

Thermoreversible gelation of biodegradable polyester (PHBV) in toluene

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Abstract

In present paper we investigate thermoreversible gelation of biodegradable polyester poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) in toluene. Hot PHBV solutions became transparent gels after cooling to room temperature. This physical gelation process was followed by light scattering and viscosity measurements for solutions of different PHBV concentrations. It has been found that gelation temperature increases with increasing polymer concentration in toluene. PHBV films have been prepared by gelation process followed by solvent removal on solid substrates. It has been demonstrated that PHBV concentration in the solution influences the surface morphology of obtained films. Homogeneous PHBV films with increased surface roughness can be obtained by means of developed technique. Hydrolytic degradation studies indicate that surface morphology of obtained PHBV layers changes considerably with degradation time.

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1. Introduction

Recently biodegradable materials have received increased interest due to the ecological and recycling reasons. Among numerous bio-polymers microbial polyesters which belong to group of poly(hydroxyl alkanooates) (PHA) have been intensively investigated by numerous research groups. It has been established that a large number of different repeat units are found in these reserve materials, depending on the bacterial species and ingested substrate. Such polyesters are biocompatible and can be bio-degraded under environmental conditions. Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) found numerous applications in medicine (implants [1], drug delivery systems [2,3], tissue engineering [4,5]) due to its attractive properties.

The conformational properties of bacterial polyesters have been intensively investigated [6–8]. Mostly these studies include SANS [6], X-ray analysis [7], molecular modelling investigations [8] and have been focused on poly(3-hydroxybutyrate) (PHB). The solution properties of PHB have been studied by Marchessault et al. [9] by means of intrinsic

viscosity, sedimentation analysis and optical rotary dispersion experiments in chloroform, ethylene dichloride, and trifluoroethanol. It has been found that the type of the solvent influences the chain conformation and it changes from coil to partially helical structure. Similarly to proteins a sharp helix-coil transition was observed by changing the solvent composition or temperature. Einaga et al. [10] investigated a series of PHB fractions in trifluoroethanol by means of light scattering and viscosity measurements. Authors reported a randomly coiled structure in dilute solution of good solvents. Baysal et al. [11] performed molecular dynamics simulation under different conditions for poly(3-hydroxy-5,8-decadienoate). They found strong persistence for rod-like helices in good solvent and sharp helix-to-coil transition was detected in going from good to poor solvent conditions.

The polymer conformational transitions mentioned above play an important role in formation of biopolymer gels and networks, which have been intensively investigated [12–14]. The crosslinking mechanism in such systems mostly involves physical bonds due to three main attractive interactions, i.e. hydrogen bonding, hydrophobic interactions, and electrostatic interactions. This is the reason why the mechanism of such crosslinking is difficult to understand. In present work we investigate thermoreversible gelation of PHBV in toluene. The big disadvantage of PHBV is bad solubility in common solvents, what complicates the processing. Usually chloroform or methylene chloride has been reported to be the best solvent for PHBV [15]. However, it has been found that PHBV can be

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also soluble in toluene after heating. The interesting feature of such solutions is formation of physical gels after cooling to room temperature. This effect is reversible and can open new possibilities for design of biomaterials on PHBV-basis with defined dimensions and morphologies. This includes preparation of membranes, fibres or particles, which can be suitable for medical applications. Therefore, the scope of present work was detailed investigation of gelation process in PHBV-toluene system what should provide better understanding of network formation process. Herein we present also first results on formation of PHBV-layers by using gelation process and report some data concerning biodegradation process.

2. Materials and methods

2.1. Materials

PHBV was received with following characteristics: hydroxyvalerate (HV) content 7.5 wt%; $M_n = 1.257 \times 10^5$ g/mol, $M_w = 4.205 \times 10^5$ g/mol and $M_z = 7.106 \times 10^5$ g/mol; polydispersity index $d = 3.344$. Toluene was obtained from Biesterfeld and used as received.

2.2. Preparation of gels

Gels were prepared by dissolving of appropriate amount of PHBV in toluene at ca. 90 °C. After cooling down transparent gels have been formed.

2.3. Preparation of films

PHBV films have been prepared by spin-coating (Specialty Coating Systems P6700) of PHBV solutions in toluene on glass substrates. Hot PHBV solutions were placed onto glass substrates (2 cm²) at rotation speed 1500 rpm. After film-formation process samples were dried to remove any trace of toluene.

2.4. Hydrolytic degradation of PHBV films

For degradation tests prepared PHBV layers on glass substrates have been placed into 0.01 M phosphate buffer

(pH=7.4) and stored at 37 ± 1 °C. Every 3 weeks samples were rinsed with distilled water, dried and investigated by SEM.

2.5. Analytical methods

2.5.1. Dynamic light scattering

A commercial laser light scattering (LLS) spectrometer (ALV/DLS/SLS-5000) equipped with an ALV-5000/EPP multiple digital time correlator and laser goniometer system ALV/CGS-8F S/N 025 was used with a helium–neon laser (Uniphase 1145P, output power of 22 mW and wavelength of 632.8 nm) as the light source. PHBV solutions in toluene (2.5, 5, 7.5 and 10 g/l) have been investigated. Hot solutions were passed through 5 µm PTFE filter before measurements and placed into glass cuvettes. Measurements have been performed in temperature range 70–90 °C.

2.5.2. Scanning electron microscopy

SEM images were taken with Gemini microscope (Zeiss, Germany). PHBV films prepared on glass substrates have been dried under reduced pressure and coated with gold layer to improve the conductivity. Pictures were taken at voltage of 4 kV.

3. Results and discussion

3.1. Thermoreversible gelation

The thermoreversible gelation process of PHBV solutions in toluene was observed in concentration range from $c_{\text{PHBV}} = 2.5$ to 10 g/l. Transparent solutions prepared by dissolving PHBV in hot toluene became gels after cooling to room temperature (Fig. 1). It has been found that this process is fully reversible and system can be transformed into liquid state by heating.

The principal gelation schema is shown in Fig. 1. Based on studies of conformational properties of biopolyesters [6–8] and gelation of other biopolymer systems [16] it can be assumed that gelation process in PHBV-toluene system proceeds in following way. PHBV chains are in random-coil conformation at a given temperature and concentration (a); later on form partial helices after being cooled (b), and then helices

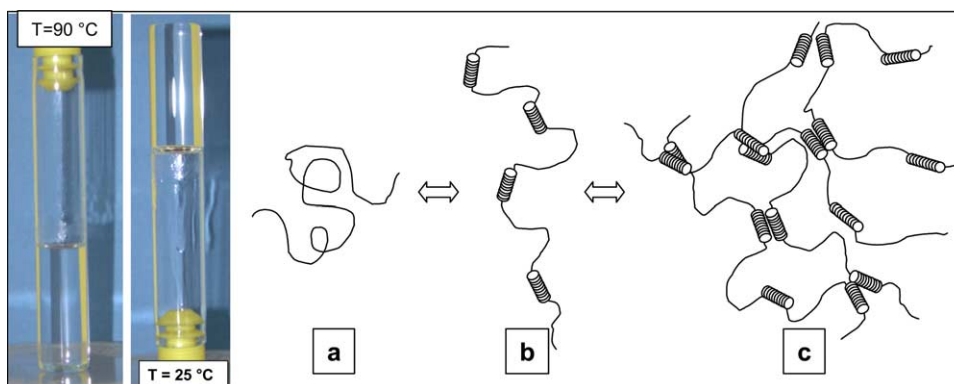


Fig. 1. Schematic representation of thermoreversible gelation in PHBV solutions (photograph shows PHBV solution in toluene at 90 °C and gel formed by cooling down to 25 °C).

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