COMMUNICATIONS

DE LA FACULTÉ DES SCIENCES
DE L'UNIVERSITÉ D'ANKARA

Série B: Chimie

TOME: 29 ANNÉE: 1983

Studies on The Modification of N-Vinylpyrrolidone – Methyl methacrylate Copolymer

By

Abo El-KHAIR B.M. MOSTAFA

14

Faculté des Sciences de l'Université d'Ankara
Ankara, Turquie

Communications de la Faculté des Sciences de l'Universite d'Ankara

La Revue "Communications de la Faculté des Sciences de l'Université d'Ankara" est un organe de publication englobant toutes les diciplines scientifique représentées à la Faculté des Sciences de l'Université d'Ankara.

La Revue, jusqu'à 1975 à l'exception des tomes I, II, III etait composé de trois séries

Série A : Mathématiques, Physique et Astronomie,
Série B : Chimie,
Série C : Sciences Naturelles.

A partir de 1975 la Revue comprend sept séries:

Série A_1 : Mathématiques,
Série A_2 : Physique,
Série A_3 : Astronomie,
Série B : Chimie,
Série C_1 : Géologie,
Série C_2 : Botanique,
Série C_3 : Zoologie.

A partir de 1983 les séries de C_2 Botanique et C_3 Zoologie ont été réunies sous la seule série Biologie C et les numéros de Tome commencerons par le numéro 1.

En principe, la Revue est réservée aux mémoires originaux des membres de la Faculté des Sciences de l'Universiteé d'Ankara. Elle accepte cependant, dans la mesure de la place disponible les communications des auteurs étrangers. Les langues Allemande, Anglaise et Française seront acceptées indifféremment. Tout article doit être accompagnés d'un resume.

Les articles soumis pour publications doivent être remis en trois exemplaires dactylographiés et ne pas dépasser 25 pages des Communications, led dessins et figures portes sur les feuilles séparées devant pouvoir être reproduits sans modifications.

Les auteurs reçoivent 25 extraits sans couverture.

l'Adresse : Dergi Yayın Sekreteri,
Ankara Üniversitesi,
Fen Fakültesi,
Beşevler – Ankara
TURQUIE

Studies on The Modification of N-Vinylpyrrolidone–Methyl methacrylate Copolymer

By

Abo El-KHAIR B.M. MOSTAFA

Chemistry Department, University College for Women, Ain Shams University, Heliopolis, Cairo, Egypt.

(Received September 5,1983, and accepted October 13,1983)

SUMMARY

The copolymerization behaviour of N-vinylpyrrolidone (NVP) and methyl methacrylate (MMA) in the presence of $ZnCl_2$ was investigated. It was observed that, the value of the monomer reactivity ratio at 65 °C for NVP (r_1) increases from 0.044 to 0.297 with the addition of $ZnCl_2$ in the polymerizing system, i.e., $[ZnCl_2]/[NVP + MMA]$ from 0.0 to 0.1. However, the value of r_2 (for MMA) decreases from 1.866 to 0.858 at the same concentration of $ZnCl_2$. This indicates that, the reactivity of NVP increases towards the copolymerization reaction, thus affecting the properties and uses of the obtained copolymers.

INTRODUCTION

The interesting applications and uses[1–9] of polyvinyl-pyrrolidone (PVP) and its copolymers such as inhibitor for the corrosion of Al and Fe in acid media[1,2], separation of phenolic compounds from aqueous solutions[3], manufacture of chewing gum[4,5], complexing agents for Co, Ni, Cu, Fe, Zn and Mn[6] and contact lenses[7] led us to study the copolymerization behaviour of N-vinylpyrrolidone (NVP) with methyl methacrylate (MMA) in the presence of zinc chloride as a modificator. This was performed by determining the monomer reactivity ratios of NVP and MMA during their bulk copolymerization in the presence of different concentrations of $ZnCl_2$. Such investigation gives a very useful information on the relationship between structure and reactivity of monomers, thus affecting the properties of the obtained copolymers.

EXPERIMENTAL

Materials:

N-Vinylpyrrolidone (Koch-Light) was distilled under nitrogen and the fraction distilling at 98 °C was used.

Methyl methacrylate (Merck) was washed several times with 5 % aqueous NaOH followed by distilled water, dried and distilled under nitrogen. The fraction distilling at 101 °C was used.

Azobisisobutyronitrile (Polysciences) was recystallized from ethyl alcohol (M. P. 103.5 °C).

Anhydrous zinc chloride (Merck) was heated for several hours at 150 °C before use.

Polymerization:

The copolymerization was carried out in 20 ml pyrex ampoules. N-vinylpyrrolidone and methyl methacrylate of known molar ratios were mixed in an external conical flask. To this mixture, the required percentage by weight of azobisisobutyronitrile and a known weight of $ZnCl_2$ were added. The mixture was introduced into an ampoule immeresed in a cooling mixture, flushed with nitrogen, sealed and then immeresed in a thermostat at 65 ± 0.2 °C.

The polymerization was stopped when 5–10 % conversion had taken place (by observing the viscosity of the ampoule content). The ampoule was opened and the content pured into a large amount of water containing very small amount of hydroquinone. The precipitated polymer was redissolved in ethyl alcohol, reprecipitated from water and dried at 60 °C to constant weight.

Copolymer anaysis:

The copolymer composition was determined from its nitrogen content by elemental analysis.

RESULTS AND DISCUSSION

Bulk copolymerization of N-vinylpyrrolidone (NVP) with methyl methacrylate (MMA) was carried out in the presence of $ZnCl_2$. Azobi-

sisobutyronitrile (ABIN), 0.2 % of the weight of the two monomers, was used as an initiator. The percent conversion of the polymerizing system does not exceed 10 %. In such case, the differential equation of Maye and Lewis[10] can be applied.

The reactivity ratios of N-vinylpyrrolidone and methyl methacrylate, r_1 and r_2 respectively, were calculated by applying the Fineman – Ross method[11] using the following equation:

$$F(f-1)/f = r_1F^2/f - r^2 \quad \ldots\ldots\ (1)$$

where F is the molar ratio of NVP to MMA in the monomer feed, and f is the molar ratio in the resulting copolymer. Thus a plot of $F(f-1)/f$ against F^2/f yields a straight line of slope r_1 and intercept $-r_2$. The monomer reactivity ratio $r_1 = k_{11}/k_{12}$, where k_{11} is the rate constant for the addition of monomer-1 (NVP) to a chain ending in radical-1 and k_{12} is the rate constant for the addition of monomer-2 (MMA) to a chain ending in radical-1. In analogous manner, $r_2 = k_{22}/k_{21}$.

Equation (1) can be represented as follows:

$$y = ax + b \quad \ldots\ldots\ (2)$$

where $y = F(f\text{-}1)/f$,

$x = F^2/f$,

$a = r_1$ and

$b = -r_2$.

The constants a and b were calculated using the following formulae:

$$a = \frac{n\sum_1^n x_i y_i - \sum_1^n x_i \sum_1^n y_i}{n\sum_1^n x_i^2 - (\sum_1^n x_i)^2} \quad \ldots\ldots\ (3)$$

and

$$b = \frac{\sum_1^n x_i^2 \sum_1^n y_i - \sum_1^n x_i \sum_1^n x_i y_i}{n\sum_1^n x_i^2 - (\sum_1^n x_i)^2} \quad \ldots\ldots\ (4)$$

where n is the number of experiments.

Table 1 shows the copolymerization of NVP with MMA in the presence of different concentrations of $ZnCl_2$ initiated by ABIN at 65 °C.

Table 1.

Bulk copolymerization of N-vinylpyrrolidone (NVP) and methyl methacrylate (MMA) initiated by azobisisobutyronitrile (ABIN) in presence of $ZnCl_2$ at 65 °C.

No.	Monomer composition (%)		N (%) in copolymer	Copolymer composition (%)	
	[NVP]	[MMA]		[NVP]	[MMA]
a–	$[ZnCl_2]/[NVP + MMA] = 0.0$				
1	90	10	7.20	54.52	45.48
2	80	20	5.50	41.06	58.94
3	70	30	4.70	34.86	65.14
4	50	50	4.50	33.32	66.68
5	40	60	2.85	20.83	79.17
6	20	80	1.80	13.04	86.96
b–	$[ZnCl_2]/[NVP + MMA] = 0.05$				
1	80	20	7.60	57.74	42.26
2	70	30	4.60	34.09	65.91
3	40	60	3.75	27.60	72.40
4	30	70	2.30	16.74	83.26
5	10	90	1.10	07.92	92.08
c–	$[ZnCl_2]/[NVP + MMA] = 0.1$				
1	80	20	8.60	65.89	34.11
2	50	50	5.40	40.28	59.72
3	40	60	3.80	27.98	72.02
4	30	70	3.70	27.23	72.77
5	10	90	3.20	23.44	76.56

Fig. 1 shows the monomer-copolymer composition curves for NVP and MMA bulk copolymerization in the presence of $ZnCl_2$. The concentrations of $ZnCl_2$ (in molar ratios) to NVP and MMA monomers were 0.0; 0.05 and 0.1. It was observed that, N-vinylpyrrolidone content in the copolymer increases with raising the concentration of $ZnCl_2$ in the system. The results of monomer reactivity ratios for NVP and MMA in absence and in presence of $ZnCl_2$ are shown in Table 2 and Fig. 2. The value of r_1 (for NVP) increases more than six times (from 0.044 to 0.297) as the concentration of $ZnCl_2$ in the monomer feed increases from 0.0 to 0.1, i.e., $[ZnCl_2]/[NVP + MMA] = 0.1$. However, the value of r_2 (for MMA) decreases from 1.866 to 0.858 at the same concentration of $ZnCl_2$.

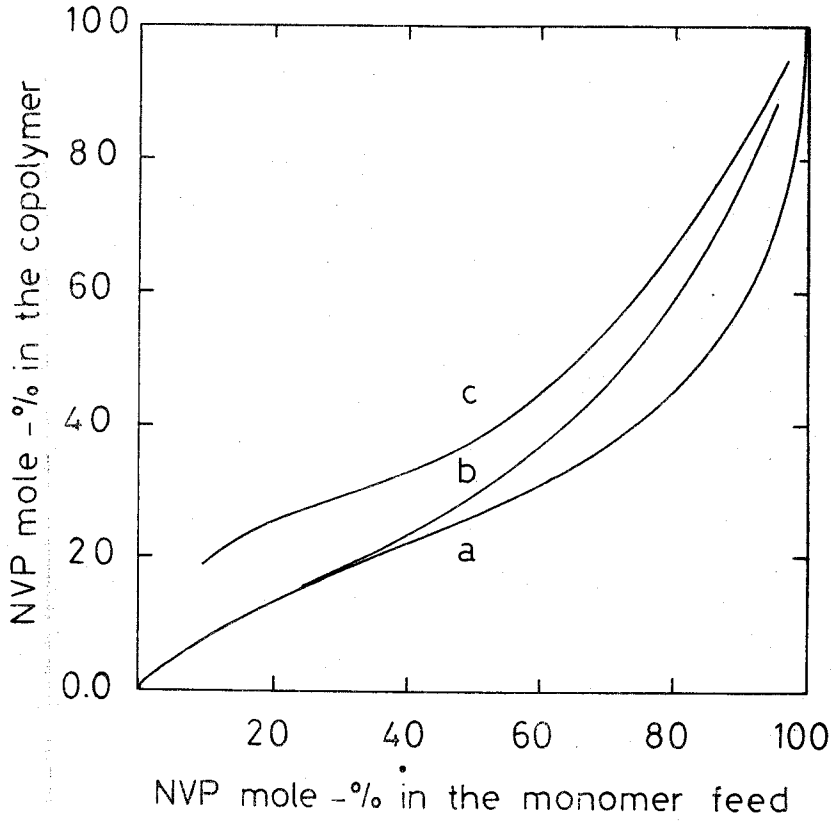

Fig. 1. Monomer/copolymer composition curves for N-vinylpyrrolidone (NVP) with methyl methacrylate (MMA)copolymerization in the presence of $ZnCl_2$ initiated by azobisisobutyronitrile.

a– $[ZnCl_2]/[NVP + MMA] = 0.0$;
b– " " " $= 0.05$;
c– " " " $= 0.1$.

Table 2.

r_1 and r_2 values of bulk copolymerization of N-vinylpyrrolidone (NVP) with methyl methacrylate (MMA) in the presence of zinc chloride at 65 °C.

$[ZnCl_2]/[NVP + MMA]$ (molar ratio)	r_1	r_2
0.00	0.044	1.866
0.05	0.088	1.444
0.10	0.297	0.858

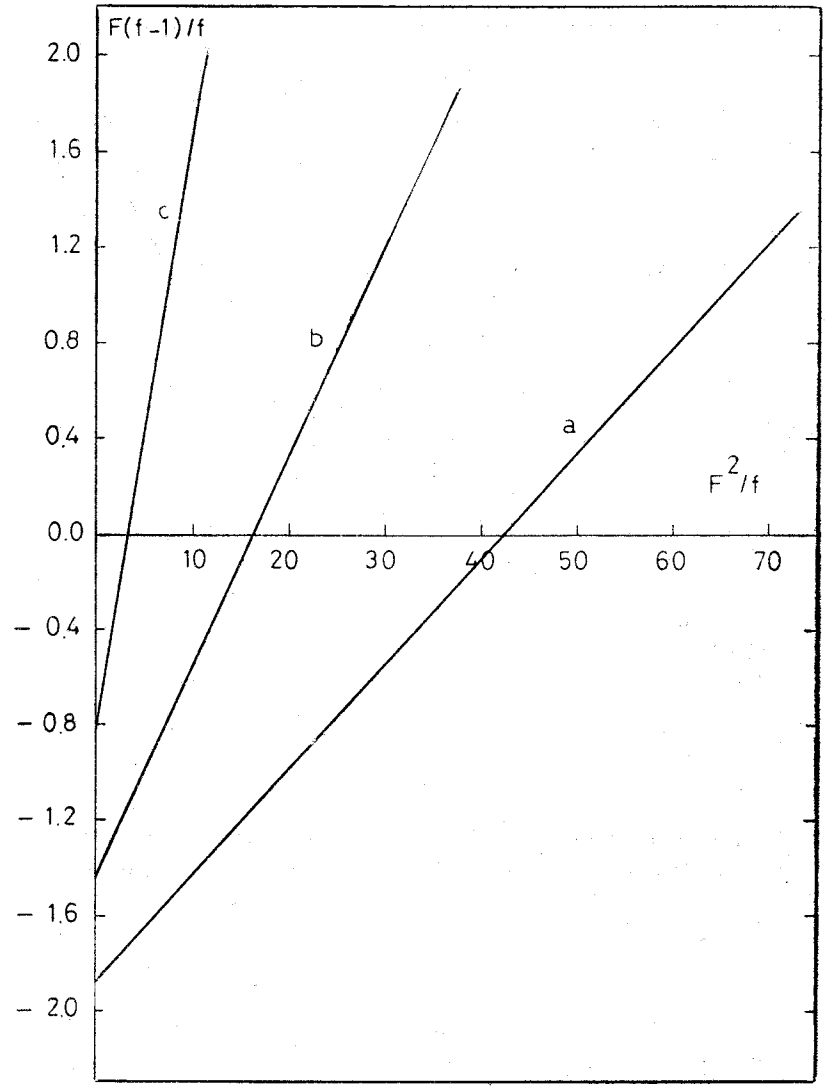

Fig. 2. Plots used to determine the relative reactivity ratios of N-vinylpyrrolidone (NVP) and methyl methacrylate (MMA) by Fineman and Ross method.

a– $[ZnCl_2]/[NVP + MMA] = 0.0$;
b– " " " $= 0.05$;
c– " " " $= 0.1$.

The increase in the value of r_1 (for NVP) and the decrease in the value of r_2 (for MMA) indicate that, the content of NVP during the copolymerization of NVP with MMA at the early stages of polymerization increases while the content of MMA decreases. It can be said that, the presence of $ZnCl_2$ increases the reactivity of NVP towards the copolymerization process, subsequently increases the flexibility of the resulting copolymer. Thus affording a better copolymer than that of poly (2-hydroxyethyl methacrylate)[12] which used in the manufacture of conventional soft contact lenses. Furthermore, usage of NVP-MMA copolymer can improve the tablets used for the detection of the ovulation in women[13].

REFERENCES

1. **B.M. Abo El-Khair,** Corrosion Prevention & Control, 1983, 30, 15.
2. **B.M. Abo El-Khair,** Corrosion Prevention & Control, 1982 (in press).
3. **A. Carpenter, S. Siggia and S. Carter,** Anal. Chem., 1976, 48, 225.
4. **E.K. Podval'naya, N.V. Meiya, D.E. Markosyan, M.E. Rozenberg, S.S. Khachatryan, L.V. Putilina and E.S. Midzhiferdzhyan,** Plast. Massy, 1978, 7, 7.
5. **Z.K. Boikova, L.I. Petrova, E.K. Podval'naya and N.V. Meiya,** Khim. Plastmass, 1979, 1, 15.
6. **S. Sh. Rashidova and M.D. Inoyatov,** Uzb. Khim. Zh., 1977, 3, 32.
7. **S.G. Starodubtsev, O.K. Boiko,** N.R. Pavlova and V.R. Ryabina, Kolloidn. Zh., 1982, 44 (2), 370.
8. **J. Burdy and W. Chernecki,** Can. J. Physiol. Pharmacol., 1968, 6, 46.
9. **I. Ismailov, A.M. Karimova,** A.T. Dzhalilov and M.A. Askarov, Dokl. Akad. Nauk Uzb. SSR, 1981, 7, 44.
10. **M.Z. El-Sabee, A.H. Ahmed and S. Mawaziny,** Eur. Polymer J., 1974, 10, 1149.
11. **M. Fineman and S.D. Ross,** J. Polym. Sci., 1950, 5, 259.
12. **S. Hosaka, A. Yamada, H. Tanzawa, T. Momose, H. Magatani and A. Nakajima,** J. Biomed. Mater Res., 1980, 14 (5), 557.
13. **W.Z. Polishuk,** Braz. Pedido PI 77 02, 481 (CI. A 61B10/00), 04 Apr. 1978, Brit. Appl. 76/1/, 020, 20 Apr. 1976.