European Polymer Journal 46 (2010) 2372–2380

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

# Coordination and morphology of metal/polyetherurethane complexes

Li-Fen Wang *

*Department of Applied Chemistry, Fooyin University, Kaohsiung, 831 Taiwan, ROC*

ARTICLE INFO

*Article history:*
Received 12 May 2010
Accepted 20 September 2010
Available online 29 September 2010

*Keywords:*
Polyetherurethane
Metal coordination
Morphology
Quantum chemical calculation

ABSTRACT

Based on infrared spectra, differential scanning calorimetry, and quantum chemical calculations, this study investigated the effects of the species of metal ($MnCl_2$, $FeCl_3$, $CoCl_2$, $CuCl_2$, $GaCl_3$), their interaction sites and binding strength on the morphologies of polyetherurethane (PU). The calculated frequency and binding energy were consistent with the experimental results, suggesting that most of the binding strength (95%) is associated with the charge transfer from the lone pairs (on the nitrogen in NH and the oxygen in CO and COC) in the PU ligand to the metal. $MnCl_2$, $CoCl_2$, and $CuCl_2$ are more soluble in soft segments of PU than $GaCl_3$ and $FeCl_3$ via coordination with one or two polyether ligands and can significantly raise the glass transition temperature of PU. Conversely, $GaCl_3$ and $FeCl_3$ interact more strongly with hard-segment NH of PU than $MnCl_2$, $CoCl_2$, and $CuCl_2$ and markedly reduce the melting temperature of PU.

## 1. Introduction

The interaction between polymer and metal systems is of interest because they can provide valuable information on the capacity of polymers to retain metallic ions and the effect of such ions on the properties of the polymers [1]. The natures of the polymer and metal species, their ratio and the strength of their interaction determine the ultimate performance of the new materials that are developed for various potential applications [2–6]. Linear polyurethane-based metal complexes have attracted substantial attention for use as polymeric electrolytes, actuators, transducers and other devices, because of their unique two-phase microstructure [7,8]. A low glass transition temperature ($T_g$) and therefore high segmental motion of their soft segments lead to the high mobility of the dissolved metallic ions, resulting in relatively high ionic conductivity. Moreover, their hard segment domains act as reinforcing fillers and therefore contribute to the mechanical strength of the polymer materials [9,10]. Accordingly, the effects of metallic ions on the morphologies and properties of polyurethane are particularly important [11–14].

Polyurethane has a hydrogen-bonded structure in which N–H groups in a chain are hydrogen-bonded both to hard-segment C═O groups and soft-segment C–O–C groups in adjacent chains. Therefore, the complexation of metal salts competes with hydrogen bonding of the polymer because potential complexation sites are also the hydrogen bond donor (N–H) and acceptor sites (C═O and C–O–C) [15]. Moroi et al. [3] studied a series of metal complexes of polyesterurethane and copper ions. They concluded that the copper ions formed coordination complexes with the urethane nitrogen atoms in the hard segment. The intermolecular complexation caused cross-linking of the hard segments, destroying the original hydrogen bonding and crystallinity of the hard-segment domains. Wen et al. [2] and Gopalan et al. [9] investigated the interactions of lithium ions ($Li^+$) with both the soft and hard segments of polyetherurethane. Significant changes in the Fourier transform infrared (FTIR) spectra indicated the formation of various complexes by the interaction of $Li^+$ ions with different coordination sites of polyurethane.

Despite much interest in metal/polyurethane complexed systems, studies of interactions that affect the morphology of polyurethanes are relatively few. Due to a

---

* Tel.: +886 7 7811151x5211; fax: +886 7 7826732.
*E-mail address:* sc112@mail.fy.edu.tw

0014-3057/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.eurpolymj.2010.09.013

big advance in computer architecture and algorithms of computational chemistry recently, molecular modeling has provided a powerful and reliable tool to give quantitative understandings on intermolecular strengths and vibration spectra of complexes [16–24]. In this work, a series of metal complexes of linear polyetherurethane and metal salts ($GaCl_3$ and transition metals $MnCl_2$, $FeCl_3$, $CoCl_2$, $CuCl_2$) were prepared and characterized by FTIR spectroscopy, differential scanning calorimetry (DSC) and complementary quantum chemical calculations to elucidate the effect of the metal species, their interaction sites and their strength of interaction on the morphology of polyetherurethane.

## 2. Methods

### 2.1. Materials

Hydroxyl-terminated poly(tetramethyl oxide) with molecular weights of 650 g/mol (PTMO; Aldrich) were dehydrated under vacuum at 60 °C for 48 h before use. 1,4-Butanediol (BD; Tedia) and dimethylacetamide (DMAc; Tedia) were distilled under vacuum from calcium hydride and then dried over 4 Å molecular sieves before use. Hexamethylene diisocyanate (HDI; Aldrich), stannous octoate (T-9; Sigma) and metallic salts (Aldrich) of gallium (III) chloride, iron (III) chloride, cobalt (II) chloride, copper (II) chloride and manganese (II) chloride were used as obtained.

### 2.2. Preparation of polyetherurethane

The polyetherurethane (PU) sample was synthesized using HDI, PTMO and chain extender BD with a 4:1:3 stoichiometry. A predetermined amount of HDI was dissolved in DMAc in a four-necked flask under nitrogen and a fixed amount of PTMO/DMAc solution that contained 0.5 wt.% stannous octoate as the catalyst was added dropwise at 60 °C. After the PTMO solution was added, the temperature was raised to 70 °C, which temperature was maintained for 1 h. In a second step, the stoichiometric amount of chain extender was added dropwise and the reaction was carried out at 90 °C. The progress of the reaction was monitored by the absence of IR-absorption by the free NCO group at 2270 $cm^{-1}$. PU obtained was precipitated in deionized water, washed thoroughly with methanol, and dried in a vacuum oven at 60 °C for one week to remove any moisture.

### 2.3. Preparation and characterization of polyetherurethane metal complexes

The metal/PU complexes were prepared by adding a stoichiometric amount of metal salts to PU solutions in DMAC to yield a metal/urethane (M/U) molar ratio of 1/1, 1/2 and 1/4, denoted MPU11, MPU12 and MPU14, respectively. (M represents metal salt) Depending on the polymer concentration, the mixture was stirred or heated to 40–50 °C until all of the metal salt dissolved. Films of metal/PU complexes were prepared for infrared and DSC analysis by casting the solution onto KBr substrates and aluminum DSC pans followed by the slow evaporation of the solvent in a vacuum at 60 °C overnight. Pure PU films were prepared similarly for comparison. FTIR experiments were performed using a Bio-Rad FTS-40A Fourier transform infrared spectrophotometer with purging with dry air. Sixty-four scans at a resolution of 2 $cm^{-1}$ were signal-averaged. The DSC experiments were conducted using a DSC 2920 differential scanning calorimeter (TA Instruments, USA) over a temperature range from −120 to 200 °C at a scanning rate of 20 °C/min. The glass transition temperature ($T_g$) is reportedly the midpoint of the transition, and the melting temperature ($T_m$) is the peak temperature.

### 2.4. Computational method

1,4-Di-(3′-propylcarbamate)butane and diethylether were employed to model the PU ligands, hard-segment urethane and soft-segment polyether, respectively [25–26]. First, the ligands were modeled and their geometry in the model was optimized to enable their geometrical parameters to be compared to those of their complexes. Then, the complexes, presented in Fig. 1, were modeled and their geometry was optimized for M=Mn, Fe, Co, Cu and Ga. The geometries of all molecules (including free ligands and complexes) were optimized using the density functional theory (DFT) method. The B3LYP functional [27–28] was applied with the 6-31G(d) basis set in the Gaussian 03 program suite [29]. Vibrational analysis was performed to ensure that the optimized structures are at the lowest point on the potential energy surface, and to obtain the harmonic frequencies for comparison with experimental observations. Also, to elucidate the nature of the intermolecular interactions in the systems of interest, the binding energy ($E_{bind}$) [30–32] between various metal salts and PU ligands was computed by a supermolecular approach, in which the ground state energy of the coordination complex was calculated and compared to the sum of the ground state energies of its individual components.

## 3. Results and discussion

### 3.1. Infrared analysis

FTIR spectra of metal/PU complexes with various metal/urethane (M/U) molar ratios of 1/1, 1/2 and 1/4, were obtained. A comparison of the FTIR spectra of the pure and metal-complexed PU samples indicates that the changes in the main bands were those anticipated upon the severing of the N–H…O=C and N–H…(COC) hydrogen bonds and the extent of variation of absorption band depends on the species of metal salt and its content. Therefore, three major spectral regions in this study are of particular interest. They are N–H stretching at 3000–3600 $cm^{-1}$, C=O stretching at 1500–1800 $cm^{-1}$, and C–O–C stretching at 1000–1200 $cm^{-1}$ [9,33]. Table 1 and Fig. 2 present the peak assignment and the IR spectra