

1-1 What are polymers?

It is difficult to visualize civilized life without polymers or polymer products. Polymer has become the most important materials due to its use in many fields from domestic use up to aerospace shuttles ⁽¹⁾.

Polymers are long chain molecules consisting of repeating units called monomers. The composition of the monomer, and the way in which the monomers are linked, determine the properties of the polymer.

Polymers have existed for centuries in the form of oil and resins which called natural polymer. It was only at the end of the nineteenth century that scientists such as Charles Good-year began to manufacture artificial polymers ⁽²⁾ by process known as polymerization.

However, polymer is produced by two main polymerization processes:

- Step-growth polymerization.
- Chain-growth polymerization.

There are four methods for polymerization:

Bulk, solution, suspension and emulsion polymerization.

1-2 Uses of polymers:

Polymers, in general, have a range of applications that far exceeds that of any other class of material available to man. Current applications extend from adhesives, coatings, foams, and packaging materials to textile and industrial fibers, elastomers, and structural plastics. Polymers are also used for most composites, electronic devices, biomedical devices, optical devices, and precursors for many newly developed high-tech ceramics ⁽³⁾.

Conjugated polymers for example are materials for electronic applications due to the tunability of their properties through variation of

their chemical structure. Their applications, which currently include light-emitting diodes (LEDs), field effect transistors (FETs), plastic lasers, batteries, and sensors, are expanding too many new areas ⁽⁴⁾.

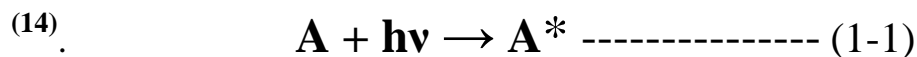
A conjugated polymer chain can be considered as a series of connected chromophores with various effective conjugation lengths ⁽⁵⁾. Therefore, an exciton travels along the energy gradient established among the chain segments with statistically distributed effective conjugation lengths.

Moreover polymer solutions in particular poly-electrolytes have significant application in many commercial products such as paints, inks, cosmetics, foodstuff and water-borne coatings ⁽⁶⁾. This importance arises as a consequence of the growing concerns about the safety of more traditional organic-based fluids. However, in the most of these applications polymers act as viscosity, rheology modifiers and used as analogous to understand biological macromolecules behavior ⁽⁷⁾. Therefore, polymer and polymer solutions have been studied widely by different classical techniques, including ¹H-NMR, viscosity measurement and potentiometric titration ⁽⁸⁻¹²⁾.

In the past two decades, the photophysical processes, fluorescence, excimer emission and energy transfer, are used as tools in order to examine conformation, compatibility, flexibility, and stereoregularity of the polymer in relation to many factors, e.g. temperature, solvents and molar mass ⁽¹³⁾.

1-3 Photophysical processes:

It is known that reaction of light with matter induces absorption of photons energy. when a species (A), for examples, absorbed photon that leads to the formation of short-lived electronically excited molecule, A*



After absorption of a photon a molecule exists in an excited state, and because it is not in thermal equilibrium with its surroundings, it will, in general, have only a short lifetime since a number of processes can contribute to the deactivation of the excited molecule to the lower state. These processes include both chemical and physical processes and are summarized in Table (1.1). If the process gives rise to chemically distinguishable products, it is said to be photochemical; otherwise, it is labeled as photo physical. The alternate pathways compete with each other for energy dissipation and the dominant routes are usually determined by factors such as the structure and environment of the molecule, the nature of the excited state, and temperature, pressure, and other experimental conditions.

Table 1.1 Modes of energy dissipation for electronically excited molecules

Photophysical processes	Conversion to thermal energy Conversion between states Energytransfer Radiative dissipation
Photochemical processes	Free radical formation Cyclization Intramolecular rearrangement Elimination

However, a convenient description of the modes of energy dissipation from possible excited states is given by the Jablonski diagram Figure(1.1)⁽¹⁵⁾.

In this diagram only the two lowest energy excited states, S_1 and T_1 , are shown. There will, of course, be higher energy singlet and triplet states, but in condensed phases these two are the most likely to be involved in photochemical reactions ⁽¹⁶⁾.

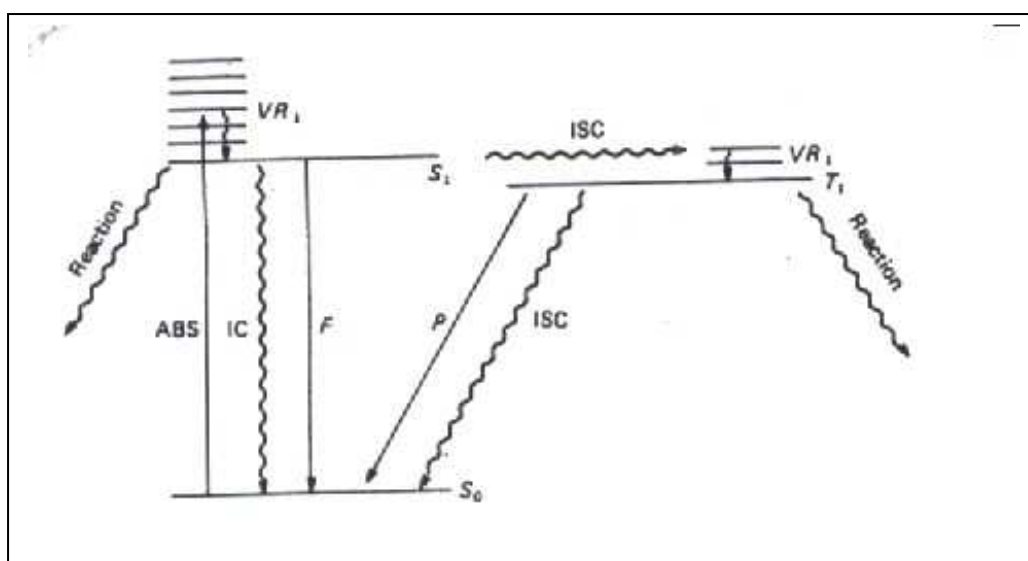
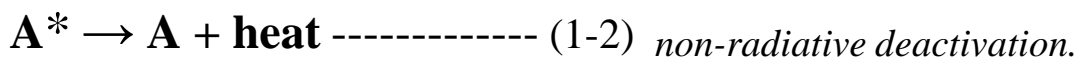


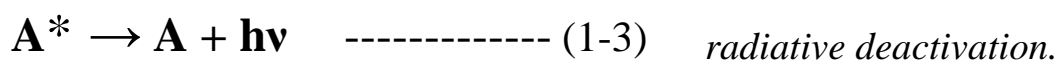
Figure (1.1) Energy level diagrams showing deactivation pathways for a typical organic chromophore. ABS= absorption, VR₁= vibrational relaxation, IC= internal conversion, F= fluorescence, ISC= inter system crossing, P= phosphorescence, S_0 = ground state singlet, S_1 = first excited singlet, T_1 = first triplet ⁽¹⁵⁾.

In general, electronic conversions between states of identical multiplicity are known as *internal conversion* (IC) ⁽¹⁷⁾, whereas those between states of differing multiplicity are known as *intersystem crossing* (ISC) ⁽¹⁸⁾. These processes are similar in that they involve a conversion of electronic energy to vibrational energy (heat) which is followed by rapid relaxation to the lowest vibrational level of the lowest

excited state. They occur without emission of a photon of light i.e. no radiation is emitted, the process is called radiationless or non-radiative deactivation process.



On the other hand, an electronically excited molecule can lose its energy by emission of radiation which is known in this case radiation deactivation or luminescence ⁽¹⁹⁾.



An electronically excited species can return to the ground state by emission of a photon. If the multiplicities of ground and excited states are the same, the emission is called “fluorescence”. If different it is called “phosphorescence” ⁽¹⁸⁾.

1-3-1 Fluorescence:

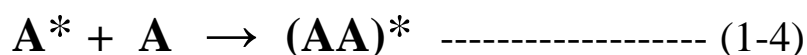
Fluorescence is light emission due to an electronic transition, without change of multiplicity ^(20, 21), and this radiative emission process occurs from the lowest excited singlet state (S_1) to the ground singlet state (S_0) ⁽²²⁾ Figure (1.1). Rapid vibrational relaxation and internal conversion in the solid and liquid state enables the emission to take place, usually from the lowest vibrational level of the first excited singlet state ⁽²³⁾. The consequence of this relaxation is that the shorter absorbed and longest emitted wavelength. One of fluorescence related processes is excimer phenomenon ⁽²⁴⁾.

Generally, fluorescence has been applied to the greatest extent in the life sciences where trace concentrations of metabolites, drugs, etc. must be determined quantitatively. For example, thiamine and riboflavin and their metabolites can be determined in trace amounts in biological

tissues and fluids. Fluorescence is also used in quality control of drug dosage ⁽²⁵⁾.

1-3-2 Excimer:

The term “excimer” has become familiar as the name of an excited-state complex (excited dimer) formed by a couple of aromatic molecules (chromophores) placed face to face at short distance. The formation of an excited dimer is due to the association of two aromatic groups one of which has electronically excited ⁽²⁶⁾ as in the following equation:



During the decomposition of excimer one may observe excimer fluorescence band at a considerably lower energy region than that of monomer fluorescence (normal fluorescence) ⁽²²⁾ as shown.



Long ago, the formation of excited dimer had been considered by Kautsky and Merkel ⁽²⁷⁾.

Stevens and Hutton ⁽²⁸⁾ proposed the name “excimer” instead of excited dimer, which became generally accepted within a few years. Klöpffer ⁽²⁹⁾, a review on excimers mentions that the absence of excimer emission does not prove the absence of excimer formation, because rapid dissociation may have taken place before emission.

Furthermore, if the life-time of the excited species is short, then a high concentration of excimer is needed in order to observe its emission. Concentration quenching of fluorescence, arising from excimer formation, is followed in some cases by rapid photochemical reaction:

e.g. in anthracene. However, there are two types of excimers, intermolecular excimer and intramolecular excimer:

1-3-2-1 Intermolecular Excimer:

In 1954 Förster and Kasper ⁽³⁰⁾ discovered that when the concentration of pyrene solution was increased a new structurless emission band appeared, red shifted relative to the normal pyrene emission which its intensity was decreasing after reaching a critical concentration, Figure (1.2).

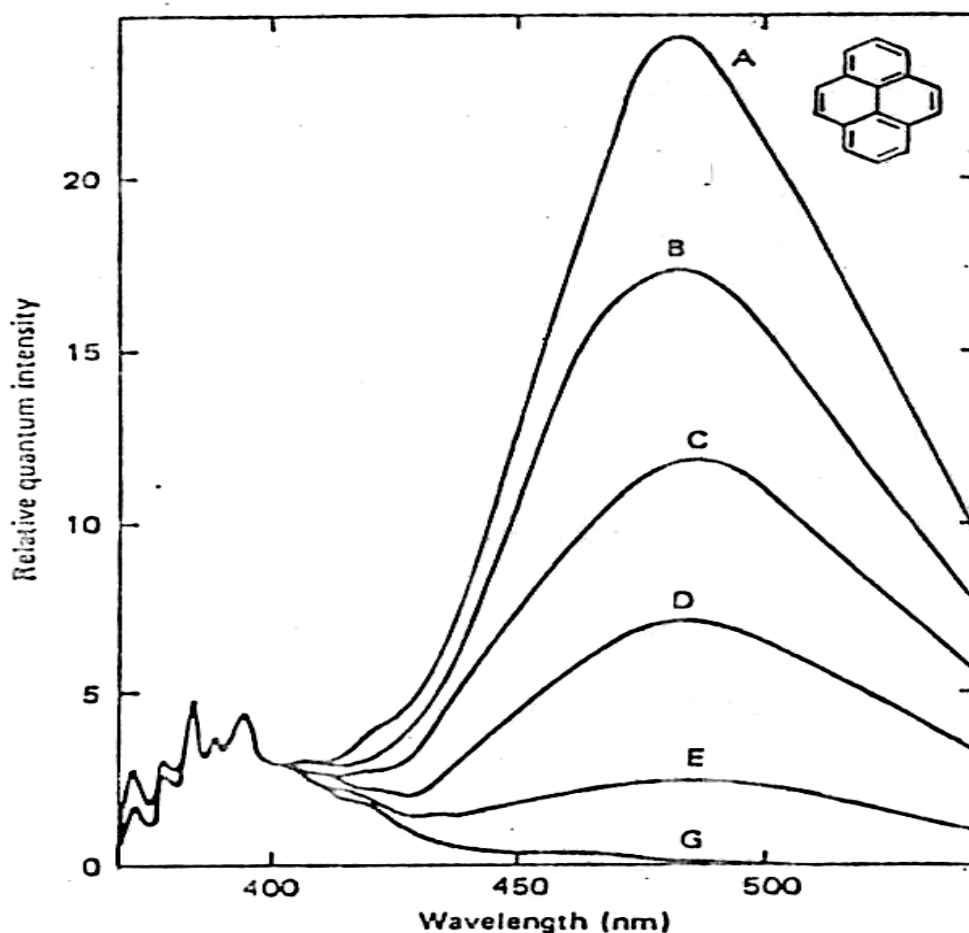


Figure (1.2) Fluorescence spectra of pyrene solutions are in cyclohexane at different concentrations.

A, 10^{-2} M; B, 7.75×10^{-3} M; C, 5.5×10^{-3} M; E, 10^{-3} M; G, 10^{-4} M.

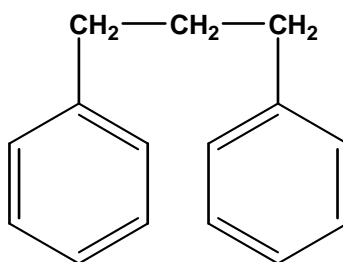
This new emission was ascribed to a complex formation between the ground singlet pyrene state (py) and the excited singlet pyrene state (py*) molecules as in the equation:



This interaction was formed between two molecules in solution; therefore it was named an intermolecular excimer.

1-3-2-2 Intramolecular Excimer:

Hirayama ⁽³¹⁾, the first to study the intramolecular excimer phenomenon, which the excimer is formed between two chromophores attached to the same molecule. This molecule can display intramolecular excimer emission and constitutes a typical small molecule model unit for a vinyl polymer with terminal chromophores. Hirayama found that 1, 3-diphenyl propane [1] exhibits typical excimer emission independent on concentration.

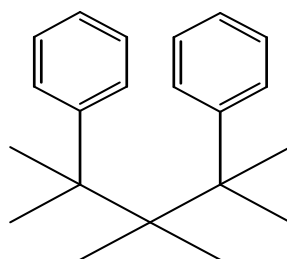


[1]

By contrast, Hirayama did not observe any excimer emission for other α - ω -diphenyl alkanes. It was believed at the time that intramolecular excimer formation was possible only if the two chromophores are linked together by three atoms bridge. This conclusion has become known as “Hirayama’s n=3 rule” and confirmed by Chandross and Dempster ⁽³²⁾ working on α - ω -dinaphthyl alkanes. Later, Zachariasse and Kuhnle ⁽³³⁾, found that such restriction does not apply to

all chromophores, and that α - ω -dipyrenyl alkanes form intramolecular excimer even with longer hydrocarbons separating the chromophores.

The reason for the $n=3$ rule is that apparently no other structure will allow a complete coplanar arrangement for adjacent 1, 3-aromatic rings where excimer have the gauche-gauche conformation with interplanar distances of ca. 3.2 \AA ⁽¹⁶⁾ as in [2]:



[2]

1-3-3 Photophysical Processes In Macromolecule:

As mentioned previously, the photophysical processes, fluorescence, excimer formation and fluorescence quenching have been used as tools to study biological and man-made macromolecules. Here a fluorescence group is introduced into a macromolecule as a molecular sensor of the environment^(34, 35). One chooses this group with acknowledge of it's spectroscopy in the hope that any change in it's emission spectrum will gives detailed information about the macromolecule system itself.

The application of this technique has been used in biology⁽³⁶⁾, where from the spectroscopy of these groups informations could be provided about hydrophobicity in proteins, local polarity at water-membrane interface, distances in antibody-antigen interaction, and other informations⁽³⁷⁻³⁹⁾.

Time resolved fluorescence spectroscopy (TRFS) was found to be particularly useful in the study of several types of polymers in solution, and in the presence of additives ⁽⁴⁰⁻⁴⁷⁾. Time resolved anisotropy decay of a fluorescent probe attached to a polymer chain reflects the rotational relaxation of the probe, and the local dynamics of the polymer segments in solution ⁽³⁵⁾.

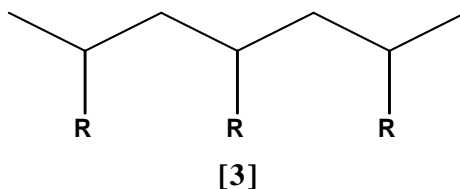
The dependence of the segmental dynamics as a function solvent viscosity was studied by (TRFS) using anthracene attached to 1,2 poly butadiene ^(48, 49). The polymer local dynamics as well as the structural properties and relaxation processes of polymer and blends were studied by steady state and dynamic fluorescence using anthranyl and pyrenyl groups ⁽⁵⁰⁻⁵²⁾. Fluorescence studies of polymethacrylic acid (PMAA) and polyacrylic acid (PAA) containing aromatic fluorescent probes such as naphthalene, anthracene and pyrene have been carried out by many authors to elucidate the properties of those poly electrolytes in different solvents, pH, and surfactant addition ⁽⁵³⁻⁵⁷⁾.

Photophysical methods also, are used to study the effect of crystallinity on the distribution and mobility of probe molecules in well-characterized polymer films. A combination of steady-state and time-resolved methods indicate that probe molecules are excluded from lamella-like crystalline zones in the polymer systems. This effect tends to concentrate the probes into the amorphous zones that exist between crystallites. Using the pyrene-perylene donor acceptor pair as a "molecular ruler", it was shown by Förster analysis that the amorphous zones form a network structure throughout the polymer film. Mobility within this region is greatly reduced from that in solution and is very size selective, as indicated by the quenching rate constants of the pyrene triplet state by oxygen, azulene and ferrocene ⁽⁵⁸⁾.

Group of researchers used probe labeled polymer in solar photosynthesis or isomerization of pre-vitamin D₃ in aqueous solution ^(59, 60) in photo-degradation of organic pollutants in water ⁽⁶¹⁾ and evolution of hydrogen from water ⁽⁶²⁾.

1-3-4 Excimer in Synthetic Macromolecules:

Synthesized polymer by addition polymerization of vinyl monomer has a general structure of the form given in [3].



In which the R groups are separated by at least three carbon atoms. If R fluorescence groups (chromophores), one should expect that these groups capable of forming excimers. This structure is efficient within the term of Hirayama's $n=3$ rule. A number of vinyl polymers have been researched by many authors including polystyrene ⁽⁶³⁻⁶⁷⁾, poly(1-vinylnaphthalene), poly(2-vinylnaphthalene) ⁽⁶⁸⁻⁷⁰⁾, poly(1-vinylpyrene) ⁽⁷¹⁾ poly(N-vinylcarbazole) ⁽⁷²⁻⁷⁶⁾, poly(acenaphthalene) ^(77,78) and poly(naphthyl methacrylate) ^(79, 80). These researches reveal that the fluorescence emission of the vinyl polymers consists of two band type; one is the chromophore's normal fluorescence emission band, and the other is a broad structureless emission band, shifted by ca. 4000 - 6000 cm^{-1} . This structureless band resembles both the emission band observed in concentrated aromatic hydrocarbons and the emission band described by Hirayama ⁽³¹⁾ in 1, 3-di phenyl propane and therefore attributed to

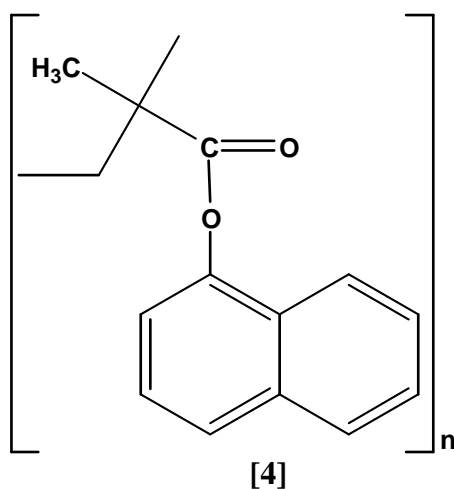
excimer emission. At the same time, it was found that these excimer spectra are independent of polymer concentration; thus they originate from an intramolecular excimer, formed between two adjacent chromophores on the same polymer chain. Vala et. al., ⁽⁶⁵⁾ have postulated a mechanism to explain excimer formation in polystyrene, poly(1-vinylnaphthylene) and poly(2-vinylnaphthylene), and also the tacticity, atactic and isotactic. Thus, once the incident light has been absorbed by a chromophore on the polymer chain, within the lifetime of the excited state, rapid rotational and vibrational motions of the chromophores create conformation which is favorable for excimer formation. Furthermore, these authors proposed that singlet excited states migrates through the polymer chain as excitons (the term used for random hopping from one chromophore to another) ⁽²⁹⁾ until a conformation favorable for excimer formation named the “excimer formation site” ⁽⁷¹⁾ is encountered. They also interpreted the normal fluorescence emission in terms of radiative return to the ground state of an excited chromophore created by direct absorption of the incident light, or as the radiation from an excited chromophore produced by dissociation of an excimer. Many observations support this mechanism, particularly the quenching of the excimer emission by oxygen to a greater extent than its normal fluorescence ⁽⁶⁵⁾. However, recently, Bunz and Coworkers ⁽⁸¹⁻⁸³⁾ suggested that the additional absorption band observed in the PPE films that is absent in solution is not due to the ground–state aggregation but to the planarization of PPE poly(phenylene ethynylene) backbones induced by morphological aggregations.

The evident difference between a ground–state aggregate and an excimer is the presence of a directly excitable red–shifted absorption

band. This fact has been used to discriminate the presence of a ground-state aggregation in conjugated polymer films.

On the other hand, Ishii et. al.,^(66, 67) and David et. al.,⁽⁸⁴⁾ have shown that tacticity has a considerable effect on excimer formation. If the polymer is atactic, then the intensity ratio for excimer emission, related to the normal fluorescence, is less than that encountered in the isotactic polymer. This difference arises because the isotactic polymer exists in 3-1 helix structure, which provides more excimer formation sites than that of atactic polymer. Harrah and Frank⁽⁶⁸⁻⁶⁹⁾, have accounted for the effect of chain conformation change on excimer formation in fluid solution. These authors suggested that in the fluid state, interconversion of chain conformation proceeds rapidly, and that the life-time of a particular conformation is limited by collision processes with solvent. If the residence time of the excitation on a chromophore at a non-excimer forming site is long enough, solvent collision with polymer will cause rotational sampling of chain conformation leading to excimer formation. If the residence time is insufficient or the rotational sampling is slow, excimer sampling may occur by competitive trapping at a suitable excimer site formed prior to the onset of excitation.

Excimer formation is not limited to the vinyl aromatic polymers in which the aromatic ring is joined directly to the backbone. Therefore, excimer formation in poly(naphthyl methacrylate)⁽⁸⁵⁾ in which a spacer between the aromatic moieties are separated by at least seven atoms as in [4] was investigate.



Guillete et. al., ^(79, 80) founds excimer emission in poly(1-naphthyl methacrylate) at 375-390 nm in addition to the monomer fluorescence at 344nm. The intensity of these spectra varied considerably with the solvent. When excimer formation being greater in a poor solvent and less in a good solvent ⁽⁸⁶⁾. It appears that excimer formation takes place between two relatively remote naphthalene chromophores in the chain loops rather than between next nearest neighbor chromophores. This is explained in terms of chain contraction anticipated in a poor solvent and the expansion in a good solvent. In poly(2-naphthyl methyl methacrylate)⁽⁷⁹⁾ excimer formation is said to be solvent-independent; and it is thought excimers are formed between next nearest neighbor groups on the chain, due to flexibility of polymer chains. Newly, excimer emission was used as a valuable tool to elucidate the state of intra- and intermolecular aggregation of aromatic groups in liquid crystalline polymers, and to deduce the spatial arrangement of these on the polymer chains ⁽⁸⁷⁻⁸⁹⁾.

1-4 Aim of the work:

It is known that cinnamic acid (monomer) does not have the ability to be polymerized as a homopolymer, but it can be copolymerized with other monomers like styrene, acrylate ---- etc .

Accordingly in our present work we try to synthesize macromolecules polymers labeled with naphthyl chromophores in their structures through copolymerization of 3-(1-naphthyl) acrylic acid with methacrylic acid and methyl acrylate monomers and study their solutions properties by photophysical processes.

2-1 Chemicals:

The following materials and chemicals used in this work were obtained from different companies as listed below:-

Compounds	Supplied form	Purity
Alpha-naphthaldehyde	B.D.H.	98%
Acetic anhydride	B.D.H.	97%
Potassium acetate	B.D.H.	98%
Sodium carbonate	Aldrich	99%
Methacrylic acid	B.D.H.	97%
Methyl acrylate	B.D.H.	97%
Methanol	Fluke	99%
Ethanol	B.D.H.	99%
Diethyl ether	B.D.H.	99%
Chloroform	Hopkins and Williams	99%
Acetonitrile	B.D.H.	99%
Petroleum ether	B.D.H.	98%
Benzoyl peroxide	B.D.H.	98%
Toluene	B.D.H.	98%
Dioxane	Fluka	99%

2-2 Instruments and Equipments:

- Shimadzu Fourier transforms infrared model F.T.IR 8300 (Kyoto, Japan) was used to record the IR spectra of the prepared polymers. Infrared spectra- photometer as KBR disc at Al – Nahrain University Chemistry Department.
- Melting points were recorded on hot stage Gallen kamp melting point apparatus, and are uncorrected.
- Double – beam UV-VISBLE spectrophotometer (UV 1650 CP), Shimadzu / (Japan), interfaced with computer via Shimadzu UV – VISBLE prop data system program at Al – Nahrain University Chemistry Department.
- Spectrofluorophotometer model (RF – 1501), Shimadzu, (Japan), with internal computer system at Al – Nahrain University Chemistry Department.
- Viscosity measurements were performed using viscometer type AVIS 300 H.W (factor= 0.03095 multiply by follow time), in Ibn- Sina Company.
- The N.M.R. spectra were recorded by NMR 300 MHz Ultra Shield Bruker Company Switzerland, in Al al – Byat University / Jordan.
- LV-08 supplies ultra pure water of $18 \mu\Omega.\text{cm}^{-1}$ with TORAY'S ion exchange fiber.
- High vacuum line to carry out reaction experiments and distillation of some chemicals was assembled in the laboratory as illustrated in Figure (2-1).

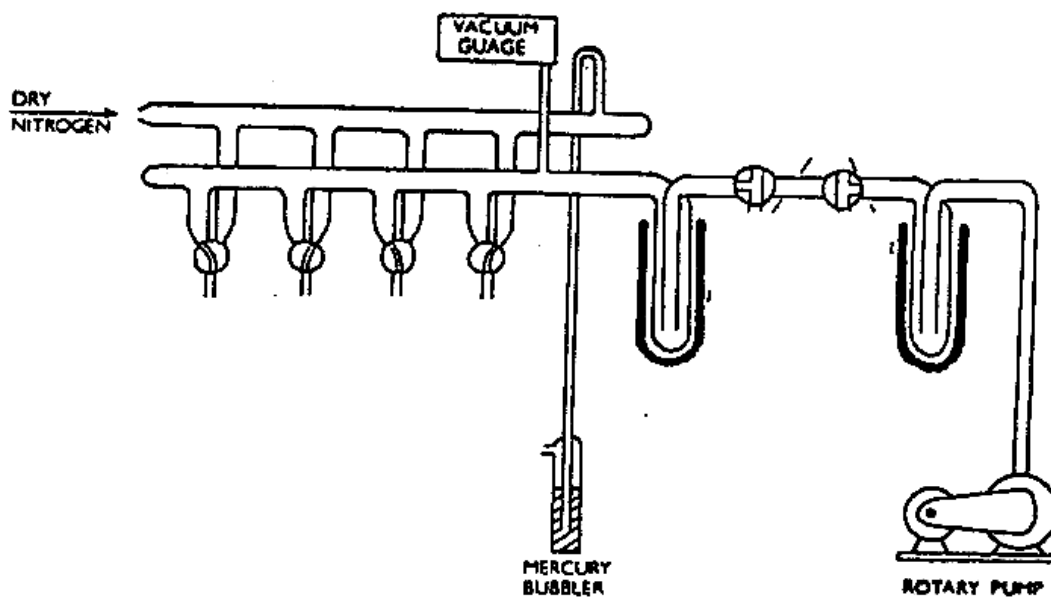


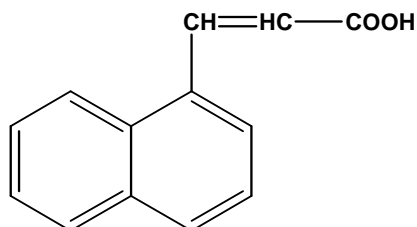
Figure (2-1)

A = Taps.

B = Liquid Nitrogen traps.

2-3 Preparation of compounds:

2-3-1 Preparation of 3-(1-naphthyl) acrylic acid:



A mixture of freshly distilled (α -naphthaldehyde) (4.6 g, 0.029 mole), potassium acetate fused (2.9 g, 0.03 mole) and excess of acetic anhydride (7.574 g, 0.037 mole) were placed in a dry 100 ml round bottom flask fitted with an air condenser carrying a silica gel guard tube. The reaction mixture was heated in a sand bath up to 160 C° for one hour, then at $170 - 180\text{ C}^\circ$ for three hours. The mixture was poured out whilst hot onto about 100–150 ml distill water and made basic by the addition of saturated aqueous sodium carbonate solution. The solution was filtered then the filtrate was acidified with concentrated hydrochloric acid with vigorous stirring until the evolution of carbon dioxide was ceased. A white precipitate was formed, filtered and dried under vacuum, final product was re-crystallization from ethanol. Yield (4g, 68%) and the melting point is $(210-212)\text{ C}^\circ$. The literature serve is $(211-212)\text{ C}^\circ$ ⁽⁹⁰⁾.

2-3-2 Preparation of polymers:

2-3-2-1 Preparation of poly(methacrylic acid) homopolymer:

Methacrylic acid monomer (2.03 g, 0.024 mole) was placed in a 50 ml round bottom flask purged with nitrogen gas for several times. Benzoyl peroxide (0.01 g) was added under nitrogen atmosphere, and the reaction mixture was heated up to 70 C° for one hour on a water bath. A faded yellow solid (polymer) was formed. The polymer was dissolved in methanol solvent and re-precipitated by diethyl ether.

2-3-2-2 Preparation of poly(methyl acrylate) homopolymer:

Methyl acrylate monomer (4.78 g, 0.056 mole) was placed in a 50 ml round bottom flask purged with nitrogen gas for several times. Benzoyl peroxide (0.015 g) was added under nitrogen atmosphere, and the reaction mixture was heated up to 70 C° for one hour on a water bath. A highly viscous (elastic) polymer was formed. This polymer was dissolved in chloroform or acetonitrile solvent and re-precipitated by petroleum ether.

2-3-2-3 Preparation of poly(methacrylic acid and 3-(1-naphthyl) acrylic acid) copolymer:

A mixture of methacrylic acid monomer (3.045 g, 0.035 mole) and 3-(1-naphthyl) acrylic acid (5×10^{-4} mole, 0.1 g) were placed in 50 ml round bottom flask then purged with nitrogen gas. Benzoyl peroxide (0.01g) was added under N₂. The reaction mixture was heated up to 70 C° for one hour on a water bath, a solid yellow polymer was formed. The polymer was purified by dissolving in methanol solvent and re-precipitated in diethyl ether for 4 times to be sure that all 3-(1-naphthyl) acrylic acid monomer was removed. Two types of copolymers were

prepared with different weights (0.15g and 0.05g) of 3-(1-naphthyl) acrylic acid.

2-3-2-4 Preparation of poly(methyl acrylate and 3-(1-naphthyl) acrylic acid) copolymer:

A mixture of methyl acrylate monomer (4.78 g, 0.056 mole) and 3-(1-naphthyl) acrylic acid (5×10^{-4} mole, 0.1 g) were placed in 50 ml round bottom flask then purged with nitrogen gas. Benzoyl peroxide (0.01 g) was added under N_2 . The reaction mixture was heated up to 70 C° for one hour on water bath, a viscous (elastic) yellow polymer was formed. The polymer was purified by dissolving in chloroform or acetonitrile solvent and re-precipitated in petroleum ether for 4 times to be sure that all 3-(1-naphthyl) acrylic acid monomer was removed. Another type of copolymer was prepared with different weight (0.05g) of 3-(1-naphthyl) acrylic acid.

2-3-2-5 Preparation of poly(methacrylic acid, methyl acrylate and 3-(1-naphthyl) acrylic acid) tricopolymer:

A mixture of 3-(1-naphthyl) acrylic acid (0.1 g, 5×10^{-4} mole) with methacrylic acid (3.045 g, 0.035 mole) and methyl acrylate (0.287 g, 3×10^{-3} mole) were placed in 50 ml round bottom flask then purged with nitrogen gas. Benzoyl peroxide (0.01 g) was added under N_2 . The reaction mixture was heated up to 70 C° for one hour on a water bath, a solid yellow precipitate was formed. The polymer was purified by dissolving in methanol solvent and re-precipitated in diethyl ether for 4 times to be sure that all 3-(1-naphthyl) acrylic acid monomer was removed.

2-3-2-6 Preparation of poly(methacrylic acid and 3-(1-naphthyl) acrylic acid) copolymer in toluene solvent:

A mixture of methacrylic acid (3.045g, 0.035 mole) with 3-(1-naphthyl) acrylic acid (0.1 g, 5×10^{-4} mole) was dissolved in dry toluene (22.452 g, 0.14 mole) and flushed with N₂ gas. Amount of benzoyl peroxide (0.01 g) was added to the reaction. The reaction mixture was heated to the boiling point of the solvent, after half hour a precipitate polymer was formed. This product was purified by methanol solvent and re-precipitated in diethyl ether for 2 times to be sure that all 3-(1-naphthyl) acrylic acid monomer was removed.

2-4 Measurements and Equipments:

2-4-1 Ultraviolet Measurement:

For U.V. spectrum measurements stock solutions of the (polymer or the monomer) (0.01 g) were prepared by dissolving the compound in (5 ml) of the solvent (methanol, acetonitrile, chloroform) and the volume completed to the mark in (10 ml) volumetric flask. Then series of dilute samples were prepared for the measurements. All samples were measured at room temperature by ultraviolet device.

2-4-2 Fluorescence Measurement:

For fluorescence measurements stock solutions of the (polymer or the monomer) (0.01 g) were prepared by dissolving the compound in (5 ml) of the solvent (methanol, acetonitrile, chloroform) and the volume completed to the mark in (10 ml) volumetric flask. Then series of dilute samples were prepared for the measurements which were carried out at room temperature.

Fluorescence measurements of 3-(1-naphthyl) acrylic acid solutions were carried out with excitation wave length of 311 nm at methanol solvent and 317 nm at acetonitrile solvent.

Fluorescence measurements for polymer solutions were carried out at the same conditions; expect the excitation wave length for naphthyl group was 282 nm ^(91a).

2-4-3 Viscosity Measurement:

The viscosities of solvent and the polymer solutions were measured at 298.15 K.

Solutions of polymer were prepared by dissolving (1 g) of the polymer in (100 mL) of the initial solvent and then diluted with calculated amount of the same solvent to get the different concentrations of the polymer solution in one solvent.

2-4-4 Determination of the molecular weight (M_v) of polymers (1 and 2) by viscosity:

Usually the molecular weights of these polymers were calculated by measurements of the viscosity of dilute solutions; the viscosity and molecular weight are related by the Mark-Houwink equation ^(91b).

$$[\eta] = K M^\alpha \text{ ----- (1)}$$

$[\eta]$ = is the intrinsic viscosity.

K, α = are constants dependent upon the polymer-solvent system at a particular temperature.

The intrinsic viscosities of polymer solutions were measured by the following equations:

Relative viscosity $\eta_{rel.}$ was calculated by follow the equation.

$$\eta_{rel.} = t/t_0 \text{-----} (2)$$

The flow time of pure solvent is t_0 and the flow time of polymer solvent is t .

Specific viscosity

$$\eta_{spc.} = \eta_{rel} - 1 \text{-----} (3)$$

And the reduced viscosity

$$\eta_{red.} = \eta_{spc.}/c \text{-----} (4)$$

c = Concentration of polymer solution (g/100 ml).

The intrinsic viscosity was calculated using

$$[\eta] = \text{Lim} \dots \eta_{red} .$$

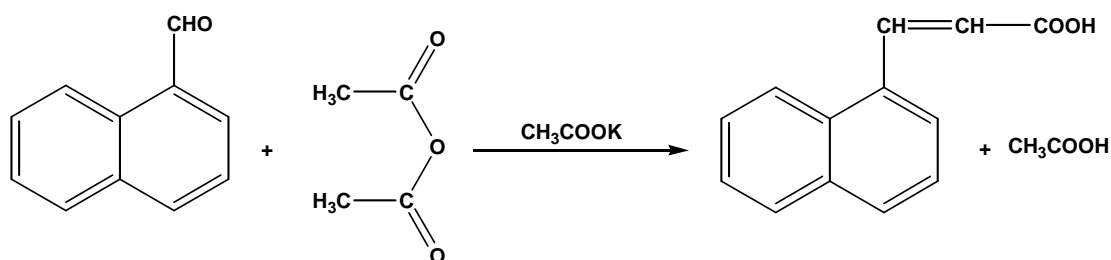
$$[\eta] = k M^a$$

a, k is constants .

η is intristic viscosity .

3-1 Synthesis and characterization of 3-(1-naphthyl) acrylic acid (compound 1):

This compound was prepared by the reaction of α -naphthaldehyde with acetic anhydride and fused potassium acetate, according to Perkins condensation ⁽⁹²⁾.



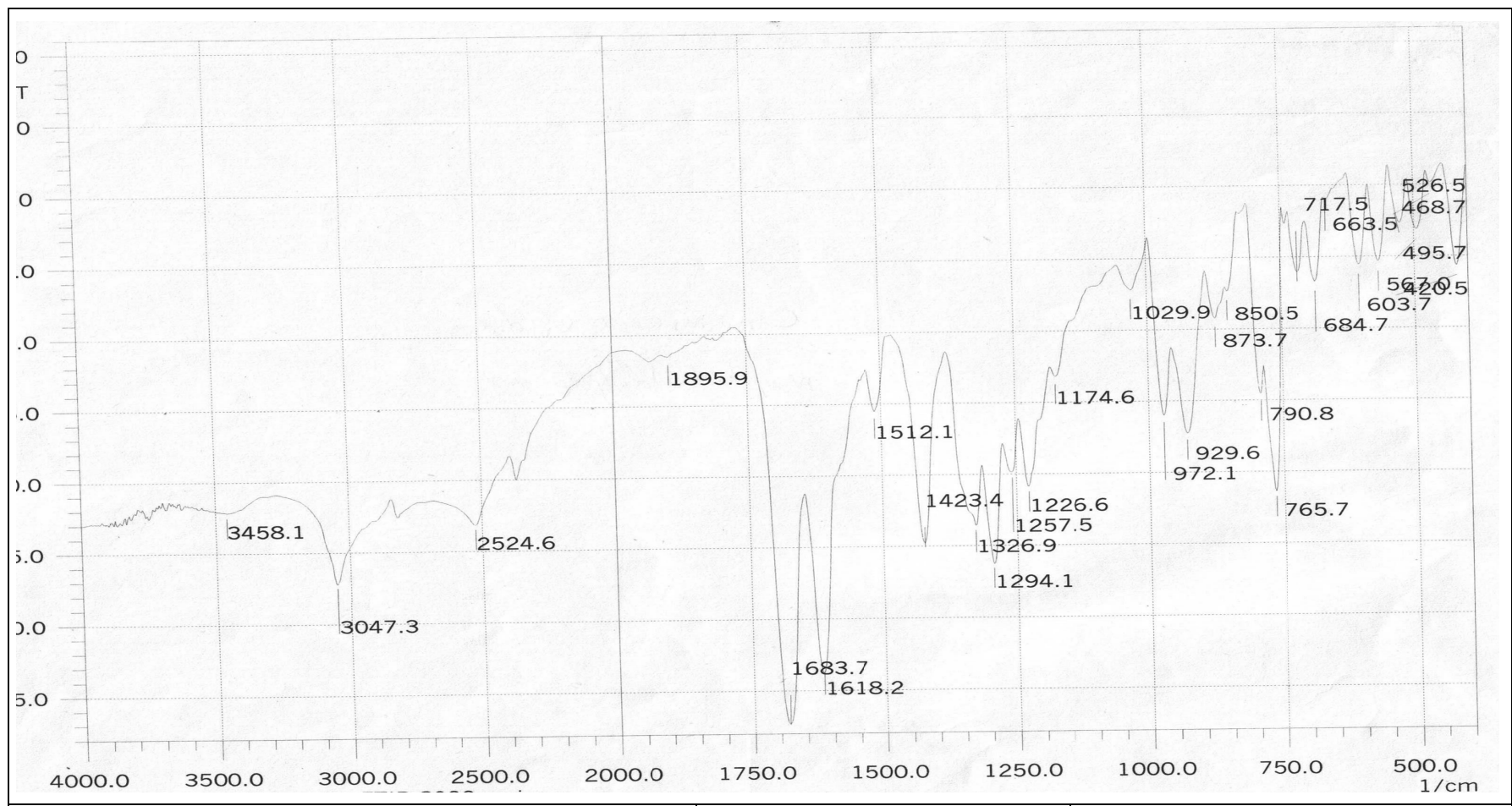
The product (compound 1) was characterized by FT.IR, U.V. spectra and steady-state fluorescence.

Figure (3-1) display the FT.IR spectrum of (compound 1) comparing with cinnamic acid as a model compound, the spectrum shows a shoulder near to 3100 cm^{-1} attributed to the (C-H) vinylic stretching vibration and an absorption band in the region 3047 cm^{-1} refer to the overlapping between carboxyl group (-OH) and the (C-H) aromatic stretching vibration, a strong absorption band appeared at the region 1683 cm^{-1} for (C=O carbonyl group) stretching vibration.

The spectrum show also, absorption band at 1618 cm^{-1} attributed to (C=C) vinylic stretching vibration, shoulder near to 1600 cm^{-1} due to (C=C) aromatic stretching vibration, absorption band in the region 1294 cm^{-1} for (C-O) stretching vibration and a medium absorption band at 765 cm^{-1} , which is attributed to the out of plane bending vibration of substituted naphthalene ring ^(91a).

The appearance of the carbonyl group at low frequency (1683 cm^{-1}) may refer to trans-conformation of (compound 1). This interpretation,

however, basically depends on comparing (compound 1) with cis and trans cinnamic acid which show (C=O group) absorption at (1705) cm^{-1} for cis and (1680) cm^{-1} for trans conformations ⁽⁹³⁾.



<p>C00857 trans-Cinnamic acid, pure $C_9H_8CH_2CO_2H$ M.W. 146.16 m.p. 133-134°</p>	M.P. : 210-212 °C	Color: yellow
	Yield: 68.5 %	Molecular Weight: 198.22 g/mol
		Molecular Formula: $C_{13}H_{10}O_2$

Figure (3-1) physical properties and FT-IR spectrum of (compound 1).

The U.V. spectrum of (compound 1), in methanol solvent at room temperature is shown in Figure (3-2a).

The spectrum exhibit the absorption band at 311 nm which belong to the overlapping between the electronic transition $\pi-\pi^*$ for the naphthalene ring and electronic transition $n-\pi^*$ for the lone pair that exists on the oxygen atom in carbonyl group. The band is red shifted from normal naphthalene absorption bands which usually appear at 282 nm^(91a). This shift may be due to the conjugation of naphthalene ring in (compound 1) with the vinylic and the carboxylic groups. (The literature refer to absorption band at 317 nm in methanol solvent)⁽⁹⁰⁾. Absorption shoulder appeared at the wave length of less than 250 nm results from the electronic transition $\pi-\pi^*$ of the naphthalene ring. Another absorption band appears at 224 nm which is also result from the electronic transition $\pi-\pi^*$.

On the other hand, the U.V. absorption of (compound 1) in acetonitrile solvent show maximum absorption band at 317 nm Figures (3-2b). However, the difference in absorption bands in methanol and acetonitrile solvents may appear from the difference in polarity between these two solvents, which indicated that $n-\pi^*$ is overlapped with $\pi-\pi^*$.

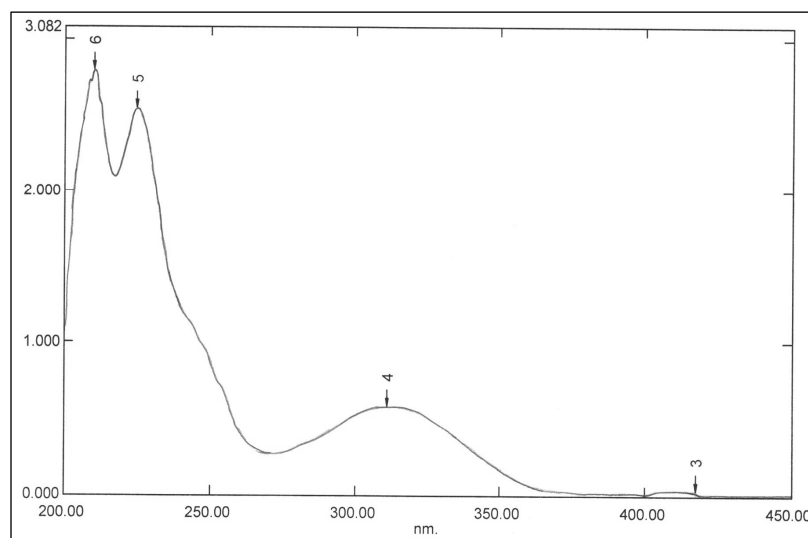


Figure (3-2a) U.V. spectrum of (compound 1) in methanol solvent.

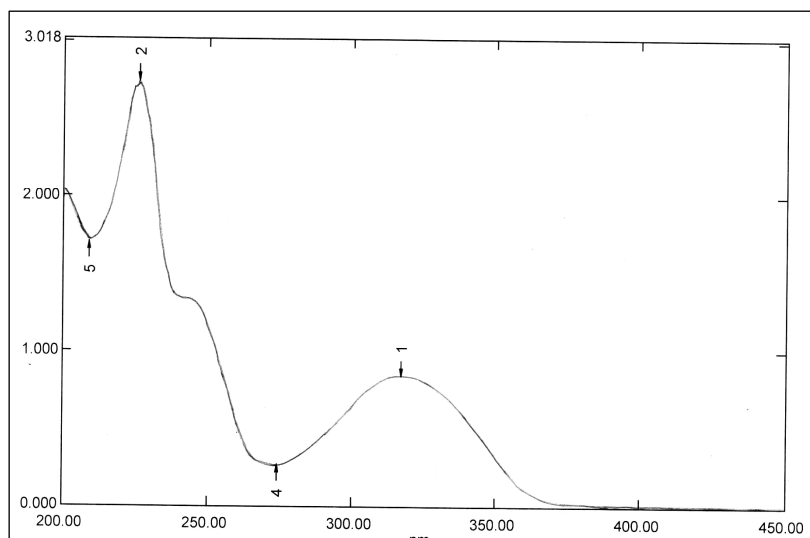
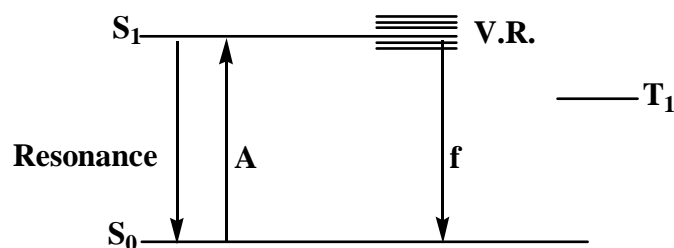


Figure (3-2b) U.V. spectrum of (compound 1) in acetonitrile solvent.

3-1-1 Steady – state fluorescence:

The fluorescence emission spectrum of (compound 1) Figure (3-3) is measured in methanol as a solvent at room temperature, with excitation wavelength 311 nm.

The spectrum shows a band at 316 nm which may result from the resonance and scattered light transition caused by the excitation state at 311 nm.



The spectrum shows red shift band at 400 nm belongs to the fluorescence emission of the naphthalene ring. This shift of fluorescence emission may arise from the conjugation system in (compound 1).

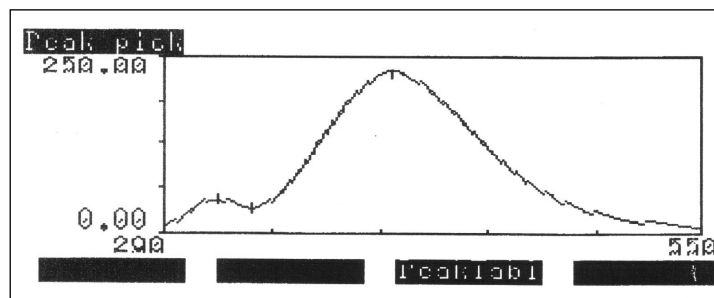
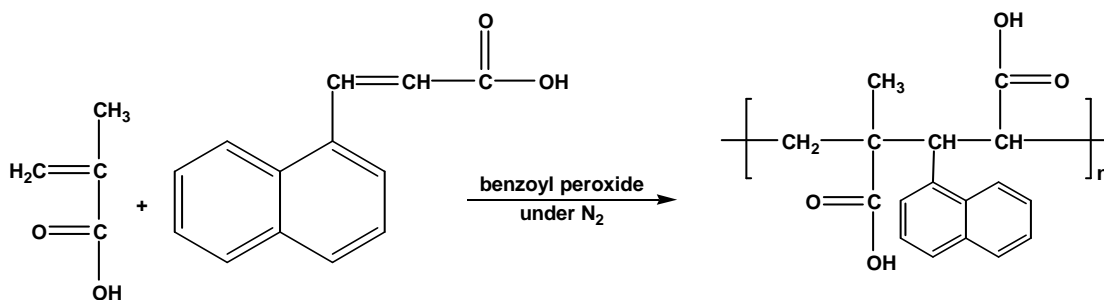


Figure (3-3) fluorescence spectrum of (compound 1) in methanol solvent.

3-2 Synthesis and characterization of methacrylic acid and 3-(1-naphthyl) acrylic acid copolymer (polymer 1):

This polymer was prepared by bulk polymerization of methacrylic acid monomer with 3-(1-naphthyl) acrylic acid and benzoyl peroxide as initiator under N_2 atmosphere.



The (polymer 1) was characterized by 1H -N.M.R., ^{13}C -N.M.R., U.V. spectra and steady-state fluorescence after four purifications to remove the unreacted compound 1.

Figure (3-4) shows the 1H -N.M.R. spectrum of the (polymer 1) in deuterated DMSO as a solvent.

The 1H -N.M.R. spectrum of (polymer 1) exhibits the expected resonance corresponding to the aromatic protons of naphthalene ring at δ (7-8) ppm. The aliphatic resonance protons are appearing at δ (0.9-1.3) ppm for methyl (CH_3) groups and at δ (1.7-1.8) ppm for methylene ($-CH_2-$) groups, the region between δ (5.5-6.2) refer to the aliphatic

resonance protons of (CH-CH) groups, while the hydroxyl of carboxylic acid protons appears at δ (12.4) ppm.

However, the low intensity of aromatic proton resonance indicates that low quantity of (compound 1) has been copolymerized with methacrylic acid.

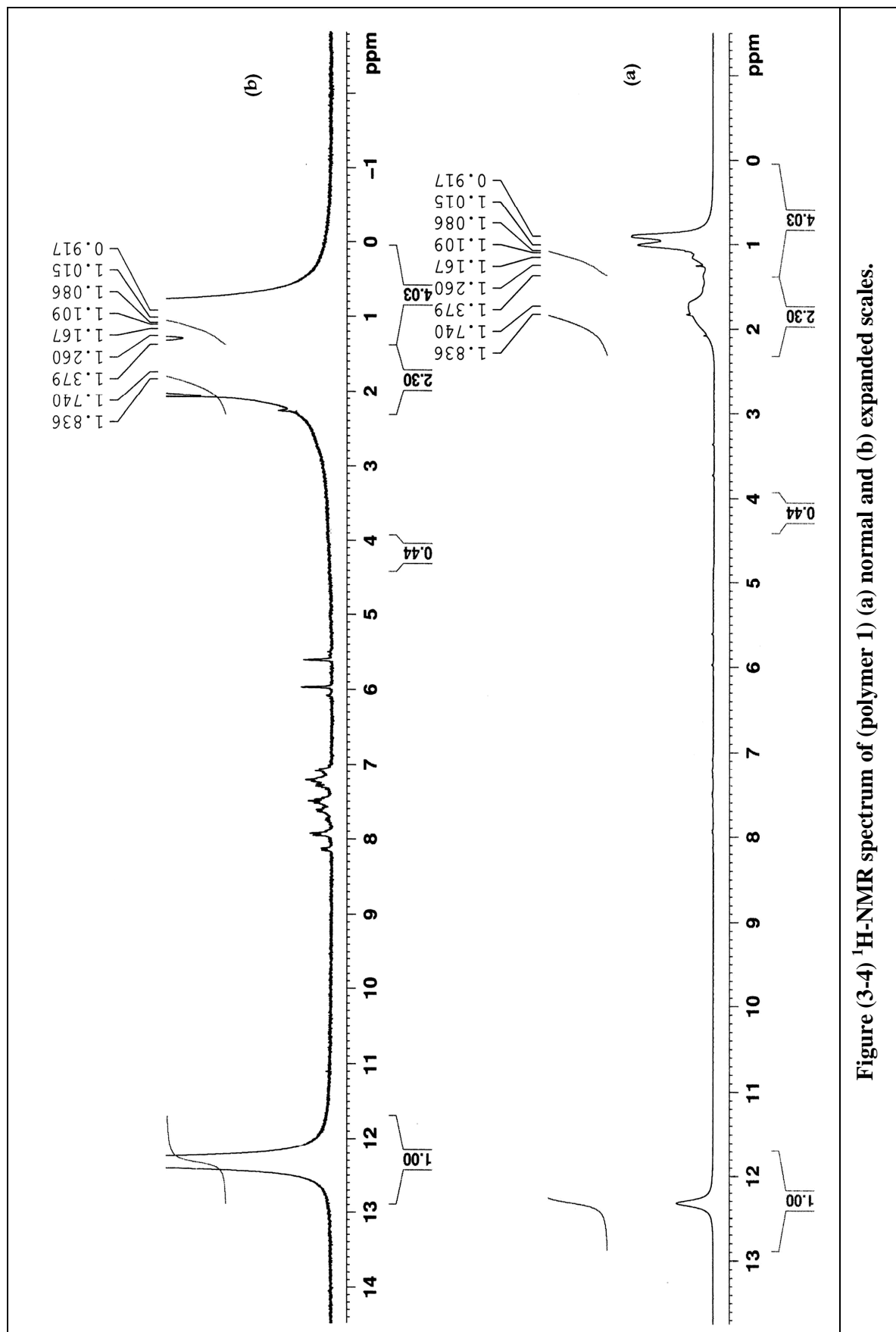


Figure (3-4) $^1\text{H-NMR}$ spectrum of (polymer 1) (a) normal and (b) expanded scales.

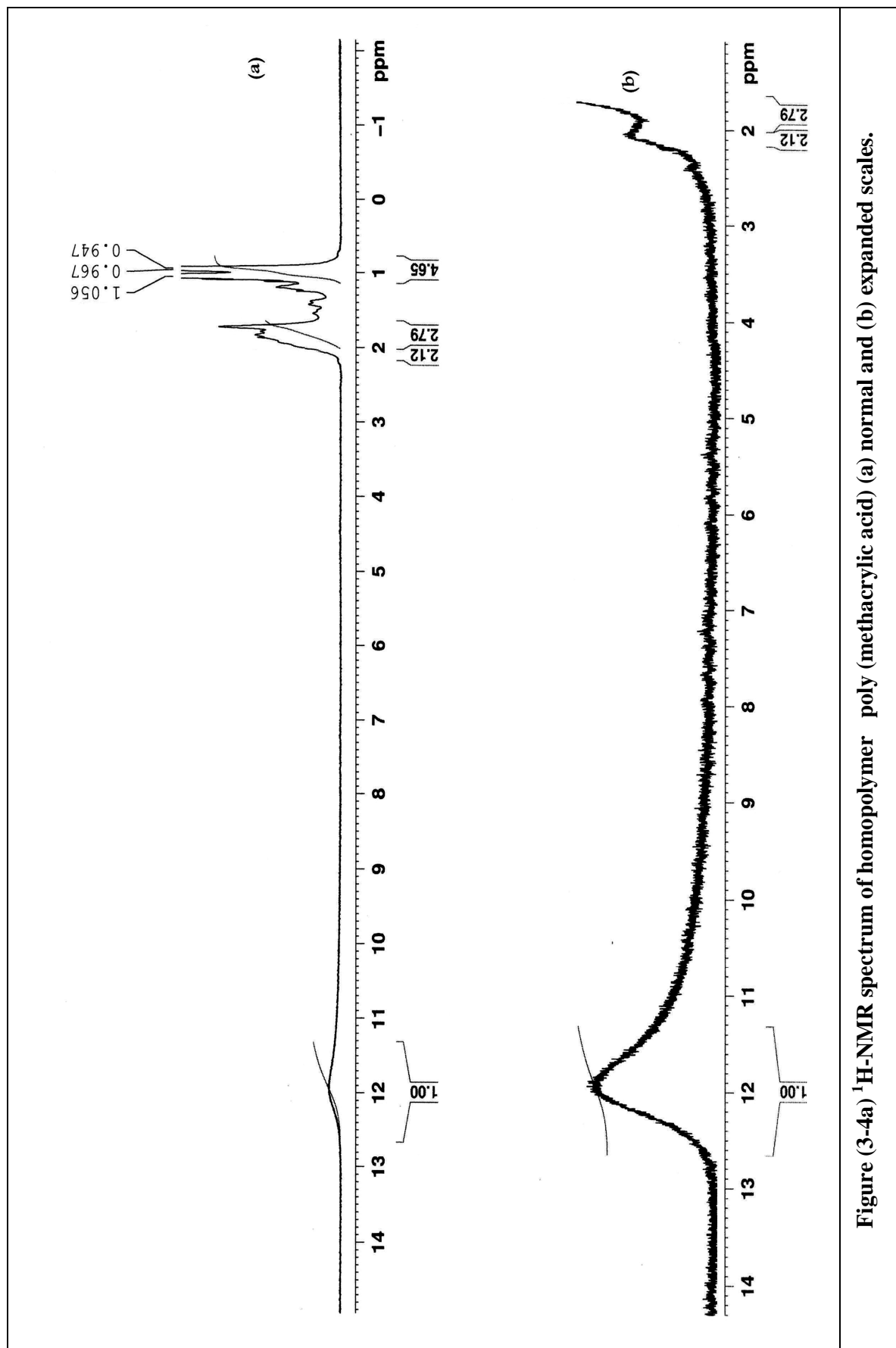


Figure (3-4a) $^1\text{H-NMR}$ spectrum of homopolymer poly(methacrylic acid) (a) normal and (b) expanded scales.

Moreover, figure (3-5) explains the ^{13}C -N.M.R. spectrum of (polymer 1) in deuterated DMSO as a solvent.

This figure shows the peaks to the carbon atoms of the aliphatic groups at different regions, in which we notice at the region lower than δ (20) ppm the appearance of peaks which belong to the aliphatic methyl groups (a) of the methacrylic acid units within polymer backbone. Appearance of powerful peaks at the region between δ (39-41) ppm belongs to the carbon atoms of the solvent. Also the appearance of peaks which belong to the quaternary carbon atom (b) at the region between δ (44-45) ppm, while we notice weak peaks that exists between δ (49-55) ppm which refer to the methylene groups (c) which has possibilities of the different bonding. The region between δ (122-125) ppm which belong to the aliphatic carbon groups (CH-CH) (d). The peaks that appear at the region between δ (129-130) ppm belongs to the carbon atoms of the naphthalene groups (e), the low intensity of these peaks show the very low ratio of copolymerization of the (compound 1) within polymer backbone. Finally the peaks between δ (178-180) ppm refer to the carboxyl groups (f) ⁽⁹⁴⁾.

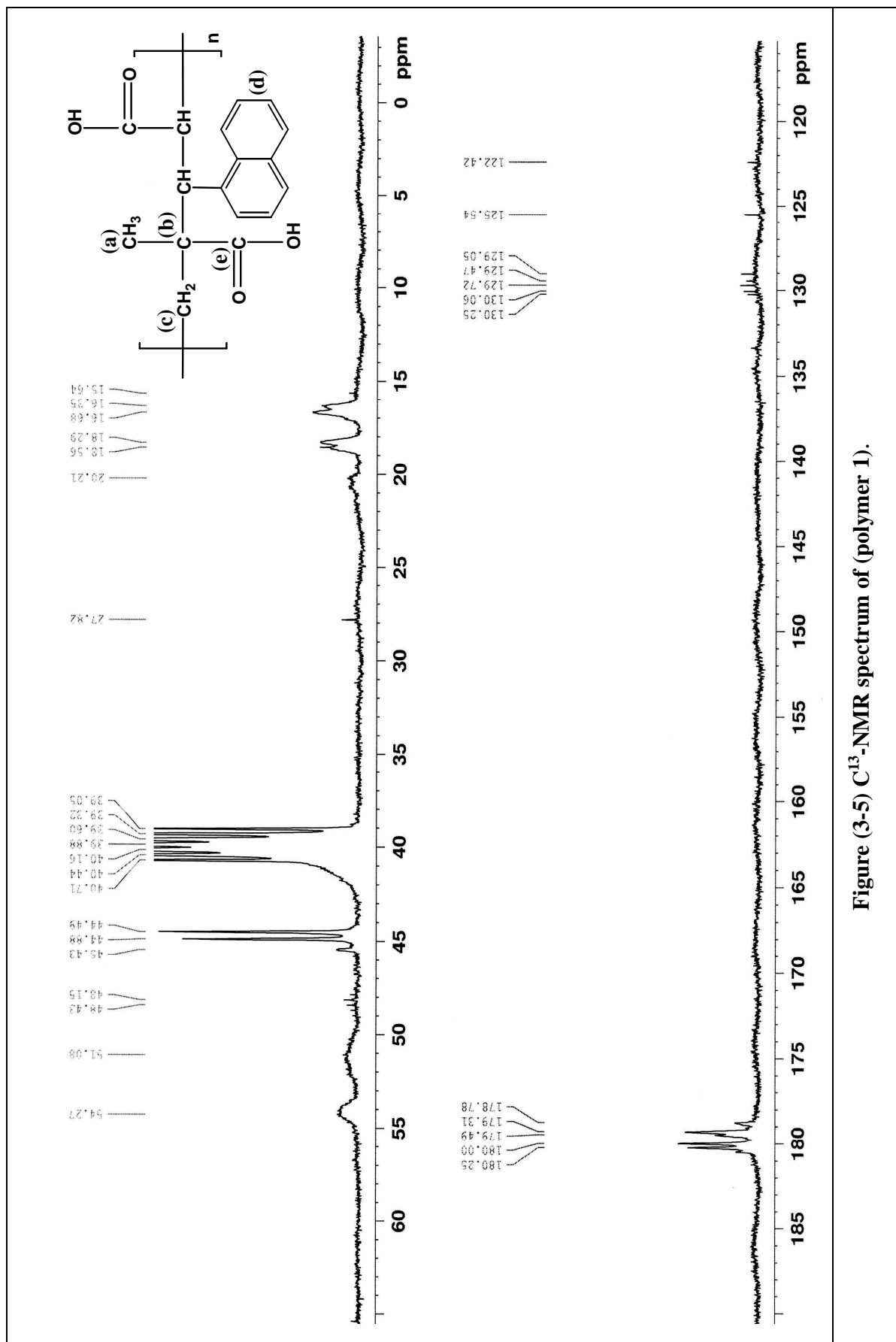


Figure (3-5) ^{13}C -NMR spectrum of (polymer 1).

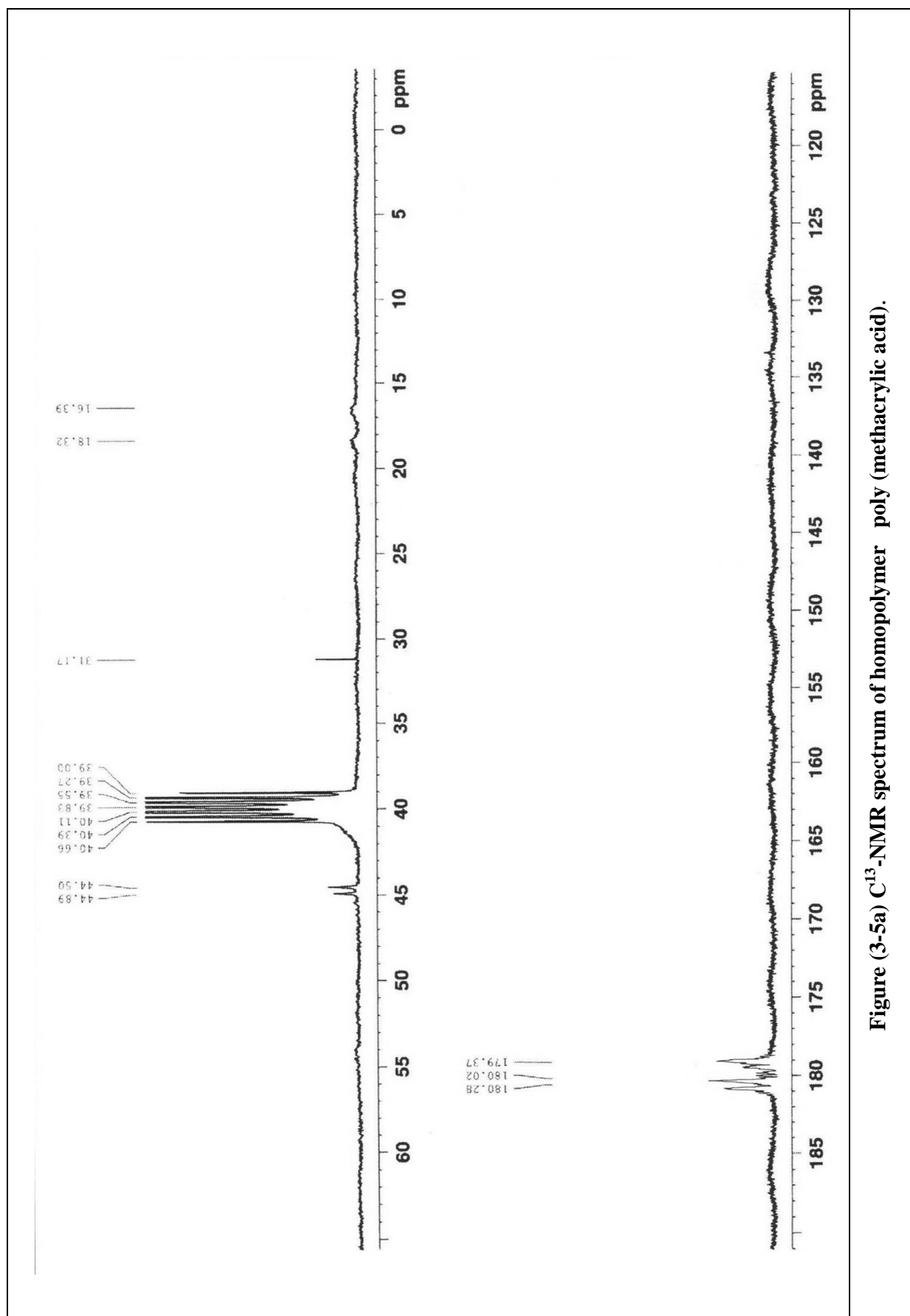


Figure (3-5a) ^{13}C -NMR spectrum of homopolymer poly(methacrylic acid).

The U.V. spectrum of (polymer 1) in methanol solvent at room temperature is shown in Figure (3-6).

The spectrum exhibit appearance of absorption bands at 264-282 nm belong to the electronic transition $\pi-\pi^*$ of the aromatic groups (naphthalene ring). These bands distinguish the copolymer from the homopolymer figure (3-6 a). From this result we notice the appearance of naphthalene absorption band at 282 nm wavelength, which is involved within the same absorption location of methyl naphthalene (91a). Absorption shoulder appeared at the wavelength less than 282 nm which belong to the electronic transition $n-\pi^*$ of the lone pair that exists on the oxygen atom in carbonyl group.

However, the discrepancy between the U.V. absorption spectrum of the monomer (compound 1) from that of copolymer attributed to the fact that (compound 1) has been copolymerized with methacrylic acid monomer and consequently lose it's conjugation system, therefore, naphthalene absorption return to it's normal state (i.e. 282 nm).

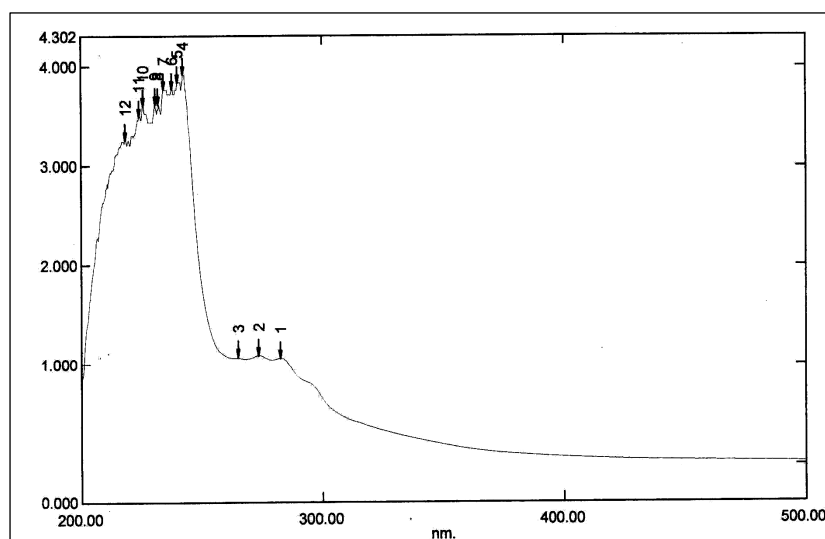


Figure (3-6) U.V. spectrum of (polymer 1) in methanol solvent.

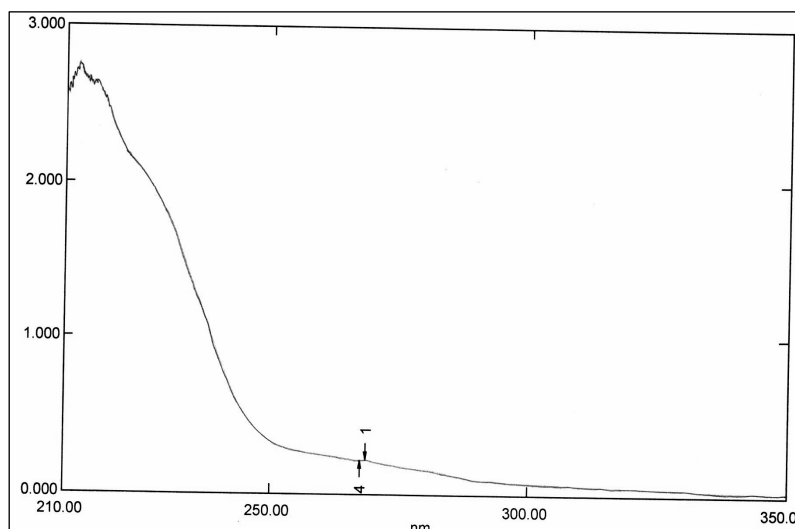


Figure (3-6a) U.V. spectrum of homopolymer poly(methacrylic acid) in methanol solvent.

However, the above results verify the attachment of 3-(1-naphthyl) acrylic acid monomer onto the polymer chains through the polymerization process.

3-2-1 Steady – state fluorescence:

The copolymer conformation, composition and behavior in solution were investigated by steady–state fluorescence at 282 nm excitation wave length.

The fluorescence emission spectrum of the (polymer 1) was recorded in methanol solvent at room temperature as shown in Figure (3-7). The spectrum display emission band at 322 nm which is identical to normal naphthalene ring fluorescence emission ^(79, 80).

However, no excimer emission has been appeared in the spectrum which may attribute to difficulty of naphthalene chromophores to form sandwich like conformation, (excimer structure) due to:

- 1- Polymer chain will adopt an open conformation in methanol solvent, because it is a good solvent for the copolymer.

- 2- The quantity of (compound 1) may by not be enough to form excimer emission.
- 3- The attachment of naphthyl groups with the polymer back bone is rigid. (i.e. there is no flexible space) as shown in structure below.

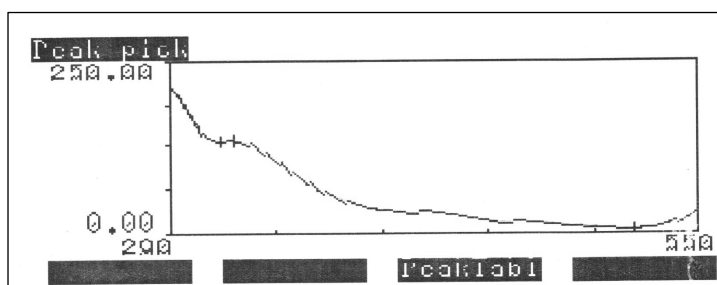
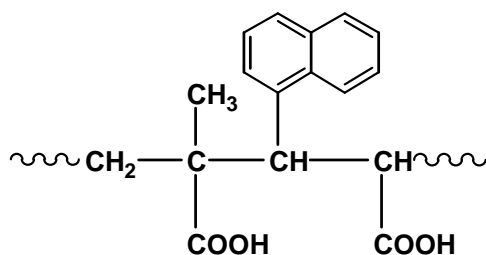
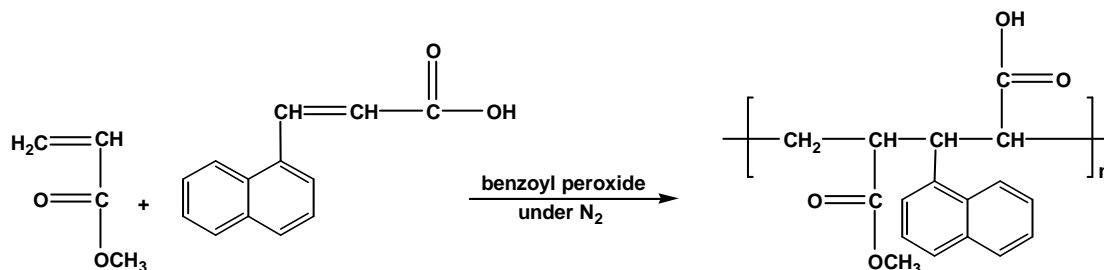


Figure (3-7) fluorescence spectrum of (polymer 1) in methanol solvent.

3-3 Synthesis and characterization of methyl acrylate and 3-(1-naphthyl) acrylic acid copolymer (polymer 2):

This polymer was prepared by bulk polymerization of methyl acrylate monomer with 3-(1-naphthyl) acrylic acid and benzoyl peroxide as initiator under N₂ atmosphere.



The polymer was characterized by ¹H-N.M.R., ¹³C-N.M.R., U.V. spectra and steady-state fluorescence after four purification to remove the unreacted of (compound 1).

Figure (3-8) show the ¹H-N.M.R spectrum of (polymer 2) in deuterated acetonitrile as a solvent.

The spectrum exhibit clearly the expected protons resonance at δ (7-8) ppm corresponding to the naphthyl chromophores, protons resonance at δ (1.5-1.9) ppm belong to groups of CH₂ and the region at δ (2.1-2.2) ppm refer to the CH₃ CN respectively. The appearance of proton resonance at δ (3.6) ppm is due to OCH₃ of the acrylate. While the region between δ (7-7.5) ppm which belong to the (CH-CH) groups. The spectrum show low intensity of proton resonance of naphthalene which seems low quantity of naphthalene chromophores within the polymer chains has been copolymerized.

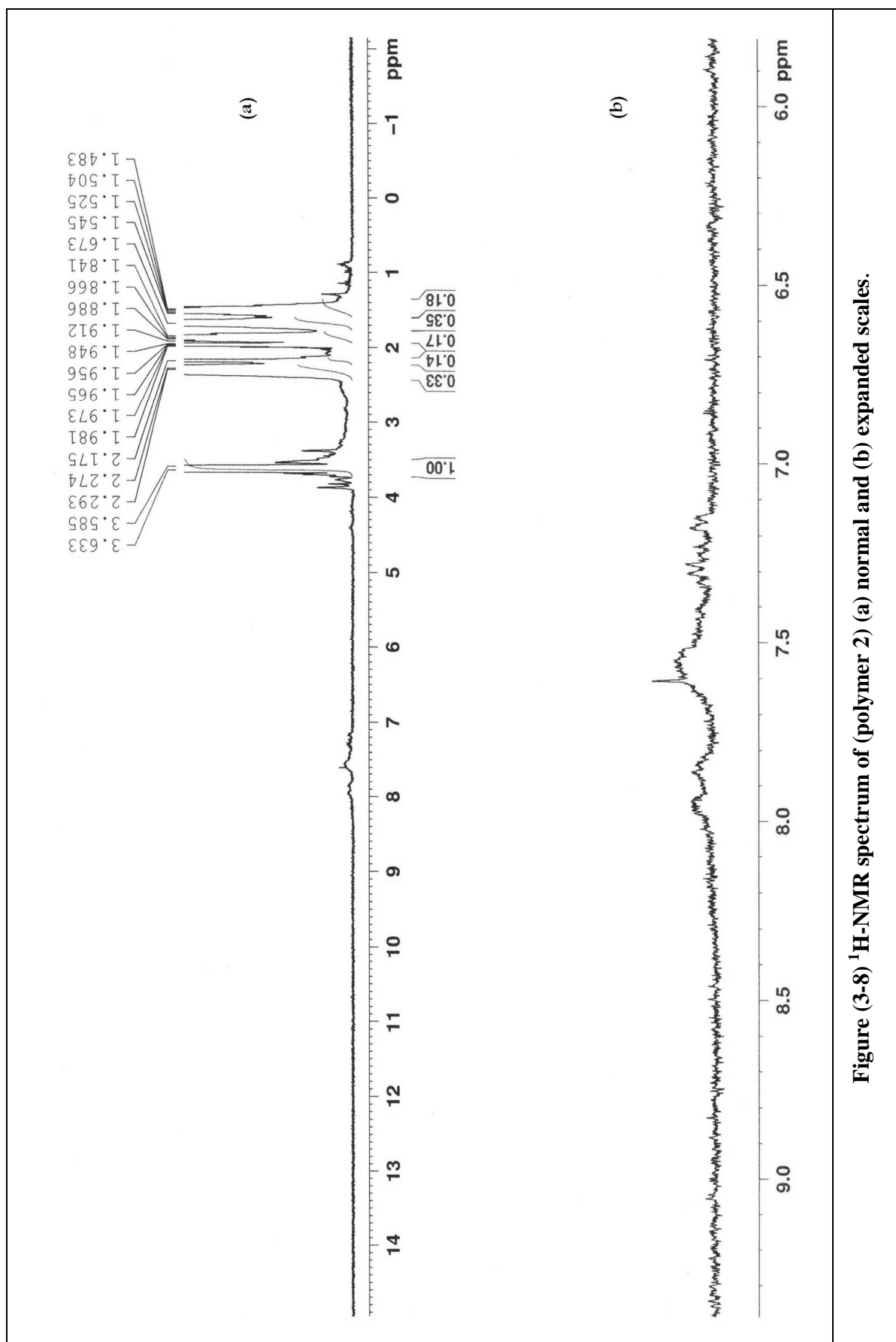


Figure (3-8) $^1\text{H-NMR}$ spectrum of (polymer 2) (a) normal and (b) expanded scales.

In addition, figure (3-9) shows the ^{13}C -N.M.R. spectra of the (polymer 2) in deuterated acetonitrile solvent.

^{13}C -NMR spectra show the appearance of the peak at the region δ (34) ppm which belong to the methylene group ($-\text{CH}_2-$).

We notice in this spectrum obvious peaks at the region between δ (39-41) ppm which belongs to the carbon atoms of the solvent, while the peaks at the region δ (44.49)ppm and δ (44.88) ppm refer to the carbon atoms of ($-\text{CH}-\text{CH}-$) group. The carbon atom of methoxy group (OCH_3) appears at the region (51.30) ppm . This spectra shows the appearance of a peak with high intensity at the region (117) ppm which belong to (CN) droup of the solvent . At the region between δ (129-130) ppm shows peaks refer to carbon atoms of the naphthalene groups , the low intensity of these peaks confirm the low ratio grafting of the (compound 1) within copolymer. The last peak shows at the range δ (174.78- 174.82) ppm which belongs to the two carbonyl groups ⁽⁹⁴⁾.

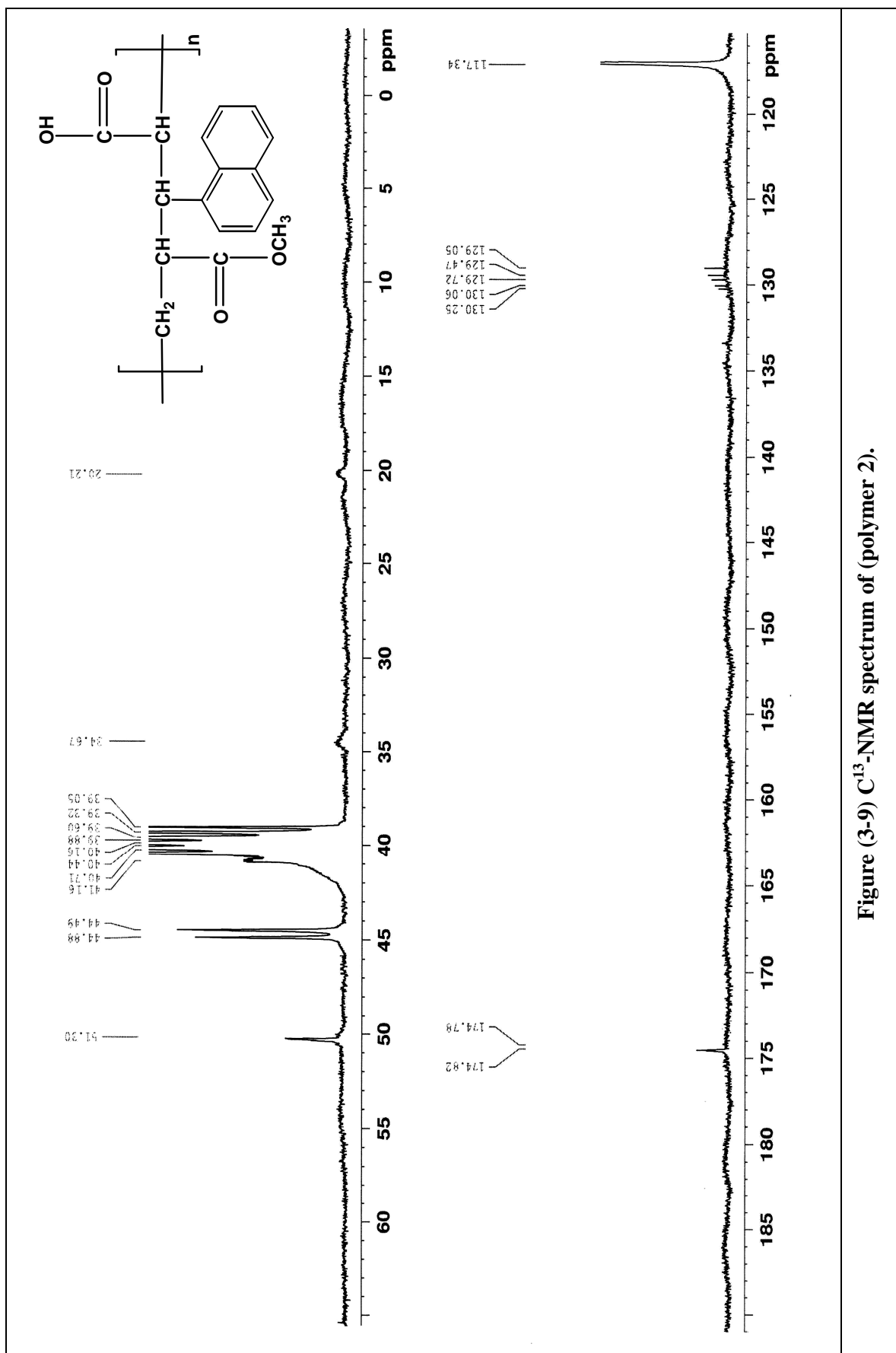
Figure (3-9) ^{13}C -NMR spectrum of (polymer 2).

Figure (3-10) shows the U.V. spectrum of (polymer 2) in acetonitrile as a solvent at room temperature.

The chart shows absorption bands at 274 nm and 284 nm which is due to the electronic transition $\pi-\pi^*$ of the naphthalene ring. These bands distinguish the copolymer from the homopolymer poly(methyl acrylate) Figure (3-10a). As mentioned previously the appearance of an absorption band within a limit range of 282 nm devote the converting of the double bond of 3-(1-naphthyl) acrylic acid to a single bond, which means losses of the conjugating system, therefore, naphthalene ring return to the natural absorption state. Show absorption shoulder at region less than 284 nm which belong to the electronic transition $n-\pi^*$ of the lone pair that exists on the oxygen atom in carbonyl group. This result confirms the polymerization of monomers to each other to form the copolymer.

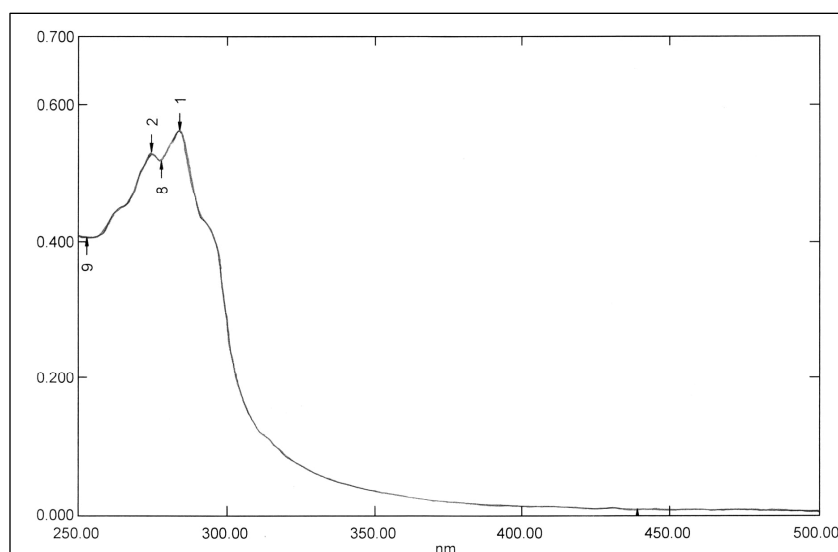


Figure (3-10) U.V. spectrum of (polymer 2) in acetonitrile solvent.

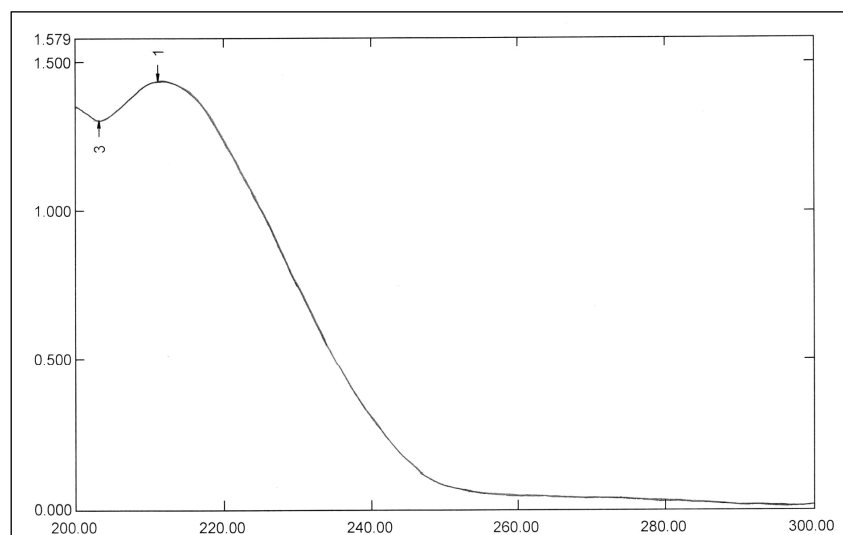


Figure (3-10a) U.V. spectrum of homopolymer poly(methyl acrylate) in acetonitrile solvent.

3-3-1 Steady – state fluorescence:

The copolymer conformation, composition and behavior in solution were investigated by steady–state fluorescence at 282 nm excitation wavelength.

The fluorescence emission spectrum of (polymer 2) in acetonitrile solvent at room temperature is shown in Figure (3-11). The spectrum exhibit emission band at 335 nm which is identical to normal naphthalene fluorescence emission ^(79, 80). This result, also, prove the attachment of 3-(1-naphthyl) acrylic acid monomer to the polymer back bone by polymerization process and the existence of (compound 1) was not as impurity retain with the polymer.

However, despite the fact that steric effect (scheme 2) to the naphthalene chromophores in (polymer 2) is less than that of (polymer 1) as shown in (scheme 1); still no excimer emission has been noticed. This result may attribute to the same reasons discussed previously in case of (polymer 1). (i.e. 3-(1-naphthyl)acrylic acids can not be homopolymerized).

This results (no excimer emission) suggest that no two 3-(1-naphthyl) acrylic acid monomer molecules can be joined together but it would be indistributed random form along the polymer chain.

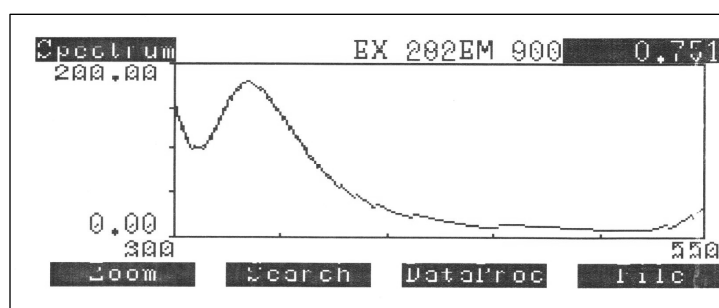
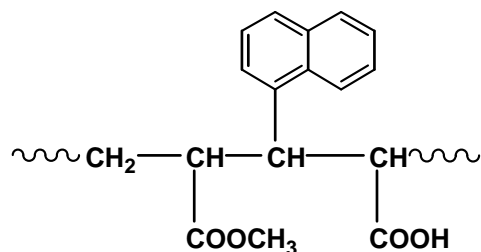
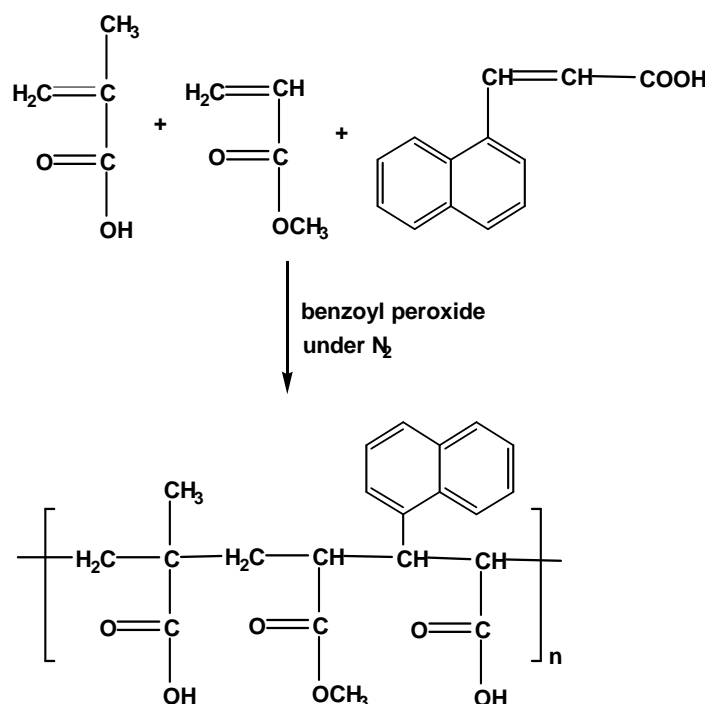


Figure (3-11) fluorescence spectrum of (polymer 2) in acetonitrile solvent.

3-4 Synthesis and characterization of methacrylic acid with methyl acrylate and 3-(1-naphthyl) acrylic acid tricopolymer (polymer 3):

Attempts to prepare the tricopolymer by bulk polymerization of methacrylic acid, methyl acrylate with 3-(1-naphthyl) acrylic acid and benzoyl peroxide as initiator under N_2 atmosphere, were not successful.



The polymer was characterized by $^1\text{H-N.M.R.}$, $^{13}\text{C-N.M.R.}$, U.V. spectra and steady-state fluorescence, after four purification to remove the unreacted of (compound 1), which proved that the tricopolymer couldn't be prepared, but instead copolymer of methacrylic acid and methyl acrylate was synthesized.

Figure (3-12) show the $^1\text{H-N.M.R.}$ spectra of (polymer 3) in deuterated methanol as a solvent.

The $^1\text{H-N.M.R.}$ spectrum of the tricopolymer shows the presence of aliphatic resonance protons at a region δ (1, 2, 2.7) ppm which belong

to the methacrylic acid and methyl acrylate and these aliphatic groups with different stereoregularity of bonding. The appearance of protons resonance between δ (3-4) ppm belongs to the methoxy groups present in the methyl acrylate which appear in less intensity relatively to the same groups in (polymer 2). This observation is expected because of the small amount that we implement in the copolymerization process.

We notice the presence of a strong peak at a region δ (5) ppm which dose not exist in all the previous polymer belong to the solvent, with noticing the disappearance of the acidic proton peaks between δ (12-13) ppm.

The striking observations of the spectrum is the disappearance of protons resonance of naphthalene groups at δ (7-8) ppm which indicate that 3-(1-naphthyl) acrylic acid has not been copolymerization with both monomers methacrylic acid and methyl acrylate.

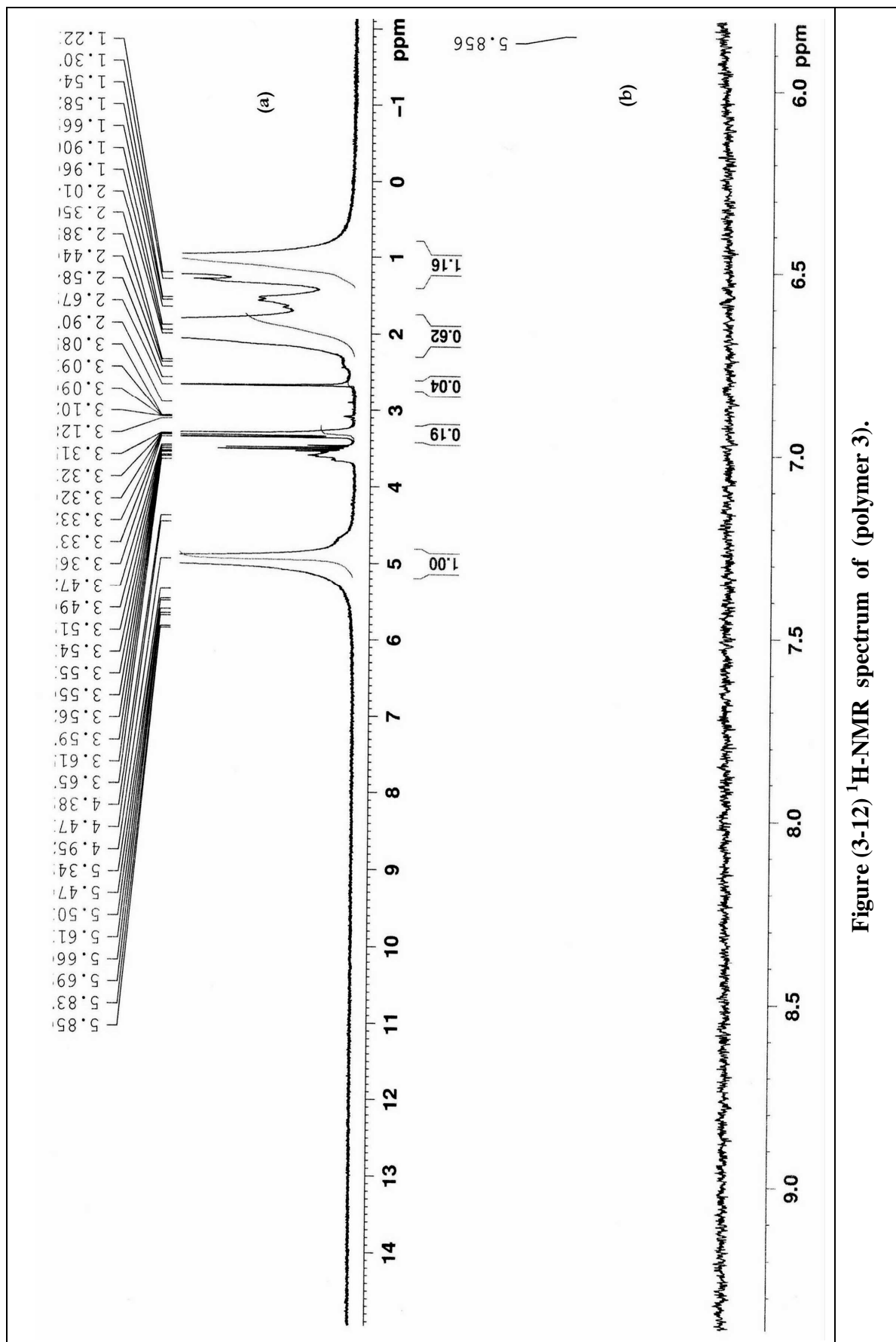


Figure (3-12) ¹H-NMR spectrum of (polymer 3).

In addition, figure (3-13) shows the ^{13}C -N.M.R. spectrum of (polymer 3) in deuterated methanol as a solvent.

This figure shows the peaks to the carbon atoms of the methyl groups at a region less than δ (20) ppm ^{13}C -NMR spectrum show the appearance of a peak at the region δ (39.41) ppm which belong to (CH_2) group . Also we notice the appearance of peaks at a region δ (44.40) ppm and δ (44.86) ppm which belong to the $(-\text{CH}-\text{CH}-)$ group but the region between δ (46.24 - 49.09) ppm belong to the solvent. This spectrum also show a peak at δ (54.29) ppm which is refers to methoxy group $(-\text{OCH}_3)$

On the other hand, we can not notice the appearance of peaks at the regions between δ (179-180) ppm represent the peaks of the carbonyl groups ⁹⁴.

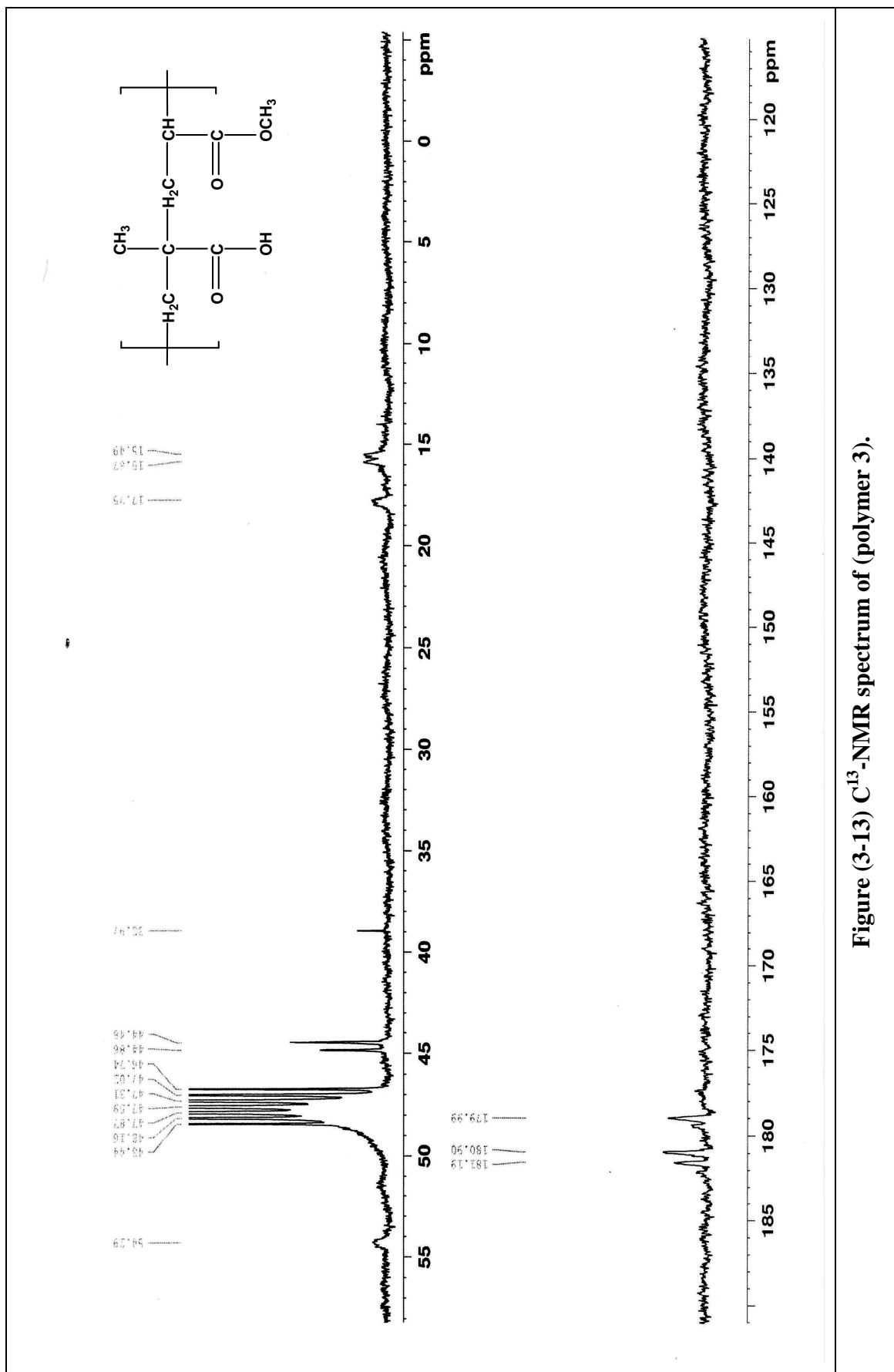


Figure (3-13) C^{13} -NMR spectrum of (polymer 3).

The U.V. spectrum of the (polymer 3) in methanol solvent at room temperature is shown in Figure (3-14).

The first absorption band shows the electronic transition $n-\pi^*$ at region 258 nm which belongs to the carbonyl groups while the band at region 215 nm belongs to the electronic transition $\pi-\pi^*$ of group that carry the double bond (CO). There is no absorption band of naphthalene ring at 282 nm.

However, these results of $^1\text{H-N.M.R.}$, $^{13}\text{C-N.M.R.}$ and U.V. spectra indicate that 3-(1-naphthyl) acrylic acid monomer has not been able to copolymerize with methacrylic acid and methyl acrylate because to the ratio reactivity of methacrylic acid with methyl acrylate is higher than with 3-(1-naphthyl) acrylic acid monomer because the steric effect of the latter monomer.

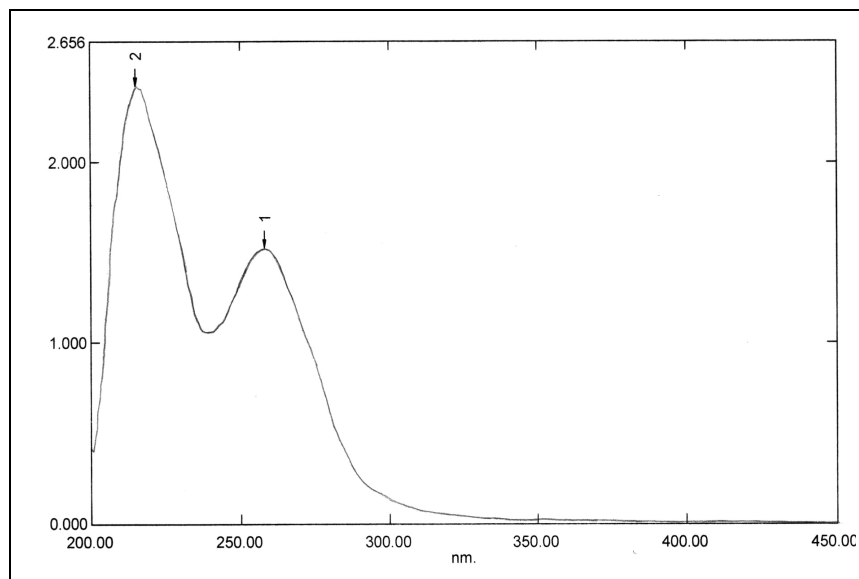


Figure (3-14) UV spectrum of (polymer 3) in methanol solvent.

3-4-1 Steady – state fluorescence:

Although, $^1\text{H-N.M.R.}$, $^{13}\text{C-N.M.R.}$ and U.V. spectra for (polymer 3) indicate that no 3-(1-naphthyl) acrylic acid monomer has been copolymerized with methacrylic acid and methyl acrylate mixture, the polymer was examined by fluorescence spectroscopy in methanol solvent at 282 nm excitation wave lengths and room temperature, which as shown in figure (3-15).

The spectrum shows low intensity of fluorescence emission at 339 nm which may attributed to low concentration of 3-(1-naphthyl) acrylic acid monomer has been copolymerized with methacrylic acid and methyl acrylate monomers.

However, the discrepancy in the results between N.M.R. and U.V. spectra with the fluorescence emission may attributed to the fact that fluorescence technique is more sophisticated and powerful technique to trace micro quantities of fluorescing groups, so, it is used widely in biological investigations, hence the fluorescence band in Figure(3-15) may be due to impurities of (compound 1).

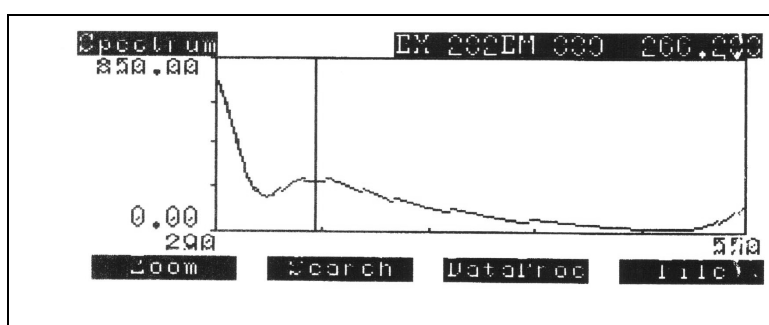


Figure (3-15) fluorescence spectrum of (polymer 3) in methanol solvent.

3-5 Synthesis and characterization of methacrylic acid and 3-(1-naphthyl) acrylic acid copolymer in toluene solvent (polymer 4):

This polymer was prepared by solution polymerization of methacrylic acid monomer with 3-(1-naphthyl) acrylic acid dissolved in dry toluene and benzoyl peroxide as initiator under N₂ atmosphere.

The polymer was characterized by U.V. spectrum and steady-state fluorescence. Figure (3-16) shows the U.V. spectrum of (polymer 4) in methanol solvent at room temperature and after twice purification.

The U.V. spectrum of (polymer 4) shows the presence of absorption bands at a region between 268-282 nm which belong to the electronic transition $\pi-\pi^*$ of the naphthalene ring.

However, when we compare the U.V. spectrum of (compound 1) with (polymer 4), we can conclude that (compound 1) has been copolymerized with methacrylic acid monomer by solution polymerization and lose its conjugation system, so, the aromatic groups absorption at a normal region (i.e. 282 nm).

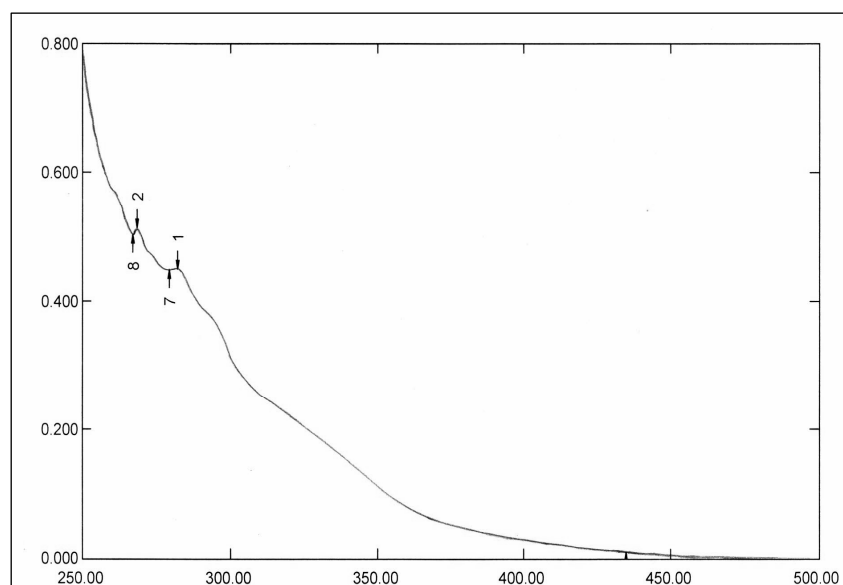


Figure (3-16) UV spectrum of (polymer 4) in methanol solvent.

3-5-1 Steady – state fluorescence:

The copolymer conformation, composition and behavior in solution were investigated by steady–state fluorescence at 282 nm excitation wave length.

The fluorescence emission spectrum of (polymer 4) in methanol solvent at room temperature is shown in Figure (3-17).

The spectrum shows the emission band at 337 nm ^(79, 80) which is identical to normal naphthalene ring fluorescence emission. This result demonstrates the copolymerization of 3-(1-naphthyl) acrylic acid within polymer backbone by solution polymerization.

In this spectrum also, no excimer emission has been appeared, this result may attribute to same reason which discussed previously in case of (polymer 1).

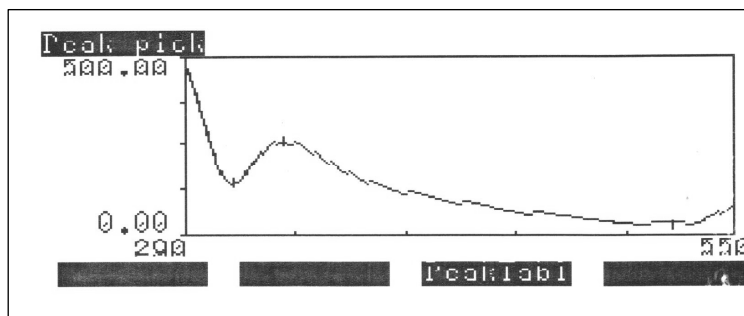


Figure (3-17) fluorescence spectrum of (polymer 4) in methanol solvent.

3-6 Steady – state fluorescence in binary mixture solvent:

As discussed previously that no excimer emission was observed in methanol and acetonitrile for both (polymer 1 and 2), respectively. These results were attributed to the open chain conformations of these polymers in such solvents.

Hence, we examined the effect of non solvent on the polymer conformation through addition of dioxane for (polymer 1) solutions and deionized water for (polymer 2) solution.

However, the fluorescence emission of (polymer 1) in 20% dioxane: methanol volume percent is shown in Figure (3-18). The spectrum show the normal naphthalene ring fluorescence only, there is no excimer emission even with such percentage of mixture.

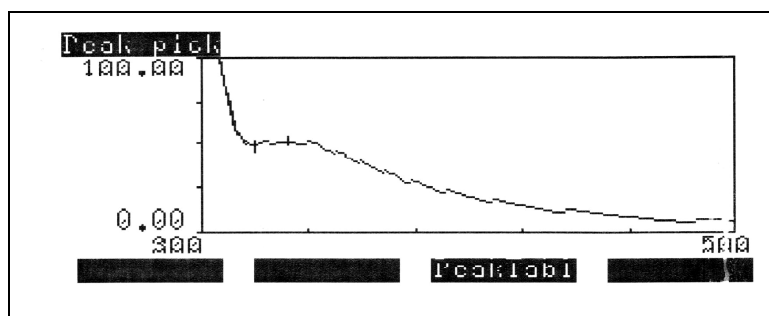


Figure (3-18) fluorescence spectrum of (polymer 1) at 20% dioxin.

On the other hand, Figure (3-19) display the fluorescence emission of (polymer 2) in acetonitrile: deionized water 80:20 volume percent. The spectrum shows no excimer emission too.

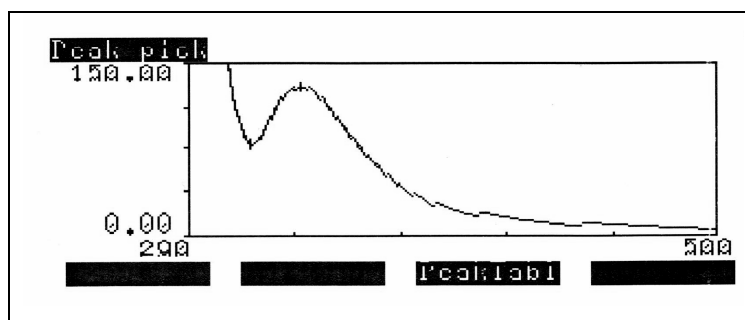


Figure (3-19) fluorescence spectrum of (polymer 2) at 20% deionized water.

These results verify the difficult formation of excimer which may be due to, as a mentioned previously, steric effect or the rigidity of joining naphthalene chromophores with the polymer backbone for both (polymer 1 and 2) schemes (1 and 2).

3-7 Molecular weight determination:

A) Polymer 1:

Molecular weight of (polymer 1) was calculated using equation (1), for intrinsic viscosity in methanol solvent⁹⁵.

$$T = 298.15 \text{ K}$$

$$[\eta] = 2.729$$

$$[\eta] = (5.02 * 10^{-4}) * M^{0.7474}$$

$$\bar{M} = 99.50 * 10^3 \text{ g/mole}$$

$$\text{Repeating units} = 1156.98$$

B) Polymer 2:

Molecular weight of (polymer 2) was calculated using equation (1), for intrinsic viscosity in acetonitrile solvent.

$$T = 298.15 \text{ K}$$

$$[\eta] = 3.5172$$

$$[\eta] = (6.33 * 10^{-4}) * M^{0.75}$$

$$\bar{M} = 98.132 * 10^3 \text{ g/mole.}$$

$$\text{Repeating units} = 1141.07$$

Conclusion:

1- Through studying the previous results of $^1\text{H-N.M.R.}$, $^{13}\text{C-N.M.R.}$, U.V. spectra and steady-state fluorescence it's became obvious that 3-(1-naphthyl) acrylic acid is copolymerized with methacrylic acid and methyl acrylate monomers to produce.

Copolymer of (methacrylic acid and 3-(1-naphthyl) acrylic acid), and copolymer of (methyl acrylate and 3-(1-naphthyl) acrylic acid).

2- Fluorescence investigation indicated that no excimer emission was observed referring to the fact that naphthalene chromophores are distributed along the polymer chains, in a way such that no two 3-(1-naphthyl) monomers are joined together in the polymer chains.

3- The excimer formation restricted by the rigidity of naphthalene chromophores on the polymer chain.

4- Tricopolymer of methacrylic acid, methyl acrylate and 3-(1-naphthyl) acrylic acid can not be synthesized may be because the ratio reactivity of methacrylic acid and methyl acrylate is higher than with 3-(1-naphthyl) acrylic acid.

Suggestion for further work:

- 1- Use of the other monomers like methyl methacrylate, acrylonitrile or acrylamide to prepare copolymer with 3-(1-naphthyl) acrylic acid.
- 2- Preparation of 3-(β -naphthyl) acrylic acid and using it in the preparation of the copolymer.
- 3- Study of the energy transfer phenomenon between the polymer chains prepared by the described method and another polymer containing difference chromophore.
- 4- Synthesis of copolymer with high percent of 3-(1-naphthyl) acrylic acid monomer and investigate the spectroscopic properties.

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