Investigation of Termination During Ultrasonic Depolymerization

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Summary: Ultrasound applications provide additional ways in polymerization and copolymerization synthesis. Ultrasonic depolymerization has wide applications in industry and is also used in copolymer synthesis. Another application of depolymerization is investigating the termination mechanism and finding the combination/disproportionation ratio for various monomer-polymer systems. In this work ultrasonic depolymerization of polyvinyl pyrrolidone and polyacrylamide were investigated. Sonications were monitored continuously by the ACOMP (Automatic continuous monitoring of polymerization) system, which provides viscosity, light scattering, ultraviolet and refractive index measurements continuously. Depolymerizations were performed in the absence and presence of a radical scavenger and disproportionation/combination ratios were discussed for each system.

Keywords: chain scission; combination; disproportionation; termination; ultrasound

Introduction

Low frequency and high intensity ultrasound is called power ultrasound and has wide applications in biology, chemistry and food industry. Dispersion of solids, homogenization of emulsions, filtration, crystallization and degassing are some of its well known industrial applications.[1–3] Polymer degradation with ultrasound is finding new areas of application. Application of ultrasound to a polymer solution decreases the molecular weight by breaking the polymer backbone without causing any changes in the chemical nature of the polymer. In high intensity ultrasound there is cavitations; that is, large negative pressure in the rarefaction phase breaks the surface tension and forms microscopic bubbles. Bubbles grow during rarefaction. The cavitation bubbles implode during the compression phase. Implosions lead to extreme temperature and pressures, shock waves and turbulence. In some cases light emission from implosion sites, known as sonoluminescence occurs.[4] It is probably this turbulence that breaks the backbones of macromolecules.

Depolymerization depends on frequency, intensity, solvent, temperature and nature of gas in the solution and applied pressure.[5] Long chains in the polymer solution are affected, however chains shorter than a certain length are immune to scission, thus heterogeneity decreases. These properties of ultrasonic degradation are similar to degradation by shear flow.[6] Ultrasonic degradation is a controlled process and scission occurs predominantly around the middle point. Sonication can be used to control the chain length and polydispersity, which is very important in terms of polymer properties. It is a physical and nonrandom process which also provides additional ways in polymer synthesis, after polymerization.[7–9]

Two macroradicals are formed as a result of one scission. Resulting macro radicals can be used further in copolymer synthesis or in block copolymer formation.

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Created macroradicals will terminate either with disproportionation or with combination. One must know the dominant mode of termination to be able to use the process in a controlled manner.

Ultrasonic scission and subsequent termination of the macro radicals was used to investigate the termination step and find the disproportionation/combination ratio for various systems. In the case of disproportionation, molecular weight decreases continuously towards the limit molecular weight. However if the macroradicals terminate solely by combination molecular weight of the system does not change substantially. If the termination is partially by disproportination and partially by combination then the molecular weight will decrease but the rate of decrease will be less than the pure disproportionation case. Thus comparison of the rate of molecular weight decrease in the presence of a chain capping agent which prevents normal chain termination and in particular the combination reaction, with the rate when the macro radicals are allowed to terminate naturally gives the fraction of chains terminating by combination.

Ultrasonic termination reactions for poly (methyl methacrylate) (PMMA) and polystyrene (PS) were investigated by this technique.[10–12] The data obtained by sequentially sampling the solution, was fitted to Schmid's molecular weight evolution model.[12–15]

$$\frac{d[C]}{dt} = S \tag{1a}$$

$$\frac{dS}{dt} = k\ \ln(P_{nt}/P_{n0}) \tag{1b}$$

Here [C] is the concentration of all chains, S the number of chain scissions per unit time per unit volume. P_{nt} and P_{n0} are the number average degrees of polymerization at time t and at the beginning of the reaction. As the weight concentration is constant, the number concentration [C] and the degree of polymerization P_n are inversely proportional.

When the termination reactions are included, the concentrations of dead polymers [P], radicals [R] and diradicals [D] must be tracked. The equation (1a) is replaced by,

$$\frac{d[P]}{dt} = -S\frac{[P]}{[C]} + \left(\frac{k_{tc}}{2} + k_{td}\right) \times [R]^2 + 2k_{td}[R][D] \tag{2a}$$

$$\frac{d[R]}{dt} = 2S\frac{[P]}{[C]} - (k_{tc} + k_{td}) \times [R]^2 + 4k_{td}[D]^2 \tag{2b}$$

$$\frac{d[D]}{dt} = S\left(1 - \frac{[P]}{[C]}\right) - 2(k_{tc} + k_{td})[R] \times [D] - 2k_{td}(k_{tc} + 2k_{td})[D]^2 \tag{2c}$$

Where k_{tc} and k_{td} are the termination rate constants for combination and disproportionation respectively. Here it is assumed that the scission probability is independent of whether a chain is a dead polymer, radical or a diradical. Comparing the experimental molecular weight evolution with numerical solution of these equations one obtains the best fit value for the ratio, k_{td}/k_{tc}.

On-line monitoring techniques developed to monitor polymerization and depolymerization reactions have enabled composition, conversion and molecular weight data to be monitored simultaneously and continuously during the reaction. Online and insitu methods allow hundreds, even thousands, of data points to be obtained from each experiment and enable monitoring of the evolution of molecular weight much more closely than is possible with traditional techniques.

In ACOMP (automatic continuous monitoring of polymerization), a steady stream of reactor solution is continuously removed from the system and pumped through a series of detectors namely, light scattering (LS), viscosity, UV spectrometry and refractive index dedectors. Data obtained are analyzed to monitor the evolutions of the molecular weight viscosity and UV absorption.[16–19]

In this work, water soluble polymers were considered and depolymerization reactions of polyvinyl pyrrolidone and polyacrylamide were monitored continuously by ACOMP. Depolymerizations were performed in the absence and presence of a radical scavenger (methanol) and disproportionation/combination ratios are discussed for each system.

The technique has several advantages. Huge amount of data reduce the experimental errors. Only the ratios instead of absolute values of molecular weights are used, eliminating the need for calibration and the calibration errors which otherwise might affect the results. There are no monomers and initiators in the sonication vessel and no reactions involving these species take place. The termination reactions are head-head, head-tail and tail-tail in the ratios valid for depolymerization environments. Of course the last would be a disadvantage if one were trying to obtain the termination mode during polymerization.

Experimental Part

Polyvinylpyrrolidone (K90) (PVP, Acros Organics, M_w 1300000) was obtained from industry and polyacrylamide (PAam) was prepared in our laboratory (M_w 1000000). Depolymerization studies were performed in ultrasound bath (Bandelin Sonorex RK 100h, 35kHz, 80W). Polymer solutions (2×10^{-3} g/g) were prepared and saturated with nitrogen bubbling for 30 minutes before the sonication and nitrogen flushed above the solution throughout the sonication. The ACOMP system has been described elsewhere.[15–18] For these experiments the sample withdrawn from the solution, was pumped directly to the detectors without dilution and returned to the system. Light scattering, viscosity and UV absorption at 235nm were measured. LS is the main molecular weight measurement, viscosity results are used to corroborate the LS data and the increase of the UV signal is used to monitor the formation of vinyl bonds as a result of disproportionation.

Results and Discussion

Chain scission and termination take place simultaneously during the sonications. Depending on the termination mode of the system, chains terminate either with

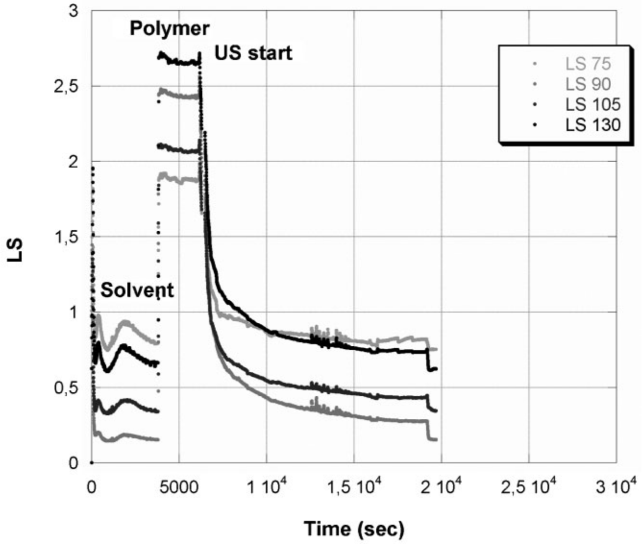


Figure 1.
Raw Light scattering signals for PVP in 10% methanol solution.

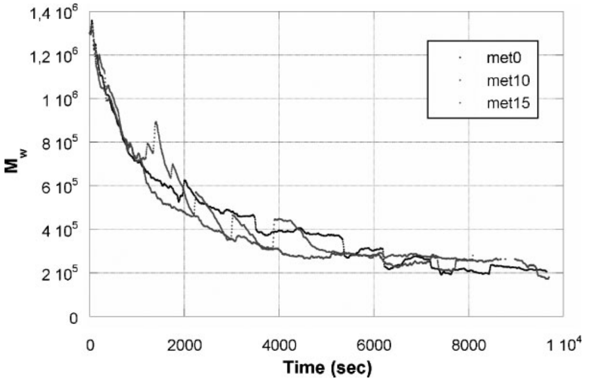


Figure 2.
Evolution of weight average molecular weight of PVP during sonication.

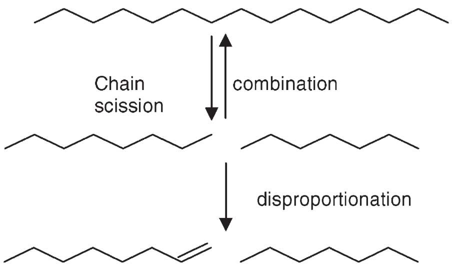
combination or disproportionation as given in the Scheme 1.

In the case of PVP sonication, molecular weight evolution did not show any dependence on the presence or absence of methanol. This implies that termination mechanism is predominantly disproportionation.

In viscosity results there is a considerable difference between the with and without methanol curves. This difference can be a result of differences in solvent quality.

UV absorption slightly increased during the sonication in water, indicating double bond formation. As methanol is added, double bond formation is suppressed and UV absorption is decreased as given in Figure 4. The concentration of chain ends formed during the sonication was much less than the 5% methanol concentration in the system. However in PVP, only 15% methanol could completely suppress the double bond formation. This implies that methanol is not a good chain capping agent for PVP.

The PAam data for experiments conducted in 0, 5 and 10% methanol are shown in Figure 5. It is seen that for approximately the first 1000s the three curves are essentially parallel. Then the curve for the 0% methanol decouples from the other two and the molecular weight decrease is decidedly slower. Both viscosity and LS results show that methanol addition causes the molecular weight and viscosity to decrease faster. This indicates that a fraction of PAam radicals terminate by combinatination.



Scheme 1.
Chains terminate either with disproportionation or with combination.

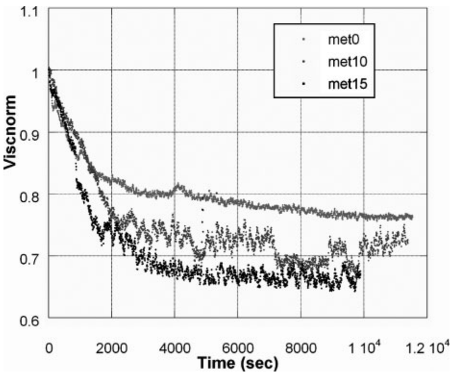


Figure 3.
Evolution of reduced viscosity (normalized to the initial value, Viscnorm) during PVP sonication.

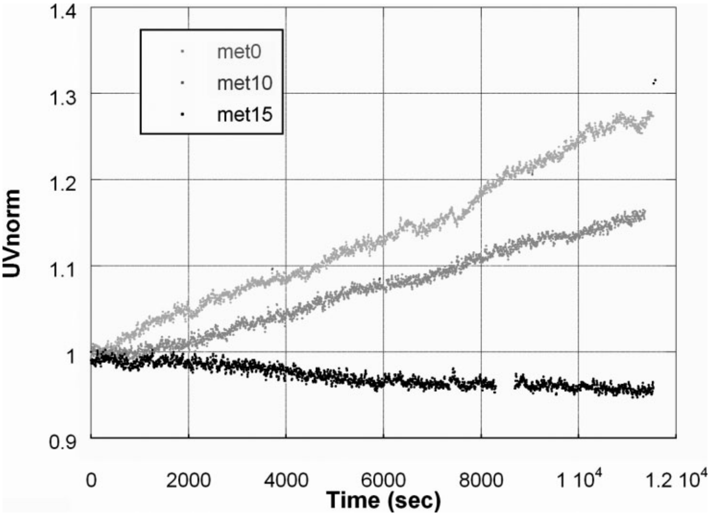


Figure 4.
Normalised UV absorption at 235 nm (UVnorm) during PVP sonication.

However during the first 1000 seconds signals with and without methanol follows exactly the same path indicating that combination reactions do not take place in this period. On the other hand the increase of UV absorption begins at the end of this period which indicates that the disproportionation reaction does not take

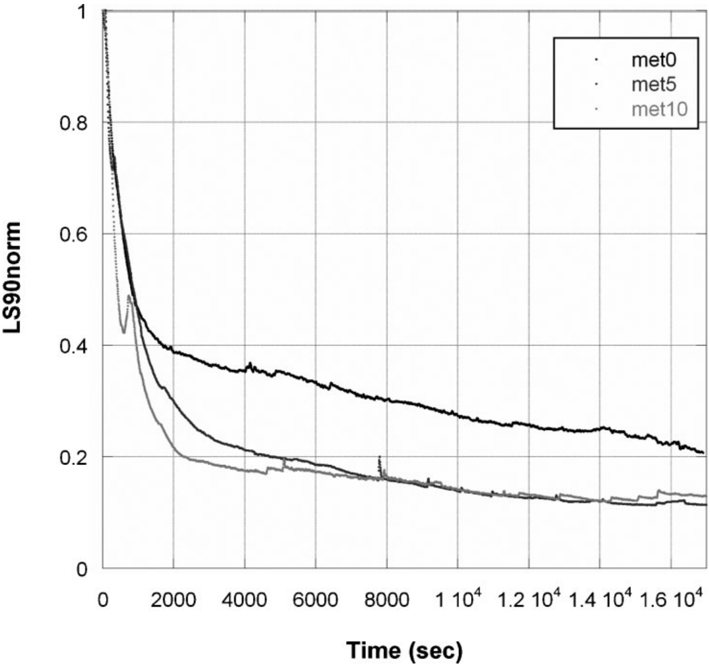


Figure 5.
Normalized light scattering signal at 90 degrees (LS90norm) during PAam sonication in 0, 5, 10% methanol.

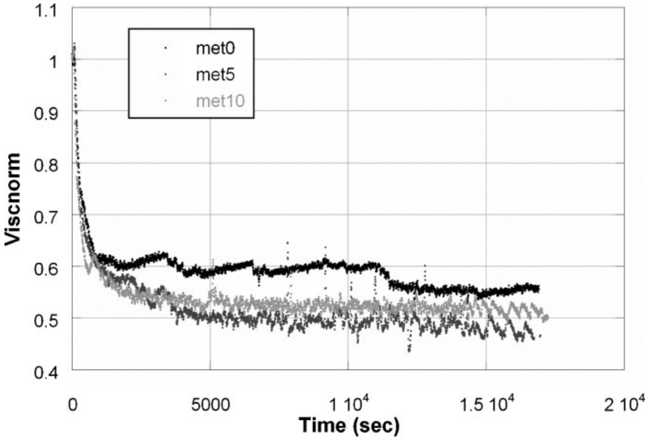


Figure 6.
Evolution of reduced viscosity (normalized to the initial value, Viscnorm) during PAam sonication.

place either. Part of the explanation is the extreme longevity of the macro radicals because of extremely dilute environment and because of their large molar masses. It is also likely that any impurities, such as dissolved oxygen, in the sonication vessel terminate the chains in the early phase of sonication, and after they are purged the termination proceeds by the natural mechanism. The molecular weight evolution with and without methanol are compared only after the two traces diverge from each other after 900–1000 seconds.

Fits to Schmid's model shown in Figure 8 results in 70–78% of PAam macro radicals terminating by combination. Here data with methanol was fitted to numerical solutions of equations 1a and b. The data without methanol were fitted to numerical solutions of equations 1b, 2a, 2b and 2c. Fits

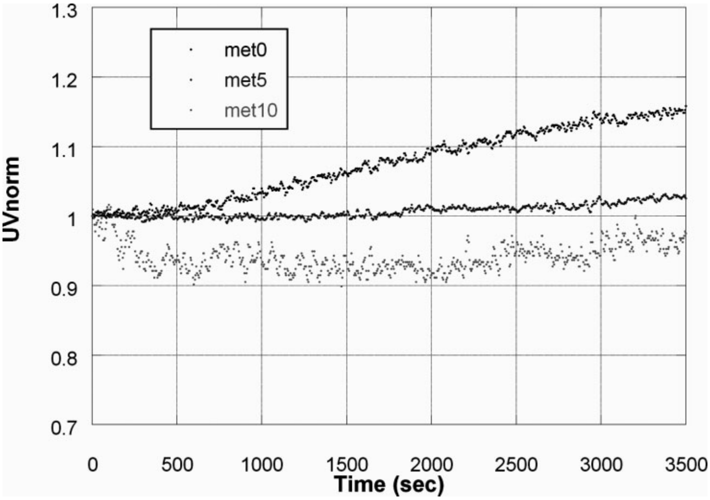


Figure 7.
Normalized UV absorption at 235 nm (UVnorm) during PAam sonication, for the first hour.

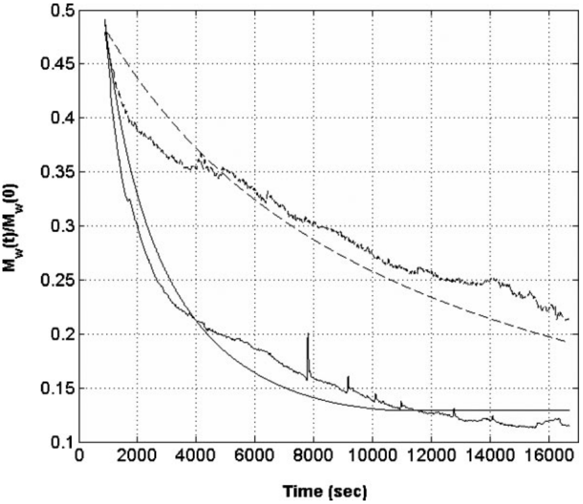


Figure 8.
Schmid fit to PAam sonication with (lower fit and data) and without (upper curve and data) methanol.

were performed by the 'nlinfit' function of MATLAB using the 'ode15s' function for solving the differential equations. As the solver uses adjustable time steps the molecular weights corresponding to the measurement times were obtained by monotonized cubic interpolation.

The estimation range is mainly due to the dependence of the results on the time when the normal termination reaction is assumed to take over. Comparison of the slopes at the 1000s when the two curves diverge, give about 70–75% of the chains terminating by combination. Taking into account model dependence of the results we can conclude that in depolymerization environments the fraction of chains terminating by combination is between 2/3 and 4/5.

In polymerization environments or when propagation is also allowed during chain scission most of the termination reactions are expected to be head-head. Since steric effects are more important in head-head reactions it is expected that if the termination is dominated by disproportionation in depolymerization as in the PVP case, it would also be dominated by disproportionation during polymerization. On the other hand we would expect disproportionation fraction to be larger in the PAam termination during polymerization than the depolymerization value obtained here.

The UV evolution with and without methanol shows that 5% methanol is nearly enough for suppression of disproportionation, which means that methanol is a better chain capping agent for PAam than it is for PVP.

Conclusion

Online monitoring during sonication was developed as a technique to determine the disproportination and combination fractions for termination in depolymerization case. The fractions obtained for depolymerization in aqueous solutions were (1 and 0) for PVP and (0.2–0.33 and 0.67–0.80) for PAam.

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