STUDIES OF ORIENTATIONAL ORDER OF LIQUID CRYSTALS IN POLYMER MATRIX

BY

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ABSTRACT

Infrared spectrophotometry was employed to obtain the order parameter, S , as a function of temperature, for nematic liquid crystal in stretched polystyrene (PS) film. The nematic solutes used in this thesis are the first six members of the homologous series P-(n-alkyloxybenzylidene) -p-n-butylanilines (ABBA). Both ABBA and PS were prepared and the mesomorphic transition temperatures of the prepared ABBA were determined by several methods.

The temperature dependence of the orientational order of 20.0% (by weight) ABBA in stretched PS film is different from that of pure ABBA and pure PS. In general, the order parameters of both the solutes and solvent decrease with increasing temperature. The implication of these results are discussed in term of the thermal motion of polystyrene. The orientation of the solute molecule originated from its properties and related to the perturbation by stretched polymer.

The absorption band at 757 cm^{-1}, due to C-H out of plane bending of the mono-substituted benzene ring, is chosen to determine the order parameter, S, of polystyrene. This absorption band shows dichroism of parallel type. The other absorption band chosen to determine the order

parameter of ABBA is 837 cm^{-1} which shows dichroism of perpendicular type. The orientation behavior of ABBA in the stretched polystyrene film has been discussed in terms of the difference in the dichroic behavior.

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CHAPTER 1

INTRODUCTION

1.1 GENERAL BACKGROUND

When semi-crystalline polymers are oriented by drawing or extrusion a marked anisotropy in the physical properties of the polymer is produced(1). Experimental evidence based on techniques such as birefringence indicates that there are principally increased alignments of the molecular chain axes along the draw direction(2). Many papers have been devoted to investigations of such molecular orientation in stretched polymers. Several amorphous or semi-crystalline polymers have been studied. *Hoshino et al.* have calculated the orientation of amorphous regions of a low density polyethylene using birefringence and X-ray diffraction measurements(3). Using fourier transform infrared (FTIR) spectroscopy, *Jasse* and *Koenig*(4,5) have shown the existence of the orientation of atactic polystyrene and isotactic polystyrene as a function of draw ratio and temperature of stretching. Recently, fluorescence polarization has been use to measure the orientation of polystyrene chain labelled by an anthacene group. Stretching was performed at constant strain rate and various temperature above T_g using equipment which was described(6). *Lefebvre et al.* (7-10) have pointed out, in the case of uniaxially oriented polymer blends, that poly-(2,6-dimethyl, 1,4-phenylene oxide) (PPO) and atactic polystyrene (PS) chains orient in a different way when subjected to an uniaxial strain in spite of the compatible nature of the blend.

Over the last decade, interest in the stretched film techniques as a way to investigate the molecular orientation of some organic molecules imbedded in stretched polymers has increased rapidly. *Thulstrup et al.*(11) have discussed ways in which those characteristics of the orientation distribution of planar molecules in stretched polyethylene which determine dichroic properties can be found from absorption measurements on stretched and unstretched sheets. Orientation factors of planar molecules in stretched polyethylene sheets are discussed in relation to molecular shape and orientation distribution(12). Linear dichroism spectra were presented for naphthalene oriented in stretched polyethylene and polypropylene matrice(13), orientational parameters have indicated different orientational mechanisms in polyethylene and polypropylene but the resolving procedure yields mainly identical component spectra. *Radziszewski* and *Michl*(14) have reported a measurement of FTIR linear dichroism of about 60 bands of the aromatic hydrocarbon, pyrene, in stretched low-density polyethylene. Some authors(15-17) use poly(vinyl alcohol) (PVA) as a film matrix for measuring the linear dichroism of dyes oriented in a stretched film.

It is well known that nematic liquids differ from normal isotropic liquids only by the more or less complete spontaneous parallel orientation of the elongated molecules. Nematic liquid crystals can be homogeneously ordered by using strong electric or magnetic fields, surface force, rubbing the surface of a substrate, or using anisotropic solvents, such as nematic liquids or stretched polymer films.

The main objective of this work is, therefore, to study the orientation and order of molecules of solutions containing nematic solutes, N-(p-alkyloxybenzylidene)-p-n-butylanilines (ABBA) in a non-mesogenic solvent, polystyrene (PS) by the measurement of the intensity of absorption bands in infrared region. The orientational order of the mixtures are obtained by embedding the nematic molecules in a stretched polymer matrix. The present experiment is (1) to investigate the temperature dependence of orientational order parameter of both polymer and nematic liquid crystals, ABBA, which alkoxy group varies from methoxy to hexyloxy, (2) to examine the effect of non-mesomorphic polymer on alignment and mesomorphic properties of nematic liquid crystals and (3) to study the odd-even effect in ABBA series where the homogeneous molecule alignment is achieved by rubbing of NaCl cell and stretched polymer film techniques.

Infrared investigation is the major technique used to study the alignment of both nematic liquid crystals and polymer. Differential Scanning Calorimeter will also be used to determine glass transition temperature of various sample films.

1.2 LIQUID CRYSTALS

1.2.1 GENERAL DESCRIPTION

Liquid crystal science really began in 1888 with the reserches of *Friedrich Reinitzer*(18), an Austrian botanist who prepared cholesteryl benzoate and found it has two interesting properties. When heated, its crystal lattice collapses at 145°C to form a turbid liquid, and then, at 179°C,the turbid liquid disappears and an isotropic solution is formed. On cooling, the process is reversed.

The term "Liquid Crystal", first used by *Lehmann* in 1890(19), designates a state of matter that is sometimes observed intermediate between a solid crystal and an ordinary liquid. Liquid crystals can flow like an ordinary liquid while other properties, as for example the birefringence, are reminicent of those of a crystalline phase. Although liquid crystals exhibit certain aspects of both of solid and liquid states, they also posses properties that are not found in either liquids or solids. Their ordering properties, for example, can be controlled by ordinary magnetic or electric fields, and some change color as a result of the sensitivity of their structure to temperature. These properties are the basis of their intermediate nature. Other words in use are mesophase (meaning intermediate phase) or mesomorphic phase.

1.2.2 CLASSIFICATION

Liquid crystals can be classified as thermotropic and lyotropic liquid crystals, depending on the principal way that the order of the parent solid state is destroyed. The thermotropic liquid crystal is formed by heating to a temperature above which the crystal lattice is no longer stable. This phase is mostly formed by organic molecules having an elongated shape. Many of these molecules are aromatic containing two or more benzene rings or cholesterol derivatives. The lyotropic liquid crystals are commonly prepared by the action of a solvent on a solid. They often are two or more component systems composed of water (or other polar solvents) and amphiphilic compounds, e.g. soaps, various detergents, and long chain saturated fatty acid.

In 1922, *Fridel*(20) was able to distinguish clearly both thermotropic and lyotropic liquid crystals into three types, viz. smectic, nematic and cholesteric mesophases, mainly on the basis of their optical, rheological and thermodynamic studies. The smectic phases can be considered as two dimensional axes aligned parallel to a reference axis in space. The packing within a layer exhibits a less or more ordered structure. The smectic mesophase is a liquid crystal of the highest order. Nematic mesophase defines a structure in which the molecules are more mobile than those in the smectic mesophase. The molecules are still oriented in parallel fashion, however, layered arrangement of the smectic type no longer exists. This structure has a parallel or one-dimensional order. However, *de Vries et al.*(21) have described a nematic phase for a compound in which they assumed that part of the molecules are arranged in regular groups. In each group the center of the molecules lies in a fairly well-defined plane. This type of arrangement is called a cybotactic nematic structure. The cholesteric mesophase represents a special case of nematic phase, occurs only in optically active materials and corresponds to a twisted nematic layer which results in a helical structure. They are called Cholesteric because many compounds exhibiting this mesophase are derived from derivatives of cholesterol. The other words in use are chiral nematic(22) or twisted nematic(23).

1.2.3 NEMATIC LIQUID CRYSTALS

Nematic liquid crystals are the most frequently encountered mesophase. They have the lowest order of the liquid crystals. They are formed by rod-shape molecules. The center of mass of molecules are randomly located but their long axes are parallel to a preferred axis. The textures observed in nematic are marble, schlieren and pseudoisotropic. Nematic mesophase may be further subdivided into three types, viz. classical nematic, cybotactic nematic and twisted nematic or cholesteric(23).

On heating, a crystal structure of nematic liquid crystal is broken down to form a turbid liquid at the melting temperature, T_m, and on further heating, it is transformed into an isotropic liquid at a certain temperature called the clearing point, T_c. Both the melting temperature and the clearing temperature are sharp and specific. At the clearing temperature, a long-range orientational order of molecules is lost, although degree of a short-range order persists. The transition from isotropic to nematic phase is always observed to be first order. But the corresponding density (ρ) , enthalpy (H) and entropy (S) changes are found to be very small(24-26), when compared to those characterizing the first order change which occurs when the nematic is cooled further to its crystallization temperature(27). The enthalpy of the nematic-isotropic phase transition has between 0.1 and 1.0 kcal.mole^{-1} (28).

The quality of the parallel orientation can be characterized by the degree of order, S, which is unity for the ideal nematic phase and zero for the isotropic phase. It has a value between 0.3 and 0.8 for normal nematic liquid crystals and decreases steadily with rising temperature, suddenly falling to zero at the transition point to the isotropic melt(29-30).

Liquid crystal may exhibit both nematic and smectic mesophases, but no materials are known to exhibit both nematic and cholesteric phases. When a liquid crystal exhibits both a smectic and a nematic mesophase, the smectic mesophase always occurs at the low temperature.

1.2.4 EFFECT OF EXTERNAL FORCES ON NEMATIC ALIGNMENT

The direction of alignment of nematic liquid crystals is very sensitive to external forces. In order to obtain an uniform parallel or slightly inclined alignment to the substrates, various techniques have been developed: rubbing on the bare glass substrates or those coated with inorganic materials, polymer and silane compound. Other orienting techniques that give similar results are liquid crystal matrix, hydrodynamic shear, electric and magnetic fields. The stretched film technique is a simple method and can be applied to a wide variety of molecules with proper choice of polymer. On stretching, previously unoriented regions in the polymer become partially aligned and hence the nematic liquid crystals in all these regions acquire similar partial orientation with respect to the stretching direction.

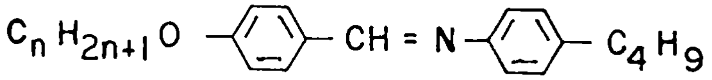
1.2.5 MIXTURE OF NEMATIC LIQUID CRYSTALS AND NON-MESOGENIC MOLECULES

Recently, interest has been growing in study of mixture of a liquid crystal with solutes which do not themselves form liquid crystal phases(31-37). Phase diagrams(31) have been determined for a large number of systems where the solutes were of molecular size less than that of the liquid crystal. As first found by *Chen and Luckhurst*(38), there is a functional relationship between the depression of the nematic-isotropic transition temperature and the lowering, by the solute, of the order parameter of liquid crystal. Recent work(31) with p-methoxybenzylidene-p-n-butylaniline (MBBA) has shown that solute size and shape affects the depression of the nematic-isotropic transition and also the free energy of solute transfer from the isotropic to the nematic phase. This perturbation affects also changes in dipole-dipole interaction or dispersion force in the solvent. On the other hand, studies of an orientational order of solute molecules in such system indicate that the order parameter of the solute decreases as its concentration increases(39). *Chingduang et al.*(36) have also observed that the decrease of the nematic-isotropic transition temperature, T_c, depends on the size and shape of the non-mesogenic guest molecules.

When macromolecular solute such as a polymer is added to a nematic liquid crystal, a second phase separation at still lower temperature can occur and the resulting phase diagram can be very complex. The phase diagrams obtained for different flexible polymer-nematic compound systems clearly show that a homogeneous nematic phase becomes anobservable when the molecular weight, Mw, of the polymer solute becomes higher than 10^4. The evolution of the two phases domain as Mw increases, seems to indicate that the nematic order is destroyed near each polymeric coil(34).

1.2.6 P-(N-ALKYLOXYBENZYLIDENE)-P-N-BUTYLANILINES

The Schiff's bases resulting from the reaction between para-substituted benzaldehydes and para-substituted anilines have been of particular interest, especially since the report(40) that p-methoxybenzylidene-p-n-butylaniline (MBBA) is nematogenic at room temperature. The compounds required for the preparation of p-n-(alkyloxybenzylidene) -p-n-butylanilines (ABBA) are p-n-alkyloxybenzaldehydes and p-n-butylaniline. The general formula of the liquid crystals investigated, usually abbreviated as ABBA, is



[1.1]

Enthalpies and entropies for certain crystal-crystal and crystal-mesophase transition temperatures of ABBA compounds have been presented by *Smith*(41). Infrared and Raman spectra of MBBA have been reported and tentative assignments were given(42-43). Infrared dichroic ratio was applied successfully to the investigation of the order parameter temperature dependence in p-ethoxybenzylidene-p-n-butylaniline (EBBA) in its nematic phase(42). *Vergoten et al.*(44) published the IR spectra of MBBA and its ethoxy homologue (EBBA) in region 4000-30 cm^{-1} for a liquid film (isotropic liquid) and for a homeotropic layer in the nematic phase. Assuming that the ring structure of many nematogens has approximately C_{2v} symmetry they gave the assignment of most bands of MBBA and EBBA in the middle IR region. Their results are supported by a normal coordinate analysis and dichroic measurements. *Ohnishi*(45) has investigated the influence of electric fields on the IR spectra of liquid crystals with weak nagative dielectric anisotropy. He has applied a d.c. electric field up to 10 V. to a cell filled with MBBA and studied the relative transmittance changes of some bands in the region 4000-100 cm^{-1} at the conditions of the dynamic scattering mode. Recently, *Kirov et al.*(46) have reported order parameter temperature dependence of the first five members of the homologous series using IR spectroscopy.

Two research groups, *Kirov et al.*(46) and *Chang et al.*(47) observed similar even-odd alternation of order parameters in the homologous series of ABBA. The first group used optical anisotropy measurements whereas the second used infrared spectroscopy for studying the orientational order parameter, S_2, for homogeneously and homeotropically aligned samples.

1.3 POLYMER

1.3.1 GENERAL DESCRIPTION

Polymer is a macromolecule built up by the linking together of large numbers of the repetition of small, simple chemical molecules. The small molecules which combine with each other to form polymer molecule are termed "monomer". The reaction by which the monomers combine is termed "polymerization". In some cases, the monomer is linear, as a chain is built up from links. In other cases, the chains are branched or interconnected to form three dimensional networks. There may be hundreds, thousands, tens of thousands or more monomer molecules linked together in a polymer molecule.

1.3.2 CLASSIFICATION

Polymers were originally classified by *Carothers*(48) in 1929 into condensation and addition polymers on the basis of the compositional difference between the polymer and the monomers from which it was synthesized. Condensation polymers were those polymers that were formed from polyfunctional monomers by the various condensation reactions of organic chemistry with the elimination of some small molecule such as water, hydrogen chloride. Addition polymers were classified as those formed from monomers without the loss of a small molecule. The repeating unit of an addition polymer has the same composition as the monomers.

Polymers have also been classified from a consideration of the chemical structure of the group present in the polymer chains(49), physical properties, preparative techniques, or processing techniques. For example, a classification according to processing techniques might divide polymer into thermoplastics and thermosets. Based on the source of the polymer, they may be classified as natural and synthetic polymers.

1.3.3 POLYMERIZATION PROCESSES

The processes of polymerization were divided by *Carothers*(48) and *Flory*(49) into two groups known as condensation and addition polymerization or, in more precise terminology, step-reaction and chain-reaction polymerization.

Condensation or step-reaction polymerization is entirely analogous to condensation in low molecular weight compounds. In polymer formation the condensation take place between two polyfunctional molecules to produce one larger polyfunctional molecule, with the possible elimination of a small molecule. The reaction continues until almost all of one of the reagents is used up. An equilibrium is established which can be shifted at will at high temperature by controlling the amounts of the reactants and products.

Addition or chain-reaction polymerization involves chain reactions in which the chain earlier may be an ion or a reactive substance with one unpaired electron called a free radical. Free radical is usually formed by the decomposition of a relatively unstable material called an initiator. The free radical is capable of reacting to open the double bond of a vinyl monomer and add to it, with an electron remaining unpaired. In a very short time, many monomers add successively to the growing chain. Finally two free radicals react to annihilate each other's growth actively and form one or more polymer molecules.

1.3.4 STRETCHED POLYMER

Polymer materials are characterized by two major types of transition temperatures, the crystalline melting temperature, T_m, and the glass transition temperature, T_g. T_m is the melting temperature of crystalline domains of a polymer whereas T_g is the temperature of which the amorphous domains of polymer take on the characteristic properties of the glassy state: britteness, stiffness and rigidity. Completely amorphous polymers show only a T_g and completely crystalline polymers only a T_m. If the polymer is below its glass transition temperature, it is a tough thermosetting plastic. If it is above its T_g , it is a tough elastomer. Even polymers such as polystyrene which do not crystallize undergo considerable molecular orientation when subjected to stress at the temperature above T_g(50) and this orientation is stable below T_g.

When a molten is allowed to crystallize, the crystallites will tend to form in a random fashion in the absence of any external force. But when an external force is applied, a rearrangement of the crystalline material takes place. Under the influence of applied stress, the crystallites become oriented, in that the chains align themselves in the direction of the applied stress.

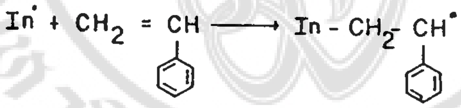
The mechanical properties of polymer are strongly influenced not only by the structure of the material but by molecular orientation. Thus a great deal of interst exists in the molecular orientation introduced by any forming process (e.g. drawing). Several techniques for evaluation of this orientation exist: birefringence, X-ray diffraction, sonic modulus, polarized fluorescence, broad-line NMR, UV, and IR dichroism, and polarized Raman spectroscopy(1).

1.3.5 POLYSTYRENE

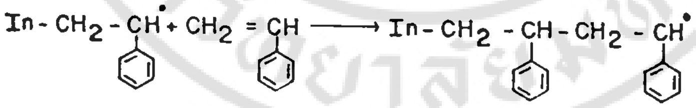
Polystyrene (PS) is a very interesting polymer from the point of view of fine structure and fine texture. Its crystallinity can be varied over wide range from amorphous to highly crystalline state by heat treatments and also a highly oriented sample can be made by hot stretching. Polystyrene as a commercially product has an average molecular weight ($\bar{M}n$) in the range 50,000-300,000. This polymer is a typical rigid plastic, a good electrical insulator, has excellent optical clearity due to the lack of crystallinity, and is easy to process since only T_g must be overcome for the polymer to flow. The deficiencies of polystyrene are overcome by copolymerization with other monomers such as acrylonitrile and butadiene: or physical blending (mixing) with other polymers or organic molecules.

The first polystyrene appears to have been prepared by *Simon*(51). Free-radical polymerization of styrene can be carried out by bulk, solution, suspension or emulsion techniques. Polystyrene prepared by free-radical mechanism is atactic, composed of head to tail sequences(52). Styrene can also be polymerized by various cationic and anionic initiators as well as with the aid of coordination catalysis.

Polymerization begins by the initiating free radical, In , adding to the double bond of alkene to form a chemical bond and a generation of a new free radical [1.2]. The new free radical then adds to another molecule of alkene to generate a still larger radical which can then add to another molecule of alkene, and so on [1.3].



$$In^{\bullet} + CH_2=\underset{C_6H_5}{CH} \longrightarrow In-CH_2-\underset{C_6H_5}{CH^{\bullet}} \quad [1.2]$$



$$In-CH_2-\underset{C_6H_5}{CH^{\bullet}} + CH_2=\underset{C_6H_5}{CH} \longrightarrow In-CH_2-\underset{C_6H_5}{CH}-CH_2-\underset{C_6H_5}{CH^{\bullet}} \quad [1.3]$$

The preparation method used in this thesis is emulsion polymerization. The main components of this system are monomer, dispersing medium, emulsifying agent and water soluble initiator. A simplified schematic representation and detail of an emulsion polymerization system was described in *Ref.50-54*. Rate of polymerization and chain length are proportional to the concentration of soap(54-56). When the number of active micelles is constant, the polymerization rate is linear with time as long as excess monomer droplets remain and the concentration of monomer is constant. At high conversions the rate decreases as the concentration of monomer decreases$^{(53)}$.

1.4 MOLECULAR ORIENTATION

1.4.1 GENERAL DESCRIPTION

In recent years the stretched polymer film linear dichroism technique has been successfully used to establish transition moment directions in a large number of organic molecules$^{(11-17,56)}$. This procedure consists of embedding the molecule of interest in a polymer matrix which is then stretched. If the guest molecule is nonspherical it will align itself with its long molecular axis along the stretched direction. If orientation is considered to occur only in one dimension, birefringence and several related phenomena such as infrared dichroism, polarized Raman spectroscopy, polarized fluorescence, etc. measure the quantity $\langle \cos^2\theta \rangle_{av}$, where the bracket indicates averaging and θ is the angle between long axis of a molecule and the preferred direction, $\vec{n}$, (or the director) at any moment in liquid crystal case, or the angle between the molecular chain direction and that of the orienting force, such as the fiber stretched axis in polymer case.

1.4.2 LINEAR DICHROISM AND ORDER PARAMETER

An important and often poorly appreciated aspect of the absorption of light by molecules is that the absorption has a directional character. If a collection of molecules is not randomly oriented, the absorption of plane polarized light will not be the same for all orientations of the electric vector of the light. If the molecular transition dipole moment is parallel to the plane of polarization of the light, the absorption will be maximum, while if the transition dipole moment is perpendicular to the plane of polarized light, no absorption will occur. This differential absorption of light with respect to two perpendicular planes of polarization is known as "linear dichroism".

Dichroism measurements in the infrared region are made using the double-beam infrared spectrometer. The oriented specimen and the infrared polarizer are placed in the sample compartment. The infrared spectra are recorded with the polarizer successively placed with the electric vector parallel and perpendicular to the sample reference axis. Dichroism measurements have usually been expressed either in terms of the dichroic ratio(15,57-60);

$$D = \frac{A_{/\!/}}{A_{\perp}} \qquad [1.4]$$

or the reduced dichroism(15);

$$\frac{\Delta A}{A} = \frac{3\,(A_{/\!/} - A_{\perp})}{(A_{/\!/} + 2A_{\perp})} \qquad [1.5]$$

where $A_{/\!/}$ and $A_{\perp}$ are the absorbances measured with light polarized parallel and perpendicular to the stretched direction of a film. It is well-known that D or $\Delta A/A$ of partially oriented rodlike molecules can be related to the transition moment angle, α, which is defined as the angle between the direction of transition moment and the orientation axis of a molecule, as(15)

$$D = \frac{2 + 2(3\cos^2\alpha - 1)\Phi}{2 - (3\cos^2\alpha - 1)\Phi} \qquad [1.6]$$

or

$$\frac{\Delta A}{A} = \frac{3}{2}(3\cos^2\alpha - 1)\Phi \qquad [1.7]$$

where Φ is the orientation function of the guest molecules.

Uniaxial partial alignment imparted to solutes included in stretched polymer induces anisotropy in the orientation of the molecular segments. Orientation of chains can be characterized by an orientation distribution function, $f(\theta)$, in the case of uniaxial stretching, where θ is the angle between the chain axis and the stretching direction in polymer case or the angle between a long molecular axis and the director of any moment in liquid crystal case. Then $f(\theta)$ is expressed as

$$f(\theta) = \sum_{n=0} (n+\tfrac{1}{2})\langle P_n(\cos\theta)\rangle_{av} P_n \cos\theta \ , \qquad [1.8]$$

where $P_n(\cos\theta)$ are the spherical harmonic functions. Infrared measurements on oriented materials determine the second moment of the orientation function, $\langle P_2(\cos\theta)\rangle_{av}$ For a given absorption band, the dichroic ratio [1.4] is related to $\langle P_2(\cos\theta)\rangle_{av}$ by the expression

$$\begin{aligned} S &= \langle P_2(\cos\theta)\rangle_{av} \\ &= \tfrac{1}{2}(3\langle\cos^2\theta\rangle_{av} - 1) \\ &= \frac{(D-1)(D_0+2)}{(D+2)(D_0-1)} \end{aligned} \qquad [1.9]$$

where $D_0 = 2\cot^2\alpha$,

α being the angle between the dipole moment vector of the vibration and the local chain axis, the angular bracket denote a statistical average, and S is the order parameter, first introduced by *Tsvetkov*(81). For perfectly parallel alignment; S=1, while for random orientation; S=0.

1.4.2.1 POLYMER ORDERING AND ORIENTATION PARAMETERS

The relationship between the infrared dichroism D, the orientation of the molecules, and the direction of the transition moments was solved by Fraser(57). Consider a fiber where all of the polymer chain axes are oriented parallel to the fiber axis. Optical-density measurements are made with the electric vector parallel and perpendicular to the fiber axis, respectively. For this ideal system, the incident electric vector E_{π} (see Fig.1.1) will be parallel to the polymer chain axis as well as to the fiber axis. The expression for the parallel principal absorption coefficient, k_{π} is

$$k_{\pi} = NP^2 \cos^2 \alpha_\nu \quad , \qquad [1.10]$$

N is the number of absorbing centers per unit volume, P is the magnitude of a vector, $\vec{P}$ proportional to the transition moment and α_ν is the transition moment angle for the centers absorbing radiation of frequency. From similar arguments for the perpendicular electric vector, $E_{\angle}$ the expression for the perpendicular principal absorption coefficient, $k_{\angle}$ is

$$k_{\angle} = \frac{1}{2} NP^2 \sin^2 \alpha_\nu \quad . \qquad [1.11]$$

Thus, for perfect alignment of the molecules parallel to the fiber axis, the dichroic ratio is related to the transition moment angle by the expression,

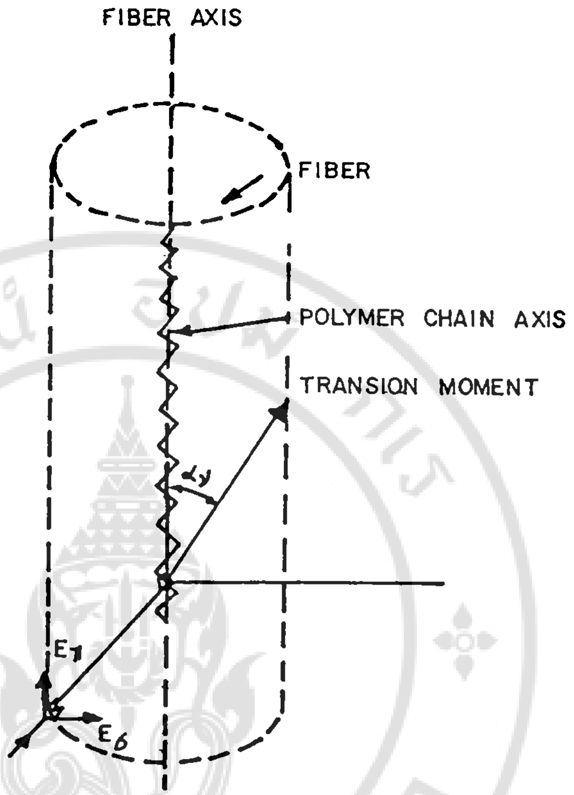


Fig.1.1 Schematic representation of perfect orientation parameters.

$$D_o = \frac{A_{/\!/}}{A_\perp} = \frac{k_\pi}{k_\sigma} = 2\cot^2\alpha_y \quad , \qquad [1.12]$$

where Do is the dichroic ratio of an ideally oriented polymer.

When all of the molecules are randomly oriented, then

$$k_\pi = k_\sigma = \frac{1}{3}NP^2 \quad , \qquad [1.13]$$

and the dichroic ratio for an unoriented specimen is

$$D = \frac{k_\pi}{k_\sigma} = 1.0 \qquad [1.14]$$

In real polymer film or fiber, the molecules are only partially oriented (see Fig.1.2). An oriented polymer system can then be considerd as composed of a perfectly oriented chains fraction, *f* and a perfectly random chains fraction,(1-*f*). From eqs.[1.10],[1.11] and [1.13], therefore,

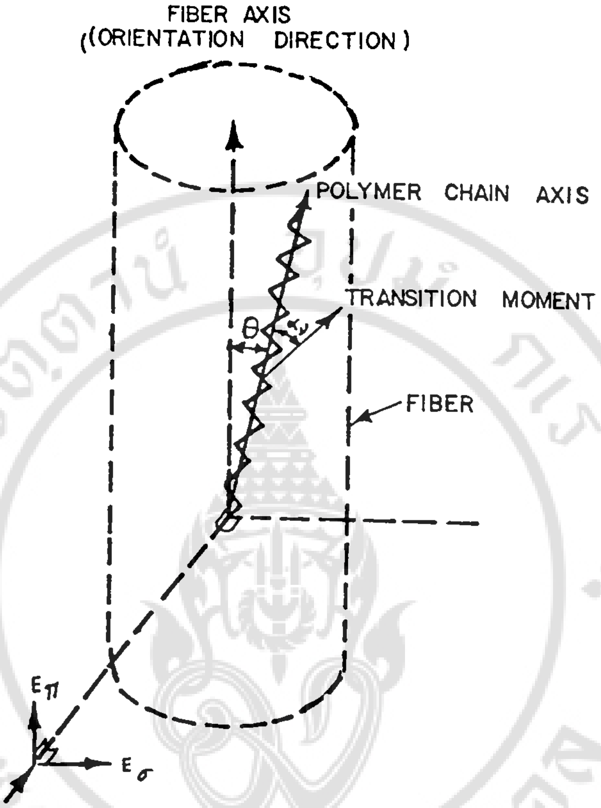


Fig.1.2 Schematic representation of uniaxial orientation parameters.

$$k_\pi = NP^2[\ f\cos^2\alpha_\nu + \frac{1}{3}(1-f)\ ] \qquad [1.15]$$

$$k_\sigma = NP^2[\ \frac{1}{2}f\sin^2\alpha_\nu + \frac{1}{3}(1-f)\ ]. \qquad [1.16]$$

The dichroic ratio in term of D_o [1.12] and f, takes the form

$$D = \frac{1+\frac{1}{3}(D_o-1)(1-2f)}{1+\frac{1}{3}(D_o-1)(1-f)}. \qquad [1.17]$$

By solving eq.[1.17], the expression can then be obtained in terms of the fraction of perfectly oriented molecules,

$$f = \frac{(D-1)(D_o+2)}{(D+2)(D_o-1)}. \qquad [1.18]$$

One method of estimating the value of f is developed by

Fraser[62], using a minimum value of the fraction of oriented molecules (f_m). This value may be obtained by allowing D_∞ to infinity for D>1, or zero for D<1 in eq.[1.18], giving

$$f_m = \frac{D-1}{D+2} \quad \text{when} \quad D>1 \qquad [1.19]$$

$$f_m = \frac{2(1-D)}{D+2} \quad \text{when} \quad D<1 \qquad [1.20]$$

1.4.2.2 NEMATIC ORDERING AND ORDER PARAMETER

The orientational order of nematic liquid crystal is usually characterized by the order parameter,

$$S = \frac{1}{2} \langle 3\cos^2\theta - 1 \rangle_{av} , \qquad [1.21]$$

or

$$S = 1 - \frac{3}{2} \langle \sin^2\theta \rangle_{av} , \qquad [1.22]$$

where θ denotes the angle between the molecular chain direction (long axis of a molecule) and the director, $\vec{n}$, at any moment of the liquid crystal (see Fig.1.3), and the

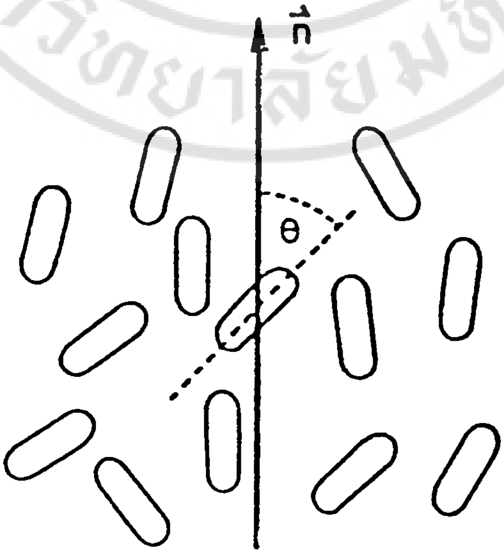


Fig.1.3 Possible orientations of nematic liquid crystal molecules with respect to the preferred directions, $\vec{n}$.

bracket indicates the ensemble average. A convenient way to determine the order parameter experimentally is by linear dichroism measurements. The relation between S and the dichroic ratio, D has been derived by *Maier* and *Saupe*(63) assuming the molecular constituting nematic phase to be cylindrically symmetric.

Consider a nematic molecule which is assumed to have a completely cylindrical symmetry (rigid rod), the orientation of molecule can be described by the Euler angles (θ, ψ and ψ') as shown in Fig.1.4. Cartesian "molecular axes" (XYZ) fixed relative to the molecular framework and related to externally-fixed "laboratory axes" ($x'y'z'$) by the Euler angles ($\theta\psi\psi'$) where OZ is taken parallel to the preferred direction, $\vec{n}$, and $\vec{M}$ is a transition moment which forms an angle α with the long molecular axis, z'.

The components of the oscillator strength, f (being proportional to the square of the transition moment) effective parallel to x', y' and z', respectively, are

$$f_{x'} = f_{y'} = f\sin^2\alpha \qquad [1.23]$$

$$f_{z'} = f\cos^2\alpha \ . \qquad [1.24]$$

The resulting components parallel to" XYZ" axes are obtained by applying the Euler transformation, then

$$f_z = f_{x'}\sin^2\psi\,\sin^2\theta + f_{z'}\cos^2\theta \ . \qquad [1.25]$$

Substitution of eqs.[1.23] and [1.24] into eq.[1.25] yields

$$f_z = f\sin^2\alpha\,\sin^2\psi\,\sin^2\theta + f\cos^2\alpha\,\cos^2\theta \ . \qquad [1.26]$$

Eqs.[1.21] and [1.22] can be rewritten as

$$\langle\cos^2\theta\rangle_{av} = \tfrac{1}{3}(2S+1) \ , \qquad [1.27]$$

and

$$\langle\sin^2\theta\rangle_{av} = \tfrac{2}{3}(1-S) \ , \qquad [1.28]$$

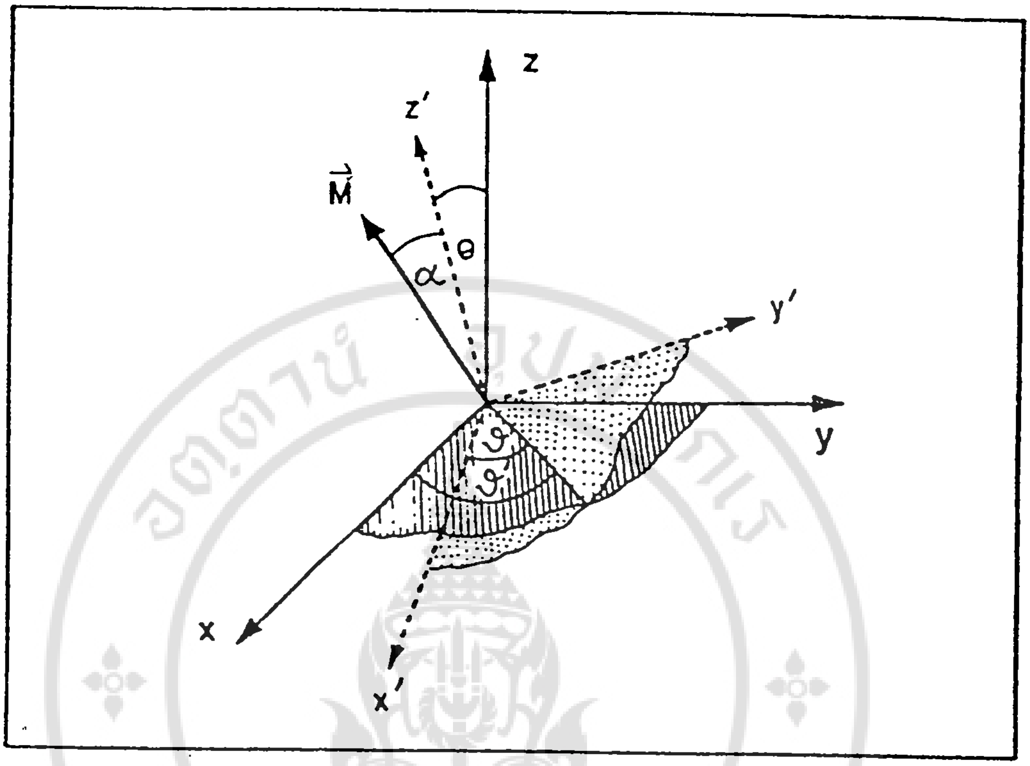


Fig.1.4 Definition of the angles used to specify the orientation of a transition moment, $\vec{M}$, with respect to the molecular axes x' ,y' and z' .

respectively. Assuming random distribution of molecules, statistical averaging leads to[64]

$$\langle \sin^2 \vartheta' \rangle_{av} = \frac{1}{2} . \qquad [1.29]$$

After substitution of the averaged values, eqs.[1.26] can then be rewritten as

$$\bar{f}_z = f[1 + 2(1 - \frac{3}{2}\sin^2\alpha)S] , \qquad [1.30]$$

the total oscillator strength is defined as

$$f = \bar{f}_x + \bar{f}_y + \bar{f}_z , \qquad [1.31]$$

for an uniaxial phase, f_x and f_y have to be equal, then

$$\bar{f}_x = \bar{f}_y = \frac{1}{2}(f - \bar{f}_z)$$

$$= \frac{f}{3}[1-(1-\frac{3}{2}(\sin^2\alpha))S] \qquad [1.32]$$

The absorbance (peak or, more precise, integral values) of a given sample for radiation linearly polarized parallel to X, Y and Z is proportional to $\bar{f}_x$, $\bar{f}_y$ and $\bar{f}_z$ respectively(63). Since $\bar{f}_x = \bar{f}_y$ and $\bar{f}_z$ are linearly related to $A_\perp$ and $A_{/\!/}$ where $A_\perp$, $A_{/\!/}$ are the absorption for linear polarized radiation which its electric vector vibrate perpendicular and parallel with director n, respectively. Using eqs. [1.30] and [1.32], the well-known expressions of the order parameter for the cylindrically symmetric molecule become

$$S = \frac{(A_{/\!/} - A_\perp)}{(A_{/\!/} + 2A_\perp)(1 - \frac{3}{2}\sin^2\alpha)} \qquad [1.33]$$

and

$$S = \frac{(D-1)}{(D+2)(1 - \frac{3}{2}\sin^2\alpha)} \qquad [1.34]$$

For a transition moment parallel to the principal axis, z, of the molecule ($\alpha = 0°$), S is obtained as

$$S_{/\!/} = \frac{D-1}{D+2} \quad \text{when } D>1 \qquad [1.35]$$

For a perpendicular transition moment ($\alpha = 90°$), then

$$S_\perp = \frac{2(1-D)}{D+2} \quad \text{when } D<1 \qquad [1.36]$$

CHAPTER 2

EXPERIMENTS

2.1 INSTRUMENTS

All instruments used in this thesis are listed below:

-Infrared spectrophotometer : Perkin-Elmer Model 683

-Infrared Data Station : Perkin-Elmer Model 3500

-Aluminum wire grid polarizer : Cambridge Physical Sciences

-Thermocouple and digital thermometer : Omega Model 2175A

-Thermostat : Colora-Kryo Model WK5

-Constant Temperature Circulator : Haake Model F4

-Air Compressor

-Pure air Heatless Dryer : Perkin-Elmer

-Temperature control unit : Mettler Model FP5

-Microscope Hot Stage for microthermal investigation with a hand control panel : Mettler Model FP52

-Trinocular microscope (with two 10xbinocular and 10xmonocular objective including a polarizer and an analyzer) : Nikon Model L-ke

-Differential Scanning Calorimeter : DuPont Model 990

-EM-360 L Proton NMR Spectrometer : Varian 60MHz

2.2 MATERIALS

Chemicals used in the experiment are :

2.2.1 POLYSTYRENE

Polystyrene was used as a polymer matrix in this study. Polystyrene was prepared by emulsion polymerization from styrene monomer (Siam Chemical Co. Ltd.).

2.2.2 LIQUID CRYSTALS

The nematogenic solutes which were used as guest molecules in polymer matrix are listed in Table 2.1. The table lists the series of p-n-alkyloxybenzylidene-p-n-butylanilines (ABBA) where name, abbreviation of name (given in parenthesis), formular and molecular weight are included. All of the compounds were prepared in the laboratory.

2.2.3 TOLUENE (A.R. : Merck)

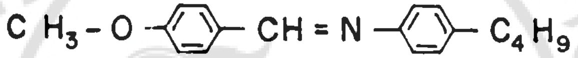
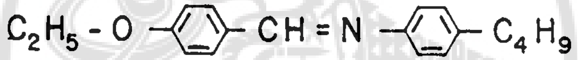
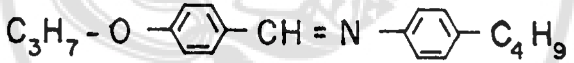
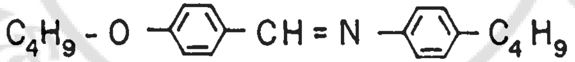
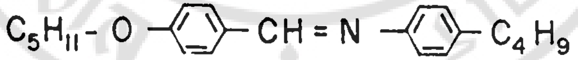
2.3 PREPARATION OF POLYSTYRENE

Polystyrene was prepared from styrene monomer using equipment set-up as shown in Fig. 2.1.

2.3.1 PROCEDURE

About 80 ml distilled water, 0.09 g potassium persulphate ($K_2S_2O_8$) and 0.09 g sodium hydrogen phosphate

Table 2.1 List of nematogenic solutes used in the thesis.

NAME	FORMULA	MOLECULAR WEIGHT
p- methoxybenzylidene-p-n-butylaniline (MBBA)		267.37
p- ethoxybenzylidene-p-n-butylaniline (EBBA)		281.40
p-n-propoxybenzylidene-p-n-butylaniline (P_3BBA)		295.43
p-n-butoxybenzylidene-p-n-butylaniline (BBBA)		309.46
p-n-pentoxybenzylidene-p-n-butylaniline (P_5BBA)		323.49
p-n-hexoxybenzylidene-p-n-butylaniline (HBBA)		337.52

($Na_2HPO_4.7H_2O$) were placed in a 500 ml two necked flask. The mixture was gently stirred until $K_2S_2O_8$ and $Na_2HPO_4.7H_2O$ were dissolved, sodium dodecyl sulphate (about 1.2g) and 60ml distilled styrene monomer were then added. The flask was immediately purged with N_2 gas for about 10 minutes to disperse the monomer and to remove air. The reaction was stirred and refluxed at about 70°C. After refluxing for 1 hour, the reaction was then removed from the water bath poured into a beaker and 30 ml of alum solution (2.5 ml $Al_2(SO_4)_3$ in 100 ml distilled water) was then poured into the beaker. The coagulated polymer was collected by filtration and washed twice with 20 ml of methanol and followed by 20 ml of distilled water. The polymer was dried in a vacuum oven at 70°C for 3-4 hours to make sure that methanol and water was

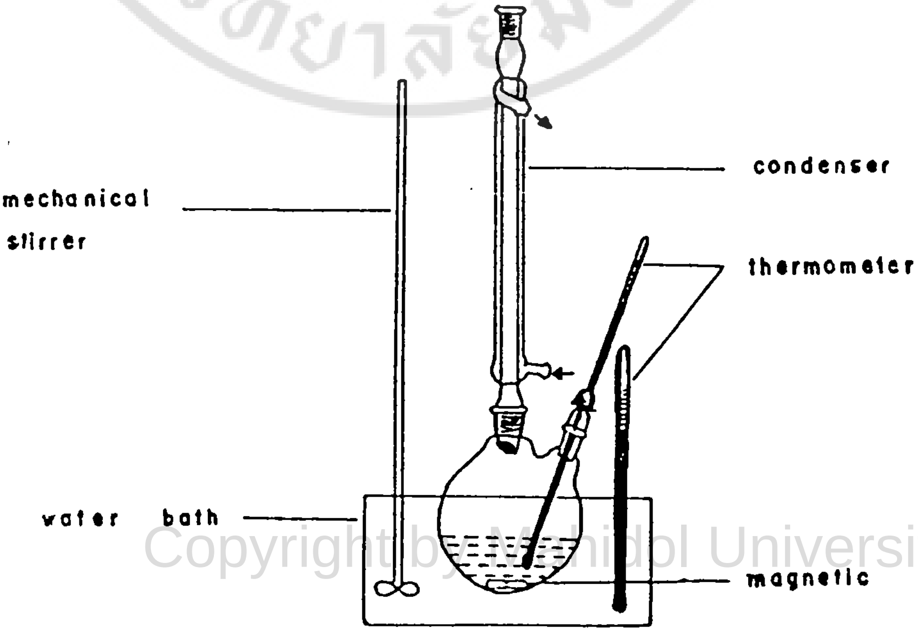


Fig.2.1 Apparatus used for Emulsion polymerization of PS.

completely evaporated. Finally the polymer was then recrystallized by dissolving in toluene and the solution dropped into distilled methanol. The precipitated polystyrene was filtered off and dried to a constant weight in the vacuum oven at 70°C. The obtained polystyrene was stored for further use in a vacuum desiccator at room temperature.

2.3.2 DETERMINATION OF VISCOSITY AVERAGE MOLECULAR WEIGHT OF POLYSTYRENE

25 ml stock solution (0.4 g (exact by weight) of purified polystyrene in 100 ml toluene) was pipetted into a volumetric flask and the solution was made up to 50 ml with toluene ; this solution will be called solution one. Solution two, three, four and five were also prepared from solution one, two, three and four respectively. The molecular weight of polystyrene was measured by viscometric method. Using Ubbelohde viscometer, the flow time of pure toluene (as solvent), t_o and of the polystyrene solutions, t are determined at tenperature 30°C.

For dilute solution, the relative viscosity was obtained form the expression

$$\eta/\eta_o = t/t_o \qquad [2.1]$$

where η and η_o are viscosity of polystyrene solution and solvent respectively. The specific viscosity was defined by subtracting the relative viscosity by unity as

$$\eta_{sp} = (\eta/\eta_o) - 1 \qquad [2.2]$$

Each specific viscosity was divided by the concentration of polystyrene solution, c (in g/100 ml) and then plotted against c. The least squares fitted straight line was drawn through the points. The intercept is the intrinsic viscosity as defined in the expression [2.3].

$$[\eta] = \lim_{c\to 0} \eta_{sp}/c \qquad [2.3]$$

The viscosity average molecular weight ($\bar{M}v$) was calculated from the measured intrinsic viscosity using Mark-Houwink-Sakarada equation(65),

$$[\eta] = K\bar{M}_v^{\,a} \qquad [2.4]$$

where $K = 9.2\mathrm{x}10^{-5}$, $a = 0.72$.

2.4 PREPARATION OF P-(N-ALKYLOXYBENZYLIDENE) -P-N-BUTYLANILINES (ABBA)

A diagram of preparation of p-(n-alkyloxybenzylidene) -p-n-butylanilines is shown in Fig. 2.2.

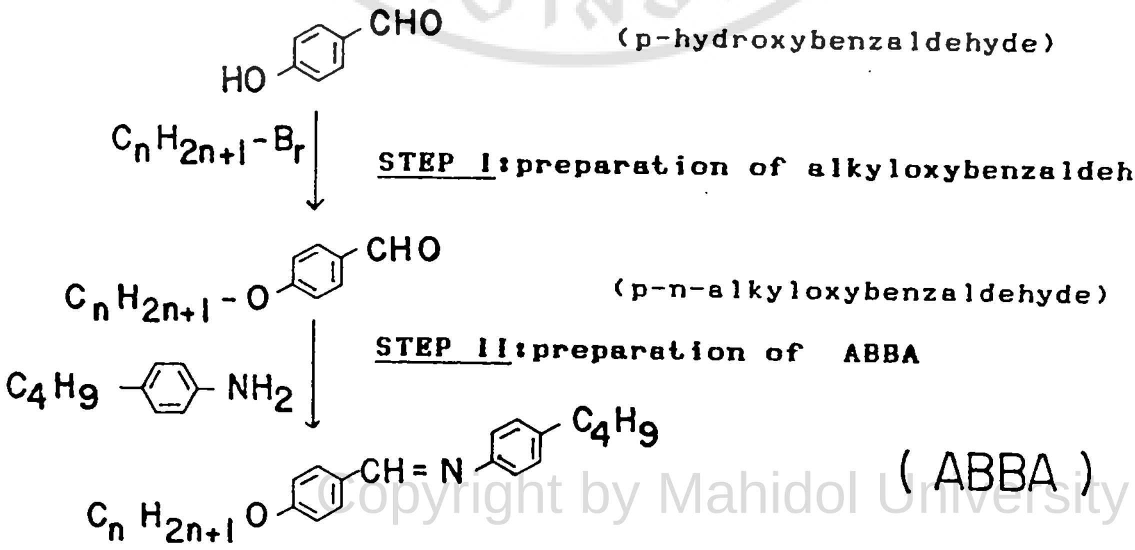
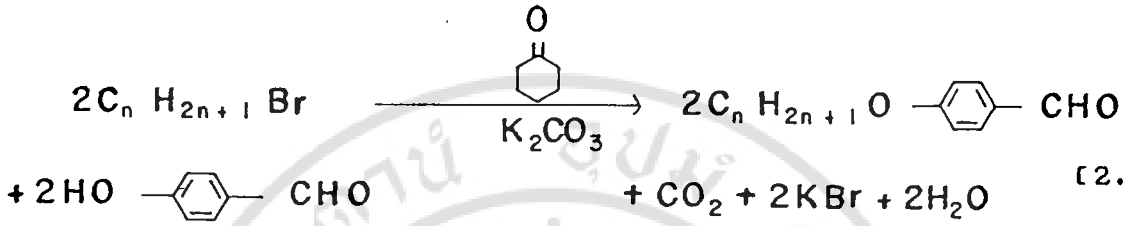


Fig.2.2 The reaction involving of the preparation of ABBA

2.4.1 PREPARATION OF P-N-ALKYLOXYBENZALDEHYDES (STEP I)

They are obtained by a one-step reaction from commercial products. The reaction is



[2.5]

2.4.1.1 PROCEDURE

12.2 g (0.1 mole) of p-hydroxybenzaldehyde, 60 g (0.4 mole) of anhydrous potassium carbonate, 80 ml of cyclohexanone (as solvent), and 0.16 mole of n-alkylbromide ($C_nH_{2n+1}Br$ where n=1-6) were introduced into an erlenmeyer flask fitted out with a reflux condenser. The mixture was stirred vigorously and heated under reflux. A significant

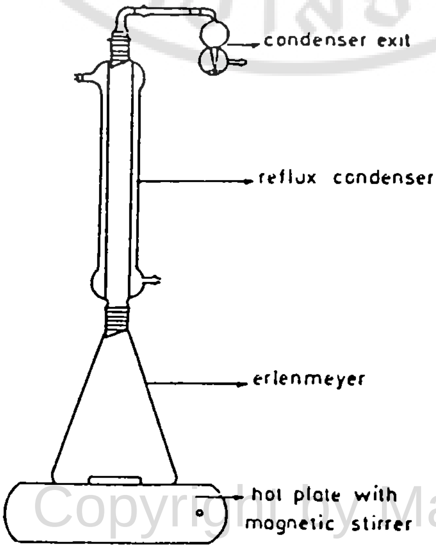


Fig.2.3 Apparatus for synthesis of p-n-alkyloxybenzaldehydes

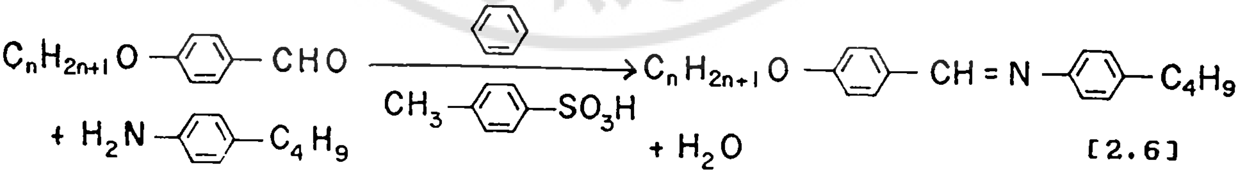
volume of gas (CO_2 formed during the reaction) is evolved. This was controlled by a bubble on the condenser exit (see Fig.2.3). After refluxing for 3 hrs, the reaction was completed.

2.4.1.2 PURIFICATION

The reaction mixture was cooled to room temperature and filtered off to remove of K_2CO_3 and KBr formed during the reaction. The precipitate was washed with 50 ml of ether. This filtrate was evaporated on a rotary evaporator to moved ether and then cyclohexanone. The obtained residue was distilled under vacuum.

2.4.2 PREPERATION OF ABBA BY BENZENE METHOD (STEP II)

The compounds required for the preperation of ABBA are p-n-alkyloxybenzaldehydes (prepared before in step I) and p-n butylaniline. The reaction is



[2.6]

2.4.2.1 PROCEDURE

In an erlenmeyer flask of 1 lit, 0.1 mole of distilled p-n-butylaniline,0.1 mole of p-n-alkyloxybenzaldehyde, 0.25g of p-toluene sulfonic acid (as acid catalyst), and 400 ml of benzene (as solvent) were refluxed for 3(1/2) hrs. The water formed during the reaction was removed azeotropically with a Dean-Stark apparatus as shown in Fig. 2.4.

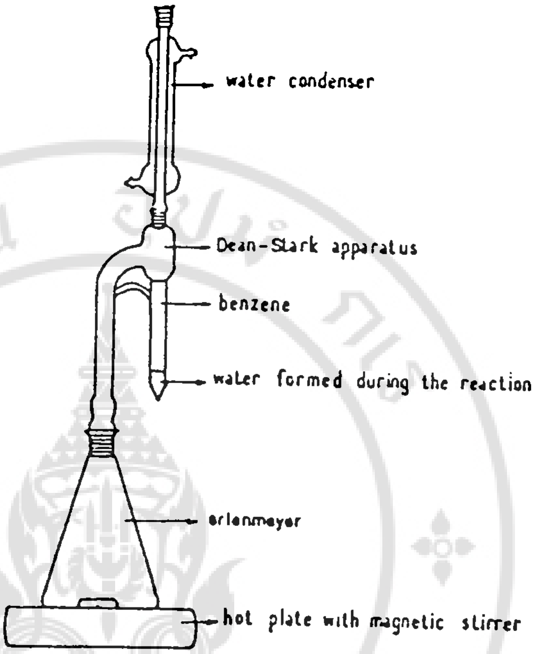


Fig.2.4 Apparatus for synthesis of ABBA by benzene method.

2.4.2.2 PURIFICATION

The mixture was fittered off warm, about 60-70°C. After cooling benzene was removed by distillation on rotary evaporator and the residue obtained was distilled under reduced pressure. The apparatus for distillation is shown in Fig.2.5 (the first distillate is often composed of the solvent residue of the reaction and the product which distills at higher temperature).

Distilled product was dissolved in absolute ethanol and crystallized in a freezer. The crystals obtained were fillered off and recrystallized several times in absolute

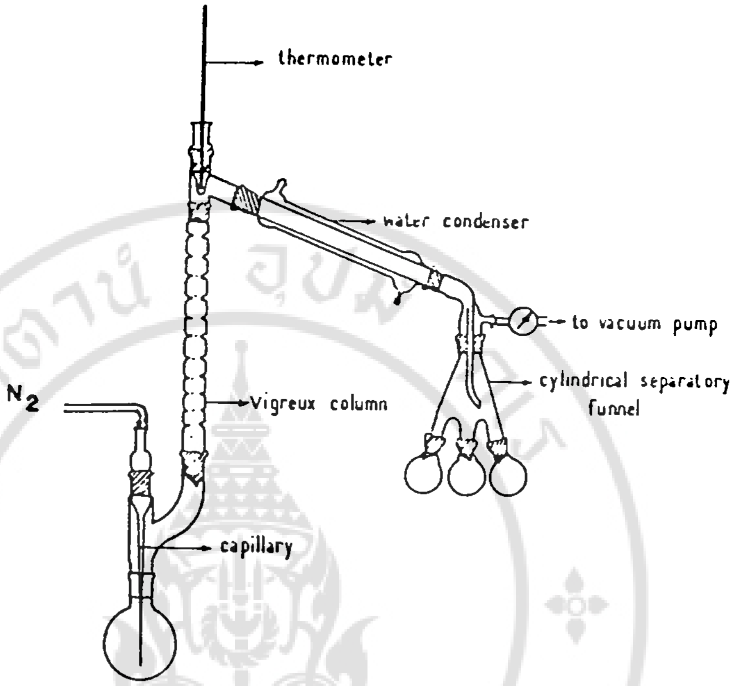


Fig.2.5 Distillation apparatus.

ethanol until the transition temperature remain constant[a]. The products were stored in refrigerator for further used.

2.4.3 PURITY DETERMINATION

After purification, the purity of the product was checked. Purity of the products were determined by Nuclear magnetic resonance (NMR) spectroscopy and the determined transition temperature. NMR spectra were determined by means of spectrometer (10% solution in CCl_4, the compound used as

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(a) Distillation under reduced pressure was used to purify in the case of MBBA.

a reference standard was tetramethylsilane, TMS). The best apparatus for the determination of transition temperature of the products is a microscope equipped with an electrically heated hot-stage and differential scanning calorimeter (see also section 2.5).

2.5 DETERMINATION OF TRANSITION TEMPERATURE OF ABBA

A small amount of ABBA was placed on a clean glass slide and the cover slip was placed over. The slide was then placed on a Mettler heating stage. The transition temperatures of the sample were obtained by observing the changes in the textures under a polarized Nikon microscope equipped with Mettler heating stage Model FP52 and Mettler FP5 temperature control unit. The samples were first heated at a rapid rate about 10°C/min to find the approximate transition temperatures. After cooling for a few degrees below the transition temperature, the samples were heated again at rate of 0.2°C/min to find the precise transition temperatures.

The transition temperatures of ABBA were also observed by DSC measurement. DSC thermograms of the prepared ABBA were obtains between -40°C to 100°C range of temperature by using the DuPont DSC thermal analyser Model 990. The heating rate of 10°C/min and the sensitivity setting of 1.0 were used. The sample size used in each measurement is 10 mg.

2.6 DETERMINATION OF GLASS TRANSITION TEMPERATURE OF THE SAMPLE FILMS.

Samples for DSC studies were prepared in the same manner as for the infrared linear dichroism studies (see section 2.7.2) but thicker films were needed (a petri-dish of diameter 5.0 cm was used to prepare sample films). Glass transition temperature (T_g) of prepared sample films were obtained between 0°C to 120°C in the case of pure polystyrene and -40°C to 100°C in the case of ABBA-PS films (about 20% ABBA by weight). The heating rate of 10°C/min was used. Sample films used in this measurement were weight to 2 mg. The sensitivity setting for determination of T_g of pure PS was 0.5 and for the other samples was 0.2.

2.7 MEASUREMENT OF INFRARED LINEAR DICHROISM

The polarized infrared spectra were obtained using a Perkin-Elmer Infrared Spectrophotometer Model 683 equipped with the Data Station Model 3500. An aluminum wire grid polarizer (Cambridge Physical Science) was placed at the entrance slit of PE683 for the polarization measurements of the sample. Using the double beem mode, twenty spectra of each sample were taken and the averaged spectra were obtained by the multiscanning method. Air compressor and pure air heatless dryer were used to generate dry air to the sample area.

In order to find the appropriate polarization direction, the polarizer was placed in the sample beam and the instrument was set at 650 cm^{-1}. The polarizer was rotated to find two positions giving maximum and minimum transmittance. These two positions must be 90° apart, and their transmittance are shown in Fig.2.6. The polarizer was then set at a position which makes an angle of 45°from the maximum or minimum position. This position was marked and the other point was 90°from it. The transmittance of these two marked points should be the same (the dashed lines in Fig.2.6). The direction of polarized light was set at these two positions for measurement of the polarized spectra in the experiment.

The sample was placed in the sample compartment so that the preferred direction ($\vec{z}$) is parallel to the grid lines of the polarizer. The absorbance of the sample in z direction,denoted as $A_{/\!/}$, is shown by the dotted line in Fig.2.7. When the polarizer was rotated 90°to the other marked point,the electric vector was changed to the x direction (see Fig. 2.8). The absorbance, denoted as $A_{\perp}$, was recorded as shown by the solid line in Fig.2.7. The base line of each band is obtained by connecting the two minimum points of the peak. $A_{/\!/}$ and $A_{\perp}$ are measured from this base line to the maximum height.

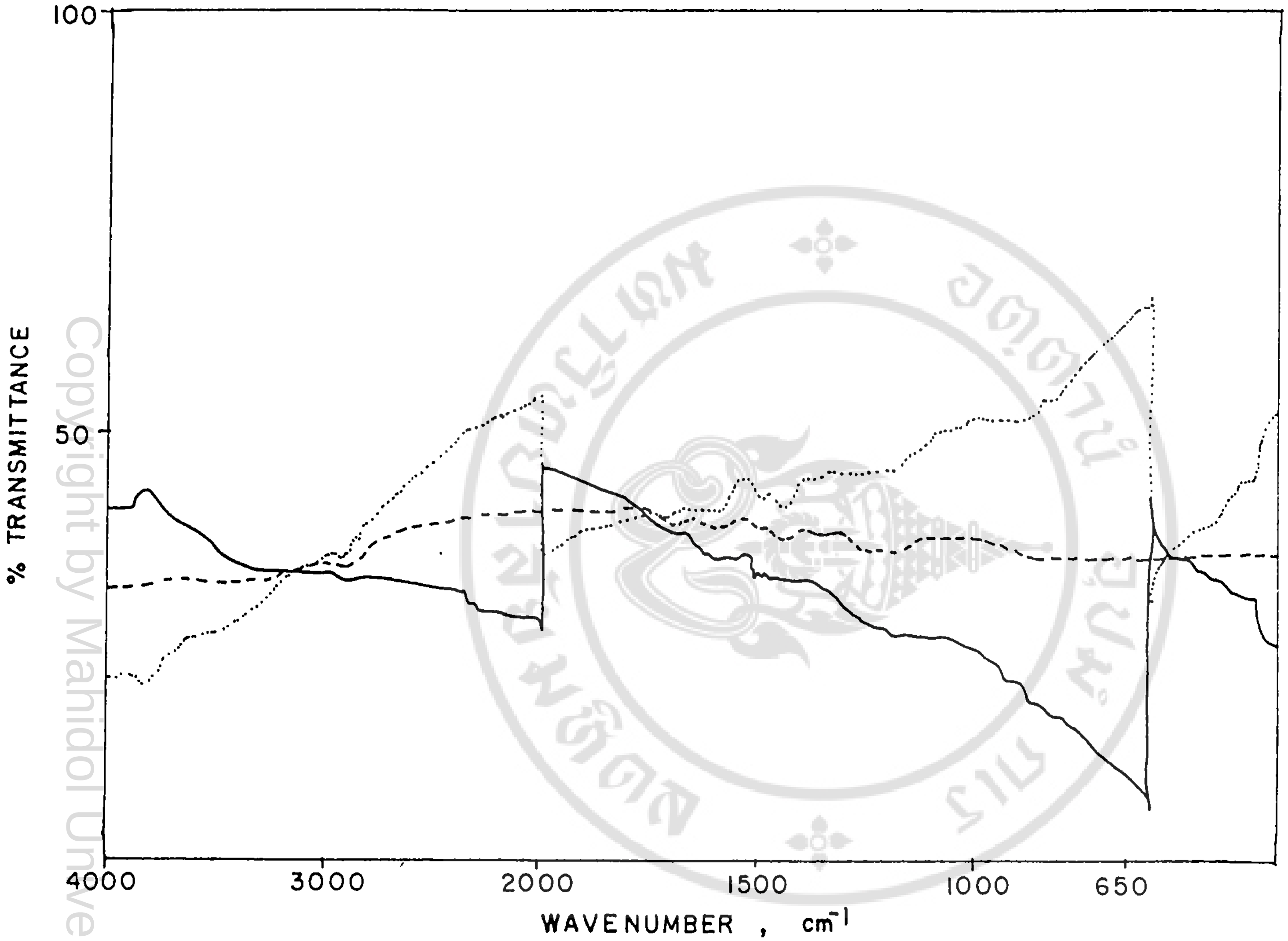


Fig.2.6 The polarized transmission spectra of the polarizer. Solid line, dotted line and dash line are the transmission at the minimum, maximum, and middle positions, respectively, as observed at 650 cm^{-1}.

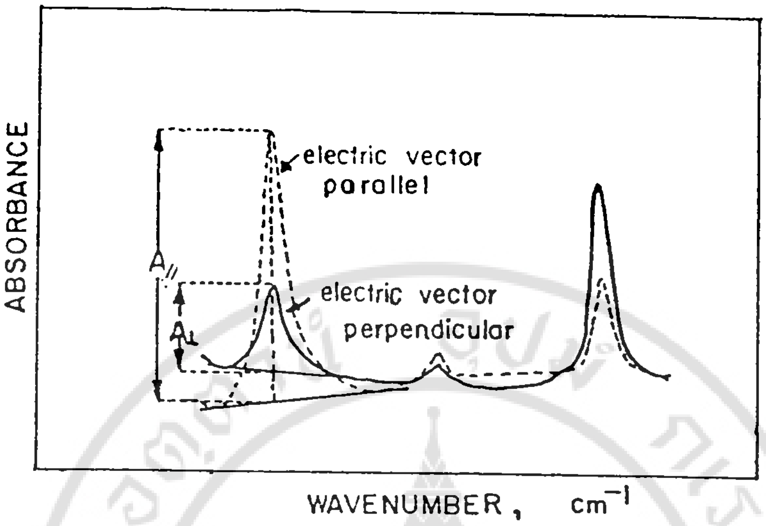


Fig.2.7 Infrared polarized spectra of a uniaxial oriented specimen.

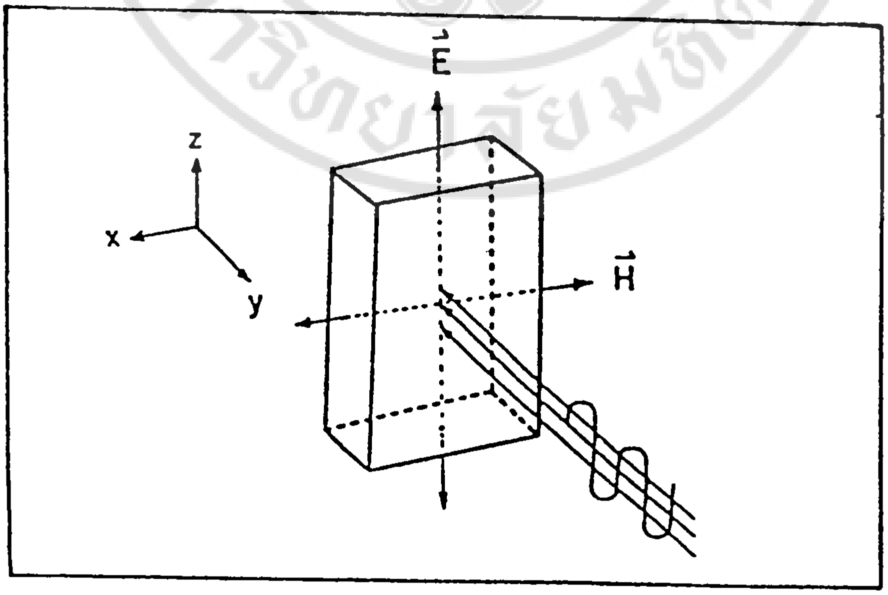


Fig.2.8 Schematic diagram of polarized light propagating through NaCl cell, where $\vec{E}$ and $\vec{H}$ are electric and magnetic vectors, respectively.

2.7.1 SAMPLE PREPARATION FOR INFRARED LINEAR DICHROISM STUDIES OF PURE ABBA

Liquid crystal molecules were aligned homogeneously by rubbing of NaCl cells and comfirmed for its homogeneity between two crossed polaroids. Therefore the preferred direction (z direction in Fig.2.8) of the liquid crystal is parallel to the rubbing direction of NaCl cells. The absorbance, $A_{\parallel}$ and $A_{\perp}$ of the selected band were taken at various temperatures. The Haake Model F4 constant temperature circulator and temperature measuring instrument were used to control and measure the temperature of sample cell. The order parameters were then determined by using eq.[1.36]. The clearing temperature was taken to be the temperature at which the order parameter is extrapolated to zero.

The band at 837 cm^{-1} was used in this thesis to determine the order parameter of p-(n-alkyloxybenzylidene)-p-n-butylanilines (ABBA). This band is due to the C-H out of plane bending of p-disubstituted benzene ring.

2.7.2 PREPARATION OF THE SAMPLE FILMS FOR INFRARED LINEAR DICHROISM STUDIES

For IR linear dichroism studies, about 20%(w/w) MBBA PS films was prepared. About 0.08 g of purified p-(methoxybenzylidene)-p-n-butylaniline (MBBA) was added in 15 ml toluene. The solution was gently stirred until MBBA was completely disolved and purified polystyrene was then added. The solution obtained was kept to swell polystyrene for 2 days in a moist environment (a desiccator with toluene instead of Drierite). The solution was stirred vigorously with a glass stirring rod for several minutes to make sure that polystyrene was completely disolved. The solution was poured into a petri-dish of diameter 7.5 cm and dried away from air currents at room temperature for 2 days. When dry, the film easily peals off. The sample film was put into the vacuum oven at 40°C for 3-4 hours and reweighed to make sure that the solvent was completely evaporated. Dried sample was cooled at room temperature for about 5 minutes and then quenched with dry ice for 1-2 minutes. The film thus prepared has a thickness of about 80 μm. The MBBA-PS film was cut into 2x3 cm^2 pieces with a razor blade. The film obtained was stored in the vacuum desiccator until use.

The sample films of the other compounds in p-(n-alkyloxybenzylidene)-p-n-butylaniline series such as EBBA, P_3BBA, BBBA, P_5BBA and HBBA were also prepared in a similar way. In the case of pure PS film, 0.4 g (exact by weight) of purified PS was used.

Table 2.2 The temperatures of stretching sample films

Sample films	Temperature of stretching (°C)
20.07% (w/w) MBBA-PS	35
20.00% (w/w) EBBA-PS	41
20.05% (w/w) P_3BBA-PS	42
20.00% (w/w) BBBA-PS	43
20.05% (w/w) P_5BBA-PS	43
20.00% (w/w) HBBA-PS	44

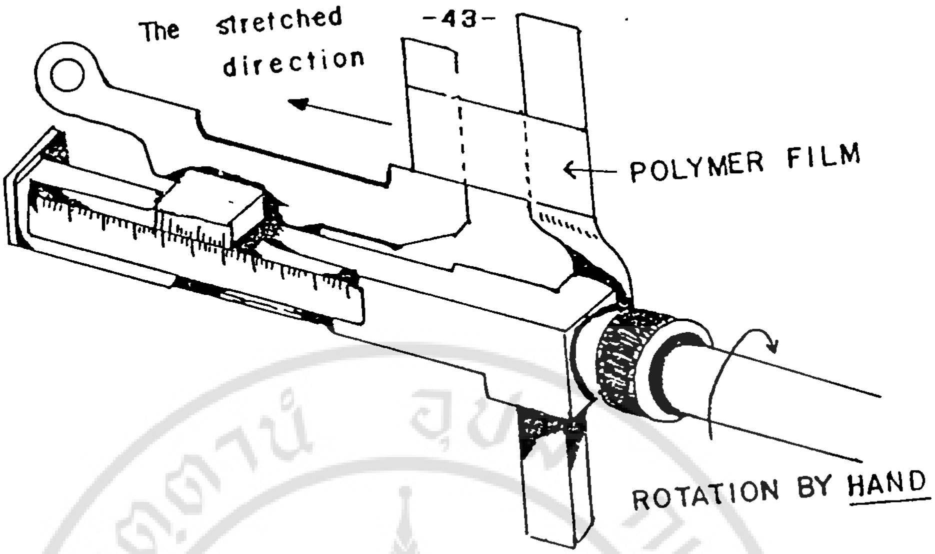


Fig.2.9 Schematic diagram of the device for stretching the sample films.

A simple mechanical stretcher, as shown in Fig.2.9, was used for stretching the sample films (PS film and ABBA-PS films). Stretch ratio may be easily calculate by measuring the distance between two marks on the film before stretching. The sample films of 20% (by weight) ABBA-PS mixture were stretched to 600% elongation. The temperatures of stretching are presented in Table 2.2. After stretching, the sample film was immediately quenched with dry ice, placed between NaCl windows in a steel holder which kept the temperature at 20°C. The sample cell set in the sample compartment was rotated so that the stretched direction is parallel to grid lines of the polarizer. Dichroic spectra of the sample films were measured on a double beem recording spectrophotometer at various temperatures.

The determination of the degree of molecular orientation by dichroic ratio measurements requires a mode of vibration which is not overlapping with those of the other compounds. One absorption band of polystyrene which does not overlap with those of liquid crystal is at the wave number 757 cm^{-1} which is due to C-H out of plane bending on the monosubstituted benzene ring. On the other hand, the absorption band which is appropriate for dichroic ratio evalution of ABBA is at the wave number 837 cm^{-1} which is due to a C-H out of plane bending on the p-disubstituted benzene ring.

In the case of pure polystyrene film, the specimen was stretched at 90°C to 600% elongation. After stretching,the specimen was quickly cooled under stress to room temperature. The double beam spectra were calculated at the wave number 757 cm^{-1}.

2.8 LIMIT OF ACCURACY.

The temperature measured by the Colora-Kryo thermostat WK5 and Haake Model F4 constant temperature Circulator can be read to within ±0.2°C , and to ±0.1°C by a Mettler FP5 temperature control unit. Differential Scanning Calorimeter (DSC) has an accuracy in the order to 0.5°C. Infrared spectrophotometer, Perkin-Elmer Model 683, has resolution 2cm^{-1} at wave number 700 cm^{-1} whereas the data station Model 3500 has resolution 2.5 cm^{-1} at 1100 cm^{-1}. The absorbances obtained from Basic programming has an error in the range of ±0.001. The order parameter evaluated from the absorption band has an error in the range of ±0.002 and from the curve fitting of ±0.003.

CHAPTER 3

RESULTS AND DISCUSSTION

3.1 RESULTS

3.1.1 CHARACTERISTIC OF PREPARED POLYSTYRENE.

the molecular weight (MW) of the prepared polystyrene was measured by viscometric method. The results of the flow times of pure toluene and polystyrene solutions are shown in Table 3.1 .

Table 3.1 Flow times of polystyrene solution in toluene at 30°C

solution	concentration	Flow times (sec)				
	c,(g/100ml)	expt.1	expt.2	expt.3	expt.4	average
stock	0.4028	185.84	186.13	185.96	185.72	185.91
one	0.2014	87.28	87.20	87.24	87.26	87.24
two	0.1007	61.10	61.06	61.04	61.04	61.06
three	0.0504	53.74	53.77	53.74	53.76	53.75
four	0.0252	51.58	51.53	51.52	51.53	51.54
five	0.0126	50.78	50.82	50.80	50.82	50.80
Toluene	-	50.30	50.32	50.31	50.30	50.31

Using the expression [2.1] and [2.2] , relative viscosity (η/η_o) and specific viscosity(η_{sp}) were calculated and the results are shown in Table 3.2 . Fig 3.1 is the plot of

η_{sp}/c as a function of the concentration, c . Using Perkin-Elmer Data station and Basic programming for least square method , the slope and intercept are 15.1376 and 0.5968 respectively with correlation coefficient 0.999 and standard deviation 2.25813 x 10^{-3}. Viscosity average molecular weight of polystyrene can then be calculated from the expression [2.4] which gives Mv ≈ 200,000 .

Table 3.2 Relative viscosity , specific viscosity and η_{sp}/c

solution	concentration c (g/100ml)	(η/η_o) $[=t/t_o]$	η_{sp}	η_{sp}/c
Stock	0.4028	3.6960	2.6960	6.6931
one	0.2014	1.7344	0.7344	3.6465
two	0.1007	1.2139	0.2139	2.1241
three	0.0504	1.0686	0.0686	1.3611
four	0.0252	1.0246	0.0246	0.9762
five	0.0126	1.0099	0.0099	0.7857

DSC thermogram of prepared polystyrene film is shown in Fig.3.2. The DSC results indicated that prepared polystyrene has the glass transition temperature at 88°C .

3.1.2 INFRARED LINEAR DOCHROISM STUDIES OF POLYSTYRENE

The polarized infrared spectra of stretched polystyrene film (stretched to 600% elongation at 90°C), recorded at 20.0°C in the region of 650 to 4000 cm^{-1}, are shown in Fig.3.3. Dotted line and solid line indicated the polarized absorption spectra with the electric vector parallel and

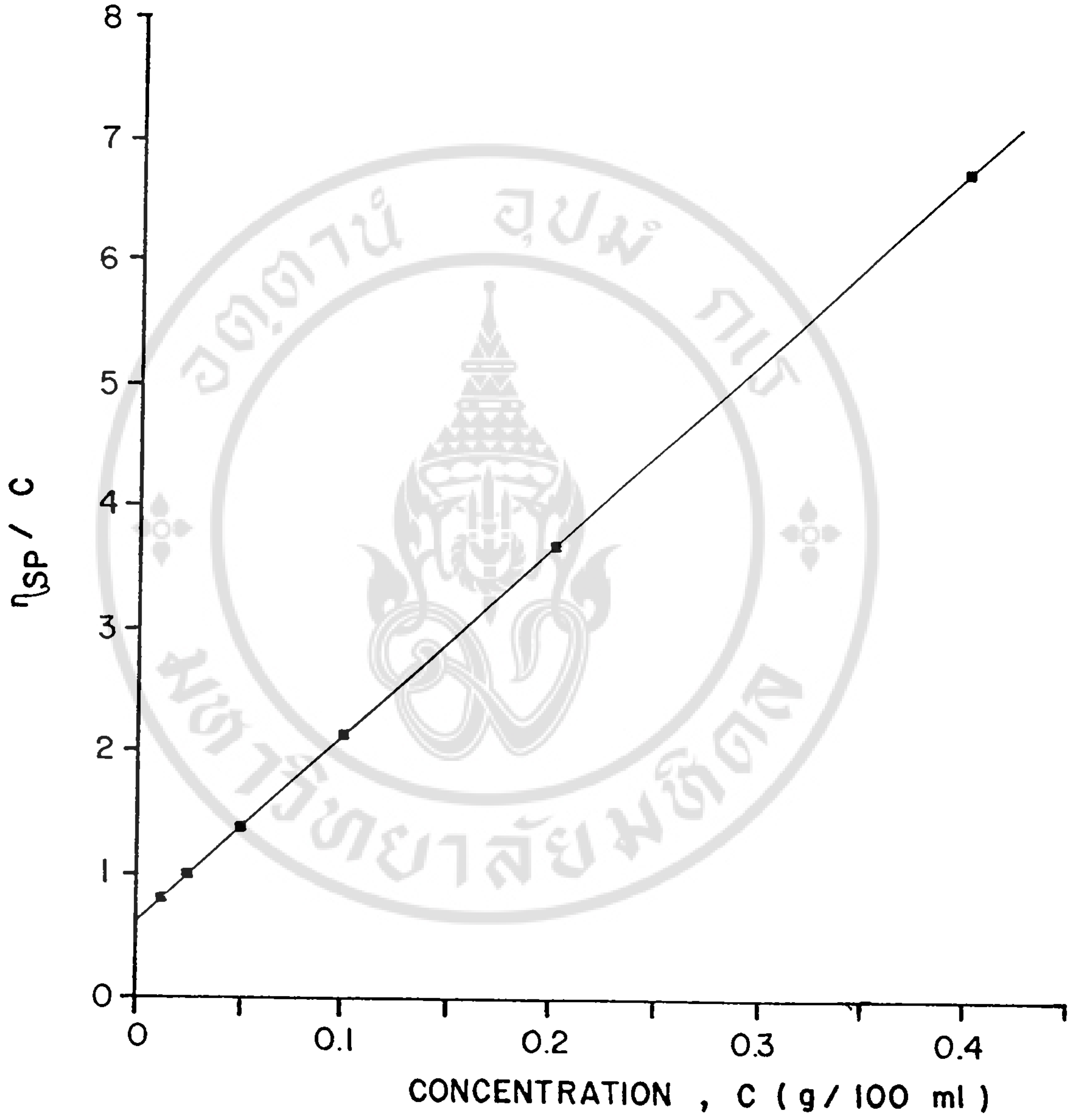


Fig.3.1 η_{sp}/c plotted as a function of the concentration of polystyrene solution, c, at 30°C.

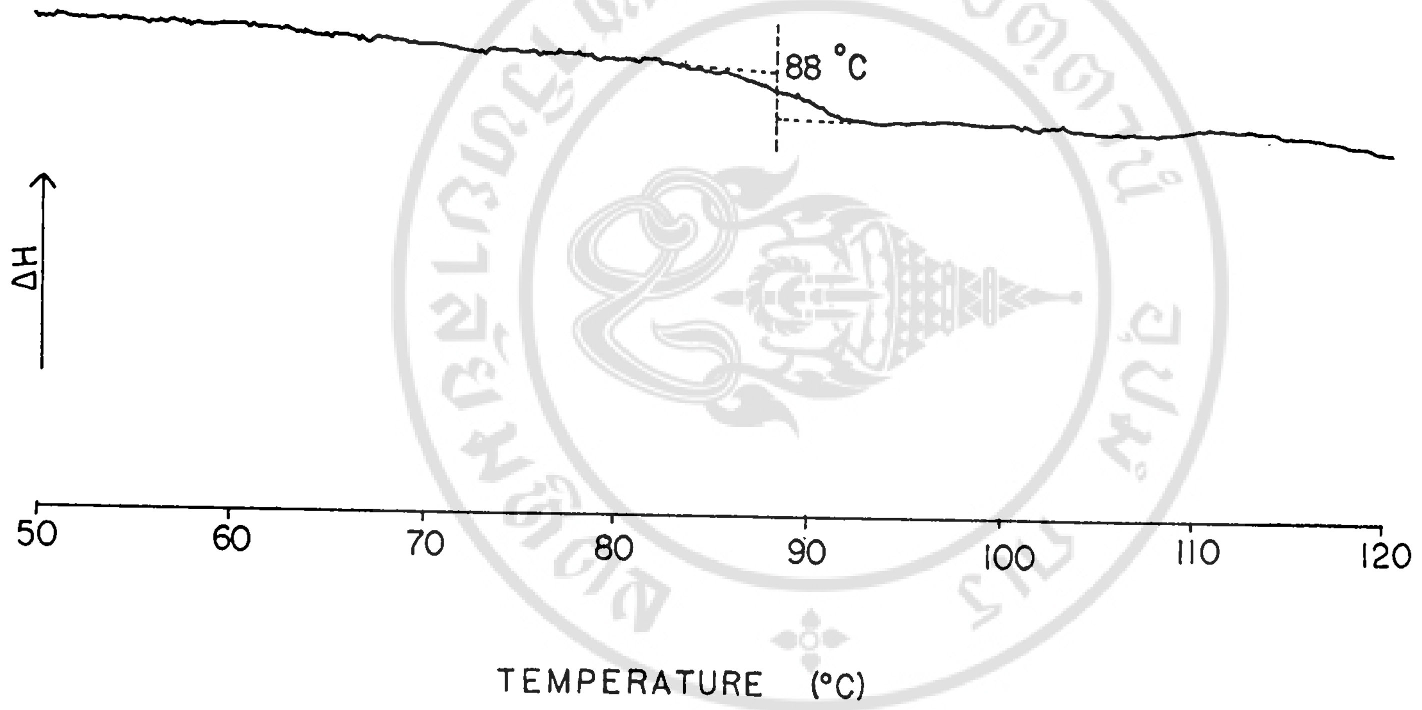


Fig.3.2 DSC thermogram of polystyrene film.

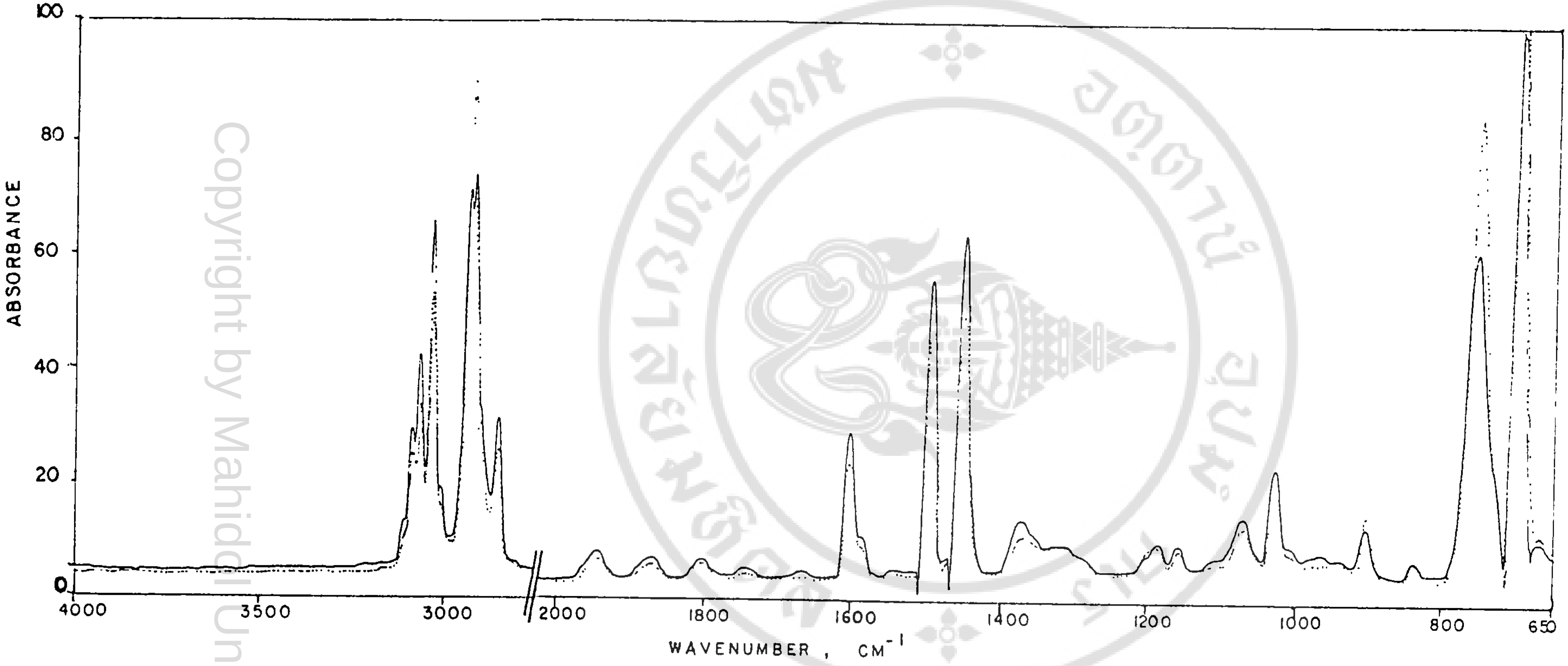


Fig.3.3 The polarized absorption spectra of pure polystyrene (PS), stretched to 600% elongation at 90°C, observed at 20.0°C. Dotted line and solid line refer to the electric vector of radiation polarized parallel and perpendicular to the optical axis, respectively.

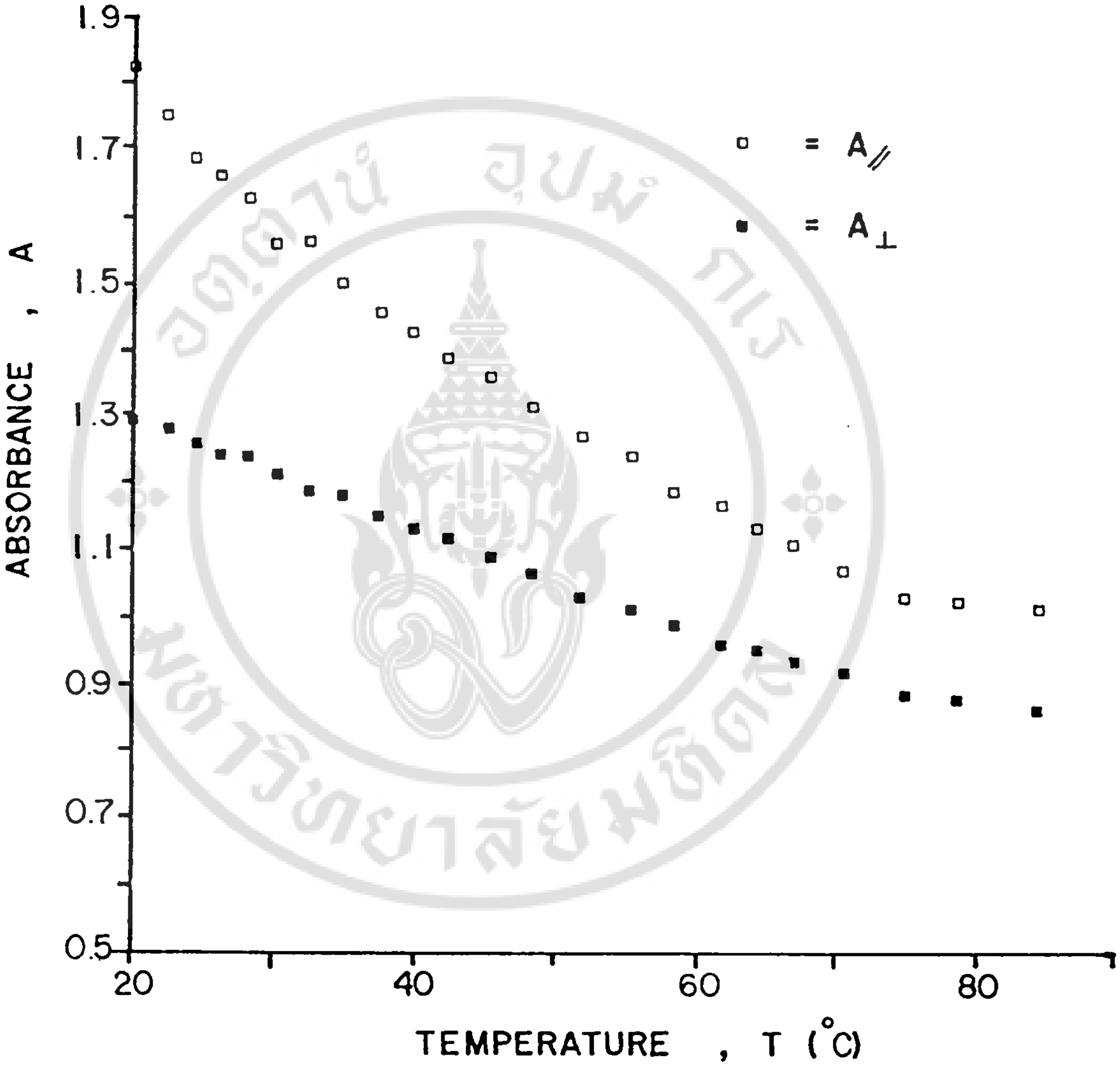


Fig.3.4 Temperature dependence of the absorbance (A) of polystyrene film, stretched to 600% elongation.

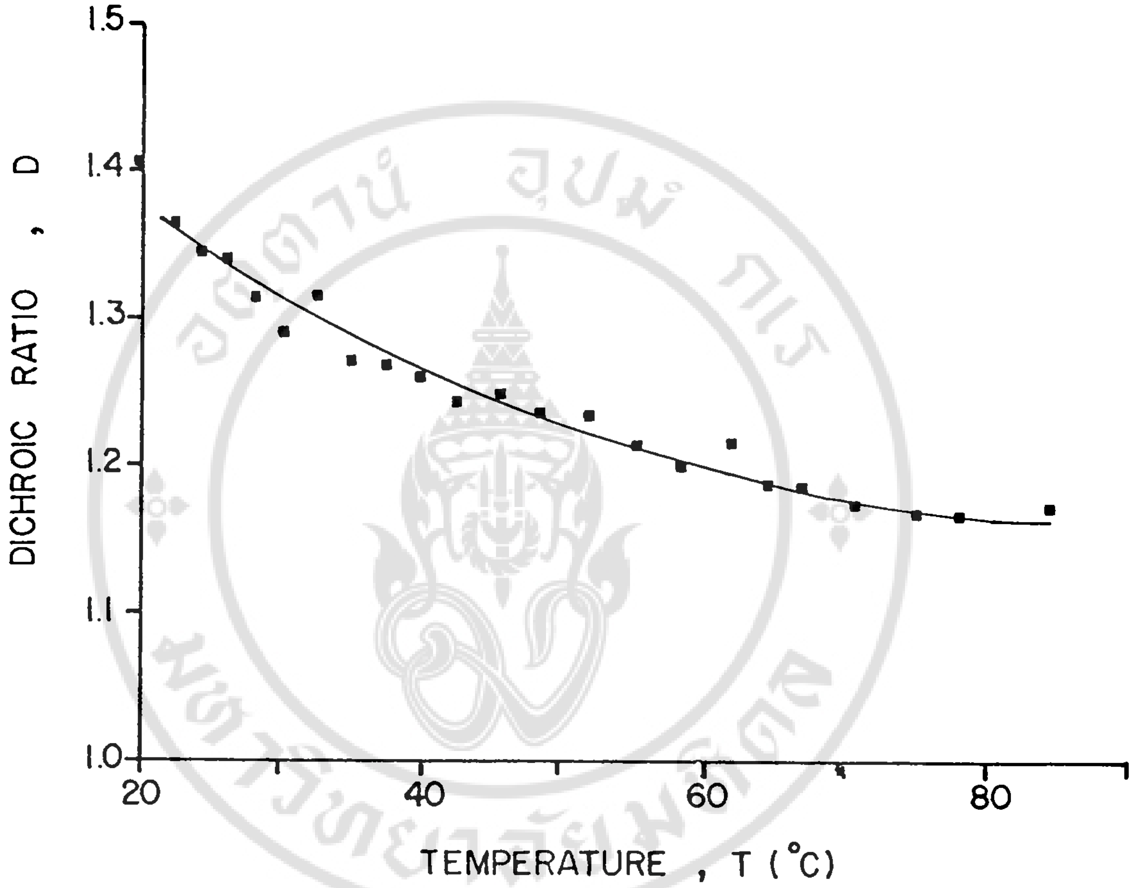


Fig.3.5 Temperature dependence of the dichroic ratio (D) of polystyrene film, stretched to 600%elongation.

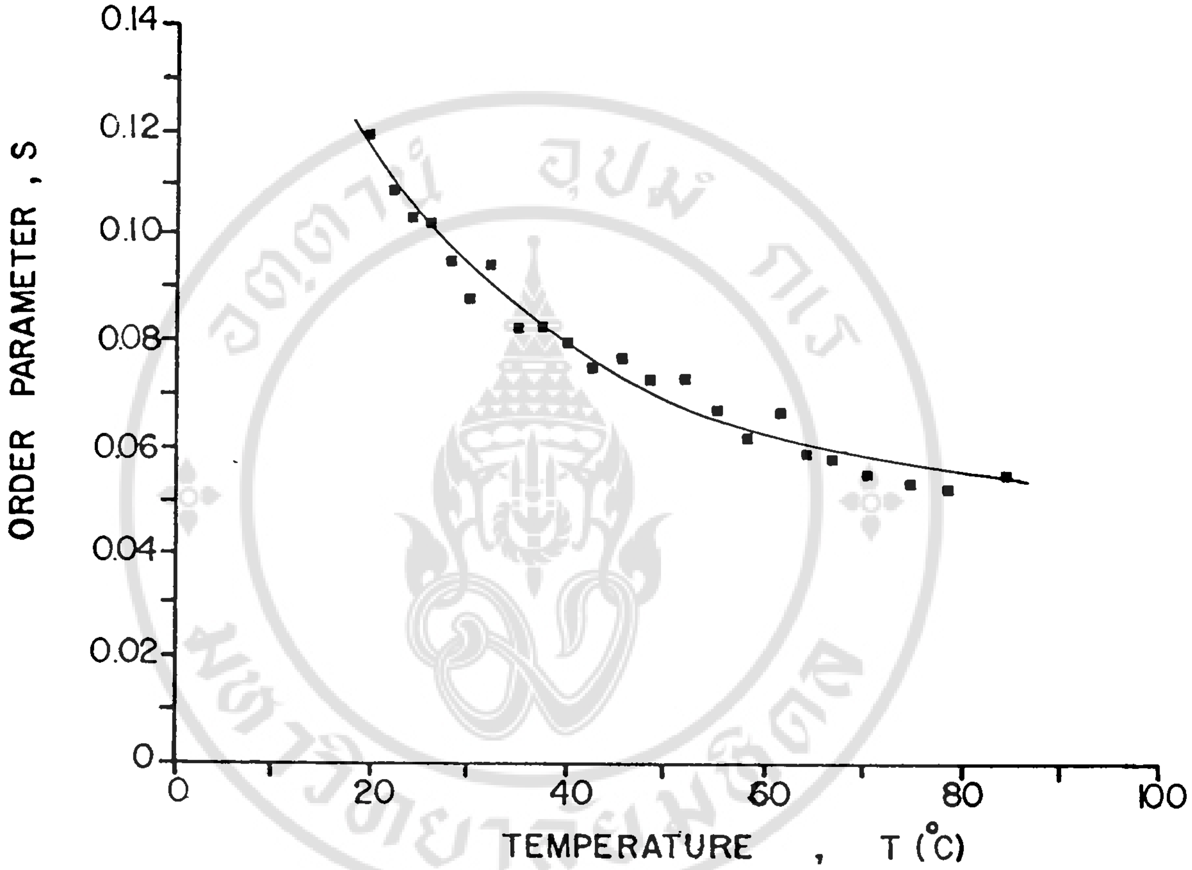


Fig.3.6 Temperature dependence of the order parameter (S) of polystyrene film, stretched to 600%elongation.

perpendicular respectively to the optical axis of the sample (stretched direction). The absorption band at 757 cm^{-1}, due to the C-H out of plane bending of the monosubstituted benzene ring is chosen to determine the order parameter of polystyrene. This absorption band shows dichroism of parallel type i.e. $A_{\parallel} > A_{\perp}$.

In Fig.3.4, the absorbances (with its electric vector parallel and perpendicular to the stretched direction defined as $A_{\parallel}$ and $A_{\perp}$) obtained by using Basic programming at the wave number 757 cm^{-1} are shown for the elongated polystyrene (stretched to 600% elongation at 90°C). The dichroic ratio , D , and the order parameter , S , obtained by using the expression [1.4] and [1.19] as a function of the temperature are given in Fig.3.5 and Fig.3.6 respectively. One can notice that the dichroic ratio and the order parameter are slightly decreased as the temperature is increased.

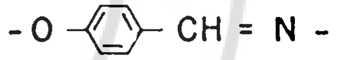
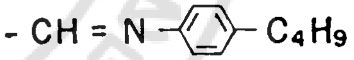
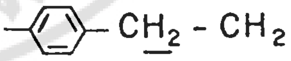
3.1.3 RESULTS FROM NMR STUDIES OF ABBA.

The nuclear magnetic resonance spectra of 10% ABBA in CCl_4 were taken by EM-360 L Proton NMR spectrometer, Varian 60 MHz, as shown in Fig 3.7-3.12. Proton resonance in certain regions of NMR spectrum is indicative of certain type of protons. Table 3.3 shows the detailed analysis of NMR spectrum of p-methoxybenzylidene-p-n-butylaniline(MBBA). However, the NMR spectra of these series are slightly different especially the peak in the 3.6-4.0 δ regions (relative to TMS) which is due to the CH_3-O- in the case of

MBBA (see Fig.3.7) and $-CH_2-O-$ in the case of the other compounds (Fig.3.8-3.12).

In NMR spectrum of EBBA (Fig 3.8), the position of 3.9 δ quartet indicates $CH_3-C\underline{H}_2-O-$. In the case of P_3BBA, BBBA, P_6BBA and HBBA (Fig. 3.9 - 3.12), the position of 3.8-3.9 δ triplet indicates $-CH_3-C\underline{H}_2-O-$.

Table 3.3 The detailed analysis of NMR spectra of ABBA.

Position	Multiplicity	Analysis
8.2 δ	singlet	$-C\underline{H}=N-$
7.8-6.7 δ	A-B quartet	proton in benzene ring: 
7.0 δ	singlet	proton in benzene ring: 
3.6 δ	singlet	$C\underline{H}_3-O-$
2.5 δ	triplet	
1.8-0.6 δ	multiplet	$-CH_2-C\underline{H}_2-C\underline{H}_3$

3.1.4 TRANSITION TEMPERATURE OF ABBA.

Fig.3.13 shows heating runs of ABBA compounds. DSC thermogram of MBBA, the first compound in ABBA series is shown in curve (a). A large endothermic peak is observed near 20°C, followed by a small transition near 42°C. The large transition represents the change from the normal

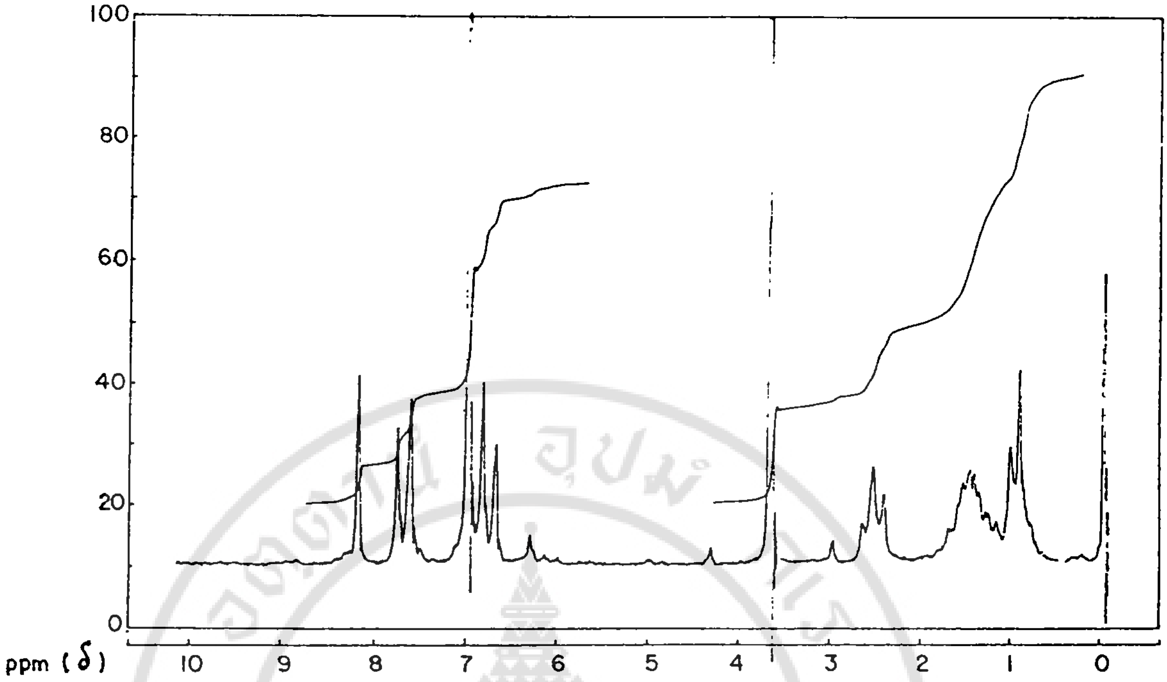


Fig.3.7 NMR spectrum of p-methoxybenzylidene -p-n-butylaniline (MBBA)

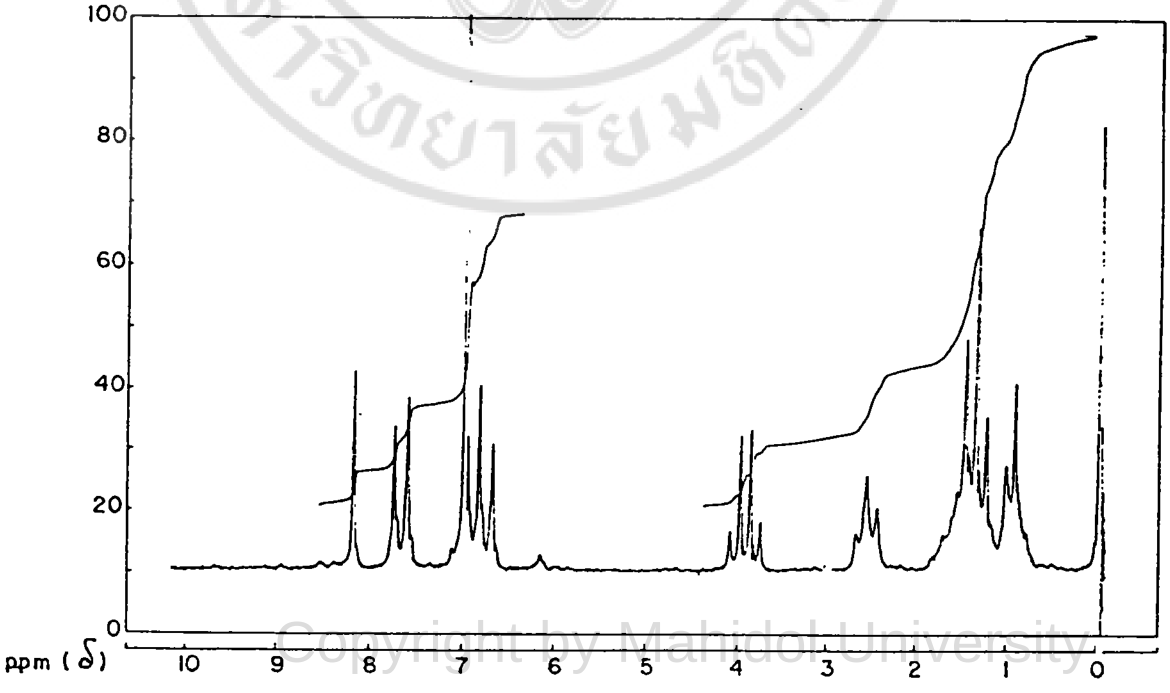


Fig.3.8 NMR spectrum of p-ethoxybenzylidene -p-n-butylaniline (EBBA)

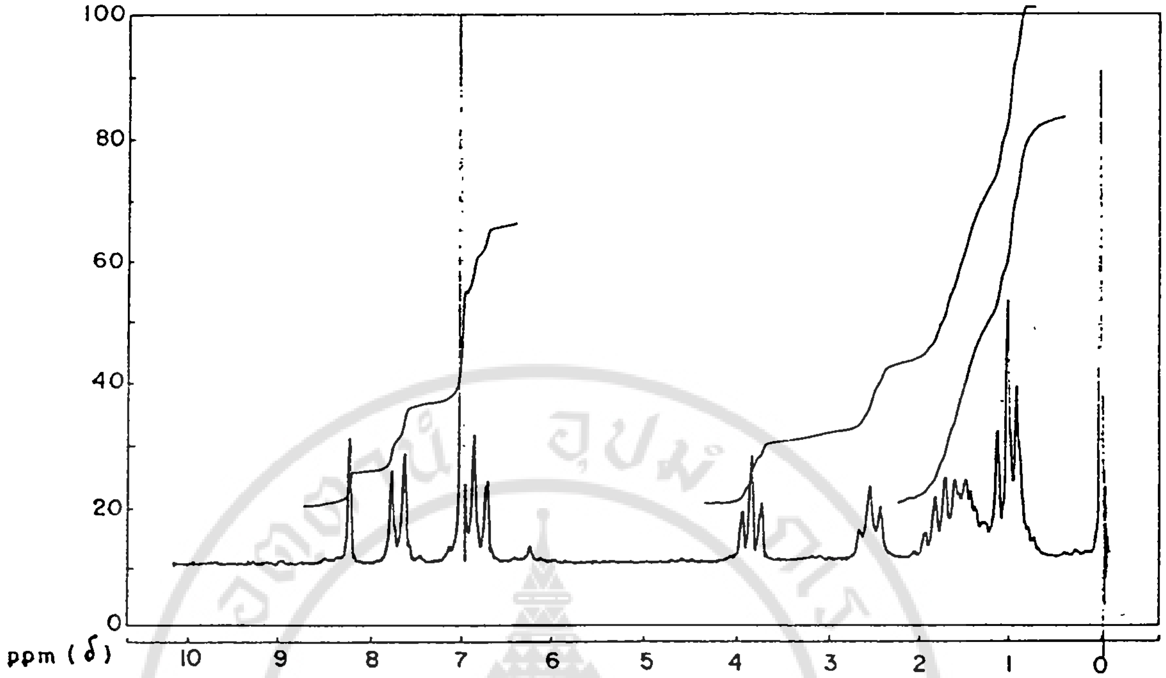


Fig.3.9 NMR spectrum of p-n-propoxybenzylidene -p-n-butylaniline (P_3BBA)

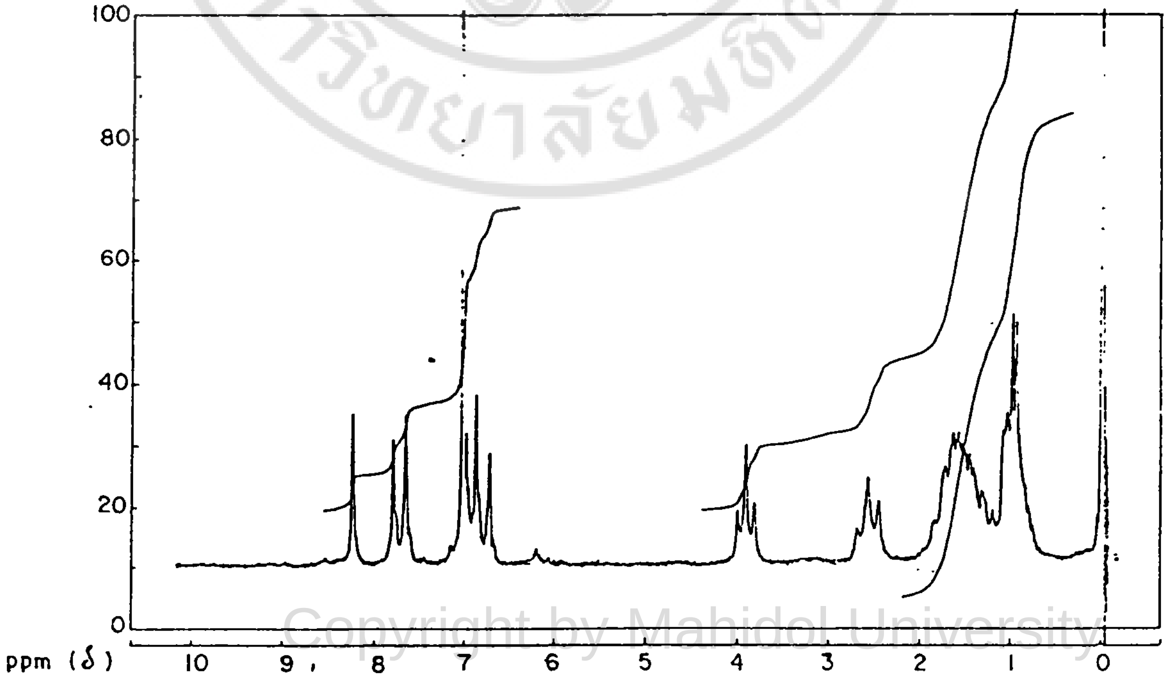


Fig.3.10 NMR spectrum of p-n-butyloxybenzylidene -p-n-butylaniline (BBBA)

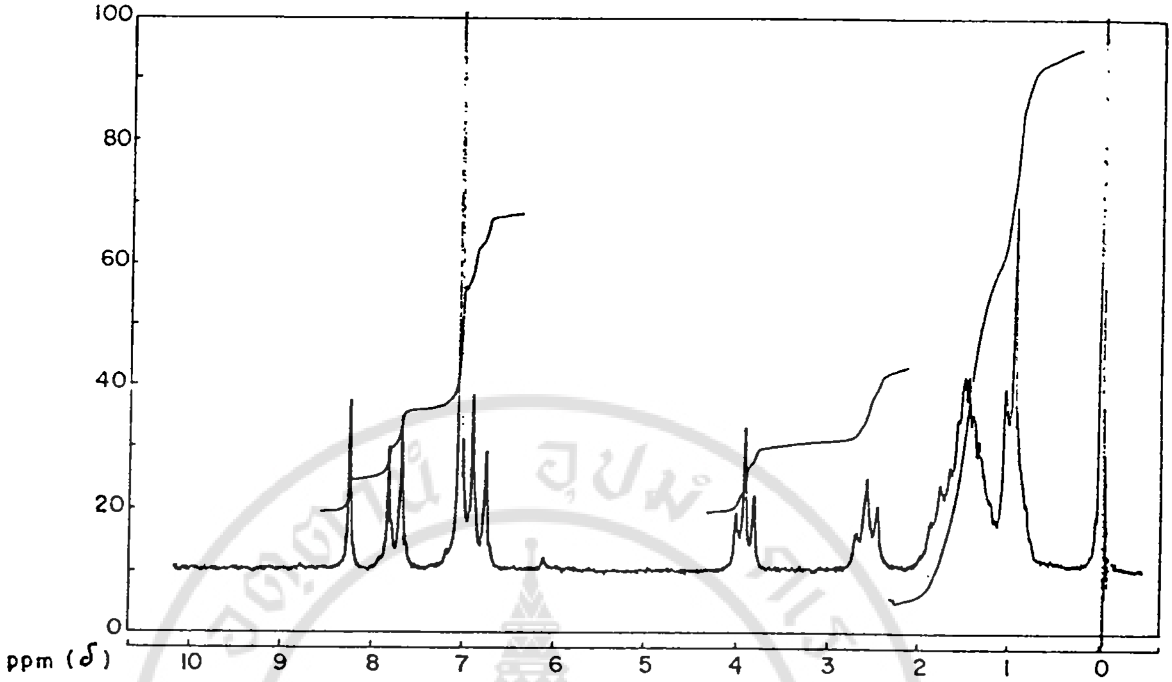


Fig.3.11 NMR spectrum of p-n-pentoxybenzylidene -p-n-butylaniline (P_5BBA)

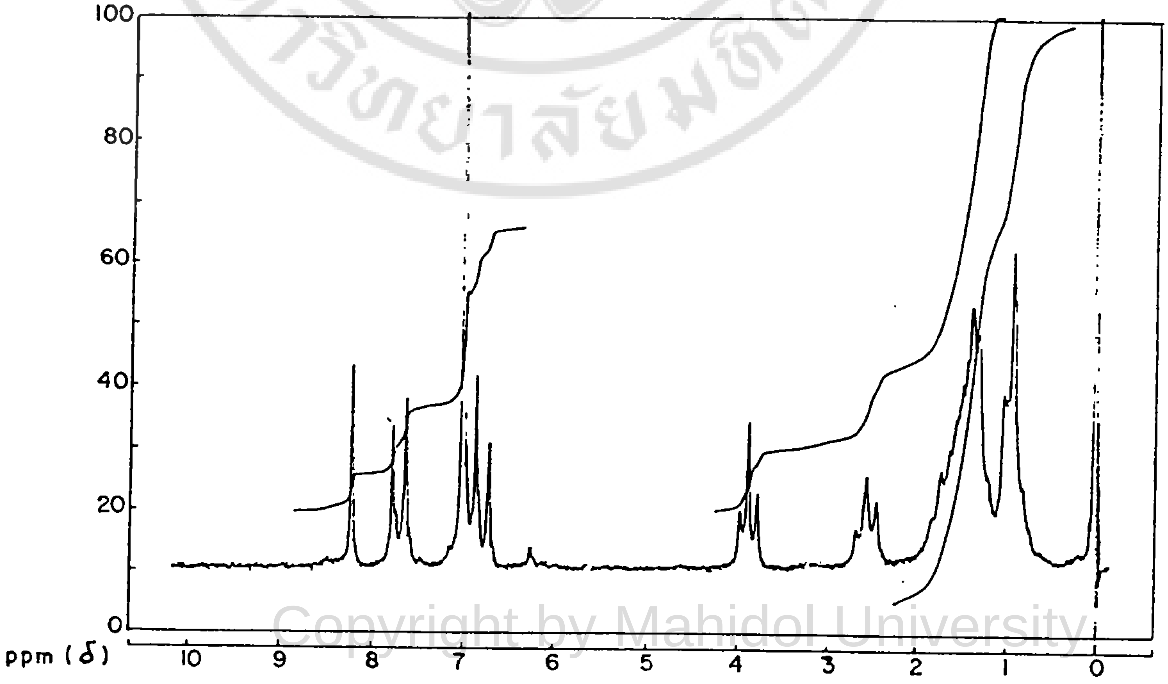
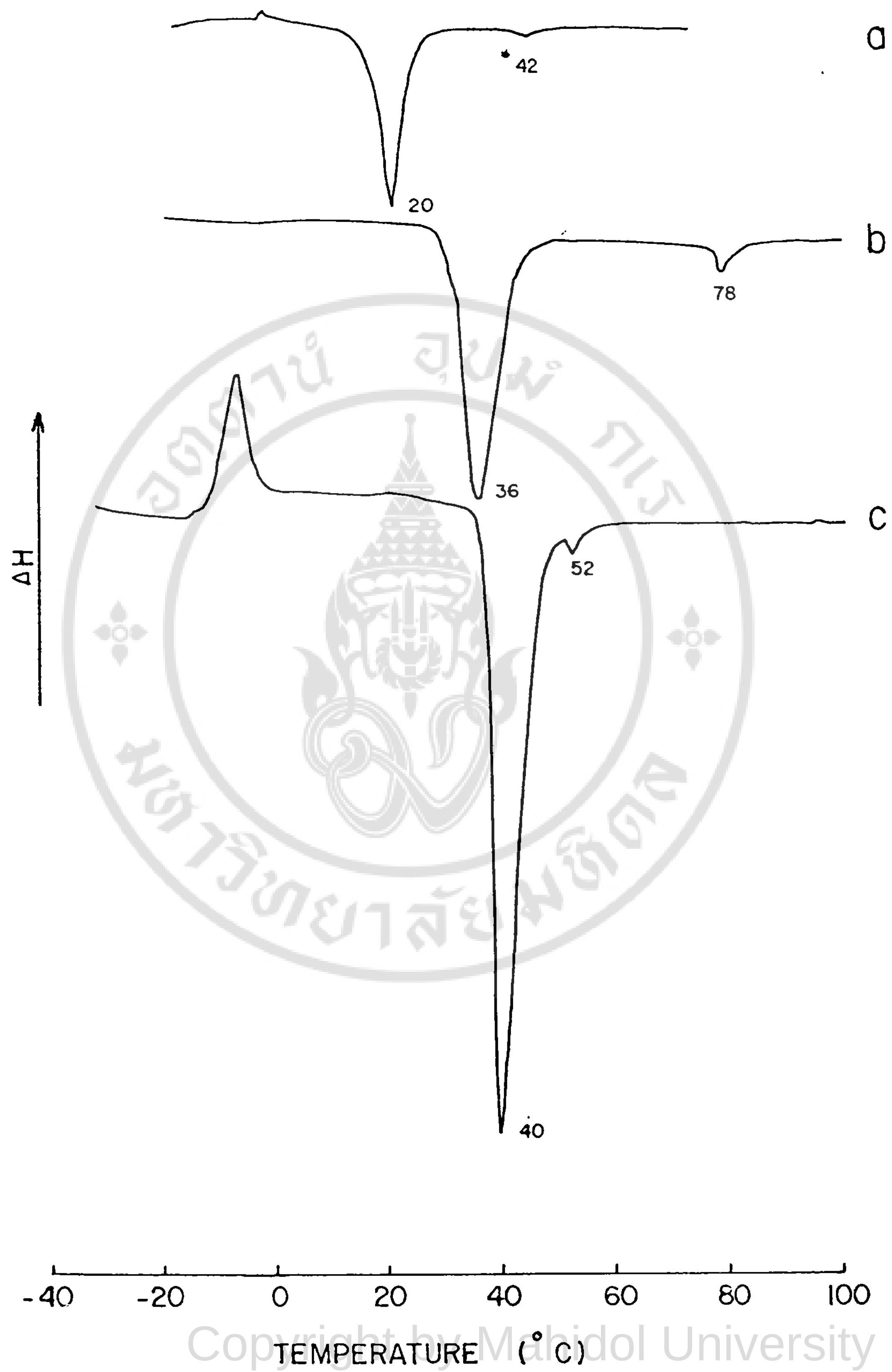


Fig.3.12 NMR spectrum of p-n-hexoxybenzylidene -p-n-butylaniline (HBBA)


a
20
42
b
36
78
c
40
52
ΔH
-40
-20
0
20
40
60
80
100
TEMPERATURE (°C)

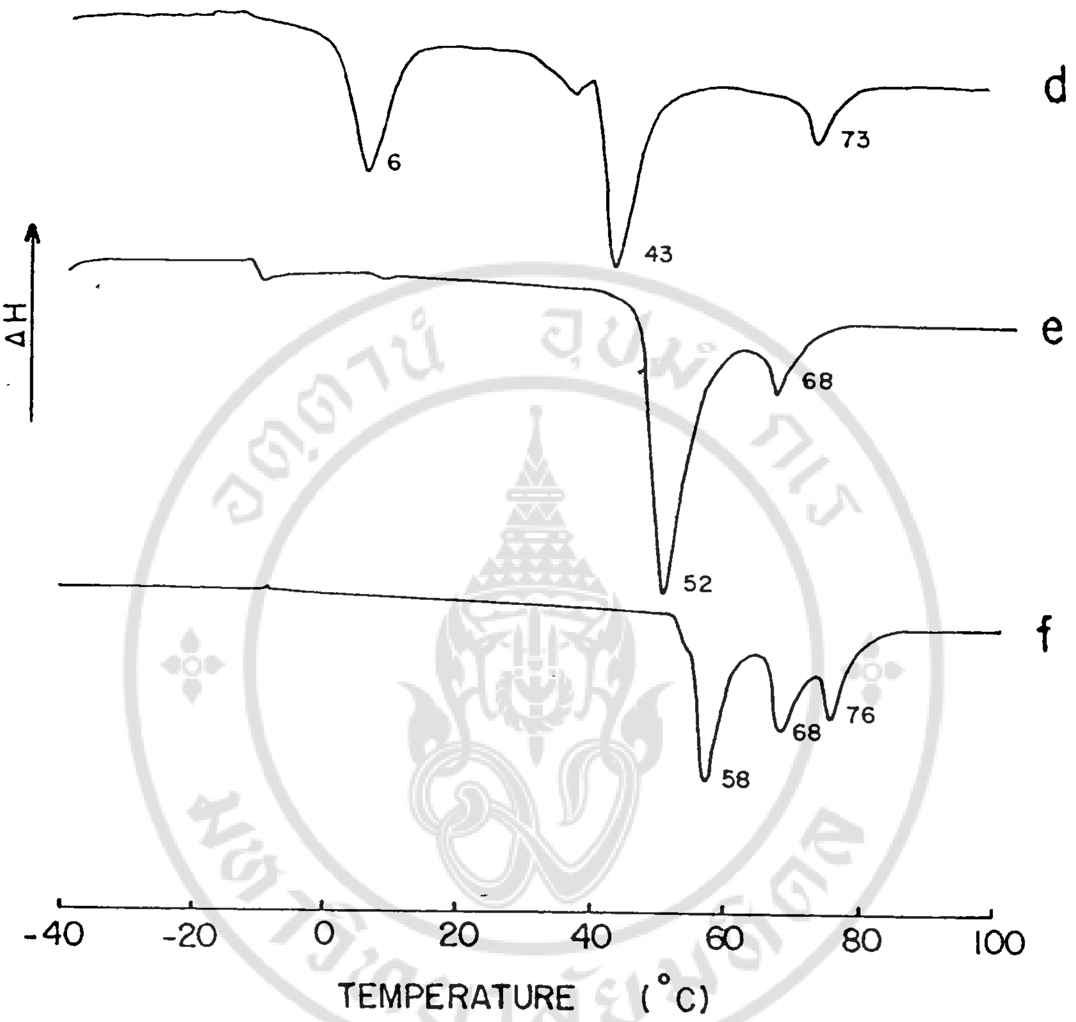


Fig.3.13 DSC thermograms of : a) MBBA, b) EBBA, c) P_3BBA d) BBBA, e) P_5BBA, f) HBBA.

crystalline state to the nematic liquid crystalline state while the small transition is the"liquid-crystal transition" from nematic to isotropic liquid. A small exothermic transition near -4°C is the crystallization which exhibits supercooling.

DSC thermograms of EBBA and P3BBA are shown in curves (b) and (c) respectively. Their phase behavior correspond to the melting point and the clearing point are also observed. However, referring to curves (d),(e) and (f), which show the DSC thermograms of BBBA, P5BBA and HBBA respectively, the detected transition peaks correspond to the solid-smectic, smectic-nematic and nematic-isotropic transitions.

The phase transition temperature from microscopic observation are shown in Table 3.4 and are compared with the results from DSC measurement. All transition are reversible and do not change on repeated cooling and heating cycles. The clearing temperature (T_c) of the investigated compounds obtained from microscope studies and DSC measurement are listed in comparison with the results from IR linear dichroism studies (see also section 3.1.5) in Table 3.5. Fig.3.14 is the plot of T_c (data from Table 3.5) versus the number of carbon atoms of the alkoxy chain in ABBA series. A clear odd-even effect can be observed in this series.

3.1.5 INFRARED LINEAR DICHROISM STURIES OF ABBA

Polarized absorption spectra of p-methoxybenzylidene-p-n-butylaniline (MBBA) at 20°C is illustrated in Fig.3.15. The solid and the dotted lines have the same meaning as

Table 3.4 Phase transition temperature of ABBA

name of compound	number of carbon atom in alkoxy chain (n)	Phase transition$^{(a)}$ in°C	
		DSC measurement	Microscopic observation
MBBA	1	k20n42i	k20n45.8i
EBBA	2	k36n78i	k36.8n78.6i
P_3BBA	3	k40s52i	k41.9s56i
BBBA	4	k6s43n73i	s46n75i
P_5BBA	5	s52n68i	$s_2$52.7$s_1$55n69.1i
HBBA	6	$s_2$58$s_1$68n76i	$s_2$59$s_1$70.5n78i

(a) The meaning of each symbol used is as follows:

k = crystal phase

s = smectic phase

n = nematic phase

i = isotropic phase

Table 3.5 Clearing temperature of ABBA

name of compound	number of C-atoms in alkoxy chain (n)	Clearing Temperature (T_c) in°C		
		DSC measurement	Microscopic observation	IR linear dicrhoism
MBBA	1	42	45.8	43.1
EBBA	2	78	78.6	75.7
P_3BBA	3	52	56.0	53.2
BBBA	4	73	75.0	71.4
P_5BBA	5	68	69.1	66.6
HBBA	6	76	78.0	75.2

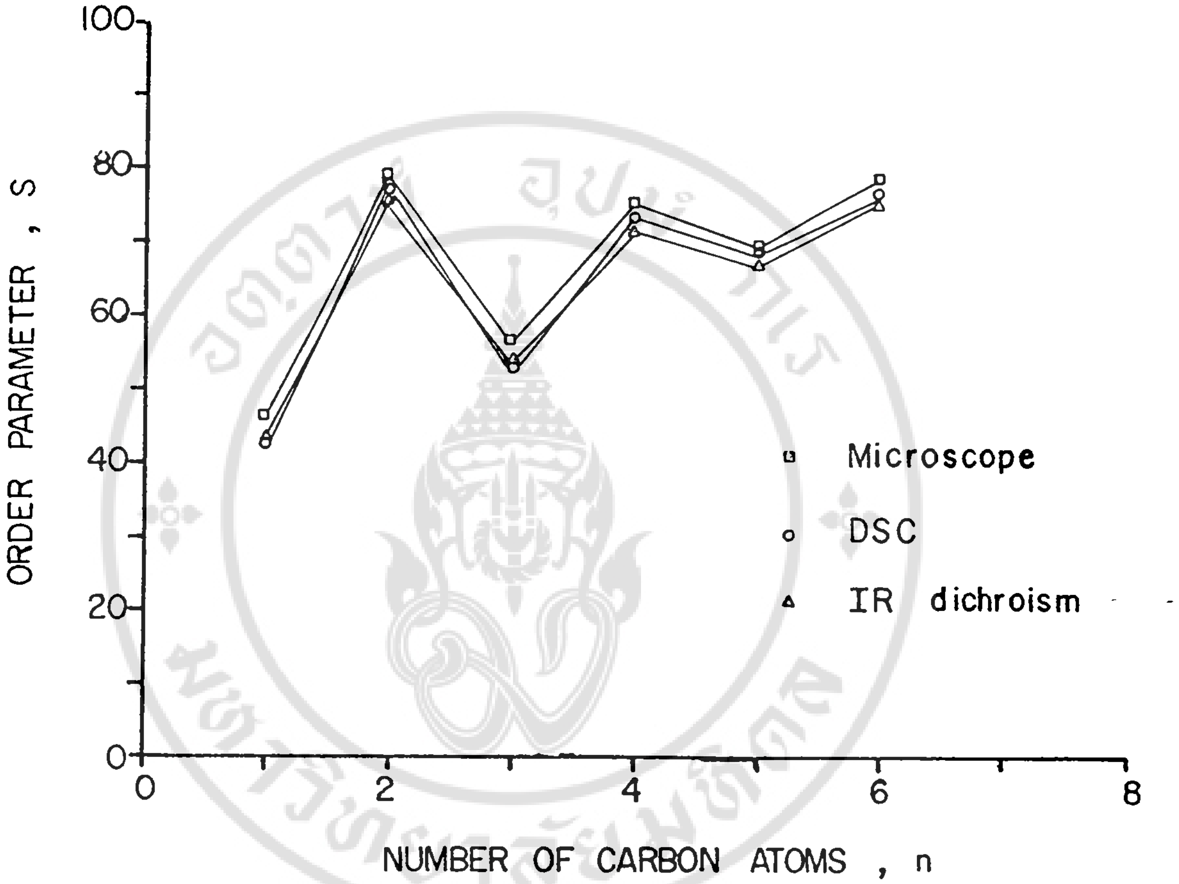


Fig.3.14 Clearing temperature (T_c) of ABBA as a function of the number of carbon atoms (n) of the alkoxy end chain.

described in Fig.3.3. The absorption at 837 cm^{-1}, due to the C-H out of plane bending of disubstituted benzene ring which shows the dichroism of perpendicular type, viz $A_{\parallel} < A_{\perp}$, are used for determination of the order parameter. Fig.3.16-3.21 represent the orientational order parameter, S , of six liquid crystals as a function of temperature. The S values in these curves decrease slowly first with increasing temperature and then suddenly approach zero at the clearing temperature as shown in Table 3.5. The plot of the order parameter versus the temperature below T_c, defined as T_c-T, of all system investigated are also shown in Fig.3.22 . The order parameter at 2°C below T_c, as shown in Fig.3.22, are plotted against the number of carbon atoms, n, of the alkoxy end chains of the homologous p-(n-alkyloxybenxylidene) -p-n-butylanilines (ABBA) series (see Fig.3.23). The order parameter, S , for the homogeneous samples exhibit an odd-even alternation with respect to the number of carbon atoms in the alkoxy end group. The similar dependence is found for the same homologous series in the clearing temperature, T_c (see also Fig.3.14).

3.1.6 GLASS TRANSITION TEMPERATURE OF SAMPLE FILMS

The glass transition temperature (T_g) of the sample films prepared by disolving the molecules of solute, ABBA in the solvent, polystyrene, were determined by DSC methods. Like pure polystyrene (see Fig.3.2), DSC thermograms, as shown in Fig.3.24, indicate that the glass transition temperature of each sample films correspond to steps. The

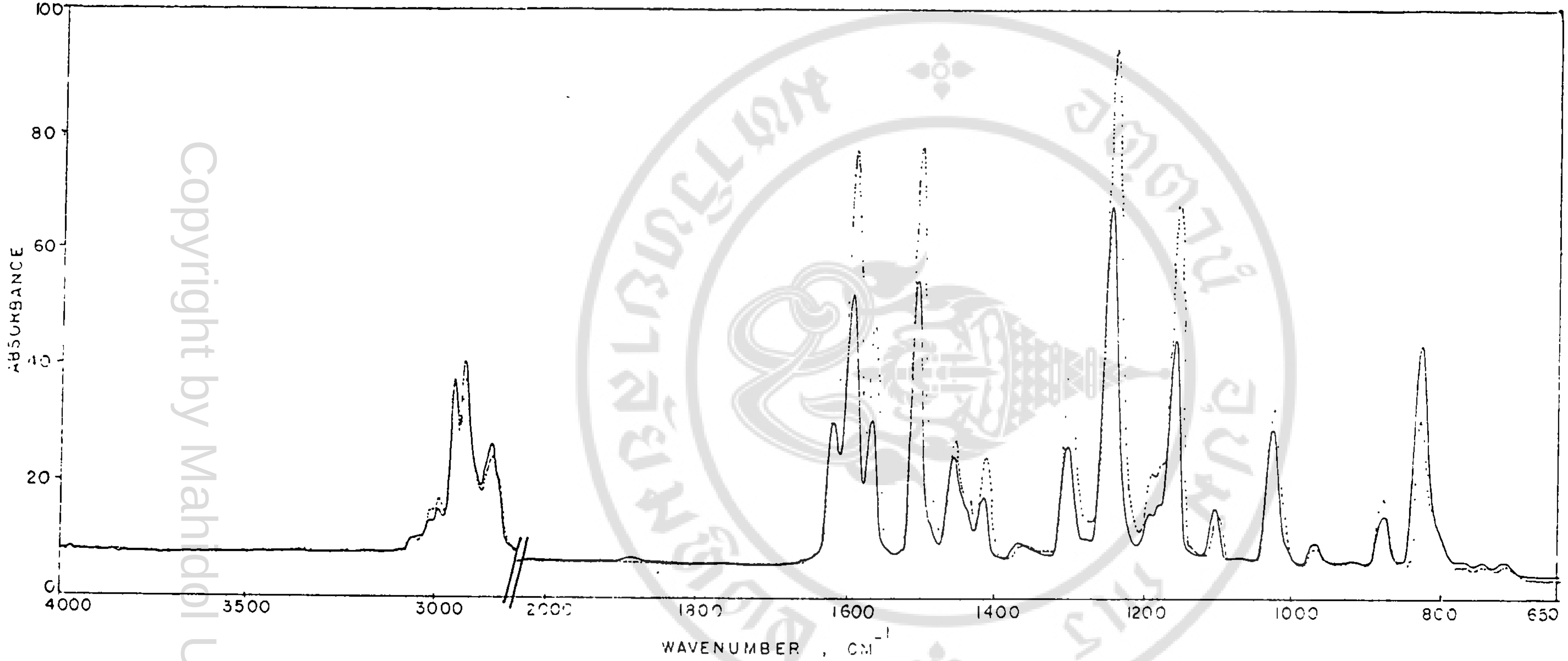


Fig.3.15 The polarized absorption spectra of p-methoxybenzylidene-p-n-butylaniline (MBBA) observed at 28.0°C. Dotted line and solid line refer to the electric vector of radiation polarized parallel and perpendicular to the optical axis, respectively.

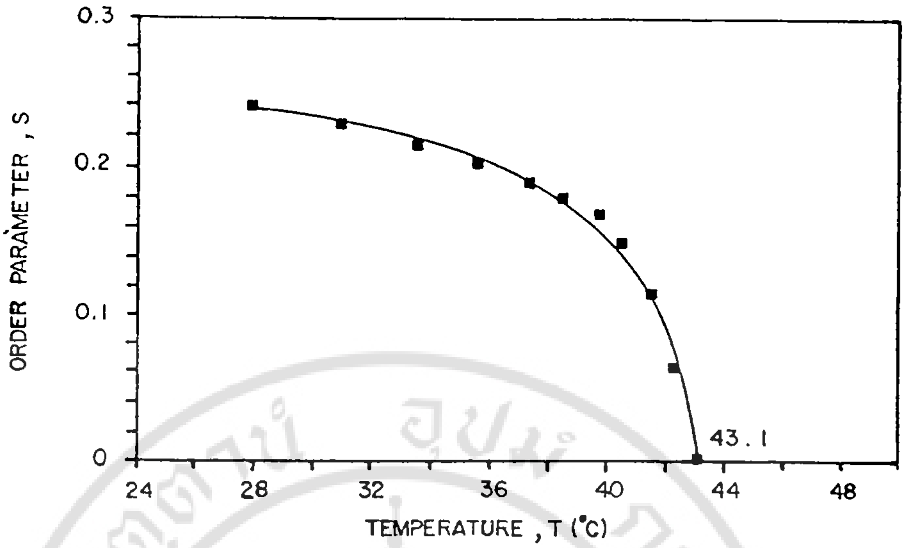


Fig.3.16 Temperature dependence of the order parameter (S) of p-methoxybenzylidene-p-n-butylaniline (MBBA) evaluated from IR linear dichroism.

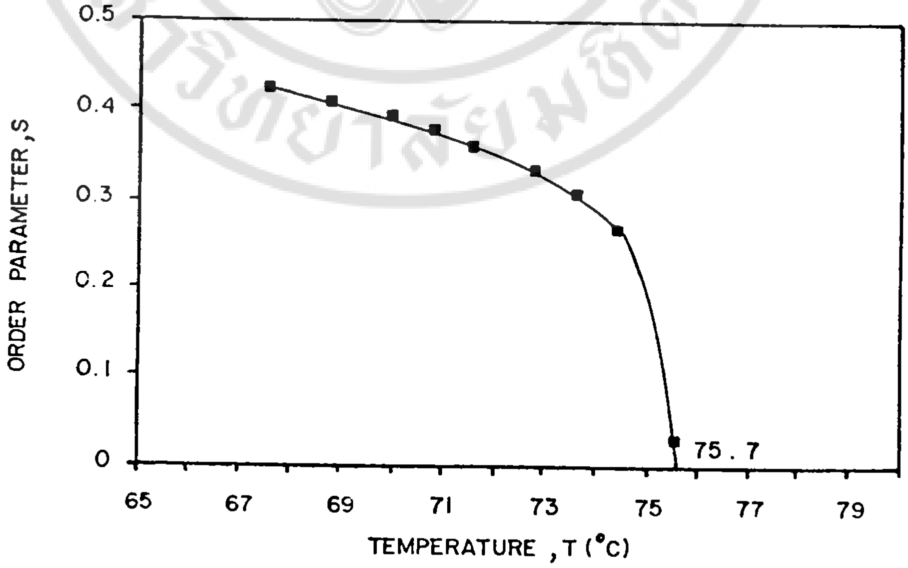


Fig.3.17 Temperature dependence of the order parameter (S) of p- ethoxybenzylidene-p-n-butylaniline (EBBA) evaluated from IR linear dichroism.

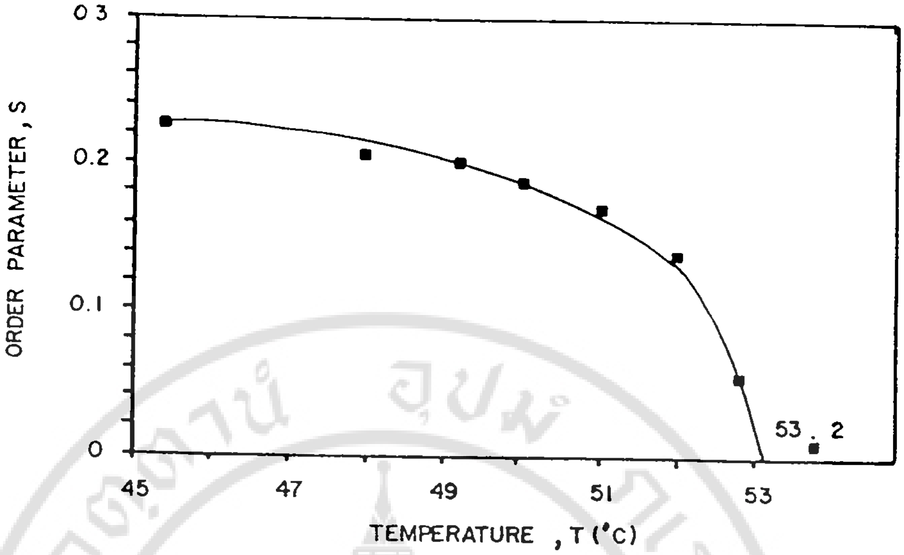


Fig.3.18 Temperature dependence of the order parameter (S) of p-n-propoxybenzylidene-p-n-butylaniline (P_3BBA) evaluated from IR linear dichroism.

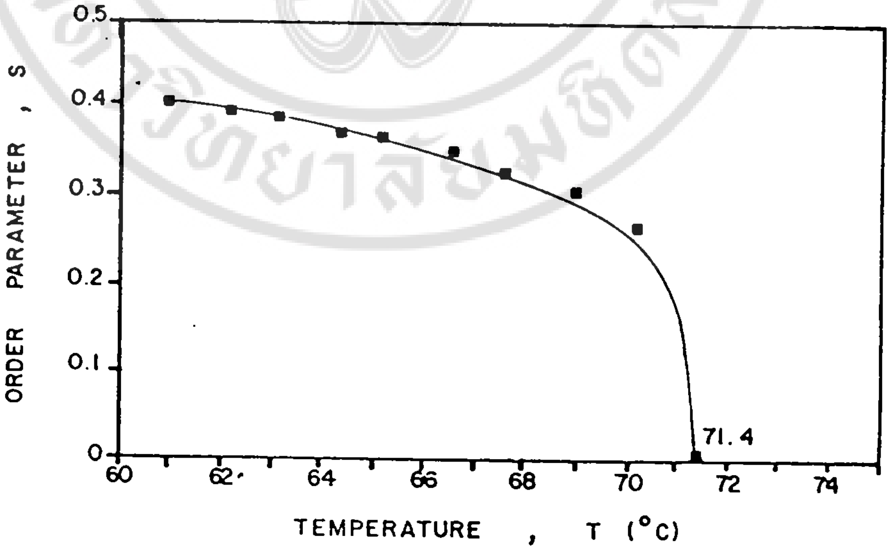


Fig.3.19 Temperature dependence of the order parameter (S) of p-n-butoxybenzylidene-p-n-butylaniline (BBBA) evaluated from IR linear dichroism.

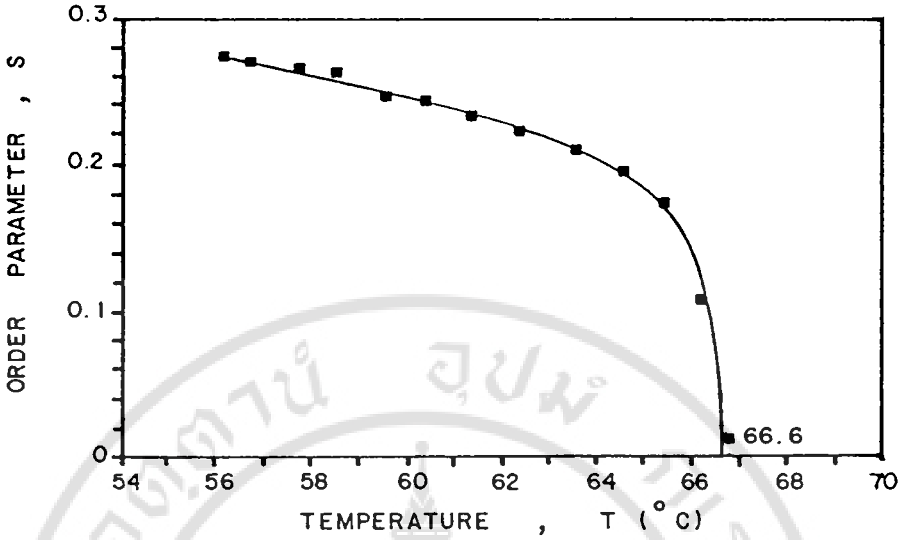


Fig.3.20 Temperature dependence of the order parameter (S) of p-n-pentoxybenzylidene-p-n-butylaniline (P_5BBA) evaluated from IR linear dichroism.

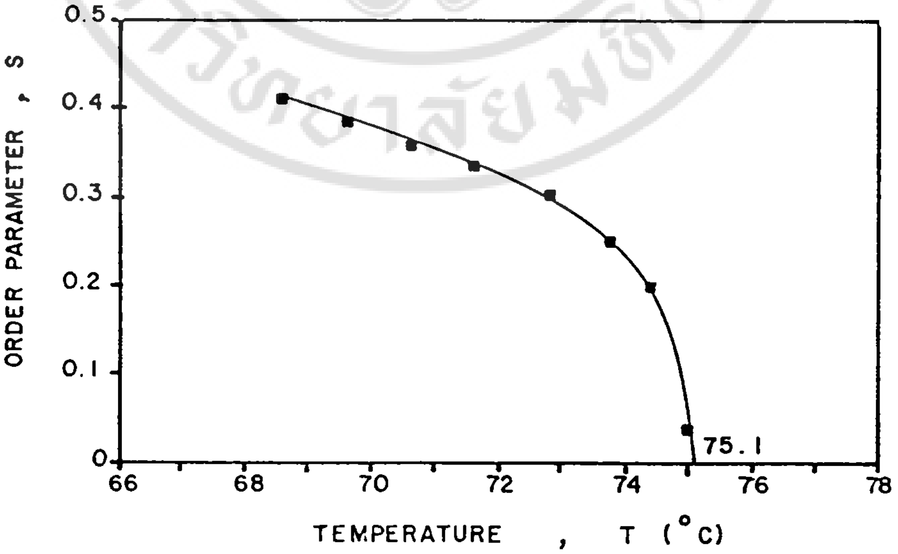


Fig.3.21 Temperature dependence of the order parameter (S) of p-n-hexoxybenzylidene-p-n-butylaniline (HBBA) evaluated from IR linear dichroism.

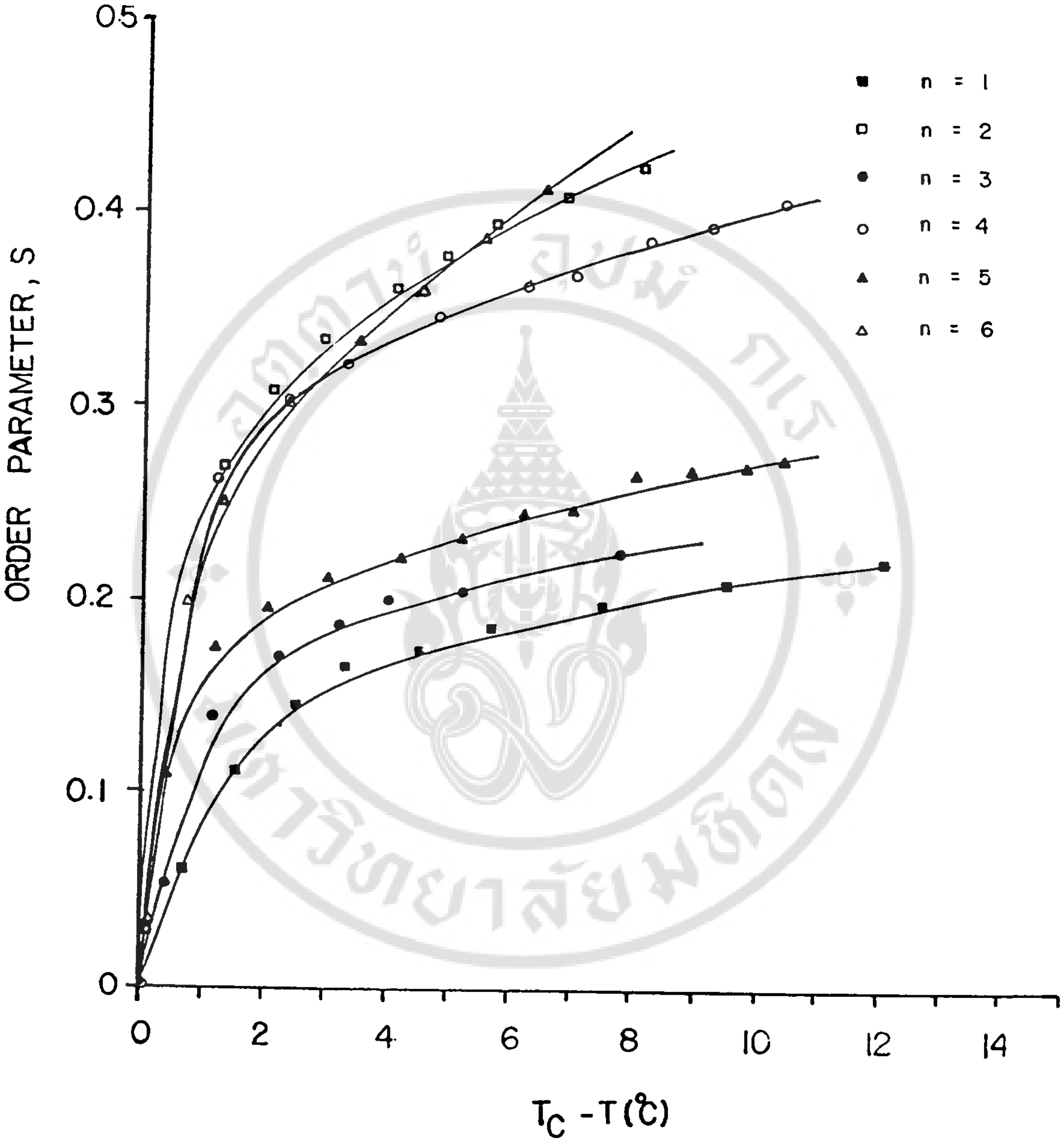


Fig.3.22 Order parameter (S) of p-n-alkyloxybenzylidene -p-n-butylaniline (ABBA) plotted as a function of the temperature below clearing temperture (T_c-T)

n = number of carbon atoms in the alkoxy chain.

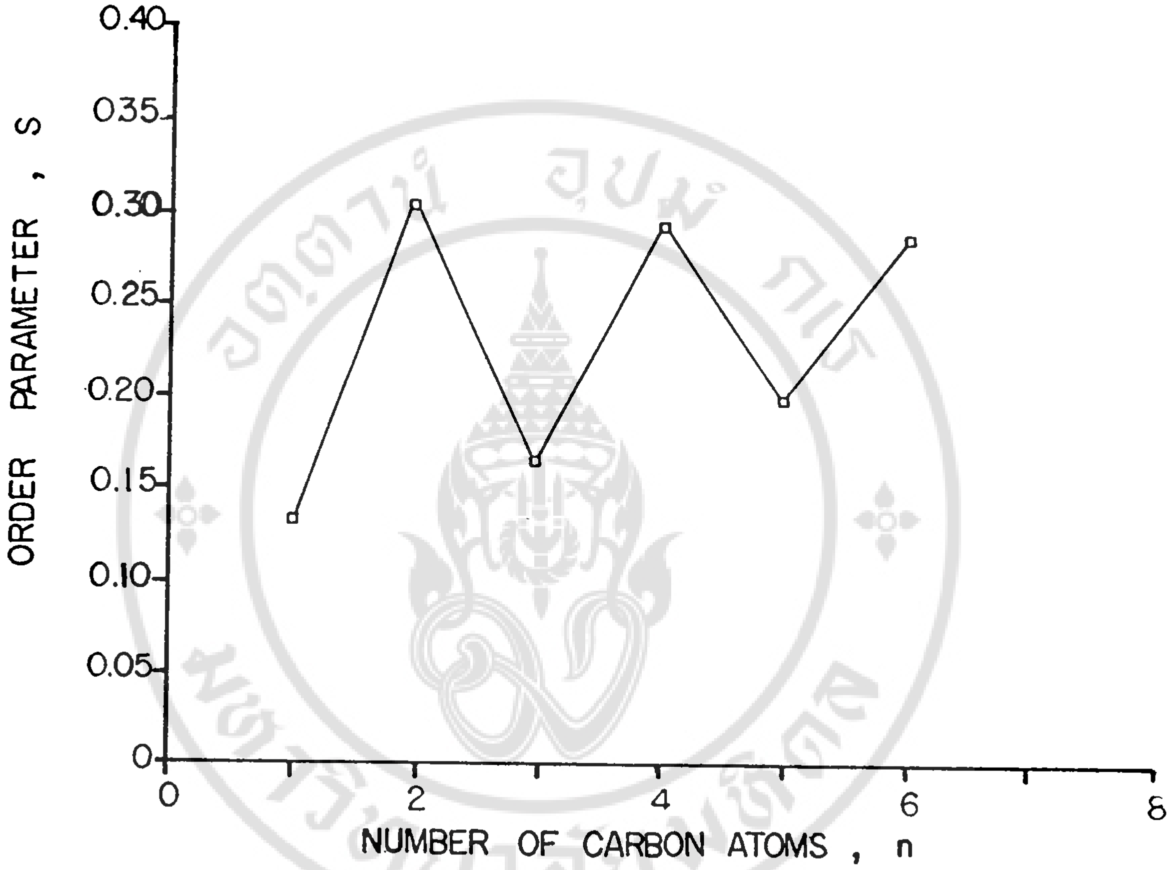


Fig.3.23 Order parameter (S)at 2°C below the clearing temperature (T_c) of p-n-alkyloxybenzylidene -p-n-butylaniline(ABBA) plotted as a function of number of carbon atoms in the alkoxy chain.

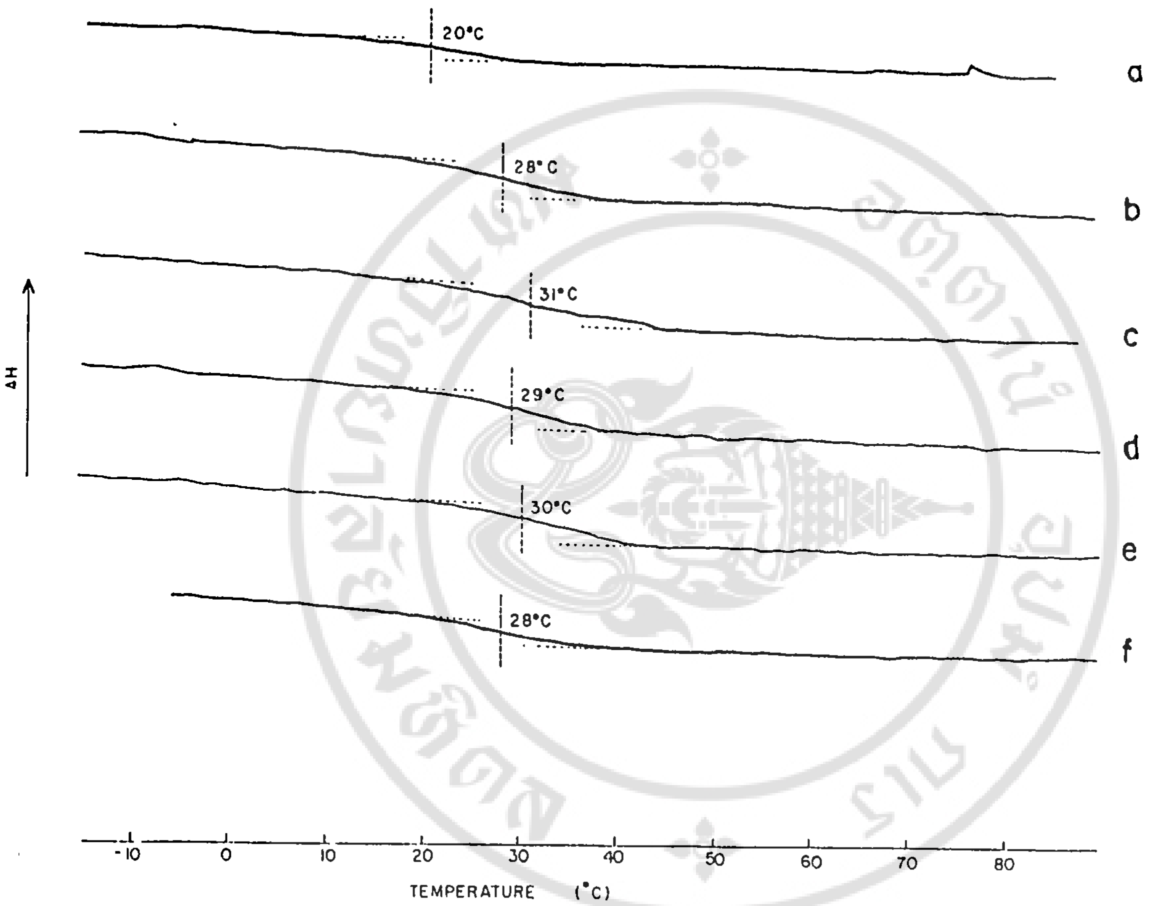


Fig.3.24 DSC thermograms of: a) MBBA-PS film, b) EBBA-PS film c) P_3BBA-PS film, d) BBBA-PS film, e) P_5BBA-PS film f) HBBA-PS film. (Before stretching)

observed glass transition temperature of the sample films are listed in Table 3.6. A comparison of these ABBA-PS films (about 20% w/w) with the pure polystyrene film shows that the glass transition temperatures of the sample films (Tg 20-31°C) are lower than that of the pure polymer (Tg 88°C).

Table 3.6 The glass transition temperature of sample films

Sample films	T_g (°C)
20.07% (w/w) MBBA-PS	20
20.00% (w/w) EBBA-PS	28
20.05% (w/w) P_3BBA-PS	31
20.00% (w/w) BBBA-PS	29
20.05% (w/w) P_5BBA-PS	30
20.00% (w/w) HBBA-PS	28

3.1.7 INFRARED LINEAR DICHROISM STUDIES OF THE SAMPLE FILMS

3.1.7.1 TEMPERATURE DEPENDENCE OF ORDER PARAMETER OF POLYSTYRENE AND ABBA

Fig.3.25 shows the typical example of polarized infrared absorption spectra recorded for MBBA-polystyrene film (20.07% MBBA by weight), stretched at 35°C to 600% elongation, obtained at 20.8°C in the range 4000-650 cm^{-1}. The solid and dotted lines have the same meaning as described in Fig.3.3 and 3.15. The absorption at the wave number 757 cm^{-1} of polystyrene (solvent) and the wave number

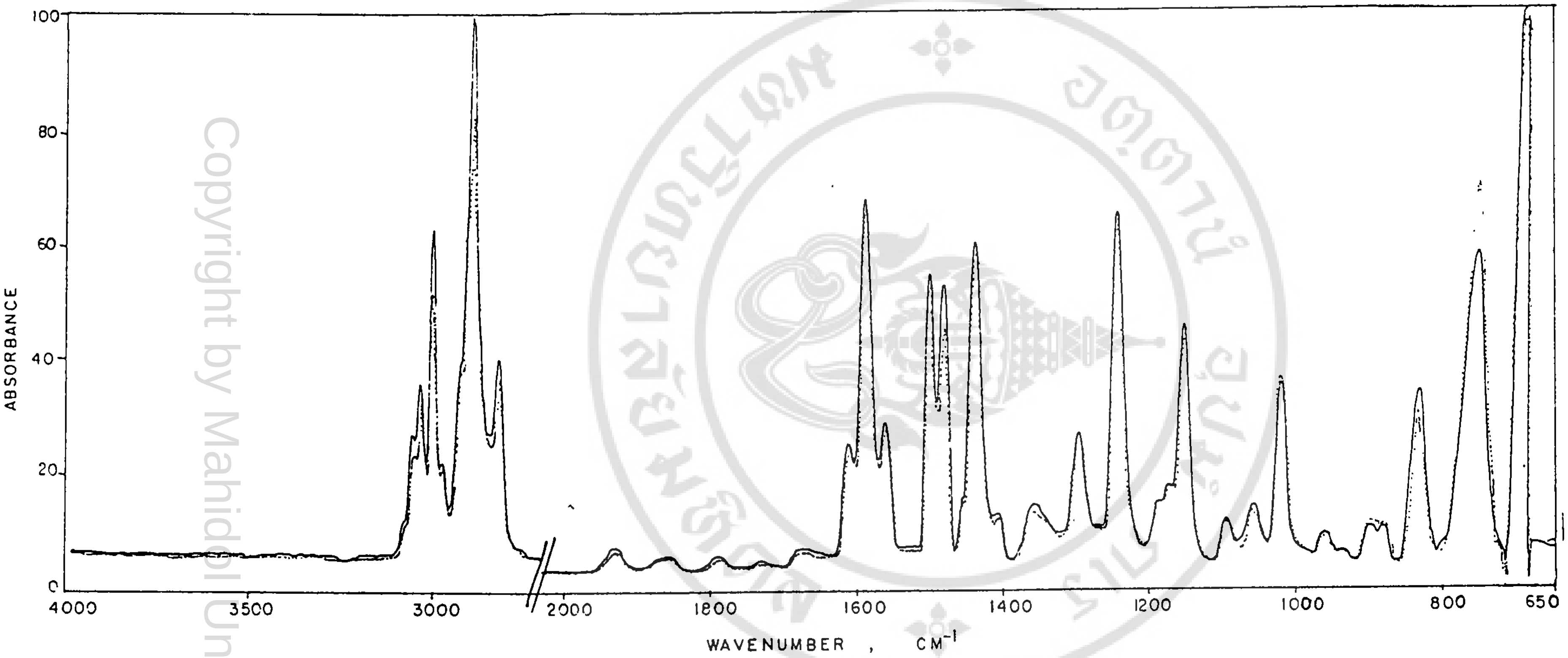


Fig.3.25 The polarized absorption spectra of 20.07% (w/w) ABBA-PS, stretched to 600% elongation at 35°C, observed at 20.8°C. Dotted line and solid line refer to the electric vector of radiation polarized parallel and perpendicular to the optical axis, respectively.

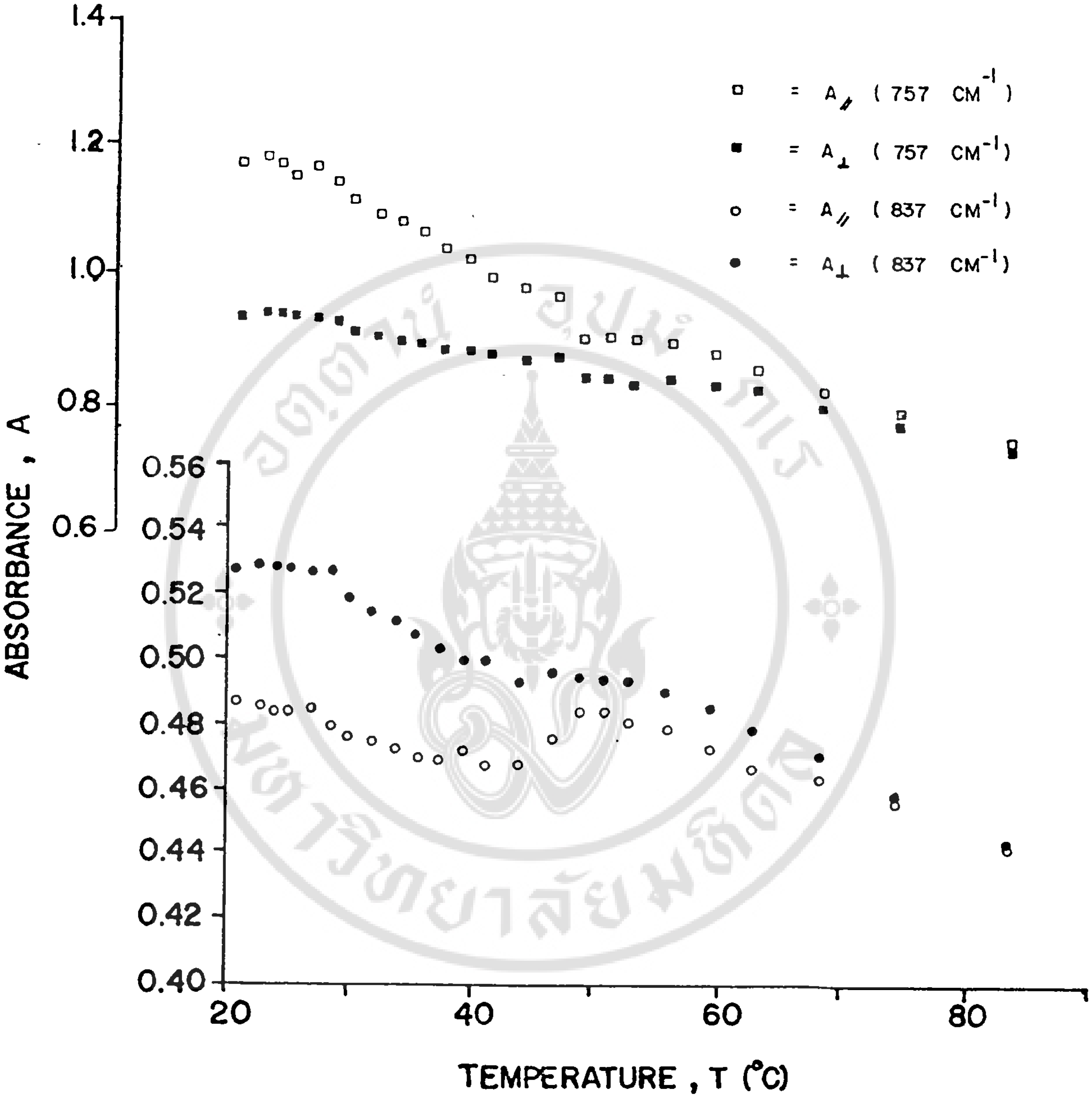


Fig.3.26 Temperature dependence of the absorbance (A) of 20.07%(w/w) p-methoxybenzylidene-p-n-butylaniline (MBBA) in polystyrene film, stretched to 600% elongation.

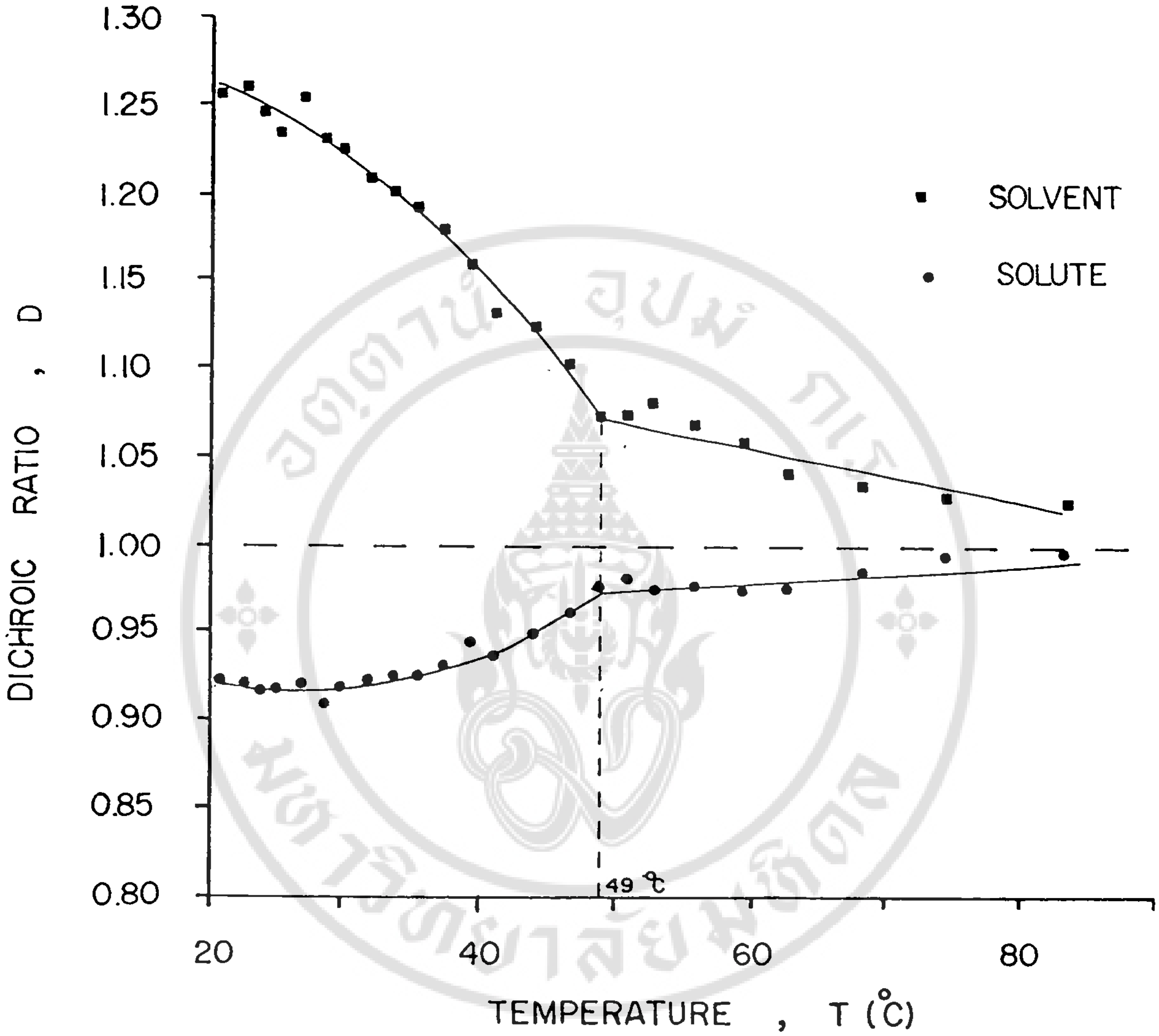


Fig.3.27 Temperature dependence of the dichroic ratio (D) of 20.07%(w/w) p-methoxybenzylidene-p-n-butylaniline (MBBA) in polystyrene film, stretched to 600%elongation.

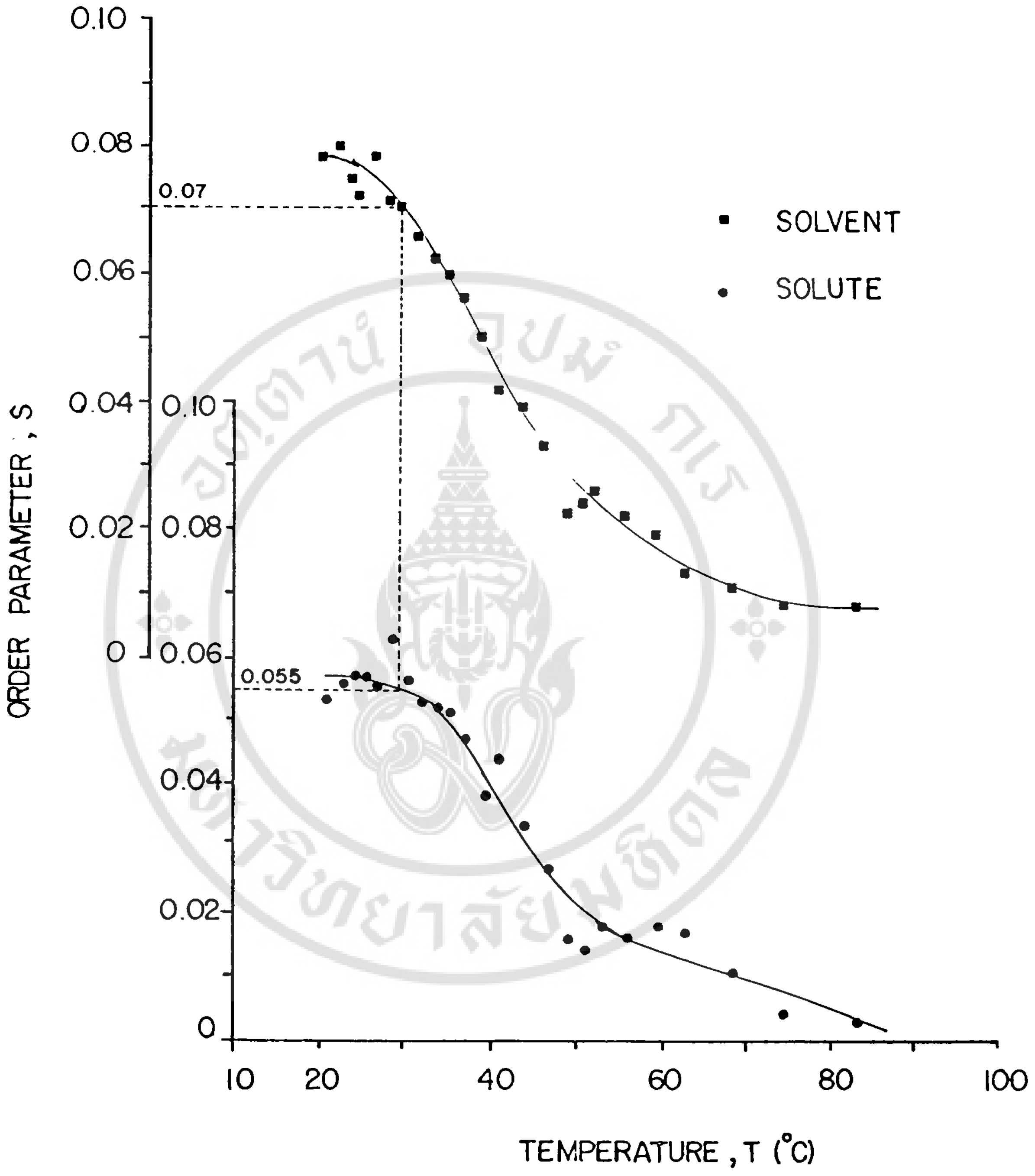


Fig.3.28 Temperature dependence of the order parameter (S) of 20.07%(w/w) p-methoxybenzylidene-p-n-butylaniline (MBBA) in polystyrene film, stretched to 600%elongation.

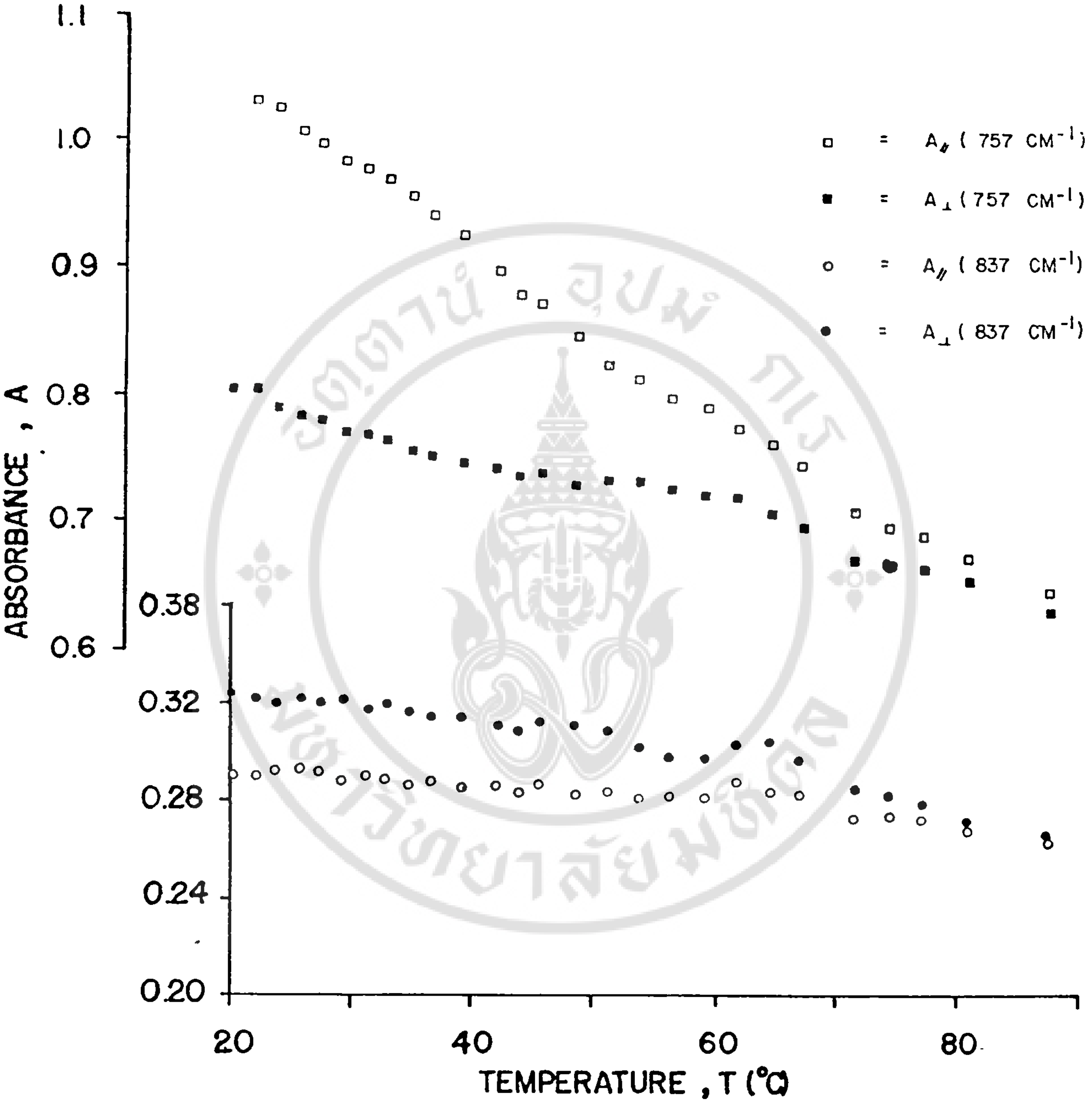


Fig.3.29 Temperature dependence of the absorbance (A) of 20.00%(w/w) p-ethoxybenzylidene-p-n-butylaniline (EBBA) in polystyrene film, stretched to 600%elongation.

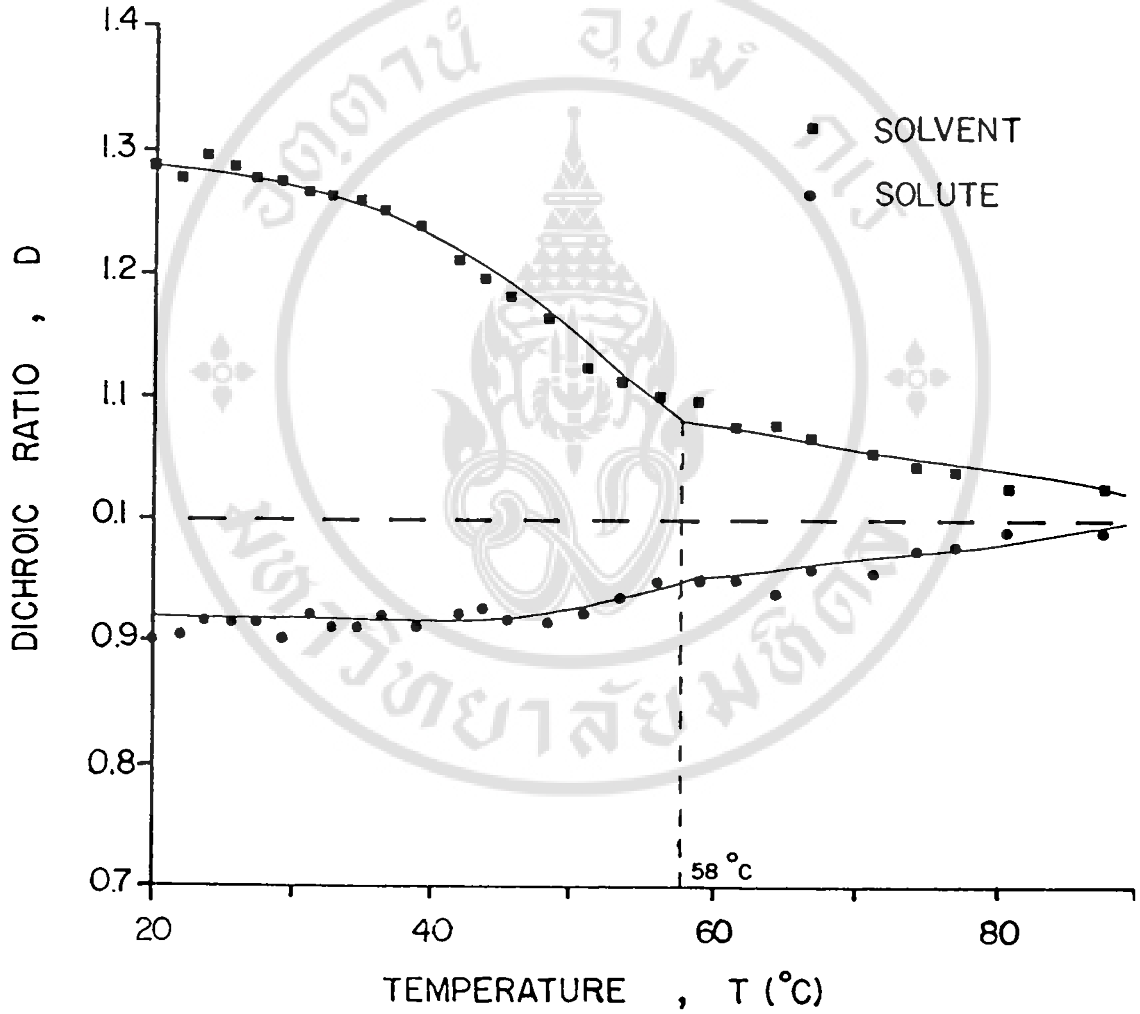


Fig.3.30 Temperature dependence of the dichroic ratio (D) of 20.00%(w/w) p-ethoxybenzylidene-p-n-butylaniline (EBBA) in polystyrene film, stretched to 600%elongation.

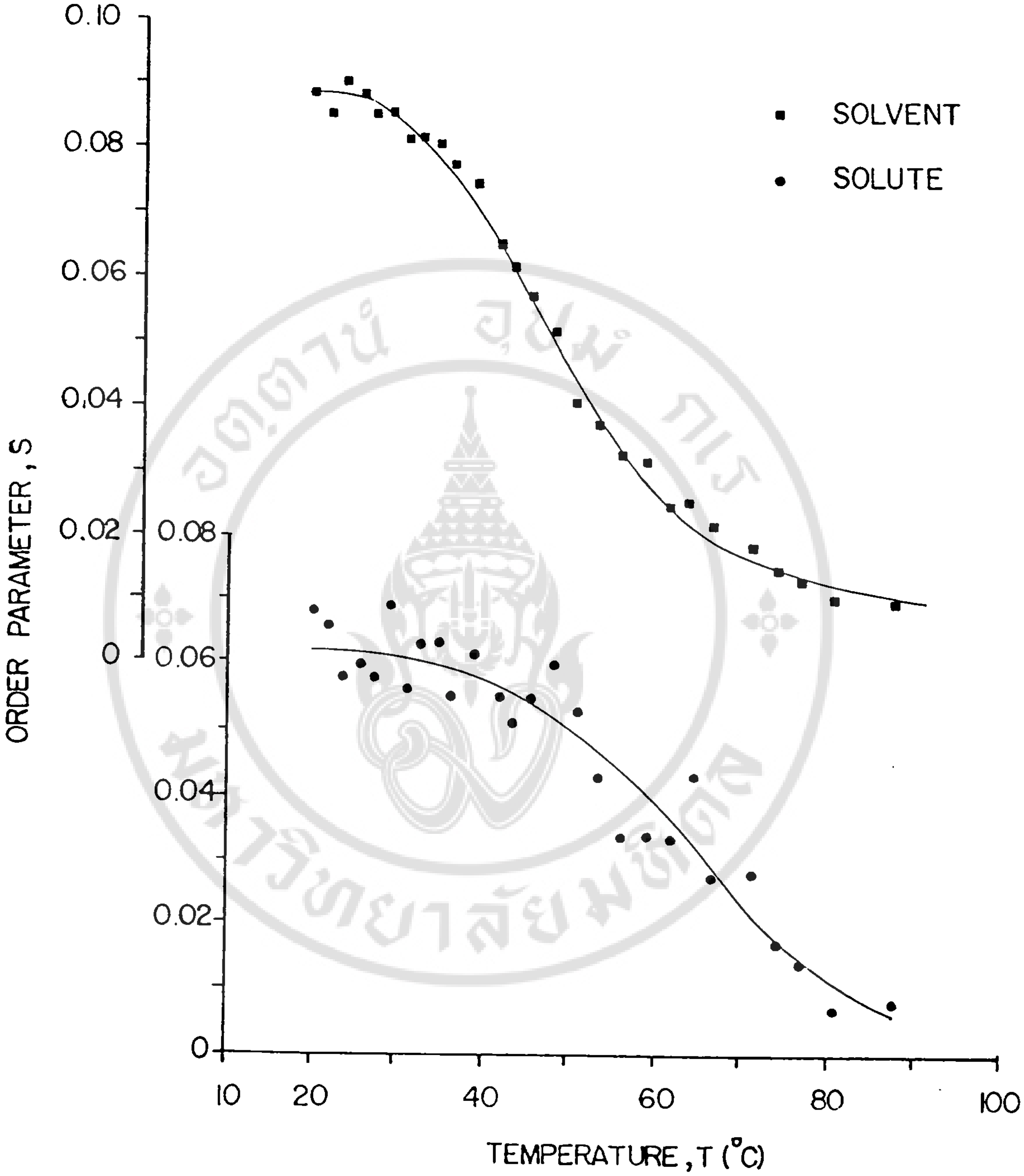


Fig.3.31 Temperature dependence of the order parameter (S) of 20.00%(w/w) p-ethoxybenzylidene-p-n-butylaniline (EBBA) in polystyrene film, stretched to 600%elongation.

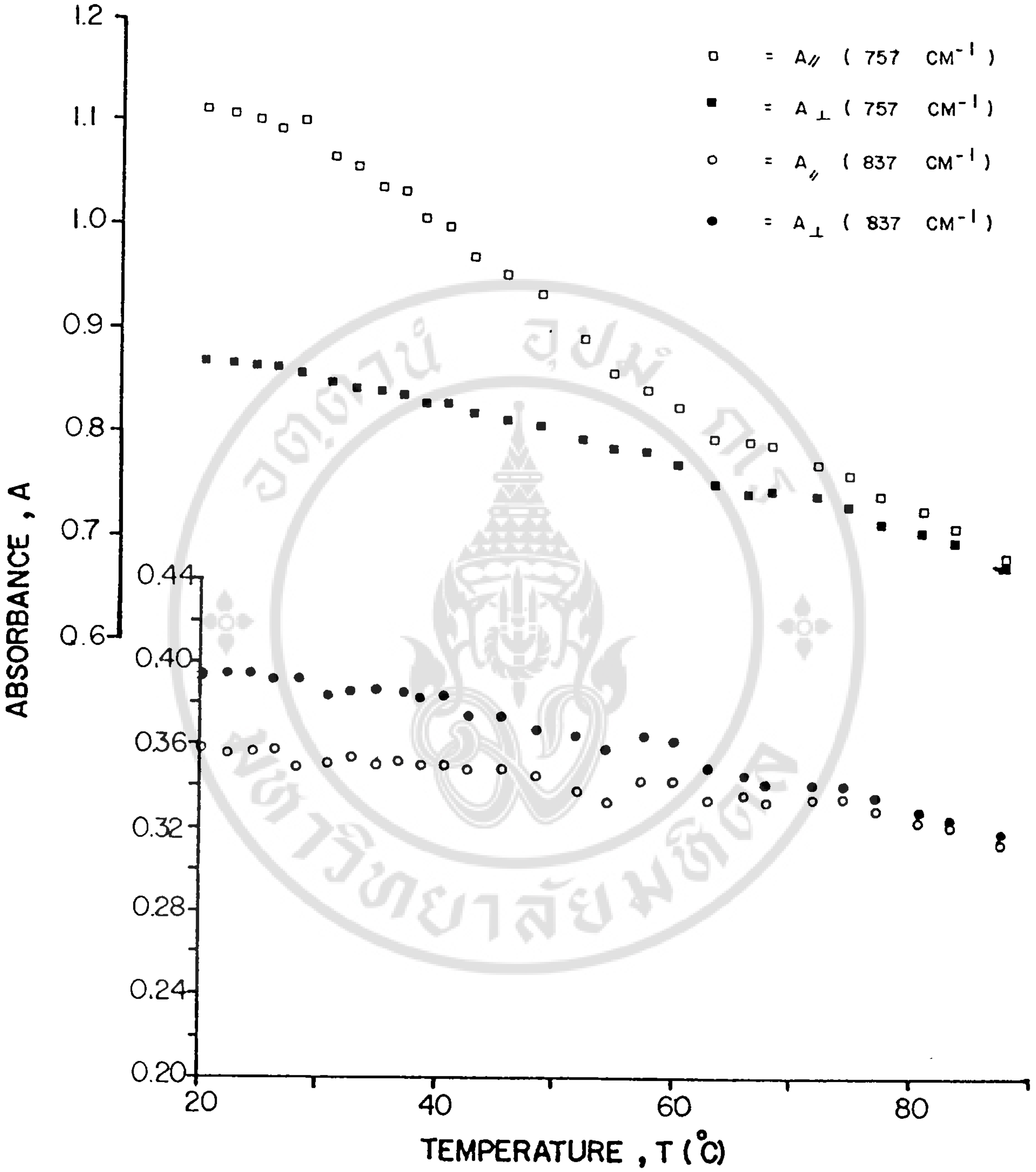


Fig.3.32 Temperature dependence of the absorbance (A) of 20.05%(w/w) p-n-propoxybenzylidene-p-n-butylaniline (P_3BBA) in polystyrene film, stretched to 600%elongation

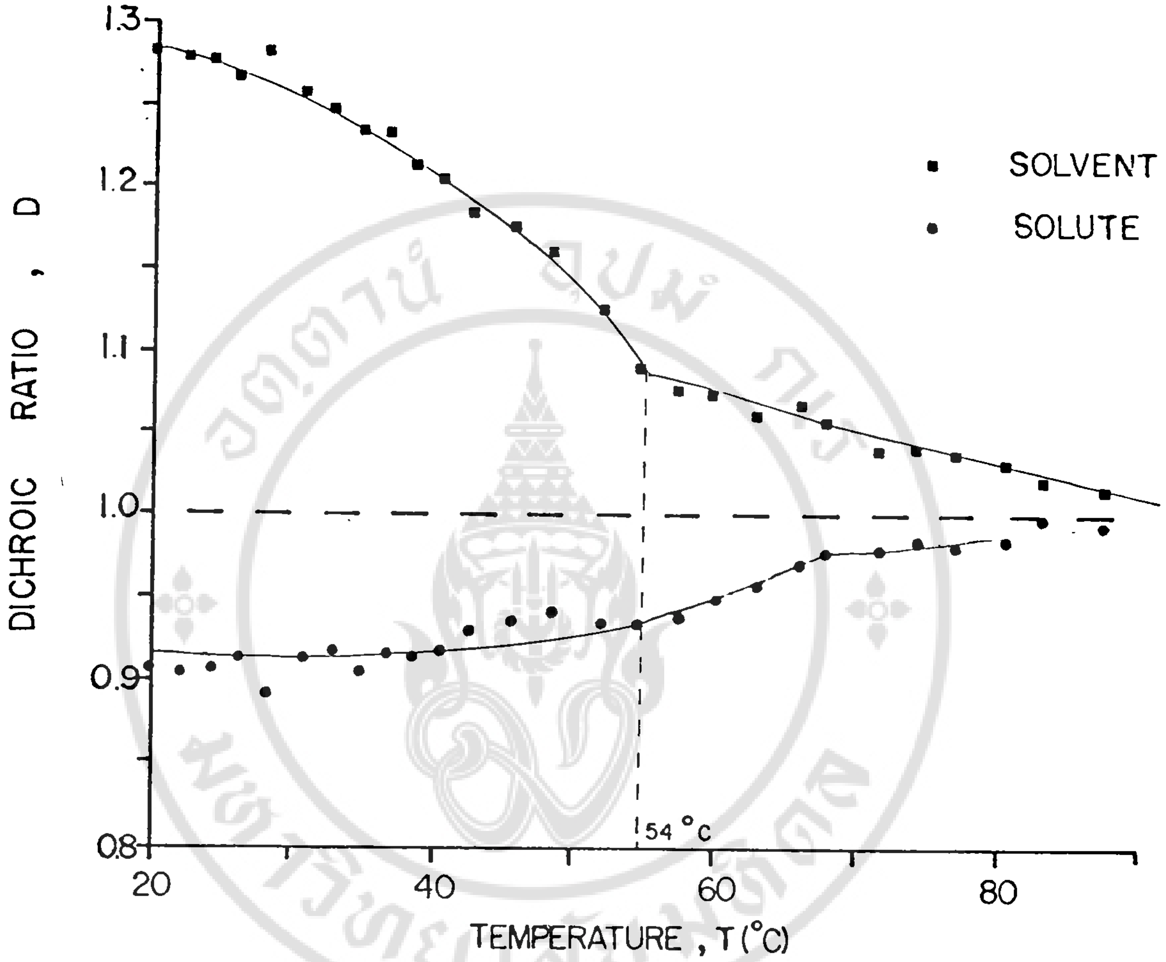


Fig.3.33 Temperature dependence of the dichroic ratio (D) of 20.05%(w/w) p-n-propoxybenzylidene-p-n-butylaniline (P_3BBA) in polystyrene film, stretched to 600%elongation.

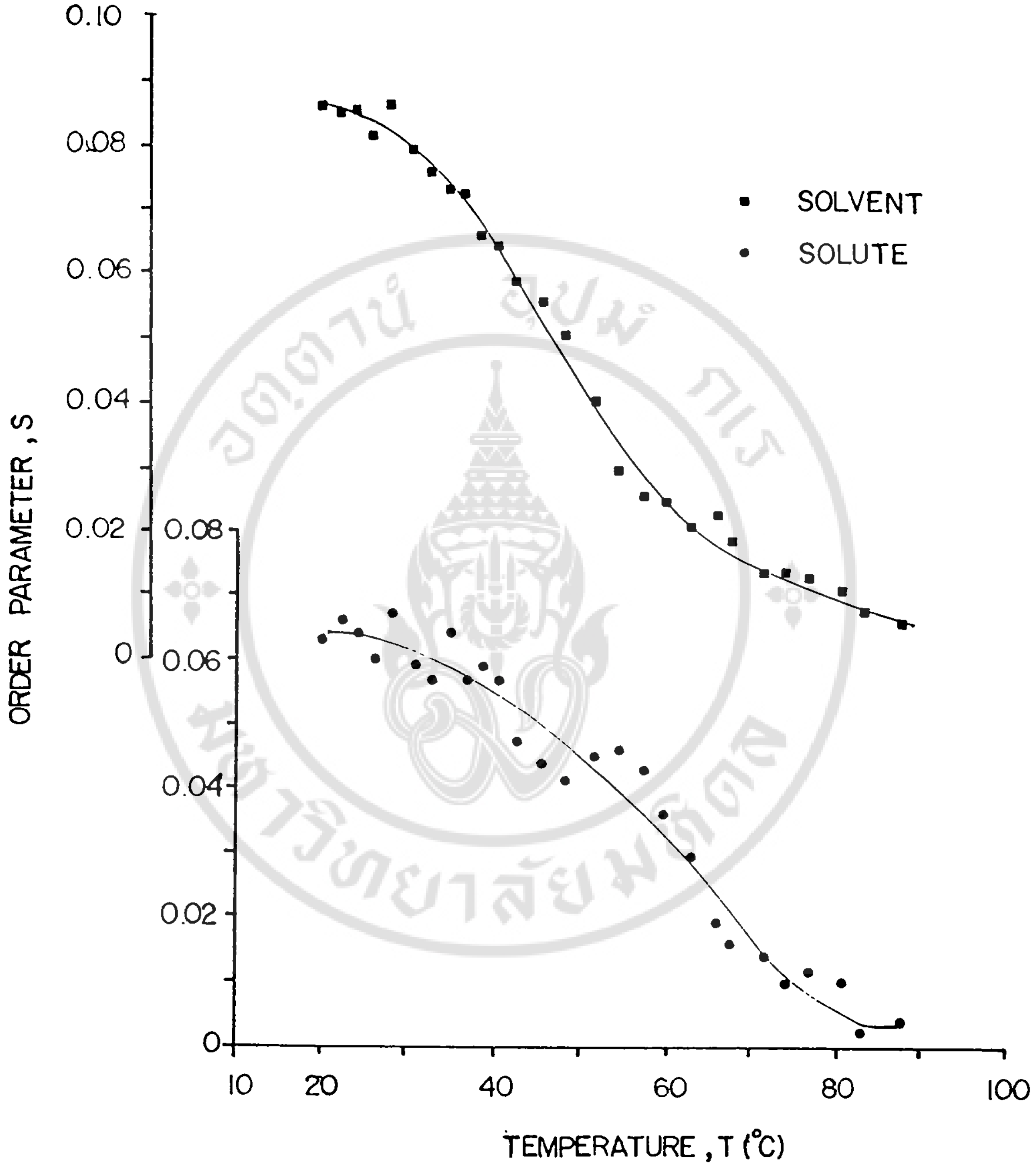


Fig.3.34 Temperature dependence of the order parameter (S) of 20.05%(w/w) p-n-propoxybenzylidene-p-n-butylaniline (P_3BBA) in polystyrene film, stretched to 600%elongation.

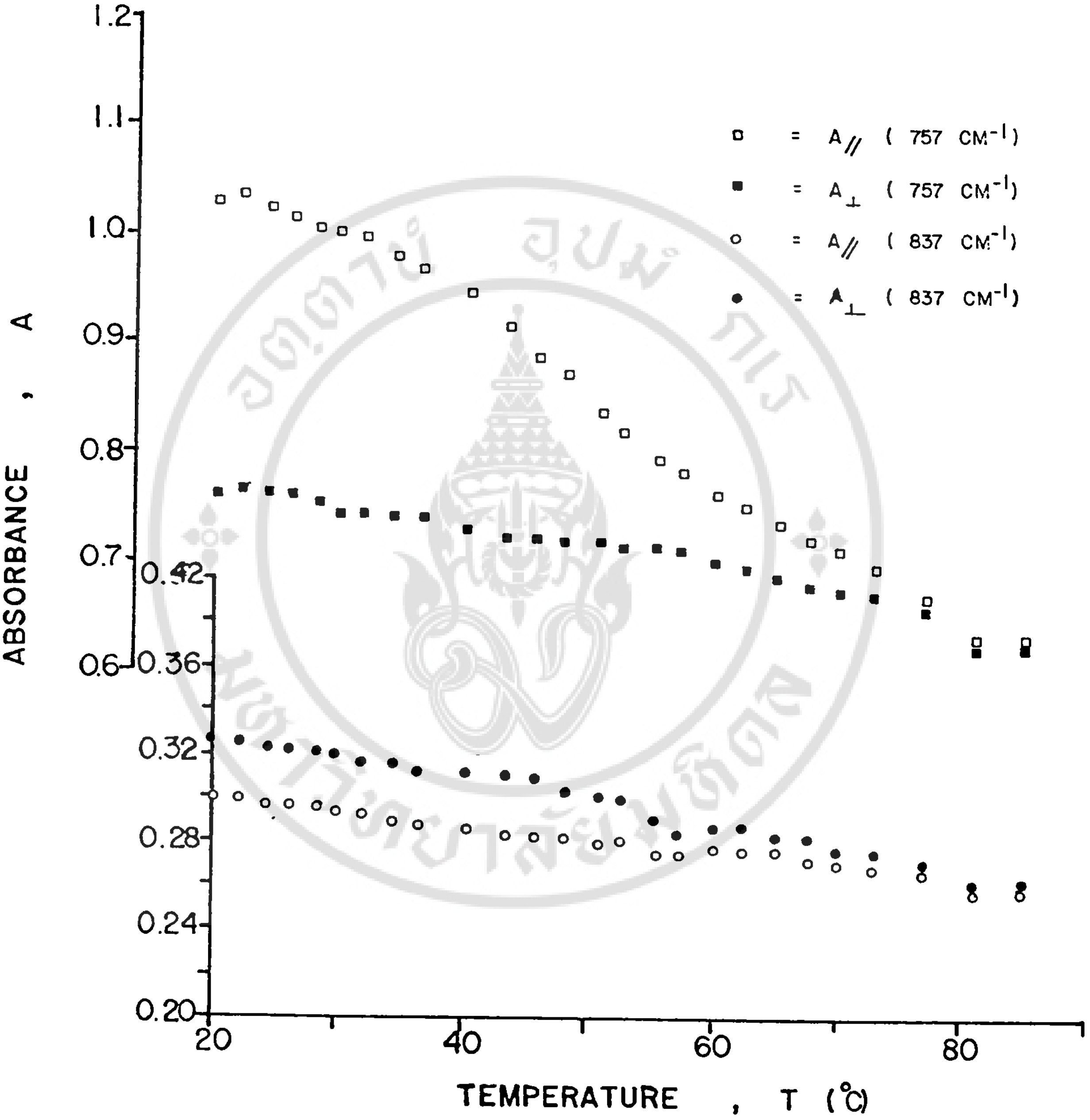


Fig.3.35 Temperature dependence of the absorbance (A) of 20.00% (w/w) p-n-butoxybenzylidene-p-n-butylaniline (BBBA) in polystyrene film, stretched to 600%elongation

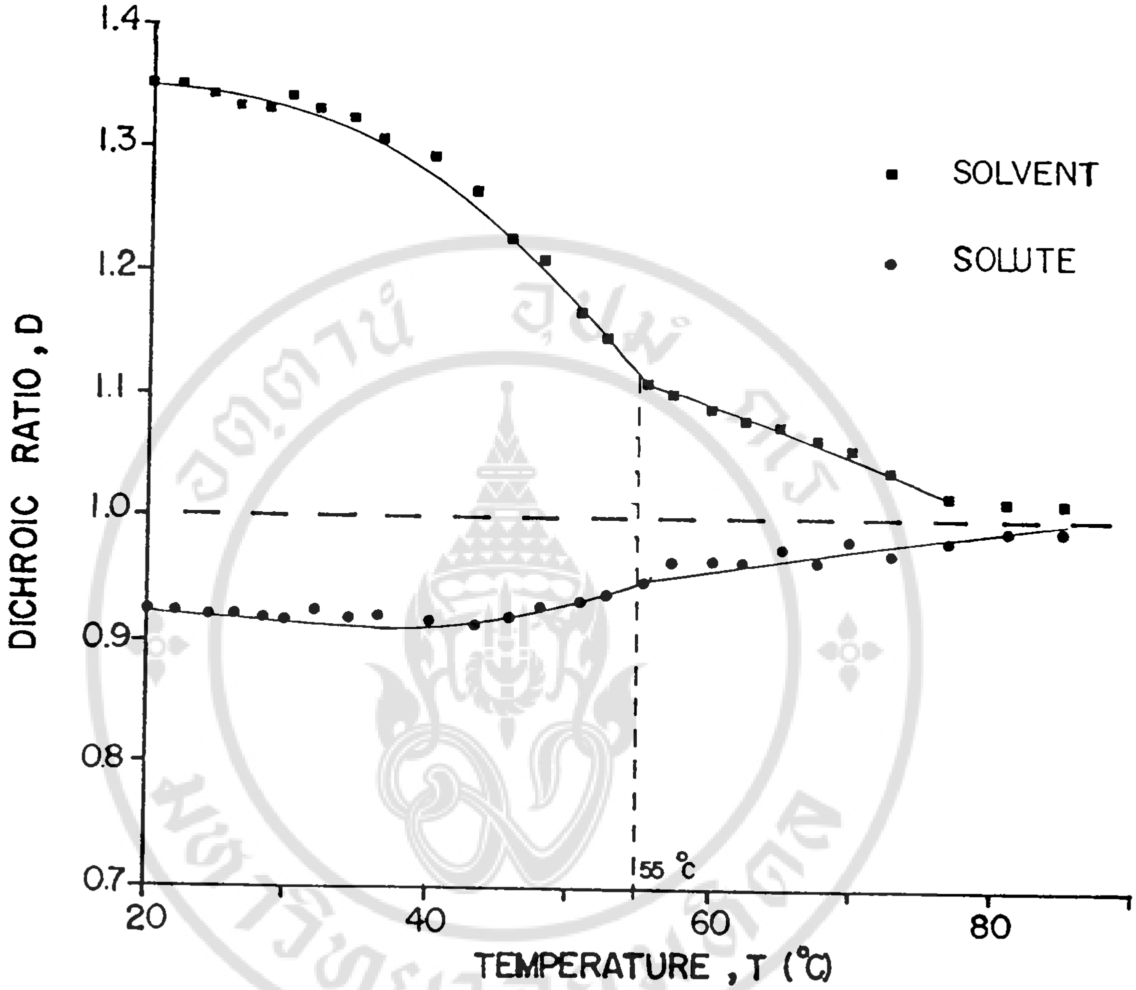


Fig.3.36 Temperature dependence of the dichroic ratio (D) of 20.00%(w/w) p-n-butoxybenzylidene-p-n-butylaniline (BBBA) in polystyrene film, stretched to 600%elongation.

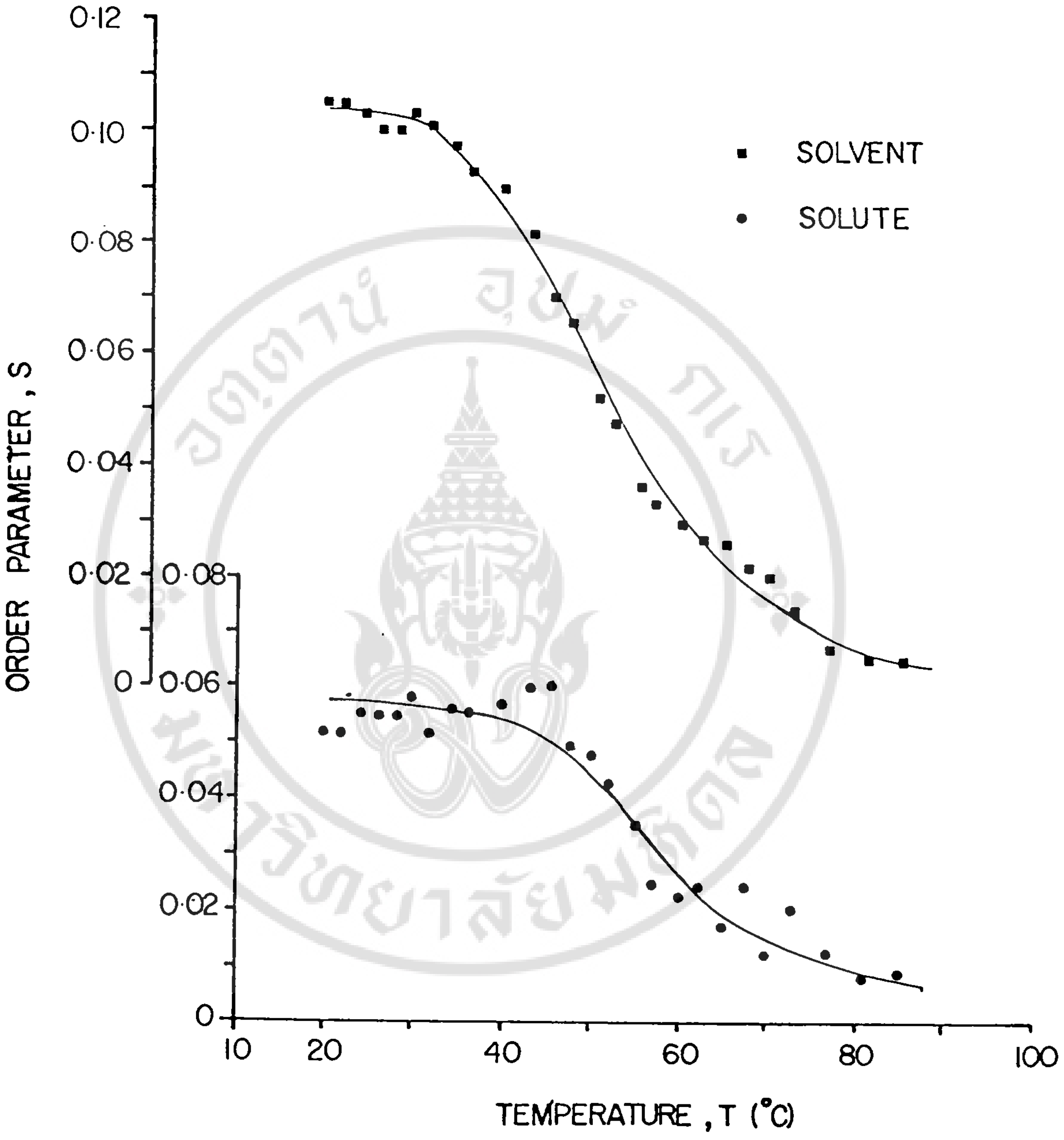


Fig.3.37 Temperature dependence of the order parameter (S) of 20.00%(w/w) p-butoxybenzylidene-p-n-butylaniline (BBBA) in polystyrene film, stretched to 600%elongation.

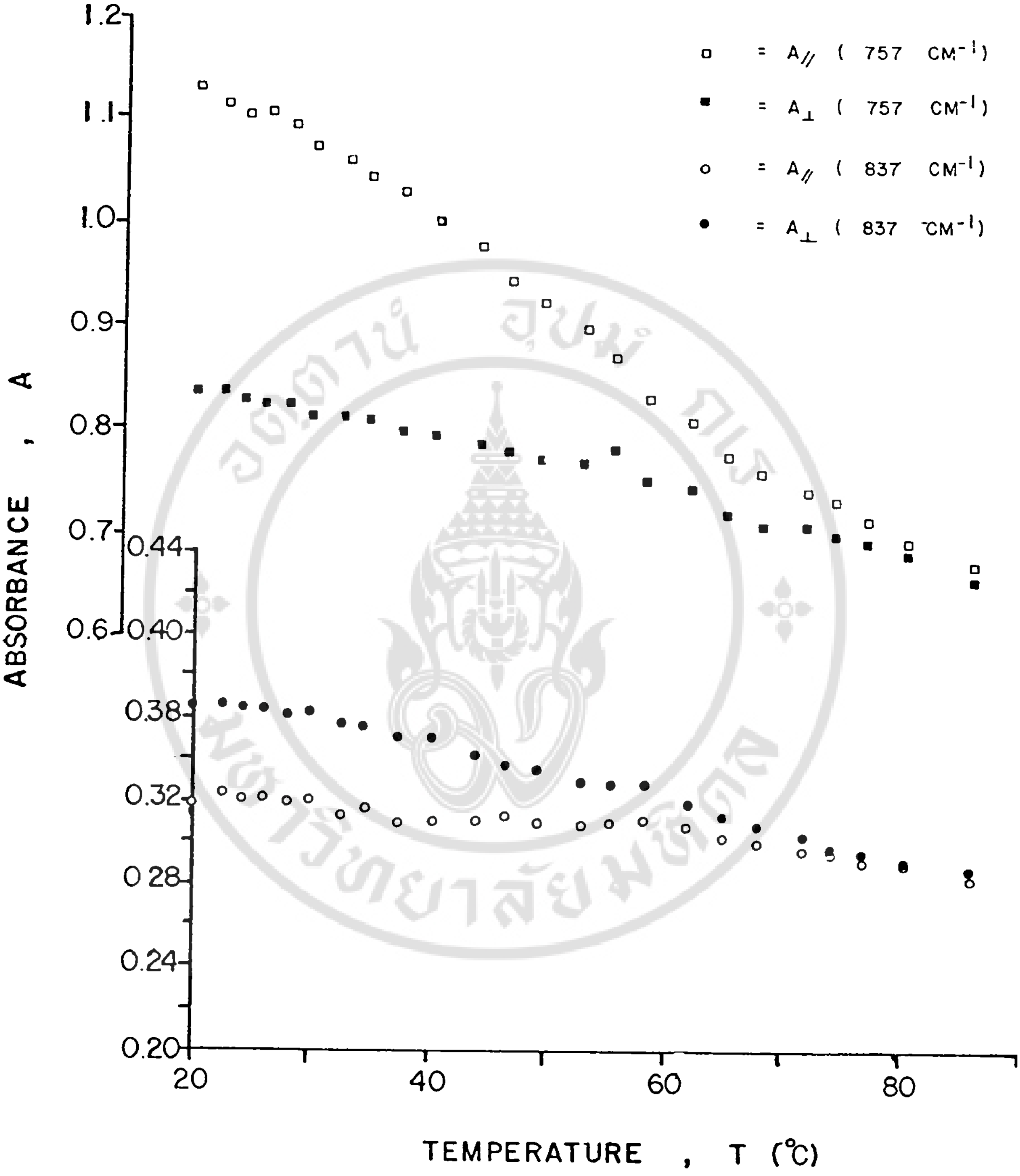


Fig.3.38 Temperature dependence of the absorbance (A) of 20.05% (w/w) p-n-pentoxybenzylidene-p-n-butylaniline (P_5BBA) in polystyrene film, stretched to 600%elongation

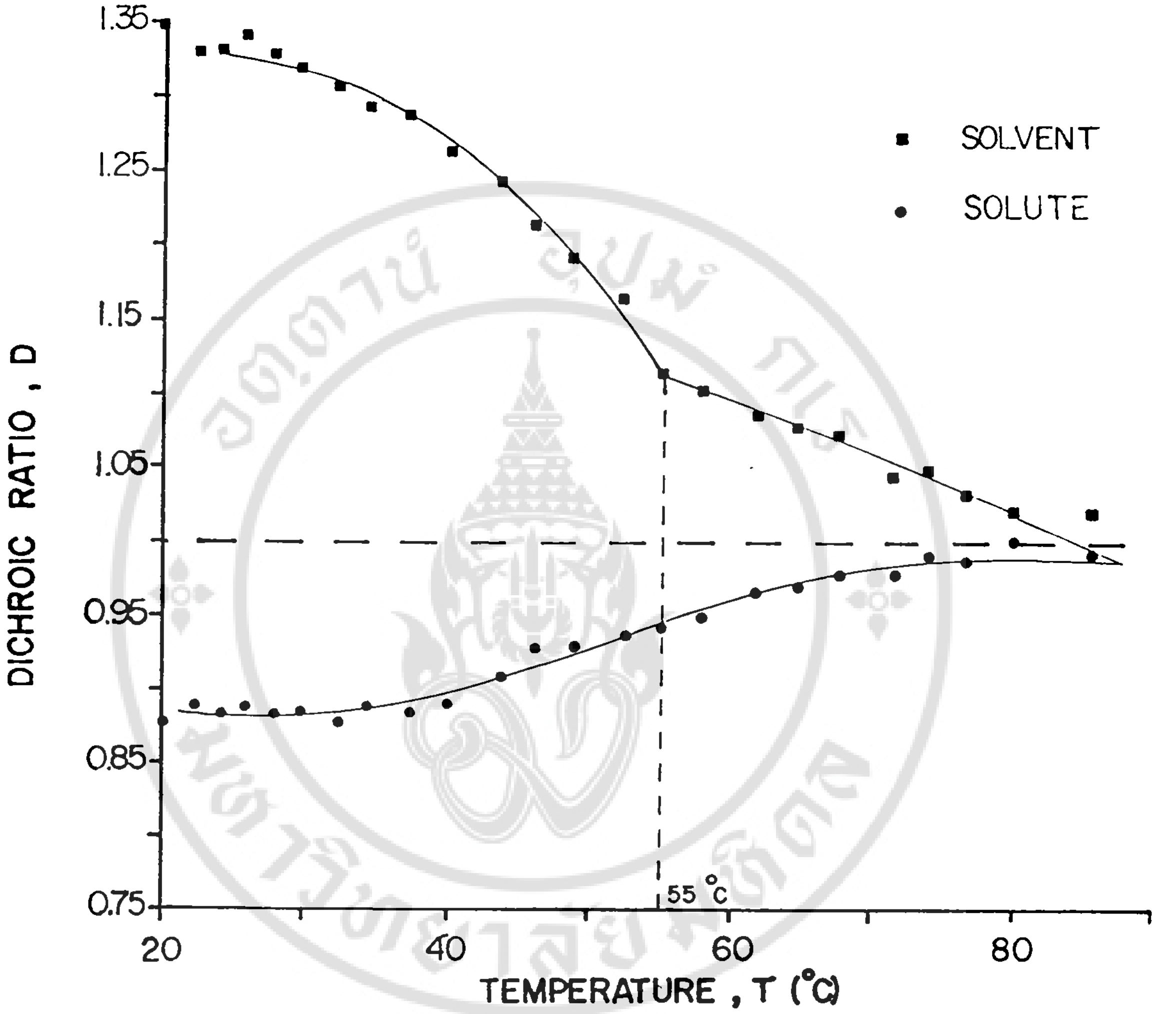


Fig.3.39 Temperature dependence of the dichroic ratio (D) of 20.05%(w/w) p-n-pentoxybenzylidene-p-n-butylaniline (P_5BBA) in polystyrene film, stretched to 600%elongation.

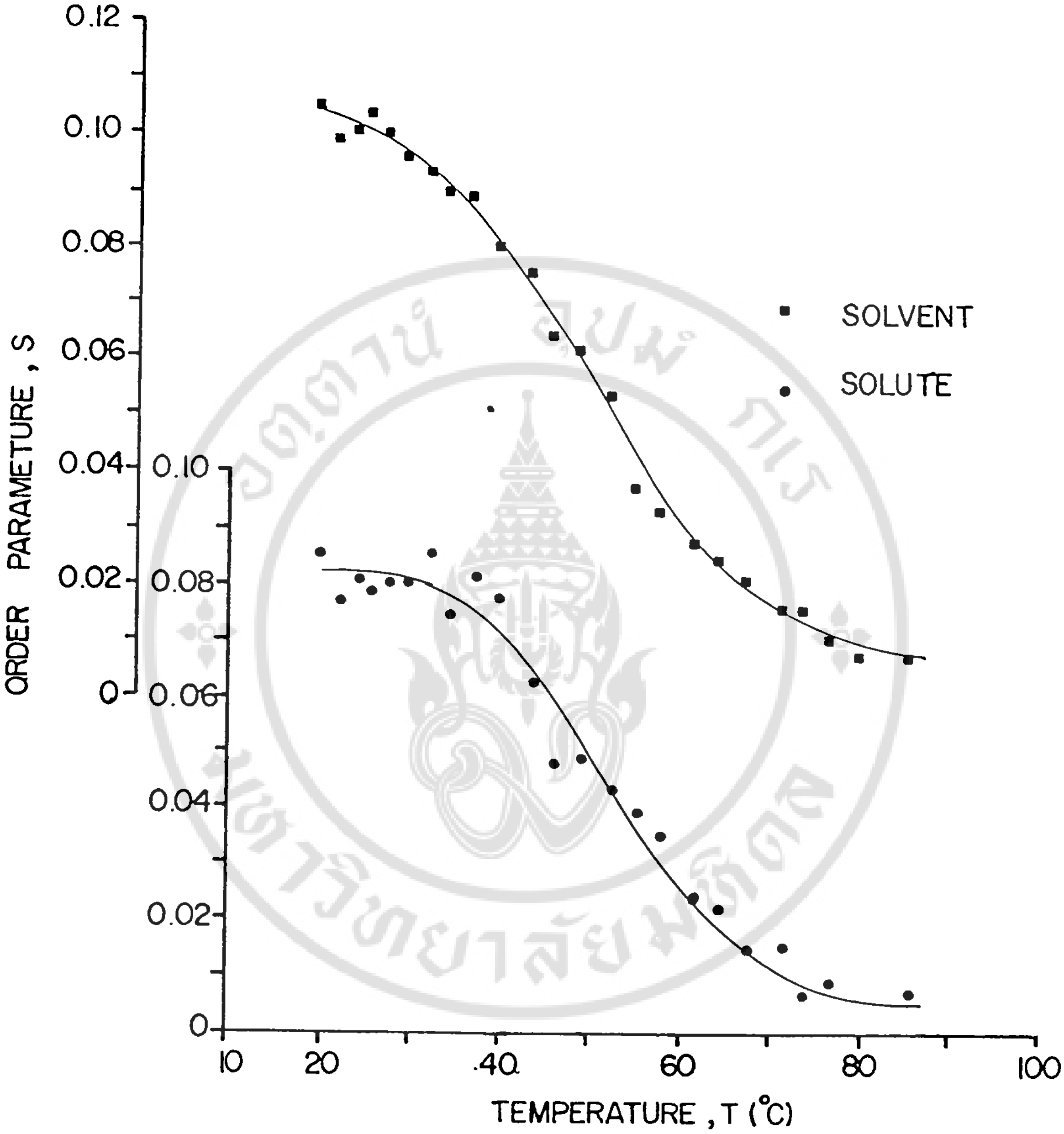


Fig.3.40 Temperature dependence of the order parameter (S) of 20.05%(w/w) n-pentoxybenzylidene-p-n-butylaniline (P_5BBA) in polystyrene film, stretched to 600%elongation.

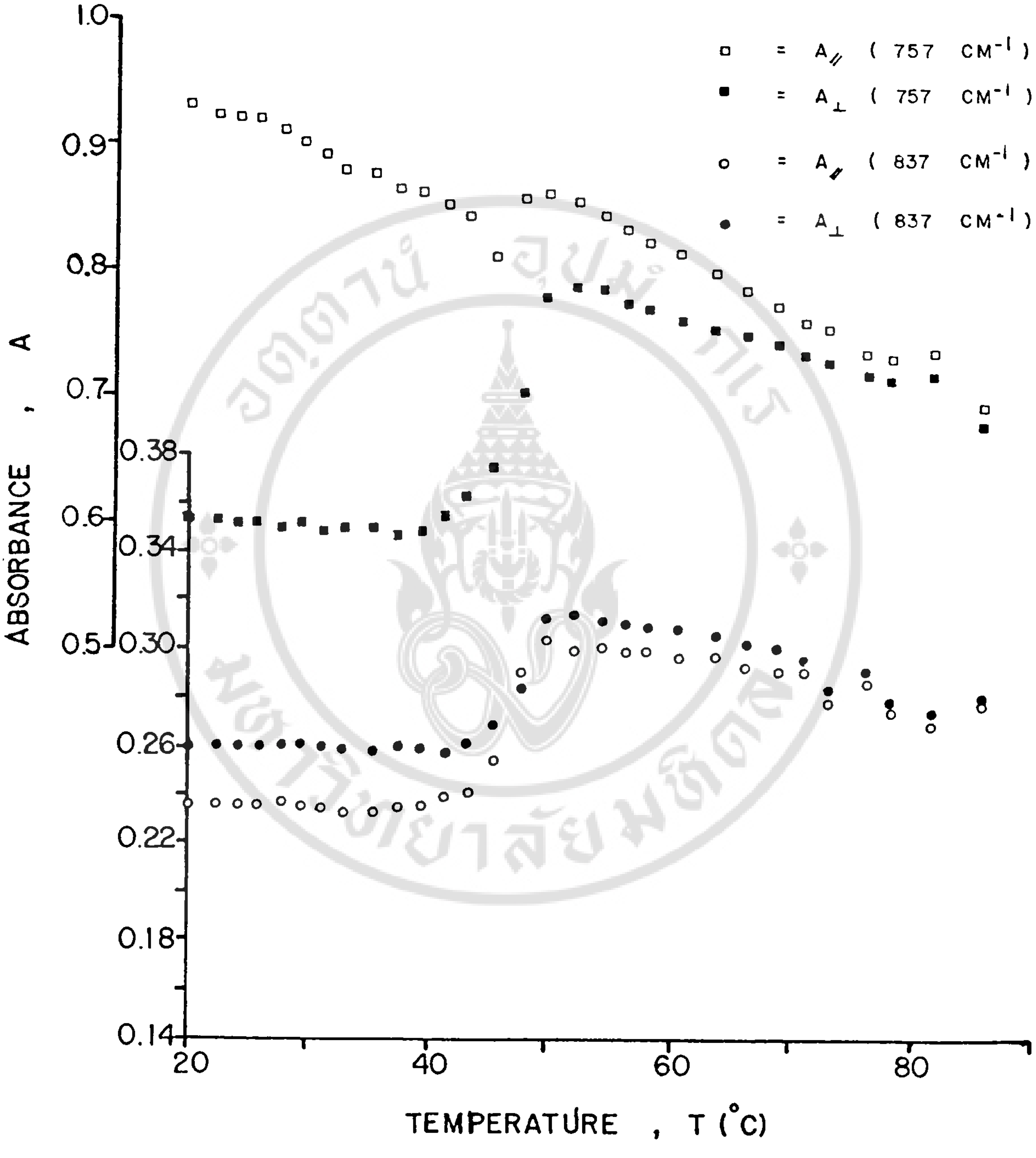


Fig.3.41 Temperature dependence of the absorbance (A) of 20.00%(w/w) p-n-Hexoxybenzylidene-p-n-butylaniline (HBBA) in polystyrene film, stretched to 600% elongation

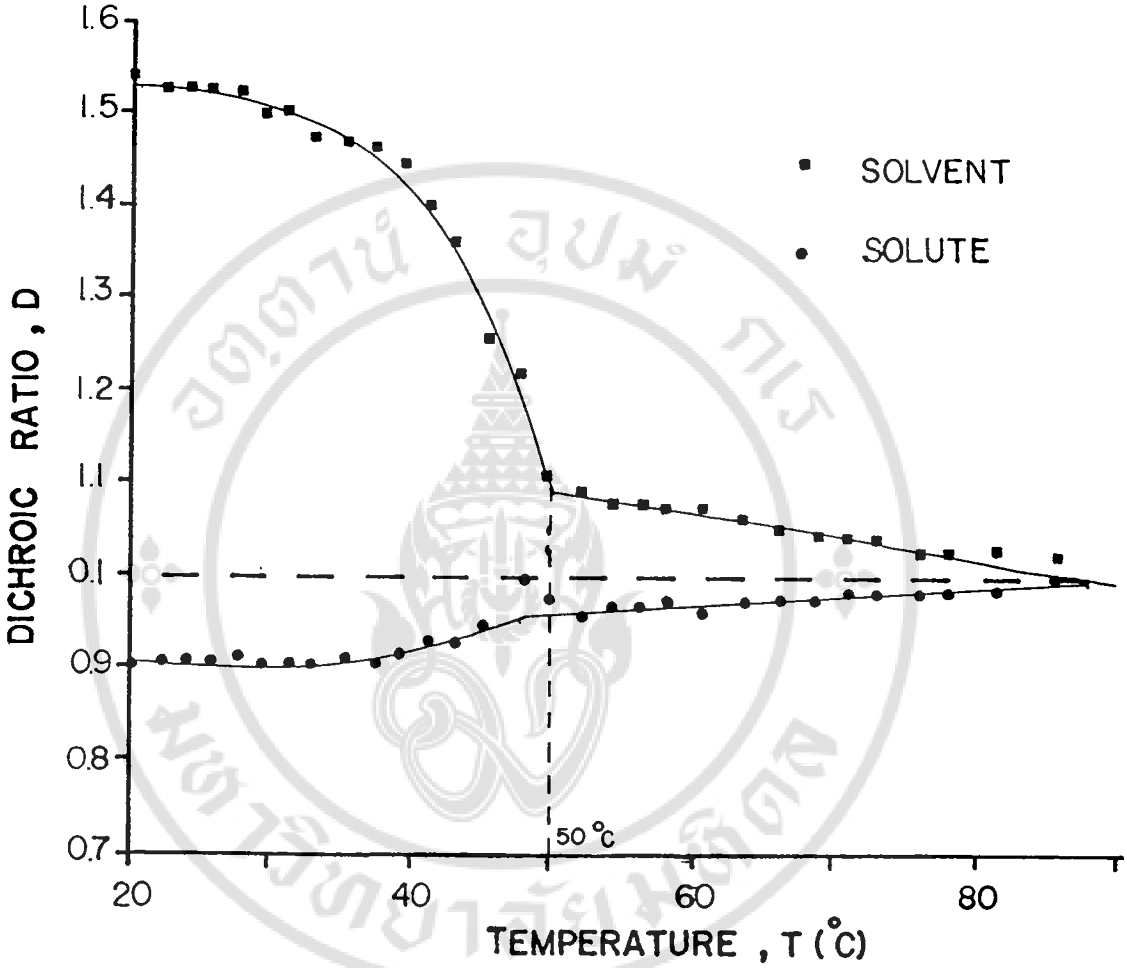


Fig.3.42 Temperature dependence of the dichroic ratio (D) of 20.00%(w/w) p-n-hexoxybenzylidene-p-n-butylaniline (HBBA) in polystyrene film, stretched to 600%elongation.

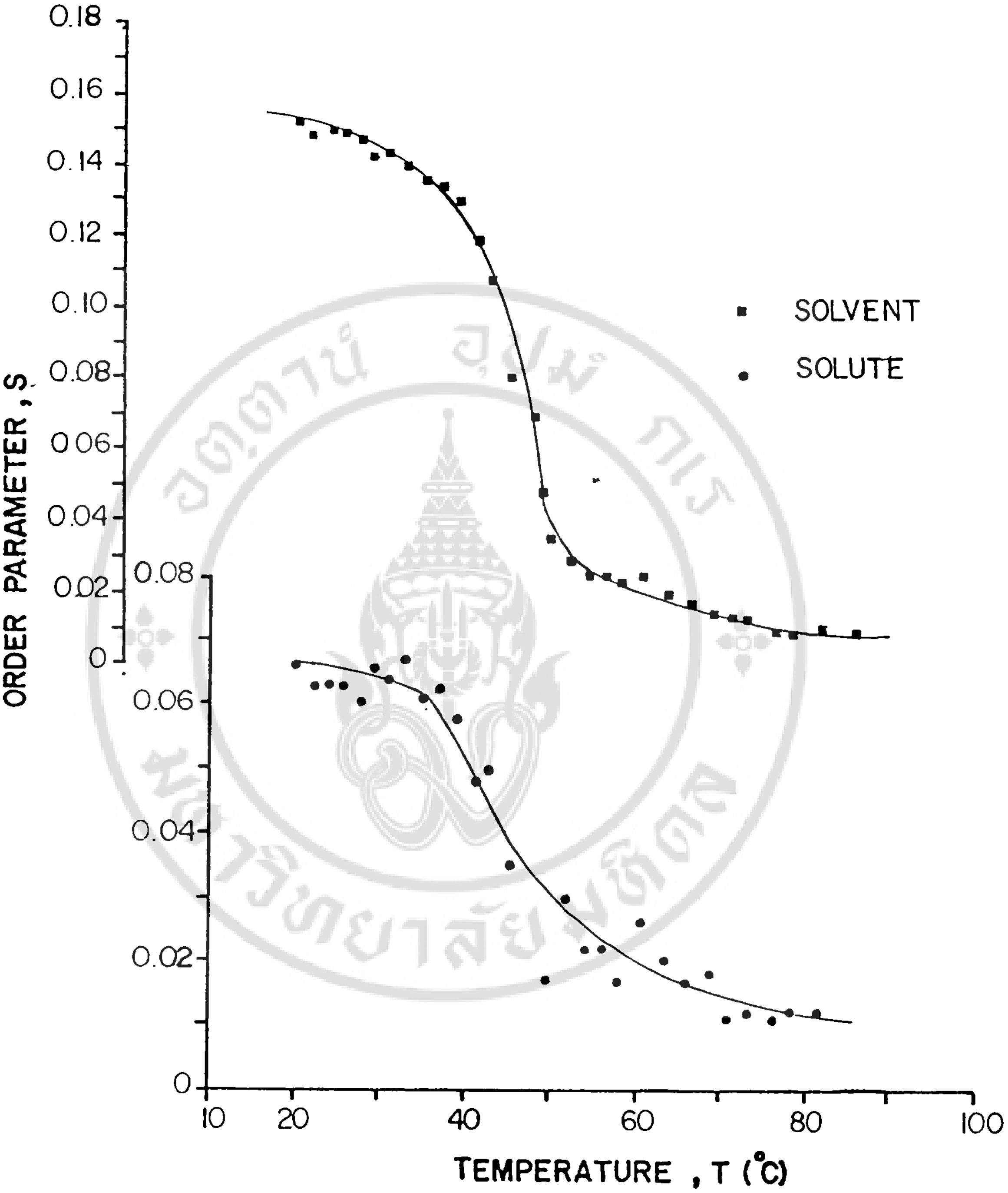


Fig.3.43 Temperature dependence of the order parameter (S) of 20.00%(w/w) p-n-hexoxybenzylidene-p-n-butylaniline (HBBA) in polystyrene film, stretched to 600%elongation.

837 cm^{-1} of MBBA (solute) which show the opposite dichroic behavior are used for the determination of the orientational order.

Using Perkin-Elmer Data Station and Basic programming for the determination of absolute absorbances (as described in section 2.7), $A_{\parallel}$ and $A_{\perp}$ at the wave number 757 cm^{-1} and 837 cm^{-1} were calculated. The absorbances so obtained are shown in Fig.3.26 as a function of the temperature. At the wave number 757 cm^{-1}, which is due to the absorption band of the solvent (PS), $A_{\parallel}$ decreases as the temperature increases while $A_{\perp}$ decreases slowly. It seems that the convergence of $A_{\parallel}$ and $A_{\perp}$ occur. On the other hand, trend of $A_{\parallel}$ and $A_{\perp}$ at 837 cm^{-1} which is due to the absorption band of the solute, MBBA, are parallel at the low temperature. When the temperature is raised to approximate 45°C, $A_{\parallel}$and $A_{\perp}$ slightly increase and converge. Dichroic ratio of the solvent and solute calculated from the formula [1.4] are then plotted, as shown in Fig.3.27, against the temperature. The clearing point (T_c) of this sample film determined from the intercept of the linear decrease of the dichroic ratio with the non-linear curve as shown in Fig.3.27 is then observed.

The data obtained from Fig.3.27 were used to calculate the order parameter of both solvent and solute. These are shown in Fig.3.28 as a function of the temperature. The upper curve shows the order parameter of the solvent (S_v) as calculated using the band at 757 cm^{-1} and the lower curve shows the order parameter of the solute (S_s) as calculated using the band at 837 cm^{-1}. It is shown that as the temperature increases, the order parameter observed decreases. At high temperature (temperature above the clearing point), rate of change order parameter seems to be slow.

Similar to Fig.3.26-3.28, the results of the other sample films are presented in Fig.3.29-3.43. The mixtures of various solutes in the stretched polystyrene films were studied and shown for EBBA (Fig.3.29-3.31), P_3BBA (Fig.3.32-3.34), BBBA (Fig.3.35-3.37), P_5BBA (Fig.3.38-3.40), HBBA (Fig.3.41-3.43). The clearing temperatures (T_c) of each sample film obtained from Fig.3.27, 3.30, 3.33, 3.36, 3.39 and 3.42 are listed in Table 3.7.

Table 3.7 The clearing points of the sample films

Sample films	T_c (°C)
20.07% (w/w) MBBA-PS	49
20.00% (w/w) EBBA-PS	55
20.05% (w/w) P_3BBA-PS	54
20.00% (w/w) BBBA-PS	55
20.05% (w/w) P_5BBA-PS	55
20.00% (w/w) HBBA-PS	50

3.1.7.2 STUDIES OF ODD-EVEN EFFECT IN THE SAMPLE FILMS.

Temperature dependence of the order parameter of polystyerne (S_v) in the sample films as shown in Fig.3.28, 3.31, 3.34, 3.37, 3.40 and 3.43 are summarized together in Fig.3.44. The order parameter, S_v, obtained temperature 30°C

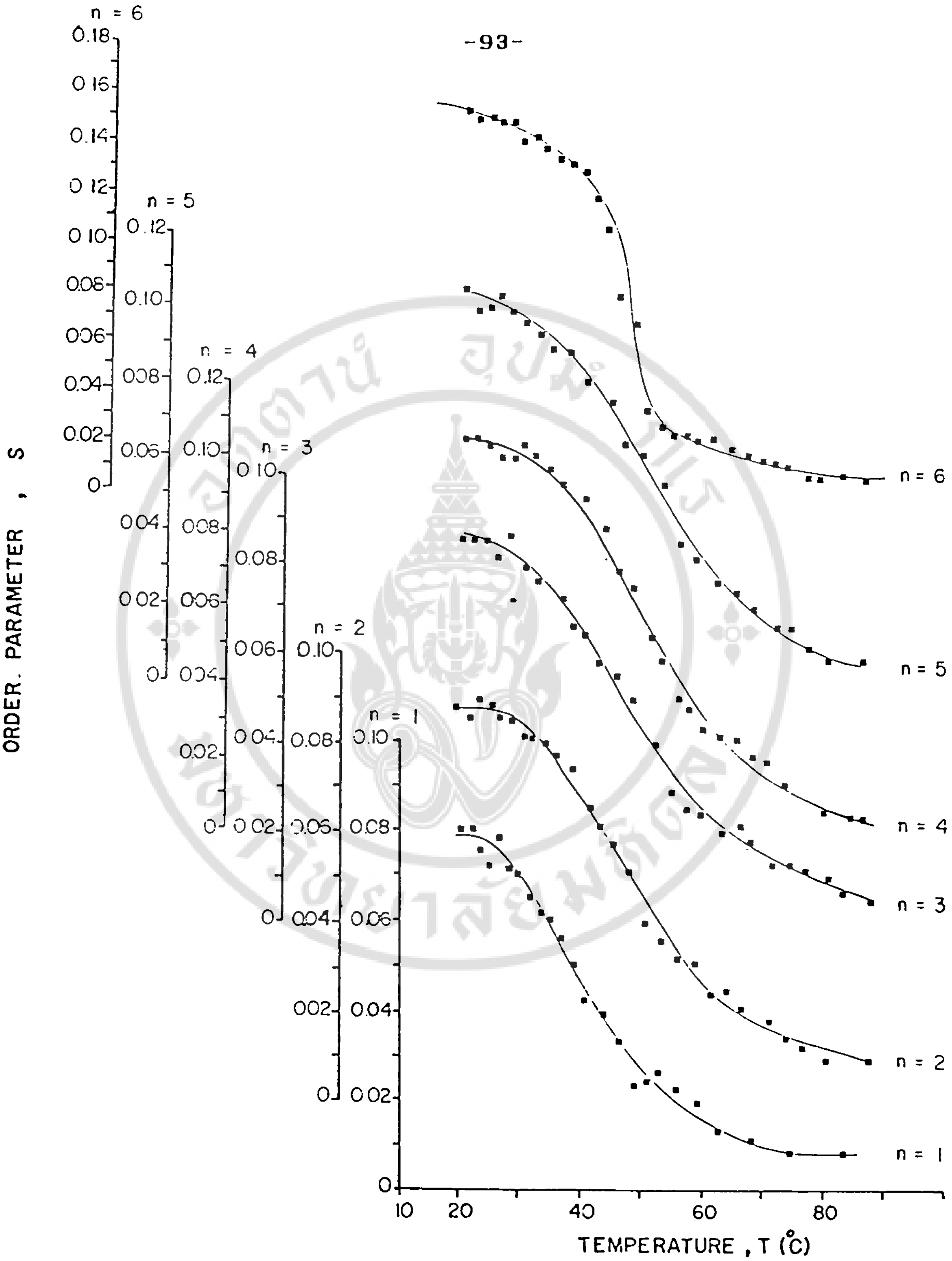


Fig.3.44 Temperature dependence of the order parameter of polystyrene(S_v) in 20%(w/w) ABBA-polystyrene film, stretched to 600%elongation.

n = number of carbon atoms in the alkoxy chain.

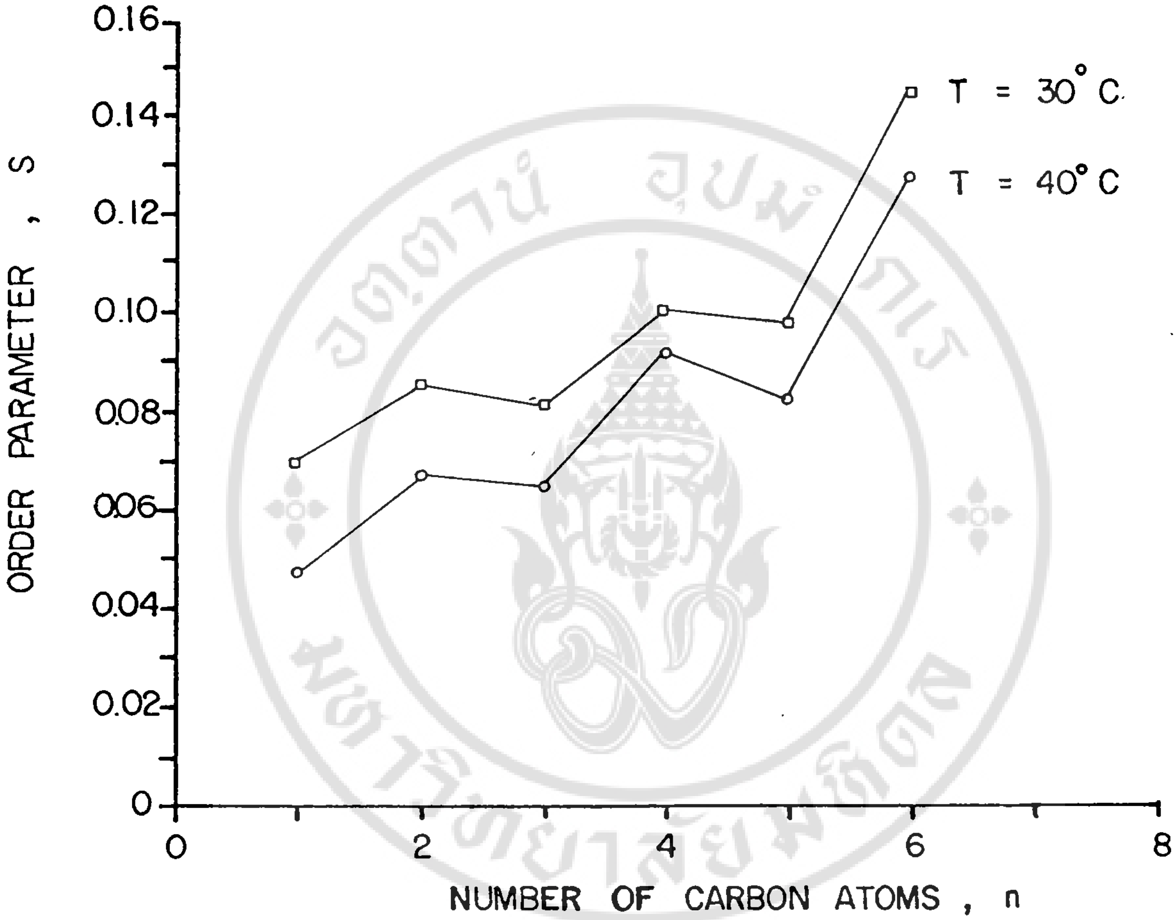


Fig.3.45 Order parameter of polystyrene(S_v) in 20%ABBA-polystyrene film (stretched to 600% elongation), read at temperature 30°C and 40°C plotted as a function of the number of carbon atoms (n) of the alkoxy chain.

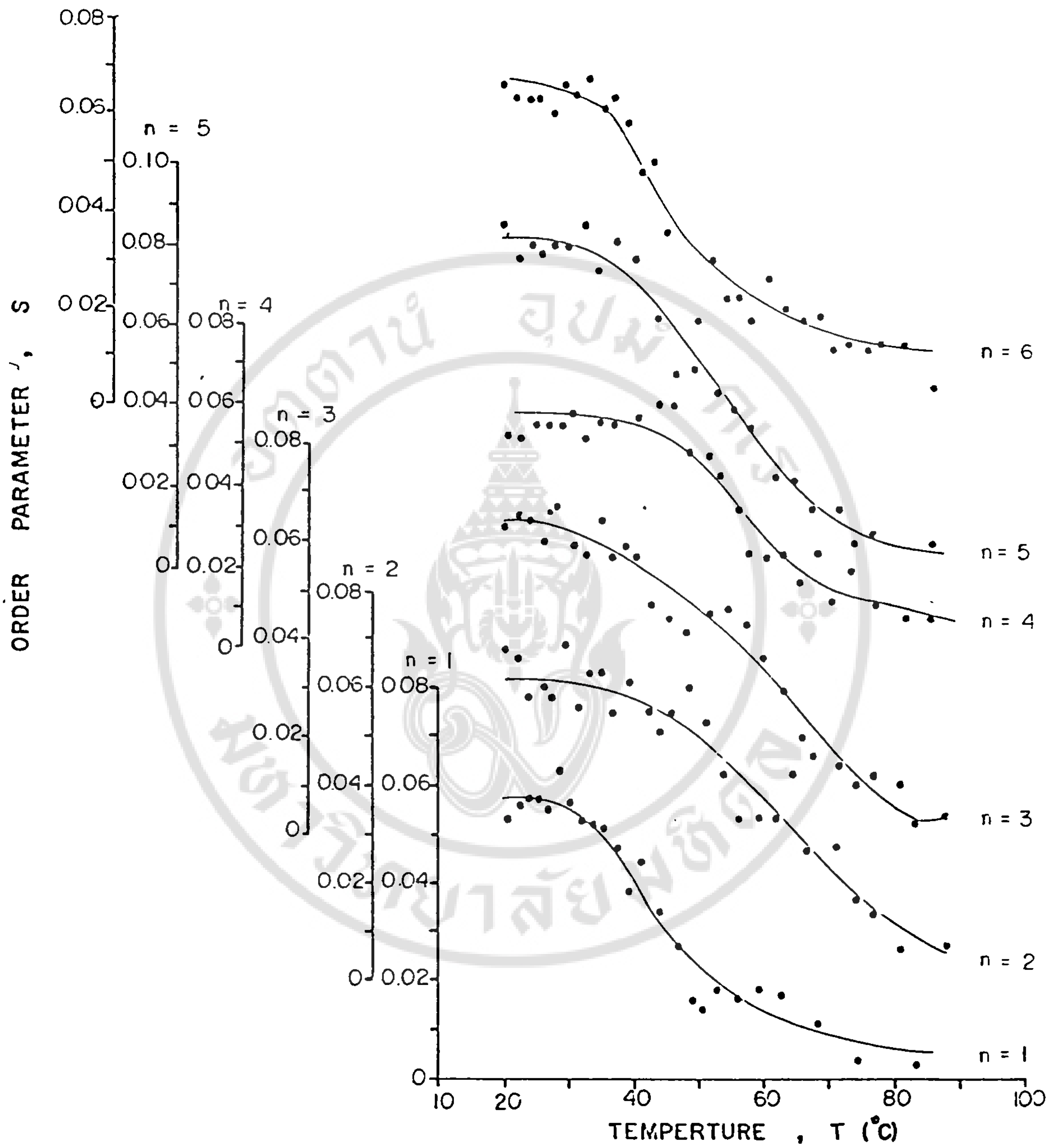


Fig.3.46 Temperature dependence of the order parameter of ABBA (S_s) in 20%(w/w)ABBA-PS film, stretched to 600%elongation.

n = number of carbon atoms in the alkoxy chain.

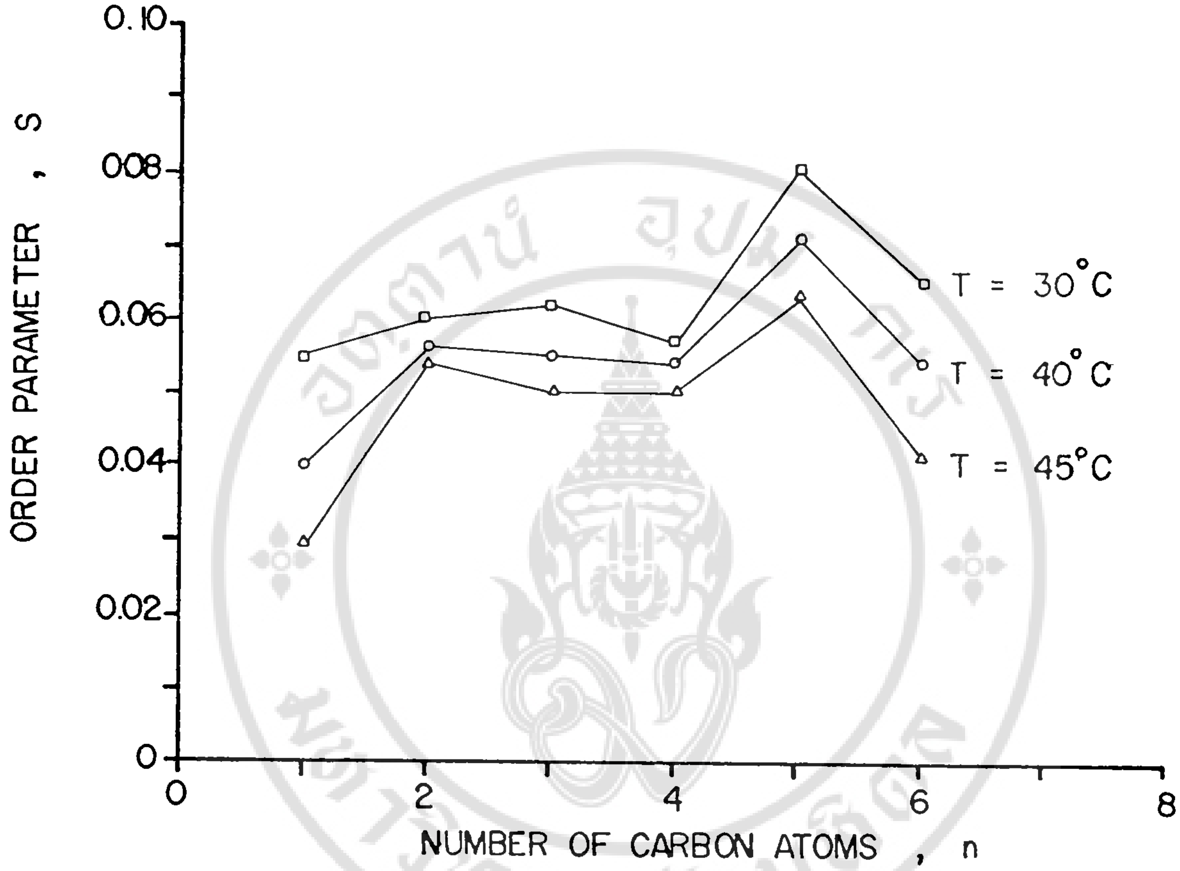


Fig.3.47 Order parameter of ABBA (S_s) in 20%(w/w) ABBA-polystyrene film (stretched to 600% elongation), read at temperature 30°C, 40°C and 45°C plotted as a function of the number of carbon atoms (n) of the alkoxy chain.

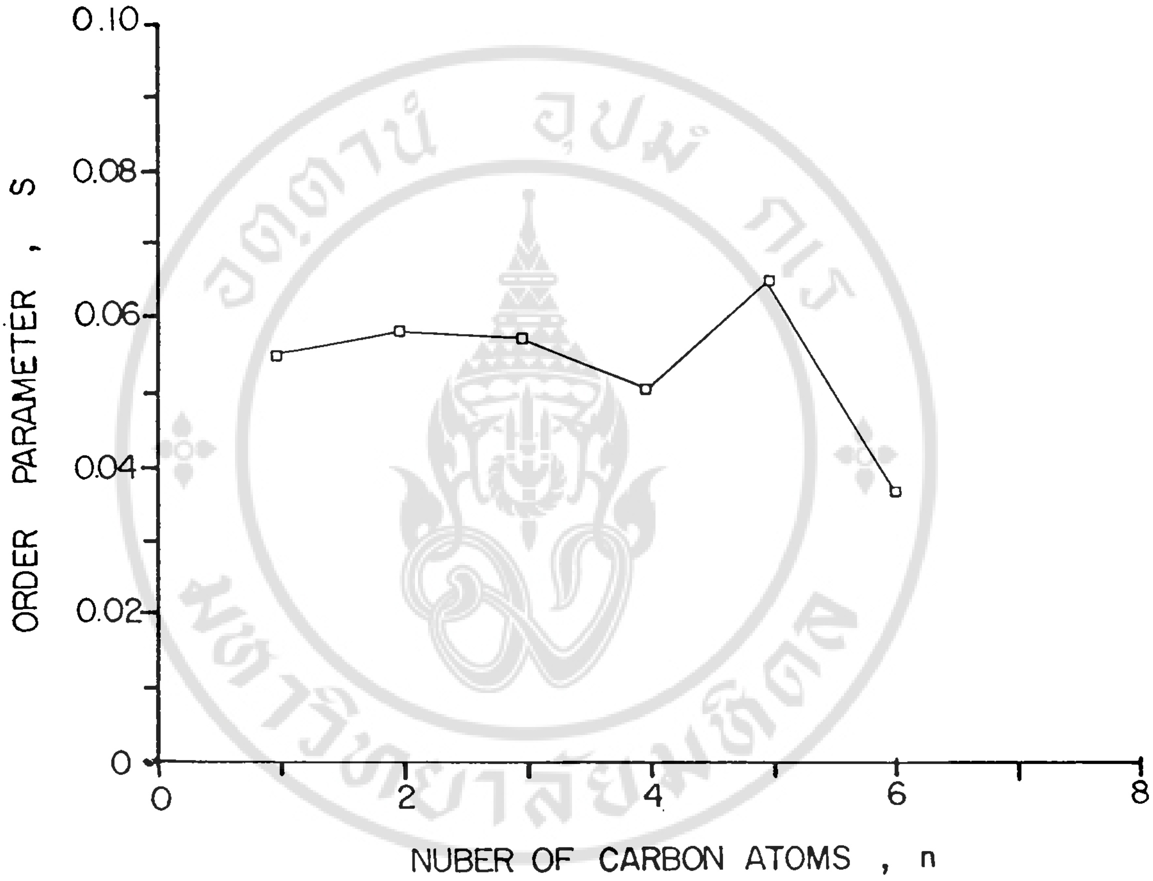


Fig.3.48 Order parameter of ABBA (S_s) in 20% ABBA-polystyrene film, stretched to 600% elongation read at S_v = 0.07, plotted as a function of the number of carbon atoms(n) of the alkoxy chain.

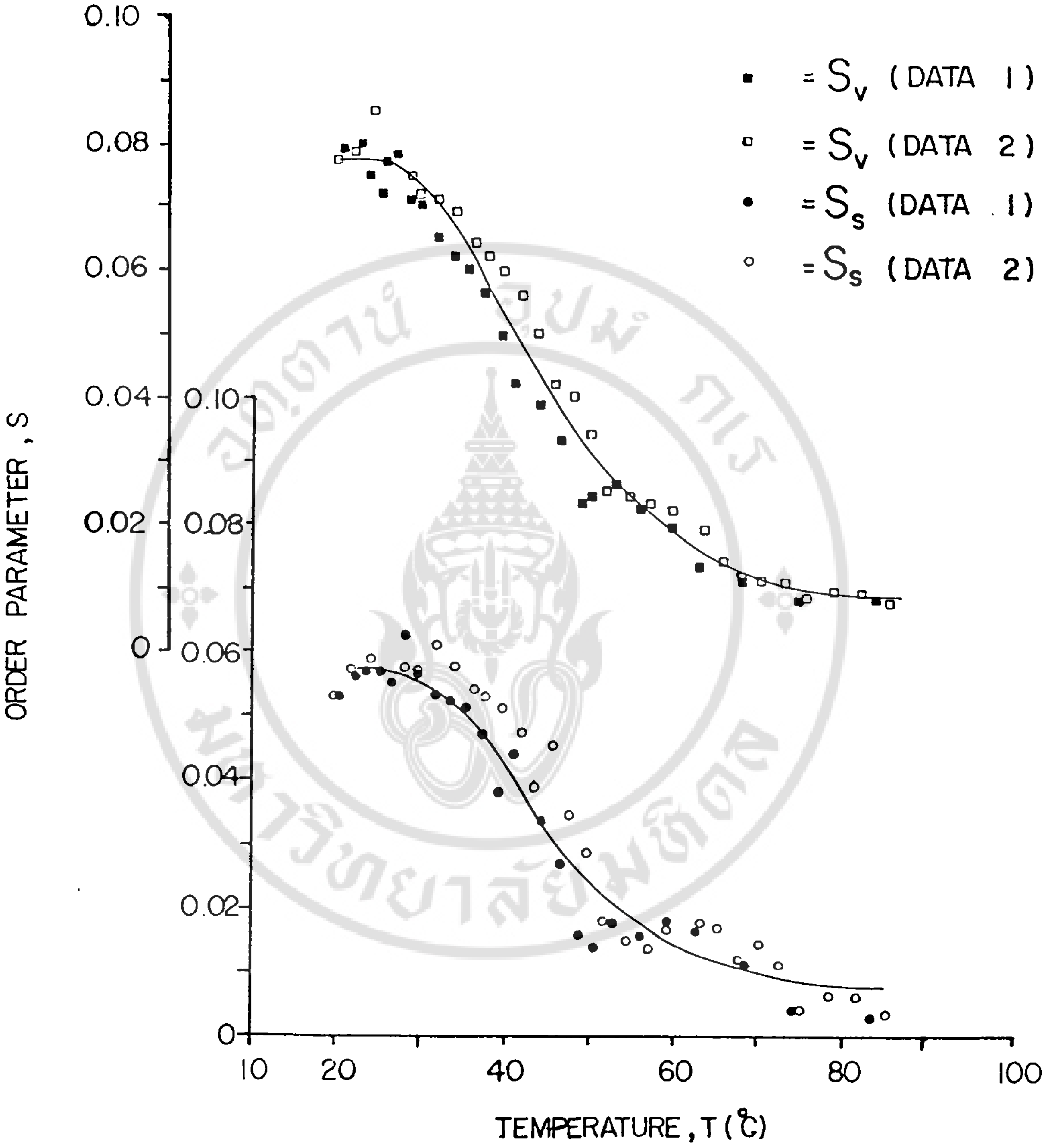


Fig.3.49 Temperature dependence of the order parameter of MBBA in polystyrene film, stretched to 600%elongation. In order to comparison two data sets

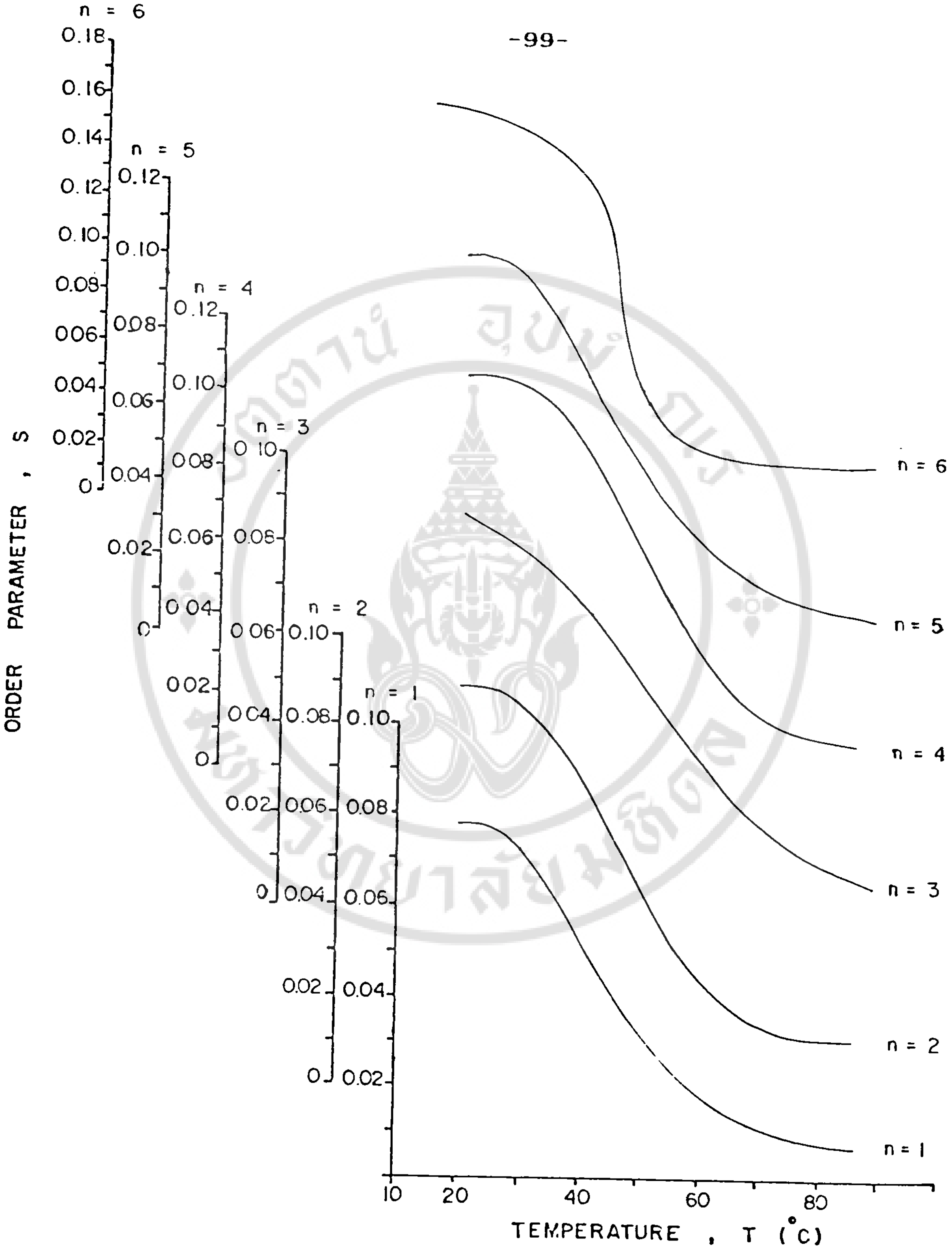


Fig.3.50 Temperature dependence of the average order parameter of polystyrene ($\bar{S}_v$) in 20% (w/w) ABBA-polystyrene film, stretched to 600%elongation.

n = number of carbon atoms in the alkoxy chain.

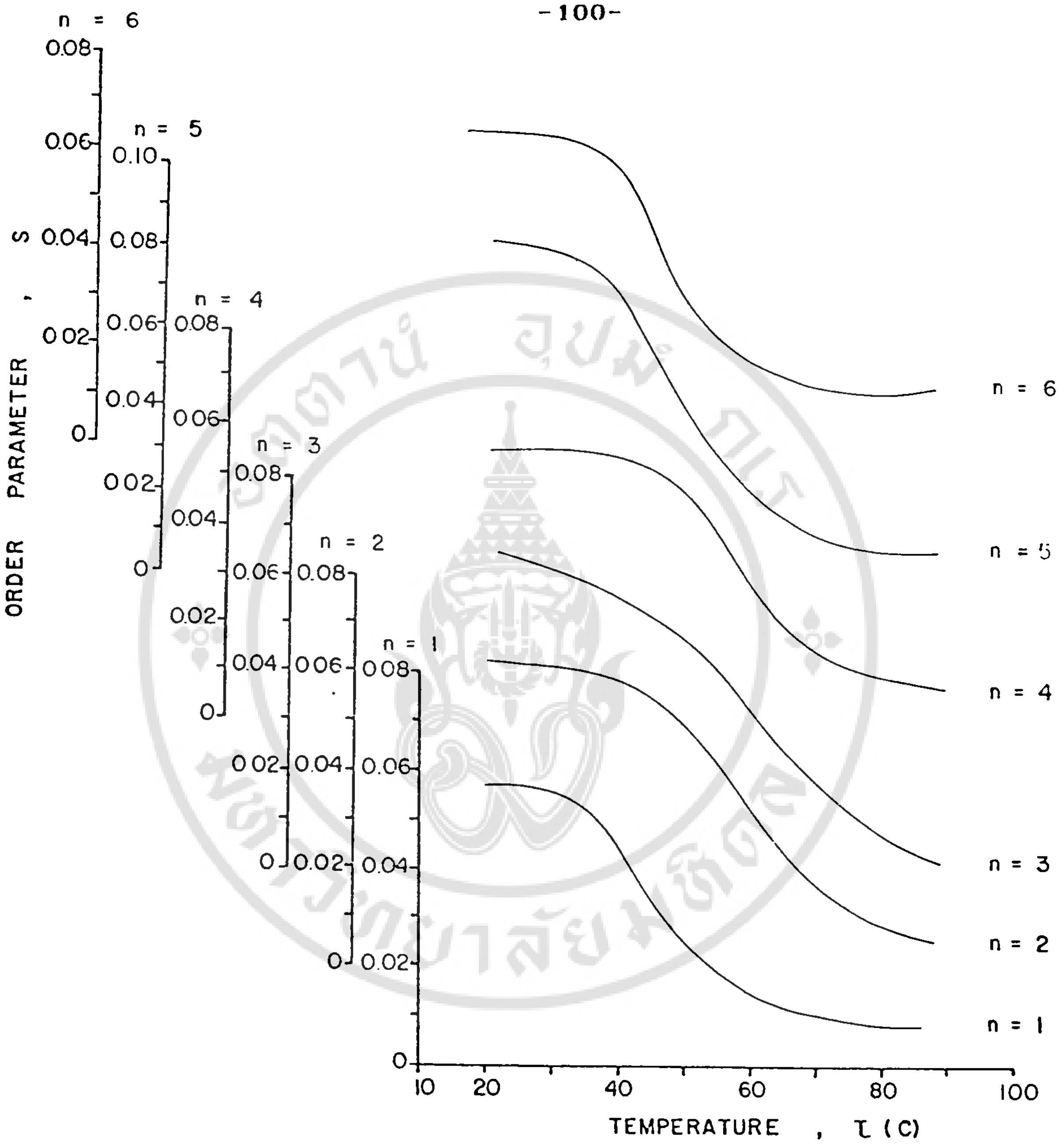


Fig.3.51 Temperature dependence of the average order parameter of ABBA ($\bar{S}_s$) in 20% (w/w) ABBA-polystyrene film, stretched to 600% elongation.

n = number of carbon atoms in the alkoxy chain.

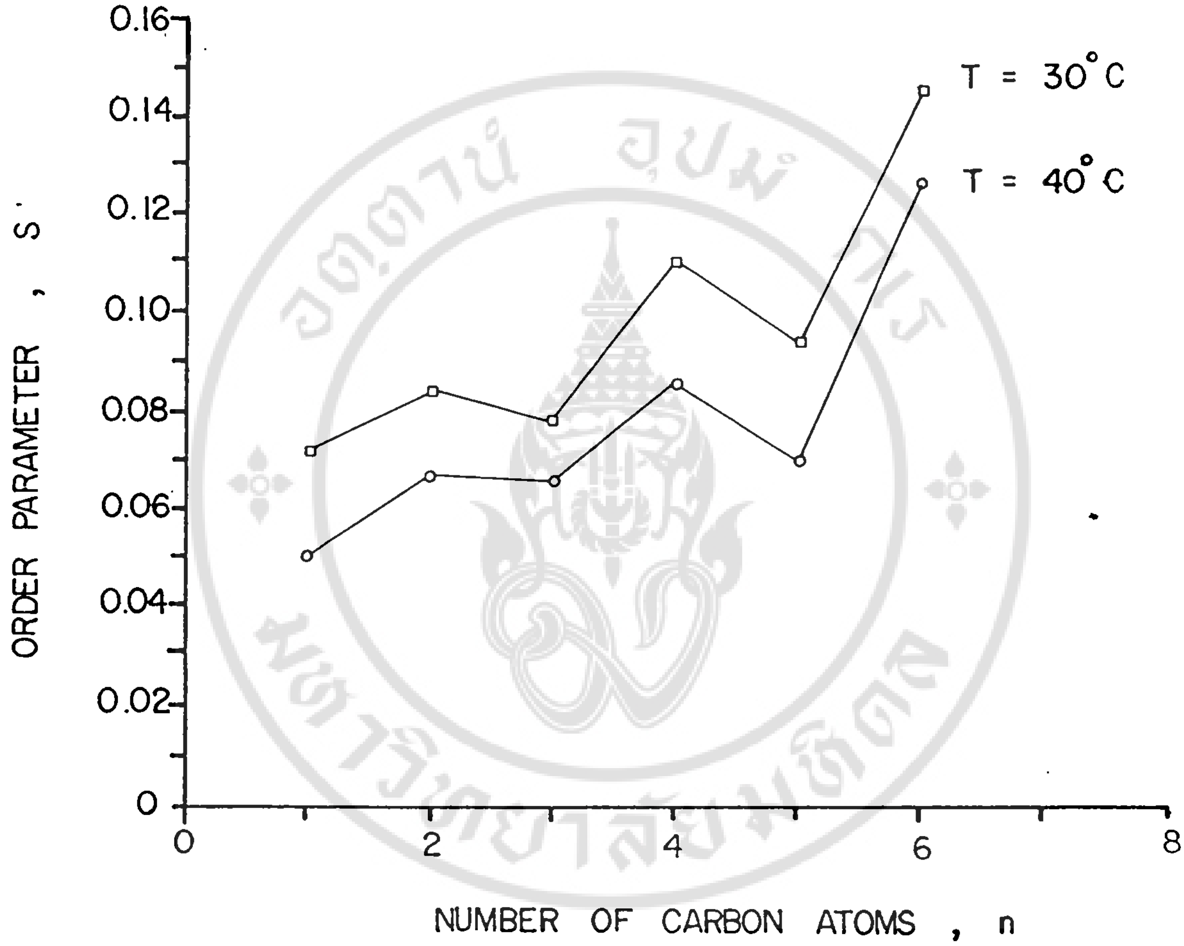


Fig.3.52 Average order parameter of polystyrene($\bar{S}_v$) in 20%(w/w) ABBA-polystyrene film (stretched to 600% elongation), read at temperature 30°C and 40°C plotted as a function of the number of carbon atoms (n) of the alkoxy chain.

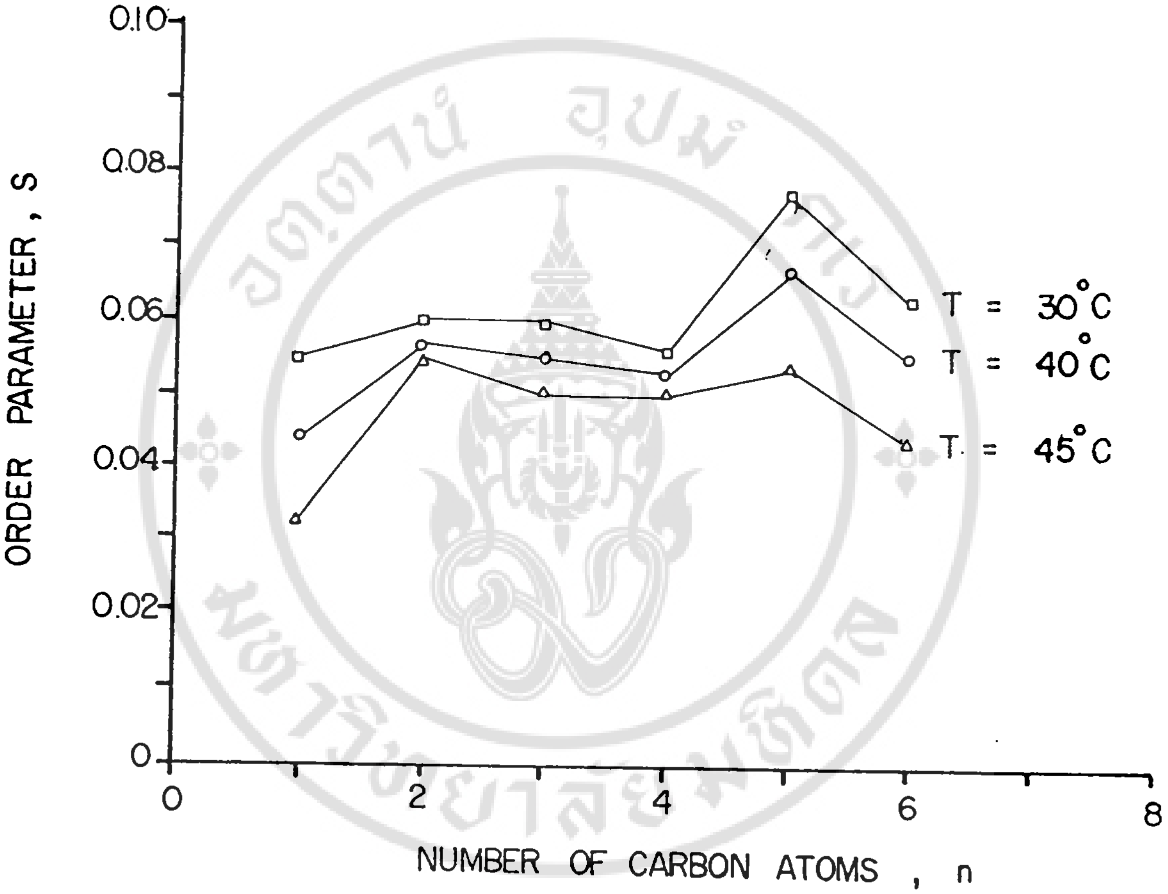


Fig.3.53 Average order parameter of ABBA (S_s) in 20%(w/w) ABBA-polystyrene film (stretched to 600% elongation), read at temperature 30°C, 40°C and 45°C plotted as a function of the number of carbon atoms (n) of the alkoxy chain.

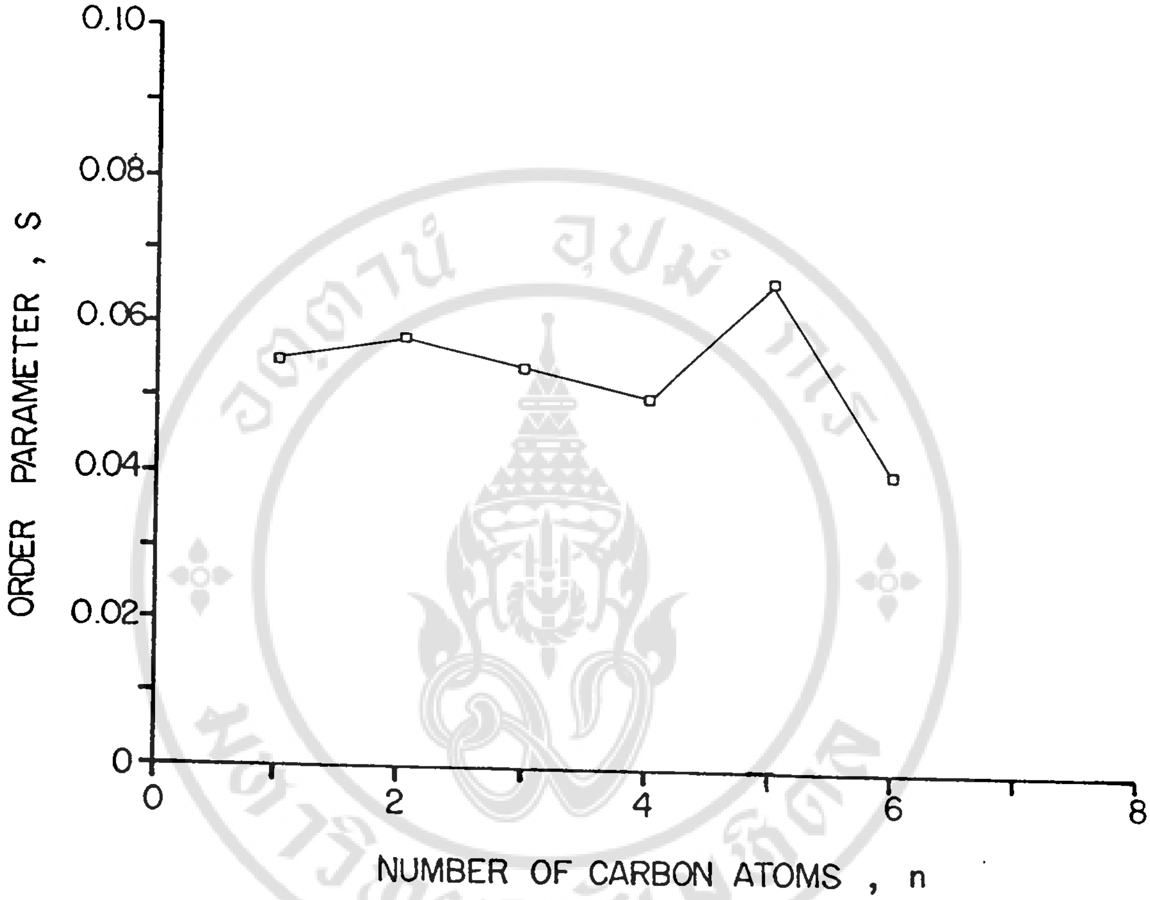


Fig.3.54 Average order parameter of ABBA ($\bar{S}_s$) in 20%(w/w) ABBA-polystyrene film, stretched to 600%elongation read at $\bar{S}_v$ = 0.07, plotted as a function of the number of carbon atoms (n) of the alkoxy chain.

and 40°C are plotted against the number of carbon-atoms (n) of the alkoxy end chain in ABBA series as shown in Fig.3.45. The alternation of S_v according to odd and even number of carbon atoms (n) is not as clear as those obtained in the case of pure ABBA (see also Fig.3.23).

Similar to Fig.3.44, the temperature dependence of order patameter of solutes (S_s) for those systems is shown in Fig.3.46. Fig.3.47 illustrates the order parameter (S_s) read at constant temperatures as a function of the number of carbon atoms (n) of the alkoxy chain in ABBA. In addition, the order parameter of the solutes (S_s), at a constant order parameter of the solvent, as shown in Fig.3.28 are plotted against the number of carbon atoms (n), and is shown in Fig. 3.48. The odd-even effect of S_s is not observed in both figures. The variations of S_s with respect to n show maximum for n = 5.

To confirm the results of the temperature dependence of the order parameter in the stretched films, the procedure was repeated. An example of the temperature dependence of order parameter of solute and solvent for the sample of 20% MBBA (weight by weight) in polystyrene, stretched at temperature 35°C to 600% elongation is shown in Fig.3.49 for the first data and the repeated data. The average order parameter of solvent ($\bar{S}_v$) and solute ($\bar{S}_s$) are obtained from the best fit as shown in Fig.3.49. The results in terms of the average fit curves of the temperature dependence of S_v and S_s are presented in Fig. 3.50 and 3.51 respectively. The estimated set of the order parameter of solvent ($\bar{S}_v$) from the best fits in Fig.3.50, taken at any constant temperature, are plotted against the number of carbon-atoms in alkoxy end chain of the solute (Fig.3.52). The odd-even effect of $\bar{S}_v$ is also observed.

However, in order to compare with Fig.3.47, the order parameter of the solutes which are obtained from the best fit curves in Fig. 3.51 ($\bar{S}_s$), were also taken at constant temperature 30°C, 40°C and 45°C respectively. These values are shown in Fig.3.53 where they are plotted against the number of carbon-atoms (n) of the solute end chain. The variation of $\bar{S}_s$ with n shows a maximum for n = 5. The order parameter of the solute ($\bar{S}_s$) taken at constant $\bar{S}_v$ ($\bar{S}_v$ = 0.07) are plotted against the number of carbon-atoms of the alkoxy end chain, n, is also given in Fig.3.54. The alternation of $\bar{S}_s$ according to odd-even of carbon-atoms is not observed.

3.1.7.3 RESULTS OF THE RELAXATION TIME EFFECT.

Fig.3.55 illustrates the time dependence of the order parameter of the solvent, polystyrene and the solute, HBBA in 20.05% HBBA-PS film, stretched to 600% elongation. The equivalent reference temperatures used in the range of this experiment are 20°C, 40°C and 60°C respectively. It is clearly seen that at the temperature of 20°C, the order parameter of polystyrene and HBBA are independent time. S_v and S_s are almost constant with increasing time. At temperature 40°C, S_v and S_s decrease almost linearly with increasing time. This indicates that the order parameter of

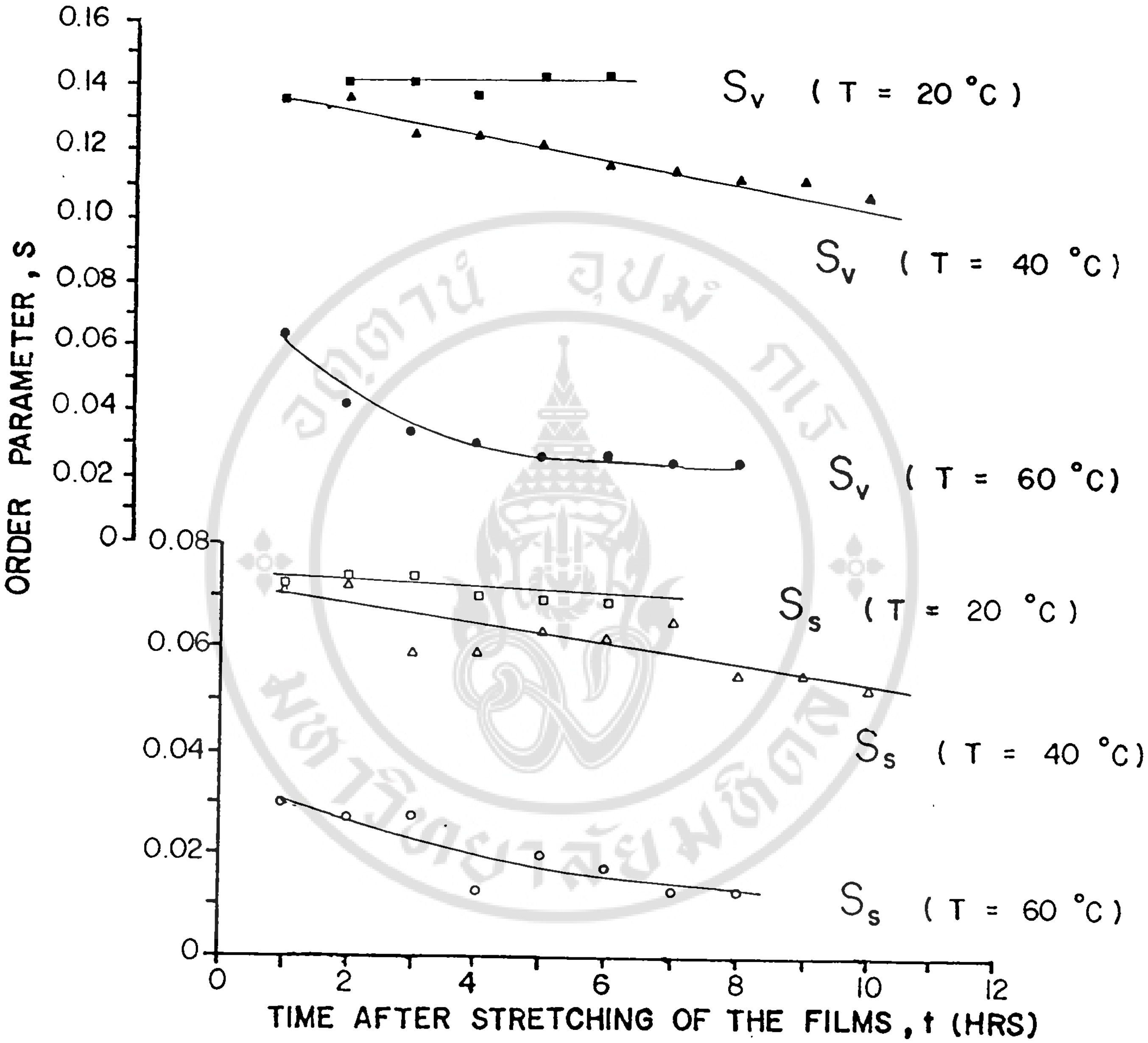


Fig.3.55 Order parameter (S) of 20.05%(w/w) p-n-hexoxybenzylidene -p-n-butylaniline (HBBA) in polystyrene film, stretched to 600% elongation, read at temperature 20°C, 40°C and 60°C, plotted as a function of time after the stretching of the film (t).

both solute and solvent depends on the time after stretching of the film. When the sample film was kept at 60°C, the behavior of the time dependence of order parameter of solute is similar to that observed at 40°C, but it can be noted that, in the case of the order parameter of polystyrene, as the time increases from 1 hour to 2 hours after stretching of the film, the order parameter decrease from 0.064 to 0.042. In the other words, the order parameter of polystyrene decrease about 34% in the first hour.

3.2 DISCUSSION

Firstly, it must be noted that the purity of solutes, P-(n-alkoxybenzylidene)-p-n-butylanilines, required for the experiment is very high. The product obtained from the preparation was recrystallized several times until the transition temperatures remain constant. The transition temperatures determined from microscopic studies (see Table 3.4) are nearly the temperatures indicated in the literature (Ref.66). In order to check that the starting materials, such as p-n-alkoxybenzaldehydes and p-n-butylaniline or the solvent used for purification, had been removed from the products, NMR measurements were taken. From the NMR spectra (see Fig. 3.7-3.12), peaks which are due to the proton in benzaldehyde and aniline group, in the regions 9.7-10.5 δ and 3.5 δ(singlet) respectively are not present. The other determination of purity is DSC analysis, which also gave excellent results. To every transition there corresponds a peak, the symmetry and sharpness of which give an indication of the purity of the product (see Fig.3.13). Thus the product obtained is pure enough to be used in this experiment.

Order parameters shown in Fig.3.23 are the spectroscopic evidence of an odd-even ordering effect in the homologous series of Schiff's base liquid crystals where the two end groups are not equivalent. The molecular end chains are known to exert important effect on the properties of this mesophase. As pointed out by Marcelja(67), the even-numbered carbon atoms of alkoxy end chains causes the molecule to align along the rubbing direction, whilst the odd-numbered methyl group tends to destroy this alignment.

DSC thermogram of ABBA-PS films revealed the behavior of each component in the mixture in which polystyrene matrix acts as the solvent and ABBA molecules act as the solutes. The addition of a small amount of the solutes in polystyrene induce a sharp decrease of the glass transition temperature. Only a glass transition temperature (T_g) is observed and no melting peak was detected on the DSC thermograms as shown in Fig.3.24. It seems to be that in the sensitivity of DSC measurement, the solute is compatible with the polymer.

Another point to consider is how to define a chain axis in polystyrene and ABBA. In order to check how the solute molecules, ABBA, is aligned in the anisotropic solvent such as stretched polymer films, one should consider the vibrational absorption frequency of polystyrene at 757 cm^{-1} and that of ABBA at 837 cm^{-1}. The intense band at 757 cm^{-1} of polystyrene is assigned to ν_{108} (B_2), due to the C-H out of plane bending on mono-substituted benzene ring (see Fig.3.56). The dichroic absorbances for linearly polarized light with the electric vector polarized parallel to the stretching direction is higher than that where the electric vector is perpendicular to the stretched direction (i.e. $A_{//} > A_{\perp}$), as shown in Fig.3.3

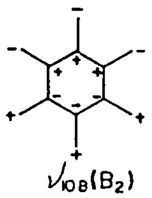


Fig.3.56 Approximate normal mode of mono-substituted benzene

and 3.25. This evidence shows that under stretched condition, the dipole moment of C-H out of plane bending mode of benzene ring is parallel with the stretched direction. For elongated molecules like polystyrene, it is usually possible to estimate an "orientation axis"which has the highest tendency of becoming aligned parallel to the stretched direction. So the benzene ring in polystyrene should arrange themselves in such a way that the plane of these rings are perpendicular to the stretching direction (see Fig.3.57). On the other hand, the out of plane C-H bending mode of benzene ring at 837 cm^{-1} presents dipole moment vector perpendicular to the stretched direction. Thus benzene rings of the solute align along the molecular axes, such that the dipole moment is perpendicular to the stretching direction, as shown in Fig.3.57.

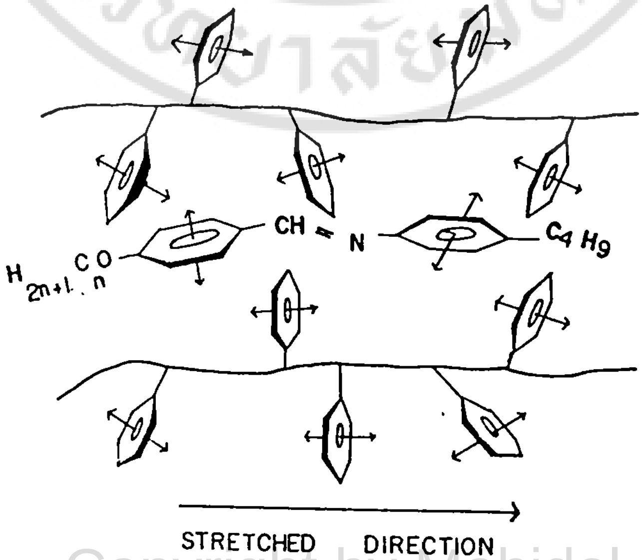


Fig.3.57 Diagram showing molecular orientation of both ABBA and PS in the stretched ABBA-PS film.

From IR linear dichroism measurements of stretched pure polystyrene film of 600% elongation (stretching at 90°C) gave a degree of orientational order parameter, evaluated from the absorption at the wave number 757 cm^{-1}, of 0.12. The orientation of pure polystyrene is still preserved although the temperature is raised to T_g of polystyrene. In fact, the order parameter obtained at the temperature above T_g is related to the orientation of the polymer which still exist. In order to comfirm this, the experiment should be carried out to higher temperature.

Temperature dependence of the order parameter of PS in ABBA-PS films stretched to 600% elongation as shown in Fig. 3.47 generally indicate that the order parameter decreases with increasing temperature. This is probably due to the fact that when the temperature is raised the thermal motion is continuously increased, leading to a decreased orientation in the interior of the polystyrene matrix. It is observed that even at high temperature the order parameter was independent of temperature. This can be understood by considering that the thermal motion of the network chain can be constrained by the presence of crosslinking and entanglement at the higher temperature. It is interesting to note that almost no orientation is achieved at high temperature as revealed by the very low values of the order parameter, it is not possible to indicate precisely the clearing point of the mixtures. However, the temperature dependence of dichroic ratio, as shown in Fig. 3.27 for example, should be used to determine the clearing point, T_c, of sample films. One can notice that after stretching, the sample films are turbid. This would arise from the alignment of the solutes in stretched polystyrene. As shown in Fig.3.26 and 3.41, it is evident that the turbidity disappears after increasing temperature to T_c. In the case of HBBA-PS film, this phenomenon is clearly observed (see Fig.3.41). Fig.3.43 was also used to determine T_c which was taken as the temperature at which the order parameter is extraporated to zero. In fact, the sample film of HBBA-PS mixture is slightly different from those of the other solutes, although DSC data is still similar to that observed for the others. Before stretching, this sample film is turbid. It seem likely that phase separation occurs. The behavior of the temperature dependence of the order parameter of polystyrene is also different from the others. It is possible to estimate that the molecule of HBBA is dissolved in polystyrene and also forms a second phase in polystyrene matrix.

Using the viscosity average molecular weight of polystyrene and the molecular weight of ABBA reported in Table 2.1, the molecular ratio of ABBA molecule and styrene monomer are calculated. From this ratio the number of MBBA molecule to the number of styrene monomer is 1:10. This means that the interaction between the molecules of solute are quite small because they are far apart from each other. It seems to be that molecules of ABBA are dissolved in the polymer and do not form a second phase in PS, but tend to orient themselves parallel to PS chains which align along the stretched direction. Comparing Fig.3.46 with Fig.3.16 -3.21, it seems to indicate that orientation of the solute does not originate from its properties but is related to the perturbation by the stretched polymer. The temperature dependence of orientation of solutes are not as clear as those obtained in the case of the solvents. The data points are more scattered and the reproducibility is rather poor. This could be explained as the alignment of solute molecules being flexible, although the mobility of solute molecules is hindered by polymer chains which act as a matrix. However, it is interesting to note that the clearing point, T_c, of the sample films have been observed as shown in Table 3.6. It is evident that liquid crystals have formed the second phase in polystyrene matrix. Although the arguments are fragmentary, they indicated that the observed anisotropy of ABBA in PS matrix is a product of two effects, one "macroscopic" due to the alignment of the polymer chains, the other "microscopic" due to the degree of regularity in the packing of the hydrocarbon end chains of ABBA.

In order to compare results, the order parameters of polystyrene were taken at various temperatures. These value are shown in Fig.3.45 where they are plotted against the number of carbon atoms of the solute end chain. A clear odd-even effect can be observed in this series. This can be explained as odd number of carbon-atoms at the alkoxy group deviating from the main molecular axis and so significantly changing of benzene ring orientation in polystyrene. The results reveal that the even number of carbon-atoms of the alkoxy group in solutes influence the ordering of polystyrene molecule more than those having odd numbers.

Odd-even effect are not observed in the case of solute orientation, although the value of order parameter of the solutes are taken from normalized environment, i.e. for constant orientation of solvent, in order to see the influence of the solute structure on their orientation.

A further point of discussion is the effect of relaxation time on orientation. From results presented in Fig.3.55 it can be noted that at 20°C, order parameters are independent of the time after the stretching of the film. At 40° C, orientation of the molecule slightly decreases with increasing time. This effect is greatest when the temperature rises to 60°C.

3.3 CONCLUSION

The orientation behavior of polystyrene (PS) and p-n-alkyloxybenzylidene-p-n-butylanilines(ABBA) in stretched polystyrene film could be specified by the orientational order parameter. Under stretched condition, molecules of the liquid crystal tend to align along the stretched direction and parallel to the polymer chains. The benzene rings in PS arrange themselves in such a way that the plane of these rings are perpendicular to the stretched direction whereas the plane of benzene rings in ABBA are parallel to the stretched direction.

The temperature dependence of the orientational order parameter for polystyrene and the first six members of the homologous series p-n-alkyloxybenzylidene-p-n-butylanilines (ABBA) were investigated by infrared linear dichroism technique for stretched film. In all the measurements, the order parameters decrease with increasing temperature, and then become almost constant. Such a reduction of the order parameter with increase in the temperature is considered to be caused by two phenomena which occur simultaneously: the first is the decrease of the crystallinity due to crystal melting, and the second is the relaxation of amorphous chains accompanying the melting of crystal. The constant value at higher temperatures (above the clearing point of the sample films) can be regarded as the order parameter which is due to the amorphous phase.

The odd-even alternation of the orientational order of pure p-n-alkyloxybenzylidene-p-n-butylanilines (ABBA) is clearly observed. When a small amount of ABBA was added to embed itself in the stretched PS film (20% ABBA by weight), the odd-even effect of the order parameter of ABBA disappeared.

CHAPTER 4

APPENDIX

Numerical results for plotting all curves are listed in this section. Table 4.1 is data from IR measurement of pure p-n-methoxybenzylidene-p-n-butylanilines (ABBA). Tables 4.2-4.3 are data from IR measurement of pure polystyrene (PS) films. Tables 4.4-4.15 are data from IR measurement of the sample films described at the beginning of each table. The meaning of each symbol used is as follows:

n = number of carbon atoms at the alkoxy end chain of ABBA

T_c = clearing temperature

ΔT = $T_c - T$

$S_{(\Delta T=2)}$ = order parameter at $\Delta T=2$

S_v = order parameter of solvent (evaluated from the absorption band at 757 cm^{-1})

S_s = order parameter of solute (evaluated from the absorption band at 837 cm^{-1})

Table 4.1 P-(n-alkoxybenzylidene)-p-n-butylaniline, sample thickness 10 μm, (evaluated from the absorption band at 837 cm^{-1}). (see Fig. 3.16 - 3.22)

n	T/°C	T_c-T/°C (ΔT)	S	
1	28.0	15.1	0.234	T_c = 43.1°C
	31.0	12.1	0.223	$S_{(\Delta T=2)}$ = 0.135
	33.6	9.5	0.209	
	35.6	7.5	0.198	
	37.4	5.7	0.186	
	38.6	4.5	0.175	
	39.8	3.3	0.164	
	40.6	2.5	0.146	
	41.6	1.5	0.113	
	42.4	0.7	0.062	
	48.2	-	0.001	
2	67.6	8.1	0.423	T_c = 75.7°C
	68.8	6.9	0.409	$S_{(\Delta T=2)}$ = 0.305
	70.0	5.7	0.394	
	71.6	4.1	0.361	
	72.8	2.9	0.334	
	73.6	2.1	0.308	
	74.4	1.3	0.266	
	75.6	0.1	0.030	
3	45.4	7.8	0.226	T_c = 53.2°C
	48.0	5.2	0.206	$S_{(\Delta T=2)}$ = 0.166
	49.2	4.0	0.201	
	50.0	3.2	0.188	
	51.0	2.2	0.171	
	52.0	1.2	0.139	
	52.8	0.4	0.055	
	53.8	-	0.011	

Table 4.1 (cont.)

n	T/ C	T_c-T/ C (T)	S	
4	61.0	10.4	0.407	T_c = 71.4°C
	62.2	9.2	0.395	$S_{(\Delta T=2)}$ = 0.292
	63.2	8.2	0.388	
	64.4	7.0	0.371	
	65.2	6.2	0.365	
	66.6	4.8	0.350	
	67.6	3.3	0.325	
	69.0	2.4	0.303	
	70.2	1.2	0.264	
	71.4	0	0.003	
5	56.2	10.4	0.274	T_c = 66.6°C
	56.8	9.8	0.270	$S_{(\Delta T=2)}$ = 0.195
	57.8	8.8	0.266	
	58.6	8.0	0.263	
	59.6	7.0	0.246	
	60.4	6.2	0.244	
	61.4	5.2	0.232	
	62.4	4.2	0.222	
	63.6	3.0	0.210	
	64.6	2.0	0.195	
	65.4	1.2	0.174	
	66.2	0.4	0.109	
	66.8	-	0.012	
6	68.6	6.5	0.411	T_c = 75.1°C
	69.6	5.5	0.385	$S_{(\Delta T=2)}$ =0.285
	70.6	4.5	0.358	
	71.6	3.5	0.334	
	72.8	2.3	0.301	
	73.8	1.3	0.250	
	74.4	0.7	0.199	
	75.0	0.1	0.036	

Table 4.2 Polystyrene film, stretched to 600% elongation at 90°C, (evaluated from the absorption band at 757 cm^{-1}).
Data set I (see Fig. 3.4 - 3.6)

T/°C	$A_{\perp}$	$A_{\parallel}$	D	S
20.0	1.296	1.821	1.405	0.119
22.4	1.281	1.750	1.366	0.109
24.4	1.255	1.687	1.344	0.103
26.2	1.237	1.657	1.340	0.102
28.2	1.238	1.629	1.316	0.095
30.2	1.209	1.561	1.291	0.088
32.6	1.185	1.559	1.316	0.095
35.0	1.178	1.500	1.273	0.083
37.6	1.148	1.458	1.270	0.083
40.0	1.130	1.426	1.262	0.080
42.6	1.117	1.389	1.244	0.075
45.6	1.086	1.358	1.250	0.077
48.4	1.063	1.315	1.237	0.073
52.0	1.027	1.268	1.235	0.073
55.4	1.012	1.229	1.214	0.067
58.4	0.986	1.183	1.200	0.062
61.8	0.959	1.166	1.216	0.067
64.4	0.951	1.129	1.187	0.059
67.0	0.932	1.104	1.185	0.058
70.6	0.912	1.070	1.173	0.055
75.0	0.881	1.028	1.167	0.053
78.8	0.876	1.021	1.166	0.052
84.6	0.860	1.009	1.173	0.055

Table 4.3 Polystyrene film, stretched to 600% elongation at 90°C, (evaluated from the absorption band at 757 cm^{-1}).
Data set II

T/°C	$A_{\perp}$	$A_{\parallel}$	D	S
20.0	1.284	1.798	1.400	0.118
22.6	1.271	1.728	1.360	0.107
24.8	1.247	1.671	1.340	0.102
27.4	1.227	1.615	1.316	0.095
29.6	1.206	1.550	1.285	0.087
32.8	1.171	1.494	1.276	0.084
35.2	1.143	1.455	1.273	0.083
38.0	1.123	1.422	1.266	0.082
40.6	1.081	1.355	1.253	0.078
43.4	1.063	1.315	1.237	0.073
46.2	1.022	1.270	1.243	0.075
49.6	1.000	1.233	1.233	0.072
53.0	.0983	1.187	1.208	0.065
56.2	0.942	1.138	1.208	0.065
59.2	0.934	1.114	1.193	0.060
64.0	0.914	1.079	1.181	0.057
68.6	0.885	1.039	1.174	0.055
72.8	0.878	1.032	1.175	0.055
76.8	0.878	1.032	1.175	0.055
83.8	0.864	1.017	1.177	0.056
86.0	0.864	1.017	1.177	0.056

Table 4.4 20.07% (by weight) p-(methoxybenzylidene)-p-n-butylaniline in polystyrene film, stretched to 600% elongation at 35°C, (evaluated from the absorption bands at 757 cm^{-1} and 837 cm^{-1}).
Data set I (see Fig. 3.26 - 3.28)

T/°C	757 CM^{-1}				837 CM^{-1}			
	$A_\perp$	$A_{/\!/}$	D	S_v	$A_\perp$	$A_{/\!/}$	D	S_s
20.8	0.939	1.179	1.256	0.079	0.528	0.487	0.922	0.053
22.8	0.943	1.188	1.260	0.080	0.529	0.486	0.919	0.055
24.0	0.944	1.175	1.245	0.076	0.528	0.484	0.917	0.057
25.2	0.941	1.160	1.233	0.072	0.528	0.484	0.917	0.057
27.0	0.936	1.174	1.254	0.078	0.527	0.485	0.920	0.055
28.6	0.934	1.149	1.230	0.071	0.527	0.479	0.909	0.063
30.0	0.916	1.122	1.225	0.070	0.519	0.476	0.917	0.057
32.0	0.908	1.097	1.208	0.065	0.515	0.475	0.922	0.053
33.8	0.906	1.087	1.200	0.062	0.512	0.473	0.924	0.052
35.6	0.899	1.071	1.191	0.060	0.508	0.470	0.925	0.051
37.4	0.889	1.048	1.179	0.056	0.504	0.469	0.931	0.047
39.4	0.888	1.028	1.158	0.050	0.500	0.472	0.944	0.036
41.2	0.884	1.000	1.131	0.042	0.500	0.472	0.944	0.038
44.0	0.877	0.984	1.122	0.039	0.493	0.468	0.949	0.035
46.6	0.882	0.972	1.102	0.033	0.496	0.476	0.960	0.027
48.8	0.847	0.907	1.071	0.023	0.495	0.483	0.976	0.016
50.8	0.849	0.911	1.073	0.024	0.494	0.484	0.980	0.013
52.8	0.841	0.908	1.080	0.026	0.494	0.481	0.974	0.017
55.8	0.847	0.903	1.066	0.022	0.491	0.479	0.976	0.016
59.4	0.837	0.885	1.057	0.019	0.486	0.473	0.973	0.018
62.8	0.831	0.863	1.039	0.013	0.479	0.467	0.975	0.017
68.2	0.805	0.831	1.032	0.011	0.471	0.463	0.983	0.011
74.4	0.778	0.798	1.026	0.009	0.459	0.456	0.993	0.005
83.4	0.739	0.756	1.023	0.008	0.444	0.442	0.995	0.003

Table 4.5 20.02% (by weight) p-(methoxybenzylidene)-p-n-butylaniline in polystyrene film, stretched to 600% elongation at 35°C, (evaluated from the absorption bands at 757 cm^{-1} and 837 cm^{-1}).

Data set II

T/ °C	757 CM^{-1}				837 CM^{-1}			
	$A_\perp$	$A_{/\!/}$	D	S_v	$A_\perp$	$A_{/\!/}$	D	S_s
20.0	0.945	1.183	1.252	0.077	0.516	0.476	0.922	0.053
22.0	0.948	1.191	1.256	0.079	0.518	0.475	0.917	0.057
24.2	0.962	1.230	1.279	0.085	0.514	0.470	0.914	0.059
26.4	0.941	1.177	1.251	0.077	0.515	0.473	0.918	0.056
28.4	0.948	1.180	1.245	0.075	0.517	0.473	0.915	0.058
30.0	0.945	1.164	1.232	0.072	0.517	0.474	0.917	0.057
32.0	0.938	1.154	1.230	0.071	0.515	0.469	0.911	0.061
34.2	0.921	1.126	1.223	0.069	0.508	0.465	0.915	0.058
36.4	0.913	1.101	1.206	0.064	0.504	0.464	0.921	0.054
37.8	0.911	1.093	1.200	0.062	0.502	0.463	0.922	0.053
39.8	0.903	1.076	1.192	0.060	0.496	0.459	0.925	0.051
42.0	0.895	1.053	1.177	0.056	0.493	0.459	0.931	0.047
43.8	0.893	1.033	1.157	0.050	0.489	0.461	0.943	0.039
45.6	0.889	1.007	1.133	0.042	0.489	0.457	0.935	0.045
47.8	0.882	0.991	1.124	0.040	0.482	0.457	0.948	0.035
50.0	0.888	0.982	1.106	0.034	0.485	0.464	0.957	0.029
52.0	0.853	0.919	1.077	0.025	0.484	0.471	0.973	0.018
54.6	0.859	0.922	1.073	0.024	0.484	0.473	0.977	0.015
57.0	0.857	0.918	1.071	0.023	0.483	0.473	0.979	0.014
59.6	0.857	0.914	1.067	0.022	0.481	0.469	0.975	0.017
63.2	0.847	0.896	1.058	0.019	0.476	0.463	0.973	0.018
65.4	0.839	0.874	1.042	0.014	0.469	0.457	0.974	0.017
68.0	0.815	0.841	1.032	0.011	0.461	0.453	0.983	0.012
70.2	0.821	0.848	1.033	0.011	0.457	0.447	0.978	0.015
72.8	0.807	0.835	1.035	0.011	0.435	0.428	0.984	0.011
75.0	0.788	0.808	1.025	0.008	0.449	0.446	0.993	0.004
78.4	0.793	0.814	1.026	0.009	0.445	0.441	0.991	0.006
81.6	0.792	0.813	1.027	0.009	0.444	0.440	0.991	0.006
85.2	0.750	0.766	1.021	0.007	0.435	0.433	0.995	0.003

Table 4.6 20.00% (by weight) p-(ethoxybenzylidene)-p-n-butylaniline in polystyrene film, stretched to 600% elongation at 41°C, (evaluated from the absorption bands at 757 cm^{-1} and 837 cm^{-1}).

Data set I (see Fig. 3.29 - 3.31)

T/°C	757 CM^{-1}				837 CM^{-1}			
	$A_{\perp}$	$A_{//}$	D	S_v	$A_{\perp}$	$A_{/}$	D	S_s
20.0	0.807	1.040	1.289	0.088	0.324	0.292	0.901	0.068
22.0	0.804	1.029	1.280	0.085	0.322	0.291	0.904	0.066
23.8	0.791	1.027	1.298	0.090	0.320	0.293	0.916	0.058
25.8	0.783	1.009	1.289	0.088	0.322	0.294	0.913	0.060
27.4	0.779	0.997	1.280	0.085	0.320	0.293	0.916	0.058
29.2	0.771	0.985	1.278	0.085	0.321	0.289	0.900	0.069
31.2	0.769	0.973	1.265	0.081	0.317	0.291	0.918	0.056
32.8	0.765	0.968	1.265	0.081	0.319	0.290	0.909	0.063
34.8	0.758	0.955	1.260	0.060	0.316	0.287	0.908	0.063
36.6	0.753	0.941	1.250	0.077	0.314	0.289	0.920	0.055
39.2	0.747	0.925	1.238	0.074	0.314	0.286	0.911	0.061
42.0	0.743	0.899	1.210	0.065	0.311	0.286	0.920	0.055
43.8	0.737	0.881	1.195	0.061	0.308	0.285	0.925	0.051
45.6	0.739	0.873	1.181	0.057	0.312	0.287	0.920	0.055
48.4	0.730	0.848	1.162	0.051	0.311	0.284	0.913	0.060
51.0	0.734	0.825	1.124	0.040	0.309	0.285	0.922	0.053
53.6	0.733	0.814	1.111	0.036	0.301	0.282	0.937	0.043
56.2	0.727	0.800	1.100	0.032	0.298	0.283	0.950	0.034
59.0	0.722	0.791	1.096	0.031	0.297	0.282	0.949	0.035
61.6	0.721	0.775	1.075	0.024	0.303	0.288	0.950	0.034
64.4	0.708	0.763	1.078	0.025	0.304	0.285	0.938	0.042
66.8	0.701	0.746	1.064	0.021	0.296	0.284	0.959	0.028
71.2	0.673	0.710	1.055	0.018	0.285	0.273	0.958	0.028
74.2	0.670	0.699	1.043	0.014	0.282	0.275	0.975	0.017
77.0	0.666	0.691	1.038	0.013	0.279	0.273	0.978	0.015
80.8	0.657	0.674	1.026	0.009	0.272	0.269	0.989	0.007
87.6	0.632	0.649	1.027	0.009	0.267	0.264	0.989	0.007

Table 4.7 20.07% (by weight) p-(ethoxybenzylidene)-p-n-butylaniline in polystyrene film, stretched to 600% elongation at 41°C, (evaluated from the absorption bands at 757 cm^{-1} and 837 cm^{-1}).

Data set II

T/°C	757 CM^{-1}				837 CM^{-1}			
	$A_{\perp}$	$A_{/\!/}$	D	S_v	$A_{\perp}$	$A_{\parallel}$	D	S_s
20.0	0.759	0.978	1.289	0.088	0.305	0.274	0.898	0.070
22.0	0.751	0.971	1.293	0.089	0.289	0.262	0.907	0.064
24.4	0.755	0.967	1.281	0.086	0.302	0.274	0.907	0.064
26.4	0.743	0.965	1.299	0.091	0.301	0.275	0.914	0.059
28.4	0.724	0.924	1.276	0.084	0.293	0.269	0.918	0.056
30.4	0.727	0.932	1.282	0.086	0.294	0.269	0.915	0.058
32.6	0.711	0.897	1.262	0.080	0.292	0.266	0.911	0.061
34.8	0.705	0.885	1.255	0.078	0.289	0.263	0.910	0.062
38.0	0.701	0.872	1.244	0.075	0.287	0.265	0.923	0.052
40.2	0.692	0.835	1.207	0.064	0.285	0.261	0.916	0.058
42.8	0.688	0.820	1.192	0.060	0.281	0.260	0.925	0.051
45.2	0.690	0.811	1.175	0.055	0.285	0.263	0.923	0.053
47.8	0.681	0.788	1.157	0.050	0.284	0.260	0.915	0.058
50.2	0.684	0.767	1.121	0.039	0.282	0.259	0.918	0.056
53.2	0.681	0.757	1.112	0.036	0.274	0.258	0.942	0.040
55.8	0.676	0.744	1.101	0.032	0.271	0.258	0.952	0.033
57.6	0.671	0.721	1.075	0.024	0.274	0.262	0.953	0.030
60.6	0.652	0.694	1.064	0.021	0.268	0.257	0.959	0.028
63.4	0.629	0.657	1.045	0.015	0.265	0.259	0.977	0.015
65.6	0.625	0.653	1.045	0.015	0.256	0.251	0.980	0.013
68.6	0.622	0.646	1.039	0.013	0.254	0.249	0.980	0.013
71.0	0.615	0.638	1.037	0.012	0.249	0.243	0.976	0.016
74.2	0.614	0.634	1.033	0.011	0.248	0.252	-	-
76.8	0.614	0.634	1.033	0.011	0.248	0.250	-	-
79.8	0.607	0.630	1,038	0.012	0.242	0.245	-	-
86.4	0.607	0.630	1.038	0.012	0.242	0.245	-	-

Table 4.8 20.05% (by weight) p-(n-propoxybenzylidene)-p-n-butylaniline in polystyrene film, stretched to 600% elongation at 42°C, (evaluated from the absorption bands at 757 cm^{-1} and 837 cm^{-1}).

Data set I (see Fig. 3.32 - 3.34)

T/°C	757 CM^{-1}				837 CM^{-1}			
	$A_{\perp}$	$A_{\parallel}$	D	S_v	$A_{\perp}$	$A_{\parallel}$	D	S_s
20.0	0.869	1.113	1.281	0.086	0.395	0.359	0.909	0.063
22.4	0.866	1.108	1.279	0.085	0.395	0.357	0.904	0.066
24.4	0.864	1.104	1.278	0.085	0.395	0.358	0.906	0.065
26.2	0.862	1.091	1.266	0.081	0.392	0.358	0.913	0.060
28.2	0.858	1.100	1.282	0.086	0.392	0.350	0.893	0.074
30.8	0.847	1.065	1.257	0.079	0.385	0.352	0.914	0.059
32.8	0.843	1.051	1.247	0.076	0.387	0.355	0.917	0.057
35.0	0.839	1.036	1.235	0.073	0.388	0.352	0.907	0.064
36.8	0.837	1.031	1.232	0.072	0.385	0.353	0.917	0.057
38.6	0.829	1.005	1.212	0.066	0.383	0.350	0.914	0.059
40.6	0.828	0.997	1.204	0.064	0.384	0.352	0.917	0.057
42.8	0.819	0.969	1.183	0.057	0.374	0.348	0.930	0.048
45.6	0.811	0.952	1.174	0.055	0.374	0.350	0.936	0.044
48.4	0.806	0.933	1.158	0.050	0.368	0.346	0.940	0.041
52.0	0.793	0.892	1.125	0.040	0.364	0.340	0.934	0.045
54.6	0.786	0.857	1.090	0.029	0.358	0.334	0.933	0.046
57.4	0.781	0.842	1.078	0.025	0.366	0.343	0.937	0.043
60.0	0.767	0.823	1.073	0.024	0.362	0.343	0.946	0.035
63.0	0.748	0.793	1.060	0.020	0.349	0.334	0.979	0.014
66.0	0.740	0.790	1.068	0.022	0.346	0.336	0.971	0.020
67.8	0.743	0.785	1.057	0.019	0.341	0.333	0.977	0.015
71.6	0.74	0.769	1.039	0.013	0.341	0.334	0.979	0.014
74.2	0.728	0.757	1.040	0.013	0.340	0.335	0.985	0.010
77.0	0.712	0.739	1.038	0.013	0.335	0.329	0.982	0.012
80.6	0.703	0.725	1.031	0.010	0.329	0.324	0.985	0.010
83.2	0.694	0.708	1.020	0.007	0.324	0.323	0.997	0.002
87.6	0.671	0.681	1.015	0.005	0.317	0.315	0.994	0.004

Table 4.9 20.01% (by weight) p-(n-propoxybenzylidene)-p-n-butylaniline in polystyrene film, stretched to 600% elongation at 42°C, (evaluated from the absorption bands at 757 cm^{-1} and 837 cm^{-1}).

Data set II

T/°C	757 CM^{-1}				837 CM^{-1}			
	$A_\perp$	$A_{//}$	D	S_v	$A_\perp$	$A_{//}$	D	S_s
20.0	0.895	1.147	1.282	0.086	0.407	0.370	0.909	0.062
22.2	0.878	1.119	1.274	0.084	0.390	0.353	0.905	0.065
24.2	0.876	1.117	1.275	0.084	0.389	0.354	0.910	0.062
26.0	0.871	1.111	1.276	0.084	0.388	0.351	0.905	0.066
28.4	0.874	1.103	1.262	0.080	0.388	0.353	0.910	0.062
32.4	0.858	1.077	1.255	0.078	0.381	0.348	0.913	0.059
34.6	0.855	1.066	1.247	0.076	0.383	0.351	0.916	0.057
36.4	0.853	1.050	1.231	0.071	0.383	0.348	0.909	0.063
38.4	0.851	1.047	1.230	0.071	0.380	0.349	0.918	0.056
40.2	0.845	1.023	1.211	0.066	0.378	0.346	0.915	0.058
43.0	0.844	1.013	1.200	0.063	0.380	0.348	0.916	0.058
45.8	0.844	1.013	1.200	0.063	0.380	0.348	0.916	0.058
48.2	0.835	0.987	1.182	0.057	0.370	0.345	0.932	0.046
50.4	0.827	0.970	1.173	0.054	0.370	0.346	0.935	0.044
54.8	0.827	0.970	1.173	0.054	0.370	0.346	0.935	0.044
58.2	0.822	0.951	1.157	0.050	0.364	0.341	0.937	0.043
60.0	0.810	0.914	1.128	0.041	0.360	0.335	0.931	0.047
62.4	0.805	0.880	1.093	0.030	0.355	0.332	0.935	0.044
65.0	0.785	0.844	1.075	0.024	0.359	0.340	0.947	0.036
67.4	0.767	0.816	1.064	0.021	0.345	0.330	0.957	0.029
70.0	0.760	0.805	1.059	0.019	0.337	0.330	0.979	0.014
72.4	0.757	0.790	1.044	0.014	0.338	0.332	0.982	0.012
76.6	0.745	0.777	1.043	0.014	0.337	0.331	0.982	0.012
78.8	0.731	0.758	1.037	0.012	0.331	0.326	0.985	0.010
81.6	0.720	0.744	1.033	0.011	0.325	0.321	0.988	0.008
83.8	0.691	0.701	1.014	0.005	0.327	0.324	0.991	0.006
86.4	0.687	0.697	1.015	0.005	0.314	0.311	0.990	0.006

<u>Table 4.10</u> 20.00% (by weight) p-(n-butoxybenzylidene)-p-n-butylaniline in polystyrene film, stretched to 600% elongation at 43°C, (evaluated from the absorption bands at 757 cm^{-1} and 837 cm^{-1}).

<u>Data set I</u> (see Fig. 3.35 - 3.37)

T/°C	757 CM^{-1}				837 CM^{-1}			
	$A_{\perp}$	$A_{//}$	D	S_v	$A_{\perp}$	$A_{//}$	D	S_s
20.0	0.761	1.030	1.353	0.105	0.327	0.302	0.925	0.052
22.2	0.767	1.036	1.351	0.105	0.326	0.301	0.923	0.053
24.4	0.761	1.023	1.344	0.103	0.324	0.298	0.920	0.055
26.2	0.761	1.014	1.330	0.100	0.323	0.297	0.920	0.055
28.4	0.754	1.005	1.333	0.100	0.322	0.296	0.919	0.055
30.0	0.745	1.001	1.344	0.103	0.321	0.294	0.916	0.058
32.0	0.745	0.995	1.336	0.101	0.317	0.293	0.924	0.052
34.4	0.741	0.980	1.323	0.097	0.316	0.290	0.918	0.056
36.6	0.740	0.967	1.307	0.093	0.313	0.288	0.920	0.055
40.2	0.731	0.945	1.293	0.089	0.312	0.286	0.917	0.057
43.4	0.722	0.913	1.265	0.081	0.311	0.284	0.913	0.060
45.8	0.721	0.884	1.226	0.070	0.310	0.283	0.913	0.060
48.0	0.719	0.870	1.210	0.065	0.304	0.282	0.928	0.049
50.8	0.718	0.837	1.166	0.052	0.301	0.280	0.930	0.048
52.6	0.713	0.793	1.112	0.036	0.300	0.281	0.937	0.043
55.4	0.713	0.793	1.112	0.036	0.290	0.275	0.948	0.035
57.2	0.709	0.781	1.102	0.033	0.285	0.275	0.965	0.024
60.0	0.699	0.762	1.090	0.029	0.288	0.278	0.965	0.024
62.4	0.693	0.749	1.082	0.026	0.287	0.277	0.965	0.024
65.0	0.683	0.735	1.076	0.025	0.283	0.276	0.975	0.017
67.6	0.676	0.719	1.064	0.021	0.282	0.272	0.965	0.024
70.0	0.671	0.709	1.057	0.019	0.276	0.271	0.982	0.012
72.8	0.666	0.692	1.039	0.013	0.276	0.268	0.971	0.020
77.0	0.653	0.664	1.017	0.006	0.271	0.266	0.982	0.012
81.2	0.620	0.628	1.013	0.004	0.261	0.258	0.989	0.007
85.0	0.620	0.628	1.013	0.004	0.261	0.258	0.989	0.007

Table 4.11 20.06% (by weight) p-(n-butoxybenzylidene)-p-n-butylaniline in polystyrene film, stretched to 600% elongation at 43°C, (evaluated from the absorption bands at 757 cm^{-1} and 837 cm^{-1}).

Data set II

T/°C	757 CM^{-1}				837 CM^{-1}			
	$A_\perp$	$A_{//}$	D	S_v	$A_\perp$	$A_{//}$	D	S_s
20.0	0.738	0.998	1.352	0.105	0.316	0.293	0.927	0.050
22.4	0.743	1.003	1.350	0.104	0.316	0.292	0.924	0.052
26.2	0.743	1.003	1.350	0.104	0.316	0.292	0.924	0.052
28.4	0.737	0.992	1.346	0.103	0.314	0.289	0.920	0.055
30.4	0.722	0.970	1.343	0.103	0.311	0.285	0.916	0.057
32.6	0.722	0.970	1.343	0.103	0.311	0.285	0.916	0.057
34.8	0.707	0.935	1.322	0.097	0.301	0.277	0.920	0.055
37.2	0.706	0.923	1.307	0.093	0.299	0.275	0.920	0.055
39.6	0.698	0.902	1.292	0.089	0.298	0.273	0.916	0.058
42.6	0.689	0.872	1.266	0.081	0.297	0.271	0.912	0.060
45.0	0.696	0.844	1.213	0.066	0.295	0.273	0.925	0.051
47.4	0.689	0.833	1.209	0.065	0.283	0.262	0.926	0.051
49.6	0.695	0.811	1.167	0.053	0.292	0.271	0.928	0.049
52.4	0.691	0.792	1.146	0.046	0.291	0.272	0.935	0.044
57.0	0.691	0.768	1.111	0.036	0.281	0.266	0.947	0.036
59.4	0.687	0.757	1.102	0.033	0.276	0.266	0.964	0.024
62.0	0.678	0.738	1.088	0.029	0.279	0.269	0.964	0.024
64.6	0.662	0.712	1.076	0.025	0.274	0.267	0.874	0.017
67.0	0.650	0.687	1.057	0.019	0.268	0.262	0.978	0.015
69.6	0.646	0.682	1.056	0.018	0.257	0.252	0.981	0.013
72.4	0.632	0.644	1.019	0.006	0.263	0.258	0.981	0.013
75.8	0.601	0.608	1.012	0.004	0.253	0.250	0.988	0.008
79.6	0.598	0.605	1.012	0.004	0.251	0.248	0.988	0.008
82.8	0.592	0.599	1.012	0.004	0.241	0.239	0.992	0.006
85.2	0.592	0.599	1.012	0.004	0.241	0.238	0.988	0.008

Table 4.12 20.05% (by weight) p-(n-pentoxybenzylidene)-p-n-butylaniline in polystyrene film, stretched to 600% elongation at 43°C, (evaluated from the absorption bands at 757 cm^{-1} and 837 cm^{-1}).
Data set I (see Fig. 3.38 - 3.40)

T/°C	757 CM^{-1}				837 CM^{-1}			
	$A_{\perp}$	$A_{\parallel}$	D	S_v	$A_{\perp}$	$A_{\parallel}$	D	S_s
20.0	0.836	1.129	1.350	0.104	0.366	0.321	0.877	0.086
22.4	0.837	1.113	1.330	0.099	0.367	0.326	0.888	0.078
24.2	0.828	1.104	1.333	0.100	0.364	0.322	0.885	0.080
26.0	0.823	1.105	1.343	0.103	0.364	0.323	0.887	0.078
28.0	0.824	1.095	1.329	0.099	0.362	0.320	0.884	0.078
29.8	0.813	1.072	1.319	0.096	0.363	0.321	0.884	0.080
32.6	0.811	1.059	1.306	0.093	0.358	0.314	0.877	0.086
34.6	0.809	1.045	1.292	0.089	0.356	0.318	0.893	0.074
37.4	0.798	1.029	1.289	0.088	0.352	0.311	0.884	0.080
40.2	0.794	1.002	1.262	0.080	0.351	0.312	0.889	0.077
44.0	0.785	0.977	1.245	0.076	0.342	0.311	0.909	0.063
46.4	0.799	0.924	1.195	0.061	0.338	0.314	0.929	0.048
49.2	0.773	0.924	1.195	0.061	0.336	0.312	0.929	0.048
52.8	0.753	0.830	1.102	0.033	0.330	0.309	0.936	0.044
55.4	0.780	0.869	1.114	0.037	0.329	0.310	0.942	0.039
58.2	0.753	0.830	1.102	0.033	0.329	0.312	0.948	0.035
61.8	0.746	0.808	1.083	0.027	0.320	0.309	0.966	0.023
64.8	0.721	0.775	1.075	0.024	0.313	0.303	0.968	0.022
67.8	0.710	0.760	1.070	0.023	0.309	0.302	0.977	0.015
71.6	0.710	0.742	1.045	0.015	0.304	0.297	0.977	0.015
74.0	0.701	0.734	1.047	0.015	0.300	0.297	0.990	0.007
76.8	0.693	0.715	1.032	0.011	0.297	0.293	0.987	0.009
80.2	0.682	0.696	1.021	0.007	0.292	0.292	1.000	0
85.8	0.659	0.672	1.020	0.007	0.288	0.285	0.990	0.007

Table 4.13 20.02% (by weight) p-(n-pentoxybenzylidene)-p-n-butylaniline in polystyrene film, stretched to 600% elongation at 43°C, (evaluated from the absorption bands at 757 cm^{-1} and 837 cm^{-1}).

Data set II

T/°C	757 CM^{-1}				837 CM^{-1}			
	$A_\perp$	$A_\parallel$	D	S_v	$A_\perp$	$A_\parallel$	D	S_s
20.0	0.803	1.062	1.323	0.097	0.341	0.303	0.889	0.077
22.2	0.794	1.055	1.329	0.099	0.339	0.299	0.882	0.082
24.4	0.789	1.055	1.337	0.101	0.339	0.300	0.885	0.080
26.4	0.790	1.045	1.323	0.097	0.337	0.297	0.881	0.082
28.0	0.780	1.023	1.312	0.094	0.336	0.298	0.887	0.078
30.0	0.778	1.012	1.301	0.091	0.332	0.292	0.880	0.084
32.4	0.765	0.984	1.286	0.087	0.327	0.290	0.887	0.078
36.8	0.754	0.935	1.240	0.074	0.318	0.289	0.909	0.063
40.0	0.744	0.888	1.194	0.061	0.312	0.290	0.929	0.048
43.0	0.739	0.864	1.169	0.053	0.307	0.287	0.935	0.044
45.6	0.747	0.836	1.119	0.038	0.305	0.288	0.944	0.038
48.2	0.725	0.801	1.105	0.034	0.306	0.290	0.948	0.035
51.0	0.718	0.778	1.084	0.027	0.297	0.286	0.963	0.025
53.8	0.709	0.767	1.082	0.027	0.288	0.278	0.965	0.023
56.2	0.694	0.706	1.075	0.024	0.290	0.281	0.969	0.021
59.0	0.691	0.732	1.059	0.019	0.287	0.280	0.976	0.016
62.0	0.693	0.732	1.056	0.018	0.281	0.280	0.996	0.002
64.8	0.684	0.716	1.047	0.015	0.283	0.276	0.975	0.017
68.0	0.675	0.706	1.046	0.015	0.279	0.276	0.989	0.007
70.6	0.667	0.689	1.033	0.011	0.276	0.272	0.986	0.100
74.0	0.634	0.646	1.019	0.006	0.267	0.264	0.989	0.008
78.4	0.635	0.647	1.019	0.006	0.262	0.259	0.989	0.008
79.8	0.635	0.647	1.019	0.006	0.262	0.259	0.989	0.008
83.8	0.635	0.648	1.020	0.007	0.255	0.252	0.988	0.008
86.0	0.620	0.632	1.029	0.006	0.240	0.238	0.992	0.006

Table 4.14 20.00% (by weight) p-(n-hexoxybenzylidene)-p-n-butylaniline in polystyrene film, stretched to 600% elongation at 44 °C, (evaluated from the absorption bands at 757 cm^{-1} and 837 cm^{-1}).

Data set I (see Fig. 3.41 - 3.43)

T/°C	757 CM^{-1}				837 CM^{-1}			
	$A_\perp$	$A_\parallel$	D	S_v	$A_\perp$	$A_\parallel$	D	S_s
20.0	0.603	0.930	1.542	0.153	0.261	0.236	0.904	0.066
22.4	0.604	0.923	1.528	0.150	0.260	0.236	0.908	0.063
24.2	0.602	0.921	1.530	0.150	0.260	0.236	0.908	0.063
25.8	0.602	0.919	1.527	0.149	0.260	0.236	0.908	0.063
27.8	0.597	0.911	1.526	0.149	0.260	0.237	0.912	0.060
29.4	0.602	0.902	1.498	0.142	0.261	0.236	0.904	0.066
31.2	0.594	0.892	1.502	0.143	0.259	0.235	0.907	0.064
33.0	0.598	0.880	1.472	0.136	0.259	0.234	0.903	0.067
35.4	0.597	0.877	1.469	0.135	0.258	0.235	0.911	0.061
37.4	0.593	0.866	1.460	0.133	0.260	0.236	0.908	0.063
39.4	0.596	0.861	1.445	0.129	0.259	0.237	0.915	0.058
41.4	0.608	0.852	1.401	0.118	0.258	0.240	0.930	0.048
43.2	0.621	0.844	1.359	0.107	0.262	0.243	0.927	0.050
45.4	0.645	0.811	1.257	0.079	0.269	0.255	0.948	0.035
47.8	0.703	0.858	1.220	0.068	0.284	0.291	-	-
49.8	0.779	0.861	1.105	0.034	0.312	0.304	0.974	0.017
52.2	0.787	0.855	1.086	0.028	0.314	0.300	0.974	0.017
54.4	0.785	0.844	1.075	0.024	0.311	0.301	0.968	0.022
56.4	0.775	0.833	1.075	0.024	0.310	0.300	0.968	0.022
58.2	0.769	0.822	1.069	0.022	0.308	0.300	0.974	0.017
60.8	0.761	0.814	1.070	0.023	0.309	0.297	0.961	0.017
63.6	0.754	0.798	1.058	0.019	0.306	0.297	0.971	0.020
66.2	0.748	0.784	1.048	0.016	0.302	0.294	0.974	0.017
68.8	0.740	0.771	1.042	0.014	0.300	0.292	0.973	0.018
71.0	0.731	0.759	1.038	0.013	0.296	0.291	0.983	0.011
73.0	0.726	0.753	1.037	0.012	0.284	0.279	0.982	0.012
76.2	0.717	0.734	1.024	0.008	0.291	0.286	0.983	0.011
78.2	0.712	0.730	1.025	0.008	0.279	0.274	0.982	0.012
81.6	0.715	0.734	1.027	0.009	0.274	0.269	0.982	0.012
85.8	0.677	0.691	1.021	0.007	0.280	0.279	0.996	0.003

Table 4.15 20.02% (by weight) p-(n-hexoxybenzylidene)-p-n-butylaniline in polystyrene film, stretched to 600% elongation at 44°C, (evaluated from the absorption bands at 757 cm^{-1} and 837 cm^{-1}).

Data set II

T/°C	757 CM^{-1}				837 CM^{-1}			
	$A_\perp$	$A_\parallel$	D	S_v	$A_\perp$	$A_\parallel$	D	S_s
20.0	0.554	0.853	1.540	0.152	0.239	0.217	0.908	0.063
22.4	0.554	0.847	1.529	0.150	0.239	0.216	0.904	0.066
25.0	0.553	0.845	1.528	0.150	0.238	0.216	0.908	0.064
27.6	0.550	0.843	1.527	0.149	0.238	0.217	0.912	0.061
29.6	0.552	0.843	1.527	0.149	0.238	0.217	0.912	0.061
32.4	0.548	0.836	1.526	0.149	0.237	0.217	0.912	0.061
34.8	0.545	0.819	1.503	0.144	0.237	0.216	0.911	0.061
36.8	0.545	0.819	1.503	0.144	0.237	0.216	0.911	0.061
38.6	0.547	0.805	1.472	0.136	0.237	0.216	0.911	0.061
40.8	0.547	0.790	1.444	0.129	0.237	0.217	0.916	0.058
43.2	0.558	0.781	1.400	0.118	0.237	0.220	0.928	0.049
45.8	0.592	0.744	1.257	0.079	0.247	0.234	0.947	0.036
48.2	0.715	0.790	1.105	0.034	0.286	0.278	0.972	0.019
50.8	0.722	0.784	1.086	0.028	0.288	0.275	0.955	0.031
53.0	0.720	0.775	1.076	0.025	0.285	0.276	0.968	0.021
56.0	0.711	0.764	1.075	0.024	0.284	0.275	0.968	0.021
58.8	0.706	0.754	1.068	0.022	0.283	0.275	0.972	0.019
61.4	0.692	0.732	1.058	0.019	0.281	0.273	0.972	0.019
64.4	0.686	0.719	1.048	0.016	0.277	0.270	0.975	0.017
67.4	0.686	0.719	1.048	0.016	0.277	0.270	0.975	0.017
70.4	0.679	0.708	1.043	0.014	0.275	0.268	0.975	0.017
73.4	0.671	0.696	1.037	0.012	0.272	0.267	0.982	0.012
76.2	0.666	0.691	1.038	0.012	0.260	0.256	0.985	0.010
79.6	0.658	0.674	1.024	0.008	0.267	0.262	0.981	0.013
83.8	0.654	0.670	1.024	0.008	0.256	0.251	0.980	0.013
86.2	0.654	0.669	1.023	0.008	0.256	0.251	0.980	0.013

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