ELSEVIER

Polymer 43 (2002) 2011–2015

polymer

www.elsevier.com/locate/polymer

Thermal polydimethylsiloxane degradation. Part 2. The degradation mechanisms

G. Camino[a,*], S.M. Lomakin[b], M. Lageard[c]

[a]Department of Material Science and Chemical Engineering of Politechnic of Turin, Viale T. Michel 5, 15100 Alessandria, Italy
[b]Institute of Biochemical Physics, Russian Academy of Sciences, 117978, Kosygin 4, Moscow, Russian Federation
[c]Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica del Materiali dell'Università, Via P. Giuria 7, 10125 Torino, Italy

Received 18 September 2001; received in revised form 20 November 2001; accepted 2 December 2001

Abstract

The products of the thermal degradation of polydimethylsiloxane (PDMS) are determined by the heating conditions, since two competing mechanisms are involved.

Cyclic oligomers are formed in the low degradation temperature range and during slow heating in programmed degradation. This involves molecular splitting of oligomers from loop conformations of the PDMS chain favoured by its flexibility, and assistance on the part of empty silicon d-orbitals.

Methane and oligomers are formed in the high temperature range and during fast heating. This shows that homolytic scission of Si–CH_3 also takes place and is followed by hydrogen abstraction.

Keywords: Polydimethylsiloxane; Thermal Degradation; Oligomer

1. Introduction

The mechanisms of the thermal degradation of polydimethylsiloxane (PDMS) end-blocked with (CH_3)Si-groups have been intensively studied [1,2]. Degradation in an inert atmosphere (N_2) and under vacuum results in depolymerisation and the production of cyclic oligomers [3,4]. The trimer is the most abundant product, with irregularly decreasing amounts of the tetramer, pentamer and hexamer and higher oligomers [3].

Examination of linear and cyclic PDMS has indicated that they share a common molecular depolymerisation mechanism [5]. Nielsen [6] has proposed that cationic reactions on a glass surface (borosilicate, quartz) contributes to the depolymerisation of linear PDMS, while Zeldin et al. [7] suggest that it may be catalysed by ionic impurities from the walls of Pyrex glass vessels. The small amounts of macro-cycles (>10 Si atoms) formed during the thermal degradation of PDMS have also been the subject of attention [8]. Their presence points to ionic ring-opening polymerisation reactions and formation of a distribution of cyclic species. Clarson and Semlyen [9], in fact, have demonstrated ring-opening polymerisation catalysed by ions of the surface of the glass, when the cyclic tetramer, octamethylcyclotetrasiloxane is heated at 420 °C under vacuum in a Pyrex vessel. The degradation products are consistent with subsequent formation of cyclic species from the linear high molecular mass PDMS [9].

It can be thus assumed that at temperatures below 500–600 °C, PDMS depolymerise completely in an inert atmosphere and do not form a solid residue, whereas in air their decomposition is accompanied by the formation of some white silica powder [10]. However, the products of the thermal PDMS degradation are essentially determined by the temperature and the heating rate. This question is examined in depth in the present paper.

2. Experimental

2.1. Materials

Polydimethylsiloxane end-blocked with trimethyl-siloxy-groups $(CH_3)_3$Si-containing a vinyl-methyl-siloxane unit every 1400th –$(CH_3)_2$–Si–O unit (V1400) with a viscosity of 8×10^6 mPa was supplied by Wacker–Chemie Gmbh. The effect of cross-linking involving –C=C– bonds during the thermal degradation of PDMS can be ignored owing to its very low cross-linking density.

* Corresponding author. Tel.: +39-0131-229-318; fax: +39-0131-229-331.
E-mail address: gcamino@mail.polial.polito.it (G. Camino).

0032-3861/02/$ - see front matter
PII: S0032-3861(01)00785-6

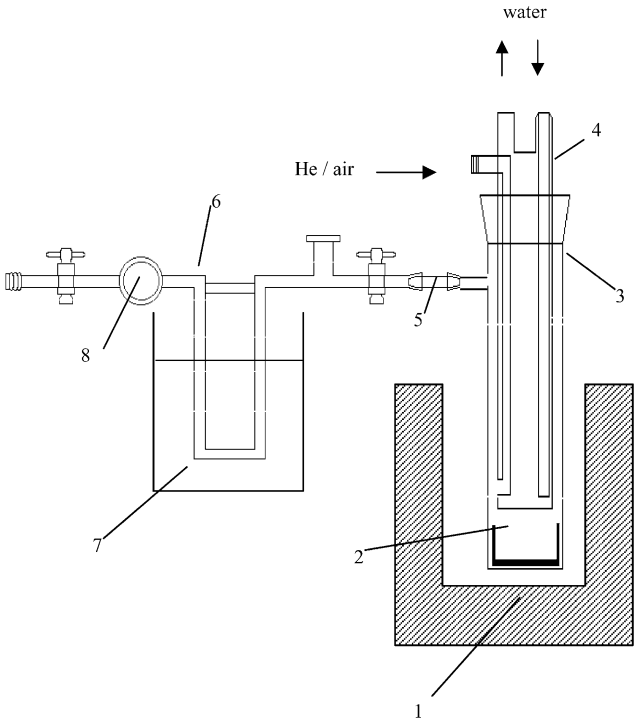


Fig. 1. Scheme of pyrolyser apparatus. 1 – furnace; 2 – quartz sample container; 3 – quartz degradation vessel; 4 – water cooled cold finger for high boiling products condensation; 5 – removal connector; 6 – U-trap for low boiling and gaseous products condensation; 7 – Dewar cooling system; 8 – KBr windows for gases IR examination.

2.2. Thermal degradation

Degradation in He or air was carried in the glass apparatus of Fig. 1. In air, methanol cooled at −78 °C was used to condense volatiles and gases in the trap and avoid oxygen condensation. In He, liquid nitrogen was used.

The 'programmed heating' conditions were 10°/min to 80 °C; equilibration for 1 min; 10 °C/min from 80 to 400 °C, then isothermal 1 h.

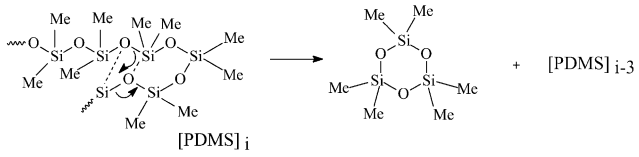
For 'flash pyrolysis', the samples were heated at 80°/min to 800 °C and kept at this temperature for 10 min.

The U-trap with low boiling gaseous and condensed liquid products of degradation was then removed. The gaseous products were analysed by FTIR, while the condensed liquid products were dissolved in $CHCl_3$ together with high boiling products condensed on the water-cooled cold finger and analysed using GC–MS. The solid decomposition residue was ground to a fine powder, mixed with KBr and then pressed into pellets for IR analysis.

2.3. Products analysis

IR spectra were obtained using a Perkin–Elmer 2000 Fourier transform, IR spectrophotometer: number of scans 16, gain 1.

GC–MS data were obtained with a Hewlett Packard CG 5890 A chromatograph coupled to a Hewlett Packard MSD 5970 mass spectrometer detector using a HP-5 capillary column filled with cross-linked 5% methyl-silicon (30 m). Detector temperature is 290 °C, injector temperature, 280 °C, oven maximum temperature, 280 °C, solvent delay time, 4.00 min, heating rate, 10 °C/min, and isothermal conditions, 4.00 min.



Scheme 1. PDMS molecular depolymerisation mechanism.

2.4. Thermal analysis

Thermogravimetry (TG) was performed on a Du Pont 1950 Vertical TG balance connected to a Du Pont 2100 thermal analyser, with a 100 ml/min nitrogen or air flow.

3. Results and discussion

3.1. Slow heating rate

The thermal degradation of PDMS to cyclic oligomers has been illustrated in a well-known depolymerisation diagram [10]. It has been suggested that the formation of an intramolecular, cyclic transition state is the rate-determining step [10]. Silicon d-orbital participation was postulated with siloxane bond rearrangement leading to the elimination of cyclic oligomers and shortening of the chain. The mechanism for formation of the smallest cyclic product, hexamethylcyclotrisiloxane, is illustrated in Scheme 1.

This transition state can be formed at any point of the polymer chain, and the process can take place indefinitely within a chain, until the residual linear structure is too short to cyclise.

Fig. 2 shows the gas chromatogram of the liquid degradation products of PDMS heated for 1 h under 50 ml/min. He

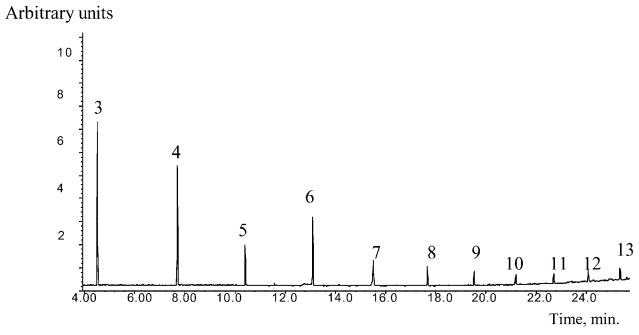


Fig. 2. Gas chromatogram of PDMS liquid degradation products (He, 400 °C), ('programmed heating' conditions). Figures on peaks: degree of polymerisation of cyclic oligomers (Table 1).