Available online at www.sciencedirect.com
ScienceDirect
European Polymer Journal 44 (2008) 1548–1555
EUROPEAN POLYMER JOURNAL
www.elsevier.com/locate/europolj

Modelling molecular weight changes induced in polydimethylsiloxane by gamma and electron beam irradiation

Angel J. Satti [b], Noemí A. Andreucetti [a], Jorge A. Ressia [b], Marie F. Vallat [c], Claudia Sarmoria [b], Enrique M. Vallés [b,*]

[a] *Laboratorio de Radioisótopos, Dpto. de Química Universidad Nacional del Sur (UNS), 8000 Bahía Blanca, Argentina*
[b] *Planta Piloto de Ingeniería Química, (PLAPIQUI-UNS-CONICET) Camino "La Carrindanga", Km 7, CC 717, 8000 Bahía Blanca, Argentina*
[c] *Institut de Chimie des Surfaces et Interfaces, UPR CNRS 9069 and Université de Haute-Alsace, 68057 Mulhouse, France*

Received 12 July 2007; received in revised form 7 February 2008; accepted 17 February 2008
Available online 23 February 2008

Abstract

A commercial linear polydimethylsiloxane (PDMS) was subject to gamma irradiation under vacuum and in air, as well as to accelerated electron beam radiolysis (EB). All irradiation treatments were done at room temperature. The molecular weight changes induced by the radiation processes have been investigated using size exclusion chromatography (SEC) with refraction index (RI) and multi angle laser light scattering (MALLS) detectors to obtain the number and weight average molecular weights of the irradiated samples.

The analysis of the data indicates that crosslinking reactions predominated over scission reactions in all cases. Gamma irradiation under vacuum was the most efficient process within the analyzed dose range, reaching the gel point earlier. Irradiation in the presence of oxygen induces oxidative effects, both in gamma and EB irradiations. A previously developed mathematical model of the irradiation process that accounts for simultaneous scission and crosslinking and allows for both H and Y crosslinks fitted well the measured molecular weight data.

Keywords: Crosslinking; Experimental; Electron beam; Gamma irradiation; Mathematical model; PDMS

1. Introduction

The radiation chemistry of polymeric materials has been a field of extensive research, motivated in part by the useful modifications that ionizing radiation may induce in them. Radiation treatment of a polymeric material always produces crosslinking and scission reactions, which affect the molecular

* Corresponding author. Tel.: +54 291 4861700 206.
E-mail addresses: asatti@plapiqui.edu.ar (A.J. Satti), andreuce@criba.edu.ar (N.A. Andreucetti), jressia@plapiqui.edu.ar (J.A. Ressia), MF.Vallat@uha.fr (M.F. Vallat), csarmoria@plapiqui.edu.ar (C. Sarmoria), valles@plapiqui.edu.ar (E.M. Vallés).

0014-3057/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.eurpolymj.2008.02.017

weight, the molecular weight distribution, and in turn the physical properties of the treated material [1–3].

In practical applications of this technology two sources are commonly available, namely gamma irradiation and electron beam irradiation. Both sources produce high energy ionizing radiation and are used to treat polymers for a variety of uses. It is known that the interaction of such sources of radiation with polymer molecules produces a great amount of ions and excited molecules along their path into the polymer. The distribution of these species throughout the polymer sample is determined by the type and energy of the ionizing radiation, and is related to the linear rate of radiation energy transfer to the polymer, denominated LET [4]. Gamma and electron beam radiations are typical examples of low LET radiations. They transfer energy predominantly in small isolated events through the polymer inducing the formation of macroradicals which in turn become involved in several chemical reactions that produce the crosslinking and scission. However one must consider that, besides the similar energy transfer, these ionizing radiations differ in several ways such as dose rate, sample temperature rise, oxygen availability and treatment duration.

From a practical point of view the study on radioinduced changes in PDMS is a suitable field of research. Polydimethylsiloxane has been widely used in medical applications. Medical devices and implants require sterilization using high energy radiation [5]. Also in controlled drug delivery from polydimethylsiloxane matrices, irradiation crosslinking has been found effective to produce useful elastomeric support without affecting the stability of the controlled drug delivery systems [6].

In the specific case of radiation modified PDMS, crosslinking predominates over chain scission reactions. Because of this, the net effect of an irradiation treatment on PDMS is an increase of the molecular weight. Molecular architecture also changes due to chain branching. After a certain radiation dose, denominated the gelation dose D_{gel}, an infusible and insoluble three-dimensional network results. Beyond this gelation dose, further irradiation transforms the originally liquid PDMS into a soft to rubberlike gel.

Fig. 1 shows the different radicals that could be radioinduced in PDMS under vacuum. The same radicals should appear in gamma in air or in electron beam irradiation, with the addition of oxidized species and macroradicals.

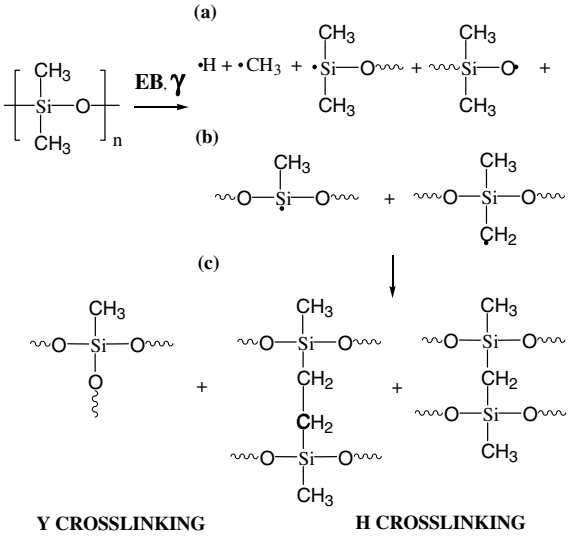

Fig. 1. (a) Radioinduced radicals due to chain scission; (b) radioinduced macroradicals due to methyl or hydrogen abstraction; (c) radioinduced H and Y crosslinks produced in PDMS irradiated with gamma rays under vacuum.

An interesting aspect related to these radicals is that they can react producing four-armed H crosslinks, and also three-armed Y crosslinks [7]. The Y-type crosslinks have been generally ignored in favor of the H-type crosslinks [3,8]. However, both of them have been reported in the literature [9,10]. It has been shown that their presence may help to explain the behavior of the molecular weights in the postgel region [7].

In this work we irradiate a commercial PDMS at room temperature using three methods: gamma irradiation under vacuum, gamma irradiation in air, and accelerated electron beam (EB) radiolysis. Of the three processes, EB is the one that has been analyzed the least in the literature. To the best of our knowledge, this is the first time that this type of experimental data on electron beam irradiated PDMS are discussed. Particular care was taken to follow the molecular weight changes of the studied polymers as a function of the applied radiation dose using double detection – refractive index and light scattering – SEC system. The experimentally measured molecular weights were compared with the predictions of a mathematical model specially developed for the PDMS irradiation process.

2. Experimental part

A commercial linear methyl terminated PDMS (Mw = 141,000 Da, Mn = 76,600 Da) purchased