

## Preparation of Thermally Stable Acrylic Polymers

ABDUL-RAHIM A. SAMARKANDY

*Faculty of Science, Chemistry Department, King Abdulaziz University  
Jeddah – Saudi Arabia*

**ABSTRACT.** Monomers of N-phenyl methacrylamide (PPM), N-(p-methyl phenyl) methacrylamide (PMPM) and N-(p-methoxy phenyl) methacrylamide (PMOM) were prepared and the optimum conditions for their polymerization were investigated by following the polymerization time, effect of ratio of initiator, as well as the effect of solvent.

The polymers obtained were characterized by determining the viscosity number, Infrared spectroscopy, elemental analysis, metal analysis, and thermo-gravimetric analysis (TGA).

Micro-analytical data and IR-spectra of PPM, PMPM, and PMOM confirmed the structures of the prepared polymers. According to IR-spectra and micro-analytical data, the structures for the polymer complexes are suggested.

Thermo-analytical results of PPM, PMPM, and PMOM and their polymer complexes showed two to three stages of decomposition.

### Introduction

Polymers provide one of the most versatile groups of materials and find widespread use as plastics, rubbers, fibers, adhesives and coatings. The advantages of these materials, especially their ease of fabrication and low density, for use in an ever widening range of products have become more appreciated by designers and engineers. However, some inherent deficiencies in these materials have prevented their employment in certain areas of application. Polymers show extreme sensitivity to temperature. Most importantly, owing to the intrinsic flexibility of their molecular chains, they exhibit very low softening points. Polymers will have high softening points if they have a high glass transition temperature ( $T_g$ ) and/or melting temperature ( $T_m$ ).

A further restriction to their use at high temperature is their susceptibility to atmospheric oxidation when used at elevated temperature. This oxidation usually leads to polymer chain scission by way of a free radical chain reaction. Many common polymers oxidize at appreciable rates at temperatures as low as 100°C, so long term use at these temperatures or above can lead to premature product failure. The susceptibility of a polymer to thermal oxidation is largely dependent on the strengths of the C-H bonds from which hydrogen atoms are abstracted by the propagating free radicals<sup>(1)</sup>.

The bond forming cross-links in network polymers contribute significantly to thermal stability. They are dimensionally stable under a wide variety of conditions due to their rigid network structure<sup>(2-4)</sup>. Polymer metal complexes are synthesized by reaction of a polymer containing donating groups such as amine, heterocyclic nitrogen, carboxylic acid, ketone, phosphonic acid, or thiol with metal ion. The reaction of polymer ligand with metal ion usually results in various coordination structures, which are divided chiefly into pendant and inter-, and/or intramolecular bridged complexes<sup>(5)</sup>.

The chelating ligand groups show excellent ability to adsorb metal ions selectively<sup>(6-9)</sup>. The polymer metal complex is insoluble in water or in organic solvents. It is usually difficult to distinguish between the inter- and intramolecular bridging<sup>(10-26)</sup>.

James *et al.*<sup>(27)</sup> reported that the glass transition temperature ( $T_g$ ) has been increased on complexation of poly (tetramethylglycol) and poly (propylene oxide) with  $ZnCl_2$ . A satisfactory model for the poly (propylene oxide) complexes has been postulated involving coordination of two adjacent ether oxygen atoms in the polymer backbone to the metal salt, thus creating five-membered rings.

The activation energies of the thermal degradation of the polymer complexes<sup>(28-32)</sup> were calculated using Arrhenius relationship and were found to be in the range (3.5 - 3.6) kJ/mol.

## Experimental

### Materials

Methacryloyl chloride, copper (II) acetate dihydrate, copper (II) chloride, p-anisidine, and p-toluidine were used as received without further purification (all from Aldrich); aniline, dimethyl formamide, petroleum ether (60-80°C), and tetrahydrofuran (all from BDH), were used without further purification. Benzene (BDH) was distilled and kept over sodium metal. 2,2-azobisisobutyronitrile (AIBN) (Fluka) was recrystallized from ethanol.

### Methods

#### **I- Preparation of N-phenyl methacrylamide, N-(p-methyl phenyl) methacrylamide and N-(p-methoxy phenyl) methacrylamide**

The monomers were prepared by the addition of equimolar amounts of methacryloyl chloride to a stirred solution of aniline, p-toluidine or p-anisidine in DMF as a solvent in an ice bath. The reaction mixtures were precipitated by pouring into a large excess of distilled water in an ice bath. The monomers were filtered, washed with distilled water and dried under vacuum.

#### **II- The optimum conditions for polymerization of N-phenyl methacrylamide were investigated as follows**

**1- Time of polymerization :** The homopolymer was prepared by boiling under reflux N-phenyl methacrylamide (0.5 g) in DMF (2 ml) as a solvent, and in the presence of 0.05 g (10% w/w) AIBN as initiator for different times.

**2- Effect of ratio of initiator :** 0.5 g of the monomer was boiled under reflux with 2 ml DMF as solvent and different ratios of AIBN as initiator for 5 hours.

**3- Effect of solvent :** The homopolymer was prepared by boiling the monomer (0.5 g) under reflux with 0.05 g (10% w/w) AIBN as initiator in the presence of different solvents (Benzene, DMF, or THF) for five hours.

### III- Preparation of poly *N*-(*p*-methyl phenyl) methacrylamide and poly *N*-(*p*-methoxy phenyl) methacrylamide

A solution of the monomer (4.9 g) in dry benzene (20 ml) with AIBN (0.2 g) as initiator was boiled under reflux for five hours. The reaction mixture was precipitated by pouring into a large excess of petroleum ether (60-80°C) and kept in the freezer for 10 days.

The precipitated polymers were filtered and dried under vacuum for several days.

### IV- Preparation of the polymer metal complexes

Polymer complexes of poly-(*N*-phenyl) methacrylamide (PPM), poly *N*-(*p*-methyl phenyl) methacrylamide (PMPM) or poly *N*-(*p*-methoxy phenyl) methacrylamide (PMOM), with copper (II) acetate and copper (II) chloride were prepared by free radical polymerization. Equimolecular amounts of monomers and metal salts were dissolved in DMF. The reaction mixture was boiled under reflux for 6 hr. The resulting solution was added to cold water acidified with HCl, and the formed polymer complex was precipitated, filtered and dried under vacuum.

### V- Characterization of the polymers

**1- Determination of the viscosity number :** A dry sample (0.05 g) was dissolved in DMF and its viscosity was measured at 25°C.

**2- Infrared spectroscopy :** IR spectra were recorded using Perkin-Elmer infrared spectrophotometer.

**3- Elemental Analysis :** (Carbon, hydrogen and nitrogen content were performed for monomers, and polymers).

**4- Metal analysis :** The metal analysis were carried out using Perkin-Elmer atomic absorption.

### VI- Thermogravimetric analysis (TGA)

TGA measurements were recorded with Perkin-Elmer, TGA 7, thermal analysis system. Samples were heated from 30°C to 700°C in a platinum pan with a heating rate 20°C/min., in air 25 ml/min.

## Results and Discussion

Table 1, shows the effect of time of polymerization on the viscosity and yield of poly (*N*-phenyl methacrylamide) (ppm). The maximum yield and viscosity were obtained at 5 hrs polymerization time.

Table 1. Effect of time of polymerization on the viscosity and yield of poly (*N*-phenyl methacrylamide) (ppm).

Time (hr)	1	2	3	4	5	6	7
Yield (g)	0.28	0.3	0.31	0.32	0.34	0.39	0.28
reduced viscosity	0.19	0.23	0.49	0.57	0.7	0.65	0.55

Table 2, shows the effect of solvents on the yield and viscosity of PPM. The results revealed that the maximum yield and viscosity were obtained using benzene as a solvent.

Table 2. Effect of solvents on the yield and viscosity of PPM.

Solvent	DMF	BENZENE	THF
Yield (g)	0.34	0.40	0.2
reduced viscosity	0.7	0.88	0.5

Table 3, shows the effect of ratio of AIBN on the polymerization of PPM. The optimum ratio of AIBN was (5% w/w).

Table 3. Effect of ratio of AIBN on the polymerization of PPM.

Ratio of AIBN (% w/w)	2.5%	5%	10%	15%
Yield (g)	0.30	0.36	0.34	0.31
reduced viscosity	0.68	0.79	0.7	0.68

It was concluded, from Tables 1-3, that the optimum conditions for polymerization of PPM were as follows:

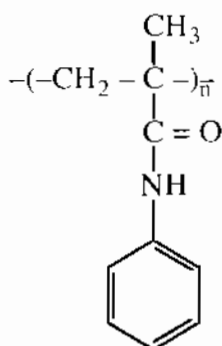
Time of polymerization is 5 hr. solvent used is benzene, and ratio of initiator is 5% (w/w).

Table 4, shows the micro-analytical data for the prepared polymers.

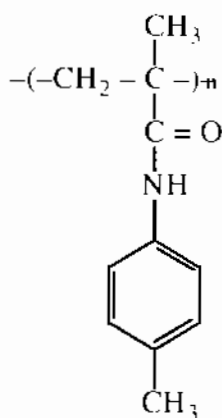
Table 4. Micro-analytical data for the prepared polymers.

Compound	Analysis (%) Found/(calculated)		
	% C	% H	% N
poly(N-phenyl)methacrylamide (PPM)	73.82 (74.49)	6.73 (6.8)	8.21 (8.69)
poly [N-(p-methyl phenyl) methacrylamide (PMPM)]	74.51 (75.38)	7.18 (7.48)	7.62 (8.0)
poly N-(p-methoxy phenyl) methacrylamide (PMOM)	68.84 (69.07)	6.54 (6.86)	7.18 (7.33)

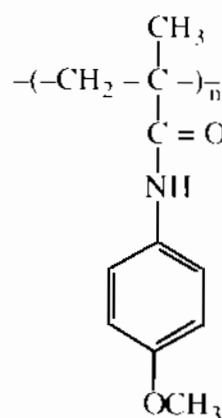
The micro-analytical data confirmed the following structures of the prepared polymers :



(PPM)



(PMPM)



(PMOM)

IR spectrum of PPM (Fig. 1-3), PMPM (Fig. 4-6), and PMOM (Fig. 7-9) confirmed the structures of the prepared polymers. The band characteristic of amide I band  $\nu$  (C=O) appeared at  $(1665 - 1650) \text{ cm}^{-1}$ . The bands at  $(1600 - 1590) \text{ cm}^{-1}$ ,  $(1510 - 1490) \text{ cm}^{-1}$  are characteristic of benzene ring. The band at  $(1380 - 1370) \text{ cm}^{-1}$  was attributed to CH symm. def. of  $\text{CH}_3$ . The amide II band  $\nu$  (C-N) +  $\delta$  (N-H) showed a band in the range  $(1560 - 1525) \text{ cm}^{-1}$ . Also a band at  $(1340 - 1310) \text{ cm}^{-1}$  was due to amide III band  $\delta$  (C-N).

Table 5. IR bands assignment for PPM.

Band	Assignment	Band	Assignment
3210	$\nu$ (N-H)	2930, 2870	$\nu$ (C-H)
1665	Amide I band $\nu$ (C=O)	1600	Benzene ring
1560	Amide II band $\nu$ (C=N) + $\delta$ (N-H)	1510, 1450	Benzene ring
1375	C-H symm. deform. of $\text{CH}_3$	1320	Amide III band $\delta$ (C-N)
910, 860	$\delta$ (C-H) bending		

Table 6. IR bands assignment for PMPM.

Band	Assignment	Band	Assignment
3290 (s)	$\nu$ (OH) free	3070	$\nu$ (N-H)
2930, 2860	$\nu$ (C-H)	1660	Amide I band $\nu$ (C=O)
1545	Amide II band $\nu$ (C=N) + $\delta$ (N-H)	1590	Benzene ring
1490, 1460	Benzene ring	1310	Amide III band $\delta$ (C-N)
1370	C-H symm. deform. of $\text{CH}_3$	900, 860	$\delta$ (C-H) bending

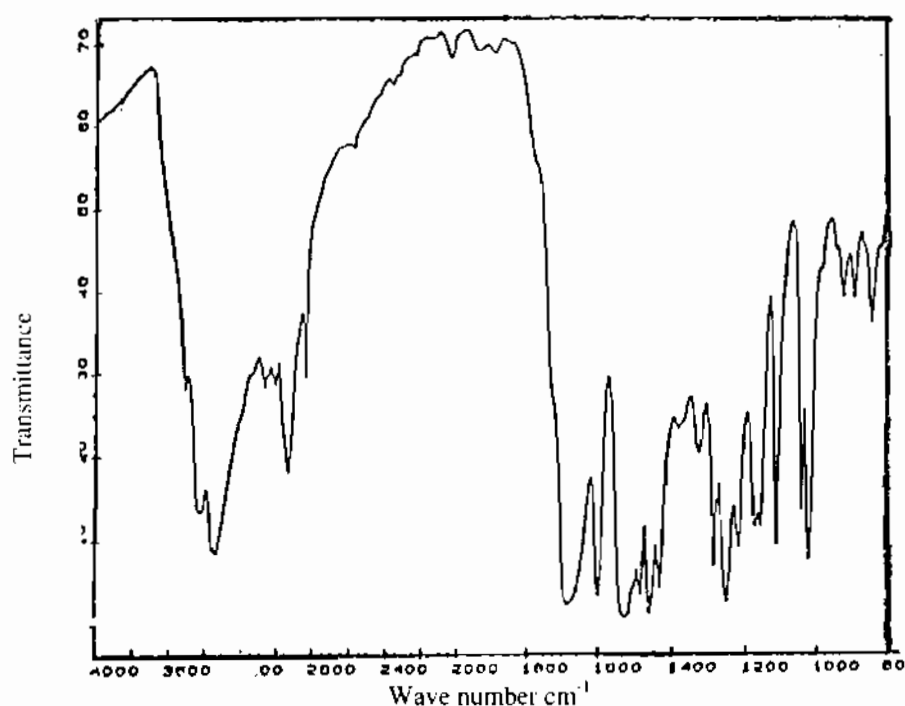


Fig. 1. IR spectrum of PPM.

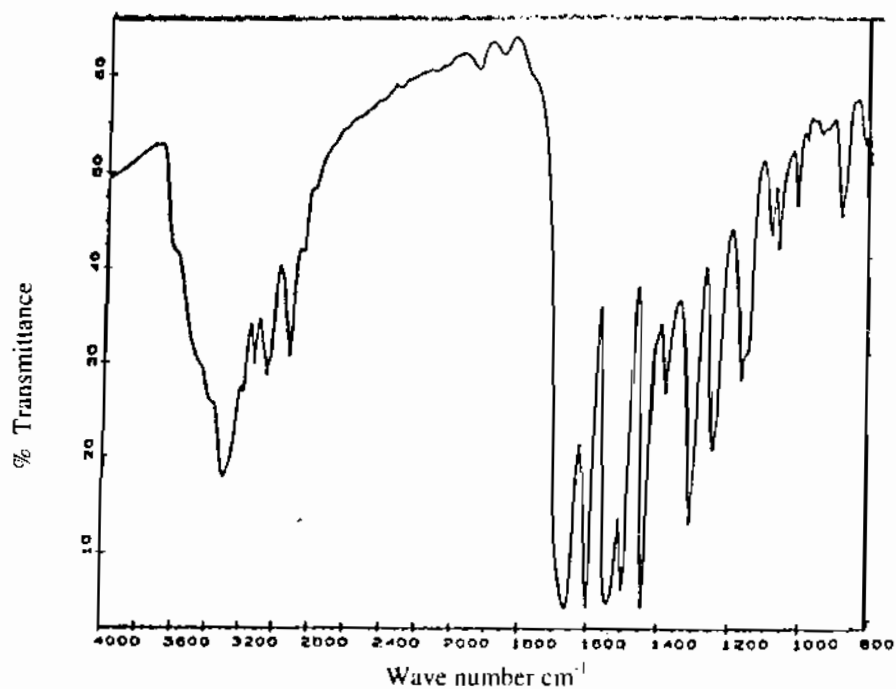


Fig. 2. IR spectrum of PPM-Copper acetate.

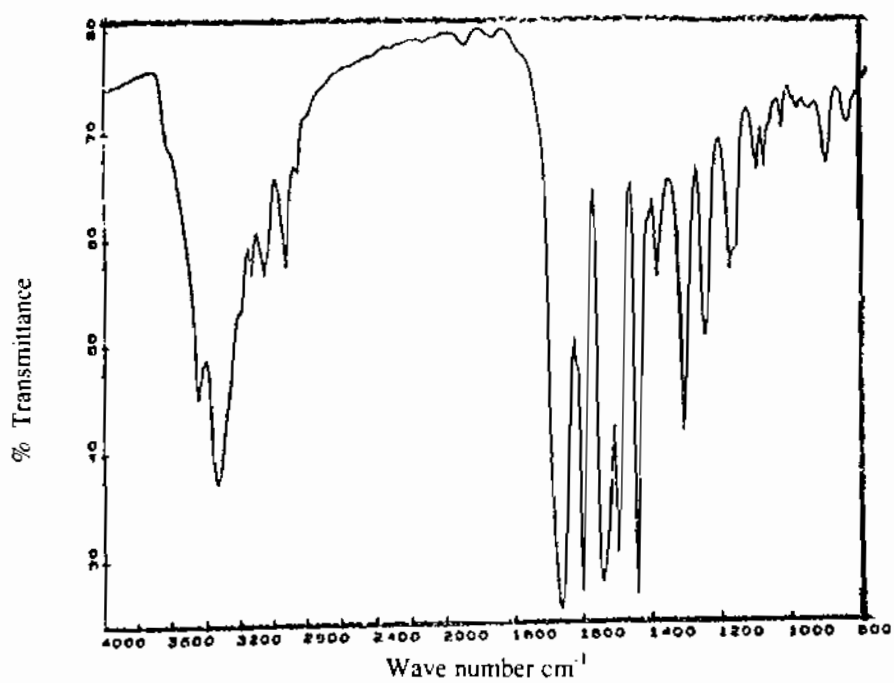


Fig. 3. IR spectrum of PPM-Copper chloride.

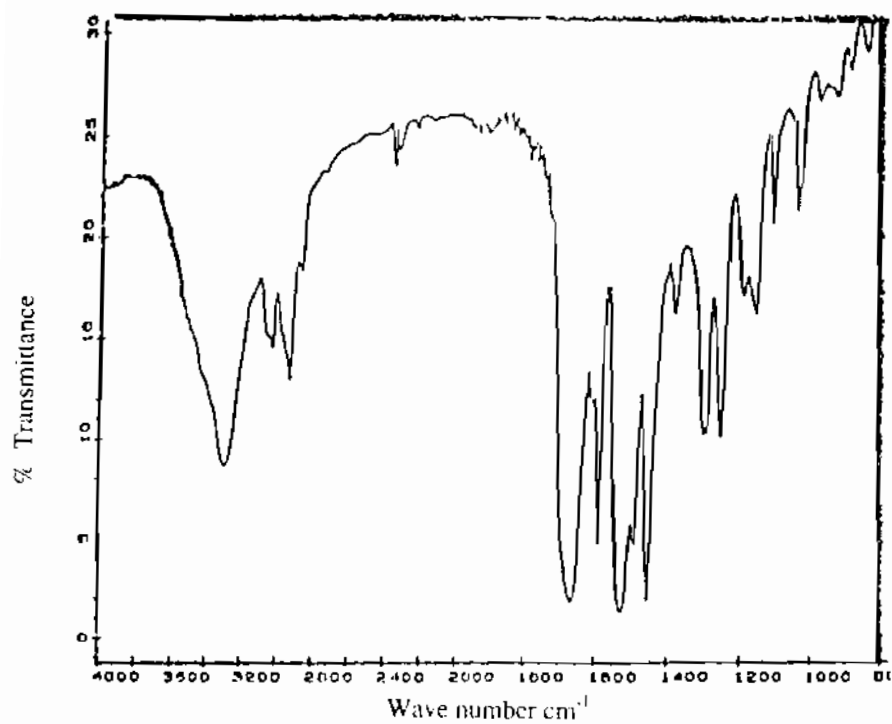


Fig. 4. IR spectrum of PMPM.

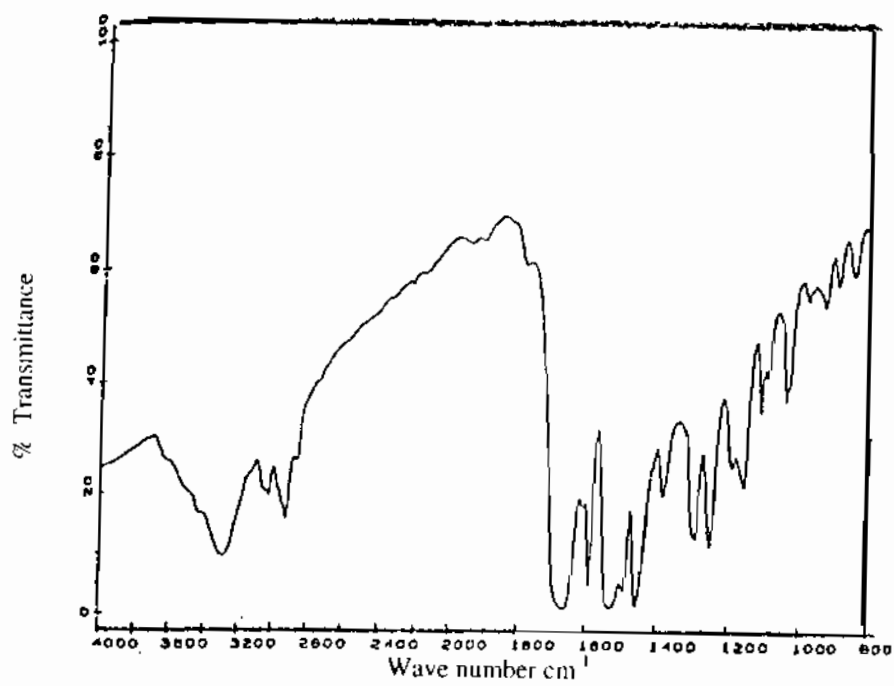


Fig. 5. IR spectrum of PMPM-Copper acetate.

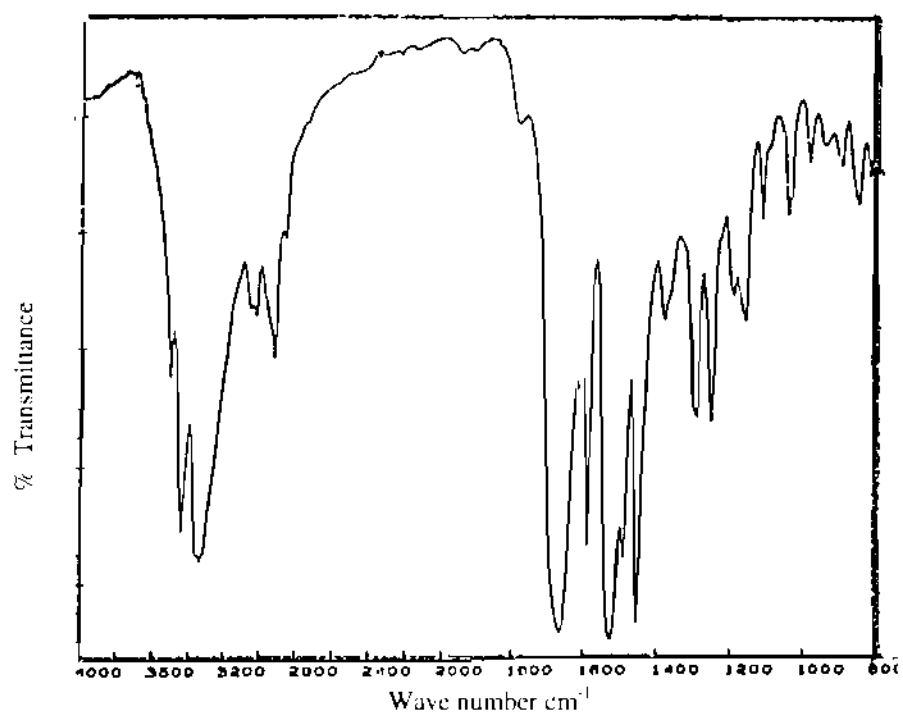


Fig. 6 IR spectrum of PMPM-Copper chloride.

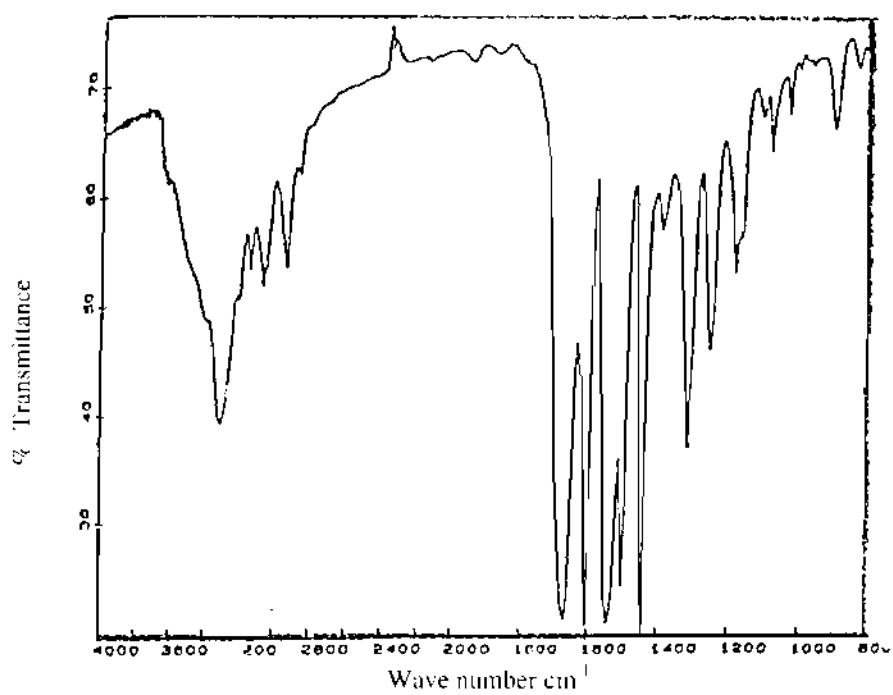


Fig. 7. IR spectrum of PMOM.



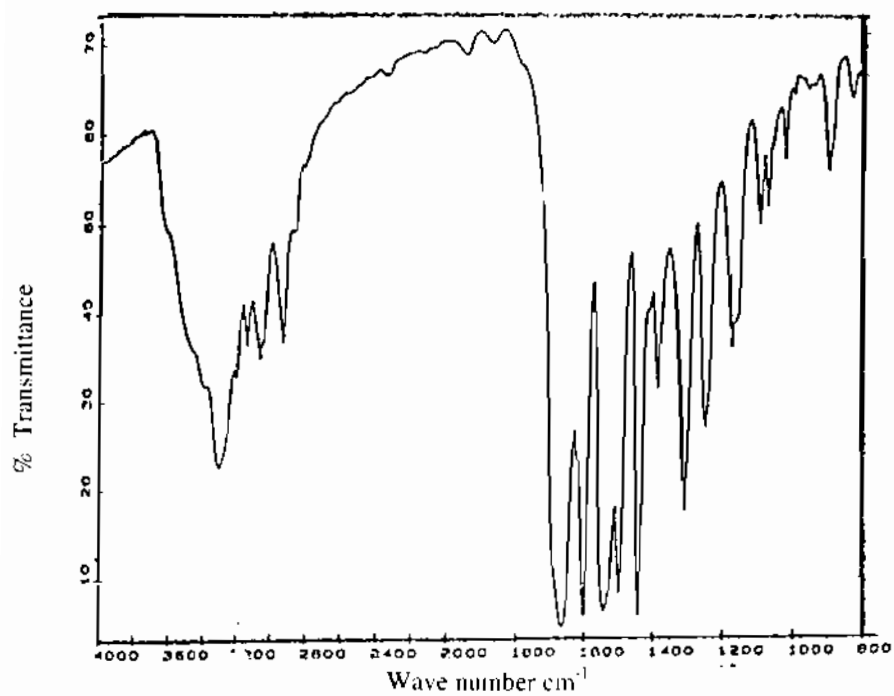


Fig. 8. IR spectrum of PMOM-Copper acetate.

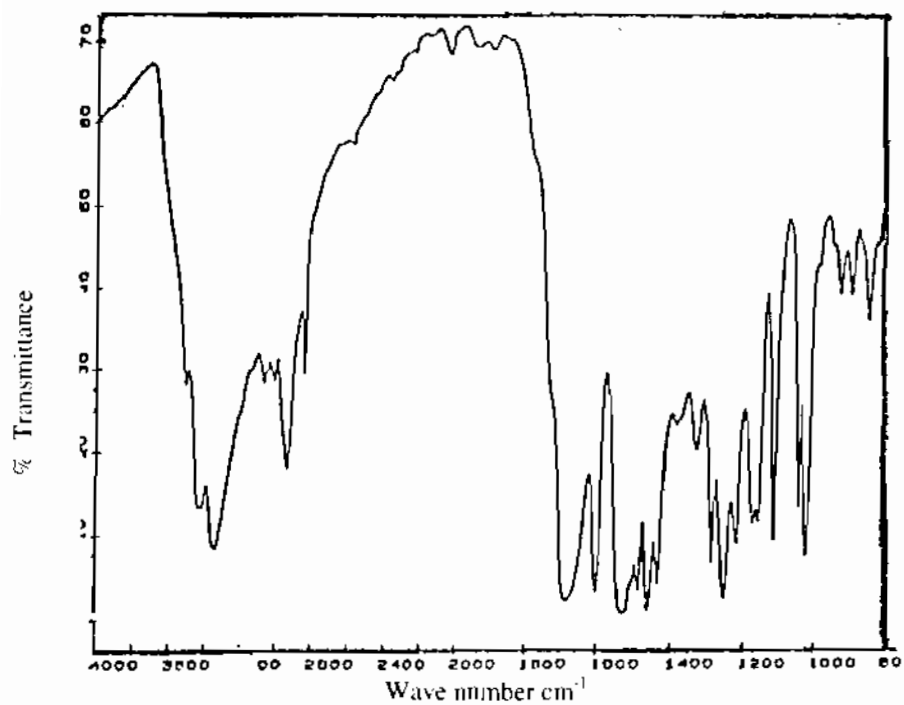


Fig. 9. IR spectrum of PMOM-Copper chloride.

Table 7. IR bands assignment for PMOM.

Band	Assignment	Band	Assignment
3380 (s)	$\nu$ (OH) free	3120	$\nu$ (N-H)
2920, 2810	$\nu$ (C-H)	1655	Amide I band $\nu$ (C = O)
1525	Amide II band $\nu$ (C=N) + $\delta$ (N-H)	1600	Benzene ring
1380	C-H symm. deform. of CH <sub>3</sub>	1490, 1450	Benzene ring
1340	Amide III band $\delta$ (C-N)	900, 850	$\delta$ (C-H) bending

Table 8. Micro-analytical data for PPM-metal complexes.

Compound	Analysis (%) Found/(calculated)			
	% C	% H	% N	% M
PPM - Cu acetate	60.1 (59.77)	6.17 (6.05)	6.30 (6.15)	8.98 (9.30)
PPM - Cu chloride	57.01 (56.65)	5.78 (5.55)	6.50 (6.61)	10.20 (9.99)

Table 9. Micro-analytical data for PMPM-metal complexes.

Compound	Analysis (%) Found/(calculated)			
	% C	% H	% N	% M
PMPM - Cu acetate	61.80 (61.27)	6.60 (6.53)	6.01 (5.79)	9.00 (8.76)
PMPM - Cu chloride	58.01 (58.45)	6.30 (6.09)	5.98 (6.20)	9.70 (9.37)

Table 10. Micro-analytical data for PMOM-metal complexes.

Compound	Analysis (%) Found/(calculated)			
	% C	% H	% N	% M
PMOM - Cu acetate	58.00 (57.47)	6.40 (6.13)	5.80 (5.43)	8.60 (8.22)
PMOM - Cu chloride	54.10 (54.58)	5.91 (5.69)	6.08 (5.79)	8.98 (8.75)

Table 11. IR bands assignment for PPM - metal complexes.

PPM - Cu acetate	PPM - Cu chloride	Assignment
	3460	$\nu$ (O - H) free
3320	3330 (s)	$\nu$ (O - H) bonded
3150	3150	$\nu$ (N - H)
2935, 2870	2940, 2870	$\nu$ (C-H)
1665 (s)	1665 (s)	Amide I band $\nu$ (C = O)
1600 (s)	1600(s)	Benzene ring
1550 (s)	1550 (s)	Amide II band $\nu$ (C = N) + $\delta$ (N - H)
1510 (s)	1510 (s)	Benzene ring
1450 (s)	1450 (s)	benzene ring
1400 (w)		$\nu$ (OAc)
1375	1375	$\nu$ (C-H) symm. deform. of CH <sub>3</sub>
1325 (s)	1325 (s)	Amide III band $\delta$ (C - N)
910 (m)	910 (m)	$\delta$ (C - H)
850 (w)	850 (w)	$\delta$ (C - H) bending

**The IR-spectra of all polymer complexes showed the following**

- 1- The  $\nu$  (N – H) are shifted to a lower frequency in the polymer complexes, suggesting the coordination of the polymers to the metal ions through the nitrogen of the (N – H) group.
- 2- The  $\nu$  (C = O) bands are unaffected upon complexation indicating that the carbonyl is not bonded to the metal ion in all complexes. Depending upon IR-spectra and micro-analytical data, the following structures (Schemes 1-3) are suggested for the polymer complexes.

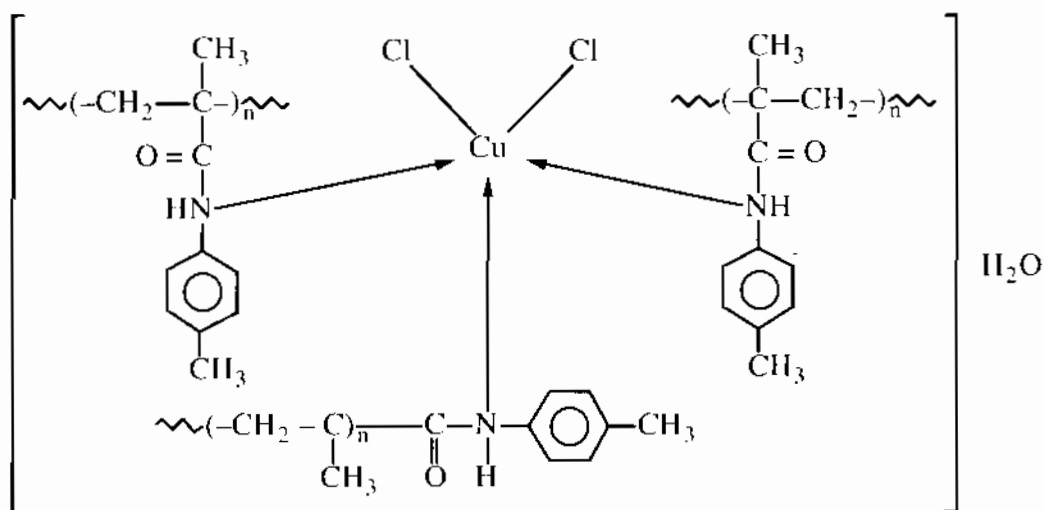
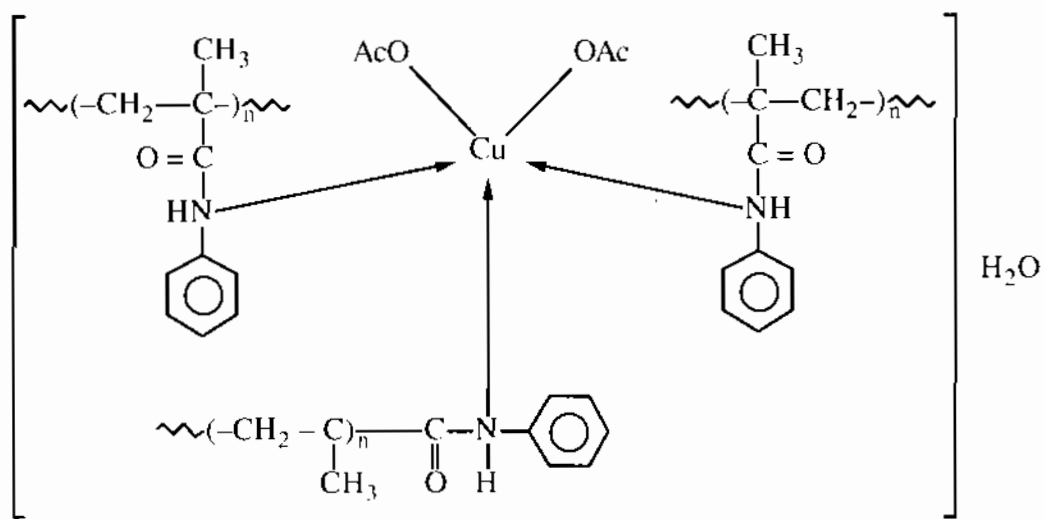
Table 12. IR bands assignment for PMPM - metal complexes.

PMPM - Cu acetate	PMPM - Cu chloride	Assignment
	3460 (s)	$\nu$ (O – H) free
3300	3330 (s)	$\nu$ (O – H) bonded
3030	3030	$\nu$ (N–H)
2930, 2860	2930, 2860	$\nu$ (C–H)
1660 (s)	1660 (s)	Amide I band $\nu$ (C = O)
1590 (s)	1590(s)	Benzene ring
1535 (s)	1535 (s)	Amide II band $\nu$ (C = N) + $\delta$ (N – H)
1490 (w)	1490 (w)	Benzene ring
1460 (s)	1460 (s)	benzene ring
1400 (w)		$\nu$ (OAc)
1380	1380	$\nu$ (C–H) symm. deform. of CH <sub>3</sub>
1300 (s)	1300 (s)	Amide III band $\delta$ (C – N)
900 (m)	900 (m)	$\delta$ (C – H)
860 (m)	860 (m)	out of plane $\delta$ (C – H) bending

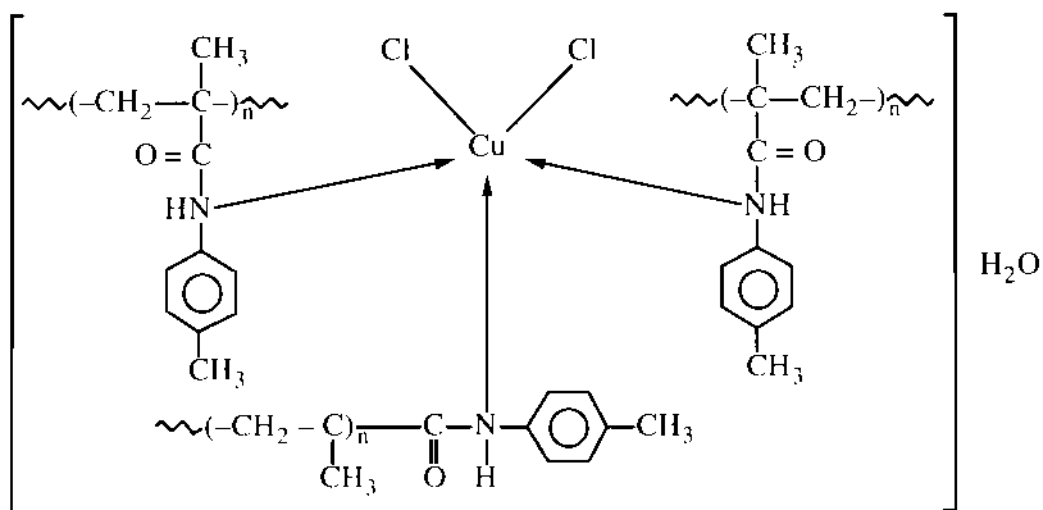
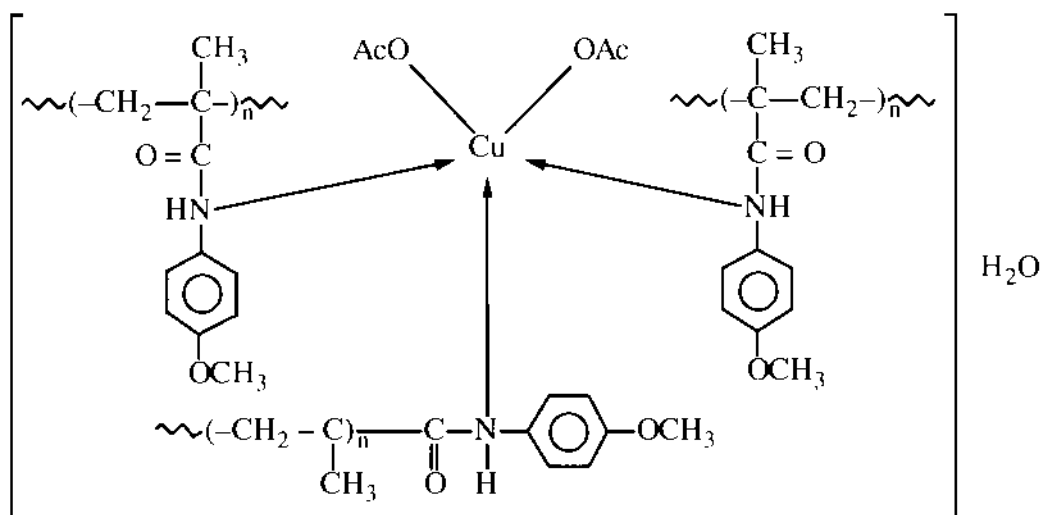
Table 13. IR bands assignment for PMOM - metal complexes.

PMOM - Cu acetate	PMOM - Cu chloride	Assignment
	3435 (s)	$\nu$ (O – H) free
3310 (s)		$\nu$ (O – H) bonded
3030	3030	
2910, 2850	2960, 2850	$\nu$ (C–H)
1655 (s)	1655 (s)	Amide I band $\nu$ (C = O)
1600 (s)	1600(s)	Benzene ring
1530 (s)	1535 (s)	Amide II band $\nu$ (C = N) + $\delta$ (N – H)
1500 (w)	1490 (w)	Benzene ring
1460 (s)	1450 (s)	benzene ring
1400 (w)		$\nu$ (OAc)
1380	1380	$\nu$ (C–H) symm. deform. of CH <sub>3</sub>
1330	1330	Amide III band $\delta$ (C – N)
900	900	$\delta$ (C – H)
850	850	out of plane $\delta$ (C – H) bending

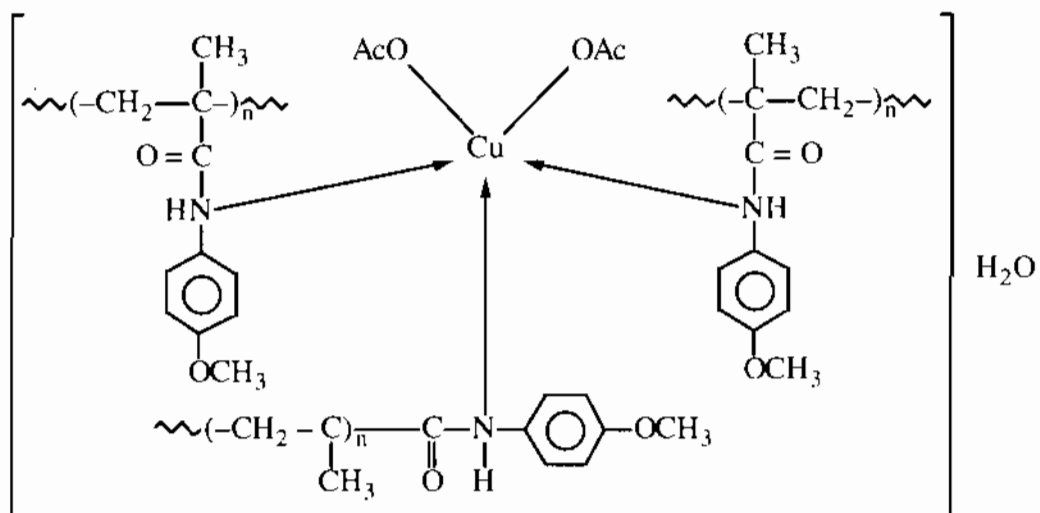
Depending upon IR-spectra and micro-analytical data, the following structures (Schemes 1-3) are suggested for the polymer complexes.



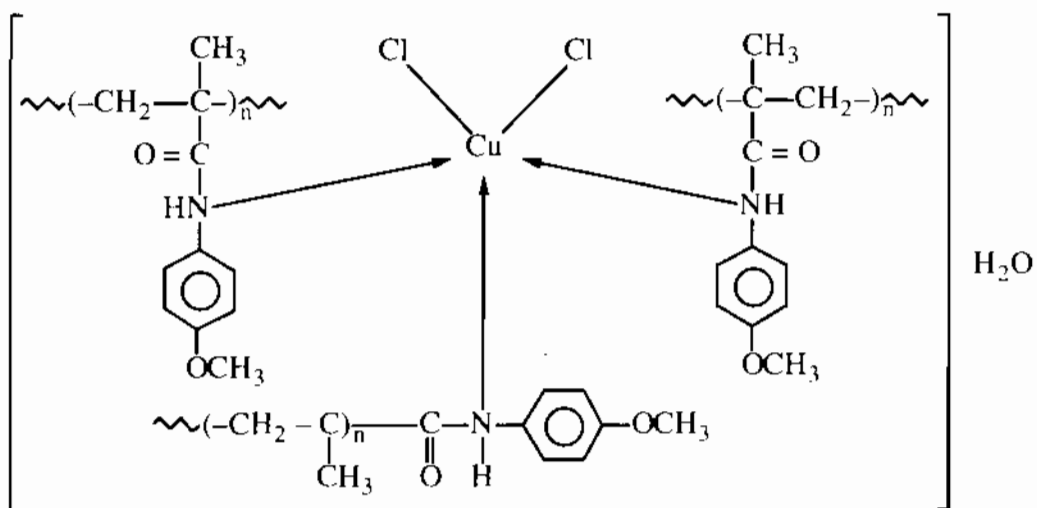
Scheme 1. Suggested structure for the PMM - Cu - complexes.



Scheme 2. Suggested structure for the PMPM - Cu - complexes.



PMOM - Cu acetate



PMOM - Cu chloride

Scheme 3. Suggested structure for the PMOM-Cu-complexes.

Thermo-analytical results of PPM and its complexes are shown in Table 14.

Table 14. Thermo-analytical results of PPM and its metal complexes.

Compound	DTA		TGA
	T <sub>range</sub> (°C)	T <sub>max</sub> (°C)	wt. loss (%) for stage
PPM		90 - 170 250 - 530	- 418
PMM - Cu acetate	95 - 192 230 - 630	- 430	3.4 77
PMM - Cu chloride	100 - 290 290 - 390 390 - 610	- 360 440	10.5 27 43.5

Two stages of decomposition were observed for PPM (Fig. 10). The first one occurs in the temperature range 90 - 170°C (3.5% wt. loss) and is assigned to a loss of solvent molecules. The second stage started at 250°C and ended at 530°C with 88% wt. loss.

Two stages of decomposition were observed for PPM - Cu acetate (Fig. 11) and three stages were observed for PPM - Cu chloride complexes (Fig. 12). The first weight loss for PPM - Cu acetate occurred between 95 - 192°C (3.4% wt. loss) and is equivalent to the loss of a water molecule. The second stage appeared between 230°C and 630°C with 77% wt. loss. For PPM - Cu chloride complex, the first weight loss occurred between 100 and 290°C with 10.5% weight loss, which may be due to the loss of a water molecule. The second step occurred in the temperature range 290 - 390°C. The third step started at 390°C and ended at 610°C (43.5% wt. loss).

Thermo-analytical results of PMPM homopolymer and its metal complexes are shown in Table 15. Two stages of decomposition were observed for the homopolymer (Fig. 13). The first one occurs in the temperature range 185 - 300°C (10.2% wt. loss). The second stage started at 350°C and ended at 525°C with 76.3% wt. loss.

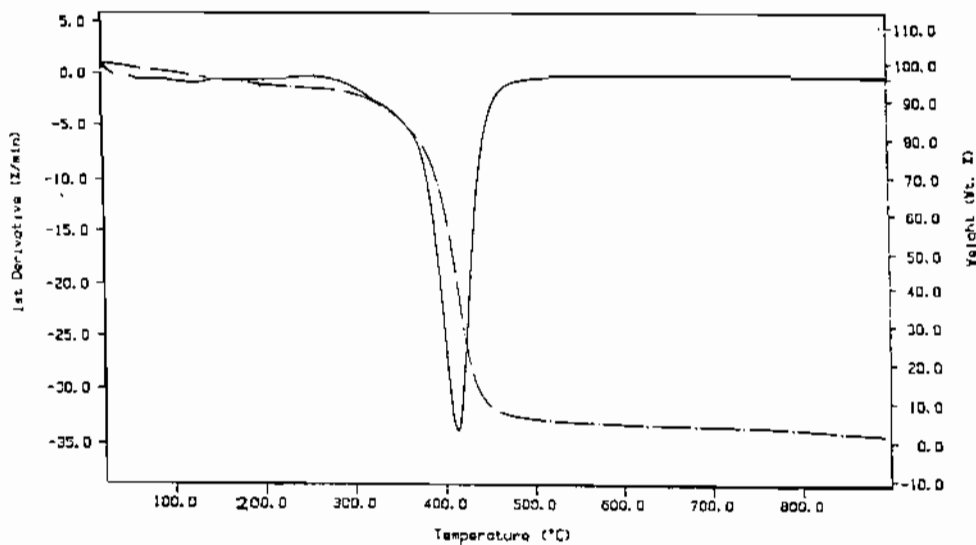


Fig. 10. Thermogravimetric analytical spectrum of PPM.

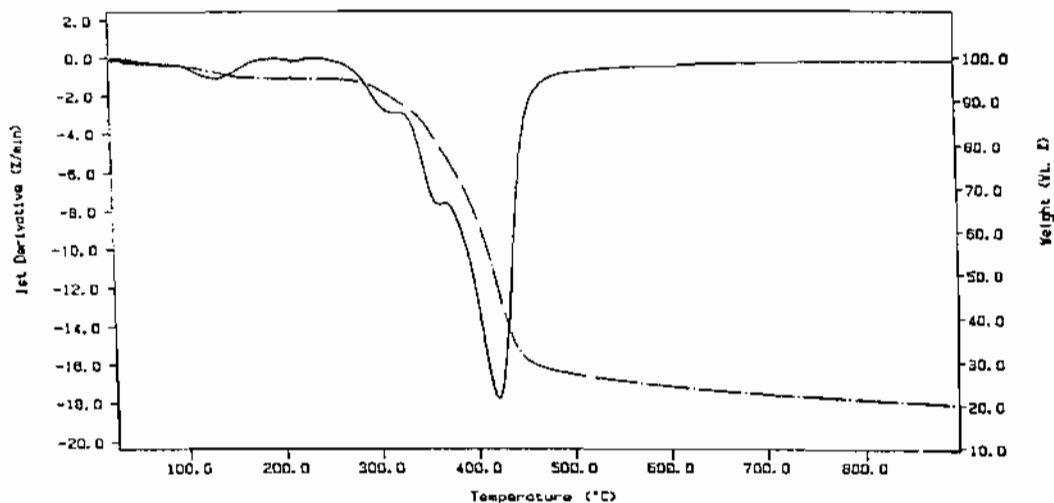


Fig. 11. Thermogravimetric analytical spectrum of PPM-Cu-acetate complex.

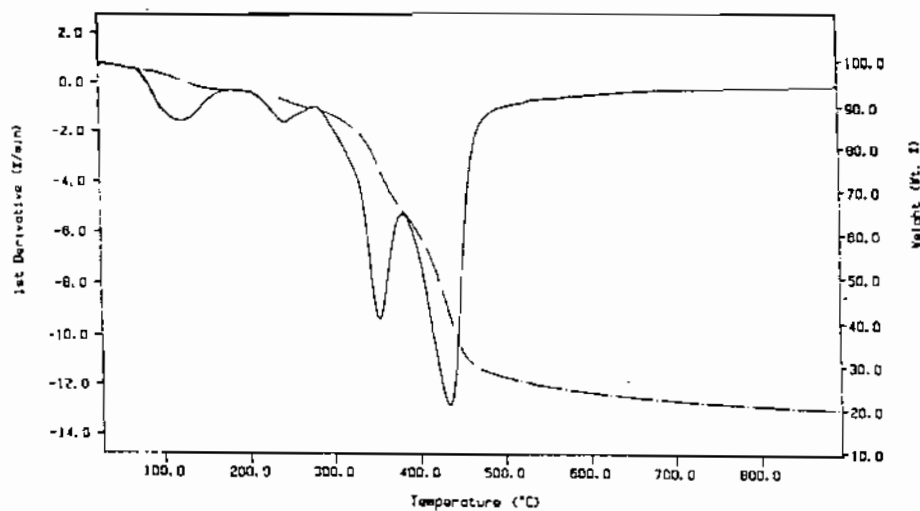


Fig. 12. Thermogravimetric analytical spectrum of PPM-Cu-chloride complex.

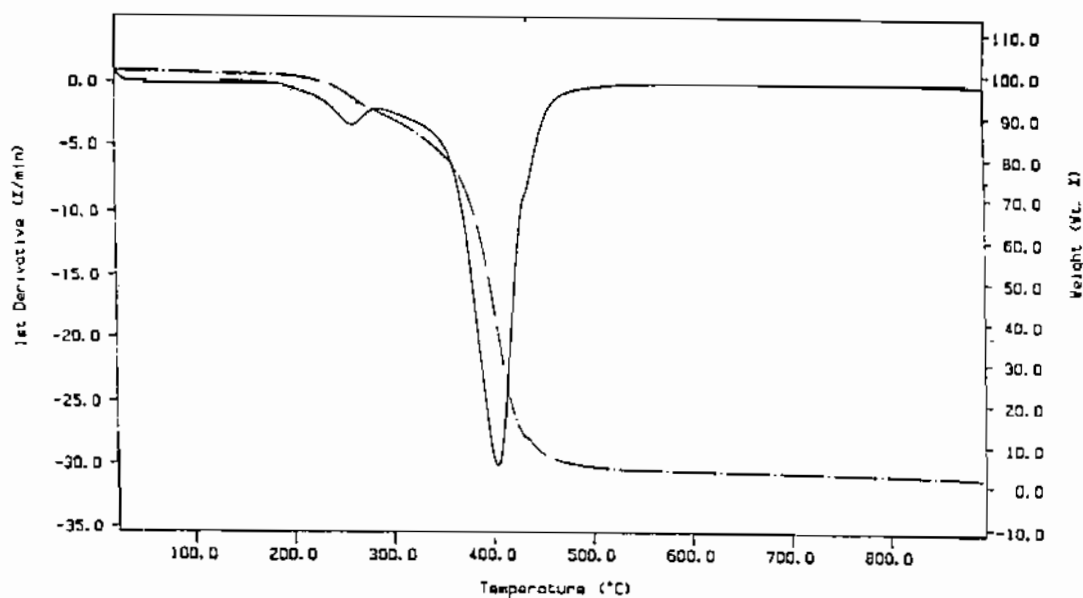


Fig. 13. Thermogravimetric analytical spectrum of PMPM.

Three stages of decomposition were observed for PMPM - metal complexes (Fig. 14) and (Fig. 15). The first step in case of PMPM - Cu acetate appeared in the temperature range 95 - 180°C with 2.8% wt. loss which may be due to the loss of a water molecule. The first weight loss stage for PMPM - Cu chloride was observed in the temperature range 100 - 316°C with a weight loss 5.25% which may be due to the loss of a water molecule. The second stage for Cu (II) acetate complex was observed in the temperature range 270 - 396°C (29% wt. loss). The second step in case of Cu (II) Chloride complex appeared in the temperature range 316 - 392°C (20.4% wt. loss). The third stage occurred in the temperature range 396 - 580°C (36.9% wt. loss) for Cu (II) acetate complex and in the temperature range 392 - 670°C (41% wt. loss) for Cu (II) chloride complex.



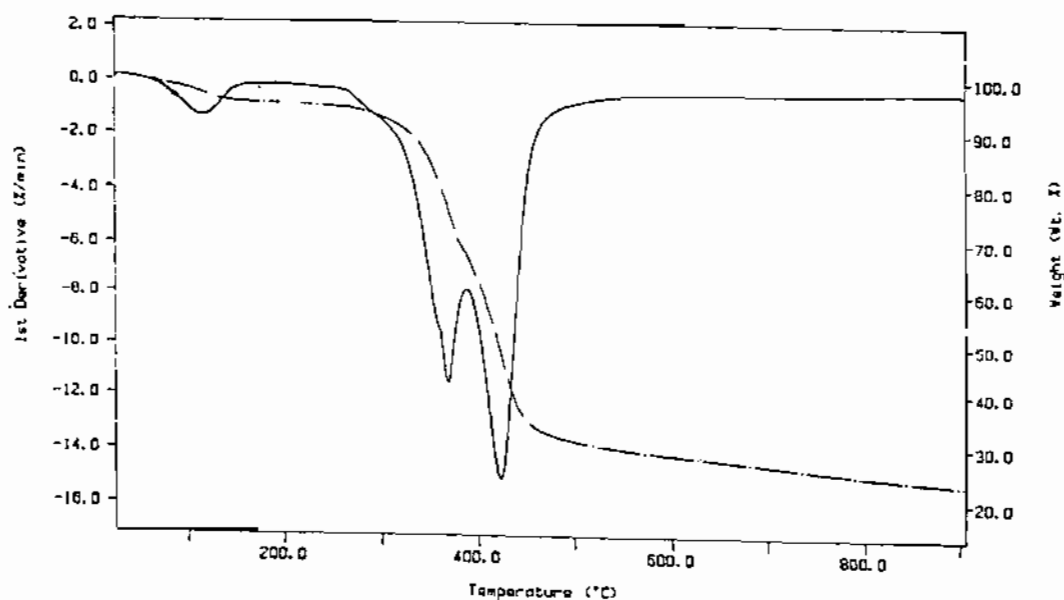


Fig. 14. Thermogravimetric analytical spectrum of PMPM-Cu-acetate complex.

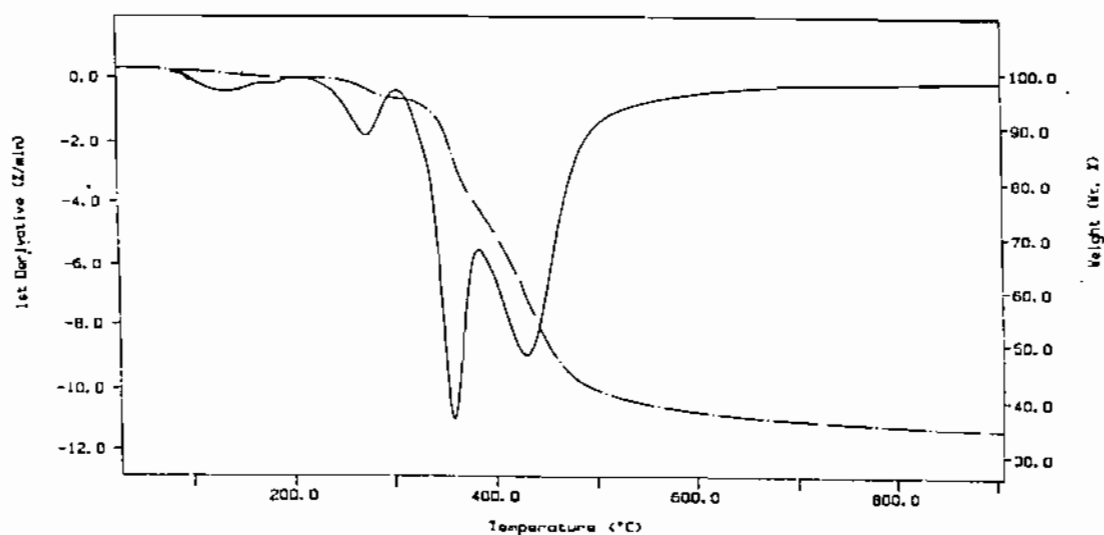


Fig. 15. Thermogravimetric analytical spectrum of PMPM-Cu-chloride complex.

Table 15 Thermo-analytical results of PMPM and its metal complexes.

Compound	DTA		TGA
	T <sub>range</sub> (°C)	T <sub>max</sub> (°C)	wt. loss (%) for stage
PMPM	185 – 300	265	10.5
	350 – 525	400	76.3
PMPM - Cu acetate	95 – 180	–	2.8
	290 – 396	382	29.0
	396 – 580	441	36.9
PMPM - Cu chloride	100 – 316	–	5.25
	316 – 392	362	20.4
	392 – 670	438	41.0

Thermo-analytical results of PMOM and its complexes are collected in Table 16. PMOM decomposed in three stages (Fig. 16).

The first one occurs in the temperature range 90 - 180°C (3.35% wt. loss) and was assigned to a loss of solvent molecules. The second stage started at 276°C and ended at 340°C with 10.2% wt. loss. The third stage of decomposition ended at 537°C with 77% wt. loss.

Cu (II) acetate and Cu (II) chloride complexes decompose in three stages (Fig. 17) and (Fig. 18). The first weight loss appeared in the temperature range 100 - 296°C (7.15% wt. loss) for Cu (II) acetate and 100 - 290°C (9.8% wt. loss) for Cu (II) chloride complex. The second step for Cu (II) acetate complex occurred between 296 and 385°C with 23.3% weight loss while for Cu (II) chloride complex appeared between 290 - 380°C (23% wt. loss). The third weight loss stage was observed in the range 385 - 570°C (42.5% wt. loss) for Cu acetate complex and in the range 380 - 650°C (40.3% wt. loss) for Cu chloride complex.

The TG and DTA results for homopolymers and their corresponding copper complexes showed that the thermal stabilities of homopolymers are lower than that of their copper complexes. This may be due to the formation of stable structures in these polymer complexes.

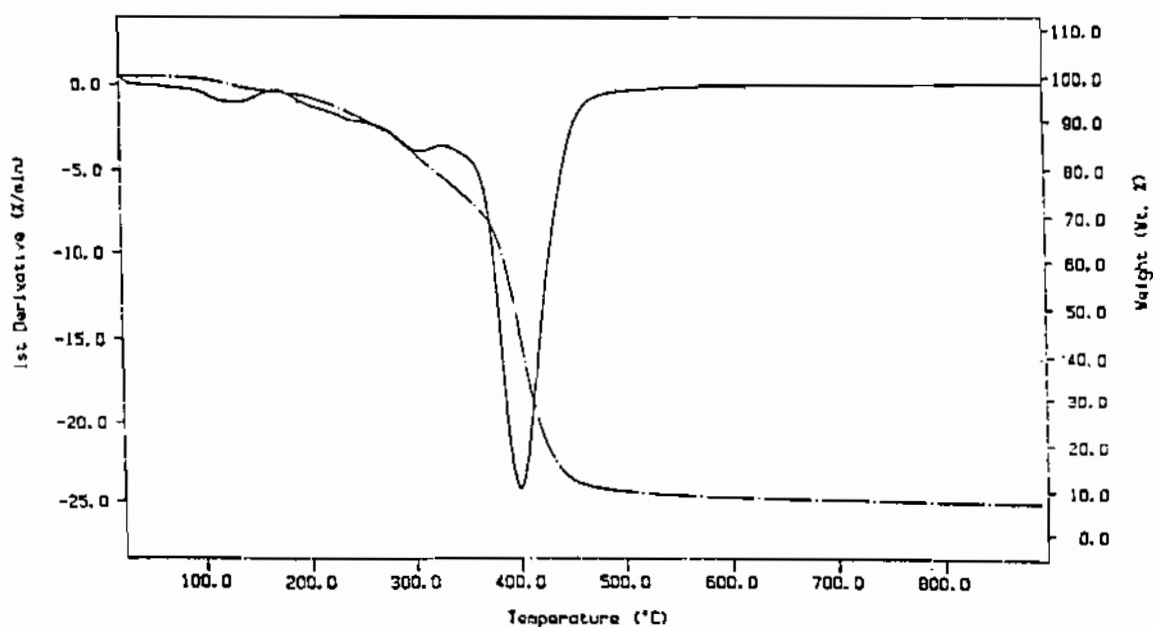


Fig. 16. Thermogravimetric analytical spectrum of PMOM.

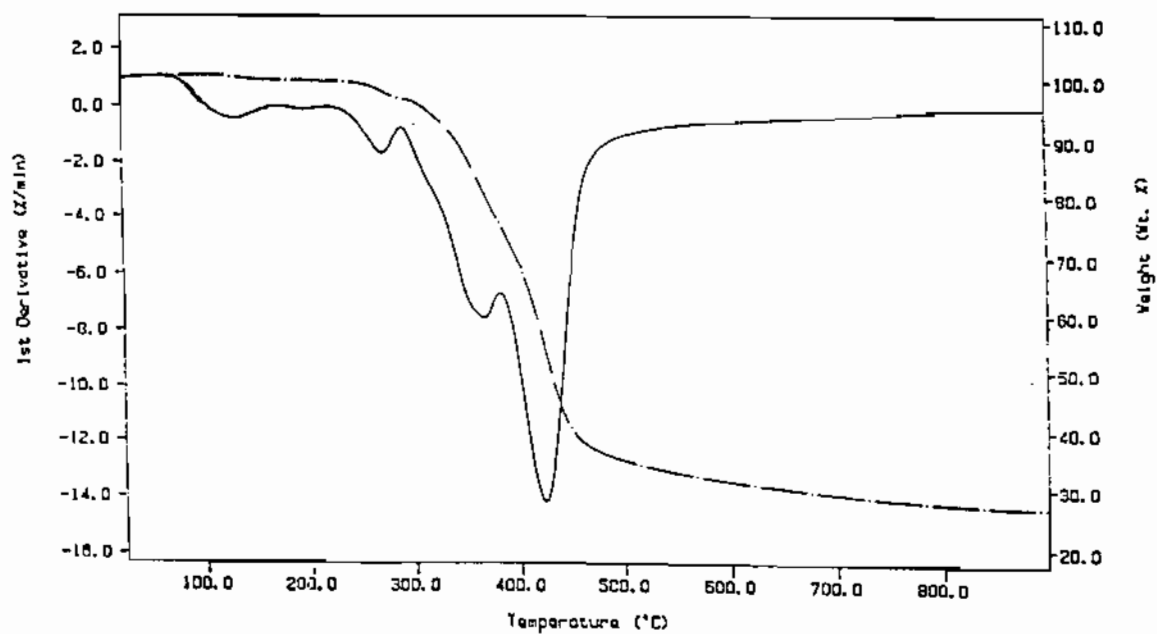


Fig. 17. Thermogravimetric analytical spectrum of PMOM-Cu-acetate complex.

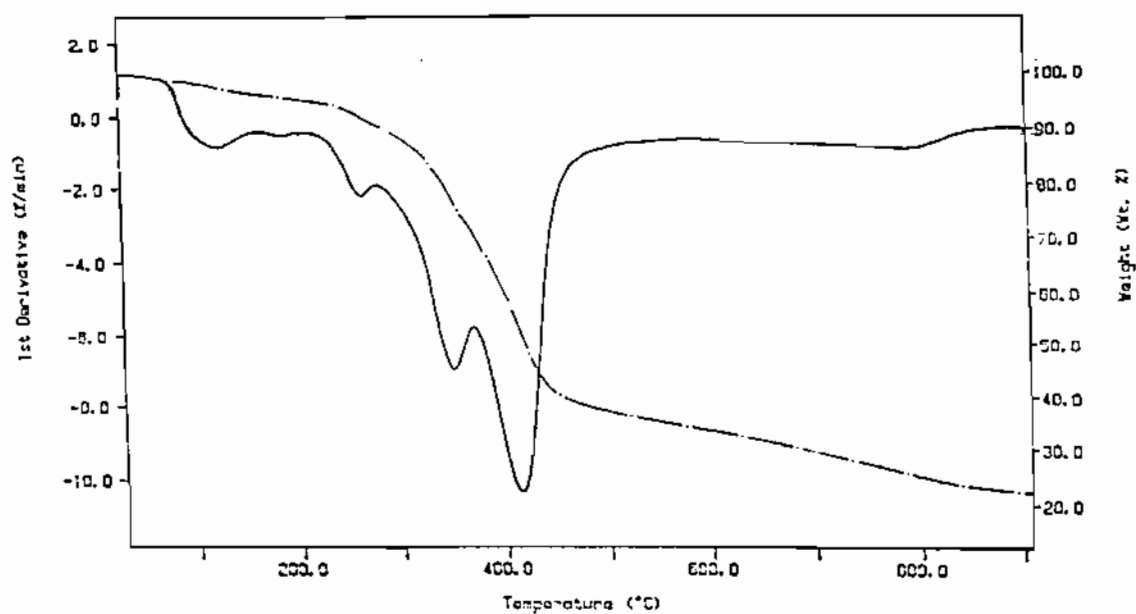


Fig. 18. Thermogravimetric analytical spectrum of PMOM-Cu-chloride complex.

Table 16. Thermo-analytical results of PMOM and its metal complexes.

Compound	DTA		TGA
	T <sub>range</sub> (°C)	T <sub>max</sub> (°C)	wt. loss (%) for stage
PMOM	90 – 180	–	3.35
	268 – 340	300	10.2
	340 – 537	405	77.0
PMOM - Cu acetate	100 – 296	–	7.15
	296 – 385	360	23.3
	385 – 570	420	42.5
PMOM - Cu chloride	100 – 290	–	9.8
	290 – 380	345	23.0
	380 – 650	415	40.3

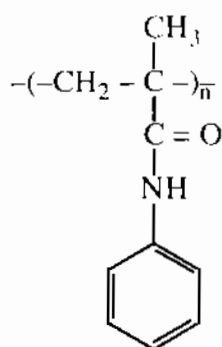
### Conclusion

- 1- In this work monomers of N-phenyl methacrylamide, N-(p-methyl phenyl) methacrylamide and N-(p-methoxy phenyl) methacrylamide were prepared and the optimum conditions for their polymerization were investigated by following the polymerization time, effect of ratio of initiator, and effect of solvent.

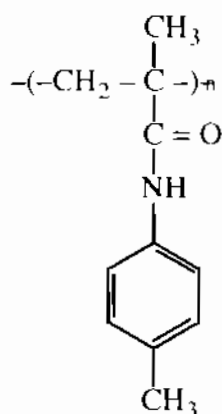
The optimum time condition of polymerization is 5 hrs, when benzene is used as a solvent, and the ratio of initiator is 5% (w/w).

- 2- The polymers obtained were characterized by determining the viscosity number, Infrared spectroscopy, elemental analysis, metal analysis, and thermo gravimetric analysis (TGA).

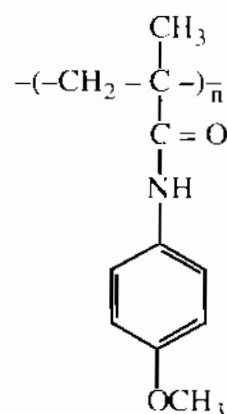
The micro-analytical data confirmed the following structures of the prepared polymers :



(PPM)



(PMPM)



(PMOM)

- 3- The TGA and DTA results for homopolymers and their corresponding copper complexes showed that the thermal stabilities of homopolymers are lower than that of their copper complexes. This may be due to the formation of stable structures in these polymer complexes.

### Acknowledgements

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### References

- (1) **Alger, M.S.M.**, "Speciality Polymers", Edited by Dyson, R.W., Blackie & Son Ltd., Glasgow and London, Chapter 3 (1987).
- (2) **Grassie, N. and Torrance, B.J.D.**, "Thermal Degradation of Copolymers of Methyl Methacrylate and Methyl Acrylate. I. Products and General Characteristics of the Reaction", *J. Polym. Sci.*, A-1, **6**, 3303-3307 (1968).
- (3) **Diab, M.A.**, "Thermal Stability of Poly (vinyl Bromide) and Vinyl Bromide-Methylacrylate Copolymers", *J. Polym. Sci., Chem. Ed.*, **21**, 3249-3254 (1983).
- (4) **Diab, M.A.**, "Thermal Stability of Poly (vinyl Bromide) Copolymers of Vinyl Bromide With Methyl Vinyl Ketone", *Eur. Polym. J.* **20**, 599-603 (1983).
- (5) **El-Agamey, A.A., Diab, M.A. and Osman, A.I.**, "Thermal Degradation of Poly ( $\beta$ -Bromostyrene) and Copolymers of  $\beta$ -Bromostyrene with Methyl Methacrylate", *J. Thermal Anal.*, **31**, 239-244 (1986).
- (6) **Diab, M.A. and El-Sonhati, A.Z.**, "Thermal Stability of Poly ( $\beta$ -Bromostyrene) and Copolymers of  $\beta$ -Bromostyrene with Methyl Acrylate", *Acta Polymerica*, **38**, 571-577 (1987).
- (7) **Odian, G.**, "Principles of Polymerization", Wiley-Interscience, New York, P. 109 (1991).
- (8) **DeWinter, W.**, *J. Macromol. Sci., Rev. Macromol. Chem.*, **1**, 329-333 (1966).
- (9) **Kaneko, M. and Tsuchida, E.**, "Formation, Characterization and Catalytic Activities of Polymer Metal Complexes", *J. Polym. Sci., Macromol. Rev.*, **16**, 397-400 (1981).
- (10) **Kurimura, Y., Tsuchida, E. and Kaneko, M.**, "Preparation and Properties of some Water-Soluble Cobalt (III)-Poly-(4-Vinyl Pyridine) Complexes", *J. Polym. Sci., A-I*, **9**, 3511-3516 (1971).
- (11) **Tsuchida, E., Nishide, H. and Takeshita, M.**, "Steric and Electrostatic Factors on the Formation and the Structure of Polymeric Cobalt (III) Complexes", *Makromol. Chem.*, **175**, 2293-2299 (1974).
- (12) **Hering, H.**, "Chelatbildnde Ionenaustauscher", Akademie Verlag, Berlin (1967).
- (13) **Barnes, J.H. and Esslemont, G.F.**, *Makromol. Chem.*, **177**, 307-311 (1976).
- (14) **Kida, S., Hirano, S., Ando, F. and Nonaka, Y.**, *Nippon Kagaku Kaishi*, 915-920 (1977).
- (15) **Leon, N.H. and Broadbent, D.**, "Novel Polymers Containing Thiocarbonyl Groups", *J. Polym. Sci. C*, **12**, 693-670 (1974).
- (16) **Hojo, N. and Shirai, H.**, "Synthesis and Thermal Stability of Mixed Amine Complexes of Metal Tetracarboxylic Diimideates", *Kogyo Kagaku Zasshi*, **73**, 1862-1865 (1970).
- (17) **Hojo, N. and Shirai, H.**, "Formation Constants of Poly (Vinyl Alcohol)-Copper (II) Complexes", *Nippon Kagaku Kaishi*, 1316-1320 (1972).
- (18) **Agnew, N.H.**, "Transition Metal Complexes of Poly (Vinyl Pyridines)", *J. Polym. Sci., A-1*, **14**, 2819-2830 (1976).
- (19) **Katon, J.E.**, "Organic semiconducting Polymers", Marcel Dekker, New York (1970).
- (20) **Amon, W.F. and Kane, K.W.**, *U.S. Pat.*, **2**, 505, 85-88 (1950).

- (21) **Wertz, D.L. and Tyvoll, J.L.**, "Effect of Hydrochloric Acid on the Mean solute Species in Copper (II) Chloride-Hydrochloric Acid solutions", *J. Inorg. Nucl. Chem.*, **36**, 3713-3717 (1974).
- (22) **Epstein, A. and Wildi, B.S.**, "Electrical Properties of Poly (Cu-Phthalocyanine)", *J. Chem. Phys.*, **32**, 324-328 (1960).
- (23) **Osada, Y.**, "Radical Polymerization Reactivities of Methacrylic Acid, Polymerization Reactivities of Methacrylic Acid Coordinated to Cobalt (III) Complexes", *Makromol. Chem.*, **176**, 1893-1898 (1975).
- (24) **Osada, Y.**, "Configuration Effects of Metal Complexes Attached to Methacrylic Acid in the Process of Radical Polymerization", *Makromol. Chem.*, **177**, 1259-1263 (1976-a).
- (25) **Osada, Y.**, "Radical Polymerization Reactivities of Methacrylic Acid Coordinated to Cobalt (III) Complexes", *Makromol. Chem.*, **177**, 1273-1277 (1976-b).
- (26) **Osada, Y. and Ishida, K.** "Alternative Copolymer with -(ABA)- Sequences from the Radical Copolymerization of Methacrylic Acid Coordinated to Cobalt (III) Complex with Sodium Styrene-4-Sulfonate", *Makromol. Chem.*, **177**, 2209-2213 (1976).
- (27) **James, D.B., Wetton, R.E. and Brown, D.S.**, "Structure and Properties of Poly (Propylene Oxide)-Metal Salt Complexes", *Polymer*, **20**, 176-191 (1979).
- (28) **Diab, M.A., El-Sonhati, A.Z., El-Sanabari, A.A. and Taha, F.I.**, "Polymer complexes. VII. Thermal Stability of Poly (2-Acrylamido Pyridine) and Complexes of 2-Acrylamido Pyridine with Transition Metal Chlorides", *Polym. Deg. and Stab.*, **24**, 1-8 (1989).
- (29) **Diab, M.A., El-Sonbati, A.Z. and El-Sanabari, A.A.**, "Thermal Degradation of Poly (Acryloyl Chloride) and Copolymers of Acryloyl Chloride with Methyl Methacrylate", *Acta Polymerica*, **40**, 112-116 (1989).
- (30) **Diab, M.A., El-Sonbati, A.Z. and Ghoniem, M.M.**, "Polymer complexes. IX. Thermal Stability of Poly [Bis(2,6-Diaminopyridine Sulfoxide)] and Polymer Complexes of [bis(2,6-Diaminopyridine Sulfoxide)] with Copper Halides", *Acta Polymerica*, **8**, 545-547 (1989).
- (31) **Zulfiqar, M., Hussain, R., Zulfiqar, S., Mohammad, D. and McNeill, I.C.**, "Thermal Stability of Some Transition Metal (Cobalt, Nickel, and Copper) Salts of Poly (Methacrylic Acid)", *Polym. Deg. and Stab.*, **45**, 115-120 (1994).
- (32) **Mehmtt., et al.**, *Polymer Degradation and Stability*, **60**, 185-193 (1998).

## تحضير مبلمرات الأكريليك مقاومة الحرارة

عبدالرحيم عبدالرحمن سمرقندي

كلية العلوم ، قسم الكيمياء ، جامعة الملك عبدالعزيز

جدة - المملكة العربية السعودية

المستخلص. تم تحضير منومرات {N-phenyl methacrylamide (PPM)} و {N-(p-methoxy phenyl) methacrylamide (PMPM)} و {N-(p-methyl phenyl) methacrylamide (PMOM)} و تمت دراسة أفضل شروط بلمرتها بمتابعة زمن البلمرة وتأثير نسبة البادئات وتأثير المذيبات . تم توصيف البوليمرات المحضرة بتحديد عدد اللزوجة واستخدام طيف الأشعة تحت الحمراء والتحليل الدقيق وتحليل العناصر كما تم فحص السلوك الحراري للبوليمرات ومركباتها باستخدام التحليل الوزني الحراري .

نتائج التحليل الدقيق وطيف الأشعة تحت الحمراء أكدت المبلمرات المحضرة وبالرجوع إليها تم اقتراح مخططات لمركبات المبلمرات مع المعادن . ومن ناحية أخرى أظهر التحليل الوزني الحراري مرحلتين إلى ثلاث مراحل تحلل للمنومرات ولمركبات البوليمرات.

