Available online at www.sciencedirect.com
SCIENCE DIRECT®
European Polymer Journal 41 (2005) 219–224
EUROPEAN POLYMER JOURNAL
www.elsevier.com/locate/europolj

Crystallization of photo-chain extended poly(ethylene glycol)

Scott R. Trenor [a,*], Timothy E. Long [b], Brian J. Love [c,*]

[a] Macromolecular Science and Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA
[b] Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA
[c] Department of Materials Science and Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA

Received 9 August 2004; received in revised form 2 September 2004; accepted 20 September 2004
Available online 18 November 2004

Abstract

Coumarin-functionalized poly(ethylene glycol) (PEG) monols and diols were isothermally crystallized at temperatures between 20 and 35 °C before and after exposure to approximately 110 J cm^{-2} of ultra-violet A ($\lambda > 300$ nm, UVA) irradiation. Irradiation dimerized the coumarin groups and chain-extended the coumarin-functionalized PEG oligomers. The higher molecular weights reduced the crystal growth rate by as much as 50% compared to the non-irradiated coumarin-functionalized PEG oligomers under ambient crystallization conditions. Hoffman's kinetic nucleation theory was utilized to evaluate the types of nucleation that occurred for the coumarin-functionalized PEG diols (COU–PEG–COU). Crystallization regimes II and III were observed for the coumarin-modified PEG oligomers before and after exposure to UVA light.

Keywords: Crystallization; Photochemistry; Poly(ethylene glycol); Coumarin

1. Introduction

Many research groups have thoroughly studied the crystallization of poly(ethylene glycol) (PEG) and poly(ethylene oxide) (PEO) via a number of methodologies including optical microscopy, differential scanning calorimetry (DSC), in situ atomic force microscopy (AFM) and small angle X-ray scattering [1–9]. In the late 1970's and early 1980's Kovacs and coworkers reported on the melting and crystallization behavior of low molecular weight PEO films. They found that the crystallization rates decreased when molecular weights increased in low molecular weight PEO (<10 000 g mol^{-1}) was due, in part, to increased melt viscosity [1]. Cheng and coworkers studied the effects of chain ends on 3000 and 7000 g mol^{-1} PEG [4,5]. For the 3000 g mol^{-1} polymer, crystallization rate decreased with increasing endgroup size (–OH, –OCH_3, –$OC(CH_3)_3$ and –OC_6H_5). However, since the endgroups are a lower weight fraction of the 7000 g mol^{-1} polymer, the endgroups had no pronounced effect on the crystallization rate. Goh and Huang also reported a similar endgroup effect during their study of C_{60} endcapped PEO (M_w = 3000 g mol^{-1}) [7]. The addition of a single C_{60} chain end only depressed the T_m from 54.6 °C (as received PEO) to 53.0 °C, while the second C_{60} chain end further depressed the T_m to 43.4 °C. A similar trend

* Corresponding authors. Address: KRATON Polymers, 3333 Hwy 6 S., Suite C-1501, Houston, TX 77082, USA. Tel.: +1 281 677 2659; fax: +1 231 668 3233 (S.R. Trenor), +1 540 231 3554 (B.J. Love).
E-mail addresses: scott.trenor@kraton.com (S.R. Trenor), blove@vt.edu (B.J. Love).

0014-3057/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.eurpolymj.2004.09.009

was observed for the crystallization rates with the bulky C_{60} chain ends retarding chain motion and thus decreasing the rate of crystallization.

There are three growth regimes observed in the crystal growth rate of PEG and other polymers; each regime displays a distinct growth curve and nucleation constants [1,3,7,9–14]. In regime I, at small undercoolings, a single nucleation occurs and the substrate is completely covered by the crystallization growth layer from the single nuclei. Multiple nucleations occur at larger undercoolings where crystal growth and additional nucleation are competing factors (regime II). At even larger undercoolings (regime III), nucleation occurs at such a high rate that the distance between nucleation sites is approximately the same size as the width of a single chain (repitation tube) as it is incorporated into the crystal [7,9,10,12,15]. Hoffman first reported and others have verified that the nucleation constants for regimes I and III are similar and are theoretically (and experimentally verified) twice that of regime II [7,9,10,12,15].

Previously, we have studied the photoreversible chain extension of coumarin-endcapped PEG monols and diols [16,17]. When exposed to UVA irradiation, the coumarin groups undergo a $[2\pi + 2\pi]$ photochemical cycloaddition forming a dimer [16–21]. The coumarin dimer was utilized as a chain extension point in the PEGs (Fig. 1). UVA irradiation of the coumarin functionalized PEG diols ($\sim$110 J cm^{-2}) doubled the M_n and increased the molecular weight distribution from 1.08 to 2.75 [16,17].

The crystallization rates of these coumarin-functionalized PEG monols and diols with and without exposure to UV light are described herein. While the effects of molecular weight and endgroup functionality on isothermal crystal growth rates is well characterized, the photodimerization reaction provides a unique chemistry with defects (coumarin dimers) introduced regularly throughout the PEG backbone. Isothermal crystalline growth rates of the coumarin-functionalized PEGs were measured with optical microscopy. Kinetic data were then calculated from the optical microscopy measurements and compared to those in the literature.

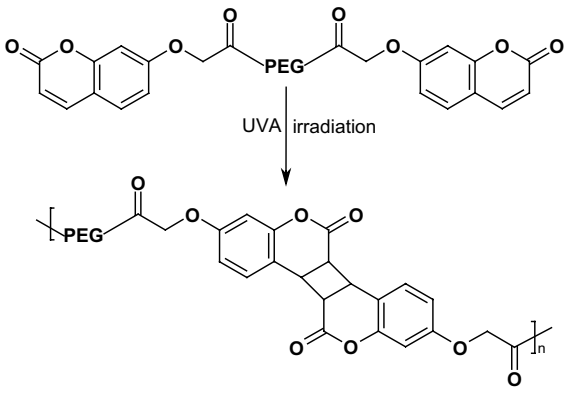

Fig. 1. Photo-chain extension of coumarin endcapped PEG diols.

2. Experimental section

2.1. Reagents

7-Hydroxycoumarin, PEG monol and diol, ethyl bromoacetate, and thionyl chloride were purchased from Sigma Aldrich Chemical Co. and used as received unless otherwise noted. All other solvents and reagents were purchased from commercial sources and were used without any further purification unless otherwise noted. Tetrahydrofuran (THF) was distilled from sodium/benzophenone under a nitrogen atmosphere prior to PEG/acid chloride reactions.

2.2. Instrumentation

^{1}H NMR spectra were recorded using either a Varian Unity 400 MHz or a Varian Inova 400 MHz spectrometer at 25 °C in $CDCl_3$ at ambient temperature. UV–Vis spectroscopy was performed using an Analytical Instrument Systems Inc. spectrometer equipped with fiber optic light guides, a DT1000CE light source, and an Ocean Optics USB2000 UV–Vis detector. FTIR–ATR spectroscopy was accomplished with an Olympus Bx51 microscope modified with a SensIR IlluminatIR ATR objective and stage. Molecular weights were determined at 40 °C in chloroform or THF (HPLC grade) at 1 mL min^{-1} using polystyrene standards on a Waters GPC equipped with 3 in-line PLgel 5 μm MIXED-C columns with an autosampler, and a 410 RI detector. Differential scanning calorimetry (DSC) was performed with a Perkin Elmer Pyris 1 at a heating rate of 20 °C min^{-1} after quenching from 120 °C at 80 °C min^{-1} under nitrogen. UVA irradiation was accomplished using an Oriel UV reactor equipped with a glass filter, which efficiently blocked wavelengths below 300 nm. Irradiance and effective energy density were measured at time intervals no longer than 5 min with an EIT UV Power Puck radiometer. PEG films were solvent cast from chloroform or THF onto quartz and drawn in a controlled manner using a doctor blade. Homogenous films of less than 3 μm thickness were prepared for optical microscopy.

2.3. Synthesis and characterization of Coumarin-functionalized PEGs

The detailed synthesis of the coumarin endcapped monols and diols is published elsewhere [16]. Briefly, PEG diol (^{1}H NMR M_n = 2020, GPC RI M_n = 3370, M_w/M_n = 1.04 versus polystyrene standards) was dried