POLYMERIZATION AND POLYMER CHARACTERIZATION OF N-BUTYL ACRYLATE

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ABSTRACT

POLYMERIZATION AND POLYMER CHARACTERIZATION OF *N*-BUTYL ACRYLATE

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Acrylic polymers are very important commercial polymers. Poly (*n*-butyl acrylate) is used especially as adhesive, in coatings and copolymer production. The molecular weight of the polymers has significant contribution on their physical properties. Chain transfer can control molecular weight of polymers. For this reason, *n*-butyl acrylate was polymerized by gamma irradiation. The product was characterized by FT-IR and DSC techniques. The product was not soluble in common solvents. The reason can be that the polymer has a very short autoacceleration time and again crosslinked in a short time. In order to overcome this problem, chain transfer agents were used; these were benzene, acetone and acetonitrile as solvents. Chain transfer constants to these solvents were calculated. It was seen that the chain transfer constants were inversely proportional to the dielectric constants. Light scattering technique was used in molecular weight determination and it was seen that chain transfer to solvent could control molecular weight. Furthermore, by measuring viscosity of the polymer in different solvents, K and α constants were determined.

Keywords: *n*-butyl acrylate, solution polymerization, chain transfer, gamma radiation, light scattering.

ÖZ

N-BUTİL AKRİLATIN POLİMERLEŞTİRİLMESİ VE POLİMER KARAKTERİZASYONU

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Akrilik polimerleri çok önemli ticari polimerlerdir. Polibutilakrilat özellikle yapıştırıcı, kaplama ve kopolimer üretiminde kullanılır. Polimerlerin molekül ağırlıklarının fiziksel özelliklerine etkisi büyüktür. Zincir transfer işlemi polimerlerin molekül ağırlığını kontrol edebilir. Bu amaçla *n*-butil akrilat gama ışınları ile polimerleştirildi. Polimerlerin karakterizasyonu FTIR ve DSC yöntemleriyle yapıldı. Elde edilen polimer bilinen çözücülerde çözünmedi. Bunun nedeni polimerin çok kısa özivme zamanına sahip olması ve yine çok kısa sürede çapraz bağlanması olabilir. Bu problemi çözmek için çözücüye transfer birimleri kullanıldı; bunlar benzen, aseton ve asetonitril gibi çözücülerdi. Bu çözücülere transfer sabitleri hesaplandı. Transfer sabitlerinin dielektrik sabitlerine ters olarak orantılı olduğu saptandı. Molekül ağırlığı tayininde ışık saçılması metodu kullanıldı ve çözücüye zincir transferinin molekül ağırlığını kontrol edebileceği görüldü. Ayrıca polimerin değişik çözücülerdeki viskoziteleri ölçülerek K ve α sabitleri bulundu.

Anahtar Kelimeler : *n*-butil akrilat, çözelti polimerizasyonu, zincir transferi, gama ışıması, ışık saçılması

To my mother

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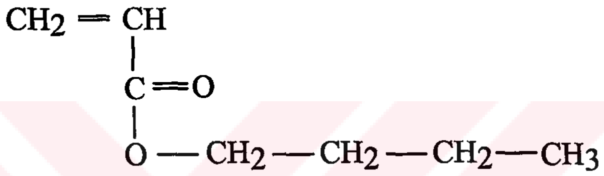
INTRODUCTION

n-butyl acrylate is the derivative of the corresponding α,β unsaturated carboxylic acid. It has the following formula :



$$\begin{array}{l} CH_2 = CH \\ \qquad\quad | \\ \qquad\quad C = O \\ \qquad\quad | \\ \qquad\quad O - CH_2 - CH_2 - CH_2 - CH_3 \end{array}$$

The monomer boils at 148 °C, freezes at -65 °C and has a density of 0.898 g/ml at 20 °C. The flash point is 49 °C and has a lower explosive limit of 1.5 %. It is a clear, colorless liquid of penetrating and disagreeable odor and is stabilized with 200 ppm of hydroquinone monomethyl ether [1].

n-butyl acrylate can be synthesized by various methods. Some of them are as follows [2,3,4] :

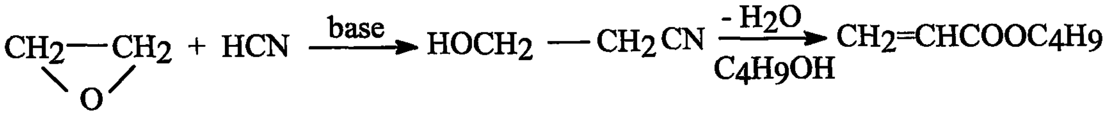
From acrylic and nonacrylic starting materials

-Dehalogenation of α,β*-dihalopropionate esters by W.Caspary and B.Tollens*

$$CH_2BrCHBrCOOC_4H_9 + Zn \rightarrow CH_2 = CHCOOC_4H_9 + ZnBr_2$$

-Dibromopropionic acid was obtained by brominating allyl alcohol, followed by oxidation.

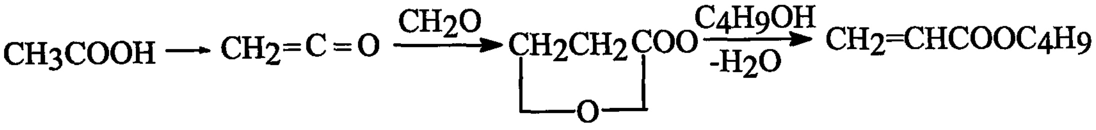
- Dehydration and esterification of ethylene cyanohydrin by Röhm and Haas



-Acetylene-carbon monoxide process by Reppe and coworkers of I.G. Farben

$$4C_2H_2 + 4C_4H_9OH + Ni(CO)_4 + 2HCl \rightarrow 4CH_2{=}CHCOOC_4H_9 + NiCl_2 + H_2$$

- Propiolactone process by Goodrich



- Acrylonitrile process

$$CH_2{=}CHCN \xrightarrow[H_2SO_4]{H_2O} CH_2{=}CHCO\overset{+}{N}H_3H\overset{-}{S}O_4 \xrightarrow[H^+]{C_4H_9OH} CH_2{=}CHCOOC_4H_9 + NH_4HSO_4$$

- Direct esterification of acrylic and methacrylic acids

- Transesterification of alcohols

$$CH_2{=}CHCOOCH_3 + C_4H_9OH \rightarrow CH_2{=}CHCOOC_4H_9 + CH_3OH$$

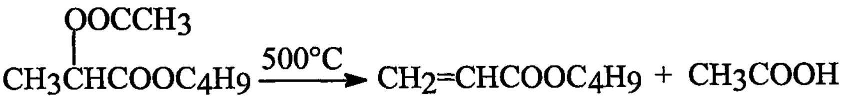
-Dehydration of hydroxypropionate esters (hydracrylic esters)

$$CH_3CHOHCOOC_4H_9 \underset{200°C}{\rightarrow} CH_2{=}CHCOOC_4H_9 + H_2O$$

- From acrylyl chloride

$$CH_2{=}CHCOCl + C_4H_9OH \rightarrow CH_2{=}CHCOOC_4H_9 + HCl$$

- Pyrolysis of acetoxy propionates derived from lactic acid



$$CH_3\underset{}{\overset{OOCCH_3}{C}}HCOOC_4H_9 \xrightarrow{500°C} CH_2{=}CHCOOC_4H_9 + CH_3COOH$$

- *From vinylidene chloride, formaldehyde and butanol*

$$CH_2{=}CCl_2 + HCHO + C_4H_9OH \xrightarrow[H_2SO_4]{} CH_2{=}CHCOOC_4H_9 + 2HCl$$

1.1 HISTORICAL BACKGROUND AND COMMERCIAL USE

Acrylic acid and acrylic esters have been known since the middle of the nineteenth century. A process for the industrial production of acrylate esters was developed in 1928 by H. Bauer of Röhm&Haas. The use of polyacrylates in many fields of application increased rapidly with the development of new methods for producing acrylic acid and acrylate esters. The first commercial acrylic polymer was produced in 1927 at the Darmstadt plant of Röhm&Haas A.G. American manufacture began at the Bristol, Pennsylvania, plant of the Rohm&Haas Co. in 1931. Emulsion polymers were first developed on an industrial scale in 1929 by H. Fikentscher and were introduced onto the market by BASF as a polymer dispersion named "Corialgrund" for the surface finishing of leather. Methyl, ethyl, *n*-butyl, and 2-ethylhexyl acrylate are produced on a large scale. Other acrylate esters such as *tert*-butyl, *iso*-butyl, or lauryl acrylate are also produced industrially, but have not yet become quantitatively important.

Although acrylic esters are in commercial use as chemical intermediates, the major portion of monomer production is converted to polymers and copolymers. The availability of a large group of esters offers the possibility of tailor-made polymers and copolymers with a wide range of physical properties suitable for a broad variety of applications. These products characteristically exhibit the same quality of film clarity and resistance to many reagents and to normal atmospheric conditions and light. The flexibility of many acrylic polymers eliminates the need for adding the plasticizers.

With the exception of *tert*-butyl acrylate, most acrylate homopolymers have extremely low glass transition temperatures. They are therefore too soft, too tacky, or have too high elongation and insufficient strength for many areas of applications. As the carbon number in the alkyl group of acrylate esters increase the softness and tackiness of the polymers increase. Poly acrylates hardly yellow under direct sunlight, because they only absorb UV radiation below 290 nm. If UV stabilizers are added, their properties do not change at all under the action of light. This is an important advantage of polyacrylates.

The industrial applications of solutions or dispersions (emulsion polymers) of acrylic ester polymers as coatings or impregnants are many and varied. In fact, the first commercial application of acrylic ester polymers, in the 1925-1930 period, was the use of acrylic polymer emulsions as base coats in the finishing of leather. The inherent stability, durability, and pigment-binding characteristics of the acrylic polymers have been important factors in the selection of such systems in the various coatings applications.

Polyacrylates are extremely resistant to oxygen, and only decompose very slowly under extreme conditions such as high temperature and in an oxygen-rich atmosphere. When heated, polyacrylates depolymerize to monomers much less readily than the corresponding polymethacrylates. They are also largely resistant to acid and alkaline hydrolysis. The longer the alkyl radical, the greater the resistance to hydrolysis.

Many important physical properties of polyacrylates and their copolymers can be varied within wide limits by a suitable choice of comonomers, auxiliaries, and polymerization process to give a large number of products for a wide variety of applications. The most important areas of application are concerned with protection, binding, and adhesion. The good pigmentability, processability and film properties, light stability and resistance to hydrolysis are the properties of polyacrylates to be used as binders for transparent and low-pigment coatings used in architectural applications. In the automobile industry, the coating systems include waterborne or low-solvent polyacrylates. Acrylic resins with hydroxyl groups are used in the clearcoat; solution polymers offer advantages as regards application, gloss, and weather resistance. In the paper industry, high-quality papers are coated with pigments to improve their printability, appearance, gloss, and other properties. Natural products (e.g., starch and casein) were first used as binders. One of the first acrylate-based dispersions, Acronal 500D, was introduced on the market in the 1950s. Laminating adhesives, pressure-sensitive adhesives, building construction adhesives, and sealing compounds are produced from polyacrylates. Homopolymers and copolymers with low glass transition temperature (usually based on 2-ethylhexyl acrylate and *n*-butyl acrylate) are used to obtain the desired tackiness. Polyacrylates are replacing natural products in pressure-sensitive adhesives (e.g., label adhesives, pressure-sensitive sheets, adhesives tapes, adhesive plasters). The advantages of polyacrylates compared with natural rubber, for example, are their better resistance to aging and temperature. Both solution polymers and dispersions are used; solution polymers have a better water resistance than dispersion adhesives. Sealing compounds are based on dispersions and must be tack-free in the dry state. One-component polyacrylate systems offer economic advantages compared with silicones. Disadvantages are their water sensitivity and poor adhesion to glass and ceramics. In the textile industry polyacrylates are used almost exclusively as emulsion polymers (e.g., as binders for pigment dyeing or printing). The treated textiles generally have to be resistant to washing and drycleaning; this is achieved by crosslinking the polyacrylates after film formation. Polyacrylates are also used as binders for textile flocking to produce velvety surfaces. In addition, fabrics may be coated with water-resistant dispersions (e.g., wax cloth and umbrella material). Polyacrylates, mainly emulsion polymers, are used in many minor areas: for example, as sizes in the production of textile and glass fibers; as polishes for floor coverings, automobiles and shoes; and as additives for hydraulic binders. Polyacrylates are used as additives in mortar and concrete, as well as in agriculture for seed protection and spraying with fertilizers. They are also employed as matrices for ion exchangers crosslinked with divinylbenzene [1,5-8]

1.2. PROPERTIES OF POLY (N-BUTYL ACRYLATE) AND IMPORTANCE OF POLYACRYLATES

Most of the physical and chemical properties of the polyacrylates can be related to the glass-transition temperature as well as their viscosity and molecular weight. The values of T_g pass through a minimum in polyacrylates as the length of the side chain of the ester is increased. The brittle points or softening points of the polymers follow the same general trend. Poly(*n*-butylacrylate) has a density of 0.898 g/ml at 20°C, its glass transition temperature is -43 °C and refractive index is 1.474 at 28°C.

The ability of polyacrylates to copolymerize with other monomers has been found extensive use in industrial applications because of their extensively low T_g's. Polymers for specific applications can be produced by copolymerization with monomers whose homopolymers have high glass transition temperatures (e.g.,styrene, acrylonitrile, methylmethacrylate, ethylmethacrylate). In general, the acrylate esters in copolymers produce an "internal plasticization" of the polymers, resulting in improved toughness, increased tensile strength, increased tear and impact strengths, and improved processibility. The use of acrylate esters in copolymers has an important contributions to the improved stability toward heat and light. These properties provide the acrylic polymers a unique position among the synthetic resins.

Poly(methyl acrylate) films have a relatively low elongation at break and an extremely high rupture strength at room temperature. The elongation of poly(ethyl acrylate) films is greater and the rupture strength is considerably lower. Poly(ethyl acrylate) is elastic and almost rubberlike. The elongation of poly(*n*-butyl acrylate) is extremely high and the rupture strength is very low; the films are not elastic, but exhibit viscous flow even at small elongation and cannot be freely handled.

Poly(methyl acrylate) is not tacky at room temperature, poly(ethyl acrylate) is only slightly tacky. Poly (*n*-butyl acrylate) is however extremely tacky. Tackiness depends on the molecular mass: tacky films can be produced from poly(ethyl acrylate) with a very low molecular mass, whereas tack-free films can be produced from poly(*n*-butyl acrylate) of very high molecular mass. Increasing chain length of the alcohol residue ($>C_8$) causes the tackiness to fall and they no longer act as internal plasticizer for the main polymer chain.

The polyacrylates become increasingly "dry" and elongation at break decreases due to crystallization of the n-alkyl chain. For example, poly(*n*-hexadecyl acrylate) is waxy and rigid at room temperature although the degree of polymerization obtained are low. The softer, more rubberlike quantities of the polyacrylate esters can be attributed in part to greater chain coiling and flexibility, resulting from a less balanced chain segment than in the methacrylate ester polymers, perhaps with easier rotation of segments about the main chain.

The isomerism also have a marked influence of the shape of the side alkyl group. Poly *n*-butyl acrylates are soft elastomers, whereas the *iso*-butyl polymers are considerably harder at room temp. *Sec*-butyl acrylate polymers are still harder, approaching poly(methyl acrylate)s. Polymeric *t*-butyl acrylates are tough, nearly rigid solids at room temperature and were the hardest uncrosslinked alkyl acrylate polymers examined by Neher [8].

The production of polyacrylates has become increasingly important since 1969. Butyl acrylate showed average growth rates around 7.3 % between 1969 and 1984.

Most polyacrylates are produced by emulsion polymerization. In the United States the proportions of solution polymers is 12%. Although the proportion of solution polymers (which are largely used for coatings and adhesives) may well fall, they will not be completely replaced by emulsion polymers. The use of polyacrylates in the adhesives and paper industries is substantially higher in Europe than in the US. The mean annual growth rate in the consumption of polyacrylates for 1984-1989 is estimated to be 3.3 % for US and 2.8 for Europe; speciality fields have the highest growth rates.

1.3 POLYMERIZATION OF ACRYLATES

Until recently, all polymerizations of acrylic ester monomers were carried out by free radical processes; these remain the predominant synthetic route in industrial manufacture. The polymerizations can be performed in homogeneous media, either in bulk or in solution, or in heterogeneous media, either emulsion or suspension.

1.3.1 Bulk and Solution Systems

1.3.1.1 Chemically Initiated Polymerization

Chemical initiation using peroxides, hydroperoxides, and azo catalysts is the normal procedure in polymer manufacture. These compounds are soluble in acrylic ester monomers and permit control of the reaction and the molecular weight of the product by selection and concentration of initiator and (for solution processes) solvent and the concentration of monomer, and by the temperature. Azo compounds are especially convenient because of their high initiating efficiency; their decomposition rates are relatively independent of solvent and concentration. Their nonoxidizing nature avoids the formation of occasional peroxide crosslinks that may result from induced secondary decomposition of peroxidic initiators and that may cause ultimate deterioration of the polymer product. Hydroperoxide are subject to chain transfer, thus lowering the molecular weight and reducing the efficieny of the initiator.

1.3.1.2. Bulk Polymerization

Bulk polymerization is a process in which the monomer is polymerized in bulk form (usually liquid) with merely the addition of initiating substances and the application of heat, UV light or high-energy radiation. The method is notable chiefly for the absence of added substances. There is, thus, no problem of separating the polymer from solvents or from dispersion media. There are no solvents present during the polymerization reaction to act as chain transfer agents and thereby to reduce the molecular weight of the product. The acrylate polymers are soluble in their monomers at all stages of conversion. Here there is no question about initiation occuring in the monomer because the system contains nothing but the monomer. As the polymerization progresses, the viscosity increases noticeably, and the propagation takes place in a medium of associated polymer chains dissolved in, or swollen by, the monomer until the monomer is consumed. Termination in a free-radical bulk polymerization can occur in two ways: by the combination of two growing chains or by chain transferring. When the viscosity is high, the termination reaction is hindered, since the macroradicals are unable to diffuse readily in the viscous medium. In contrast, the monomer may diffuse readily and high molecular weight macroradicals are produced as the result of propagation in the absence of termination. This autoacceleration, called the Norrish-Trommsdorff or gel effect causes the formation of unusually high molecular weight polymers. The dissipation of the heat of polymerization becomes an increasing problem as the viscosity increases, the product is likely to be of variable structure owing to local increases of temperature which may occur, and the polymer which is produced in the latter stages of the reaction is often highly branched or crosslinked.

Burlant et al. studied crosslinking and degradation in γ-irradiated poly *n*-alkyl acrylates including *n*-butyl acrylate. They examined also the effects of irradiation temperature (-196 to 56 °C). Crosslinking, was found to occur predominantly on the alkyl side chain, is independent of temperature above and below the polymer softening point, but is severalfold higher for irradiations above the softening point. This reflects the importance of segmental mobility of radiation produced polymer radicals in the crosslinking step [10].

The bulk polymerization of monomeric acrylic esters on a commercial scale has been, limited primarily to the production of cast sheets of methyl methacrylate polymer. This process requires careful control of the polymerization, particularly during the accelerated stage in order to obtain a bubble-free product with good optical clarity and other properties desired. The principal difficulties are removal of dissolved gases, adjustment for the shrinkage in volume and adequate control of the highly exothermic polymerization reaction in the early stages, especially after the material has reached the gel consistency.

1.3.1.3. Solution Polymerization

Because of the difficulty of dissolving polymers of the acrylic esters prepared by bulk polymerization, they may also be polymerized in solution using good or poor solvents for homogeneous and heterogeneous systems, respectively. Solvents with low chain-transfer constants should be used whenever possible to minimize reduction in molecular weight. The method is especially suited to the preparation of polymers of low to medium molecular weight. High molecular weight polymers are not only difficult to prepare by solution polymerization, but the high viscosity of the solutions of such polymers makes the handling of them difficult and costly. While telogens decrease molecular weight, the molecular weight and the rate of polymerization are independent of the polarity of the solvent in homogeneous solution systems.

Solvents used in the polymerization may be a good solvent for the monomer as well as for the polymer. If it is, then the end-product of the reaction is a solution of polymer in solvent; if it is not, then the polymer precipitates from the system as it forms, and the result is a slurry of polymer. Under the former circumstance, the polymerization system will remain fluid over the whole course of the reaction, if sufficient solvent is present. In the latter case, the reaction system is, in part at least, heterogeneous.

The principal reason for using a solvent is to prevent the polymerizing system from becoming intractably viscous during the course of the reaction. The problem of heat dissipation is thereby mitigated to some extent. Beside these advantages, the process of solution polymerization has a number of serious disadvantages as the requirement of expensive, toxic and often inflammable solvents. Separation of the polymer from the solvent is necessary at the end of the reaction unless, of course, the polymer precipitates during the reaction, thereby forming a slurry. A further disadvantage is that the molecular weight of the product may be seriously reduced by the reaction of transfer to solvent. For simple reactions uncomplicated by branching and crosslinking, it is found that, for a given concentration of active centers, the reciprocal degree of polymerization of the product varies linearly with the ratio of solvent to monomer. The slope of the relationship depends upon the chemical nature of the solvent. In particular, halogenated hydrocarbon solvents are especially prone to participation in transfer reactions.

Raghuram et al. [11] studied the chain transfer of alcohols in the polymerization of methyl, ethyl and butyl acrylates. They determined the transfer constants from the thermal polymerization at 80 °C utilizing mixed-solvent system wherever necessary. They observed that the chain transfer constant for alcohols is not much affected by lengthening of the ester group in the acrylates, and the reactivities of the solvent is enhanced by an increased substitution at the α-carbon atom in the alkyl group.

1.3.1.4. Thermal Polymerization

Certain monomers including acrylates, that have been carefully purified and freed of all possible initiators, will still polymerize at elevated temperatures. This is believed to be due to thermally induced decomposition of monomers to radicals. The rates for such reactions appear to be smaller than those with chemical initiators. When no catalyst is added, thermal initiation of acrylates is of relatively low order of magnitude. Attempts to determine the thermal rate of polymerization of acrylates have run into difficulties because of trace materials in the monomers which act as initiators. However, thermal effects can usually be neglected in the study of catalyzed polymerizations. During organic or polymerization reactions of the common acrylic esters, thermal polymerization at high temperatures probably results from boiling out the dissolved oxygen which is part of the inhibitory system or from the presence of adventitious initiators [8,12-15].

1.3.1.5.Initiation of Polymerization with Radioactive Sources and Electron Beams

The types of high-energy radiation which have been used to initiate free radical chain reactions include principally α-particles (fast moving helium ions), β-rays (fast electrons), and γ- and *x*-rays. These forms of energy are so powerful that the mechanism and the result of their interaction of matter are usually quite different than that of ultraviolet light. Most often, the energy absorbed by the molecule is so excessive that an electron is not just excited into a higher energy state, but it is completely ejected from the molecule, and for this reason, these types of high energy radiation are frequently referred to as ionizing radiation.

Electron ejection and ionization of a stable molecule produces a radical-cation containing one unpaired electron and a positive charge (1). In equation (1) the symbol

$$AB \rightsquigarrow AB^{\cdot\oplus} + e \tag{1}$$

$\rightsquigarrow$ is used in keeping with the convention for designating a primary act caused by the absorption of radiation. Such ion-radicals are often unstable, and may dissociate (2) into

$$AB^{\cdot\oplus} \longrightarrow A^{\oplus} + B^{\cdot} \tag{2}$$

a free radical and a cation, but this dissociative process can also occur in the same step in which the electron, *e*, is ejected from the molecule (3).

$$AB \rightsquigarrow A^{\oplus} + B^{\cdot} + e \tag{3}$$

If the electron doesn't have excessive energy it will be attracted back to the cation, and the net result will be the production of two free radicals. Otherwise, the ejected electron will eventually be trapped by a neutral molecule to form (4) either a radical-anion or to

$$AB + e \longrightarrow AB^{\cdot\ominus} \tag{4}$$

cause (5) molecular dissociation and generate one radical and one anionic species. The net effect, therefore, of the ejection of one electron by ionizing radiation can be to produce two free radicals, one cationic fragment, and one anionic fragment.

$$AB + e \longrightarrow A^{\cdot} + B^{\ominus} \tag{5}$$

Charge neutralization may occur before dissociation and excited molecules rather than free radicals will be formed (6). If the primary energy absorption causes only

$$AB^{\cdot\oplus} + CD^{\cdot\ominus} \longrightarrow AB^{*} + CD^{*} \tag{6}$$

promotion of an electron to an excited state in the molecule, (7), then subsequent

$$AB \rightsquigarrow AB^{*} \tag{7}$$

reactivity of the excited molecule will often be the same as that of photochemically excited molecules. Excited molecules may show several different types of reactions before quenching can occur, including: *(a)* dissociation into free radicals (8), sometimes

$$AB^{*} \longrightarrow A^{\cdot} + B^{\cdot *} \tag{8}$$

producing hot radicals, that is, radicals containing a large excess of energy, which may undergo reactions different from radicals produced by thermal dissociation, *(b)* dissociation into stable molecular products (9), and *(c)* direct reaction with other

$$AB^* \longrightarrow C + D \tag{9}$$

molecules (10) by some mechanism other than the transfer of energy (sensitization).

$$AB^* + CD \longrightarrow \text{Products} \tag{10}$$

Radiation-initiated polymerization reactions of vinyl monomers are generally, but not always, free-radicalic reactions. The effect of free-radical inhibitors and the results from copolymerization and kinetic studies indicate that the polymerization of most vinyl monomers in the liquid state proceeds by a free radical mechanism. In contrast, there is good evidence that, for some vinyl and diene monomers in solution at very low temperatures or in the solid state, the mechanism of initiation and propagation is ionic. [16].

1.4. THEORETICAL BACKGROUND OF THE KINETICS

Kinetic studies and rate coefficients of free radicalic polymerizations are both scientific interest and technical importance. According to the classical kinetic treatment of radical polymerization, the rate of polymerization is directly proportional to monomer concentration and to the square root of initiator concentration. The proportionality factor is the overall rate constant. For several monomers, however, the orders with respect to initiator and monomer concentration are different from the theoretical values. For acrylic acid esters, the literature shows great deviations in the order with respect to monomer [17,18,19].

Buback et al. studied the free radical polymerization of *n*-butyl acrylate between 25 and 80 °C at pressures up to 2500 bar. They measured the reaction by applying excimer laser techniques in conjunction with time-resolved high pressure near infrared spectroscopy. They obtained rate coefficients of propagation, k_p, and termination, k_t, for and extended temperature, pressure and conversion range [19].

Kamachi et al. measured the propagation and termination rate constants k_p and k_t for the radical polymerization of *n*-butyl acrylate initiated by biacetyl using the rotating-sector method, in various solvents at 30 °C [20].

From the studies of Subrahmanyam et al. [21], it appears that the monomer order increases and initiator order decreases as the length of the alkyl chain is increased. The overall rate constant decreases and the activation energy increase, as the alkyl chain is increased [22].

In the study of copolymerization kinetics of systems having butyl acrylate as one of the comonomers, a significant lack of knowledge of the homopolymerization rate constants for *n*-butyl acrylate has been noted [23].

1.4.1. Polymerization Rate

The initiator, I, decomposes into two free radicals, R•, via the following scheme :

$$I \xrightarrow{k_d} 2R\cdot \tag{1}$$

k_d is a temperature dependent rate constant for initiator decomposition. The decomposition proceeds with an efficiency, *f*. The radicals, also known as primary radicals, add to monomer *M* as follows:

$$R\cdot + M \xrightarrow{k_i} M\cdot \tag{2}$$

If k_d and *f* are known, k_i is not required. The rate of initiation is then given by:

$$R_i = 2fk_d\left[I\right] \tag{3}$$

In the propagation step, a monomer unit adds to an active site on a growing radical chain and the active site is transferred to the terminal unit on the chain.

$$R_r\cdot + M \xrightarrow{k_p} R_{r+1} \tag{4}$$

The rate of polymerization is defined as

$$R_p = k_p[M][M\cdot] \tag{5}$$

The growing radical may, at some point in the reaction, transfer its active center to a small molecule (T), such as solvent, monomer, initiator, impurity, or chain transfer agent (CTA). Thus, the polymerization is terminated prematurely, creating a shorter (dead) polymer molecule of length r (P_r). The transferred radical may or may not continue to react. This is shown below:

$$\begin{gathered} M_r\cdot + T \xrightarrow{k_{fT}} P_r + T\cdot \\ T\cdot + M \xrightarrow{k_{pI}} R_I\cdot \end{gathered} \tag{6}$$

In a way analogous to the transfer of the active center to small molecules, the active center may transfer to a dead polymer chain, thus creating branched instead of linear polymers. The reaction proceeds as follows:

$$M_r\cdot + P_s \xrightarrow{k_{fp}} P_r + M_s\cdot \tag{7}$$

Chain transfer to polymer in emulsion polymerization of *n*-butyl acrylate by ^{13}C

-NMR and GPC was studied by Lovell et al [24].

Another cause of long chain branching (trifunctional or tetrafunctional) is the reaction of a growing polymeric radical with a dead polymer molecule containing a terminal or internal double bond, as shown below:

$$M_r\cdot + P_s \xrightarrow{k_p} M_{r+s} \tag{8}$$

Should a growing radical chain not undergo any transfer reaction, it will eventually terminate when it encounters another growing radical chain end. The active centers coming together may terminate either by combining to form a larger polymer molecule, or disproportionating to form two separate dead polymer molecules one with an unsaturated end bond of $CH=CH_2$. The reactions are shown below :

$$\begin{gathered} M_r\cdot + M_s \xrightarrow{k_{tc}} P_{r+s} \\ M_r\cdot + M_s \xrightarrow{k_{td}} P_r + P_s \end{gathered} \tag{9}$$

The termination rate R_t is defined as

$$R_t = k_t\left[M\cdot\right]^2 \tag{10}$$

A steady-state hypothesis can be applied, stating that $R_I \cong R_t$, or that the total radical concentration is as follows:

$$[M\cdot] = (R_I / k_t)^{1/2} \tag{11}$$

The termination rate constant, is not really a constant, but changes with the viscosity of the reaction medium. In other words, k_t is diffusion-controlled [23]. The rates of the three steps may be written in terms of the concentrations (in brackets) of the species involved and the rate constants. The rate of initiation is

$$R_i = \left[\frac{d[M\cdot]}{dt}\right]_i = 2fk_d[I] \tag{12}$$

where the factor *f* represents the fraction of the radicals formed by eqn. (1) that is succesful in initiating chains formed by eqn. (2), the factor 2 comes from availability of 2 radicals from each homolytic dissociation. The rate of termination is

$$R_t = -\left[\frac{d[M\cdot]}{dt}\right]_t = 2k_t[M\cdot]^2 \tag{13}$$

In the polymerization system when the reaction starts, the concentration of forming free radicals from dissociation of initiator increase. Suppose the concentration of all types of free radicals is

$$[M\cdot] = \sum[RM_n\cdot] \tag{14}$$

From eqn.(9) it can be seen that the destruction rate of radicals in the termination step is proportional with the square of the concentration of radicals. After a very short time from the start of reaction, the radicals are formed and destroyed at identical rates. In this step, the steady-state concentration of radicals is achieved. Each termination reaction results destruction of two polymer radicals, it can be written;

$$R_i = (2k_{tc} + 2k_{td})[M\cdot]^2 \tag{15}$$

The rate of propagation is essentially the same as the overall rate of disappearance of monomer, since the number of monomers used in eqn.(2) must be small compared to that used in eqn.(4) if polymer is obtained. Then,

$$\frac{-d[M]}{dt} = R_p = k_p[M][M\cdot] \tag{16}$$

From eqn. (15) and (16)

$$R_p{}^2 = \frac{[M]^2 k_p{}^2 R_i}{2(k_{tc} + k_{td})} \tag{17}$$

If we replace R_i in the above equation with that was defined in eqn. (12) into eqn. (17) we obtain ;

$$R_p{}^2 = \frac{k_p{}^2 f k_d}{(k_{tc} + k_{td})}\,[I][M]^2 \tag{18}$$

If we call all the termination reactions as k_t then R_p ;

$$R_p = k_p[M]\left(\frac{f k_d [I]}{k_t}\right)^{1/2} \tag{19}$$

In the polymerizations that are initiated by catalyst, for the reaction rate, R_p , the following relation is obtained.

$$R_p{}^2 = K^2[I][M]^2 \tag{20}$$

Then we can write it as

$$R_p = \frac{-d[M]}{dt} \approx K[I]^{1/2}[M] \tag{21}$$

From eqn.(8), it can be understood the polymerization rate is in the first order with respect to monomer concentration. In the case of polymerizations where the percent conversion is low, it can be written approximately;

$$\frac{-d[M]}{dt} \approx \frac{-\Delta[M]}{\Delta t} \tag{22}$$

Also, $[M]$ and $[I]$ can be assumed to be equal to the initial concentration $[M]_0$ and $[I]_0$, and for the experimental rate constant

$$K = -\frac{\Delta M}{\Delta t}\frac{1}{[I]_0^{1/2}[M]_0} \tag{23}$$

can be found. The eqn. (21) can be integrated in the form as follows

$$log\left([M]_0/[M]\right) = \frac{K[I]_0^{1/2}t}{2.303} \tag{24}$$

In this case, conversion-time data should be plotted as $log\,[M]$ vs. time. The intercept of the line will give us $log\,[M]_0$ and the slope $K[I]_0^{1/2}/2.303$.

The suggestion was first advanced by Flory [25] that in vinyl polymerization processes a reaction may occur which limits the growth of polymer molecules, without reducing the number of active centers. It can be assumed that the chain length of the polymer is controlled by a reaction of the type

$$R_r\cdot + M \rightarrow P_r + M\cdot$$

in which the activity of the growing radical is transferred to a monomer molecule, yielding a radical $M\cdot$. The above reaction may be visualized as taking place in either of two ways, depending on whether the polymer radical transfers an atom to the monomer or *vice versa*. It is reasonable to infer that a similar transfer of activity from polymer radicals can also be made to molecular species other than monomer, and in fact Flory [25] was able to point to previously published results on polymerizations in the presence of solvents which indicated that transfer to solvents must take place. Such a reaction can be represented by

$$R_r\cdot + S \rightarrow P_r + S\cdot$$

where S is a molecule of solvent, or some species other than monomer, from which an atom (of hydrogen, for example) can be abstracted by a polymer radical. The radicals newly formed from the solvent molecules may then continue the kinetic chain by resumption of propagation reactions

$$S\cdot + M \rightarrow R_1\cdot$$
$$R_1\cdot + M \rightarrow R_2\cdot \text{ , } etc.$$

fragments of solvents (or transfer agent) being incorporated into the polymer molecules as end groups [6].

The degree of polymerization is therefore

$$\bar{P}_n = \frac{rate\ of\ growth}{\sum rates\ of\ all\ reactions\ leading\ to\ dead\ polymers}$$

$$\frac{1}{\bar{P}_n} = \frac{fk_d[I] + k_{tr,M}[M][M\cdot] + k_{tr,S}[S][M\cdot] + k_{tr,I}[I][M\cdot]}{R_p} \qquad (25)$$

where the terms in the numerator represent termination by combination and transfer to monomer, solvent, and initiator, respectively. If termination is by disproportionation, the first term becomes $2fk_d[I]$. If transfer constants are defined as

$$C_M = \frac{k_{tr,M}}{k_p}, \qquad C_S = \frac{k_{tr,S}}{k_p}, \qquad C_I = \frac{k_{tr,I}}{k_p} \qquad (26)$$

then (assuming termination by combination)

$$\frac{1}{\overline{P}_n} = \frac{k_t}{k_p}\frac{[M\cdot]}{[M]} + C_M + C_S\frac{[S]}{[M]} + C_I\frac{k_t}{fk_d}\frac{[M\cdot]^2}{[M]} \qquad (27)$$

in other words in terms of R_p ;

$$\frac{1}{\overline{P}_n} = \frac{k_t}{k_p^2}\frac{R_p}{[M]^2} + C_M + C_S\frac{[S]}{[M]} + C_I\frac{k_t}{k_p^2 fk_d}\frac{R_p^2}{[M]^3} \qquad (28)$$

The above analysis assumes that the radical formed in the transfer process is approximately as reactive as the original chain radical, otherwise retardation or inhibition results.

In the presence of a solvent, and by properly choosing conditions to keep other types of chain transfer to a minimum, eqn. (27) reduces to

$$\frac{1}{\overline{P}_n} = \left(\frac{1}{\overline{P}_n}\right)_0 + C_S\frac{[S]}{[M]} \qquad (29)$$

where $(1/\overline{P}_n)_0$ combines the polymerization and transfer to monomer terms. There is a linear dependence of $1/\overline{P}_n$ on $[S]/[M]$.

Chain-transfer agents with transfer constants near unity are quite useful in depressing molecular weight in polymerization reactions. This is often of great commercial importance. The choice of transfer constant near unity ensures that the transfer agent, or *regulator*, is consumed at the same rate as the monomer so that $[S]/[M]$ remains constant throughout the reaction. Too large quantities are needed of chain-transfer agents with constants much lower than unity, and agents with transfer constants greater than about 5 are used up too early in the polymerization [26,27].

1.5. POLYMERIZATION OF N-BUTYL ACRYLATE

The most commonly used polymerization technique of butyl acrylate is the emulsion polymerization. The success of this technique is due in part to the fact that this method yields high molecular weight polymers. In addition, the polymerization rate is usually high.

In 1961 Richard W. Rees [28] worked on emulsion polymerization of butyl acrylate for use in coatings. He mixed butyl acrylate monomer, water, and small portions of SO_2 and tertiary alkyl aromatic hydroperoxide forming a stable aqueous emulsion of the monomer. A small portion of a H_2O-sol. polymerization catalyst is also added. After continuous stirring and heating as necessary the polymerization takes place.

In 1969 John W. Vanderhoff [29] polymerized butyl acrylate by aqueous emulsion technique without use of catalyst in the presence of pulsed electromagnetic radiation.

In the last decade starting from 1985, especially I. Capek and his colleagues worked on emulsion [30,31] and microemulsion [32,33] polymerization of butyl acrylate.

Also the polymerization of butyl acrylate using different catalysts and initiators have been found special interest. P. Lambrinos et al. [34] worked on the BA polymerization initiated with N,N-Diethyl Dithiocarbamate derivatives. E. Ihara et al.

[35] studied living anionic polymerization using rare-earth-metal complexes as catalyst.

Anionic polymerizations can also be initiated in an electric field. B.Z.Lubentsov et al. electrosynthesized butyl acrylate [36].

N-butyl acrylate can also be polymerized using high-energy radiation, ^{60}Co source, especially for coating uses. T. Sasuga et al. [37] and N.V. Fomina and coworkers [38] studied the radiation-induced polymerization of *n*-butyl acrylate

Hayashi et al. [39] studied the polymerization of *n*-butyl acrylate and other acrylates in a wide range of dose rate, 10-10^6 rad/s by γ-ray and electron beam irradiation. They examined the steady-state kinetics.

Recently, Matyjaszewski et al. [40] published a paper about the polymerization of *n*-butyl acrylate by atom transfer radical polymerization in 1998. They studied the effects of ethylene carbonate and other solvents on it.

1.6 AIM OF THIS WORK

In this study, the polymerization of butyl acrylate was carried out by radiation. This monomer is expected to be polymerized with a high rate to high molecular weight when initiated by radiation. In order to obtain products that are processible and have controled molecular weight, the polymerization was carried out in bulk and in solution. In the last case, the chain transfer to solvent was caused a decrease in molecular weight. Therefore, polymerization in different solvents was examined to observe the effect of solvents, dielectric constants and other natural effects. The molecular weights of samples were measured by viscosity method. However, the K and α values in Mark-Houwink-Sakurada equation were determined by light scattering technique. The comparison with the results obtained for ethyl acrylate was done.

CHAPTER 2

EXPERIMENTAL

2.1 PURIFICATION OF MATERIALS

2.1.1 Purification of Monomer

Reagent quality *n*-butyl acrylate, *n*-BA, (Merck) was distilled under reduced pressure. The freshly distilled sample was used for polymerization.

2.1.2 Solvents

Acetonitrile, benzene, dichloromethane, toluene, acetone were all reagent grade and used without further purification. Reagent quality acetone (Surechem Product Ltd.) was distilled once for the light scattering measurements.

2.2 INSTRUMENTATION

2.2.1 Irradiation tubes

They were 1-3 cm. in diameter, 10 cm. in length Pyrex tubes. The open ends of the Pyrex irradiation tubes were attached to another tube of smaller diameter, which allows to be connected to the vacuum line easily.

2.2.2 Radiation Source

Irradiation were made in "220 Model Gamma Cell" product of "Atomic Energy of Canada Ltd. Co.". In this gamma source unit the cobalt (12400 curie in April, 1968) is in the forms of cylinders and placed around a hollow cylinder into which the sample is introduced by means of the moving drawer; spiral tubes through the drawer allow wires and samples to be led into irradiation cavity without the escape of irradiation. The dose rate of source was about 15 krad/h. during the experiments.

2.2.3 High Vacuum System

High vacuum system was used to evacuate the irradiation tubes containing the monomer at 10^{-4} to 10^{-5} mmHg pressures for about 5-6 hours. It was consisted of the following parts:

a) Duo-Seal Vacuum Pump

It was a product of "Sargent-Welch Scientific Co." model 1399 and capable of pressure reduction and down to 1.5×10^{-2} mmHg.

b) Mercury Diffusion Pump

It was a water-cooled one stage diffusion pump with an approximate of capacity of 200 ml of mercury. Mercury was heated by a 143 W metallic bond resistive heater operating at 130 V which is a product of "Pilz Co." type 62.

c) Main Manifold

A Pyrex glass tube of length 110 cm., diameter 4.53 cm. was employed. It was connected to the first trap by a high vacuum stopcock and to the sample holder tubes to high vacuum stopcocks with standard joints.

d) Liquid Nitrogen Traps

Two Pyrex traps were used to protect the pumps from the chemicals evaporated at low pressures and placed before the connection of each pump.

2.2.4 Viscometer

Viscosities of polymer solutions were measured in acetone, toluene and dichloromethane by using Ubbelohde glass viscometer.

2.2.5 Infrared Spectrometer

Infrared spectrum of monomer and the obtained polymers were taken from KBr pellets by using two different spectrometers.

1) Nicolet 510 FT-IR Spectrometer
2) Mattson 1000 FTIR Spectrometer

2.2.6 Differential Scanning Calorimetry

The thermal analysis of the samples were recorded by TA-DSC 910S differential scanning calorimeter. Heating rate was 5 °C/min. from -100 to 300 °C under nitrogen atmosphere.

2.2.7 Light Scattering

Molecular weight of poly(*n*-butylacrylate) was determined by light scattering method.

Zimm plot was obtained using Dawn B Laser Photometer produced by Wyatt Technology Corporation.

2.3 EXPERIMENTAL PROCEDURE

2.3.1 Radiation-Induced Bulk Polymerization

Radiation-induced polymerization of *n*-butyl acrylate in bulk was studied at room temperature using ^{60}Co γ-source. For this purpose, purified monomer was placed into irradiation tubes, made of pyrex glass and connected to high vacuum system. Sample tubes were evacuated for about 6 hours at 10^{-4} to 10^{-5} mmHg.

The removal of dissolved oxygen from monomers is of particular importance in careful theoretical studies. As a matter of fact, it is very possible that many of the contradictory and irreproducible observations in polymer kinetics may be attributed to variations in the quantity of residual oxygen in the monomers under study. The method of removing dissolved oxygen is not particularly difficult, although it is troublesome.

The unhibited *n*-butyl acrylate monomer is placed in a heavy-walled vessel fitted with a suitable stopcock which in turn is attached to a high-vacuum train. The stopcock is closed and the monomer is frozen in liquid nitrogen. Then the stopcock is opened to the high-vacuum system and the vessel evacuated with an oil-diffusion pump while maintaining the monomer in a frozen condition. When the high-vacuum gauge indicates a constant low pressure in the system, the stopcock is closed and the monomer is allowed cautiously to thaw. After reaching room temperature and when ebullition has subsided, the monomer is refrozen. Then the stopcock is opened to the vacuum system again and the space above the solid monomer is again evacuated. This procedure is repeated at least four times. After finally returning the monomer to room temperature, the glass apparatus is sealed with a torch so that it will no longer expose it to oxygen. It is best to protect the monomer from excessive exposure to daylight throughout this procedure.

2.3.2 Solution Polymerization

The polymerization of *n*-butyl acrylate in different solvents was studied at room temperature and under vacuum. 2 ml solutions of *n*-butyl acrylate at 20,30,40,50,70 % concentrations were prepared in acetonitrile, acetone, benzene. The radiation-induced solution polymerization of *n*-butyl acrylate in different solvents was carried out similar to bulk polymerization. The polymer formed at the end of irradiation and the residual monomer was removed by evaporation in a draft and then in a vacuum oven up to constant weight. Polymer yield for samples was determined gravimetrically.

2.3.3 Molecular Weight Determination

The methods employed most frequently to determine the molecular weights of polymer in solution are

I. Freezing Point Depression or Boiling Point Elevation ($\overline{M_n}$)
II. Vapor Pressure Lowering ($\overline{M_n}$)
III.Osmotic Pressure ($\overline{M_n}$)
IV.End Group Analysis ($\overline{M_n}$)
V. Viscosity ($\overline{M_v}$)
VI.Gel Permeation Chromatography ($\overline{M_n}, \overline{M_w}$)
VII.Light Scattering ($\overline{M_w}$)
VIII.Sedimentation ($\overline{M_z}$)

In this work both viscosity and light scattering method was applied to determine the molecular weight of polymers.

2.3.3.1 Viscosity Measurement

In viscosity method, flow time for certain volume of solvent and solution are compared. If the flow time for the solvent is t_0 and that of solution is t, relative viscosity, η_r , is

$$\eta_r = \frac{t}{t_0}$$

specific viscosity, η_{sp} , in terms of η_r

$$\eta_{sp} = \eta_r - 1 = \frac{t - t_0}{t_0}$$

The experiment is repeated by diluting the sample solution several times. If specific viscosity over concentration (η_{sp} / c) is plotted against concentration, the intercept of the straight line gives intrinsic viscosity [η]. The concentration in this case is in terms of g/100 ml. The relation between molecular weight and intrinsic viscosity known as Mark-Houwink-Sakurada equation is as follows:

$$[\eta] = KM^{\alpha}$$

where; K and α are constants depending on the nature of the solvent and temperature. For poly(*n*-butyl acrylate) the relation of degree of polymerization to the viscosity in acetone solution at 25 °C was reported [41] :

$$\overline{P_n} = 2.774 \times 10^3 [\eta]^{1.333}$$

In these experiments, Ubbelohde type of glass viscometers were used and all viscosity measurements were done at 25 °C by using acetone, toluene and dichloromethane as solvent.

2.3.3.2 Light Scattering Measurement

Molecular weight determination of poly(*n*-butyl acrylate) was carried out by light scattering measurements in solutions having the concentration range 18.10^{-4}- 9.10^{-4} g/ml by using Zimm Method. Acetone was used as solvent in the solutions. Solutions were dedusted by filtration two times through filtering crozets having pore size 3 μm. The dn/dc value for acetone-poly(*n*-butyl acrylate) system were taken from Immergut's Polymer Handbook.

The light scattering measurement were carried on Dawn B photometer from Wyatt Technology Co., that use a laser as light source. The Dawn B photometer, is a multiangle light-scattering photometer for the analysis of relatively large samples (10 cm^3) in batch mode. The sample is placed in a cuvette at the center of the stage and is illuminated by a fine laser beam. The cuvette stage is surrounded by an array of fifteen detectors with high-gain photodiodes. The detector angles are set equidistantly in $\sin(\theta/2)$ from 0.2 to 0.9. Employing the multiangle detectors, the measurement time for static light scattering is reduced by between 30 and 90 % compared with measurements using a scanning type apparatus. The analysing software AURORA allows one automatically to estimate $\overline{M}_w$, $<s^2>_z$ and A_2 by Zimm plots.

CHAPTER 3

RESULTS AND DISCUSSION

3.1. POLYMERIZATION OF *n*-BUTYL ACRYLATE IN BULK

n-Butyl acrylate was polymerized by γ-irradiation. The polymerization was carried at room temperature in bulk form by γ-irradiation. The percent conversions versus time for polymerization at room temperature are given in Table 3.1. The percent conversions against irradiation time are plotted in Fig. 3.1. The change of percent conversion with irradiation time shows slight autoacceleration character at room temperature. The conversion reaches to 100 % as limiting value. The induction period was observed as in most of the radiation-induced polymerization. The polymer obtained was partially soluble up to a certain extent and insoluble after this. About 67 % of the obtained polymer is insoluble after 88 % conversion, and nearly 100 % is insoluble in most common solvents at about completion of polymerization.

Table 3.1 The % conversion vs. time results for bulk polymerization of *n*-ba

Time (min.)	% conversion
0	0
10	1.72
20	11.32
30	15.34
40	29.19
50	40.78
60	57.47
70	65.34
80	78.58
90	82.06
100	87.65
110	92.24
120	95.91
130	96.02

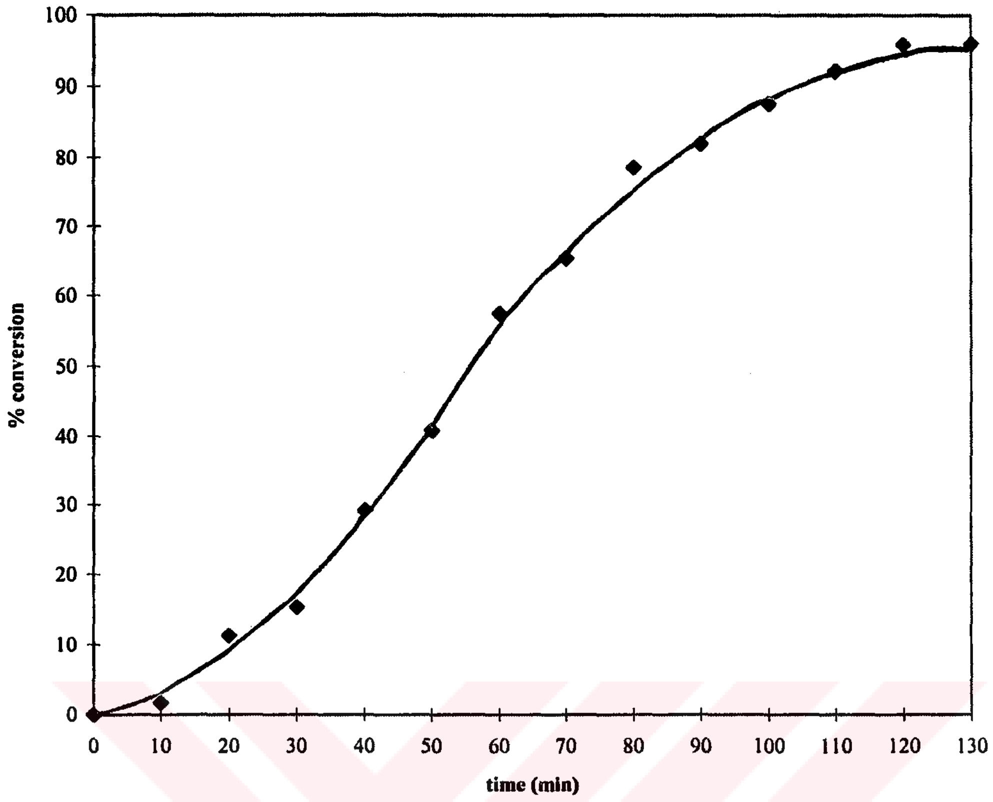


Fig. 3.1 % conversion vs. time graph for bulk polymerization of *n*-ba

This autoacceleration behavior can be explained by the gel effect. The polymer yield increases almost linearly with time up to 25 % conversion and then R_p increases significantly. In the initial stage, up to a critical conversion and an abrupt increase in R_p the polymerization proceeds smoothly at a constant rate, which follows the steady state kinetics. At the intermediate stage, autoacceleration of R_p takes place because of the reduction in the termination rate constant due to the viscosity increase in the reaction medium. In the final stage, R_p is greatly decreased with conversion because of the difficulty of monomer diffusion and the polymerization ceases at a limiting conversion, leaving immobilized radicals in the system. This autoacceleration, Norrish-Trommsdorff or gel effect, causes the formation of unusually high molecular weight polymers.

The rate constant was calculated by the application of the kinetic equation 24. log (M_0/M) is plotted against t. The results are shown in Table 3.2 and the plot is shown in Fig. 3.2. The slope of this line gives us rate constant. Rate constant is calculated as 0.00540. It is around the same value compared with ethyl acrylate which is 0.00426 [42].

Table 3.2 Time vs. log (M_0/M) results

Time (min)	log (M_0/M)
0	0
10	0.0075
20	0.052
30	0.072
40	0.15
50	0.23

The molecular weight of polymer samples could not be determined because they were insoluble in common solvents. Polymerization of *n*-butyl acrylate initiated by radiation was also carried out in open atmosphere at room temperature. The relation between % conversion and irradiation time was not regular and the results were not reproducible and consistent.

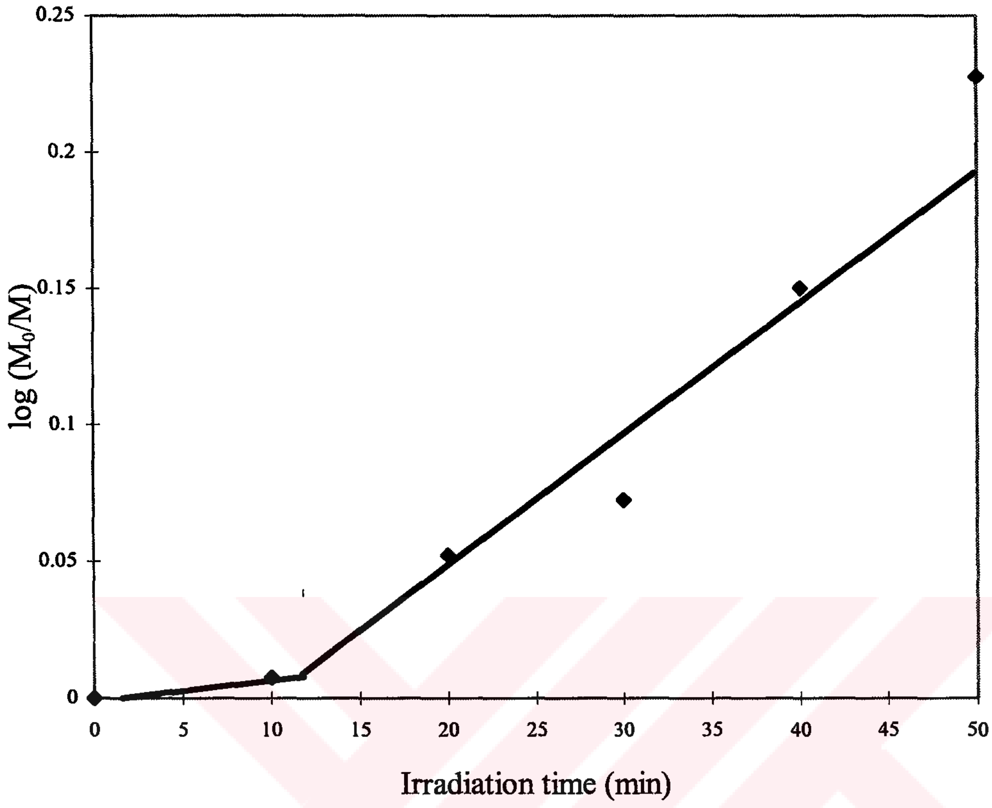


Fig. 3.2 log (M_0/M) vs. irradiation time graph for *n*-butyl acrylate

3.2. Polymerization of n-butyl acrylate in solution

The polymer obtained by bulk polymerization was not soluble in common solvents because of high molecular weight and perhaps crosslinking. This problem was overcome by performing solution polymerization in order to have a better control on molecular weight.

The chain transfers to different solvents were achieved. The solvent choice was due to their dielectric constants in order to study the effect of the polarity of the medium to the chain transfer constant.

Solutions of 20, 30, 40, 50 and 70 % (w/w) *n*-butyl acrylate and solvents were polymerized by γ-radiation for an irradiation time of 75 min. at room temperature. The type of solvent, percentages of monomer, % conversion, dielectric constants and viscosity average molecular weights of the polymer samples obtained are given in Table 3.3.

The percent conversion follows the following trend; highest in acetonitrile > acetone > lowest in benzene. This is entirely related with their dielectric constants. This result does not agree with that of ethyl acrylate [42]. The relations between dielectric constants and percent conversion were not regular as shown in Table 3.4.

In all cases, the percent conversions were lower than the conversion in bulk polymerization. From Table 3.1. the percent conversion in bulk polymerization for 75 min. at room temperature, between 65 and 78 %, which is much more larger than any of the polymerization performed in solution given in Table 3.3.

Several factors were discussed about the solvent effect on the k_p values of some vinyl monomers [43]. It was claimed by Imoto et al. [44] that the charge-transfer from the monomer to the polymer radical plays an important role in the propagation.

Table 3.3 Experimental results after solution polymerization of *n*-ba in some solvents

% *n*-butyl acrylate	% conversion	dielectric constant ε	$\overline{M}_v \times 10^{-6}$
poly (*n*-butyl acrylate) in benzene			
19.88	5.02	2.28	0.74
30.08	9.69		1.73
39.86	10.69		3.03
49.29	14.86		4.39
70.31	16.42		4.85
poly (*n*-butyl acrylate) in acetone			
20.03	16.07	20.70	0.66
29.95	19.97		1.30
39.88	23.01		2.04
49.52	25.06		2.74
68.33	32.36		4.43
poly (*n*-butyl acrylate) in acetonitrile			
19.88	22.50	36.0	0.73
30.00	27.15		1.12
39.40	30.88		1.40
49.94	39.93		2.03
69.93	43.92		3.78

Table 3.4 Experimental results for solution polymerization of ethyl acrylate [42]

50 % ethyl acrylate in	% conversion	dielectric constant ε	$\overline{M_v} \times 10^{-6}$
benzene	15.0	2.28	4.8
acetone	36.0	20.70	4.7
acetonitrile	13.0	36.0	2.2

Such a charge-transfer should make the transition state more polar compared with the reactants. So, the polymerization would be accelerated in polar solvents. Donor-acceptor interaction between the propagating polymer radicals and solvents was also reported to be a dominant factor of the solvent effect on k_p in the polymerizations of vinyl esters, acrylates and methacrylates [45]. The interaction is known to be pronounced in aromatic solvents. Kamachi et al. found that the variation of k_p with solvent is larger in the polymerizations of acrylates than in those of methacrylates [20]. The propagating radicals of the latter are considered to interact less favorably with the solvent owing to sterical requirement of the methyl group at the terminal radical center. Thus in the present system, it is assumed that the type of such interaction operate and exerts some effect on k_p. The interaction of polymer chain with solvent also possibly affects the k_p value. The solubility parameter may be able to be used as a rough measure of such interaction. The polymer chains are extended in good solvents, whereas they are contracted in poor solvents. The radical center of the growing polymer chain appears to be more crowded with the bulky *n*-butyl group in poorer solvents. Such crowding suppresses the propagation, leading to a lower k_p. The solubility parameters of the solvents and the polymer was taken from *Immergut's Polymer Handbook* and given in Table 3.5.

Table 3.5 Solubility parameters of the solvents and the polymer

Solvent	$\delta_{solvent}$ (cal/cm^3)$^{1/2}$	$\delta_{polymer}$ (cal/cm^3)$^{1/2}$
benzene	9.2	7-12.7 poor
acetone	9.9	7.4-12.1 moderate
acetonitrile	11.9	9.5-12.7 strong

As the above Table supports the R_p , it can be now understood better why the percent conversion is higher in acetonitrile, moderate in acetone and smaller in benzene with the other supporting idea.

The molecular weight of polymers obtained in all solvents were quite high ($>5\times10^4$ up to 5×10^6). Differences in molecular weights can not be explained with the differences either in percent conversion or dielectric constant of the solvents. Therefore, there are more factors relating to nature of solvents affecting the percent polymerization of *n*-butyl acrylate and the molecular weights of polymer obtained.

The results for polymerization of *n*-butyl acrylate are given in Table 3.6. The polymerization was in benzene and it was irradiated 75 min.

Table 3.6 Experimental results for the solution polymerization of *n*-butyl acrylate in benzene for irradiation time of 75 min.

Run no	% *n*-BA	[S]/[M]	% conversion	[η] dl/g	$\overline{M}_v \times 10^{-6}$	$1/\overline{P}_n \times 10^5$
1	19.88	6.61	5.02	1.41	0.74	17.32
2	30.08	3.81	9.69	2.74	1.73	7.41
3	39.86	2.48	10.69	4.24	3.03	4.23
4	49.29	1.69	14.86	5.66	4.39	2.92
5	70.31	0.69	16.42	6.12	4.85	2.64

The molecular weights were calculated from the measured viscosities by using the Mark-Houwink-Sakurada equation $[\eta]=KM^{\alpha}$ having $K=3.73\times10^{-5}$ and $\alpha=0.78$ as constants calculated from light scattering measurements as described in section 3.4. The percent polymerization was calculated gravimetrically. The percent conversion against percent *n*-BA in benzene is shown in Fig. 3.3.

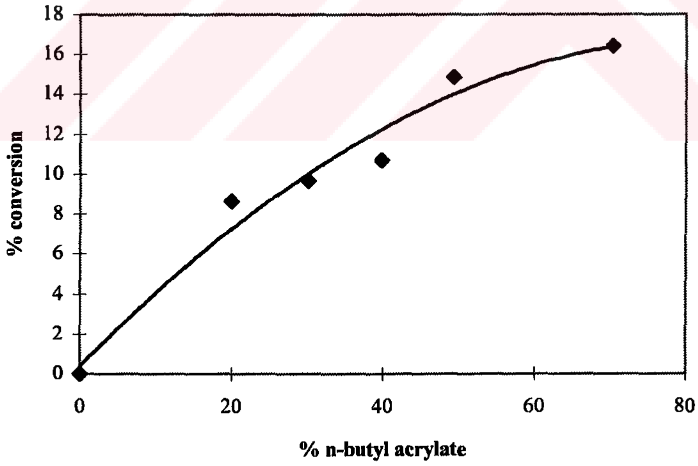


Fig.3.3 The plot of % conversion against % *n*-BA in benzene solution

The percent conversion increases with % *n*-BA, rapid increase at the beginning and constant increase up to completion takes place. The values of $1/\overline{P}_n$ against [S]/[M] are plotted in Fig. 3.4. C_s is found from the slope of the straight line that is 2.59×10^{-5}.

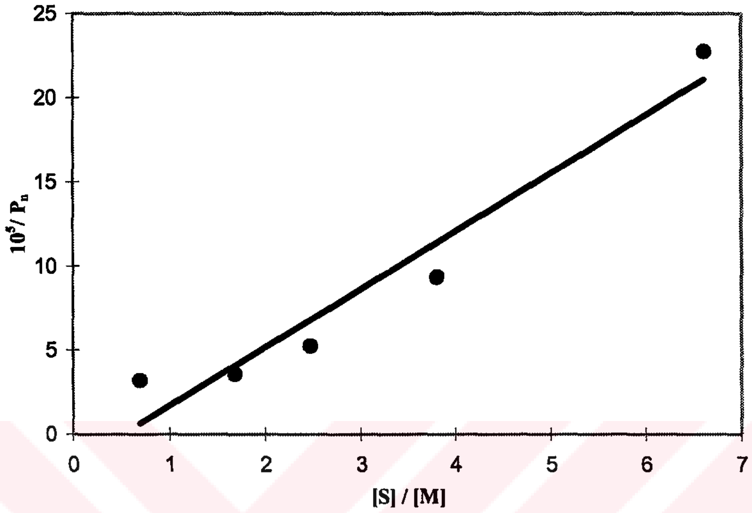


Fig. 3.4 The plot of $1/\overline{P}_n$ against [S]/[M] for *n*-BA in benzene solution

The results for the polymerization of *n*-BA in acetone by irradiation of 75 min. γ-radiation are given in Table 3.7.

Table 3.7 Radiatio*n*-induced polymerization of *n*-BA in acetone at room temperature irradiated for 75 min.

Run no	% *n*-BA	[S]/[M]	% conversion	[η] dl/g	$\overline{M}_v \times 10^{-6}$	$1/\overline{P}_n \times 10^{5}$
1	20.03	8.81	16.07	1.29	0.66	19.42
2	29.95	5.16	19.97	2.19	1.30	9.86
3	39.88	3.33	23.01	3.12	2.04	6.28
4	49.52	2.25	25.06	3.92	2.74	4.68
5	68.33	1.02	32.36	5.70	4.43	2.89

The percent conversion against percent *n*-BA in acetone solution is given in Fig. 3.5

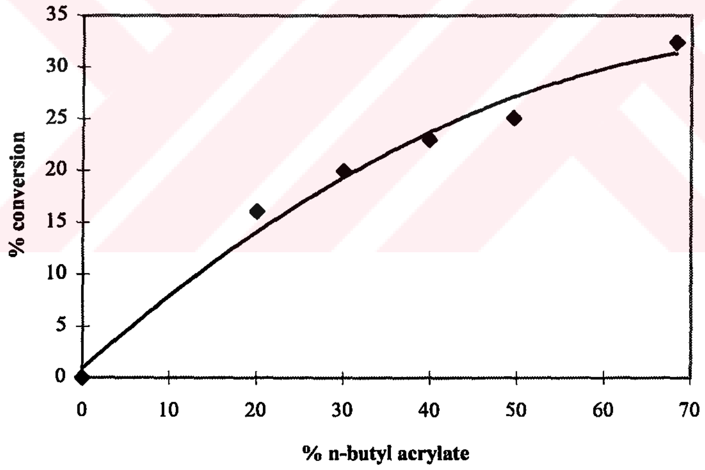


Fig. 3.5 The plot of % conversion against % *n*-BA in acetone solution

Again % conversion increases with increasing % *n*-BA up to a limiting conversion. The values of $1/\overline{P}_n$ against [S]/[M] are plotted in Fig. 3.6

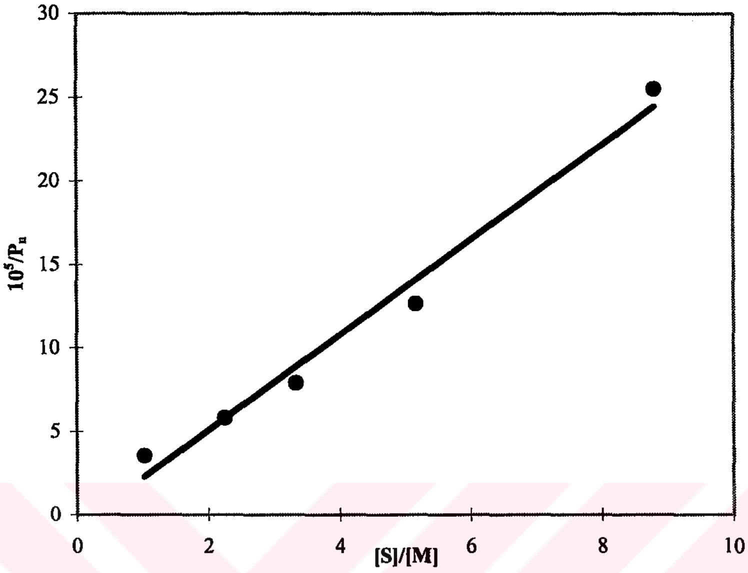


Fig. 3.6 The plot of $1/\overline{P}_n$ against [S]/[M] for *n*-BA in acetone solution

A straight line is obtained. The value of C_s determined from the slope of the straight line in Fig. 3.6 is 2.14×10^{-5}.

The results for the polymerization of *n*-BA in acetonitrile by irradiation of 75 min. are given in Table 3.8.

Table 3.8 Radiation-induced polymerization of *n*-BA in acetonitrile at room temperature irradiated for 75 min.

Run no	% *n*-BA	[S]/[M]	% conversion	[η] dl/g	$\overline{M}_v \times 10^{-6}$	$1/\overline{P}_n \times 10^5$
1	19.88	12.59	22.50	1.40	0.73	17.56
2	30.00	7.28	27.15	2.04	1.12	11.44
3	39.40	4.80	30.88	4.08	1.40	9.16
4	49.94	3.13	39.93	5.07	2.03	6.31
5	69.93	1.34	43.92	7.28	3.78	3.39

The % conversions against % *n*-BA are given in Fig. 3.7 for 75 min. irradiation.

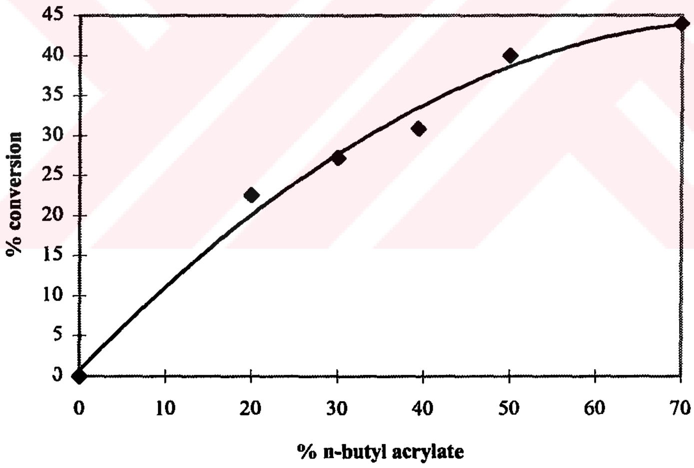


Fig. 3.7 The plot of % conversion against % *n*-BA in acetonitrile solution

This curve shows quite similar character like the others. In the initial stage up to a limiting conversion, and an abrupt increase in % conversion takes place finally the polymerization ceases at a limiting conversion.

The values of $1/\bar{P}_n$ against [S]/[M] are plotted in Fig. 3.8

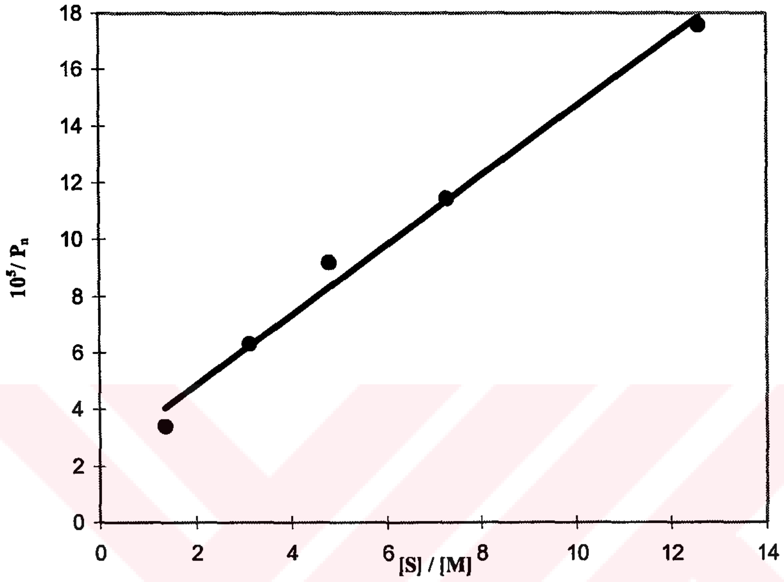


Fig. 3.8 **The plot of $1/\bar{P}_n$ against [S]/[M] for *n*-BA in acetonitrile solution**

The chain transfer constant to solvent C_s determined from the slope of straight line is 1.23×10^{-5} for the polymerization of *n*-BA in acetonitrile initiated by radiation. The correlation factor in all plots is near 0.99. This shows that the results are successful. In literature these transfer constant are not available. The only constants related with PBA are chain transfer to some alcohols [11] and they can be seen in Table 3.9.

Table 3.9 Chain transfer constants of alcohols in the polymerization of acrylic esters at 80 °C [11].

Solvent	*n*-butyl acrylate		
	[S]/[M]	$10^4/P_n$	$C_s \times 10^4$
Methyl alcohol	0.18	2.38	0.47
	0.44	2.54	
	0.89	2.77	
	1.33	2.96	
Ethyl alcohol	1.22	6.97	4.28
	2.45	12.23	
	3.06	14.81	
Propyl alcohol	0.96	5.22	3.78
	1.92	8.85	
	2.40	11.65	
	2.84	12.70	
Isopropyl alcohol	0.94	14.60	14.12
	1.87	26.30	
	2.34	34.20	
	2.81	42.70	

3.3 MOLECULAR WEIGHT DETERMINATION BY LIGHT SCATTERING TECHNIQUE

The light-scattering method has been extensively applied to determine the weight average molecular weight, $\overline{M}_w$, as well as the molecular dimensions of polymer molecules and the degree of polymer-solvent interaction in polymer solutions. The amount of experimental work is greater than that involved in osmotic methods (e.g. more complicated purification procedures) but is justified by the wealth of information obtained. The spatial expansion, i.e. radius of gyration and/or end-to-end distance of the dissolved macromolecules and their geometric shape can be determined from the angular dependence of the scattering intensity of the light scattered by a polymer solution. The theoretical basis of light scattering from polymer solutions was first established by Zimm et al. [46] in the 1940's. They derived a relation between the intensity of scattered light from the polymer solution and the $\overline{M}_w$, size and shape of the solute molecule in the solution.

In light scattering investigations, one measure the reduced scattering intensity at a scattering angle θ, R_θ, sometimes referred to as Rayleigh's ratio, which is defined as:

$$R_\theta = i_\theta r^2/(I_0 V) = I_\theta/(I_0 V)$$

$$I_\theta = i_\theta r^2$$

where; i_θ is the intensity of scattered light per unit area ($erg.s^{-1}.cm^{-2}$) at a distance (r) of the observer from the sample solution with volume V; I_0 is the intensity of the incident beam and I_θ the radiant intensity of the scattered light ($erg.s^{-1}$ per unit solid angle).

For a dilute solution consisting of a monodisperse polymer with molecular weight $\overline{M}_w$ and a solvent, R_θ is expressed by :

$$\frac{Kc}{R_\theta} = \frac{1}{\overline{M_w}} + \frac{1}{\overline{M_w}} \cdot \frac{16}{3}\pi^2 \frac{<s^2>_z}{\lambda^2}\sin^2\frac{\theta}{2} + 2A_2c\cdots\cdots$$

where K is the optical constant, c is the concentration, A_2 is the second virial coefficient, $<s^2>_z$ is radius of gyration and λ is the wavelength of the incident beam in the solution. If we derive the eqn. step by step, we obtain,

$$\lim_{c\to 0}\frac{Kc}{R_\theta} = \frac{1}{\overline{M_w}} + \frac{1}{\overline{M_w}} \cdot \frac{16}{3}\pi^2 \frac{<s^2>_z}{\lambda^2}\sin^2\frac{\theta}{2}$$

$$\lim_{\theta\to 0}\frac{Kc}{R_\theta} = \frac{1}{\overline{M_w}} + 2A_2c$$

or

$$A_2 = \frac{1}{2}\lim_{c\to 0}\left\{\frac{d}{dc}\left(\lim_{\theta\to 0}\frac{Kc}{R_\theta}\right)\right\}$$

and

$$<s^2>_z = \overline{M_w}\frac{3}{16}\cdot\frac{\lambda^2}{\pi^2}\lim_{\theta\to 0}\left\{\frac{d}{d\sin^2\frac{\theta}{2}}\left(\lim_{c\to 0}\frac{Kc}{R_\theta}\right)\right\}$$

In order to estimate $\overline{M_w}$, $<s^2>_z$ and A_2 from experimental data of R_θ versus c for solutions at various scattering angles θ at constant temperature, it is convenient to use a graphical method, proposed by Zimm [47]. In this method, Kc/R_θ is plotted against $(\sin^2(\theta/2)+kc)$, where k is an arbitrary constant chosen to produce a reasonable spread of data points. In Zimm's method, $<s^2>_z$ and A_2 are estimated from the relations of

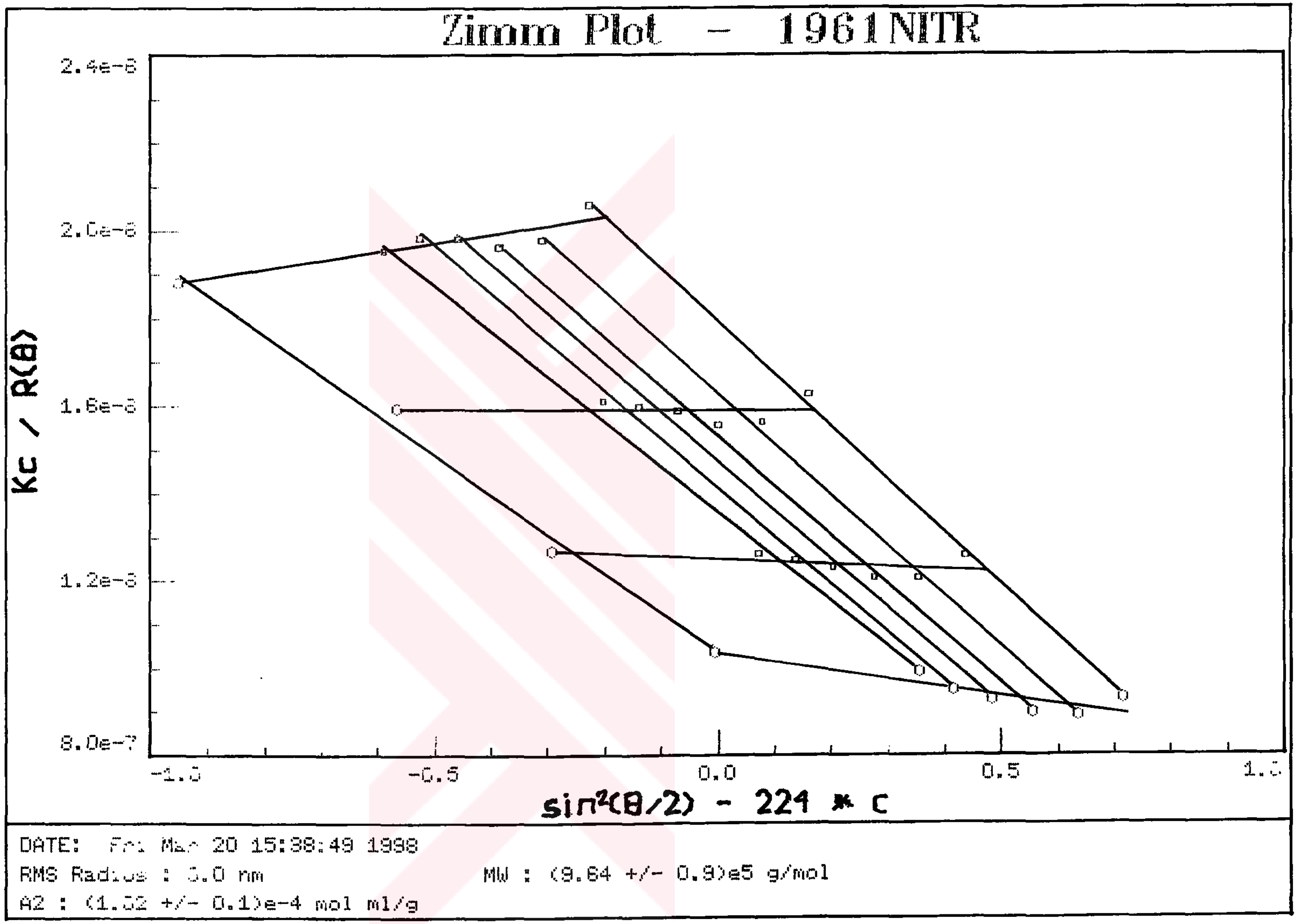
$\lim_{c\to0} Kc/R_\theta$ versus $\sin^2(\theta/2)$ and $\lim_{\theta\to0} Kc/R_\theta$ versus c, respectively that was given before. $\overline{M_w}$ is obtained as the inverse of the value of the intercept of a line of $\lim_{c\to0} Kc/R_\theta$ at $\theta=0°$ or that of a line of $\lim_{\theta\to0} Kc/R_\theta$ at c=0. It should be noted that the intercepts of the two lines coincide with each other. Zimm's procedure is a double extrapolation method.

Viscosity and light scattering measurements have been carried out with poly(*n*-butyl acrylate). For the diluted solutions of the polymer in acetone, toluene and dichloromethane at 25 °C, the constant K and the exponent α of the function $[\eta]=KM^\alpha$ have been calculated from the measured values. Acetone seems to be a good solvent for PBA whereas dichloromethane and toluene are moderate solvents. This graduation is made obvious by the values of the exponent α. The results can be seen in Table 3.10. Weight average molecular weights were determined automatically by the software used in laser photometer. No further calcultions were performed. The final Zimm plots can be seen in Fig. 3.9-3.12.

Table 3.10 Viscosity-Mwt. relation of poly (*n*-butyl acrylate)

Percentage of *n*-ba in acetonitrile during polymerization	Solvent	Intrinsic Viscosity (dl/g)	$\overline{M}_v \times 10^{-6}$	[a]$\overline{M}_w \times 10^{-6}$
19.61	acetone	1.62	0.88	0.96±0.09
	dichloromethane	2.34	0.74	
	toluene	2.40	0.79	
28.27	acetone	2.43	1.48	1.36±0.1
	dichloromethane	3.72	1.46	
	toluene	3.81	1.46	
47.09	acetone	4.45	3.22	2.88±0.6
	dichloromethane	6.56	3.37	
	toluene	6.84	3.19	
67.57	acetone	7.04	5.81	6.14±1.0
	dichloromethane	8.44	4.88	
	toluene	9.93	5.24	

a: Found by light scattering at room temperature using acetone as solvent.



```
DATE:   Fri Mar 20 15:38:49 1998
RMS Radius : 0.0 nm                 MW : (9.64 +/- 0.9)e5 g/mol
A2 : (1.02 +/- 0.1)e-4 mol ml/g
```

Fig. 3.9 Zimm Plot of 19.61 % *n*-butyl acrylate dissolved in acetone

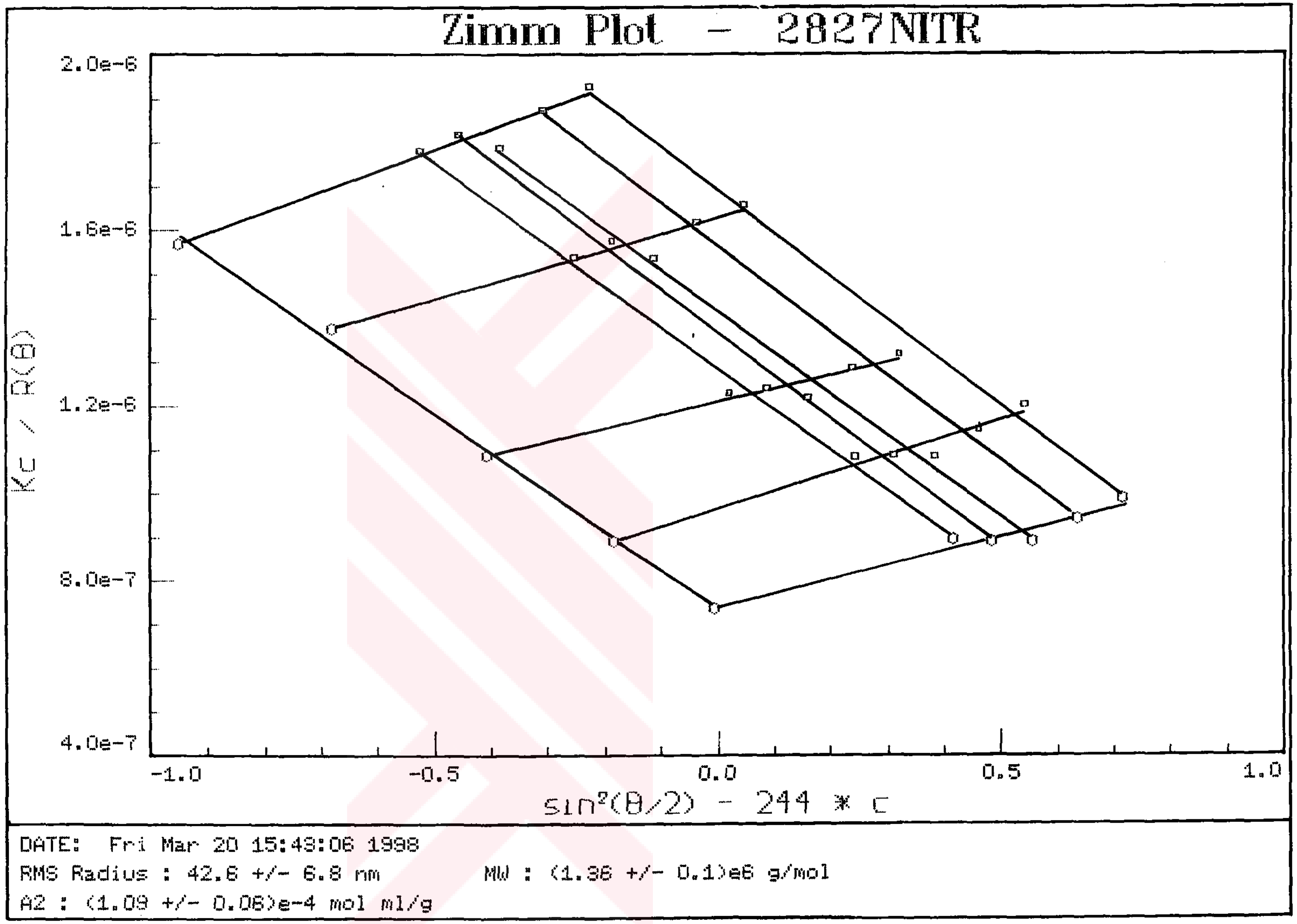
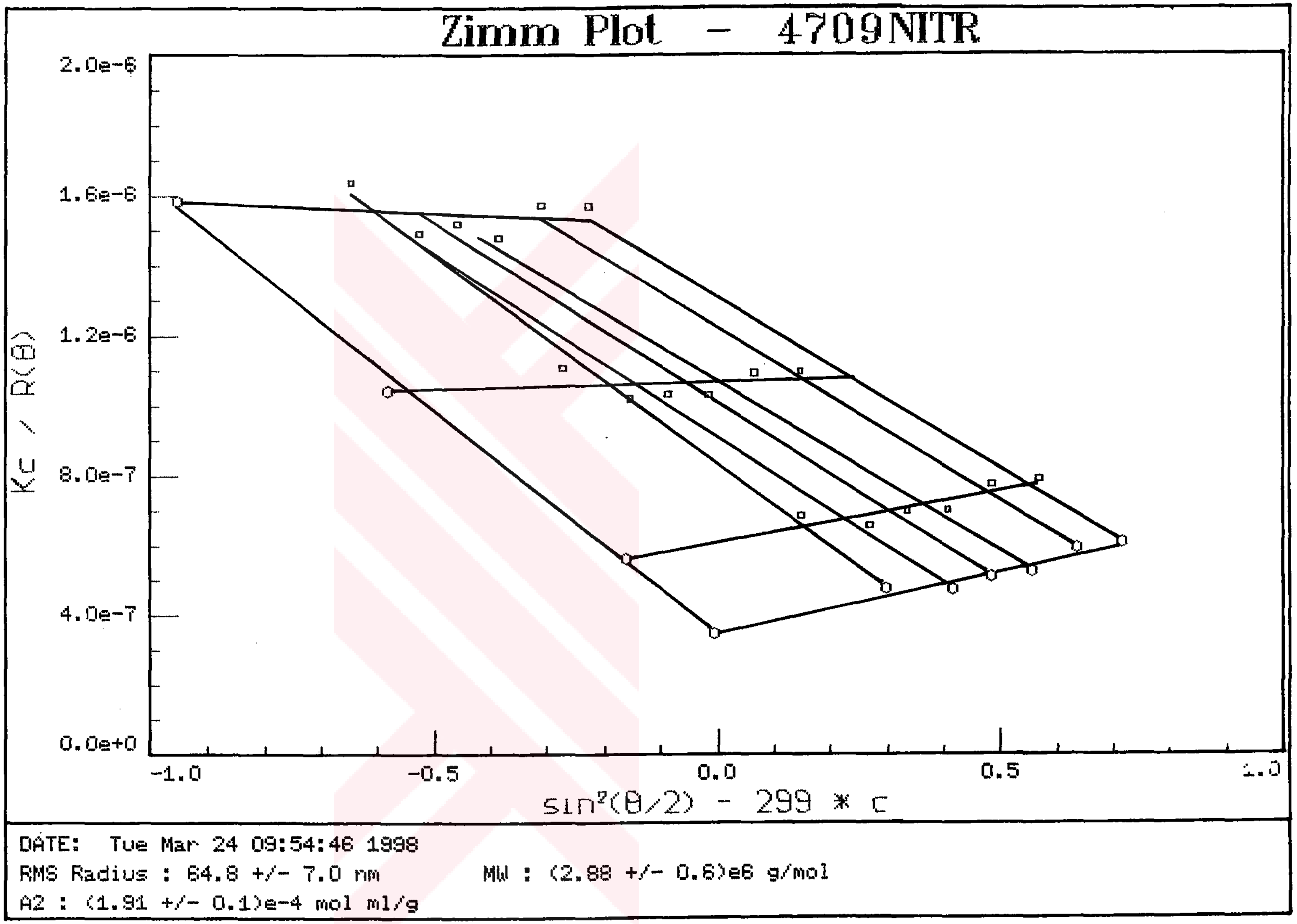


Fig 3.10 Zimm Plot of 28.27 % *n*-butyl acrylate dissolved in acetone



DATE: Tue Mar 24 09:54:46 1998

RMS Radius : 64.8 +/- 7.0 nm MW : (2.88 +/- 0.6)e6 g/mol

A2 : (1.91 +/- 0.1)e-4 mol ml/g

Fig 3.11 Zimm Plot of 47.09 % *n*-butyl acrylate dissolved in acetone

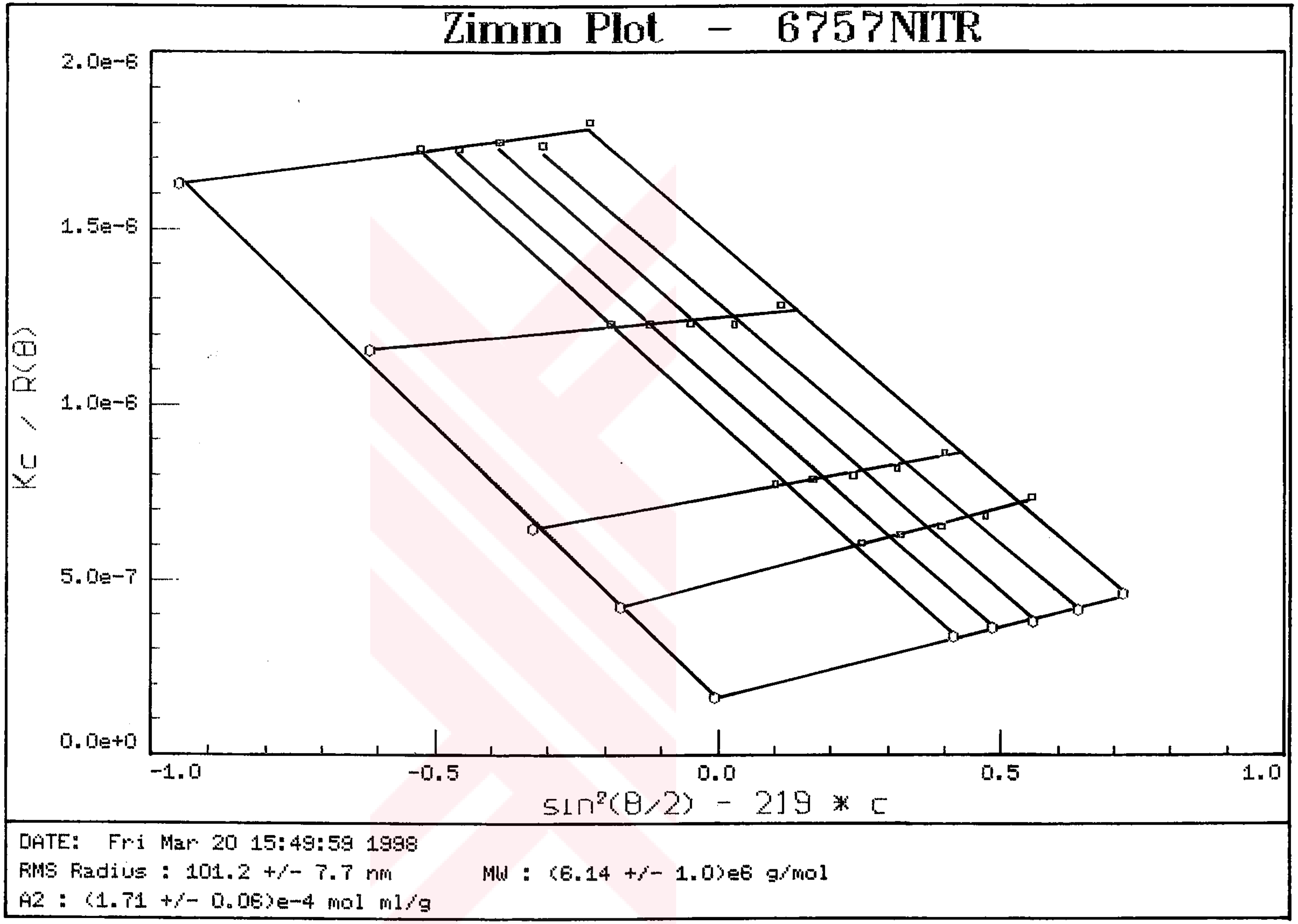


Fig 3.12 Zimm Plot of 67.57 % *n*-butyl acrylate dissolved in acetone

3.3.1 Determination of K and α constants from light scattering measurements

Four polymer samples of different molecular weights dissolved in acetone. Acetone was chosen as solvent because of high refractive index increment. The weight average molecular weights were determined by Zimm plots. $<s^2>_z$ and A_2 were also calculated.

From the Mark-Houwink-Sakurada eqn.,

$$[\eta]=KM^{\alpha}$$

if we take the logarithms of both side we obtain

$$\log[\eta] = \alpha \log \overline{M}_w + \log K$$

If we plot log [η] versus log ($\overline{M}_w$), we obtain α from the slope and log K from the intercept. The results for different percentages of *n*-ba dissolved in acetone are given in Table 3.11 and the log-log plot is given in Fig. 3.13.

Table 3.11 Results obtained for *n*-ba dissolved in acetone

$\overline{M}_w \times 10^{-6}$	η (dl/g)	log $\overline{M}_w$	log η	α	K×10^5 (dl/g)
0.96	1.62	5.984	0.211	0.78	3.73
1.36	2.43	6.134	0.385		
2.88	4.45	6.459	0.649		
6.14	7.04	6.788	0.848		

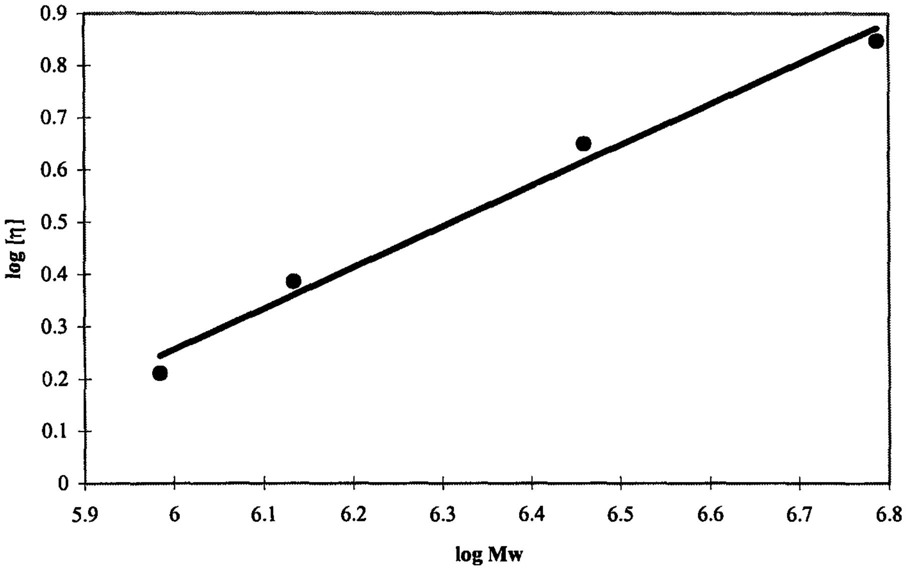


Fig. 3.13 log-log plot of limiting viscosity number [η] versus weight average molecular weight $\overline{M}_w$ for *n*-ba dissolved in acetone

The results for *n*-ba dissolved in dichloromethane are given in Table 3.12 and the log-log plot is given in Fig. 3.14.

Table 3.12 Results obtained for *n*-ba dissolved in dichloromethane

$\overline{M}_w \times 10^{-6}$	η (dl/g)	log $\overline{M}_w$	log η	α	K×10^5 (dl/g)
0.96	2.34	5.984	0.369	0.68	23.9
1.36	3.72	6.134	0.571		
2.88	6.56	6.459	0.817		
6.14	8.44	6.788	0.926		

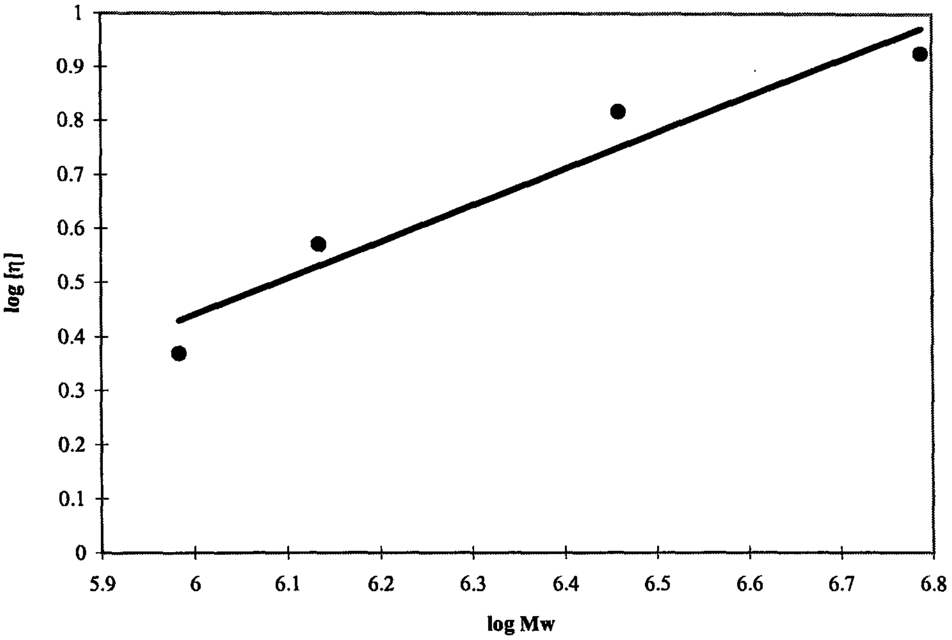


Fig. 3.14 log-log plot of limiting viscosity number [η] versus weight average molecular weight $\overline{M}_w$ for *n*-ba dissolved in dichloromethane

The results for *n*-ba dissolved in toluene are given in Table 3.13 and the log-log plot is given in Fig. 3.15.

Table 3.13 Results obtained for *n*-ba dissolved in toluene

$\overline{M}_w \times 10^{-6}$	η (dl/g)	log $\overline{M}_w$	log η	α	K×10^5 (dl/g)
0.96	2.40	5.984	0.381	0.75	9.07
1.36	3.81	6.134	0.581		
2.88	6.84	6.459	0.835		
6.14	9.93	6.788	0.997		

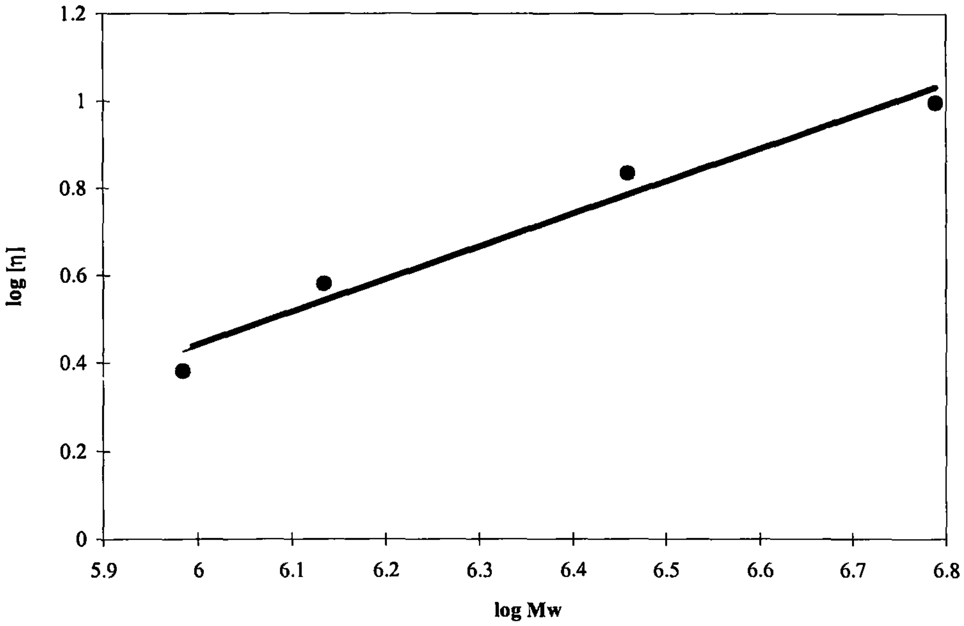


Fig. 3.15 log-log plot of limiting viscosity number [η] versus weight average molecular weight $\overline{M}_w$ for *n*-ba dissolved in toluene

In literature, K and α constants are available only for chloroform and acetone for *n*-ba. The constants with those obtained in this work are shown in Table 3.14.

Table 3.14 K and α constants available in the literature and found in this work

	PBA-Acetone (25°C)		PBA-Chloroform (20°C)	PBA-Acetone (25°C)^c	PBA-Dichloromethane (25°C)^c	PBA-Toluene (25°C)^c
K×10^5 (dl/g)	13.1^a	6.85^b	5.2^a	3.73	23.9	9.07
α	0.69^a	0.75^b	0.73^a	0.78	0.68	0.75

a: Ref. 48
b: Ref. 49
c: Found in this work

The results obtained from Zimm plots are tabulated in Table 3.15.

Table 3.15 Results obtained from Zimm plots

Polymer sample no	$^{a}\overline{M}_w \times 10^{-6}$	$^{a}A_2 \times 10^4$ (mol.ml/g)	$^{a}< s^2 >_z^{1/2}$ (nm)
1	0.96±0.09	1.02±0.1	0.0
2	1.36±0.1	1.09±0.06	42.6±6.8
3	2.88±0.6	1.91±0.1	64.8±7.0
4	6.14±1.0	1.71±0.06	101.2±7.7

a: Measured in acetone at room temperature

3.4. CHARACTERIZATION

3.4.1. Fourier Transform Infrared Spectrometry

The infrared spectrum of monomer and amorphous poly (*n*-BA) have been examined in the range from 4000 to 500 cm^{-1} in order to determine the mode of addition reaction of monomer. The amorphous polymer was so tacky that it was difficult to make solid films from them, and therefore, infrared measurements were made on specimens prepared by dropping the acetone solution directly on a KBr pellet followed by removing the solvent under vacuum. The infrared spectrum of monomer and polymer can be seen in Fig 3.16.

The IR spectrum of monomer (Fig. 3.16a) gives peaks at 1610-1640 cm^{-1} and these bands corresponds to CH_2 =CH— stretching modes of vibration and the peak at 986 cm^{-1} corresponds to again CH_2=CH— out of plane bending mode of vibration. It can be clearly seen that these two bands disappeared completely as in the Fig. 3.16. It can be concluded from the spectrum that the polymerization proceeds with addition reaction by opening carbon-carbon double bond. The IR spectrum of monomer can be seen in Fig. 3.17. For the complete discussion about the IR spectrum of the polymer, shown in Fig. 3.18, the explanation is given below. One can follow the discussion through the expanded scale between the region 600-1800 cm^{-1} as seen in Fig. 3.19.

In the range from 3200-2600 cm^{-1} the only significant band arise from the fundamentals associated with the C-H stretching. The spectrum shows three bands at about 2960, 2930 and 2874 cm^{-1} in this region. The band at about 2960 cm^{-1} is associated with the asymmetrical C-H stretching mode of the methyl groups. The band at about 2874 cm^{-1} may be assigned to the symmetrical methyl and methylene C-H stretching modes. In the series of oxygenated molecules, sometimes a weak shoulder appeared on the low frequency side of the more intense band. Thus, the weak shoulder near 2930 cm^{-1} can be explained by this way.

The stretching vibration of the carbonyl group may be found in 1730-1735cm^{-1} region. A very weak band in the vicinity of 3460 cm^{-1} is assigned as the overtone of the carbonyl stretching band.

The 1458 cm^{-1} band corresponds to the methylene groups in the polymer main chain and the band at 1397 cm^{-1} corresponds to the methylene groups in the *n*-butyl groups. The band at 1379 cm^{-1} may be assigned to the symmetrical methyl bending mode. In cases in which a second methyl group is attached to the same carbon atom, resonance splitting occurs and two separate bandd appears (1397-1379 cm^{-1}). The 1336 cm^{-1} band corresponds to the C-H bending mode of C-H groups.

The 1303 cm^{-1} band was considered at first sight to be due to the methylene wagging mode of the methylene groups directly attached to the oxygen atoms.

From its position, the 740 cm^{-1} band is assigned to the methylene rocking mode. A shoulder appears, on the high frequency side of the 740 cm^{-1} band, at 752 cm^{-1} and it may also be ascribed to the methylene rocking mode. The methylene rocking band of the *n*-butyl groups is expected to be seen in the 742-734 cm^{-1} region [50], and therefore, the 752 cm^{-1} band corresponds to the methylene groups in the polymer main chains and 740 cm^{-1} may be connected with the methylene groups in the *n*-butyl groups.

Two strong bands appears at 1252 and 1171 cm^{-1}. These bands are mainly ascribed to the asymmetrical and symmetrical C-O-C stretching modes of the *n*-butyl ester groups respectively.

Two medium bands occur at 1118 and 1067 cm^{-1}. These bands may be ascribed to the vibrations associated with the *n*-butyl groups of the polymer. The 1027 cm^{-1} band corresponds to the skeletal stretching modes of the polymer main chain.

A doublet is found near 950 cm^{-1}. The skeletal stretching mode of the polymer main chain is expected to be found in this region.

A weak band occurs at 841 cm^{-1} and a very weak band is also found at 803 cm^{-1} . These two bands may be ascribed to the modes corresponding to the *n*-butyl groups of the polymer. The above results are summarized in Table 3.16.

Table 3.16 Infrared spectrum assignments for poly (*n*-BA)

	Amorphous (cm^{-1})
$\nu_a(CH_3)$	2960
$\left.\begin{array}{l}\nu_s(CH_2)\\ \nu_s(CH_3)\\ \nu(CH)\end{array}\right\}$	2874
$2\times\nu(C=O)$	3460
$\nu(C=O)$	1733
$\delta(CH_2)\begin{cases}\text{main chain}\\ n-\text{butyl}\end{cases}$	1459 1397
$\delta_s(CH_3)$	1379
$\delta(CH)$	1335
$\gamma_w(CH_2)\begin{cases}\text{main chain}\\ n-\text{butyl}\end{cases}$	1303 —
$\gamma_t(CH_2)\begin{cases}\text{main chain}\\ n-\text{butyl}\end{cases}$	— —
$\gamma_r(CH_2)\begin{cases}\text{main chain}\\ n-\text{butyl}\end{cases}$	752 740
$\nu_a(COC)$	1255
$\nu_s(COC)$	1171
n-butyl	$\left\{\begin{array}{l}\begin{cases}1118\\ 1067\end{cases}\\ \begin{cases}960\\ 943\end{cases}\\ \begin{cases}841\\ 803\end{cases}\end{array}\right.$

Table 3.16 (continued)

ν(CC)	1118 1027 960 943

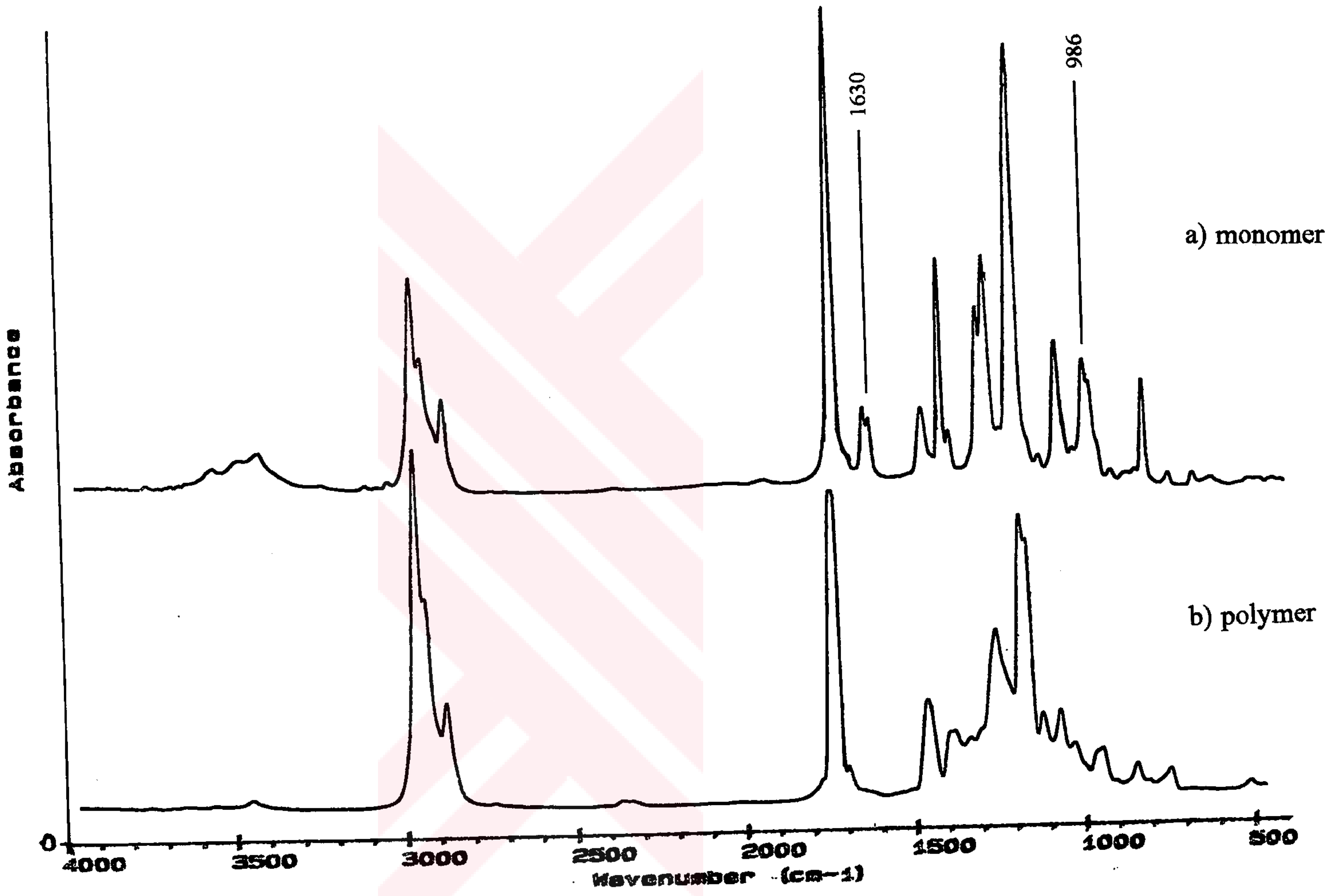


Fig. 3.16 IR spectra of a) monomer and b) polymer together

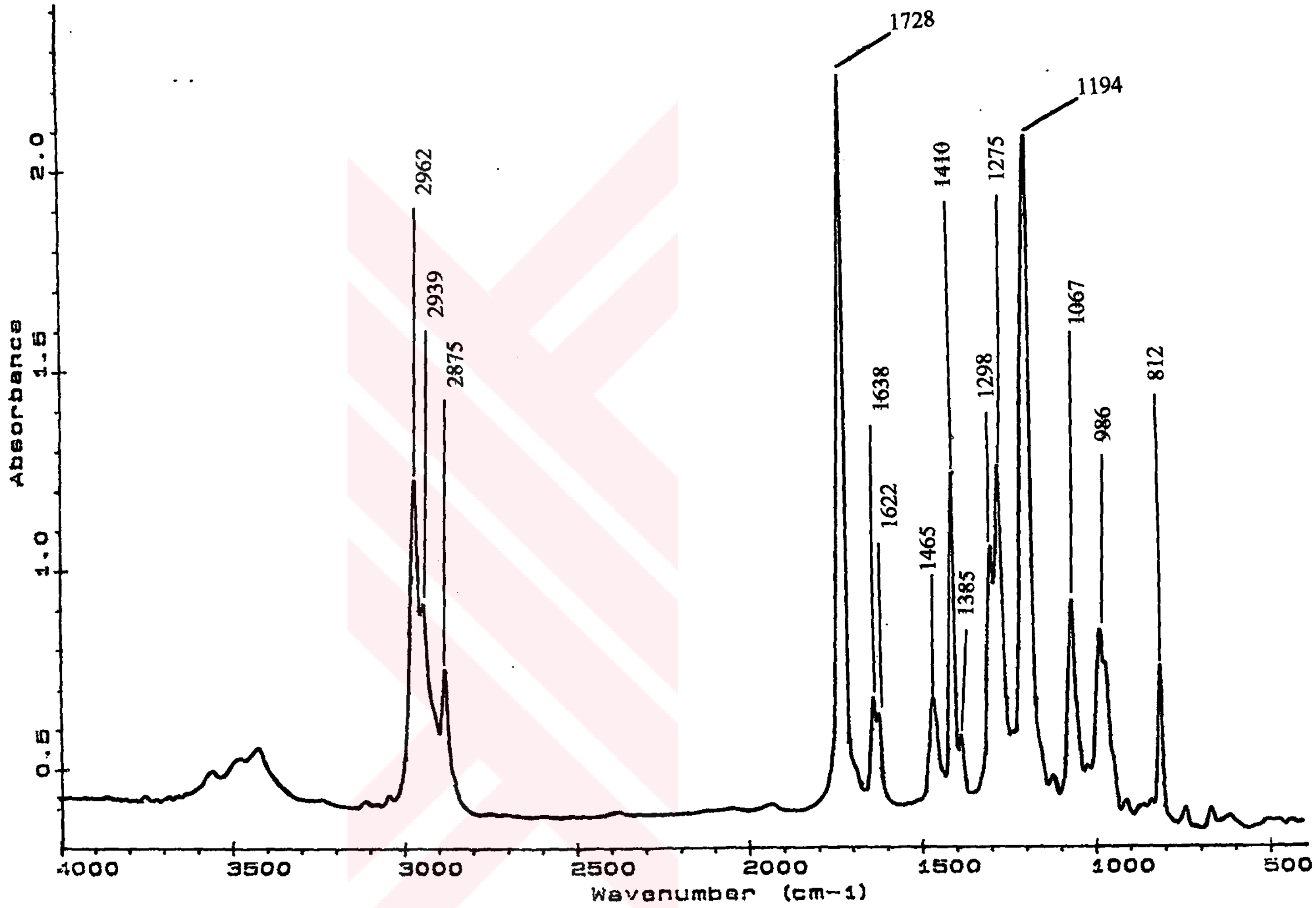


Fig 3.17 IR spectra of monomer

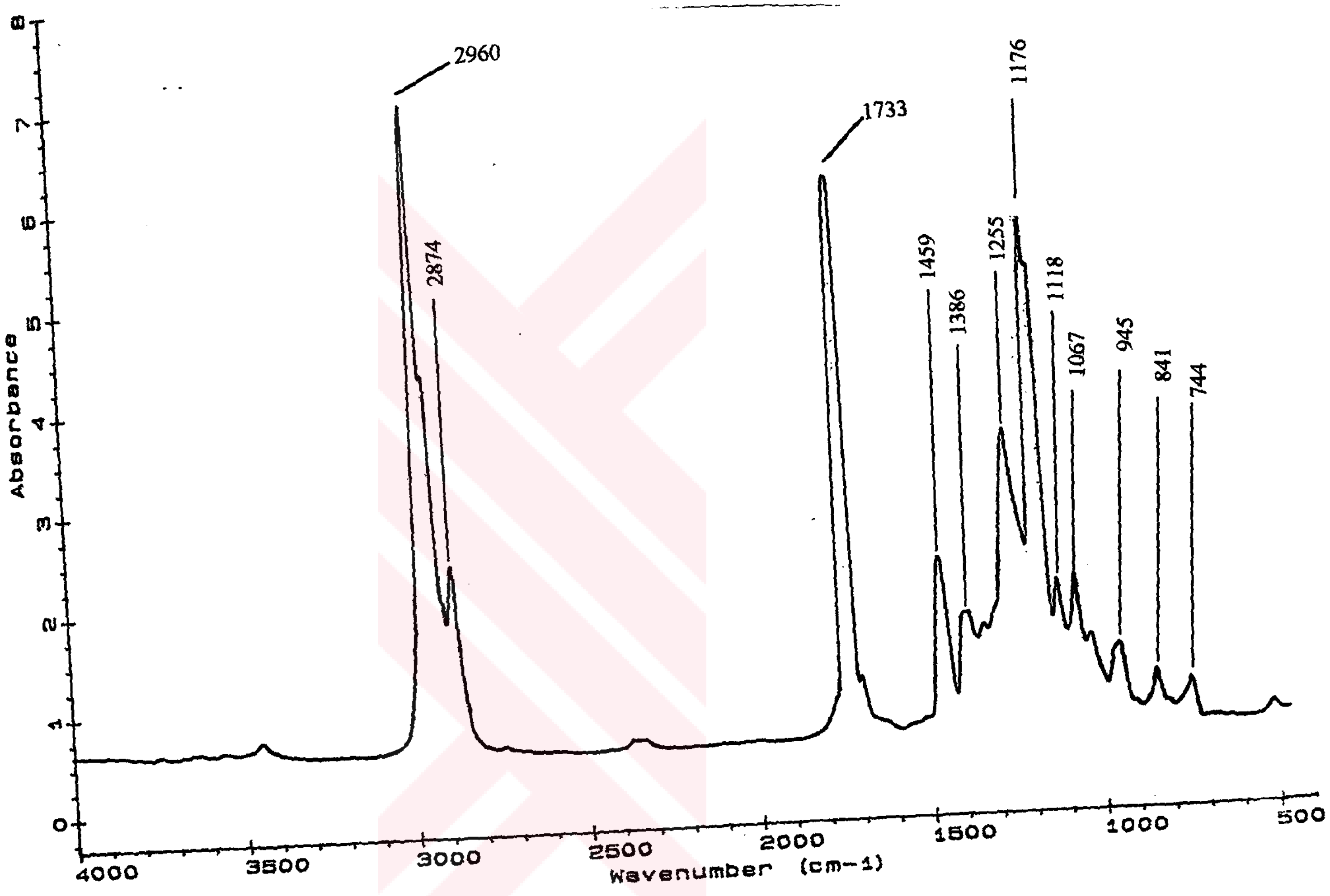


Fig 3.18 IR spectra of polymer

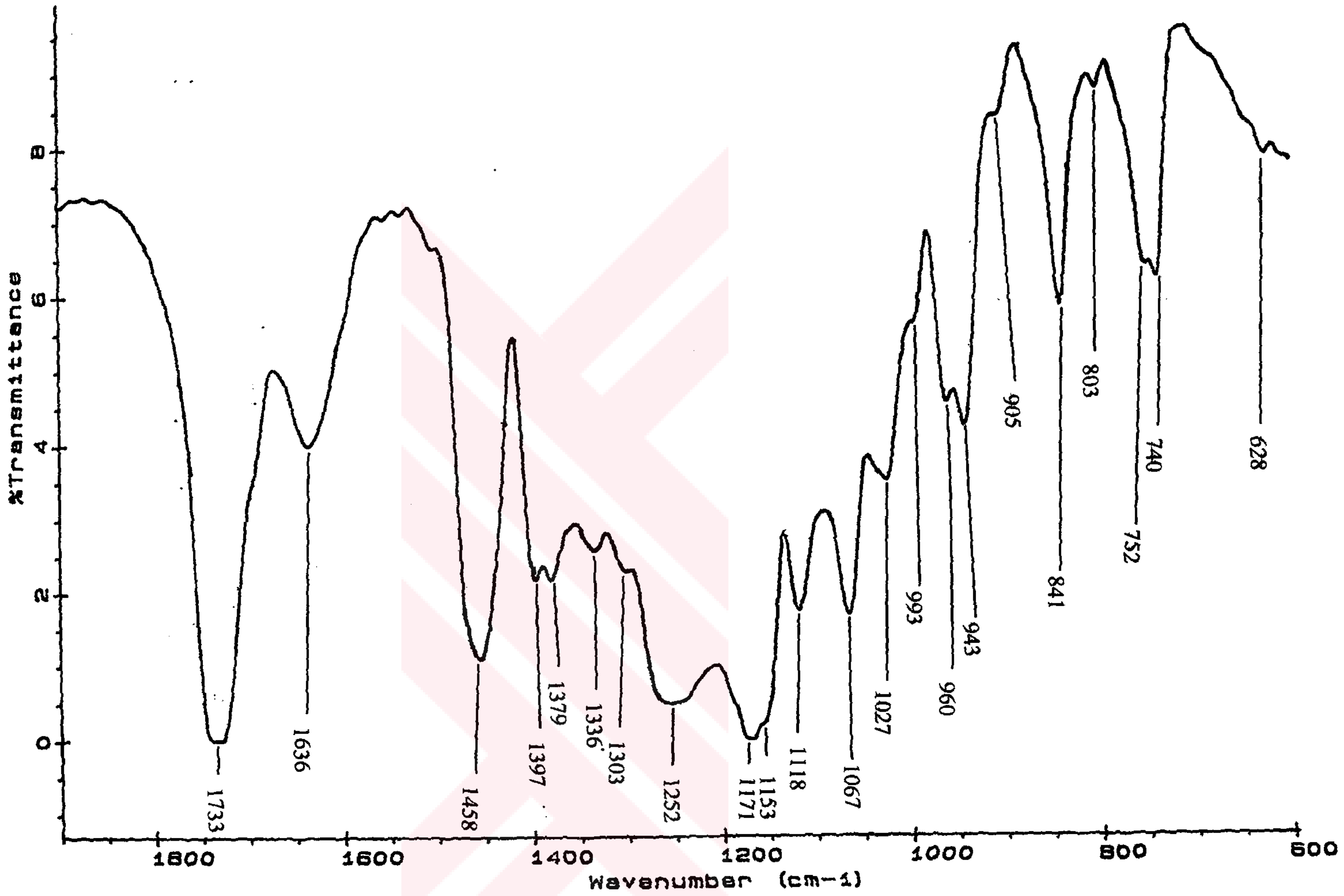


Fig 3.19 Expanded scale IR spectra of polymer (600-1800 cm^{-1})

3.4.2 Differential Scanning Calorimetry

Physical and chemical properties of the polyacrylates are also influenced by the molecular weight of the polymer. For example T_g and associated properties such as brittle point, softening temperature, and hardness increase rapidly as the molecular weight increases from a low value, then becomes practically constant for molecular weight values greater than about 10000. Especially for the polyacrylates having average molecular weight in the range of 10^5 -10^7, these values are almost constant after a certain value. With increasing molecular weight, toughness of the polymer increases and the polymer becomes less easily dissolved. Likewise, crosslinking of polyacrylates has a profound influence upon the physical and chemical properties, especially solubility, hardness, and chemical resistance value.

Supporting the above explanation three polymer samples having different molecular weights has very similar DSC thermograms. The results can be seen in Fig. 3.20, 3.21 and 3.22. All three polymers having different molecular weights have T_g values around -45 °C.

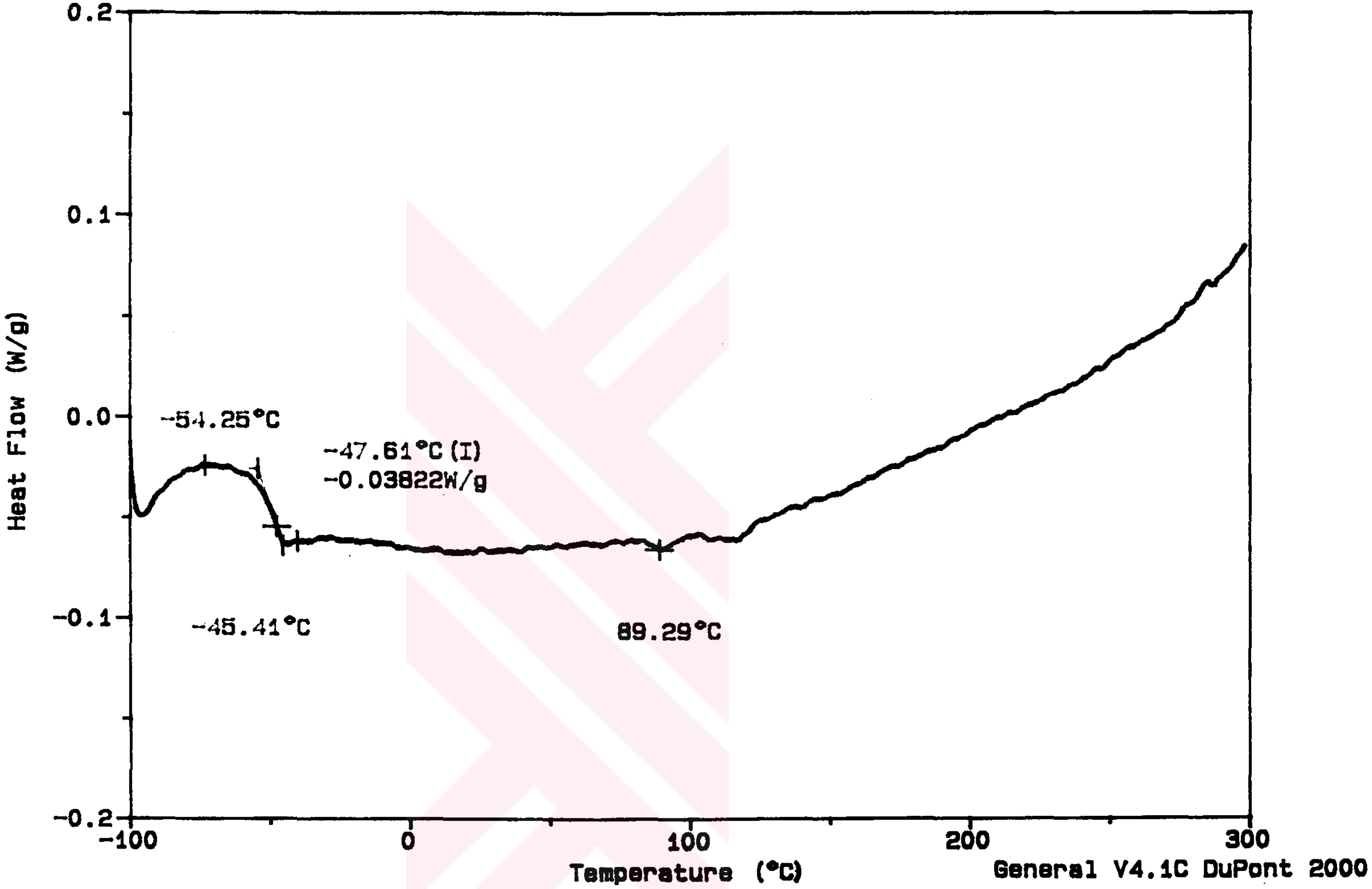


Fig 3.20 DSC thermogram no:1 of poly (*n*-butyl acrylate)

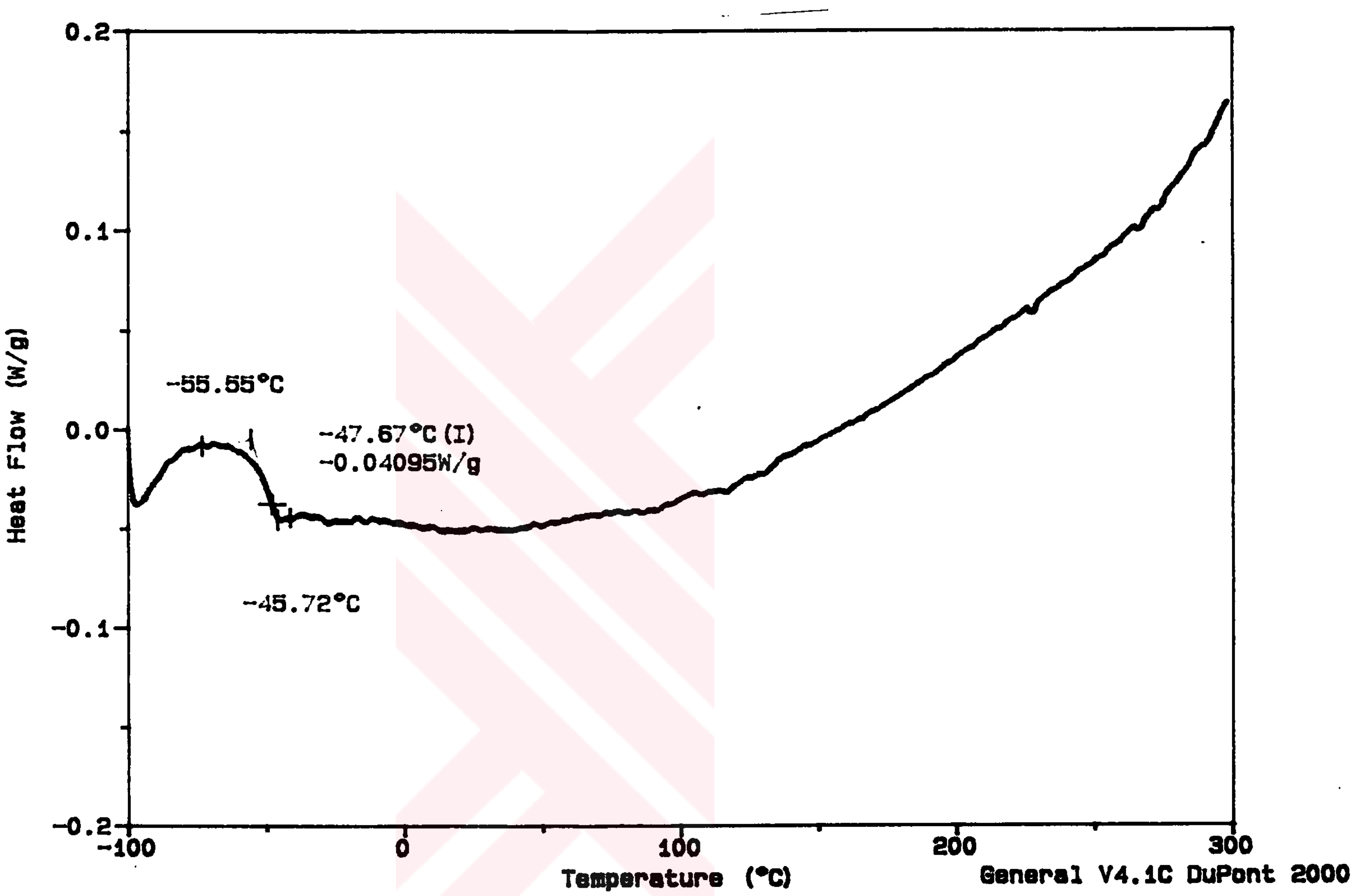


Fig 3.21 DSC thermogram no:2 of poly (*n*-butyl acrylate)

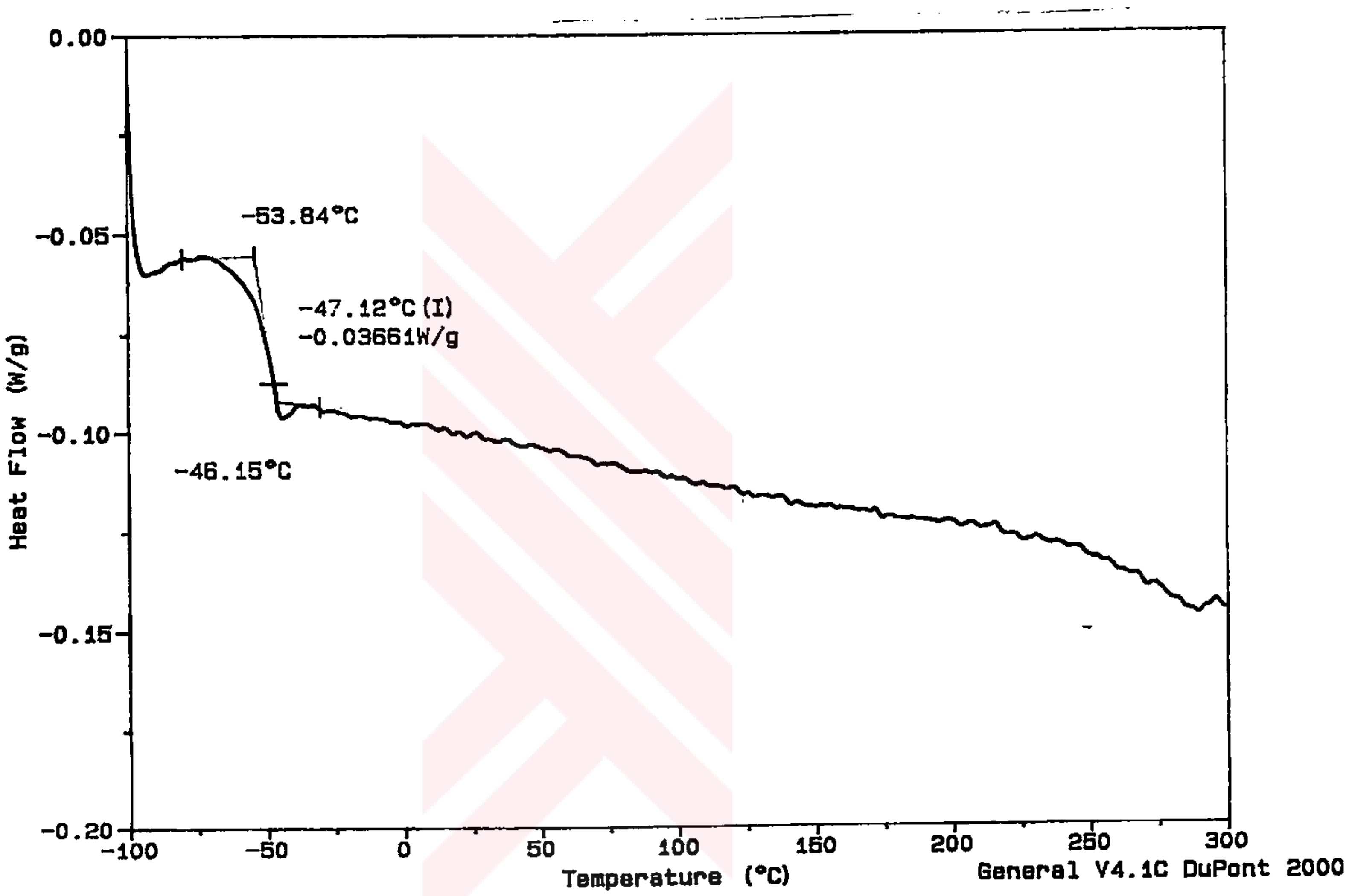


Fig 3.22 DSC thermogram no:3 of poly (*n*-butyl acrylate)

CHAPTER 4

CONCLUSION

In this work, the polymerization of *n*-butyl acrylate was carried out by γ-irradiation initiation in bulk form and in solution. The rate constant was calculated and compared with smaller alkyl acrylates. No further kinetics has been investigated. The rate of polymerization was very high in bulk polymerization. Also molecular weights were very high and the control of molecular weight was not possible. Furthermore, they were not soluble in common solvents and they were in gel form. In order to overcome this problem, the polymerization was carried out in solution. In this case, the molecular weights were still high but now they were soluble in common solvents. It means chain transfer to solvents is achieved. Chain transfer to solvents is dependent on polarity of the medium. The rates of polymerizations as followed through the Figures of % conversion versus % *n*-butyl acrylate were not different from each other so much. It can therefore be concluded that *n*-BA polymerized readily in solutions by radiation initiation. It has advantage over thermal or chemically initiated polymerization with respect to smaller chain transfer constants to solvents. The IR and DSC investigations had been done to support the polymerization through double bond and non-changing character of T_g after a certain molecular weight. The molecular weights of polymers have been found by light scattering method and from the viscosities, the constant K and the exponent α in the Mark-Houwink-Sakurada equation were determined for several solvents which were not available in the literature. The only constants in the literature were for PBA-acetone at 25 °C and PBA-chloroform at 20 °C. The constants found in this work seems to be more reliable because the laser photometer used is among the recently improved machines and the probability of making errors is minimized.

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