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Synthesis and characterization of UV-curable maleimide-terminated imide oligomers

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ABSTRACT

Three maleimide-terminated imide (MTI) oligomers/polymers with varying molecular weight were synthesized and characterized by Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, mass spectroscopy, and size exclusion chromatography (SEC). The MTI oligomers were formulated with two reactive diluents, *N*,*N*-dimethylacrylamide (DMAA) or *N*-vinylpyrrolidone (NVP), and were photopolymerized with and without a photoinitiator. The kinetics of film formation was investigated using real-time FTIR and photo-differential scanning calorimetry (DSC). Thermal and viscoelastic properties of UV cured films were studied by thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), and differential scanning calorimetry (DSC). The reaction rate and conversion were improved by adding a photoinitiator. MTI oligomer with low molecular weight ($\bar{M}_n \sim$ 2 kg/mol) MTI-2k had the highest reaction rate and final conversion. More than 90% of conversion was achieved after exposure to UV light for 60 s. A wide α-transition (tan δ) for all UV cured films was observed, indicating a heterogeneous system. When no photoinitiator was used, the MTI/NVP formulations polymerized, while the MTI/DMAA formulations did not. It was proposed that the NVP could react with MTI oligomers via a donor/acceptor complex, and the DMAA could not due to the electron-poor double bond.

1. Introduction

Polyimides were first developed in 1955 as thermoplastics [1–3]. Their rigid aromatic ring of polyimides provides a high glass transition temperature (T_g) and good mechanical strength. Polyimides have been widely used in electronic and aerospace engineering due to their excellent thermal stability, chemical resistance, and low dielectric constant [3–11]. Most thermoplastic aromatic polyimides in the fully imidized state are insoluble and infusible; thus, polyimides are typically processed in the form of poly (amic acid) (PAA) precursors [2]. After casting, the films or coatings, however, are imidized at elevated temperature (~300 °C). The high processing temperature limits polyimide usage. Another problem with this process is that the PAA solution is sensitive to humidity, which may result in the chain scission during the storage period. In addition, water released from the imidization process may cause voids in the products, especially when processing relatively high molecular weight polymers to produce thick films or composites [12]. More recently, thermoplastic polyimides have been developed with good solubility in common solvents [13–15]; however, a drawback of the soluble polyimides is the poor chemical resistance.

To ameliorate some of the processing issues with thermoplastic polyimides, thermosetting polyimides were developed by NASA in early 1960s [16]. Thermosetting polyimides are oligomers with reactive functional groups on the backbone or side chain which crosslink upon heating. The reactive functional groups, such as nadimide, maleimide and acetylene, can undergo homo or copolymerization upon heating [17]. However, the high cross-linking temperature is still a major concern for application beyond its current niche. Lowering the cure temperature of polyimides is one of the requirements for expanding the applications of polyimides.

Photopolymerization can be performed at room temperature, which is good for heat sensitive substrate. Photopolymerization of maleimide-terminated imide (MTI) oligomers was studied by several research groups [14,18–22]. These studies showed that maleimide group exhibits a strong UV absorbance in the 300 nm region due to the C=C double bond conjugated with the carbonyl group [16]; therefore, it is capable of undergoing homopolymerization or copolymerization without any additional photoinitiator (PI) [2,23]. Photopolymerization of N-substituted maleimide and bismaleimide have been studied in the past by a number of researchers [13,14,18,24]. Three possible reactions may account for consumption of the maleimide groups: initiation of polymer chains through

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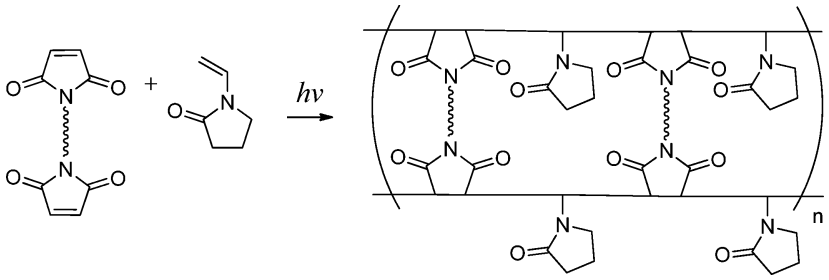


Scheme 1. Polymer network formed by bismaleimide and NVP.

hydrogen atom abstraction or electron/proton transfer processes, copolymerization with the other monomers, as shown in Scheme 1, or maleimide [2 + 2] cycloaddition reaction [13,14,18,22,24–28], as shown in Scheme 2. However, most of the research focused on the mechanism studies of photopolymerization with model compounds, and not polymeric materials.

The overall goal of this research is to develop a UV-curable imide oligomer. MTI oligomers were synthesized and characterized by FTIR, NMR, mass spectra, and SEC. Those oligomers were formulated with reactive diluents, *N*, *N*-dimethylacrylamide (DMAA), and *N*-vinylpyrrolidone (NVP). T_g and thermal stability of UV-cured films were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Viscoelastic properties were investigated by dynamic mechanical analysis (DMA). Real-time FTIR and photo-DSC were used to study the UV-curing kinetics. The structure of MTI oligomers and the films cured were characterized by wide angle X-ray diffraction (XRD).

2. Experimental

2.1. Materials

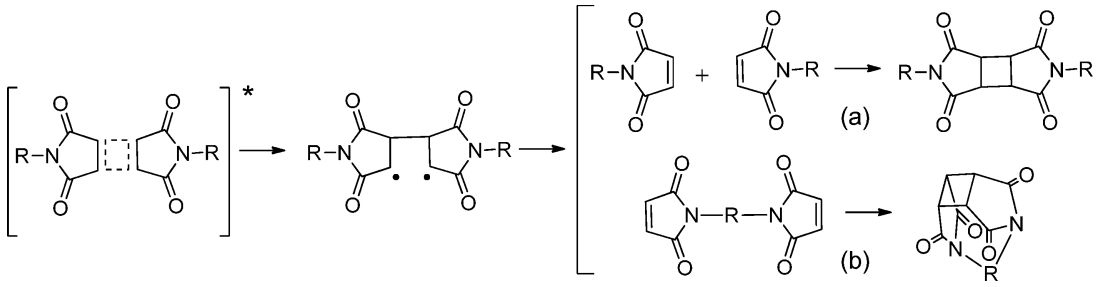
N-Methyl-2-pyrrolidinone (NMP) (anhydrous, 99.5%, dried over molecular sieve) dimethylacrylamide (DMAA) (99%), *N*-vinylpyrrolidone (NVP) (>99%), *m*-xylene (anhydrous, >99%) and methanol (ACS reagent, 99.8%) were purchased from Sigma–Aldrich. 4,4-(Hexafluoroisopropylidene) diphthalic anhydride (6FDA) (purity > 99%) was purchased from Akron Polymer Systems, Inc (Akron, OH) and recrystallized from acetic anhydride and dried under vacuum at 160 °C for 24 h before use. Maleic anhydride (>95%) was purchased from Sigma–Aldrich and recrystallized from toluene before use. 4, 4′-(1,3-Phenylenediisopropylidene) *m*-bisaniline (bisaniline M) was obtained from Mitsui Chemicals Inc. and vacuum dried before use. Irgacure 184 was obtained from BASF. All of the other reagents and solvents are commercially available ACS reagents and were used without further purification.

2.2. Instrumentation and characterization

FTIR spectra were recorded on a Thermo Scientific Nicolet 380 Fourier transform infrared spectrometer by casting thin film on KBr crystal from chloroform solution. Data spacing is 4 cm^{-1}, resolution is 32. UV–vis spectra were recorded on a Perkin-Elmer Model LS-5 spectrometer. The maleimides and reactive diluents were diluted in acetonitrile to obtain UV–vis data. ^{1}H NMR and ^{13}C NMR were recorded on Mercury-300 spectrometer (Varian) in chloroform-*d*. Mass spectrometry experiments were performed with a Bruker REFLEX III time-of-flight (TOF) mass spectrometer (Billerica, MA) equipped with a single-stage pulsed ion extraction ion source. Size exclusion chromatography (SEC) with tetrahydrofuran as the mobile phase was used to determine polymer molecular weight and polydispersity index (PDI) using a Waters 1515 isocratic pump, three Waters styragel columns (HR 3, HR 4, HR 4E), and a Waters 2414 refractive index detector. The columns were calibrated with narrow-distribution polystyrene standards.

UV radiation was performed on a bench top conveyor LC-6 with an ultraviolet lamp system (Fusion UV systems, Inc). The Fusion lamp system uses microwave radiation to energize the lamp. Intensity was measured by a UV POWER PUCK® high energy UV integrating radiometer. Thermal stability was studied on a TGA 2950 (TA Instruments, Inc). Samples were put on a platinum pan and heated up with a heating rating of 20 °C/min. Nitrogen was used as the furnace purging gas. The decomposition temperature and the first derivative were reported. The T_g was measured by DSC Q-2000 (TA Instruments, Inc). DSC thermograms were obtained by using 3–5 mg samples that were sealed in aluminum hermetic DSC pans and heated from room temperature at heating rate of 10 °C/min. The value of T_g was taken as the midpoint of the transition region using TA Universal Analysis. A DMA test was performed on DMA Q-80 (TA Instruments, Inc). Films were tested under the following conditions: tension mode, heating rate of 3 °C/min, and a frequency of 1 Hz. The maximum of the tan δ transition was used to determine the T_g, while the cross-link density was determined by utilizing the storage modulus (E') in the rubbery plateau (T_g + 50 °C). The cross-link density of the film has been defined as the moles of elastically effective network chains per cubic meter of film. The cross-link density was calculated by using the following equation derived from the theory of rubber elasticity [29]:

$$\nu_e = \frac{E'}{3RT} \quad (1)$$



Scheme 2. Photoinduced cycloaddition reaction of bismaleimides.

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