



Ultrasonic degradation of poly(methyl methacrylate-co-alkyl acrylate) copolymers

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ARTICLE INFO

Article history:

Received 1 June 2009

Received in revised form 20 August 2009

Accepted 21 August 2009

Available online 31 August 2009

Keywords:

Ultrasonic degradation

Methyl methacrylate copolymers

Alkyl acrylates

Continuous distribution kinetics

ABSTRACT

The copolymers, poly(methyl methacrylate-co-methyl acrylate) (PMMAMA), poly(methyl methacrylate-co-ethyl acrylate) (PMMAEA) and poly(methyl methacrylate-co-butyl acrylate) (PMMABA), of different compositions were synthesized and characterized. The effect of alkyl acrylate content, alkyl group substituents and solvents on the ultrasonic degradation of these copolymers was studied. A model based on continuous distribution kinetics was used to study the kinetics of degradation. The rate coefficients were obtained by fitting the experimental data with the model. The linear dependence of the rate coefficients on the logarithm of the vapor pressure of the solvent indicated that vapor pressure is the crucial parameter that controls the degradation process. The rate of degradation increases with an increase in the alkyl acrylate content. At any particular copolymer composition, the rate of degradation follows the order: PMMAMA > PMMAEA > PMMABA. It was observed that the degradation rate coefficient varies linearly with the mole percentage of the alkyl acrylate in the copolymer.

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1. Introduction

Ultrasound has been used in several applications such as polymer degradation [1], copolymerization [2], emulsion polymerization [3], organic reactions [4], and for removing high molecular weight tails from fractionated polymers. Polymer degradation by ultrasound has been used as an effective technique for the degradation of polymer compounds because of its *nonrandom* nature of depolymerization unlike thermal and chemical degradation methods [1]. The effect of ultrasound is due to cavitation of microbubbles and collapsing walls of the microbubbles, which produce intense shear on polymer molecules near the bubbles [1]. Since the polymer scission occurs by mechanical shearing, the scission occurs primarily at the mid point of the chain [5].

The effect of different parameters such as ultrasound intensity, temperature, solvent, dissolved gases, polymer concentration, initial molecular weight, viscosity, surface tension and alkyl group substituents on the ultrasonic degradation of different polymers has been reported in literature [6–9]. The kinetic studies for the ultrasonic degradation of polymer solutions by using continuous distribution kinetics [5,8,9] and viscometry [7,10,11] have been reported. Akyüz et al. [12,13] have compared several theoretical and phenomenological models for the evolution of molecular weight with sonication time and observed that the

models that use continuous distribution kinetics describe the results adequately [12,13]. Taghizadeh and Mehrdad have determined the kinetics for the ultrasonic degradation of poly(vinyl alcohol) and poly(vinyl acetate) using viscometry [14,15]. A few studies on the ultrasonic treatment/degradation of polymer blends and melts have also been reported in literature [16–18].

Alkyl methacrylates can form copolymers with alkyl acrylates [19] and these poly(methyl methacrylate-co-alkyl acrylate) copolymers are used in adhesives, coatings and in multigrade lubricating oils [20]. One of the important applications of ultrasound is to investigate the stability of polymer additives. So, it is very useful to study the effect of ultrasound on the stability of these copolymers.

To the best of our knowledge, this is the first detailed kinetic study on the ultrasonic degradation of poly(methyl methacrylate-co-alkyl acrylate) copolymers in solution. In the present study, different compositions of poly(methyl methacrylate-co-methyl acrylate) (PMMAMA), poly(methyl methacrylate-co-ethyl acrylate) (PMMAEA) and poly(methyl methacrylate-co-butyl acrylate) (PMMABA) copolymers were synthesized and ultrasonic degradation of these polymers was studied. The objective of this study was to investigate the effect of composition (percentage of monomer), alkyl group substituents and solvents on the ultrasonic degradation of poly(methyl methacrylate-co-alkyl acrylate) copolymers. Continuous distribution kinetics was used to model the kinetics of degradation process and the degradation rate coefficients were obtained by fitting the experimental data with the model. It is shown for the first time that the degradation rate coefficient varies linearly with the mole percentage of the alkyl acrylate in the copolymer.

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2. Experimental details

2.1. Materials

Methyl methacrylate (MMA), methyl acrylate (MA), ethyl acrylate (EA) and *n*-butyl acrylate (BA) were purchased from Sigma Aldrich (USA) and washed with 5% caustic solution to remove the inhibitor followed by distillation under pressure. The solvents tetrahydrofuran, *o*-dichlorobenzene, chlorobenzene, toluene, *o*-xylene and benzene were purchased from S.D. Fine chemicals (India). The solvents were distilled and filtered using 0.2 μm nylon filter paper before use. The initiator, azo-bis-isobutyronitrile (AIBN) was purchased from S.D. Fine chemicals (India). Polystyrene standards, used for the calibration of molecular weights, were procured from Polymer labs (USA).

2.2. Polymerization

All the homopolymers PMMA, PMA, PEA, PBA and different compositions of PMMAMA, PMMAEA, and PMMABA copolymers were synthesized by solution polymerization technique using AIBN as the initiator at 60 °C. Calculated amounts of monomers (MMA, MA, EA and BA), benzene and AIBN were taken in culture tubes and the mixture was flushed with inert gas N_2 for 15 min. The tubes were then kept in the incubator shaker maintained at 60 °C. The homopolymers and copolymers formed were precipitated in methanol and dried at 50 °C. The initial molecular weight, limiting molecular weight and polydispersity for all the homopolymers and the copolymers are shown in Table S1 (see Supplementary information).

2.3. NMR characterization

^1H NMR (400 MHz, Bruker) spectroscopy was used to determine the composition of the synthesized copolymers, using CDCl_3 as solvent and tetramethylsilane as a reference substance for resonance frequency.

2.4. Degradation experiments

Polymer solutions of concentration 2 g L^{-1} for all the homopolymers and copolymers of different compositions in *o*-dichlorobenzene were prepared to study the effect of alkyl acrylate content. PMMAMA-36 (36 mol percentage of methyl acrylate) polymer solutions of concentration 2 g L^{-1} in different solvents (*o*-dichlorobenzene, chlorobenzene, toluene, *o*-xylene and benzene) were prepared to study the effect of solvent. 70 mL of polymer solution was ultrasonically degraded by using a horn-type ultrasonic processor (Vibronics, India) with an intensity of 36 W cm^{-2} and frequency of 25 kHz at 30 °C. The temperature of the solution was maintained constant ($\pm 1\text{ }^\circ\text{C}$) using a thermostated water bath. The samples were collected at various intervals of time for further analysis by gel permeation chromatography (GPC). The limiting molecular weight was obtained by conducting each experiment for eight hours and it is listed in Table S1 (see Supplementary information).

2.5. Gel permeation chromatography (GPC) analysis

The molecular weight distributions (MWDs) of the samples were determined by using GPC. The GPC consists of a high pressure liquid chromatography (HPLC) pump (Waters 501), three size exclusion columns (Styragel HR 5E, HR 4 and HR1) in series packed with poly(styrene-divinyl benzene), a differential refractometer (Waters RI 2410) to monitor the refractive index and a data acqui-

sition system to store the data. The sonicated samples were injected through a Rheodyne 7725i valve with a sample loop of 50 μL . The eluent tetrahydrofuran (THF) was pumped at a flow rate of 1 mL min^{-1} . The system was calibrated by using narrow molecular weight polystyrene standards. The same universal calibration curve was used for all the polymers and copolymers. Multiple analyses to determine the molecular weight of the same sample indicated the error was less than 2% while the rate coefficients determined in the study have errors less than 4%.

3. Theoretical model

The mid chain scission of polymer chain under ultrasound irradiation yields two daughter products nearly having same chain length. Thus, the overall degradation reaction with a rate coefficient, κ , can be represented by



where $P(x)$ represents polymer chain of molecular weight x , whose molar concentration can be indicated by $p(x,t)$. By applying continuous distribution kinetics to the above equation it becomes [5,21]

$$\frac{\partial p(x,t)}{\partial t} = -\kappa(x)p(x,t) + 2 \int_x^\infty \kappa(x')p(x',t)\delta\left(x - \frac{x'}{2}\right)dx' \quad (2)$$

The degradation coefficient, $\kappa(x)$, is assumed to be of the form $\kappa(x) = k(x-x_l)$, where x_l is the limiting molecular weight [21]. This clearly indicates that no further degradation takes place at limiting molecular weight i.e. when $x = x_l$ which is consistent with the experimental observation. Further, the rate coefficient, k , is independent of molecular weight and thus the rate coefficient for different systems can be compared even if the initial molecular weights of the polymers are different. The moments of the MWDs are defined as

$$p^{(j)}(t) = \int_0^\infty p(x,t)x^j dx \quad (3)$$

Applying the above moment operation to Eq. (2), yields [21]

$$\frac{dp^{(j)}}{dt} = k(2^{1-j} - 1)(p^{(j+1)} - p^{(j)}x_l) \quad (4)$$

The above equation represents the variation of MWD moments of the polymer with time, and is solved by using corresponding initial conditions. The above equation is solved for the zeroth moment ($j = 0$) with the initial condition, $p^{(0)}(t = 0) = p_0^{(1)}$ to get

$$\left(\frac{p^{(1)} - p_0^{(0)}x_l}{p^{(1)} - p_0^{(0)}x_l}\right) = e^{kx_l t} \quad (5)$$

where $p^{(0)}$ and $p^{(1)}$ are zeroth and first moments which represent the molar and mass concentrations of the polymer. The variation of the first moment obtained by putting $j = 1$ in Eq. (4) indicates that the variation with time is zero. Thus, mass is conserved and $p^{(1)} = p_0^{(1)}$ at all times. The number average molecular weight, M_n , is defined as $p^{(1)}/p^{(0)}$. So, the Eq. (5) can be rewritten as [21]

$$\ln\left(\frac{\frac{1}{M_{no}} - \frac{1}{x_l}}{\frac{1}{M_n} - \frac{1}{x_l}}\right) = \ln H = kx_l t \quad (6)$$

where $H = [(1/M_{no}) - (1/x_l)] / [(1/M_n) - (1/x_l)]$. The above equation represents the variation of M_n with time t , in terms of initial molecular weight, M_{no} , and limiting molecular weight, x_l . The values of the degradation rate coefficient at various conditions are obtained by fitting the experimental data with the model.

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