

SYNTHESIS AND DILUTE SOLUTION  
PROPERTIES OF POLYACENAPHTHYLENE

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By

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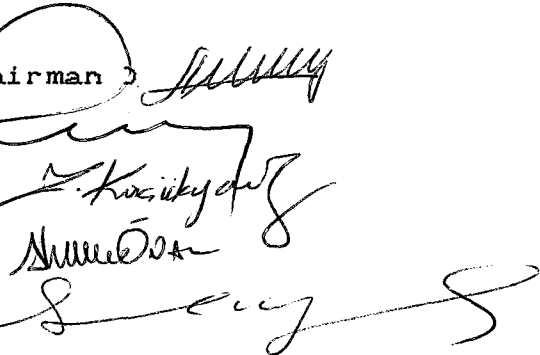
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## ABSTRACT

### SYNTHESIS AND DILUTE SOLUTION PROPERTIES OF POLYACENAPHTHYLENE


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In this study , polyacenaphthylene was obtained by radiation induced and thermal bulk polymerizations. The backbone of polyacenaphthylene chain is a part of cyclic repeating unit. Due to the locked linkages and the steric hindrance of large aromatic ring, it is expected to be a stiff chain. Dilute solution properties of it were studied. Relationships for molecular weight dependence of intrinsic viscosity and an unperturbed dimension were determined in both theta as 1,2-dichloroethane and in good solvents as toluene and chloroform. The chain rigidity was quantitatively calculated by the characteristic ratio ,  $C_{\infty}$  , and steric factor ,  $\sigma$  , . These values were found as  $C_{\infty} = 18.0$  and  $\sigma = 3.0$  respectively at theta condition. Therefore, it was concluded that polyacenaphthylene is a semi-rigid chain.



Key words: Acenaphthylene, polyacenaphthylene, dilute  
solution properties , unperturbed chain dimension.

405.04.02 Polymer Chemistry

## ÖZET

### ASENAFTİLEN'İN SENTEZİ VE ÇÖZELTİ ÖZELLİKLERİNİN İNCELENMESİ

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Bu çalışmada, poliasenaftilen, iki ayrı metotla, radyasyonla başlatılarak ve ısısal kütle polimerizasyonu ile sentezlendi ve bu örneklerin çözelti özellikleri incelendi. Poliasenaftilen zinciri üzerinde yinelenen aromatic halkalar bulunan bir yapıdır. Zincir hareketinin az oluşu ve aromatic halkaların neden olduğu sterik etkiler sonucunda zincirin, rijit olması beklenmektedir. Molekül ağırlığı, intrinsik viskozite ilişkisi ve bozulmamış boyutlar, teta çözücü olarak 1,2-dikloroetan ve iyi çözücü olarak kloroform ve toluende incelendi. Zincirlerin bükülebilirliği, nicel olarak karakteristik oran,  $C_{\infty} = 18.0$ , ve sterik faktör,  $\sigma = 3.0$ , hesaplanarak belirlendi. Sonuçlara göre, poliasenaftilen'in yarı-rijit bir polimer olduğu yargısına ulaşılmıştır.



Anahtar kelimeler: Asenaftilen, poliasenaftilen, çözelti  
özellikleri,bozulmamış zincir boyutları  
405.04.02 Polimer Kimyası

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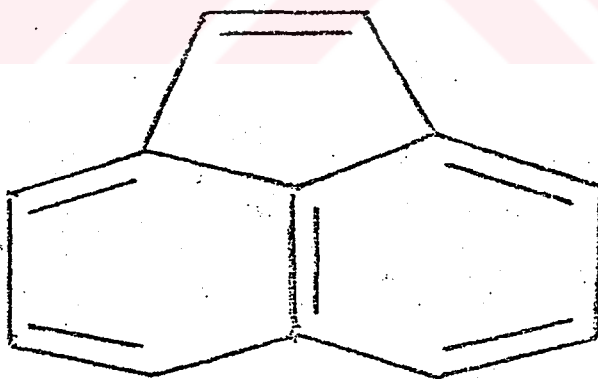
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## NOMENCLATURE



Acenaphthylene

## 1 INTRODUCTION

### 1.1 Historical Development of Acenaphthylene Polymerization

Acenaphthylene, ACN, is a yellow crystal that exists abundantly in coke oven tar. It has a melting point of  $92^{\circ}\text{C}$  and easily polymerizes in both solid and liquid states. Investigations of its polymerization was first carried out by German workers: K.Dziewonski with F.Rapalski (1912); Z.Leyko (1914); J.Dolinski (1915) and T.Sotoloyhow (1924) about 80 years ago, by the action of heat alone and by strong acids, but polymers obtained were of low molecular weight. In 1947, polymers of high molecular weight of about 150000 were successfully prepared by the action of  $\text{BF}_3$  gas at low temperatures and benzoyl peroxide at  $80^{\circ}\text{C}$  [1] and thereafter further research on its polymerization and copolymerization by various catalysts, availabilities of polymer and copolymer as films, paper impregnants and electrical insulation at high temperatures were carried out widely in USA [2] and England [3,4]. Because polyacenaphthylene has good heat and electrical properties.

Up to 1955, however, no mechanism for its polymerization has ever been proposed by previous workers. The polymerization reaction was studied by using complex of  $\text{BF}_3$  with ether as ionic initiator and overall rate

of polymerization was shown to be first order with respect to initial concentrations of both monomer and catalyst used [5].

It has been well known that acenaphthylene polymerizes with cationic catalysts (Borontrifluoride [1], stannic chloride  $\text{SnCl}_4$  [6],  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  [7]) ,free radicalic catalysts (Benzoyl peroxide, BPO, [8] ) and anionic catalysts (Butyllithium [9], Na,Li in THF [10] ) in solution.

Solid state reactions of acenaphthylene have been carried out extensively considering radiation induced polymerization [11,12] and free radicalic and cationic polymerization. Electroinitiation [13,14] and emulsion [15,16] polymerization have also been investigated.

#### 1.2. Studies on Solid State Polymerization of Acenaphthylene

Acenaphthylene offers interesting possibilities as a monomer for solid state polymerization studies, the polymerization reaction should be capable of being initiated readily or most advantageously by irradiation techniques.

In 1962, the polymerization of acenaphthylene in solid state initiated by  $\gamma$ -rays have been undertaken in air, under nitrogen, and in vacuum [12]. Results on the polymerization of acenaphthylene in the presence of air showed that the

percent polymerization was directly proportional to the total dose after a certain induction period. On the other hand, no induction period was present and the percent polymerization was directly proportional to the total dose for the polymerization under nitrogen. However the overall rate of polymerization was slower than that of first case which was carried out in air. This can be explained by impurities including oxygen which increase the rate of polymerization.

The molecular weight distribution of polyacenaphthylene formed in the solid state in the presence of isobis(isobutyronitrile) (AIBN) indicated the presence of two polymerization processes due to the changed phase condition caused by the appearance of polymer and by the presence of initiator and its decomposition fragments. The most important aspect of the phase condition was the freedom of mobility of molecule which was different in melt, viscoelastic medium and glassy phase. The crystallized monomer was not present in the liquid or the plasticized phase [11].

The phase diagram of ACN-PACN was determined in connection with study of solid state polymerization. It was pointed out that in matrix of acenaphthylene containing polyacenaphthylene, PACN, a molten highly elastic or glassy



polymer-monomer solution phase and crystalline phase exist together depending on the temperature and composition of system. It was established that, below 50°C, polymerization could take place only when crystalline monomer was an equilibrium system which demonstrated direct connection between kinetics of solid state polymerization and phase diagram. Later in 1974, examination of molecular mobility and interactions between monomer and polymer were done in polymerizing system by ir, x-ray and spin lattice relaxation measurements which confirm previous results on the phase diagram of the ACN-PACN system as well as the structure of polyacenaphthylene formed in the solid state polymerization. The mobility of molecules is higher than those in the solid phase resulting in a higher polymerization rate [17].

The crystal structure of acenaphthylene and the products of its solid state oligomerization initiated by iodine was investigated by x-ray, analytical and ir spectroscopic methods [18,19]. In these studies, the configurations of oligomer molecules and distances between atoms in the lattice were found. It was seen that in the course of rotation of the acenaphthylene molecule, some vinyl to vinyl contacts occur repeatedly. It was concluded that the conditions of topotactic solid state polymerization

were realized in acenaphthylene crystals.

In 1976, the effects of inhibitors on  $\gamma$ -ray initiated solid state polymerization of acenaphthylene was studied [20]. Chloranil (tetrachloroquinone) KA and Bromanil (tetrabromoquinone) BA which are effective inhibitors of radical polymerization were chosen as the inhibitors of that study. KA and BA which have otherwise similar radiation chemical properties affect the solid state polymerization of acenaphthylene in different manner. KA decreases the rate of polymerization proportionally to its concentration and besides it also decreases the conversion limit of the polymerization. This limit, above 8 mole% BA content is independent of BA concentration. The reason for the different behavior is that while BA forms an ideal eutectics with acenaphthylene, KA forms a solid solution of limited miscibility at the temperature of the experiments. Both pairs of compounds give charge transfer complexes in the solid state.

It was reported that acenaphthylene forms amorphous polymer on irradiation with  $\gamma$ -rays [12] while dimer called heptacyclene was produced under uv irradiation by Dziwonski [21]. Examination of the possibility of vapour phase grafting of Acenaphthylene on various polymer films by  $\gamma$  and uv irradiation was studied by Hayakawa [22]. The colour of

acenaphthylene homopolymer depended on the state of monomer, in the liquid phase, colourless polymer was produced while yellowish polymer was produced in the solid state by  $\gamma$ -rays. Chen [12] attributed the difference in colour of polyacenaphthylene to a difference in the molecular weight of polymer, that is, shorter polymer was yellow and longer polymer was colourless. According to his results, it seems probable that the graft copolymer produced by the vapour phase method has shorter branches, while that by liquid phase method has longer branches.

Recently, the  $\gamma$ -ray induced solid state polymerization of binary mixtures consisting of a maleimide derivative as the first component and acenaphthylene and trans-stilbine as the second component was investigated regarding the occurrence of copolymerization. Vapour pressure of monomers as a measure of diffusibility has been considered to play a large role in the solid state polymerization and copolymerization proceeded by the radical mechanism. Therefore, higher temperature, if it did not exceed the melting point was preferable for the solid state copolymerization [23].

### 1.3 Dilute Solution Properties of Polyacenaphthylene

First, Moacanin and his coworkers were studied the solution properties of polyacenaphthylene and poly(4-vinylbiphenyl) in both good and  $\theta$ -solvents. They showed that the unperturbed dimensions of polyacenaphthylene, poly(4-vinylbiphenyl), polystyrene, poly( $\alpha$ -methylstyrene) are similar. The small differences which may exist in those dimensions can be reconciled with differences in rotational barriers estimated from  $T_g$ , glass transition temperature [24].

In 1966-1967, the photodecomposition of polyacenaphthylene in benzene were studied and attempts to find possible causes for polyacenaphthylene degradation by measuring solution viscosities under various conditions and by investigating influence of several effects such as heat, light, iodine addition were made [25,26]. In both work, they observed a viscosity decrease with time. They too found that process is strongly accelerated by the light and dependent on wavelength, concentration and molecular weight. Opposing proposals were done about the mechanism of degradation. The first mechanism proposed was photoinitiated preponderant random chain scission as compared with the second one, a mixed chain-chain scission-"Unzipping Process". According to a recent article on this process,

the polyacenaphthylene sample when irradiated in solution undergoes random chain scission. The photodegradation is solvent and temperature dependent and leads to a lower limit of degree of polymerization. Polymer analogous reactions and crosslinking can be found to occur simultaneously. A certain fraction of "weak links" was detected in the polymer [27].

Polyacenaphthylene has a cyclic repeating unit, as a result, in contrast to polystyrene or other vinyl aromatic polymers only one half of backbone bonds can rotate. This structural feature along with bulkiness of substituent should impart considerable stiffness to polymer chain and lead to expanded coil conformation in solution. The high  $T_g = 260^\circ\text{C}$  for this polymer as compared to polystyrene, is an expected consequence of greatly hindered bond rotation. Another feature is that in each repeating unit both carbons are asymmetric which leads to four possible stereoconfigurations: threo(trans) and erythro(cis) each configuration being either diiso and disyndiotactic. The stereoregular placements are expected to have widely different probabilities because of the hindrance to cis placement caused by the bulky substituent [28]. Thus three such placements in diisotactic configuration would bend the backbone into ring and three in disyndiotactic configuration would lead to gross overlap of rings. Trans(threo) additions

are, on the other hand, relatively unhindered. Regular sequences would produce a helix (trans-diisotactic) or a "stepped chain" (trans-disyndiotactic) .

Moacanin and his coworkers found that in dilute solution this polymer appears to behave as flexible chains. This was contrary to the extremely high degree of hindrance to rotation as indicated by examination of molecular models. They reported  $\theta$ -temperature as 35°C in 1,2-dichloroethane. The polymers were obtained by benzoyl peroxide initiation in bulk. A number of fractions were characterized by means of light scattering, osmotic pressure, viscosity determinations in theta solvent and in benzene. The observation of crystalline x-ray patterns for the polymer suggests a considerable degree of stereoregularity [29].

The samples examined in Barrels-Rienda's [30] study were prepared by thermal polymerization. They are presumed to be completely atactic, but with a predominance of trans form and only relatively infrequent cis placement. From their study on Flory- $\theta$ -temperature in ethylenedichloride  $\theta$ -temperature was found to be 20°C, that is, lower than the value(35°) reported by Maocanin. Polyacenaphthylene, even its atactic form, its chain might be expected to be rather inflexible, since as well as having bulky substituent and "locked" bonds.

In their second paper, the unperturbed dimension of polyacenaphthylene chain in solution was derived and steric hindrances to rotation were estimated [31]. Because of these values of polyacenaphthylene when compared to those of polystyrene, the anticipated "stiffening effect" of bulky substituent was therefore much less than expected. These samples of polyacenaphthylene gave solution properties that are quite normal and the large substituents and "locked" alternate bonds in the chain do not impose abnormally large coil dimensions.

More recently, Agbaje reported  $\theta$ -temperature as  $41.1^{\circ}\text{C}$  and different Mark-Houwink-Sakurada (M-H-S) relationships in various solvents. The evaluated values of exponent ( $a$ ) of M-H-S equation for polyacenaphthylene in benzene, toluene and tetrahydrofuran confirm previous reports (Moacanin and Barrales-Rienda) that polyacenaphthylene in dilute solutions behaves in a manner similar to that of flexible coils [32].

Another result on the occurrence of branching during thermal polymerization of acenaphthylene was agreed with that of Utracki [26]. However, Moacanin suggested that branching, if it occurs at all, cannot be extensive.

It was reported that polyacenaphthylene macromolecules can be treated as statistical coils which are thermodynamically fairly flexible and have strong

hydrodynamic reactions between chains [33]. The hydrodynamic properties of polyacenaphthylene samples studied in benzene solutions at 24°C by viscometry, progressive diffusion and sedimentation rate. The obtained data were used to determine the equilibrium skeletal rigidity of polyacenaphthylene chains. This was characterized by the length A of the Khun segment. The A value of polyacenaphthylene calculated was twice as large as those found for flexible polymer chain. To clarify the question of the likely polyacenaphthylene chain conformations, the optical properties of this polymer were studied by the structural similarity method. The most probable molecular chain conformation of polyacenaphthylene in the solution will be a trans-disyndiotactic chain or  $4_1$  coil. Due to the size of bulky naphthylene ring, molecular rotation relative to these is practically impossible. This state permits consideration of polyacenaphthylene as polymers with half-ladder(comb-like) macromolecular structure.

Chain stiffness of polyacenaphthylene was studied by Chu [34] because polyacenaphthylene chain has extreme steric hindrance, only weak intramolecular forces and locked linkages. The most probable molecular structure for polyacenaphthylene was first examined on the basis of a space filling molecular model. The spectroscopic evidence



for the chain structure was later interpreted in accordance with the proposed model. Trans-disyndiotactic configuration was found to be predominant microstructure in polyacenaphthylene samples. Some thermal properties and crystallizability of polyacenaphthylene were also studied. Both a non crystallizable and an inflexible nature of polyacenaphthylene chain were found in bulk state. The unperturbed chain dimension results indicate that polyacenaphthylene is expanded only approximately 10% more than polystyrene. This unexpected chain flexibility of polyacenaphthylene is explained in terms of hindered rotation that is compensated by a mixed chain microstructure.

## 2. POLYMERIZATION TECHNIQUES AND SOLUTION PROPERTIES

### 2.1 Brief Summary On Polymerization Techniques

#### 2.1.1 Radiation Induced Solid State Polymerization

In the case of interaction of matter with  $\gamma$ -rays, the energy absorbed by the molecule is so excessive that an electron is not just excited into a higher energy state, but it is completely ejected from the molecule and for this reason this type of high energy radiation is often referred to "Ionizing Radiation".

Higher energy ionizing radiation, such as  $\gamma$ -rays, is not subject to the transparency difficulties and will usually pass through any reasonable thickness of solid monomer without any appreciable decrease in the intensity. Accordingly ionizing radiation has been used to cause the polymerization of a wide variety of solid monomers. Sometimes polymerization is permitted to occur during irradiation and this technique is termed as insource polymerization. In some cases, it has been shown that the irradiation only serves to introduce the initiating species into the solid monomer and that polymerization may take place after removal of the monomer from the source. This sort of polymerization is named as postpolymerization.

There are some disadvantages on insource polymerization method, firstly the radiation damage on the reaction product is not prevented. Secondly in the insource polymerizations, branched polymers may be obtained because of the new active centers on the chain arising from the irradiation damage. Finally, during irradiation the crystal environment is continuously changing and at the latter stages of irradiation many ionizations and excitations may occur on or near polymer chains which can interfere with further growth of polymer in the insource method.

The radiolysis of vinyl type monomers results in the formation of cations, anions and free radicals. It is then possible for these species to initiate chain polymerizations. Most radiation induced polymerization are radical polymerizations, especially at ambient or higher temperatures.

Radical chain polymerization is a chain reaction consisting of a sequence of three steps namely initiation, propagation and termination. It is not necessary to exist an effective termination step for some chain polymerizations of solid state polymerization. In such cases, further growth of polymer chain is prevented by trapping the radicals in the polymer matrix.

### 2.1.2 Thermal Bulk Polymerization

Polymerization in bulk, is the most obvious method of synthesis of polymers. Bulk polymerization of vinyl monomers is more difficult, since the reactions are highly exothermic and with the usual thermally decomposed initiators, proceed at a rate which is strongly dependent on temperature.

The polymerization of unsaturated monomers typically involves a chain reaction. The characteristic of chain polymerizations are the active center that consists of cation, anion or free radical responsible for the growth of the chain and polymer molecules are formed from the beginning of the reaction.

Many reactions take place through intermediates having an unpaired electron which are called free radicals. They can be generated in a number of ways including thermal decomposition of peroxides or azo compounds. The other ways of generating free radicals used to initiate polymerization include dissociation of covalent bonds by high energy radiation, reduction-oxidation reaction and electrochemical processes.

A common reaction used to produce radicals for the polymerization is the thermal decomposition of benzoyl peroxide:



## 2.2 Conformation and Viscosity Measurement

### 2.2.1 Conformation of Polymer Chain

The geometrical arrangement of atoms in a polymer chain can be divided into two groups [35]:

(1) The arrangements which are fixed by synthesis, for example, cis and trans isomers or d- or l- forms are termed as configuration. Configuration of polymer chains can not be altered unless chemical bonds are broken and reformed.

(2) The arrangements arising from rotation about single bonds, manifold forms that polymer chain may have in solution are termed as conformation.

In dilute solution where the polymer chain is surrounded by small solvent molecules, polymer molecule is in the continual motion because of its thermal energy assuming many different conformations in rapid succession. The random coil arises from relative freedom of rotation associated with chain bonds of most polymers.

The interpretation of conformation of linear polymeric chain molecule dispersed in a dilute solution can be resolved into short range and long range interactions. The former is determined by geometrical parameters such as bond angles and bond lengths as well as with potential energies which are affected by steric and electrostatic interactions between neighbouring atoms and groups in the chain sequence. The latter involves pairs of units which are distant in chain sequence but come near to one another in space when involved mutual interaction because of continual thermal motion of the chain molecule. Because of mutual interaction between chain units, out of total number of random-flight conformations, only a small fraction will be altogether free of self-interactions and hence acceptable conformations for real chain molecule. As a sequence of retaining latter conformations to exclusion of all others, the average size of real molecule is perturbed relative to its random-flight analog. This effect is also called excluded volume effect and includes interactions between chain groups with solvent.

In order to make more easy to understand above concept  $\langle r^2 \rangle_0$  denotes the mean square end to end distance which would be obtained in absence of perturbation of long range interactions. Actual dimension of chain molecule is related

to unperturbed dimension through the equation,

$$\langle r^2 \rangle = \alpha^2 \langle r^2 \rangle_0$$

where the average expansion  $\alpha$  of the molecule arising from long range interactions.

Through selecting solvent and temperature, excluded volume for chain unit can be compensated exactly by mutual attraction between chain units in poor solvents, temperature at which perturbation of chain conformation vanishes is called  $\theta$ -temperature by Flory [36a]. Thus chain assumes unperturbed dimensions at  $\theta$ -temperature, the  $\alpha$  parameter equals unity and

$$\langle r^2 \rangle = \langle r^2 \rangle_0$$

Since chain conformation is strickly related to short and long range interactions which determines dimensions of the chain, determination of chain dimensions at different conditions is one of the most widely used methods to study chain conformations.

The values of unperturbed dimension can be obtained experimentally from dilute solution measurements made either directly in a theta (ideal) solvent or by using indirect measurements in non-ideal solvents and employing extrapolation procedure [37].

Two principle methods currently in use for determining dimension of polymers, both are operative in very dilute solutions only. One depends on determination of angular dependence of light scattered by dispersed polymers, the other involves determination of the intrinsic viscosity.

### 2.2.2 Viscosity Of Polymer Solutionn

A parameter of considerable importance is the viscosity ratio or relative viscosity  $\eta_r$  which is defined as  $(\eta / \eta_o)$  and can be related to the flow times  $(t)$  and  $(t_o)$  which lead to;

$$\eta_r = \eta / \eta_o = t\rho / t_o\rho_o \quad (2.1)$$

This equation can be further simplified since for a dilute solution  $\rho \simeq \rho_o$  and so  $\eta_r$  is normally taken as  $t / t_o$ . Since  $\eta_r$  becomes unity for an infinitely dilute solution, it is more useful to define the specific viscosity,  $\eta_{sp}$ , which is given by,

$$\eta_{sp} = \eta_r - 1 = (t - t_o) / t_o \quad (2.2)$$

The specific viscosity then corresponds to the fractional increase in viscosity of the solvent due to the presence of polymer molecules.

It is obvious that this increase in viscosity will depend upon the concentration of polymer molecules in the solution and it is possible to represent the variation of



specific viscosity with concentration as a power series in concentration such as,

$$\eta_{sp} = [\eta]c + k[\eta]^2 c^2 + \dots$$

or

(2.3)

$$\eta_{sp} / c = [\eta] + k[\eta]^2 c + \dots$$

where  $k$  is a constant.

The term  $(\eta_{sp})$  is often called the viscosity number. The limiting viscosity number (or intrinsic viscosity)  $[\eta]$  describes the ability of the polymer molecules to increase the viscosity of the solvent in the absence of any intermolecular interaction. The second term represents the interactions between molecules in the solution.

Measurements of  $(\eta_{sp})$  are normally made of a series of solutions of different concentration by determining flow times.

### 2.2.3 Limiting Viscosity Number And Molecular Weight

The limiting viscosity number  $[\eta]$  can be readily related to the molecular weight of a monodisperse polymer,  $M$ , through a semi-empirical equation of the form,

$$[\eta] = K.M^a \quad (2.4)$$

This is often called the Mark-Houwink-Sakurada equation and is usually treated as a semi-empirical equation. The M-H-S

constants are the characteristic for a given polymer solvent system. Usually the value of  $(a)$  is typically between 0.5 and 1. In fact, it is found to be about 0.5 for a solution in the theta condition and is higher for better solvents.

When  $[\eta]$  is measured for a polydisperse sample, the value of  $M$  obtained in this case is an average one and it is often called the viscosity average molecular weight  $\bar{M}_v$ .

It can be shown that  $\bar{M}_v$  is given by,

$$\bar{M}_v = \left( \frac{\sum N_i M_i^{1+a}}{\sum N_i M_i} \right)^{1/a} \quad (2.5)$$

for a polydisperse polymer sample. Because  $(a)$  normally lies between 0.5 and 1, the value of  $\bar{M}_v$  is between  $\bar{M}_n$  and  $\bar{M}_w$ . It is normally close to  $\bar{M}_w$  and in the special case when  $a=1$ ,  $\bar{M}_v \simeq \bar{M}_w$ .

#### 2.2.4 Determination of The Unperturbed Dimension of Polymers from Viscosity Measurements.

The viscosity method depends upon the relationship suggested by Flory and Fox for random coiled polymers and confirmed in a manner of instances [36b]

$$[\eta] = \phi ( \langle r^2 \rangle^{3/2} ) / M \quad (2.6)$$

where  $M$  is the molecular weight and  $\phi$  is a universal

constant. If measurements are carried out at the  $\theta$ -point, this expression is appropriately written

$$[\eta]_{\theta} = \phi \left( \langle r^2 \rangle_0 / M \right)^{3/2} \cdot M^{1/2} \quad (2.7)$$

for chain molecules of sufficient length. The unperturbed mean square end to end distance  $\langle r^2 \rangle_0$  is proportional to the chain length and therefore to  $M$ . Hence the equation (2.1) may be written as

$$[\eta]_{\theta} = K_{\theta} \cdot M^{1/2} \quad (2.8)$$

where  $K_{\theta}$  is a constant for the given type of polymers,

$$K_{\theta} = \phi \left( \langle r^2 \rangle_0 / M \right)^{3/2} \quad (2.9)$$

$$\text{or } \left( \langle r^2 \rangle_0 / M \right)_{\infty} = \left( K_{\theta} / \phi \right)^{2/3} \quad (2.10)$$

The subscript  $\infty$  serves as a reminder that the ratio has been assigned its limiting value. The ratio of the unperturbed mean square end to end distance to molecular weight is the quantity which provides complementary information of polymer chains [38]. The applicable value of  $\phi$  at  $\theta$ -point or near  $\theta$ -point is  $2.5 \times 10^{23}$  for monodispersed polymers with  $\langle r^2 \rangle$  in  $\text{cm}^2$  and  $[\eta]$  in  $\text{ml/g}$ .

#### 2.2.5 The Characteristic Ratio

The quantity most widely used to characterize random coil conformations of chain molecules is the characteristic ratio.

$$C_{\infty} = \langle r^2 \rangle_0 / nl^2 \quad (2.11)$$

where  $\langle r^2 \rangle_0$  is the mean square end to end distance of the chain as unperturbed by long range interactions (excluded volume effects) and  $n$  is the number of skeletal bonds, each of length  $l$ .

The requirement that the molecule be in its unperturbed state parts from the desire that its dimension truly reflected the nature of the chain with regard to its structural geometry and short range intramolecular interactions.

#### 2.2.6 The Steric Factor

Steric factor provides a measure of chain stiffness in dilute solution.

$$\sigma = ( \langle r^2 \rangle_0 / \langle r^2 \rangle_{of} )^{1/2} \quad (2.12)$$

where  $\langle r^2 \rangle_0$  and  $\langle r^2 \rangle_{of}$  are the mean square end to end distance of unperturbed and freely rotating chains respectively. This value represents a measure of restriction to free rotation in the chain. This conformation factor depends on generally temperature and sometimes also solvent.

### 3 EXPERIMENTAL

#### 3.1 Apparatus

##### 3.1.1 High Vacuum System

It was made of Pyrex glass and consists of a fore pump, an oil diffusion pump, main manifold, liquid nitrogen traps and Mcleod-gauge.

The figure and more information about the system can be seen in the related reference [39].

##### 3.1.2 Co-60 irradiation source

The samples were irradiated by Gamma Cell 220 of Atomic Energy of Canada ltd which has a  $^{60}\text{Co}$  source. The dose rates at the beginning and at the end of the study were 0.71 and 0.65 kGy/hour, respectively.

The figure and more information about the system can be seen in the related reference [40].

##### 3.1.3 UV spectrophotometer

The spectra of monomer and polymer were taken from uv-160 spectrophotometer which consists of a micro-computer controlled double-beam recording spectrophotometer.

##### 3.1.4 Viscometer

The viscosities of polymer solutions were measured by using Ubbelohde type glass viscometers.

### 3.1.5 Constant Temperature Bath

The experiments were carried out at different temperatures. Therefore a thermomix was used to adjust the temperature. A water-bath was used in viscosity measurements. The temperatures were measured with a sensitive thermometer with an accuracy of  $\pm 0.01^{\circ}\text{C}$ .

## 3.2 Materials and Purification of Reagents

### 3.2.1 Monomer

The monomer was a product of BDH company. It was purified by recrystallization thrice from ethanol. After recrystallization, the crystals were filtered and dried in a vacuum oven to overnight. The melting point of acenaphthylene crystals was found to be  $91-92.5^{\circ}\text{C}$ .

### 3.2.2 Methanol

Methanol was technical grade, distilled prior to use. Its boiling point was  $61^{\circ}\text{C}$ .

### 3.2.3 Ethanol

Ethanol was technical grade, distilled prior to use. Its boiling point was  $75^{\circ}\text{C}$ .

### 3.2.4 Toluene

It was a product of Merck company, was used without further purification.

### 3.2.5 1,2-Dichloroethane

It was a product of Merck company, distilled under vacuum over  $\text{Al}_2\text{O}_3$ .

### 3.2.6 Chloroform

It was a product of BDH company and was used without further purification.

## 3.3 Experimental Procedure

### 3.3.1 Insource Polymerization

Samples of 5 grams of monomer were placed into the 12 cm length and 12 mm width Pyrex-glass polymerization tubes and the inner contents were degassed in vacuum system for 5 hours and sealed under a pressure of  $10^{-4}$ – $10^{-5}$  torr whilst in liquid nitrogen. The sealed tubes were irradiated with Co-60  $\gamma$ -rays at room temperature. The inner contents were dissolved in toluene and poured into large excess methanol. The polymers were collected by filtration, then vacuum dried to constant weight. From known amount of monomer, percent conversions of monomer to polymer were calculated.

### 3.3.2 Thermal Bulk Polymerization

Samples of 8 grams of the monomer and varying amount of benzoyl peroxide as an initiator were placed into 15 cm length and 12 mm wide Pyrex-glass polymerization tubes.

The inner contents were degassed in vacuum and sealed. Then the polymerization was carried out in a constant temperature bath at  $100 \pm 3^\circ\text{C}$ . The polymer recovery was obtained with the same procedure as in the case of insource polymerization.

### 3.3.3 Viscosity Measurements

The relative viscosity " $\eta_r$ " is obtained by measuring flow times of solvent " $t_o$ " and the solution " $t$ "

Specific viscosity " $\eta_{sp}$ " is

$$\eta_{sp} = \eta_r - 1 = \frac{t - t_o}{t_o} \quad (3.1)$$

Intrinsic viscosity,  $[\eta]$ , is defined as,

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} \quad (3.2)$$

Therefore intrinsic viscosities were obtained by plotting  $\frac{\eta_{sp}}{c}$  and  $\frac{\ln \eta_r}{c}$  against  $c$  (gr/100 ml) and extrapolating to zero concentration according to

$$\text{Huggin's equation} \quad \frac{\eta_{sp}}{c} = [\eta] + k' [\eta]^2 c \quad (3.3)$$

and

$$\text{Kramer's Equation} \quad \frac{\ln \eta_r}{c} = [\eta] + k'' [\eta]^2 c \quad (3.4)$$

The intrinsic viscosities of resultant polyacenaphthylene samples were measured by using an Ubbelohde type of viscometer.



Viscosity measurements were done in toluene at 25°C. Viscosity-average molecular weights,  $\bar{M}_v$ , were calculated with the relation [32] of  $[\eta] = 8.64 \times 10^{-3} \bar{M}_v^{0.65}$ , where  $[\eta]$  unit is ml/g.

In order to evaluate the solution properties of polyacenaphthylene, the viscosity data were also obtained for polyacenaphthylene solutions in 1,2-dichloroethane and chloroform.

## 4. RESULTS AND DISCUSSION

### 4.1 Insource Polymerization

Insource polymerization of acenaphthylene was carried out at room temperature. The sample tubes were exposed to the  $\gamma$ -irradiation with total doses ranging from 167 kGy to 2140 kGy. Chen [12] reported that there is an induction period in solid state polymerization of acenaphthylene initiated by  $\gamma$ -rays in air, however, no induction period is present under nitrogen atmosphere. It was also observed that impurities including oxygen increase the rate of polymerization.

The percent conversion versus exposure time plot for samples irradiated at room temperature is shown in Figure (4.1). The plot shows that the percent conversion curve is dependent on the total irradiation dose. The initial rate of polymerization can be estimated from the slope of initial linear part of time-conversion curve. Since the curve seems to exhibit an induction period of about 250 hours, the initial rate of polymerization may be calculated from time interval of 250 - 1000 hours where the curve is nearly a straight line. The limiting conversion is estimated to be about 70% from this time-conversion curve.

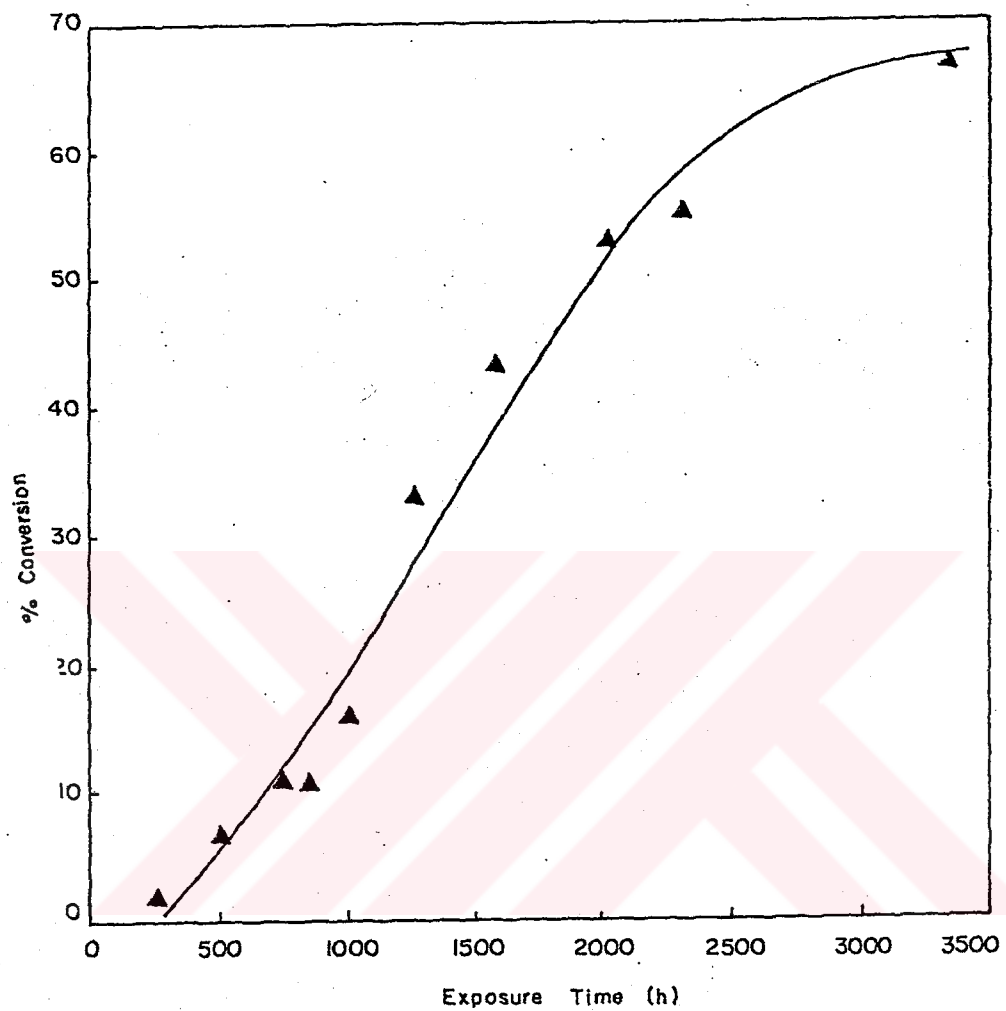


Figure 4.1 : Exposure time-% conversion curve for the solid state polymerization of acenaphthylene

Percent conversions and molecular weights of polymers obtained by the solid state polymerization are tabulated in Table (4.1). It can easily be seen from Figure (4.2) that intrinsic viscosities of polymer increase as the irradiation time is increased up to 2000 hours. Polymers obtained at very high irradiation doses had low intrinsic viscosities attributed to the existence of chain scission processes. Present results suggest that chain scission processes have important effects on the chain length of polymers at high irradiation doses. The degradative effect of radiation on the polymers formed at the initial stages of polymerization can be clarified by determining the molecular weight distributions of polymers.

#### 4.2 Thermal Bulk Polymerization

Thermal bulk polymerization of acenaphthylene was carried out at 100°C using benzoyl peroxide as the initiator. The initiator concentrations and polymerization times were chosen as obtaining sufficient amounts of polymers with certain molecular weights. Since the solid state polymerization of acenaphthylene gave relatively low molecular weight polymers, the higher molecular weight samples were obtained by this method. The results are shown in Table (4.2).

Table 4.1: Solid State Insource Polymerization of  
Acenaphthylene at 0.65 kGy/h dose rate and  
room temperature.

Run	Time (hr)	Dose (kGy)	% Conversion	$[\eta]^*$ (ml/g)	$\bar{M}_v \times 10^{-4}$
R1	260	166.8	1.74	6.19	2.50
R2	509	327	6.67	7.20	3.10
R3	757	486.1	10.61	8.20	3.80
R4	860	547	10.43	7.81	3.50
R5	1010	642.6	15.55	9.27	4.60
R6	1274	844.2	32.94	10.15	5.30
R7	1586	1050.9	42.98	11.13	6.10
R8	2026	1290.5	52.56	12.32	7.10
R9	2310	1485.3	54.97	11.34	6.30
R10	3350	2137.2	66.66	8.25	3.85

\* in toluene, at 25°C.

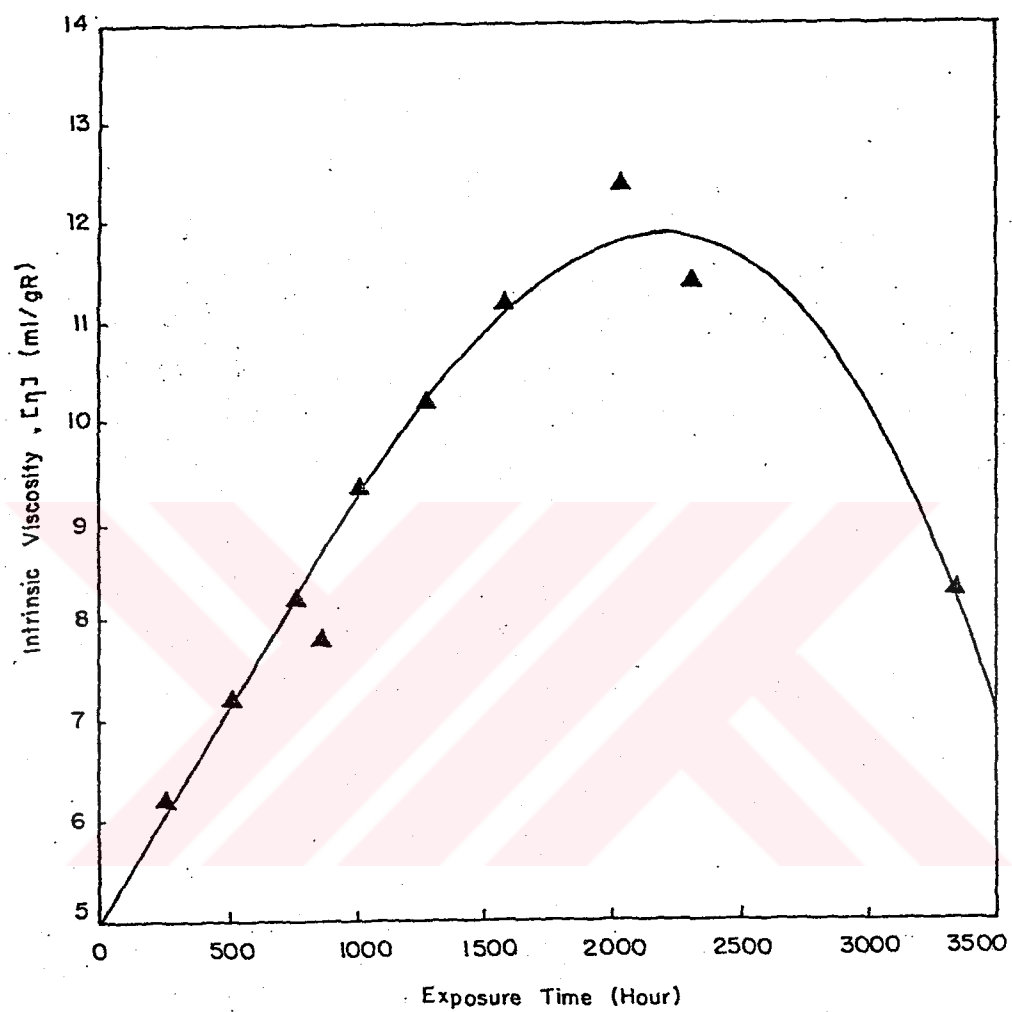


Figure 4.2 : Intrinsic viscosity-exposure time curve for the solid state polymerization of acenaphthylene

Table 4.2: Thermal Bulk Polymerization of Acenaphthylene  
at 100°C .

Run	Initiator $\times 10^{-2}$ concentration (wt%)	Time (Hr)	% Conversion	$[\eta]_{25^{\circ}\text{C}}^{\text{toluene}}$	$\bar{M}_v \times 10^{-5}$
T1	2.5	24	44.19	75.74	11.64
T2	10	24	61.80	53.64	6.85
T3	30	16	66.90	31.20	2.98
T4	60	16	76.07	19.84	1.48

#### 4.3 Characterization of Polymers

UV absorption spectra of the monomer and polyacenaphthylene obtained from both polymerization are shown in Figure (4.3). The maximum absorption wavelength,  $\lambda_{\text{max}}$ , for the monomer and polymer were 323.6 and 297 nm, respectively.

The viscosity average molecular weights of polymers were obtained from the intrinsic viscosities measured in toluene at 25°C. In the determination of intrinsic viscosities, both Huggins (  $\eta_{\text{sp}} / c$  versus  $c$  ) and Kraemer's (  $\ln \eta_r / c$  versus  $c$  ) plots were used. The intrinsic viscosities were found as common intercepts of Huggins and Kraemer's plots. All these plots were nearly perfectly linear and the Huggins and Kreamer's constants found from the slopes of these lines well agreed with the theory. Two such plots are shown in Figures (4.4 and 4.5). The viscosity average molecular weights of all samples were calculated from the intrinsic viscosities in toluene according to the relation [32]:

$$[\eta] = 8.64 \times 10^{-3} \bar{M}_v^{0.65} \quad (4.1)$$

1,2-dichloroethane (1,2-DCE ) is known to be  $\theta$ -solvent for polyacenaphthylene [24]. However, three different  $\theta$ -temperatures which were 41.1, 35 and 20°C, were reported for polyacenaphthylene in 1,2-dichloroethane [32,29,30].



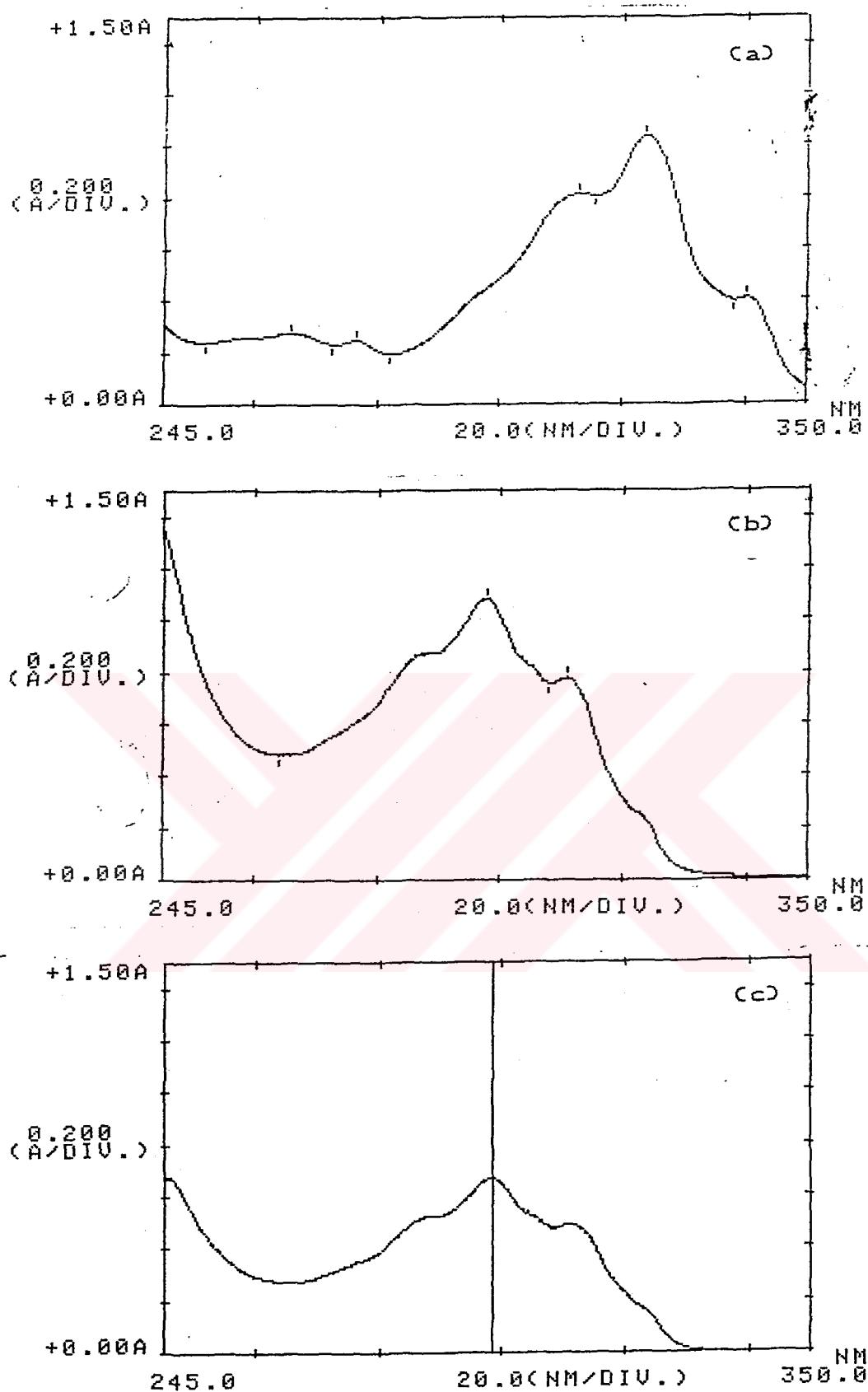


Figure 4.3: The UV Spectra of Acenaphthylene (a) and its polymers (b,c).

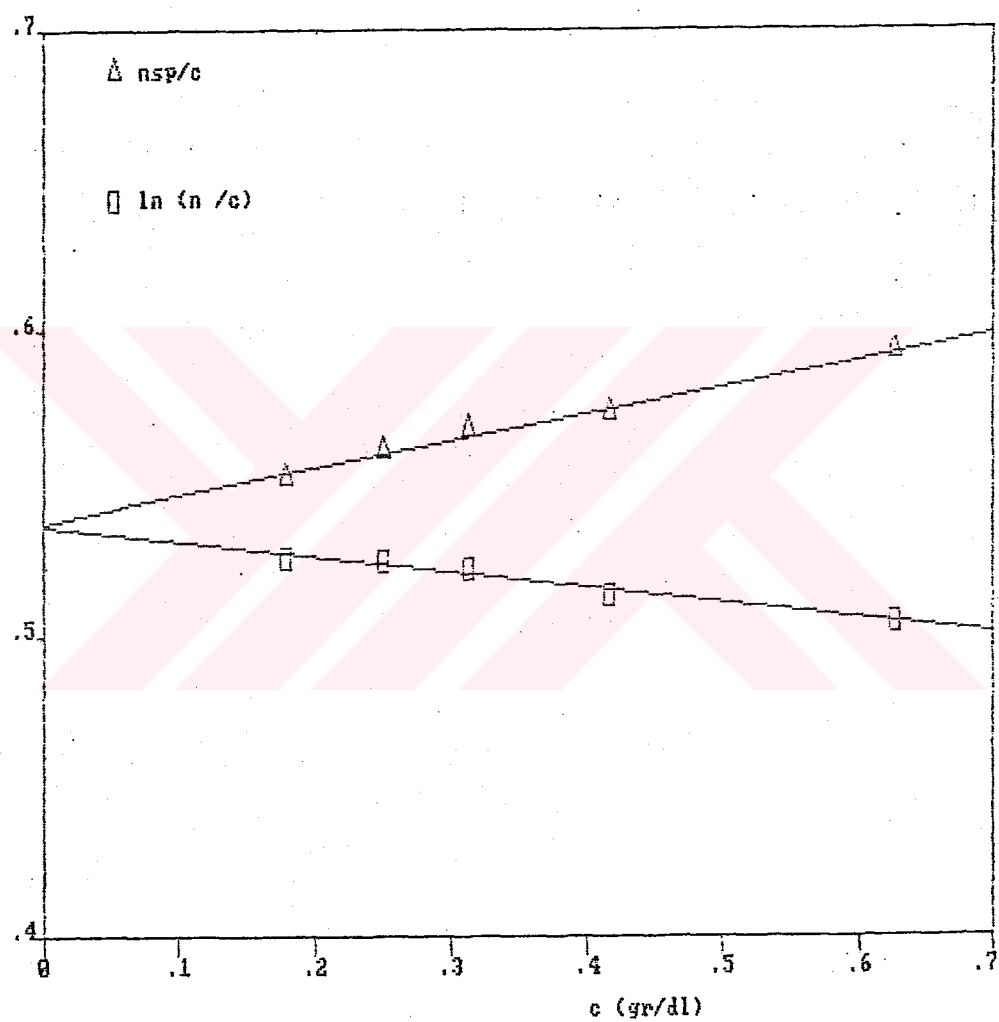


Figure 4.4 : Viscosity Measurements of PACN-T2 sample in toluene at 25°C

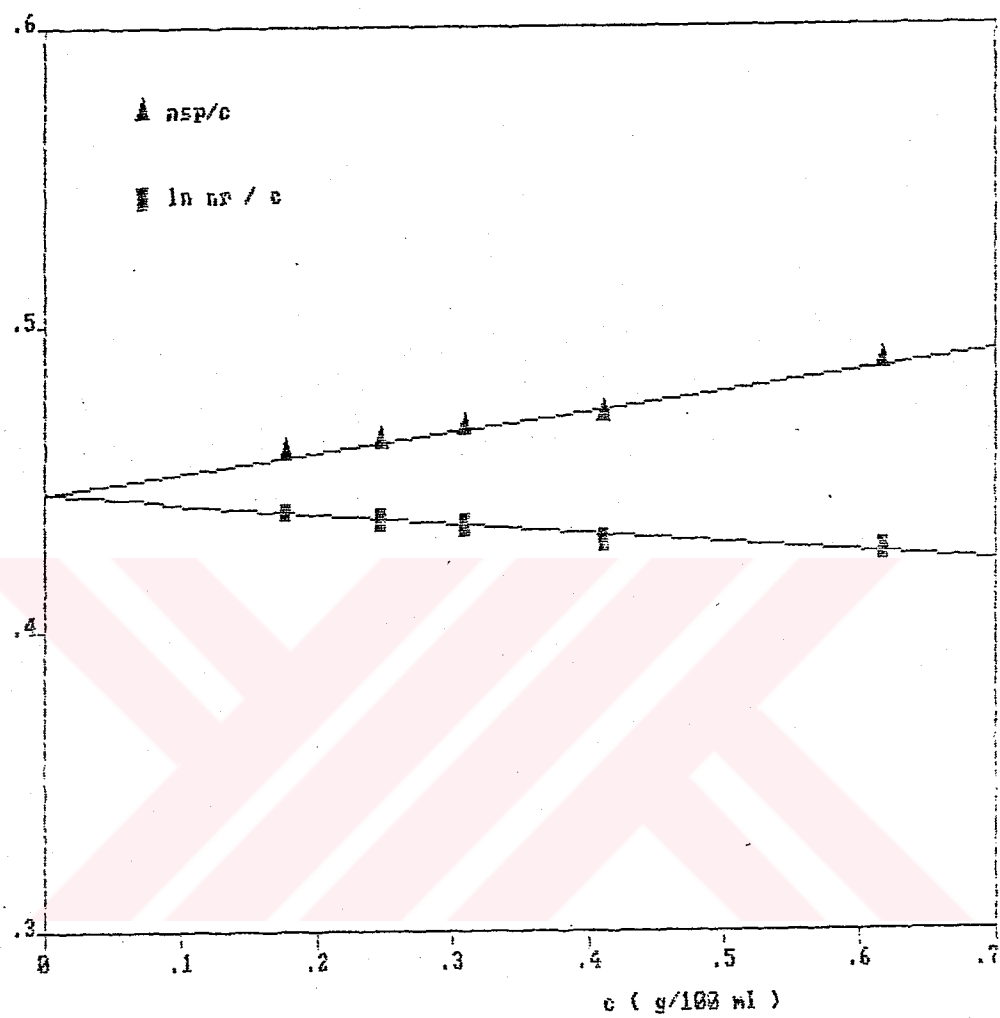


Figure 4.5 : Viscosity Measurements of PACN-T1 sample in 1,2-dichloroethane at 41°C.

The viscosity measurements in 1,2-dichloroethane at 41 and 35°C tried in the present study. Log  $[\eta]$  versus  $\log \bar{M}_v$  plots are shown in Figures (4.6 and 4.7). Following Mark-Houwink-Sakurada relations were obtained from these plots.

$$[\eta] = 4.15 \times 10^{-2} \bar{M}_v^{0.50} \quad (\text{at } 41^\circ\text{C}) \quad (4.2)$$

$$[\eta] = 3.81 \times 10^{-2} \bar{M}_v^{0.50} \quad (\text{at } 35^\circ\text{C}) \quad (4.3)$$

where  $[\eta]$  's are in the unit of ml/g. These results suggested that  $\theta$  condition occurs in a broad range of temperatures for polyacenaphthylene in 1,2-dichloroethane solution. This behavior was observed before other polymers like poly(p-t-butylstyrene) [41].

The intrinsic viscosities of polyacenaphthylene were measured in chloroform at 25°C. Log  $[\eta]$  versus  $\log \bar{M}_v$  plot is shown in Figure (4.8). The M-H-S equation for this system is found to be

$$[\eta] = 6.77 \times 10^{-3} \bar{M}_v^{0.68} \quad (4.4)$$

#### 4.4 Unperturbed Dimension of Polyacenaphthylene

The unperturbed dimension of polyacenaphthylene was determined at  $\theta$ -temperature by using the equation :

$$[\eta] = K_\theta M^{1/2}$$

Table 4.3: Viscosity data of polyacenaphthylene

Run	Intrinsic Viscosity, $[\eta]$ , (ml/g)			
	Toluene *	1,2-dichloro ethane **	1,2-dichloro ethane ***	Chloroform *
T1	75.74	44.48	41.55	86.25
T2	53.64	35.30	33.35	67.90
T3	31.10	23.80	—	39.22
T4	19.84	15.97	—	24.64
R9	11.34	10.77	10.32	13.07
R6	10.15	9.46	—	—
R5	9.27	8.98	7.99	—
R10	8.25	—	—	8.48

\* T = 25°C ,    \*\* T = 41°C ,    \*\*\* T = 35°C .

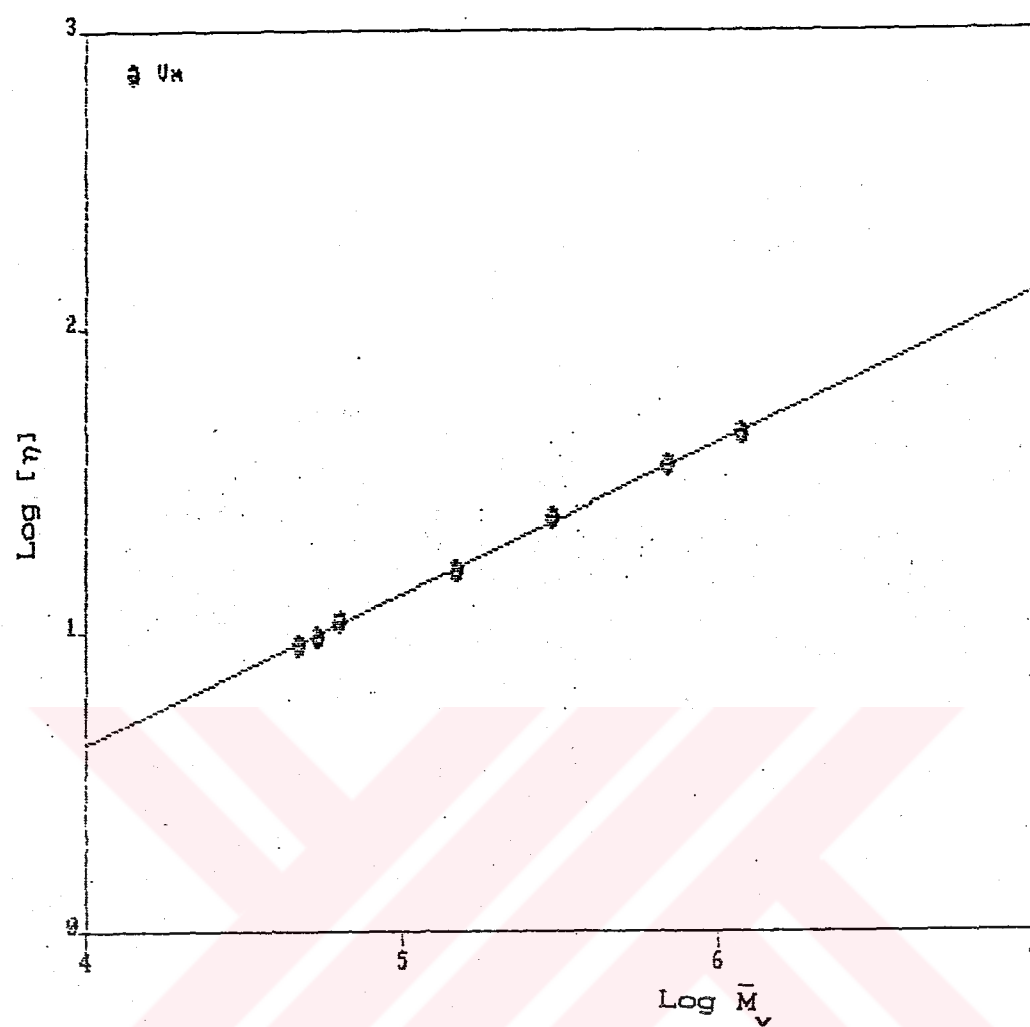


Figure 4.6 : Double Logarithmic Plot of  $[\eta]$  versus  $\bar{M}_v$   
for PACN samples in 1,2-dichloroethane at 41°C.

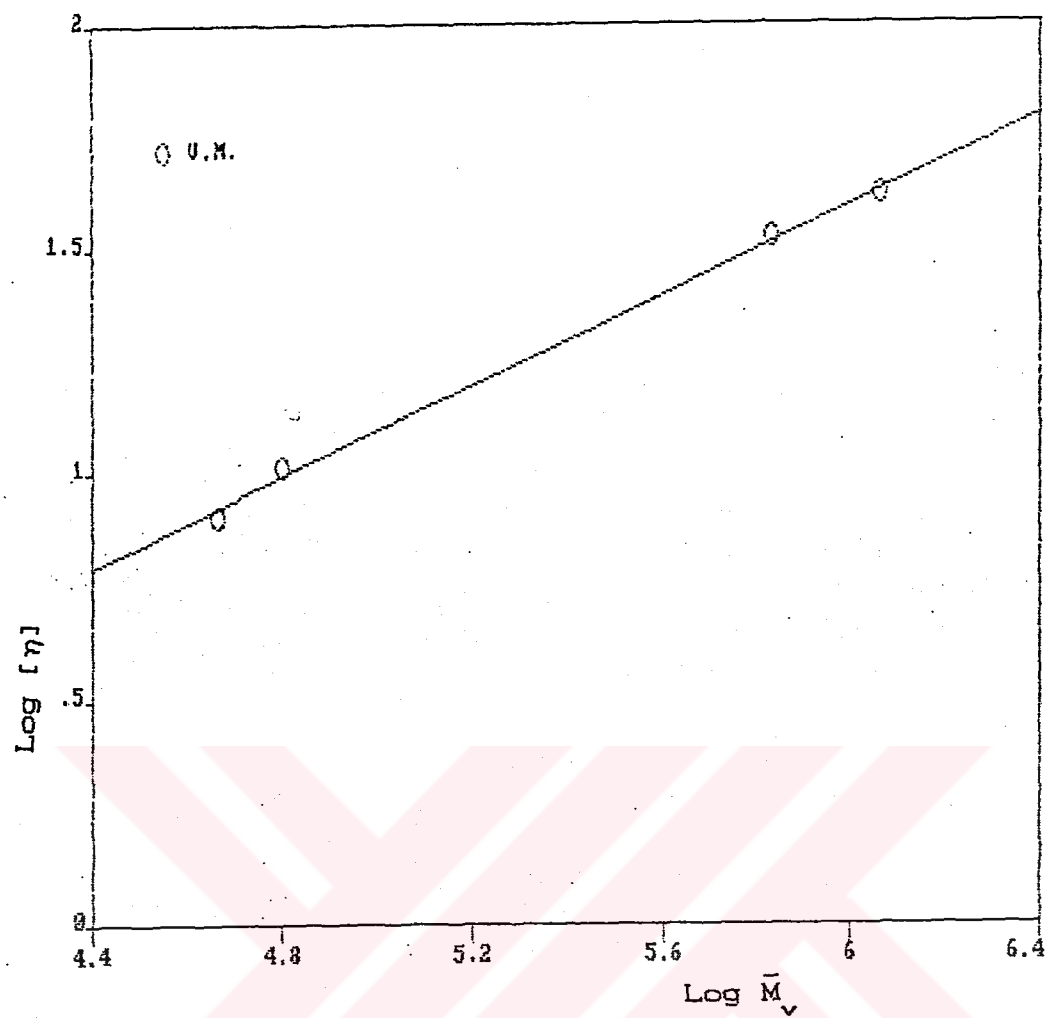


Figure 4.7 : Double Logarithmic Plot of  $[\eta]$  versus  $\bar{M}_v$   
for PACN samples 1,2-dichloroethane at 35°C.

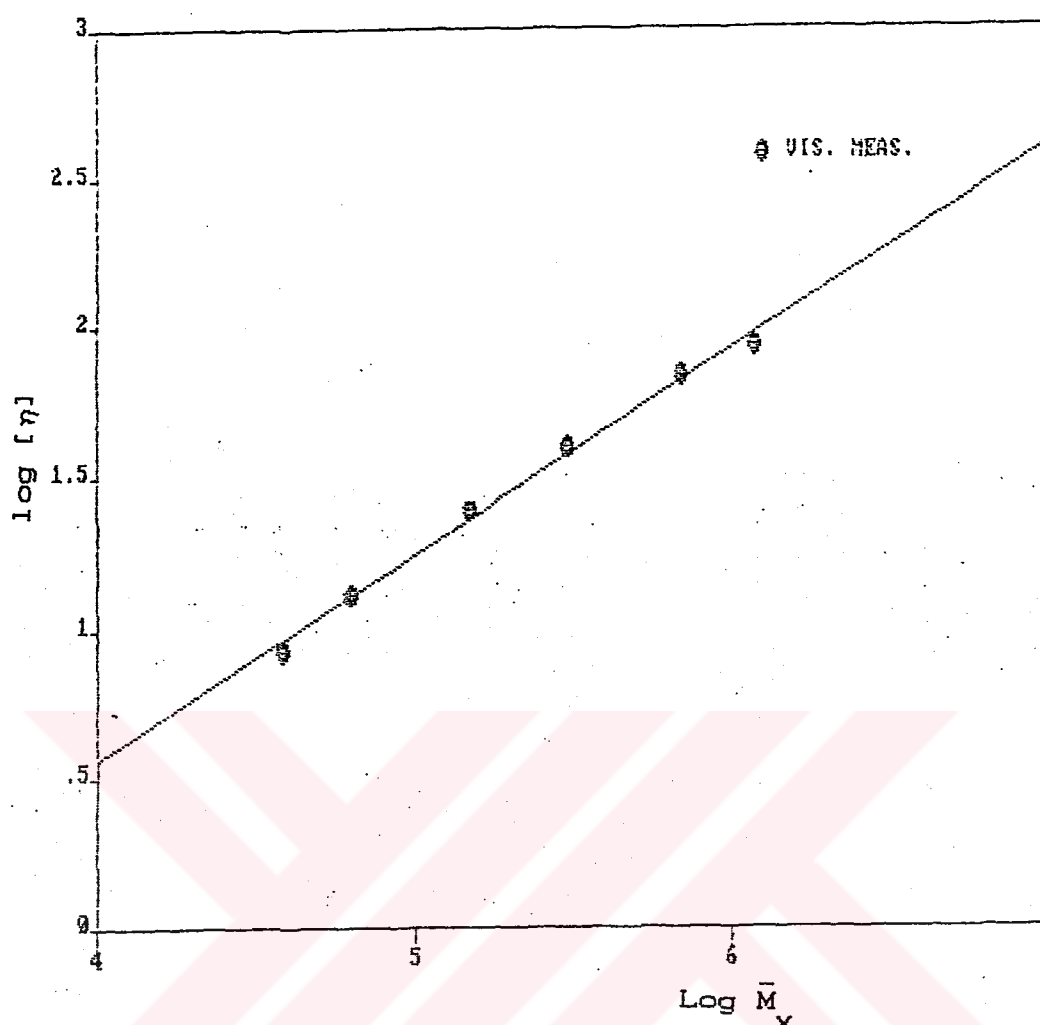


Figure 4.8 : Double Logarithmic Plot of  $[\eta]$  versus  $\bar{M}_v$  for PACN samples in  $\text{CHCl}_3$  at  $25^\circ\text{C}$ .



where

$$K_{\theta} = \phi \left[ \frac{\langle r^2 \rangle_0}{M} \right]^{3/2} \quad (4.6)$$

The  $K_{\theta}$  value for polyacenaphthylene in 1,2-dichloroethane at 41°C where M-H-S exponent is 0.5 was found as  $4.15 \times 10^{-2}$  ml/g. The characteristic ratio was calculated from the following equation

$$C_{\infty} = \lim_{n \rightarrow \infty} \frac{\langle r^2 \rangle_0}{nl^2} = \left[ \frac{K_{\theta}}{\phi} \right]^{2/3} * \frac{M_b}{l^2} \quad (4.7)$$

where  $M_b$  is the mean molecular weight per skeletal bond,  $n$  is the number of bonds on chain backbone and  $\bar{l}^2$  is mean squares of bond lengths. The C — C bond length in the monomer was reported as 0.128 nm [18]. Assuming that this length does not change by the occurrence of an addition reaction and taking the C — C bond length as 0.154 nm,  $\bar{l}^2$  was calculated to be  $2.00 \times 10^{-16} \text{ m}^2$ . In the viscosity measurements, unfractionated samples were used. Therefore correction of  $\phi$  parameter was necessary. The method of correction will be given in section 4.6. The characteristic ratio of polyacenaphthylene was calculated as  $C_{\infty} = 18.00$  by using  $\bar{l}^2 = 2.00 \times 10^{-16} \text{ m}^2$  and  $\phi = 1.28 \times 10^{-23}$  (in cgs units) in theta condition.

#### 4.5 Determination of Unperturbed Dimension

from Buchard-Stockmayer-Fixman ( B-S-F ) equation

The unperturbed dimensions can be estimated from intrinsic viscosities measured under nontheta conditions using various extrapolation procedures. The most useful and common employed procedure is based on the relation given by Buchard [42] and Stockmayer-Fixman [43]. The B-S-F relation is given as

$$[\eta] / \bar{M}_v^{1/2} = K_\theta + 0.51.B.\phi.M_v^{1/2} \quad (4.8)$$

where B is the parameter characterizing long range interactions. It is known that such plots (  $[\eta] / \bar{M}_v^{1/2}$  versus  $\bar{M}_v^{1/2}$  ) are not reliable for good solvents and deviate from linearity in the region of large molecular weight.

The intrinsic viscosity data obtained in chloroform at 25°C was treated according to B-S-F method. A deviation from linearity was observed and from the intercept of non linear regression,  $K_\theta$  was found as  $4.07 \times 10^{-2} (\text{ml/g})$  in chloroform. The characteristic ratio of polyacenaphthylene from B-S-F method was calculated as  $C_\infty = 18.7$  by using the corrected value of  $\phi$  as  $1.18 \times 10^{-23}$ .

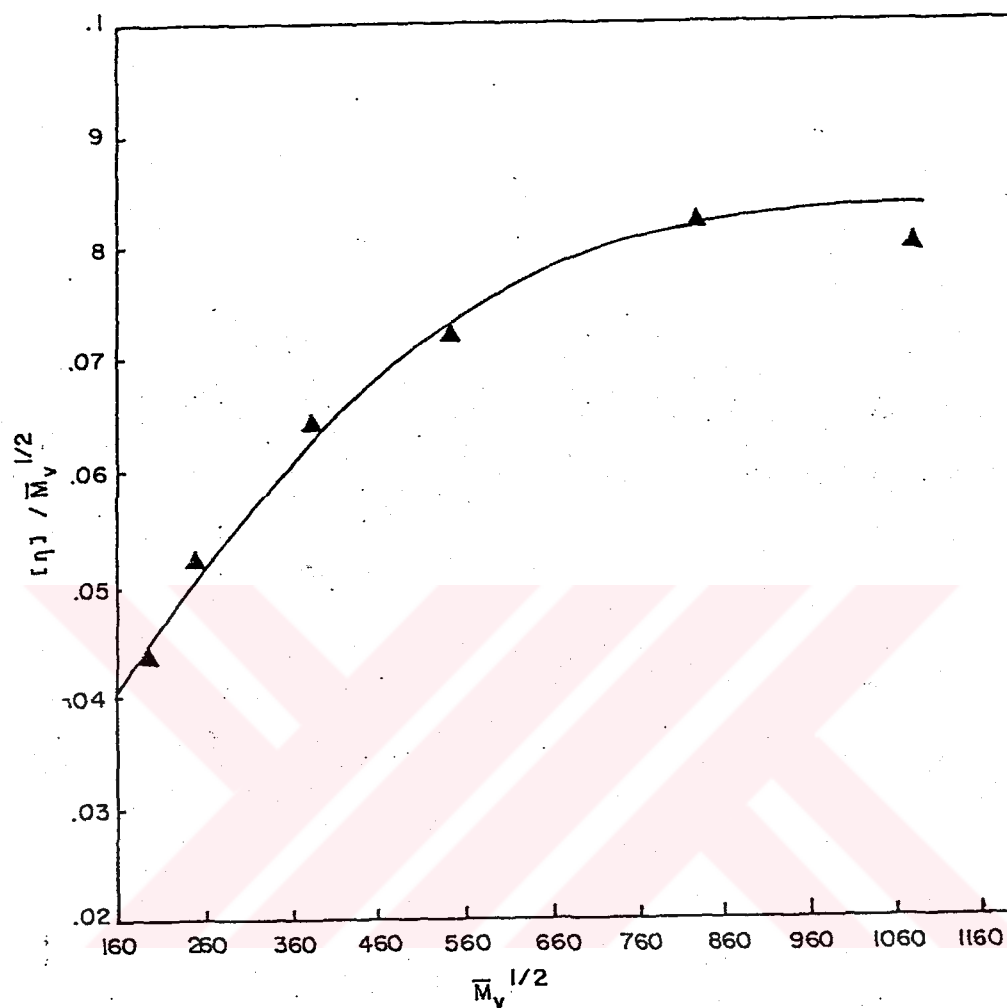


Figure 4.9 : Stocmayer-Fixman Plot For PACN samples in  $\text{CHCl}_3$ .

#### 4.6 Correction on $\phi$

A reasonable estimate of  $\phi$ , Flory Viscosity Function, can be made using

$$Q_{\phi} = \phi_{\text{corr}} / \phi_{0,\infty} \quad (4.1)$$

This quantity depends on distribution function of molecular weight and solvent power ( $\epsilon$ ). The solvent power ( $\epsilon$ ) that is called Ptitsyn-Eizner parameter and obtained from equation (4.12). The value of polydispersity,  $\bar{M}_w / \bar{M}_n$ , was used as the most probable distribution for free radicalic methods, as  $(\bar{M}_w / \bar{M}_n) = 2$ . From below equations, the correction was done [44].

$$\frac{1}{b^*} = \frac{\bar{M}_w}{\bar{M}_n} - 1 \quad (4.10)$$

where  $b^*$  is the polydispersity parameter.

$$\phi = (b^* + 1) \frac{\Gamma(b^* + 3/2 + 3/2\epsilon)}{\Gamma(b^* + 1)} \left[ \frac{\Gamma(b^* + 2)}{\Gamma(b^* + 3 + \epsilon)} \right] \quad (4.11)$$

where  $\Gamma$  is the generalized factorial function (gamma function).

For ideal solvents,  $\epsilon = 0$  and  $Q_{\phi}$  found as 0.51. In good solvent, equation (4.3) was used by introducing  $\epsilon$  value to equation (4.11)

$$\epsilon = \frac{2a-1}{3} \quad (4.12)$$

where  $a$  is the M-H-S constant.

In our case,  $a$  has value of 0.68 in chloroform. Therefore  $Q_\phi$  calculated as 0.47.

The best experimental value of  $\phi_{o,\infty}$  is  $2.5 \times 10^{23}$  (cgs) for monodispersed polymers [38]. Its corrected value at  $\theta$  condition  $\phi_{\text{corr}} = 1.28 \times 10^{23}$  and non theta condition  $\phi_{\text{corr}} = 1.18 \times 10^{23}$ .

In previous papers, on dilute solution properties of polyacenaphthylene [29,33], the correction of  $\phi$  values also were made. Their corrected  $\phi$  values were very close to ours values.

#### 4.7 Short Range Interactions- The Steric Factor

The steric factor,  $\sigma$ , is defined as :

$$\sigma = \frac{(\langle r^2 \rangle_o / M)^{1/2}}{(\langle r^2 \rangle_{of} / M)^{1/2}}$$

With no restrictions on bond rotation, a chain of  $n$  bonds of length  $l$  joined at valance angle  $\theta$  ( $\pi - \alpha$ ) has a mean square end to end distance [36c]

$$\langle r^2 \rangle_{of} = nl^2 \frac{(1 + \cos \alpha)}{(1 - \cos \alpha)}$$

For polyacenaphthylene chain where  $\bar{l}^2$  is  $2.00 \times 10^{-16} \text{ m}^2$ ,  $\theta = 109.5^\circ$ ,  $\cos \alpha = 1/3$  and  $n = \frac{2M}{M_o}$  where  $M_o$  is the monomer molecular weight.

$$\left[ \frac{\langle r^2 \rangle_{of}}{M} \right]^{1/2} = \frac{2.83 \times 10^{-8}}{M_o^{1/2}}$$

The steric factors ,  $\sigma$  , of polyacenaphthylene , polystyrene (PS) and poly( $\beta$ -vinyl naphthylene) (P $\beta$ VN) are tabulated in Table (4.4), in order to get a comparison between them. It appears that higher  $\sigma$  values are due to bulky rigid side groups and to specific interactions between them and solvent. It is clearly apparent that polyacenaphthylene has a steric factor which is very close to that for poly( $\beta$ -vinyl naphthylene). Both polymers having nearly identically bulky side groups and they can be classified as semi-rigid polymers.

Table 4.4 : The Mark-Houwink-Sakurada Parameters For Polyacenaphthylene and Some Vinylaromatic polymers in unperturbed state.

Polymer	$K_{\theta} \times 10^{-2}$ (ml/g)	$\theta$ -solvent	$\theta$ -temp. (°C)	$\alpha$		Ref.
				$\left[ \frac{\langle r^2 \rangle_0}{M} \right]^{1/2}$	$\left[ \frac{\langle r^2 \rangle_{\theta f}}{M} \right]^{1/2}$	
PACN	4.15	1,2-DCE	41	6.88	2.30	3.0 [8]
from B-S-F PACN	4.07	CHCl <sub>3</sub>	25	7.01	2.30	3.05 [8]
PS	8.20	cyclo- hexane	34	6.70	3.02	2.23 [43]
PβVN	5.20	decalin/ toluene	30.2	8.10	2.49	3.2 [44]
PACN	2.12	1,2-DCE	20	5.20	2.50	- [30]
PACN	4.56 <sup>α</sup>	1,2-DCE	35	6.00	-	- [29]
PACN	4.27 <sup>α</sup>	1,2-DCE	41.1	-	-	- [32]

\* unit : cm.mol<sup>1/2</sup>. g<sup>-1/2</sup> and  $\times 10^{-9}$ .

<sup>α</sup> from  $K_v$ , others  $K_v$ .

## 5. CONCLUSION

The following conclusions has been deduced from the results of this study :

1. It has been shown that acenaphthylene polymerization can be initiated by gamma radiation at room temperature (20°C) .
2. The percent conversion increases with the irradiation dose.
3. Benzoyl peroxide initiated polymerization of acenaphthylene at 100°C follows a typical free radical chain polymerization kinetics.
4. The characteristic ratios of polyacenaphthylene obtained from theta condition and indirectly at good solvent are respectively 18.0 and 18.7.
5. The  $C_{\infty}$  found for polyacenaphthylene is higher than that of polystyrene (  $C_{\infty} = 10.0$  ). These results show that the presence of naphthlene group decreases the flexibility of chain and increases the unperturbed dimension of it.
6. For polyacenaphthylene in 1,2-dichloroethane the M-H-S constant remains the same  $a = 0.5$  in the temperature range 41-35°C.
8. The steric factor values of PACN are found as  $\sigma = 3.00$  and  $\sigma = 3.05$  respectively in  $\theta$  and good solvents .



# LIST OF REFERENCES

- [11] Flowers, R.G., and Miller, H.F., J. Am. Chem. Soc., 69, 1388, (1947).
- [12] Flowers, R.G., and Miller, H. F., U.S. Patent 2,510,647 (1950); U.S. Patent 2,563,524 (1951).
- [13] Jones, J.I., J. Appl. Chem., 568, (1951).
- [14] Kaufman, M., and Williams, A.F., *ibid* , 489, (1951).
- [15] Imoto, M., and Takemoto, K., J. Polym. Sci., 15, 271 (1955).
- [16] Cohen, S., Belliard, P., and Marechal, E., Polymer , 14, 352, (1973).
- [17] Giusti, P., Cerrai, P., Andruzzi, F., and Magagnini, P.L., Eurp. Polym. J., 7, 165, (1971).
- [18] Ayrey, G., and Bevington, J. Macromol. Sci. Chem., A22(2), 229, (1985).
- [19] Lindsell, W.E., Service, D.M., and Soutar, I., Polym. Commun., 25, 108, (1984).
- [110] Moacanin, J., and Rembaum, A., Polym. Letters, 2, 979, (1964).
- [111] Hardy, Gy., Kovacs, G., Koszterszitz, Gy., Fedorova, N., and Cser, F., Proceedings of the third Thiany Symposium on Radn. Chem., 601, (1972).
- [112] Chen, C.S., J. Polym. Sci., S62, 538, (1962)

- [13] Kikuchi, Y., and Mitoguchi, H., *Die. Macro. Chem.*,  
173,233, (1973).
- [14] Mano, B.E., and Calafate,B.L., *J. Polym. Sci., Poly.  
Chem. Ed.*, 19, 3325, (1981).
- [15] Chen,Y.C., and Piirma, I., *ibid*, 18, 1979, (1980).
- [16] Piirma, I., and Chen, Y.C., *J. Am.Chem.Soc.Div. Polym.  
Chem.Polym. Preprints.*,19(2),608,(1978).
- [17] Cser,F., Hardy,Gy.,and Veksli, Z., *Eur.Poly.J.*,  
10,1217,(1974).
- [18] Cser, F., *Acta,Chim.Acad.Sci.Hung.*,80(3),317,(1974).
- [19] Hardy, Gy., Kovacs, G.,Cser, F., and Kosterszitz, Gy.,  
*ibid* ,75(3),303,(1973).
- [20] Mahr, L., Cser, F., Kovacs, G., Hardy, Gy., *Fourth  
Symposium on Radn.Chem.*,377,(1976).
- [21] Dziewonski, K.,and Rapalski, G., *Ber.Dtssch.Chem.Ges.*,  
45,2491,(1912).
- [22] Hayakawa, K., Kawase, K., and Yamakita, H.,  
*J.Polym.Sci. PartA-1*,10,2463,(1972).
- [23] Hayakawa, K., Kawase, K., and Yamakita, H.,  
*J.Polym.Sci.Polym.Chem.Ed.*, 23,2739, (1985).
- [24] Moacanin, J., Rembaum, A., and Laudenslager, R.K.,*J.  
Am.Chem.Soc.Polym.Preprints.*,4(2),179, (1963).
- [25] Springer,J., Uebberreiter, K., and Wenzel, R.,  
*Die.Makro.Chim.*,96,122,(1966).

- [26] Utracki, L., Eliezer, N., and Simha, R.,  
Polym. Letters., 5, 137, (1967).
  - [27] Steller, T., and Springer, J., Macromol. Chem., 185, 1719  
(1984).
  - [28] Yamada, A., Yanagita, M., and Kobayashi, E.,  
J. Polym. Sci., 61, S14, (1962).
  - [29] Moacanin, J., Rembaum, A., Laudenslager, R.K., and  
Adler, R., J. Macromol. Sci. Chem. A1(8), 1497, (1967).
  - [30] Barrales-Rienda, J.M., and Pepper, D.C., Polymer, 8,  
337, (1967).
  - [31] Barrales-Rienda, J.M., and Pepper, D.C., Polymer,  
8, 351, (1967).
  - [32] Agbaje, H., and Springer, J., Eur. Polym. J., 22, 943,  
(1986).
  - [33] Tsvetsov, V.N., Vitovskaya, M.G., Lavrenko, P.N.,  
Zakharova, E.N., Gavrilenko, I.F., and  
Stefanovskaya, N.N., Vysokomol. Soeid. A13,  
No: 11, 2532, (1971).
  - [34] Chu, E.F., PH.D., the university of Akron, (1987).
  - [35] Billmeyer, F.W., Text Book of Polymer Science, Wiley,  
Second Edition, (1971).
  - [36] Flory, P.J., Principles of Polymer Science, Cornell  
University Press, Ithaca, N.Y., (1953).
- a) PP 425                      [36a]

- b) PP 611-612 [36b]  
c) PP 415-418 [36c]
- [37] Cowie, J.M., Polymers: Cemistry and Physics of Modern Materials, Intext Educational Publishers, N.Y., (1973).
- [38] Flory, P.J., Statical Mechanics of Chain Molecules, Chapter 2, PP 35-39, (1969).
- [39] Nugay, T., M.S. Thesis, M.E.T.U., (1984).
- [40] Instruction Manual, " Gamma Cell 220 ", Ed. No.5, Atomic Energy of Canada Ltd., Ottawa, (1968).
- [41] Küçükyavuz, S., and Küçükyavuz, Z., Polym. Commun. (in press).
- [42] Buchard, W., Macromol. Chem., 50,20,(1960).
- [43] Stockmayer, M.J., and Fixman, M.J., Poly. Sci., C-1, 137 (1963).
- [44] Jenkins, A.D., Viscosity of Polymer Solutions, Chapter 2, PP 51-53 , Elsevier, (1982).
- [45] Krigbaum, W.R., and Flory, P.J, J. Polym. Sci., 11,37, (1953).
- [46] Eskin, V.E., and Korotkino, O.Z., Vsokomol. Soeid., 3,435, (1961).