Contents lists available at SciVerse ScienceDirect

European Polymer Journal

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



Effect of slight crosslinking on the mechanical relaxation behavior of poly(2-ethoxyethyl methacrylate) chains



M. Carsí^{a,*}, M.J. Sanchis^a, R. Díaz-Calleja^a, E. Riande^b, M.J.D. Nugent^c

^a Energy Technological Institute (ITE), Universitat Politècnica de València, Camino de Vera s/n, 46022 Valencia, Spain ^b Institute of Polymer Science and Technology (ICTP), Spanish National Research Council (CSIC), Juan de la Cierva 3, 28008 Madrid, Spain

^c Athlone Institute of Technology, Dublin Rd., Athlone, Co. Westmeath, Ireland

ARTICLE INFO

Article history: Received 21 June 2012 Received in revised form 26 November 2012 Accepted 16 December 2012 Available online 5 January 2013

Keywords: Dynamic-mechanical spectroscopy Crosslinking Poly(2-ethoxyethyl methacrylate) Nanodomains structure

ABSTRACT

The synthesis, thermal and mechanical characterizations of uncrosslinked and lightly crosslinked poly(2-ethoxyethyl methacrylate) are reported. The uncrosslinked poly(2-ethoxyethyl methacrylate) are reported. The uncrosslinked poly(2-ethoxyethyl methacrylate) exhibits in the glassy state two relaxations called in increasing order of temperature, the gamma and beta processes respectively. These are followed by a prominent glass-rubber or alpha relaxation. By decreasing the chains mobility by a small amount of crosslinking, the beta relaxation disappears and the peak maximum associated with the alpha relaxation is shifted from 268 K to 278 K, at 1 Hz. An investigation of the storage relaxation modulus of the crosslinked polymer indicates two inflexion points that presumably are related to segmental motions of dangling chains of the crosslinked networks and to cooperative motions of the chains between crosslinking points. Nanodomains formed by side-groups flanked by the backbone give rise to a Maxwell–Wagner–Sillars relaxation in the dielectric spectra that have no incidence in the mechanical relaxation spectra.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Chains dynamics is a flourishing field of research in polymer science due in part to the practical applications of these studies in engineering [1]. Furthermore, the prediction of the mechanical performance of polymeric structures requires an understanding of the chain dynamics of polymers. As is well-known, the glass–rubber or α -relaxation that arises from segmental motions of molecular chains, freezes at T_g . This characteristic, in conjunction with the fact that the α relaxation is the dominant process in chain dynamics until molecular chains disentanglement occurs, leads us to consider the glass–rubber relaxation as the precursor of the glassy state and the viscous flow. Moreover, the α relaxation also occurs in oligomers of low molecular weight, well below the entanglement condition [2,3]. Besides the glass rubber relaxation, the relaxation

spectra of polymers in the frequency domain present secondary relaxations produced by conformational transitions of the chains backbone or motions of flexible side-groups [4–6]. Unlike the glass–rubber relaxation and the normal mode process [7] that reflects chains disentanglement, secondary relaxations remain operative below T_{g} .

Secondary relaxations can have a great impact on the mechanical properties of polymers in the glassy state [4–6,8,9]. For example, chair-inverse-chair conformational transitions of cyclohexyl in poly(cyclohexyl methacrylate) produce an ostensible secondary β relaxation that causes a significant decrease of the real relaxation modulus of the polymer in the glassy state [10–12]. Since to date, while no quantitative theory that describe the glass–rubber relaxation and the secondary relaxations in terms of the chemical structure has been formulated, (i) the theory of the total dielectric relaxation strength for the α -process is well-established in terms of molecular dipole moments [4–6,13–22] and (ii) much success has been achieved in understanding the characteristic behavior of the dielectric

^{*} Corresponding author. Tel.: +34 96 3879327; fax: +34 96 3877329. *E-mail address:* mcarsi@ter.upv.es (M. Carsí).

^{0014-3057/\$ -} see front matter \odot 2013 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.eurpolymj.2012.12.012

 α relaxation through computer "molecular dynamics" simulations [23–29]. In this sense, actually the design of polymers with specific physical properties relies on empirical rules based on experimental studies of the relaxation properties of polymers with different chemical structures.

Poly(n-alkyl methacrylate)s and poly(n-alkyl acrylate)s have been widely used in the study of chain dynamics owing to the great dependence of the properties of the members of the series on the length of the alkyl residue [4-9,30-53]. The first member of the series, poly(methyl methacrylate) (PMMA), is widely used in household and automotive applications [54]. The fact that PMMA has a glass-transition temperature ca. 100 K above that of poly(methyl acrylate) (PMA) puts in evidence that hindering of the conformational transitions by effect of the methyl group rigidly attached to the polymer backbone. This results in the increase of the T_g of PMMA [4]. Moreover, the tacticity of the PMMA has a significant influence in the dynamics of this polymer, thus the T_g value of the isotactic form is lower than that corresponding to the syndiotatic form. The β peak is located at somewhat lower temperatures for the isotatic polymer than for the sindiotactic polymer. Moreover, the magnitude of the β -relaxation is also very influenced by tacticity. Thus, whereas the height of the β peak is about twice that of the α peak for the conventional polymer, the opposite situation exists in the case of the isotatic polymer [4]. Moreover, the X-ray spectra of poly(n-alkyl methacrylate)s melts with $n \ge 2$, which shows that these polymers are heterogeneous systems formed by nanodomains integrated by side-chain groups flanked by the chains backbone [37,44,45]. Cooperative motions of the side chains in the domains produce an α_{EP} peak located at higher frequencies than the glass-rubber relaxation arising from segmental motion of the chains backbone.

Recently, the dielectric relaxation behavior of poly (2-etoxyethyl methacrylate) (PEOEMA) was studied [55]. PEOEMA can schematically be obtained by replacing a methylene group of poly(pentyl methacrylate) for an ether group. This polymer has been used as drug-eluting stent coating for percutaneous coronary interventions, providing durable, robust coatings with precise control over rapamycin elution rates [56]. The formation of nanodomains visible in the X-ray spectra of poly(n-pentyl methacrylate)s is not detected in poly(2-ethoxyethyl methacrylate) (PEOEMA) [40,41,45]. The X-ray pattern of this polymer only shows a single peak that reflects the average distance of side chains groups. However, the X-ray spectra of slightly crosslinked PEOEMA exhibit, in addition to the peak appearing in the uncrosslinked polymer, another transition presumably arising from correlations between the chains backbone [55]. The similarity of these spectra with those of poly(n-alkyl methacrylate)s suggests the presence of nanodomains in the crosslinked PEOEMA network. Hereinafter, the acronym of crosslinked polymer will be CEOEMA. In view of these antecedents, a mechanical-dynamical study was undertaken on PEOEMA and CEOEMA. The aim of the study was to determine whether the differences observed in the mesoscopic structure of the uncrosslinked and crosslinked polymers, which affect the dielectric spectra of these systems, will also affect their mechanical relaxation spectra.

2. Experimental section

Commercial monomer 2-ethoxyethyl methacrylate (Aldrich, 99%) (Fig. 1) and the cross linker diethylene glycol dimethacrylate (Aldrich, 98%) (Fig. 2) were purified by distillation under high vacuum. Dioxane (Aldrich; 99%) was distilled twice: the first time over sodium hydroxide and the second time over sodium. 2, 2'-Azobisisobutyronitrile (AIBN, Fluka; 98%) was recrystallized from methanol and dried under high vacuum at room temperature. All other materials and solvents used for the synthesis were commercially available and they were used as received unless otherwise indicated.

Poly 2-ethoxyethyl methacrylate (PEOEMA) was obtained by radical polymerization of 2-ethoxyethyl methacrylate in dioxane solution using 2.5 wt% of 2,2'-azobisisobutyronitrile (AIBN) as initiator. The reaction was carried out in nitrogen atmosphere, at 343 K, for 5 h. The polymer was precipitated with methanol, washed several times with this organic compound and finally dried under high vacuum at room temperature. The number and weight average molecular weights of PEOEMA were measured by size exclusion chromatography (SEC) in a Perkin-Elmer apparatus with an isocratic pump serial 200 connected to a differential refractometric detector (serial 200a). Two Resipore columns (Varian) were conditioned at 70 °C and used to elute the samples (1.0 mg/mL concentration) at 0.3 mL/min HPLC-grade N,N'-dimethyl formamide (DMF) (Scharlau) supplemented with 0.1 v/v% LiBr. Calibration of SEC was carried out with monodisperse standard poly(methyl methacrylate) samples in the range of $2.9 \times 10^3 - 480 \times 10^3$ obtained from Polymer Laboratories. The values of M_n and M_w were 82,600 and 250,800 g mol⁻¹, respectively.

CEOEMA was prepared by radical copolymerization of 2-ethoxyethyl methacrylate and ethylene glycol dimethacrylate, the mass fraction of the latter comonomer or crosslinking agent in the feed being 1 wt%. The polymerization reaction took place at 343 K in a silanized-glass mold of about 100 μ m thickness, in oxygen free atmosphere. A crosslinked film, without bubbles, was obtained which was washed with methanol and further dried at room temperature under vacuum.

In order to characterize the polymer, Fourier Transform Infrared Spectroscopy (FTIR) was used to study the structure and complexation of the polymers. Infrared spectroscopy was performed on a Nicolet Avator 360 FTIR spectrometer, with a 32 scan per sample cycle. For each sample, scans were recorded from 4000 to 400 cm⁻¹ with a resolution of 4 cm⁻¹. The spectra obtained show a signal at 1700 cm⁻¹ associated with the C=O stretching vibration of carboxylic group, one signal at 2900 cm⁻¹ due to CH₂ stretching and the signal at 1125 cm⁻¹ associated with C-O-C asymmetric stretching.



Fig. 1. Structure of 2 ethoxyethyl methacrylate (EEMA).

Download English Version:

https://daneshyari.com/en/article/10609529

Download Persian Version:

https://daneshyari.com/article/10609529

Daneshyari.com