Polymer 135 (2018) 285–294

Contents lists available at ScienceDirect

Polymer

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

The nature of bonding matters: Benzoxazine based shape memory polymers

Hannes Schäfer [a, b], Andreas Hartwig [a, b], Katharina Koschek [a, *]

[a] Fraunhofer Institute for Manufacturing Technology and Advanced Materials IFAM, Wiener Strasse 12, Bremen, D-28359, Germany
[b] University of Bremen, Chemical Department, Leobener Str., Bremen, D-28359, Germany

ARTICLE INFO

Article history:
Received 29 September 2017
Received in revised form
8 December 2017
Accepted 9 December 2017
Available online 11 December 2017

Keywords:
Shape memory polymers
Benzoxazines
Ring opening polymerization
PCL
Thermosets
Thermo-responsive polymers

ABSTRACT

A novel shape memory polymer is presented based on polybenzoxazine and poly(ε-caprolactone) (PCL). Polybenzoxazines with unbound and covalently incorporated PCL were prepared applying hydroxyl and tosyl terminated PCLs, respectively. Thermo-responsive and shape memory behavior with high shape fixity and recovery were demonstrated for samples containing a high ratio of covalently bonded PCL in a crosslinked benzoxazine structure. Samples with exclusively non-bonded PCL chains proved to be brittle, possessing a heterogeneous morphology and lacking shape memory properties. The type of bonding into benzoxazines network – covalent versus non-covalent bonding of PCL – strongly affects materials structure property relationship.

1. Introduction

Shape memory polymers (SMP) represent a group of smart materials gaining more and more relevance in recent studies and applications [1–6]. Those polymers are able to memorize their original shape after being manipulated and fixed in a temporary shape after a specific external stimulus [7]. A broad variety of stimuli such as temperature [8–10], light [11], electrical fields [12], pH value [13,14], solvents [15,16] or ions [17] was reported.

SMPs exhibit great potential for applications ranging from hinges for solar arrays [18] and adaptive wing constructions [19] in the aerospace industry over seat assemblies and morphing vehicle structures in automotive productions [20,21] up to thermally-tightening sutures [22] and blood clot removal devices [23] for biomedical purposes.

One major group of thermoresponsive SMPs consists of hard and soft segments. The hard segment makes up a network and defines the permanent shape, whereas the soft segment enables a phase transition at a distinct temperature, e.g. T_g or T_m, allowing for modulation and fixation from the memorized to a temporary shape, respectively [1,24]. The most common scaffolds for SMPs are polyurethanes and epoxy resins as hard segments reacting for instance with semi-crystalline polyesterpolyols such as poly(ε-caprolactone)s (PCL) and poly(lactide)s (PLA) as switchable soft segments [25–29]. Shape memory polymers based on poly(ε-caprolactone) were prepared for example by radiative crosslinking of neat PCL [30], by blending PCL with polymethylvinylsiloxane (PMVS) [31] as well as by polymerization of acrylate functionalized PCLs using benzoyl peroxide [32] or by photo curing [33,34].

Benzoxazines have a great potential to serve as hard segments in SMP as they exhibit outstanding thermal and mechanical properties combined with high char yields, near zero shrinkage and few condensation by-products upon polymerization [35–38]. Only a few studies have been recently reported dealing with polybenzoxazine based SMPs. Y. Liu et al. reported SMPs based on polyetheramine or tetramethyldisiloxane, which were end group-functionalized with benzoxazine moieties [39,40]. Furthermore, shape memory systems were described by linking hydroxyl groups of polybenzoxazines with isocyanate-polytetrahydrofuran or -polypropylenglycol prepolymers [41–43]. Epoxy based shape memory polymers with benzoxazines as curing agents were recently reported by S. Rimdusit et al. and T. Tanpitaksit et al. [44,45] Beside SMPs, further smart materials based on benzoxazines were reported such as recyclable [46] and self-healing polybenzoxazines [47,48], self-assembling systems [49], low-surface-free-energy

* Corresponding author.
E-mail address: katharina.koschek@ifam.fraunhofer.de (K. Koschek).

https://doi.org/10.1016/j.polymer.2017.12.029
0032-3861/

polymers based on polybenzoxazines [50] as well as high-performance polybenzoxazoles generated through crosslinking of a main-chain poly(benzoxazine amic acid) [51]. A general overview about polybenzoxazine blends and copolymers was given by Rimdusit et al. in 2013 [52].

The thermal ring opening polymerization (ROP) of benzoxazines, however, requires high temperatures. Various approaches aiming at lowering the curing temperatures were studied. Lewis acids [53], transition metal complexes [54], metal organic frameworks [55] and salts of the trifluoromethanesulfonic acid [56] were described as accelerators and initiators among others. Furthermore, highly reactive benzoxazine monomers have been studied by introducing substituents into the benzoxazine scaffold [57–60] or applying bi- and trifunctional benzoxazines [61–63].

This contribution reports on thermo-responsive polybenzoxazines showing a shape memory effect based on poly(ε-caprolactone) as soft segment. In order to gain a deeper insight into the feasibility and applicability of benzoxazine based SMPs, structure-property relationships were studied considering thermal, mechanical and shape memory behavior of various PCL/benzoxazine mixtures. A special focus lays on the differences in morphology and shape memory behavior caused by the way of bonding and interaction of the thermoplastic PCL while benzoxazine crosslinking polymerization.

2. Experimental part

2.1. Characterization

2.1.1. 1D and 2D NMR spectroscopy

NMR spectra (^{1}H, ^{13}C, HH-COSY) of the poly(ε-caprolactone)s were recorded on a *Bruker AVANCE DPX-200* in deuterated chloroform at room temperature (RT). The chemical shifts δ are reported in parts per million (ppm) and referred to residual protons in the solvent as internal standard (^{1}H: 7.26 ppm and ^{13}C: 77.16 ppm for $CDCl_3$).

2.1.2. Infrared (IR) spectroscopy

The measurements were performed on a *Bruker Equinox 55* FT-IR spectrometer in attenuated total reflection (ATR) with a *Golden Gate* cell at room temperature with a resolution of 4 cm^{-1} (32 scans).

2.1.3. MALDI-ToF-MS

MALDI-ToF-MS measurements were carried out on an *autoflex speed™ LRF MALDI-ToF-MS* from *Bruker Daltonic* with a *MALDI-Perpetual™ ion source* and *BRUKER smartbeam™-II* laser. The samples were prepared on steel targets using 2,5-dihydroxybenzoic acid (DHB) as matrix and lithium chloride as ionization agent.

2.1.4. Gel permeation chromatography (GPC)

Molecular weight and molecular weight distribution were determined using a GPC system from *PSS Polymer Standards Service GmbH* equipped with three PSS-SDV high combination columns (Styrene-divinylbenzene copolymer network with a molecular range: 100-3,000,000 Da) and a refractive index detector (SECurity RID) a diode array detector (SECurity DAD), a viscosimeter detector (DVD 1260) and a light scattering detector with 3D spectra option (SECurity Multichrom SLD 1000). The apparatus was calibrated using polystyrene standards (PSS) and THF (HPLC grade without stabilizer) was used as an eluent at 35°C. The columns where heated at 35°C with a column thermostat (SECurity TCC6000).

2.1.5. Differential scanning calorimetry (DSC)

DSC measurements were performed on a *DSC 2920 Modulated calorimeter* from *TA Instruments* with a sealed pan in a temperature range from 0°C to 250°C and a heating rate of 10°C/min under air. The diagrams are presented “exo up”.

2.1.6. Determination of gel content

The gel content was determined by performing soxhlet extractions. The hackled polymerized samples were extracted for 24 h with dichloromethane. The solid parts were dried in a vacuum oven (50°C, <100 mbar) until constant weight. The extraction solvent was removed under reduced pressure and the extracted residue was analyzed by NMR spectroscopy.

2.1.7. Elemental analysis (EA)

The *Mikroanalytisches Labor Pascher* (Remagen, Germany) performed elemental analyses.

2.1.8. Dynamic mechanical analysis (DMA)

DMA was performed using a single cantilever with a *DMA 2980* from *TA Instruments* with a heating rate of 2°C/min and a frequency of 1 Hz.

2.1.9. Thermogravimetric analysis (TGA)

Thermogravimetric measurements were carried out on a *Q5000* from *TA Instruments* with a temperature range from RT to 800°C and a heating rate of 10°C/min under nitrogen.

2.1.10. Scanning electron microscopy (SEM)

Scanning electron microscopy images of fracture surfaces, prepared by cryofracture in liquid nitrogen, were recorded with a *LEO 1530 Gemini microscope* from *Zeiss*.

2.2. Materials

The bisphenol A based benzoxazine *Araldite® MT 35600* (Fig. 1) was obtained from *HUNTSMAN* and used after drying in an oven under reduced pressure (2 h, 35°C, <100 mbar).

Hydroxy-terminated poly(ε-caprolactone) (PCL) *Capa™ 2402* (M_n: 4000 g/mol) was obtained from *Perstorp* and was used as received (M_n determined by MALDI-ToF-MS (*m*/*z*): $[M+Li]^+$ 3182.3).

2.3. Synthesis

2.3.1. Tosylation of poly(ε-caprolactone) (PCL-(OTs)$_2$)

While stirring a solution of poly(ε-caprolactone) (PCL-(OH)$_2$) (40.0 g, 10.0 mmol, 1 eq.) and triethylamine (34.6 mL, 250 mmol, 25 eq.) in THF (80 mL) 4-toluenesulfonyl chloride (9.6 g, 50 mmol, 5 eq.) was added. The mixture was stirred for 20 h at room temperature. The formed white by-product was separated by filtration and the product was precipitated in cold methanol (600 mL) from the clear solution and stored for two hours at 5°C. The white solid was filtered, washed three times with cold methanol and dried under reduced pressure yielding 34.3 g of PCL-(OTs)$_2$ as a fine, white powder (7.96 mmol, 80%).

PCL-(OTs)$_2$: ^{1}H NMR (200 MHz, $CDCl_3$, δ, ppm): 7.78 (d, 4H, ArH), 7.34 (d, 4H, ArH), 4.05 (t, 76H, CH_2–O), 2.44 (s, 6H, Ar–CH_3), 2.30 (t, 76H, CH_2–COO), 1.64 (m, 152H, CH_2), 1.39 (m, 76H, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$, δ, ppm): 173.6, 129.9, 128.0, 70.4, 64.2, 63.9, 32.2,

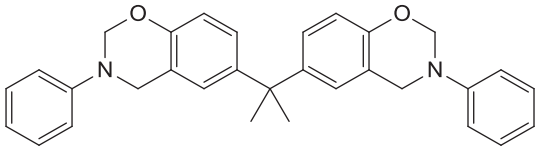

Fig. 1. Bisphenol A based benzoxazine Araldite® MT 35600.