Ultrasonics Sonochemistry 16 (2009) 273–279

Contents lists available at ScienceDirect

Ultrasonics Sonochemistry

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

Kinetics of the ultrasonic degradation of poly (alkyl methacrylates)

Nagu Daraboina, Giridhar Madras *

Department of Chemical Engineering, Indian Institute of Science, Bangalore 560012, India

ARTICLE INFO

Article history:
Received 29 April 2008
Received in revised form 15 July 2008
Accepted 31 August 2008
Available online 11 September 2008

Keywords:
Ultrasound
Degradation
Poly (alkyl methacrylate)s
Initiator
Continuous distribution kinetics

ABSTRACT

The influence of the alkyl group substituents on the ultrasonic degradation of poly (alkyl methacrylate)s, namely poly (methyl methacrylate) (PMMA), poly (ethyl methacrylate) (PEMA) and poly (butyl methacrylate) (PBMA) was studied. The rate coefficient increased with an increase in the number of carbon atoms in the alkyl group: thus the order of degradation was PBMA > PEMA > PMMA. This was attributed to the scission of the main chain, which increases with the length of the side chain. The ultrasonic degradation of PBMA was investigated in various solvents, at different temperatures and at different ultrasound intensities. The degradation rate coefficients increased logarithmically with the decrease in vapor pressure and increased linearly with an increase in viscosity of the solvent and ultrasound intensity. The effect of three different initiators, benzoyl peroxide (BPO), dicumyl peroxide (DCP) and azo-bisisobutyronitrile (AIBN) on the ultrasonic degradation of PBMA was also studied. The degradation of the polymer decreased in the presence of the initiator. A continuous distribution model was developed for the radical mechanism involved in degradation and was used to determine the degradation rate coefficients of PBMA in presence of initiator. The model indicated that the degradation rate coefficient of the interaction of the PBMA radical with the initiator is independent of the dissociation constant of the initiator.

1. Introduction

Among several methods used for degrading polymers like thermal, mechanical, radiative, chemical, biological, etc., the ultrasonic assisted degradation of polymers is the among the fastest. When an ultrasonic wave passes through the polymer solution, it produces cyclic tensions and compressions causing cavitation. The microbubbles formed during cavitation are the main cause for degradation of the polymer [1–6]. Microbubbles collapse and produce intense shear and shock waves on the polymer molecules near the bubble. Because of this high shear polymer molecules near the collapsing microbubble move faster than the polymer molecules far from the cavitation. Due to this relative motion of polymer chains and mechanical stress generated, the polymer chain breaks almost at the mid-point [3,7]. The molecular weight decreases continuously till it reaches a limiting molecular weight [3].

The effect of various parameters such as vapor pressure [8–13], initial molecular weight [9], temperature [10,14], pH [13], concentration [8,13,15] and viscosity [10,16] on the ultrasonic degradation of polymers has been investigated. The ultrasonic degradation of many polymers such as dextran [5], poly (alkyl acrylates) [10], polyacrylamide [14], poly (methyl methacrylate) [16], polyvinylacetate [17], polyethyleneoxide [14,18], poly (ethylene adipate) [18], poly (dimethylsiloxane) [18], polybutadiene [19], polypropylene [19] and polystyrene [20] has been studied. Initiator plays an important role in both polymerization and degradation of polymers [17,21–25]. The previous studies on the ultrasonic degradation of polymers have been summarized in literature reviews [3,26].

There is a considerable interest on the thermal decomposition of poly (methacrylic esters) and a number of studies have reported the thermal degradation (by pyrolysis) of these polymers [27–30]. The degradation of these polymers in solution would have several advantages like better heat transfer and uniform temperature distribution compared to that of thermal degradation by pyrolysis. Thus thermal degradation of PMMA has been investigated in solution [16,31,32]. The effect of solvent on the ultrasonic degradation of PMMA was studied and correlated to the vapor pressure of the solvent and kinematic viscosity of the solution and polymer-solvent interaction parameters [16]. Recently the effect of alkyl group on thermal degradation of poly (alkyl methacrylate)s in supercritical fluids has been determined [33]. The degradation of poly (alkyl methacrylate)s under SF_5^+ primary ion bombardment using time of flight secondary ion mass spectroscopy has been also investigated [34].

In this study, we have investigated the effect of three radical generators namely benzoyl peroxide (BPO), dicumyl peroxide (DCP) and azo-bisisobutyronitrile (AIBN) on the ultrasonic degradation of PBMA. Because these compounds are used as radical ini-

---

* Corresponding author. Tel.: +91 80 22932321; fax: +91 80 23600683.
E-mail addresses: giridhar@chemeng.iisc.ernet.in, giridharmadras@gmail.com (G. Madras).

1350-4177/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.ultsonch.2008.08.007

tiators in polymerization, these are referred to as initiators in this study.

This is the first study that investigates the effect of alkyl group on the ultrasonic degradation of poly (alkyl methacrylates) and the effect of solvent, temperature, intensity and initiator on the degradation of PBMA. A new continuous distribution model has been developed to determine the degradation rate coefficients. The model indicates the rate coefficient of the interaction of the PBMA radical with the initiator is independent of the initiator dissociation constant.

2. Materials

Methyl methacrylate, poly (ethyl methacrylate) (initial molecular weight, M_{n0} = 112,000; polydispersity, PD = 1.8), poly (isopropyl methacrylate) (M_{n0} = 90,000; PD = 1.6) and poly (butyl methacrylate) (M_{n0} = 98,000; PD = 1.5) were purchased from Sigma–Aldrich. Poly (methyl methacrylate) (M_{n0} = 176,000; PD = 1.7) was synthesized by bulk polymerization technique with benzoyl peroxide as the initiator at 60 °C. The solvents tetrahydrofuran, chlorobenzene, *o*-dichlorobenzene, toluene, benzene and *o*-xylene were purchased from S.D. Fine Chemicals (India). The solvents were distilled and filtered through 0.22 μm nylon filter paper before use. The radical generators (initiators), azo-bisisobutyronitrile (AIBN), benzoylperoxide (BPO) and dicumylperoxide (DCP) were purchased from S.D. Fine Chemicals, Rolex, and N.R. Chemicals, respectively.

2.1. Degradation experiments

About two gram per liter of polymer solutions were prepared and 50 mL solution in various solvents was taken in a 100 mL glass beaker. Horn-type ultrasonic processor (Vibronics, India) with an intensity 36 W cm^{-2} and frequency 25 kHz was used for degradation process. Experiments were conducted by varying the intensity from 16 to 36 W cm^{-2} and temperature from 30 to 60 °C. The temperature of the polymer solution was maintained at the desired temperature (±1 °C) using a thermostated water bath. Further details of the experimental setup can be found elsewhere [13,14].

Samples of 0.5 mL were collected at various time intervals for analysis by gel permeation chromatography (GPC). The limiting molecular weight (MW) was obtained by conducting experiments for 10 h, when the molecular weight reaches a constant value of 40,000. Multiple experiments indicated that the error in rate coefficient is approximately 3%.

2.2. Gel permeation chromatography analysis

The samples were analyzed in gel permeation chromatography. The system consists of a high pressure liquid chromatography (HPLC) pump (Waters 515) for pumping the eluent, THF at a flow rate of 1 mL/min, Rheodyne (7725i) injector, three size exclusion columns packed with crosslinked poly (styrene-divinyl benzene) (Styragel HR-5E, 4, 1) maintained at 50 °C. A differential refractive index detector (Waters RI 2410) was used for detection and stored using a data acquisition system. The chromatograph was converted to molecular weight distribution using a universal calibration based on polystyrene standards (Polymer Lab, UK). The same universal calibration curve was used for all the three polymers. Multiple analyses to determine the molecular weight of the same sample indicated the error was less than 1%.

2.3. Initiator degradation rate

The dissociation rate coefficient of the initiators in presence of ultrasound was determined using the same equipment under the same experimental conditions. The experiments were conducted for several hours and the concentration of the initiators, AIBN, BPO and DCP was determined by high pressure liquid chromatography (HPLC). 20% (v/v) water and 80% (v/v) methanol was used as eluent at 0.5 mL/min. The absorbance was continuously monitored using a UV detector at 340, 235 and 288 nm for AIBN, BPO and DCP, respectively. The system was calibrated with known concentration samples. Based on the time evolution of the concentration, it was found that the dissociation rate was first-order. The dissociation constants ($k_d \times 10^3$) of AIBN, BPO and DCP in ultrasound were determined to be 13, 9 and 3.7 min^{-1}, respectively. These dissociation rate constants are comparable to that ($2\text{–}4 \times 10^{-3}\ \text{min}^{-1}$) obtained at 70 °C thermally. This indicates the enhancement of degradation of the initiators in ultrasound compared to the degradation obtained thermally. Further, no degradation of the polymers occurs at ambient conditions in absence of ultrasound indicating the enhancement observed with ultrasound.

2.4. Theoretical model

The model developed using continuous distribution kinetics was used to determine the rate coefficient for the ultrasonic degradation of polymer. Though the proposed radical mechanism for polymer degradation discussed below is new, it builds upon the existing models that discuss ultrasonic degradation in the absence [13,14] of and in the presence of initiators [10]

$$P(x) \underset{k_t}{\overset{k_i}{\rightleftharpoons}} R^*(x') + R^*(x - x') \tag{1}$$

$$P(x) \underset{k_H}{\overset{k_h}{\rightleftharpoons}} R^*(x) \tag{2}$$

$$R^*(x) \xrightarrow{k_s} P(x') + R^*(x - x') \tag{3}$$

$$D_2 \xrightarrow{k_d} 2D^* \tag{4}$$

$$R^*(x) + D_2 \xrightarrow{k_D} P(x) + D^* + DH \tag{5}$$

The initiation and termination steps are represented by Eq. (1). $P(x)$ represents the polymer molecule with molecular weight x and R^* represents the radical formed after fission. According to the long-chain approximation (LCA) the initiation and the termination rates are assumed to be zero [35]. The LCA is based on the insignificant effect of initiation and termination reactions compared to the predominant influence of the depropagation reactions. This assumption is based on the relatively insignificant magnitude of the thermally induced initiation rate because of the high activation energy and the low probability of bimolecular addition reactions (termination) between radicals at small concentrations. Hydrogen abstraction and the depropagation reaction of the polymer are represented by Eqs. (2) and (3), respectively. The initiator undergoes cleavage and produces free radicals, as given by reaction (4). Reaction (5) represents the formation of stable polymer by the interaction of the polymer radical with the initiator. Because the initiator does not influence the scission of the polymer, Eq. (1), the overall degradation is non-random both in the presence and in the absence of the initiator. Thus, the molecular weight distributions obtained in both cases are similar and do not indicate random chain scission.

An additional reaction where $P(x)$ can react with D^* to yield radicals can be included but this will result in more scission in presence of an initiator. However, the experimental data indicates that the degradation rate actually decreases in the presence of the initiator and thus the initiator acts as a capping agent for the radicals.

$p(x, t)$ and $D(t)$ represent the molar concentrations of polymer, $P(x)$ and initiator, D_2. The population balance equations for the var-