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Preparation of Organic Nanoacid Catalyst for Urethane Formation

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Metal-free catalysts are preferred during these days in organic synthesis or in polymerizations. Sulfonic acid is reported to be efficient in catalyzing reactions between isocyanates and alcohols. In this work, synthesis of sulfonic acid immobilized organic nanoparticles (nanoacid) and its application in catalyzing urethane formation, are elaborated. The nanoacid can be simply prepared by miniemulsion polymerization with a reactive surfactant, namely sodium 4-((perfluoronon-8-en-1-yl)oxy)benzenesulfonate, followed by an acidification. From the images of scanning electron microscope, the nanoacid obtained is found to be narrowly dispersed and the average diameter is around 90 nm. The measured sulfur content is 0.5%, from which the content of sulfonic acid in the nanoparticles is calculated to be 0.16 mmol/g. When catalyzing urethane formation based on hexamethylene diisocyanate and *n*-butanol, the nanoacid catalyst exhibits considerable efficiency.

Key words: Nanoacid, Catalysis, Urethane, Miniemulsion

I. INTRODUCTION

Polymer-supported solid acids (PSAs), such as Amberlyst-15, Nafion NR50 and Dowex 50WX2 have been widely utilized as heterogeneous catalysts in organic synthesis [1–7]. Compared with homogeneous acids, PSAs have attracted environmental and economic attention due to its non-corrosion, easy separation, and high efficiency in catalyzing organic reactions, *e.g.*, alkylation, etherification, hydration, hydrogenation, nitration, oxidation and esterification [8–15]. However, the particle size of such traditional PSAs are in millimeter scale so that they must be removed from the polymer, otherwise it would affect the mechanical properties of the final products. Moreover, Nafion NR50 does not swell in a lot of organic solvents so that the acid groups are not active in reactions, and the low specific surface area (about 0.02 m^2/g) is another factor limiting the catalytic efficiency [11, 16]. To increase the specific surface area of PSA, one of the most feasible way is to make it into nanoscale. It is feasible for nanoparticles to leave in polymer materials since they are usually applied as additives to enhance the mechanical properties of polymer materials, and furthermore the particles do not migrate during processing or in use.

Polyurethanes (PUs) are a versatile class of polymers with carbamate linkages in polymer backbone. Since it is convenient to tailor the properties of PUs by adjusting their chemical and morphological makeup, these diverse materials are widely utilized as foams, elastomers, coatings, adhesives, composite materials, *etc.* [17]. Generally, PUs are primarily synthesized via polyaddition of diisocyanates and diols in which organotins are the most commonly-used catalysts for their remarkable catalytic activity. However, organotins are difficult to be removed from PU products and the residual tin causes adverse effects, such as unwanted toxicities and side reactions, thus it limits the application of PUs in some sensitive areas, especially in biomedical applications [18–20]. Less toxic metal catalysts [21–23] and even metal-free organic compounds [20, 24] are therefore introduced to replace the organotins. Metal-free organic catalysts are preferable because of their high substrate tolerance and selectivity [25]. Among the organic catalysts, organic acids, especially sulfonic acids, show considerable catalytic efficiency in the polymerization of PUs [26]. Moreover, organic acids are better choices for base-sensitive PUs [18, 27] and the residual organic acid catalysts do not cause the degradation of PUs while organic bases do [26].

In this work, we elaborate the preparation and the application of organic nanoparticles embedded with sulfonic acid group on the surface (abbreviated as nanoacid). Since there is no monomer transfer in miniemulsion system [28–30], nanoacid is proposed to be prepared by miniemulsion polymerization in which a reactive surfactant bearing both carbon-carbon double bond (C=C) and sulfonate is possible to react on the surface of the particles.

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II. EXPERIMENTS

A. Materials

Hexamethylene diisocyanate (HDI, 99%) and styrene (St, 99%) were purchased from Aladdin Industrial Corporation (Shanghai, China). Divinylbenzene (DVB, 80%) and hexadecane (98%) were bought from Energy Chemical Corporation (Shanghai, China). Sodium 4-((perfluoronon-8-en-1-yl)oxy)benzenesulfonate (OBS) was from Hongjia Technology Corporation (Jiangsu, China). All chemicals mentioned above were used as received without further treatment. Azobisisobutyronitrile (AIBN) was purchased from Fuchen Chemical Corporation (Tianjin, China) and was purified by recrystallization in ethanol before use. Toluene (AR, from Guangzhou Chemical Reagent Factory, Guangzhou, China) and *n*-butanol (AR, from Chinasun Specialty Products Corporation, Jiangsu, China) were dried over calcium hydride and distilled *in vacuo*.

B. Characterizations

^{1}H NMR was detected at 25 °C on a Bruker AVANCE III HD 600 (600 MHz) spectrometer (Germany) and chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (DMSO-D$_6$: δ 2.50 ppm). Elemental analysis was carried out in an Elementar Vario EL cube elemental analyzer (Germany). *In situ* Fourier transform infrared (FTIR) spectra were collected every 30 s during the monitored reaction by a Mettler Toledo ReactIR 15 spectroscope with a DiComp diamond probe.

C. Synthesis of nanoacid

OBS (3.60 g) was first dissolved in 144 g deionized water. St (28.80 g), DVB (7.20 g), AIBN (0.72 g) and hexadecane (2.88 g) were mixed into a homogeneous liquid and then was added dropwise into the OBS water solution. After stirring for 15 min, the 'presheared' emulsion was subjected to probe-typed sonication (JY98-IIIDN, 800 W, from Ningbo Xinzhi, China) for another 15 min in an ice bath (an on-pulse period of 10-10 seconds and an output power of 66%). The obtained miniemulsion was then transferred into a three-necked flask equipped with an argon inlet, a gas outlet and an overhead mechanical stirrer. Under argon flow, the reaction was heated to 70 °C for 4 h. After reaction, the formed miniemulsion was cooled to room temperature and freeze-dried for 48 h to get white powder. By acidification with HCl solution (0.1 mol/L) and then by extraction in a Soxhlet extractor for 12 h, excess monomers and sodium chloride were removed. The residue was freeze-dried again to receive the final product.

D. Nanoacid-catalyzed reactions of HDI with *n*-butanol

n-Butanol (21 mmol, 1.56 g), nanoacid and 10 mL toluene were added in a three-neck flask equipped with an argon inlet, a gas outlet and a DiComp probe of ReactIR under argon. Then the flask was heated at 75 °C. HDI (10 mmol, 1.68 g) was added to start the reaction and the process was monitored by *in situ* ReactIR spectroscope. Samples were taken in the end of each reaction for ^{1}H NMR measurements to determine the final conversion.

III. RESULTS AND DISCUSSION

A. Synthesis and characterizations of nanoacid

In this work, organic acid functionalized nanoparticle (nanoacid) was synthesized through miniemulsion polymerization. St and DVB were used as comonomers in order to obtain cross-linking particles so that the formed particles are able to remain heterogeneous in any reaction system with good chemical resistance. OBS (chemical structure see Scheme 1) is chosen to be a reactive surfactant in order to introduce and immobilize the acid groups on the surface of nanoparticles. The hydrophobic fluorinated moieties of OBS prefer to embed in the hydrophobic monomer droplets so that the C=C could copolymerize with the monomers while the moiety of sodium benzenesulfonate prefers staying on the surface of the droplets. Azobisisobutyronitrile was used as the initiator and hexadecane was applied as a costabilizer. After miniemulsion polymerization, the formed mixture was freeze-dried to keep the original shape as nanoparticles. Cross-linking particles bearing sodium benzenesulfonate on the surface were obtained. By acidification with dilute hydrochloric acid solution and then by extraction in a Soxhlet extractor, the excess monomers and sodium chloride were simply removed. The targeted nanoparticles with sulfonic acid can be obtained after another freeze-drying process.

The scanning electron microscope image (SEM, FIG. 1) tells that the particles obtained are narrowly dispersed and the average diameter is around 90 nm. The sulfur content of the obtained nanoacid measured by elemental analysis is found to be 0.5%, from which the sulfonic acid content can be calculated as 0.16 mmol/g. The measured content of sulfonic acid is slightly higher than its corresponding theoretical value (0.14 mmol/g) since the conversion of the monomers did not achieve 100% and the unreacted ones were removed during the purification process.

B. Nanoacid-catalyzed urethane formation

As mentioned above, the obtained nanoacid is supposed to be applied in catalyzing the synthesis of urethane from isocyanate and alcohol. To evaluate the catalytic efficiency, nanoacid was then utilized in a model
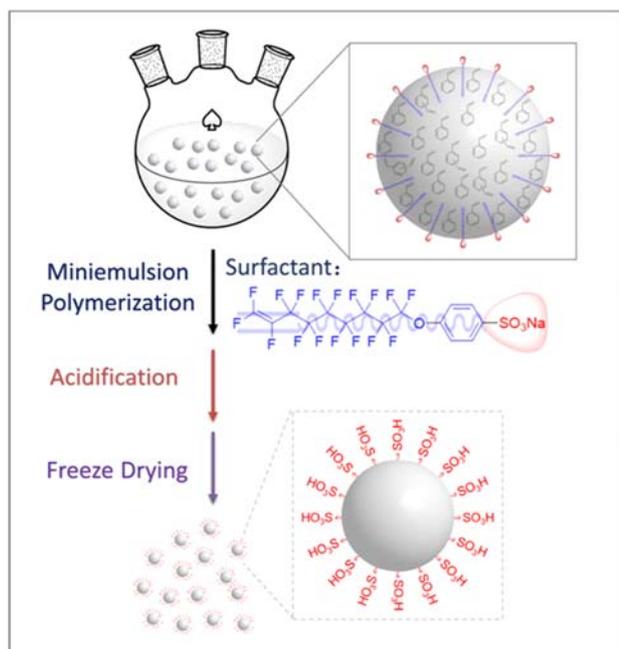
Scheme 1 Synthetic scheme for nanoacid via miniemulsion polymerization.
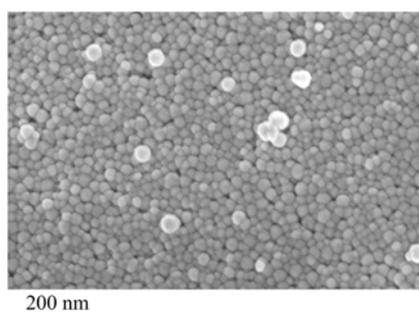

FIG. 1 SEM image of the obtained nanoacid.

FIG. 2 *In situ* ReactIR monitoring the reaction of *n*-butanol and HDI catalyzed by nanoacid at 75 °C. ([BO]/[HDI]=2.1, 0.1 mol% nanoacid was used).

FIG. 3 ^{1}H NMR spectra (DMSO-D$_6$) of the products catalyzed by nanoacid (0.1 mol%, 0.2 mol%, and 0.4 mol%).

reaction of HDI and *n*-butanol at 75 °C under argon. The progress of the reaction was monitored by *in situ* ReactIR spectroscope (see FIG. S1−S4 in the supplementary materials). As shown in FIG. 2, in the model reaction, as soon as the HDI was added, new peaks at 1728 (v(C=O)), 1510 (δ(NH)) and 1234 cm^{-1} (v(COC)) were observed in the IR spectra. It indicates that the reaction between the NCO and the OH groups takes place to form carbamate groups. In particular, v(C=O) (1728 cm^{-1}) which demonstrates the formation of carbamate is chosen to monitor the conversion of the reaction. The relationship between the absorbance and the concentration of carbamate product approximately follows the Beer-Lambert Law, which means they are in a positive correlation. Samples were also taken for ^{1}H NMR measurements to determine the absolute value of final conversion of HDI (see FIG. 3). Based on the data of both *in situ* ReactIR and ^{1}H NMR, the conversion
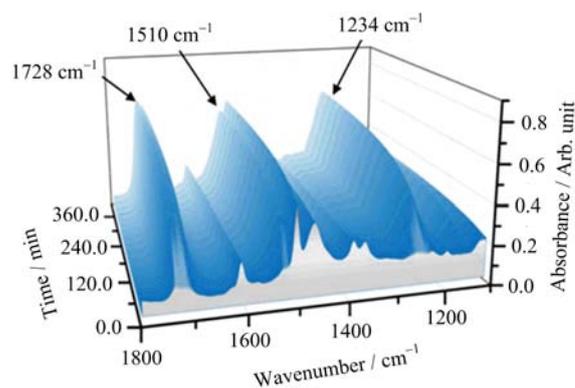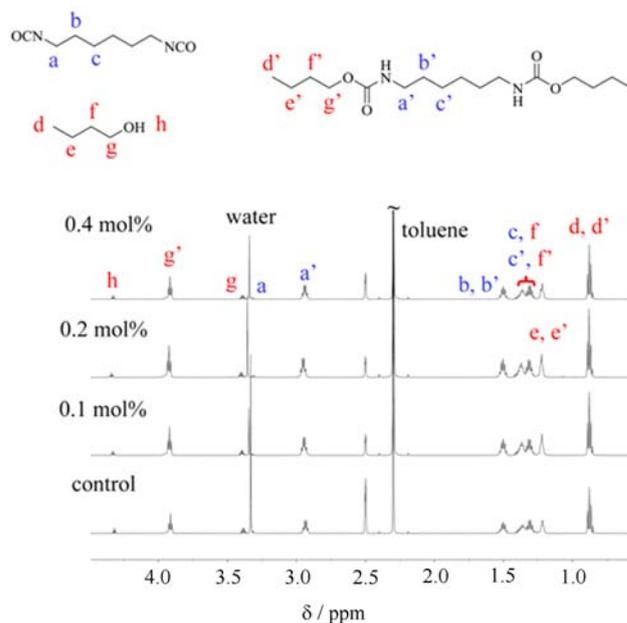
of HDI were calibrated and the final results are shown in FIG. 4. It is found that the reaction catalyzed by nanoacid runs faster than that without any catalyst, especially in the first hour. It took 90 min for the conversion of HDI to reach 50% without any catalyst while the time reduced to 33 min and even shorter when catalyzed by nanoacid. When the amount of nanoacid increases, the reaction rate keeps similar. To achieve a HDI conversion of 95%, it took 276, 273 and 255 min when the catalyst loading was 0.1 mol%, 0.2 mol%, and 0.4 mol%, respectively. 0.1 mol% of nanoacid is sufficient and efficient enough for catalyzing the reaction of HDI with *n*-butanol.
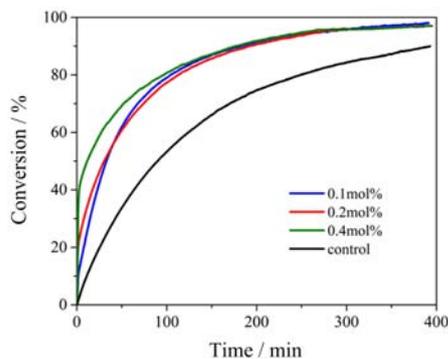
FIG. 4 The conversion curves of HDI catalysed by nanoacid. ([BO]/[HDI]=2.1, at 75 cm^{-1}).

IV. CONCLUSION

A novel organic nanoacid was synthesized via miniemulsion polymerization in which styrene and divinylbenzene were applied as comonomers while a reactive surfactant OBS was utilized to offer and immobilize sulfonic acid groups on the surface of the formed particles. The size of the particles is found to be narrowly dispersed and the average diameter is around 90 nm. The sulfonic acid content of the nanoparticles is calculated to be 0.16 mmol/g. Monitored by *in situ* ReactIR, the nanoacid is proven to be an efficient catalyst in the urethane formation from NCO and OH groups. Further investigation and development of utilizing nanoacid in other organic reactions, *e.g.*, (trans)esterifications, urea formation, Biginelli reactions, *etc.*, is underway in our group.

Supplementary materials: *In situ* ReactIR spectra monitoring the reaction of *n*-butanol and HDI at 75 °C and ^{1}H NMR spectra of the urethane products catalyzed by nanoacid are shown.

V. ACKNOWLEDGMENTS

[1] E. Lotero, Y. J. Liu, D. E. Lopez, K. Suwannakarn, D. A. Bruce, and J. G. Goodwin Jr., Ind. Eng. Chem. Res. **44**, 5353 (2005).
[2] A. A. Kiss, A. C. Dimian, and G. Rothenberg, Adv. Synth. Catal. **348**, 75 (2006).
[3] M. Di Serio, R. Tesser, L. Pengmei, and E. Santacesaria, Energy Fuels. **22**, 207 (2008).
[4] J. A. Melero, J. Iglesias, and G. Morales, Green Chem. **11**, 1285 (2009).
[5] N. Mizuno and M. Misono, Chem. Rev. **98**, 199 (1998).
[6] G. Gelbard, Ind. Eng. Chem. Res. **44**, 8468 (2005).
[7] S. V. Ley, I. R. Baxendale, R. N. Bream, P. S. Jackson, A. G. Leach, D. A. Longbottom, M. Nesi, J. S. Scott, R. I. Storer, and S. J. Taylor, J. Chem. Soc. Perkin Trans. **1**, 3815 (2000).
[8] N. D. Ghatge, J. Appl. Polym. Sci. **8**, 1305 (1964).
[9] M. M. Sharma, React. Funct. Polym. **26**, 3 (1995).
[10] K. Tanabe and W. F. Hölderich, Appl. Catal. A-Gen. **181**, 399 (1999).
[11] M. A. Harmer and Q. Sun, Appl. Catal. A-Gen. **221**, 45 (2001).
[12] J. H. Clark, Acc. Chem. Res. **35**, 791 (2002).
[13] M. Benaglia, A. Puglisi, and F. Cozzi, Chem. Rev. **103**, 3401 (2003).
[14] J. A. Melero, R. van Grieken, and G. Morales, Chem. Rev. **106**, 3790 (2006).
[15] Y. Chang and C. Bae, Curr. Org. Synth. **8**, 208 (2011).
[16] D. E. Lpez, J. G. Goodwin Jr., and D. A. Bruce, J. Catal. **245**, 381 (2007).
[17] H. W. Engels, H. G. Pirkl, R. Albers, R. W. Albach, J. Krause, A. Hoffmann, H. Casselmann, and J. Dormish, Angew. Chem. Int. Ed. **52**, 9422 (2013).
[18] D. J. Coady, H. W. Horn, G. O. Jones, H. Sardon, A. C. Engler, R. M. Waymouth, J. E. Rice, Y. Y. Yang, and J. L. Hedrick, ACS Macro Lett. **2**, 306 (2013).
[19] H. Sardon, A. Pascual, D. Mecerreyes, D. Taton, H. Cramail, and J. L. Hedrick, Macromolecules **48**, 3153 (2015).
[20] W. N. Ottou, H. Sardon, D. Mecerreyes, J. Vignolle, and D. Taton, Prog. Polym. Sci. **56**, 64 (2016).
[21] H. Sardon, L. Irusta, and M. J. Fernndez-Berridi, Prog. Org. Coat. **66**, 291 (2009).
[22] W. J. Blank, Z. A. He, and E. T. Hessell, Prog. Org. Coat. **35**, 19 (1999).
[23] B. Bantu, G. M. Pawar, K. Wurst, U. Decker, A. M. Schmidt, and M. R. Buchmeiser, Eur. J. Inorg. Chem. **2009**, 1970 (2009).
[24] J. Alsarraf, F. Robert, H. Cramail, and Y. Landais, Polym. Chem. **4**, 904 (2013).
[25] M. K. Kiesewetter, E. J. Shin, J. L. Hedrick, and R. M. Waymouth, Macromolecules **43**, 2093 (2010).
[26] H. Sardon, A. C. Engler, J. M. W. Chan, J. M. Garca, D. J. Coady, A. Pascual, D. Mecerreyes, G. O. Jones, J. E. Rice, H. W. Horn, and J. L. Hedrick, J. Am. Chem. Soc. **135**, 16235 (2013).
[27] H. Sardon, J. M. W. Chan, R. J. Ono, D. Mecerreyes, and J. L. Hedrick, Polym. Chem. **5**, 3547 (2014).
[28] P. A. Lovell and M. S. El-Aasser, *Emulsion Polymerization and Emulsion Polymers*, New York: John Wiley and Sons, (1997).
[29] J. M. Asua, Prog. Polym. Sci. **27**, 1283 (2002).
[30] K. Landfester, Angew. Chem. Int. Ed. **48**, 4488 (2009).