

Effects of Moisture on Reaction of Hexamethylene Diisocyanate and HO-Terminated Poly(lactide-co-p-dioxanone) in DMF System

MEINA HUANG^{1,2,3,*}, SHUANG CUI¹, SHAOHU XU¹ and FUSHENG PAN²

¹College of Mechanical Engineering, Chongqing Technology and Business University, Chongqing 400067, P.R. China

²National Engineering Research Center for Magnesium Alloy, College of Materials Science and Engineering, Chongqing University, Chongqing 400030, P.R. China

³Chongqing Key Laboratory of Manufacturing Equipment Mechanism Design and Control, Chongqing Technology and Business University, Chongqing 400067, P.R. China

*Corresponding author: Tel: +86 15320437026; E-mail: meinahuang1982@163.com

Received: 12 June 2014;

Accepted: 10 September 2014;

Published online: 26 May 2015;

AJC-17215

A novel poly(urethane-urea) shape memory polymer (PUU-SMP) was synthesized by a systematic two-step reaction process in DMF system. Initially, isocyanate-terminated prepolymer was prepared from reaction of hydroxyl-terminated poly(lactide-co-p-dioxanone) with hexamethylene diisocyanate with NCO/OH ratio of 1.2:1 for 3 h under 70-75 °C. Secondly, the excessive NCO reacted with butanediamine, aiming to realize chain extension. However, the reaction phenomena indicated that reaction between hexamethylene diisocyanate and HO-terminated poly(lactide-co-p-dioxanone) was affected by moisture from solvent or reaction materials in this system. In order to confirm the effects of moisture on above reaction, the obtained poly(urethane-urea) shape memory polymer (PUU-SMP) were characterized with Fourier transform-infrared (FT-IR) spectroscopy, which indicated that moisture may participate in the reaction and play an important role in reaction products *via* hydrogen bond and crosslinked ureido ways. The reaction heat in reaction systems with different types of moisture content were determined by differential thermal analyzer and thermogravimetric analyzer. Differential scanning calorimetry showed that, comparing to the mixture without moisture, the activation energy and reaction enthalpy of mixtures with moisture are higher, however, heat flow were not obviously different. According to the results of FT-IR and thermal analysis, we can inference that if moisture content as well as contact of H₂O and -NH-C=O increased, the hydrogen bond interaction will be strengthened, resulting in the probability of a crosslinking reaction.

Keywords: Moisture, Hydrogen bond, Thermal analysis, Polyurethane, Poly(lactide-co-p-dioxanone).

INTRODUCTION

Shape memory polyurethane is an emerging class of smart polymer, which can change its shape under the external conditions, such as heat stimulus and have great potential for biomedical applications, especially in the area of minimally invasive surgery¹. One of the trends of biomedical polyurethane is realizing shape memory property and biodegradability². Biodegradable shape memory polyurethanes, attributing to its biodegradability and biocompatibility have attracted growing research interest in recent years³⁻⁶.

Poly(lactide-co-p-dioxanone) is a kind of popular biomedical material, since poly(lactide-co-p-dioxanone) has biodegradability and shape memory property. Moreover, glycolic acid (GA) was incorporated into poly(lactide-co-p-dioxanone), which exhibited the fastened and controllable degradation rate due to the better hydrophilicity of polyglycolic acid⁷. In addition, poly(ethylene

glycol) (PEG) was copolymerized with poly(lactide-co-p-dioxanone) and the obtained block copolymers PLA-PEG-PLA, compared to poly(lactide-co-p-dioxanone), showed the improved flexibility, because of the introduction of ether bonds into poly(lactide-co-p-dioxanone) backbone. Based on the above information, the combination of glycolic acid and ethylene glycol, together with poly(lactide-co-p-dioxanone) will hopefully create copolymers that possesses many advantages. *p*-Dioxanone (PDO) is in structure a cyclic compound condensed from one molecule of glycolic acid and one of molecule ethylene glycol (EG), which makes *p*-dioxanone have good flexibility. Moreover, the T_g of poly(*p*-dioxanone) is -10 °C, while the T_g of PDLLA is 50-60 °C, so the T_g of copolymer can be regulated easily by changing the ratio of *p*-dioxanone to lactide acid.

In this study, *p*-dioxanone (PDO) was employed to copolymerize with lactide using Sn(Oct)₂ as an initiator and ethylene glycol (EG) as a co-initiator, producing a series of

macro-diols based on polylactic acid and poly(*p*-dioxanone) (PPDO) [HO-P(LA-PDO)-OH]. Secondly, biodegradable and shape memory polyurethane based on poly(D,L-lactic acid-*co*-*p*-dioxanone) [HO-P(LA-PDO)-OH] and hexamethylene diisocyanate (HDI), butanediamine (BDA) was synthesized in DMF system, which is expected to an ideal biomedical material.

However, the reaction phenomena of preparing polyurethane suggested that presence of moisture have significant effects on the reaction of HO-P(LA-PDO)-OH with hexamethylene diisocyanate in DMF system. He and Yan⁸ reported the effect of moisture content on curing kinetics of pMDI resin and wood mixtures, showing that moisture can react with isocyanate to form polyurea and biuret-type structure, which competes strongly with the reaction of diols and isocyanate. There is some controversy on the various reactions during preparation of polyurethane^{9,10}. FT-IR analysis indicated that urethane bonds could be formed under anhydrous conditions, when excessive isocyanate was used. Chrissafis *et al.*¹¹ synthesized a kind of hyperbranched polyurethane-urea by the reaction of isocyanate-terminated prepolymer from a hyperbranched polyester polyol with isophorone diisocyanate under atmospheric moisture and room temperature for 20 days, finally obtained the HBPU-urea coating.

In our study, we found the following results: First, when hexamethylene diisocyanate was added to the reaction system without HO-P(LA-PDO)-OH, but with equimolar water, the content of hexamethylene diisocyanate slight declined. Second, the rigidity of polyurethane, obtained from hexamethylene diisocyanate and HO-P(LA-PDO)-OH, increased with increasing of moisture, however, the shape memory property did not decreased. How does moisture affect the reaction of HO-P(LA-PDO)-OH with hexamethylene diisocyanate at the present of Sn(Oct)₂ as the catalyst in the DMF system? Studying the effects is a key problem for preparing the HO-P(LA-PDO)-OH-based shape memory polyurethane in the solvent system.

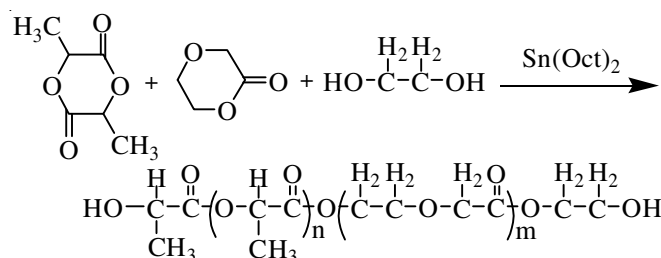
To illuminate the effects of moisture on reaction of hexamethylene diisocyanate with HO-P(LA-PDO)-OH, Fourier transform-infrared (FT-IR) and differential scanning calorimetry (DSC) are chosen. On the basis of isocyanate chemistry, the variation in thermodynamical parameters and characteristic peaks of FT-IR were used to interpret the reaction characteristics of hexamethylene diisocyanate and HO-P(LA-PDO)-OH with moisture.

EXPERIMENTAL

Hexamethylene diisocyanate (HDI) and butanediamine (BDA) were purchased from Sigma-Aldrich Corporation. Dimethylformamide (DMF) was purchased from Chongqing Oriental Chemical Factory. hexamethylene diisocyanate and DMF were dried with CaH₂ and then the hexamethylene diisocyanate was centrifugated and DMF was vacuum distilled, the obtained hexamethylene diisocyanate and DMF contained less than 0.01 % moisture. D, L-lactide (D, L-LA) was synthesized and purified in my laboratory with a purity of greater than 99.9 %. *p*-Dioxanone was supplied by Jinan Biotechnology Corporation.

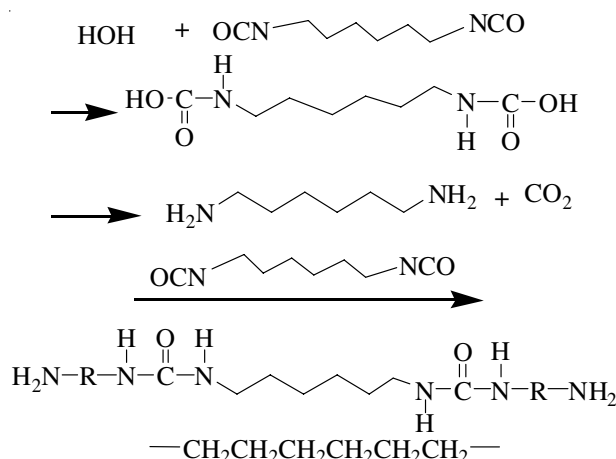
Synthesis of HO-P(LA-PDO)-OH: In brief, HO-P(LA-PDO)-OH was synthesized by melt ring-opening polymerization

of D, L-lactide (LA) and *p*-dioxanone (PDO) in the presence of Sn(Oct)₂ as an catalyst and ethylene glycol as a co-initiator at 140 °C for 24 h in vacuum (**scheme-I**). The obtained copolymer was purified through co-precipitation in chloroform-*n*-absolute ethyl alcohol system at room temperature. The purified copolymer was then vacuum dried at room temperature for 48 h. In the process, the number average molecular weight (\bar{M}_n) of HO-P(LA-PDO)-OH can be controlled by regulating the ratio of L-lactide to *p*-dioxanone and the content of Sn(Oct)₂ and ethylene glycol. [FTIR (KBr, ν_{\max} , cm⁻¹): 3509 (ν_{OH} in hydroxyl terminated), 2996, 2882 (ν_{CH} in alkyl), 1754 ($\nu_{\text{C=O}}$ in carbonyl group), 1455 ($\delta_{\text{C-H}}$ in methane and methylene), 1382 ($\delta_{\text{C-H}}$ in methyl); ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 5.0-5.2 (-CH- in polylactic acid segment), 3.77 (-CH₂- in -O-CH₂-CH₂-O-CO- in *p*-dioxanone segment), 1.456-1.572 (-CH₃- in polylactic acid segment), 4.12-4.40 (-CH₂- in -O-CH₂-O-CH₂-CH₂-O-CO- and -O-CH₂-O-CH₂-CH₂-O-CO- in the PPDO segments), 3.86 (-CH₂-) in the ethylene glycol connected with -OH, 4.48(-CH₂-) in the ethylene glycol connected with -OCO-].



Scheme-I: Synthetic route of HO-P(LA-PDO)-OH mearodiols

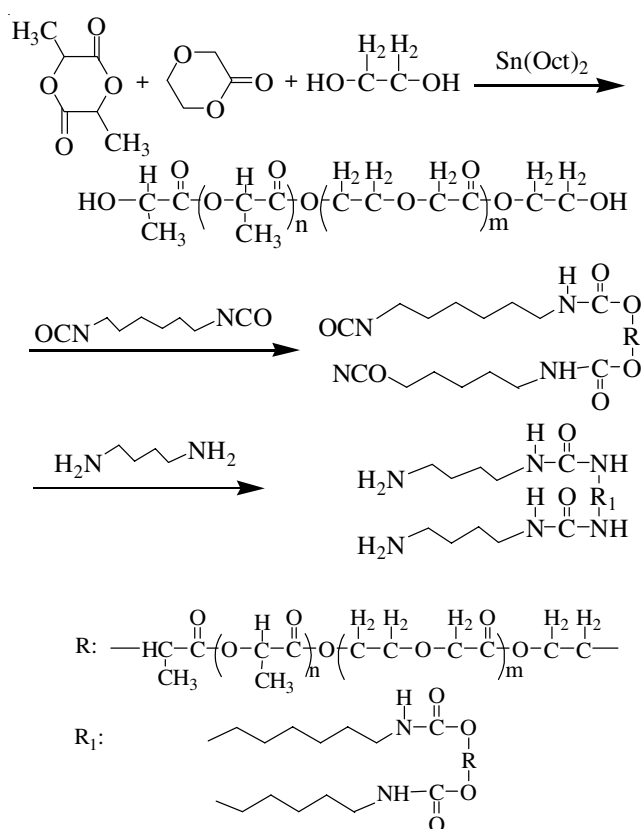
Synthesis of polyurethane from HO-P(LA-PDO)-OH and hexamethylene diisocyanate: The polyurethane was prepared as follows (**Scheme-II**): predetermined amounts of HO-P(LA-PDO)-OH, hexamethylene diisocyanate, Sn(Oct)₂ and anhydrous DMF were added into a 250 mL three-neck round-bottomed flask with thermometer, magnetic stirrer and drying tube. And purge flow of nitrogen was continuously introduced into the flask through above drying tube. The prepolymer [OCN-HDI-P(LA-PDO)-HDI-NCO] based on HO-P(LA-PDO)-OH and hexamethylene diisocyanate was obtained at 60-75 °C for 3 h. Then butanediamine, the molar number of which was equal to the molar difference value between



Scheme-II: Reaction of hexamethylene diisocyanate with moisture

hexamethylene diisocyanate and HO-P(LA-PDO)-OH, dissolved in DMF was added into reaction system slowly for chain extension below 5 °C. The chain extending reaction lasted for 2 h below 5, thereafter obtained polyurethane was purified through co-precipitation in a DMF/water system at room temperature. In order to remove unreacted monomers, the obtained polyurethane was immersed in isopropyl alcohol for 3 days and then vacuum dried for 48 h under room temperature. [FTIR (KBr, ν_{\max} , cm^{-1}): Comparing to the FTIR of HO-P(LA-PDO)-OH: 1523.94, 1627 ($\delta_{\text{N-H}}$ in -CO-NH- and $\nu_{\text{C=O}}$ in -CO-NH-), 1587 ($\delta_{\text{C=O}}$ in -HN-CO-NH-), 3350 ($\delta_{\text{N-H}}$ in -NH₂); ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 2.90 (-CH₂- in BDA segment), 5.7 (-NH- in -HN-CO-NH-), 7.4 (-NH-in-NH-CO-O-)].

Reaction phenomena of the reaction of hexamethylene diisocyanate with HO-P(LA-PDO)-OH: In the study, the molar feed ratio of HO-P(LA-PDO)-OH to hexamethylene diisocyanate and butanediamine is 1/1.2/0.2 as the reaction process showed in **Scheme-III**. Regulating the reactant in the system may get different results. Firstly, when \overline{M}_n of HO-P(LA-PDO)-OH was constant at 3000, regulating moisture content (MC) from 0 to 20 %. Secondly, when moisture content was constant at 5 %, regulating \overline{M}_n of HO-P(LA-PDO)-OH from 1850 to 5800. And then primarily determine the effects of moisture on reaction of hexamethylene diisocyanate with HO-P(LA-PDO)-OH by the reaction phenomena and the production properties.



Scheme-III: Reaction of hexamethylene diisocyanate with HO-P(LA-PDO)-OH and chain extension

Preparation of samples for FT-IR: Preparing polyurethane as **Scheme-III**, we can get following results. When

\overline{M}_n of HO-P(LA-PDO)-OH was constant at 3000, regulating moisture content from 0 to 20 %, different amount of precipitate were produced. Clarified solution and white solid from different reaction systems were obtained by high-speed centrifugation and then detected by FT-IR *via* paint film method and tableting method, respectively.

FT-IR instrumentation: A small drop of clarified solution was spread on dry KBr disc and stored at room temperature and humidity for 2 days. Later on, the samples coated KBr disks were vacuum dried at 80 °C for 10 min in order to remove the solvent and absorbed water. The white solid was mixed with KBr and then was made to mixed disc. Each sample was scanned in mid-IR from 4000 to 400 cm^{-1} .

Preparation of samples for differential scanning calorimetry: The last step of synthesis of polyurethane was chain extension by butanediamine below 5 °C. In brief, butanediamine reacts with NCO-terminated prepolymer, which is easy to achieve, since the high reactivity of -NH₂ with NCO. The reactivity of -NH₂ with -NCO is much higher than the reactivity of hydroxyl group and water to -NCO and the effects of moisture on chain extension reaction is slimmer than the first step at below 5 °C, so we chose reaction of hexamethylene diisocyanate with HO-P(LA-PDO)-OH as the study object is adequate.

Mixtures of hexamethylene diisocyanate, HO-P(LA-PDO)-OH with target moisture content were prepared for thermodynamic study. Initial, HO-P(LA-PDO)-OH ($\overline{M}_n = 3000$) and hexamethylene diisocyanate at 1/1.2 molar ratio were dissolved in methylene chloride and then added the water at the molar ratio of 0, 5 and 20 %; secondly, dried the mixtures under vacuum at room temperature to remove the methylene chloride, which last for about 0.5 h; finally, the moisture content in samples, determined by Karl Fisher moisture titration instrument (ZKF-1), were 0.1, 5.3 and 20.9 %, respectively.

Differential scanning calorimetry instrumentation: All differential scanning calorimetry measurements and analyses were made using STA449C comprehensive thermal analyzer. High-volume pans that can withstand vapor pressure up to 3.8 MPa were used to prevent components of the test samples from evaporating at higher temperature up to 250 °C. Dynamic scans were made at heating rates of 10, 15, 20, 25 °C/min and the samples were scanned from 25 to 300 °C. Two replicated were done for each scan. The maximum variability was 1 for peak temperature and 5 % for reaction enthalpy.

RESULTS AND DISCUSSION

Reaction phenomena of the reaction of hexamethylene diisocyanate with HO-P(LA-PDO)-OH: When \overline{M}_n of HO-P(LA-PDO)-OH as well as the ratio of hexamethylene diisocyanate to HO-P(LA-PDO)-OH were constant and moisture content increased from 0 to 20 %, the amount of precipitation increased and the time appearing precipitation advanced. When the moisture content was constant at 5 % and the \overline{M}_n of HO-P(LA-PDO)-OH decreased, the amount of precipitation decreased and the time appearing precipitation lagged. Table-1 showed the \overline{M}_n of macrodiols and their corres-

TABLE-1
 \overline{M}_n OF MACRODIOL AND THEIR
 CORRESPONDING PREPOLYMER

	\overline{M}_n		
Macrodiol	1800	3000	4500
Prepolymer	12900	9800	7400

ponding prepolymers. We can see that the \overline{M}_n of prepolymer from HO-P(LA-PDO)-OH ($\overline{M}_n = 1800$) is 12900, while the \overline{M}_n of prepolymer from HO-P(LA-PDO)-OH ($\overline{M}_n = 3000$) is 17400. The results may be primarily due to different reactivity of HO-P(LA-PDO)-OH with different \overline{M}_n (Table-1). When \overline{M}_n of HO-P(LA-PDO)-OH is low, it is easy for it to move in the reaction system, which is beneficial to the contact of HO-P(LA-PDO)-OH and -NCO and then the effect of moisture decreased. Moreover, the reaction of low \overline{M}_n HO-P(LA-PDO)-OH prepared prepolymers with much higher \overline{M}_n (Table-1), which determined the effect of reactivity of HO-P(LA-PDO)-OH on the reaction of HO-P(LA-PDO)-OH with hexamethylene diisocyanate. According to above analyses, we preliminary inferred that when the moisture content existed in reaction systems, the structure or kinds of products will change. However the detail information, structure of products and thermal property, obtained by FT-IR and differential scanning calorimetry.

Fourier transform-infraredspectroscopy (FT-IR): FT-IR is an analytical technique for functional group analysis that provides information about the chemical make up of materials. FT-IR spectra of clarified solutions are showed in Fig. 1, showing no absorption at 2237 cm^{-1} and with characteristic peaks of $\delta_{\text{N-H}}$ in -CO-NH- at 1524 cm^{-1} , which confirmed that isocyanate was completely blocked and the reaction of hexamethylene diisocyanate and HO-P(LA-PDO)-OH and chain extension had realized. However, the allophanate is not obvious. When moisture content increased from 0 to 20 %, the characteristic peaks at 1631 cm^{-1} decreased [Fig. 1(a), 1(b), 1(c)]. Owen *et al.*¹⁰ reported that the characteristic peak of carbamate at about 1631 cm^{-1} and the hydrogen bond can result in the characteristic peak of carbamate changing to high field direction deviation.

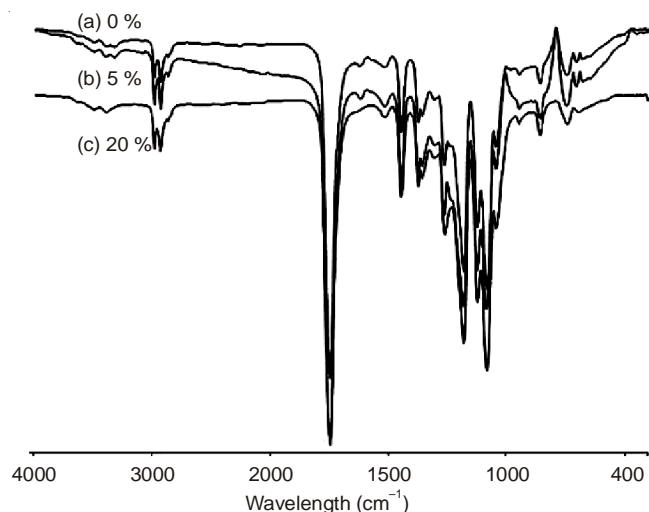


Fig. 1. FT-IR of the polyurethane from different reaction systems

FT-IR spectra of precipitation from reaction with high moisture content [Fig. 2(a)] is similar with clarified solutions, besides the peak of carbonyl group at 1587 cm^{-1} , attributing to allophanate. The sample with 20 % moisture showed broad peak at $1563\text{--}1520\text{ cm}^{-1}$ ($\delta_{\text{N-H}}$, $\delta_{\text{C=O}}$), which can be attributed to that the carbonyl group is hydrogen bonding completely and the participation of moisture, while the precipitation from reaction with 5 % moisture [Fig. 2(b)] showed the different carbonyl group absorption of 1587 cm^{-1} , attributing into the carbonyl groups hydrogen bonded partly and the less participation of moisture¹⁰.

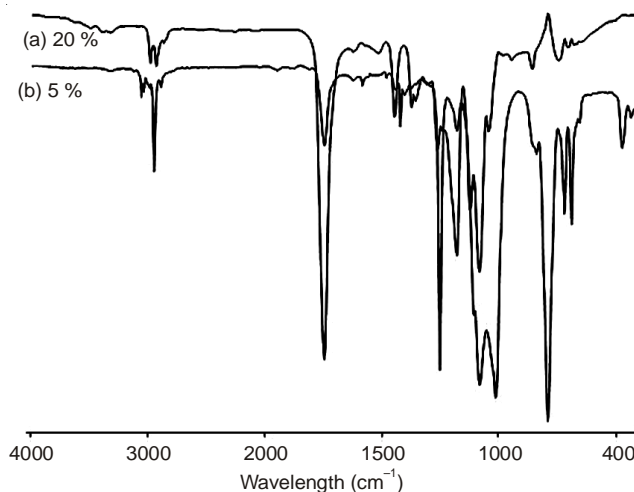
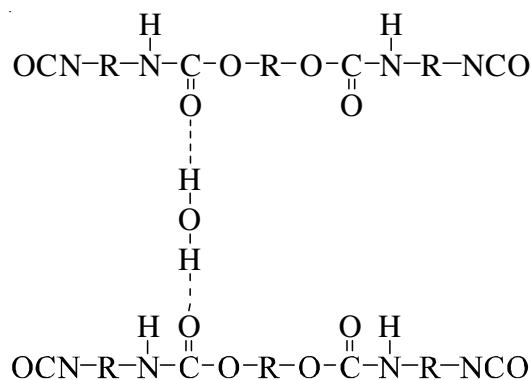


Fig. 2. FT-IR of the precipitation of the reaction with moisture

Comparing the reaction phenomena and the similarity between FT-IR spectra of clarified solutions and precipitation, we proved elementarily that when moisture content participates in reaction, hydrogen bond and crosslinked ureido from water generated not only the biuret-type structure which is different with literature⁸, showing moisture reacted with hexamethylene diisocyanate to form biuret-type or polyurea-type structure (**Scheme-II**).

These results can be explained by following reasons: Firstly, in the reaction system, the concentration of HO-P(LA-PDO)-OH is much more than H_2O and distributes uniformly, which is beneficial to the reaction of HO-P(LA-PDO)-OH, even some reaction of HO-H with hexamethylene diisocyanate. Secondly, the hydrogen bond is formed between of excessive HO-H and the formed -NH-C=O, since the polarity and electronic structure of H_2O (**Scheme-IV**).



Scheme-IV: Hydrogen bond of H_2O of -NH-C=O

Differential scanning calorimetry kinetic evaluation:

The activation energy of reaction hexamethylene diisocyanate with HO-P(LA-PDO)-OH having moisture was evaluated from thermogravimetric analysis at four different heating rates. Based on the assumption that the isothermal rate of conversion da/dt is a linear function of the temperature-dependent rate constant, $k(T)$ and a temperature-independent function of the conversion, $f(\alpha)$, that is:

$$\frac{d\alpha}{dT} = k(T) \cdot f(\alpha) \quad (1)$$

α being the fractional extent of reaction. In eqn. 1, $f(\alpha)$ depends on the particular decomposition mechanism. According to Arrhenius equation:

$$k(T) = A \cdot \exp\left(-\frac{E}{RT}\right) \quad (2)$$

wherein A is the pre-exponential factor, that is assumed to be independent of temperature, E is the activation energy, T is the absolute temperature and R is the gas constant. Combining eqn. 1 and 2, we have

$$\frac{d\alpha}{dt} = A \times \exp\left(-\frac{E}{RT}\right) \times f(\alpha) \quad (3)$$

For non-isothermal measurements at constant heating rate $\beta = dT/dt$, eqn. 3 transforms to

$$\beta \frac{d\alpha}{dt} = A \times \exp\left(-\frac{E}{RT}\right) \times f(\alpha) \quad (4)$$

Activation energy E can be calculated by various methods. Someone is an isoconversional one. Based on eqn. 1 and the Arrhenius eqn. 2, applying the logarithm of the conversion rate $d\alpha/dt$ as a function of the reciprocal temperature, from eqn. 4, in the form of

$$\ln\left(\beta \frac{d\alpha}{dt}\right) = -\frac{E_a}{R} \cdot \frac{1}{T} + \ln A \cdot f(\alpha) \quad (5)$$

It is obvious from eqn. 5 that if the function $f(\alpha)$ is constant for a particular value of α , then the $\ln A \cdot f(\alpha)$ is also constant.

By plotting $\ln\left(\beta \frac{d\alpha}{dt}\right)$ against $1/T$, the value of the $-E_a/R$ and the pre-exponential factor can be obtained, respectively.

Kinetic analysis of reaction between hexamethylene diisocyanate and HO-P(LA-PDO)-OH: It has been shown that moisture in wood has a significant influence on the synthesis of polyurethane⁸. He and Yan⁸ reported that the main reaction of hexamethylene diisocyanate with diols in presence of moisture may include primary reaction and secondary reaction. First, isocyanate reacts with hydroxyls of diols to form urethane and with moisture to form urea. Urethane and urea then react with isocyanate, as the secondary reaction, to form allophanate and biuret, respectively. These primary and secondary reactions are the main factors that affect kinetics of reactions between hexamethylene diisocyanate and diols or water.

However, in present study, we speculated different results based on FT-IR spectra. In order to prove these results, the heat of reaction was anatomized by comparing the heat flow among reactions of hexamethylene diisocyanate with HO-P(LA-PDO)-OH.

The differential scanning calorimetry scanning curves for different HDI/HO-P(LA-PDO)-OH/moisture mixtures are shown in Fig. 3. The curves do not show obvious changing in heat flow. From which we can prove that the moisture do not participate in the primary reaction and the reaction of HO-P(LA-PDO)-OH with hexamethylene diisocyanate is the key reaction in the primary reaction. The different results can be contributed to the effect of $\text{Sn}(\text{Oct})_2$ on the competition reaction between moisture and HO-P(LA-PDO)-OH with $-\text{NCO}^{12}$.

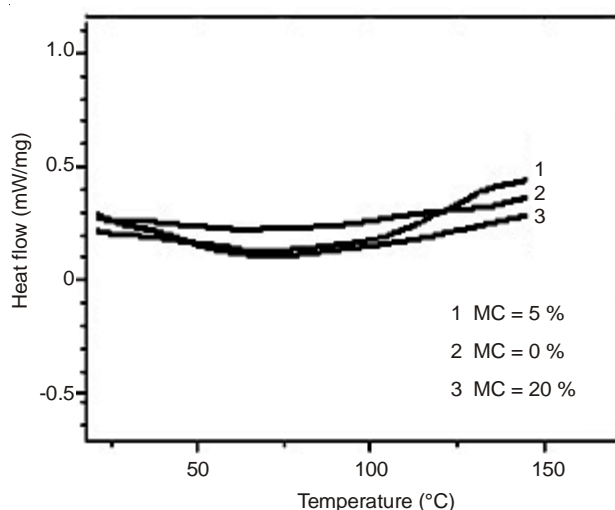


Fig. 3. DSC scanning curves for the reaction process of HDI/ HO-P(LA-PDO)-OH mixtures (heating rate: 10 °C/min)

In order to confirm the participation of moisture, the TG, enthalpy, peak temperature of differential scanning calorimetry curves are further analyzed.

Table-2 summarizes the peak temperatures (T_p) and calculated activation energy (E_a) based on the eqn. 5 for the different mixtures T_p increased from 157 to 162 °C with moisture content increasing from 0 to 20 %, when the heat rate is 10 °C/min, which suggested that the decomposition temperature (T_d) of structure of products from different mixtures of hexamethylene diisocyanate, HO-P(LA-PDO)-OH and moisture were different. It can be seen that the activation energy increases when the moisture content change from 0 to 20 %. The most possible explanation is that the structure of product was affected by the moisture, resulting in different contributions to the T_p and E_a .

TABLE-2 PEAK TEMPERATURES AND ACTIVATION ENERGY			
Moisture content	0 %	5 %	20 %
Peak temperature (°C)	157	159	162
E_a (KJ/mol)	113	127	144

The reaction enthalpy generally increased with increasing of moisture content (Fig. 4). It is evident that the increase mainly occurred between the reaction system with 0 % moisture and 5 % moisture. The difference value between 0 and 5 % was equivalent to the difference value between 5 and 20 %, which showed that the reaction of moisture with carbamate did not increase proportionally to the increasing of moisture content.

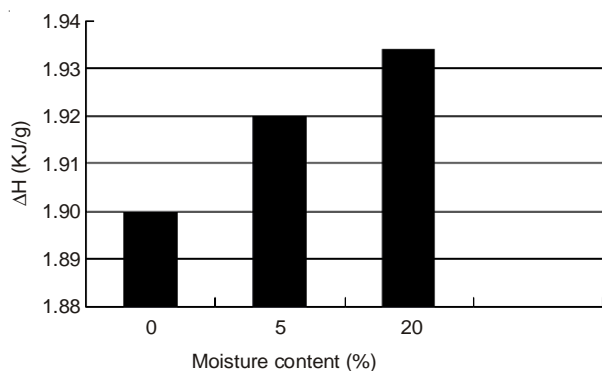


Fig. 4. Reaction enthalpy of curing for diols/HDI/moisture systems

This is reasonable because in the case of mixture without water, there is very limited amount water could react with the prepolymer to form hydrogen bond, which reaction is exothermic. Moreover, in the case of mixture without water, HO-P(LA-PDO)-OH reacted with hexamethylene diisocyanate slowly and reaction rate increased with increasing of reaction temperature and dissolution time of HO-P(LA-PDO)-OH in solvent. So we can prove that the effect of moisture on the reaction of hexamethylene diisocyanate with HO-P(LA-PDO)-OH is significant for all reaction systems. However, the reaction of isocyanate with moisture may not be same as reported by previous researchers^{8,11}.

It should be noted that literature⁷ reported that the isocyanate/moisture reactions without Sn(Oct)₂ probably had a lower energy and when moisture content was high, the activation energy showed lower value. However, in the hexamethylene diisocyanate/macrodior/moisture reaction systems, the activation energy increased with increasing of moisture. The results showed that the moisture in the reaction system did not participate in the primary reaction to form urea, while we can speculate the formation of hydrogen bond. The formation of hydrogen bond is an exothermic reaction, while the reaction of moisture with hexamethylene diisocyanate is endothermic reaction. So we proved further that the formation of hydrogen bond is dominated in the mixtures with water.

The dependence of activation energy on degree of conversion for the mixture of HDI/HO-P(LA-PDO)-OH/moisture is shown in Fig. 5. In Fig. 5 the values for the activation energy at very low and very high degrees of cure were in general more variable, since they are typically more sensitive to the baseline selection. We found that the trend was same for all repeated scans and replicate samples even at low and high degrees of cure. However, it is obvious that the relationship between activation energy and degree of conversion was different for the system without moisture and the mixtures with moisture. The differences revealed that the reaction of hexamethylene diisocyanate with HO-P(LA-PDO)-OH was influenced by the moisture in the mixtures.

For the mixture without moisture, activation energy increased with degree of conversion at the beginning of the reaction, indicating that the parallel reaction occurred simultaneously, which is similar to the literature⁸. The activation energy then remained almost constant and decreased at the high conversion. This trend was probably the result of the degradability to form monomer at high temperature, which can be proved by the further

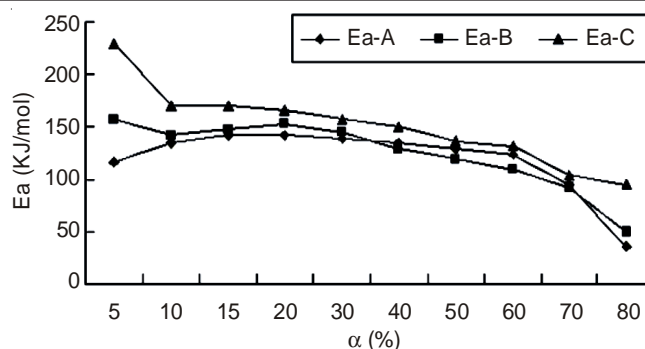


Fig. 5. Dependence of activity energy on the degree of conversion; (A: Without moisture; B: With moisture 5%; C: With moisture 20%)

detection about the material from the detector. The decomposition crosslinked OCN-HDI-P(LA-PDO)-HDI-NCO, whose structure is similar to biuret, has a activation energy and, therefore, gives a higher activation energy.

The reaction processes of HDI/HO-P(LA-PDO)-OH mixture became very different after moisture was introduced into the reaction system. At the beginning of reaction, the activation energy decreased. In addition, comparing to mixture with 5% moisture, the decreasing degree *versus* the degree of conversion had a more concave shape of the mixture with 20% moisture. This phenomena can be explained by that, the initial activation energy of mixture with 20% moisture is more than the mixture with 5% moisture, which can be attributed the exist of hydrogen bond between H₂O and OCN-HDI-P(LA-PDO)-HDI-NCO and then the reaction of moisture with -NH-COO- in carbamates, which led to the decreasing of activation energy. When the degree of conversion increased from 10 to 70%, the activation energy decreased gradually and the constant reaction was not found in the mixture with moisture, indicating that the individual reaction was affected by moisture and the structure of the product varied constantly in the reaction processes.

Conclusion

Generally, in the reaction, having Sn(Oct)₂ as the catalyst, hexamethylene diisocyanate primarily reacted with HO-P(LA-PDO)-OH, but not reacted with moisture in the primary reaction. In this research, the effects of moisture on reaction of hexamethylene diisocyanate with HO-P(LA-PDO)-OH are tested with FT-IR and DSC/TGA. The reaction of hexamethylene diisocyanate with HO-P(LA-PDO)-OH is influenced by moisture and influence degree increased with increasing of moisture content, however, it is not very obvious and the shape memory properties are not affected significantly.

For the HDI/HO-P(LA-PDO)-OH/moisture mixtures, the reaction of -NCO occurred mainly with HO-P(LA-PDO)-OH and limited bonded water. When moisture content is low and even no moisture, the values of activation energy, enthalpy of reactions and reaction rate are all lower. Considering the characteristics of FT-IR and DSC/TGA measurement, we preliminarily conjectured that the isocyanate react with both moisture and hydroxyls in mixtures, however, the reactions of isocyanate with HO-P(LA-PDO)-OH preferred to the reaction of isocyanate with moisture and moisture may reaction with -NH-COO- in carbamates, the reaction products of hexamethylene

diisocyanate with HO-P(LA-PDO)-OH, which reactions resulted in products hardness increasing.

Moreover, the synthesis of the novel shape memory polymer in toluene system was studied, from which we can find the different results. This may be contributed into the intersolubility between H₂O and DMF or between H₂O and toluene. More detail phenomena and causes will be study in future.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support from the Postdoctoral special funding of Chongqing (20110-2009) and Natural Science Foundation of Chongqing (CSTC 2013jcyjA50019).

REFERENCES

1. F. El Feninat, G. Laroche, M. Fiset and D. Mantovani, *Adv. Eng. Mater.*, **4**, 91 (2002).
2. M. Behl and A. Lendlein, *Mater. Today*, **10**, 20 (2007).
3. A. Lendlein and R. Langer, *Science*, **296**, 1673 (2002).
4. A. Alteheld, Y. Feng, S. Kelch and A. Lendlein, *Angew. Chem. Int. Ed.*, **44**, 1188 (2005).
5. W.S. Wang, P. Ping, X.S. Chen and X.B. Jing, *Eur. Polym. J.*, **42**, 1240 (2006).
6. Q.H. Meng, J.L. Hu, Y. Zhu, J. Lu and Y. Liu, *J. Appl. Polym. Sci.*, **106**, 2515 (2007).
7. T. Musumeci, C.A. Ventura, I. Giannone, B. Ruozi, L. Montenegro, R. Pignatello and G. Puglisi, *Int. J. Pharm.*, **325**, 172 (2006).
8. G.B. He and N. Yan, *Int. J. Adhes. Adhes.*, **25**, 450 (2005).
9. F.W. Weaver and N.L. Owen, *Appl. Spectrosc.*, **49**, 171 (1995).
10. N.L. Owen, W.B. Banks and H. West, *J. Mol. Struct.*, **175**, 389 (1988).
11. K. Chrissafis, K.M. Paraskevopoulos and D.N. Bikiaris, *Polym. Degrad. Stab.*, **91**, 60 (2006).
12. Y. Nakayama, R. Yamaguchi, C. Tsutsumi and T. Shiono, *Polym. Degrad. Stab.*, **93**, 117 (2008).