Colloids and Surfaces A: Physicochem. Eng. Aspects 393 (2012) 17–26

Contents lists available at SciVerse ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

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

In situ miniemulsion polymerization for waterborne polyurethanes: Kinetics and modeling of interfacial hydrolysis of isocyanate

Qinghua Zhang[a], Ying Shi[b], Xiaoli Zhan[a,*], Fengqiu Chen[a]

[a] *Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou, Zhejiang 310027, People's Republic of China*
[b] *SINOPEC Beijing Research Institute of Chemical Industry, Beijing 100013, People's Republic of China*

ARTICLE INFO

Article history:
Received 19 August 2011
Received in revised form 8 October 2011
Accepted 14 October 2011
Available online 20 October 2011

Keywords:
Interfacial polycondensation
Hydrolysis
Miniemulsion
Modeling
Polyurea microcapsule

ABSTRACT

Isocyanates hydrolysis, an important side reaction in direct synthesis of waterborne polyurethanes by miniemulsion polymerization has been studied experimentally and theoretically in the paper. A kinetic model has been developed considering the resistances due to the diffusion through the formed polymer and interfacial reaction in monomer miniemulsion. This model studied the hydrolysis process quantitatively by reaction degree as a function of time in terms of the reaction rate-controlling step. Both experimental results and reported data from literatures fit the kinetic model well. It has been found that the hydrolysis of aromatic isocyanate with high reactivity is a diffusion controlled fast reaction process, while the hydrolysis of aliphatic isocyanate with moderate reactivity is a reaction-controlled process. The hydrolysis of aliphatic isocyanate at different temperatures has also been studied and it was also found a reaction-controlled process.

1. Introduction

Polyurethane (PU) is one of the most versatile polymer material utilized in a variety of industrial parts, building materials, adhesives and coatings. To meet the ever increased demand for cost reductions and the progressive restrictions of organic solvent emissions, there has been a strong preference for waterborne polyurethanes (PUs) compared with solvent type in recent years [1–4]. Waterborne PUs have become a potential commercial material for the excellent properties, such as solvent resistance, toughness, film formation and abrasion resistance. Such waterborne PUs have been discussed widely in many publications [5–8].

Waterborne PUs are commonly prepared by the incorporation of ionic groups into the polymer structure to be dispersed well in the water phase, i.e. self-emulsification process [1–7]. Due to the relatively high surface free energy of the hydrophilic segments in PU backbone, the water and oil repellency of waterborne PUs is inferior to those hydrophobic ones prepared by solvent-based polymerization [9,10]. One method to tackle this problem is to synthesize PU in the water dispersion directly. Landfester et al. [11,12] and Soldi et al. [13] directly obtained hydrophobic PU dispersion by miniemulsion polymerization. The hydrophobe in miniemulsion suppresses the mass exchange between the different oil droplets by osmotic force (the Ostwald ripening) [14], so that the polymerization is initiated in each small stabilized droplet and the droplet nucleation favors the formation of PU.

During the miniemulsion polymerization of waterborne PUs, two main reactions compete. The first one is the main reaction of polyaddition of isocyanate compound with diol to form urethane. The second one is the side reaction of hydrolysis of isocyanate compound to form urea. This side reaction is responsible for the loss of stoichiometry, and the forming urea groups break the well-defined structures of waterborne PUs. The hard segments formed by hydrogen-bonded urea groups tend to phase separate to affect the product's property [15]. The quantitative FTIR characterization of waterborne PUs prepared by miniemulsion polymerization confirmed the existence of urea group in the polymer [16]. Since the hydrolysis of isocyanate compound is unavoidable in the miniemulsion polymerization of waterborne PUs and no literature has been reported on this side reaction, attention should be paid to the reaction mechanism of hydrolysis to investigate the competition of polyaddition with hydrolysis.

Owing to the different localizations of the reactants (water and monomers), and the high hydrophobicity of monomers and the costabilizer, the hydrolysis reaction should take place near the interface [11–13]. The preparation of polyurethane nanocapsules by interfacial polyaddition of isophorone diisocyanate (IPDI) and hydrophilic diol in miniemulsion also confirmed the interfacial hydrolysis of isocyanate compound by the presence of urea unit in the polymeric wall [17]. In order to understand the hydrolysis mechanism during the miniemulsion polymerization of waterborne PUs, some simple system, i.e. isocyanate monomer

---

* Corresponding author.
E-mail address: xlzhan@zju.edu.cn (X. Zhan).

0927-7757/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.colsurfa.2011.10.016

Nomenclature

A	water
B	isophorone disocyanate
$C_A(r_0, t)$	concentration of monomer **A** at the outer surface of the capsule wall at time t, as shown in Fig. 1 (kmol/m^3)
$C_A(R, t)$	concentration of monomer **A** in the reaction zone at time t, as shown in Fig. 1 (kmol/m^3)
$C_B(R, t)$	concentration of monomer **B** in the capsule core at time t, as shown in Fig. 1 (kmol/m^3)
D_M	constant defined in Eq. (6), $D_P M_U/\rho_P$ (m^5/(kmol s))
D_P	diffusion coefficient of monomer **A** in polymeric phase (m^2/s)
D_V	diffusion coefficient of monomer **A** in micro void (m^2/s)
k	apparent reaction rate constant, $k_r\delta$ (m^4/(kmol s))
k_I	constant defined in Eq. (4), $k_r\delta M_U/\rho_P$ (m^7/(kmol^2 s))
k_r	second order reaction rate constant (m^3/(kmol s))
K_A	partition coefficient of monomer **A** between the capsule wall and the continuous aqueous phase
M_P	average molecular weight of polymer, PM_U (kg/kmol)
M_U	molecular weight of the repeat unit, $M_A + M_B - M_{CO_2}$ (kg/kmol)
P	average degree of polymerization
r	radial coordinate normal to the spherical surface, as shown in Fig. 1 (m)
S	membrane area (m^2)
t	reaction time (s)
υ_P	volume of the capsule wall, zone II in Fig. 1 (m^3)
X	degree of hydrolysis reaction
δ	thickness of reaction zone, as shown in Fig. 1 (m)
φ_P	volume fraction of the polymer in capsule wall
ρ_P	density of the capsule wall formed by the interfacial polymerization (kg/m^3)

miniemulsion is adopted. Under this extreme condition, no diol exists in the droplets and no polyaddition happens, only the hydrolysis of isocyanate compound proceeds at the interface. Then the isocyanate–water reaction in the monomer miniemulsion could be regarded as encapsulation by interfacial polymerization. Therefore, the research on the reaction mechanism of hydrolysis in the monomer miniemulsion could refer to the mathematical model of microcapsule's synthesis by interfacial polymerization in water dispersion.

There have been a few studies on the kinetics of the encapsulation by interfacial polymerization in the emulsion [18–25]. Most of the available literatures are about polyamides, while several other reports discussed the reaction of isocyanate compounds. Pearson and Williams [18] studied the encapsulation involving the interfacial polymerization of an isocyanate with a diol, and developed a theoretical model on a reaction- and diffusion-controlled process. Yadav et al. [19] conducted experiments on the encapsulation in polyurea wall from a diisocyanate in droplets and a hydrophilic diamine, and concluded that the process was kinetically controlled under the conditions employed. Suresh et al. [23] presented a theoretical and experimental study on the interfacial polycondensation with a microencapsulation kinetic model, and indicated that the reaction is under kinetic control. Although some works have been reported in this area, no specific model for the interfacial isocyanate–water polycondensation has been published yet.

In this article, the interfacial hydrolysis of isocyanate compound in monomer miniemulsion is studied. A model is proposed for the process that considers the resistances due to the diffusion through the formed polymer and surface reaction. This model describes the hydrolysis process quantitatively by reaction degree as a function of time. The effects of diffusion and reaction resistances on the process are discussed in terms of reaction-controlling step. The model developed is fitted with experimental data to obtain the kinetic feature of hydrolysis in miniemulsion. The hydrolysis of different isocyanates is simulated by the theoretical model, and some proper conditions to restrain the hydrolysis in miniemulsion are deduced from the kinetic model analysis.

2. Experimental

2.1. Materials

Isophorone diisocyanate (IPDI; BASF), hexadecane (HD; Aldrich), sodium dodecyl sulfate (SDS; Guangzhou Pharmaceuticals Co.), dibutyltin dilaurate (DBTDL; Shanghai Chemical Reagent Co.), and deionized water (conductivity <4 μs/cm) were used as received. The chemicals used for the determination of the isocyanate concentration, including anhydrous di-n-butylamine (Sinopharm Chemical Reagent Co.), anhydrous toluene (Sinopharm Chemical Reagent Co.), isopropanol (Sinopharm Chemical Reagent Co.), standard hydrochloric acid (HCl; Shanghai Chemical Reagent Co.), Bromocresol green (Shanghai SSS Reagent Co.) and potassium chloride (KCl; Sinopharm Chemical Reagent Co.) were used as received.

2.2. Preparation of monomer miniemulsion

As a typical recipe, the surfactant SDS (3.0 g) was dissolved in deionized water (140.0 g) to obtain the surfactant solution. The monomer IPDI (35.0 g) and hydrophobe HD (1.0 g) were stirred together for 5 min at room temperature to obtain a homogenous oil phase. The two phases were mixed by magnetic stirring for 10 min at room temperature, and then the miniemulsion was prepared by ultrasonication the mixture for 120 s at 60% amplitude (Scientz sonifier JY92-II) in an ice bath to prevent the polymerization. The size of the monomer miniemulsion size was 85 nm measured by laser light scattering with a Mastersizer 2000.

2.3. Procedure for kinetic study

The reactions for the kinetic study were conducted in a 250-mL, round-bottom, three-necked flask fitted with a sampling outlet, a mechanical stirrer and a condenser. The monomer miniemulsion was preheated to a certain temperature (20, 30, 45, 50, or 60 °C) in the three-necked flask. DBTDL (0.3 wt% based on the monomer) used as catalyzer was then added to the flask and mixed at the initial time ($t = 0$). At each time interval, a 5-mL aliquot of miniemulsion was withdrawn from the flask and the isocyanate content was determined by modified titration method.

2.4. Modified titration method

The NCO content of the monomer miniemulsion is determined using a slightly modified procedure for the water in the system. The sample miniemulsion in a conical flask was first demulsified by saturated KCl solution, and 1 mol/L di-n-butylamine toluene solution (25 mL) was then added to the flask to react with isocyanate group. The mixture was rapid heated to 50 °C under magnetic stirring for 10 min, and then quenched to room temperature with isopropanol. The excess amine was back-titrated with standard hydrochloric acid (0.5 mol/L) to a Bromocresol green endpoint. The NCO content