

Characterization of Some Poly(methyl Methacrylate)s Prepared by Emulsifier-Free Emulsion Polymerization in Presence of Some Organic Ligands and Their Nickel Complexes

S. M. SAYYAH, S. H. H. EL-HAMOULY,* and
M. A. ABD EL-GHAFFAR,† *Chemistry Department, Faculty of Science,
Al-Azhar University, Nasr City, Cairo, Egypt*

Synopsis

The aqueous polymerization of methyl methacrylate (MMA) was studied using sodium bisulfite as initiator in absence and presence of tetraoxalyl urea (TOU), tetraoxalyl thiourea (TOthioU) and tetraoxalyl paraphenylene diamine (TOP-phD). The effect of their nickel complexes on the polymerization rate has also been studied. Ligands with free carboxyl groups have a retarding effect on the polymerization reaction, while their nickel complexes have a catalytic effect. The polymers obtained in presence of nickel complexes were found to have wider molecular weight distribution than those obtained in their absence; this was deduced by thin layer chromatographic analysis in a binary mixture (benzene/methanol). The apparent energy of activation was found to be 5.83×10^4 J/mol, 1.87×10^4 J/mol, 2.11×10^4 J/mol, and 3.95×10^4 J/mol in absence and in presence of 0.5 g of Ni complex of TOP-phD, TOthioU and TOU, respectively.

INTRODUCTION

A study of the aqueous polymerization of methyl methacrylate was previously carried out in absence and in presence of various inorganic substances and complexes.¹⁻¹⁰ The effect of such substances on the rate of polymerization, obtained average molecular weights, and apparent energy of activation was also studied.

A number of investigations have been carried out on the separation of homopolymers according to their molecular weights using thin layer chromatographic (TLC) analysis, which proved to be a very good and rapid technique for determination of the molecular weight distribution of the obtained polymers.^{8,11-14}

In this article we intend to study the emulsifier-free emulsion polymerization of methyl methacrylate (MMA) in the presence of some organic ligands and their nickel complexes. Their effect on the obtained viscosity average molecular weights and molecular weight distribution by means of thin layer chromatography (TLC) were also determined.

*Chemistry Department, Faculty of Science, El-Mounofia University, Egypt.

†Laboratory of Polymers and Pigments, National Research Centre, Dokki, Cairo, Egypt.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) monomer, a product of Merck-Schuchardt, was of 99% purity, stabilized with 100 ppm hydroquinone. It was washed with a small amount (10%) of sodium hydroxide and distilled water. The methyl methacrylate was separated with a separating funnel, dried over anhydrous sodium sulfate, and finally fractionated using a fractionating column of about 15 theoretical plates. The fraction boiling at 100–100.5°C was collected and used.

All chemicals and reagents used were pure research grades. The silica gel type (G 60) which contains gypsum (13.3%) was used as stationary phase in TLC experiments.

Tetraoxalyl-urea, thiourea and paraphenylene diamine were prepared according to Abd Ellah et al.¹⁵ and Sayyah et al.¹⁶. The chemical formula, molecular weights, acid values, and Pk values are given in Table I. The nickel complexes of the tetra functional organic ligands are prepared by dropwise addition of nickel sulfate (0.02 mol) in 50 mL distilled water to 50 mL of 0.01 molar solution of the organic ligand. The mixture was refluxed for 3 h under nitrogen atmosphere and the products were filtered, washed with water and absolute ethanol, then dried till constant weight. Nickel content was determined using atomic absorption spectrophotometer SP 191. The chemical formulas and nickel weight percentage are given also in Table I.

Emulsifier-Free Emulsion Polymerization

In a well-stoppered conical flask of 500 mL capacity, the amount of initiator in 200 mL distilled water followed by the organic ligand or nickel complex (in case of studying their effects), and finally the amount of monomer (MMA) (2.6 g) were added to the reaction mixture under nitrogen atmosphere. The order of addition of substances was kept constant in all the performed experiments. The conical flasks were then put in an automatically controlled thermostat at the required temperature. The flasks were shaken (10 shakings/10 s every 30 min) for definite periods of time. The reaction was stopped at will by the addition of few drops of sodium hydroxide solution (5%) and cooling in ice bath. The polymer or mixture of polymer and organic ligands or their nickel complexes was then filtered using Buchner funnel, washed thoroughly with distilled water, methanol and finally dried in an electric oven at 105°C till constant weight.

Purification of the Polymer

The polymer was dissolved in pure benzene (thiophene free) to obtain approximately a 2% polymer solution, and filtered to separate the organic ligands or their Ni complexes and obtain a very clear polymer solution. The polymer was then precipitated by the addition of its solution to a suitable amount of methanol and stirring for a suitable period of time. The white precipitated polymer was then filtered and dried in an electric oven at 105°C.

TABLE I
Some analytical data of the Ligands Used and Their Nickel Complexes

Chemical and molecular formula of the substances used	Ni content (wt %)	Molecular weight (Req/Found)	Acid value (Req/Found)	Pk ₁ — Pk ₄ values
 $C_{14}H_8N_2O_{12} \cdot 8H_2O$ (TOp-phD)	—	396	566.77	3.00, 3.65
 $C_9H_4N_2SO_{12} \cdot 8H_2O$ (TOthioU)	—	364	617	2.95, 3.70
 $C_9H_4N_2O_{13} \cdot 8H_2O$ (TOU)	—	348	645	2.85, 3.75
 $C_{14}H_{12}N_2O_{16}Ni_2$ $Ni_2(TOp-phD)$	20.19	581.4	—	— —
 $C_9H_8N_2SO_{16}Ni_2$ $Ni_2(TOthioU)$	21.37	549.4	—	— —
 $C_9H_8N_2O_{17}Ni_2$ $Ni_2(TOU)$	20.93	565	—	— —
 $C_9H_8N_2O_{17}Ni_2$ $Ni_2(TOU)$	22.01	533.4	—	— —
 $C_9H_8N_2O_{17}Ni_2$ $Ni_2(TOU)$	21.82	550.0	—	— —

W = H₂O

Determination of Intrinsic Viscosity and Average Molecular Weights

The intrinsic viscosity $[\eta]$ for each polymer sample was determined by the usual method of extrapolation. The viscosity average molecular weights \bar{M}_v for the respective polymers were calculated from the following equation:

$$[\eta] = 0.94 \times 10^{-4} \cdot \bar{M}_v^{0.76}$$

The viscosity measurements were carried out in thiophene-free benzene at 25°C.¹⁷

Thin Layer Chromatographic Analysis

We have applied TLC technique for characterization of poly(methyl-methacrylate) (PMMA) samples obtained by emulsifier-free emulsion polymerization in absence and in presence of different amounts of nickel complexes. The stationary phase material for the TLC experiments was Merck silica gel (G 60). The Kirschner apparatus was used to adjust the thickness of the stationary phase film to 500 μm . The activation of the plates was then carried out in an oven at 110°C for 3 h. The charged plates with polymer samples were then placed into a chromatographic vessel containing the developing solvent (benzene : methanol 1 : 1.5 by volume). The chamber type used was normal saturation system at 30°C. The position of the polymer spots after development was marked by spraying a 5% $\text{KMnO}_4\text{-H}_2\text{SO}_4$ (8 N) solution followed by charring at 120°C.

RESULTS AND DISCUSSION

Effect of Organic Ligand

The polymerization of methyl methacrylate (2.6 g) in water (200 mL) using NaHSO_3 (0.03 mol/L) under nitrogen atmosphere at 40°C in absence and in presence of different amounts of ligands was performed. The conversion percentage of the monomer to polymer in absence of organic ligand was found to be 63% after 4 h. The conversion percentage after 4 h was also determined for systems containing different amounts of organic ligands. The data are graphically represented in Figure 1, the decrease in the conversion percentage is due to the presence of the organic ligands with four carboxylic groups in their structures. This means that the organic ligands have an inhibition effect on the emulsifier free emulsion polymerization of MMA. The inhibition effect decreases in the following order: TOU > TOrthioU > TOp-phD. This could be explained by the acid values of the ligands (cf. Table I), which have the order TOU > TOrthioU > TOp-phD. The ionization of the ligands in aqueous medium leads to the formation of hydrogen ions in solution, which consequently affects the ionization of NaHSO_3 , that is, less radical formation occurs.

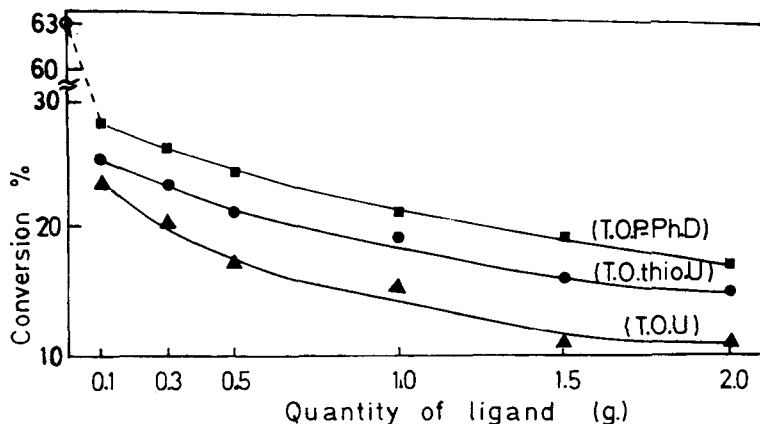
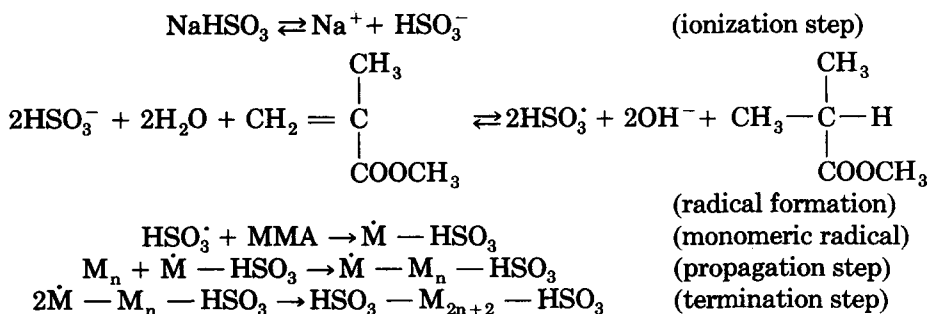
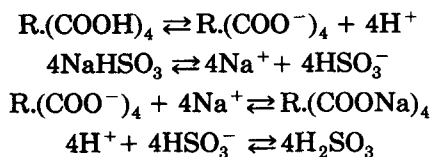


Fig. 1. Relation between conversion percentage after 4 h at 40°C using initiator concentration (0.03 mol/L) and ligand quantity in grams. (■) ToP-phD; (●) TOrthioU; (▲) TOU.

In the absence of ligands:



In presence of organic ligands

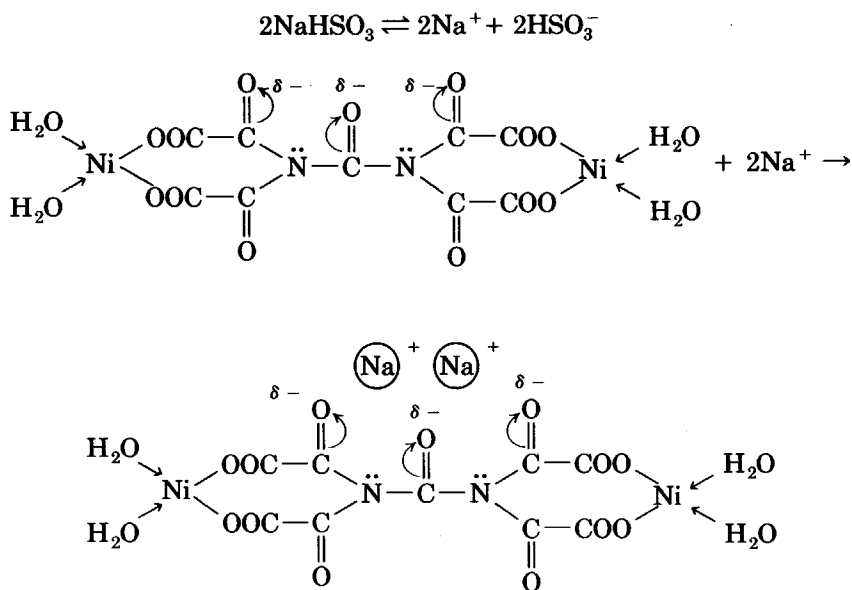


where R = C₅N₂O₅ in case of TOU,
 R = C₅N₂SO₄ in case of TOrthioU, and
 R = C₁₀H₄N₂O₄ in case of TOp-phD.

The first ionization step of the initiator could be affected by the above ionization reactions of the organic ligands in aqueous medium. The ionization of TOU is higher than that of TOrthioU due to the more electronegativity of oxygen than sulfur. The order of ionization of the ligands in solution is in good agreement with the order of their inhibition effect. (cf. Table I and Fig. 1).

Effect of Nickel Complexes

The emulsifier-free emulsion polymerization of MMA (2.6 g) in water (200 mL) was performed under nitrogen atmosphere using NaHSO_3 (0.03 mol/L) as initiator at 40°C in absence and in presence of different amounts of nickel complexes of TOU, TOTHIOU and TOP-PHD. The conversion percentage, viscosity average molecular weights, and R_f values on TLC plates for the obtained polymer samples after 4 h were determined. The data are graphically represented in Figure 2, from which it is clear that the conversion percentage increases from 63% in absence of nickel complexes to 81%, 88%, and 94% in presence of 0.1 g of nickel complexes of TOTHIOU, TOU, and TOP-PHD, respectively. This indicated that the nickel complexes have a catalytic effect on the polymerization processes, which is in good agreement with what was found by Moustafa et al.^{18,19} in case of nickel salts and that of phthalocyanine complexes. The catalytic effect of the nickel complexes can be explained on the basis of the following equations:



The attraction of sodium ions to the partially negative charges oxygen atoms of $\text{C}=\text{O}$ or $\text{S}=\text{O}$ groups leads to the more ionization of NaHSO_3 in aqueous medium and consequently to more radical formation (i.e., catalytic effect of the Ni complexes of TOU and TOTHIOU). In case of the Ni complex of TOP-PHD, the attraction of sodium ions toward oxygen atoms of the $\text{C}=\text{O}$ groups could also take place. The delocalization of electrons of benzene ring and the lone pair of electrons of nitrogen atoms leads to the increase of electron density on the oxygen atoms of the carbonyl groups and, consequently, more attraction of sodium ions which also increases the ionization of the initiator molecules in aqueous medium (i.e., more radical formation and higher catalytic effect). The conversion percentage decreases from 0.1 g to 0.5 g of nickel complex, then slightly increases to 2.0 g. The highest catalytic effect

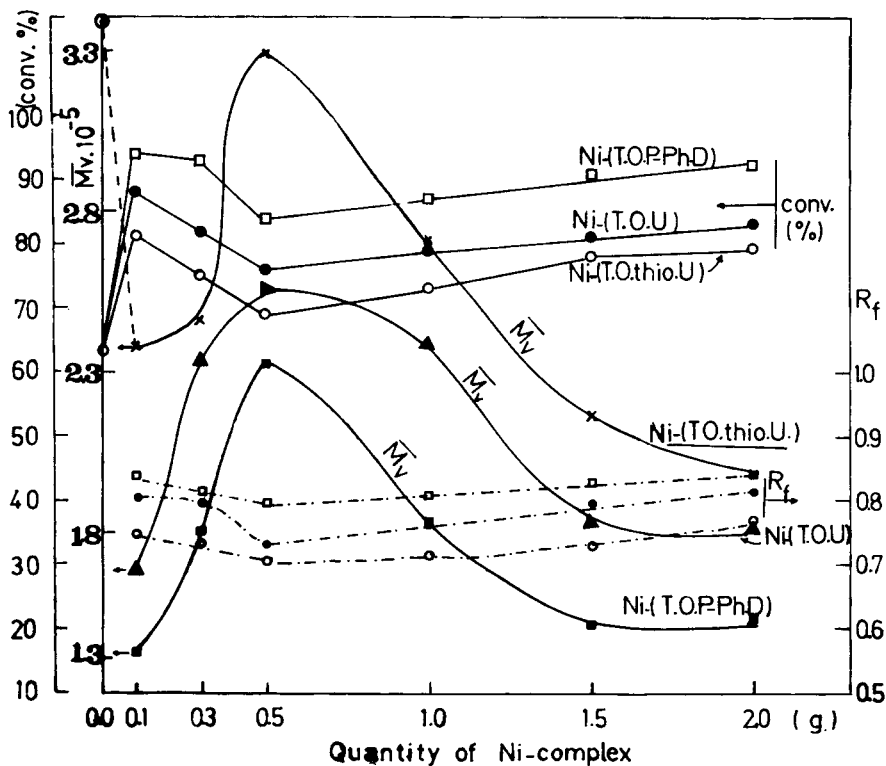


Fig. 2. Conversion %, \bar{M}_v , and R_f values vs. weight of Ni complexes (for polymers obtained after 4 h at 40°C using initiator concentration 0.03 mol/L).

is found in the presence of 0.1 g of nickel complex. The catalytic effect increases in the order $\text{Ni}_2(\text{TOrthioU}) < \text{Ni}_2(\text{Tou}) < \text{Ni}_2(\text{TOp-phD})$, which may be attributed to the greater electronegativity of carbon over sulfur, and consequently more attraction of sodium ions toward oxygen of the carbonyl groups than in case of $\text{S}=\text{O}$ groups.

On one hand, the viscosity average-molecular weight of the obtained polymer samples was found to decrease in presence of 0.1 g nickel complexes in the following order:

$$\bar{M}_v(\text{PMMA})_{\text{Ni}_2(\text{TOrthioU})} > \bar{M}_v(\text{PMMA})_{\text{Ni}_2(\text{Tou})} > \bar{M}_v(\text{PMMA})_{\text{Ni}_2(\text{TOp-phD})}$$

On the other hand, the viscosity average molecular weight increases with increasing the nickel complex quantity up to 0.5 g then decreases with higher nickel complex quantities. The highest values of the viscosity average molecular weights were found for polymer samples prepared in presence of 0.5 g nickel complex in all cases.

The R_f values of the obtained polymer samples in presence of different amounts of nickel complexes were found to be in good agreement with the viscosity data. The R_f values decrease for all cases, in presence of nickel complex up to 0.5 g, then slightly increase up to 2.0 g. The R_f values of the obtained polymer samples in presence of the same amounts of nickel com-

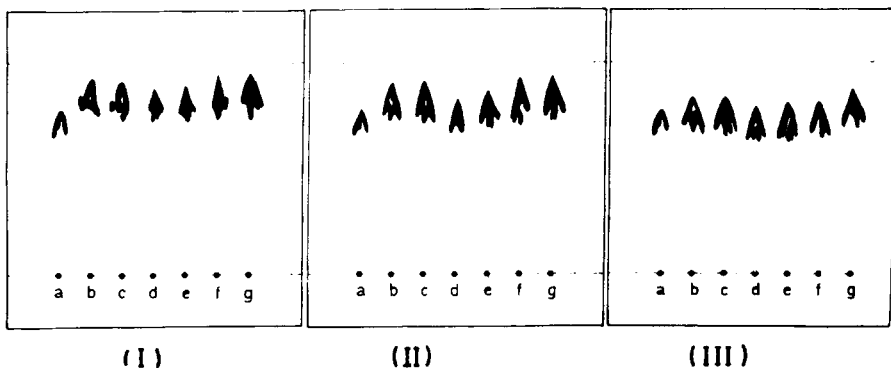


Fig. 3. TLC chromatograms for PMMA samples prepared in absence and presence of Ni complexes. (I) in presence of different amounts of $\text{Ni}_2(\text{TOP-phD})$; (II) in presence of different amounts of $\text{Ni}_2(\text{TOfthioU})$; (III) in presence of different amounts of $\text{Ni}_2(\text{TOU})$; (a) in absence; (b) in presence of 0.1 g Ni complex; (c) in presence of 0.3 g; (d) in presence of 0.5 g; (e) in presence of 1.0 g; (f) in presence of 1.5 g; (g) in presence of 2.0 g, respectively.

plexes were found to have the following order:

$$R_f(\text{PMMA})_{\text{Ni}_2(\text{TOP-phD})} > R_f(\text{PMMA})_{\text{Ni}_2(\text{TOU})} > R_f(\text{PMMA})_{\text{Ni}_2(\text{TOfthioU})}$$

The thin layer chromatograms for the obtained polymer samples prepared in the absence and in the presence of different amounts of Ni complexes are represented in Figure 3 (I, II, and III). From the chromatograms, it is clear that both the spot areas and R_f values, for polymer samples prepared in presence of 0.1 g Ni complexes are higher than those for polymer sample obtained in the absence of nickel complexes; this means a decreased viscosity average molecular weight and increased polydispersity. The increase of the amount of nickel complex in the reaction medium up to 0.5 g leads to the decrease of the R_f values and the spot areas of the obtained polymer samples. Higher amounts of nickel complex, up to 2.0 g, lead to an increase in the spot areas and R_f values. Consequently, the polydispersity of the obtained polymer samples increase with the increasing of nickel complex amounts from 0.5 g up to 2.0 g. The lowest polydispersity was found for polymer samples obtained in presence of 0.5 g of Ni complexes. (sample d in all chromatograms).

Effect of Temperature

The emulsion polymerization of MMA (2.6 g) in water (200 mL) using NaHSO_3 (0.03 mol/L) as initiator in nitrogen atmosphere in absence and presence of 0.5 g ligands or their Ni complexes for different periods of time with mild shakings (10 shakings/10 s every 15 minutes) was carried out at different temperatures (40 and 50°C). The viscosity average molecular weights and R_f values were measured for polymer samples obtained after 3 h, and the data are summarized in Table II. It was found that, the initial rates of the polymerization reactions increase with raising the reaction temperature. The induction period decreases from TOU to TOP-phD in the following order: TOU > TOfthioU > TOP-phD. The initial rate of the polymerization reaction

TABLE II
Emulsifier-Free Emulsion Polymerization of MMA in Absence and in Presence of 0.5 g Organic Ligands or Their Ni Complexes in Nitrogen Atmosphere
at 40 and 50°C Using NaHSO₃ (0.03 mol/L) as Initiator

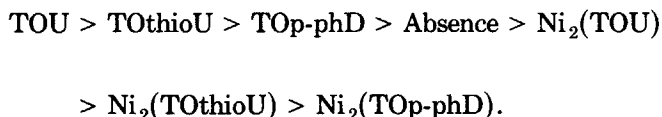
Run no.	Name of additives	Conversion %															Initial rate × 10 ⁶ mol L ⁻¹ s ⁻¹	Activation energy (J/mol)	$\bar{M}_v \cdot 10^{-5}$	R_p values
		Time (min)																		
		15	30	45	60	75	90	105	120	150	180	210	240							
1 ^a	—	—	4	7.5	13.5	17	22	24	27	32.5	39	50	63	4.50	5.83	3.390	0.705			
2 ^b	—	6.5	13	18	26	31	38	44	50	61.0	67	70	83	9.01	—	2.550	0.735			
3 ^a	TOP-phD	—	—	—	—	2.0	7.5	11	13	17.5	20	23	24	2.40	6.41	—	—			
4 ^b	—	—	4	12	19	25	30	34	38	42	46	48	51	5.15	—	—	—			
5 ^a	TOthioU	—	—	—	—	—	1.0	4.0	7.0	10	12	14	21	1.44	7.29	—	—			
6 ^b	—	—	—	—	9.0	20	28	32	35	39	42.5	45	47	3.43	—	—	—			
7 ^a	TOU	—	—	—	—	—	—	—	—	5.0	7.5	11	17	1.11	8.89	—	—			
8 ^b	—	—	—	—	2.5	15	25	30	33	36	37	38	42	3.20	—	—	—			
9 ^a	Ni ₂ (TOP-phD)	26	38	44	51	54	57	60	62	70	79	84	94	28.82	1.87	2.320	0.790			
10 ^b	—	34	45	51	56	60	62	65	69	75	82	88	96	36.02	—	1.840	0.810			
11 ^a	Ni ₂ (TOU)	18	30	36	43	47	50	54	57	64	69	75	88	18.01	3.95	2.550	0.735			
12 ^b	—	24	36	43	48	50	53	56	60	68	75	84	92	28.82	—	1.990	0.770			
13 ^a	Ni ₂ (TOthioU)	11	17	22	27	30	33.5	36.5	41	50	60	70	81	16.01	2.11	3.290	0.710			
14 ^b	—	13	25	31	36.5	41.5	46	50	53	64	72	79	86	20.58	—	2.390	0.740			

^aAt 40°C.

^bAt 50°C.

at the same temperature increases in the same order. In case of the Ni complexes, the initial rates are higher than in cases of the ligands, which indicates the catalytic effect of the Ni complexes. The order of the catalytic action of the three complexes is as follows: $\text{Ni}_2(\text{TOP-phD}) > \text{Ni}_2(\text{TOU}) > \text{Ni}_2(\text{TOthioU})$. In all cases the initial rate and conversion percentage increase while the \bar{M}_v values decrease with higher reaction temperature (cf. Table II). The R_f values confirm the viscosity measurements (i.e., R_f values increase with higher reaction temperature).

The apparent activation energy (E_a) of the different polymerization systems was calculated between two different temperatures 40 and 50°C. The data are also given in Table II. The E_a values decrease in the following order:



CONCLUSION

Thin layer chromatographic analysis is a good and rapid technique for characterization of polymer samples, especially in the determination of molecular weights, and gives an idea of their molecular weight distribution (MWD). The chromatograms obtained from TLC studies on PMMA samples show the effect of the different Ni complexes on both \bar{M}_v and MWD as shown from R_f values and spot shapes of the polymer samples on TLC plates. The Ni complexes catalyzed the polymerization of MMA, while ligands inhibited the polymerization processes. The higher catalytic effect is recorded by using $\text{Ni}_2(\text{TOP-phD})$ as a catalyst and the highest inhibition effect in the case of addition of TOU to the reaction medium.

References

1. N. A. Ghanem, A. A. Yehia, A. B. Moustafa, and N. A. Rizk, *Eu. Polym. J.*, **7**, 717 (1971).
2. A. B. Moustafa, M. A. Abd-El-Ghaffar, A. S. Badran, and A. M. Rabie, *J. Polym. Sci. (Polym. Chem. Ed.)*, **19** (3), 719 (1981).
3. A. B. Moustafa, A. M. Rabie, and A. S. Badran, *Angew Makromol. Chem.*, **103**, 87 (1982).
4. A. B. Moustafa and A. S. Badran, *Angew Makromol. Chem.*, **103**, 153 (1982).
5. A. B. Moustafa, M. A. Abd-El-Ghaffar, and A. S. Badran, *Acta Polymerica*, **34** (4), 235 (1983).
6. A. B. Moustafa, M. A. Abd-El-Ghaffar, and A. S. Badran, *Acta Polymerica* **35** (1), 68 (1984).
7. A. B. Moustafa, S. M. Sayyah, A. S. Badran, and M. S. Hassanin, *J. Appl. Polym. Sci.*, **29**, 3677 (1984).
8. A. B. Moustafa, S. M. Sayyah, A. S. Badran, and M. S. Hassanin, *J. Appl. Polym. Sci.*, **30**, 3443 (1985).
9. A. B. Moustafa, S. M. Sayyah, Z. H. Abd El-Latif, and L. I. Amer, *Acta Polymerica*, **37** (11), (1986).
10. A. B. Moustafa, Z. H. Abd El-Latif, L. I. Amer, and S. M. Sayyah, *J. Polym. Sci. Part A. Polymer Chem. Ed.*, **24** (1986).
11. E. P. Otocka and M. Y. Hellman, *Macromolecules*, **3**, 392 (1970).
12. E. P. Otocka, *Macromolecules*, **3**, 691 (1970).
13. H. Inagaki, F. Kamiyama, and T. Yagi, *Macromolecules* **4**, 133 (1971).

14. H. Inagaki and F. Kamiyama, *Macromolecules*, **6**, 107 (1973).
15. I. M. Abd-Ellah, A. A. Salman, M. A. Abd El-Ghaffar, and A. M. Naser, *J. Chem. Soc. Pak.* **4** (1), 7 (1982).
16. S. M. Sayyah, A. A. Bahgat, and M. A. Abd El-Ghaffar, *Pakistan J. Sci. Ind. Res.*, **28** (6), 382 (1985).
17. A. L. Goldberg, W. P. Hohenstein, and H. Mark, *J. Polym. Sci.*, **2**, 502 (1947).
18. A. B. Moustafa, A. M. Rabie, and A. S. Badran, *Die Angew. Makromol. Chemi*, **103**, 87 (1982).
19. A. B. Moustafa, M. A. Abd El-Ghaffar, and A. S. Badran, *Acta Polymerica*, **34**, 235 (1983).

Received September 14, 1987

Accepted December 21, 1987