SPECTROSCOPIC ANALYSIS OF CIS-POLYISOPRENE AND POLYMETHYL METHACRYLATE GRAFT COPOLYMERS

by

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Abstract

This paper explains the used of Fourier Tranisform Infra-Red Spectroscopy (FTIR) Nicolet MX-1 in analysing the PMMA content of the graft copolymer cis-polyisoprene/PMMA leading to its suspected mechanism. Both qualitative and quantitative applications were used.

Graft copolymers were synthesized by free-radical polymerisation utilising benzoyl peroxide as an initiator and toluene as the solvent. Samples were analysed for three different polymerisation time. The proposed grafting mechanism were confirmed by the FTIR analysis on the product obtained after the degradation of the backbone chain.

Calibration of the FTIR was accomplished with the used of PMMA standard of number average molecular weight, M_n 125,000.

Keyword:-

FTIR	–	*Fourier Transform Infra-Red Spectroscopy*
PMMA	–	*Polymethyl Metha crylate*
PI	–	*cis-Polyisoprene*
MMA	–	*Methyl Methacrylate*

Introduction

In the characterization of grafted and ungrafted copolymers both qualitative and quantitative analysis were used. The qualitative applications of infra-red spectroscopy to polymer characterization include the followings[1]:-

.i) structure determination, using the group frequency region

ii) structure determination in copolymers, information about the sequence distribution and tacticity in copolymers can be obtained

The group frequency region determine the difference between the grafted and ungrafted cis-polyisoprene and the composition of the PMMA grafted on to cis-polyisoprene. The following absorption bands were used in the determination;

Absorption band an^{-1} Characteristic Group

1,735 $>c = 0$ of PMMA

1,620-1,650 $>c = c<$ cis-polyisoprene

The quantitative analysis is based on the application of the BEER-LAMBERT LAW, which is given by:

$$A = \log(I_o/I) = acl = \log 100/\% \ T$$

where,

A   = absorbance, directly determined from the spectrum

I_o = intensity of incident radiation

I   = intensity of transmitted radiation

a   = the absorption coefficient ($dm^3 \ g^{-1} \ cm^{-1}$)

c   = concentration fo solute (gdm^{-3})

l   = path length of sample (cm)

T   = transmittance = I/I_o

This method is especially convenient because it could be calibrated with polymer solutions of known concentration.

In order to analyse the grafting mechanism, studies on the backbone polymer is a useful method. Grafted cis-polyisoprene, in solution, could be broken down by hydroperoxide in the presence of osmium tetroxide. The PMMA graft chains, since they do not contain ethylenic bonds (excluding the end groups) remain unaltered. The unattacked PMMA was isolated by precipitation with ethanol, whereas with small fragments of cis-polyisoprene are readily soluble (aldehydes of low molecular weight). Therefore separation of the PMMA consist merely of precipitating the hydroperoxide degradation mixture into methanol and filtering off the PMMA.

Equipment

Fourier Transform Infra-Red Spectrophotometer (FTIR)

A Nicolet MX-1 Fourier Transform infra-red spectrophotometer (Figure 1) was used for the determination of the weight percentage of MMA grafted on to the cis-polyisoprene. This technique differs from conventional dispersive spectrophotometers in using an interferometer, instead of a monochromator eg: a Michelson interferometer. This interferometer consisted of two plane mirrors at right angles to each other and a beam splitter at an angle of 45° to the mirrors. The beam splitter divides the incoming light from the source -50% is transmitted and 50% is reflected. A compensator is placed in one arm of the interferometer to equalise the optical path lengths in both arms. From the compensator the incoming radiation goes into the sample compartment and to the detector. The output information from the detector is digitalised in a computer and transformed to the FREQUENCY DOMAIN - each individual frequency is filtered out from the complex interferogram (FOURIER TRANSFORMS). Then the signals are converted into a conventional infra-red spectrum. An entire spectrum can be recorded, computerised and transformed in a few seconds.

Experimental Methods:

Calibration of FTIR

Calibration of the FTIR was accomplished with the use of polymethyl methacrylate standard of number average molecular weight, M_n 125,000. Methyl methacrylate solution were made from a known weight of the PMMA in 10 cm^3 of dried toluene. Various solutions were obtained by diluting the stock solution. Six solutions with concentration ranging from 0.46 to 2.72 g/cm^3 were prepared and the six infra-red measurements made. Two measurements were made on each solution and the mean value of the absorption peak was utilised in constructing a calibration curve, (Figure 2).

Sample Preparation

Graft copolymer cis-polyisoprene/PMMA was synthesised in toluene utilising benzoyl peroxide as an initiator by a free radical polymerisation. Three sets of samples were prepared at 2 hr, 4 hr and 6 hr intervals. Prior used, the samples were Soxhlet extracted to remove any unreacted PMMA homopolymers and dried under vacuum to a constant weight.

A graft copolymer solution of 1.0% was made from the required weight of the copolymer followed by 10 cm^3 of dried toluene. The mixture was heated under reflux until the graft copolymer appeared to have dissolved completely. The solution was allowed to cool to room temperature before IR measurements were made. This was repeated twice and the average value of the absorbance taken.

Degradation of graft copolymer

The technique employed was developed by Kolthoff et.al.[2] p-Dichlorobenzene (40-50g) contained in a 100 cm^3 round bottom flask was heated to 50° - 60°C. Graft copolymer samples (0.5 g) were added and the solution heated to about 130°C. The temperature was maintained until the graft copolymers had dissolved.

The solution was cooled to 80° - 90°C and 10 cm^3 of tert-butyl hydroxide added. 1.0 cm^3 of 0.003M osmium tetroxide solution in benzene was then added and the solution heated to 110 - 150°C. The temperature was maintained for 20 minutes and then cooled to 50° - 60°C.

After cooling, 20 cm^3 of benzene was added to the solution. Finally the solution was slowly poured into 250 cm^3 of methanol containing a few drops of concentrated sulphuric acid. The mixture was continuously stirred during this addition. A small portion of benzene was then used to wash the flask and the mixture was stired until the PMMA had coagulated. This solution was left overnight for PMMA to precipitate fully.

The precipitate was then filtered, washed and dried before it was redissolved in a minimum amount of acetone and reprecipitated in methanol. This precipitate was collected, washed and dried to constant weight under reduced pressure in a vacuum oven at 45°C. The product was then analysed by the Nicolet MX-1 Fourier Transform IR Spectrophotometer.

Results and Discussion

The spectrum of synthesis cis-polyisoprene is shown in Figure 3, and that of a graft copolymers in solution in Figure 4. An additional band at 1,735 cm^{-1} due to PMMA can be seen. The absorption band is due to the carbonyl absorption [>c = 0] and so is the characteristic of PMMA. From figure 4, the intensity of this absorption band increases as the weight percentage of PMMA grafted on the cis-polyisoprene increases. Increasing the weight precentage of PMMA grafted on the cis-polyisoprene, means increasing the number of carbonyl group in the graft copolymers.

From either grafted or ungrafted cis-polyisoprene the characteristic double bond stretching band (>c = c<) in region 1620 - 1680 cm^{-1} ie. 1668 cm^{-1} was observed. This absorption band has the same intensity for all the three different graft copolymers.

The presence of the carbonyl absorption peak in the spectra of the grafted copolymers confirmed that cis-polyisoprene grafted with different percentages of PMMA was actually prepared by the free radical polymerisation. Table 1 shows the weight percentage of PMMA presence in the grafted copolymers as calculated from the FTIR analysis using the *BEERS-LAMBERT LAW*. Hence, the infra-red analysis, analysed the weight percentages of PMMA content of the copolymers.

The unchanged intensity of the double bond stretching band observed for all the graft copolymers meant that no detectible amount of the unsaturation of the cis-polyisoprene were utilised in the graft copolymerisation of MMA on the cis-polyisoprene with time. Therefore, there is little or no copolymerisation of MMA with cis-polyisoprene units. The grafting of PMMA units on to cis-polyisoprene chains must come from transfer. The results, therefore, give useful information in elucidating the possible mechanism of the graft copolymerisation.

The result from the analyses, using the degradation technique, of the PMMA content of the graft copolymers are presented in Table 2. The weight decreased linearly with extent of polymerisation as shown in figure 5. This meant more PMMA chains of lower molecular weight such as oligomers grafted on to the cis-polyisoprene with increasing extent of polymerisation. Those would not be recovered on degrading the cis-polyisoprene backbone. Very low molecular weight oligomers would be particularly soluble in the precipitating agent. Further losser of PMMA also occur during purification.

On analysis by FTIR spectroscopy the spectra obtained, Figure 6, confirm that all the polymers collected were PMMA only. This spectrum was obtained on the PMMA isolated from the degradation of the graft copolymer, G4. Hence degradative technique support the results obtained by the FTIR that unsaturation of the cis-polyisoperene were not utilise in the graft copolymerisation of MMA onto cis-polyisoprene with time.

Conclusion

Analysing the products formed at different time of polymerisation indicate that graft copolymers of varying content have been synthesised. Therefore free radical copolymerisation in solution can be utilised in the synthesis of graft copolymers. FTIR concludes that the amount of PMMA grafted increased linearly with the percentage of conversion consistant with a constant production of graft formation with polymerisation time.

Mechanism of graft copolymerisation is considered to be of chain transfer to polymer with abstraction of H-atom from the polymer backbone either by an initiator radical or a growing polymer radical. The grafting mechanism for MMA on to cis-polyisoprene can be represented by the following reaction scheme;
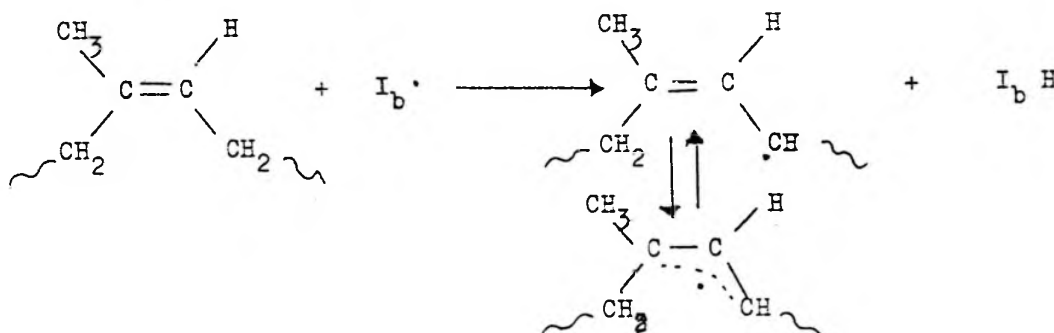
Generation of free-radical,

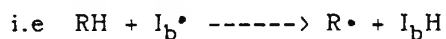Benzoyl peroxide which was used as an initiator, undergoes decomposition, i.e,

i.e, $I_2 \longrightarrow 2I_b\cdot$

$I_b\cdot + M \longrightarrow P\cdot$
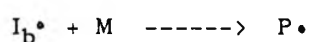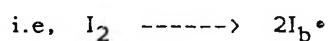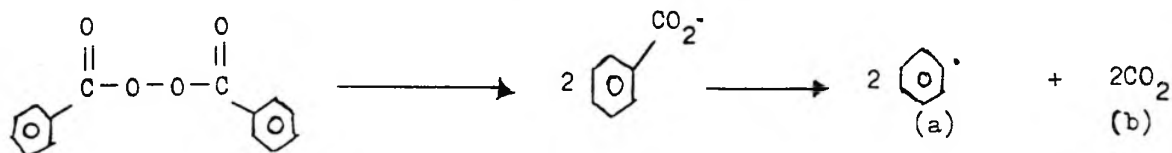
where I_2 is initiator and M the manomer.
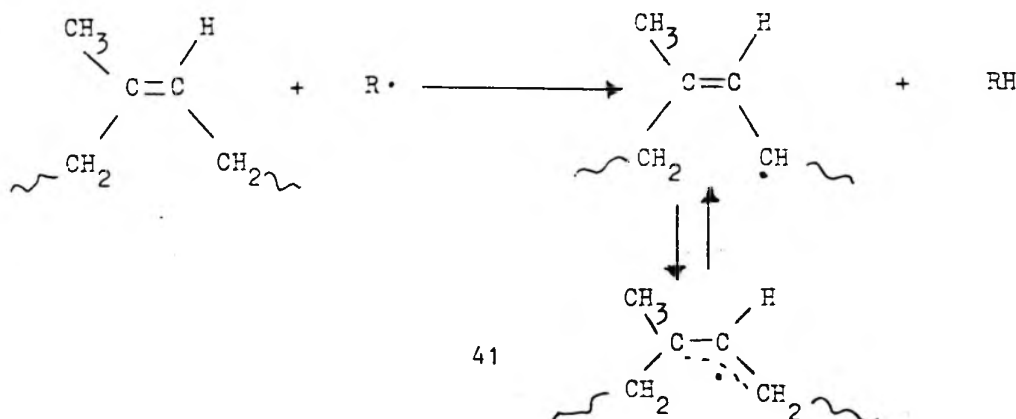
Graft initiation

Transfer to the polymer backbone by initiator radical occurs on the methylene group[3] producing a stabilised allylic radical, i.e,
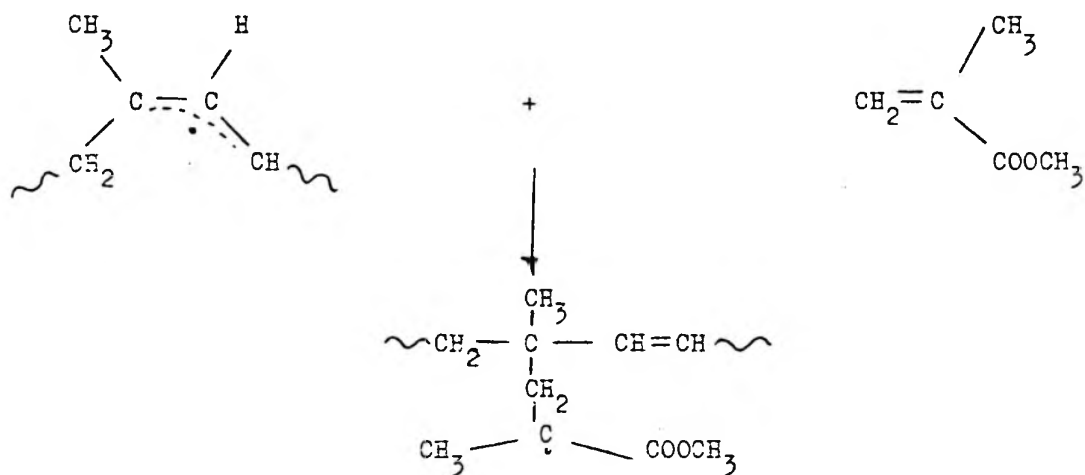

Transfer to the methyl group-would be equivalent.
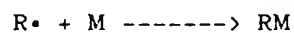
i.e $RH + I_b\cdot \longrightarrow R\cdot + I_bH$

The cis-polyisoprene radicals will initiate graft copolymerisation and also be terminated by transfer to the polymer backbone producing a new polymer radical i.e,
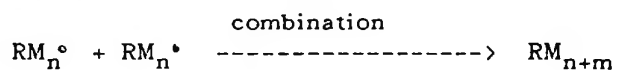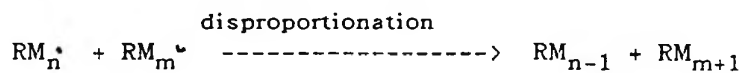

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Graft propagation

$$\underset{\displaystyle \sim\!\!\!CH_2 \quad\quad CH\!\!\!\sim}{\overset{\displaystyle CH_3 \quad\quad H}{\underset{}{C \,\overset{\cdot}{-\!\!\!-}\, C}}}$$

$$+$$

$$CH_2\!\!=\!\!C\overset{\displaystyle CH_3}{\underset{\displaystyle COOCH_3}{}}$$

$$\downarrow$$

$$\sim\!\!CH_2\!-\!\overset{\displaystyle CH_3}{\underset{\displaystyle CH_2}{C}}\!-\!CH\!=\!CH\!\sim$$

$$CH_3\!-\!\overset{}{\underset{}{C}}\!\!\sim\!COOCH_3$$

and so,

$$R\bullet \;+\; M \;-\!-\!-\!-\!-\!-\!-\!> \; RM$$

This graft radical will propagate by addition of monomer until termination or transfer occurs.

Termination step

$$RM_n^{\bullet} \;+\; RM_m^{\cup} \quad \overset{\text{disproportionation}}{-\!-\!-\!-\!-\!-\!-\!-\!-\!-\!-\!-\!-\!-\!-\!-\!-\!>} \quad RM_{n-1} \;+\; RM_{m+1}$$

$$RM_n^{\circ} \;+\; RM_n^{\bullet} \quad \overset{\text{combination}}{-\!-\!-\!-\!-\!-\!-\!-\!-\!-\!-\!-\!-\!-\!-\!-\!-\!>} \quad RM_{n+m}$$
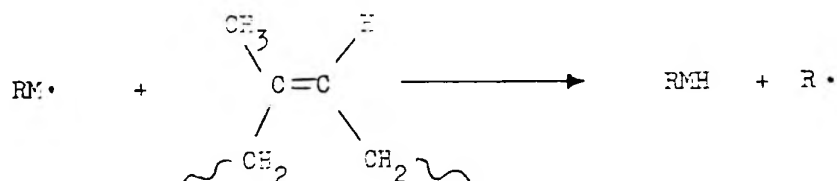
Termination by disproportionation is considered to be more likely, since termination by combination is considered to be less likely in MMA than disproportionation and termination by combination produces a crosslinked graft copolymers and the copolymers were soluble.

Transfer reaction

(i) To monomer

$$RM\bullet + M \quad ------------> \quad RMH + M\bullet$$

(ii) To polymer,

### (iii) To solvent,

$$RM\bullet + SH \quad ----------> \quad RMH + S\bullet$$

Transfer to monomer, polymers and solvent can occur but transfer does not change the kinetic chain length and further grafting or homopolymerisation occurs. The reaction proceeds by transfer of a hydrogen atom from the transfer molecule to the growing polymer chain. The transfer constant of MMA radicals to PI is high $(8-11 \times 10^4)$[4-5] compared with that to toluene (0.2×10^4)[6], but concentration differences makes this less.

The above mechanism is deduced from the IR and chemical analyses in that the cis-polyisoprene double bonds do not appear to be involved in copolymerisation — within the experimental accuracy of these measurements. The studies of the graft copolymers by degradative techniques indicated that only the ethylenic double bond were intact after grafting since PMMA was the sole product of the degradation.

However, the possibility of a small amount of copolymerisation occuring, cannot be ruled out, i.e,
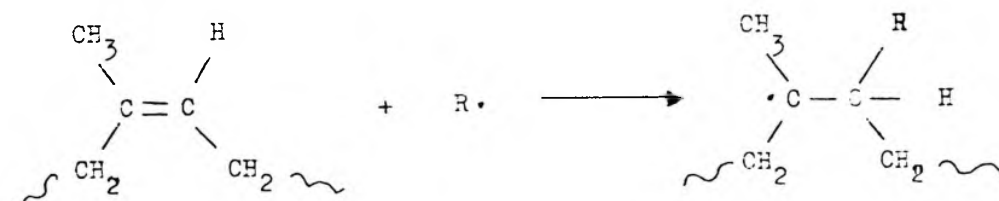
References

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7.   W.A. Wan Abdul Rahman, Master Thesis, University of Birmingham (1988).

TABLE I

Weight % of PMMA content determined by FTIR analysis

| Graft Copolymer type	Copolymerisation time / h	PMMA content determined by / weight %	PMMA content by FTIR analysis / weight %
G 6	6	17.9	16.7 $\pm$ 1.5
G 4	4	12.5	11.6 $\pm$ 2.0
G 2	2	6.7	6.3 $\pm$ 1.0

TABLE 2

Determinations of PMMA content from the graft copolymers

Graft copolymer serial no.	Polymerisation time / h.	* PMMA content / wt. %	PMMA recovered ** / wt. %
G 2	2	6.7	89.9 $\pm$ 0.5 %
G 4	4	12.5	69.6 $\pm$ 0.7 %
G 6	6	17.9	51.9 $\pm$ 1.0 %

* Weight % of PMMA content = $\dfrac{W_G}{W_o + W_G}$ x 100

* * Determination by degradation technique

Figure 1
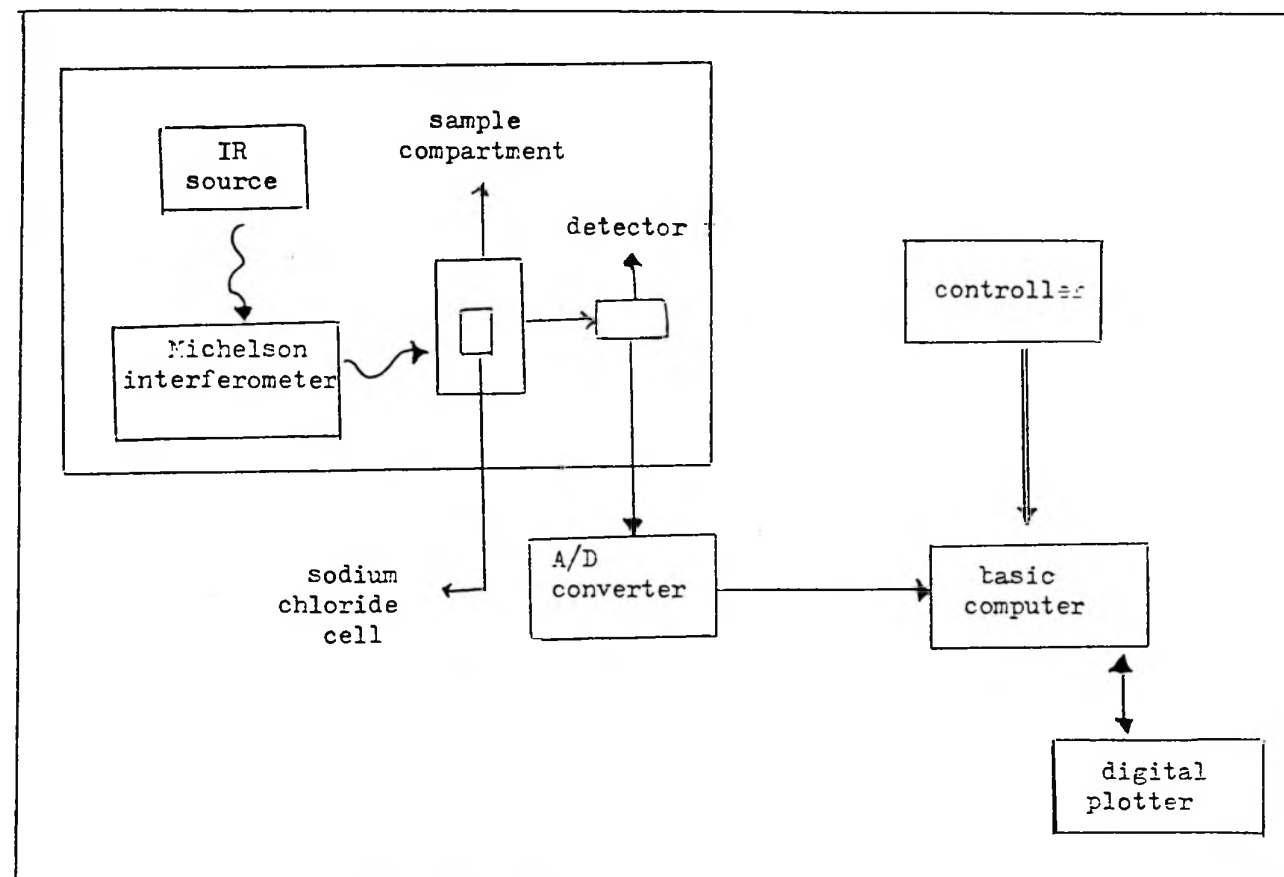
BLOCK DIAGRAM OF THE BASIC COMPONENTS OF A F.T INFRA-RED SPECTROPHOTOMETER

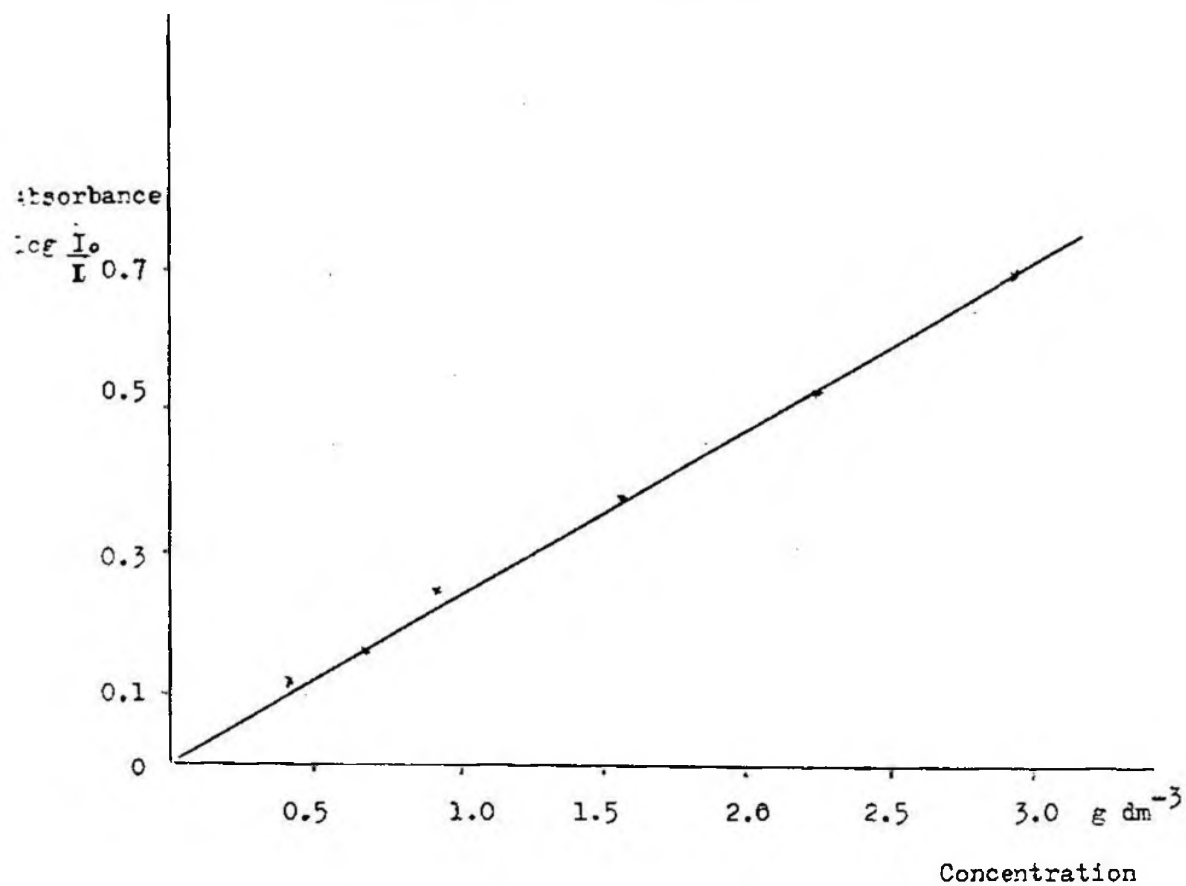## Figure 2

FTIR Calibration Graph
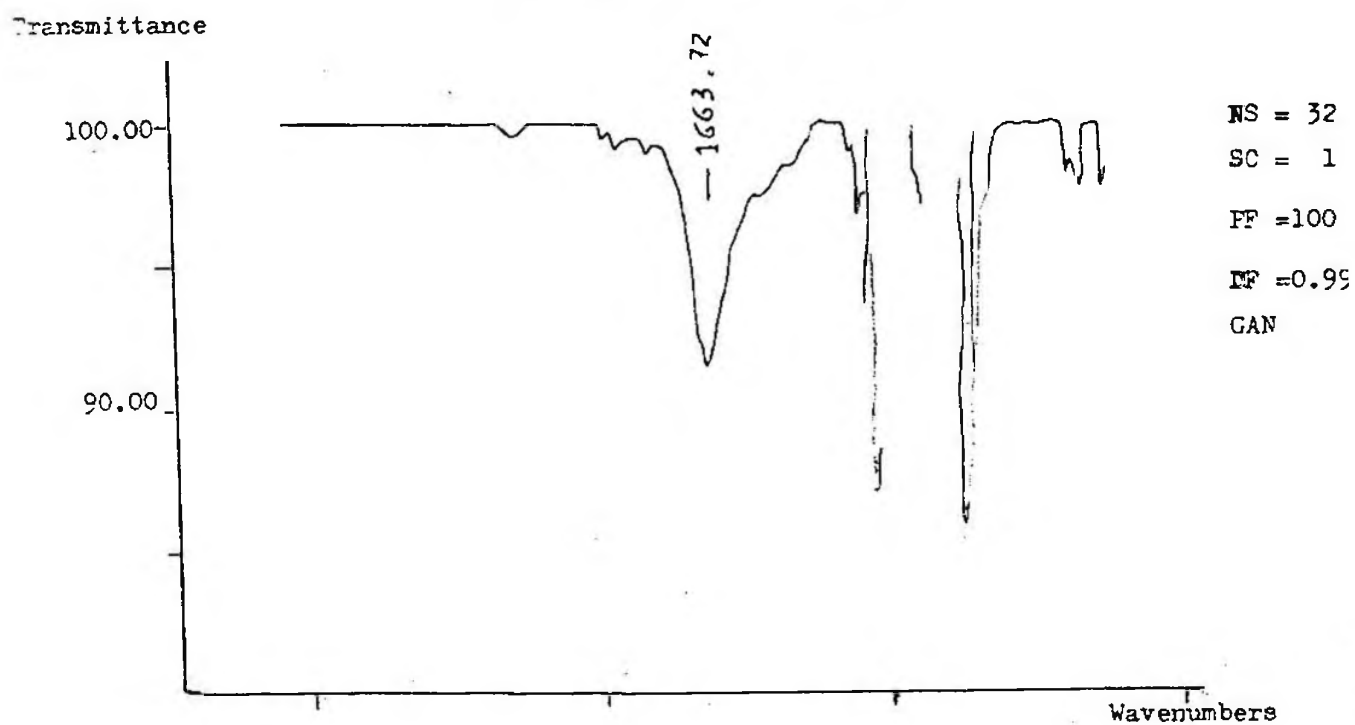

Figure 3

Infra- red of extracted cis-polyisoprene

NS = 32

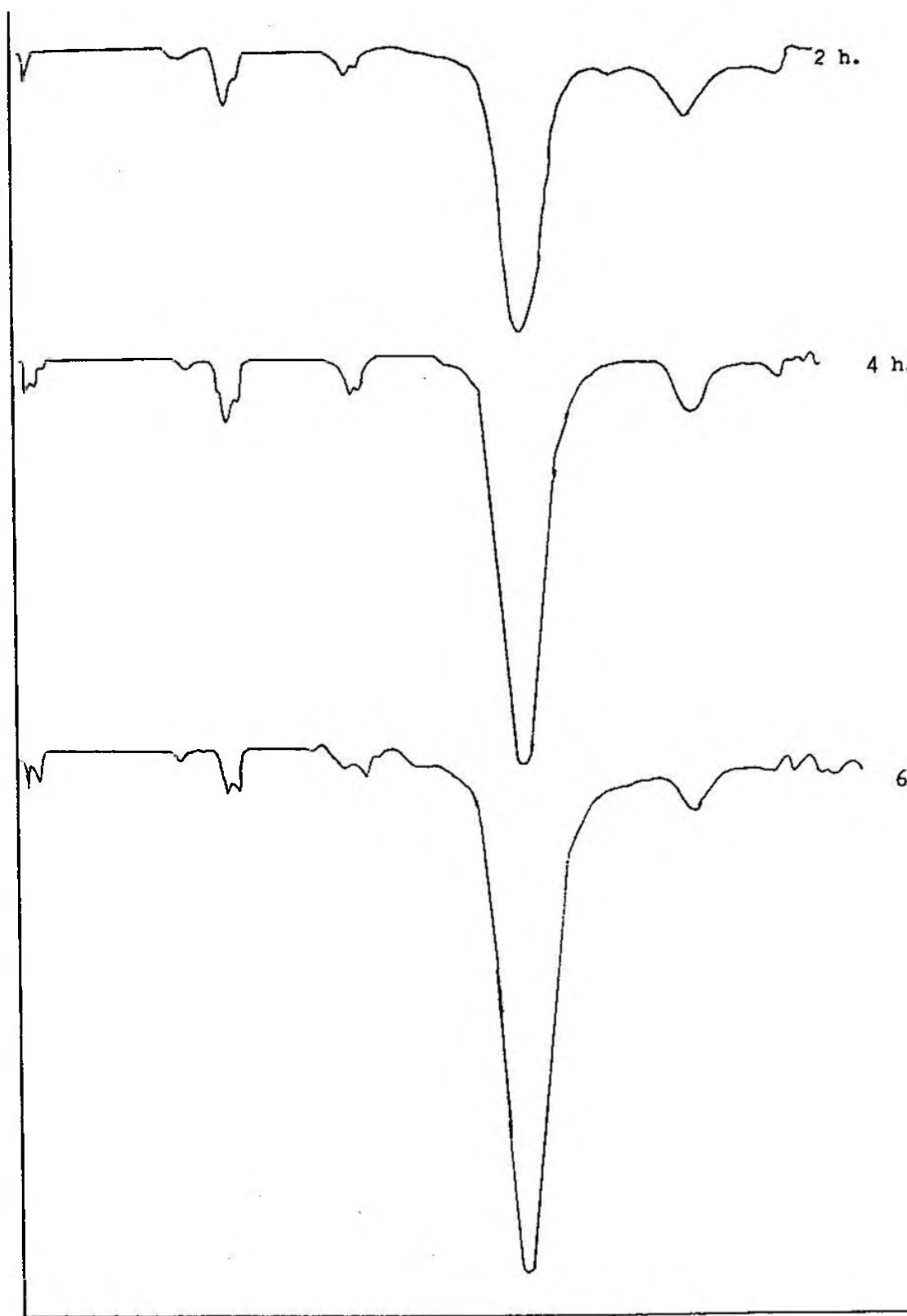SC = 1

FF =100

DF =0.99

GAN

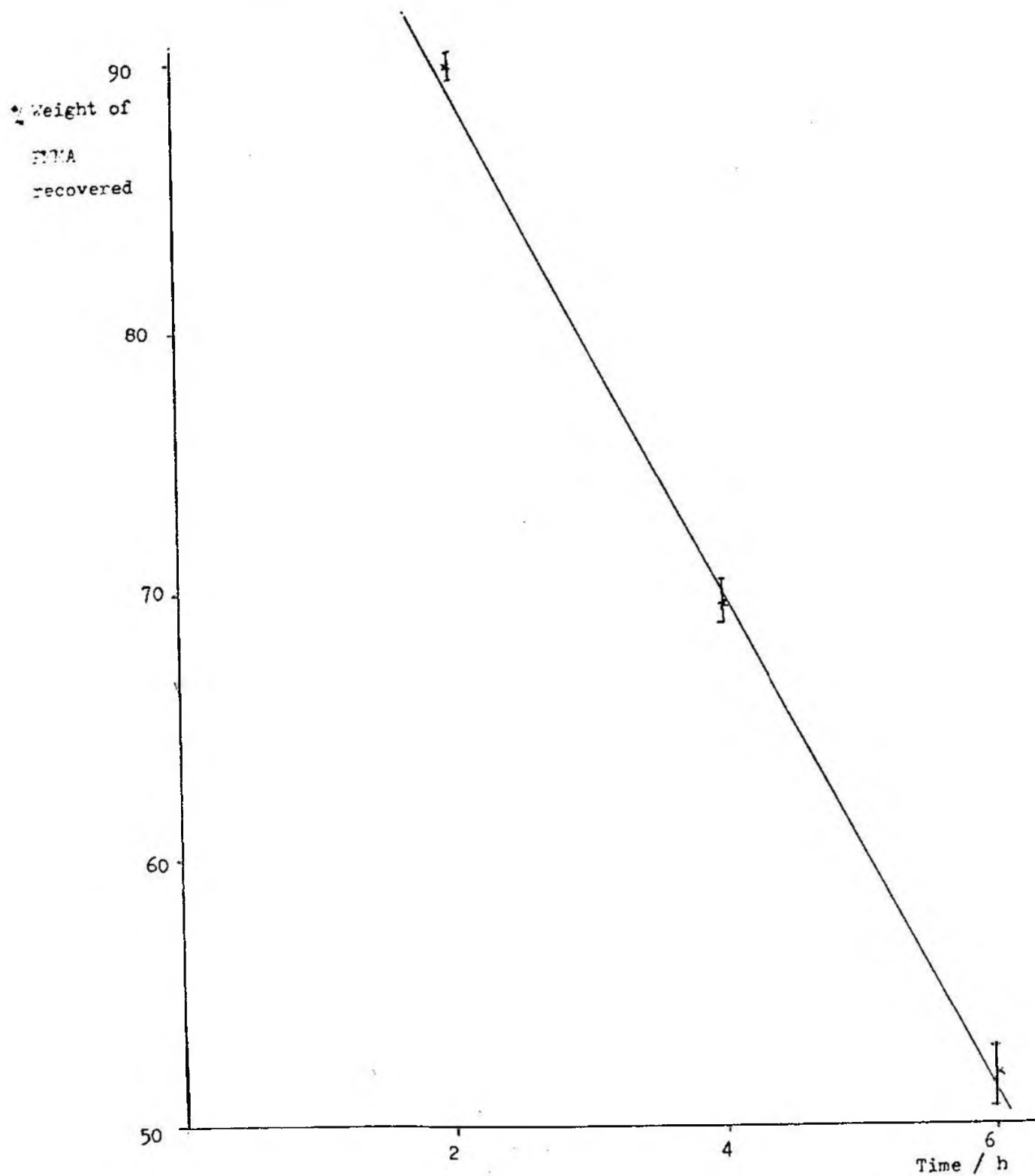Figure 4

Figure 5

Average weight percentage of PMMA recovered vs time of polymerisation

Figure 6

Extracted PMMA , isolated from G 4

100.00

75.00

50.00

25.00

4400   3200

1734.13

2000　　　1400

50