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Thermogravimetric studies of poly(oxymethylene-co-dimethylsiloxane) copolymers

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Abstract

The thermal stability and kinetic parameters of a series of poly(oxymethylene-co-dimethylsiloxane) copolymers have been studied by thermogravimetry from 303 to 846 K under nitrogen flow. The new copolymers, obtained by ring-opening copolymerization of 1,3,5-trioxane and hexamethylcyclotrisiloxane, contain different concentrations of oxymethylene and dimethylsiloxane comonomer units. The results of the thermal studies were compared with data corresponding to pure poly(oxymethylene) and poly(dimethylsiloxane). The copolymers with low concentration of dimethylsiloxane comonomer units show only one degradation process, but copolymers richer in this co-unit degrade in two stages. Copolymers with an even higher concentration of dimethylsiloxane co-unit have three decomposition processes. The TGA results indicate that the molecular structure of the copolymers correspond to block copolymers and random copolymers bonded to segments formed by both pure poly(oxymethylene) and poly(dimethylsiloxane). The structures depend on the composition of the copolymers. The pre-exponential factors, the reaction orders and the activation energies have been determined from non-isothermal thermogravimetric data.

INTRODUCTION

Thermogravimetric analysis (TGA) measures the amount and rate of the change in sample weight as the temperature is varied, providing definitive data for materials selection and product design. Typical applications include analysis of the composition of materials, and their thermal and oxidative stability, and kinetics studies. In the electronics industry, materials used for printed-circuit boards and electronic components must meet rigid electrical, thermal, and mechanical specifications. TGA techniques have been applied to both research and development and

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quality-assurance areas to test these materials. Polymers in the form of thermoplastic materials or thermosetting resins have, over the past several years, greatly increased their areas of applications. It is therefore pertinent to describe how TGA can be used to characterize these products.

Kinetic parameters such as activation energy, pre-exponential factor and reaction order, give a quantitative measure of thermal stability [1]. The present work reports on a study of the non-isothermal degradation of poly(oxymethylene-co-dimethylsiloxane) copolymers prepared from 1,3,5-trioxane (TOX) and hexamethylcyclotrisiloxane (D_3) [2]. The influence of the copolymer composition on the thermal decomposition process was analysed and their kinetic parameters determined.

EXPERIMENTAL

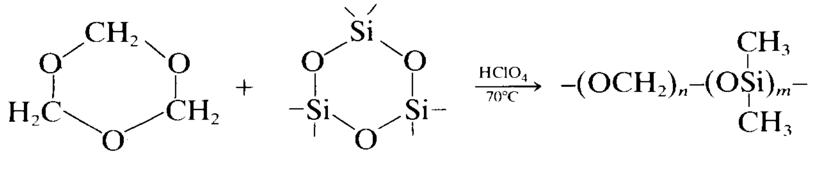
The poly(oxymethylene-co-dimethylsiloxane) copolymers were obtained by ring-opening copolymerization of TOX with D_3 in the molten state at 343 K, using anhydrous perchloric acid as cationic initiator. The samples were washed with dichloromethane and methanol and dried under vacuum at room temperature. The composition of the comonomer units, oxymethylene ($-OCH_2-$) and dimethylsiloxane ($-OSi(CH_3)_2-$), in the copolymers depends on the concentration of TOX and D_3 in the initial reaction mixture [2]. The composition was determined by elemental analysis expressed as the molar fraction of dimethylsiloxane comonomer units, X_{DMS}.

The TGA was carried out on samples obtained directly from the reaction medium. Thermogravimetric data were obtained using a Perkin-Elmer PC-series TGA-7 thermobalance. Samples (2–6 mg) were placed in aluminium pans and heated under flowing nitrogen (50 cm^3 min^{-1}) at a rate of 10 K min^{-1} between 303 and 846 K.

RESULTS AND DISCUSSION

Thermal decomposition temperatures

The poly(oxymethylene-co-dimethylsiloxane) copolymers were synthesized according to the reaction



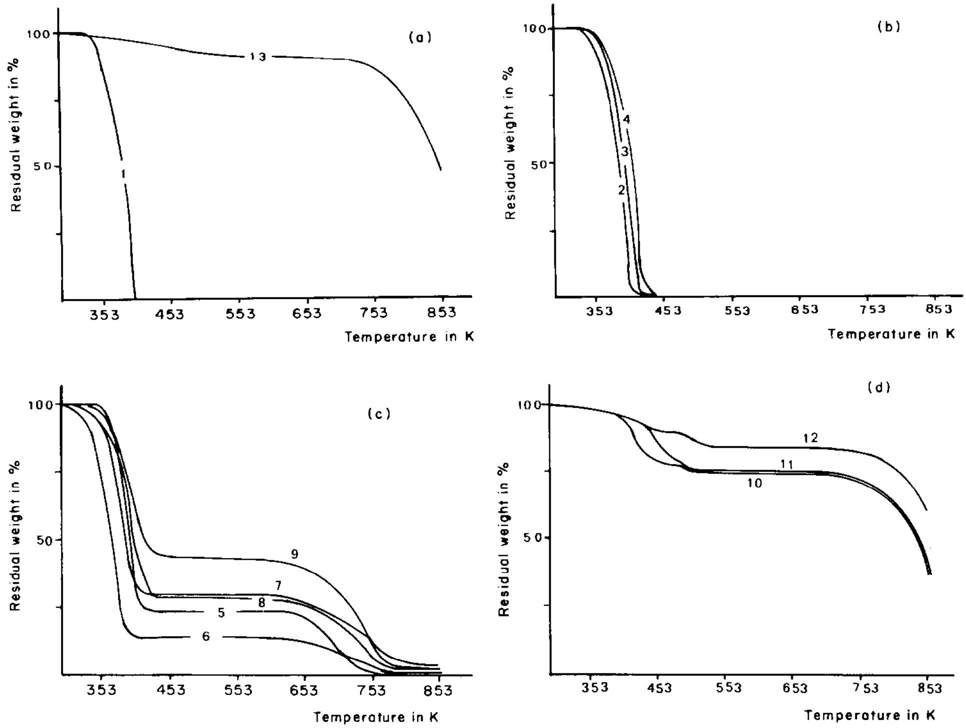


Fig. 1. (a)–(d) Thermogravimetric curves of poly(oxymethylene-co-dimethylsiloxane) copolymers recorded at a heating rate of 10°C min^{-1}: curve 1, poly(oxymethylene); curves 2–12, copolymers; curve 13, poly(dimethylsiloxane).

Figure 1 shows the change in sample weight as a function of time and temperature when the poly(oxymethylene-co-dimethylsiloxane) copolymers were heated from 303 to 846 K.

The thermogravimetric curves for poly(oxymethylene) (Fig. 1(a), curve 1) and also of the copolymers 2, 3 and 4 (Fig. 1(b)) show a single-stage process and similar thermal decomposition temperatures (T_{D1}) because the concentration of the dimethylsiloxane comonomer units is very low. In general, the T_{D_1} values increase when the mole fraction X_{DMS} also increases (see Table 1).

The copolymers 5–9 (Fig. 1(c)) show a two-stage degradation process; the first has a T_{D1} which is very similar to that of pure poly(oxymethylene), and the T_{D3} of the second process is analogous to that of pure poly(dimethylsiloxane). This suggests that the molecular structure of copolymers 5–9 corresponds to block copolymers.

In copolymers 10–12 (Fig. 1(d)), a three-stage degradation process can be observed (most clearly in sample 12), corresponding to degradation of segments formed by almost only oxymethylene comonomer units (first stage), of those bonded to segments of random copolymers (second stage)

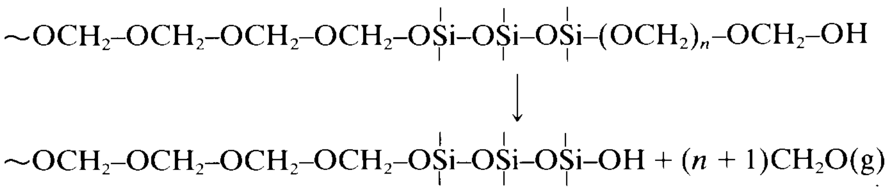
TABLE 1

Thermal decomposition temperatures of different degradation stages (T_{D1}, T_{D2}, T_{D3}) and residual masses for poly(oxymethylene-*co*-dimethylsiloxane) copolymers

Copolymer	X_{DMS} [a]	T_{D1}/ K	r_{m1}/ %	T_{D2}/ K	r_{m2}/ %	T_{D3}/ K
1	0.00	335	0.00	–	–	–
2	0.016	338	0.73	–	–	–
3	0.017	350	1.45	–	–	–
4	0.026	352	0.78	–	–	–
5	0.028	355	23.75	–	–	643
6	0.031	332	14.38	–	–	646
7	0.042	339	28.75	–	–	672
8	0.044	347	28.13	–	–	668
9	0.050	352	43.75	–	–	693
10	0.054	393	76.88	483	75.00	752
11	0.330	431	79.06	486	75.63	753
12	0.350	405	89.38	488	85.00	765
13	1.00					768

[a] Mole fraction of dimethylsiloxane comonomer units in the copolymers.

and of those bonded to segments formed by almost exclusively dimethysiloxane comonomer units (third stage). Figure 1(d) also shows that the concentration of the random segments is low. The weight loss curve of the random copolymer segments lies in a temperature range between its two homopolymers. However, the block copolymers 5–9 show an initial weight loss step that reflects the oxymethylene content. The same behaviour was found for styrene-α-methyl styrene blocks and random copolymers obtained by anionic polymerization [3]. The higher thermostability of the random copolymer segments in comparison to pure poly(oxymethylene), which thermally decomposes via a free radical mechanism with production of gaseous formaldehyde [4, 5], is explained by the presence of $-OSi(CH_3)_2-$ co-units that are distributed statistically on the POM chains, inhibiting the degradation process:



$$\sim\mathrm{OCH_2{-}OCH_2{-}OCH_2{-}OCH_2{-}O\overset{|}{\underset{|}{Si}}{-}O\overset{|}{\underset{|}{Si}}{-}O\overset{|}{\underset{|}{Si}}{-}(OCH_2)_{\mathit{n}}{-}OCH_2{-}OH}$$
$$\downarrow$$
$$\sim\mathrm{OCH_2{-}OCH_2{-}OCH_2{-}OCH_2{-}O\overset{|}{\underset{|}{Si}}{-}O\overset{|}{\underset{|}{Si}}{-}O\overset{|}{\underset{|}{Si}}{-}OH} + (n+1)\mathrm{CH_2O(g)}$$

Sample 13 (Fig. 1(a)) corresponds to pure poly(dimethylsiloxane) and shows only one degradation process. A free radical mechanism was proposed in order to explain the routes of the dimethylsiloxane degradation [6].

Table 1 shows the thermal decomposition temperatures T_{D1}, T_{D2} and T_{D3} for the different degradation processes for each copolymer. These values were taken from the first large change in the slope of the TG curve. It is interesting to note that the T_{D1} values move away from the T_D value of pure POM, and that the T_{D3} values approach to T_D value of pure poly(dimethylsiloxane), when the mole fraction X_{DMS} increases.

According to the above discussion, the molecular structures of the copolymers are given in Scheme 1.

Homopolymer 1	■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■■
Copolymers 2–4	■■■■■■■■○■■■■■■■■■○■■■■■■■■■■■■■■■■■
Copolymers 5–9	■■■■■○■■■■■■■■■■■—○○○○○○■○○○○○○○○○○○
Copolymers 10–12	■■■■○■■—■○■■○■○■■■○■—○○○■○○○○○○○○○○○
Homopolymer 13	○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○○

Scheme 1. Molecular structures of the copolymers. ■, $-OCH_2-$; ○, $-OSi(CH_3)_2-$.

Kinetic parameters

The decomposition reaction is irreversible and the rate-dependent parameters such as activation energy and reaction order can be calculated from a single experimental curve [7].

The thermal decomposition kinetics of the thermogravimetric weight loss was attributed to the kinetic equations

$$-\mathrm{d}\alpha/\mathrm{d}t = K(1-\alpha)^n \tag{1}$$

where α is the fraction of sample weight reacted at time t, n is the reaction order and K is the specific rate constant. The reaction rate $\mathrm{d}\alpha/\mathrm{d}t$ was calculated using a differential technique which included the heating rate v (10°C min^{-1}), and using temperatures versus sample weight-fraction data [8].

By combining the Arrhenius equation

$$K = Z\exp(-E/RT) \tag{2}$$

where Z is the frequency factor, E the activation energy, R the gas constant and T the absolute temperature, with eqn. (1), and after introducing v, we obtain the logarithmic equation

$$\beta = \ln\left[-v\frac{\mathrm{d}\alpha/\mathrm{d}T}{(1-\alpha)^n}\right] = \ln Z - \frac{E}{RT} \tag{3}$$

A linear multiple regression program was used to calculate the kinetic parameters E and Z. Plotting β against $1/T$ should give a straight line, and

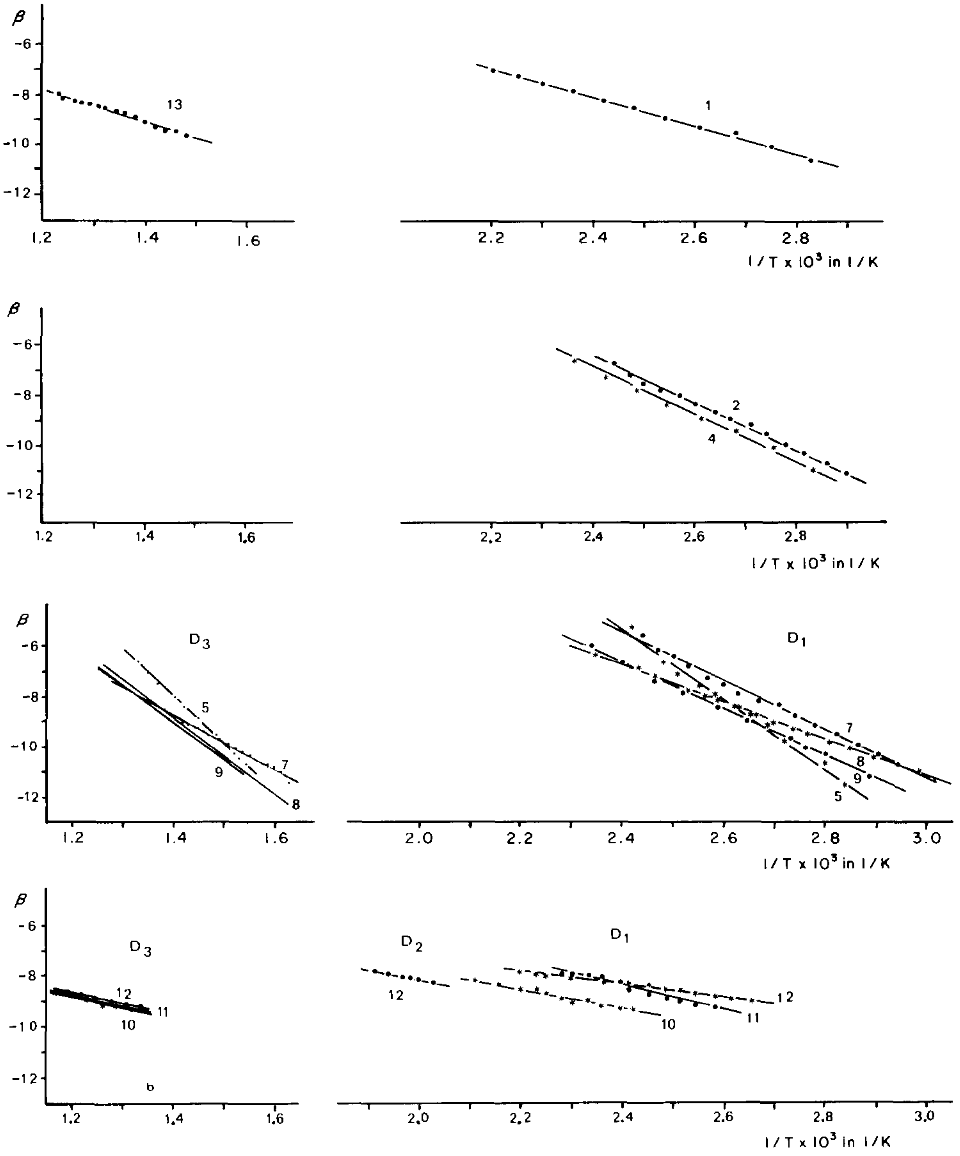


Fig. 2. Arrhenius plots for the thermal degradation of poly(oxymethylene-co-dimethylsiloxane) copolymers according to eqn. (3). D_1, D_2 and D_3 corresponds to the first, second and third stages of the degradation processes: plot 1, poly(oxymethylene); plots 2–12, copolymers; plot 13, poly(dimethylsiloxane).

E and *Z* are determined from the slope and intercept (see Fig. 2). The degradation processes were considered to be independent, and *E*, *Z* and *n* were determined for each stage. The linear relationships obtained indicated that the reactions are of order −0.25 for the homopolymers and copolymers that have a single-stage process (samples 1, 2, 4 and 13) and −0.50 for those

TABLE 2

Kinetic parameters of poly(oxymethylene-*co*-dimethylsiloxane) copolymers

Copolymer	Z_1/s^{-1}	E_1/(kcal mol^{-1})	n_1	Z_2/s^{-1}	E_2/(kcal mol^{-1})	n_2	Z_3/s^{-1}	E_3/(kcal mol^{-1})	n_3
1	2.6×10^2	11.30	−0.25						
2	2.2×10^6	17.53	−0.25						
4	7.9×10^5	17.12	−0.25						
5	5.8×10^{11}	26.89	−0.50				1.1×10^8	37.54	−0.50
6	7.3×10^5	15.46	−0.50				2.3×10^6	32.46	−0.50
7	8.3×10^4	14.92	−0.50				3.4×10^5	30.50	−0.50
8	3.4×10^6	17.64	−0.50				3.8×10^5	30.87	−0.50
9	3.6×10^7	18.99	−0.50				4.4×10^2	21.17	−0.50
10	0.781	7.53	0	–	–	–	0.023	8.24	0
11	84.3	10.61	0	–	–	–	0.031	8.75	0
12	0.144	5.28	0	1.32×10^{-2}	3.78	0	0.032	8.78	0
13							1.013	12.88	−0.25

that show two degradation processes (samples 5–9). A negative value of *n* indicates that the decomposition rate is higher with lower amounts of material being degraded. Depending on the analytical methods, a reaction order of −0.15 was found for poly(oxymethylene) [9]. For the copolymers 10–12, with three degradation processes, the linear relationships obtained indicated that the order of the reactions is zero. It seems likely that they exhibit a complex decomposition kinetics because of their mixed molecular structures. The coefficients of linear correlation varied from 0.980 to 0.999. The kinetic parameters *n*, *E* and *Z* calculated from these plots are summarized in Table 2. For copolymers 10 and 11, it was not possible to determine the kinetic parameters of the second degradation process due to the small weight loss corresponding to this stage.

The *E* value for POM of 11.30 kcal mol^{-1} is similar to that reported in the literature [9]. In general, the activation energies increase at higher frequency factors.

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