>PAM3>PAM4>PAM2>PAM5;
- for PAM7-PAM9 and $T_{10\%}$, $T_{15\%}$ and $\%\Delta m_T$ (T=400°C) criteria: PAM9>PAM7>PAM8;
- for PAM7-PAM9 and $\%\Delta m_T$ (T=390°C) criterion: PAM9>PAM8>PAM7.

The obtained results suggest that the thermo-oxidative degradation begins with the destruction of the ether bond from Si–CH_2–O-phenyl groups and not by the break of siloxanic $(Si(CH_3)_2–O)_6$ groups. A support of this assumption is the relative high thermo-oxidative stability of PAM6, which has $(Si(CH_3)_2–O)_6$

Table 3 The calculated and experimental values of the total mass loss

Polymer	(calc)/%	(exp)/%	*e*%
PAM1	76.4	72.8	4.95
PAM2	79.6	85.8	–7.23
PAM3	80.1	85.6	–6.43
PAM4	75.4	78.6	–4.07
PAM5	72.5	79.4	–8.69
PAM6	64.8	62.1	4.35
PAM7	83.4	80.1	4.12
PAM8	82.9	87.0	–6.22
PAM9	84.7	88.4	–4.19

$$e\%=\frac{\Delta m(\text{calc})-\Delta m(\text{exp})}{\Delta m(\text{exp})}\cdot 100$$

groups and the lowest number of Si–CH_2–O-phenyl groups per mass unit.

Unlike the thermal stability, PAM4 exhibits a thermo-oxidative stability lower than PAM3. This means that thermo-oxidative reactivity depends on not only the number of aromatic rings from R_2, but also on the kind of bonding of R_2 within the macromolecular chain (*p*, *p*' in PAM3 and *m*. *m*' in PAM4) and the nature of the aliphatic group.

The results obtained for PAM7-PAM9 show that –O– function bonded with two aromatic rings determines the highest thermo-oxidative stability of PAM9. The lower thermo-oxidative reactivity of PAM7 and PAM8 could be due to aliphatic–O–aliphatic and aliphatic–O–aromatic groups from R_2.

Conclusions

- The processes that occur at the progressive heating of some poly(siloxane-azomethine)s in inert (argon) and oxidative (air) atmospheres were put in evidence by simultaneous TG, DTG and DSC analyses.
- The non-isothermal data were used for establishing of orders of thermal and thermo-oxidative stabilities of these polymers.
- The obtained orders of thermal and thermo-oxidative stabilities were discussed in relation with the structures of investigated polymers.
- The obtained results associated with those resulted by other methods of characterization can be used for the proper selection of the poly(siloxane-azomethine) in some applications.

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References

1 C. Racleş, V. Cozan and I. Sajo, High Perform. Polym., 19 (2007) 541.
2 H. Niu, Y. Huang, X. Bai, X. Li and G. Zhang, Mater. Chem. Phys., 86 (2004) 33.
3 I. A. Alkskas and B. A. El-Gnidi, Macromol. Sci-Pure Appl. Chem., 43 (2006) 1435.
4 A. El-Shekeil, M. A. Khader and A. Abu-Bakr, Synth. Met., 143 (2004) 147.
5 Z. I. Ali, H. A. Youssef, H. M. Said and H. H. Saleh, Thermochim. Acta, 438 (2005) 70.
6 J. Chrusciel, G. Janowska, P. Rybinski and L. Slusarski, J. Therm. Anal. Cal., 84 (2006) 339.
7 E. Rudnik, G. Matuschek, N. Milanov and A. Kettrup, J. Therm. Anal. Cal., 85 (2006) 267.

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