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Probing electric field response of LC thermosets via time-resolved X-ray and dielectric spectroscopy

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ABSTRACT

Curing of LCTs in an AC electric field was studied to understand the interplay between crosslink reaction and formation of a liquid crystalline (LC) phase and its effect on mechanical thermal properties on resulting thermosetting films. We show that dicyanate thermosetting monomers with ester functionality exhibit the ability to realign even after long curing times and allow poling of the LC director in resulting thermosetting films. To probe the details of the underlying process that leads to reorientation of the LC director model compounds were synthesized and their frequency and temperature dependent behavior under electric fields was studied. Curing reactions under electric fields show that the dual-frequency characteristics of the dicyanate mesogens behave very differently than epoxy thermosets. Size exclusion experiments reveal a prolonged gelation point in this system responsible for orientational switching even after long curing times. Finally, the ability to change orientation of the LC director allows tuning of modulus and thermal coefficient of expansion, making these thermoset films potential candidates for underfills, encapsulation materials and protective coatings for LC displays and active matrix substrates which require match in refractive index and mechanical/thermal properties.

1. Introduction

Densely crosslinked LCTs have many of the properties of conventional thermosets as well as the order of the LC phase "locked" into the network, even above the glass transition temperature. Crosslinking of LC monomers in the presence of external fields leads to macroscopically oriented LCTs [1–6]. The material no longer shows LC phase transitions before it decomposes at high temperatures. This macroscopic orientation is thermally stable until degradation, which takes place at temperatures often as high as 400 °C for cyanate ester resins. In the absence of external fields, crosslinking of LC monomers usually leads to polydomain structures [7].

There has been an increasing interest recently, in densely crosslinked systems based on rigid-rod, LC molecules [8–12]. Possible applications for these new thermosets include electro-conductive adhesives [13], new matrix materials for composites, as protective film, TFT active matrix substrate, liquid crystal display device [14], and a variety of applications in the microelectronics industry, including underfills and encapsulation materials. Several review articles discuss and compare different LC thermoset systems including bismaleimide, bisacetylene and epoxy rigid-rod thermosets [6,15,16]. Research by several groups on LC thermosets has focused on mesophase-forming dicyanate esters, which cure into LC triazine networks [17,18].

Cyanate ester resins have been attractive, especially in electronics applications, because of their excellent dielectric properties and their good thermal stability even at high temperatures [19]. Barclay et al. reported the first LCT material based on cyanate esters [20]. In this work macroscopically oriented samples were obtained by crosslinking in strong magnetic fields. The same LC dicyanate monomer of 1,4-benzenedicarboxylic acid bis (4-cyanatomethylphenyl) ester was also successfully oriented and polymerized in an ac electric field. Orientation of the molecules was achieved to be either parallel or perpendicular to the electric field by changing the frequency of the applied field [3]. Dicyanate curing behavior in electric fields is distinctly different than similar LC epoxy thermosets [21], which lock in after short curing times and cannot be altered in alignment via dual-frequency addressing. The goal of this work is to shed some more light into the process of reorientation and curing chemistry of dicyanate esters to find reasons for the discrepancy.

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A detailed study of the interrelationship between the polymerization reaction and the formation of the LC phase in external fields has not yet been undertaken. Alignment can translate the molecular anisotropy of the mesogens into a macroscopic anisotropy. However, under the influence of external fields these materials are not usually in thermodynamic equilibrium, especially in a reacting system.

In this work, X-ray scattering is used to identify and probe the packing of oriented LC thermosets. Researchers studying the electric field alignment of LC polymers typically observe the influence of temperature, applied voltage, and frequency by using dielectric relaxation spectroscopy (DRS) and polarizing optical microscopy (POM) [22–25]. The DRS technique depends on certain assumptions about the electronic structure of the mesogens and POM yields information on large macroscopic scales. X-ray scattering, however, looks at the physical arrangements of the mesogens with respect to their neighbors on a molecular scale. X-ray studies involving the effect of applied electric fields on LC systems have focused on side-chain LC polymers and small molecules [26–28]. In this study we combine X-ray analysis with DRS to examine the dual-frequency addressing behavior of LCT's. X-ray can unequivocally determine the nature of a relaxation mode observed in DRS, while DRS alone can only make assumptions whether the long axis of the molecules is rotating or molecules are merely rotating around their short axis in an LC system.

Application of a high frequency electrical field is the typical method to align LC monomers. However, only one direction can be obtained depending on the sign of the dielectric anisotropy. In this work, we use a monomer which orientation can be controlled by change of frequency and temperature. A combination of frequency addressable orientation typical of many low molar mass LC materials with the good mechanical and film-forming properties of polymers can be used to produce robust films with tunable mechanical and thermal properties. Only the combination of characterization methods such as DRS and X-ray can give detailed answers to the complex non-equilibrium field mediated reaction of LCTs.

2. Experimental

The dicyanate of 1,4-benzenedicarboxylic acid bis(4-cyanatomethylphenyl) ester (DCN) was synthesized, as described elsewhere [29]. A detailed study of the curing kinetics of DCN is described in Ref. [30]. A modification in the core of the mesogen leads to the LC dicyanate cyclohexanedicarboxylic acid bis(4-cyanatomethylphenyl) ester (CHDCN). In addition to the thermosetting monomers, model compounds were synthesized starting from the bis (hydroxymethylphenyl) precursors of the LC dicyanate monomer. Instead of a cyanato end group, allyl ether and cyclohexene ester end groups were attached to the mesogen and yielded non-curing LC equivalents to the dicyanate, in the following referred to as M1 and M2. The model compounds allowed studying the field effects without the interfering crosslinking reaction. The chemical structures of the compounds are summarized in Fig. 1.

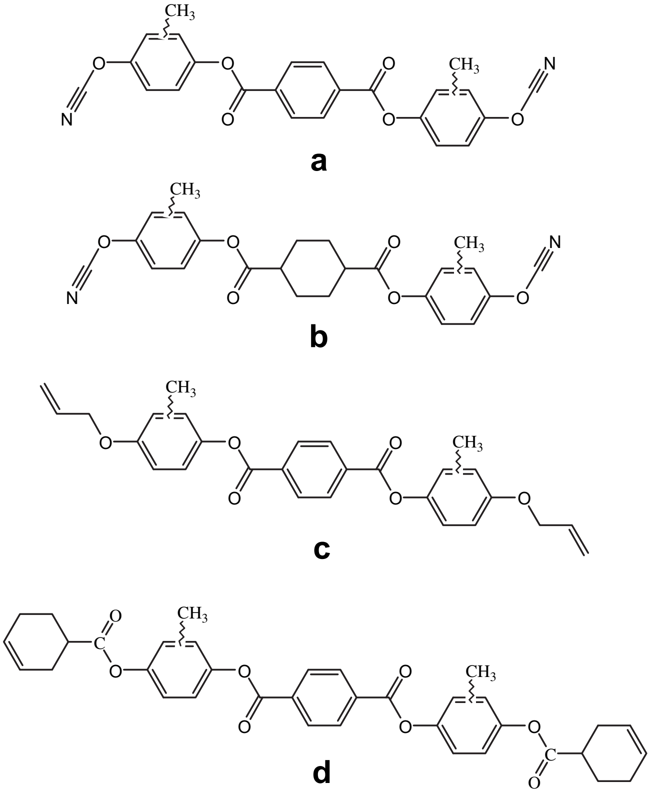

Fig. 1. Chemical formula of investigated compounds. a) thermosetting fully aromatic dicyanate DCN, b) thermosetting cyclohexyl dicyanate CHDCN, c) Allyl Ether M1, d) Cyclohexane Ester M2.

A DuPont 910 differential scanning calorimeter (DSC) was used for investigation of phase and curing behavior. DSC studies were carried out with a heating rate of 10 °C/min. Size exclusion chromatography (SEC) was carried out to study the composition of the crosslinking thermoset. Chromatographic methods like size exclusion chromatography can be used to measure the amount of the monomer and the first oligomers. The first oligomer formed from a dicyanate with one complete crosslink site is a trimer. Three cyanate end groups participate in an electron insertion reaction to form a triazine ring. If equal reactivity of the functional groups is assumed, then the OCN-conversion can be calculated using the relationship $\alpha = 1 - w_1^{0.5}$ where w_1 is the weight fraction of the monomer. Because the refractive index increment of a trimer is about twice the value of a monomer, a calculation of the conversion for a dicyanate from the ratio of the areas under the peaks of the monomer and the trimer without any calibration produces incorrect results because changes in the refractive index will lead to changes in the FT/IR signal [29]. Therefore, an area under the trimer- or any oligomer peak corresponds to a lower weight fraction than the same area under the monomer peak in the dicyanate system. The ratio of the calculated fractions was used to get qualitative information about the beginning of the curing reaction and to interpret the switching in the LC phase in this particular dicyanate system.

Dielectric measurements were carried out using a Solartron 1280 Gain Phase/Impedance analyzer and a LC optical cell over a frequency range of 10^{-1} Hz to 10^{5} Hz. Liquid crystal cells consisted of two transparent indium-tin oxide (ITO) glass electrodes with a rubbed poly (imide) alignment layer and a poly (ester) film insulator of 10.0 μm thickness.

The experimental setup for E-field alignment [31] was used at the F1 beamline of the Cornell High Energy Synchrotron Source (CHESS) to obtain real-time X-ray diffraction data. Sample cells consisted of two 500 μm thick stainless steel electrodes, which were separated by a controlled gap spacing of 100 μm–200 μm using a poly (imide) film. The cell was mounted in the Mettler hotstage and the temperature was changed by a PC driven controller. A 1 V/μm field strength was applied across a 200-μm gap at temperatures of 120 °C–170 °C with frequencies from 1 Hz to 1 MHz. Typical procedures for the thermosets involved heating the compounds to the melting temperature and subsequent increasing of the temperature to the desired curing temperature. Voltage and frequency were generated by a HP 8116A frequency generator and amplified ×1000 by a Trek model 10/10 high voltage operational