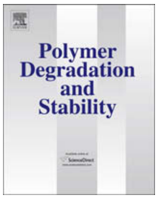
Polymer Degradation and Stability 94 (2009) 584–590

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab



Determination of scission, crosslinking and branching parameters of electron beam irradiated methacrylate–acrylamide copolymer

Khelil Slimani [a], Laurence Moine [b,*], Caroline Aymes-Chodur [a], Alexandre Laurent [c], Denis Labarre [b], Najet Yagoubi [a]

[a] Université Paris-Sud11, EA 401, IFR 141, Faculté de Pharmacie, 92296 Châtenay-Malabry, France
[b] Université Paris-Sud11, UMR 8612 CNRS, IFR 141, Faculté de Pharmacie, 92296 Châtenay-Malabry, France
[c] Service de Neuroradiologie et Angiographie Thérapeutique, AP-HP Hôpital Lariboisière, 75010 Paris, France

ARTICLE INFO

Article history:
Received 20 November 2008
Received in revised form
8 January 2009
Accepted 12 January 2009
Available online 20 January 2009

Keywords:
Irradiation
Scission
Crosslinking
Branching
Poly(methacrylate-*co*-acrylamide)

ABSTRACT

The aim of this work was to investigate the impact of electron beam irradiation at different dose rates on the molecular structure of linear methacrylate–acrylamide copolymer. In the first part, the radiation chemical yields of scission (G_s) and crosslinking (G_x) have been determined after irradiation for various initial molecular weights CL1 (40 000 g/mol), CL2 (90 000 g/mol) and CL3 (425 000 g/mol). Based on this calculation, solvent (ethanol) was found to increase the impact of irradiation especially at low concentration of copolymer. In the second part, the presence of branching in samples before and after e-beam irradiation was explored, and branching calculation was performed.

1. Introduction

Ionizing radiation is often used in various applications and is one suitable method to obtain hydrogel for biomedical applications without having recourse to any crosslinker or initiator [1,2]. Irradiation is also used as an alternative method able to modify polymers' surface properties and to enhance the surface functionalisation of some biomaterials [2,3]. Grafting reactions on polymers by irradiation techniques are also efficiently performed [4,5]. Furthermore, this technique is an effective way for sterilisation of biodegradable medical devices [6] or drugs [7–9] that do not support traditional sterilisation such as steam sterilisation. However, this technique may alter polymer properties because of crosslinking and/or scission reactions that could occur on backbone chains [10,11]. The scission reaction leads to the degradation of polymers by rupture of covalent bond inducing a decrease of molecular weight and intrinsic viscosity. In contrast, crosslinking reactions lead to the formation of inter- and intramolecular bonds, which increases molecular weight and intrinsic viscosity. For high crosslinking yields, gelation may occur [12]. According to the chemical structure of polymers, crosslinking or scission will predominate. The absence of tri or tetra substituted carbon atoms, as in polyethylene, polypropylene, polystyrene promotes crosslinking. Polymers with lateral side chains, like poly(methyl methacrylate) preferentially show scission reactions [13]. In addition to the chemical structure, these two effects depend on other parameters such as the physical state of the polymer (crystalline or amorphous solid, solution), the temperature and irradiation atmosphere [10]. Indeed, the presence of oxygen during irradiation tends to favour scission reactions [10,12,14] due to the oxidative action of formed peroxides [15]. Irradiation involves the formation of radicals that tend to react more rapidly with oxygen than with molecular chains. The radical recombination or diffusion is strongly affected by molecular mobility. When temperature rises close to the glass transition of the polymer, chain mobility and oxygen diffusion in the structure rise and may have different impact on the kinetics of radical decay [16,17].

In this study, we focused on the effect of irradiation by means of electron beam on a methacrylate–acrylamide copolymer. This copolymer has shown suitable properties to be used like an effective material in embolization treatment of hypervascularized processes such as arterio-venous malformations and tumours or vein dilations such as varicoceles [18].

Previous studies [19–22] have shown that ionizing radiation on polymethacrylates like poly(methyl methacrylate) or

---

* Corresponding author. Tel.: +33(0)146835994; fax: +33(0)146835312.
E-mail address: laurence.moine@u-psud.fr (L. Moine).

0141-3910/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymdegradstab.2009.01.011

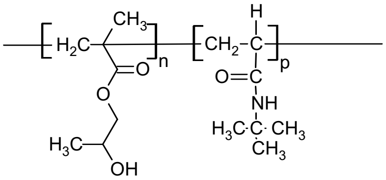


Fig. 1. Molecular structure of hydroxypropyl methacrylate-*co*-*N*-*tert*-butylacrylamide copolymer.

poly(ethyl methacrylate) lead to scission. Shultz et al. [20] found for the poly-*n*-alkyl methacrylate series that there was a competitive effect between scission and crosslinking reactions: an increase of the number of carbon atoms in pendent *n*-alkyl groups leads to an increase of crosslinking. Acrylamide polymers unlike methacrylate polymers show preference for crosslinking under gamma treatment. Using this property, hydrogels were successfully synthesized after irradiation of acrylamide monomers [23–26]. Gel formation was also obtained from polyacrylamide irradiated in solid state [27] and the initial moisture content revealed a high impact on the yield of crosslinking [28].

These two opposite behaviours between acrylamide and methacrylate polymers under irradiation do not let us predict which reaction (scission and/or crosslinking) will predominate after irradiation of our copolymer. We have tried to elucidate the behaviour of the copolymer after irradiation by investigating the molecular weight distribution and determining the radiation chemical yields of scission (G_s) and crosslinking (G_x).

The presence of branching in polymers before and after e-beam irradiation was also explored.

2. Experimental

2.1. Materials

Monomers, reagents and solvents were used as received without any treatment. Hydroxypropyl methacrylate (HPMA 97%) was purchased from Aldrich (Saint Quentin Fallavier, France) and *N*-*tert*-butylacrylamide (TBA: 97%) and 2,2′-azobisisobutyronitrile (AIBN 98%) from Acros Organics (Halluin, France).

2.2. Sample preparation

The copolymer hydroxypropyl methacrylate-*co*-*N*-*tert*-butylacrylamide (Fig. 1) was obtained by bulk polymerization of HPMA and TBA in ethanol using AIBN as initiator, under nitrogen atmosphere at 85 °C during 4 h. Ratio of AIBN and volume of solvent was varied to obtain different molecular weights (M_w). Synthesis conditions and results are summarized Table 1. Three copolymers having the same ratio of [HPMA]/[*t*BA] (70/30) but with different M_w were obtained: CL1 (40 000 g/mol), CL2 (90 000 g/mol), CL3 (425 000 g/mol). The polydispersity indexes (PI) were 1.9, 2.5 and 2.7 respectively.

2.3. Analysis

2.3.1. SEC

Molecular weight distributions of the copolymers were measured by Size Exclusion Chromatography (SEC) at 30 °C on a system equipped with a guard column and two GMH HRm columns (Viscotek, Irigny, France) with THF as eluent and flow rate of 1 ml min^{-1}. A differential refractometer (Waters 410) and a double SEC detector (model 270 Dual, Viscotek) with RALS and viscometer in series were used to analyze the samples. The data obtained were treated with OmniSEC 4.0 software (Viscotek). Branching index (g) of copolymers were also calculated from the OmniSEC software.

2.3.2. ^{1}H NMR spectroscopy

Products were analyzed by ^{1}H Nuclear Magnetic Resonance (NMR) spectroscopy using a Bruker DPX 300 FT-NMR spectrometer employing the solvent peak as reference. Analyses were performed on solutions of polymer in $(CD_3)_2SO$.

Copolymer composition was measured by ^{1}H NMR and calculated according to Eq. (1):

$$\%\text{HPMA} = \frac{\frac{a}{3}}{\frac{a}{3} + \frac{b - \frac{8}{3}a}{12}} \times 100 \tag{1}$$

where a and b are the integral values of the peaks at $\delta = 2.8$–3.6 ppm and 0.2–1.8 ppm respectively. Results of monomer ratio measurement are summarized in Table 2.

2.3.3. Irradiation

Irradiations were carried out under electron beam (e-beam) (IONISOS – Orsay – France). Samples were irradiated at a constant dose rate of 300 kGy/h in air at room temperature to get total doses of 25, 50, 75, 100, 125 and 150 kGy.

All samples CL1, CL2, CL3 were irradiated in solid form and CL2 sample was also irradiated in ethanol solution at different concentrations: 10%, 20% and 30% (w/v).

3. Results and discussion

3.1. Analysis of scission/crosslinking effect

3.1.1. Irradiation in the solid state

We studied the effect of the irradiation of the methacrylate–acrylamide copolymers of different molecular weights (CL1, CL2 and CL3) as a function of the absorbed dose (25, 50, 75, 100, 125 and 150 kGy). The intrinsic viscosities of irradiated ($[\eta]_{irr}$) and corresponding non-irradiated ($[\eta]_0$) copolymers in THF at 30 °C were measured and the ratio ($[\eta]_{irr}/[\eta]_0$) as the function of the absorbed dose was plotted (Fig. 2). This ratio was found in all cases below unity and decreased with the doses suggesting that scission of main-chain polymer occurred under e-beam treatment.

Impact of irradiation on copolymers having different molecular weights was done by analyzing the variation of radiation chemical

Table 1
Polymerization conditions of copolymers CL1, CL2 and CL3.

Sample	Initial monomers composition (10^{-3} mol)		AIBN (10^{-3} mol)	Ethanol (ml)	Conversion (%)	M_w (g mol^{-1})	PI
	HPMA	TBA					
CL1	57	24	0.97	360	81	40 000	1.9
CL2	226	97	0.97	360	85	90 000	2.5
CL3	57	24	0.12	30	88	425 000	2.7