

level of the  $C^1\pi_u$  electronic state into the dipole-dipole resonance attraction well of a  $^1\pi_g$  repulsive state<sup>24</sup> that dissociates to  $H(n=1) + H(n=3)$ .

A potential well at ca. 3 Å of about 800-cm<sup>-1</sup> depth exists for repulsive states of hydrogen with the appropriate symmetry and which dissociate to  $H(n=1) + H(n=2)$ .<sup>24</sup> This well is due to a resonance dipole-dipole attraction between the atoms at separations for which the shorter range electronic repulsion term is negligible. The resonance aspect, which greatly amplifies the dispersion force attraction (or repulsion), arises from exchange of excitation between the identical atoms. States dissociating to  $H(n=1) + H(n=3)$  should also produce a dipole-dipole resonance well.

This speculative mechanism is further suggested by the fact that a bound electronic state at this energy (ca. 133 000 cm<sup>-1</sup>) should strongly overlap the  $H_2^+$  well and rapidly autoionize to the molecular ion instead of leading to protons. Proton formation is postulated to occur by absorption of a third red photon to the repulsive  $^2\Sigma_u^+$  curve of  $H_2^+$  at an internuclear distance of ca. 3 Å, producing protons in a concerted ionization-dissociation process. This mechanism requires the molecule to attain total energies very near the  $H(n=1) + H(n=2)$  threshold after absorption of the first probe laser photon and very near the  $H(n=1) + H(n=3)$  thresholds

after absorption of the second probe laser photon.

## Conclusions

Proton formation in laser excitation of prepared E,F states is shown to occur by dissociation of electronically excited  $H_2$ , either by process 3, ionization of excited fragments, or by dissociative ionization, process 2, depending on the energy of the dissociation-causing photon. The second ( $H(n=1) + H(n=2)$ ) dissociation threshold is clearly seen by one-photon absorption from the E,F levels when the  $H(n=2)$  atoms are detected by (1 + 1) REMPI via  $H(n=3)$ . The third dissociation limit ( $H(n=1) + H(n=3)$ ) is observed by proton production following absorption of two photons from the F3 level. In both cases the observed thresholds lie surprisingly close to the asymptotic limits. The observation of proton production from the E,F( $v=6$ ) state below these one- and two-photon thresholds is tentatively ascribed to reaching the  $H(n=1) + H^+$  threshold with three photons, i.e., dissociative ionization of the four-photon excited molecule rather than ionization of an excited H atom.

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## Sonolysis of Polymers in Aqueous Solution. New Observations on Pyrolysis and Mechanical Degradation

Arnim Henglein\* and Maritza Gutiérrez

Hahn-Meitner-Institut Berlin GmbH, 1000 Berlin 39, FRG (Received: March 18, 1988)

Aqueous solutions of DNA, pectin, poly(acrylamide), poly(vinyl alcohol), poly(vinylpyrrolidone), poly(methacrylic acid), and poly(ethylene glycol) were sonicated under argon and the yields of CO and  $H_2O_2$  determined. The CO yield is a measure of the pyrolysis of the polymers. DNA is least sensitive toward thermal decomposition, while poly(ethylene glycol) decomposes most rapidly. The  $H_2O_2$  yield is most strongly decreased by polymers producing the most CO. These polymers also decrease the surface tension of water the strongest. It is concluded that pyrolysis and OH radical scavenging require the accumulation of polymer molecules in the interfacial region around the cavitation bubbles. The mechanical degradation of poly(acrylamide) under various gases (He, Ar,  $H_2$ ,  $CH_4$ ,  $C_2H_4$ ,  $CO_2$ ,  $N_2O$ , air) was also studied. The nature of the gas plays a much smaller role than in other sonolytic reactions, such as pyrolysis and oxidation of solutes. It is concluded that, for the various gases, there is no simple correlation between the high temperatures in the cavitation bubbles and the hydrodynamic shear forces near the bubbles. In the presence of small amounts of oxygen in argon, the rate of degradation is increased, which is explained by the suppression of macroradical combination by  $O_2$ .

## Introduction

For about 50 years it has been known that macromolecules experience rupture of bonds in the main chain when ultrasound sufficiently intense to produce cavitation passes through polymer solutions.<sup>1</sup> This degradation is of a mechanical nature, due to strong hydrodynamic shear forces in the neighborhood of cavitation bubbles. When a bond is ruptured in the main chain, macroradicals may be formed that can initiate various chemical reactions.<sup>2</sup>

Aqueous solutions of polymers are of special interest when the damage which may be caused during the medical applications of

ultrasound is discussed. It has been shown recently that poly(vinylpyrrolidone) in aqueous solution is not only degraded in the main chain but also yields gaseous products which are typical for pyrolysis.<sup>3</sup> In the present paper several water-soluble macromolecules are investigated with respect to their sensitivity toward pyrolysis in an ultrasonic field.

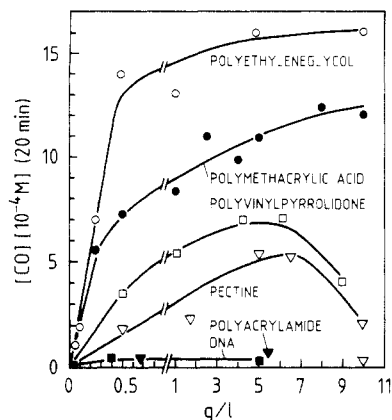
When considering aqueous solutions, one should also remember that ultrasound initiates many redox processes in this solvent, the first step being the formation of H atoms and OH radicals.<sup>4</sup> The yield of these reactions strongly depends on the nature of the dissolved gas, monoatomic and diatomic gases being very much more efficient than polyatomic ones. The dependence of the rate of polymer degradation on the nature of the dissolved gas has

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**Figure 1.** Concentration of carbon monoxide after 20-min irradiation of various polymer solutions.

scarcely been studied.<sup>5</sup> Only polymers in organic solvents were investigated, and no systematic study was made for aqueous solutions. In the present paper the main-chain degradation of a polymer in water is also described and the effect of various gases investigated.

### Experimental Section

The setup for irradiation with ultrasound at an intensity of 2 W/cm<sup>2</sup> has been previously described.<sup>6</sup> A volume of 60 cm<sup>3</sup> of solution was irradiated in a vessel of 135 cm<sup>3</sup> total volume. The solution was bubbled with argon prior to irradiation. In a few experiments, argon-oxygen mixtures were used. During irradiation, the vessel was closed. It carried a septum through which samples could be taken for analysis in a gas chromatograph. The frequency of the ultrasound was 1 MHz.

The polymers were commercial samples with the exception of DNA which was prepared from calf thymus. All samples were purified by precipitation, dissolution in water, and removal of the solvent by freeze-drying. The latter procedure was applied to ensure that the polymer samples did not contain any low molecular weight organic material that could evaporate into the cavitation bubbles and be pyrolyzed there.

Surface tension measurements were made with a digital tensiometer, type K 10 from Krüss, Hamburg. Hydrogen peroxide was determined via reaction with iodide and measurement of iodine formed ( $\epsilon_{350\text{ nm}} = 2.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ).

### Results and Discussion

**Pyrolysis of Polymers.** Ultrasonic irradiation of the polymer solutions in Figure 1 resulted in a reduction of the viscosity which is explained by the decrease in molecular weight. In the case of DNA a small contribution to degradation by free-radical attack may be present.<sup>7</sup> The gas chromatographic investigation showed that carbon monoxide was the main gaseous product. Roughly 10 times smaller amounts of carbon dioxide and methane were also detected. The CO yield is plotted in Figure 1 as a function of polymer concentration. Each carbon atom in a polymer may contribute to CO formation. As the total number of C-atoms present is practically proportional to the weight amount of polymer, the concentration in Figure 1 was expressed in grams per liter. At low concentrations up to 0.5–1 g/L the yield increases linearly with polymer concentration and then starts to level off. In some cases the yield even decreases at higher concentrations. The leveling off and decrease are explained by less efficient cavitation due to the high viscosities of the solutions at high polymer concentrations, although it cannot be excluded that the leveling off reflects a limited accumulation of polymer at the surface of the

**TABLE I: Change in Surface Tension, CO Concentration after a 20-min Irradiation, and Half-Concentration for Suppression of H<sub>2</sub>O<sub>2</sub> Formation**

macromolecule	$\Delta\delta$ , dyn/cm	[CO] after 20 min, 10 <sup>-4</sup> M	$c_{1/2}$ , g/L
DNA	+0.6	0.3	1.0
poly(acrylamide)	+0.40	0.6	3.0
pectin	-1.0	5.2	0.3
poly(vinylpyrrolidone)	-4.3	7.0	0.02
poly(methacrylic acid)	-1.7	11	0.05
poly(vinyl alcohol)	-7.7	12	0.01
poly(ethylene glycol)	-9.7	16	0.003

cavitation bubbles. The fact that the yields at lower concentrations, where the cavitation quality is the same, are quite different for the various polymers indicates that they have different sensitivity toward pyrolysis in an ultrasonic field. Only the DNA solutions still had appreciably higher viscosity at low concentrations. An experiment was also carried out with a DNA sample that had already been degraded by 20-min irradiation, i.e., had lower viscosity. This sample did not yield more CO than the sample that had not been pretreated. It is recognized from Figure 1 that DNA was most stable and poly(ethylene glycol) was most strongly affected. The mechanical degradation (decrease in viscosity), however, was also present in the DNA solution as already mentioned.

The polymers have no substantial vapor pressure; they cannot evaporate into the gas bubbles. However, around the bubbles exists an interfacial region where high temperatures prevail. In order to be decomposed thermally a polymer has to be present in this region. Furthermore, the polymer molecule or at least a segment of it has to be dehydrated before the thermal decomposition can occur. Both effects are expected to be more pronounced for the more hydrophobic polymers. On the other hand, the extent to which a polymer changes the surface tension of water may be taken as an indication of how readily the polymer accumulates at the water-gas interface. Table I shows a comparison of the rate of pyrolysis as measured by CO production and the change  $\Delta\delta$  in surface tension. It was observed that the surface tension decreased with polymer concentration (with the exception of DNA and poly(acrylamide) where a slight increase was observed) and reached an almost constant value above about 2 g/L. The  $\Delta\delta$  values in Table I were determined at a polymer concentration of 5 g/L. With respect to  $\Delta\delta$  the polymers are grouped into ionic and nonionic ones. In both groups a correlation exists between the decrease in surface tension and the rate of pyrolysis. As expected, the pyrolysis is more efficient for the polymers that strongly influence the surface tension.

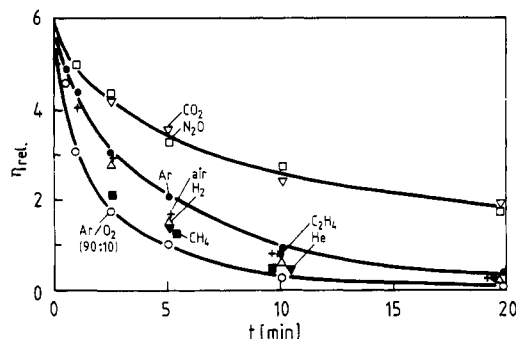
Hydrogen peroxide is formed in the irradiation of water under argon. It was shown previously that organic solutes decrease the H<sub>2</sub>O<sub>2</sub> yield, which was explained by the scavenging of intermediate OH radicals.<sup>8</sup> Furthermore, it was concluded from the concentration dependence of the yield that the OH radicals, which are generated in the gas phase, form H<sub>2</sub>O<sub>2</sub> in a somewhat cooler interfacial region, where they arrive at a high local concentration. In order to scavenge effectively, a solute has to be present in high concentration in this region. Hydrophobic solutes generally are more efficient than hydrophilic ones. Polymers also decrease the H<sub>2</sub>O<sub>2</sub> yield. The half-concentration,  $c_{1/2}$ , at which the yield is decreased by a factor of 2, is also listed in Table I. As expected, polymers having a small value of  $c_{1/2}$  strongly decrease the surface tension and produce the most CO. The correlation between CO yield,  $\Delta\delta$ , and  $c_{1/2}$  underlines the importance of a factor that determines the kinetics of sonolysis reactions: the availability of a solute in the interfacial region (where it is attacked by free radicals or is thermally decomposed) is at least as important as its specific reactivity toward radicals or its thermal stability. We may finally add that the importance of reactions in the interfacial region has also been recognized by Suslick and co-workers in their

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**Figure 2.** Sonication of a poly(acrylamide) solution under argon. Relative viscosity as a function of time. Polymer concentration: 2.5 g/L.

studies on the sonolysis of organic liquids.<sup>9</sup>

**Mechanical Degradation: Effect of Dissolved Gas.** Figure 2 shows the relative viscosity,  $(\eta - \eta_0)/\eta_0$ , of a poly(acrylamide) solution as a function of irradiation time. The irradiation occurred under various gases. It is seen that the nature of the gas plays an important role. However, the influence of the gas is considerably less than for other reactions, such as the oxidation or thermal decomposition of solutes or dissolved gases. For example, hydrogen peroxide is formed and iodide oxidized at a 20 times lower rate when water is sonicated under helium as compared to argon.<sup>10</sup> The degradation of poly(acrylamide), however, proceeds at a higher rate under helium. No oxidations occur when aqueous solutions are irradiated under carbon dioxide, and nitrous oxide is decomposed more than 100 times more slowly than in presence of Ar.<sup>11</sup> The polymer can, however, be degraded under CO<sub>2</sub> and N<sub>2</sub>O, the rate being only 2.5 times smaller than under argon. Furthermore, the polymer is rapidly degraded under methane and ethylene, although thermal decomposition reactions in these gases have very low rates.<sup>12</sup>

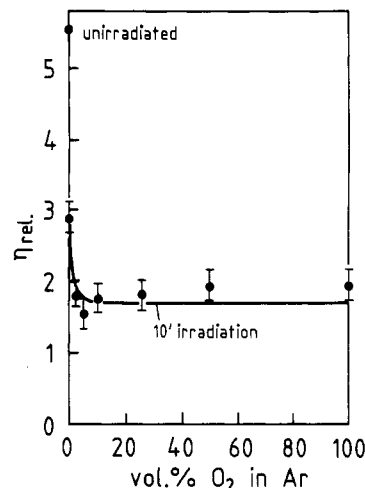
These results show that the degradation of a polymer is a process substantially different from oxidation and pyrolysis of solutes. The degradation is of a mechanical nature, bonds in the main chain of a polymer being ruptured under the influence of strong hydrodynamic shear forces in the neighborhood of a vibrating gas bubble. The oxidations and thermal decompositions result from the high temperatures in the adiabatic compression phase of the vibrating bubbles. High temperatures are reached in the case of monoatomic and diatomic gases, which possess a high value of the ratio  $\gamma$  ( $\gamma$  = ratio of specific heats) and a low thermal conductivity, while polyatomic gases are less effective. It seems that the velocity gradients and shear forces in the neighborhood of a vibrating bubble depend little, if at all, on the nature of the gas. Or, in other words, shear forces around the bubble and temperatures in the bubble do not parallel each other.

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**Figure 3.** Degradation of poly(acrylamide) under argon-oxygen mixtures. Relative viscosity after a 10-min irradiation as a function of the oxygen concentration in the gas mixture.

One recognizes from the results in Figure 2 that the rate of degradation tends to be greater with decreasing solubility of the gas. For example, CO<sub>2</sub> and N<sub>2</sub>O are much more soluble than He, H<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub>H<sub>4</sub>. A similar observation was reported by Brett and Jellinek,<sup>5</sup> who studied the degradation of polystyrene in benzene. They explained the effect by assuming that the more soluble gases from nuclei in the solution having a reduced efficiency to initiate cavitation upon sonication. A curious result in Figure 2 may also be mentioned: the rate of degradation under argon is strongly increased when the gas contains 10 vol % oxygen. This effect was further investigated by irradiating solutions under various argon-oxygen mixtures. Figure 3 shows the results. The relative viscosity after a 10-min irradiation is plotted here vs the percentage of oxygen in the gas mixture. It is seen that the polymer is degraded faster under oxygen than under argon. One percent oxygen in argon is already sufficient to secure the higher rate of degradation. This effect is explained by reactions of the macroradicals which are formed upon the rupture of bonds in the main chain. Part of the radicals disproportionate and others combine.<sup>2</sup> In the irradiation under pure argon, part of the ruptures in the main chain is "healed" by macroradical combinations. In the presence of oxygen the radicals are scavenged, the resulting peroxy radicals undergoing reactions which do not lead to a restoration of the main chain.

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**Registry No.** CO, 630-08-0; H<sub>2</sub>O<sub>2</sub>, 7722-84-1; CO<sub>2</sub>, 124-38-9; N<sub>2</sub>O, 10024-97-2; H<sub>2</sub>, 1333-74-0; Ar, 7440-37-1; CH<sub>4</sub>, 74-82-8; C<sub>2</sub>H<sub>4</sub>, 74-85-1; He, 7440-59-7; O<sub>2</sub>, 7782-44-7; poly(acrylamide), 9003-05-8; poly(vinylpyrrolidone), 9003-39-8; poly(methacrylic acid), 25087-26-7; poly(vinyl alcohol), 9002-89-5; poly(ethylene glycol), 25322-68-3.