

Microstructure in Shape-memory Chemical-Physical Co-networks

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1. Abstract

Polymers possessing shape memory are exciting materials, based on a combination of controlled degradation and triggered actuation that enables the design of unique medical devices. This research focus on physical “double-networks” that feature a superposition of a covalent network with a percolative physical network. Block copolymers based on polyethylene glycol (PEG) and polycaprolactone (PCL) were synthesized. We report the influence of composition on the microstructure and thermal properties. Furthermore, the recrystallization kinetics was investigated using small-angle light scattering, the results showed a competitive crystallization between the two species in the network.

2. Introduction

Shape memory polymers (SMPs) are an exciting class of stimuli-responsive materials that can undergo dramatic shape changes based on specific environmental conditions. Two broad classes of SMPs have been elaborated in the literature: one-way (1W-SMP) and two-way (2W-SMP) [1, 2]. For 1W-SMPs, the sample is deformed into a temporary shape and “fixed” through cooling. The material can then spontaneously return to its original shape through subsequent heating [3]. Biodegradable SMPs are exciting materials, based on a combination of controlled degradation and triggered actuation that enables the design of unique medical devices. However, their synthesis requires precise control over thermo-mechanical properties often not possible with common building blocks for biodegradable polymers. In the present work, we report the preparation of “double networks” that feature a superposition of a covalent network with a percolative physical network. The blocks consist of bio degradable partially crystalline polymers, polyethylene glycol (PEG) and polycaprolactone (PCL)

3. Experimental

3.1 Materials

A series of block copolymers based on PEG and PCL with varying composition and constant molecular weight were synthesized. The blocks consisted of PCL 2,000 g/mol and PEG of 6,000 g/mol. To determine the chemical structure and molecular weight (M_n) of the PCL-PEG diols, ^1H NMR spectroscopy (Varian Inova spectrometer, 600 MHz, 128 scans) was performed at room temperature using deuterated CHCl_3 as the solvent. Gel permeation chromatography (GPC) was conducted in HPLC-grade tetrahydrofuran (THF) using a Varian Pro Star system with a Viscotek dual detector attachment used for viscosity and light scattering tests. Solutions were prepared from THF (~5 mg/mL) and passed through a 0.45 μm PTFE filter prior to injection. The GPC operated at a rate of 1 mL/min with two columns of cross-linked PS beads. The columns were 5 and 30 cm long (Polymer Laboratories, Inc.), each packed with 3 μm particles designed for separations of polymers with $M < 25,000$ g/mol. The copolymers were photo cured in the presence of a tetrathiol cross-linker, Table 1.

Table 1 PCL-PEG double molecular networks

Sample	PCL 2K / PEG 6K	Gel fraction (%)	T_m (°C)	T_c (°C)	ΔH_m (J/g)
1-A	100 % / 0%	98.3	34.4	7.5	46.2
1-B	80 % / 20%	98.4	35.0	5.4	53.2
1-C	60 % / 40%	98.6	37.9	4.7	52.2
1-D	50 % / 50%	97.9	41.5	12.1	53.4
1-E	40 % / 60%	98.0	42.7	18.8	60.2
1-F	20 % / 80%	97.4	48.3	28.5	83.9
1-G	0 % / 100%	97.2	51.3	36.3	112.4

3.2 Thermal Analysis

The transition temperatures (T_m) were determined using differential scanning calorimetry (DSC, TA Instruments Q100) under a nitrogen purge. The networks were heated to 100 °C, then cooled to -90 °C at a rate of 10 °C/min and heated once more to 100 °C using the same rate. Values reported for T_m , T_c , and ΔH_m are taken from the second heating traces.

3.3 Microstructure

Isothermal recrystallization was carried out using a Leitz microscope and a Mettler FP-90 hot-stage. Images were acquired using a Moticam 100 digital camera manufactured by

Motic Inc. H_V small-angle light scattering patterns were obtained using an in-house built diffractometer equipped with a He-Ne laser ($\lambda=632.8$ nm).

4. Results and discussion

The gel fraction determination (Table 1) showed that the crosslinking reactions were nearly complete for each sample. On the other hand, thermal transitions were determined by DSC, these are listed in Table 1. The results show that the thermal transition temperatures of the copolymer networks vary continuously between the neat components.



Figure 1. Polarized optical microscopy of PCL-PEG 50%/50% networks. Isothermal recrystallization at room temperature (material was first taken to the melt and then quenched to room temperature).

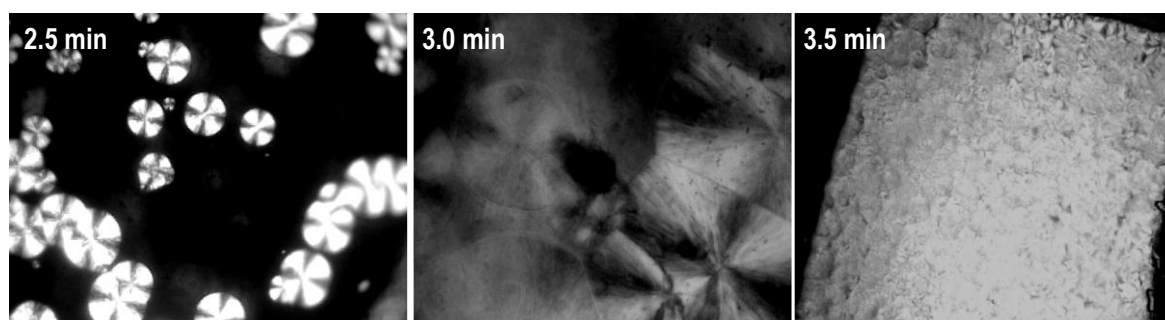


Figure 2. Polarized optical microscopy of PCL-PEG 20%/80% networks. Isothermal recrystallization at room temperature (material was first taken to the melt and then quenched to room temperature).

The kinetics of crystallization was investigated via POM and SALS. For this, the materials were taken into the melt and then quenched to room temperature; Figure 1 shows POM micrographs for the PCL-PEG 50-50 network as a function of time. Within the first minute there is no evidence of crystallization. At 1 min the sample exhibits a striped texture. This texture slowly develops into well-defined spherulites. After 15 min the spherulitic

microstructure can still be clearly appreciated. On the other hand, the PCL-PEG 20:80 network (Figure 2) shows a significantly faster rate of crystallization. Although the first spherulites are appreciated after about 2.5 min, these rapidly grow covering the field of view (3 min). Strikingly, after 3.5 min no individual spherulites can be identified. The mean size of spherulites can be determined by SALS. Figure 3 shows a series of H_V SALS patterns corresponding to the PCL-PEG 0-100 network. The 4-lobe scattering pattern is clearly seen after 1 min. The spherulites grow and impinge over each other rapidly saturating the field of view, giving rise to a circular pattern with an intensity maximum corresponding to the mean size of spherulites. The plot in Figure 3 shows the time evolution of intensity maximum; after the initial rapid grow, there is no change in spherulite size. This behavior was observed in the PEG-rich networks.

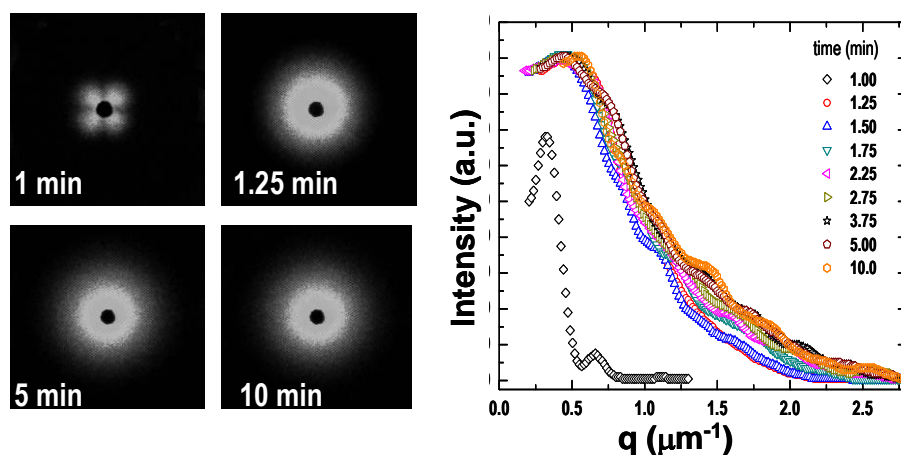


Figure 3. H_V SALS patterns vs. time for PCL-PEG 0%/100% networks. Isothermal recrystallization at room temperature. Plot of scattered intensity as a function of time and scattering vector q .

5. Conclusions

A series of block copolymers based on polyethylene glycol (PEG) and polycaprolactone (PCL) with constant molecular weight and varying composition were investigated. In-situ small-angle light scattering and polarized optical microscopy showed a competitive crystallization between the two species in the network.

B Alvarado-Tenorio was supported by a scholarship from CONACyT, ME Romero-Guzmán was supported by a postdoctoral fellowship from DGAPA-UNAM. This research was supported by CONACyT (CIAM-2006, grant 58646) and the Materials World Network program, NSF.

6. References

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