Utilization of a hollow copper cathode laser in producing polymers

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Abstract: A Pulsed, home- built, hollow copper cathode discharge laser (HCCL) in the visible region and 1.76 mj energy per pulse, was used to irradiate a monomer so as to produce polymer. Three different categories of samples were irradiated for different intervals of time: 30, 60 and 90 minutes. Infrared Spectrometry was carried for the samples before and after irradiation and the collected spectra were analyzed and discussed. The results showed that the polymerization process starts in a very short time (30min), which indicates the efficiency of this type of laser in such application.

Keywords: Laser, hollow copper cathode, polymerization.

Theory

Lasers are considered being as one of the most significant tools in chemistry for its remarkable characteristics, which are: narrow spectral range, high intensity and the possibility of producing pulses of very short duration. Lasers can be used to drive chemical reaction in a chosen direction or to initiate reactions instead of the traditional method of adding thermal energy. Also, another area of laser - enhanced chemistry is the systemization of reactions by the excitation of species that it dose not change. In addition to that, they are capable of monitoring the dynamics of the chemical reactions and polymers production (John F. Ready, 1997).

A *Polymer* is a large molecule comprised of repeated structural units. These structural units are much related to the starting material from which the polymer is originated (*Monomer*).

The Degree of Polymerization (n), is the average number of monomer units that have polymerized together. It depends on the nature of the monomer and the conditions under which they formed (Fred & Bill Meyer, 1971). Some examples of the structures of polymers and monomers are shown in Table 1, (Malcolm P. Stevens, 1984).

The physical properties of a polymer material are largely determined by: molecular weight, strength of intermolecular forces, regularity of the polymer structure, flexibility of the polymer molecule.

Polymers are classified according to many parameters such as the origin, the physical properties, and how the structural groups are joined. According to the origin, polymers are classified into natural and synthetic polymers. According to the physical properties, are classified into: elastomers, fibers and plastics: when considering the functional group, polymers are classified into (a)linear, (b)branched and (c)net- work or cross-linked polymers as shown in Fig.1 (Malcolm P. Stevens, 1984).

Polymerization process can be preceded by many chain reactions. It may be subdivided into many types, such as free radical addition polymerization, an ionic addition polymerization, and cationic polymerization. A simple picture for the dynamic of polymerization by free radical addition is on the following steps:

Initiation

Free radical activates the monomer by opening the double bond.

Initiation steps are as follows:

- The initiator (I) decomposed into free radical (R*):

Initiator (I) $\rightarrow$ R*
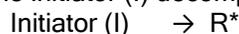
- The second step; the free radicals are added to the monomer unit M to form a chain radical M_1*

R* + M $\rightarrow$ Mi*

where k_d, k_i are the speed constants for decomposition and initiation of the previous reactions.

Fig.1. Types of polymers

Propagation

The chain radical formed in the previous step is capable of adding successive monomers to propagate the chain as follows:

M_1*   + M $\rightarrow$ M_2*
M_2*   + M $\rightarrow$ M_3*
M_x*   + M $\rightarrow$ $M^*_{(x+1)}$
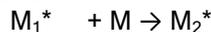
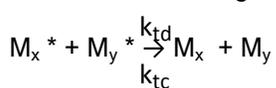where k_p is the speed constant for the propagation.

Termination

The process of propagation can keep in continuing until the supply of monomers is finished. Termination process can take place in two ways:

- The coupling of two radicals:

$M_x^* + M_y^* \rightarrow M_{(x+y)}$

- Two radical undergo disportionation:

$$M_x^* + M_y^* \underset{k_{tc}}{\overset{k_{td}}{\rightarrow}} M_x + M_y$$

where k_{tc}, k_{td} are the speed constants for the termination by coupling and disportionation reactions, respectively (Burnett,1954).

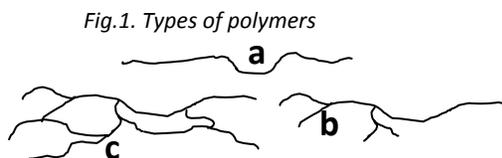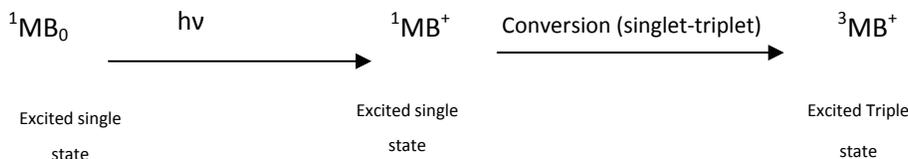Free radical polymerization, for some monomers, can be obtained by a photochemical system (Malcolm P. Stevens,

Table.1. Structures of some monomers and Polymers

Monomer Structure	Monomer Name	Polymer Repeating unit	Polymer Name
$CH_2= CH_2$	Ethylene	[CH_2 CH_2]	Polyethylene
$CH_3CH=CH_2$	Propylene	[CH_2–CH- CH_3]	Polyproplyene
$F_2C=CF_2$	Tetrafluoroethylene	[CF_2 CF_2]	Polytetrafluoroethylene

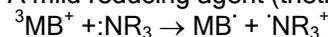1984). Some photochemical systems are capable of producing free radical polymerization, for some monomers.

Lasers have been utilized to activate some organic dyes that have selective absorption for the laser light at a certain range of wavelengths, and then it will be excited to a higher state. At this excited state it becomes strong oxidizer, capable of participating in a redox reaction with mild reducing agent (Zare *et al.,* 1995). Then this reaction results in generation of free radicals that ready to attack the monomer which leads to homoletic opening of the double bond.

That mean formation of radicals chain reaction and the reaction propagates, and hence the polymer is produced. An example will be given below:

Table 2. The hollow copper cathode laser parameters

Active medium	Cupper ions
Wavelength	513.5 nm
Gas carrier	Helium
Helium pressure	28 mbar
Discharge current	1.96 Ampere
Temporal mode	Pulsed
Output energy	1.76 mJ
Pulse repetition rate	0.675 kHz
Pulse duration	1.4 msec

Fig. 2. Block diagram for irradiation process

$$^1MB_0 \xrightarrow{h\nu} {}^1MB^+ \xrightarrow{\text{Conversion (singlet-triplet)}} {}^3MB^+$$

Excited single state   Excited single state   Excited Triple state

tryethanolamine in 100ml volumetric flask. The volume was adjusted to 100 ml using the 15% gelatin solution, and then well mixed.

One drop from the prepared reactants mixture was applied on clean microscopic slide. The diameter of each sample was 5mm approximately. These samples were exposed to the laser radiation for different intervals of time (½, 1, and 1½) hours. Some samples were kept as a control, i.e. not exposed to the radiation. The beam was focused so that the entire volume of the sample was uniformly irradiated as shown in Fig.2. The beam was reflected by a plane mirror downwards perpendicularly on the sample.

Note that the process of irradiation was completed in a dark room to avoid any source of illumination except the laser beam that may affect the polymerization process.

The irradiated samples were subjected to spectroscopic measurements by an infrared spectrometer. The spectra of the samples indicate whether the polymer is produced or not.

The sample was scratched from the slide and grounded finely in a mortar. Then a 0.5 mg of a KBr powder (analar) was added to the sample in the mortar. The mixture was transferred to the compressing machine and pressed (8 Tons) to form a transparent disk. The disk was mounted in a suitable holder and kept in a desiccator to avoid moisture.

The spectra of the samples were collected using IR Spectrometer (Thermo- Nicot) in the wavenumber range (500-4000) cm^{-1} with resolution of 4 cm^{-1}.

Results and discussion

The action of the high focused energy of the laser beam is to breakdown the strong covalent bonds C=C, which normally characterize the monomers, and subsequently allows another molecule to be attached. Furthermore, it speeds up the polymerization reaction rate. The results of the obtained spectra are as follows:

IR Spectrum of the mixed reactants of polymerization before Irradiation:

The I.R spectrum of the mixture of reactants, comprising the polymerization mixture, is depicted in Fig.3. The mixture reactants include the monomer, the oxidizing agent and the reducing agent in a gelatin

In forming the Poly Acrylamide polymer, a Methylene Blue dye is used as strong oxidizer. The mechanism of the reaction is as follows:

A mild reducing agent (triethanolamine NR_3) is added,

$$^3MB^+ + :NR_3 \rightarrow MB^. + {}^.NR_3^+$$

This photochemical redox reaction results in generation of two radicals. Now the radicals are ready to attack the Acrylamide molecules and the polymerization reaction propagates to produce the monomer.

Experimental work

A home built hollow cupper cathode discharge laser was used to irradiate samples prepared of mixture of monomers and other reactants. Analytical grade of reagents was used to prepare the reactants. The IR spectra of the irradiated samples, with different intervals of time, were collected using infrared spectrometer. The specifications of the laser which was used as a source of irradiation are listed in Table 2.

For the sample preparation, 15% gelatin solution was prepared as follows:
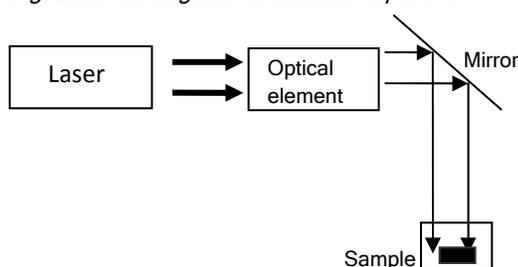
15g of gelatin was weighted and added to 10 ml of hot (50-60 ^0C) distilled water in a conical flask (100ml). The gelatin was dissolved and the volume was adjusted by addition of the hot water to 100 ml. The solution was kept warm using a magnetic stirrer ready for use.

Second, the mixture of the reactant was prepared as: 15.57 g of the monomer (acrylamide) was weighted and added to 0.025 g of methylene blue and 3.3ml of

Table 3. Spectral data of the mixed reactants before irradiation

Present work band position (Cm⁻¹)	Previous work (Elameer,2005) band position (Cm⁻¹)	Reference data (James *et al.*, 1988) band position (Cm⁻¹)	Probable assignment
1658.74	1675	1630-1690	C=O stretch
3359.84	3425	3200-3400	N-H stretch
1567.77	1620	1560-1690	C=C stretch
1454.21	1425	1450-1575	N-H bend
2924.40	2950	2850-2960	C-H stretch

solution. The experimental data of the band positions are compared with a previous study as illustrated in Table 3 and with referenced data in correspondence of its probable assignment. Only the major vibration frequencies are listed here. The obtained results from a KBr disc of the mixture spectrum shows an agreement with the referenced data (Table 3).

IR spectrum of mixed reactants after laser irradiation for 30 min (Fig.4):

The degradation of the bond C=C which considered as a significant criteria of the monomer, nearly disappeared. It means that the polymerization reaction

become obvious after 30min.

The data collected from the spectrum of a KBr disc of mixture reactant irradiated for half an hour using the hollow cathode discharge laser are listed in Table 4. The results obtained in the present work are compared with a previous data where the irradiation was done with the helium- neon laser for the same mixed reactant and irradiation time of 36 hours. The data shows a good agreement with both previous work (Elameer, 2005) and that data obtained from reference (James D. Ingle & Crouch, 1988) although the irradiation time of the present

Fig.3. IR spectrum of mixture reactants before irradiation

Fig.4. The IR spectrum after irradiation for half an hour

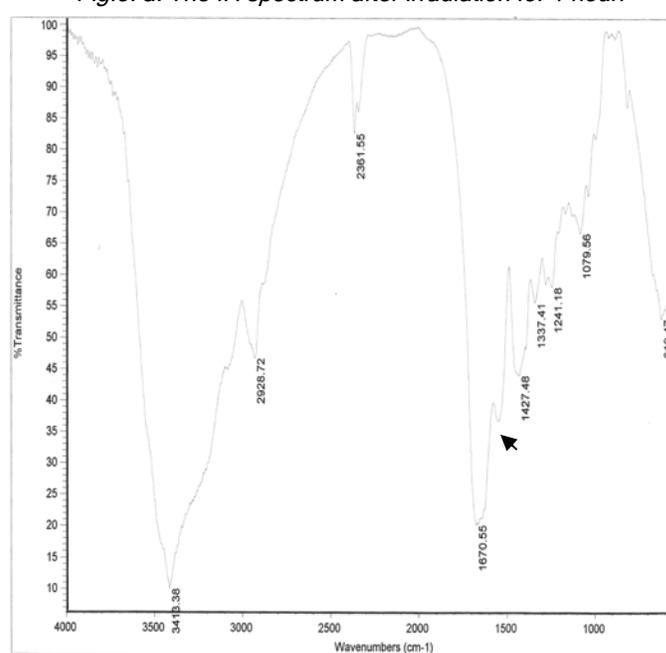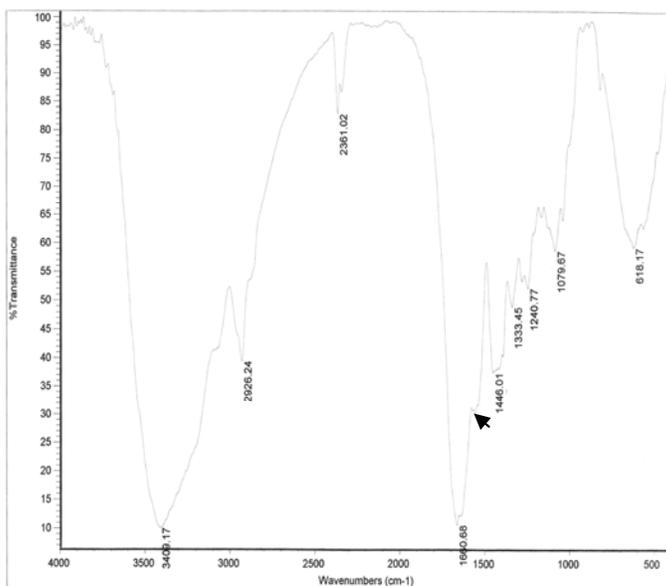*Fig.5. a. The IR spectrum after irradiation for 1 hour.*

*Fig. (5.b) The IR spectrum after irradiation for (1½) hour*

work is just 30min. The band position 3413.38 cm^{-1} is slightly out of the range and that may be due to the laser beam direction which makes a new orientation as a result of polarization.

Table. 4. Comparison of obtained data with that of previous work & the referenced data

Present work band position (Cm^{-1})	Previous work (Elameer,2005) band position (Cm^{-1})	Reference data (James et al., 1988) band position (Cm^{-1})	Probable assignment
1658.74	1673	1630-1690	C=O stretch
3393.38	3384	3200-3400	N-H stretch
1427.84	1423	1450-1575	N-H bend
2928.40	2925	2850-2960	C-H stretch

Fig.6. The effect of the exposure time on the polymerization rate
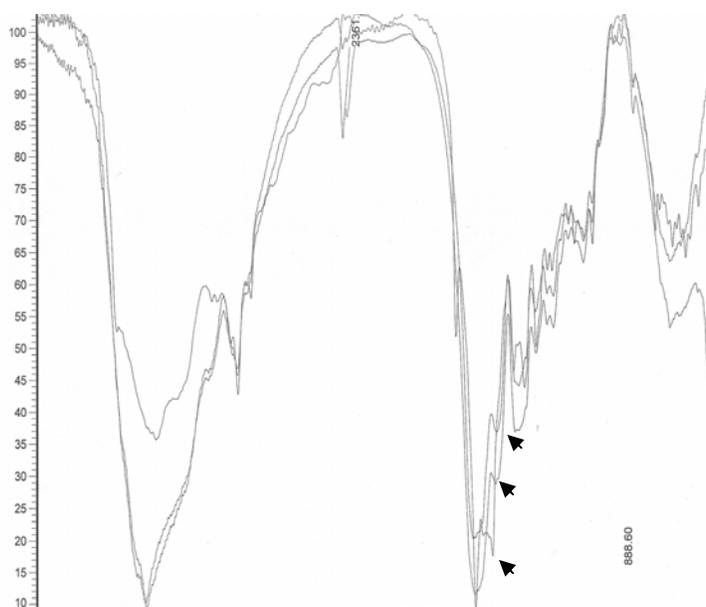
The effect of exposure time on rate of polymerization:

After the successful experiment of producing polymer from monomer using the technique of HCCL irradiation, other samples of the mixture reactants were exposed to different irradiation time: 1 and 1½ hour. The IR spectra that show the transmittance as a function of the wave number are shown in Fig. 5 a,b for 1 hour and 1 ½ hour, respectively. The gradual declination of the C=C bond can be observed. In other words, increasing the irradiation time increase the polymerization rate. This can be explained easily since the laser energy deposited in mixed reactant is time dependent. Fig.6 shows the effect of exposure time on the polymerization rate. In our view, this rapid change may be due to increase of photon energy since the wavelength of the produced laser is 513.8 nm which is greater than the He-Ne laser (632.8nm). The other factor is the energy per pulse as a result of the pulsed mode of the laser (1.76 mJ).

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