Thermochimica Acta 634 (2016) 31–37

Contents lists available at ScienceDirect

Thermochimica Acta

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

# Kinetics of isothermal miniemulsion polymerization of 1,6-hexanediol diacrylate

Quoc-Thai Pham, Ming-Chin Hsu, Chorng-Shyan Chern *

*Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan*

ARTICLE INFO

*Article history:*
Received 10 March 2016
Received in revised form 18 April 2016
Accepted 23 April 2016
Available online 25 April 2016

*Keywords:*
Miniemulsion polymerization
Hexanediol diacrylate
Isothermal kinetics
Microgel particles

ABSTRACT

Kinetics of miniemulsion polymerization of 1,6-hexanediol diacrylate (HDDA) was investigated. The particle size of microgel particles remained relatively constant (ca. 270 nm) during polymerization in the temperature range 65–75 °C. The model-fitting method in combination with the model-free method was used to determine the relevant kinetic parameters. The droplet nucleation involved in the miniemulsion polymerization process was satisfactorily predicted by the nucleation Avrami-Erofeyev model $\{g(\alpha)=[-\ln(1-\alpha)]^{1/2}\}$. The overall activation energy ($E$ = ca. 75 kJ mol$^{-1}$) determined by the model-fitting and model-free methods is quite close to the overall activation energy (ca. 80 kJ mol$^{-1}$) for polymerization initiated by a thermal initiator. By contrast, the conventional model $[g(\alpha)=-1/2\ln(1-\alpha)]$ was incapable of adequately predicting the polymerization kinetic data. The miniemulsion polymerization was characterized by DSC, DLS and TEM.

## 1. Introduction

With two reactive terminal –C═C– groups, 1,6-hexanediol diacrylate (HDDA) undergoes highly crosslinked free radical polymerization initiated by initiators such as water-soluble sodium persulfate (SPS) or oil-soluble 2,2′-azobisisobutyronitrile and benzoyl peroxide in heterogeneous oil-in-water polymerization systems to form reactive microgel particles (MPs, ca. $10^0$–$10^3$ nm in diameter). MPs first observed by Staudinger and Husemann [1] comprising polymeric materials with an intramolecular crosslinked network structure show excellent physicochemical properties and find wide industrial applications such as coatings, fillers, carriers for dyes and substrates for biomedical and diagnostic purposes [2]. The pioneering work of Funke [3] involves preparation and characterization of reactive MPs via free radical polymerizations of multifunctional monomers (e.g., tetrafuntional divinylbenzene (DVB), ethylene glycol dimethacrylate (EGDMA) and multifunctional unsaturated polyester). In addition to free radical polymerization, some other techniques that can be employed to synthesize reactive MPs include anionic polymerization of DVB [2,4] and polymerization of *N*,*N*′-bismaleimide-4,4′-diphenylmethane and barbituric acid via a mixed mode of free radical and Michael addition polymerization mechanisms [5,6]. It is noteworthy that it is the free radical polymerization mechanism that is responsible for the formation of MPs from the reaction of bisphenol A diglycidyl ether diacrylate with barbituric acid [7]. Processes commonly used to prepare MPs include solution polymerization, conventional emulsion polymerization, microemulsion polymerization, non-aqueous dispersion polymerization and precipitation polymerization [2]. For environmentally friendly products prepared by conventional emulsion polymerization or microemulsion polymerization, the requisite transport of monomer species from gigantic monomer droplets to monomer-swollen polymer particles is imposed on the former process, whereas quite high levels of surfactant and cosurfactant are generally required in the latter [8–11].

Miniemulsions are aqueous dispersions of oil droplets (ca. 50–500 nm in diameter), which are prepared by homogenizing a mixture of monomer, water, surfactant and costabilizer. Subsequently, these numerous submicron miniemulsion droplets (acting as micro-bulk reactors) can be transformed to latex products via free radical polymerization [8,11–13]. Miniemulsion is thermodynamically unstable in nature and, therefore, it tends to undergo Ostwald ripening and/or droplet coalescence process upon aging in order to reduce the total oil-water interfacial energy. If miniemulsion is adequately stabilized by surfactant against coalescence, the former would be the predominant mechanism responsible for the substantial degradation of miniemulsion droplets. Ostwald ripening phenomenon is the growth of larger droplets with lower chemical potential at the expense of smaller ones with higher chemical potential via molecular diffusion of monomer molecules

---

* Corresponding author.
*E-mail address:* cschern@mail.ntust.edu.tw (C.-S. Chern).

http://dx.doi.org/10.1016/j.tca.2016.04.016
0040-6031/© 2016 Elsevier B.V. All rights reserved.

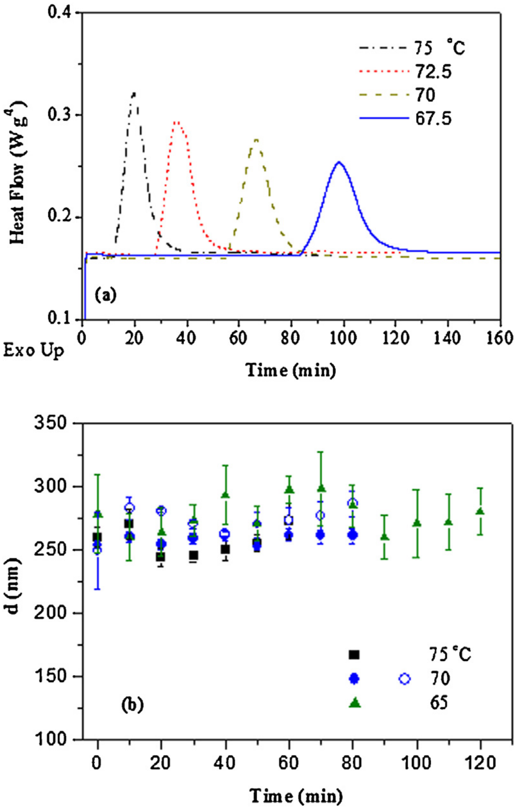

**Fig. 1.** (a) Representative DSC curves and (b) d versus t data for the miniemulsion samples were carried out at different temperatures. The pairs (● ○ ) represent experimental data in duplicate.

from smaller droplets to larger ones [11,14–16]. However, incorporation of a small level of an extremely hydrophobic low molecular weight costabilizer (e.g., *n*-hexadecane (HD)) into the disperse phase results in effective suppression of the Ostwald ripening effect by the osmotic pressure effect [17–19]. Under the circumstances, kinetically stable monomer miniemulsions can be achieved for subsequent free radical polymerization. The objective of this work was therefore to investigate the kinetics of isothermal miniemulsion polymerization of HDDA to gain a fundamental understanding of relevant polymerization kinetics and mechanisms. The key kinetic parameters of miniemulsion polymerization including the reaction rate constant (K), activation energy (E), frequency factor (A) and integral model [g(α)] were determined by differential scanning calorimetry (DSC). Model-free (isoconversional) and model-fitting methods were used to calculate the kinetic parameters.

## 2. Theory

Free radical polymerization mechanism generally involves three steps in sequence, namely, initiation, propagation and termination [20]. The rate of polymerization ($R_p$) for bulk, solution or emulsion polymerization can be expressed as below [11,20]:

$$R_P = -\frac{d[M]}{dt} = k_p[M][R] \qquad (1)$$

where [M] is the concentration of monomer, t the reaction time, [R] the total radical concentration, and $k_p$ the propagation rate constant. For miniemulsion polymerization initiated by a water-soluble initiator such as SPS, the initial condition is a large number of monomer droplets (~$10^2$ nm in diameter) containing monomer and costabilizer. Thus, polymerization primarily occurs within miniemulsion droplets (each miniemulsion droplet just acts as a micro-bulk reactor) immediately after absorption of oligomeric radicals originated from the thermal decomposition of initiator in water (termed the droplet nucleation [11]). In this case, [M] is the concentration of monomer within miniemulsion droplets and [R] is represented by $\bar{n}N_p/N_A$, where $\bar{n}$ is the average number of radicals per particle, $N_p$ the total number of particles per unit volume of water and $N_A$ the Avogadro number [10,11]. The rate of polymerization (dα/dt) can be expressed as follows:

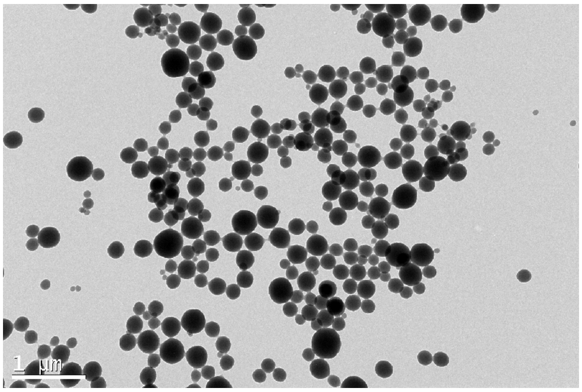

**Fig. 2.** Representative TEM image of dried polymer particles at the end of the miniemulsion polymerization of HDDA.

$$\frac{d\alpha}{dt} = k_p(1-\alpha)\left(\frac{\overline{n}N_p}{N_A}\right) \qquad (2)$$

where α is the fractional conversion of monomer into polymer.

The parameter $\bar{n}$ value is a function of α, which is dependent upon $N_p$, the particle volume, the rate of absorption of radicals by particles, the rate of desorption of radicals out of particles and the termination rate constant ($k_t$) within particles [10,11]. In miniemulsion polymerization involving formation of MPs, $k_t$ decreases with increasing α due to the increased viscosity of the reaction medium inside miniemulsion droplets during polymerization, thereby leading to a significant increase in [R] with the progress of polymerization (termed the gel effect). Therefore, it is postulated that $\bar{n}$ is some function of α [$\bar{n} = f(\alpha)_{\bar{n}}$], and Eq. (2) becomes

$$\frac{d\alpha}{dt} = k_p(1-\alpha)f(\alpha)_{\overline{n}}(N_P/N_A) \qquad (3)$$

The presence of an extremely hydrophobic low molecular weight costabilizer (e.g., HD) in the disperse phase of miniemulsion results in suppression of the Ostwald ripening effect by the osmotic pressure effect. As a consequence, $N_p$ can be regarded as a constant during subsequent polymerization provided that these colloidal particles are well stabilized by surfactant. Thus, the miniemulsion polymerization can be described by the following equation.

$$\frac{d\alpha}{dt} = \frac{N_P}{N_A}k_P(1-\alpha)f(\alpha)_{\overline{n}} = K(1-\alpha)f(\alpha)_{\overline{n}} \qquad (4)$$

where K [$=(N_p/N_A)k_p$] is a compound reaction rate constant. Nucleation models (e.g., Avrami-Erofeyev models (Am) in the solid-state reaction shown in Table 1 [21]) were of choice in Eq. (4) in determining the kinetic parameters since droplet nucleation predominates in the MP formation process. Furthermore, Eq. (4) can be described by the following equation.

$$\frac{d\alpha}{dt} = Kf(\alpha) = A\left[\exp\left(-\frac{E}{RT}\right)\right]f(\alpha) \qquad (5)$$