



Glass-like dynamics of new cross-linked polymeric systems: Behavior of the Boson peak



B. Rossi ^{a,*}, A. Fontana ^a, M. Giarola ^b, G. Mariotto ^b, A. Mele ^c, C. Punta ^c, L. Melone ^c, F. Toraldo ^c, F. Trotta ^d

^a Department of Physics, University of Trento, via Sommarive 14, 38123 Povo (Trento), Italy

^b Department of Computer Science, University of Verona, Strada le Grazie 15, 37134 Verona, Italy

^c Department of Chemistry, Materials and Chemical Engineering "G. Natta", Politecnico di Milano, Via Mancinelli 7, 20131 Milano, Italy

^d Department of Chemistry, University of Torino, Via Pietro Giuria 7, 10125 Torino, Italy

ARTICLE INFO

Article history:

Received 12 July 2013

Received in revised form 23 December 2013

Available online 21 January 2014

Keywords:

Cross-linked polymers;

Cyclodextrin;

Boson peak;

Raman scattering;

Nanostructured materials

ABSTRACT

Cyclodextrin nanosponges (CDNS) provide a very promising class of cross-linked polymers consisting of cyclodextrins as building blocks and showing a characteristic nanoporous structure capable of effectively encapsulating and carrying a variety of both lipophilic and hydrophilic compounds. Hereafter, we investigate the vibrational dynamics of CDNS in the low-wave number region, with the aim to provide physical descriptors correlated to the elastic properties of this innovative glass-forming material. By means of Raman scattering measurements, we explore the modifications occurring to the boson peak (BP) as a function of the cavity size of the cyclodextrin and the relative amount of the cross-linking agent with respect to the monomer cyclodextrin, which can be varied during the synthesis of the polymer. The shift and intensity variations of the BP are discussed in terms of the modification of the elastic properties of CDNS, and a master curve for the boson peak can therefore be obtained. The experimental approach adopted here is a useful tool for investigating the structural and physico-chemical properties of novel nanoporous soft materials of interest for biolife applications.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Cyclodextrin nanosponges (CDNS) represent a very promising class of cross-linked polymers showing a unique three-dimensional architecture that consists of both hydrophilic and hydrophobic nanosized pores, where a large variety of guest compounds can be effectively encapsulated [1–3]. The monomeric units of CDNS are constituted by cyclodextrins (CD), natural cyclic oligosaccharides formed by 6–8 glucose units linked by 1,4- α -glycosidic bonds leading to form α -, β -, and γ -CD, respectively. CD show a characteristic structure of a truncated cone, with an internal hydrophobic cavity and an outer hydrophilic surface [4–6], and they are well known for their capability of including a large variety of organic compounds via non-covalent interactions. The reaction of polymerization of CD with suitable polyfunctional agents leads to highly cross-linked amorphous structures, referred to as cyclodextrin nanosponges, characterized by unique molecular encapsulation properties. These polymeric networks play a key role in the rational design of new soft materials for application as carrier systems in many different technological fields, including agriculture [7], environmental control [8] cosmetic and pharmaceutical domain [9–14].

In this scenario, the deep knowledge of the architecture of the network connectivity or an estimation of the cross-linking density of CDNS is a crucial step to understand how the molecular structure can

affect the functional properties of these polymers. This is an important challenge in view of the possibility to control and tune the molecular encapsulation ability inside the matrix of these very promising amorphous systems. On the other hand, despite the easy synthesis and the versatility of CDNS, carrying out a systematic structural and dynamic characterization of cross-linked polymeric networks suffers from many intrinsic difficulties, mainly due to the random nature of the growing process which leads to the formation of the polymer.

Recent experimental-numerical works [15–20] showed how the study of the vibrational dynamics of CDNS is a powerful tool to characterize amorphous polymeric networks, from a structural point of view, too. The detailed analysis of the high-frequency vibrational dynamics of nanosponges revealed a clear dependence of the hydrogen-bonded network involving the OH groups of the polymers on the temperature and on the cross-linking degree of CDNS [20]. Moreover, the inspection of the vibrational spectra of the polymers over a broad spectral range [15–19] allowed us to demonstrate that the cross-linking density of the polymeric network and the stiffness (i.e., rigidity) of the whole material can be effectively tuned by varying the chemical structure of cross-linking agent and the reaction conditions. In particular, the relative amount of crosslinking agent with respect to the monomer CD (i.e., $n = \text{crosslinking agent/CD molar ratio}$) was observed to be the parameter which mainly can affect the covalent connectivity [17–19] and the elastic properties of the polymeric matrix [15–17].

In this paper, the low-energy vibrational excitations of cyclodextrin nanosponges, obtained by polymerization of α - and γ -CD with the

* Corresponding author.

E-mail address: rossi@science.unitn.it (B. Rossi).

cross-linking agent ethylenediaminetetraacetic acid (EDTA), are investigated by means of Raman scattering experiments. The structure of α - and γ -CD differs by the number of glucose units, composed of macrocycle (6 and 8, respectively), and this is reflected in a different size of the cavity diameter of the CD (≈ 4.7 and 7.5 Å for α - and γ -CD, respectively). The aim of this work is exploring as how the steric hindrance and the number of reactive sites on each CD unit (which varies from 12 secondary and 6 primary OH groups to 16 secondary and 8 primary groups per CD residue passing from α -CD to γ -CD) can affect the stiffness properties of the polymer network over a mesoscopic length scale. For this purpose, the spectral evolution of the so-called Boson peak (BP), a vibrational feature usually observed in the low-energy vibrational spectra of a wide range of different amorphous materials [21–24], will be analyzed and discussed in terms of a physical descriptor correlated to the elasticity properties of these amorphous polymeric networks [16,17].

2. Experimental methods

2.1. Synthesis and purification of nanosponges

The nanosponges were obtained following a synthetic procedure previously reported [1,2,25]. In order to obtain α -CDEDTA1*n* and γ -CDEDTA1*n* nanosponges, anhydrous α -CD (γ -CD) was dissolved at room temperature in anhydrous DMSO containing 1 mL of anhydrous Et₃N. Then the cross-linking agent ethylenediaminetetraacetic acid dianhydride (EDTAn) was added at molecular ratios of 1:*n* (with *n* = 2, 6, 10) under intense stirring. The polymerization was complete in few minutes obtaining a solid that was broken up with a spatula and washed with acetone in a Soxhlet apparatus for 24 h. The pale yellow solid was finally dried under vacuum obtaining finally an apparently homogeneous powder.

2.2. Raman scattering measurements

All the Raman measurements were carried out at room temperature from dried specimens of nanosponges placed on a glass slide exposed to air. Cross-polarized (HV) anti-Stokes and Stokes Raman spectra were recorded over the wave number range between about -400 cm^{-1} and $+370$ cm^{-1} in backscattering geometry, by means of a triple-monochromator spectrometer (Horiba-Jobin Yvon, model T64000) set in double-subtractive/single configuration and mounting three holographic gratings with 1800 grooves/mm. Micro-Raman spectra were excited by the 632.8-nm wavelength of a helium/neon or by the 647.1-nm wavelength of an argon/krypton ion laser and detected by a multichannel detector (CCD with 1024×256 pixels) cryogenically cooled by liquid nitrogen. The laser beam was focused onto the sample surface with a spot size of about $1 \mu\text{m}^2$ through an $80\times$ objective of the microscope with $\text{NA} = 0.75$. The resolution was better than $0.4 \text{ cm}^{-1}/\text{pixel}$.

No appreciable damage due to possible heating of the sample was observed by means of an accurate inspection of the irradiated sample surface throughout the camera coupled to the microscope objective and carried out after each measurement. Moreover, four Raman spectra were recorded from different regions of each examined sample in order to verify their reproducibility.

3. Results

Cross-polarized Raman intensity $I_{\text{Raman}}(\omega, T)$ of α -CDEDTA110 nanosponge is shown in the wave number region between $+200$ cm^{-1} and -200 cm^{-1} (Fig. 1). The experimental profile shows two different contributions, which appear evident in both the anti-Stokes and Stokes components of the spectrum: a quasi-elastic (QE) signal, related to diffusive and relaxational dynamics of the system, which appears as a

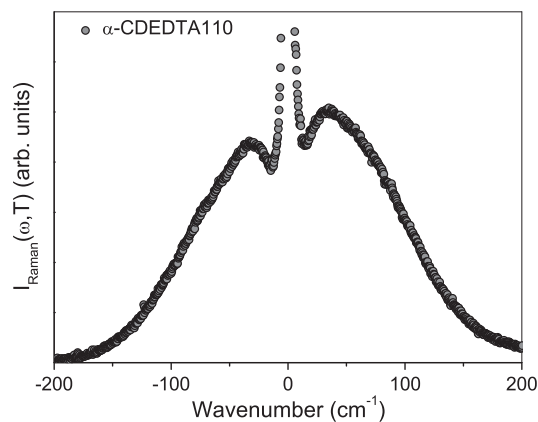


Fig. 1. Cross-polarized (HV) Raman intensity $I_{\text{Raman}}^{\text{HV}}$ of α -CDEDTA110 nanosponge in the wave number region between $+200$ cm^{-1} and -200 cm^{-1} .

broadening of the elastic peak, and the broad bump, characteristic of disordered systems, usually referred as the boson peak (BP).

According to Shuker and Gammon model [26], the experimental intensity $I_{\text{Raman}}(\omega, T)$ of Raman scattering Stokes processes turns out to be proportional to the density of states $g(\omega)$ through the following relation:

$$I_{\text{Raman}}(\omega, T) = C(\omega)g(\omega) \frac{[n(\omega, T) + 1]}{\omega} \quad (1)$$

where $n(\omega, T) = [\exp(\hbar\omega/kT) - 1]^{-1}$ is the temperature Bose factor and $C(\omega)$ is the coupling function between light and vibrational mode of frequency ω of the system.

In order to rule out the temperature dependence of the Raman spectra, the measured intensity can be converted into the reduced Raman intensity, defined as

$$I^{\text{Red}}(\omega) = \frac{I_{\text{Raman}}(\omega, T)}{[n(\omega, T) + 1]\omega} = C(\omega) \frac{g(\omega)}{\omega^2} \quad (2)$$

The reduced Raman intensity $I^{\text{Red}}(\omega)$ derived from the Stokes component of the cross-polarized spectrum of three different α -CDEDTA1*n* nanosponges in the low-energy region (0 – 200 cm^{-1}) is shown in Fig. 2, as an example.

In order to compare Raman spectra acquired on different samples of EDTA nanosponges, the experimental data were preliminary normalized to the total measured area.

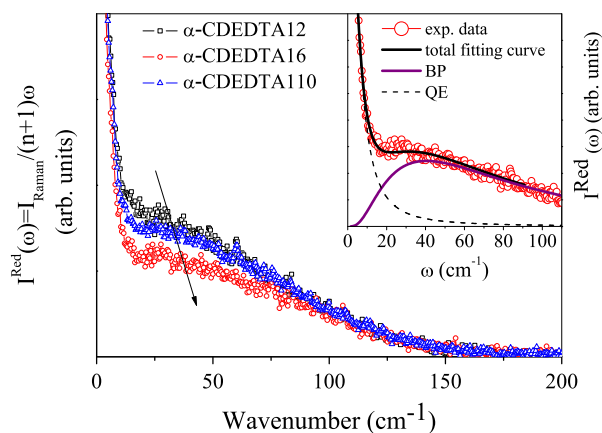


Fig. 2. Reduced Raman spectra of α -CDEDTA1*n* nanosponges (*n* = 2, 6, 10) in the energy range 0 – 200 cm^{-1} ; the arrow indicates the evolution of the BP peak frequency. (Inset) Typical example of the best fitting results for α -CDEDTA16: the experimental data (red circles) are shown together with the total fitting curve and the different components (QE, quasi-elastic; BP, boson peak).

Download English Version:

<https://daneshyari.com/en/article/1480882>

Download Persian Version:

<https://daneshyari.com/article/1480882>

[Daneshyari.com](https://daneshyari.com)