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Some Aspects of the Properties and Degradation of Polyacrylamides

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I. Introduction

The polyacrylamide family of polymers and copolymers is a highly versatile group used in a multitude of applications including clarification of drinking water[1−4] flocculants for wastewater treatment,[5,6] oil recovery,[7] soil conditioning,[8−11] agriculture,[12,13] and biomedical applications.[14−17]

However, the neurotoxicity of the acrylamide monomer has led to some concerns and even reluctance to accept polyacrylamides as safe materials particularly in situations where the polymer is in direct contact with bodily fluids (e.g., renal dialysis, blood filtration, etc.) or where the polymer is used in making therapeutic products. There are lingering concerns regarding the possibility that residual acrylamide is present in the polymeric materials and whether polyacrylamides can degrade back to the monomer.

The nomenclature of naming polymers has also added some confusion to the debate; the convention used for naming polymers is to construct the name using “poly” (meaning many) followed by the monomer from which the polymer is derived. Thus, polyacrylamide is many units of the monomer acrylamide. This can be somewhat misleading when considering properties without taking into account the chemical nature of the polymer since, for example, the monomer has a C═C double bond, which is not present in the polymer. Chemically the polymer and the monomer are quite different. This fact seems to be lost on some scientists who are not familiar with polymers.

We therefore felt it timely to review the 40 or so years of experimental work regarding the properties of acrylamide and polyacrylamides (homo-, co-, and cross-linked), and to examine, from a polymer chemist’s point of view, their likely or known degradation pathways and products.

II. Acrylamide

Before discussing the properties of polyacrylamides, it is useful to first examine the monomer acrylamide.

A. Acrylamide: Production, Chemical and Physical Properties

Acrylamide is a white odorless crystalline solid with a melting point of 84.5 °C.[18] It is soluble in many

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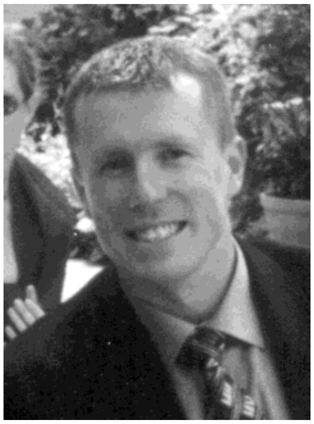
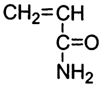


Marcus Caulfield was born in Melbourne, Australia, in 1970. He received a B.Sc. degree in organic chemistry from the University of Melbourne (1993) and his Ph.D. (1998) in polymer science from the same university. He is currently undertaking postdoctoral research in the Polymer Science Group, Department of Chemical Engineering, University of Melbourne, with Professor David Solomon. His research has focused on the development and application of synthetic hydrogel materials with particular emphasis on the design, synthesis, and application of novel architectures.

Greg Qiao was born in Shanghai, China, and received his B.Eng. in polymer engineering at East China University in 1982. He completed his Ph.D. at the University of Queensland with Professor Curt Wentrup in 1996 studying novel nitrogen containing cumullenes. He then served as a postdoctoral fellow in the Polymer Science Group under Professor David Solomon at the University of Melbourne, where he worked on the synthesis and characterization of novel polymeric materials. He is currently a lecturer in the Department of Chemical Engineering, The University of Melbourne. His main research interests include the synthesis of novel nanoparticles through controlled free radical polymerization techniques and the development and application of other unique polymeric architectures useful in biological separations.

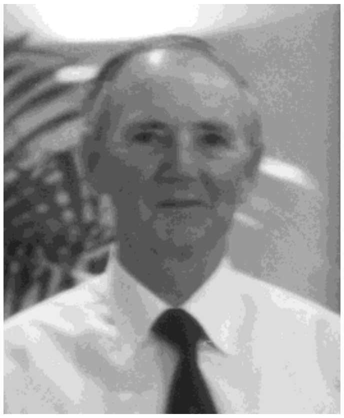


$$CH_2{=}CH{-}C({=}O){-}NH_2$$

Figure 1. Structure of acrylamide.

polar solvents, including acetone, acetonitrile, and water, where 215.5 g can be dissolved in 100 mL of water at 30 °C. Acrylamide contains two principle functional groups, the vinylic carbon−carbon double bond and an amide group (Figure 1).

The German scientist Moureu first synthesized acrylamide in 1893; however, it was not widely commercially available until the 1950s, when Hercules started making commercial quantities.[19] Acrylamide is generally formed from the hydration of acrylonitrile with either sulfuric acid at between 90 and 100 °C or more recently by catalytic hydration using copper catalyst.[20] The total world production capacity for acrylamide is more than 300 000 metric tons per year.[6, 21]

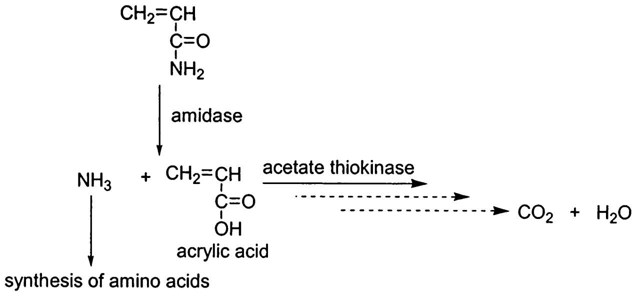


David Solomon was born in Adelaide, Australia, in 1929. He received his B.Sc. degree in 1952 and his M.Sc. in 1955 from NSW University of Technology. He received his Ph.D. (1959) and his D.Sc. (1968) degree from the University of NSW. He began working with Balm Paints (Dulux) in 1946 and gained experience in all aspects of the paint industry. In 1963, he moved to the Division of Applied Mineralogy of Commonwealth Science Industry Research Organization (CSIRO) and in 1968 was seconded to Georgia Kaolin Company in Elizabeth New Jersey to further develop his work on the interaction between mineral fillers and organic polymers. In 1970, he became Chief Research Scientist in the Division of Applied Chemistry of CSIRO and established the Polymer Research Group of the Division. At his time at CSIRO, he initiated the research into Plastic Banknotes and during 1980–81 was seconded by the Reserve Bank of Australia to assist in the transfer of the technology related to Australian Plastic Banknotes. He was appointed foundation Chief of the Division of Chemicals and Polymers in 1974 and in 1990 he became Deputy Director of the CSIRO Institute of Industrial Technologies. He was elected a Fellow of the Australian Academy of Science in 1975 and became a Foundation Fellow of the Academy of Technological Science and Engineering in the same year. From 1991 to 1995, he moved to the University of Melbourne where he served as the ICI Australia Masson Professor of Chemistry and Head of School. From 1995 to the present, he has been a Professorial Fellow in the Department of Chemical Engineering at the University of Melbourne. Professor Solomon is the author of a number of books on polymer chemistry and has published over 250 publications in polymer synthesis, degradation, and characterization. His most recent book *The Chemistry of Free Radical Polymerization* is a defining publication and represents a major advance in the understanding of this area of polymers. Professor Solomon has been involved in the synthesis and properties of hydrogels based on acrylamide for over 20 years and has collaborated with Dr. Caulfield and Dr. Qiao in the design of novel hydrogel matrixes. Together they have published over 20 publications including six patents in the field.

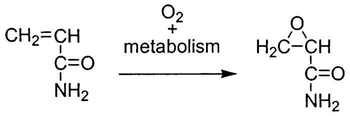
The electron deficient double bond of acrylamide is susceptible to a wide range of chemical reactions including nucleophilic additions, Diels−Alder, and radical reactions.[2] Thus, ammonia, aliphatic amines, phosphines, chlorine, bromine, bisulfite, and dithiocarbamates readily react with the vinylic double bond as do proteins, hence the reasons for concern in biological systems. Reactions of the amide residue include hydrolysis, dehydration, alcoholysis, and condensation with aldehydes.[22]

Acrylamide's extreme water solubility contributes to it being readily absorbed by a variety of microorganisms such as bacteria from widely diverse habitats, including soil, aquatic, and sewage.[22] Once absorbed, enzymes are involved in its transformation to water, carbon dioxide, ammonia, and other constituent products.[23−26] Shanker et al.[27] have shown

Scheme 1. Proposed Pathway for Biodegradation of Acrylamide by Bacteria



Scheme 2. Formation of the Epoxide Derivative of Acrylamide (Glycidamide)



that acrylamide can act as the sole carbon and nitrogen sources for microbial growth. Shanker's proposed pathway for the metabolism of acrylamide in bacterium is outlined in Scheme 1.

Higher animals are also capable of absorbing compounds such as acrylamide and metabolising them via suitable enzymes.[28]

B. Acrylamide: Acute and Chronic Toxicity

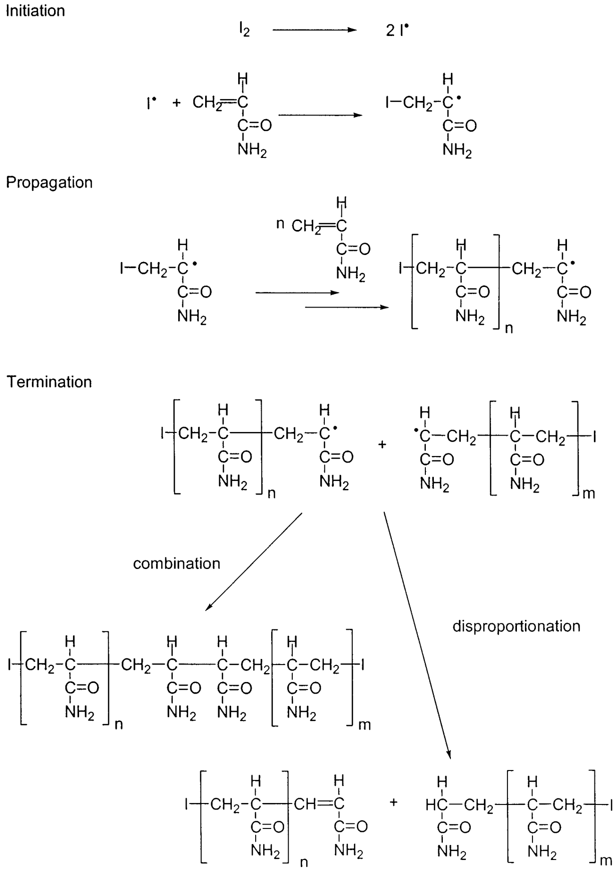
Acrylamide is an acute eye, skin, and respiratory tract irritant and is absorbed by all routes of exposure, including intravenous, intraperitoneal, subcutaneous, intramuscular, oral, and dermal. The toxicity of acrylamide has been exhaustively examined and well documented in several articles and reviews.[20,21,29−35]

In higher animals, once absorbed, acrylamide causes damage to the central nervous system, producing an ascending central/peripheral axonopathy. The severity and length of the axonopathy is depended on the level of intoxication, and is generally characterized by disruption of sensory, motor, and autonomic function of the peripheral and ascending tracts of the spinal chord. Acrylamide has been classified by the U. S. Environmental Protection Agency (EPA) as a Group B2 probable carcinogen.[36]

Acrylamide is metabolized by organisms to a variety of different compounds and excreted. Recent work by Dearfield et al.[28] has shown that some metabolites of acrylamide are responsible for the observed mutagenic properties of acrylamide. For example, oxidation of the double bond of acrylamide forms the relatively stable epoxide derivative, glycidamide (Scheme 2). Glycidamide is mutagenic to Salmonella and would be expected to be generally mutagenic in other assay systems.[28] Therefore, when assessing the toxicity of acrylamide it is important to also examine the toxicity of acrylamide metabolites and degradation products.

The literature contains numerous reports on the toxicological effects of acrylamide during animal trials; however, establishing safe exposure limits to acrylamide has been hampered by the scarcity of data from human studies. The common convention when describing the concentration of acrylamide used in these studies is parts-per-million (ppm). It has been determined for animals that the no observable effect level (NOEL), 0.2 to 2 ppm, and the lowest-observable-effect level (LOEL) is between 1 and 3 ppm acrylamide. Certain assumptions are necessary to translate the data from animal studies into what is acceptable for humans. It is generally acknowledged that an acceptable level for humans is about 1000 times less than for animals; therefore, the USA's environmental protection agency (EPA) has recommended that the safe acrylamide exposure or reference dose for acrylamide (RfD) to be 0.0002 ppm, which is often conveniently quoted as 0.3 ppb (parts-per-billion).[21]

Scheme 3. Free Radical Polymerization of Acrylamide



III. Polyacrylamides

Polyacrylamides are generally prepared via the free radical polymerization of acrylamide using a large variety of initiation methods in aqueous solution or dispersions.

A. Free Radical Polymerization of Acrylamide

The free radically induced polymerization of acrylamide follows the classical vinyl polymerization mechanism involving initiation, propagation, and termination processes.[2,6,37,38] The basic mechanism involved in the free radical polymerization of acrylamide is outlined in Scheme 3.

Polymerization can be initiated by a number of systems including peroxides, persulfates,[39] redox couples,[40−42] azo compounds, and photochemical.[43−45]

Termination leads to the cessation of growth of one or more of the polymer chains leading to the formation of a dead polymer chain. This can occur via self-reaction of the propagating radicals by combination or disproportionation. Combination introduces a head-to-head linkage in the polymer backbone, while disproportionation affords two dead polymers, one with an unsaturated end group and the other one with a saturated end group. Chain transfer can also occur between the growing propagating radical with a nonradical substrate, producing a dead polymer and a new radical species capable of adding more monomer. In addition, termination can occur when a propagating radical reacts with a primary radical.[46]

The free radical polymerization of acrylamide is very sensitive to residual oxygen, which efficiently scavenges primary carbon radicals down to 1 ppm forming peroxide radicals.[6] It has been postulated[47] that these peroxide radicals can also participate in monomer addition forming backbone O−O bonds. The consequences of the inclusion of peroxide groups in the polymer backbone will be discussed further in a later section.

Concomitant with the formation of high molecular weight polyacrylamides in solution, there is also the development of extremely high viscosities, even at low polymer concentrations. This high viscosity leads to problems associated with the large-scale industrial production of polyacrylamides in solution, particularly in relation to inhomogeneous mixing and heat transfer. To overcome these limitations, linear polyacrylamides are often produced through a heterophase water-in-oil polymerization.

B. Synthesis of Polyacrylamides through Water-in-Oil Polymerization

Water-in-oil polymerization or inverse emulsion polymerization comprises emulsifying the aqueous monomer solution in a continuous hydrophobic organic phase (oil) containing a water-in-oil emulsifier, homogenizing the mixture to form a water-in-oil emulsion, degassing, and then polymerizing the monomer in the emulsion. The initiating species can reside in either the dispersed aqueous phase, suspension polymerization, or in the continuous organic phase, emulsion polymerization. Because polymerization occurs in the particles there is efficient heat removal, and in emulsion polymerization chain termination processes are altered.[48,72]

The resultant polymer is dispersed in the continuous oil phase as nonsettling latex particles and can have molecular weights upward of 20 million. The viscosity of the solution is that of the continuous oil phase, greatly simplifying the transport and handling of the products.[6] However, before use the latex polymer needs to be dissolved in a continuous aqueous phase, and this process is called polymer inversion.[49,50] Polymer inversion involves transforming the water-in-oil emulsion into an oil-in-water emulsion, where the polymer is dissolved in the continuous aqueous phase. This is accomplished by adding a small amount of an inverting surfactant with a high hydrophilic lypophilic balance (HLB) and massive amounts of water. Care must be taken during this process to ensure that complete dissolution of all the latex particles is achieved and to avoid the formation of "fish eyes". Fish eye formation results from the inefficient dissolution of latex particles whereby polymer aggregation occurs. These particles age over time, and dissolution can occur over extended periods of time.[51]

Table 1. Calculated Concentration of Acrylamide (ppm) at a Range of Conversions for 100 mL of a 20% (w/v) Aqueous Acrylamide Solution

conversion	concentration acrylamide (ppm)
50	100000
90	20000
95	10000
99	2000
99.5	1000
99.95	100
99.995	10
99.9995	1

C. Copolymerization of Acrylamide

The physical properties of polyacrylamides are manipulated by copolymerizing with a variety of different vinylic monomers. One of the most useful examples is produced by copolymerizing acrylamide with sodium acrylate to form an ionic polymer at normal pHs. A polymer gel is formed when acrylamide is copolymerized with *N,N′*-methylenebisacrylamide (BIS), forming a cross-linked infinite three-dimensional network which is a useful media for biological separations.

D. Residual Monomers in Polyacrylamides

The two primary areas of concern associated with the use of polyacrylamides are the presence of residual monomer (particularly acrylamide) in the polymer product and the possible formation of acrylamide or other toxins from polyacrylamide by some degradation mechanism.[21,52,53]

The very nature of the chain growth reaction to form the polymeric species dictates certain limitations on the realistically possible conversion.

It is convenient to consider the issue of conversion in terms of the concentration acrylamide monomer remaining in the system as parts-per-million (ppm), Table 1.

Reported experimental conversions vary considerably depending on the reaction conditions employed, although they generally range from 90%,[54] 95%,[44,43] to greater than 99.5%.[25,40]

Mandatory government regulations play an important role in ensuring polyacrylamide-based products meet strict requirements on the allowable monomer content.[8,21,50,53,55] For example, polyacrylamides used in drinking water clarification must contain no more than 0.05% residual acrylamide (which equates to 500 ppm).[20,25,56] It is therefore convenient to discuss some of the methods employed by industry to reduce the residual monomer content of polyacrylamide products.

E. Removal of Residual Monomers

The concentration of residual unchanged monomers present in polyacrylamide-based products can be reduced by application of appropriate purification procedures. For linear polyacrylamides, there are a variety of different techniques including repeated precipitation techniques and methodology based on further chemical reactions. For example, the Dow Chemical Company in the early 1960s developed a method whereby unchanged residual acrylamide monomer could be substantially reduced in linear polyacrylamide by the addition of sodium sulfite (Na_2SO_3) just prior to the drying process.[57] Dow also describes methods whereby unchanged acrylamide in polyacrylamide samples was removed or substantially reduced by treatment with NH_3 or amines.[58] The American Cyanamid Company[59] describes a method whereby the polymer is heated to between 80 and 150 °C for 30 min while maintaining the water content. More recently, Allied Colloids Ltd. has reported a method of reducing the acrylamide content of polyacrylamide products by exposing a solution of the polyacrylamide to a bacterial derived enzyme amidase, where the amidase is believed to convert the unchanged monomeric acrylamide into acrylic acid.[60] A similar method has been described by Nalco Chemical Company for reducing the acrylamide content of water-in-oil emulsions.[61]

The patent and journal literature also contains numerous techniques for reducing the monomer content of cross-linked polyacrylamide gels. For example, the Japanese patent[62] describes methodology whereby monomer is extracted from the ground gel using a 90:10 $MeOH-H_2O$ mixture, thus effectively reducing the monomer content of the polyacrylamide gel to less than 0.02%. The US patent by Chmelir[63] describes methodology whereby the polymer products are treated with a compound that reacts with the residual acrylamide monomer's double bond to convert it to a "safe, saturated compound". Examples included describe the reaction of residual acrylamide monomer with bromine and thio compounds.

F. Chemical Properties of Polyacrylamide

The process of polymerizing acrylamide affords polyacrylamide that has completely different chemical and biological characteristics to the monomer. Acrylamide is chemically a very reactive species primarily due to the electron deficient double bond, but the polymerization process to form polyacrylamide removes the double bond, and, as such, polyacrylamides are relatively chemically inert under normal conditions.[2] Unlike acrylamide, polyacrylamides are not readily prone to nucleophilic addition across the backbone since they now possess only a C−C single bond. The amide group of polyacrylamide can undergo reactions such as hydrolysis, dehydration, and will be further discussed in the section on the degradation of polyacrylamides.

G. Biological Toxicity of Polyacrylamides

The toxicity of polyacrylamides is of major interest as they are used in applications where there is direct contact with either humans or animal livestock. The issue of the toxicity of polyacrylamides has been the subject of extensive toxicological studies since the early 1950s, as exemplified by McCollister et al.[64] who studied the toxicology of ingested polyacrylamides. They studied both rats and dogs and feeding durations ranging from single acute oral doses to chronic one- and two-year feeding trials. No adverse effects in both the physical and pathological examinations of the subject animals were found. Work was also conducted on the toxicity of polyacrylamide toward fish where it was found that concentrations of up to 6000 ppm were tolerated with no apparent ill effects.

McCollister's early work has since been extended and his conclusions supported by a number of other authors.[20−22,30,31,56] For example, Seybold[8] concluded, "Polyacrylamide has been shown to be nontoxic to humans, animals, fish, and plants."

Thus far, we have considered some of the properties of acrylamide and polyacrylamides, and it has been noted that one of the main concerns with the use of polyacrylamide products is the presence of unchanged acrylamide. Methods have been discussed whereby the amount of residual acrylamide can be minimized during polymerization and further reduced in subsequent purification steps. Special care is therefore exercised by manufacturers to ensure that polyacrylamide products meet strict mandatory guidelines set for particular applications. However, polyacrylamides are susceptible to a number of different degradative processes depending on the nature of the polymer, impurities present, and the conditions to which they are exposed. Degradation reactions are generally irreversible and alter the physical and chemical properties of the polymer. The byproducts from degradation are also of interest because they can possibly contribute to the toxicity of the degraded system. The remainder of this review is devoted to discussing the current understanding of the degradation pathways of polyacrylamides. The major pathways examined include thermal, photo-, biological, chemical, and mechanical degradation. Many of these reaction pathways involve radical species, and therefore the reactivity of these radical systems is of particular interest.

IV. Thermal Degradation of Polyacrylamides

The thermal degradation of polyacrylamides is influenced by a number of factors including molecular weight, copolymer composition, mode of synthesis, oxygen content, thermal history, and the presence of impurities. However, it has been suggested[65,66] that there are certain common temperature regions where thermal degradation primarily occurs. The thermal aging of polyacrylamide can therefore be divided into several regions depending on the temperature, the first below about 200 °C, the second between approximately 200−300 °C, and the third above 300 °C.[67]

A. Region I: Temperatures up to 200 °C

Below temperatures of about 200 °C, polyacrylamides are generally thermally stable and undergo very little physical change apart from a slight mass loss. This slight weight loss is probably due to

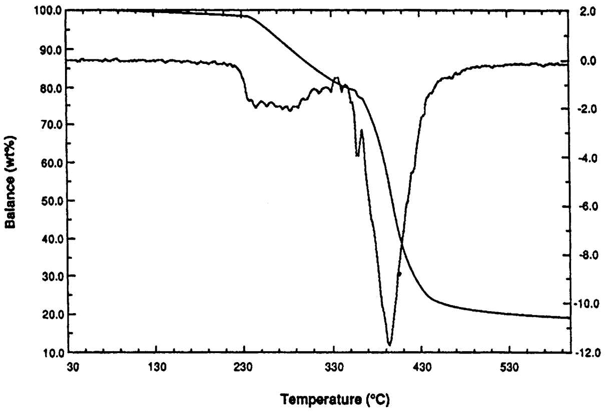


Figure 2. TG and DTG curves for polyacrylamide heated to 600 °C (Reprinted from ref 71 with permission. Copyright 1993 John Wiley & Sons, Inc.).

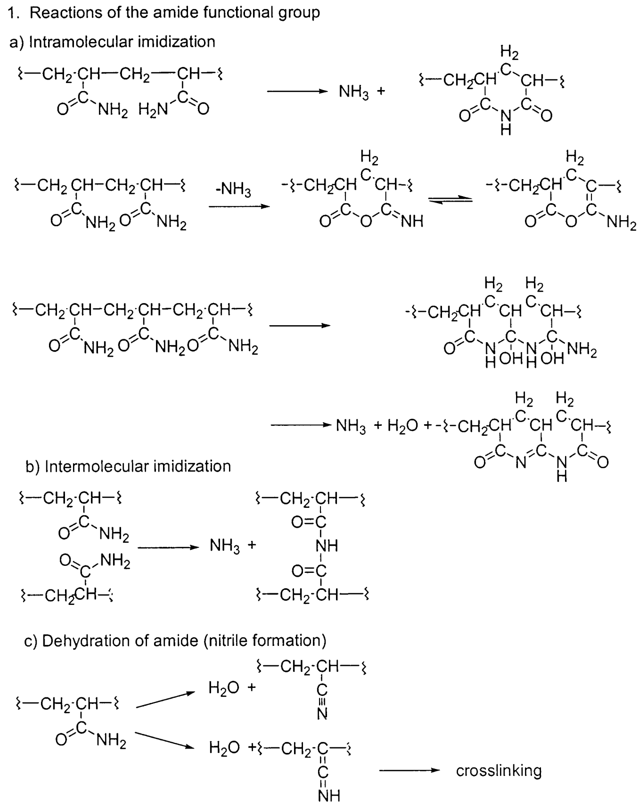
absorbed water from the environment and other volatile impurities.[68,69] Vilcu et al.[70] studied polyacrylamide samples via thermogravimetric analysis (TGA) and observed an 11% weight loss up to 200 °C. They attributed this weight loss to the release of both surface and matrix-bound water from the polymer. Later work by Van Dyke and Kasperski[71] employed a drying step before analysis where the polyacrylamide samples were crushed into small particles and dried under vacuum at 115 °C for 2 h. The dried polymer samples were characterized by microanalysis to ensure no reactions occurred during the drying process. The authors subsequently noted no weight loss before approximately 220 °C from these pretreated polyacrylamide samples during thermal analysis. Figure 2 shows the thermogram (TG) and differential thermogram (DTG) by the authors for a dried sample of polyacrylamide heated at 10 °C/min from 30 to 600 °C. There is an almost straight line from the TG curve before approximately 220 °C corresponding to no release of volatiles.

While studying the thermal degradation of polyacrylamide and other copolymers, the same authors earlier proposed that acrylamide was formed upon heating of polyacrylamide up to 115 °C.[66] These results were not substantiated in their subsequent reexamination of the thermal degradation pathways of polyacrylamide.[71] The observation of acrylamide only in the first study at comparatively low temperatures (~155 °C) suggests that it was probably present in the starting material. These contradictory results highlight the need for careful purification of the starting materials used for degradation studies. However, we note that the polymer samples used in both studies were used as received without stringent purification, and could contain a measurable concentration of residual monomer at the beginning of the degradation experiments.

B. Region II: Temperatures between 200 and 300 °C

At temperatures above approximately 200 °C, polyacrylamides begin to undergo irreversible chemical changes resulting from thermal degradation.[71] Leung et al.[66] and others[65,69] have proposed that these events occur just after the softening temperature. It has been shown that both intra-[66] and intermolecular[70] imidization reactions occur via the pendant amide groups. At this stage, H_2O, NH_3, and minor quantities of CO_2 are released as byproducts of the imide formation and degradation.[71,73–75] It has also been proposed that some breakdown of the cyclic imides groups occurs at this stage.[66,76]

Scheme 4. Proposed Degradation Pathways for Polyacrylamide up to 300 °C



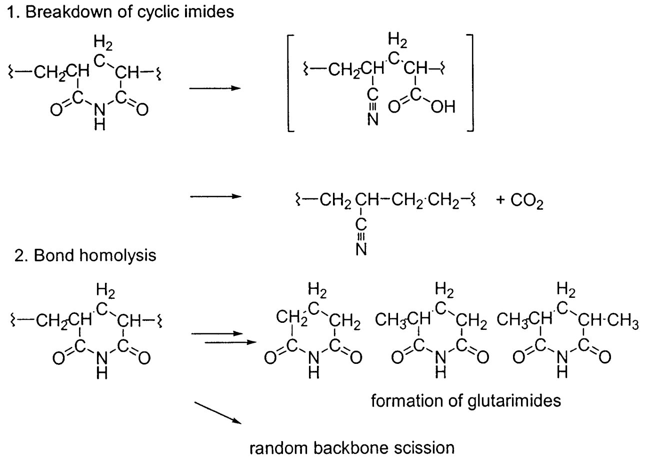
These reactions initially involving the amide residue irreversibly alter the chemical properties of the polyacrylamide and introduce new functional groups into the polymeric structure. The cross-linked intermolecular imidization reaction can render the polymer water insoluble. It has also been noted[66,70,75] that there is relatively little involvement of the polymeric backbone in the degradation reactions, and there is no evidence for the formation of acrylamide.[71]

A summary of the proposed thermal degradation reactions of linear polyacrylamide up to approximately 300 °C is outlined in Scheme 4.

C. Region III: Temperatures above 300 °C

The third degradation region is initially characterized by the decomposition of imides[74,77] to form nitriles and the release of volatiles such as CO_2 and H_2O. Further degradation occurs, and there is evidence for some main chain scission affording various substituted glutarimides.[66] At higher temperatures, the predominant reactions are random bond scission of the polymeric main chain backbone forming long chain hydrocarbons.[66,71,75] The proposed degradation pathways for reactions above 300 °C are summarized in Scheme 5.

Scheme 5. Proposed Reaction Scheme for the Thermal Degradation of Polyacrylamide



D. Thermal Degradation of Copolymers of Polyacrylamide

The chemistry of the thermal degradation of copolymers of acrylamide has also been extensively studied due to their usefulness in many applications. Leung et al.[66] examined the thermal degradation of poly(acrylamide-co-acrylate), and found that the thermal behavior is between that of two homopolymers and depends on the composition of the copolymer. Analogous degradation reactions are observed at approximately the same temperatures when compared to those seen for the individual homopolymers. For example, at approximately 220−270 °C the majority of the reactions involve the imidization of the amide group. At elevated temperatures, there is evidence for the decomposition of the acrylate with the release of CO_2 and concurrent degradation of the imides. The level of intramolecular imidization reactions that occurs is reduced, as there is a limited number of neighboring amide groups.

Vilcu et al.[70,75] studied the thermal degradation of various copolymers between acrylamide and maleic anhydride. It was found that at high acrylamide residue contents, the normal thermal degradation behavior of polyacrylamides was observed where both intra- and intermolecular imidization reactions dominate the initial degradation reactions. As expected, alternating copolymers undergo only intermolecular imidization reactions. Again, random bond scission of the main polymeric backbone dominates the reactions above 350 °C. There was no evidence of monomer formation at any of the temperatures examined.

In conclusion, when considering the thermal degradation of a polymer and the possible toxicity of the degradation products, careful attention should be directed toward not only the possibility of monomer formation but also the toxicity of the compounds that are released. For example, we have discussed the formation of a multitude of compounds during the thermal degradation of polyacrylamides including NH_3, H_2O, glutarimides, and CO_2. Each of these compounds will have certain physical and chemical properties, which need to be taken into consideration. In connection with the reported formation of various glutarimides and derivatives during the high temperature (>350 °C) degradation of polyacrylamides, the literature contains only a few references to these compounds, and therefore their toxicity has probably not been adequately established. One paper by Michalska et al.[78] describes glutarimide's interaction with specific receptors involved in transport of uracil and thymine nucleosides, and it was suggested that it could therefore easily be absorbed across biological membranes into cells. Their work was focused on developing drug delivery methodology; however, the biological effects of incorporation of this family of compounds were not discussed.

Table 2. Energy of a Mole of Photons at a Particular Wavelength

region	wavelength (nm)	energy (kJ mol^{-1})
infrared (IR)	>700	170
visible (Vis)	~400−700	300−170
ultraviolet (UV)	<400	390

V. Photodegradation of Polyacrylamides

Polyacrylamide photodegradation is largely a free radical process that can lead to cleavage of the polymer backbone (bond scission), cross-linking, introduction of new functional groups including unsaturation, and the formation of lower molecular weight products.[79,80] These irreversible changes are responsible for the observed loss of mechanical and other physical properties of the polymer. The presence of oxygen and other impurities in the system can also have a deleterious effect on the observed rate of degradation. The general aspects of photodegradation processes such as absorbance of light, photophysical processes, stabilization, factors controlling degradation mechanisms, photooxidation, etc., have recently been discussed in a number of review articles and books.[81−84] It is convenient to restrict the discussion of these processes to those that are applicable to polyacrylamides.

A. General Aspects of Photodegradation of Polymers

Polymeric photodegradation results from the absorption of energy via photons of light where the energy is proportional to its wavelength and the lower the wavelength, the higher the energy. An important source of photons is the sun, which produces a wide spectrum of photoradiation. The energy of a selection of wavelengths is presented in Table 2.

The energy required to break a chemical bond depends on the nature of the bond, with the average energies for homolytic cleavage of selected bonds presented in Table 3.[84]

The atmosphere absorbs most of the lower spectrum (less than approximately 300 nm) which still leaves components from the UV and visible regions with sufficient energy to disrupt chemical bonds.[84] The following section details the proposed pathways for the photodegradation of polyacrylamides.

B. Absorption of Light by Polyacrylamides

The photodegradation of polyacrylamides is facilitated by the absorption of incident photoradiation.

Table 3. Energies and Corresponding Wavelengths for Dissociation of Typical Chemical Bonds

bond	energy (kJ mol^{-1})	λ (nm)
C=C	669	179
C−C	355	336
C−H	397−418	286−301
C−O	334−418	286−357
O−O	146	817
O−H	355−480	249−336

Chromophoric groups within the polymer absorb light energy, and the energy is transferred to susceptible bonds within the polymer resulting in homolytic bond scission and the formation of free radicals. Thus, in polyacrylamide, the chromophoric carbonyl group of the amide is capable of absorbing incident radiation. There may also be other impurities present in the polymer sample that can act as chromophoric groups, including unsaturated carbon−carbon double bonds resulting from disproportionation during synthesis,[65] polymer hydroperoxy groups resulting from radical reactions with oxygen[6,47] and initiator residues.

The free radicals formed from bond scission are extremely unstable and will react with any suitable substrate.[85] The reactions include combination to reform the saturated carbon−carbon polymer backbone (no reduction in molecular weight), disproportionation to form an unsaturated and saturated polymer chain end (reduction in molecular weight), and reaction with other entities present. Whenever oxygen is present in the system, the carbon-centered radical will have a strong propensity to react to afford a peroxy radical that can undergo further reaction; the reaction pathways for this system are discussed in the following section.

C. Photooxidation of Polyacrylamides

Hunkeler et al.[6,39] have reported that the carbon-centered polyacrylamide derived radicals are extremely sensitive to the presence of oxygen and will have an effect at concentrations as low as 1 ppm. Others workers[86] have directly observed via ESR studies the free radical resulting from the addition of oxygen during irradiation with UV light.

The presence of oxygen in the system can lead to a complicated series of reactions collectively known as photooxidative, which generally includes the following steps, Scheme 6.[83]

The detailed mechanism and kinetics of the photooxidation for polyacrylamides will vary slightly from study to study depending on the reaction condition employed and is beyond the scope of this review. It should be noted that in polymer systems exposed to the appropriate irradiation in the presence of oxygen, the above mechanisms dominate the radical reactions. These reactions can lead to a reduction of molecular weight, introduction of new functional groups into the polymer (peroxy groups), and the possibility of cross-linking.[87]

One study examined the photooxidation of polyacrylamides samples in aqueous solutions via high energy irradiation.[88] The authors note that the observed radical processes are dominated by the reaction of oxygen and the formation of hydroxyl radicals ($^{\bullet}$OH). It was determined that only a small proportion of the hydroxyl radicals formed (approximately 1%) are involved in main chain scission reactions, with the remaining involved in other radical reactions including hydrogen abstraction.

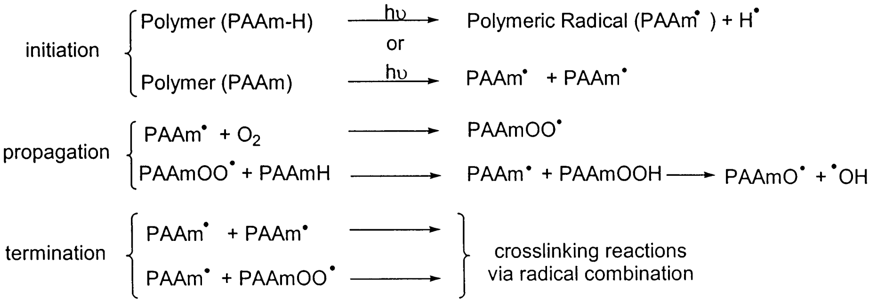
In the next section, we discuss some of the observed reaction pathways for polyacrylamide photodegradation under a variety of different reaction conditions. For simplicity, reactions of the free radicals with oxygen have been omitted from the discussion but the reader should bear them in mind.

D. Mechanisms of Photodegradation of Polyacrylamides

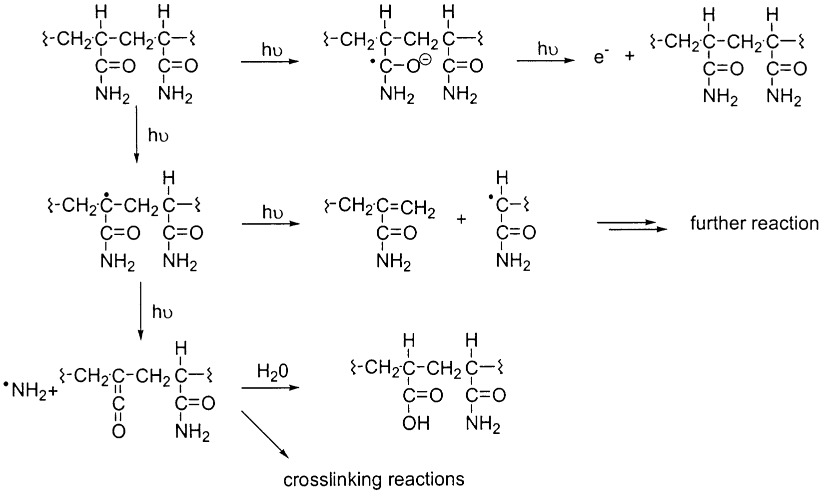
A major agricultural application of polyacrylamides is to increase the viscosity of herbicide solutions during spray application. In normal practice, the polymer and herbicide solutions are in contact with each other and in the presence of sunlight; it is therefore of interest to determine the possible environmental degradation mechanisms. Smith et al. have studied this system both in controlled laboratory experiments[52] and under environmental (outdoor) conditions.[89] They suggest that polyacrylamide samples degraded via some photochemical mechanism to form acrylamide upon exposure to UV radiation. The authors concluded that polyacrylamides are unstable to environmental conditions and depolymerized to monomers, particularly in the presence of the herbicide, glyphosate.

These results have since been challenged by a number of authors.[51,53] Vers[51] has recently reported work using analogous degradation conditions but yielding different results from Smith. Unlike Smith, Vers concluded that polyacrylamide does not degrade to acrylamide monomer in the presence of either sunlight or glyphosate. Further, it was suggested that if the polymeric starting materials were not properly prepared (especially in the case of polymers derived

Scheme 6. Proposed Reaction Pathways for the Photo-Oxidation of Polyacrylamide



Scheme 7. Proposed Radical Reactions Involved in the Photodegradation of Polyacrylamide



from emulsion polymerization), misleading results were often obtained. This problem was particularly evident for the glyphosate containing samples. Thus, before any degradation studies are attempted, it is suggested that the polymer solutions are carefully prepared. Other authors have also challenged Smith's results, suggesting that if depolymerization were occurring, the observed acrylamide concentration would be significantly higher than that claimed to be observed.[90]

Kay-Shoemake et al.[53] have also recently published results that further question the reliability of previous conclusions on the chemical nature of the degradation products derived from polyacrylamides. The authors have shown that UV irradiation of samples of high molecular weight anionic polyacrylamides (i.e., copolymers with COO^-) results in a reduction of the molecular weight of the degraded polymer. They found that the photodegraded polyacrylamide samples did not support bacterial growth. As it is well recognized that acrylamide is completely biodegradable, these results suggest that acrylamide is not formed during the photodegradation of the polyacrylamide.

Other studies have focused on characterizing the observed radical intermediates for the photodegradation of polyacrylamides.[80] The authors propose a series of radical intermediates with the relative abundance and stability of each species dependent on the temperature at which they are formed. The results obtained suggest a reduction in the molecular weight of the degraded polymer, highlighting the importance of chain scission during photodegradation. Their experiments were conducted in the absence of oxygen, and it was noted that cross-linked products were formed due to reactions of the carbenes formed. The authors do not suggest the formation of acrylamide during the course of the experiments. A brief overview of the main intermediates is presented in Scheme 7.

Thus, in conclusion, polyacrylamides are susceptible to a wide range of photodegradative processes depending on the reaction conditions. The majority of photodegradation processes involve the generation of free radicals and result in often irreversible changes in both the physical and chemical properties of the polyacrylamides. These changes include the introduction of branching, other functional groups, and a reduction of the molecular weight of the degraded polymer. However, there is argument about whether the photodegradation of polyacrylamide leads to the formation of acrylamide. In connection with early conclusions, the apparent tendency of polyacrylamides to degrade under photochemical reaction conditions to form acrylamide needs further clarification. More detailed experiments need to be conducted on well-characterized and purified polyacrylamide samples to determine explanations that more closely conform to the recognized modes of degradation of polymers with the structures of polyacrylamides.

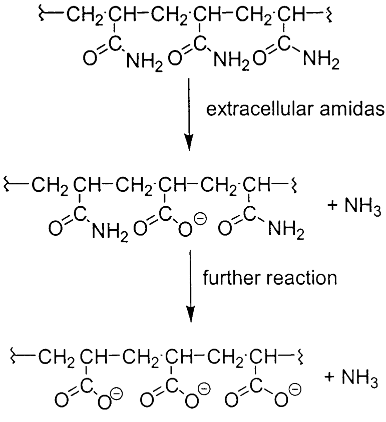
VI. Biological Degradation of Polyacrylamides

Various polyacrylamides are used in applications where contact with microorganisms can occur. For example, one of the major agricultural uses of polyacrylamides is in the control of soil erosion associated with flood-furrow and sprinkler irrigation.[91] Generally high molecular weight (1−2 million molecular weight) copolymers consisting of approximately 80% acrylamide and 20% acrylic acid residues are used.[9] The number of acrylic acid residues is also commonly referred to as the degree of hydrolysis, where in the above example, the degree of hydrolysis would be 20%. At environmental pH's of 6 or above, this copolymer is generally an anionic species (negatively charged). The anionic characteristics of the polymer are responsible for the soil stabilizing effects.

A. Polyacrylamide as a Nitrogen Source

Kay-Shoemake et al.[53] examined the degradation of polyacrylamides via microorganisms present in agricultural soil. The potential for biotransformation of polyacrylamide was examined via a bacterium's capacity to utilize the polymer as a sole nutrient source. Samples were prepared that contained polyacrylamide, and the growth of a variety of bacteria was monitored. When cultures were produced on samples with no other source of nitrogen besides the

Scheme 8. Amidase Induced Biological Degradation of Polyacrylamide



amide of polyacrylamide, bacterial growth was observed. This indicated that there were enzymes capable of biological hydrolysis of the amide to form NH_3 and an acid, effectively increasing the number of COO^- groups present in the polymer at the environmental pH's.

An analogous amidase type enzyme has already been discussed in relation to acrylamide metabolism. However, as polyacrylamides are high molecular weight polymers, they are unable to pass biological membranes and be absorbed into the bacterium.[30,64] Therefore, the action of the enzyme must be extracellular in nature, with the resulting low molecular weight byproducts subsequently being absorbed. This severely limits the possibility of the polymer being totally degraded. The proposed reaction pathway for the biological hydrolysis of polyacrylamide is outlined in Scheme 8.

The amidase activity has been determined by quantifying the concentration of the ammonia released. Changes in the physical properties of the polyacrylamides including their viscosity are evident and are due to the introduction of acrylic acid groups. The action of the amidase does not however lower the molecular weight of the polymer, but alters the nature of the substituents attached to the polymer backbone.[92]

Other workers have also noted that polyacrylamides can act as a sole nitrogen source for bacterium growth, but none have noted the formation of acrylamide.[93,94]

B. Polyacrylamide as a Carbon Source

A bacterium's ability to utilize polyacrylamides as a sole nutrient source for carbon has also been examined. Kay-Shoemake studied a range of bacteria commonly found in soils, and it was noted that the polymer was incapable of sustaining normal growth in the absence of another carbon source.[53] This is indicative of the bacterium studied not containing the necessary enzymes to degrade the main chain carbon backbone to satisfy their carbon nutritional requirements.

Earlier work by MacWilliams[95] also noted that biodegradation of polyacrylamide did not result in the formation of acrylamide and that polyacrylamide was generally very resistant to microbial degradation. Similar conclusions have also been reached by Karol,[96] King,[22] Zohdy,[97] Magdaliniuk,[98] and Conway.[99]

Seybold studied the environmental fate of polyacrylamides in soil conditioning and concluded that the observed changes in the polymer were most likely due to environmental factors such as sunlight, chemical hydrolysis, and mechanical degradation. He demonstrated that polyacrylamides are generally resistant to microbial degradation and that there was no evidence supporting the formation of monomer.[8] Similar observations have been made by El-Mamouni et al.[100] who noted that the mineralization (biological utilization) of native or untreated polyacrylamides was only between 0.6 and 0.7%. However, upon exposure to UV light there was an increased propensity for microbial growth. The authors attributed this to a molecular weight reduction of the polyacrylamide after photolysis, and the extent of mineralization was related to the length of exposure reaching a maximum of approximately 30% after 48 h. The reduction in average molecular weight allows for the absorption of the lower molecular weight oligomers by the bacteria leading to further biodegradation. They did not however observe the formation of acrylamide after the photolysis of the polymer. In contrast, Kay-Shoemake et al.[53] had earlier attempted a similar experiment where a polyacrylamide sample was exposed to UV radiation but the resultant polymer was unable to support bacterial growth. The authors also noted a reduction in the molecular weight distribution of the polymer, but it was incapable of being the sole carbon source for the bacteria.

Wallace et al. noted that polyacrylamide may also be degraded during cultivation (mechanical degradation) but is very resistant to microbial degradation.[101] Montgomery studied aqueous solutions of polyacrylamides and found that they were not subject to attack by microorganisms but could act as a substrate if additional nutrients are available.[102]

Cross-linked polyacrylamides also have agricultural applications in aiding water retention by sandy soils. These synthetic highly absorbent polymer gels are used in situations where slow water release is desirable. Johnson studied the microbial stability of the gels under strictly controlled conditions and concluded that polyacrylamides are resistant to microbial degradation over long periods of time. There was little or no degradation of the polymer over the life of the experiment, and the polymer maintained the essential characteristics needed for the application.[103] Other workers have also noted that cross-linked polyacrylamides are not subject to biological degradation on short to medium time scales when used in agricultural applications.[104]

We have found only few reports in the literature claiming that high molecular weight polyacrylamides can undergo biological degradation, and these reports deserve further comment. Nakamiya and Kunichika[105] claim to have isolated from soil samples two polyacrylamide degrading bacterial strains, *Enterobacter agglomerans* and *Azomonas macrocytogenes*. The authors report that both bacterial strains grew on media containing polyacrylamide as the sole source for both carbon and nitrogen. It was noted that after 27 h incubation 20% of the total organic carbon in the initial medium had been consumed and the average molecular weight of the polyacrylamide had been reduced from approximately 2 million to 500 000 as a result of degradation.

Recent studies have also focused on examining the degradation of polyacrylamides via enzymes extracted from bacteria. Thus, it was found that the lignin degrading enzyme, hydroquinone peroxidase, from the soil *Azotobacter beijerinckii* HM121 bacterium, was capable of degrading a variety of synthetic polymers including polyacrylamides. Extracting the enzyme and applying it to the polymer sample overcomes the limitations encountered due to the inability of high molecular weight polymer absorption into biological cells.

In conclusion, from the literature reviewed, the biodegradation of polyacrylamides under the influence of microbial interaction produces changes in the structure of the polymer. The amide nitrogen has been found to be susceptible to microbial degradation forming an acrylic acid residue and the release of NH_3. There is a large body of evidence to support this theory including nitrogen utilization experiments where the polymer was able to support growth as the sole nitrogen source. On the other hand, there appears to be only a few reports in the literature suggesting polyacrylamides can act as a sole carbon source for microbial growth. These references tend to suggest that microbial degradation occurs as a consequence of other degradation that lowers the molecular weight of the polymer. Differences in biologically induced polymer degradation observed by different authors can be attributed to a number a factors including differences in the physical properties of the polymers studied (molecular weight, copolymers, degree of hydrolysis, history), experimental conditions, and importantly the almost infinite genetic variation that exists in nature. We have found no evidence to suggest that polyacrylamide can undergo biodegradation to form free acrylamide monomer units.

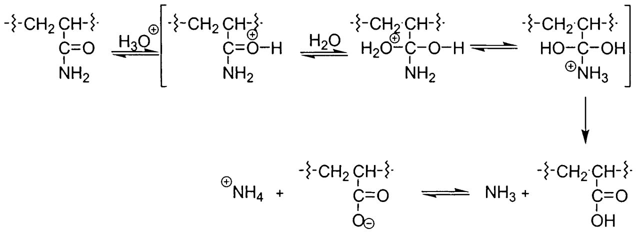
VII. Chemical Degradation of Polyacrylamides

The chemical literature is replete with studies examining the chemical degradation of polyacrylamides. Examining the degradation pathways is a complex issue owing to the almost infinite number of reaction conditions that the polymer can be exposed to. The majority of the chemistry is however concerned with the reactivity of the amide group. It is therefore convenient to restrict the current discussion to relatively mild reactions that the polymers would be exposed to in day-to-day applications.

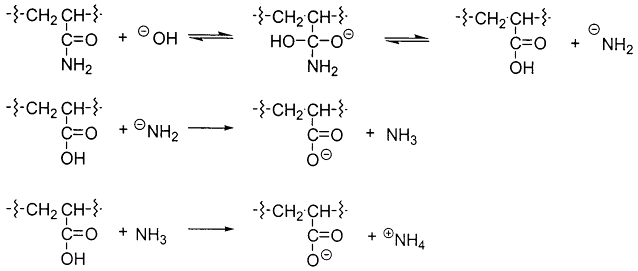
A. Hydrolysis of Linear Polyacrylamides under Acidic Reaction Conditions

Polyacrylamides are known to undergo hydrolysis under acidic conditions to yield poly(acrylamide-co-acrylic acid). Forcing conditions of low pH and long reaction times can afford almost complete hydrolysis of all the amide groups.[37] The reaction involves the nucleophilic addition of water to the protonated amide, followed by the loss of NH_3. The proposed reaction pathway for the acid-catalyzed hydrolysis of polyacrylamide is presented in Scheme 9.

Scheme 9. Acidic Hydrolysis of Polyacrylamide



Scheme 10. Hydrolysis of Polyacrylamide under Alkaline Conditions



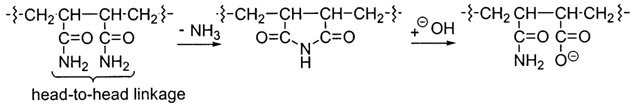
Muller et al.[106] studied the hydrolysis of polyacrylamides under slightly acidic conditions (pH 4). The author's results show that the rate of hydrolysis is increased as a function of higher temperatures and lowering of the pH. The authors noted changes in the viscosity and pH of acidic solutions of polyacrylamides upon aging at various temperatures. Their results point to conformation changes of the polymer in solution upon degradation. Light scattering data collected suggested that the molecular weight of the polymer remained relatively static during the hydrolysis.

B. Hydrolysis of Linear Polyacrylamides under Basic Reaction Conditions

Polyacrylamides are also susceptible to hydrolysis under basic or alkaline conditions at moderately low temperatures (60−100 °C). The reaction involves the nucleophilic addition of hydroxide to the amide carbonyl, followed by elimination of the amide ion ($^-NH_2$) to afford an acrylic acid residue.[107,108] The amide ion then removes a proton from the acrylic acid residue to form the more stable carboxylate anion and ammonia. The hydrolysis of the amide proceeds as a first order reaction with respect to the amide and to the hydroxyl ions. The molecular weight of the degraded polyacrylamides was examined via light scattering techniques, and no reduction in the length of the polymer chain was observed. The hydrolysis of the amide groups introduces negative charges into the polymer and effectively affords an acrylamide−acrylic acid random copolymer. Hydrolysis becomes extremely slow when residual amide content falls below about 30% in the polyacrylamide.[37] The proposed reaction pathway for the alkaline catalysed hydrolysis of polyacrylamide is outlined in Scheme 10.

The hydrolysis reaction pathway is essentially irreversible as the amide anion readily removes a

Scheme 11. Proposed Reaction Pathways for the Initial Rapid Hydrolysis of Polyacrylamides



proton from the acrylic acid residue rather than attack a carbonyl carbon atom, and the carboxylate anion will be unsusceptible to nucleophilic attack from both NH_3 and NH_2.[109,110]

Muller has studied the effect of higher temperatures on the hydrolysis of commercial samples of polyacrylamides.[111] He noted in addition to the formation of acrylic acid residues in the hydrolyzed polyacrylamides, a concurrent reduction in molecular weight of the degraded polymers. The experimental results were rather contradictory to the normal mode of hydrolysis of polyacrylamides, and the author attributed this to a synergistic effect of temperature, residual initiator impurities, and oxygen present in the unpurified experimental samples. Muller subsequently followed this initial study on commercial samples with further work on purified polyacrylamides.[112] Contrary to his earlier results, he found that the molecular weight of the polyacrylamides was not changed by the basic hydrolysis. He also showed that even in the presence of oxygen, the purified polymer was not susceptible to degradative chain scission reactions to afford lower molecular weight polymers. These later results are more in line with the generally accepted degradation pathways for polyacrylamides in basic conditions. This highlights the need for careful sample preparation before degradation experiments are conducted.

Sawant et al.[113−115] in a series of papers have shown that the structure of the polyacrylamide also has an effect on its hydrolytic properties. They showed that the initial part of the hydrolysis occurred at a much greater rate than the remainder. This rapid initial reaction was characterized by the transient appearance of an absorption band with a peak at 235 nm, which corresponded to the formation of a cyclic imide intermediate. The imide rapidly decomposes to form the acrylic acid residue. This basic hydrolysis behavior is analogous to that described by Vigneron et al. for succinamide,[116] which they attributed to the up to 4.5% head-to-head linkages of the acrylamide residues present in the polymer chain. The proposed reaction pathway for the initial hydrolysis of polyacrylamides is presented in Scheme 11.

C. Hydrolysis of Polyacrylamide Gels

The hydrolysis of polyacrylamide cross-linked gels has been shown to occur via a similar reaction mechanism to the linear polymer in solution.[107,117] Thus, Mallo et al.[117] has shown that the hydrolysis of polyacrylamide gels under basic conditions affords carboxylate groups in the network and the release of ammonia albeit at a reduced rate compared to the linear polymer in solution.

Other workers[118] have shown that residual initiator fragments, such *N*,*N*,*N′*,*N′*-tetramethylethylenediamine (TEMED) in redox systems, trigger the hydrolysis. The authors attributed this increased rate of hydrolysis to the basic nature of TEMED. Iiavsky had also previously suggested effects on the rate of hydrolysis on the concentration of TEMED.[107]

D. Chemically Induced Free Radical Degradation of Polyacrylamide

The degradation of polyacrylamides via the action of free radicals has also been well studied. The decomposition of certain compounds causes the formation of free radicals, which are capable of a number of subsequent reaction pathways. This characteristic is often utilized during the formation of polymers, but can also have consequences for the stability of the polymeric species.

Recent work by Gao et al.[119,120] has shown that the molecular weight of polyacrylamides is reduced via a free radical mechanism in the presence of peroxides. The authors discussed the controlling factors that included temperature, concentration, and molecular weight of polymer and peroxide characteristics. The degradation degree was found to be greatest in samples containing potassium persulfate ($K_2S_2O_8$) and less pronounced with samples containing hydrogen peroxide (H_2O_2). The authors concluded from their results that initiating systems that produce higher concentrations of free radicals were not necessarily going to cause more degradation, as the probability of radical−radical termination processes will also be increased.

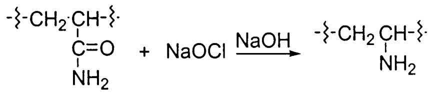
Ramsden et al. in a series of articles have discussed the degradation of polyacrylamides via the action of hydroxyl radicals.[121−123] Their results suggest that hydroxyl radicals formed in the presence of dissolved oxygen can cause chain scission of the polyacrylamide and a reduction in the molecular weight of the polymer. In the absence of oxygen, chain scission did not occur.

Traces of polymerization initiator have also been shown to contribute to the degradation of polyacrylamides, especially in the presence of oxygen. For example, even residues of the initiator potassium persulfate used for the synthesis of polyacrylamides can cause measurable changes in the molecular weight distribution in the presence of oxygen.[124]

The chemical literature contains numerous references regarding other contributing factors in the degradation of polyacrylamides. Shupe[125] has reviewed the chemical stability of polyacrylamides and discussed a range of chemical degradation modes. Many of these are ultimately free radical processes; for example, metal ions in solution have been known to cause degradation of polyacrylamides. Thus, Fe^{2+} ions in conjunction with dissolved oxygen can potentially cause severe and rapid degradation, primarily involving chain scission. This resulted in a reduction of the molecular weight of the polyacrylamide and concomitant viscosity decrease of the polymer solutions.

These studies highlight the need for correct purification of linear polyacrylamides, and indeed, the need to minimize the concentration of initiators during the formation of polymer gels, where removal of impurities is more difficult.

Scheme 12. Hoffman Degradation of Polyacrylamides



E. Hoffman Degradation of Polyacrylamides

Polyacrylamides react with alkaline sodium hypochlorite (NaOCl) to afford primary amine groups following the Hoffman degradation (Scheme 12).[126] Reaction conditions are controlled so as to avoid cross-linking at high polymer concentrations.[49,127]

In conclusion, the chemical degradation of polyacrylamides involves a variety of chemistries. There are innumerable reaction conditions and possible products, and in this review we have not attempted to cover every possible situation but have endeavored to give the reader a feel for the types of chemistries involved. There is however one generality from all the literature examined. PAAm behaves as a typical monosubstituted vinyl monomer, and no studies have shown release of acrylamide upon chemical degradation.

VIII. Mechanical Degradation of Polyacrylamides

Mechanical degradation irreversibly changes the structure of a polymer and is caused by chemical reactions initiated by the input of mechanical energy. The process of mechanical degradation can be facilitated by a variety of external stimuli including high shear or elongational flow (polymer solutions) or by direct mechanical load or agitation (solid phase).[128] Sufficient energy can be transferred to the polymer chain to cause bond scission and the formation of free radical species, which are extremely unstable and are quickly involved in other chemical reactions.

Evidence for the free radical nature of mechanical degradation has been shown by the observation of an electron spin resonance (ESR) spectra. The observed ESR spectrum provides direct evidence for the formation of unpaired electrons (free radicals). Analyzing the shape of the ESR spectrum can also help identify the nature of the free radical species. Additionally, the intensity of the ESR spectrum is proportional to the number of free radicals formed and thus the number of bonds broken.[128,129]

Polyacrylamides experience various forms of mechanical degradation depending upon the application for which they are being utilized. The next few sections describe some of the known mechanisms via which polyacrylamides are mechanically degraded.

A. Mechanical Degradation of Polyacrylamide Solutions

Industrial applications of aqueous solutions of polyacrylamides often involve varying degrees of stirring, pumping, injecting, and movement through porous media.[65,130] Each of these processes has the potential to cause mechanical degradation of the polymer used. For example, enhanced crude oil recovery (ECOR) involves injecting aqueous solutions of linear polyacrylamides with high molecular weight ($>$1 million) and up to 20% hydrolysis into porous oil bearing rock formations or reservoirs. The polymer reduces the mobility of the injected fluids during flow through the reservoir by increasing the viscosity of the solution and also by decreasing the permeability of the reservoir to water. A polymer solution flowing through such an oil-bearing reservoir will encounter drastically different flow velocities. This can induce excessive mechanical stresses within the polymer chain and subsequently to deteriorate the physical properties of the polyacrylamide solutions. These changes are primarily observed as a reduction in viscosity leading to a decline in their performance properties and a general reduction of their efficiency for a particular application.[65]

Early work by Maerker et al.[131,132] examined changes in the degraded molecular weight distributions compared to native polyacrylamides by band sedimentation of fluorescently tagged samples. Their results suggested a slight reduction in the molecular weight of the polymers post mechanical degradation.

Shear induced degradation has also been studied[130,133,134] by viscometry and gel permeation chromatography (GPC) techniques.[135] It was found that there was a marked reduction in the GPC calculated molecular weight of the polyacrylamide and it was suggested that this was due to main chain bond scission. Abdel-Alim and Hamielec[136] also studied the mechanical degradation of polyacrylamides but under highly reproducible shear stress conditions. Their GPC results indicated a reduction in the molecular weight of the degraded polymer that was more pronounced with the higher molecular weight fractions.

Some workers have suggested that there is a chain length dependence on the observed mechanical degradation,[65,137,138] and chain scission is more likely to occur at the midpoint of the polymer.[139,140]

Mechanical degradation has also been observed for semidilute solutions of nonhydrolyzed polyacrylamides in laminar flows in multipass capillary tubes.[141,142] The rheological behavior was examined for a series of polymer solutions subjected to varying amounts of mechanical loads. It was proposed that degradation of the polymer primarily occurs at the entry point of the capillary where stretching of the macromolecules is at a maximum and extensional forces are sufficiently strong to cause bond scission.

Linear polyacrylamide solutions are used in electrophoretic channels as polymer matrixes during DNA separations. The polyacrylamide solution is pumped into the channel such as a capillary tube prior to the separation, and thus there is the possibility of shear induced degradation. Vazquez et al.[143] have measured mechanical degradation at injection rates down to a minimum of 1 μL/min. They have also correlated the decrease in electrophoretic performance to changes in the rheological properties and the decrease in molecular weight of the degraded polyacrylamide. This paper emphases the susceptibility of polyacrylamide solutions to mechanical degradation given the seemingly innocuous conditions they were exposed to.

Recent work has focused on measuring the absolute molecular weight distributions of degraded polymers using multi angle laser light scattering (MALLS) techniques.[144,145] Noik et al.[146] have quantified the rate of macromolecular breakage in terms of several factors including molecular weight, concentration, and nature of electrolytes. Their results suggested a decrease in the molecular weight of the samples after exposure to mechanical loads. Other workers[147,148] have also observed a reduction in the molecular weight distribution on studies of both nonionic and anionic (hydrolyzed) polyacrylamides used as flocculants.

B. Branching during Mechanical Degradation of Polyacrylamides

Some authors[65,149,150] have suggested that there is not a significant reduction in the molecular weight distribution in degraded samples but rather macromolecular chain scission leads to branching. Moan et al.[149] have measured the absolute molecular weight distribution before and after passage through a porous medium of a partially hydrolyzed polyacrylamide (anionic) solution. They observed a large decrease in the observed intrinsic viscosity but only a slight reduction in the average molecular weight. It was noted that prolonged exposure of the polymer solution to high extensional and shear stresses lead to bond scission and the subsequent formation of branched polymers. These branched macromolecular species have approximately the same molecular weight but a smaller hydrodynamic volume. Further evidence supporting the proposed nonlinear or branched species in the degraded polymer solutions was found in the observed increase in the Huggins coefficient. Bauer et al.[151] have shown in other systems that an increase in the Huggins coefficient correlates to a certain degree of branching of the polymer.

Stupnikov et al.[150] have also suggested that branching contributes significantly to the observed physical changes in degraded polyacrylamide solutions. Under their experimental conditions, it was suggested that macromolecular radicals are involved in a number of reactions including hydrogen abstraction, disproportionation, combination, and other reactions with acceptors such as oxygen ultimately leading to the introduction of branching. Branching of the polymer chains caused changes in size, flexibility, and solution behavior of the degraded polymer. The authors concluded that the observed mechanical degradation was not associated with a decrease in the molecular weight but with the formation of inter- and intramolecular cross-links. It is useful to consider the proposed mechanism for the free radically induced formation of these branching points.

Mechanical load can exert enough shear-induced stress to cause bond scission and the formation of a macromolecular radical. As mentioned earlier, radicals are extremely unstable species and are quickly involved in a variety of further reactions. For the purposes of illustrating the proposed branching mechanism, we consider only the essential features:

(a) Combination reaction to reform the original polymer chain,

(b) Disproportionation reaction to form a saturated chain end and an unsaturated double bond end group, or

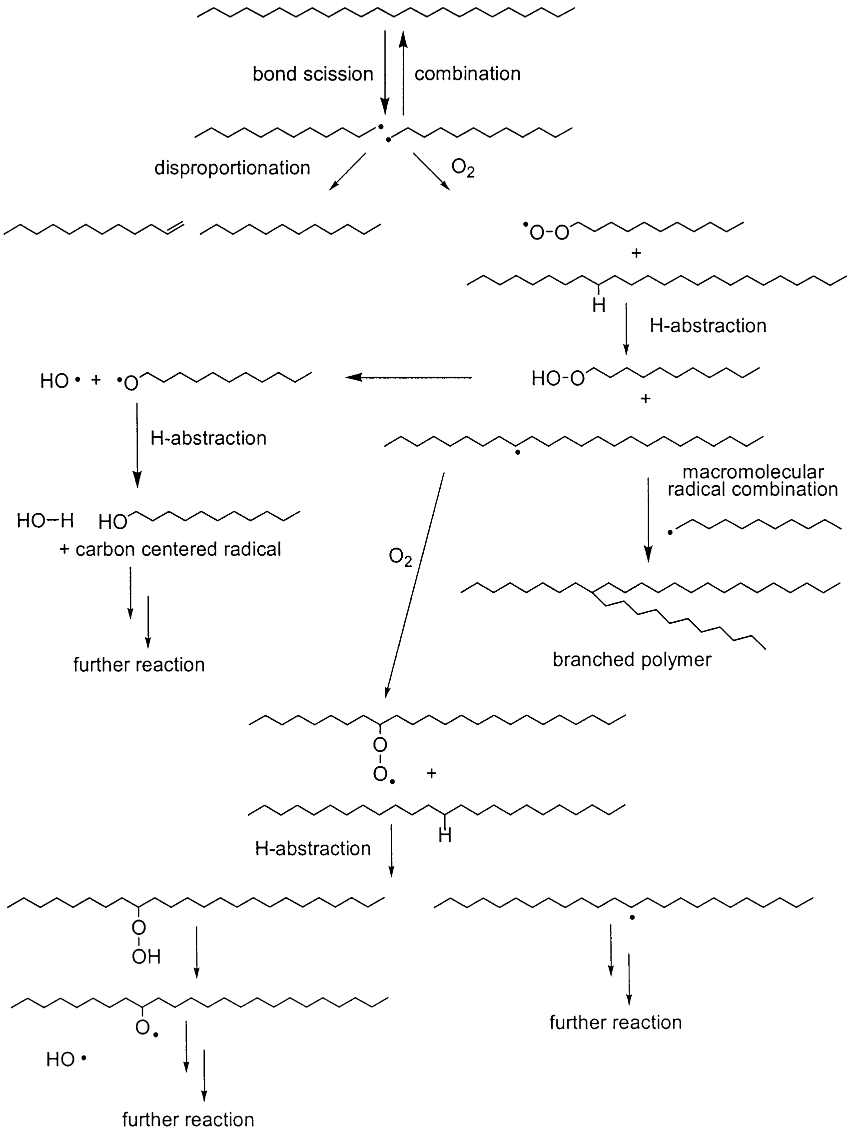
(c) Reaction with oxygen to form a peroxy macromolecular radical.

Combination reforms a stable high molecular weight polymer, which can undergo further possible bond scission. On the other hand, the radical−radical reactions by disproportionation involve the formation of two polymeric species and the introduction of a new functional group, an unsaturated double bond. Evidence in favor of the formation of unsaturated functional group in polyacrylamide samples is provided by the observed reaction of the double bonds with aqueous solutions of $KMnO_4$, Br_2, or $AgNO_3$.[65]

If the polymer solution contains even a trace of oxygen, carbon-centered radicals react with this oxygen at near diffusion-controlled rates[82,152] affording a peroxy macromolecular radical. Hunkler and Hernandez have suggested that oxygen efficiently scavenges free radicals during acrylamide polymerization down to 1 ppm.[6,39,153] Peroxy radicals have an extremely strong propensity for hydrogen atom abstraction[154] and will do so with any available hydrogen atoms. The polymer backbone forms a convenient source of hydrogen atoms and thus the peroxy radical is likely to H-abstract to form a slightly more stable hydroperoxide species and a new radical species. This new macromolecular carbon-centered radical is able to undergo further reactions including with oxygen or undergo radical−radical reactions such as disproportionation or combination with another carbon-centered radical. Combination will afford a branch point in the polymer backbone that is more likely to occur in systems with limited amounts of oxygen.[155] In addition, the hydrogen peroxide end group can readily decompose to form an oxygen-centered radical and a hydroxyl radical, both of which can abstract further hydrogen atoms, thus forming new carbon centered radicals. Hydroxy radicals in other systems have also been linked to other radical reactions including main chain scission.[88,155,156] An analogous reaction scheme has been proposed[157] for the formation of branched species in the presence of polyacrylamide macromolecular free radicals. The proposed pathways for the formation of branched species via mechanically induced radical reactions are presented in Scheme 13.

It is well recognized that application of excessive mechanical loads to polyacrylamide solutions causes deterioration in their physical properties. These irreversible physical changes are observed as differences in the rheological properties of the polyacrylamide solutions before and after degradation. There is disagreement between different authors concerning the chemical basis for these physical changes. Some studies indicate a dramatic reduction in molecular weight, while others note less significant changes. This can partially be explained by taking into account the different techniques employed by some authors when assessing changes in the polymer structure and the variable concentration of impurities such as oxygen. Much of the early work relies on viscometry and GPC techniques that provide information con-

Scheme 13. Proposed Mechanism for Free Radically Induced Branching of Polyacrylamides during Mechanical Degradation



cerning the effective hydrodynamic volumes of the polymers but not necessarily accurate molecular weight data. Recent work has focused on absolute molecular weight measurements using laser light scattering techniques; however, there are still some variations in the observed results.

Experimental conditions are not always well defined and can affect the observed polyacrylamide degradation products, where branching can occur under certain conditions by combination of macromolecular radicals. While in other systems, mechanical degradation results in a narrowing of the molecular weight distribution, a decrease in the average molecular weight, and a decrease in intrinsic viscosity.

In conclusion, care must be taken when comparing data from mechanical degradation of polyacrylamides from different research groups. However, some generalities can be drawn; first, mechanical degradation involves irreversible changes of the polymeric material including a marked reduction in viscosity. Second, mechanical degradation leads to main chain bond scission and thus the generation of free radicals. The literature contains a number of theories regarding the chemical nature of the physical changes and the fate of the free radicals. One explanation is that the physical changes are a consequence of the formation of lower molecular weight polymeric species after degradation. Others propose that the molecular weight distribution of the degraded polyacrylamide remains relatively stable and that branching is responsible for the observed changes in the physical properties.

To the best of our knowledge, there are no reports in the literature suggesting that under the influence of a mechanical load polyacrylamides degrade to form their constituent monomeric units such as acrylamide.

IX. Concluding Remarks and Future Considerations

This review has summarized the literature concerning the degradation of polyacrylamides via a number of pathways. Thermal, photo-, biological, chemical, and mechanical degradation have been discussed in relation to both linear and cross-linked polyacrylamides. The chemistry of polyacrylamide degradation can be divided into two main categories: (i) side chain substituent reactivity and (ii) polymer backbone reactivity.

There is general agreement in the literature that the degradation chemistry is dominated by the reactivity of the substituent amide group. Further studies, particularly in relation to photodegradation, have shown evidence for the degradation of the polymer backbone to form monomer. However, some of these results are questionable, as the authors have failed to indicate the purity of the starting materials and also the history of the polymer; both points are critically important to draw meaningful conclusions. Researchers therefore need to pay particular attention to reporting the initial characteristics of the polymer systems studied. Important factors include the purity of the polymer, polymerization method (solvent, initiator used, etc), sample preparation, and possible defect groups present in the polymeric backbone from, for example, head-to-head linkages.[158,159] Indeed, it is evident that some previous work has been conducted on impure polymers that most likely contained starting materials such as acrylamide.

The chemical and physical properties of polyacrylamides make them ideally suited for many applications, particularly in the growing biotechnology area. Pure polyacrylamides are nontoxic, relatively stable to a variety of reaction conditions, and, most critically, do not undergo unzipping type reactions to form significant amounts of acrylamide. To ensure that the development of polyacrylamides is unencumbered by lingering doubts over its stability, in future studies more attention needs to placed on reporting the way in which polymers are produced and purified.

X. References

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