CHAPTER
9

PHOTOPOLYMERIZATION

9.1 INTRODUCTION

The discovery of polymers has much contributed to the change of day-to-day life. In fact the use of polymers in human history dates back as early as Egyptian mummies. Before the mummies were wrapped, the cloth was soaked in a solution of oil lavender. When the cloth was dried by exposure to the sunlight, the oil was converted into a protective polymer. This was a typical application of photopolymerization. Polymers are involved in almost all aspects of our lives. Some examples include their use in textile, automotive and electronic industries and as building and packing materials.

The most widely used and simple method of polymer formation is radical-chain addition polymerization. Polymerization involves initiation, propagation, transfer and termination steps. Initiation is the step where initiating radicals are formed by external stimulation such as light, heat, gamma-radiation and redox processes. Light induced photopolymerization has several advantages over the other methods. These are low temperature conditions, usually room temperature, and controllability via selective wavelength irradiation and light intensity. Moreover, light can be focused onto a particular site, thus polymer can be formed only at desired places.

Photopolymerization is a very flexible process and can be used in various technological applications such as photo-resists in modern electronics. In this process, a film of monomer mixture is placed on a surface of and a light illumination is focused on the areas in which a polymer covering is desired. After polymerization has occurred, the unpolymerized material can be washed away, leaving the photopolymer intact. The polymer-covered areas on a silicon wafer then resist chemical etching, resulting in integrated circuit formation or printed circuit board construction. This technology has allowed billions of transistors to be placed on a single integrated circuit.

Another example of the use of polymers is in gel electrophoresis. Electrophoresis is a method for separating proteins based on the charge on the enzyme surface. Application of an electric field causes charged particles to migrate towards the electrodes. Thus, enzymes may be separated on the basis of relative charge on their surface, with grater charge giving a faster migration rate. Further negatively charged species will migrate in the opposite direction from the positively charged species.

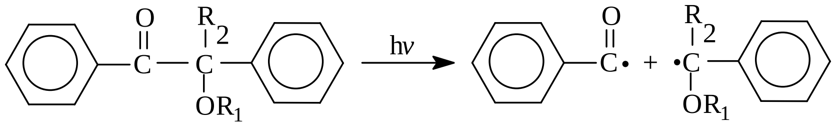
A gel is a polymer “fishnet” in which chemical bonds form the pores which are interwoven to catch chemical fish (i.e. the enzymes). The size of the holes can be varied by changing the amount of crosslinking agent in the polymer network. Small enzymes or proteins are able to move easily through gel, while the larger enzymes have more difficulty moving through the pores of the gel. Thus, separation of enzymes is accomplished on the basis of size, with smaller enzymes being able to move faster and further through a gel than larger enzymes. The combination of these two principles results in the technique of gel electrophoresis, which is a powerful technique for the separation of proteins and enzymes.

9.2 CHEMISTRY OF PHOTOINITIATION

Photoinitiators for radical polymerization may be placed in two clases: (1) those which undergo intramolecular bond cleavage, notably acetophenone and derivatives, and (2) those which undergo intermolecular H-abstraction from a H-donor, benzophenone and derivatives.

9.2.1 INTRAMOLECULAR BOND CLEAVAGE (-CLEAVAGE)

An important criterion for photoinitiators in this class is the presence of a bond with dissociation energy lower than the excitation energy of the reactive excited state, on the other hand sufficiently high to provide thermal stability. Benzoin derivatives are the first class of photoinitiators utilized in photopolymerization applications such as particleboard finishing. These compounds undergo photo-cleavage to produce benzoyl and hyroxybenzyl radicals as shown below.



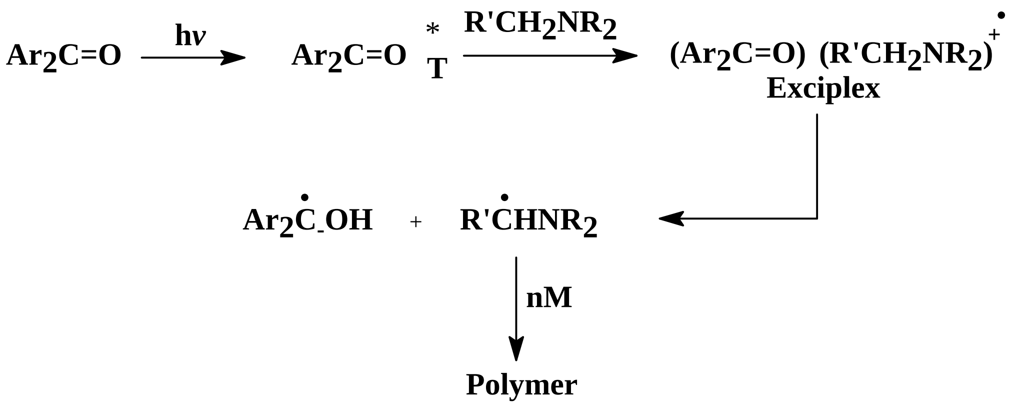
R_1 = H, Alkyl
R_2 = H, Alkyl

(1)

Although at different rates depending on the structure of the monomers employed both radicals are capable of initiating free radical polymerization.

9.2.2 INTERMOLECULAR H-ABSTRACTION

Photoinitiators of this type include benzophenone and derivatives, Michler’s ketone, thioxanthones, benzyl and quinones. In contrast to cleavage type photoinitiators, which are capable of generating radicals independently, this type of initiators must undergo a bimolecular reaction with hydrogen donors. Tertiary amines with abstractable -hydrogen atoms are particularly effective H-donors for UV curing of acrylate monomers.



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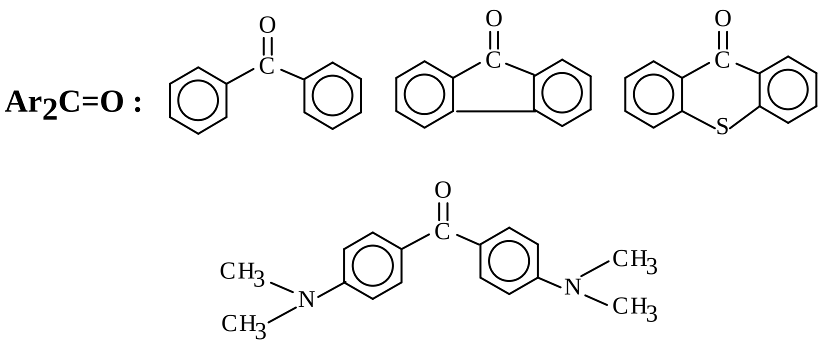


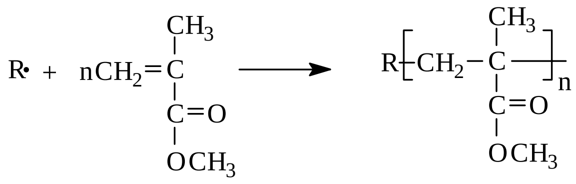
(3)

9.3 EXPERIMENTS

9.3.1 PHOTOPOLYMERIZATION OF MMA WITH BENZOIN

Poly (methylmethacrylate) (PMMA) is used in a variety of applications due to its optical properties. It may be prepared by a radical mechanism using thermal and photoinitiators. Upon irradiation radicals generated according to the reaction 4 react with the double bond of the monomer to yield PMMA.

$$I \xrightarrow{h\nu} 2R\bullet \qquad (4)$$



$$R\bullet + nCH_2{=}\overset{\displaystyle CH_3}{\underset{\substack{|\\ C=O\\ |\\ OCH_3}}{\overset{|}{C}}} \longrightarrow R\left[CH_2-\overset{\displaystyle CH_3}{\underset{\substack{|\\ C=O\\ |\\ OCH_3}}{\overset{|}{C}}}\right]_n \qquad (5)$$

9.3.1.1 Materials required

Pyrex glass tube
Methylmethacrylate (1 ml)
Methylene chloride (1 ml)
Benzoin (5 mg)
Methanol (20 ml)
Photoreactor

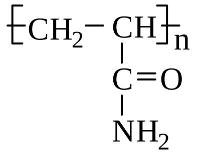
9.3.2 EXPERIMENTAL PROCEDURE

Prepare a solution of 5 mg of benzoin in 1 ml methylene chloride in a pyrex tube. Then add 1 ml of methyl methacrylate to the solution and close the tube with a stop-cock. Irradiate the solution by a photoreactor. Check the viscosity of the solution after 30 min of irradiation. When the viscosity of the solution is high, precipitate it into methanol. Determine the conversion of the polymerization after filtering and drying the polymer in a vacuum oven. Further experiments may be performed at different irradiation times and deaerated solutions with nitrogen in order to see the effect of irradiation time and air on the polymerization yield.

9.3.2.1 PREPARATION OF A PAAm GEL BY PHOTOPOLYMERIZATION

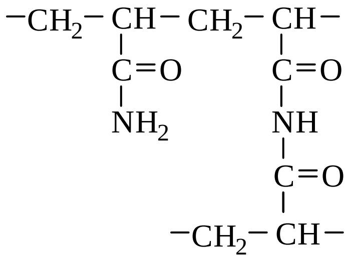
Polyacrylamide (PAAm) is a polymer which is used commonly in the separation of proteins by gel electrophoresis. To initiate the polymerization in our experiment, we begin exciting riboflavin molecules with light. The excited riboflavin (Rib) molecule undergoes a charge transfer reaction, taking an electron from the tetramethyleneethylene diamine. This produces a riboflavin radical anion and a TEMED radical cation. These species then serve as initiators for polymerization. The structure of the final polymer is given below, along with a representation of the reaction mechanism.

$$\mathrm{Rib} \xrightarrow{h\nu} \mathrm{Rib}^{*} \xrightarrow{\mathrm{TEMED}} \mathrm{Rib}^{\overset{\bullet}{+}} + \mathrm{TEMED}^{\overset{\bullet}{-}} \xrightarrow{\mathrm{Acrylamide}} \mathrm{Polymer} \qquad (6)$$



$$-\!\!\left[CH_2-CH(C(=O)NH_2)\right]_n\!\!-$$

Homopolymer



Crosslinked Polymer

The product polymer is fine and threadlike when formed. To obtain a product which is easily seen and isolated, bisacrylamide (BIS) is added as a crosslinking agent. BIS has two double bonds to which the radical may add. If one radical adds to one double bond and another radical adds to the other double bond, the two chains of polymer are joined by a crosslink. This causes the threads to become joined like a fishnet. The size of a fishnet may be varied by changing the amount of BIS which is added to the prepolymer mix.

9.3.2.1 Materials required

50 ml beaker
20 ml measuring cylinder
Acrylamide, 1 g
Bisacrylamide 50 mg
Riboflavin 1 mg
Tetramethyleneethylenediamine 0.01 ml
Photoreactor

9.3.2.2 Experimental procedure

Prepare a solution of 1 g of acrylamide, 50 mg of bisacrylamide, 1 mg of riboflavin and 0.01 ml of teramethylethylenediamine in 20 ml distilled water. Place the solution in a beaker. Irradiate the solution with the photoreactor for 1.5 h. The polyacrylamide formed will have a gel-like consistency.

REFERENCES

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2. S.P.Pappas, UV Curing, Science and Technology, Volume II, Technolgy Marketing Corp., 1993