

## CW-CO<sub>2</sub> Laser photoinitiated polymerization of Methyl Methacrylate

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:

.(10.6 μm)

(T<sub>m</sub>,T<sub>c</sub>,T<sub>g</sub>)

(TGA,DSC)

PMMA

.(10,15,20)

(T<sub>g</sub>)

.MMA

### **Abstract**

Photoinitiated polymerization of methyl methacrylate has been observed using cw-CO<sub>2</sub> laser radiation of (10.6 μm). Both of DSC and

TGA thermal analysis techniques were used for identification of the thermal characteristics ( $T_g$ ,  $T_c$ , and  $T_m$ ) as well as the thermal stability of the laser photoinitiated PMMA and they compared with that corresponding to classical, conventionally initiated PMMA.

In cw-CO<sub>2</sub> laser radiation, each of powers (10, 15, and 20W) was used. Although a definite increase in  $T_g$  value and thermal stability were observed while power are (10W, 15W and 20W), the polymerization pattern remained basically the same in all these cases.

Multi-Photon absorption reaction phenomenon was attributed to elucidate the mechanism of interaction between the CO<sub>2</sub> laser light and MMA monomer molecule.

### **Introduction:**

Methyl Methacrylate (MMA) [H<sub>2</sub>C=C (CH<sub>3</sub>) CO<sub>2</sub>CH<sub>3</sub>] is considered nowadays as the most important methacrylic acid ester commercially available, it is in particular used as a monomer for the fabrication of poly methyl methacrylate (PMMA). This polymer is in its turn widely used as a contact lens material and as a resist in microelectronics, among other applications [1].

The mechanism of CO<sub>2</sub> laser photoinitiated polymerization can be performed via free radical polymerization process which is chain reaction process and it consists of three main steps: initiation, propagation, and termination. Laser photo-initiated polymerization has demonstrated distinctive features such as it is free-initiator as well as free-solvent process. Other interesting attributes were observed for laser-initiated polymers like high crosslinking and high thermal stability than the conventional initiated polymers [2].

Infra-red laser-induced process studied most extensively is multiphoton excitation of molecules to high vibrational states from which reaction, usually dissociation, may occur. First reason is especially connected with (CW) lasers, that the high intensities associated with laser radiation can, by increasing the transient concentration of radical intermediates, substantially increase the extent to which sequential absorption processes enter into the reaction. A second reason is more directly connected with pulsed nature of the radiation. The radical chain propagation responsible for linking successive monomer units proceeds between pulses; subject the normal radical decay kinetics, only until the onset of a succeeding pulse [3]. Then, the sudden increase in initiator radical concentration leads to radical-radical termination process that prevents further chain lengthen. Laser-produced polymer has a high molecular weight and it is tougher and it displays better tensile and

thermal properties than the polymer that produced using conventional photo-initiation [4].

Multi-photon absorption process involving interaction of two or more photons with a molecular entity; The multi-photon absorption processes which can be induced by intense radiation become particularly efficient if one or more resonance condition can be satisfied by the molecular energy levels. Where a single frequency of uv/visible radiation is involved, the unequal spacing of most electronic levels means that it is rare to obtain even one intermediate state resonance. Vibrational energy levels are more or less equally spaced, at least for the lowest levels of excitation. Hence, with infra-red radiation of the appropriate wavelength, multi-photon absorption can become highly significant [5].

### **Experimental:**

#### **Materials:**

Methyl Methacrylate (Supplied by Fluka):

It is washed twice with aqueous 5% NaOH (to remove inhibitors such as hydroquinone) and twice with water. Dried with  $\text{CaCl}_2$ , and distilled under vacuum, the distillate is stored at low temperatures and redistilled before use. Also it is purified by boiling  $\text{H}_3\text{PO}_4$  solution and finally with saturated NaCl solution. It was dried for 24 hours over anhydrous  $\text{CaSO}_4$ , distillation at (0.1mm Hg) at room temperature and stored in the freezer as described in ref. [6].

#### **Techniques:**

The photo-initiated polymerization process of studied monomers using  $\text{CO}_2$  laser (CW mode,  $\lambda=10.6 \mu\text{m}$ ) has the following features:

1. Bulk Polymerization.
2. Solvent-free process.
3. Initiator-free process.
4. Initiation process is taken place owing to absorption of laser light (IR region).

Features of the laser system used are:

- Continuous wave coherent  $\text{CO}_2$  surgical laser system, sealed refillable tube, radio frequency (RF) excited.
- Laser power (up to 40W), laser wavelength (10.6  $\mu\text{m}$ ) infrared beam in the ( $\text{TEM}_{00}$ ) mode.
- The laser output power and all internal functions are controlled by an on-board microprocessor-based control unit.
- The laser system is provided with articulated arm for targeting laser beam.
- Aiming beam: (2 mW He-Ne laser).

## CW-CO<sub>2</sub> Laser photoinitiated polymerization of Methyl Methacrylate.

The CO<sub>2</sub> Photo-initiated polymerization process has performed according to the following procedure:

Each monomer was photo-polymerized via free radical addition mechanism using CW CO<sub>2</sub> laser as an initiation source. The process was done at room temperature in absence of chemical initiator and solvent. As in conventional polymerization processes, a current of N<sub>2</sub> gas was passed for (10 min.) through the polymerization reaction ampoule (Pyrex) that contain the monomer only (5 g) to avoid inhibition of free radical addition mechanism by oxygen. The (CW CO<sub>2</sub>) laser irradiation process for power densities each monomer with different incident intensity (10, 15, and 20 W.cm<sup>-2</sup>) for a certain exposure time (5 min.) was performed by exposing test tubes to the laser beam vertically. The process led to the formation of polymer chains with different properties depending on the varied applied laser parameter (laser power) [Table 1]. After the irradiation step is completed, the contents of test tubes were precipitated in (20 ml) of the proper solvent for each monomer. After filtration, polymer samples were washed and dried in a vacuum oven at room temperature and weighed, in order to calculate the ratio of conversion and testing the solubility afterwards [Table 2].

**Table (1): The parameters which applied in cw CO<sub>2</sub> laser photo-initiated polymerization process.**

CO <sub>2</sub> laser power (W)	Power Density (W/cm <sup>2</sup> )	Percentage of conversion (%)
10	50	72.8
15	75	81.4
20	100	86.2

**Table (2): The solubility of (10,15, and 20 W CO<sub>2</sub>) laser photo-initiated polymers.**

Solvent	PMMA
Acetone	-
Benzene	X
Toluene	X
Methanol	-
Ethanol	-
Chloroform	-
Hexane	-
Diethyl ether	-
THF	-
DMF	-
DMSO	-
Dioxane	-
P-Xylene	-
Methyl Ethyl Ketone	-

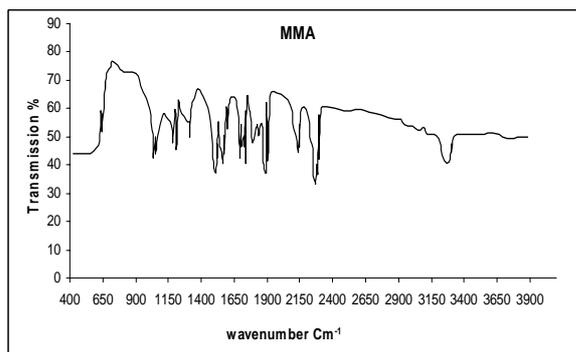
[(-): Insoluble; (x): Swelled slightly]

**Results & Discussion:****1- Infra-red analysis:**

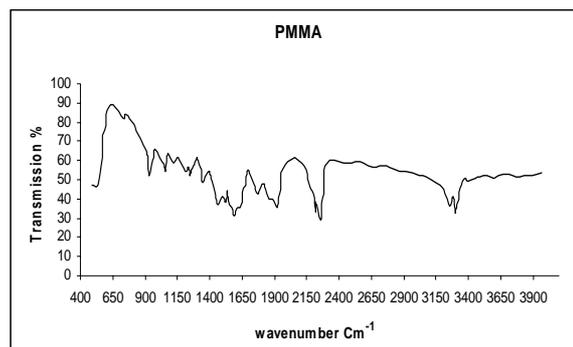
Infra-red spectra was recorded using Sodium Chloride cells for liquid monomers and (Potassium Bromide) disks for synthesized solid polymers by using “Pye-Unicam model SP-3-300s” infrared spectrophotometer. The IR spectra of [(MMA), and its polymer] are shown in Figures [(1, 2)] and the corresponding major band assignments are summarized in table (3).

The IR spectra of monomers have showed strong absorption bands in the region of ( $1610-1630\text{ cm}^{-1}$ ) ascribed to the stretching vibration of (C=C) bond [7] in which the free radical addition polymerization proceeds through its cleavage in the propagation step. This is the reason of disappearance of their absorption bands in the spectra of polymers, verifying the occurrence of polymerization processes.

Besides the (C=C) band, another strong absorption bands could be seen in the region of ( $1680-1730$ ) in the spectra of monomers and polymers as well, were assigned to the stretching vibration of (C=O) that specific for vinyl compounds [8].



**Fig. (1): IR spectrum of Methyl Methacrylate (MMA).**



**Fig. (2): IR spectrum of poly Methyl Methacrylate (PMMA).**

**Table (3): IR band assignments of (MMA), and its polymer:**

Assignment	Wavenumber ( $\text{cm}^{-1}$ )	
	MMA	PMMA
N (C=C)	1630	-----
N (C=O)	1723	1720
v (C-H) in $\text{CH}_3$	2940	2940
v (C-H) in $\text{CH}_2$	2980	3000
N (C-O)	1015	1060

## 2- Thermal analysis results of polymers (DSC Analysis)

Synthesized polymers were investigated by differential scanning calorimetry technique (DSC) using “PERKIN-ELMER (7 series Thermal Analysis System)” under identical conditions: (sample weight: 9-12 mg; heating rate: 10 °C / min.; maximum temperature: 500 °C; nitrogen atmosphere).

DSC scans were obtained for PMMA polymer in different laser power {10, 15, and 20 W} that synthesized by laser initiated photopolymerization methods {CW CO<sub>2</sub>, laser}, reveal clear indications of the thermal characteristics (T<sub>g</sub>) in an increasing values that corresponding to power of CO<sub>2</sub> laser used.

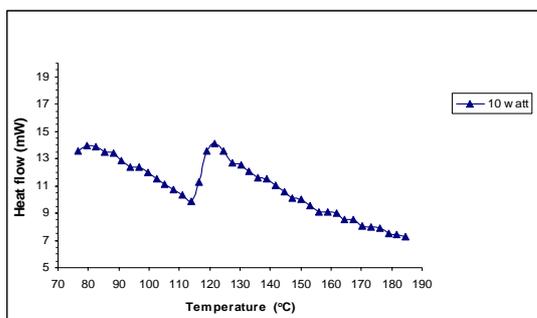
This inconsistency may attribute to these influencing effects:

1. Crystallinity effect.
2. Crosslinking effect.

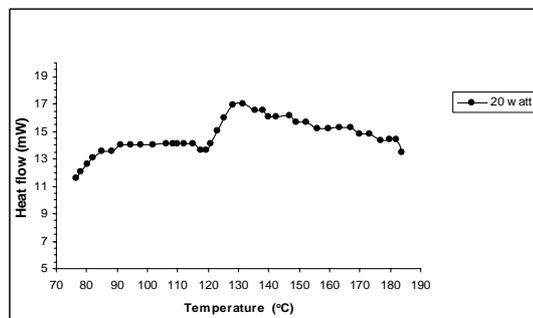
Figures (3, 4, and 5) demonstrate DSC curves and Table (4) lists the associated values of thermal characteristics of (10 W CO<sub>2</sub>) laser initiated synthesized polymers.

**Table (4): T<sub>g</sub>, T<sub>c</sub>, and T<sub>m</sub> values of (10, 15, and 20 W CO<sub>2</sub>) laser initiated synthesized PMMA polymer.**

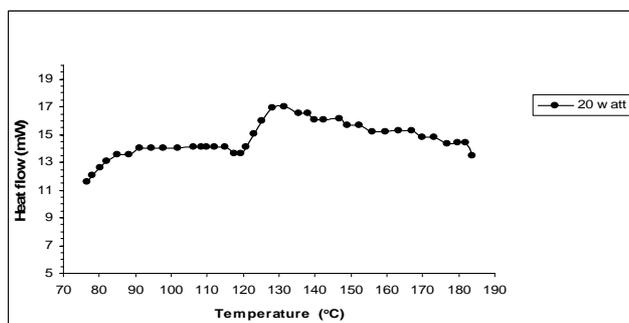
CO <sub>2</sub> laser power (W)	T <sub>g</sub> (°C)
10	119
15	123
20	129



**Fig. (3): DSC scan of PMMA 10W CO<sub>2</sub> laser photoinitiated.**

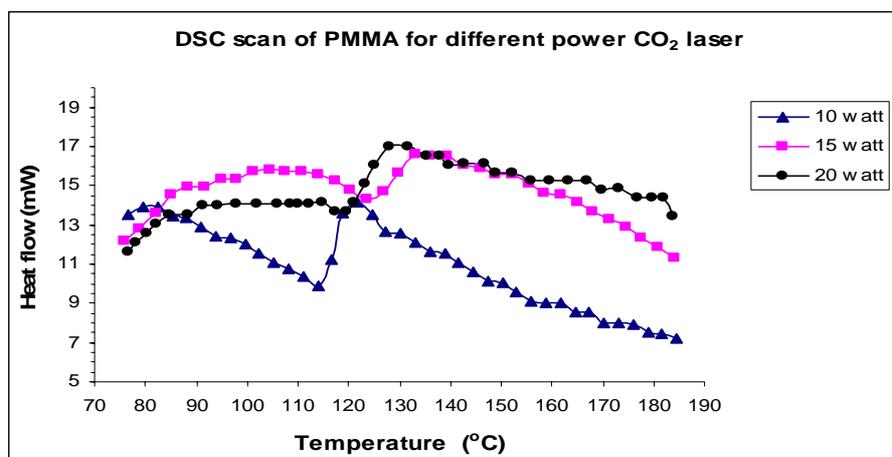


**Fig. (4): DSC scan of PMMA 15W CO<sub>2</sub> laser photoinitiated.**



**Fig. (5): DSC scan of PMMA 20W CO<sub>2</sub> laser photoinitiated.**

Figures (6) shows the DSC scan of PMMA for different powers (10, 15 and 20) W CO<sub>2</sub> laser photoinitiated.



**Fig. (6):** DSC scan of PMMA for different power CO<sub>2</sub> laser photoinitiated.

### 3- TGA analysis:

Thermal stability of synthesized polymers was measured by Thermogravimetric Analysis (TGA) using: “Du Pont TA 951 thermogravimetric Analyzer”. The rate of the TGA scans was (10 °c/min.) from 25 to 800 °c under nitrogen atmosphere; the sample weight was about (10 mg). Figures [(7, 8, and 9)], display these TGA scans.

TGA scans clearly showed the steps of the thermal degradation of synthesized polymers, which can yield critical information concerning the changes which occur on thermal processing of polymer.

As well as Crystallinity and Crosslinking degree, there are two other effects that may influence on thermal stability and resulted TGA curves of laser photo-initiated polymers:

1. Molar mass.
2. Polymerization degree.

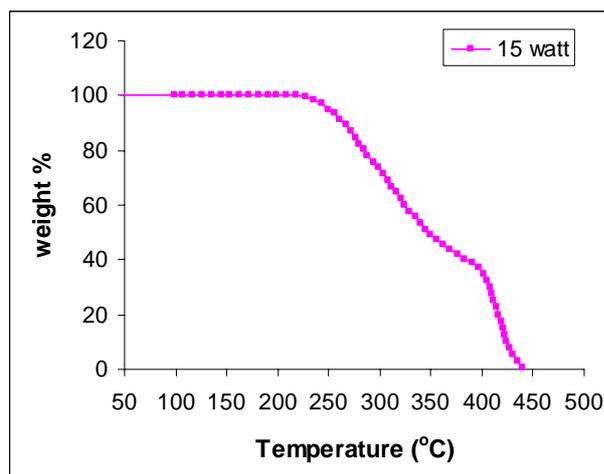
Higher thermal stability accord greatly with higher onset values of thermal decomposition of polymers, such a phenomenon was greatly demonstrated especially for the polymers that synthesized using (CW CO<sub>2</sub>) laser as a photo-initiated source. It was plausible from TGA curves for polymers which photo-initiated with (20W CO<sub>2</sub>) laser system that it possesses the relatively maximum onset values of thermal degradation owing to factors above.

Figures (7, 8, and 9) illustrate TGA curves and Table (5) lists the onset values of thermal degradation of CO<sub>2</sub> laser (10, 15, 20 W) initiated synthesized polymers.

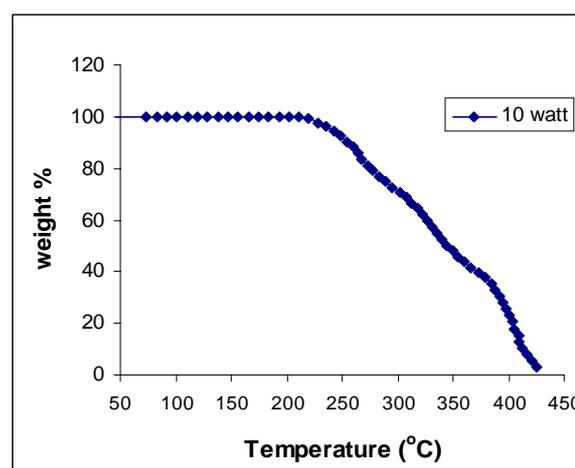
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*Table (5): The onset values of thermal degradation of CO<sub>2</sub> laser (10, 15, 20 W) initiated synthesized polymers.*

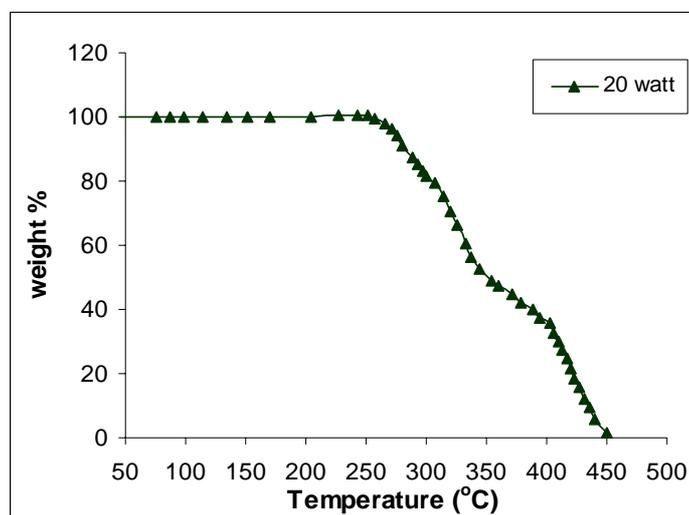
CO <sub>2</sub> Power W	Onset value of thermal degradation of the PMMA (C <sup>o</sup> )		
	First step	Second step	Third step
10	215-275	275-383	383-434
15	228-289	289-392	392-441
20	247-307	307-400	400-453



*Fig. (7): TGA scan of PMMA 10W CO<sub>2</sub> laser photoinitiated.*

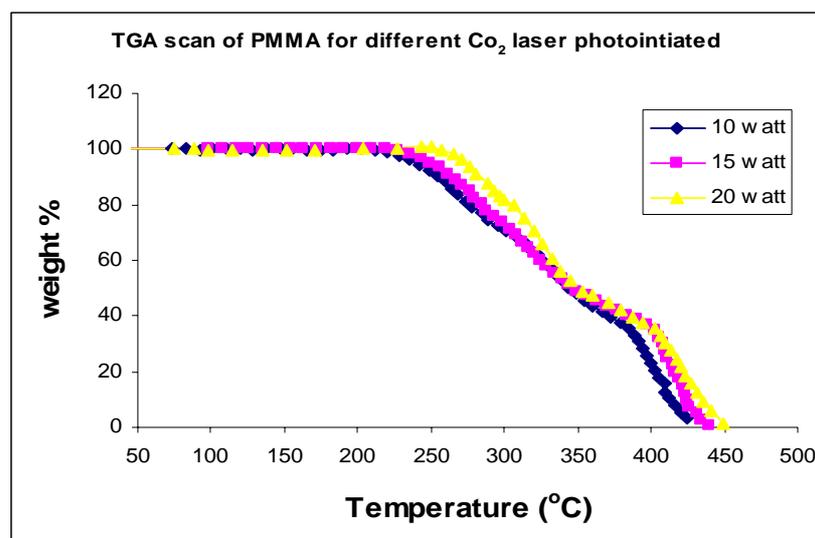


*Fig. (8): TGA scan of PMMA 20W CO<sub>2</sub> laser photoinitiated.*



*Fig. (9): TGA scan of PMMA 20W CO<sub>2</sub> laser photoinitiated.*

Figures (10) shows the TGA scan of PMMA for different powers (10, 15 and 20) W CO<sub>2</sub> laser photoinitiated.



**Fig. (10): TGA scan of PMMA for different power CO<sub>2</sub> laser photoinitiated.**

There are two influences may affect on the DSC scans behavior of the laser-initiated polymers, which are: Crosslinking and Crystallinity, where their effects depend on the laser type and its intensity [9]. DSC scans of CO<sub>2</sub> laser-initiated polymers for figures (3,4, and 5) showed that T<sub>g</sub> values continue in shifting to higher temperatures but accompanying with decreasing and broadening in their peaks intensities, and that may attributed to domination of crosslinking effect on the crystallinity effect in the polymer produced, which causes the polymeric chains to be more crosslinked and that means more restricted and hindered partial positional mobility of the polymeric chains. As a result of that, T<sub>g</sub> peaks may adopt higher values.

As example of that; for the laser-initiated PMMA: comparison between the DSC scans of PMMA showed that generally the T<sub>g</sub> values shifted to higher temperatures accompanying with decreasing in their peaks intensities until reach the lowest one in the 20W CO<sub>2</sub> laser-initiated PMMA, Fig.(5). T<sub>m</sub> peaks didn't appear in the laser-initiated PMMA scans, but they appeared in conventionally initiated ones conventionally initiated ones [10] owing to absence of Crosslinking in the latter one. It is remarkable that T<sub>g</sub> and T<sub>m</sub> peaks intensities of the conventionally initiated polymers DSC scans are low compared to that in the laser initiated polymers DSC scans [11]. This behavior may imputed to the amorphous nature of Acrylic and Methacrylic polymers.

Thermal degradation studies of conventionally and laser synthesized Acrylic and Methacrylic polymers were investigated as a function of their thermal stability which is reveals the polymer resistance against thermal degradation. Basically, it is renowned that laser-photoinitiated polymers are more crosslinked than conventionally initiated polymers.

As shown in Figs. (7, 8 and 9), TGA scans were conducted to compare between Crosslinking behavior in both of conventional (thermal and photochemical) synthesized polymers and laser synthesized polymers. In general; as the intensity of laser used increased, as a result, the thermal stability of the synthesized polymer increased too. This behavior may ascribe to the increasing amount of crosslinked chains within the polymer content with increasing of laser intensity.

For example, conventionally synthesized PMMA degraded at a remarkable lower temperature [6] than laser synthesized PMMA did (about 77 °C lower in the case of 20W CO<sub>2</sub> laser initiated PMMA). Thermally synthesized PMMA starts to lose its weight from the temperature of 170 °C whereas the laser initiated PMMA start to change their weight between (180-247 °C). It could be seen that CO<sub>2</sub> laser initiated PMMA polymers start to lose their weight in the range of (215-247 °C, and the higher intensity of 20W CO<sub>2</sub> laser used, significantly led to make PMMA lose its weight at the temperature of 247 °C .

#### **4- Solubility Tests:**

Substantially, solubility tests were made in common organic solvents of the vinyl polymers that synthesized by conventionally and laser initiated free radical polymerization in this study have cleared that laser initiated polymers withstand to solve in most organic solvents which are appropriate solvents to solve conventionally synthesized vinyl polymers.

From the solubility results mentioned in table (2) in the experimental part It could be inferred that with increasing of applied output power of CO<sub>2</sub> laser, it could be seen that the resistance of polymer synthesized by such a laser against most organic solvents increasing too.

The results mentioned above are indicating great evidences of the relatively high degree of Crosslinking which emergent as a result of using laser in initiation process instead of conventional initiation methods, and it is noteworthy that (CW 20W CO<sub>2</sub> laser) photo-synthesized polymers have the great deal of solvent resisting due to the relatively higher degree of Crosslinking within.

#### **Polymerization mechanism:**

Under the intense infrared irradiation, the vibrations of the nuclear framework of these molecules are in fact most realistically represented by an essentially random mixture of the normal and different modes of vibration, between which there is completely free energy flow. Hence, absorption of CO<sub>2</sub> laser light by monomer molecule at one particular frequency (wavelength: 10.6 μm) corresponding to a fundamental vibration, may lead to dissociation of more than one bond [i.e., other

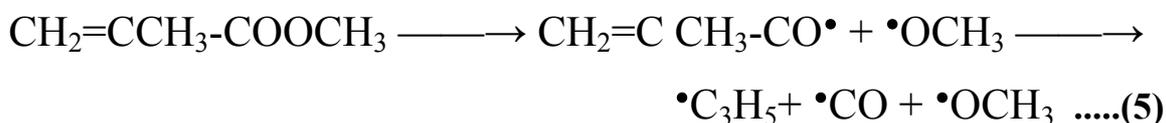
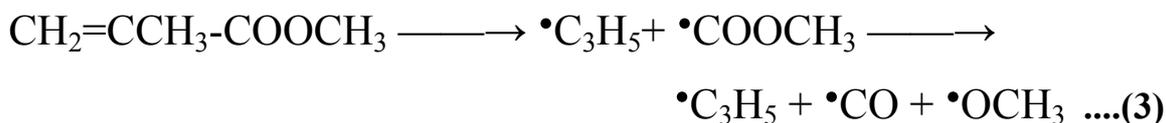
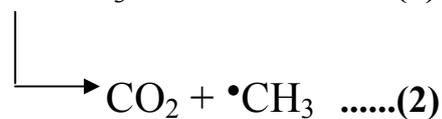
bonds as well as  $\alpha$ -carbon bond (C-C bond)], through multi-photon absorption process owing to the resulted various amounts of energy being deposited in each of the vibrational modes. Then, it may suggest that absorption of CO<sub>2</sub> laser light by acrylic and methacrylic molecules in this study, plausibly results in dissociation of the weakest bonds in their structure and consequently formation of relatively higher number of free radicals comparing with that when the laser photo-initiated polymerization of these monomers done with N<sub>2</sub> and (He-Ne) lasers [11], according to the wavelength and laser intensity employed.

It conclude by increasing of the applied (CW CO<sub>2</sub>) laser light power outputs up to (20W) reveals in increasing of the number and types of free radical species, and the corresponding DSC and TGA figures virtually demonstrate that the thermal behavior and thermal stability are relatively high and better for 20W CO<sub>2</sub> laser synthesized acrylic and methacrylic polymers, this may ascribed to the highly Crosslinking and Crystallinity produced as a result of this increased number of free radicals.

The weakest chemical bonds within MMA molecular structure are [12]:

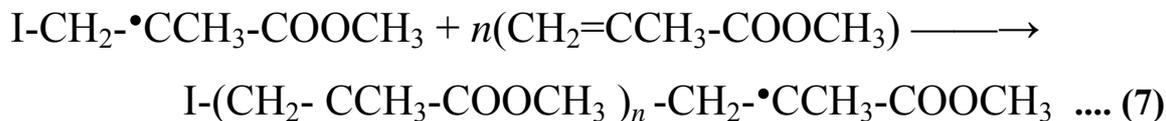
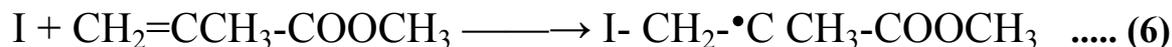
1.  $\alpha$  (C-C) bond , bond energy: 82.6 k.cal.mol<sup>-1</sup> or ( 3.58 eV).
2. (C-O) bond, bond energy: 85.5 k.cal.mol<sup>-1</sup> or (3.7 eV).
3. (C-H) bond, bond energy: 98.7 k.cal.mol<sup>-1</sup> or (4.28 eV).

However, the photo-initiation step by multi-photon absorption process using (CW CO<sub>2</sub>) laser in the sequence of free radical polymerization of MMA monomer schematically demonstrated below, by take (MMA) monomer as an instance, and taking in account that the dissociation may occur for some or all the above bonds in the monomer molecule and further dissociation of the emergent free radicals is possible:



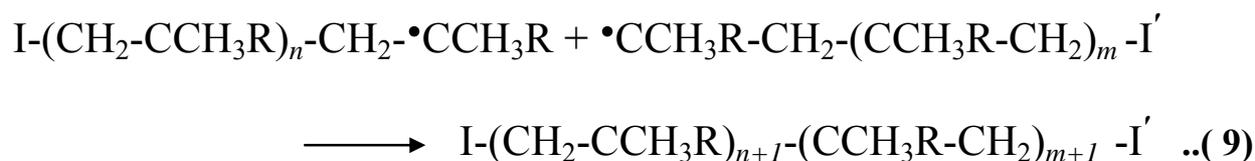
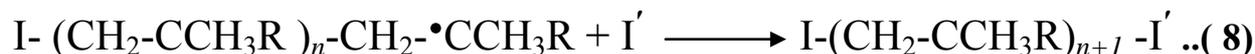
**CW-CO2 Laser photoinitiated polymerization of Methyl Methacrylate.**

All the produced radicals above (hereafter, denoted by I) can initiate free radical polymerization of other (MMA) molecule:

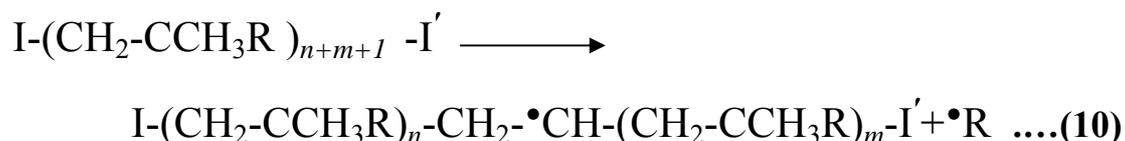


The polymer radical produced in Eq. 7 proceeds in propagation and termination steps:

Free Radical polymerization that initiated by laser radiation terminates by the recombination of the propagating polymer radical with either another polymer radical or initiating radical (I):



By increasing the irradiation duration, multi-photon absorption of IR laser light possibly occur, as a result, poly (methyl Methacrylate) dissociates the pendent group, R ( i.e., COOCH<sub>3</sub> group ) as was suggested from the photolysis of PMMA [13]:



This polymer radical (p<sub>0</sub>) can again initiate radical polymerization with MA monomer to result in the formation of a long side polymer chain as in the case of graft co-polymerization. Propagation of long side polymer chains occurs at many photo-generated active sites in the polymer structure directly exposed to the laser light. Furthermore, recombination between the two polymer radicals, (i.e., p<sub>0</sub>-p<sub>0</sub>) results in Crosslinking between the polymer chains to make the polymer final product insoluble into most organic solvents.

**References:**

- 1) Hong, K, H. Zhang, J. W. Mays, and R. D. Rogers, "Chem.Commun", 1368, (2007).
- 2) Harrisson, S., S. R. Mackenzie, and D. M. Haddleton, "Macromolecules", 36, 5072, (2008).
- 3) Akgun, M., Daran, N., and Dincer, S., "Polymer International", 54, 374-380, (2005).
- 4) Decker C., Moussa K., "*J. Coat. Technol.*", 65: 819, 49, (1993).
- 5) Tylor K., Dundast D., "*Phil. Trans. R. Soc.*", London, A, 1331, (1999).
- 6) Armarego W., Perrin D., "Purification of Laboratory Chemicals", 4<sup>th</sup> ed., 270, 1996.
- 7) Fleming I., "*Spectroscopic Methods in Organic Chemistry*", 2<sup>nd</sup> ed., McGraw-Hill, England, 87, (1973).
- 8) Urbanski J., Czerwinski W., "*Handbook of Analysis of Synthetic Polymers and Plastics*", Halsted Press, 45, (1977).
- 9) Wee S., Park S., "*Bull. Korean Chem. Soc.*", Vol. 22, No.8, 914, (2001).
- 10) Morita H., Sadakiyo T., "*J. Photochem. Photobiol.*" A: Chem., 87, 163, (1995).
- 11) Morita H., Freitas J., El-Sayed M., "*J. Phys. Chem.*", 95, 1664, (1991).
- 12) Gray H., "*Electrons and Chemical Bonding*", W. A. Benjamin Inc., New York, 90, (1965).
- 13) Pallix J., Schuhle U., "*Anal. Chem.*", 61, 805, (1989).