CHAPTER - 4

GRAFT COPOLYMERS

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Graft Copolymer

4.1 Introduction :

4.1.1 Graft copolymers

Graft copolymerisation is a wellknown method for modification of chemical and physical properties of polymeric material [1-4] and is of particular interest for achieving specially desired properties without altering the core structure of the substrate. Usually the main chain and the branch chain are thermodynamically in compatible. Most graft copolymers can be classified as multiphase polymers in the solid state, analogous to polymer blends, block copolymers and interpenetrating polymer networks [5-6]. As the immiscible phases are joined by covalent bonds, analogous to block copolymers, a limited range of composition sensitive phase and morphological behaviour is expected [7-14]. Microphase-separated graft copolymers can exhibit many of the unique thermal and mechanical properties observed in block copolymers, including thermoplastic elasticity. Since the morphology of heterophase polymers can be affected by the casting solvent and the nature of its interaction with polymer blocks [5,8,14], the physical properties are expected to depend also on the casting solvent.

4.1.2 Synthesis of graft copolymers

There are three general approaches [15] to the preparation of graft copolymers, namely:

(a) the chain transfer mechanism, (b) the radiative or photo-chemical activation of polymer molecules (used to create active sites for grafting), and (c) either the use of polymer molecules with labile functional groups or the chemical modification of polymers to create active sites for grafting. The first and the third can be applied to both radical and ionic graft copolymer preparation reactions.

4.1.3 Historical review of grat copolymers

Graft copolymers were unknowingly prepared by the chain-transfer mechanism in the early 1930's during investingations on the polymeristion of liquid vinyl monomers containing dissolved rubber [16,17]. The ability of a growing polymer chain to attach to a preformed chain of the similar type was recognised as early as 1933 [18] and this type of polymer reaction was clearly defined by Flory in 1937 [19] in a treatment of the kinetics of free-radical polymerisation reactions [20]. The first all-synthetic graft copolymer prepared by a transfer mechanism and so characterised was poly(methyl methacrylate-g-p-chloro styrene which wasreported in 1946 [21,22].

4.1.4 Brief survery of graft copolymers of acrylates/methacrylates.

There is an abundance of literature on the grafting of acrylates and methacrylates onto a wide variety of substances [1,2,23-31]. Typical examples include the grafting of MMA onto rubbers by a variety of methods : chemical [32.34], photochemical [35], radiation [35,36] and mastication [37]. MMA has been grafted onto substrates such as cellulose [38], poly(vinyl alcohol) [39], polyester fibers [40], poly ethylene [41], polystyrene [42], poly (vinyl chloride) [43], and other alkyl methacrylates [44]. Graft copolymers of acrylic monomers onto other synthetic [35,45] and natural polymers (33,46] are also well documented. Reports of grafting of MMA onto other synthetic polymers are also available [47-53] and its graft copolymers are studied extensively. The references mentioned here represent only a fraction of the available material.

4.1.5 Work done on PAN-g-MMA system :

Poly acrylonitrile as a backbone material in the graft copolymers has been reported earlier [54-73]. However, not many attempts were made to study the grafting of MMA onto PAN [54,58,64] eventhough the random and block

copolymers of the system have been studied extensively. Pieniazek [54] synthesised poly(acrylonitrile-g-methylmethacrylate) by radiation induced method in alcohol medium. Sengupta and Palit [60] carried out the grafting of MMA onto PAN through the formation of thioamido group: treating PAN with hydrogen sulphide (H_2S) and using halogen as initiator. Bamford et al. [58] synthesised graft copolymers of MMA and AN using triethylamine initiator. Novoselova et al [61] synthesised graft copolymers of MMA and AN by a two-stage process involving initial formation of living poly acrylonitrile and subsequent addition of PMMA. They used BuLi as a catayst. Beevers et al. [59] studied the X-ray scattering for powdered sample of poly(acrylonitrile-g-methyl methacrylate) and found that X-ray scattering from the AN block remained unaffected in the graft copolymers.

4.2 **Proposed work :**

From the available literature it has been observed that benzoyl peroxide has not been used as an initiator for the grafting of MMA onto PAN (with chain transfer mechanism). Hence we have undertaken this system for investigation. Another objective of the proposed work is to compare the properties of random and graft copolymers of MMA and AN. A detailed discussion about random copolymer of MMA and AN is done in section 3 and in this section synthesis and study of physico-chemical properties of poly(acrylonitrile-g-methyl methacrylate) is presented followed by the comparative account of a properties of random and graft copolymers.

4.3 **Graft copolymerisation**

Since in the present study benzoyl peroxide is used as initiator, the graft copolymerisation will proceed via chain-transfer mechanism. Three types of

products are formed in all transfer grafting reactions ; these are unmodified back bone polymer, graft copolymer and a homopolymer of the monomer to be grafted. The problem of grafting efficiency, which is the amount of grafted copolymer as a fraction of the total amount of polymer of all three types present at the end of the reaction, is a problem common to all methods of graft polymer formation. In transfer grafting, efficiency is a function of large number of variables, including the type of initiator, the structure of the polymeric substrate, the type of of monomer and the ratio of reactions, and the reaction conditions. Efficiency of grafting reaction based solely on chain transfer depends on several competing reactions. [74-77].

1. Competition between monomer and back bone for the initiator radicals. Under some conditions, the initiating fragment attacks the back bone directly resulting in the formation of a macro radical capable of initiating graft copolymerisation.

2. Competition between monomer, solvent, and backbone for the growing polymer radicals i.e. between chain growth and the various chain transfer steps. In order to obtain grafts with linear branch, and in order to suppress homopolymerisation, the chain transfer step to the back bone polymer must be the favoured process.

3. Competition between the various terminating processes for the initially formed polymer radical. For example, the back bone radical might stabilize itself by (a) eliminating an H from an adjacent carbon atom thus forming an unsaturated group or (b) disproportionating into an olefin and a smaller radical.

4. Competition between the various termination process for the growing graft species. Should the latter terminate via mutual recombination, a possible mechanism if the number of potential chain transfer sites per chain of back bone polymer is high [76] , gelation may occur so that a low grafting efficiency is observed.

4.4 EXPERIMENTAL

4.4.1 Materials Used

Poly acrylonitrile	: Synthesised as described in section 2.2.2 with $\overline{Mn} = 3.61 \times 10^4$
Methyl methacrylate	: Fluka
Benzoyl peroxide	: Fluka
Dimethyl formamide	: BDH, India
Dimethyl sulfoxide	: BDH, India.
Methanol	: Merck, India
Chloroform	: Merck, India
Absolute alcohol	: Alembic Chemicals,Baroda, India.
Cyclohexane	: Merck, India
Propanol-1	: Merck, India
Ethylene glycol	: BDH, India
Acetaldehyde	: Merck, India
Glycerol	: High purity chemicals (HPC), India.

4.4.2 Synthesis of Polyacrylonitrile

Poly acrylonitrile was synthesised from purified AN by solution polymerisation process, using benzoyl peroxide as initiator and toluene as reaction medium The purification of monomers AN and MMA is discussed in section 2.1.3 and synthesis of polyacrylonitrile (PAN) is discussed in section 2.2.2.

4.4.3 Grafting of MMA on PAN backbone

Grafting was carried out in a reaction vessel equipped with stirrer, cooling facility and thermometer. The reaction temperature was maintained with an accuracy of ±0.5°. A precised amount of PAN (2g) was dissolved in 70 cm^3

of DMF in the reaction vessel at 75°. Benzoyl peroxide (0.206 g, i.e. 10^{-2} M) was added to the reaction mixture. After 10 minutes of stirring 10.65 cm^3 (10g) of MMA was added and the reaction was continued for 6h. The graft copolymer was precipitated by pouring the reaction mixture into four fold excess of chloroform under vigorous stirring. Hompolymer of MMA remained in solution. The mixture was kept undisturbed for 24h for complete precipitation. The isolated precipitate was washed several times with chloroform to remove traces of unreacted MMA and homoplymer of MMA (i.e PMMA). The precipitate was again soxhlet extracted with chloroform for 48h to remove the traces of any impurities and hompolymer. The precipitate was dried under reduced pressure in an oven at 60° to constant weight.

The combined chloroform extract was concentrated by evaporating the chloroform. The homopolymer of MMA was recovered from concentrated chloroform using methanol as a non-solvent. PMMA was dried under reduced pressure at 60° to constant weight. For the confirmation of the effectiveness of the product separation techniques the graft copolymer was additionally purified by dissolving in DMF and then reprecipitating it in chloroform. The results of the elemental analysis of both the products were similar indicating the negligible amount of impurity of unreacted monomer, or homopolymer present in the synthesised graft copolymer. Blank exeriment conducted with PAN, without the addition of monomer indicates no degradation of PAN during the reaction process. Percentage of total conversion, percentage grafting, grafting efficiency (G.E.) rate of polymerisation (R_p), rate of grafting (R_g), and rate of homopolymerisation (R_h) were determined gravimetrically following the procedure given by Vijay Kumar et al. [78].

$$\text{Percentage conversion} = \frac{\text{weight of grafted polymer + weight of homopolymer}}{\text{weight of monomer charged}} \times 100$$

$$\text{Percentage grafting (P.G.)} = \frac{\text{weight of grafted polymer}}{\text{weight of backbone}} \times 100$$

$$\text{Grafting efficiency (G.E.)} = \frac{\text{weight of grafted polymer}}{\text{weight of grafted polymer + weight of homopolymer}} \times 100$$

Rate of polymerisation (R_p) (mol dm^{-3} sec^{-1}) =

$$= \frac{\text{weight of grafted polymer + weight of homopolymer}}{\left(\begin{matrix}\text{mol.wt.of}\\ \text{monomer}\end{matrix}\right) \cdot \left(\begin{matrix}\text{time of the}\\ \text{reaction (sec)}\end{matrix}\right) \cdot \left(\begin{matrix}\text{volume of the}\\ \text{reaction mixture } (cm^3)\end{matrix}\right)} \times 1000$$

Rate of graft copolymerisation (R_g) (mol dm^{-3} sec^{-1}) =

$$= \frac{\text{Weight of grafted polymer}}{\left(\begin{matrix}\text{mol.wt.of}\\ \text{monomer}\end{matrix}\right) \cdot \left(\begin{matrix}\text{time of the}\\ \text{reaction (sec)}\end{matrix}\right) \cdot \left(\begin{matrix}\text{volume of the}\\ \text{reaction mixture } (cm^3)\end{matrix}\right)} \times 1000$$

Rate of homopolymerisation (R_h) (mol l^{-1} sec^{-1}) =

$$= \frac{\text{Weight of homopolymer}}{\left(\begin{matrix}\text{mol.wt.of}\\ \text{monomer}\end{matrix}\right) \cdot \left(\begin{matrix}\text{time of the}\\ \text{reaction (sec)}\end{matrix}\right) \cdot \left(\begin{matrix}\text{volume of the}\\ \text{reaction mixture } (cm^3)\end{matrix}\right)} \times 1000$$

It is recognised that the percentage grafting determined in this way is an apparent value as the copolymer may contain ungrafted PAN. Due to similarity in the solubility of PAN and its graft copolymer, the removal of ungrafted PAN (if any) was not possible in the present work. We also recognise the sources of heteoogeneity in the product as :

a) heterogeneity in the backbone,

b) heterogeneity in the grafted branches.

However, this particular aspect is not studied in the present work.

4.4.4 **Optimisation of reaction conditions :**

The reaction conditions for grafting of MMA onto PAN were optimised by varying monomer : polymer ratio (i.e. by changing monomer concentration), initiator concentration, reaction time and temperature.

4.4.4a **Monomer concentration :**

To study the effect of monomer concentration on the grafting of MMA onto PAN, all other paramerters except monomer concentration were kept constant.

The reaction was carried out for six hours at 75° with 2g PAN. Total volume of the reaction mixure was maintained at 85 cm^3 and 10^{-2} M (0.206 g in 85 cm^3) benzoyl peroxide was used as an initiator. MMA concentration was varied from 2.57 x 10^{-3}M to 13.66x10^{-3}M (2g to 12g). Grafting reaction was carried out in DMF medium. After completion of the reaction, the reaction mixure was poured into four fold excess of chloroform with vigorous stirring. Isolation, purification and drying of graft copolymer and homopolymer was done in the same way as described in section 4.4.3.

4.4.4b Initiator concentration

To study the effect of initiator concentration on the grafting of MMA onto PAN, the reaction was carried out using 2g of PAN and 10.6 cm^3 (10g) of MMA in DMF having a total volume of 85 cm^3 for a constant period of six hours. Reaction temperature was maintained at 75°. The initiator concentration was varied from 0.25x10^{-2}M to 10^{-1}M. Further treatment for the separation of graft and homopolymer was same as discussed in section 4.4.3.

4.4.4.c Reacton time

To study the influence of reaction time on the grafting reaction, the grafting was carried out as mentioned in section 4.4.4b using 10^{-2}M (0.206 g) initiator but varying reaction time from 1h to 12h. The method of precipitation of graft copolymer and separation and isolation of homopolymer from graft copolymer was similar to the one discussed in section 4.4.3.

4.4.4d Reaction temperature

The effect of temperature on the grafting of MMA onto PAN was studied following the procedure described in section 4.4.4b by using 10^{-2}M (0.206 g)

initiator concentration but varying the reaction temperature in between 75 - 90°. Precipitation, separation and drying of graft copolymer and homopolymer was carried out as discussed in section 4.4.3.

4.4.5 Characterisation of graft copolymers

The graft copolymers were characterised through spectral, thermal, viscosity studies and swelling behaviour in various solvents. Surface characterisation of the graft copolymer was carried out through contact angle measurement. The details about the measurement is discussed in section 4.5.6.

4.4.5a IR spectra

IR spectroscopic information of the graft copolymer was obtained using Shimadzu IR-408 spectrophotometer and KBr pellet technique.

4.4.5b Scanning electron micrography (SEM)

SEM study of the graft copolymer was done with a scanning electron microscope JEOL 15 operated at 15.25 KV. To avoid any charging under an electron beam, the samples were mounted on a SEM stub using a double-sided tape. The samples were then coated using a polaroin S-5000 diode sputtering coater, with 200 Å gold coating. Magnification was done at 250 times .

4.4.5c Thermal analysis

4.4.5c (i) Differential scanning calorimetry

Du Pont 2000 differential scanning calorimeter was used for the characterisation of graft copolymers. Brief principle and experimental details are discussed

in section 2.4.3.a and followed in the similar way for graft copolymer analysis.

4.4.5.c (ii) Thermogravimetric analysis

The principle and the method of TG analysis is discussed in Section 2.3.3.b. All measurements were made under nitrogen at a flow rate of 50 cm^3 per minute. The thermograms of the copolymers were analysed to obtain information about the perccentage weight loss at different temperatures. The thermograms of all the graft copolymers were analysed by the Broido method [79] with a view to estimate the kinetic parameter of the degradation reaction.

4.4.5d X-ray analysis

X-ray Cystallography of the graft copolymers was carried out using Siemens crystalloflex 4 model, coupled to a Hilton brooks/phillips diffractometer. The materials to be analysed were placed in 2 mm diameter sample tubes. The sample tubes were then mounted and centered on a standard goniometer stage. The X-ray generated were Cu_{α} rays at 40 Kv and 20 mA.

4.4.5 e Viscometric study

Viscosity study of the graft copolymers was carried out using Ubbelohde suspended viscometer at different temperature using DMF and DMSO as solvent. From the viscometric data, intrinsic viscosity, activation parameters, hydrodynamic volume and Simha Shape factors for the graft copolymers were calculated. The detailed procedures and principles involved are discussed in section 2.4.4.

4.4.5 f Contact angle measurement

Contact angle measurements of the films of graft copolymers were carried

out using a contact-θ-meter developed at the University of Leeds, U.K. The experimental procedure and the mode of action was same as described in details in section 2.4.7. The critical wetting tension of the graft copolymers was determined by plotting $\cos\theta$ (θ = angle of contact) values against the surface tension of contacting liquid.

4.4.5 g Swelling

The swelling behaviour of graft copolymers with different percentage grafting was studied using powdered (approximately uniform size) sample and different solvents such as distilled water, methanol absolute alcohol, 1-propanol, cyclohexane and n-heptane. The procedure for swelling study was same as the one described for random copolymers in section 2.4.10.

4.4.5 h Differential refractometry

Differential refractive index measurements of the graft copolymers were carried out with a Brice-Phoenix Differential Refractometer, at a wave length of 63.2nm with light supplied by He-Ne gas laser. The details of the working procedure are mentioned in Section 2.4.11.

4.5. Results and Discussion

4.5.1 Optimisation of reaction conditions

4.5.1.a Monomer concentration

The effect of monomer concentration on the grafting reaction is shown in Fig. 4.1. It was observed that percentage grafting increases continuously with increase in monomer concentration. With increasing MMA concentration in the reaction mixuture, the rate of grafting as well as homopolymerisation increases leading to increase in percentage grafting but decreasing grafting efficiency.

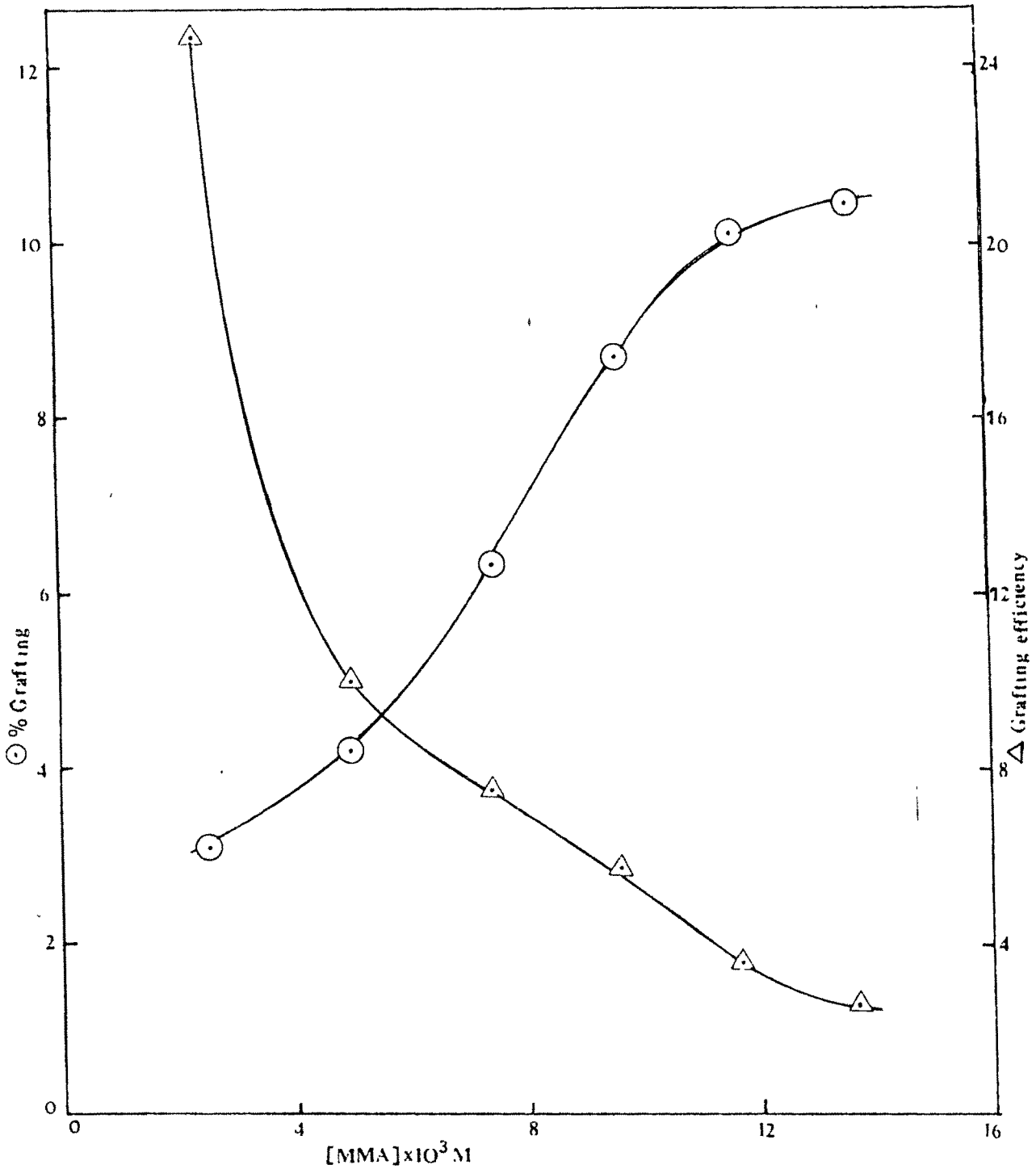


Fig.4.1 Effect of monomer concentration on percentage grafting and grafting efficiency. PAN: 2g, concentration of benzoyl peroxide: 0.01M, reaction time: 6h, temperature : 75°, total volume:85 cm^3.

This is due to the fact that within the monomer concentration range studied, with increasing MMA concentration, the rate of homopolymerisation increases to a greater extent than the rate of grafting, leading to a decrease in percentage grafting efficiency. This is clearly indicated by the steady growth in the rate of homopolymerisation (Table 4.1).

4.5.1.b Initiator concentration

Fig.4.2 shows the effect of initiator concentration on the grafting reaction. The observed trend is a typical character of grafting reactions occuring via chain transfer. The initial increase in the percentage grafting and grafting efficiency is caused due to an increase in the concentration of free radicals formed through the decomposition of initiator. Thus the higher the concentration of initiator, the higher the chain transfer to the polymer and higher will be the percentage grafting and grafting efficiency. But further increase in the initiator concentration (beyond 10^{-2} M) decreases the molecular weight of the side chains due to the increased consumption of monomer in the process of homopolymerisation and mutual termination reaction. This results into decrease in percentage grafting. These two opposite tendencies give rise to the appearance of maxima.

Effect of initiator concentration on R_p, R_g and R_h is given in Table 4.2. It is observed that R_p, R_g and R_h initially increase and then decrease with increasing concentration of initiator. As mentioned earlier with initial increase of initiator concentration the number of radical sites for polymerisation increase, thereby increasing the rate of reaction (i.e R_p, R_g and R_h). Further increase in the initiator concentration increases the mutual termination reaction, thereby decreasing Rp, Rg and Rh. In addition at these conditions concentration of the monomer added must have been quantitatively exhausted during polymerisation reaction due to excess of free radical concentration. The extent of homopolymerisation was brought down considerably by delaying the addition of monomer after addition of initiator. Similar results were observed by Hebeish and

Table-4.1

Effect of monomer concentration in the graft copolymerisation of MMA onto PAN.

PAN	: 2g
Benzoyl peroxide concentration	: 10^{-2} M
Temperature	: 75°
Reaction time	: 6h
Total volume	: 85 cm^3

Sample code	[MMA]x10 (M)	Total conversion (%)	$R_p \times 10^6$ $mol.dm^{-3}$ s^{-1}	$R_g \times 10^6$ $mol.dm^{-3}$ s^{-1}	$R_h \times 10^6$ $mol.dm^{-3}$ s^{-1}
G_1	2.57	12.67	1.37	0.34	1.03
G_2	5.06	21.08	4.59	0.46	4.13
G_3	7.44	30.87	15.56	0.69	14.87
G_4	9.60	37.79	16.47	0.95	15.52
G_5	11.68	56.46	30.75	1.09	29.66
G_6	13.66	66.39	43.39	1.14	42.25

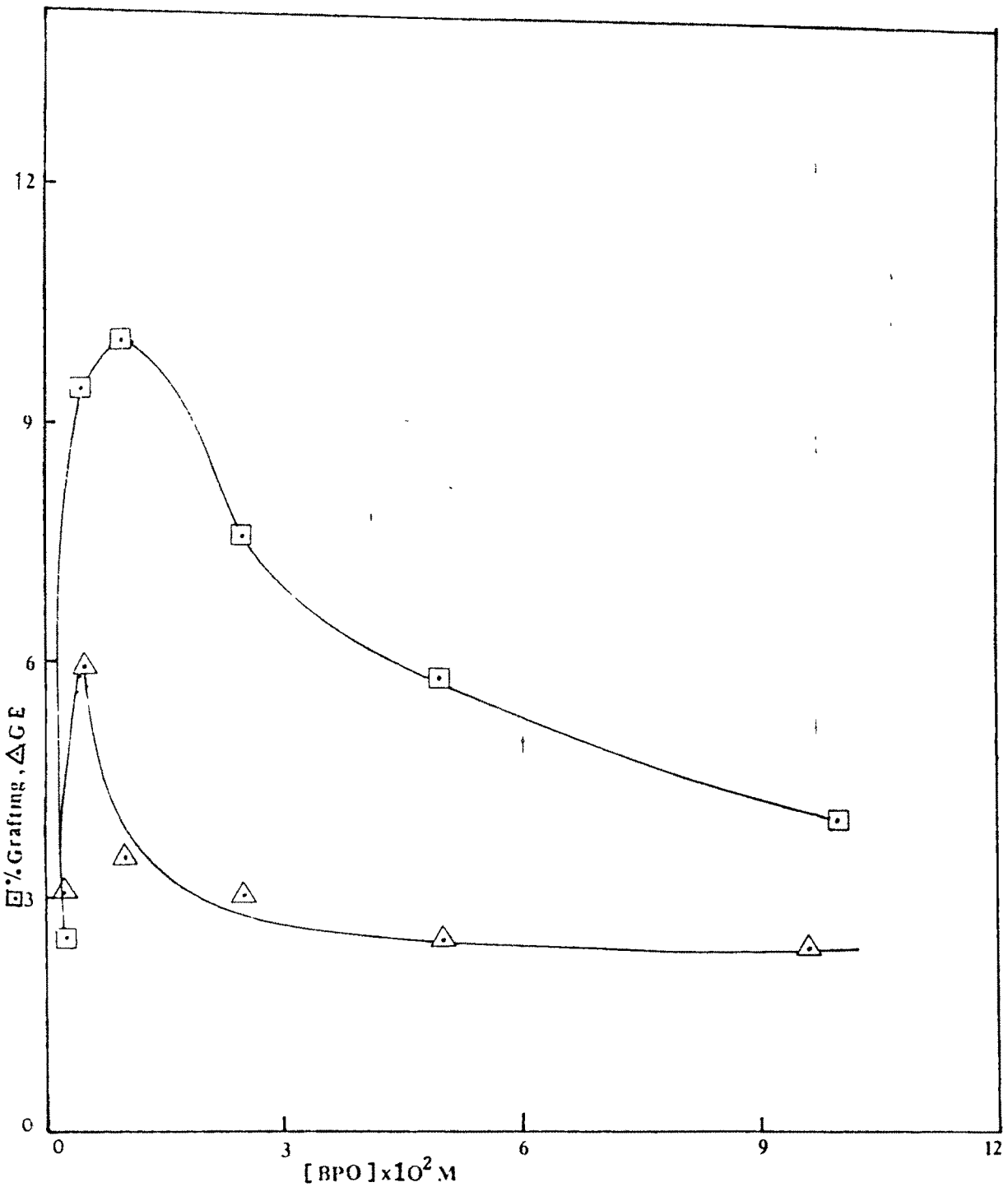


Fig.4.2 Effect of initiator concentration on percentage grafting and grafting efficiency. PAN: 2g, MMA concentration: 1.168 M, reaction time: 6h, temperature: 75°, total volume: 85 cm^3.

Table - 4.2

Effect of initiator concentration in the graft copolymerisation of MMA onto PAN.

PAN	: 2g
MMA concentration	: 1.168M
Temperature	: 75°
Reaction time	: 6h
Total volume	: 85 cm^3

Initiator concentration (M) $\times 10^2$	Total conversion (%)	$R_p \times 10^6$ $mol.dm^{-3} s^{-1}$	$R_g \times 10^6$ $mol.dm^{-3} s^{-1}$	$R_h \times 10^6$ $mol.dm^{-3} s^{-1}$
0.25	16.37	8.90	0.27	8.63
0.50	31.74	17.29	1.03	16.26
1.00	56.46	30.75	1.09	29.66
2.50	42.63	23.22	0.83	22.39
5.00	40.07	20.09	0.63	20.46
10.00	33.78	18.40	0.45	17.95

Mehta [80]. This is expected due to the elimination of direct contact of free radicals with the monomer.

4.5.1c Temperature

The influence of temperature on grafting reaction is shown in Fig 4.3. On increasing temperature, both percentage grafting and grafting efficiency pass through a maximum. R_p, R_g and R_h are also observed to give a similar trend (Table-4.3). Increase in temperature is expected to casue a higher rate of decomposition of initiator as well as diffusion and mobility of the monomer to the polymer backbone increase. As a result grafting yield increases. But percentage grafting also depends on other factors like molecular weight of the grafted side chains. Therefore a further increase in temperature causes degradation of side chains leading to a decrease in percentage grafting, grafting efficiency, R_p, R_g and also R_h.

4.5.1.d Reaction time.

The effect of reaction time on the grafting of MMA onto PAN is shown in Fig. 4.4. With increase in reaction time both percentage grafting and grafting efficiency initially increase and then decrease. Because with increase in reaction time, number of radicals taking part in the reaction will increase resulting into increase in percentage grafting and grafting efficiency. Further increase in reaction time causes the deplation of initiator and monomer with time under the given reaction conditions, lowering the percentage grafting and grafting efficiency. The rate of polymerisation decrease with increasing reaction time. This effect can be attributed to the fact that the relative increment in the total yield is comparatively less when compared to that of time, and in the expression for R_p, the numerator becomes almost constant, and when the time for the reaction is raised, the denominator becomes larger thus reducing R_p accordingly. Since R_g and R_h are related to R_p, the relative decrease of R_g

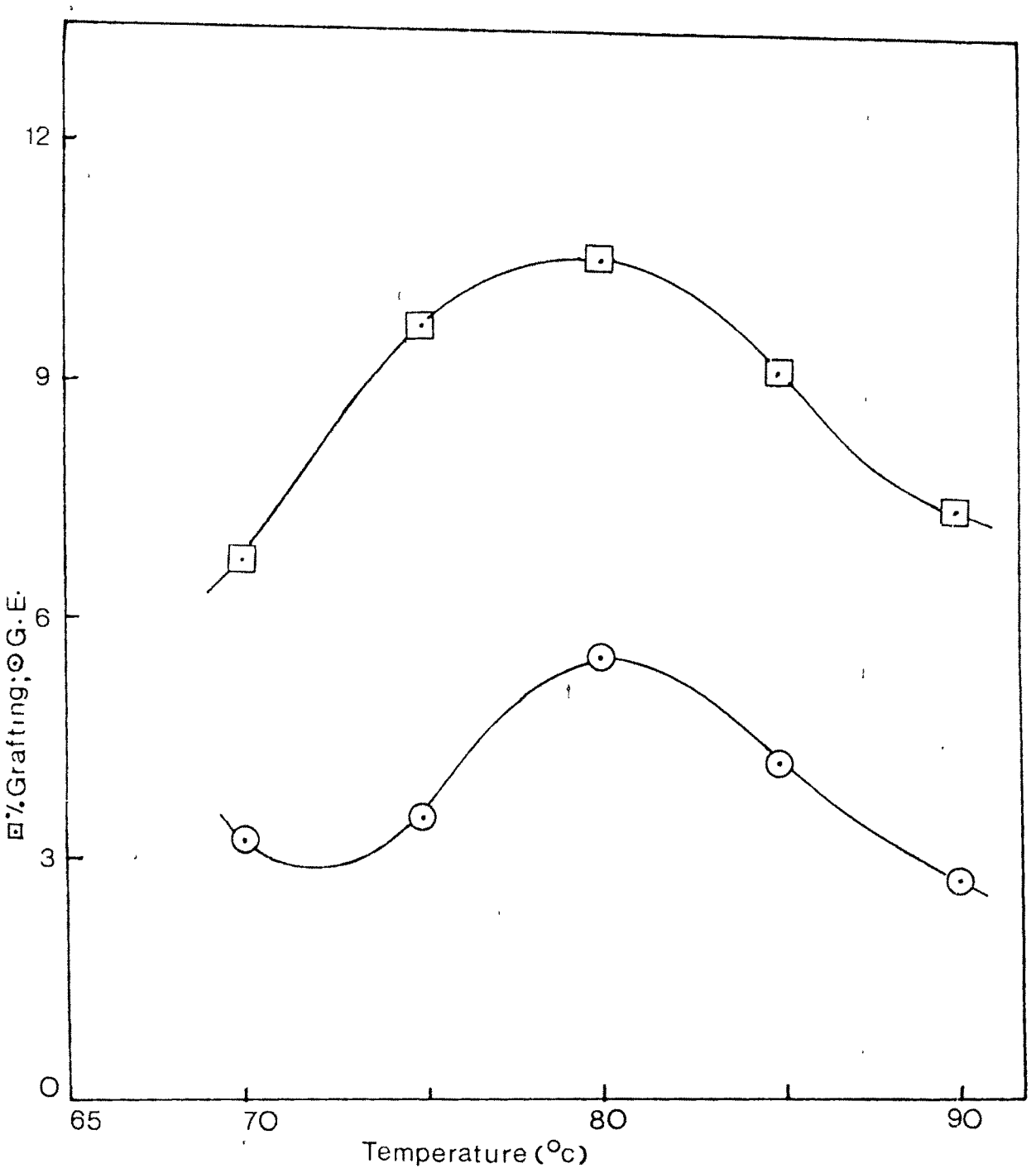


Fig. 4.3 Effect of temperature on percentage grafting and grafting efficiency. PAN: 2g, MMA concentration: 1.168 M, benzoyl peroxide concentration: 0.01 M, reaction time: 6h, total volume: 85 cm^3

Table - 4.3

Effect of temperature in the graft copolymerisation of MMA onto PAN.

PAN	: 2g
MMA concentration	: 1.168 M
Benzoyl peroxide conc.	: 10^{-2} M
Reation time	: 6h
Total volume	: 85 cm^3

Temperature (° C)	Total conversion (%)	$R_p \times 10^6$ $mol.dm^{-3}s^{-1}$	$R_g \times 10^6$ $mol.dm^{-3}s^{-1}$	$R_h \times 10^6$ $mol.dm^{-3}s^{-1}$
70	41.35	22.52	0.73	21.79
75	56.46	30.75	1.09	29.66
80	58.00	20.70	1.16	19.54
85	42.93	17.38	1.01	16.38
90	40.61	15.20	0.82	14.38

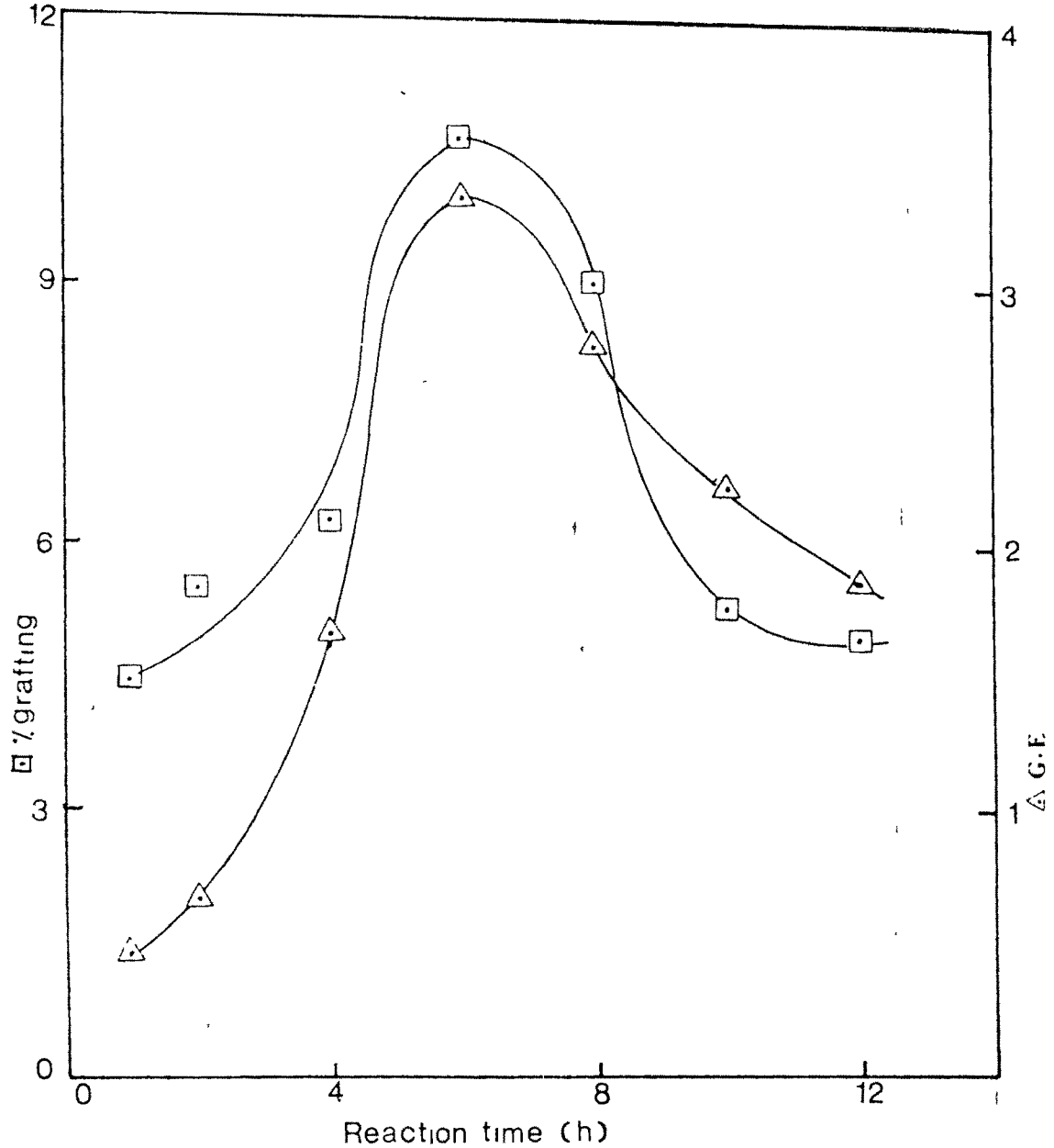


Fig. 4.4 Effect of reaction time on percentage grafting and grafting efficiency. PAN: 2g, MMA concentration: 1.168 M, benzoyl peroxide concentration: 0.01 M, temperature: 75°, total volume: 85 cm^3.

and R_h with time can be understood (Table 4.4)

4.5.2 Evidence of grafting

4.5.2.a.(i) IR spectroscopy

Figs. 3.4 and 4.5 show the i.r. spectra of PAN and poly(acrylonitrile-g-methyl methacrylate) repsectively. A comparison of the i.r. spectra of PAN and graft copolymer shows that the i.r. spectra of the latter has additional stretching frequency bands at 1735 cm^{-1} and 1148 cm^{-1} characteristics of $-\overset{|}{C}=0$ and $-\overset{|}{\underset{|}{C}}-0-$ groups respectively indicating the presence of ester groups from methyl methacrylate into the grafted sample.

4.5.2.a.(ii) SEM analysis

Figs. 4.6 - 4.9 show the scanning electron micrographs of PAN and PAN-g-MMA. The rough surfaces of the grafted polymer with respect to ungrafted one (PAN) is due to the grafted branches of PMMA on PAN and confirms the occurance of grafting. A clear change in the nature of the polymer was observed during transition from PAN to PMMA as the percentage grafting went on increasing.

4.5.2.b Wide angle x-ray scattering study

The X-ray scattering pattern for PAN, the graft copolymer and mixture of PAN and PMMA are shown in Figs. 3.34,4.10 and 4.11. PAN shows a peak at d=5.27 Å with additional unresolved peak arising from spacing 3-4 Å suggesting orthorhombic unit cell structure. The X-ray scattering curve for graft copolymer shows similar scattering pattern as that of PAN. This suggest that the X-ray scattering from acrylonitrile block appears to be unaffected by the presence of poly(methyl methacrylate) in the graft copolymer.

Table - 4.4

Effect of reaction time in the graft copolymerisation of MMA onto PAN.

PAN : 2g
Benzoyl peroxide concentration : 10^{-2} M
MMA concentration : 1.168 M
Temperature : 75°
Total volume : 85 cm^3

Reaction time (h)	Total conversion (%)	$R_p \times 10^6$ $mol.dm^{-3}s^{-1}$	$R_g \times 10^6$ $mol.dm^{-3}s^{-1}$	$R_h \times 10^6$ $mol.dm^{-3}s^{-1}$
1	18.84	61.56	0.91	60.65
2	25.35	41.42	0.65	40.77
4	48.16	39.35	0.83	38.52
6	56.46	30.75	1.09	29.66
8	58.34	22.61	0.69	21.92
10	65.52	20.68	0.44	20.24
12	67.60	18.40	0.30	18.10

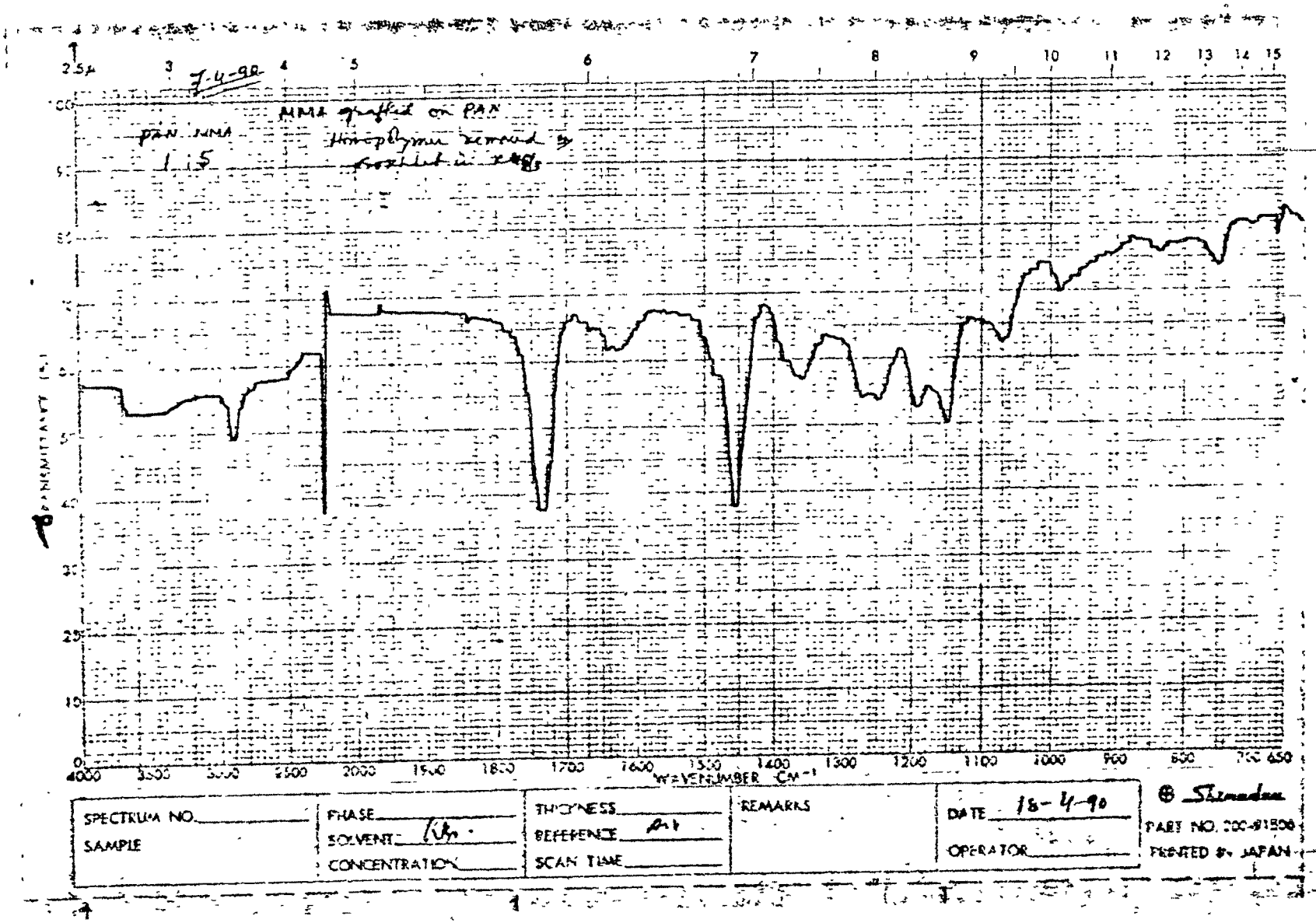


Fig.4.5 IR spectra of graft copolymer (G_2), 10.05% grafting.

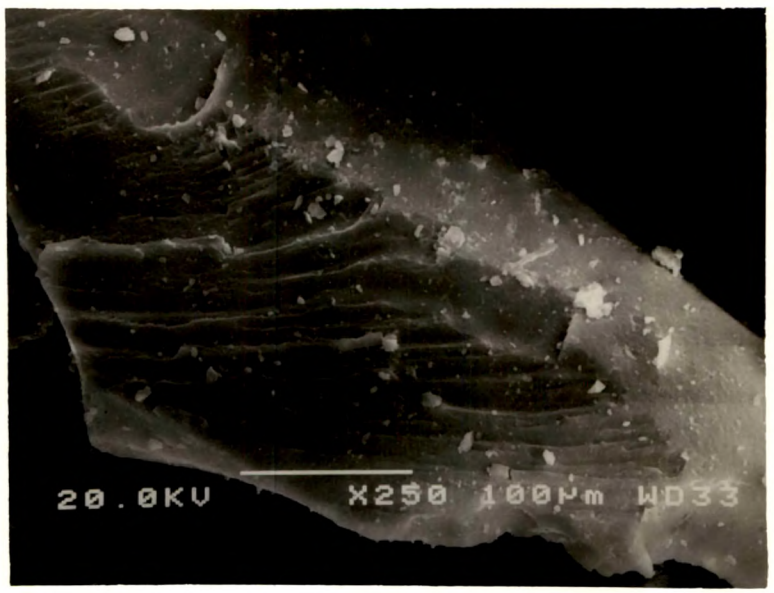


Fig.4.6 : SEM micrograph of PAN x 250

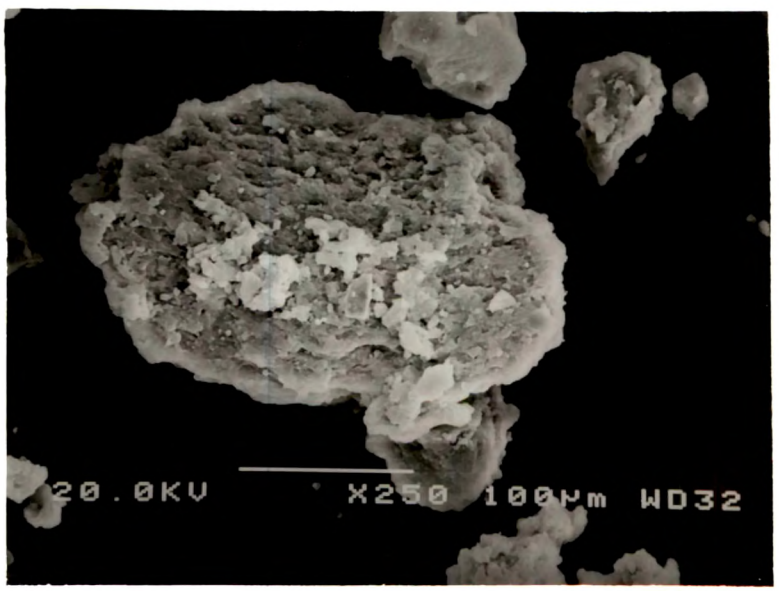


Fig.4.7 : SEM micrograph of sample G_3
(6.33% grafting) x 250

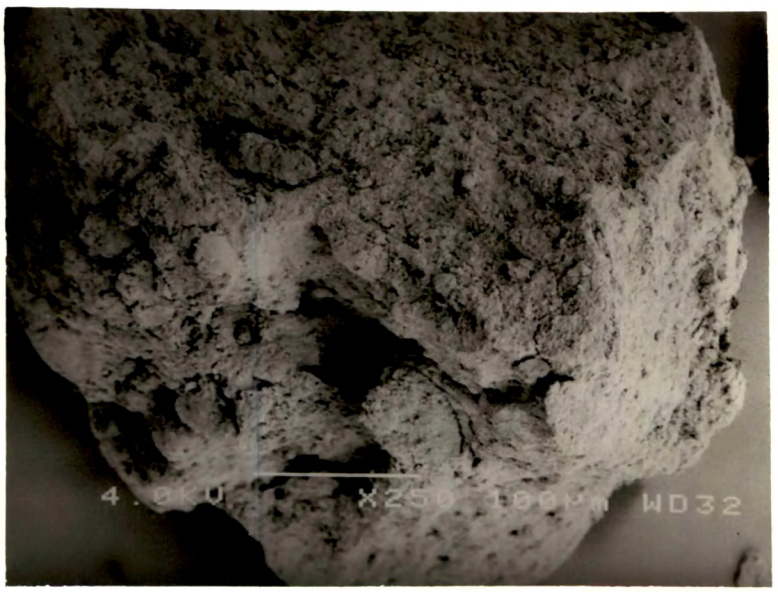


Fig.4.8 : SEM micrograph of sample G_6
(10.5 % grafting) x 250

Fig.4.9 : SEM micrograph of PMMA x 250

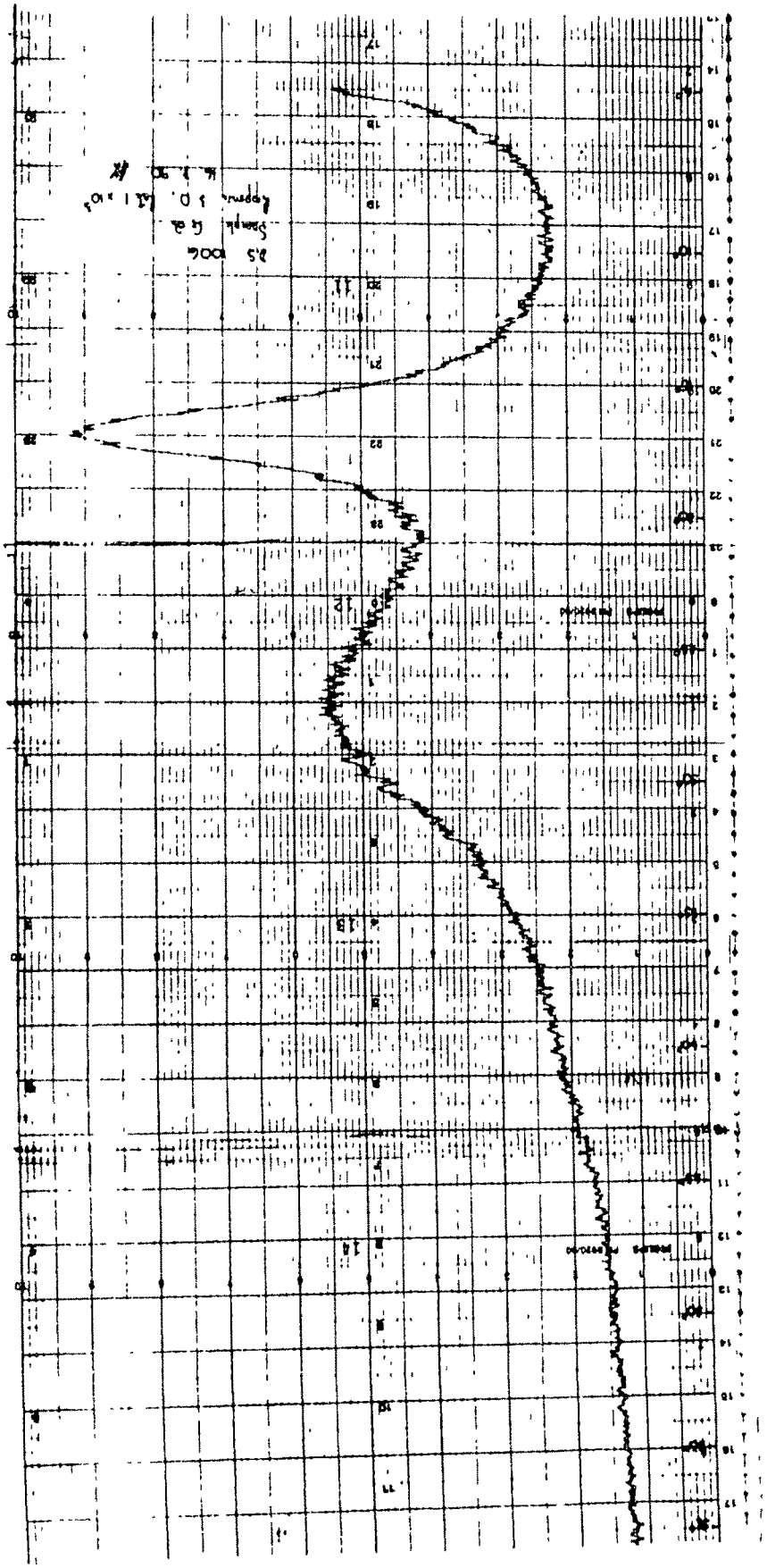


Fig. 4.10 X-ray diffraction pattern of graft copolymer (G_2)

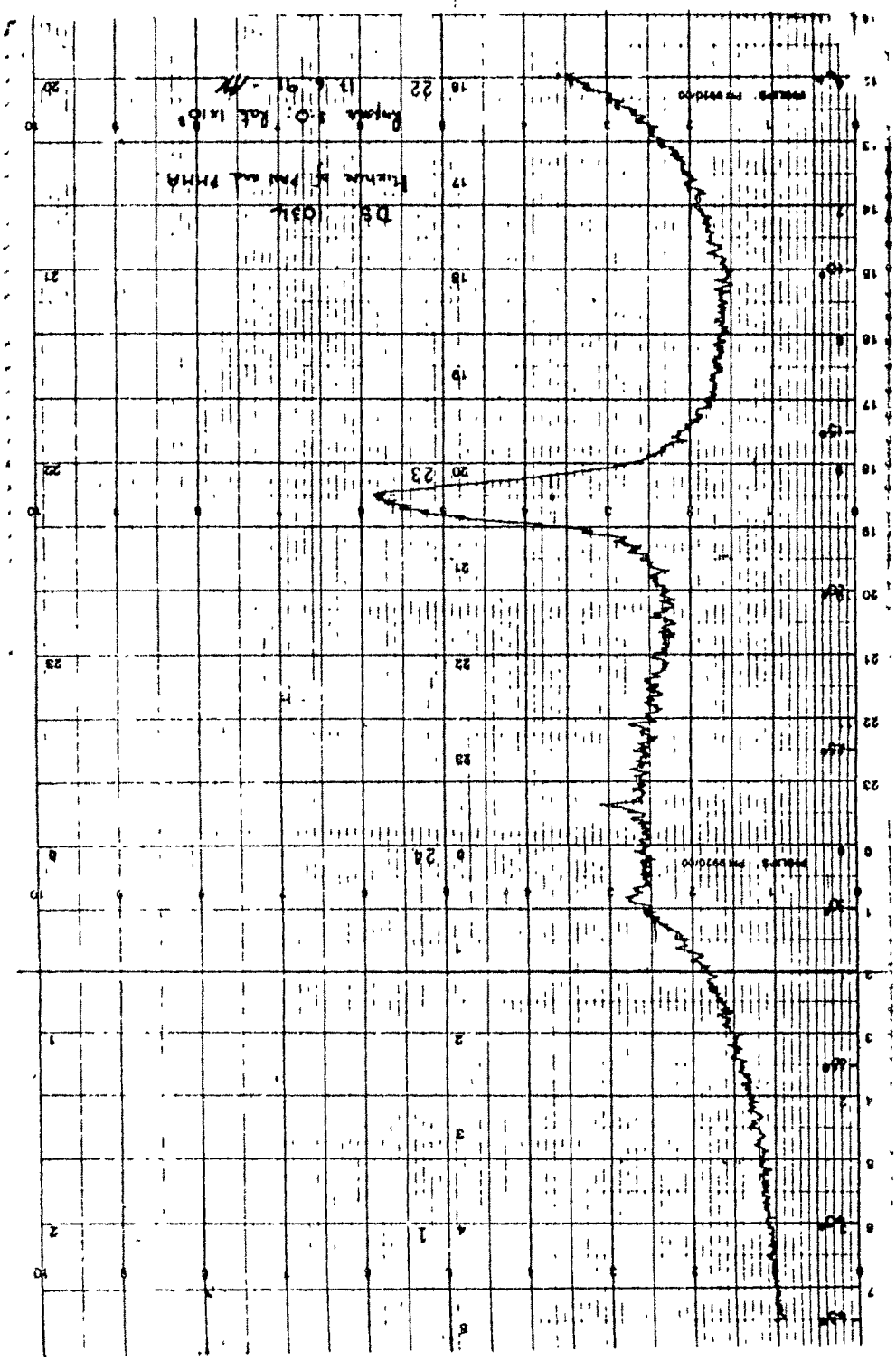


Fig.4.11 : X-ray diffraction spectra of mixture of PMMA and PAN

4.5.3 Thermal study

4.5.3.a Differential scanning calorimetry (DSC)

DSC analysis data for graft copolymers and homopolymers is given in Table 4.5. No remarkable change in the melting temperature of polyacrylonitrile was observed due to lower percentage grafting. However, the heat of crystallisation is observed to decrease with increase in the percentage grafting due to the lower crystalline character of the graft copolymer. Graft copolymers are observed to give the single glass transition values (Fig. 4.12) indicating the compatibility of the graft chain with the main chain polymers.

4.5.3.b Thermogravimetric analysis

Fig. 4.13 shows the TGA and DTGA of a representative graft copolymer. The initial decomposition temperature (IDT) for graft copolymer is 273.26° and that of PAN is 278.7° (Fig.3.27). The weight loss in the first stage could be associated with nitrile oligomerisation [81, 82] which produces volatile products (NH_3, HCN, CH_3CN etc) and subsequent chain scission. The second stage degradation of graft copolymers occurs at 417.25°. The activation energy associated with thermal breakdown of the graft copolymers was calculated following Broido method discussed earlier and was found to be 25.67 KJ mol^{-1} for first transition and 44.73 KJ mol^{-1} for the second transition.

4.5.4 Swelling behaviour

Swelling behaviour of the graft copolymers was studied in different solvents. Fig. 4.14 represents the results obtained. It was observed that extent of swelling of the graft copolymers in a given solvent decreases with the increase in percentage grafting. This may be due to increased concentration of bulky hydrophobic methyl methacrylate groups in PAN back bone. When extent of swelling is compared in different solvents for the same sample it was observed that swelling is more in polar solvents. This is because, for a particular sample MMA content is fixed and larger part of copolymer being hydrophilic (PAN), its

Table - 4.5

DSC analysis for Poly (AN-g-MMA) copolymer

Sample No.	Percentage grafting (%)	Melting temperature (°C)	Heat of crystallisation (J/g)	Glass transition temperature (°C)
PAN	-	268.0	390.0	98.0
G_1	3.10	262.5	-	96.63
G_2	4.20	265.2	370.8	97.93
G_3	6.33	266.6	322.8	-
G_4	8.66	268.1	-	94.61
G_5	10.05	266.2	265.7	-
G_6	10.47	271.0	-	-
PMMA	-	178.1	81.4	99.33

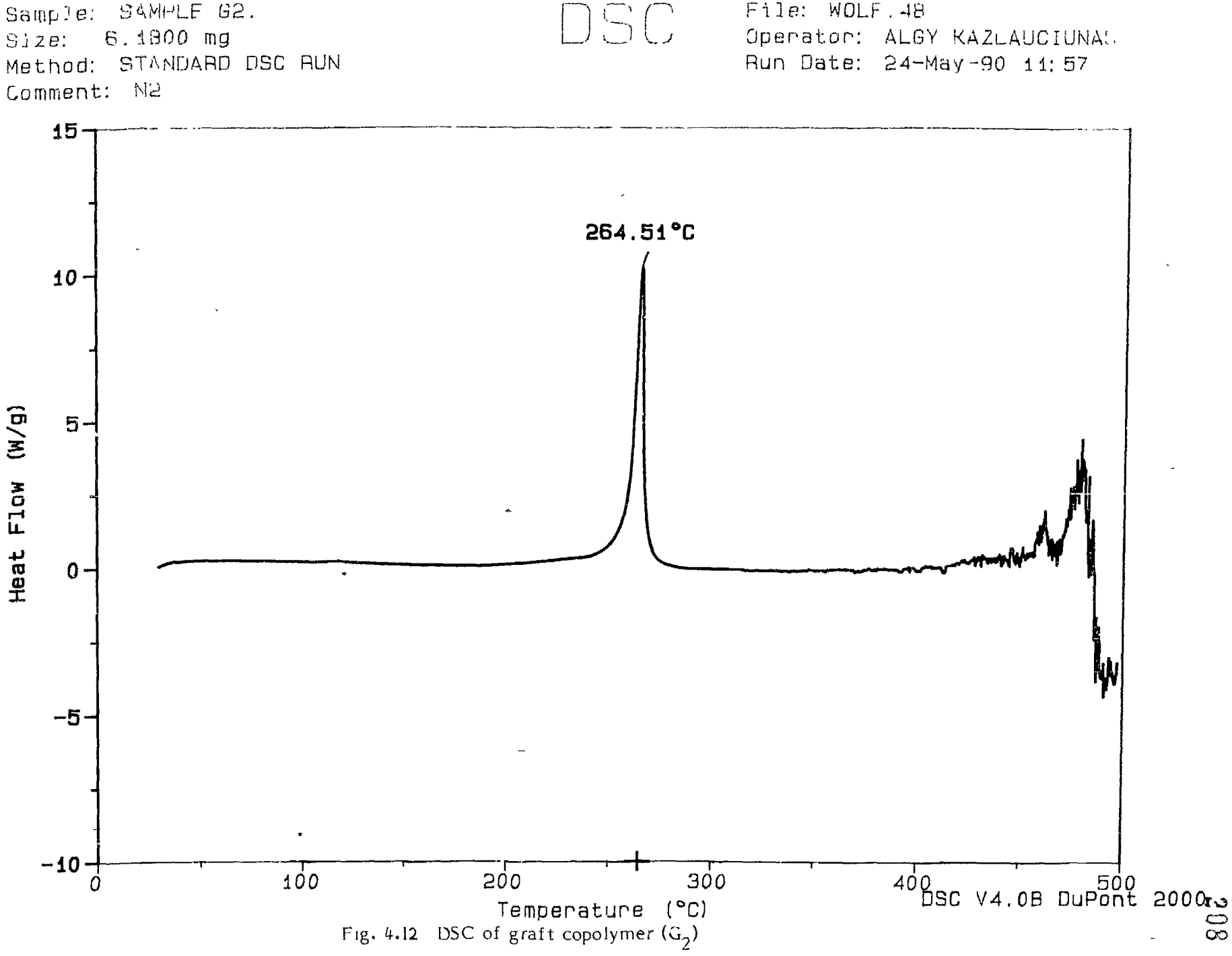


Fig. 4.12 DSC of graft copolymer (G_2)

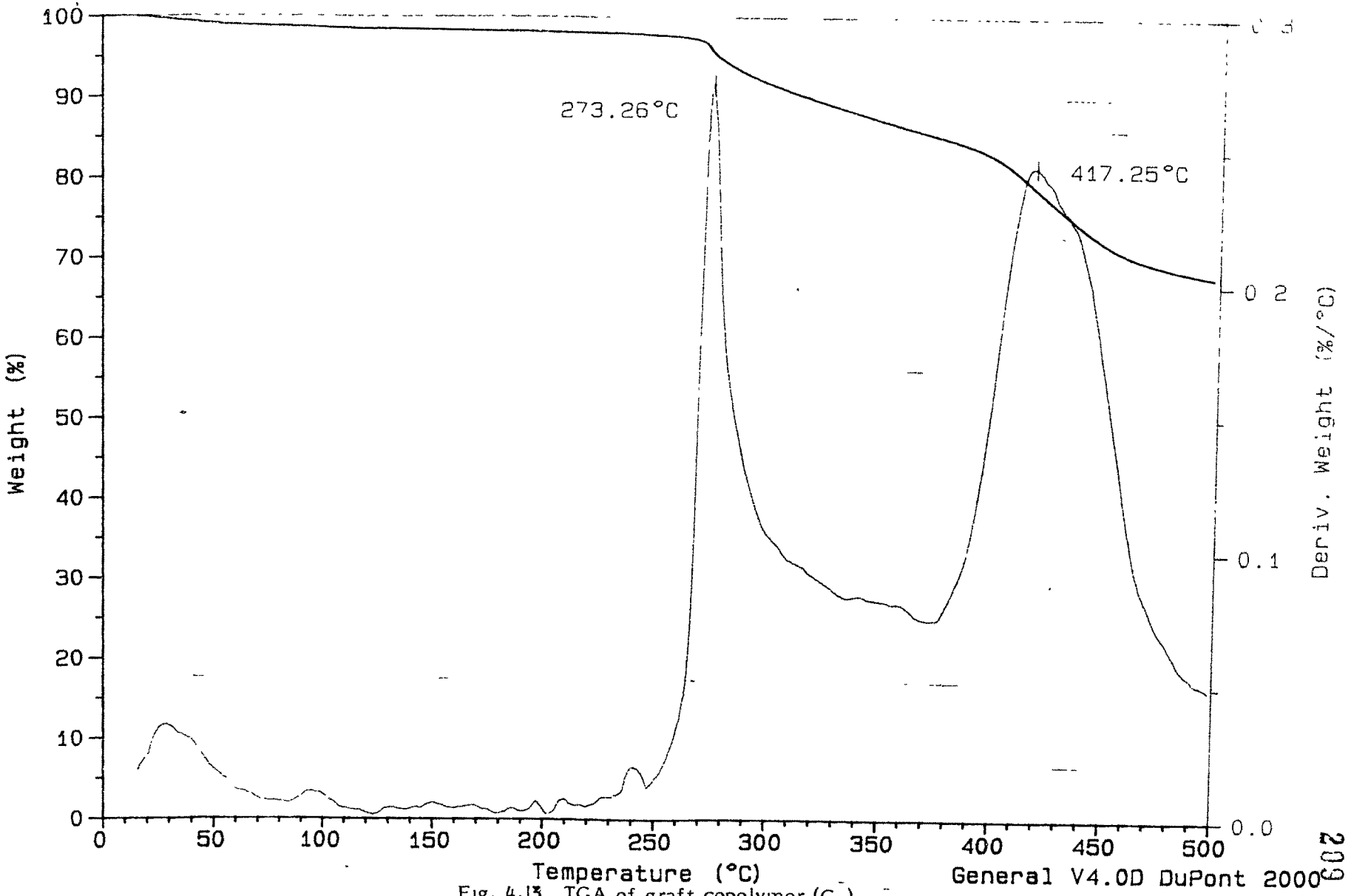


Fig. 4.13 TGA of graft copolymer (G_2)

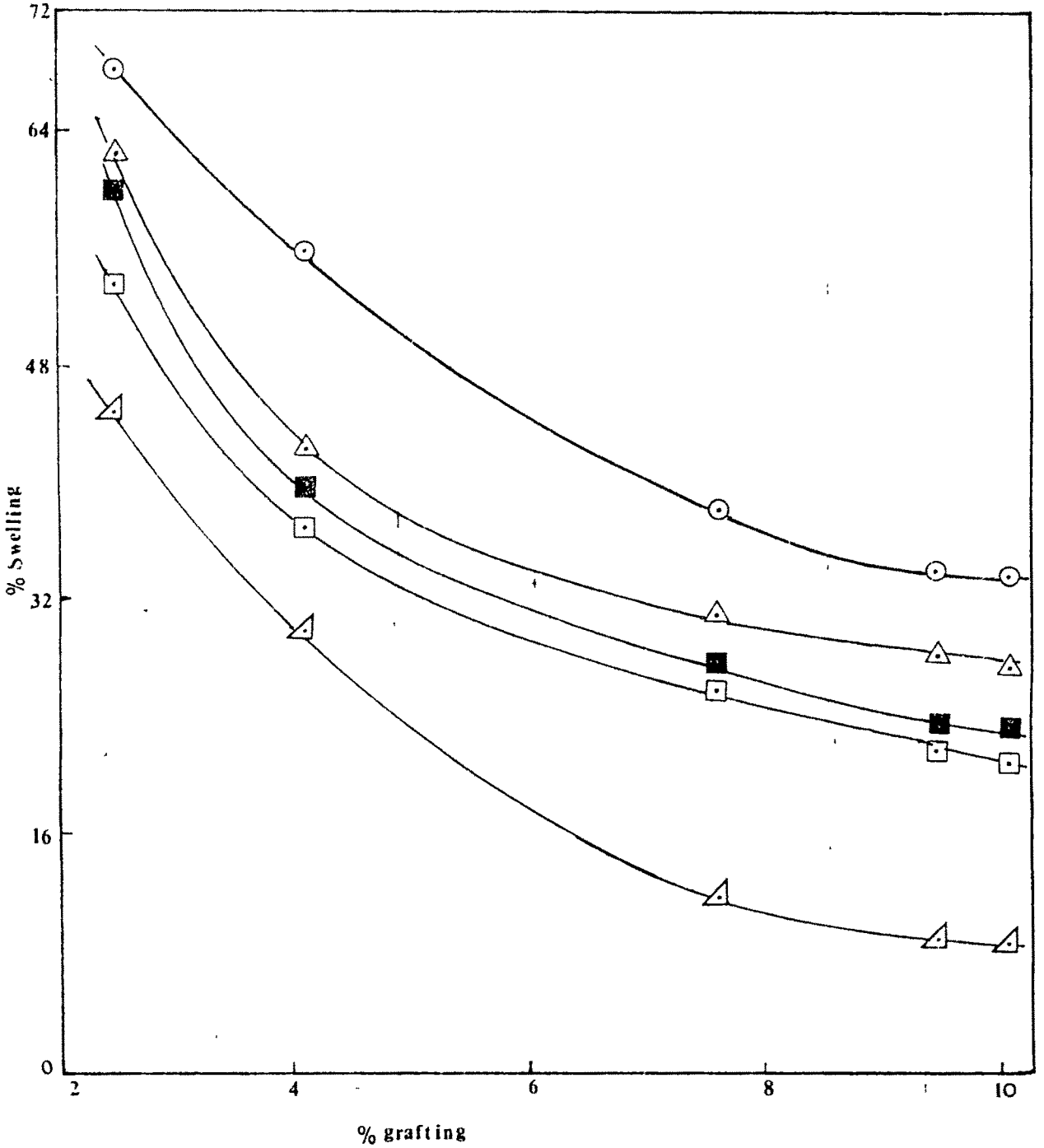


Fig.4.14 Effect of percentage grafting on swelling in different solvents. ⊙ methanol. △ absolute alcohol, ■ 1-propanol, ⊡ cyclohexane, ◿ water.

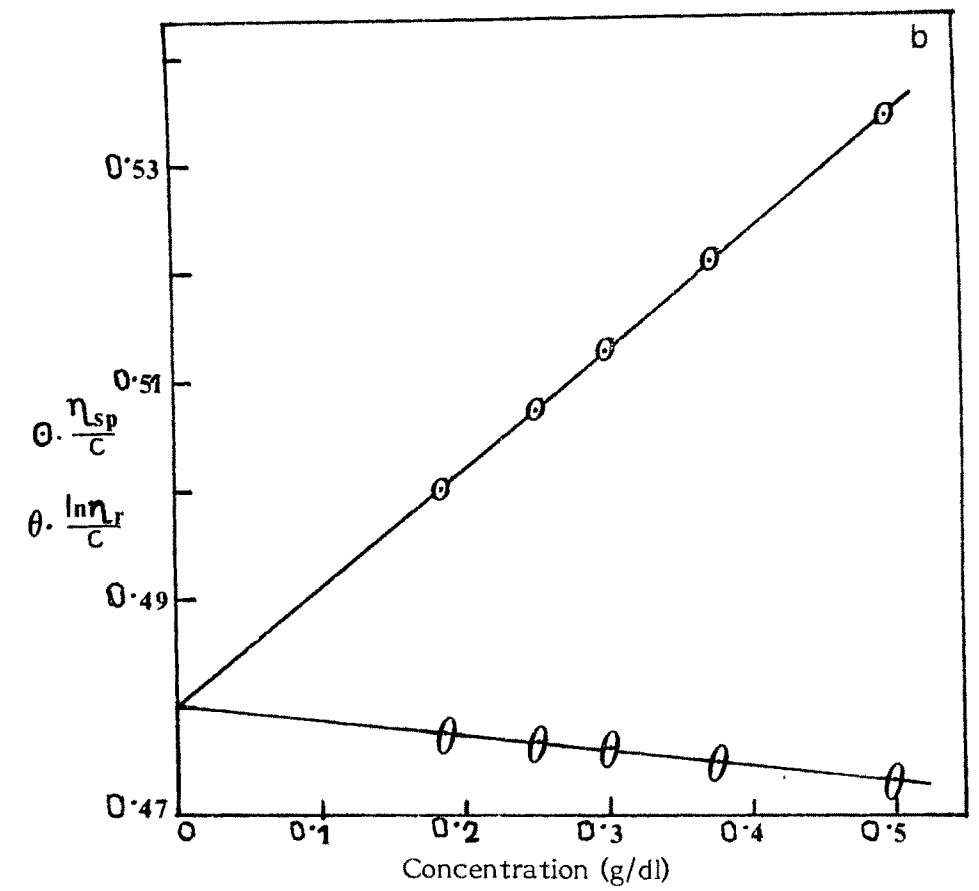
swelling behaviour is governed by the PAN backbone, resulting into increased swelling in polar solvents.

4.5.5 Viscometry

The intrinsic viscosities of graft copolymers of MMA and AN with various percentage grafting were determined in DMF and DMSO at 30, 35, 40 and 50° [Figs.4.15 - 4.17]. The results are given in Table 4.6.

From intrinsic viscosity data it is observed that the intrinsic viscosity of the graft copolymers is less than that of the parent homopolymer PAN due to the incorporation of MMA unit to the polymer backbone. Though percentage grafting obtained varies between 3-10% it influences the intrinsic viscosities considerably. The difference in intrinsic viscosity observed is 15-26% with respect to backbone PAN indicating the influence of arrangement of graft chains on the flow properties. The introduction of bulky hydrophobic groups in graft copolymers has decreased the solubility and hence viscosity. Decrease in solubility was also noticed from the solubility study where it was observed that graft copolymers show limited solubility in selected solvents such as DMF, DMSO, DMA ; whereas random copolymers were comparatively freely soluble in variety of solvents.

Using Frankel Eyring equation for viscous flow (as mentioned in section 3.2.6) the activation parameters $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$ are calculated for graft copolymers [Figs. 4.18 - 4.22] and are given in Table 4.7. It is observed that the graft copolymers with different percentage grafting did not show noticeable change in these thermodynamic parameters in a given solvent. It is also interesting to note that $\Delta S^{\ddagger}$ values in DMF are all negative wheras those corresponding in DMSO are positive. This indicates that the graft copolymers in DMF are more ordered in comparison with those in DMSO solution. This may be due to the higher polar nature of DMSO which influences the interaction between graft copolymer and solvent to a larger extent in comparison with that in



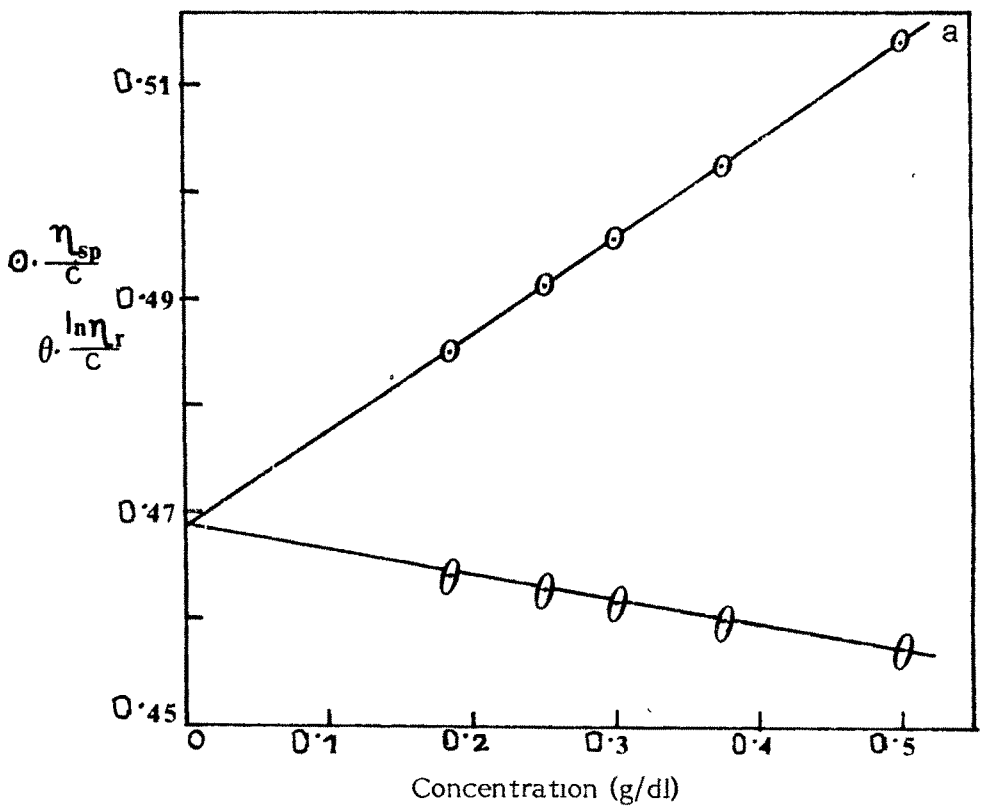


Fig. 4.15 Intrinsic viscosity of graft copolymer in DMF at 30°. a. G_1, b. G_2.

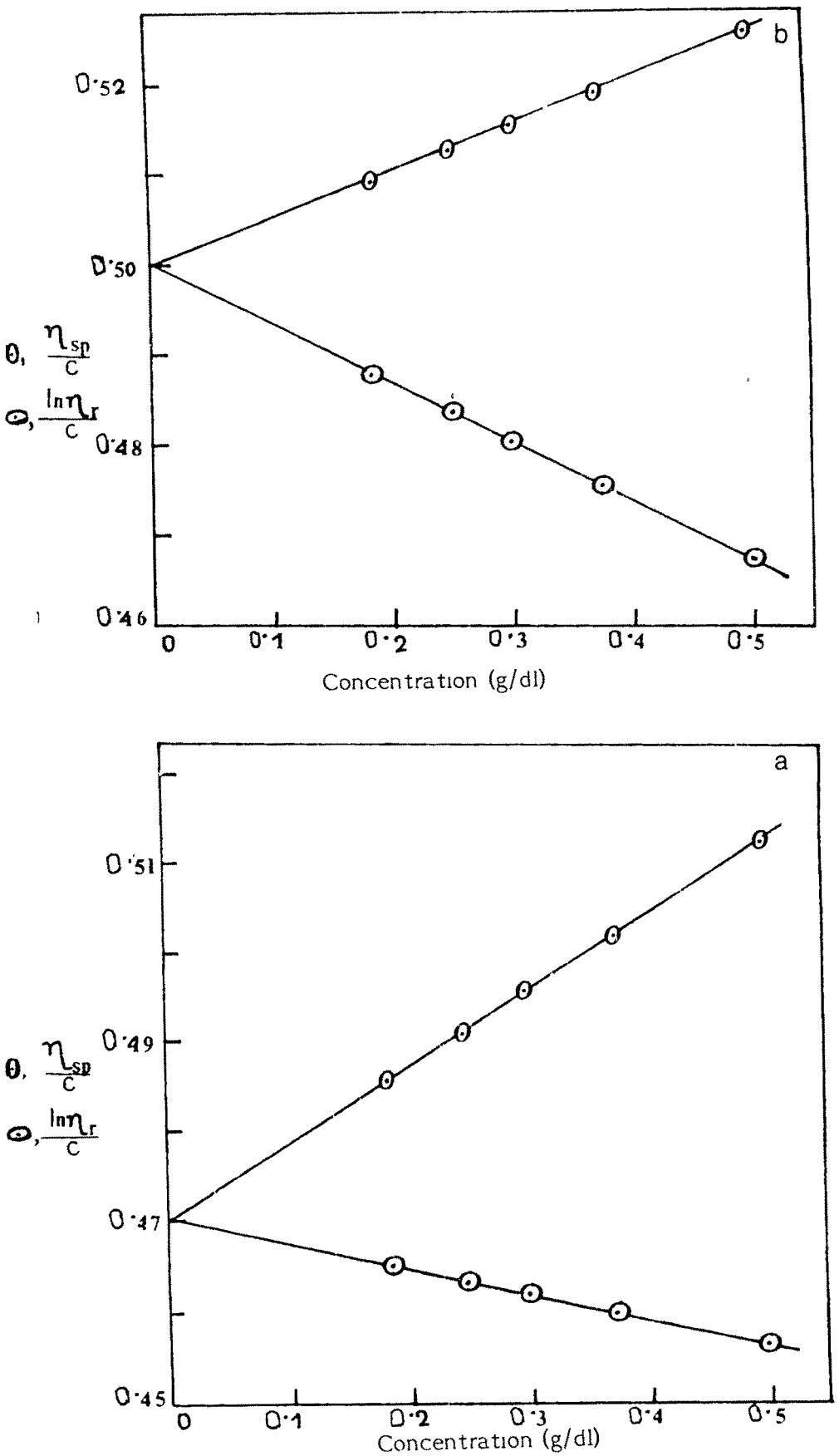


Fig. 4.16 Intrinsic viscosity of graft copolymer in DMF at 30°. a. G_3. b. G_4.

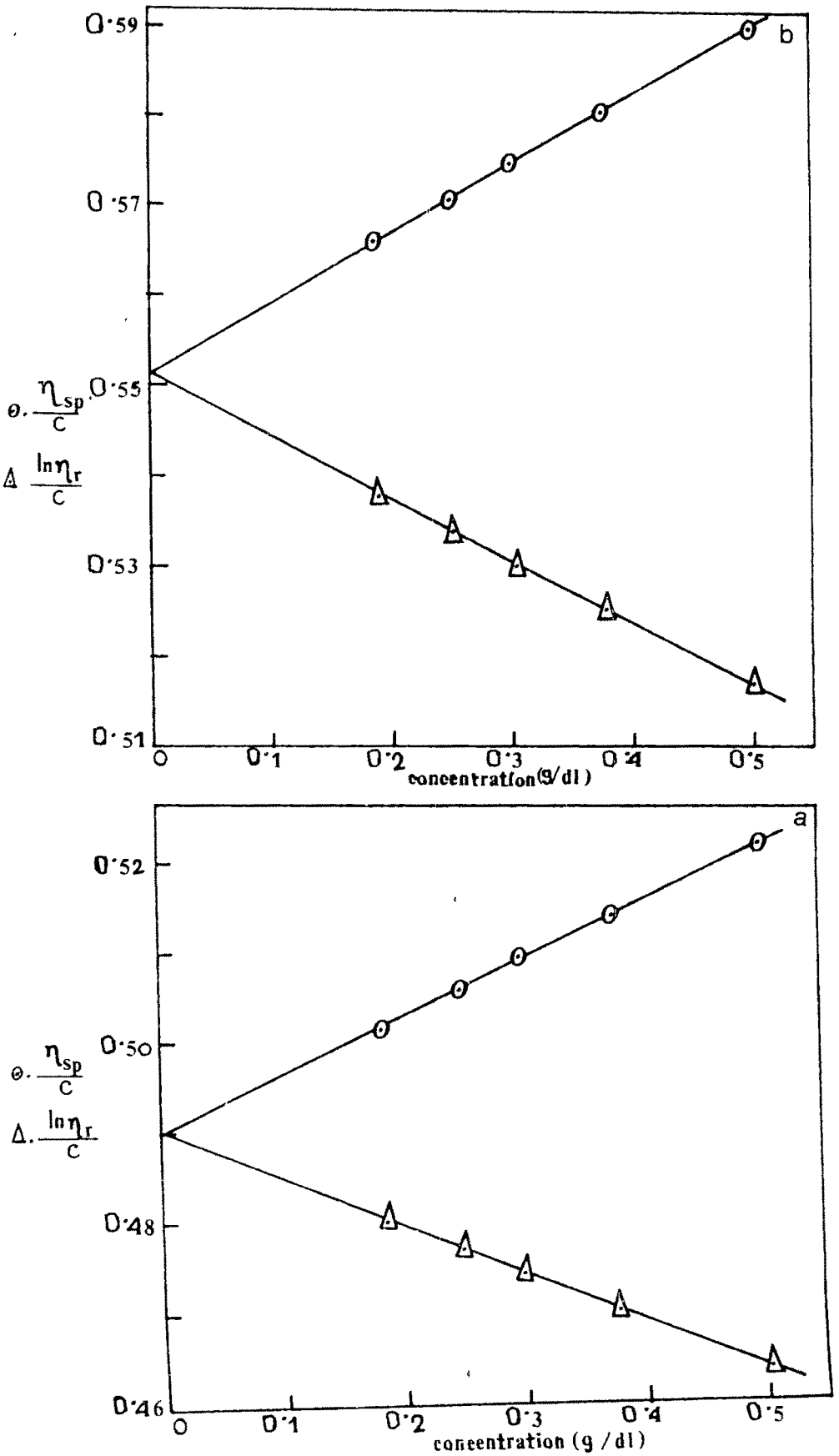


Fig. 4.17 Intrinsic viscosity of graft copolymer in DMF at 30°. a. G_5, b. G_6.

Table 4.6

Intrinsic viscosity of graft copolymer

Sample No.	Intrinsic viscosity in DMF (dl/g)				Intrinsic viscosity in DMSO (dl/g)			
	30°	35°	40°	50°	30°	35°	40°	50°
G_1	0.47	0.46	0.45	0.44	0.49	0.47	0.46	0.45
G_2	0.48	0.47	0.46	0.45	0.50	0.49	0.48	0.47
G_3	0.47	0.46	0.45	0.45	0.48	0.47	0.46	0.45
G_4	0.50	0.49	0.46	0.45	0.51	0.49	0.47	0.46
G_5	0.49	0.48	0.46	0.45	0.48	0.47	0.46	0.45
G_6	0.55	0.54	0.52	0.48	0.56	0.54	0.53	0.51
PAN	-	-	0.61				0.61	

Table - 4.6.a

Molecular weight of graft copolymer

Sample	$\overline{Mn} \times 10^{-4}$
G_1	1.27
G_2	1.29
G_3	1.31
G_4	1.40
G_5	1.42
G_6	1.65

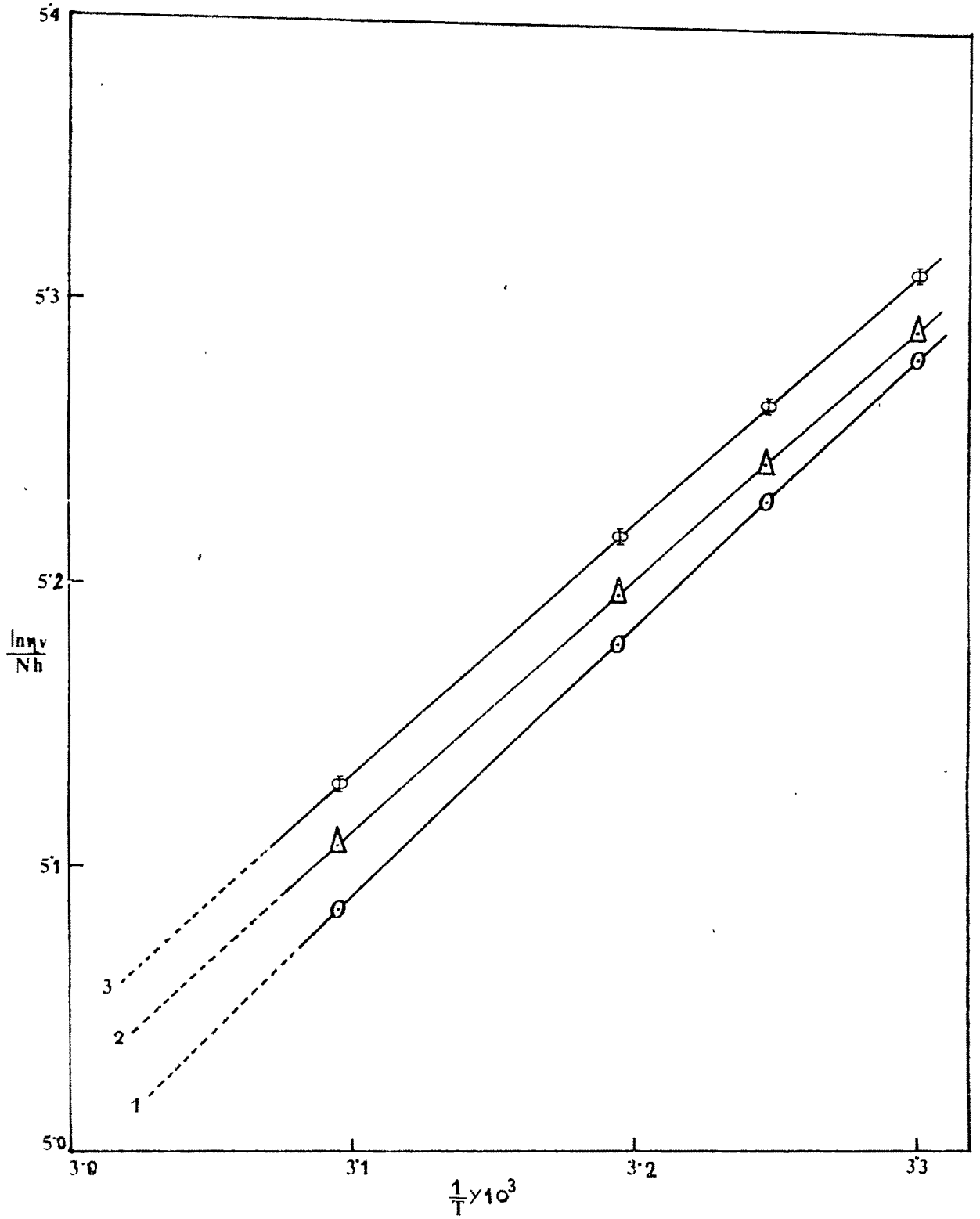


Fig. 4.18 ln ηV/Nh versus 1/T for 0.5 g/dl solution in DMF for 1. G_1, 2. G_2, 3. G_6.

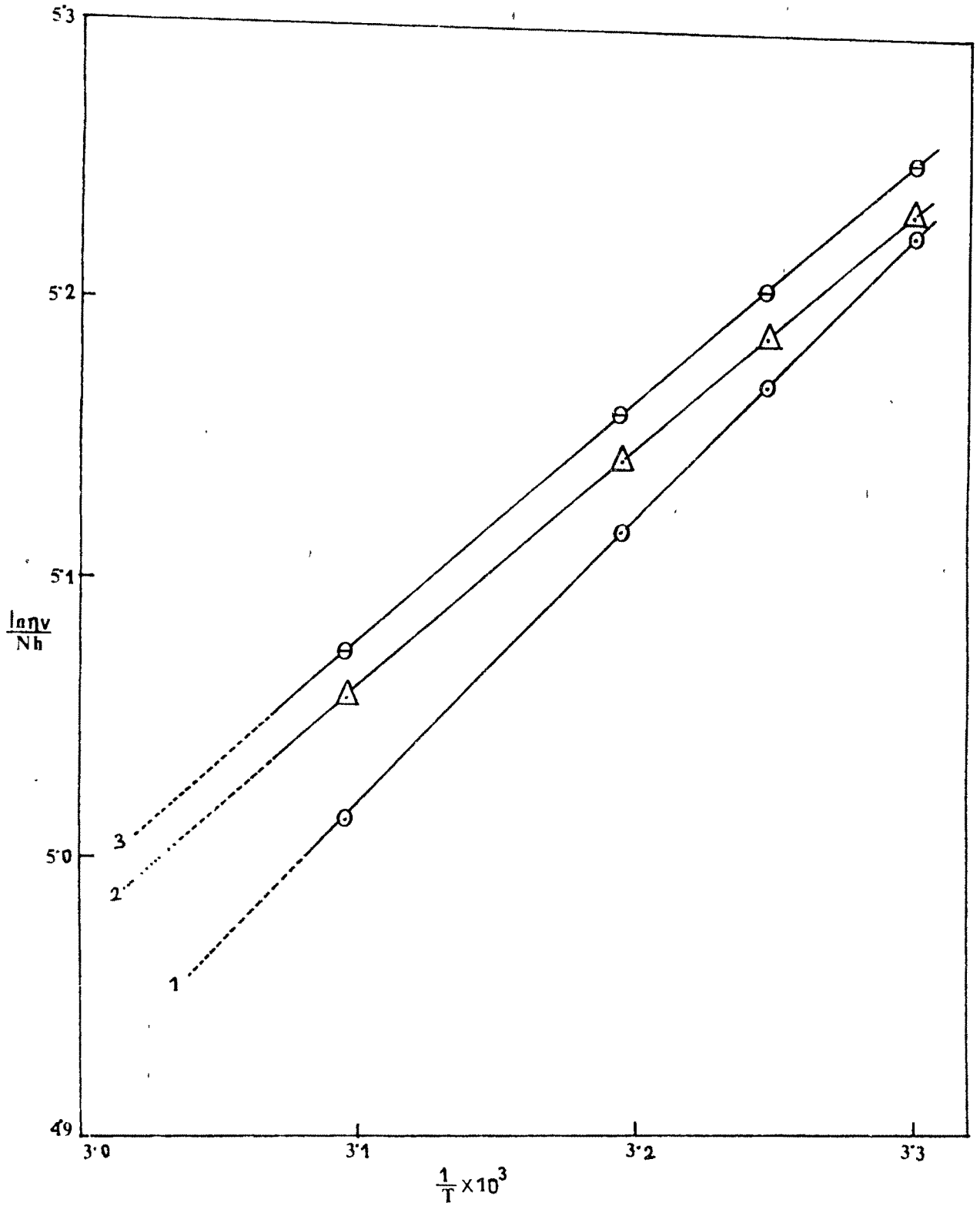


Fig. 4.19 $\ln\eta V/Nh$ versus 1/T for 0.375 g/dl solution in DMF for 1. G_1, 2. G_2, 3. G_6.

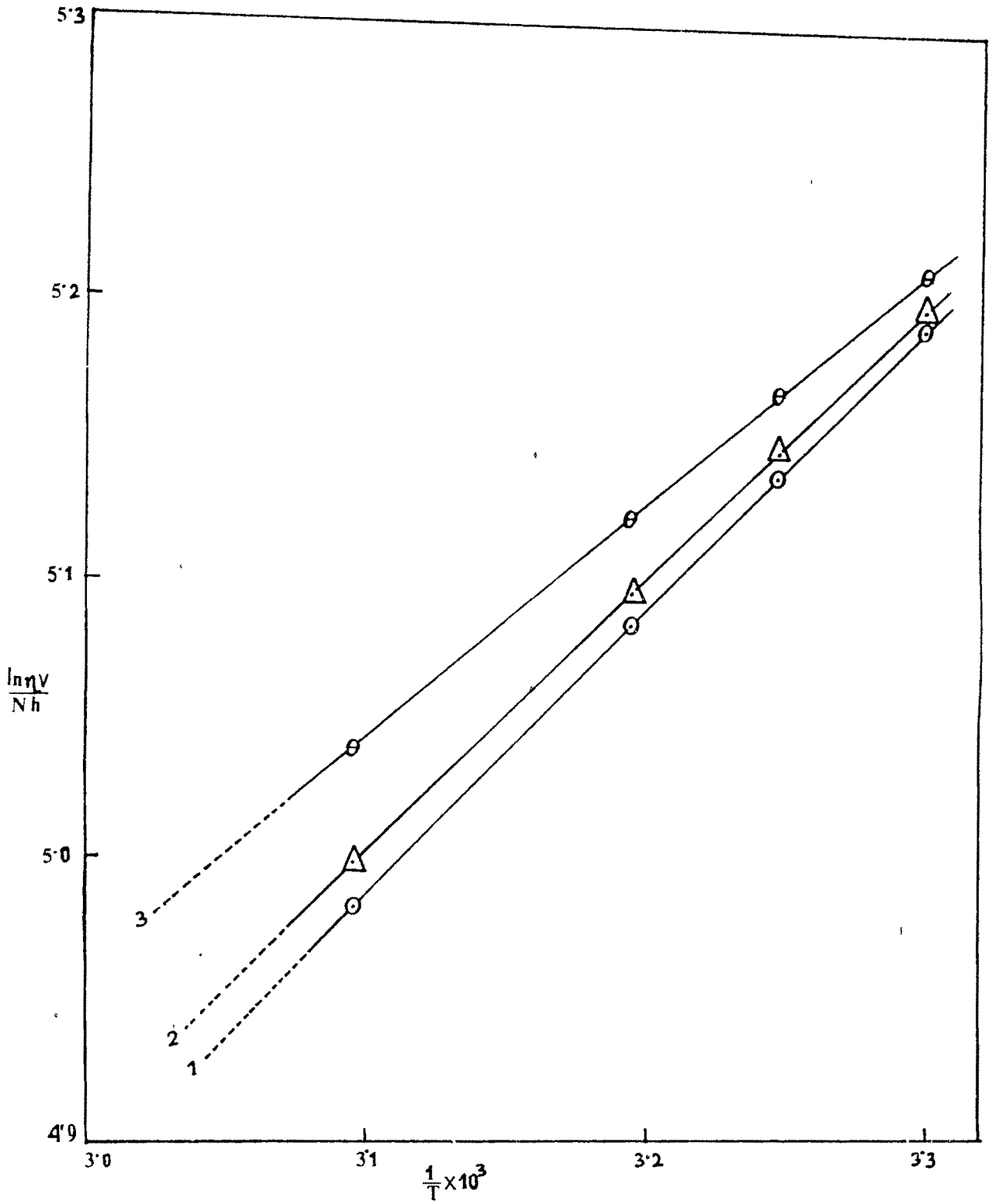


Fig. 4.20 $\ln \eta V/Nh$ versus $1/T$ for 0.3 g/dl solution in DMF for 1. G_1, 2. G_2, 3. G_6.

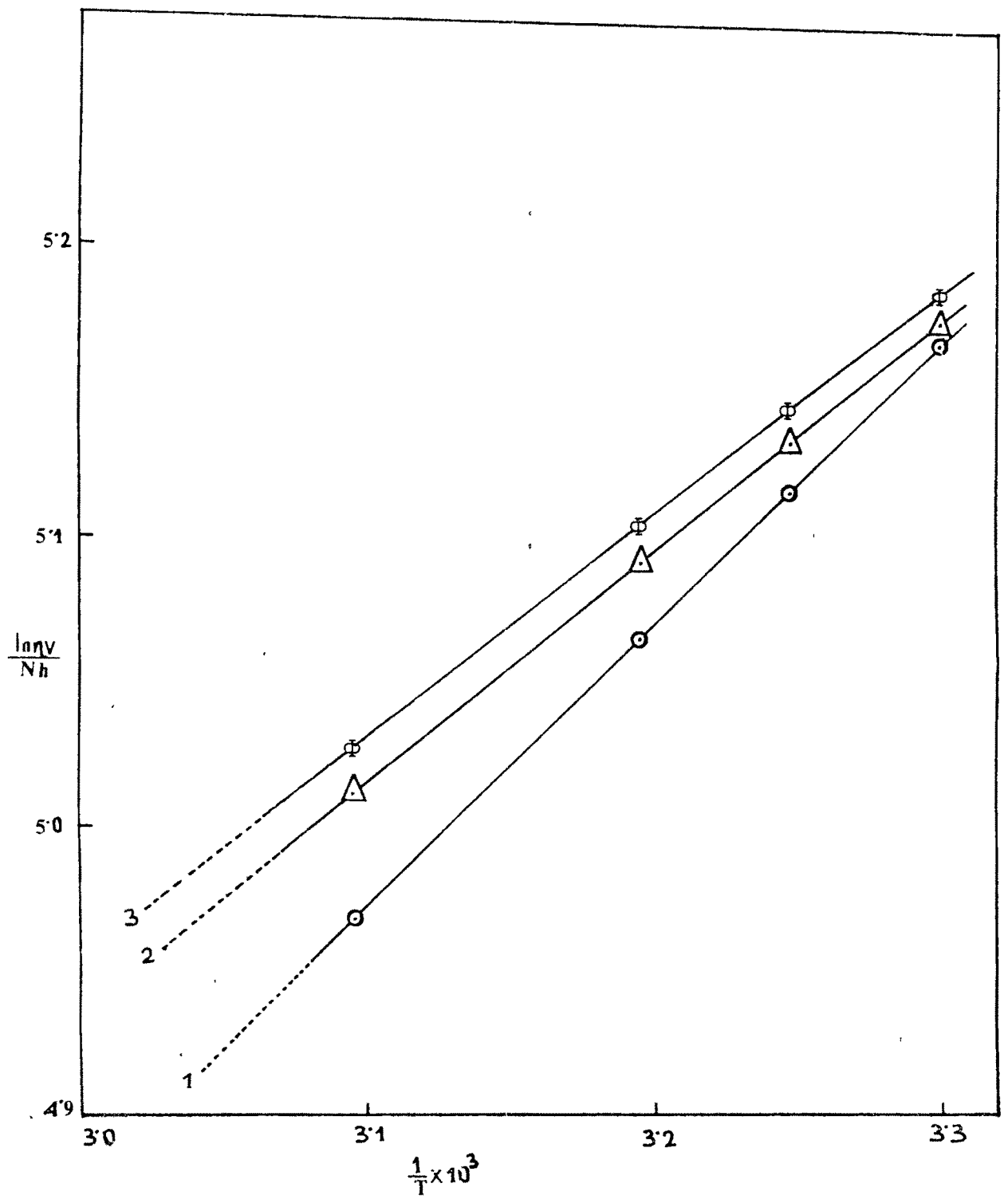


Fig. 4.21 $\ln \eta V/Nh$ versus 1/T for 0.25 g/dl solution in DMF for 1. G_1, 2. G_2, 3. G_6.

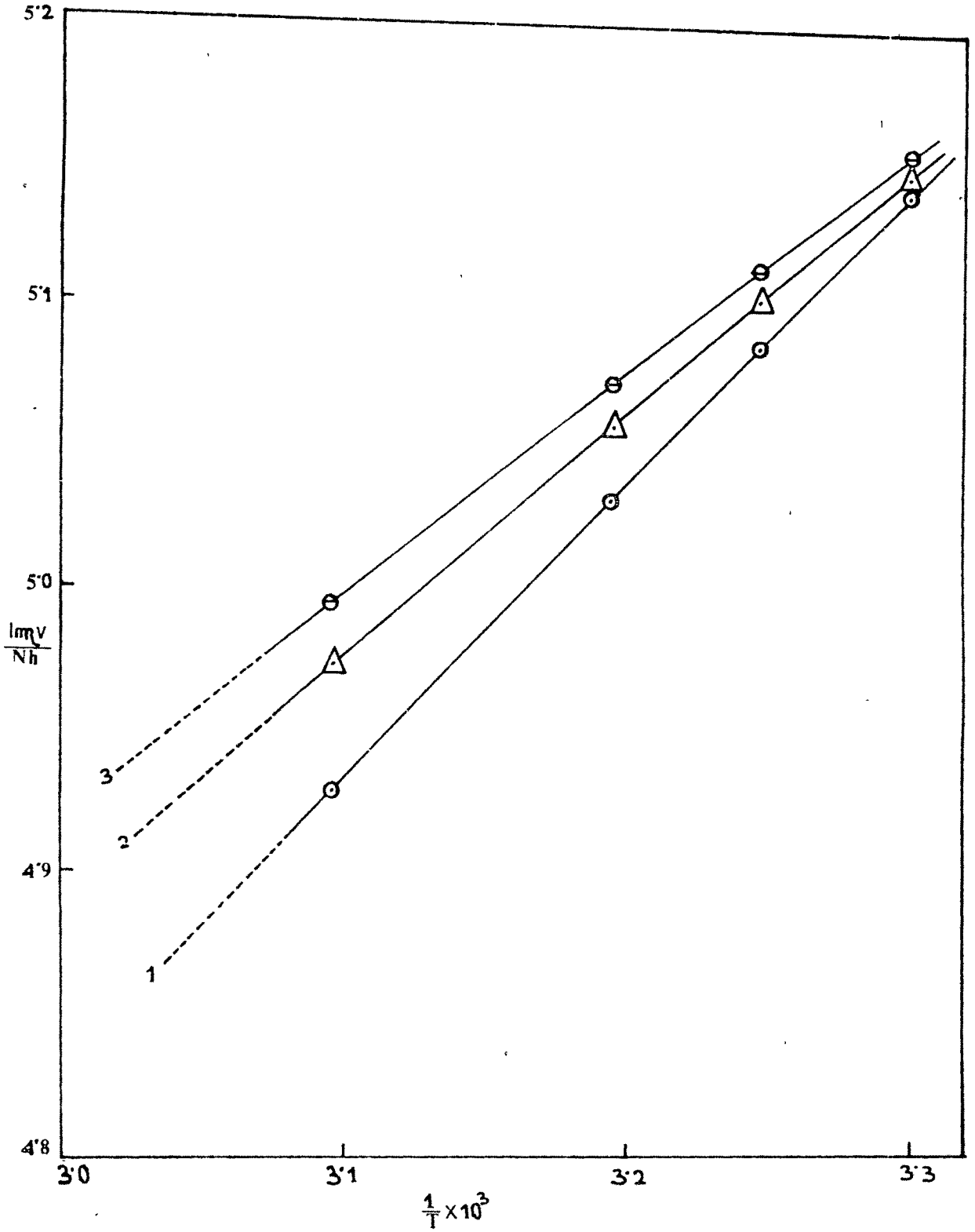


Fig. 4.22 $\ln \eta V/Nh$ versus 1/T for 0.1875 g/dl solution in DMF for 1. G_1, 2. G_2, 3. G_6.

Table - 4.7

Activation parameters for graft copolymers.
concentration of solutions : 0.5 g/dl

Sample	$\Delta H^{\ddagger}$ KJ mol^{-1}	$-\Delta S^{\ddagger}$ J deg^{-1}	$\Delta G^{\ddagger}$ KJ mol^{-1} 30°	35°	40°	50°
In DMF						
G_1	9.93	11.25	13.34	13.40	13.45	13.56
G_2	10.10	10.73	13.35	13.40	13.46	13.57
G_3	9.72	11.93	13.33	13.39	13.45	13.57
G_4	10.27	10.19	13.36	13.41	13.46	13.56
G_5	10.01	11.02	13.35	13.40	13.46	13.57
G_6	10.27	10.35	13.41	13.46	13.51	13.61
In DMSO						
G_1	15.69	−2.58	14.91	14.90	14.88	14.86
G_2	15.15	−0.80	14.91	14.91	14.90	14.89
G_3	15.35	−1.42	14.92	14.92	14.90	14.89
G_4	15.74	−2.65	14.94	14.93	14.92	14.88
G_5	14.99	−0.31	14.90	14.90	14.89	14.89
G_6	15.73	−2.47	14.98	14.97	14.96	14.93

DMF. The values of overall activation enthalpy $\Delta H^{\neq}$ of graft copolymer in DMF are smaller than the corresponding values in DMSO (Aprox. 35%) indicating that for the systems studied, thermodynamic properties of polymer solutions are influenced by the polymer-solvent interactions. $\Delta G^{\neq}$ values in DMF are also less than (51%) those corresponding in dMSO. The hydrodynamic volumes (Ve) of the graft copolymers are determined using Narang's equation [83] (section 3.2.6), and are shown in [Fig.4.23]. The values are given in Table 4.8. From the hydrodynamic volume, Simha shape factors [84] are calculated (Table 4.8). It is observed that the values of Simha shape factor for all systems at all temperatures remains almost constant at 2.44, hence the shape of the polymer in solvent is spherical.

Viscosity $\overline{M}n$ was calculated for the graft copolymers with 4 to 11 % grafting. The molecular weights were calculated as described earlier in section 3.2.6. The viscosity $\overline{M}n$ for PAN was observed to be 36000 whereas incorporation of MMA as <12 % graft decreases $\overline{M}n$ drastically to 12000. The further increase in % grafting from 4 to 11 resulted in the copolymers with 12000 - 15000 molecular weights. The results are given in Table 4.6.a.

4.5.6 Contact angle measurement

Table 4.9 shows the angle of contact (θ) of the graft copolymers in different solvents. It is observed that in a particular solvent the angle of contact decreases with the increase in percentage grafting. Critical surface tension of the graft copolymers was calculated by plotting cosθ values against surface tension of the contacting liquid. The results are given in Table-4.10. It is observed that critical surface tension of graft copolymer increases with the increase in percentage grafting.

4.5.7 Differential refractometry :

Fig. 4.24 shows the plot $\Delta n/C$ versus concentration for calculating dn/dc values

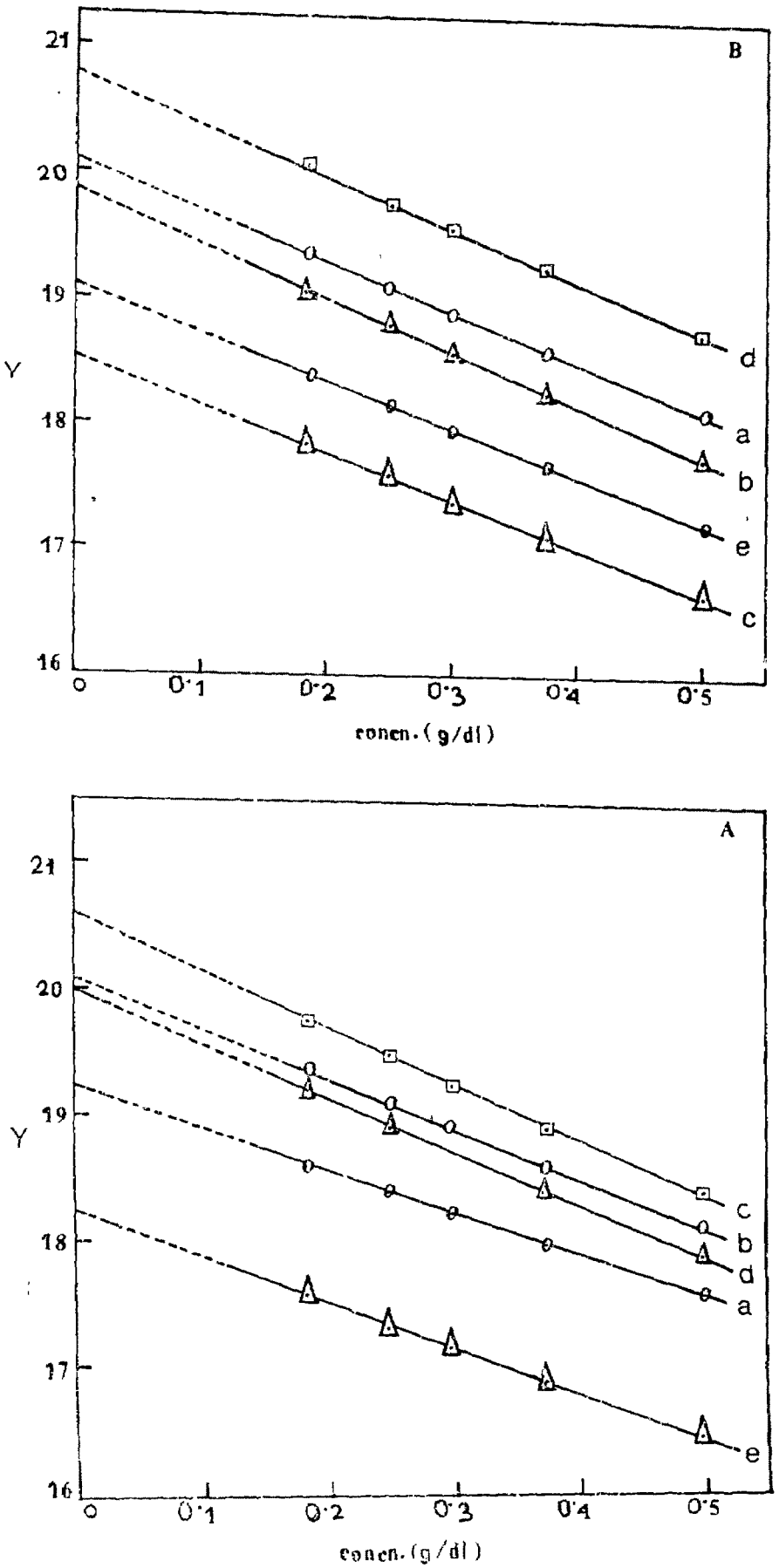


Fig. 4.23 Y versus concentration curve for graft copolymer. A. in DMF, B. in DMSO.
A:- a. G_1 at 30°, b. G_2 at 30°, c. G_3 at 40°, d. G_4 at 30°, e. G_5 at 50°.
B:- a. G_1 at 30°, b. G_2 at 30°, c. G_3 at 35°, d. G_4 at 30°, e. G_5 at 30°.

Table - 4.8

Hydrodynamic volume (Ve) and Simha shape factor (ν) of graft copolymer in DMF and DMSO

DMF	30°		35°		40°		50°	
Sample	Ve	ν	Ve	ν	Ve	ν	Ve	ν
G_1	19.21	2.45	19.65	2.34	18.44	2.44	18.03	2.44
G_2	19.67	2.44	20.05	2.34	18.85	2.44	18.44	2.44
G_3	19.36	2.43	19.18	2.40	18.52	2.43	18.44	2.44
G_4	20.22	2.47	20.23	2.42	18.78	2.45	18.51	2.43
G_5	19.99	2.45	19.70	2.44	18.78	2.45	18.52	2.43
G_6	22.53	2.44	22.17	2.44	21.17	2.46	19.59	2.45
DMSO								
G_1	20.00	2.45	19.34	2.43	18.85	2.44	18.52	2.43
G_2	20.41	2.45	20.08	2.44	19.95	2.45	19.26	2.44
G_3	19.67	2.44	19.26	2.44	18.85	2.44	18.44	2.34
G_4	20.90	2.44	20.08	2.44	19.18	2.45	18.93	2.43
G_5	19.75	2.43	19.34	2.43	18.93	2.43	18.93	2.43
G_6	22.76	2.46	22.13	2.44	21.72	2.44	20.90	2.44

Table - 4.9

Contact angle measurement of poly (acrylonitrile-9-methyl-methacrylate) copolymer at 30°.

Solvent	Contact angle (deg). of graft copolymer				
	4.2% grafting	6.33% grafting	8.66% grafting	10.05% grafting	10.47% grafting
Water	70	69	65	62	61
Ethylene glycol	55	53	51	48	47
Glycerol	64	63	60	57	56
Acetaldehyde	64	62	59	56	55
30% Ethanol	53	51	49	47	46

Table - 4.10

Critical surface tension of poly (acrylonitrile-g-methyl-methacrylate) copolymer.

% grafting	Critical surface tension $X 10^3$ Nm.
4.20	5.0
6.33	6.5
8.66	8.0
10.05	10.0
10.47	12.0

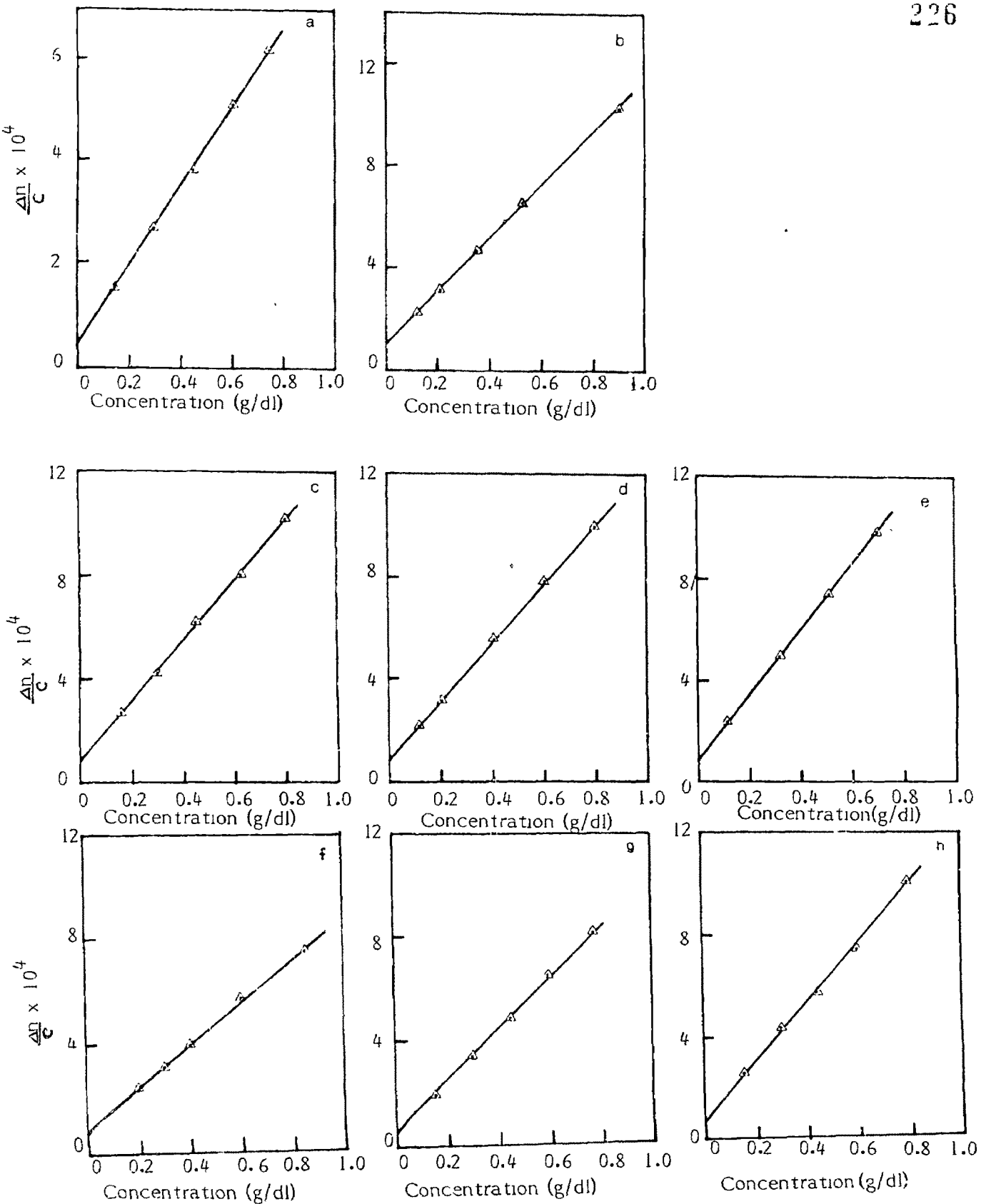


Fig.4.24 $\Delta n/c$ versus concentration plot of homopolymer and graft copolymer in differential refractometry. a. PMMA, b. PAN, c. G_1, d. G_2, e. G_3, f. G_4, g. G_6, h. G_5.

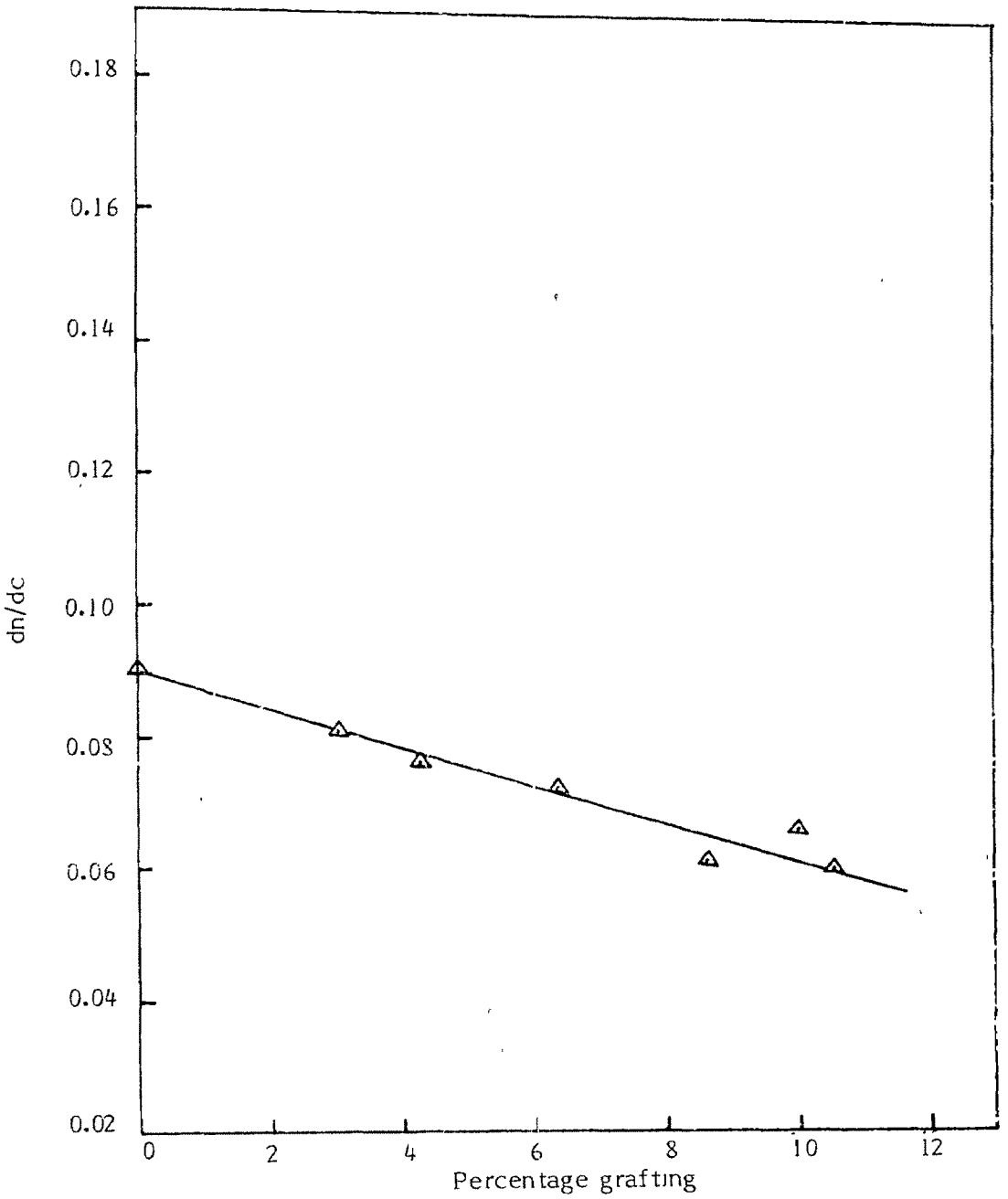


Fig.4.25 Effect of percentage grafting on the dn/dc values in differential refractometry.

for graft copolymers. It was observed that with increasing MMA content in the graft copolymer. i.e. with increasing percentage grafting dn/dc values go on decreasing and approaches closely to the dn/dc value for PMMA. Plot of dn/dc against percentage grafting (Fig 4.25) shows a reasonable linear relationship with a correlation co-efficient of 0.97.

4.5.8 Comparison between random and graft copolymers

As it is mentioned earlier the physico-chemical properties of the copolymers not only depend upon the composition but also on the arrangement of monomer units and hence on morphology. The random copolymers and graft copolymers are distinctly different in their morphologies. Hence we are giving here a comparative account of the selected properties of the random and graft copolymers of acrylonitrile and methyl methacrylate.

The i.r. spectra of random and graft copolymers exhibited peaks at 2250 cm^{-1} corresponding to -C≡N stretching and at 1735 cm^{-1} and 2930 cm^{-1} corresponding to carbonyl and methyl stretching vibrations of - $COCH_3$. I.R. being a structural property and not morphological, no difference in i.r. properties of the two types of copolymers was observed.

Solubility behaviour of random copolymers (Table 3.3) reveals that these are soluble in some common solvents such as acetone, chloroform, toluence, nitrobenzene, IBMK, DMF, DMSO, DMA etc. and graft copolymers are soluble in limited number of solvents such as DMF, DMSO, DMA. In case of graft copolymers the solubility is governed by the backbone material PAN. The grafting of MMA unit onto PAN does not have much influence on the solubility. This may be because of lower extent of grafting.

From intrinsic viscosity data for random copolymers (Table-3.6) and for graft copolymers (Taple 4-6) it is observed that intrinsic viscosities go on decreasing

with increased temperature irrespective of the morphology of the copolymer. The thermodynamic parameters (Table 3.7 and 4.7 for random and graft copolymes respectively) also show that the trend observed for random and graft copolymers are similar but $\Delta S^{\neq}$ values are comparatively lower (negatives) for graft copolymers than random copolymers indicating that the graft copolymers are more ordered.

Viscosity molecular weights of the random and graft copolymers differ widely. In case of random copolymers increased mole fraction of AN in the copolymer increases the molecular weight of the resulting copolymer. However the copolymers rich in MMA showed lower molecular weights than PMMA.

In case of graft copolymers backbone PAN has 36000 molecular weight and incorporation of MMA as graft chains decreases it drastically to 12000. Further increase in grafting upto 10% increases the molecular weight only upto 15000. Hence in case of random as well as graft copolymers incorporation of MMA results into low molecular weight products. No specific regularity was observed in molecular weights of random and graft copolymers suggesting that molecular weight is a structural property and not the morphological. Glass transition temperatures of graft copolymers (Table 4.5) are higher than those of the random copolymers (Table 3.10). The former has glass transition temperature above 90° and the latter below 90°. But the crystallisation temperatures of graft copolymers are much lower (below 271°) than those for random copolymers (above 300°). This is expected because in Table 3.10 the crystallisation temperature decreases with increase in AN content andPAN has crystallisation temperature of 268°. In grafting the crystallisation temperature increases with the increase of percentage grafting i.e with the increase of MMA content on the PAN backbone. Hence comparatively random copolymers show better processibility. From thermogravimetric analysis (Figs. 3.28, 3.29 for random copolymers and Fig. 4.13 for graft copolymers) it is observed that the graft copolymers have higher initial decomposition temperature (IDT) (above 270°) than

the random copolymers (150-180°), but the activation energy associated with thermal breakdown for graft copolymers are lower ($\sim$45 KJ mol^{-1}) than the random copolymers (above 130 KJ mol^{-1} Table 3.12)

The d-spacing for graft copolymer was found to be 5.21Å indicating close resemblance with backbone material PAN which has d-spacing at 5.27Å . This is due to low percentage grafting ; whereas for random copolymers the peaks are observed in the range 5.37-6.14 A. X-ray analysis as well as higher IDT temperatures for graft copolymers indicate higher crystallanity in them in comparison with random copolymers.

Swelling studies reveal that (Fig. 4.14 for graft copolymer and Figs 3-46, 3.47 for random copolymers) the graft copolymers exhibited higher swelling in a particular (polar) solvent than the random copolymers. This is expected due to the more polar nature of the backbone polymer PAN, which helps in developing a miceller structure comprising polar outskirts & nonpolar central cores, which have higher interaction with polar solvents hence increased swelling. The formation of miceller structure is less pronounced in random copolymers resulting into lower extent of swelling. In differential refractive index measurement it is observed that graft copolymers give a straight line when the values of dn/dc is plotted against percentage grafting (Fig. 4.25) whereas for random copolymers the plot of dn/dc against mole fraction of AN shows a 25% deviation from the calculated result (Fig. 3.49) which is due to randomness.

From the comparative account it can be summarised that crystallanity, swelling, refractive index, X-ray and electron microscopic properties depend upon the morphology of the copolymer. Thermal and viscosity properties show less dependence on morphology and IR, NMR and molecular weight show no dependence on morphology of copolymers.

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