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Preparation of eugenol-based polyurethane

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Preparation of eugenol-based polyurethane

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Abstract. The regenerative eugenol was used as the starting material to prepare diol species by two steps, with a total yield of 28%. Furthermore, the prepared diol reacts with 1,6-hexadiisocyanate(HDI) to afford the corresponding polyurethane (PU). The structure of intermediates and PU are characterized by 1H-NMR or IR.

1.   Introduction

Resource and energy crisis has become a serious problem in recent decades, due to increasing consumption of resources and energy, unsustainable fossil resources, population growth, and environmental pollution. Resources from plants and animals can be regenerated, which are renewable and inexhaustible in some sense. Therefore, importance of these renewable resources is reemphasized and has attracted more scientists to be involved in the research of these fields[1][2][3]. Eugenol, a main component of clove oil, is the derivative of phenol[4]. This interesting molecule has found wide practical or potential applications in pharmaceuticals, life science, materials, etc.   Polyurethane is one of the plastic materials, which exhibits excellent comprehensive performance among others, and growing demand for this material has made the output reach 21 million tons in 2012 [5][6].

2.   Experimental

Material and characterization

Potassium ferricyanide, dichloromethane (DCM), 25% aqueous ammonia, acetone, anhydrous sodium sulfate, aqueous HCl (36-38%), petroleum ether, ethyl acetate, 2-bromo ethanol, anhydrous potassium carbonate, 1,6-hexadiisocyanate(HDI), dibutyl tin dilaurate (DBTDL), tetrahydrofuran (THF), and methanol are AR grade, and eugenol is industrial grade. All the reagents are used straightly without any treatment.

^{1}H NMR pectra were recorded on a Bruker AV 400 MHz spectrometer using $CDCl_3$ as a solvent for deuterium locking,with etramethylsilane (TMS) as the internal standard. FTIR spectra of the samples were obtained using the KBr pellet method by a Bruker V70 FTIR spectrophotometer.

*Synthesis of dieugenol (**1**)*

Eugenol (12.5 g, 74 mmol) is dissolved in the mixed solvent acetone (50 mL) and water (25 mL), followed by adding aqueous ammonia (160 mL). After 10 min, saturated aqueous potassium ferricyanide (26 g, 79 mmol) was added dropwise. The resulting mixture is stirred at ambient temperature for 24 h. Aqueous 2 mol/L HCl is added to the reaction mixture to neutralize access ammonia. The resulting subsidence is filtered, rinse with water, and dried. The colatuie is extracted with DCM for three times, and the organic phase is dried, distilled to give another crop of the product. The total amount of light brown solid product **1** is 8.75 g (70% yield). ^{1}H NMR : δ 6.77 (m, 4H), 6.00

(m, 4H), 5.08 (m, 4H), 3.92 (s, 6H), 3.37 (m, 4H).

Synthesis of di(hydroxyethyl) dieugenol (2)

To the solution of dieugenol (**1**) (0.326 g，1 mmol) in DCM (5 mL) and acetone (5 mL) is added anhydrous potassium carbonate (0.69 g, 5 mmol),　followed by adding dropwise 2-bromoethanol (0.5 g, 4 mmol) within about 1 h. After completion of adding materials, the brown solution is stirreded and fluxed for 24h . Then cool to room temperature, and water is poured. The solution is extracted with DCM for three times. The organic phase is combined, dried on anhydrous sodium sulfate, distilled to afford gross product **2**. Purifying on silica gel column with the eluent (PE:EAC= 2 : 1, v : v) gives pure 2 as white powder (0.15 g, 40%). ^{1}H NMR δ 6.75 (s, 4H), 5.97 (m, 2H), 5.09 (m, 4H), 3.89 (s, 6H), 3.78 (m, 4H), 3.58 (m, 4H), 3.36 (m, 4H), 2.65 (m, 2H).

Synthesis of eugenol-based polyurethane (3)

To the 100 mL of flask are added sequentially di(hydroxyethyl) dieugenol (**2**) (0.828 g, 2 mmol), HDI (0.336 g, 2 mmol), DBTDL (10 mg) and THF (18g). Stir the solution is at 60 °C for 10 h. Then access methanol is added to precipitate the product. After filtration and dried, the eugenol-based polyurethane (**3**) (0.885 g, conversion c.a. 76%) is obtained.

3.　Results and discussion

Characterization of di(hydroxyethyl) dieugenol (2)

The ^{1}H NMR spectrum of di(hydroxyethyl) dieugenol (**2**) is demonstrated in Figure 1. The peak at 6.75 ppm represent from four protons (H^a) on aryl rings. The two multiplet peaks at 5.97 and 5.09 ppm represent vinyl protons (H^e and H^d) of allylic groups on the phenyl rings. The singlet peak at 3.89 ppm results from six protons (H^b) of two methoxy groups. The signal at 3.86 ppm corresponds to the four protons (H^f) of two methylene groups. The peak at about 3.58 ppm is the signal of another two methylene groups (H^g). The signal of four benzyl protons (H^c) is located at 3.36 ppm. The peak at 2.65 ppm may stem from the hydroxyl groups. Note that some peaks at high field are the signal of water and solvent remnants, which have not downside influences on the next reactions.
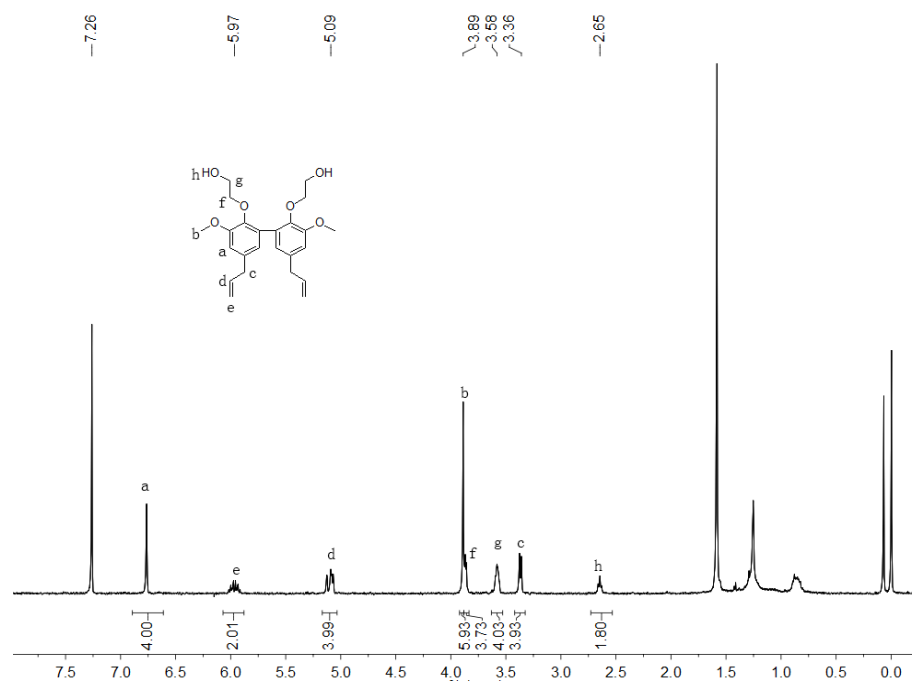

Fig.1 ^{1}H NMR spectrum of di(hydroxyethyl) dieugenol (**2**)

Synthesis of di(hydroxyethyl) dieugenol (2)

According to literature, phenols, aryl amines as well as their derivatives can be oxidized to obtain the corresponding coupling products[7][8][9]. In this contribution, dieugenol is synthesized by using potassium ferricyanide as the weak oxidant[8] (Scheme 1). With dieugenol in hand, we then study the

synthesis of di(hydroxyethyl) dieugenol (**2**) by utilizing 2-bromoethanol as the other reactant. In general, common reaction conditions of *O*-alkylation are that acetone is as the solvent and access potassium carbonate as the base. Other related factors are molar ratio of dieugenol and 2-bromoethanol, reaction temperature, reaction time. Results of controlled experiments are illustrated in Table 1. From the reaction equation, theoretical ratio of dieugenol and 2-bromoethanol is 1 : 2, so we firstly conduct the reaction at this ratio under mild conditions, and the yield of **2** is only 11%, accompanied by some byproducts (Entry 1, Table 1). Then, the ratio is raised from 1 : 3 to 1 : 4 and 1 : 5, and acceptable 28% yield at 1 : 4 is obtained. Therefore the optimal molar ratio of dieugenol and 2-bromoethanol is 1 : 4. When the reaction temperature is increased from 25 $^{\circ}$C to refluxing for 10 h, the yield is achieved as 36%. After the reaction time is extended to 24 h, the yield is increased a little, i.e. 40% ((Entry 6, Table 1)). Further extending the time to 48 h, the yield is only increased to 42%. So, the optimized reaction conditions are: molar ratio of dieugenol and 2-bromoethanol is 1 : 2, refluxing temperature, reaction time 24 h.
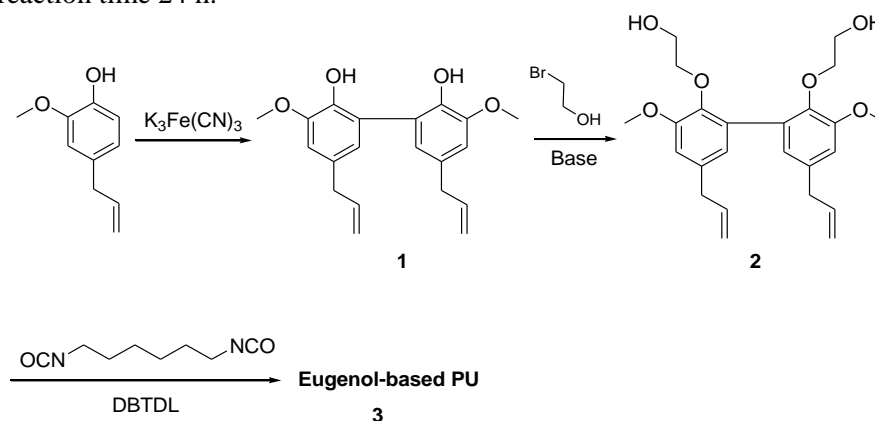
Scheme 1   preparation of eugenol-based PU **3**

Table 1   Effects of reaction conditions on the yield of **2**

Entry	molar ratio [a]	Temperature ($^{\circ}$C)	Time (h)	Yield of **2** (%) [b]
1	1 : 2	25	10	11
2	1 : 3	25	10	23
3	1 : 4	25	10	28
4	1 : 5	25	10	29
5	1 : 4	refluxing	10	36
6	1 : 4	refluxing	24	40
7	1 : 4	refluxing	48	42

[a] molar ratio means the ratio of dieugenol and 2-bromoethanol; [b] isolated yield

*Preparation of eugenol-based polyurethane (**3**)*
There are two hydroxyl groups on the compound **2**, which means that this intermediate can be used as the diol reactant for preparation of polyurethane. Thus, compound **2** reacts with HDI catalyzed by DBTDL to give the corresponding PU (**3**) (Scheme 1). The polymer 3 can come into beinga light green-yellow film on a glass matrix (Figure 2A). The IR spectrum of **3** is illustrated as Figure 2B. The peak at 1740 cm^{-1} is the signal of -NHCOO-.

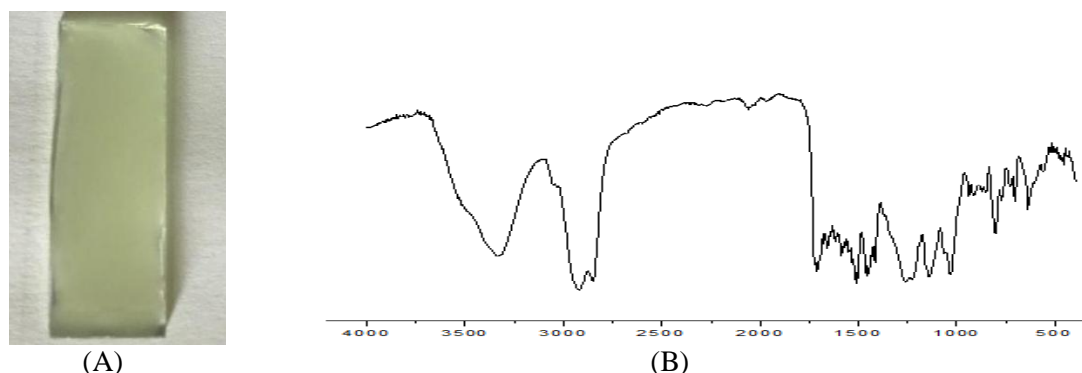(A)   (B)

Fig.2 (A) the film of PU **3** on a glass substrate; (B) IR spectrum of the PU **3**.

4.   Conclusion

The cheap and renewable resource eugenol is used to synthesize its dimmer and further the diol derivative. The optimized conditions for the synthesis of di(hydroxyethyl) dieugenol are as follows: molar ratio of dieugenol and 2-bromoethanol is 1 : 2, refluxing temperature, reaction time 24 h. Finally, the polymer PU is prepared and characterized by IR

Acknowledgement

References

[1] T. Iwata. Chem. Int. Ed. 2015, 54, 3210-3215.
[2]   A. Gandini, T.M. Lacerda. Prog. Polym. Sci. 2015, 48, 1-39.
[3]   A. Llevot, P.-K. Dannecker, M. von Czapiewski, L.C. et al. Chem. Eur. J. 2016, 22, 11510-11521.
[4]   Guy P. Kamatou, Ilze Vermaak and Alvaro M. Viljoen. Molecules 2012, 17, 6953-6981.
[5]   H.-W. Engels, H.-G. Pirkl, R. Albers, et al. Chem. Int. Ed. 2013, 52, 9422-9441.
[6]   L. Maisonneuve, O. Lamarzelle, E. Rix, E. et al. Chem. Rev. 2015, 115, 12407-12439.
[7]   H. Gang, D. Lee, K.-Y. Choi, H.-N. et al. ACS Sustainable Chem. Eng., 2017, 5, 4582-4588.
[8]   M. Shibata, N. Tetramoto, A. Imada, M. et al.. Sugimoto. React. Funct. Polym. 2013, 73, 1086-1095.
[9]   J. Pan, J.Q. Li, R.F. Huang, X.H. et al. Zhu. Tetrahedron, 2015, 71, 5341-5346.