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by

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TURQUIE

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SUMMARY

The copolymerization of N-vinylpyrrolidone (NVP) with ethyl methacrylate (EMA) was studied in the presence of $ZnCl_2$ as complexing agent. It was found that the monomer reactivity ratio of NVP (r_1) decreases since for EMA (r_2) increases with increasing the molar content of $ZnCl_2$ in the reaction medium. The variation of r_1 and r_2 from the characteristic point of view was explained in terms of the effects of $ZnCl_2$ on the reactivity of ethyl methacrylate and poly (ethyl methacrylate) radical. Consequently, the copolymerization reaction can be taken as a multicomponent system where nine reactions have to be taken into consideration.

INTRODUCTION

Copolymerization of two or more vinyl monomers ordinarily yields polymers whose composition differs from that of the starting monomer mixture. Therefore, much work has been reported on the determination of the relative reactivity ratios for many pairs of monomers¹⁻⁴. These ratios, r_1 and r_2 , are defined as the ratio k_{11}/k_{12} and k_{22}/k_{21} , respectively, where k_{11} is the rate of addition of a polymeric radical from monomer 1 to a molecule of monomer 1. The other k values are similarly defined, i.e., the first subscript refers to the radical and the second to the monomer with which the radical reacts. However, the medium of the polymerization reaction such as solvents and complexing agents play an important part on the values of copolymer parameters, i.e., r_1 and r_2 , thus affecting the structure of the obtained copolymers and hence their applications and uses.

The present work investigate the effect of $ZnCl_2$ as complexing agent on the copolymerization behaviour of N-vinylpyrrolidone and ethyl methacrylate.

EXPERIMENTAL

Materials

N-vinylpyrrolidone (NVP), ethyl methacrylate (EMA) and 2,2'-azobisisobutyronitrile (ABIN) were purified as described before^{5,6}. Anhydrous $ZnCl_2$ was heated for several hours at 150°C before use.

Copolymerization

The copolymerization of NVP with EMA in absence and in presence of $ZnCl_2$ initiated by ABIN at 65°C was carried out by the same method as was reported previously⁵. The percent conversion of the polymerizing system does not exceed 10 %.

Copolymer analysis

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

Monomer reactivity ratios determination

The relative reactivity ratios of N-vinylpyrrolidone (NVP) with ethyl methacrylate (EMA), r_1 and r_2 respectively, were calculated by applying the Fineman-Ross method⁷ using the following equation:

$$F(f-1)/f = r_1 F^2/f - r_2$$

where F is the molar ratio of NVP to EMA in the monomer feed and f is the molar ratio in the resulting copolymer. Thus a plot of $F(f-1)/f$ versus F^2/f yields a straight line of slope r_1 and intercept $-r_2$. The straight line is best drawn using the least mean square method.

IR Spectra

IR spectra of NVP and EMA in absence and in presence of $ZnCl_2$ were measured by the Nygel method using SP 200G grating spectrophotometer (Germany).

RESULTS AND DISCUSSION

Copolymerization of N-vinylpyrrolidone (NVP) with ethyl methacrylate (EMA) in bulk was investigated in the presence of $ZnCl_2$. 2,2'-

Azobisisobutyronitrile (ABIN), 0.2 % of the weight of the two monomers, was used as an initiator. Table 1 shows the bulk copolymerization of NVP with EMA in the presence of different concentrations of $ZnCl_2$

Table 1. Bulk copolymerization of N-vinylpyrrolidone (NVP) and ethyl methacrylate (EMA) in the presence of $ZnCl_2$ at 65°C initiated by azobisisobutyronitrile.

No.	Monomer composition (%) [NVP]	composition (%) [EMA]	N (%) in copolymer	Copolymer composition (%) [NVP]	[MEA]
a- $[ZnCl_2]/[NVP + EMA] = 0.0$					
1	90	10	7.40	59.31	40.69
2	80	20	6.50	52.21	47.79
3	60	40	5.20	41.88	58.12
4	40	60	4.20	33.89	66.11
5	10	90	0.90	07.32	92.18
b- $[ZnCl_2]/[NVP + EMA] = 0.05$					
1	90	10	5.70	45.85	54.15
2	80	20	4.00	32.29	67.71
3	60	40	3.80	30.69	69.31
4	50	50	1.80	14.60	85.40
5	40	60	1.25	10.15	89.85
c- $[ZnCl_2]/[NVP + EMA] = 0.1$					
1	90	10	5.55	44.66	55.34
2	80	20	3.10	25.08	74.92
3	70	30	2.40	19.44	80.56
4	50	50	2.30	18.63	81.37

initiated by ABIN at 65°C. Fig. 1 shows the monomer-copolymer composition curves for the copolymerization of NVP and EMA in the presence of $ZnCl_2$ at 65°C. It is clear that, the composition of NVP in the resulting copolymer decreases with increasing the concentration of $ZnCl_2$. For example, for NVP of 90 % molar ratio in the monomer feed, its content in the copolymer changes from 59.31 % to 44.66 % with raising the concentration of $ZnCl_2$ from zero to 0.1, i.e., $[ZnCl_2]/[NVP + EMA]$ changes from 0.0 to 0.1.

Table 2 shows the results of the relative reactivity ratios for the copolymerization of NVP with EMA in the presence of $ZnCl_2$. The results indicate that, the value of r_1 (for NVP) decreases from 0.068 to 0.026 with raising the molar concentration of $ZnCl_2$ from zero to 0.1. However, the value of r_2 (for EMA) increases from 0.879 to 6.330, in-

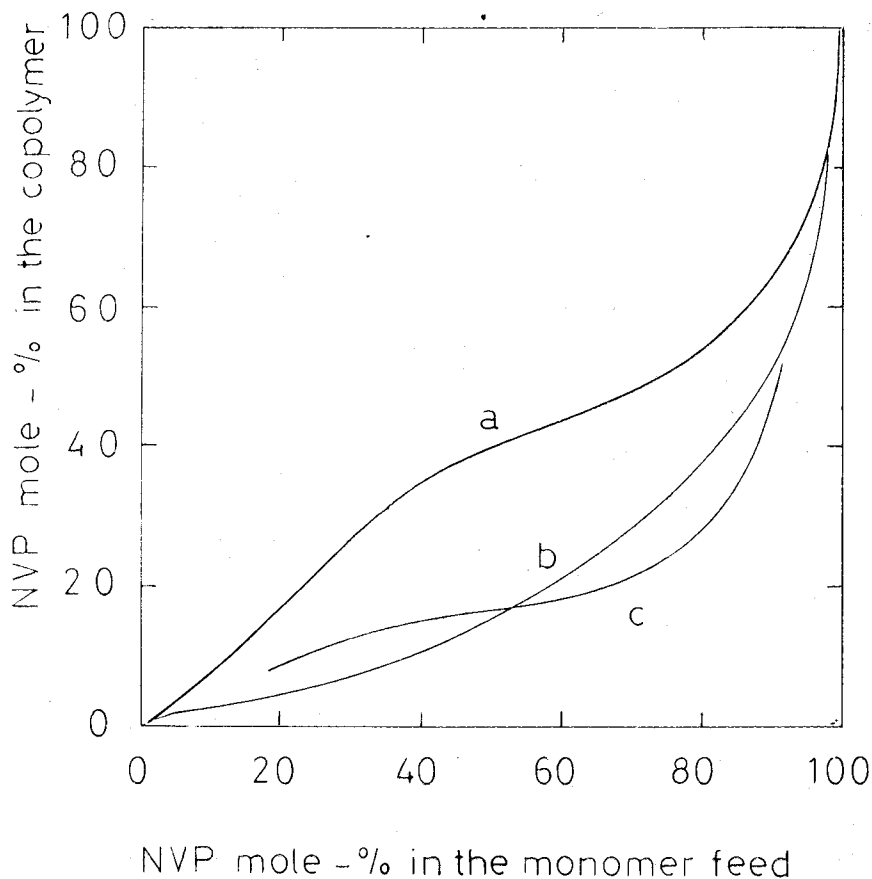


Fig. 1: Monomer/copolymer composition curves for N-vinylpyrrolidone (NVP) with ethyl methacrylate (EMA) copolymerization in the presence of $ZnCl_2$ initiated by azobisisobutyronitrile.

- a- $[ZnCl_2]/[NVP + EMA] = 0.0$;
- b- $[ZnCl_2]/[NVP + EMA] = 0.05$;
- c- $[ZnCl_2]/[NVP + EMA] = 0.10$

Table 2. The relative reactivity ratios of N-vinylpyrrolidone (NVP) and ethyl methacrylate (EMA) during their copolymerization in the presence of $ZnCl_2$ at $65^\circ C$.

$[ZnCl_2]/[NVP + EMA]$ (molar ratio)	r_1	r_2
0.00	0.068	0.879
0.05	0.025	4.328
0.10	0.026	6.330

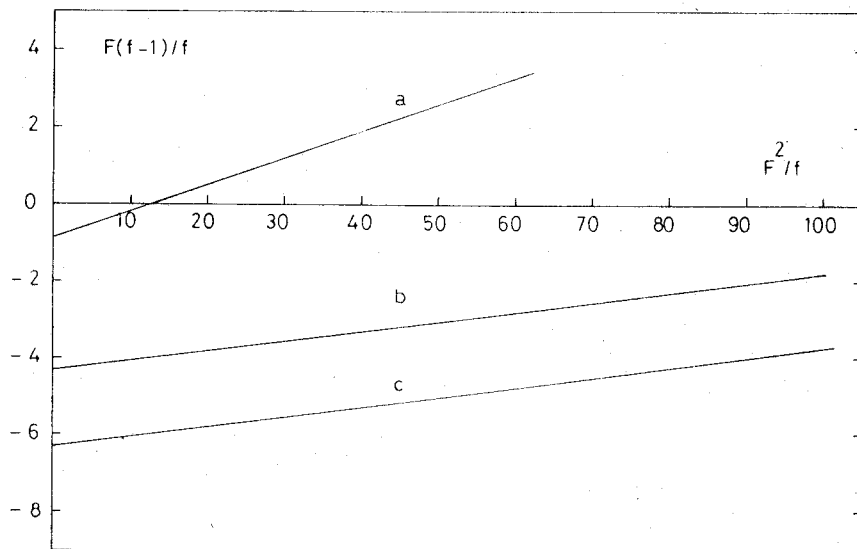


Fig. 2: Plots used to determine the relative reactivity ratios of N-vinylpyrrolidone (NVP) and ethyl methacrylate (EMA) by Fineman and Ross method.

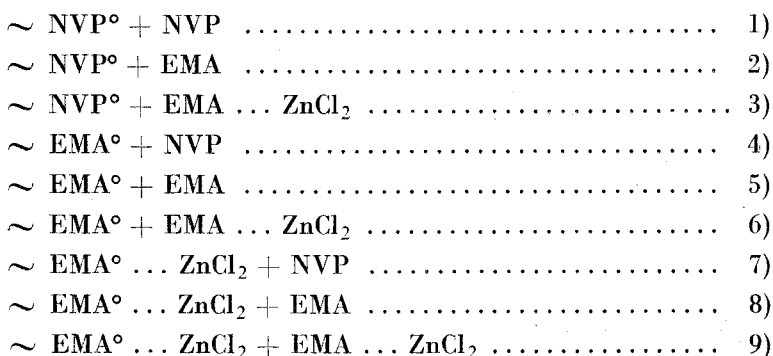
- a- $[ZnCl_2]/[NVP + EMA] = 0.0$;
 b- " " " = 0.05;
 c- " " " = 0.1.

dicating that the reactivity of EMA towards the copolymerization process increases in the presence of $ZnCl_2$.

According to the above results, it can be concluded that, $ZnCl_2$ increases the conjugation energy of the π -electrons of the C=C double bond of EMA monomer. This occurs within the interaction of $ZnCl_2$ with the carbonyl group of the methacrylic ester, i.e., $ZnCl_2$ forms complex through its coordination with the ester group of the ethyl methacrylate monomer. The formation of such complexity has a direct relation to the change in the relative reactivity ratios of NVP and EMA in the presence of $ZnCl_2$. This can be confirmed from the IR analysis. Thus, the IR spectrum of EMA with $ZnCl_2$ shows that the band due to C=O group of the methacrylic ester shifts towards higher frequency region, compared to that of the pure monomer. However, the IR spectrum of NVP with $ZnCl_2$ indicates that, the vinyl absorption bands of it remain

unchanged. Therefore, the increase in the value of r_2 (for EMA) as compared with the results of r_1 (for NVP) may arise from the simultaneous coordination of the ethyl methacrylate monomer and its radical by the zinc chloride molecule⁸.

On the basis of the previous results, the copolymerization of NVP with EMA in the presence of $ZnCl_2$ can be taken as a multicomponent system where the following nine types of elementary reactions have to be taken into consideration:



here NVP, EMA and $EMA \dots ZnCl_2$ are free and complexed monomers and $\sim NVP^\circ$, $\sim EMA^\circ$ and $\sim EMA^\circ \dots ZnCl_2$ are free and complexed propagating radicals.

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