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Dielectric studies of molecular mobility and microphase separation in segmented polyurethanes

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Abstract

This work deals with molecular mobility and microphase separation studies on segmented polyurethanes with different fragments, including crown ethers, as chain extenders and/or chain end groups. The techniques used include thermally stimulated depolarization current (TSDC) in the temperature range –185°–30°C and broadband dielectric relaxation spectroscopy (DRS) in the frequency and temperature ranges of 10^{-2}–10^{6} Hz and –55°–80°C. The combination of these techniques allowed the secondary γ and β mechanisms, the primary α mechanism, the Maxwell–Wagner–Sillars (MWS) mechanism associated with interfacial polarization and dc conductivity σ_{dc} to be recorded. The results suggest that addition of crown ethers promotes microphase separation. Specific characteristics of the primary α and the MWS relaxations and σ_{dc} were found to systematically change with the degree of microphase separation. They should be further quantified and tested on selected systems. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

Segmented polyurethanes are typical representatives of linear block copolymers. Their versatile physical properties are generally attributed to their microphase-separated structure. The latter arises due to the thermodynamical incompatibility of the hard segment and the soft segment. However, the microphase separation is not complete, even at complete incompatibility of the segments, due to covalent bonds between them [1]. Several factors affect the degree of microphase separation (DMS), such as polarity and length of the hard and soft segments and flexibility of the hard segments [2]. According to Koberstein and coworkers [3] a critical hard-segment length is required for microphase separation, whereas DMS generally improves with an increase in the hard-segment content. Chu and coworkers [4] pointed to the significance of kinetic factor, besides the thermodynamic one, for the phase structure formation.

Several experimental techniques have been employed to investigate the DMS and the microphase composition in polyurethanes [1–9]. They include among others, differential scanning calorimetry (DSC) [1–3, 7, 8], wide-angle X-ray scattering (WAXS) [2, 3], small-angle X-ray scattering SAXS [1–4], high-voltage electron microscopy [5], electron spin resonance (ESR) [6], dielectric relaxation spectroscopy (DRS) [7], nuclear magnetic resonance (NMR) [8], ultrasonic spectroscopy (US) [9], dynamic light scattering [9] and dynamical mechanical thermal analysis (DMTA) [9]. Koberstein and coworkers [10] and Chen and

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coworkers [1] developed models to calculate the microphase composition using DSC and SAXS data. Apart from their fundamental interest, these studies are also of practical interest, since the DMS and the microphase composition control to a large extent the technologically important properties of polyurethanes.

The incorporation of crown ethers into the rigid chain blocks has been found to affect the phase morphology and the physical properties of polyurethanes [11]. There are also indications that crown ethers increase the biological activity and the complex-forming ability of segmented polyurethanes [2]. In the case of solid polymeric electrolytes based on poly (ethylene oxide)-grafted poly(-methylmethacrylate) (PEO–PMMA) and lithium (Li), blending with crown ethers was found to affect the conductivity properties [12].

This work deals with molecular mobility and microphase separation studies in segmented polyurethanes with different fragments as chain extenders and/or chain ends, including crown ethers. The polyurethanes studied are based on oligotetramethylene glycol 1000 (TMG-1000), 4,4′-diphenylmethane diisocyanate (MDI) and different chain extenders. In a previous work we used small angle X-ray scattering (SAXS) and differential scanning calorimetry (DSC) to study the morphology of polyurethanes including the samples of the present study [2]. The main results of that study can be summarized as follows. All samples exhibit microphase separation, in addition the overall degree of DMS increases due to dilution of dihydrazide of isophthalic acid (DIPA) and/or blocking of chain ends with crown ether-containing di- and monohydrazides. The samples with higher DMS have lower T_g and lower specific heat capacity jump ΔC_p than the samples with smaller DMS. Here we focus on molecular mobility. The techniques employed in the present study include broadband dielectric relaxation spectroscopy (DRS), 10^{-2}–10^{6} Hz, and thermally stimulated depolarization currents (TSDC) techniques, −180°–30°C. The broad frequency range of DRS and the high sensitivity and peak resolving power of TSDC [13] make dielectric techniques very attractive for molecular mobility studies in complex polymeric systems [7, 14]. Beside that, our interest in this work is focused on methodological aspects of using dielectric techniques for microphase separation studies [14].

2. Experimental

2.1. Materials

The elementary chain fragment of the studied samples may be represented as follows: H-[-BCE-MDI-TMG-MDI-]-MCE, where BCE is the bifunctional chain extender (dihydrazide of isophthalic acid, DIPA; dihydrazide of disulfonyl-dibenzo-18-crown-6, DDDC), TMG-1000 is the oligotetramethylene glycol (molar mass 1000 g/mol), and MCE is the monofunctional chain end (monohydrazide of sulfonyl-benzo-18-crown-6, MHBC). The segmented polyurathenes were prepared by reaction of a BCE with isocyanate end groups of a prepolymer [15, 16]. Commercial DIPA was used as received. DDDC and MHBC were synthesized according to existing recommendations [15]. The chemical formulas of the different chain fragments mentioned above are shown in Fig. 1; sample coding, chemical composition of BCE and MCE, densities ρ, and intrinsic viscosities $[\eta]$ (in dimethyl formamide, DMFA) are given in Table 1. Table 2 lists the results of SAXS and DSC measurements [2].

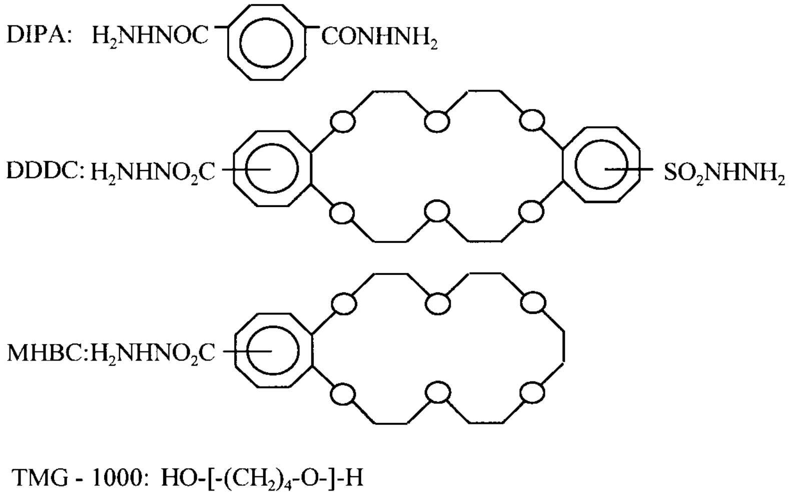

Fig. 1. Chemical formulas of chain fragments of SPUs.