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# Thermodynamic behavior and mechanisms of deformation of phase-separated multiblock copolymers as revealed from deformation calorimetry

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## Abstract

The thermodynamic analysis of the uniaxial stretching of block copolymers of various chemical compositions and hard block contents was carried out using a deformation calorimetry method.

It was found that the initial small deformations result from the volume elasticity of the hard phase, independent of its content and chemical nature. The intramolecular energy contributions of soft blocks to the deformation thermodynamics were estimated. It was shown that the hard block contributions depend on their content and degree of sample stretching. The samples were divided into two groups with respect to their thermodynamic behavior.

*Keywords:* Calorimetry; Copolymer; Deformation; Hysteresis; Thermodynamics

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## 1. Introduction

Linear multiblock copolymers consisting of alternate soft and hard blocks (segments), similar to their di- and triblock analogs, undergo microphase separation if their blocks are sufficiently incompatible [1–3]. As a result of this microphase separation, such a block copolymer self-organizes into periodic microdomains. Normally, the glass transition or melting temperatures of the blocks are sufficiently different. The morphology of these two-phase systems varies with the hard block concentration from a continuous soft phase with dispersed hard domains, to a

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continuous hard phase with dispersed soft domains. In typical multiblock copolymers, such as segmented polyurethanes or polyesters, the glass transition temperature of the soft blocks is below room temperature.

One of the important features of these microphase-separated multiblock copolymers is that their mechanical behavior can be varied from being typically rubber-like at low concentrations of the hard blocks, to typically plastic-like at high concentrations of the hard blocks. At the optimum sample composition up to the temperature of hard-component softening, such block copolymers possess unique mechanical properties, namely a combination of high rubbery deformability and rigid plastic tensile strength. Hard domains in the soft phase play the role of physical crosslinks, allowing reversible high elastic deformations. Hence, this type of block copolymer, together with “classical” SBS block copolymers, is an advanced rubber-like material, a thermoplastic elastomer, with many applications in various fields. The peculiar mechanical behavior of block copolymers results from the micro-scale level of phase segregation, the existence of chemical bonds between the components, and the extent of their interaction. However, the contributions of each component to the block copolymer deformation mechanism are not yet completely understood.

Within the last two decades, the structure and properties of thermoplastic elastomers have been studied extensively by various methods including static and dynamic mechanics, DSC, X-ray crystallography, electron microscopy, dielectric properties, etc. [1–3]. It has been demonstrated that, in contrast to di- and triblock copolymers, the extent of microphase separation in multiblock copolymers is very often incomplete, which affects both the morphology and the mechanical properties of the thermoplastic elastomers. Therefore, the deformation mechanism in these materials reflects the highly heterogeneous and ordered structure on various levels. Hence both the soft and hard segments may contribute to the mechanical behavior of these thermoplastic elastomers.

At the end of the 1970s, we applied deformation calorimetry for the first time in the study of the thermodynamics and molecular mechanisms of the uniaxial stretching of thermoplastic elastomers [4–9], such as styrene–diene–styrene triblock copolymers, segmented polyurethanes and polyesters with various chemical structures of hard and soft blocks. The following aspects have been studied and clarified:

1. The stress-softening phenomenon observed in the first loading cycle, i.e. the strain-induced plastic-to-rubber transition, resulting from the breakage of stress-supporting rigid phases.
2. The re-formation phenomena of stress-softened samples in stress-free states which involves restoration of the initial continuity of the hard phase.
3. The intra- and intermolecular entropy and energy effects during the stretching of the stress-softened thermoplastic elastomers and the contributions of the soft and hard blocks to these effects.
4. The limited chain extensibility of the soft segments with large deformations.

The main aim of the present paper is to summarize briefly our previous results with particular emphasis on the principle possibility of deformation calorimetry in

studying the thermodynamic behavior of thermoplastic elastomers and on the mechanisms of deformation which can be revealed from deformation calorimetry measurements.

## 2. Thermodynamics of deformation and treatment of calorimetric results

The complete thermodynamic analysis of various deformation processes in polymers is given in Refs. [9] and [10]. Here only the major aspects necessary for treating the experimental results will be considered.

### 2.1. Small initial (reversible) deformations

The mechanical work  $W$ , heat effect  $Q$  and internal energy changes  $\Delta U$  of the initial plastic-like behavior of block copolymers can be expressed by

$$W = \frac{E\varepsilon^2}{2} \quad (1)$$

$$Q = \beta T\sigma = \beta TE\varepsilon \quad (2)$$

$$U = \frac{E\varepsilon^2}{2} \left( 1 + \frac{2\beta T}{\varepsilon} \right) \quad (3)$$

where  $E$  is Young's modulus,  $\varepsilon$  is the strain,  $\beta$  is the coefficient of linear thermal expansion, and  $T$  is absolute temperature.

### 2.2. The energy balance of stress-softening and the hysteresis effect

The complete energy balance of the loading–unloading cycles is

$$\Delta W = \Delta U - \Delta Q \quad (4)$$

where  $\Delta$  indicates the difference in the corresponding values for the loading and unloading cycles.

### 2.3. Large rubber-like deformations

The main expressions for treating the deformation calorimetric results are

$$W_{P,T} = C \frac{(\lambda - 1)}{\lambda} (\lambda^2 + \lambda - 2) \quad (5)$$

$$Q_{P,T} = -C \left[ \left( 1 - T \frac{d \ln \langle r^2 \rangle_0}{dT} \right) - \frac{2\alpha T}{\lambda_2 + \lambda - 2} \right] \frac{(\lambda - 1)}{\lambda} (\lambda^2 + \lambda - 2) \quad (6)$$

$$U_{P,T} = C \left( T \frac{d \ln \langle r^2 \rangle_0}{dT} + \frac{2\alpha T}{\lambda^2 + \lambda - 2} \right) \frac{(\lambda - 1)}{\lambda} (\lambda^2 + \lambda - 2) \quad (7)$$

$$C = \frac{1}{2} \nu k T V_0^{-1} \frac{\langle r^2 \rangle_i}{\langle r^2 \rangle_0} \quad (8)$$

$$\left( \frac{Q}{W} \right)_{P,T} = -1 + T \frac{d \ln \langle r^2 \rangle_0}{dT} + \frac{2\alpha T}{\lambda^2 + \lambda - 2} \quad (9)$$

Eq. (10) can be used for obtaining the intramolecular contribution to the elasticity of rubber-like materials

$$(\Delta U/W)_{V,T} = T d \ln \langle r^2 \rangle_0 / dT = (\Delta U/W)_{P,T} - 2\alpha T (\lambda^2 + \lambda - 2) \quad (10)$$

### 3. Calorimetry

The thermal effects accompanying simple elongation and contraction were studied with the aid of the microcalorimetric instrument which has been described in detail in Refs. [10] and [11].

The typical experimental procedure was as follows. The clamped sample was placed in the working cell of the calorimeter and, after stabilization of the baseline, the experiments were performed. Three experimental modes were applied: (1) extension–contraction with an intermediate pause, (2) gradual extension with stepwise elongations of 10–50%, and (3) an extension–contraction cycle without a pause. It should be noted that a low rate was used with small deformations (mode (1) only). For recording force and strain, an automatic tensometric bridge was used. The values of mechanical work and thermal effect at a given deformation were determined as the areas under the corresponding curves whose shapes are shown in Fig. 1.

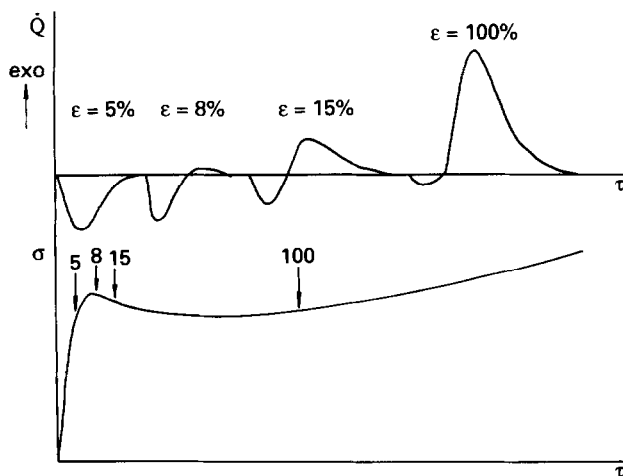


Fig. 1. Thermal heat flow and mechanical tension effects during stretching.

Table 1  
Composition of the polyurethanes studied

BCP	Hard block	Soft block
PBU <sup>a</sup>	Diphenylmethanediisocyanate + triazine-containing diol (23–79 wt%)	Oligobutadiene $M_M = 2000$
PEU <sup>b</sup>	Diphenylmethanediisocyanate + butanediol (11–58 wt%)	Oligoethylenebutylenadipate $M_M = 1940$
H-55	Polybutyleneterephthalate (55 wt%)	Oligotetramethyleneoxide $M_M = 1000$
PSU <sup>a</sup>	Diphenylmethanediisocyanate + toluilenediol (18–55 wt%)	Oligodimethylsiloxane $M_M = 1500$

<sup>a</sup> Samples prepared by Dr A.R. Korogodsky (MCTI). <sup>b</sup> Samples prepared by Dr. M.P. Letunovsky (SRISR).

#### 4. Materials

The experiments were performed using several types of polyurethanes, including polybutadieneurethanes (PBU), polyesterurethanes (PEU) [8], polysiloxaneurethanes (PSU) [13] and the polyetherester block copolymer (PE) “Hytrel” (Du Pont), see Table 1.

PBU consist of oligobutadiene soft blocks ( $M_M = 2000$ ) and diphenylmethane-diisocyanate with triazine-containing diol as hard blocks [12]. The hard block content was varied from 24 to 63 wt%. PEU was produced from ethylenebutyleneglycoladipate ( $M_M = 1940$ ) and diphenylmethanediisocyanate with butanediol as extender. The content of the hard blocks varied from 11 to 58 wt%. PSU consists of polydimethylsiloxane ( $M_M = 1800$ ) as the soft phase and diphenylmethanediisocyanate with butanediol (18–55 wt%) as the hard phase. The content of the hard blocks varied from 11 to 58 wt%. “Hytrel” contains polybutyleneterephthalate hard block (55 wt%) and oligotetramethyleneoxide ( $M_M = 1000$ ).

DSC analysis has shown that the PBU and PSU are completely phase-segregated systems. PEU and Hytrel are heterogeneous, but the phases are mixed.

#### 5. Samples

The test specimens were cut from 0.1–0.3-mm thick films prepared from solution or by hot pressing. The length of the samples used in the study was 20–70 mm.

#### 6. Initial small-strain reversible deformations

With increasing hard block content, the mechanical behavior of thermoplastic elastomers varies from that of typical rubber-like materials to that of rigid plastics.