

Spiropyran Based Smart Composites: Memorizing Polymer with Enhanced Molecular Switches

S. Shree¹, M. Schulz-Senft², X. Jin¹, Y.K. Mishra¹, A. Staubitz², and R. Adelung¹

¹ University of Kiel, Functional Nanomaterials, Institute for Materials Science, Kiel, Germany

² University of Kiel, Otto-Diels-Institute for Organic Chemistry, Kiel, Germany

Abstract— We demonstrate the fabrication and response of a smart material combined with spiropyran molecules. Spiroyrans belong to a class of compound that constitute molecular switch. They change color in response to different stimuli such as heat, UV light or mechanical stress. These molecules have been incorporated in polythiourethane (PTU) which is a shape memory polymer. The observations revealed that the molecular switches do not alter the physical properties of the PTU in general; however, both, the spiropyran molecules and smart polymer show changes individually when exposed to heat. The microscopic mechanisms of switching process in response to external stimuli have been discussed in detail.

Keywords— Spiropyran , Merocyanine), Polythiourathene, Shape memory polymer.

I. INTRODUCTION

Polymer based functional composites, which exhibit the capability to respond to any external triggers, e.g., heat, UV light, stress, etc., are important material candidates for various applications. This kind of smart polymeric materials equipped with shape memory features, have found enormous applications in various fields ranging from aerospace to building industries [1]. Very recently, there has been significant progress in the direction of self-healing/reporting materials and these auto-responsive polymers are the most appropriate candidates in this context. The major drawbacks of the present heat/light sensitive smart polymer coatings are that they contain toxic metals and permanent deformations of the polymer decrease the life-time of the material.

The shape memorizing polymer matrix used in this paper is polythiourethane, a thermo-set polymer, which can be polymerized under solvent free conditions and is thermally stable. Hence it could have tremendous applications as a smart polymer. To make this shape memory polymer more efficient, spiropyran is added to the polymer matrix as a heat indicator.

Spiropyran has been used for its photo-responsive properties for several applications such as light modulated sensors [2] and for drug delivery [3].

These molecular switches have been used in our work and were incorporated into PTU. The usual ways of integrating spiropyran in a polymer matrix are either by

polymerization of spiropyran based monomers or grafting of spiropyran on pre-formed polymer [4]. The downside of these methods of well defined covalent integration into a polymer is the accessible amount of material and its comparatively high cost, which might limit industrial usefulness. By adopting a simple strategy of dispersion of spiropyran molecules in the co-monomer, larger amounts can be obtained which is the main focus in present work.

II. EXPERIMENTS

A. Materials

Solvent free PTU, a two component system, was purchased from Fluid-& Prozesstechnik GmbH (Waltershausen, Germany). Preparation of the polymer was achieved by a poly-addition reaction between pentaerythritoltetrakis- (3 mercaptopropio-nate) (Tol) (2 mmol, 1 g) and 1.6-diisocyanatohexane (Iso) component (8.0 mmol, 1.4 g).

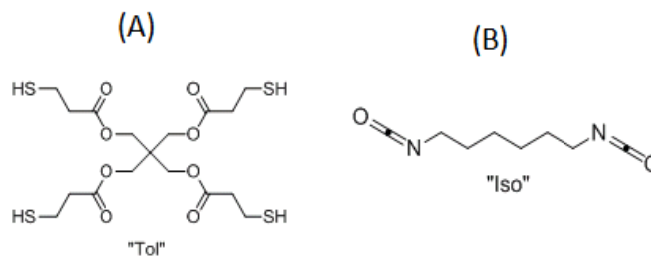


Fig. 1 Molecular structures of (A) the Tol component, and (B) the molecular structure of Iso the component.

B. Sample Preparation

The samples were prepared by dispersing 0.01 wt% spiropyran in the co-monomer Tol for 20 min at 2000 rpm in a Netzsch Mini-Master dispersion machine to obtain homogeneous distribution of spiropyran. To this mixture, an appropriate amount of Iso was added. After degassing the mixture in a desiccator, the polymer blend was set into the moulds and placed in an oven for 2 h at 75 °C for polymerization process.

C. Response of PTU to Heat

When heated, a pure PTU (without spiropyran) above its glass transition temperature (85 °C), softened. This allowed

us to give the polymer any kind of shape which was maintained upon cooling. The deformed polymer returned to its original shape by an external stimulus such as heat.

D. Switching Mechanism of Spiropyran in Response to an External Stimulus

Spiropyran undergoes a reversible isomerization to the corresponding merocyanine form under the influence of an external stimulus such as heat. This causes changes in the molecular structure of thermochromic Spiropyran [5], resulting in the open ring structure called merocyanine as illustrated in Figure 2.

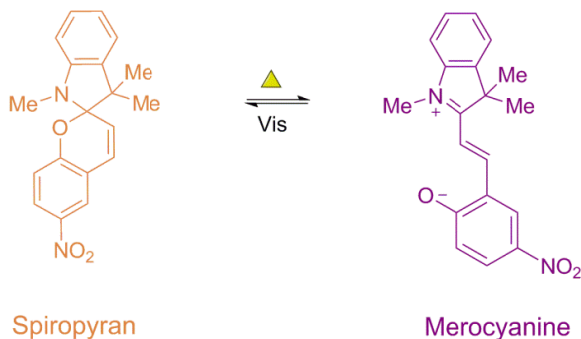


Fig. 2 Reversible isomerization between spiropyran and merocyanine in response to heat

III. RESULTS AND DISCUSSION

The PTU/spiropyran samples with a given flat shape (A) were heated to $T = 100\text{ }^{\circ}\text{C}$ slightly above their glass transition temperature which softened the samples. While cooling down from $100\text{ }^{\circ}\text{C}$, different shapes have been given to the polymer, such as (B) and (C) [Figure 3 (B, C)].

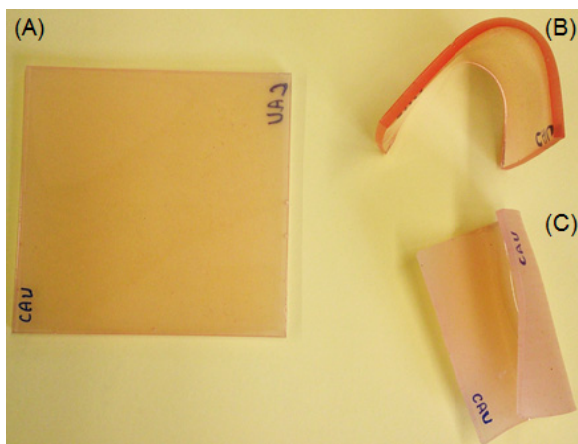


Fig. 3 Different shapes of the PTU/spiropyran under temperature controlled conditions. (A) Corresponds to the original shape of PTU/spiropyran, (B) and (C) are folded and twisted shape of PTU/spiropyran respectively

A folded PTU/spiropyran sample (Figure 3B) was clamped on one side and solely its free end was heated up to $100\text{ }^{\circ}\text{C}$ gradually with a heating gun (Figure 4). Under heat treatment, a complete shape recovery of the folded sample could be achieved as demonstrated clearly in by Figure 4 (a-h).

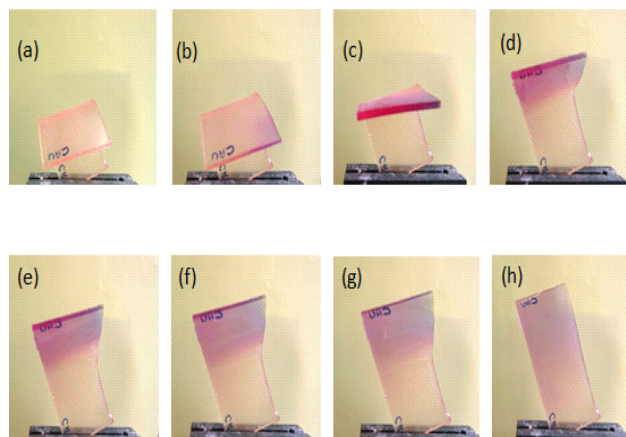


Fig. 4 PTU/spiropyran sample clamped on one end and only the folded end is heated with a heating gun. From (a) to (h) the sample was heated gradually up to $100\text{ }^{\circ}\text{C}$ and the shape recovery behavior was clearly visible.

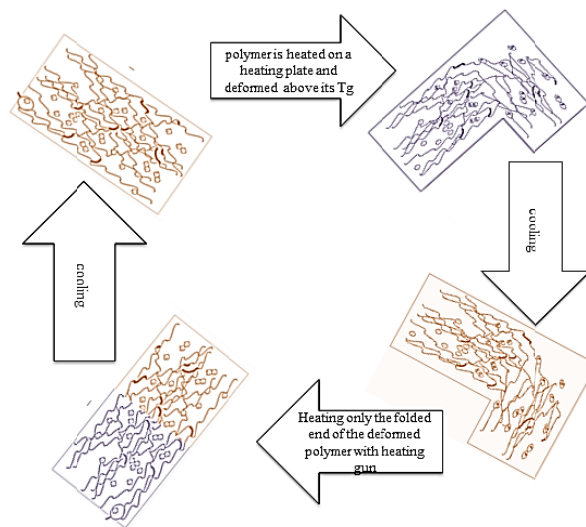


Fig. 5 Schematic representation of polymer chains incorporated with spiropyran undergoing structural changes independently

The PTU matrix consisted of a thermo-plastic and a thermo-set part. The thermo-plastic part of the polymer deforms upon heating. The thermo-set part of the polymer restrains deformation due to the cross-linking of SH-groups present in the Tol component with the NCO-groups in Iso

component. When the temperature is above T_g , the polymer chains overcome inter-chain forces resulting in softening the polymer which is enough for deformation. Again when the polymer with temporary shape is heated, the chain relaxes which results in returning the polymer to its original shape. This has been described by schematic representation in the Figure 5.

The added heat indicator gains enough energy for ring opening reaction at around 100°C as presented in the Figure 2. When cooled merocyanine returns to the closed form independent of the changes taking place in the polymer chains.

IV. CONCLUSION

A shape memory polymer with an integrated heat Indicator has been successfully fabricated in a very simple approach. With mere PTU, it is difficult to recognize the reasons for the deformation process that the polymer undergoes when it returns to its original shape. However, with the spiropyran in the matrix, it enables one to recognize if the deformation of the polymer was due to the heat applied by the change of its color. This PTU/spiropyran matrix was synthesized in an intelligent way where the physical properties of both the materials involved, were maintained independent of each other.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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Author: Sindu Shree
 Institute: University of Kiel, Functional Nanomaterials,
 Institute for Materials Science
 Street: Kaiserstrasse 2
 City: Kiel
 Country: Germany
 Email: sisi@tf.uni-kiel.de