# Turning Polybutadiene into Shape Memory Polymers

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A semi-crystalline, shape memory polymer (SMP) is fabricated by free radical cross-linking, polymerization, and grafting in a blend of *n*-octadecyl acrylate and polybutadiene (PB). Poly(*n*-octadecyl acrylate) (PODA) is a side-chain crystalline polymer, which serves as the structure-fixing network counterbalancing the elastically deformed, cross-linked polymer network. At a constant 50/50 ratio of monomer and polymer the amount of free radical initiator, dicumyl peroxide (DCP) is varied from 1% to 5% w/w PB. From swelling measurements and calculation of the cross-link density it is determined that DCP produces greater than one cross-link per DCP molecule. It is found that lower cross-linking efficiency is favorable for higher shape fixity. This lower efficiency is found to produce a higher degree of crystallinity of the PODA in the 2–5% DCP samples, which is determined to be the main driver of higher shape fixity of the polymer. A SMP with >90% fixity and 100% recovery at uniaxial strains from 34–79% is achieved. This material should be useful for mold processing of shape memory articles. This approach provides a method to decouple the elastomeric and thermoplastic portions of a SMP to convert commodity elastomers into SMPs and tailor the shape memory response.

Shape memory polymers polybutadiene side-chain crystallinity dual-network elastomers octadecyl acrylate thermal actuation smart materials polymer networks

## 1. Introduction

Shape memory polymers (SMPs) are smart materials that can be deformed into a temporary shape and later recover their original configuration when exposed to an external stimulus such as heat, light, or moisture. Compared to shape memory alloys, SMPs are lightweight, easily processable, and capable of very large recoverable strains, which makes them attractive for applications ranging from biomedical devices to soft robotics and deployable structures. At the molecular level, shape memory behavior arises from the coexistence of two distinct but cooperative networks: a permanent elastic network that stores deformation energy and a reversible fixing network that stabilizes the temporary shape until recovery is triggered. While many SMP systems have been developed using polyurethanes, polyesters, or epoxy-based networks, polydiene elastomers such as polybutadiene (PB) have received comparatively little attention, despite their excellent elasticity and widespread industrial use. This work highlights a strategy to convert commodity polybutadiene elastomers into high-performance shape memory polymers by incorporating a chemically integrated, side-chain crystalline polymer network derived from *n*-octadecyl acrylate (ODA).

## 2. Why Polybutadiene Needs Help to Become a Shape Memory Polymer

Crosslinked polybutadiene is an outstanding elastomer, but on its own it lacks two essential requirements for shape memory behavior. First, its glass transition temperature lies well below room temperature, which prevents conventional thermally induced switching. Second, polybutadiene does not possess intrinsic crystallinity, limiting its ability to fix a deformed shape once the external load is removed. To overcome these limitations, an additional solid phase capable of reversible physical transitions must be introduced. Traditional strategies often rely on blending elastomers with crystalline small molecules such as waxes or fatty acids; however, these approaches frequently suffer from blooming, leaching, and poor long-term stability. A more robust solution is to chemically integrate the shape-fixing phase directly into the elastomer network, ensuring durability and reproducible performance.

## 3. One-Pot Formation of a Dual-Network SMP

In this approach, polybutadiene is blended with *n*-octadecyl acrylate and a free-radical initiator, dicumyl peroxide, and then subjected to thermal treatment. During heating, multiple reactions occur simultaneously: the polybutadiene chains undergo chemical crosslinking, the octadecyl acrylate monomers polymerize into poly(octadecyl acrylate) (PODA), and the newly formed PODA chains become grafted onto the polybutadiene network. This single, one-pot thermal process leads to the formation of a dual-network system consisting of a permanent elastic polybutadiene network and a reversible side-chain crystalline PODA network. Upon cooling, the long alkyl side chains of PODA crystallize, creating a physical fixing phase that is essential for stabilizing the temporary shape in shape memory applications.

## 4. Network Structure and Crosslinking Efficiency

Swelling experiments and gel fraction measurements demonstrate that most of the material becomes part of an insoluble, crosslinked network, confirming strong chemical coupling between the polybutadiene and PODA components. Interestingly, increasing the amount of peroxide initiator does not lead to a proportional increase in effective crosslink density. Instead, crosslinking efficiency decreases at higher initiator concentrations due to enhanced radical termination reactions. This reduction in efficiency plays a beneficial role, as lower effective crosslink densities provide greater molecular mobility for the PODA side chains, allowing them to crystallize more effectively. Enhanced side-chain crystallization directly improves shape fixity, illustrating that crosslinking efficiency, rather than initiator concentration alone, is a key parameter governing shape memory performance.

## 5. Thermal Behavior and Crystallinity

Differential scanning calorimetry reveals a broad melting transition in the range of approximately 38–43 °C, which corresponds to the melting of the PODA side-chain crystals. The degree of crystallinity is found to depend strongly on crosslinking efficiency rather than simply on the amount of peroxide used. Samples with lower effective crosslink densities exhibit higher PODA crystallinity, as the side chains experience fewer topological constraints. The resulting side-chain crystallization provides a tunable thermal switching temperature close to ambient and physiological conditions, making these materials particularly suitable for heat-triggered shape memory applications.

## 6. Shape Memory Performance

Dynamic mechanical analysis demonstrates excellent shape memory behavior in the PB–PODA system. The materials exhibit shape fixity values exceeding 90% and shape recovery ratios approaching 100%, even over multiple thermomechanical cycles. Recoverable strains range from approximately 30% to nearly 80%, highlighting the large deformation capability of the elastomeric backbone. When heated above the melting temperature of the PODA crystals, the crystalline fixing network melts rapidly, allowing the elastic polybutadiene network to drive fast shape recovery, often occurring within one to two seconds.

## 7. Mechanism of Shape Memory

The shape memory mechanism in this system arises from a clear separation of functions between the two networks. Deformation above the PODA melting temperature allows the polybutadiene network to store elastic energy. Subsequent cooling under load induces crystallization of the PODA side chains, which fixes the temporary shape. After removal of the load, the material retains this shape at room temperature. Reheating above the melting transition causes the PODA crystals to melt, releasing the stored elastic energy and enabling rapid recovery to the original shape. This well-defined division between elastic energy storage and reversible shape fixation is characteristic of high-performance SMPs.

## 8. Advantages of This SMP Design Strategy

The PB–PODA shape memory system offers several notable advantages over conventional elastomer-based SMPs. Because the fixing phase is chemically integrated, the material does not suffer from blooming or leaching issues commonly associated with small-molecule additives. The system remains melt-processable and is compatible with standard techniques such as compression and transfer molding. Its properties can be readily tuned through control of crosslinking efficiency and composition, enabling the transformation of commodity elastomers into functional smart materials. Furthermore, this design strategy is general and can be extended to other polydiene backbones and side-chain crystalline monomers.

## 8. Outlook and Applications

This work demonstrates a scalable and versatile route to shape memory polymers that combine excellent mechanical durability with robust shape memory performance. Future studies may explore alternative polydiene matrices such as styrene–butadiene rubber or natural rubber, as well as different alkyl acrylates to further tailor the switching temperature and mechanical response. Improved control over crosslinking efficiency through initiator chemistry or processing conditions could offer additional design flexibility. With potential applications in soft actuators, biomedical devices, deployable structures, and adaptive materials, the combination of industrial elastomers with side-chain crystallinity provides a powerful platform for developing robust, tunable, and application-ready shape memory polymers.

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