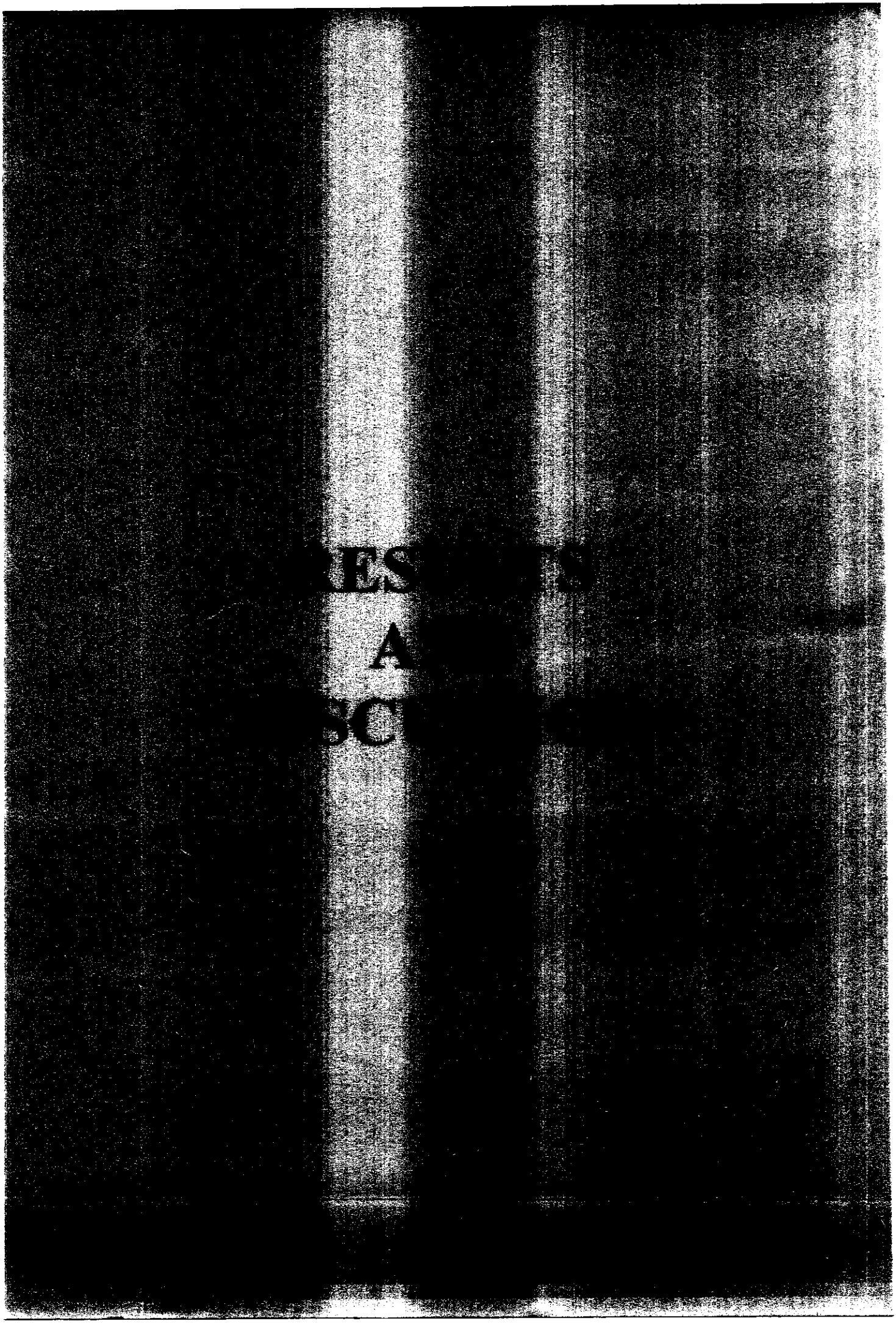
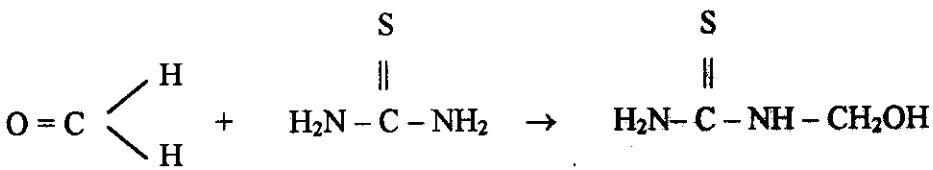


RESULTS AND DISCUSSION

1- Preparation of fire-retardant polymers

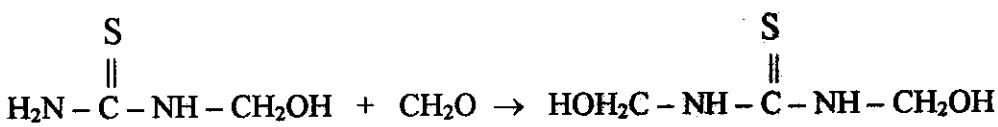
(i) Preparation of thiourea-formaldehyde resin :

Thiourea-Formaldehyde (TUF) resin was prepared through a polycondensation of thiourea and formaldehyde in basic medium according to the method described in page (34). In a slightly alkaline medium of $pH^- = 7.5$ there is an electrophilic attack by formaldehyde on a nucleophilic thiourea forming monomethylolthiouarea (MMTU)



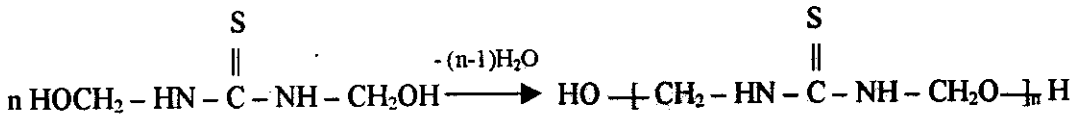
(MMTU)

(MMTU) will then further react with another molecule of formaldehyde giving rise to dimethylolthiourea (DMTU).



(DMTU)

Thus the step-growth condensation is random, giving rise to the mixture of MMTU and DMTU. Consequently, concentration of free methylol group in the polymer is very large but very little $\diagdown N–CH_2–N \diagup$ is formed. This can be explained as the amide group of $–NH–CH_2OH$ in the growing polymer chain reacting with formaldehyde to form a dimethylol compound and finaly into linear compound by the elimination of water:



The product is concentrated to 65 % solid content by distillation of water. Then the product was purified by dissolving in DMF and filtering into a large amount of a rapidly stirred cold dry ethanol. The white product has m.p. = 204-206°C and its structure was established from IR spectra Fig. (8) which illustrates the following signals:

A broad band at 3280 cm^{-1} due to the NH streching vibrations of the thiamide NH group, band at 2950 cm^{-1} due to the C–H streching vibrations of the CH_2 group; band at 1560 cm^{-1} due to the streching vibrations of the C=S group and a band at 1020 cm^{-1} due to asymmetric streching vibrations of the alkyl ethe $-CH_2-O-CH_2-$ group.

Also ^1H – NMR spectrum of (TUF) resin Fig. (9) shows the following signals:

doublet at δ = 4.7 ppm. corresponding to the two protons of $-\overset{|}{N}-CH_2O-$ group and a singlet band at δ = 8.5 ppm. corresponding to the –NH proton.

The addition of a crosslinking and fire retarding orthophosphoric acid to the above resin giving rise to the following cross linked polymer[51].

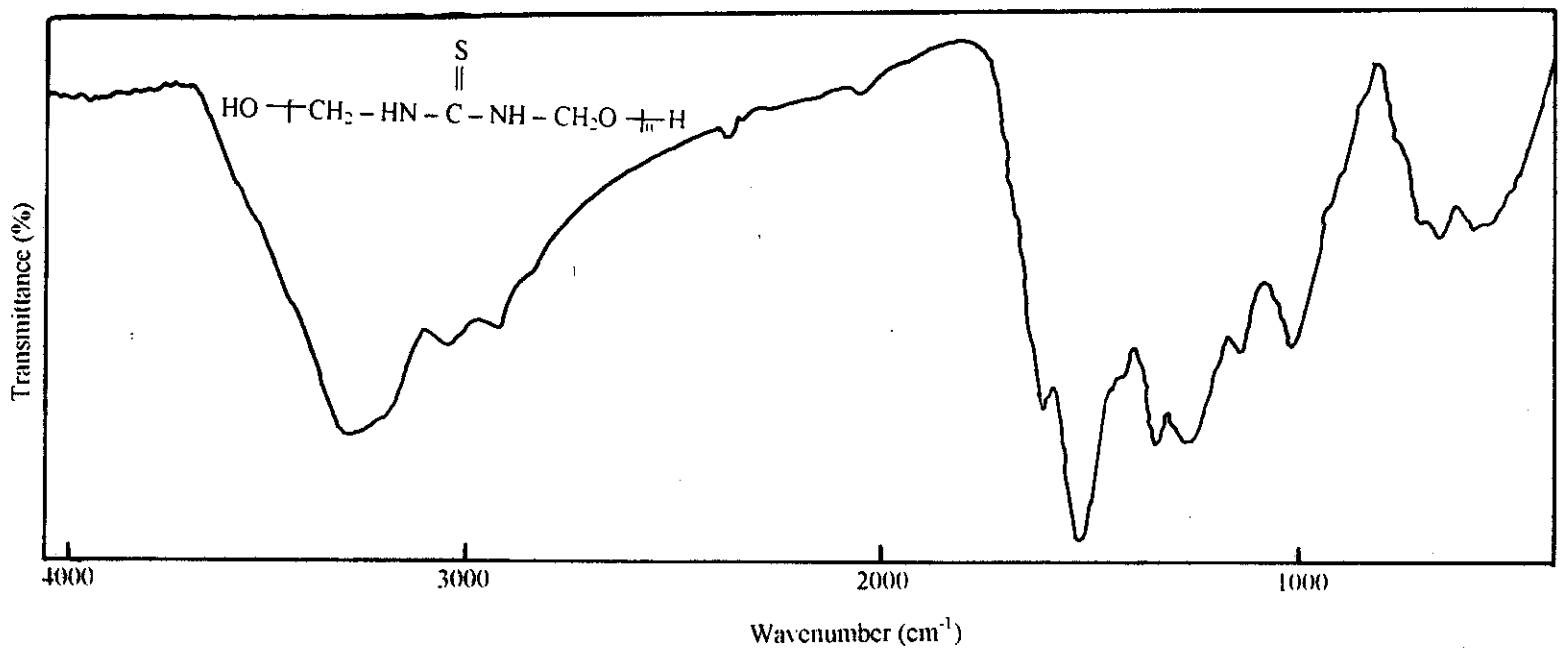


Fig. (8): IR spectrum of thiourea-formaldehyde resin.

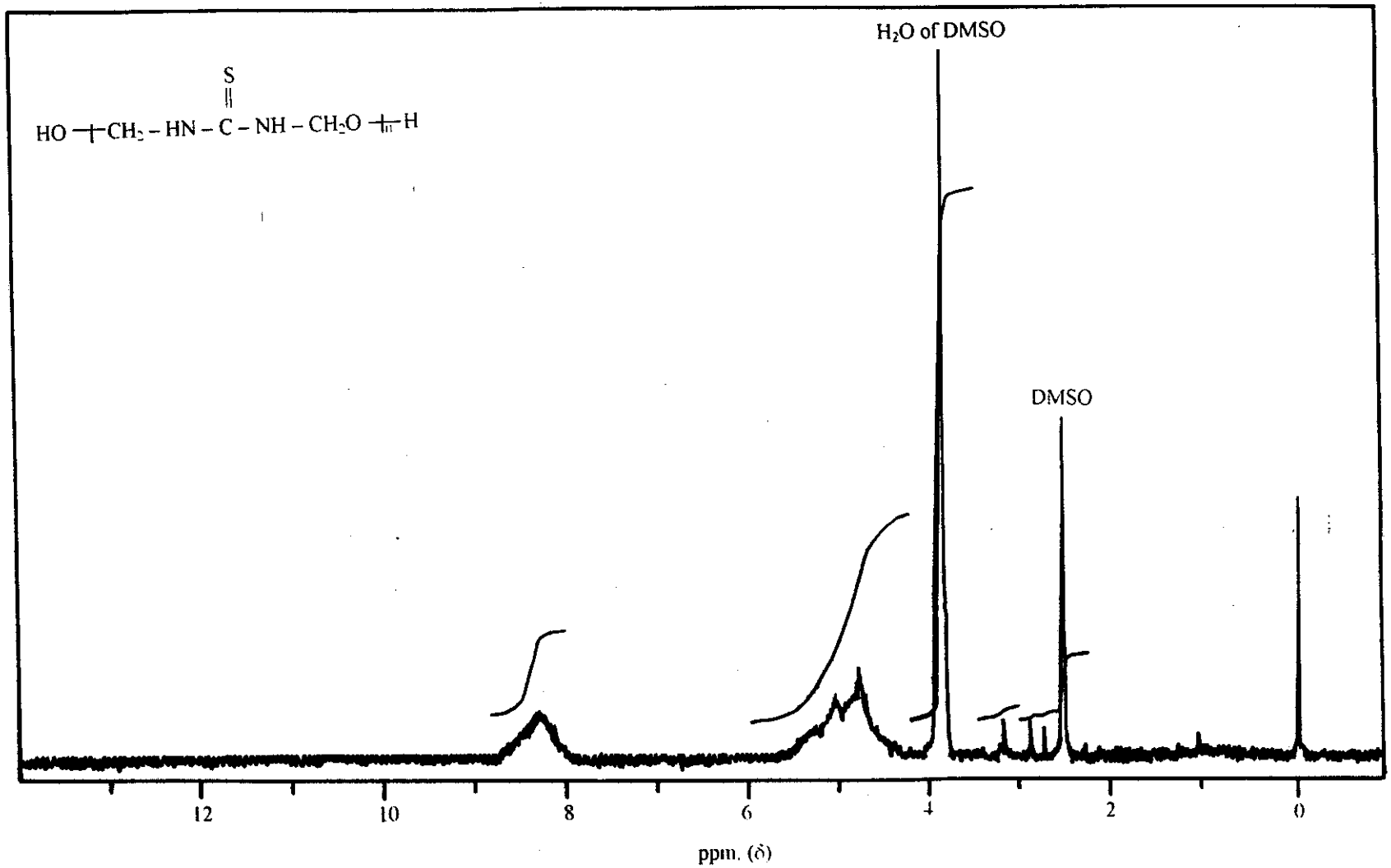
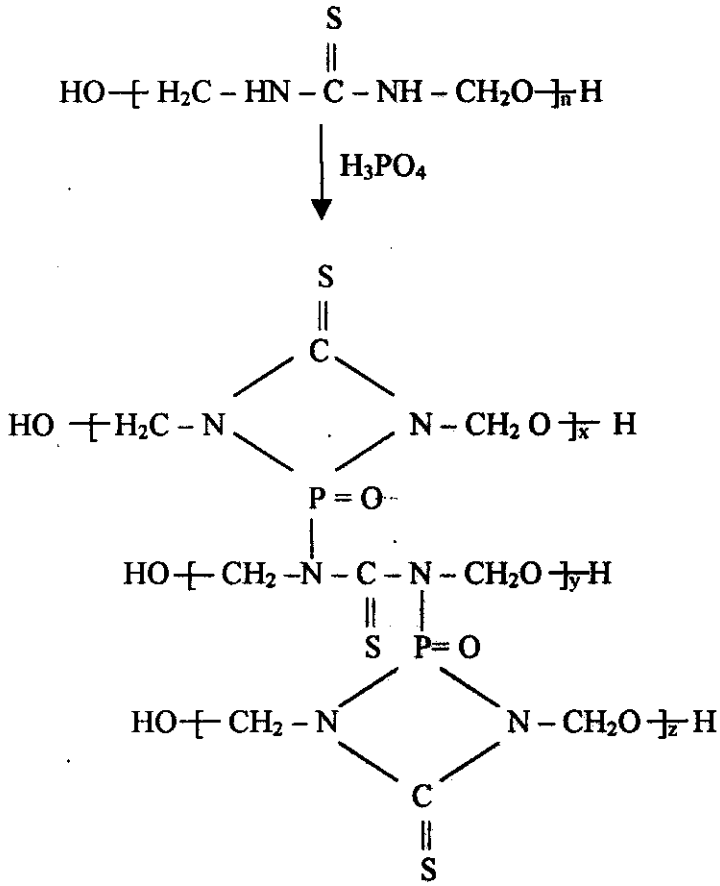
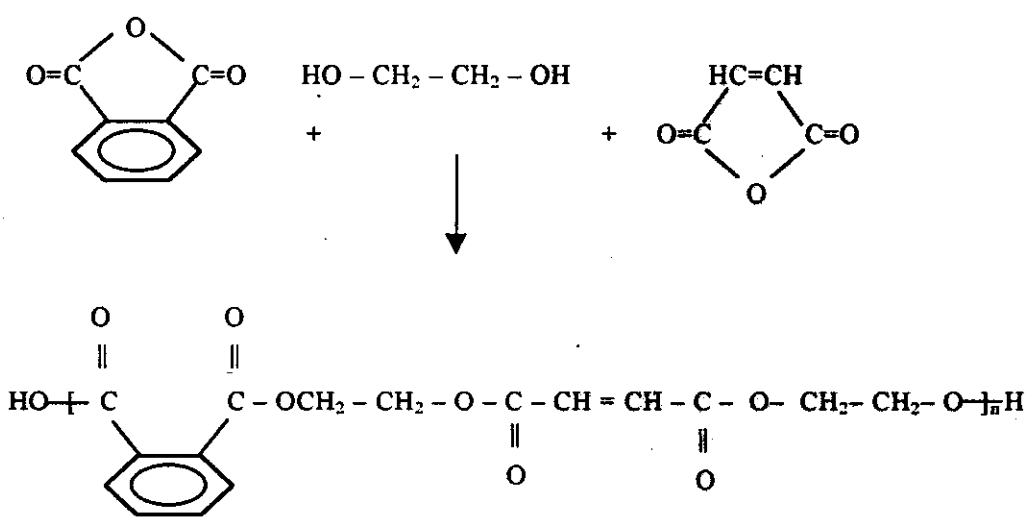


Fig. (9): ^{1}H-NMR spectrum of thiourea-formaldehyde resin.



(ii) Preparation of unsaturated polyester resins

A free bromine unsaturated polyester sample was prepared by the polyesterification reaction between phthalic anhydride, maleic anhydride and ethylene glycol according to the method described in page 34.



The product was purified by dissolving in chloroform and filtering into a large amount of a rapidly stirred cold dry methanol. The precipitated viscous yellowish polyester decanted and air dried then oven at 70°C. The structure of the prepared polyester was established from its IR-spectrum Fig. (10) which shows the following signals:

A broad band at 3500 cm^{-1} due to the streching vibrations of the O-H group; band at 3060 cm^{-1} due to the streching vibrations of the Ar-H group; band at 2960 cm^{-1} due to the C-H streching vibrations of CH_2 group; a strong band at 1750 cm^{-1} characteristic for the asymmetric streching vibrations of the carbonyl group and a band at 1635 cm^{-1} due to the C-H streching vibrations of the –HC=CH– group.

The ^{1}H-NMR spectrum of the free bromine unsaturated polyester sample was illustrated in Fig. (11) shows two signals at δ = 3.8 and 4.4 ppm. corresponding to the two different methylene groups of ethylene glycol unit the more shielded signal was due to the $-CH_2-$ neibrouring to phthalic anhydride unit and the other corresponding to the $-CH_2-$ neibrouring to maleic anhydride unit; two signals at δ = 6.3 and 6.8 ppm corresponding to the two protons of maleic anhydride unit –CH=CH– and a signal at δ = 7.5 ppm corresponding to the four aromatic protons.

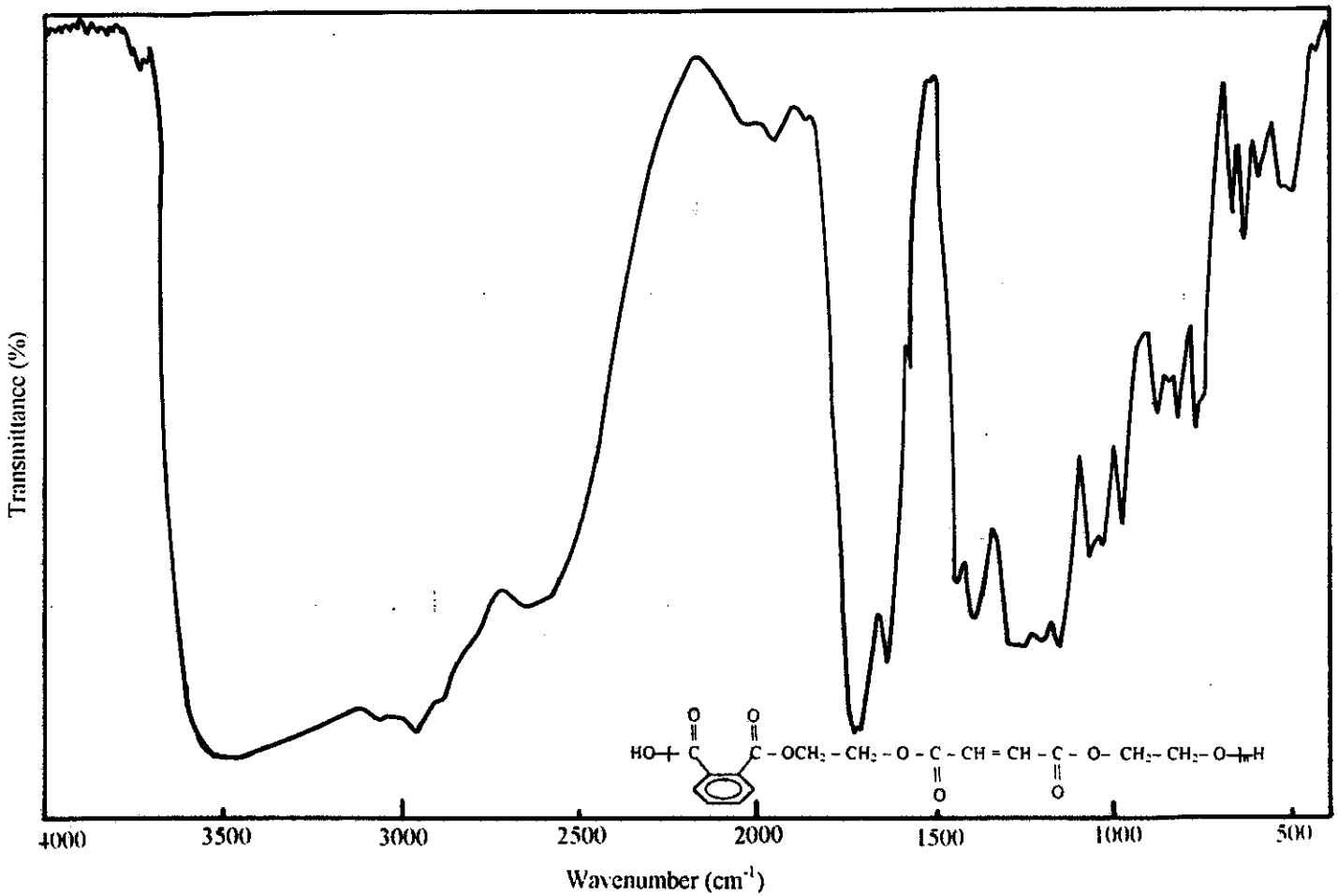


Fig. (10): IR spectrum of the free bromine unsaturated polyester sample.

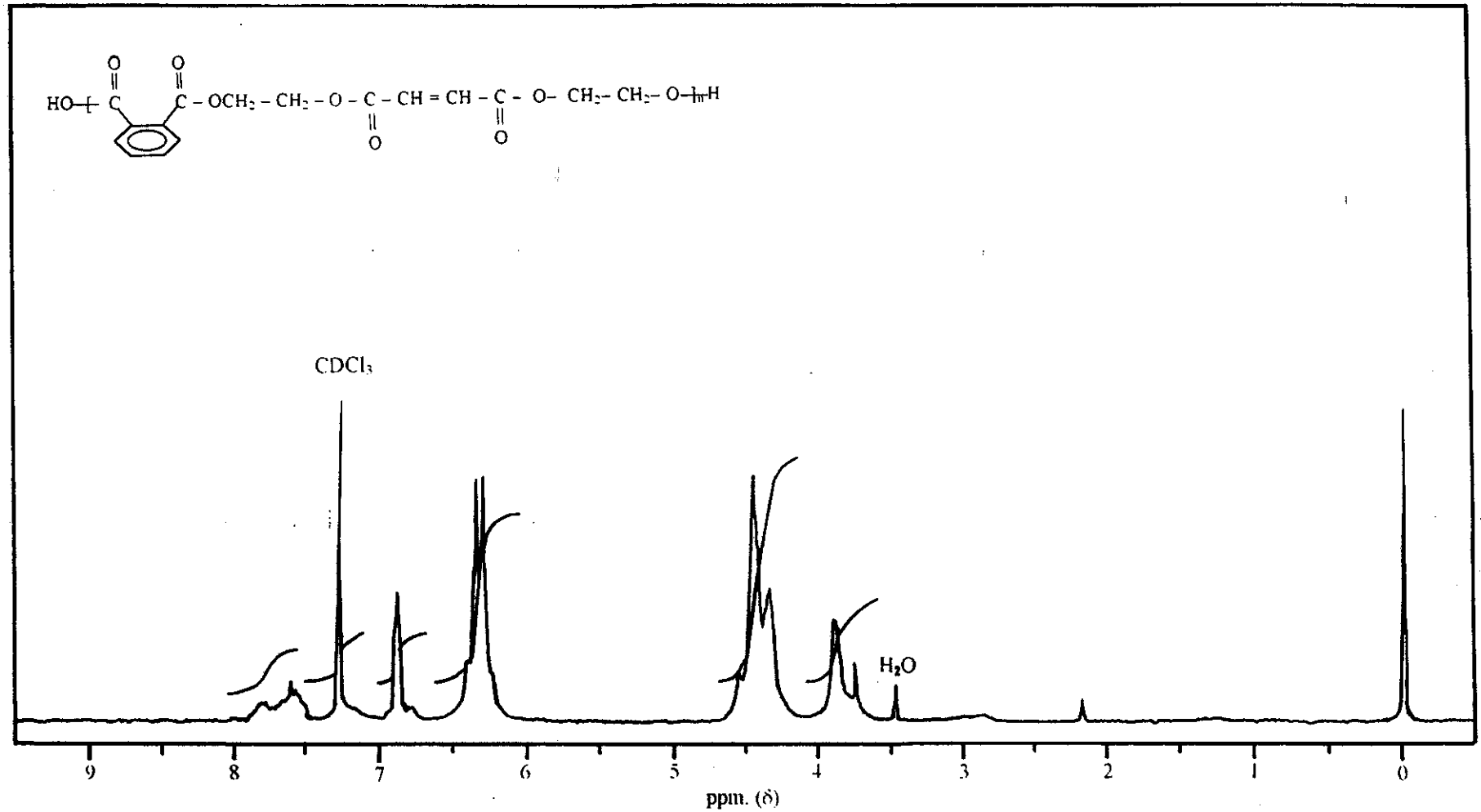
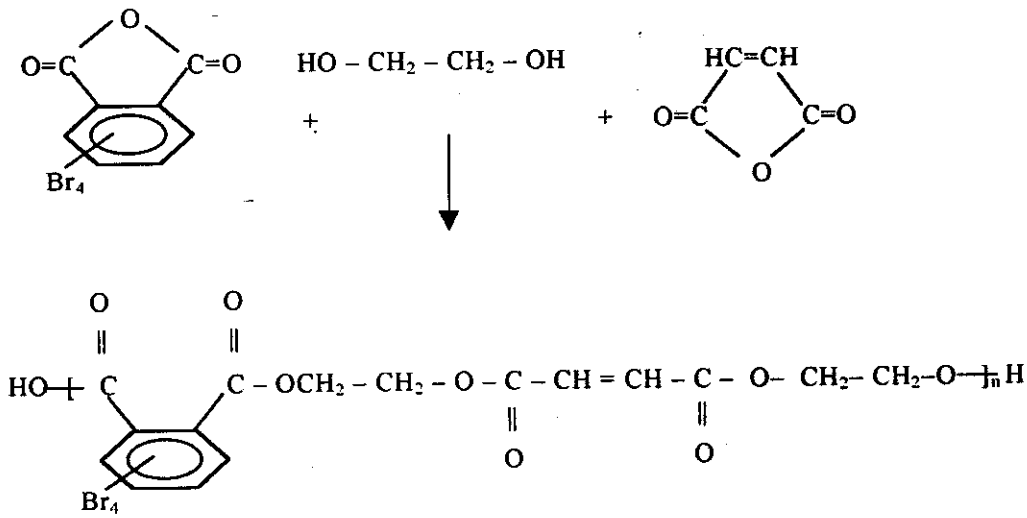


Fig. (11): ^{1}H-NMR spectrum of the free bromine unsaturated polyester sample.

Other three bromine containing unsaturated polyester resins were prepared by the polyesterification of tetrabromophthalic anhydride, maleic anhydride and ethylene glycol by the same method described for the free bromine unsaturated polyester sample.



The products were purified by the same method used in purification of the free bromine sample. The structure of the brominated polyester resins were established from their IR-spectra Figs. 12(a), (b) and (c) which are very quite similar and show the following signals:

A broad band at 3550-3620 cm^{-1} due to the streching vibrations of the O-H group; band at 2950 cm^{-1} due to the C-H streching vibrations of the $C\text{-}H_{(aliph)}$ group, a strong band at 1750 cm^{-1} characteristic for the asymmetric streching vibrations of the carbonyl group and a band at 1640 cm^{-1} due to the C-H streching vibrations of the –CH=CH– group. and a strong band at 1160 cm^{-1} corresponding to $\nu_{C\text{-}O\text{-}C}$ group.

^{1}H-NMR spectrums of the brominated polyesters are shown in Figs. 13 (a), (b) and (c) which are very quite similar to each other and

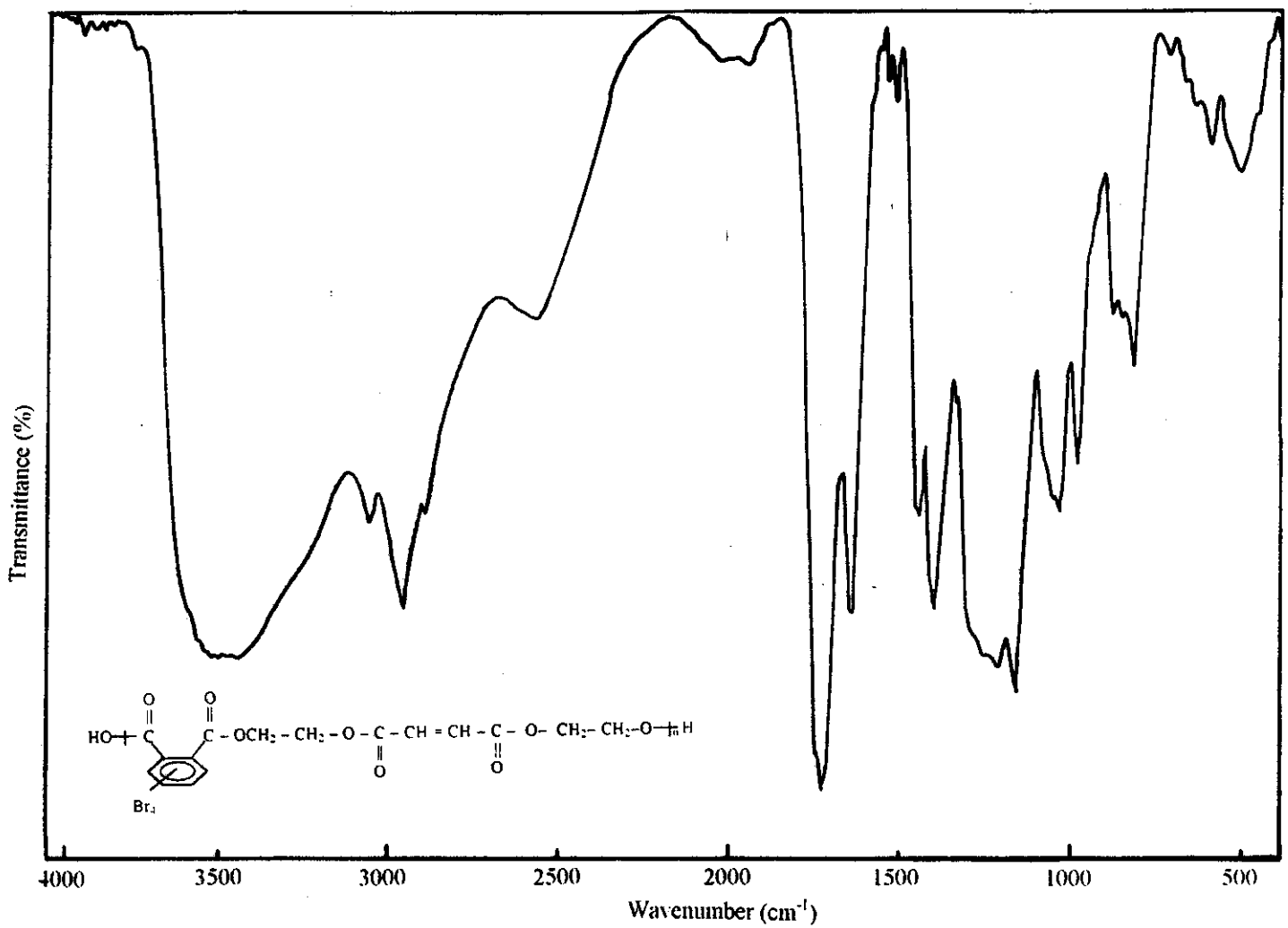


Fig. (12a): IR spectrum of unsaturated polyester sample of 8 Wt.% bromine content.

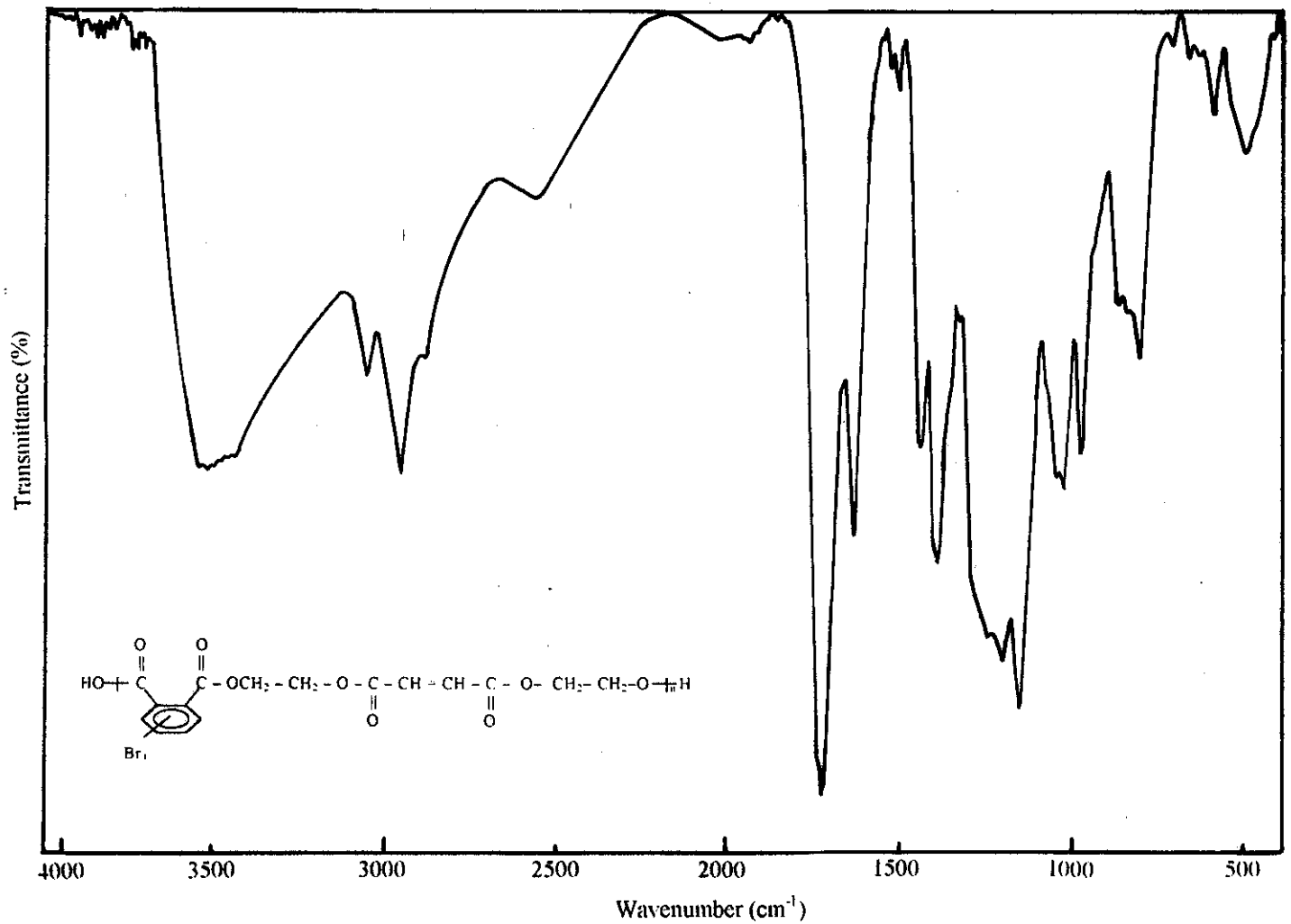


Fig. (12b): IR spectrum of unsaturated polyester sample of 12 Wt.% bromine content.

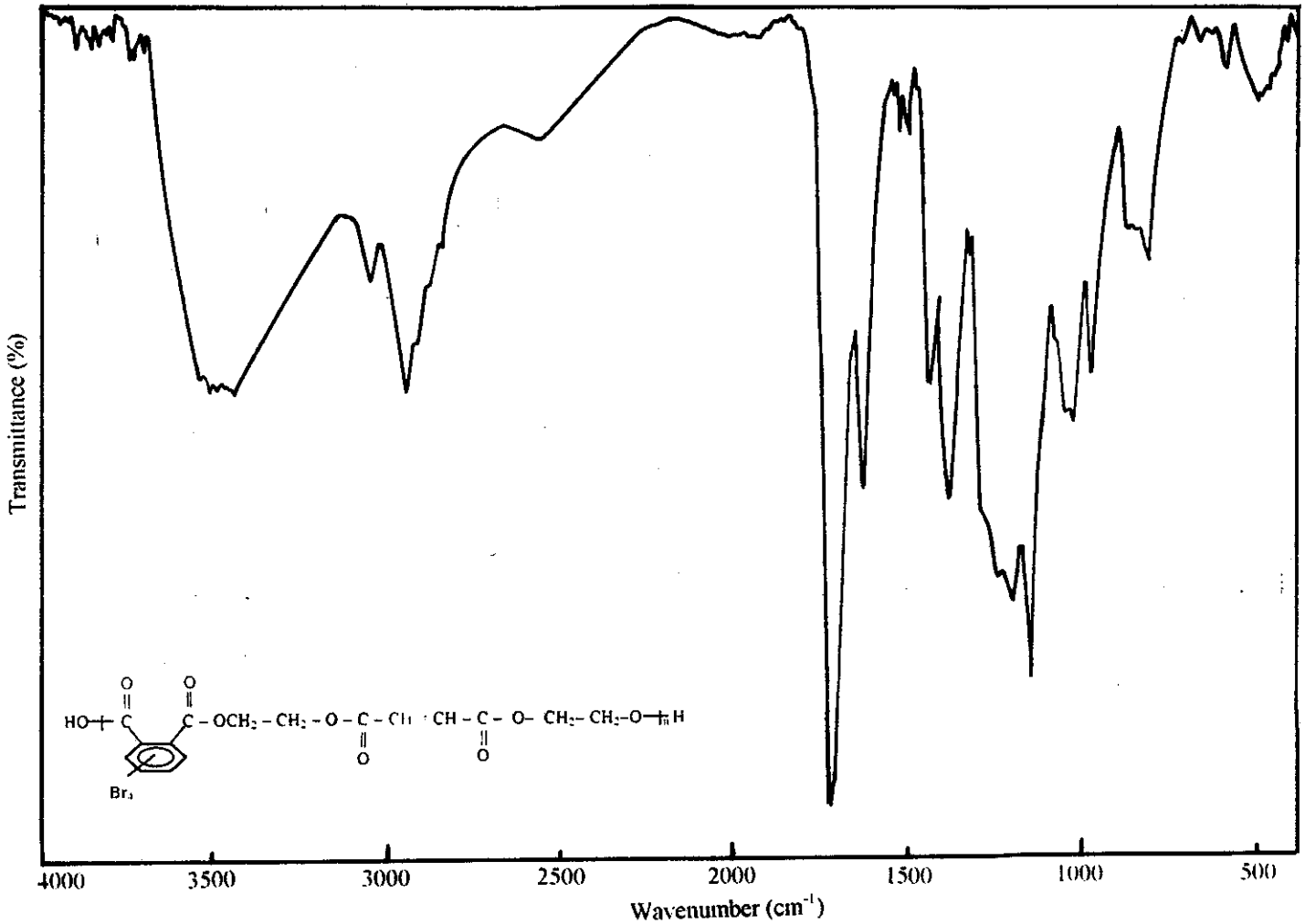


Fig. (12c): IR spectrum of unsaturated polyester sample of 16 Wt.% bromine content.

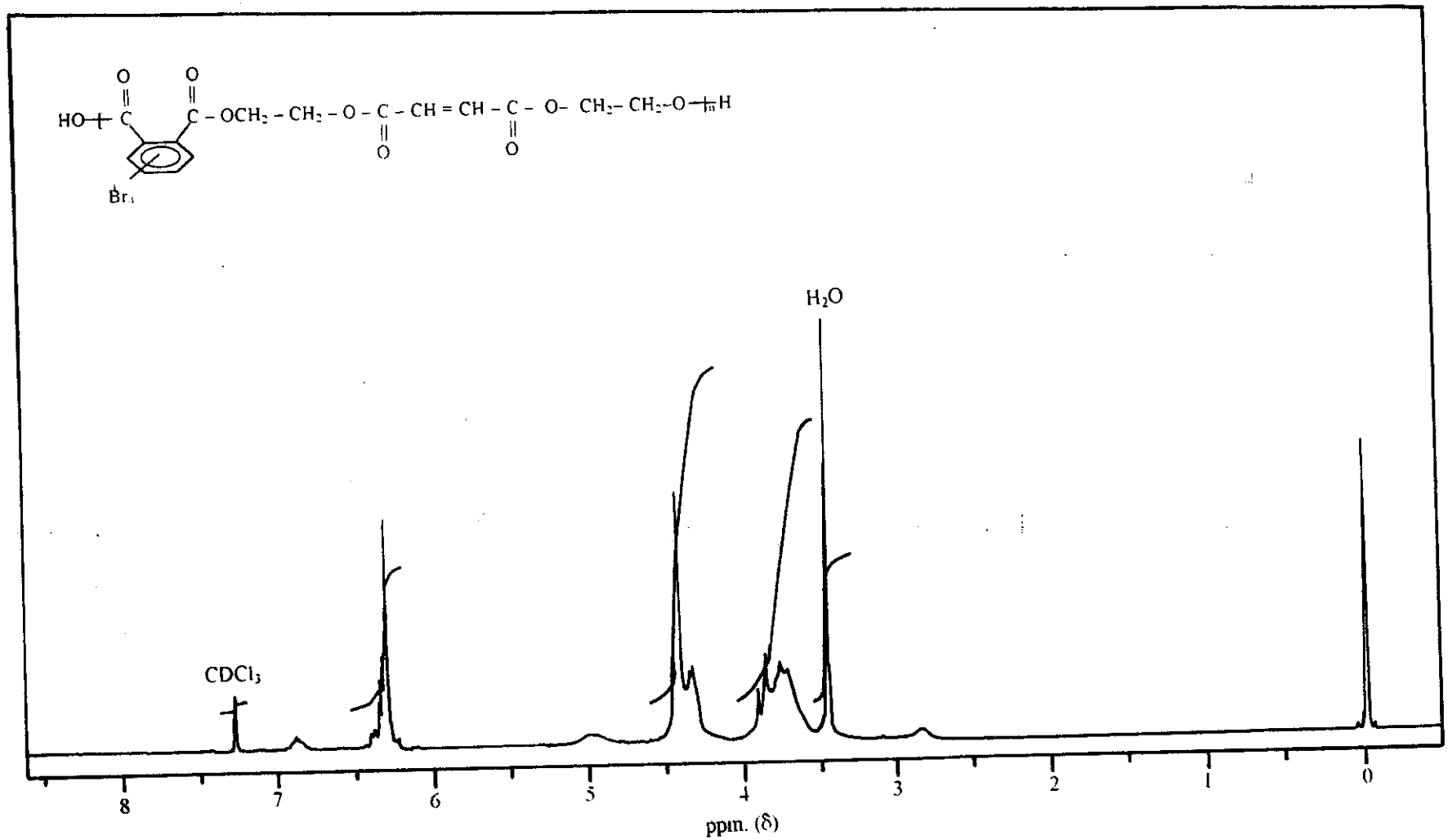


Fig. (13a): ^{1}H-NMR spectrum of unsaturated polyester sample of 8 Wt.% bromine content.

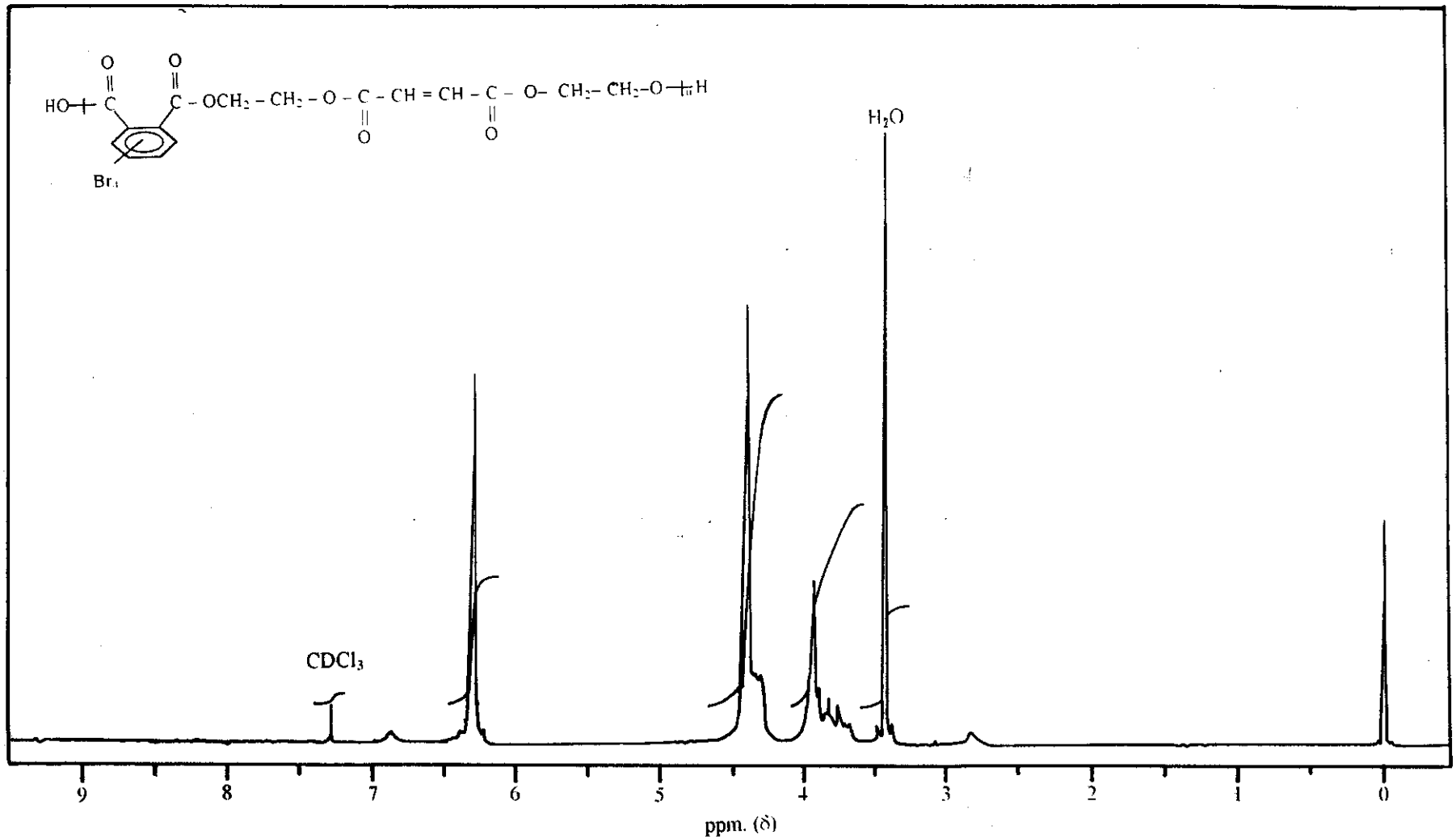


Fig. (13b): ^{1}H-NMR spectrum of unsaturated polyester sample of 12 Wt.% bromine content.

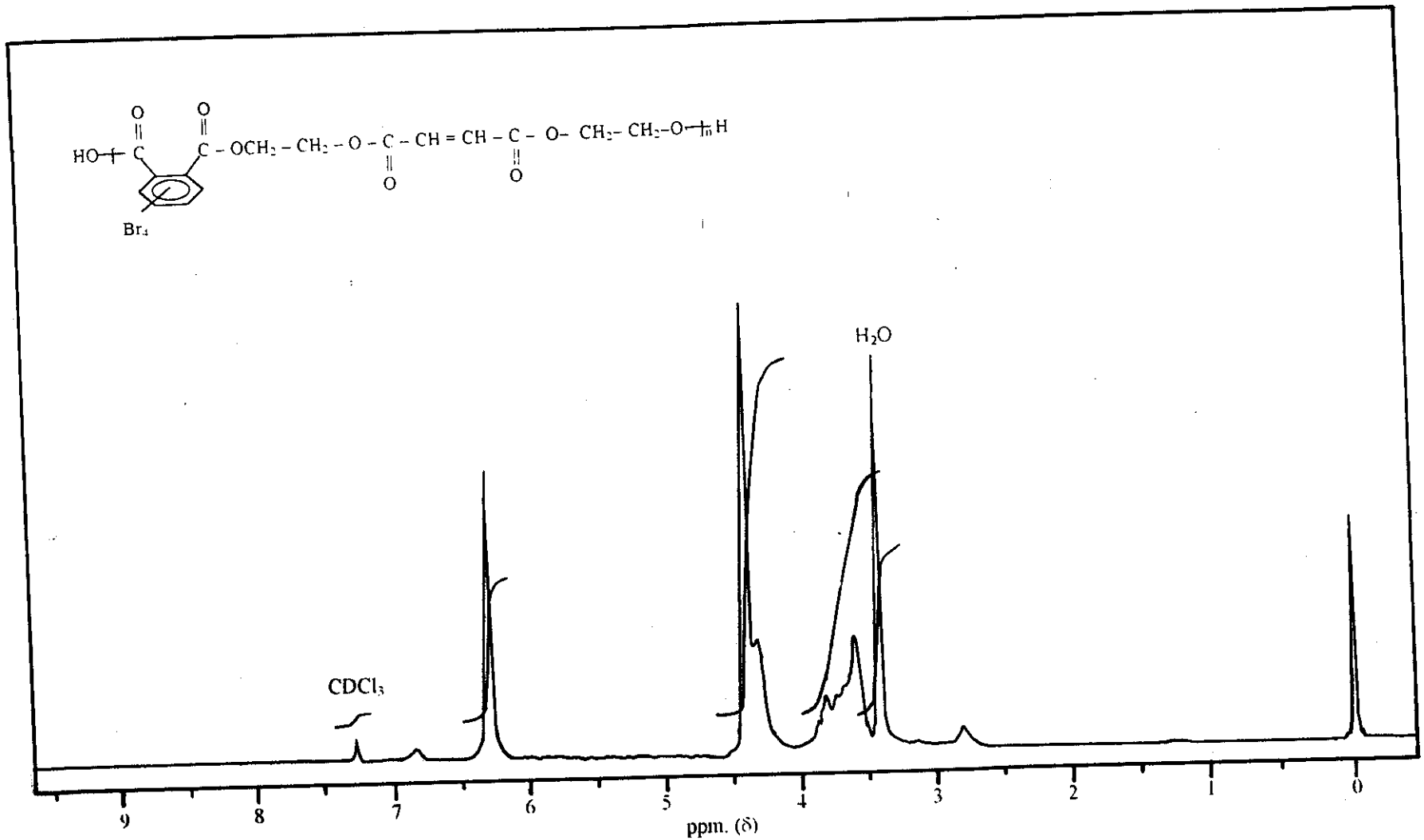
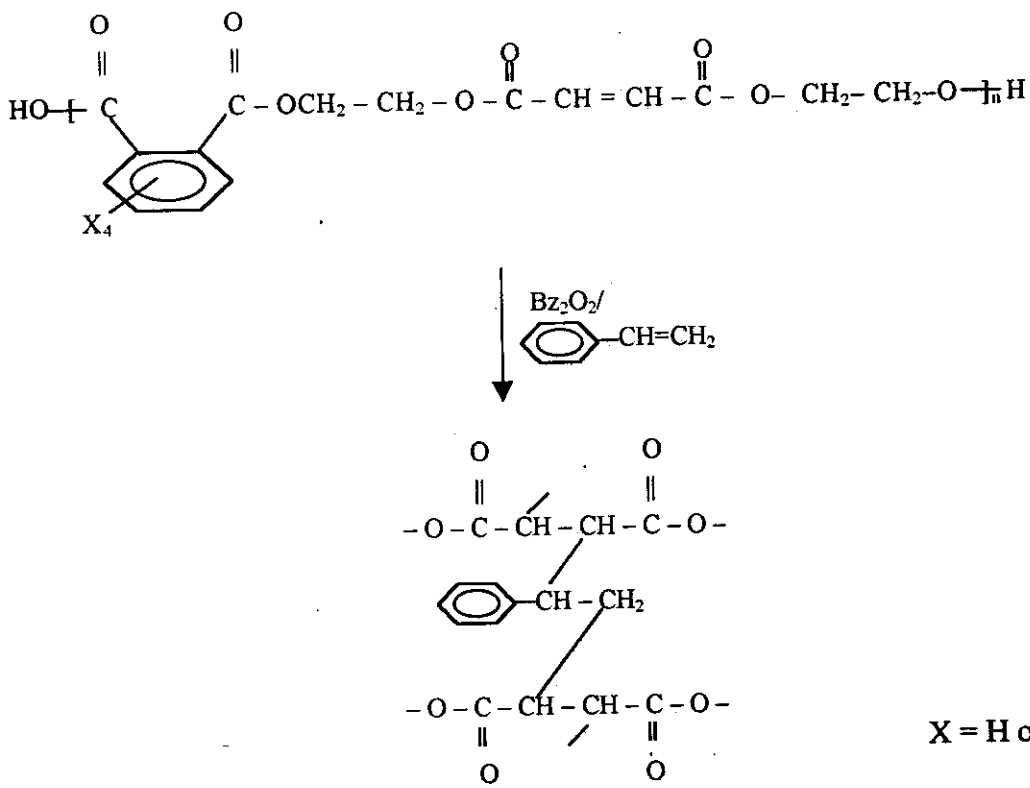


Fig. (13c): ^{1}H-NMR spectrum of unsaturated polyester sample of 16 Wt.% bromine content.

to the ^1H NMR spectrum of the free bromine sample except the absence of the band characteristic for the aromatic protons.

(iii) Reactions of unsaturated polyesters with styrene

It is known that any unsaturated polyesters generally found in liquid or other soluble form can be cured with styrene in the persence of benzoyl peroxide as initiator by the method described in page 35 to form solid thermoset materials.

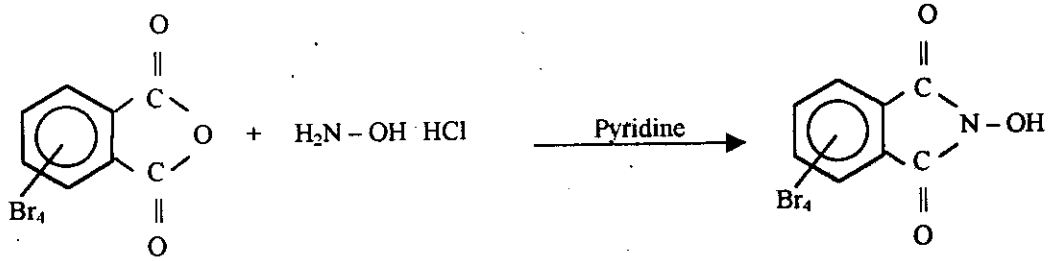


X = H or Br

The ratio of styrene to unsaturated polyester make the copolymerization reaction of styrene with the unsaturated polyesters predominate over the homopolymerization of styrene and of unsaturated polyesters[(67)].

(iv) Preparation of N-hydroxytetrabromophthalimide:

N-hydroxytetrabromophthalimide was prepared by the reaction of tetrabromophthalic anhydride with hydroxyl amine hydrochloride in basic medium[58] according to the method described in page35.



The product was recrystalized form ethanol as yellowish crystals, m.p.>300°C and the yield were 75%.

The structure of N-hydroxytetrabromophthalimide was investigated from bromine analysis which was found to be 67.3 % against a calculated value of 66.81%.

Also the structure of N-hydroxytetrabromophthlimide was established from its IR-spectrum, (Fig. 14) which shows the following signals:

A broad band at 3550 cm^{-1} due to the streching vibrations of OH group and two strong bands at 1780 cm^{-1} and 1730 cm^{-1} characteristic for coupling bands of cyclic imides, a band at 1630 cm^{-1} due to the streching vibrations of aromatic C = C and a strong band at 660 cm^{-1} for bending vibrations of C – Br bonds.

^{1}H-NMR spectrum of N-hydroxytetrabromophthalimide was illustrated in Fig. (15) which express the only signal at δ = 11.2 ppm. corresponding to the only proton of hydroxyl group.

N-hydroxyphthalimide was prepared by the same procedure, by using phthalic anhydride insteade of tetrabromophthalic anhydride

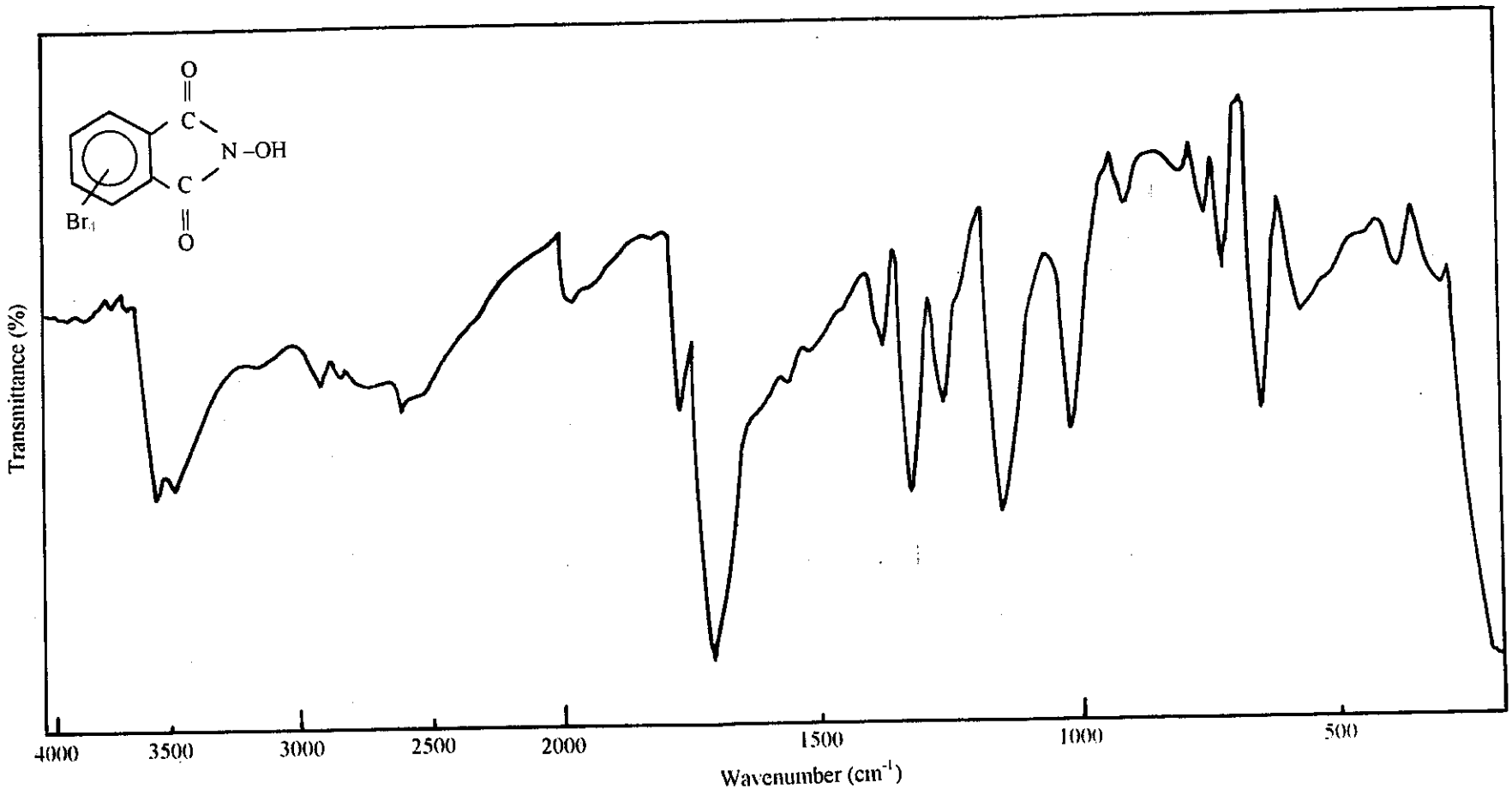


Fig. (14): IR spectrum of N-hydroxytetrabromophthalimide.

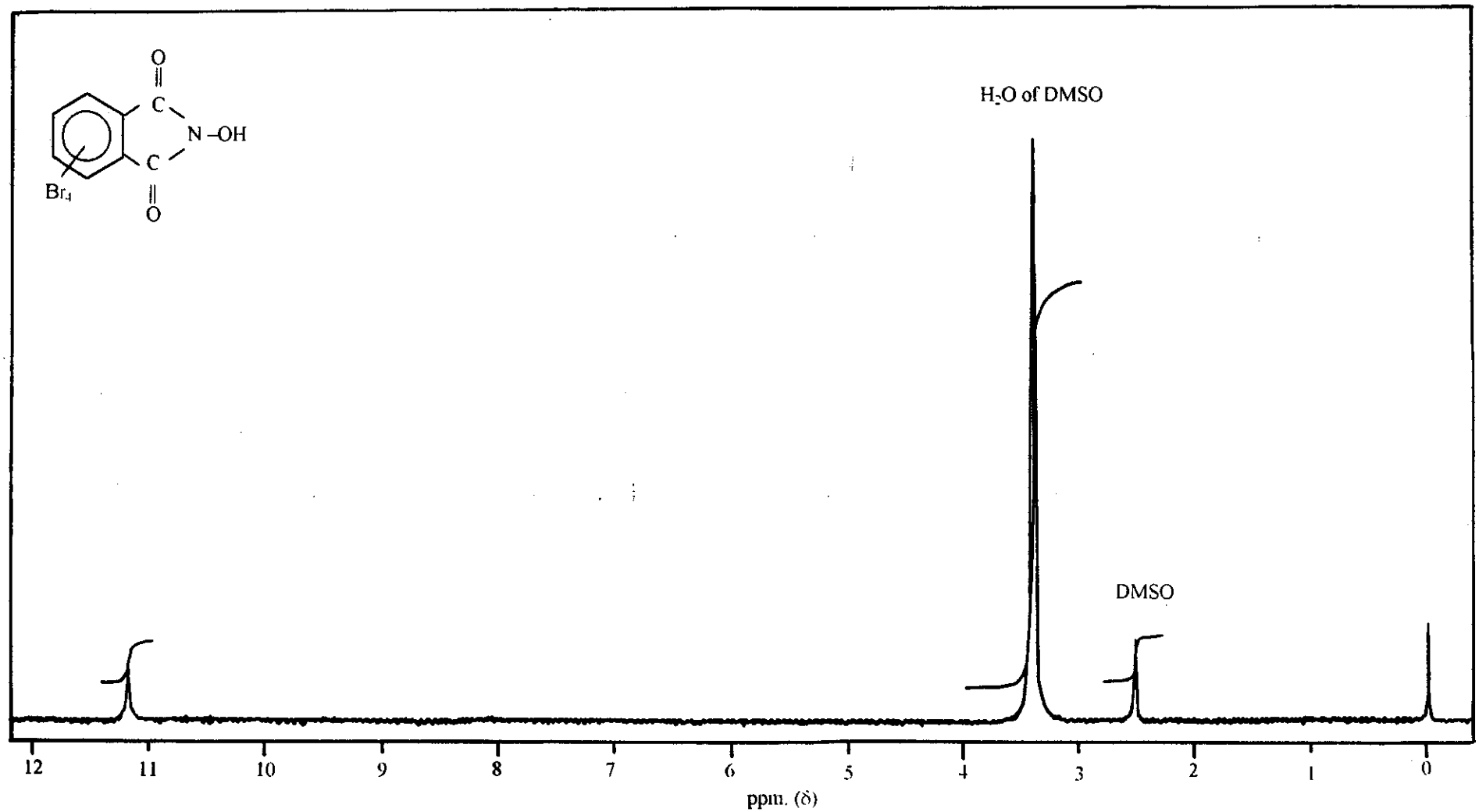


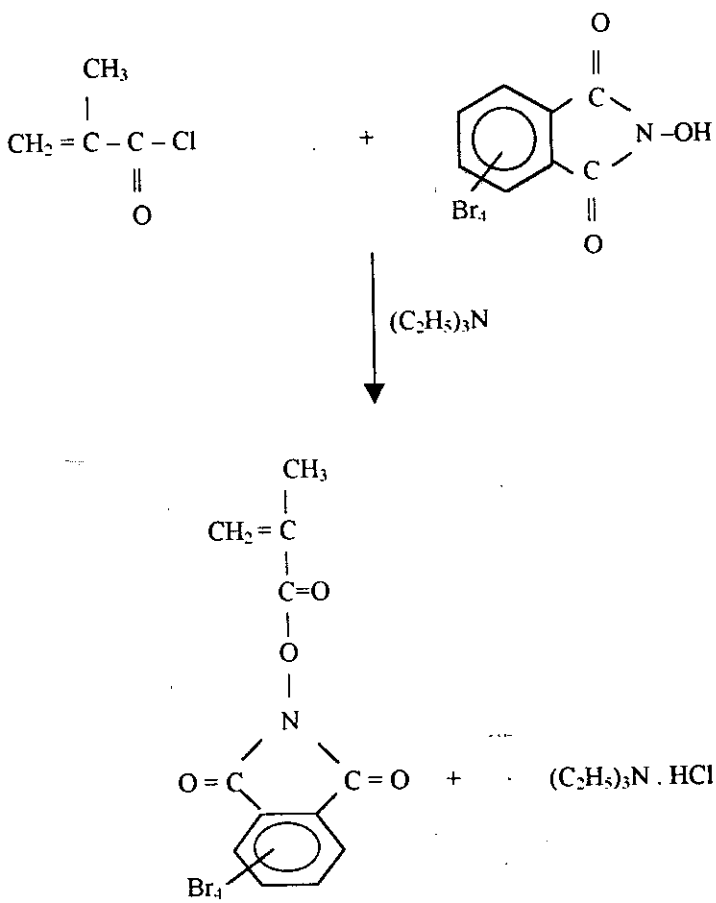
Fig. (15): ^{1}H-NMR spectrum of N-hydroxytetrabromophthalimide.

giving up a whitish yellow product, m.p. 230-232°C after crystalization from ethanol.

(v) Preparation of N-methacryloyloxytetrabromophthalimide

a- Acid chloride method[59]:

N-methacryloyloxytetrabromophthalimide monomer was prepared by the reaction of methacryloyl chloride with N-hydroxytetrabromophthalimide in the persence of triethylamine according to method described in page (36).



The resulting N-methacryloyloxytetrabromophthlimide was obtained as yellowish-white crystals and was recrystalized from benzene/methanol (30:70, v/v). The yield of recrystalized product was

98.5%, m.p. 186°C. The structure of N-methacryloyloxytetrabromo-phthalimide was investigated from bromine analysis which was found to be 58.1% against a calculated value of 58.5% for $C_{12}H_5NO_4Br_4$.

The IR-spectrum of N-methacryloyloxytetrabromophthalimide Fig. (16) shows the following signals:

Signal at 2950 cm^{-1} due to the streching vibrations of $C\text{-}H_{(aliph)}$ group; at 2870 cm^{-1} due to the C–Br streching vibrations; a strong band at 1680 cm^{-1} characteristic for the C=O streching vibrations of phthalimide group; a strong band at 1700 cm^{-1} due to the C=O streching vibrations of the carboxylate group. The spectrum also shows a strong band at 1640 cm^{-1} which is due to the C = C of vinylidene group and a strong band at 660 cm^{-1} characteristic for the C–Br bending vibrations of bromine compounds.

Also, the structure of N-methacryloyloxytetrabromophthal-imide was established from its ^{1}H-NMR spectrum which shows signals at δ = 6.3 ppm. and δ = 6.5 ppm. due to the two protons of CH_2 = C group and a signals at δ = 2.0 ppm. corresponding to the three protons of – CH_3 group Fig.(17).

N-methaxryloyloxyphthalimide was prepared by the same manner using N-hydroxyphthalimide instead of N-hydroxytetrabro-mophthalimide.

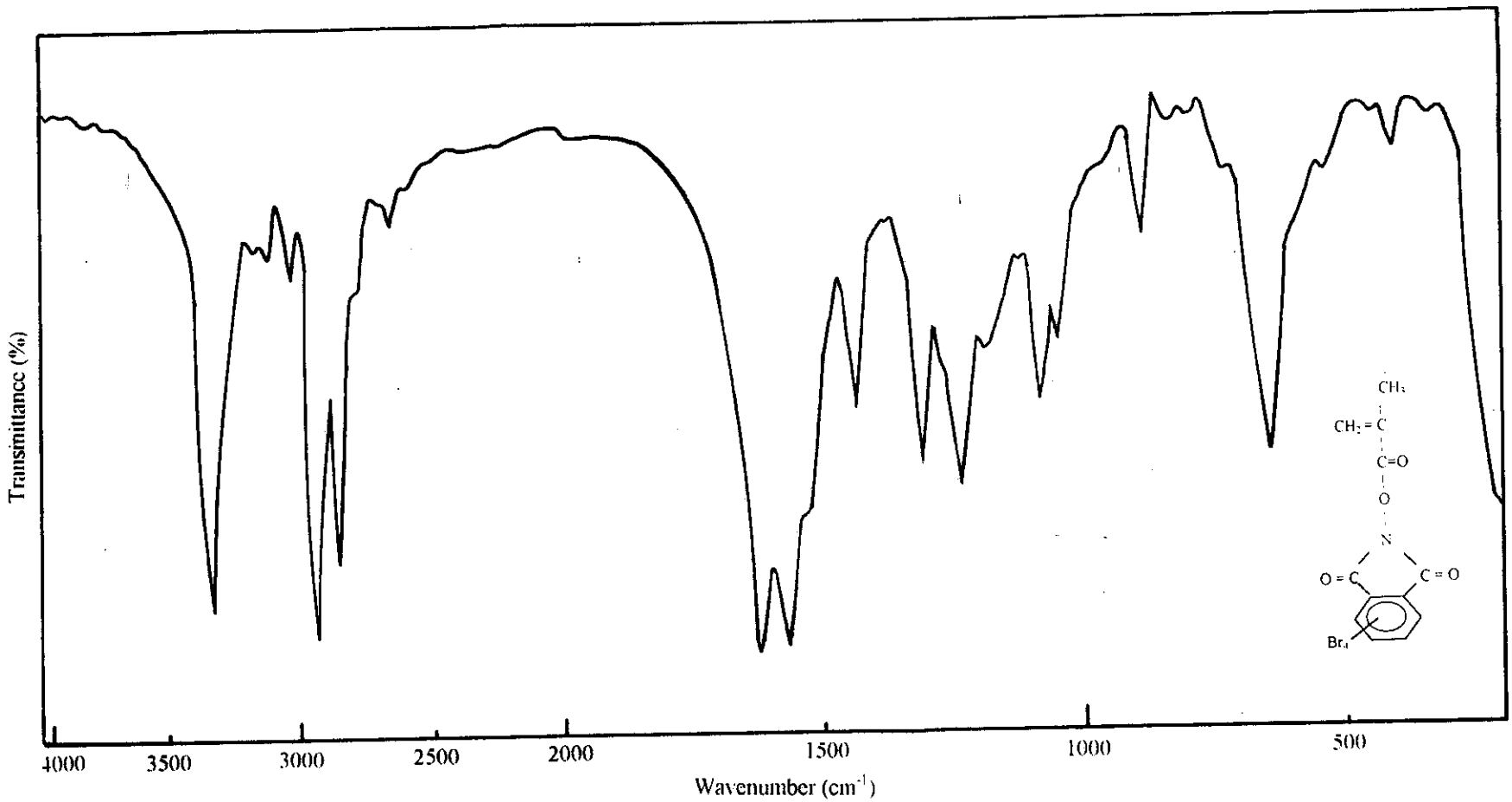


Fig. (16): IR spectrum of N-methacryloyloxytetrabromophthalimide.

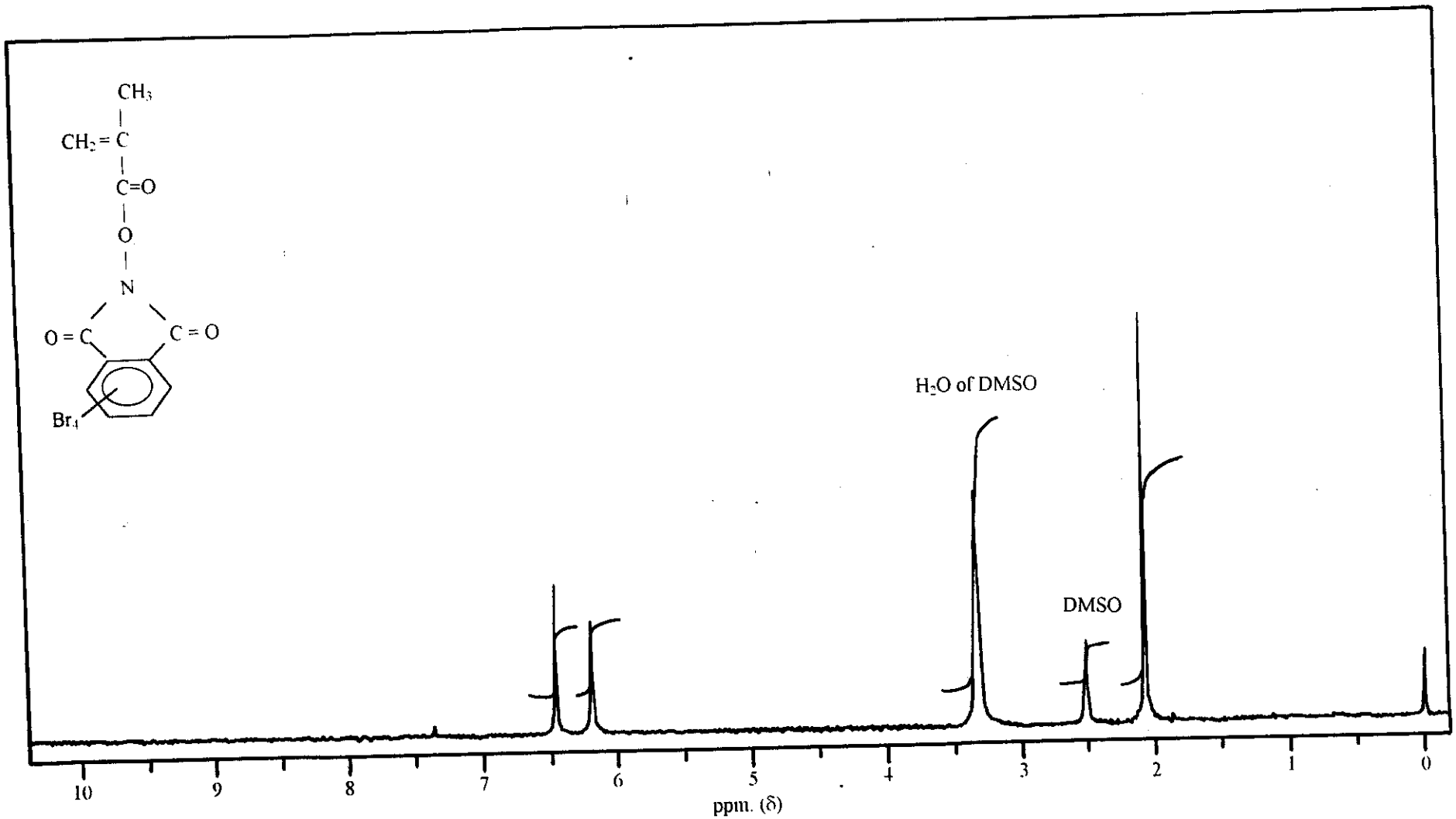
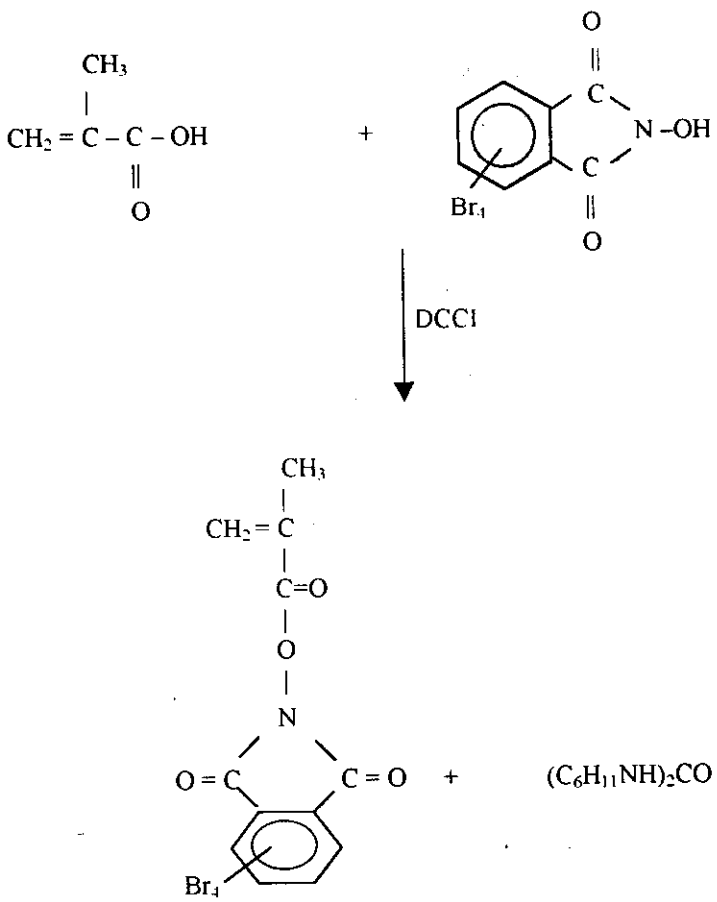


Fig. (17): ^{1}H-NMR spectrum of N-methacryloyloxytetrabromophthalimide.

b- N, N′-Dicyclohexylcarbodiimide method[60]

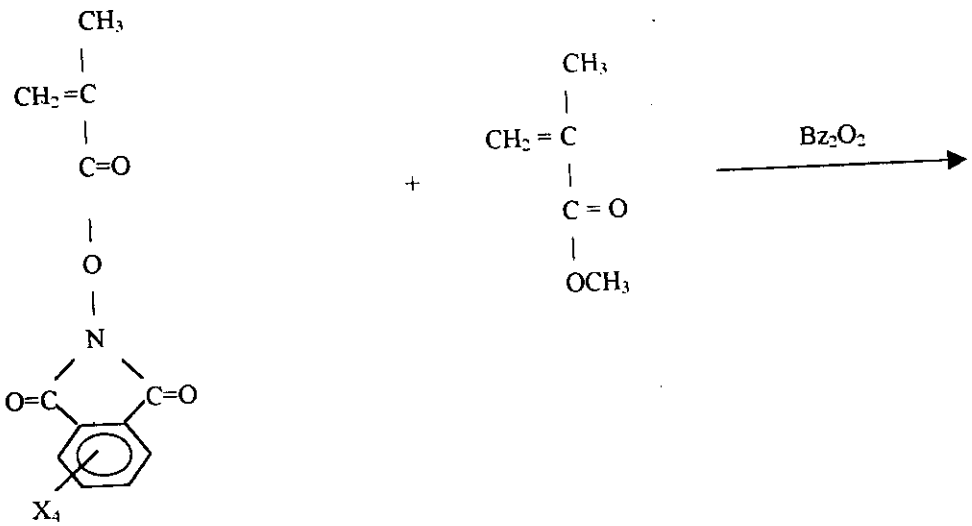
Also, N-methacryloyloxytetrabromophthalimide was prepared by the reaction of methacrylic acid with N-hydroxytrabromophthalimide in presence of N, N′-dicyclohexylcarbodiimide (DCCI) according to the method described in pages 36 and 37.

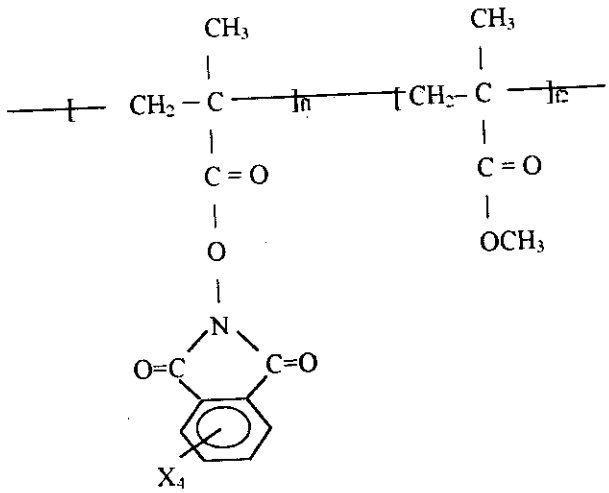


The resulting N-methacryloyloxytetrabromophthalimide was obtained as yellowish-white crystals, recrystalized from benzene methanol (30:70, v/v) to give NMTP as a yellowish solid m.p. 186°C, yield 98.5%. analytical calculations for ($C_{12}H_5NO_4Br_4$) = C, 26.33%; H, 0.91%; N, 2.56% and Br, 58.50%. Found C, 26.21%; H, 0.79%; N, 2.5% and Br, 58.46%.

(vi) Copolymerization of methyl methacrylate with N-methacryloyloxyphthimide and N-methacryloyloxytetrabromophthimide

The copolymerization reactions of methyl methacrylate with both N-methacryloyloxylphthimide and N-methacrylayloxytetrabromophthalimide were carried out by solution polymerization technique in the presence of benzoyl peroxide as initiator as described in page 37





X = H or Br

The prepared low molecular weight copolymers were yellowish solids soluble in most organic solvents. The structure of the copolymer systems were studied by IR spectroscopy. IR-spectra of the prepared copolymers are shown in Figs. 18 (a), (b) , (c) and (d) which have the following bands:

A broad band at 3500 cm^{-1} due to the streching vibrations of a hydroxyl group resulted from interamolecular H–band; a band at 3010 cm^{-1} corresponding to $C–H_{(arom.)}$ streching vibrations of the four aromatic protons (in case of free bromine sample); a strong band at 2960 cm^{-1} due to the C–H streching vibrations of $–CH_2–$ and $–CH_3$ groups and a strong band at 1750 cm^{-1} corresponding to the C = O group streching vibrations of the carboxylate ester group.

Also ^{1}H-NMR of the four prepared copolymers Figs. 19 (a), (b), (c) and (d) show broad signals at δ = 0.7-1.4 ppm due to the protons of $–CH_3$ and $–CH_2–$ groups and signals at δ = 3.4- 3.5 ppm corresponding to the three protons of $CH_3O–$ and only one signal at δ = 8.0 ppm due to the four protons of the aromatic ring (in case of nonbrominated copolymer sample).

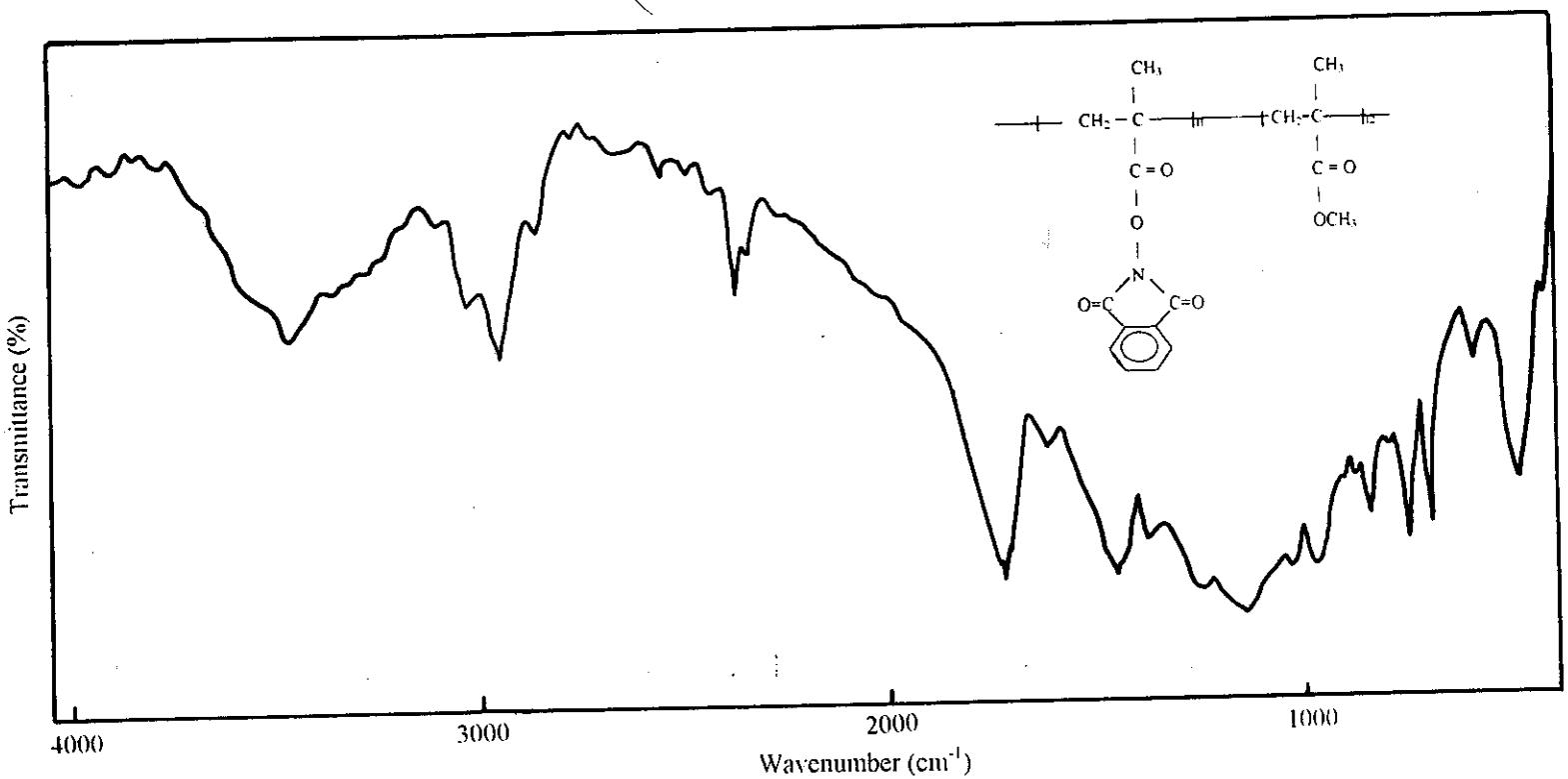


Fig. (18a): IR spectrum of (MMA/NMP) copolymer (free bromine sample).

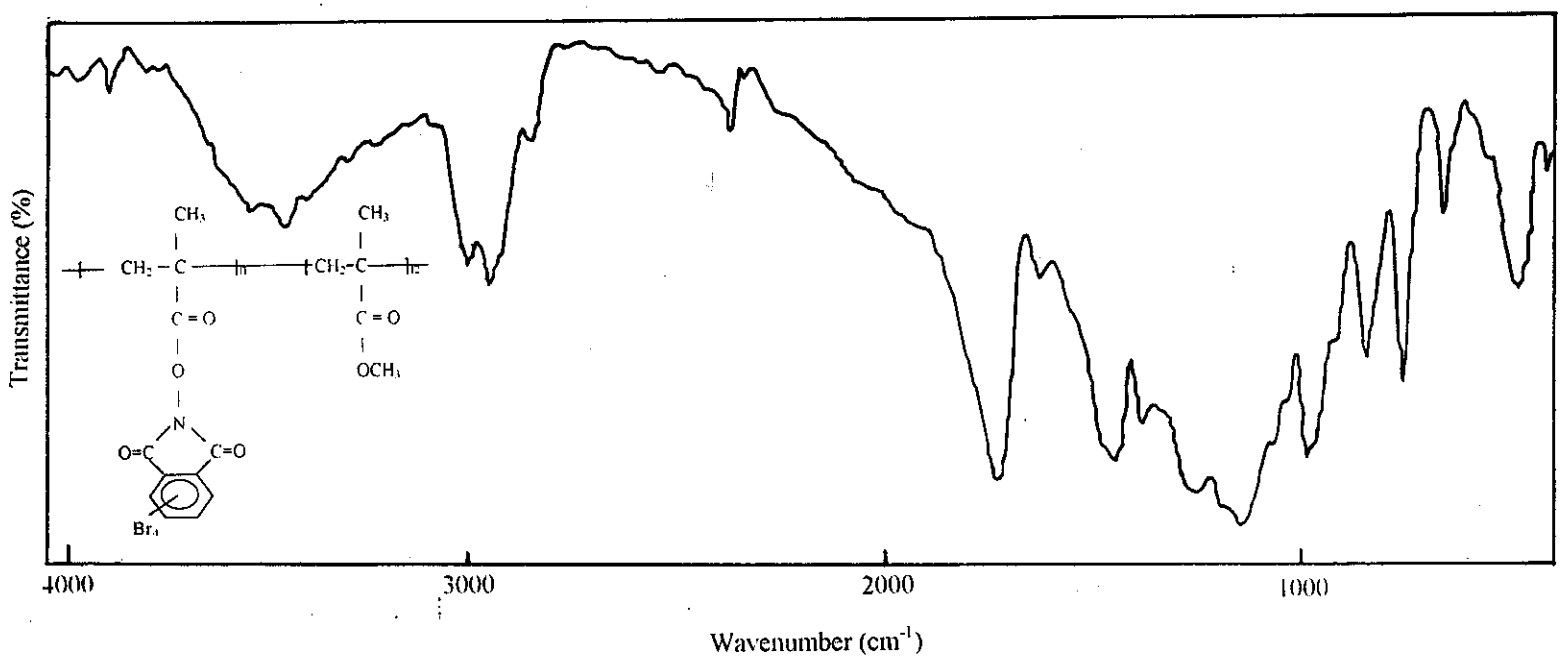


Fig. (18b): IR spectrum of (MMA/NMP) copolymer of 5.8 Wt.% bromine content.

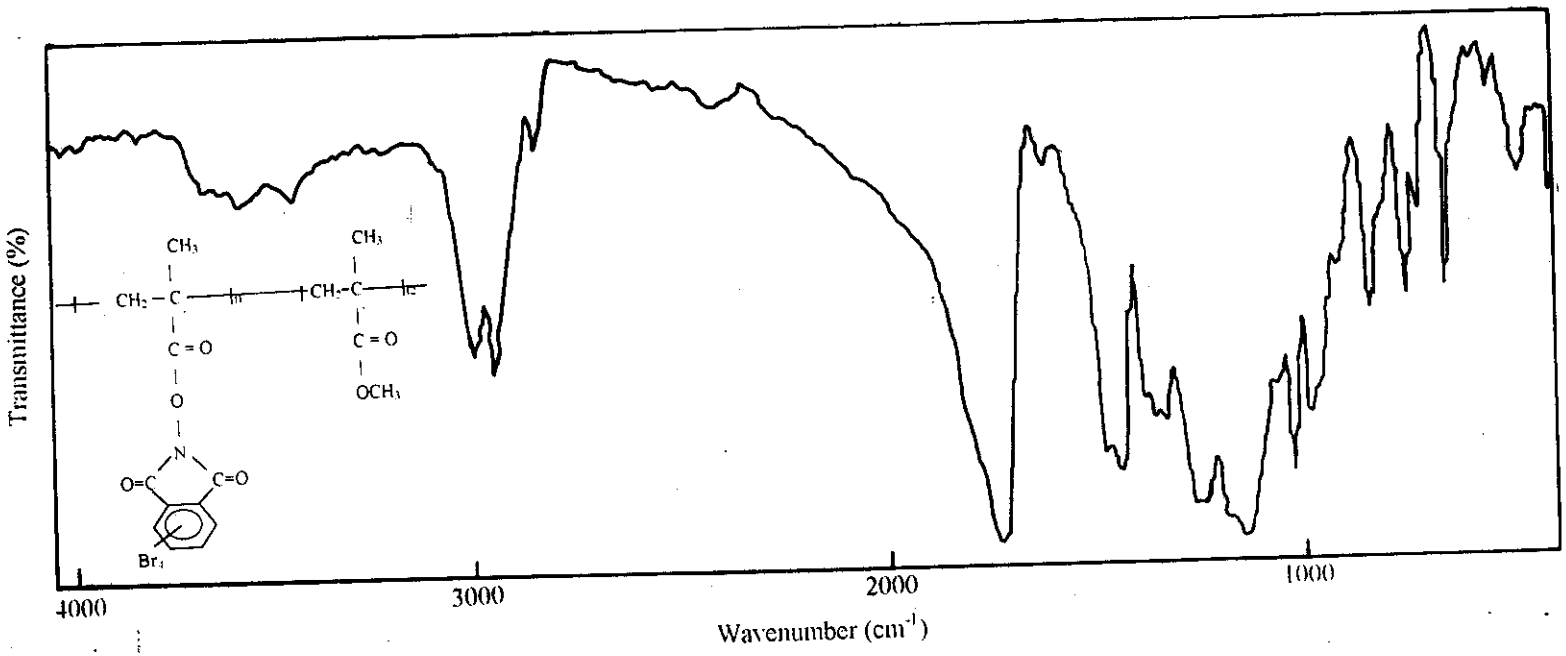


Fig. (18c): IR spectrum of (MMA/NMP) copolymer of 11.5 Wt.% bromine content.

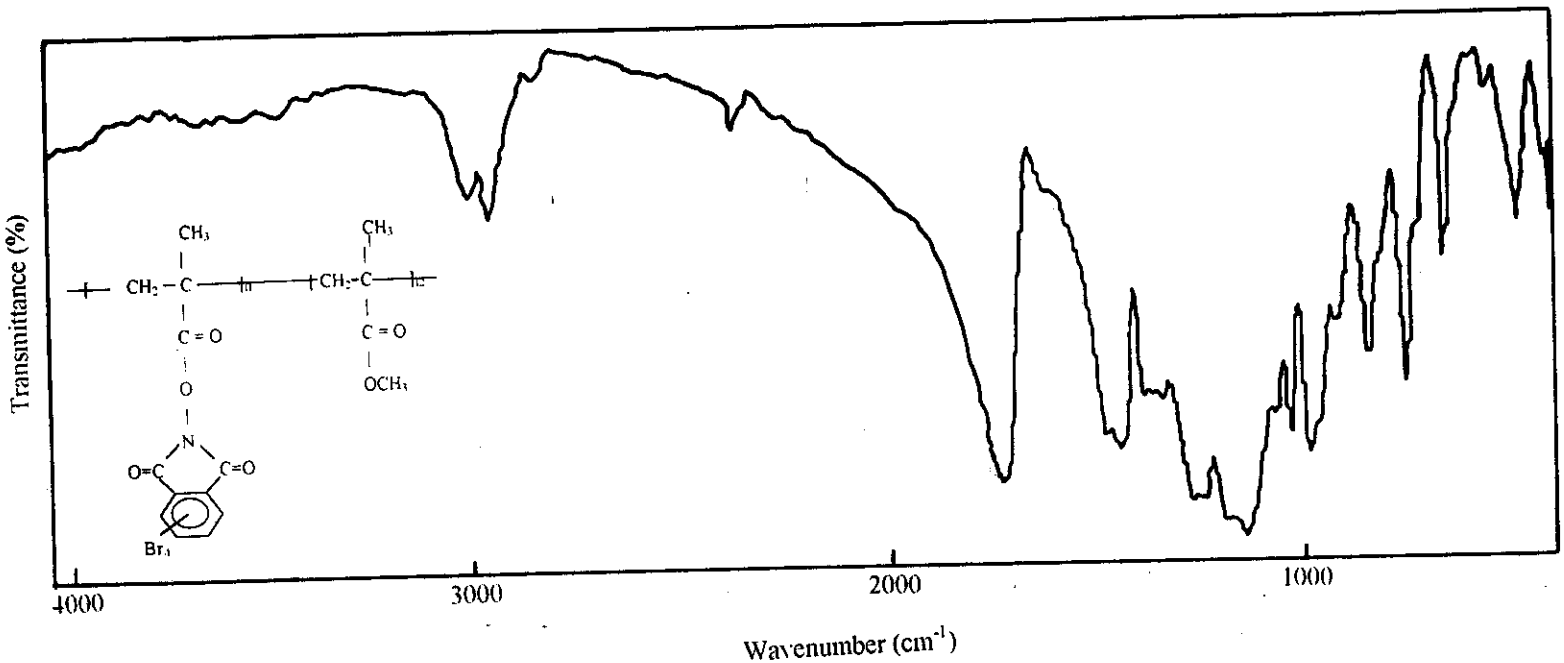


Fig. (18d): IR spectrum of (MMA/NMP) copolymer of 17.5 Wt.% bromine content.

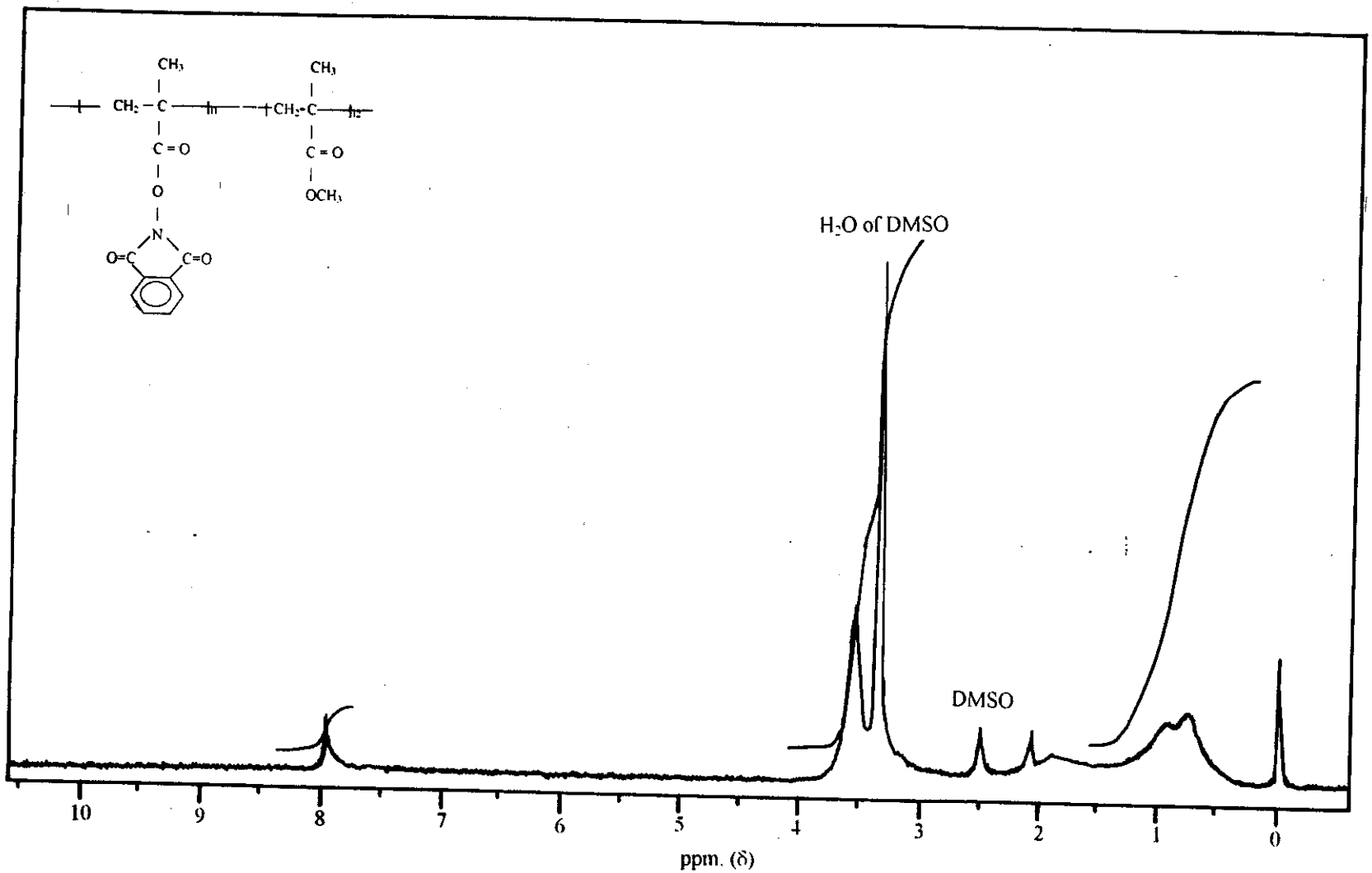


Fig. (19a): ^{1}H-NMR spectrum of (MMA/NMP) copolymer (free bromine sample).

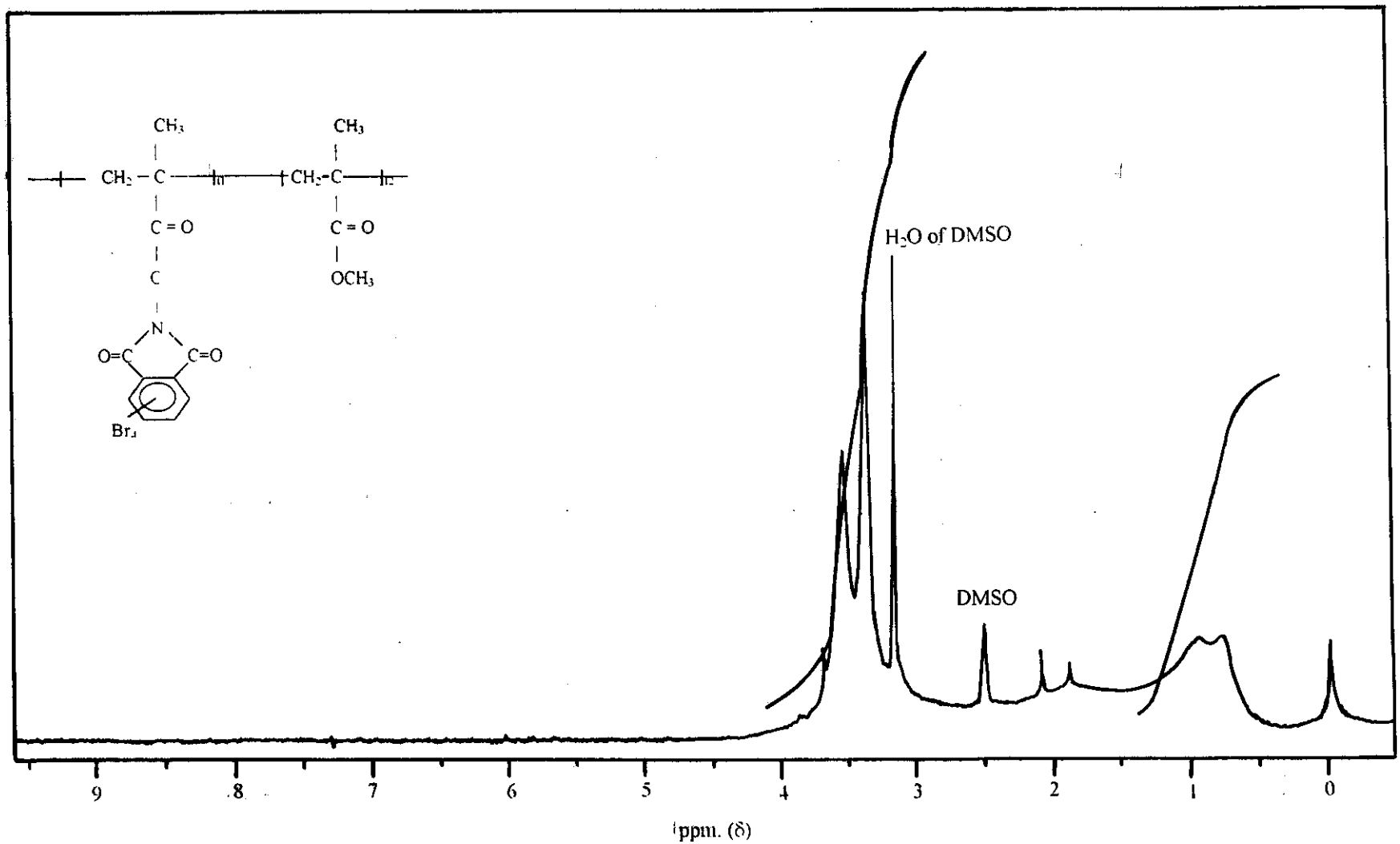


Fig. (19b): ^{1}H-NMR spectrum of (MMA/NMP) copolymer of 5.8 Wt.% bromine content.

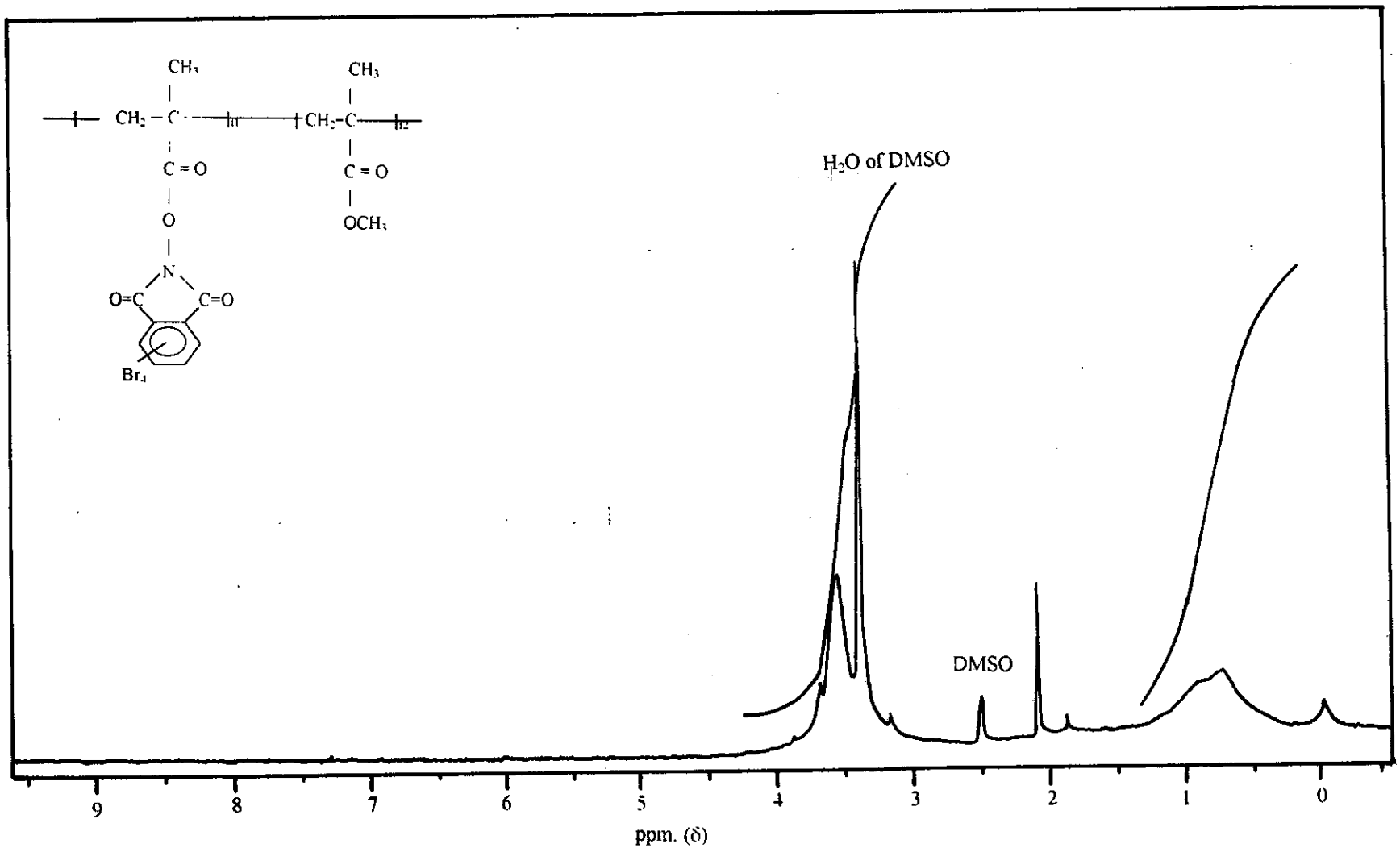


Fig. (19c): ^{1}H-NMR spectrum of (MMA/NMP) copolymer of 11.5 Wt.% bromine content.

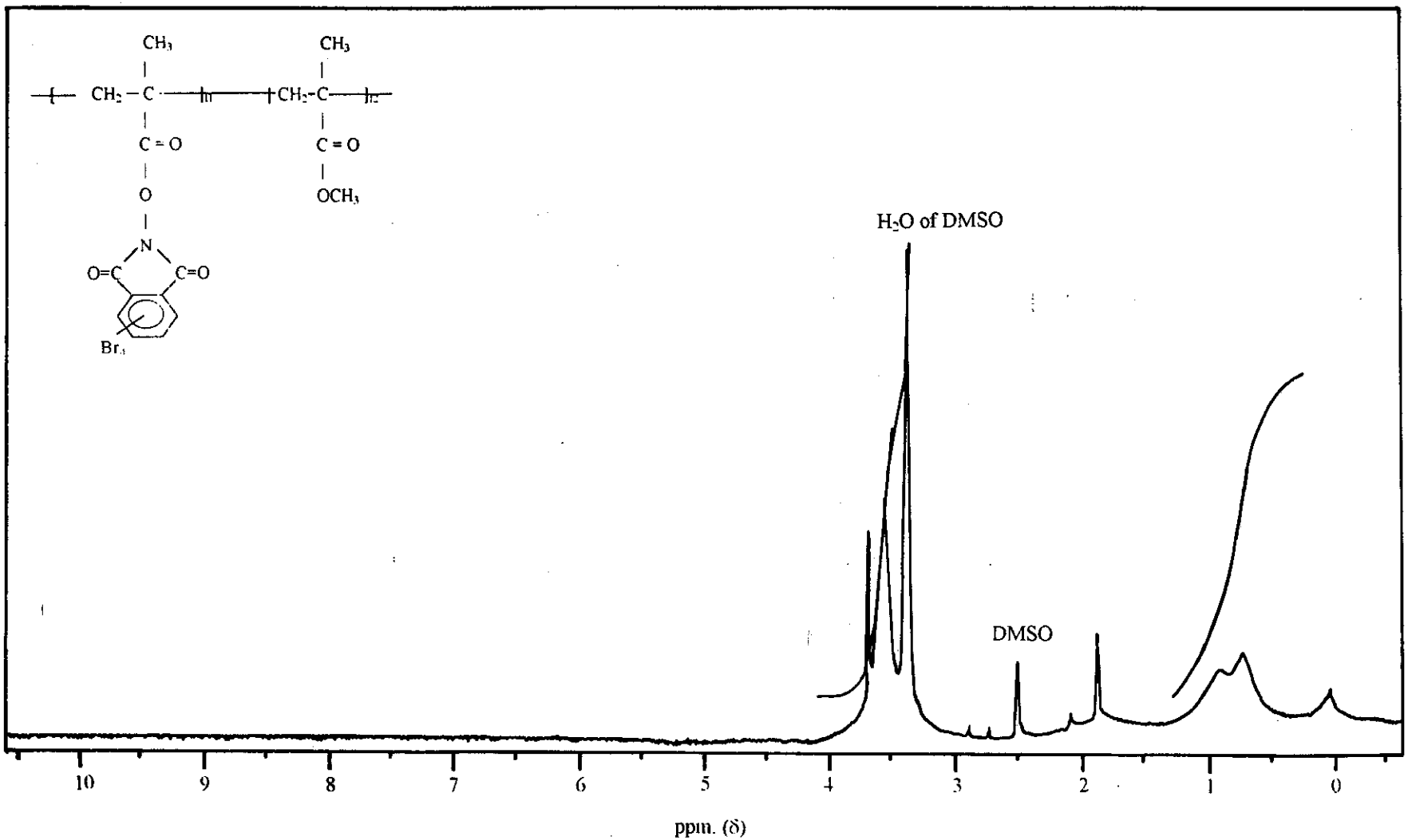


Fig. (19d): ^{1}H-NMR spectrum of (MMA/NMP) copolymer of 17.5 Wt.% bromine content.

2-IMPROVEMENT OF WHITE PINE WOOD PROPERTIES BY IMPREGNATION WITH THIOUREA-FORMALDEHYDE RESIN AND ORTHOPHOSPHORIC ACID.

The white pine wood was impregnated with TUF resin and OPA (various concentrations) as a flame – retardant and catalyst for the cross-linking reaction[51]. Each impregnation process was carried out under reduced pressure for 1 hour Tables 3 (a), (b) illustrate the (WPG)weight percent gain, volume change (%), and density of treated wood samples (grain in the tallest and smallest dimension, respectively). WPG was determined to be 27-67% and 55 - 138%. Volume change values of treated wood samples were found to be between 4.13 - 9.00% and 8 - 18%.

In addition, the density of the whole treated wood samples was found from 0.55 to 0.68 g/cm^3 and from 0.62 to 0.85 g/cm^3 for each type of treated wood sample, respectively. There is a good agreement between our results (WPG, volume change, density) and the literature[71,72].

The water uptake values (%) of the wood specimens are shown in Tables 4 (a), (b) (grain in the tallest and smallest dimension respectively). From Table 4 (a), during the first 2 hours of water soaking, control sample took about 64% water, whereas samples impregnated with TUF resin and 85 % OPA took about 8% water. After 168 hours of water soaking, the control samples gained about 106% water, whereas treated wood samples gained about 38%. From Table 4 (b), after the first 2 hours of water soaking, control samples took up water about 90%, whereas samples impregnated with TUF resin and 85% OPA took up about 8 % water. After 168 hours of

Table (3): Impregnation of white pine wood with TUF resin and OPA at different concentrations.

(a) Grain In Tallest Dimension

Sample No.	Concentration of OPA (%)	Wood Weight[a] W_o	Final Weight[b] W_t	WPG[c] (%)	Wood Volume[a] V_o	Final Volume[b] V_t	Volume Change[c] (%)	Density[d] (g/cm^3)
1	85	1.80	3.00	67	4.04	4.40	9.00	0.68
2	70	1.73	2.87	66	4.12	4.44	7.77	0.65
3	55	1.86	2.85	53	4.14	4.46	7.73	0.64
4	40	1.76	2.66	51	4.15	4.36	5.00	0.61
5	25	1.88	2.41	28	4.11	4.30	4.62	0.56
6	10	1.85	2.35	27	4.12	4.29	4.13	0.55

(b) Grain In Smallest Dimension

Sample No.	Concentration of OPA (%)	Wood Weight[a] W_o	Final Weight[b] W_t	WPG[c] (%)	Wood Volume[a] V_o	Final Volume[b] V_t	Volume Change[c] (%)	Density[d] (g/cm^3)
1	85	1.75	4.16	138	4.14	4.87	18	0.85
2	70	1.68	3.86	130	4.16	4.82	16	0.80
3	55	1.60	3.62	126	4.20	4.81	14	0.75
4	40	1.81	3.35	85	4.14	4.65	12	0.72
5	25	1.96	3.21	63	4.19	4.65	11	0.69
6	10	1.82	2.81	55	4.19	4.55	8	0.62

[a]After drying at 105 °C for 7 hrs.

[b]After complete impregnation of untreated wood samples and drying at 105 °C for 12hrs.

[c]Wt. % Gain average data from five samples.

[d]Average density of untreated wood samples: 0.4241 g/cm^3.

Table (4): Water uptake values of white pine wood impregnated with TUF resin and OPA at different concentrations.

(a) Grain In Tallest Dimension

Sample No.	Concentration of OPA (%)	Water uptake[a] % Soaking time (h.)							
		2	4	8	24	48	72	144	168
1	85	8	11	15	23	28	32	37	38
2	70	10	13	18	26	31	34	39	40
3	55	15	18	23	33	40	44	48	49
4	40	18	21	26	35	42	45	50	51
5	25	22	27	37	50	57	60	69	70
6	10	26	31	40	52	60	64	75	75
Untreated	-	64	69	75	83	90	95	103	106

(b) Grain In Smallest Dimension

Sample No.	Concentration of OPA (%)	Water uptake[a] % Soaking time (h.)							
		2	4	8	24	48	72	144	168
1	85	8	8	9	11	15	18	23	23
2	70	8	10	12	15	18	20	24	25
3	55	19	18	21	24	27	29	33	33
4	40	19	21	26	31	35	37	42	43
5	25	21	23	29	35	40	42	48	49
6	10	33	38	44	53	60	62	70	72
Untreated	-	90	94	102	112	122	129	142	144

[a]Average data from five samples.

water soaking the control sample took up about 144 % water, where as treated wood samples took up water about 23 %.

It may be seen from Figs. 20 (a), (b) that water uptake values (%) decreases with increasing the concentration of OPA, it is clear that water uptake values (%) of treated wood when grain in the direction of the smallest dimension are less than water uptake values of treated wood samples when grain in direction of the tallest dimension. For all wood species there is an inverse relationship between water uptake (%) and WPG (%). Our results for water uptake are in good agreement with those listed in the literature[68].

Dimensional stability and water repellency were measured using a simple water-soaking test. This test estimated not only dimensional stability (from data obtained for various periods) but also water repellency (from data obtained for long-term water soaking) as shown in Tables 5 (a),(b) for treated wood samples (grain in the direction of tallest and smallest dimension, respectively), from Table 5 (a), WRE values for periods of 2 hours were between 40 - 81%, whereas those for a period of 144 hours was between 6-45%. Also, in Table 5 (b), WRE values for a period of 2 hours were between 38-83% whereas those for a period of 144 hours were between 18-63%. For the entire soaking time, the white pine wood samples impregnated with 85% OPA solution gave the higher WRE values. As seen in Tables 5 (a), (b), decreases in WRE values are proportional to soaking times (2, 4, 8, 24, 48, 72, and 144 hours) for all species. There is a good agreement between our WRE results and those in the literature [68,69].

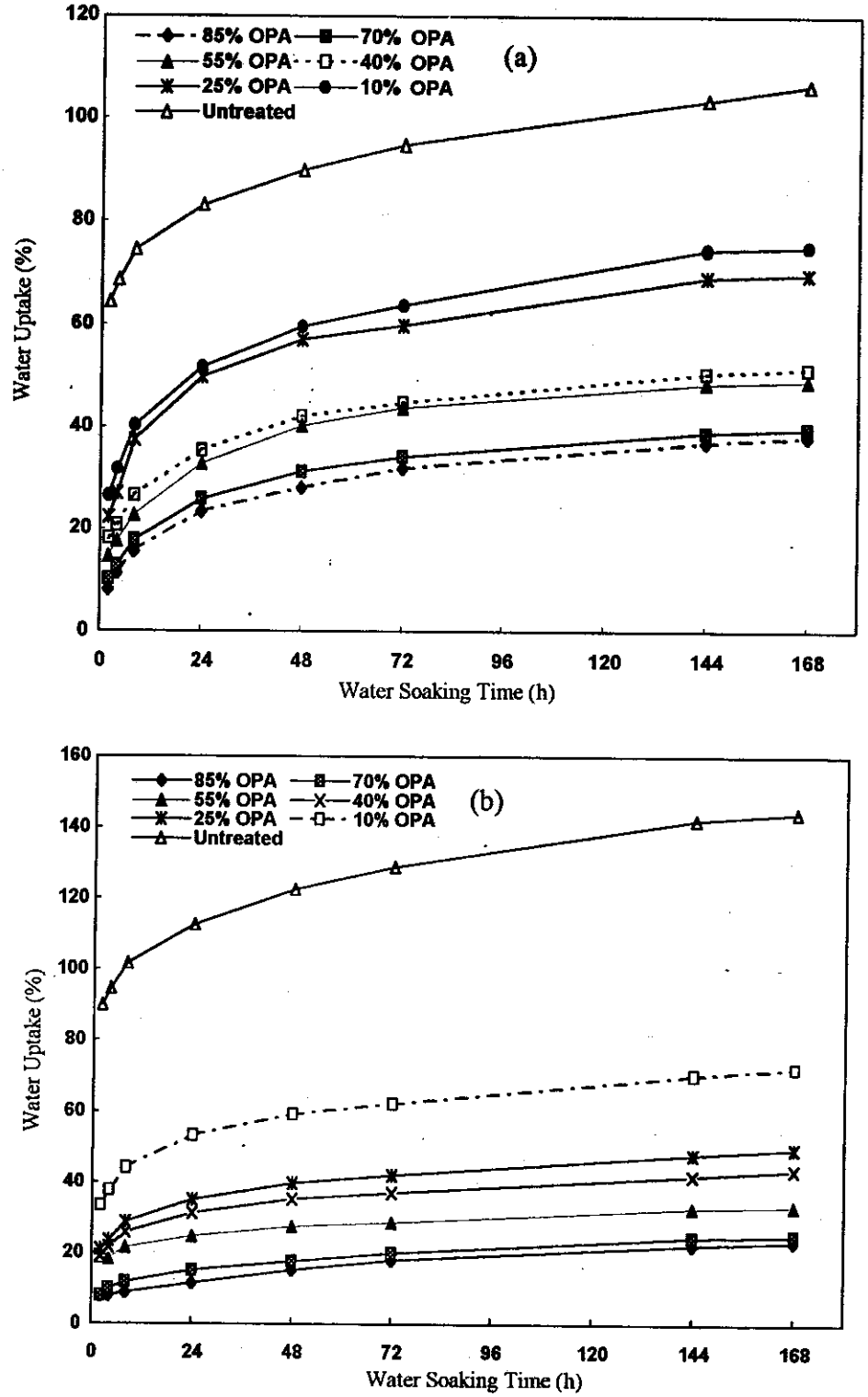


Fig. (20): Effect of soaking time on percent water uptake of white pine wood impregnated with TUF resin and OPA at different concentrations compared to untreated control, where (a) grain in the tallest dimension and (b) grain in the smallest dimension.

Table (5): Water Repellent Effectiveness (WRE) of white pine wood samples impregnated with TUF resin and OPA at different concentrations.

(a) Grain In Tallest Dimension

Sample No.	Concentration of OPA (%)	WRE[a] Soaking time (h)							
		2	4	8	24	48	72	144	168
1	85	81	75	69	53	48	46	45	43
2	70	75	70	63	55	51	47	43	29
3	55	66	62	52.	42	34	32	31	33
4	40	58	55	49	37	31	31	28	29
5	25	55	50	37	23	18	19	14	16
6	10	40	40	32	14	13	13	6	9

(b) Grain In Smallest Dimension

Sample No.	Concentration of OPA (%)	WRE[a] Soaking time (h)							
		2	4	8	24	48	72	144	168
1	85	83	81	80	77	72	69	63	64
2	70	40	76	72	69	66	64	61	61
3	55	60	59	56	53	52	51	51	52
4	40	58	55	51	45	42	41	41	43
5	25	50	44	40	37	37	36	35	36
6	10	38	33	27	20	18	18	18	20

[a]Average data from five samples.

Volumetric swelling (%) in 1-week water - soaking test is shown in Tables 6 (a),(b) (grain in the tallest and smallest dimension, respectively). It is clear that during 1week, treated wood samples have ASE values between 3 and 15% for 10 and 85% OPA solutions, respectively, for the wood samples that had grain in the tallest dimension. These results showed that wood samples treated with 85% OPA solution had greater ASE value than other solutions. The same behavior was obtained for grain in direction of the smallest dimension as shown in Table 6 (b). This may result from the amount of (%) WPG.

Compressive strength

(A) Compression parallel to grain:

Data average of three runs for compressive strength parallel to grain of treated wood compared to untreated controls, (grain in the smallest dimension) are illustrated in Fig. 21 (a) highest values were observed for the wood samples impregnated with TUF resin and 70% OPA solution.

(B) Compression perpendicular to grain

Data for compressive strength perpendicular to grain of treated wood samples compared to untreated controls, (grain in the smallest dimension) are illustrated in Fig. 21 (b), the highest values were observed for the wood samples impregnated with TUF resin and 55% OPA solution.

Table (6): Antiswelling Efficiency (ASE) of white pine wood impregnated with TUF resin and OPA at different concentrations after 7 days of immersion in distilled water at 25°C.

(a) Grain In Tallest Dimension

Sample No.	Concentration of OPA(%)	S (%)	ASE[a] (%)
Untreated	-	19.16	-
1	85	16.64	15
2	70	17.26	11
3	55	17.76	8
4	40	18.06	6
5	25	18.51	3.5
6	10	18.65	3

(b) Grain In Smallest Dimension

Sample No.	Concentration of OPA(%)	S (%)	ASE[a] (%)
Untreated	-	16.75	-
1	85	14.19	18
2	70	14.84	13
3	55	15.46	8
4	40	15.57	6
5	25	16.09	4
6	10	16.14	3.7

[a]Average data from five samples.

Fire retarding property of treated wood: -

White pine wood impregnated with TUF resin followed by another impregnation with OPA solution at various concentrations, the original, final weights, glowing and flaming time are listed in Tables 7 (a), (b).The loss in weight is expressed as a percentage of the original weight of the specimen. From Table 7 (a), (b), (grain in the tallest and smallest dimension, respectively) it is clear that all treated wood samples had fire retardency compared with untreated wood samples. In the case of treated wood samples with grain in the direction of the smallest dimension, maximum and minimum weight losses were found to be 13 and 4%, respectively. On the other hand, the treated wood samples with grain in the direction of tallest dimension showed maximum and minimum weight loss of 52 and 33%, respectively. The treated wood samples with grain in the direction of smallest dimension were found to possess excellent flame retardant properties.

A possible explanation for this phenomenon is the greater percentage of WPG for the treated wood samples with grain in the smallest dimension than for samples with grain in the tallest dimension because more wood cells are open and exposed to the impregnated solution in wood samples with grain in the smallest dimension.

Table (7): Crib fire test results for white pine wood impregnated with TUF resin and OPA at different concentrations.

(a) Grain In Tallest Dimension

Sample No.	Concentration of OPA (%)	W_o[a]	W[b]	%wt. loss	Observations	
					Flaming time (min)	*Glowing* time (min)
Untreated	-	130	2	98	14 - 16	9 - 10
1	85	189	116	38	5 - 6	0.85 - 1
2	70	170	113	33	5 - 6	1 - 2
3	55	157	79	52	7 - 8.5	8 - 9
4	40	160	85	47	6 - 7.5	5 - 6
5	25	156	73	53	7 - 8	7 - 8
6	10	154	86	44	6 - 7	5 - 6

(b) Grain In Smallest Dimension

Sample No.	Concentration of OPA (%)	W_o[a]	W[b]	%wt. loss	Observations	
					Flaming time (min)	*Glowing* time (min)
Untreated	-	136	4	97	9 - 10	8 - 9
1	85	253	242	4	-	-
2	70	257	244	5	-	-
3	55	244	230	6	-	-
4	40	243	227	6	1.5 - 2	0.166
5	25	222	201	9	2 - 3	0.5 - 0.7
6	10	205	178	13	2 - 3	0.85 - 1

[a]Weight of wood samples after drying at 105 °C for 12 hrs. and before applying the igniting flame.

[b]Weight of wood samples after the removal of igniting flame and after all flaming and glowing ceased.

3-IMPROVEMENTS OF WHITE PINE WOOD PROPERTIES BY IMPREGNATION WITH UNSATURATED POLYESTERS IN ADMIXTURE WITH STYRENE

Effect of changing bromine content in the PE/St resins on the percent retention (R) and percent crosslinking:-

Data in Table (8) indicates that values of weight percent gain (WPG) (after the removal of uncured monomers) and values of percent retention for treated wood samples (103-143%),the highest value was obtained for wood samples impregnated with PE/St resin of zero bromine content. Also high percent crosslinking values was obtained for all wood polymer composites (wpc) (94 - 98 %) especially for impregnated wood samples by resin of zero bromine content.

Volume change (%) and density of treated wood samples are given in Table (9). The highest value of volume change (%) was obtained for impregnated wood samples with the PE/St mixture of zero bromine content (139.00 %) and decreases with increasing bromine content to reach its lower value (91%) for PE/St mixture of 12.5 Wt.% bromine content. The density of the whole-polymerized wood was found to be from 0.87 g/cm^3 (for impregnated wood samples with PE/St of zero bromine content) to 0.77 g/cm^3 (for impregnated wood samples with PE/St mixture of 12.5 Wt.% bromine content).

In addition the values of average volume change of wood samples were found to be (4.00, 2.13, 1.18 and 0.24%) for impregnated wood samples with PE/St resins of 0.0, 6.3, 9.3 and 12.5 Wt.% bromine content, respectively. There is a good agreement between our results and the literature[71,72]

Table (8): Effect of bromine content in PE/St resins on the weight percent gain (WPG), percent retention (R) and percent crosslinking of wood polymer composites (wpc).

Sample No.	Bromine content (%)	W_o (g)	W_1 (g)	W_2 (g)	WPG[a] (%)	% Retention[a] (R)	% Crosslinking[a]
1	0.0	1.54	3.75	3.69	139	143	98
2	6.3	1.61	3.85	3.74	132	139	97
3	9.3	1.60	3.51	3.37	110	120	96
4	12.5	1.79	3.63	3.42	91	103	94

[a]All weights are average of six samples.

Table (9): Effect of bromine content in PE/St resins on the volume change (%) and density change wood polymer composites (wpc).

Sample No.	Bromine content (%)	W_o (g)	V_o (cm^3)	V_t (cm^3)	Vol. change (%)	d_o[a] (g/cm^3)	d[a] of (WPC)
1	0.0	1.54	4.24	4.41	4.00	0.37	087
2	6.3	1.61	4.23	4.32	2.13	0.38	0.87
3	9.3	1.60	4.24	4.29	1.18	0.38	0.78
4	12.5	1.79	4.22	4.23	0.24	0.42	0.77

[a] d_o and d are average densities of untreated and treated wood samples after drying at 105°C for 12hrs. (average data from six samples).

The water uptake values (%) of the wood specimens are shown in Table (10) during the first 2 hours of water soaking, control samples have taken about 84 % water and wood polymer composites (wpc) have taken about 39, 7, 7.5 and 10% water for impregnated samples with PE/St mixtures of 0.0, 6.3, 9.3 and 12.5 Wt.% bromine content, respectively. After 168 hours of water soaking the control samples took up about 130 % water whereas wpc took up about 74, 30,46 and 51 % water for impregnated wood samples with PE/St mixtures of 0.0, 6.3, 9.3 and 12.5 Wt.% bromine content, respectively.

The highest water uptake value of treated samples with PE/St mixture of zero bromine content was due to the higher impregnation yield as measured by WPG after final cure and drying, for all of the other three impregnated wood samples as bromine concentration increases from 6.3 to 12.5 Wt.% in the impregnating mixture the average water uptake values of the whole treated wood samples increase due to the increasement in hydrophilicity as seen in Fig. (22). Our results for water uptake are in good agreement with those listed in the literature[72]

Dimensional stability and water repellency were measured using a simple water - soaking test. This test estimates not only water repellency (from data obtained for various periods) but also provides a measure of dimensional stability (from data obtained for long - term water soaking). As shown in Table (11), WRE was greatly improved for the samples contain bromine.

Table (10): Effect of soaking time on percent water absorption of white pine wood impregnated with PE/St resins of various bromine contents compared with untreated wood.

Sample No.	Bromine content (%)	Water Uptake[a] (%)							
		Soaking Time (h.)							
		2	4	8	24	48	72	144	168
Control	-	84	86	90	98	107	112	126	130
1	0.0	39	45	52	62	66	68	71	74
2	6.3	7	11	15	24	27	28	29	30
3	9.3	7.5	15	21	36	41	43	45	46
4	12.5	10	16	23	40	45	47	50	51

[a]Average data from six samples.

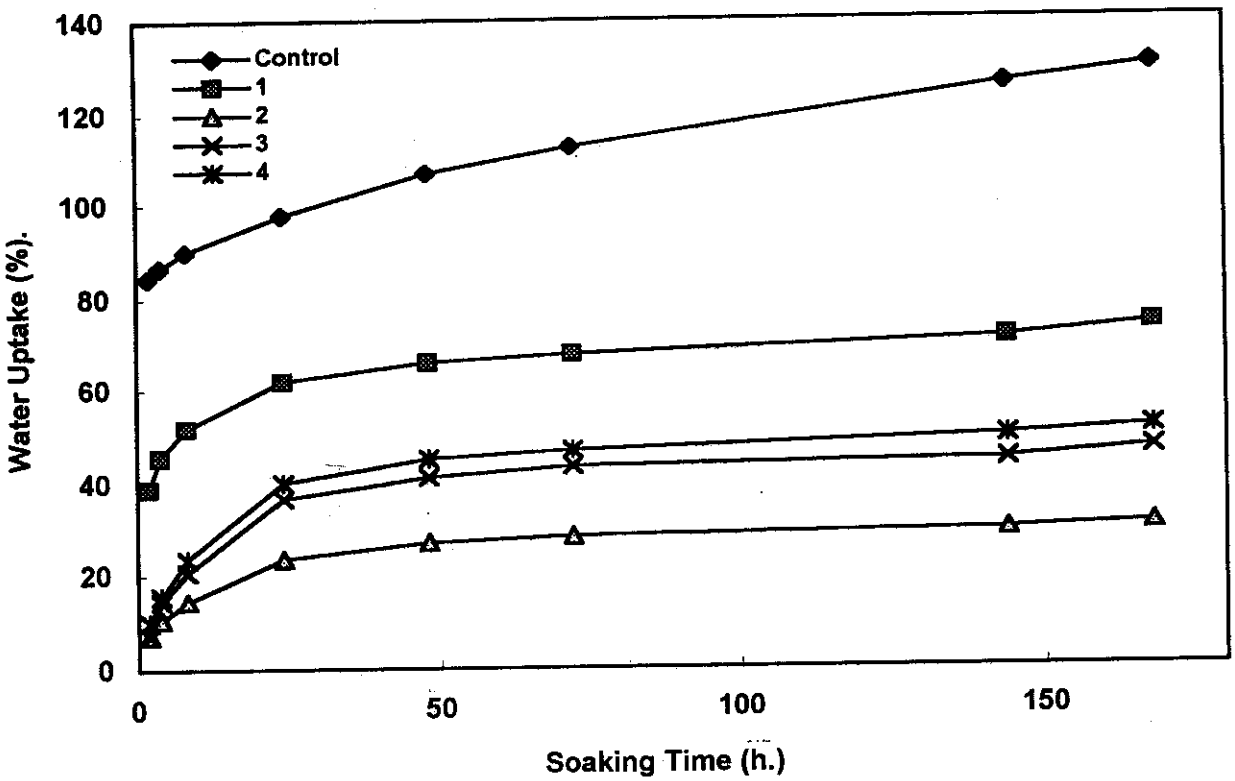


Fig. (22): Effect of soaking time on percent water uptake of white pine wood impregnated with PE/St resins of various bromine contents, compared to untreated wood samples.

Table (11): Water repellent effectiveness (WRE) of white pine wood impregnated with PE/St resins of various bromine contents.

Sample No.	Bromine content (%)	WRE[a] (%)							
		Soaking Time (h.)							
		2	4	8	24	48	72	144	168
1	0.0	27	17	6	0.66	3	5	12	12
2	6.3	82	73	63	47	45	45	49	49
3	9.3	78	67	53	27	24	24	30	31
4	12.5	76	63	46	19	16	17	21	21

[a]Average data from six samples.

Table (12): Antiswelling efficiency (ASE) of white pine wood impregnated with PE/St resins of various bromine contents after 7 days of immersion in distilled water at 18 °C.

Sample No.	Bromine content (%)	Swelling Coefficient (S)	ASE[a] (%)
Control	-	15.26	-
1	0.0	13.52	13
2	6.3	11.80	29
3	9.3	11.02	39
4	12.5	10.28	48

[a]All samples are dried at 105 °C for 12 hrs., average data from six samples.

grain) of all samples were improved compared to untreated wood samples. The highest value for compressive strength were 66 and 15 KN/m^2 in the parallel and perpendicular directions, respectively for impregnated wood samples with PE/St mixture of zero bromine content. But the compressive strength for the impregnated wood samples by PE/St mixtures of highest bromine content were found to be 47 and 9.5 KN/m^2 while of untreated wood samples were 40.00 and 5.00 KN/m^2 in the parallel and perpendicular directions, respectively see Fig. 23 (a), (b).

Fire Retardancy

(a) Relative flammability of PE/St resin sheets

PE/St resin sheets of zero bromine content continues to burn after the first ignition and judged as a *burning* substance, with a burning rate = 81.08 in/min. but the other three samples containing bromine were judged as *self extinguishing* substances and flame dose not reach to the 4 - in. mark after the second ignition and the extent of burning has its lowest value (0.40 in.) for the polymer sample of highest bromine content, as illustrated in Table (14).

(b) Crib-test for treated wood

The original, final weights, glowing and flaming time were determined. The loss in weight after all flaming and glowing shall be expressed as a percentage of the original weight of the specimen. It is obvious that all impregnated wood samples have little fire retardancy due to shrinking of polymer into the bulk of

Table (13): Compression strength parallel and perpendicular to grain of white pine wood impregnated with PE/St resins of various bromine contents, compared to untreated control.

Sample No.[a]	Bromine content (%)	Compression strength parallel to grain (KN/m^2)	Compression strength perpendicular to grain (KN/m^2)
Control	-	40.00	5.00
1	0.0	66.00	15.00
2	6.3	58.60	12.23
3	9.3	55.71	10.85
4	12.5	47.00	9.50

[a]Average date from three samples.

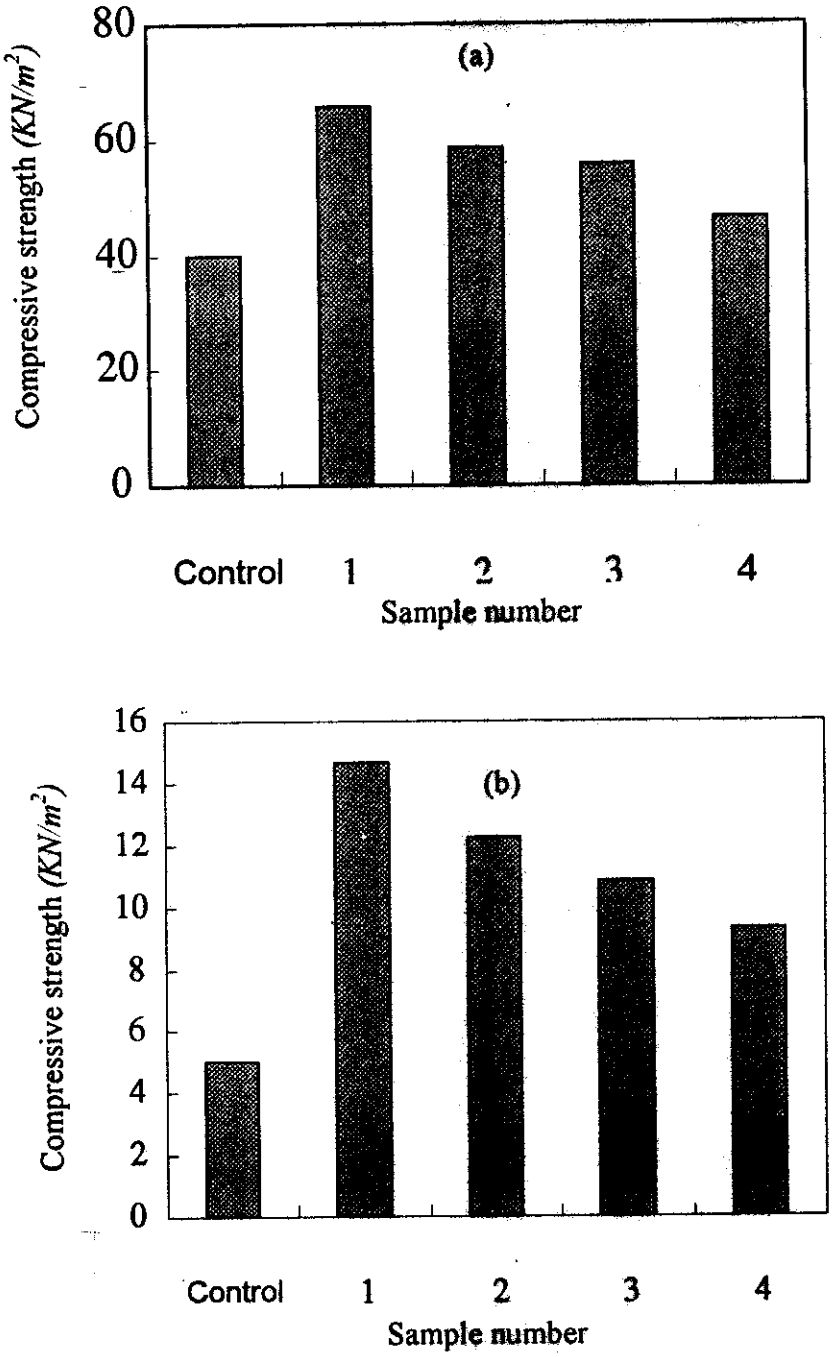


Fig. (23): Compression strength of white pine wood impregnated with PE/St resins of various bromine contents, compared to untreated control (average of three samples), where (a) is the compression strength parallel to grain and (b) is the compression strength perpendicular to grain.

Table (14): Relative flammability of PE/St resin sheets of various bromine contents.

Sample No.[a]	Bromine content (%)	Extent of burning (in.)	Burning rate (in./min.)	Classification of samples
1	0	-	81.08	Burning
2	5.3	0.63	-	Self-Extinguishing
3	7.8	0.45	-	Self-Extinguishing
4	10.6	0.40	-	Self-Extinguishing

[a] Number of specimens tested = 10 and thickness of specimen = 0.08in.

wood specimens treated with PE/St resins of various bromine contents.

(c) Flame spread test for coated wood samples.

On the bases of ASTM.D635-56T, the data in Table (15) shows that an inverse relation between bromine content (wt.%) and the distance burnt from the free end which had its highest value for wood sheets coated by a free bromine PE/St resin sample to give a burning rate = 160 in./min., but the smallest burnt distance was obtained for coated wood sheets by PE/St resin of highest wt. % of bromine to give an extent of burning = 0. 575 in.

On the other hand the burning rate of uncoated wood sheets was found to be 265 in./min. which judged as burning substances.

Table (15): Flame spread test of whit pine wood sheets coated by PE/St resins of various bromine contents.

Sample No.[a]	Bromine content (%)	Extent of burning (in.)	Burning rate (in./min.)	Classification of samples
Control	-	-	265.0	Burning
1	0.0	-	160.0	Burning
2	6.3	1.538	-	Self-Extinguishing
3	9.3	1.136	-	Self-Extinguishing
4	12.5	0.575	-	Self-Extinguishing

[a]Data obtained were average from 10 samples for each PE/St resin, thickness of the coated polymer on one side of a wood sheet = 0.0063 in.

4-IMPROVEMENT OF WHITE PINE WOOD PROPERTIES BY IMPREGNATION WITH MIXTURES OF METHYL METHACRYLATE AND PHTHALIMIDE MONOMERS AND SUBSEQUENT IN SITU COPOLYMERIZATION BY FREE – RADICAL INITIATOR

White pine wood was impregnated with a mixture of methyl methacrylate (MMA) and N-methacryloyloxyphthalimide (NMP) and other three mixtures were prepared by mixing (MMA) and N-methacryloyloxytetrabromophthalimide (NMTP) (different moles) in the presence of benzoyl peroxide as a free – radical initiator, composition of such mixture were illustrated in page 37.

Table (16) illustrates weight percent gain (WPG), volume change and density of treated wood samples, the highest WPG value(63%) were obtained for the impregnated wood samples with the comonomer mixture of zero bromine content and decrease with increasing bromine content in the comonomer mixture to reach its lower value (36%) for the impregnated wood samples with the comonomer mixture of 12.7 Wt. % bromine content. The densities of treated wood samples were found to be 0.51 and 0.60 g/cm^3 for impregnated wood samples with the brominated (Br%,12.7) and non - brominated comonomer mixtures, respectively. In addition, the values of average volume change were found to be (7.6, 7.1, 6.1 and 5.3%) for impregnated wood samples with comonomer mixture of 0, 4.2, 8.5 and 12.7 Wt .% bromine content, respectively.

Table (16): Effect of bromine content in (MMA/NMP) and (MMA/NMTP) comonomer mixtures on weight percent gain WPG, volume change % and density of wood polymer composites (wpc).

Sample No.	Comonomer mixture	Bromine content (%)	Wood weight[a] W_o	Final weight[b] W_t	WPG (%)	Wood volume[a] V_o	Final volume[b] V_t	Volume change[c] (%)	Density[d] (g/cm^3)
1	MMA/NMP	0.0	1.83	2.98	63	4.73	5.09	7.6	0.60
2	MMA/NMTP	4.2	1.89	2.97	57	4.78	5.12	7.1	0.58
3	MMA/NMTP	8.5	1.85	2.77	50	4.86	5.16	6.1	0.54
4	MMA/NMTP	12.7	1.96	2.65	36	4.92	5.18	5.3	0.51

[a]After drying at 105°C for 9 hrs.

[b]After complete impregnation of wood samples and in situ polymerization at 60°C for 2 hrs., 80°C for 4 hrs. and 100-105°C for 9hrs.

[c] weight percent gain average data from six samples.

[d]Average density of untreated wood samples = 0.39 g/cm^3.

The water uptake values of the wood specimens are shown in Table (17), during the first 2 hours of water soaking control sample took up about 73% water, and wood polymer composites (wpc) took up about 15, 18, 23 and 28 % water for impregnated wood samples with comonomer mixture of 0.0 , 4.2, 8.5 and 12.7 Wt. % bromine content, respectively. After 168 hours of water soaking the control sample took up about 130% water whereas wood polymer composites took up about 54, 58, 66 and 71% water for impregnated wood samples with comonomer mixture of 0.0, 4.2, 8.5 and 12.7 Wt.% bromine content, respectively.

It may be seen from Fig. (24) water uptake values increase with increasing bromine content (from 0.0 to 12.7%) in the comonomer mixture this is attributed to the higher impregnation yield as measured by WPG after final in situ polymernization and drying. Our results for water uptake are in good agreement with those listed in the literature[72].

Dimensional stability and water repellency were measured using a simple water-soaking test. This test estimates not only dimensional stability (from data obtained for various periods) but also water repellency (from data obtained for long-term water soaking), as shown in Table (18). Water repellent effectiveness WRE was greatly improved for all treated wood samples especially for impregnated wood samples by comonomer mixture of 0.0% bromine content then WRE % values decrease from 61 to 49% for

Table (17): Water uptake values of white pine wood impregnated with (MMA/NMP) and (MMA/NMTP) comonomer mixtures compared to untreated wood samples.

Sample No.	Comonomer mixture	Bromine content (%)	Water Uptake[a] %							
			Soaking Time (h.)							
			2	4	8	24	48	72	144	168
1	MMA/NMP	0.0	15	19	23	30	38	44	53	54
2	MMA/NMTP	4.2	18	22	25	33	42	48	57	58
3	MMA/NMTP	8.5	23	27	30	40	48	55	64	66
4	MMA/NMTP	12.7	28	30	34	43	53	60	70	71
Untreated	-	-	73	75	79	92	106	115	129	130

[a]Average data from six samples.

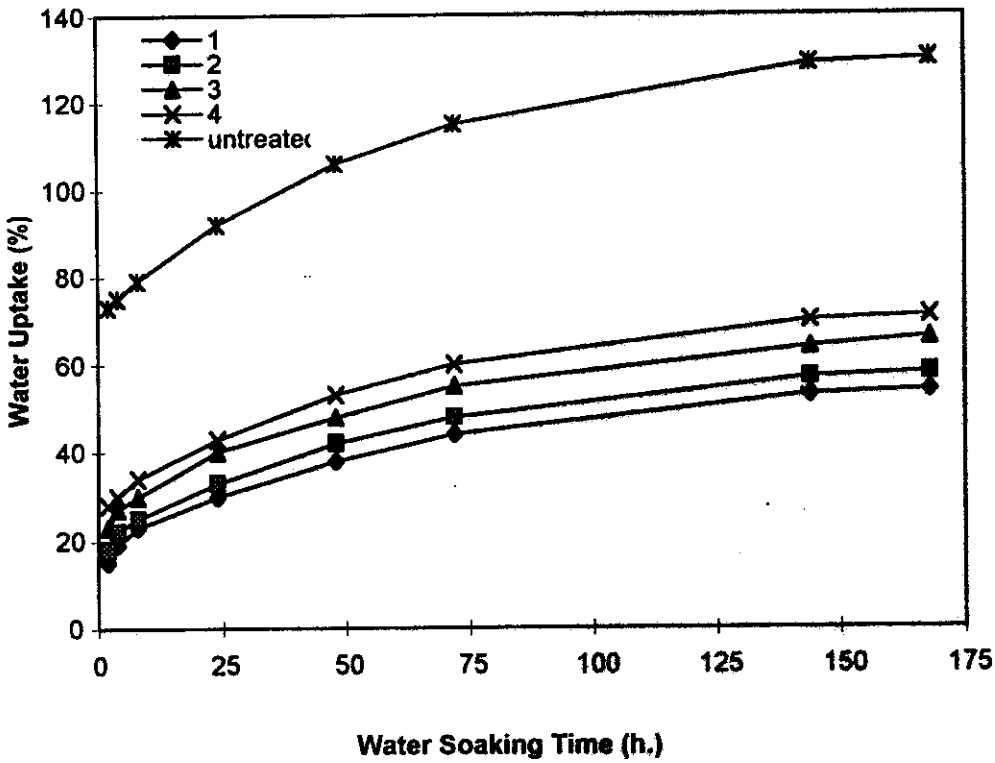


Fig. (24): Effect of soaking time on percent water uptake of white pine wood impregnated with (MMA/NMP) and (MMA/NMTP) comonomer mixtures of various bromine contents compared to untreated wood samples.

Table (18): Water repellent effectiveness (WRE) of white pine wood impregnated with (MMA/NMP) and (MMA/NMTP) comonomer mixtures.

Sample No.	Comonomer mixture	Bromine Content (%)	WRE[a] % Soaking Time (h.)							
			2	4	8	24	48	72	144	168
1	MMA/NMP	0.0	68	61	56	51	48	41	37	36
2	MMA/NMTP	4.2	61	55	52	48	45	38	34	32
3	MMA/NMTP	8.5	55	50	46	38	37	33	30	28
4	MMA/NMTP	12.7	49	45	43	33	32	29	26	25

[a]Average data from six samples.

impregnated wood samples by comonomer mixtures of 4.2 and 12.7 Wt.% bromine content, respectively. During soaking time WRE decreases with increasing time. There is a good a greement between our results and literature[72] .

Volumetric swelling (%) in a one - week- soaking test is shown in Table (19), the antiswelling efficiency ASE values for wood polymer - composites (wpc) of bromine contents varied inversely with increasing bromine contents in comonomer mixtures. All impregnated wood samples showed significant gain in antiswell efficiency, indicating improved resistance to swelling. On long-term exposure to water the highest value of ASE (48%) was obtained for the impregnated wood samples by comonomer mixture of zero bromine content, whereas ASE values decreases from 47 to 44% when bromine content increases from 4.2 to 12.7% in the comonomer mixture. Thus ASE values decrease with increasing concentration of N-methacryloyloxytetrabromophthalimide in the impregnant mixture.

Compression strength

Data of three runs for compression strength parallel and perpendicular to grain of treated wood samples compaired to untreated control are illustrated in Table (20).

Table (19): Antiswelling Efficiency (ASE) values of white pine wood impregnated with (MMA/NMP) and (MMA/NMTP) comonomer mixtures after 7 days of immersion in distilled water at 18°C.

Sample No.	Comonomer mixture	Bromine Content (%)	Swelling coefficient S[a]	ASE [a] (%)
Untreated	-	-	17.19	-
1	MMA/NMP	0.0	11.59	48
2	MMA/NMTP	4.2	11.69	47
3	MMA/NMTP	8.5	11.88	45
4	MMA/NMTP	12.7	11.96	44

[a]All samples were dried at 105°C for 9hrs., average data from six samples.

Table (20): Compression strength parallel and perpendicular to grain of white pine wood impregnated with (MMA/NMP) and (MMA/NMTP) comonomer mixtures, compared to untreated control.

Sample No.	Comonomer mixture	Bromine content (%)	Compression strength parallel to grain[a] (KN/m^2)	Compression strength perpendicular to grain[a] (KN/m^2)
Untreated	-	-	40	5
1	MMA/NMP	0.0	59	11
2	MMA/NMTP	4.2	55	10
3	MMA/NMTP	8.5	49	8
4	MMA/NMTP	12.7	47	7

[a]Average data from three samples.

(a) Compression strength parallel to grain

Values of compression strength parallel to grain are illustrated in Fig. 25 (a). The highest value (59 $KN\,m^2$) was observed for the wood samples impregnated with comonomer mixture of zero bromine content while the compression strength of wood samples impregnated with the comonomer mixture of 12.7 Wt.% bromine content was found to be 47 $KN\,m^2$.

(b) Compression strength perpendicular to grain

Data for compression strength perpendicular to grain are illustrated in Fig. 25 (b). Also, the highest value (11 $KN\,m^2$) was obtained for the free bromine comonomer mixture and it decreases to 7 $KN\,m^2$ for comonomer of 12.7 Wt.% bromine content.

Fire Retardancy

Crib- test for treated wood .

The original, final weights, glowing and flaming time were determined and listed in Table (21). The loss in weight is expressed as a percentage of the original weight of the specimen, it is clear that all treated wood samples aquire fire retardancy compared to untreated wood samples. In case of impregnated wood samples with comonomer mixture of 12.7 % bromine content the maximum weight loss was 15%. On the other hand percent weight loss increase as the bromine content decrease from 12.7 to 0.0% to reach its higher value of 38% for zero bromine percent.

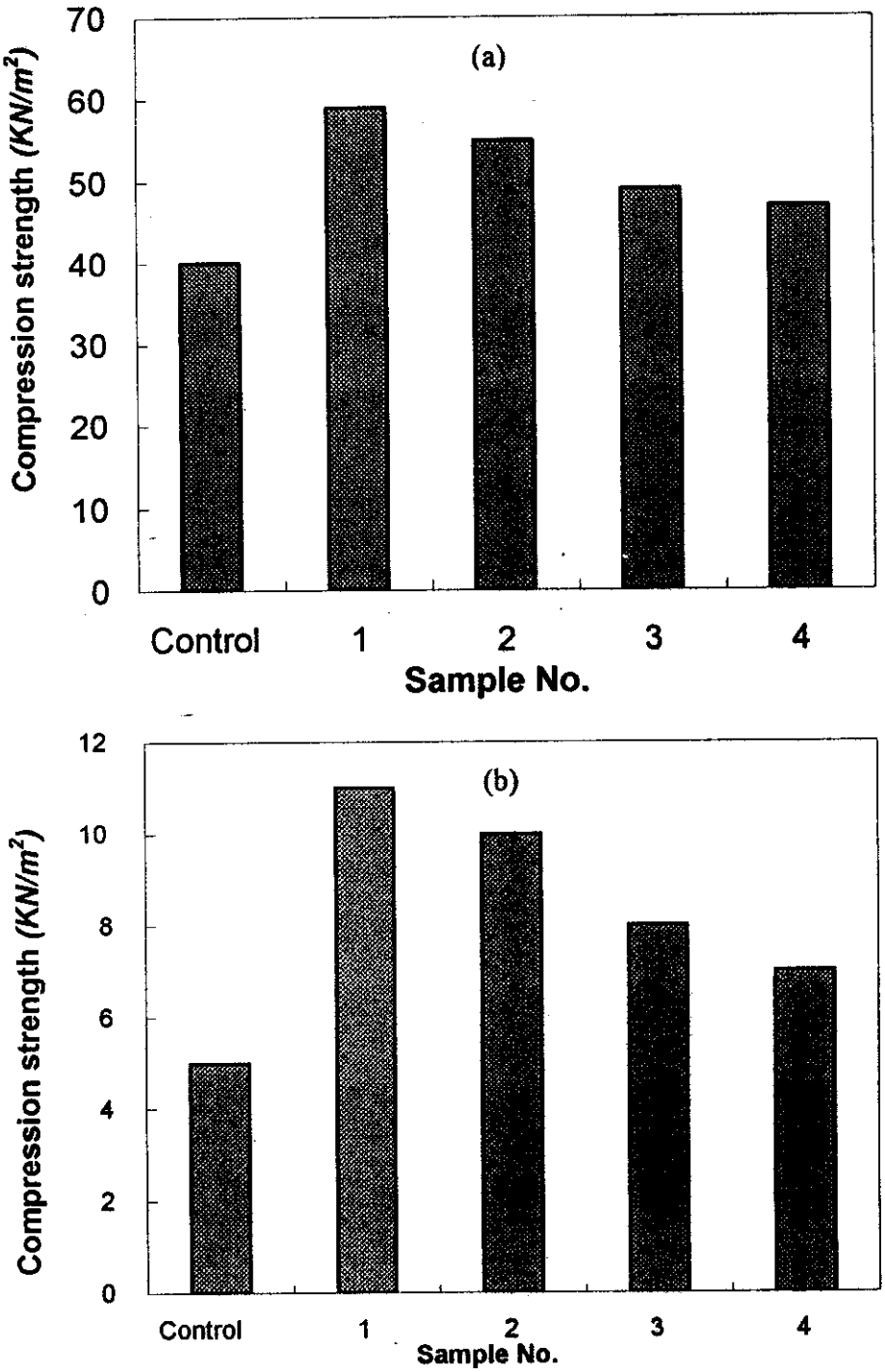


Fig. (25): Compression strength of white pine wood impregnated with (MMA/NMP) and (MMA/NMTP) comonomer mixtures of various bromine contents, compared to untreated wood samples, where (a) is the compression strength parallel to grain and (b) is the compression strength perpendicular to grain.

Table (21): Crib fire test results for white pine wood impregnated with (MMA/NMP) and (MMA/NMTP) comonomer mixtures.

Sample No.	Comonomer mixture	Bromine content (%)	W_o[a] (g)	W[b] (g)	% Wt. Loss	Observations	
						Flaming time (min)	*Glowing time* (min)
Untreated	-	-	142	5	96.5	10-11	9-10
1	MMA/NMP	0.0	201	125	38	6-7	6-7
2	MMA/NMTP	4.2	198	144.5	27	4-5	4-4.5
3	MMA/NMTP	8.5	190	149	22	2-2.5	1-2
4	MMA/NMTP	12.7	182	154	15	1-1.5	0.5-0.75

[a]Weight of treated and untreated wood samples after drying at 105°C for 9 hrs. and before applying the igniting flame.

[b]Weight of treated and untreated wood samples after the removal of igniting flame and after all flaming and glowing ceased.

5-IMPROVEMENT OF WHITE PINE WOOD PROPERETIES BY IMPREGNATION WITH COPOLYMERS OF VARIOUS BROMINE CONTENTS

The pre-determined amounts of comonomer mixtures in the previous section were undergone solution polymerization by the procedure described in page 37, to give brominated (Br %, 5.8, 11.5 and 17.5) and non-brominated copolymers. Each copolymer was dissolved in 300 ml dry acetone and used for impregnating and coating of white pine wood.

(a) Effect of changing bromine content in the copolymers on the (%) percent rention R, volume change % and density of wood polymer composites.

Data in Table (22) indicated that, a high percent retention (37%) was obtained for all treated wood samples, especially for wood samples impregnated with non - brominated copolymer solution and it decreases to reach its lower value (22%) for wood samples impregnated with brominated (Br %, 17.5) copolymer solution. Values of average volume change of wood polymer composites were found to be 3.66, 3.00, 2.24 and 1.34 % for impregnated wood samples with copolymers of 0.0 , 5.8, 11.5 and 17.5Wt.% bromine content, respectively. In addition the density of the whole-polymerized wood was found to be 0.44 and 0.48g/cm^3 for impregnated wood samples by brominated and non-brominated copolymer, respectively. These results of volume change % and

Table (22): Effect of changing bromine content in (MMA – NMP) and (MMA – NMTP) copolymers on weight percent gain (WPG), volume change (%) and density of wood polymer composites (wpc).

Sample No.	Copolymer	Bromine content (%)	W_o[a] (g)	W_1[b] (g)	WPG (%)	Wood volume[a] $V_o(cm^3)$	Final volume[b] $V_1(cm^3)$	Volume change[c] (%)	Density[d] (g/cm^3)
1	MMA-NMP	0.0	1.59	2.18	37	4.37	4.53	3.66	0.48
2	MMA-NMTP	5.8	1.64	2.15	31	4.46	4.59	3.00	0.47
3	MMA-NMTP	11.5	1.63	2.10	29	4.46	4.56	2.24	0.46
4	MMA-NMTP	17.5	1.66	2.02	22	4.47	4.53	1.34	0.44

[a]After drying at 105°C for 9 hrs.

[b]After complete impregnation of white pine wood samples and drying at 105°C for 9 hrs.

[c]Average data from six samples.

[d]Average density of untreated wood samples = 0.39 g/cm^3.

density of wood polymer composites were attributed to the percent retention values. There is a good a greement between our results and literature[71,72].

(b) Dimensional stability and water repellency

Dimensional stability and water repellency were measured using a simple water-soaking test. This test estimates not only water repellency (from the data obtained for various periods), but also provides a measure of dimensional stability (from the data obtained for long-term water soaking).

(i) Water uptake

As shown in Table (23) values of water uptake during the first 2 hours of water soaking control sample took up about 85% water and wood polymer composites took up about 17, 19, 25 and 34% water for impregnated wood samples with copolymer solutions of 0.0, 5.8, 11.5 and 17.5 % bromine percent, respectively. After 168 hours of water soaking the control sample took up about 133% water while wood polymer composites took up about 66, 72, 78 and 89 % water for impregnated wood samples with copolymer solutions of 0.0, 5.8, 11.5 and 17.5 bromine percent, respectively. Thus it was seen from Fig. (26) that water uptake values increase with increasing bromine content in the copolymer, this is attributed to the highest value of weight percent gain for treated wood samples by non-brominated copolymer compared to the lower value of weight percent gain for treated wood samples by brominated

Table (23): Effect of changing bromine content in (MMA–NMP) and (MMA–NMTP) copolymers on the water uptake % of wood polymer composites (wpc).

Sample No.	Copolymer	Bromine (%)	Water Uptake[a] % Soaking Time (h.)							
			2	4	8	24	48	72	144	168
1	MMA-NMP	0.0	17	24	27	38	51	59	65	66
2	MMA-NMTP	5.8	19	30	36	47	60	67	72	73
3	MMA-NMTP	11.5	25	32	41	53	67	74	78	79
4	MMA-NMTP	17.5	34	39	45	59	72	80	87	88
Untreated	-	-	85	88	92	105	121	128	132	133

[a]Average data from six samples.

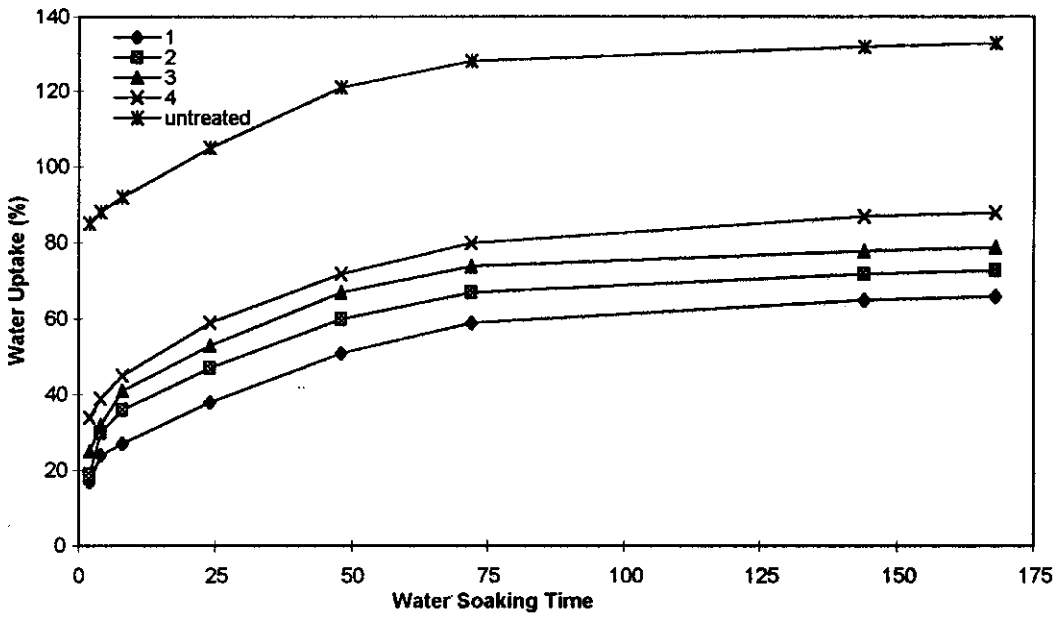


Fig. (26): Effect of soaking time on percent water uptake of impregnated wood with (MMA–NMP) and (MMA–NMTP) copolymers of various bromine contents, compared to untreated wood samples.

(Br %, 17.5) copolymer. Our results for water uptake are in a good agreement with previous results by ***Hazer*** [71] and ***Alma*** [72].

(ii) Water repellent effectiveness

Water repellent effectiveness (WRE) was generally improved specially for treated wood with non-brominated copolymer as shown in Table (24) WRE values for a period of 2 hours were between 52-75 %, whereas those for a period of 168 hours were between 19-35 %. These results may be due to the higher impregnation yield .

(iii) Volumetric swelling coefficient (S) and Antiswell efficiency (ASE)

Volumetric swelling % in a one -week water – soaking test is shown in Table (25). It is clear that during one week, control samples had a swelling coefficient (S) value of 16.63 % while treated wood samples had approximately equal values of swelling coefficient (average ≅ 14.44 %) As seen in this table ASE values were 18, 17, 16 and 10.5 % for treated wood samples with copolymer solutions of 0.0, 5.8, 11.5 and 17.5 % bromine contents, respectively. This may resulted from the amounts of (%)WPG.

Table (24): Effect of bromine content in (MMA – NMP) and (MMA–NMTP) copolymers on water repellent effectiveness (WRE) of wood polymer composites (wpc).

Sample No.	Copolymer	Bromine Content (%)	WRE[a] % Soaking Time (h.)							
			2	4	8	24	48	72	144	168
1	MMA-NMP	0.0	75	65	61	52	39	35	35	35
2	MMA-NMTP	5.8	71	56	56	41	34	32	31	30
3	MMA-NMTP	11.5	62	54	54	36	31	28	26	24
4	MMA-NMTP	17.5	52	46	46	30	26	25	20	19

[a]Average data from six samples.

Table (25): Antiswelling efficiency (ASE) values of white pine wood impregnated with (MMA–NMP) and (MMA – NMTP) polymers after 7 days of immersion in distilled water at 18°C .

Sample No.	Copolymer	Bromine content (%)	Swelling coefficient S[a]	ASE [a] (%)
Untreated	-	-	16.63	-
1	MMA-NMP	0.0	14.14	18
2	MMA-NMTP	5.8	14.21	17
3	MMA-NMTP	11.5	14.37	16
4	MMA-NMTP	17.5	15.05	10.5

[a]All samples were dried at 105°C for 9hrs., average data from six samples.

(c) Compression strength

Data of three runs for compression strength parallel and perpendicular to grain of treated and untreated wood samples were listed in Table (26).

(i) Compression strength parallel to grain

Data for compression strength parallel to grain of wood plastic composites (wpc) as compared to untreated control are illustrated in Fig. 27 (a). The highest value *(68 KN/m^2)*was observed for wood samples impregnated with a non- brominated copolymer solution.

(ii) Compression strength perpendicular to grain

Also, the same behaviour was obtained. The highest value *(15 KN/m^2)*was observed for the wood samples impregnated with a non- brominated copolymer solution, as illustrated in Fig. 27 (b).

Table (26): Compression strength parallel and perpendicular to grain of white pine wood impregnated with (MMA – NMP) and (MMA – NMTP) copolymers, compared to untreated control.

Sample No.	Copolymer	Bromine content (%)	Compression strength parallel to grain[a] (KN/m^2)	Compression strength perpendicular to grain[a] (KN/m^2)
Untreated	-	-	40	5
1	MMA-NMP	0.0	68	15
2	MMA-NMTP	5.8	61	12
3	MMA-NMTP	11.5	54	10
4	MMA-NMTP	17.5	50	7

[a]Average data from three samples.

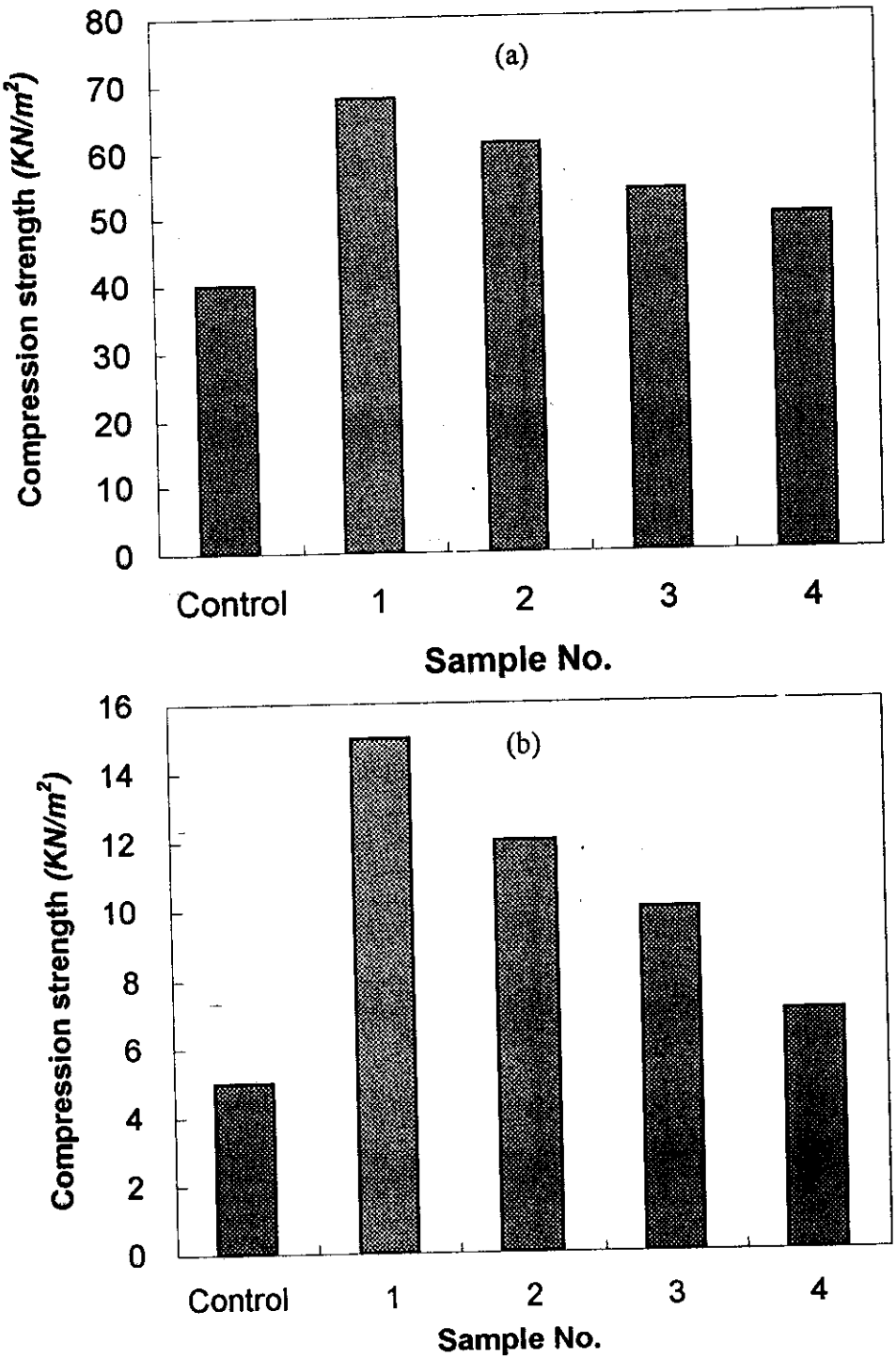


Fig. (27): Compression strength of impregnated wood with (MMA–NMP) and (MMA–NMTP) copolymers of various bromine contents, compared to untreated wood samples, where (a) is the compression strength parallel to grain. and (b) is the compression strength perpendicular to grain.

(d) Fire Retardancy

(i) Flammability- test of rigid plastics

All brominated and non-brominated copolymer were continued to burn after the first ignition and were classified as burning substances with burning rates (180/t) = 450, 231, 189 and 155 in./min. for copolymer sheets of 0.0,5.8,11.5 and 17.5Wt.% bromine contents, respectively as illustrated in Table (27).

(ii) Crib- test for treated wood

The original, final weights, glowing and flaming time were determined and listed in Table (28). The loss in weight is expressed as a percentage of the original weight of the specimen, it is clear that maximum weight loss (%) was 23 % for the impregnated wood samples with copolymer solution of 17.5 % bromine content. Values of percent weight loss was increased as the bromine content decrease in the copolymer solution to reach its higher value (56 %) for wood samples impregnated with a non-brominated copolymer solution.

(iii) Flammability test for coated wood samples.

On the bases of ASTM : 635 – 56 T (1956) measurements, we obtain the data included in Table (29) which illustrates a parallel relation between bromine content and time consumed when the flame passes from the mark 1-in. to the mark 4-in. from the free end. Thus burning rates of the coated white pine wood sheets had its best (lower) value 86 in./min. for the coated wood sheets by

brominated (Br %, 17.5) copolymer while coated wood sheets with a non-brominated copolymer had the bad (higher) value 209 in./min.. In addition all coated wood sheets were classified as burning substances with different burning rates inversely proportional to bromine content in the copolymer solutions used in coating process.

Table (27): Relative flammability of (MMA–NMP) and (MMA–NMTP) copolymer sheets of various bromine contents.

Sample No.[a]	Copolymer	Bromine content %	t[b] (min.)	Burning rate (in./min.)	Classification of samples
1	MMA-NMP	0.0	0.4	450	Burning
2	MMA-NMTP	5.8	0.78	231	Burning
3	MMA-NMTP	11.5	0.95	189	Burning
4	MMA-NMTP	17.5	1.16	155	Burning

[a]Number of specimens tested = 10 samples, thickness of specimens = 0.136 in.

[b]Time consumed by passing the flame from the mark 1-in. to the mark 4 - in. from the free end.

Table (28): Crib fire test results for white pine wood impregnated with (MMA– NMP) and (MMA – NMTP) copolymers of various bromine contents.

Sample No.	Copolymer	Bromine content (%)	W_o[a] (g)	W^b (g)	% Wt. Loss	Observations	
						Flaming time (min.)	*Glowing time* (min.)
Untreated	-	-	142	5	96	10 –11	9 –10
1	MMA-NMP	0.0	177	78	56	10 –11	14 –15
2	MMA-NMTP	5.8	184	96	48	9 –10	7 –8
3	MMA-NMTP	11.5	175	111	37	6 –7	5 –6
4	MMA-NMTP	17.5	174	133	23	2.5 –3	1 –2

[a]Weight of treated and untreated wood samples after drying at 105°C for 9 hrs. and before applying the igniting flame.

[b]Weight of treated and untreated wood samples after the removal of igniting flame and after all flaming and glowing ceased.

Table (29): Flame spread test of white pine wood sheets coated by (MMA – NMP) and (MMA – NMTP) copolymers of various bromine contents.

Sample No.[a]	Copolymer	Bromine content %	t[b] (min.)	Burning rate (in./min.)	Classification of samples
Untreated	-	-	0.64	281	Burning
1	MMA-NMP	0.0	0.86	209	Burning
2	MMA-NMTP	5.8	1.15	156	Burning
3	MMA-NMTP	11.5	1.35	133	Burning
4	MMA-NMTP	17.5	2.09	86	Burning

[a]Data obtained were average from ten samples, thickness of coated polymer on one side of wood sheet = 0.005 in.

[b]Time consumed by passing the flame from the mark 1-in to the mark 4-in from the free end.