



Molecular dynamics in polymer networks containing caprolactone and ethylene glycol moieties studied by dielectric relaxation spectroscopy



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ARTICLE INFO

Article history:

Received 28 May 2014

Received in revised form 1 August 2014

Available online xxxx

Keywords:

Copolymer networks;

Hydrogels;

Dielectric relaxation;

Molecular mobility

ABSTRACT

Copolymer networks with methacrylate main chain and caprolactone and ethylene glycol side groups were obtained by free radical copolymerisation of caprolactone methacrylate (CLMA) and poly(ethylene glycol) methacrylate (PEGMA). Dielectric relaxation spectroscopy was used to analyse molecular mobility of the different groups in the system. Only one main dielectric relaxation process was found in CLMA/PEGMA copolymer networks, located between those of the corresponding homonetworks, indicating that the system does not present phase separation. The copolymers show a secondary relaxation process at temperatures below $-50\text{ }^{\circ}\text{C}$, which can be assigned to the overlapping of the corresponding secondary processes for the homopolymer networks; one of them was related to the local mobility of caprolactone units in CLMA and the second one was assigned to the twisting motions within ethylene glycol moiety in PEGMA. Besides the relaxation processes, the mobility of space charges has been analysed by means of conductivity and electric modulus formalisms.

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1. Introduction

Poly(ethylene glycol), PEG, hydrogels have been frequently used to encapsulate and culture different types of cells in three dimensional environments for tissue engineering applications. It has been shown that elastic properties and cross-linking density of these gels influence in large extent the biological response [1,2]. It is well known that PEG is not adhesive for cells, as probed in monolayer culture of a variety of cells [3]. On the other hand very good attachment of different cells to poly(caprolactone methacrylate) substrates has been shown both in monolayer and in 3D supports.

Recently our group presented polymer networks that combine these two materials in order to modulate cell adhesion response for neural regeneration [4]. The polymer network was produced by copolymerisation of caprolactone methacrylate, CLMA, and poly(ethylene glycol) methacrylate, PEGMA. The result of the polymerisation is a methacrylate main chain with side chains containing caprolactone and/or poly(ethylene glycol) groups. These networks absorb increasing amounts of water with increasing PEGMA contents [4] whilst caprolactone segments provide attachment points for proteins that mediate cell adhesion.

We hypothesise that the behaviour of these materials as cell culture supports is in a large extent determined by the spatial distribution and mobility of the different molecular groups. The main objective of this work is to provide a deeper insight in the structure of the system by means of dielectric relaxation spectroscopy (DRS), analysing the relaxational modes that take place in the networks as a function of the CLMA/PEGMA ratio in the copolymers. Dielectric relaxation spectroscopy (DRS) is a powerful technique in investigating molecular mobility in polymer systems with the advantage that it can be used in an extremely wide frequency range analysis, from MHz to GHz [5]. This technique, together with dynamic-mechanical spectroscopy and differential scanning calorimetry has been extensively used to study the structure and molecular mobility of polymers, polymer blends [6–10] and copolymers [11–13].

2. Materials and methods

2.1. Materials

Caprolactone 2-(methacryloyloxy)ethyl ester (CLMA), purchased from Sigma-Aldrich with a molecular weight of 244.28 g/mol and poly(ethylene glycol) methacrylate (PEGMA) (Sigma-Aldrich, 96% pure) with a molecular weight of 526 g/mol were employed without further purification. Ethylene glycol dimethacrylate (EGDMA) (Aldrich, 99% pure) and 2,2'-azobisisobutyronitrile (AIBN) (Aldrich, 98% pure) were used as crosslinking agent and initiator respectively. As solvent

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N,N-dimethylformamide (DMF) (Aldrich, 99.8% pure) and ethanol (Aldrich, 99.5% pure) were employed.

2.2. Preparation of the samples

Copolymer networks were synthesised by radical polymerisation. Different proportions of CLMA and PEGMA (30/70, 50/50 and 70/30) were dissolved in DMF (50 wt.%). 0.1 wt.% of AIBN and 1 wt.% of EGDMA were employed as initiator and crosslinker respectively. The reaction was carried out at 60 °C for 24 h. Low molecular weight substances were extracted by boiling in ethanol for 24 h and dried in vacuum until constant weight. The homopolymer networks were obtained by applying the same procedure. The molecular structures of both monomers and copolymer are shown in the schemas of Fig. 1.

The samples obtained were designed as polyCLMA and polyPEGMA for the homopolymers networks and poly(CLMA-co-PEGMA) XX/YY for copolymer networks, where XX and YY are the weight ratio of CLMA and PEGMA respectively. The molecular weight obtained for the copolymers 30/70, 50/50 and 70/30 was 291.04, 333.62 and 390.79 g/mol respectively [4].

2.3. Experiments

The measurements were carried out in an impedance analyser ALPHA-S (Novocontrol Technologies) in a frequency range from 0.1 Hz to 1 MHz. Samples around 0.5 mm thickness were dried in vacuum at 25 °C for 48 h to remove traces of humidity. After that, the samples were placed in a parallel plate capacitor with 10 mm of diameter mounted on a temperature controlled cryostat (BDS 1100) and exposed to a heated gas stream evaporated from a liquid nitrogen Deward. The temperature control was assured by a Quatro Cryosystem from Novocontrol GmbH. The isothermal experiments were performed from –140 °C up to 100 °C with a thermal stability of 0.5 °C and the complex permittivity, $\epsilon^* = \epsilon' + i\epsilon''$, was determined as a function of frequency each 5 °C. The standard deviation in the measurements motivated by the uncertainties in the determination of the sample thickness is lower than 6%.

3. Results

Fig. 2 shows the dielectric loss factor (ϵ'') for polyCLMA network in the interval from –130 °C to 50 °C. Two dipolar relaxation processes can be identified, a low temperature process, shown between –140 °C and –50 °C (Fig. 2a), and at higher temperatures,

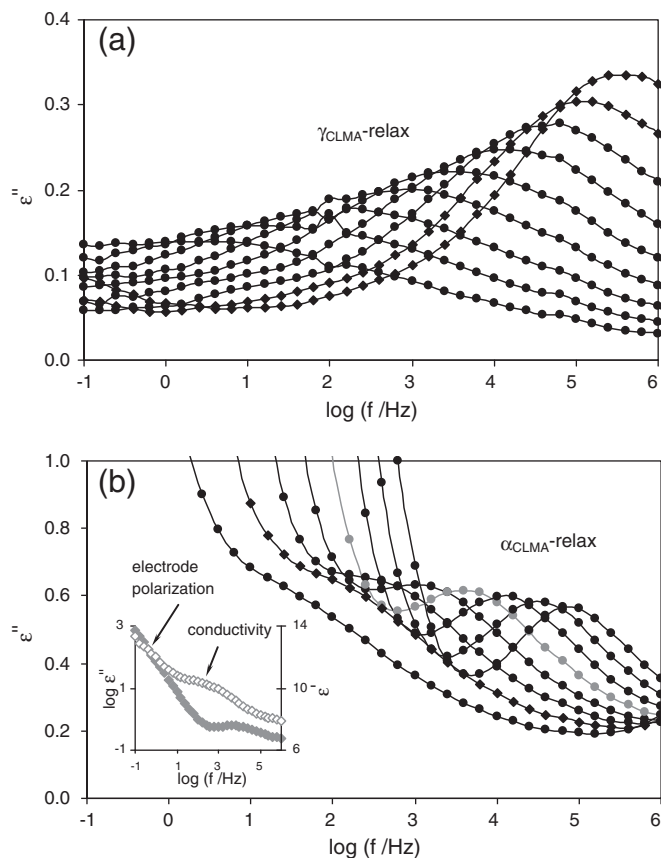


Fig. 2. Frequency dependence of ϵ'' in polyCLMA network. Isothermal curves between –130 °C and –50 °C (a) and between 20 °C and 90 °C (b), both by steps of 10 °C. The curve at 60 °C is in grey. The inset in plot b shows the real (open symbol) and imaginary (full symbol) parts of the permittivity in the isothermal curve obtained at 60 °C. The error bars are smaller than the size of the symbols. The solid lines are guides for the eye.

between 20 °C and 90 °C (Fig. 2b), a second one overlapped with conductivity.

The temperature dependence of the dielectric loss factor for both homopolymers and copolymers networks is shown in Fig. 3 at $1 \cdot 10^4$ Hz. The homopolymer networks polyCLMA and polyPEGMA show a relaxation process between –120 °C and –60 °C, with lower amplitude for polyPEGMA network. Copolymer networks show a relaxation process in the same temperature interval, whose amplitude is between the corresponding homonetworks. This process has been analysed in the

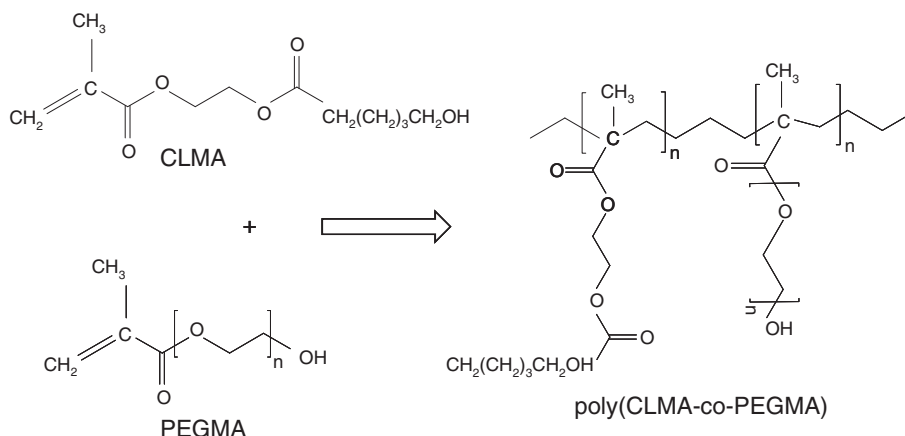


Fig. 1. Molecular structure of caprolactone methacrylate (CLMA), poly(ethylene glycol) methacrylate (PEGMA) and poly(CLMA-co-PEGMA).

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