

# Synthesis of 2-Phenyl-3-hydroxyethyl-1,3-oxazolidine and Its Application as Latent Curing Agents

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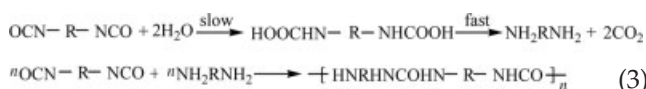
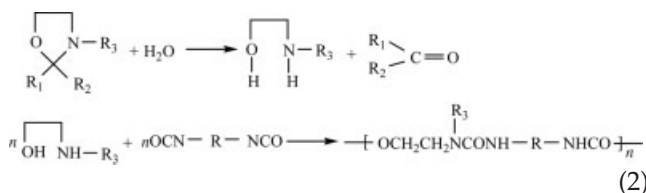
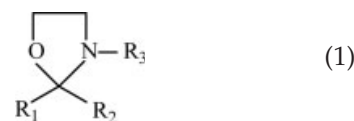
**ABSTRACT:** A kind of new compound of 2-phenyl-3-hydroxyethyl-1,3-oxazolidine was successfully synthesized by addition–condensation reaction of phenyl aldehyde and  $\beta$ -hydroxyethanolamine and purified by vacuum distillation. Its purity was examined by gas chromatographic analysis. Its structure was confirmed by <sup>13</sup>C NMR and FTIR. When this compound was added as a latent curing agent in single-component moisture-curable polyurethane system (SPU), bubbles of SPU formed during curing was

obviously restrained, and the elongation at break of the cured SPU contained a certain content of 2-phenyl-3-hydroxyethyl-1,3-oxazolidine was increased to 16 times when compared with that uncontained this oxazolidine derivative. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1343–1346, 2007

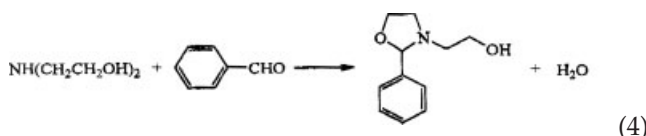
**Key words:** oxazolidine; latent curing agents; single-component moisture-cured polyurethane (SPU)

## INTRODUCTION

It is known that oxazolidine is a saturated heterocyclic compound [eq. (1)] that could react with water, and have different reactivity with different substituting groups ( $R_1$ ,  $R_2$ ,  $R_3$ ) and different substituting position.<sup>1</sup> It can be added to the single-component moisture-curable polyurethane system (SPU) for playing a role of latent curing agents.<sup>2–4</sup> SPU is widely used in the adhesives/sealants production.<sup>5</sup> Under moisture-absence condition, it can coexist with SPU for a long time; but in the presence of moisture, it can react faster with water than it does with SPU, and products of reaction further react with SPU as curing agent without carbon dioxide ( $\text{CO}_2$ ) generation [eq. (2)].<sup>2</sup> This pattern could overcome the inherent disadvantages of traditional SPU curing system. Curing principle of traditional SPU is that isocyanate reacts with water to form amines and  $\text{CO}_2$  [eq. (3)], and amines formed will react further with isocyanates, rapidly increasing polymer molecular weight as well as viscosity of the system. Generation of  $\text{CO}_2$  gas formed in the reaction, which is difficult to escape from the cured SPU, therefore causes pinholes and bubbles within cured SPU material. So these  $\text{CO}_2$  byproducts can adversely affect the final properties of the cured SPU, for example, reducing the mechanical properties.



In this article, 2-phenyl-3-hydroxyethyl-1,3-oxazolidine was synthesized by reacting phenyl aldehyde with  $\beta$ -hydroxyethanolamine [eq. (4)], and applied in SPU system as curing agent to improve SPU material properties.



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## EXPERIMENTAL

### Materials

Phenyl aldehyde,  $\beta$ -hydroxyethanolamine, and toluene are analytically pure grade.

### Synthesis of 2-phenyl-3-hydroxyethyl-1,3-oxazolidine

The preparation of 2-phenyl-3-hydroxyethyl-1,3-oxazolidine was accomplished by addition–condensation reaction of phenyl aldehyde and  $\beta$ -hydroxyethanolamine. The azeotropic distillation of toluene and water was used to remove water formed in the addition–condensation reaction from the reactant mixtures to improve the yield of the target product, stoichiometrically mixing  $\beta$ -hydroxyethanolamine with toluene into a flask assembled with mechanical agitator, thermometer, and dropping funnel. Then phenyl aldehyde was uniformly dripped into the flask from dropping funnel with stirring at 60°C. After dripping, the reaction was held under reflux for about 30 min. The dropping funnel was replaced by a water separator for azeotropic distillation to remove water, toluene, and the other impurities, so that a crude product was obtained. The crude product was purified by vacuum distillation at a pressure of 80 mmHg and a temperature of 135°C. Gas chromatographic analysis (GC) demonstrated that the purified product was 2-phenyl-3-hydroxyethyl-1,3-oxazolidine. Its structure was confirmed by  $^{13}\text{C}$  NMR and FTIR.

### Preparation of moisture-curable type polyurethane prepolymer with two isocyanate end groups

One hundred sixty grams of polyether polyol (PPG300) was added into a flask and dried in vacuum for 24 h at 100°C to remove the water, and then cooled to room temperature. 2,4-Toluene diisocyanate (15.26 mL), and 1 g dibutyltin dilaurate and 1 g triethylamine catalysts were added into the same flask containing PPG, after removal of water. The reaction was done for 30 min under mechanical stirring at ambient temperature, and then heated to 60°C for 3 h to complete the reaction. The product was discharged at once and stored in a vacuum dryer.

### Preparation of the cured SPU sheet

Ten grams of the prepared polyurethane prepolymer and 1 g of 2-phenyl-3-hydroxyethyl-1,3-oxazolidine synthesized as mentioned earlier were taken into a 50-mL glass flask and stirred vigorously to form a homogeneous fluid. This fluid was cast onto a mold ( $5 \times 10 \times 0.1 \text{ cm}^3$ ) precoated with silicone, and subsequently cured in a moisture circulating oven (at temperature of 30°C and humidity of 55%). The cured sheets were taken pictures for the observation of the surface bubbles and used for mechanical properties

tests, and then compared with those of the cured polyurethane sheet without 2-phenyl-3-hydroxyethyl-1,3-oxazolidine under the same condition.

### Measurement and characterization

#### GC characterization

GC spectra were measured with GC9790 Gas chromatographic spectrometer made in Fuli Analytical Instrument Co., Ltd. (Zhejiang Province, China). The detailed GC conditions were as follows—detector: hydrogen flame, sensitivity:  $10^{10} \text{ mv/g/s}$ , capillary column:  $50 \text{ m} \times 0.32 \text{ mm} \times 1 \mu\text{m}$ , carrier gas: nitrogen ( $\text{N}_2$ ), injector temperature: 250°C, initial temperature: 70°C with 3-min hold, ramp 1: 10°C/min to 180°C 2-min hold, ramp 2: 5°C/min to 300°C 7-min hold.

#### FTIR characterization

FTIR spectra have been taken as KBr pellets, with a Nicolet FTIR 20SXB infrared spectrometer made in America.

#### $^{13}\text{C}$ NMR characterization

$^{13}\text{C}$  NMR proton noise decoupling spectra and also under distortionless enhancement by polarization transfer (DEPT) conditions have been obtained with Varian INOVA-400MHz NMR spectrometer made in America, using  $\text{CDCl}_3$  as solvent and tetramethylsilane [ $\text{Si}(\text{CH}_3)_4$ ] as internal standard.

#### Mechanical properties measurement

The elongations at break of the cured polyurethane sheets were performed by Instron 4302 Material Tester made in America. All the test samples of the cured sheet were prepared as strips of  $50 \text{ mm} \times 6 \text{ mm} \times 0.1 \text{ mm}$ , cut from the center of the cured sheets, with a rate of extension at 50.0 mm/min. The elongations at break were calculated from the stress–strain curves as average of five measurements.

## RESULTS AND DISCUSSION

### GC results

Figure 1 is GC spectra of the synthesized compound purified by vacuum distillation. Only one very high and sharp peak at retention time of 20.572 min can be observed. It shows that a purified sample can be obtained by vacuum distillation.

### FTIR results

Figure 2 is the FTIR spectra of the purified compound. IR spectra show that an absorption peak at  $\sim 3401.32 \text{ cm}^{-1}$  is attributed to O–H characteristic stretching vibration frequency. Two absorption peaks

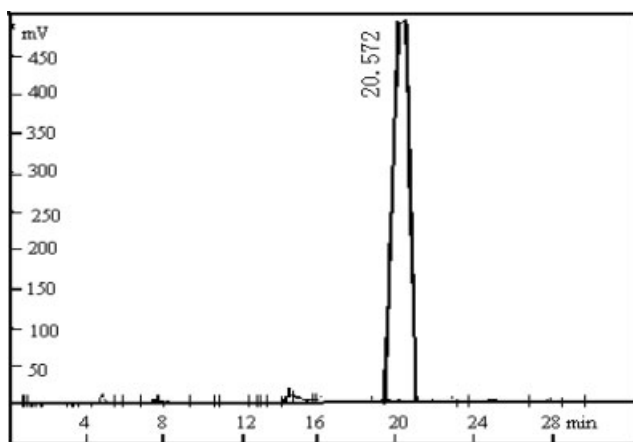


Figure 1 Gas chromatogram of purified compound.

at  $\sim 2945.63$  and  $2945.63 \text{ cm}^{-1}$  are attributed to saturated carbon-hydrogen bond ( $\text{sp}^3 \text{ C-H}$ ) stretching vibration frequency. Absorption bands in region  $1650\text{--}1450 \text{ cm}^{-1}$  are attributed to  $\text{C}=\text{C}$  bond of benzene ring. Two absorption peaks at  $\sim 759.267$  and  $700.57 \text{ cm}^{-1}$  are attributed to the characteristic peaks of single-substituted benzene ring. One absorption peak at  $\sim 1056.40 \text{ cm}^{-1}$  is attributed to  $\text{O-C-N}$  group. All characteristic absorption bands correspond to that of 2-phenyl-3-hydroxyethyl-1,3-oxazolidine, showing that the target product has been synthesized.

### $^{13}\text{C}$ NMR results

Figure 3 is the  $^{13}\text{C}$  NMR proton noise decoupling spectra of the purified compound. Figure 4 is  $^{13}\text{C}$  NMR DEPT spectra. Table I shows the chemical shifts of C atom and data obtained from the DEPT spectra. The signals for C-1 and C-2 atoms connecting directly with N-atom were observed at  $\delta_{\text{C}}$  51.449 and 53.632

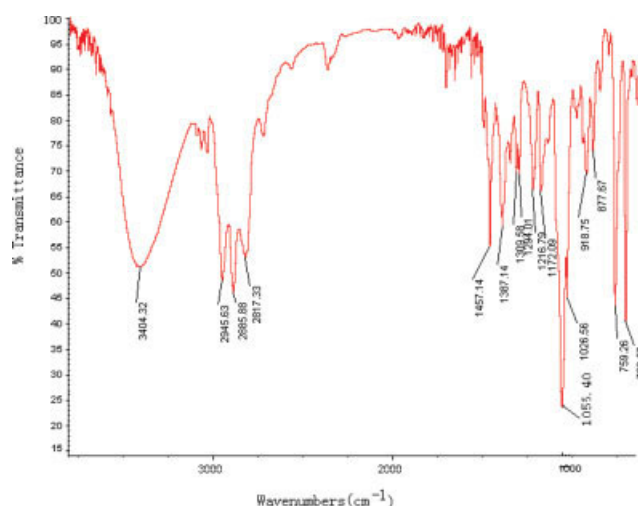


Figure 2 Infrared spectra of purified compound. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

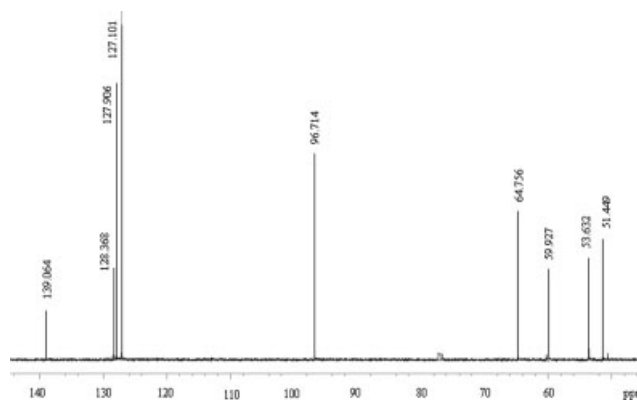


Figure 3  $^{13}\text{C}$  NMR proton noise decoupling spectrogram.

ppm, and C-2 being in heterocyclic ring shifts to a high value. At a similar condition, C-3 and C-4 atoms connecting directly with O-atom were observed at  $\delta_{\text{C}}$  59.927 and 64.756 ppm, and C-4 being in heterocyclic ring shifts to a high value. C-7 and C-10 with the same chemical environment were observed at  $\delta_{\text{C}}$  of 127.906 ppm. At a similar condition, the signals for C-8 and C-11 with the same chemical environment were observed at  $\delta_{\text{C}}$  128.368 ppm. The chemical shifts on  $^{13}\text{C}$  NMR spectra for C-7, C-8, C-10, and C-11 are obviously higher than that of other carbon atom except C-9, a tertiary carbon atom with a chemical shift of 139.064 ppm.

The  $^{13}\text{C}$  NMR analysis also confirm that the purified compound is 2-phenyl-3-hydroxyethyl-1,3-oxazolidine.

### Polyurethane cured film results

Figure 5 is the photographs of the cured sheets of SPU with [Fig. 5(a)] and without [Fig. 5(b)] the syn-

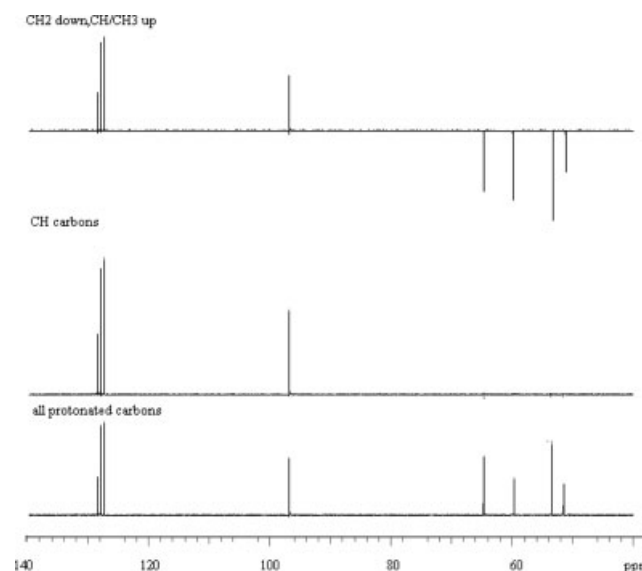


Figure 4  $^{13}\text{C}$  NMR DEPT spectrogram.

**TABLE I**  
Chemical Shifts of C Atom and Data from DEPT

C atom	$\delta C$ (ppm)	DEPT	Most probable structure
1	51.449	CH <sub>2</sub>	
2	53.632	CH <sub>2</sub>	
3	59.927	CH <sub>2</sub>	
4	64.756	CH <sub>2</sub>	
5	96.714	CH	
6	127.101	CH	
7, 10	127.906	CH	
8, 11	128.368	CH	
9	139.064	Tertiary C	

thesized 2-phenyl-3-hydroxyethyl-1,3-oxazolidine. The bubbles in Figure 5(b) is much less than that in Figure 5(a); this indicates that 2-phenyl-3-hydroxyethyl-1,3-oxazolidine can restrain bubbles in SPU during curing.

#### Mechanical properties results

The data listed in Table II are the test results of the elongations at break of the cured sheets of SPU with and without the synthesized 2-phenyl-3-hydroxyethyl-1,3-oxazolidine. The elongation at break



**Figure 5** The photographs of the cured sheet of SPU with or without the synthesized 2-phenyl-3-hydroxyethyl-1,3-oxazolidine. (a) SPU/2-phenyl-3-hydroxyethyl-1,3-oxazolidine: 100/0, (b) SPU/2-phenyl-3-hydroxyethyl-1,3-oxazolidine: 100/10. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

**TABLE II**  
Mechanical Properties of the Cured Sheet of SPU With or Without 2-Phenyl-3-hydroxyethyl-1,3-oxazolidine

SPU/2-phenyl-3-hydroxyethyl-1,3-oxazolidine	100/0	100/10
Elongation at break (%)	24	375

of SPU with 2-phenyl-3-hydroxyethyl-1,3-oxazolidine is about 16 times of that of SPU without 2-phenyl-3-hydroxyethyl-1,3-oxazolidine. The substantial increase of the elongation at break of the cured SPU using 2-phenyl-3-hydroxyethyl-1,3-oxazolidine as assistants is likely caused by the decrease of bubbles formed during curing. It indicates that the synthesized compound of 2-phenyl-3-hydroxyethyl-1,3-oxazolidine is a kind of good latent curing agent to improve the final property of the cured SPU.

#### CONCLUSIONS

2-Phenyl-3-hydroxyethyl-1,3-oxazolidine can be synthesized successfully by addition–condensation reaction of phenyl aldehyde and  $\beta$ -hydroxyethanolamine. The bubble formed in the moisture-curable type polyurethane prepolymer can be obviously restrained by adding a proper content of this oxazolidine derivative, leading to that the elongation at break of the cured polyurethane prepolymer containing the oxazolidine derivative is improved to 16 times when compared with that not containing the oxazolidine derivative. It is shown that the oxazolidine derivative can be used as a good latent curing agent in SPU to restrain the bubble formation, and hence improve its final properties.

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