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Material Properties

Thermal stability and structural anisotropy of semiaromatic poly(ester amides) from aromatic bis(2-oxazolines) and aliphatic dicarboxylic acids

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ABSTRACT

Semiaromatic poly(ester amides) containing three different aromatic units and aliphatic spacers with five different chain lengths were investigated using various experimental methods, with a focus on the effect of structural changes in the mesogenic groups and the length of the flexible alkylene spacer on the observed physical properties. The results of thermal stabilities and crystallographic measurements indicate that the thermal stability is dependent on the content of the amorphous phase in the polymer. The results from the thermal stability, differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD), and optical microscopy of the poly(ester amides) containing aromatic moieties were compared to the dielectric properties recorded using dielectric relaxation spectroscopy (DRS). DRS contributed to the description of four relaxation regions detected by matching the temperature and frequency dependencies of the dielectric functions. For the poly(ester amides) containing biphenyl units, the presence of a liquid-crystalline (LC) phase was observed.

1. Introduction

Polymers with rigid and flexible segments in their main chains are of increasing interest, and they are typically prepared by step-growth polymerization processes. Aromatic and semiaromatic polyesters, polyamides, polycarbonates, polyurethanes or polysulfones can be reported as examples for such a type of polymers. Most of these polymers are particularly attractive because they display liquid-crystalline properties, and their phase transitions can be controlled through an appropriate balance between rigid aromatic segments and flexible alkylene segments [1]. Liquid-crystalline polymers (LCPs) represent an important type of material systems in soft matter research due to their applications in optical, electrical, and mechanical devices that are responsive to various types of stimuli [2,3]. LCPs typically exhibit improved mechanical and other physical properties [4]. Various ordered systems are formed when rigid mesogenic groups are combined with flexible spacers, such as $(CH_2)_n$, because both LC and isotropic states are present in these polymers. The direct linkage of mesogens to the polymer backbone or linkage through a spacer of one or two atoms typically results in only isotropic thermal behavior above T_g because the thermally induced main-chain and side-chain motions are coupled. Most of the studies on flexible main-chain motion have been performed on polyacrylates [5] and polysiloxanes [6] as a function of temperature.

The step-growth reaction of monomers containing a 2-oxazoline ring is a very effective method for preparing poly(ester amides) with different structures [7–14]. Typically, AB, AA + BB or AB_2 types of polyadditions proceed as thermally induced processes above the melting point of at least one monomer (melt polymerization) or in high boiling solvents [8,9]. Poly(ester amides) containing an aromatic moiety have rigid structures and improved thermal properties [12,13]. In our previous studies, poly(ester amides) containing phenyl, naphthalene and biphenyl moieties were prepared [8,9,12,13]. Wilsens et al. [14] reported renewable 2,5-furandicarboxylic acid-based cross-linked poly(ester amides) *via* the polymerization of a 2,5-furandicarboxylic acid-based bis(2-oxazoline) monomer (2,5-bis(4,5-dihydrooxazol-2-yl) furan) with sebacic acid. In this case, an increased tendency to form branches or provide cross-linking was due to the presence of intramolecular hydrogen bonding of the 2,5-furandicarboxamide moiety. Another type of semiaromatic poly(ester amides) was synthesized by the condensation of aromatic bis(2-oxazolines) containing triphenylphosphine units with adipic, sebacic and 1,4-cyclo-hexanedicarboxylic acids [15]. An alternative approach for the preparation of poly(ester

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amides) containing aromatic moieties was reported by Yin et al. [16], who used a chain extension of pre-prepared poly(ester amides) from N,N′-bis(2-hydroxyethyl)oxamide and adipic acid or sebacic acid followed by a chain extension with 1,4-phenylene-2,2′-bis(2-oxazoline). The thermal properties of prepared polymers have been characterized by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA). The crystalline structure of formed polymers has been confirmed by wide angle X-ray diffraction (WAXD). Another method for the preparation of semiaromatic poly(ester amides) involves the polycondensation of 1,4-butyleneterephthalamide with glycols [17].

Poly(ester amides) containing aromatic rings in the main backbone are semicrystalline and thermally stable polymers. For poly(ester amides) containing biphenyl groups, the presence of nematic texture has been observed [12]. The temperature of the phase transition depends on the alkyl chain of the aliphatic dicarboxylic acid. The temperature of isotropization decreases as the alkyl chain length increases. The thermal behavior and physical states have been studied using DSC and optical microscopy with polarized light.

Dielectric relaxation spectroscopy (DRS) that is performed over broad frequency and temperature regions is an effective tool for characterizing the molecular motion of polymer systems. Many studies of polar polymers have demonstrated that DRS is a relevant tool for recharging their molecular dynamics [18]. This means that additional insight into the structure of the measured materials at molecular and macroscopic levels is possible using DRS. Several relaxation peaks have been observed for flexible polymers whose position depends on the frequency and temperature [19]. The information regarding the various relaxation mechanisms can be expressed in terms of relaxation times or the temperature dependence, magnitude, and shape of the dielectric response. The local, rapid motion is essentially determined by the chemical structure of the polymers and observed at low temperatures and high frequencies. At higher temperatures and lower frequencies, the relaxation of the polymer chains with transverse B-type dipoles is influenced by the chain connectivity, and such behavior is very similar for polymer chains with different chemical structures [20]. Due to the free motion of flexible polymer chains, various types of molecular motions in the polymers are controlled by broad length scales ranging from segmental motion (α-process), which corresponds to the glass transition temperature (T_g), to cooperative motions involving the entire polymer chain, including parallel A-type dipoles [21]. The relaxation normal mode relaxation was first observed by Stockmayer in linear poly (propylene)oxide [22]. In this case, the characteristic time of the relaxation was dependent on the molar mass, and this observation was due to an end-to-end vector fluctuation. Polymers with normal mode relaxation have been recently studied by several groups. In general, the dependence of the frequency of the loss peak on the temperature for the segmental and normal mode obeys a non-Arrhenius but WLF dependence.

This study focused on the investigation of semiaromatic poly(ester amides) with three different aromatic motifs and five different lengths of flexible alkylene spacers, comparing their thermal, dielectric, and crystallographic data. The aim was to better understand the microstructure of semiaromatic poly(ester amides) and the relevance of their phase transitions to macroscopic properties.

2. Experimental section

2.1. Materials

Poly(ester amides) containing benzene rings were prepared by the polyaddition reaction of 1,4-phenylene-2,2′-bis(2-oxazoline) (TBOX) or 1,3-phenylene-2,2′-bis(2-oxazoline) (IBOX) and dicarboxylic acids with different chain lengths according to previously reported protocols [8]. Poly(ester amides) containing biphenyl rings were analogously prepared from 4,4′-biphenyl-2,2′-bis(2-oxazoline) (BIBOX) and dicarboxylic acids with different chain lengths [12].

2.2. Molecular characteristics

The number average molar masses were measured using vapor pressure osmometry (VPO, Knauer, Germany) in DMSO at 90 °C. Benzil was used as a standard.

2.3. Differential scanning calorimetry

Thermal analysis was performed using a Mettler Toledo DSC821 instrument (METTLER-Toledo GmBh Analytical, Schwerzembach, Switzerland) in a temperature range from 25 to 300 °C at a heating rate of 10 °C/min. All the thermal characteristics were recorded during the 2nd heating in triplicate. All the measurements were performed under nitrogen.

2.4. Thermogravimetric analysis

TGA measurements were performed using a Mettler Toledo TGA/SDTA 851 instrument under nitrogen or oxygen flows (30 mL/min) using a heating rate of 10 °C/min over a temperature range from 25 to 550 °C. Indium and aluminum were used for temperature calibration. The amount of sample used was 2 mg. Three parallel runs were performed for each sample.

2.5. WAXD measurements

The X-ray powder diffraction profiles of pressed powder samples were recorded on a PANalytical EMPYREAN X-ray powder diffractometer with Cu Kα radiation (Kα1 = 0.154060 nm and Kα2 = 0.154443 nm). The patterns were scanned in a 2θ range of 5–50° with a step of 0.013° and 90 s per step. The pattern manipulations were performed using the HighScore Plus software package.

2.6. Dielectric relaxation spectroscopy

The dielectric measurements of the complex permittivity ($\varepsilon^* = \varepsilon' - i\varepsilon''$, where ε' is the real storage and ε'' is the imaginary loss component) were performed with a Novocontrol α-Analyzer in a frequency range from 0.01 Hz to 10 MHz at various constant temperatures. The temperature was controlled by Novocontrol cryosystem. The powder sample was placed on a rust-free circular electrode with a diameter of 15 mm and heated above its melting point. After the polymer melted, the upper electrode with a diameter of 11 mm was applied to the sample at a fixed distance between the electrodes, which was maintained using two quartz fibers (0.05 mm in diameter). All dielectric measurements were performed in a nitrogen atmosphere.

The frequency dependence of the measured dielectric response is composed of two parts: dielectric (ε_d^*) and conductivity (ε_c^*).

$$\varepsilon^* = \varepsilon_d^* + \varepsilon_c^* \tag{1}$$

The dipole (relaxation) contribution (ε_d^* or the ratio $tg\delta = {}^{\varepsilon''}/_{\varepsilon'}$) for all detected regions could be described with a sufficient accuracy by the Cole-Cole equation, which is simpler and more symmetrical in comparison to the Havriliak–Negami empirical equation [23].

$$\varepsilon_d^* = \varepsilon_\infty + \Delta\varepsilon/[1 + \mathrm{i}(f/f_\mathrm{m})^a] \tag{1a}$$

Here, the four temperature-dependent parameters are described as follows: a) the high-frequency (unrelaxed) value of the real portion of the permittivity (ε_∞), b) the relaxation strength $\Delta\varepsilon$ ($\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty$, where ε_0 is the relaxed low-frequency value of the permittivity), c) the frequency (f_m) corresponding to the most likely relaxation time (τ_m) that is related to the peak frequency (f_m) at which the loss component (ε'') reaches its maximum ($\tau_\mathrm{m} = 1/2\pi f_m$) and d) the shape parameter (a).

A computer program based on the Marquardt procedure [24] was