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Model polydimethylsiloxanes subjected to thermal weathering: effect on molecular weight distributions

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Abstract

We have subjected samples of model polydimethylsiloxanes of narrow molecular weight distribution to thermo-oxidation in an air circulating oven. Samples remained for up to 1760 h at 200°C under a standard atmosphere. Loss of average molecular weight and broadening of molecular weight distributions was observed. We have modeled the process assuming that both crosslinking and scission are present simultaneously. We have tried to interpret the experimental data in two different ways: either assuming that the ratio of crosslinking to scission was not constant, or that there is an induction period with no reaction before the polymer shows measurable effects of the attack. We discuss the relative merits of both interpretations. © 2000 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Thermal degradation; Model polydimethylsiloxanes; Crosslinking; Scission; Mathematical model

1. Introduction

Many polymers are used in hostile environments where heat, oxidizing atmospheres or ultraviolet radiation combine to create favorable conditions for degradative processes. These processes consist mainly in a series of crosslinking and scission reactions which induce changes in the properties of the material. It is generally accepted that both reactions occur simultaneously, and almost always one predominates over the other one. The relative importance of these reactions depends on the material and the environmental conditions. For example, in vacuum irradiation of polyethylene and polydimethylsiloxane crosslinking predominates, while in polypropylene scission is more important. Since in the degradative process the material loses part of its original properties, it may in time become inappropriate for its intended use. For this reason it is important to quantify the damage that the molecular properties of a given material will undergo under degradation.

The utilization of materials with a narrow molecular weight distribution is extremely useful to detect clearly the onset and evolution of species of higher and lower molecular weights that result from the scission and crosslinking reactions. In previous publications [1–3] we have shown that the use of size exclusion chromatography (SEC), applied to narrow distribution hydrogenated polybutadienes subjected to irradiation, simplifies considerably the quantitative analysis of those reactions. In this work we report the results of a study on the degradation of a narrow distribution model polydimethylsiloxane (PDMS) obtained by anionic polymerization of hexamethylcyclotrisiloxane. The degradation was performed by thermo-oxidation in an air circulating oven. The changes in the molecular weight distribution at different exposure times have been followed by SEC. A mathematical model that was previously proposed to explain the alterations of the molecular structure of hydrogenated polybutadienes subjected to irradiation has been modified to explain the degradation process. We found that two different scenarios could explain the observed experimental data, and we discuss the relative merits of these two different interpretations.

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2. Experimental

A linear polydimethylsiloxane (PDMS) with a vinyl end termination was synthesized by anionic polymerization of hexamethylcyclotrisiloxane. The reaction was carried out under vacuum on a specially designed glass reactor. *n*-Butyl-lithium in hexane was used as initiator, *n*-hexane was employed as solvent and tetrahydrofuran (THF) was used as solvating agent to allow the propagation of the reaction. Vinyldimethylchlorosilane was employed as termination agent. When the polymerization was completed, the terminal vinyl group of the linear chains was deactivated by reaction of the polymer with triethylsilane in the presence of chloroplatinic acid as catalyst. More details on the synthesis procedure may be found on previous publications [4,5].

The synthesized PDMS was characterized with SEC by dissolving the polymer in distilled tetrahydrofuran and injecting 200 μl of 0.2% solution in a modular chromatographic system composed by a Waters M-45 pump, a Rheodyne 7010 injection valve, injection loop, and an ERMA 7510 differential refractometer as a detector. Four PL-gel columns, 5 μm average particle size and nominal porosities 500, 1000, 10^4 and 10^5 Å, were employed for the separations at 1 ml/min flow rate with distilled tetrahydrofuran as eluent. Before injection, polymer solutions were passed through 0.45 μm membrane filters. Only the soluble part of the material was analyzed in postgel samples.

Molecular weights of initial PDMS, as well as those after thermal oxidative degradation, were calculated by applying the universal calibration method. Primary calibration was performed with narrow distribution linear polystyrene standards, and the following viscosimetric equation.

$$[\eta] = 6.5 \times 10^{-3} \mathrm{M}^{0.77}$$

valid for PDMS in tetrahydrofuran at 25°C [6], was used to obtain the PDMS average molecular weights.

PDMS films, thickness ca. 100 μm, were prepared by casting hexane solutions on Petri dishes. The dishes containing the dried films were located into an air circulating oven maintained at 200°C, and at selected time intervals a suitable amount of polymer was extracted and analyzed by SEC with the results shown in Table 1. Samples exposed for more than 1350 were only partially soluble indicating the presence of gel fractions.

A PDMS film was cast on a KBr dish and subjected to the complete thermal treatment, during which FTIR measurements of the sample were taken with a Perkin Elmer 1710 instrument at 4 cm^{-1} resolution.

2.1. Mathematical model

We have modeled this system using an extension of a previous model for simultaneous scission and crosslinking of monodisperse polymer chains [3]. That model was developed for polymers which were irradiated with gamma-rays, but most of the assumptions made there should be valid for this particular system: untreated polymer chains are considered to have equal length, any monomeric unit is equally likely to be subject to either crosslinking or scission, all reactions are independent and intramolecular reactions are not explicitly allowed. Similarly to the previous model, since crosslinking and scission are considered to be independent reactions, they are modeled as sequential steps for convenience. It is mathematically easier, and the results are equivalent to a simultaneous crosslinking-scission situation. Unlike the previous model, the ratio of crosslinking to scission is not necessarily constant.

Table 1
Molecular weights of the soluble fraction of PDMS after thermal-oxidation at 200°C[a]

Time (h)	M_n	M_w
0	62 100	78 300
310	61 300	81 200
445	61 700	81 500
600	60 400	88 000
700	60 200	90 900
810	57 300	98 000
900	59 600	106 500
1000	63 700	110 500
1140	66 800	144 300
1250	73 900	177 800
1350	49 600	232 700
1445	83 100	223 100
1510	78 400	195 500
1600	86 100	209 000
1760	90 800	378 100

[a] Polymer remains totally soluble up to 1350 h of treatment.

At any given time of exposure, crosslinking has advanced to a certain conversion α and scission has advanced to a conversion β. It is admissible to talk of "degree of crosslinking" α and "degree of scission" β. Since both α and β are conversions, they may take values between zero and unity. $\alpha = 1, \beta = 0$ would correspond to an extremely densely crosslinked system, where every monomeric unit is connected to another one in a different chain. $\alpha = 0, \beta = 1$, on the other hand, would correspond to a polymer so badly degraded that only monomer remained. For the system at hand we are not interested in such extreme cases. In the situation under study in this work, both α and β are well below unity.

We also admit the possibility of an induction period where neither crosslinking nor scission is present, and assume that the time of exposure in excess of the induction period is directly proportional to $\alpha + \beta$. That is,

$$t - t_{\mathrm{ind}} = k(\alpha + \beta)$$

where t is the time, t_{ind} is the induction period and k is a proportionality constant. This assumption is always valid under the conditions used in this work. In order to completely define the mathematical model, we need either independent determination of α or β as functions of time, or a relationship between the two conversions. We have considered a variety of possible relationships between α and β: constant, linear or quadratic. Details are given in the Appendix.

3. Results and discussion

As indicated in Table 1, the PDMS samples were under treatment at 200°C anywhere from 310 to 1760 h. The treated material remained completely soluble up to 1350 h; the sample treated during 1445 h already contained some gel. The "gel time", then, is somewhere between those times. Molecular weights decrease after the "gel time" because only the soluble part may be analyzed. The larger data dispersion in the postgel region is due to errors introduced by the many manipulations necessary to separate the sol from the gel. The last point is an outlier and should not be considered as valid data.

Siloxane polymers are known to have high thermal and oxidative stability, in comparison with hydrocarbon type polymers, and the thermal reactions are accelerated by oxygen [7]. In PDMS thermally induced radicals of two different types may be formed, either the one on Si atom, following abstraction of a methyl group, or the methylene radical deriving from hydrogen abstraction on the CH_3. Reaction of such radicals with oxygen will lead to introduction of hydroxyl groups in the polymer chains. Infrared spectra were taken on the PDMS samples during the whole thermal treatment, and no signs of oxidized functional groups were detected.

Fig. 1 shows SEC traces of pre-gel samples. The increase in polydispersity is evident. Note also that there is an increase of the amount of material of low molecular weight in excess of what was present in the original sample, an indication of scission. The crosslinking reactions producing high molecular weight chains may occur through recombination between macroradicals, originating different types of stable crosslinks, namely:

$> Si-CH_2-Si <$; $> Si-Si <$; $> Si-CH_2-CH_2-Si <$; $> Si-CH_2-O-CH_2-Si <$.

Chain scission, on the other hand, derive from rupture of the Si–O bond, either directly or induced by neighboring radicals. Intramolecular transfer reactions may also take place with production of cyclic and linear oligomers [7,8]. We then tried to fit the measured average molecular weights to different models. If one decides to neglect scission, which does not seem to be realistic in view of the low molecular weight tails detected by SEC, then the only way to approximate the experimental data points is to consider a delay period where no reaction takes place. Fig. 2 shows the results of this approach for two different delay times. The results are not very good, since no single delay time curve fits adequately all the experimental data points. The measured gel fraction at 1760 h is about 30%, a figure that none of the delay times in Fig. 2 approximates. The predicted values range from 38% for no delay, to 64% for 800 h delay.

Another approach is to consider simultaneous crosslinking and scission. A constant rate of crosslinking to scission does not give good results. A linear variation, however, improves predictions dramatically. We used Powell's method for linearly constrained optimization problems to calculate the best values for the relationship between α and β that would fit the pregel experimental data. The values to be optimized were m_0 and m_f (see

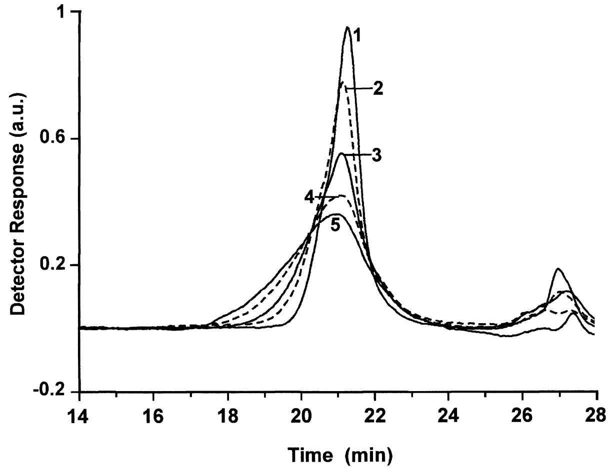

Fig. 1. SEC curves of PDMS sample: initial (1) and after thermal oxidation at 200°C for 600 h (2), 810 h (3), 1140 h (4) and 1350 h (5).

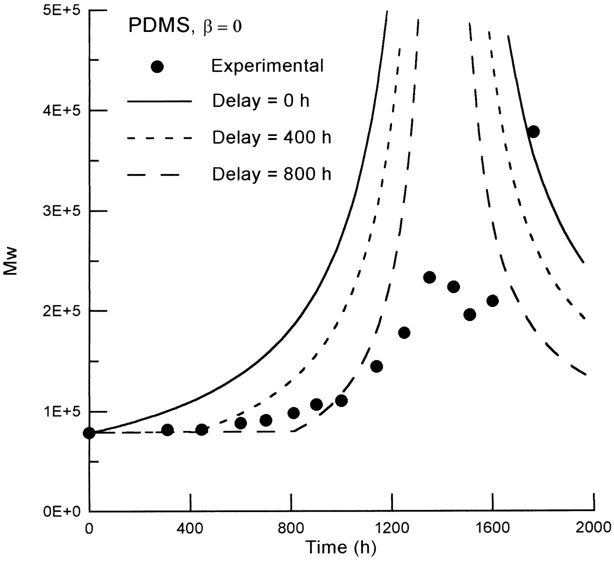

Fig. 2. Prediction of weight average molecular weight as a function of time for a model without scission with different delay times.

the Appendix), while the objective function to be minimized was

$$F = \sum_{i=1}^{N_{\text{data}}} \left| M_{\text{wcalc}} - M_{\text{wexp}} \right|_i$$

where M_{wcalc} is the calculated weight average molecular weight, M_{wexp} is the experimental molecular weight, and N_{data} is the number of experimental data. We found that several sets of values for m_0 and m_{f} gave essentially the same results. Fig. 3 shows the results for one such set. In order to draw this figure we have assumed a linear variation of β with α, starting with scission proceeding at higher rate than crosslinking ($\beta = 2.5\ \alpha$) and ending at $\beta = 1.3\ \alpha$. The starting value is for time zero, and the end value of β is taken to occur at the maximum exposure time. The agreement is better. The objective function reaches a value of 523 328, while for the model without scission and with 800 h delay it was 950 433. Even the predicted gel fraction is closer to the measured value when simultaneous crosslinking and scission are considered. The calculated gel fraction at 1760 h is 28%. Of the two proposed models, the simultaneous crosslinking and scission with the ratio of β to α varying linearly with α gives the best fit to the experimental data.

Contrary to what is seen in γ-irradiation of PDMS, where crosslinking predominates [9,10], low temperature thermal degradation seems to proceed by a different mechanism where scission predominates at the beginning.

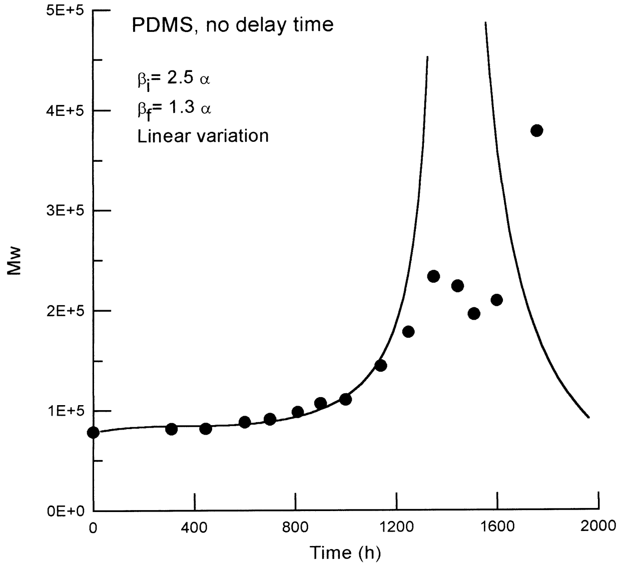

Fig. 3. Prediction of weight average molecular weight as a function of time for a model with simultaneous crosslinking and scission with no delay time. Filled circles indicate experimental data, the full line corresponds to the model predictions.

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Appendix: Possible relationships between α and β

In the proposed model of simultaneous crosslinking and scission we assume that the sum of $\alpha + \beta$ is proportional to the exposure time. We have considered three possibilities for the relationship between the degree of crosslinking α and the degree of scission β. The first one, the simplest, is to assume that the ratio of β to α is constant. In other words,

$$\beta = m\alpha \tag{A1}$$

where the proportionality factor m is constant. This model has not given good results with our data.

A second possibility is to assume that m is not constant, but a linear function of α. The proposed relationship changes to:

$$\beta = m(\alpha)\cdot\alpha = \left(m_0 + \frac{\alpha}{\alpha_{\text{f}}}(m_{\text{f}} - m_0) \right)\cdot\alpha \tag{A2}$$

where subscripts "0" and "f" correspond to initial and final values, respectively. β becomes a quadratic function of α.

The choice of m_{f} and m_0 is subject to some limitations, so that $\alpha + \beta$ will always grow with time. The necessary condition is

$$\frac{\mathrm{d}(\alpha+\beta)}{\mathrm{d}t} = \frac{\mathrm{d}\alpha}{\mathrm{d}t} + \frac{\mathrm{d}\beta}{\mathrm{d}t} = \frac{\mathrm{d}\alpha}{\mathrm{d}t} + \frac{\mathrm{d}\beta}{\mathrm{d}\alpha}\cdot\frac{\mathrm{d}\alpha}{\mathrm{d}t} > 0 \tag{A3}$$

It is reasonable to expect that both α and β should grow with time, since they have been defined as conversions. Assuming that α always grows with time, we get from Eq. (A3) that the condition to be fulfilled is

$$\frac{\mathrm{d}\beta}{\mathrm{d}\alpha} > -1 \tag{A4}$$

This leads to the relationship

$$m_{\text{f}} > \frac{m_0}{2} - \frac{1}{2} \tag{A5}$$

Similarly, if $m(\alpha)$ is taken as a quadratic function of α as indicated in Eq. (A6)

$$m(\alpha) = m_0 + \left(\frac{\alpha}{\alpha_{\text{f}}}\right)^2 (m_{\text{f}} - m_0) \tag{A6}$$

so that β is now the cubic function of α shown in Eq. (A7)

$$\beta = m(\alpha)\cdot\alpha = \left(m_0 + \left(\frac{\alpha}{\alpha_f}\right)^2 (m_f - m_0)\right)\cdot\alpha \tag{A7}$$

then in order to ensure that $\alpha + \beta$ is an increasing function of time we must impose that

$$m_f > \frac{2}{3}m_0 - \frac{1}{3} \tag{A8}$$

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