Available online at www.sciencedirect.com
SCIENCE DIRECT
Polymer 46 (2005) 12523–12531
polymer
www.elsevier.com/locate/polymer

Effect of physical aging on nano- and macroscopic properties of poly(methyl methacrylate) glass

A. Wypych [a,b,c], E. Duval [b], G. Boiteux [c], J. Ulanski [a,*], L. David [c], A. Mermet [b]

[a] *Department of Molecular Physics, Technical University of Lodz, ul. Zeromskiego 116, 90-924 Lodz, Poland*
[b] *Laboratoire de Physico-Chimie des Matériaux Luminescents, UMR CNRS 5620, Université Claude Bernard Lyon 1, 43, Bd. du 11 Novembre, 69622 Villeurbanne Cedex, France*
[c] *Laboratoire des Matériaux Polymères et Biomatériaux, UMR CNRS 5627/IMP, Université Claude Bernard Lyon1, 43, Bd. du 11 Novembre, 69622 Villeurbanne Cedex, France*

Received 22 June 2005; received in revised form 4 October 2005; accepted 25 October 2005
Available online 14 November 2005

Abstract

Physical aging of amorphous poly(methyl methacrylate) has been studied by low frequency Raman scattering, broad-band dielectric spectroscopy, low frequency high resolution mechanical spectroscopy and differential scanning calorimetry. The material was subjected to different thermal histories by isothermal aging. A consistent relationship between the changes caused by the physical aging in nanostructure and molecular dynamics has been found. The aging makes the structure more homogeneous at a scale of few nanometers, bringing it to a structural state of lower energy. These structural changes affect mainly the α-relaxation, however, some increase in the relaxation strength as well as an increase in the activation energy of the β-relaxation is also observed.

Keywords: Poly(methyl methacrylate); Physical aging; Nanostructure

1. Introduction

Amorphous polymers below the glass transition temperature (T_g) are far from their thermodynamic equilibrium. Indeed, fast cooling from temperature above T_g to temperature lower than glass transition temperature leads to high viscosity and lower mobility of the system resulting in a non-equilibrium structure. In glasses, in a time scale a molecular (and structural) rearrangements appear, in which the chains tend to reach thermodynamic equilibrium. This process is called 'physical aging' and was introduced by Struik [1] to distinguish these effects from other aging processes such as chemical reactions, i.e. degradations. The aging phenomenon affects thermodynamical parameters [1–4], influences molecular dynamics [5–8] and changes the structure at nanometric level [9]. Different thermo-mechanical treatments may induce structural rearrangements in amorphous polymers. The aging temperature and the aging time are regarded as main factors in the case of physical aging phenomenon, but structural changes also may be induced by plastic deformation [11] or by low molecular weight host molecules like methanol in poly(methyl methacrylate) [9,12]. The investigations carried out so far have been performed by many authors and by using different techniques. Nevertheless, the different aging procedures applied during these experiments and different material parameters like: molecular mass or tacticity, make direct comparison between them difficult. The involvement of molecular relaxations in the physical aging process is clear, but the choice of the relevant structural parameters that determine molecular mobility in polymers is still debated. In the case of poly(methyl methacrylate) (PMMA) the involvement of the sub-T_g β-relaxation is especially a contentious matter. An issue connected with this, it is the relation between structural relaxation and the disordered polymer structure at the nanometric level. For these reasons the studies on physical aging phenomena with the use of different experimental techniques for one material aged due to some normalized procedure, are still up to date and purposeful. They allow a deeper understanding of the relation between the structural state and dynamics of glass-forming systems.

In the present work, the aging processes were studied for amorphous PMMA aged for different times and at different temperatures in glassy state. Aging effects were investigated by: Low frequency Raman scattering (LFRS), broadband

* Corresponding author. Tel.: +48 42 631 32 05; fax: +48 42 631 32 18.
E-mail address: julanski@p.lodz.pl (J. Ulanski).

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.10.116

dielectric spectroscopy (BDS), low frequency high resolution mechanical spectroscopy (LFHRMS) and differential scanning calorimetry (DSC).

The LFRS of amorphous polymers arises from the partial localization of acoustic vibrational modes which, being non-propagative in the disordered structures, become Raman active. Hence they give rise to a broad feature at frequencies lower than ca. 200 cm^{-1}. The so-called Boson peak located between 10 and 30 cm^{-1} is a characteristic feature of amorphous materials. It appears as an excess of vibrational density of states (VDOS) in comparison to that predicted by the Debye theory. The Boson peak is, therefore, sensitive to the nanostructure changes and gives information about the size of the heterogeneities in glassy matter [9,11,12]. In this work the obtained results are analysed in frame of the model of non-homogenous nanostructure of glasses proposed by Duval et al., in which it is assumed that the more strongly bonded regions (more cohesive nanodomains) are separated by weakly bonded channels (soft zones) [13].

The application of BDS and LFHRMS allows to investigate the influence of the physical aging on dielectric and dynamic-mechanical properties of PMMA. The information received through applying different techniques makes it possible to understand better the correlations between the thermal history, structure at different size scale and relaxation phenomena in glass-forming systems.

2. Experimental

2.1. Materials

The investigated polymer is a PMMA for optical purposes and has a weight average molecular mass (M_w) equal 120,000 g/mol with polydispersity-$I_p = 1.6$ as assessed by size exclusion chromatography (SEC) measurements. The NMR measurements (^1H and ^{13}C) indicate the presence of syndiotactic triads (rr) of about 0.48, isotactic triads (mm) 0.09 and atactic triads (mr) 0.43. These values are very similar to the theoretical data of fully atactic PMMA.

The glass transition temperature $T_g = 111$ °C was determined from the DSC measurements (mid point) with a heating rate of 10 K/min.

The LFRS and DSC measurements were performed for the extrusion grade pellets, while the BDS and LFHRMS measurements were performed for the films. Before the aging, all the pellets were heated above T_g in nitrogen atmosphere (30 min at 135 °C) in order to erase its earlier thermal and mechanical history (reference state). The PMMA films with a thickness of ca. 0.2 mm were compression-moulded at 150 °C during ca. 10 min under the pressure of ca. 4 bars. To eliminate the internal stresses, the films were additionally annealed without pressure at 150 °C for about 5–10 min. The samples prepared according to this procedure were quenched to room temperature with a rate of about 75 K/min. Some of them were investigated immediately after the quenching as the reference (not aged samples). Other samples were aged by: (a) annealing at 95 and 80 °C (i.e. T_g-16 and T_g-31 °C, respectively) in nitrogen atmosphere during 3 weeks, or (b) storage at room temperature (25 °C) for about 9 months. The pellets and the films were aged simultaneously in the same conditions.

To rule out any additional effects (like degradation) from the obtained results, SEC measurements and Raman spectroscopy in conventional frequency range were applied. SEC measurements performed for PMMA samples after different thermal treatments have exhibited only negligible changes of the molecular weight. Raman spectra around 1640 cm^{-1} (the location of PMMA monomer's band, which is ascribed to C=C vibrations) were also studied to detect possible depolimerization, which might appear during thermal treatments [14] and no such effects were detected.

2.2. Techniques

The physical aging affects the macroscopic properties (enthalpy and entropy level) [2,3] of amorphous polymers, but also cause the changes in the polymer structure at nanoscale. To investigate this effect in PMMA the LFRS was used since it enables the investigation of the structure (and its evolution) at nanometric level by observing the Boson peak. The Raman Boson peak reflects principally the low energy VDOS excess, comparing with Debye regime. Thus, it is a source of information on the supermolecular structure of glasses. Such a relation is expressed by Eq. (1), which gives the LFRS intensity $I(\omega)$ for Stokes scattering:

$$I(\omega) = C(\omega)g(\omega)\frac{n(\omega)+1}{\omega} \tag{1}$$

where: $C(\omega)$ is the light-vibration coupling coefficient, $g(\omega)$ is the VDOS, ω is the frequency and $n(\omega)$ is the Bose factor. The reduced intensity: $I_R(\omega) = I(\omega)/[n(\omega)+1]$ is approximately proportional to the VDOS. The Boson peak in such representation appears as a shoulder on a low-frequency wing of bell-shaped curve (acoustic band), which has a maximum at about 80 cm^{-1}. For easier comparisons the normalized form was chosen, which is given by Eq. (2):

$$I_n(\omega) = \frac{I(\omega)}{[n(\omega)+1]\omega} \tag{2}$$

In this representation the Boson peak appears as the band located between 10 and 30 cm^{-1}. In order to compare LFRS intensities of reference and aged samples, they were additionally normalized at the maximum of acoustic band visible in the reduced Raman spectra. This band is believed not to be affected by physical aging since the high cohesive domains are not involved in the reorganization of the structure in nanoscale. As a result, the normalized Raman spectra presented in Fig. 1 are perfectly matched in higher frequencies, while the low frequency region reveals changes caused by physical aging.

The LFRS was analysed with a high-resolution five-grating monochromator equipped with a photon counting system. The sample was illuminated with an argon laser beam of