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INFLUENCE OF STANNIC CHLORIDE ON THE COPOLYMERIZATION BEHAVIOUR OF VINYL ACETATE WITH ACRYLONITRILE

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ABSTRACT

The influence of $SnCl_4$ as modifier on the copolymerization of vinyl acetate (VAc) with acrylonitrile (AN) was studied in bulk using azobisisobutyronitrile as an initiator at 65°C. The kinetic results show that the overall copolymerization rates increase with increasing the concentration of $SnCl_4$ in the reaction medium. In addition, higher relative rates were obtained in the medium containing higher content of AN in the monomer feed. The copolymerization parameters of the two monomers approach to each other with raising the molar ratio of $SnCl_4$ in the system. Thus, the presence of $SnCl_4$ increases the reactivity of VAc towards the copolymerization process and hence it raises the alternating character of the resultant copolymers. Consequently, the copolymerization of VAc and AN in the presence of $SnCl_4$ can be suggested as a multicomponent system, since the monomers can form complexes with $SnCl_4$ as was observed from IR spectra and sixteen elementary polymerization reactions can be considered in the propagation process. The effect of modifier on the structure of the resultant VAc-AN copolymer as indicated from x-ray diffraction patterns are very useful in industry, since such copolymers are used for manufacture of membranes and for preparing fibrous activated carbon of high adsorption capacity and strength.

INTRODUCTION

Free radical polymerization is one of the most important methods of obtaining synthetic polymers. The kinetic parameters of the polymerization reaction depend principally on the nature of the monomer, the formed radical and the reaction medium. However, the polymerization reaction by free radical mechanism cannot be controlled easily, and this is the main disadvantage of this process. As it is known, the propagation reaction affects the rate of the overall polymerization process, the molecular weight of the polymer, the configuration of the macromolecules and the composition of the obtained copolymer. Recently, extensive studies have been published on homo-and copolymerization of vinyl monomers in presence of some inorganic salts, such as: LiCl, $MgCl_2$, $ZnCl_2$,

$AlBr_3$ and $SnCl_4$ (Kargin -1971, Seizo- 1976 and Kabanov- 1980). These salts form complexes with functional groups of such monomers and show a considerable effect on the reaction rate and the composition of the resulting polymers (Mokhtar 1984).

In the present work the effect of $SnCl_4$ as modifier on the copolymerization behaviour of vinyl acetate (VAc) and acrylonitrile (AN) in bulk was investigated. The study was performed by measuring the kinetics of the copolymerization reaction, the structure of the obtianed copolymers and by determining the copolymerization parameters.

EXPERIMENTAL

Materials:

Vinyl acetate (BDH) and acrylonitrile (BDH) were distilled before use. Azobisisobutyronitrile was purified by recrystallizing from ethanol (m.p. = 104 °C). Anhydrous stannic chloride (GDR) was used without further purification.

Copolymerization RATES:

Vinyl acetate (VAc) and acrylonitrile (AN) of different molar ratios were mixed with a calculated amount of azobisisobutyronitrile (AIBN) as an initiator and $SnCl_4$ as modifier. The mixture was introduced into a dilatometer, flushed with nitrogen, sealed and then immersed in a thermostat at 65 $\pm$ 0.1 °C. The decrease in the volume during initial polymerization was followed as a function of time.

Copolymer Analysis:

Copolymerization was carried out in pyrex ampoules. The reaction was stopped when 5–10 % conversion had taken place. The obtained polymers were purified by precipitation and dried for several hours in vacuum oven at 60 °C. The copolymer compositions were calculated on the basis of nitrogen content of the copolymers. Nitrogen analysis was performed at the central microanalytical unit, Cairo University.

Monomer Reactivity Ratios:

Copolymerization parameters were calculated by Fineman-Ross method (Ross-1950) and by Kele -Tüdos method (Tüdos-1975).

Infrared Spectroscopy:

Infrared spectra were measured using PERKIN-ELMER 398 Infrared Spectrophotometer.

X-Ray Diffraction:

X-ray diffraction patterns were obtained by an apparaturs of Philips (PW 1390 channel control and PW 1373 goniometer supply) using Cu-Kα beam by the film method.

RESULTS AND DISCUSSION

Fig (1) illustrates the results of the percent conversion-time for the copolymerization of vinyl acetate (VAc) and acrylonitrile (AN) of 20

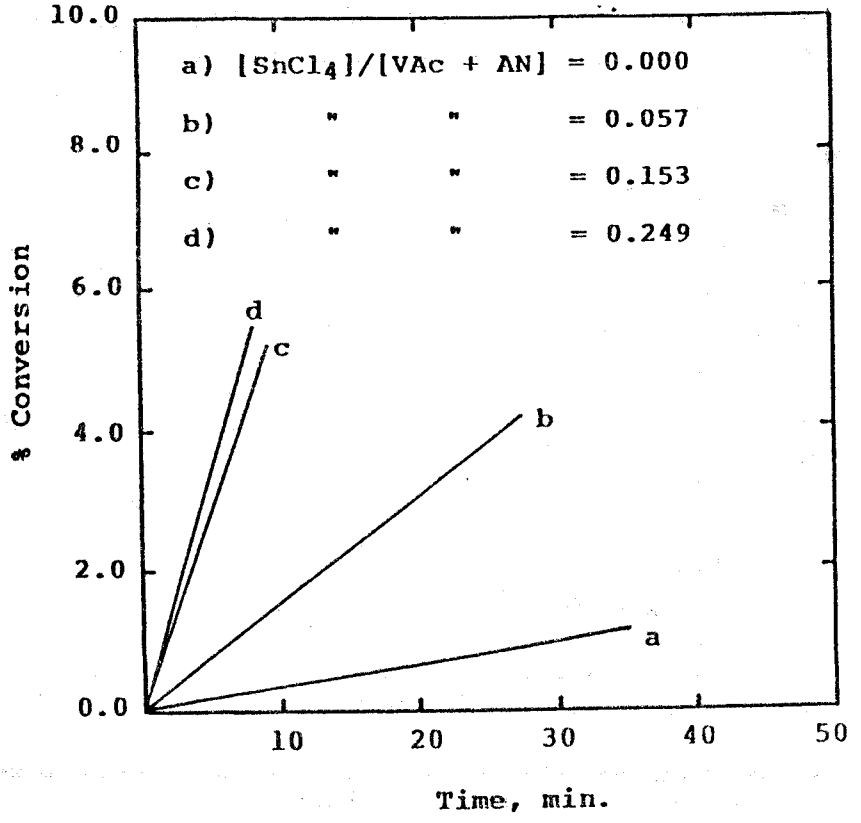

Fig. 1. Percent conversion-time curves for bulk copolymerization of vinyl acetate with acrylonitrile initiated by azobisisobutyronitrile in presence of $SnCl_4$ at 65°C. ([VAc]/ [AN] = 20 to 80 molar ratio).

to 80 molar ratio, respectively, in presence of different concentrations of $SnCl_4$. It was found that as the concentration of $SnCl_4$ increases the overall rate of the reaction increases. Fig. (2) shows the relative rates of VAc and AN copolymerization in absence and in presence of $SnCl_4$. Obviously, the relative rate of the copolymerization reaction increases about 19 times with increasing $SnCl_4$ content in the reaction medium from 0.0 to 0.249 (in molar ratio), i.e., $[SnCl_4]/(VAc+AN)$ changes from 0.0 to 0.249. These results indicate that, $SnCl_4$ is more effective on the reaction kinetics of VAc-AN copolymerization than $ZnCl_2$ (Mokhtar, 1984) .Similar behaviour was also observed for the copolymerization system of VAc and AN of 50 to 50 and of 70 to 30 molar ratio, respectively (cf. Figs. 2, 3 and 4). As shown, the copolymerization reaction of VAc and AN is more efficient to produce copolymer with higher rate with increasing the contents of both AN and $SnCl_4$ in the monomer feed. The same trend was reported previously for the copolymerization of some vinyl monomers in presence of Lewis acids (Kabonov, 1980).

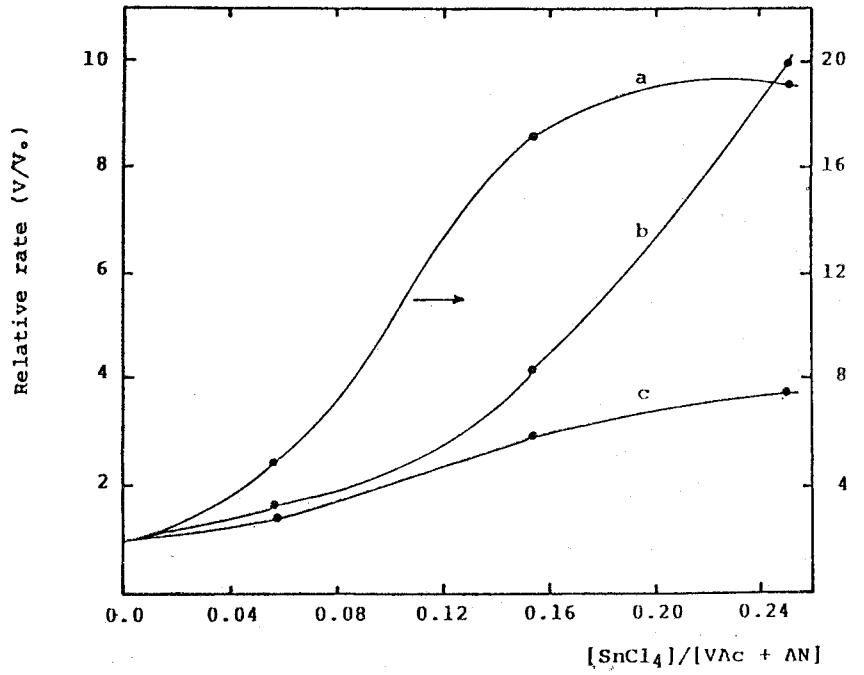

Fig. 2. Dependence of the relative rates of VAc-AN copolymerization in presence of azobisisobutyronitrile initiator on $SnCl_4$ concentration at 65°C.

a) [VAc]/ [AN] = 20 to 80 (molar ratio).
b) [VAc]/ [AN] = 50 to 50 (molar ratio).
c) [VAc]/ [AN] = 70 to 30 (molar ratio).

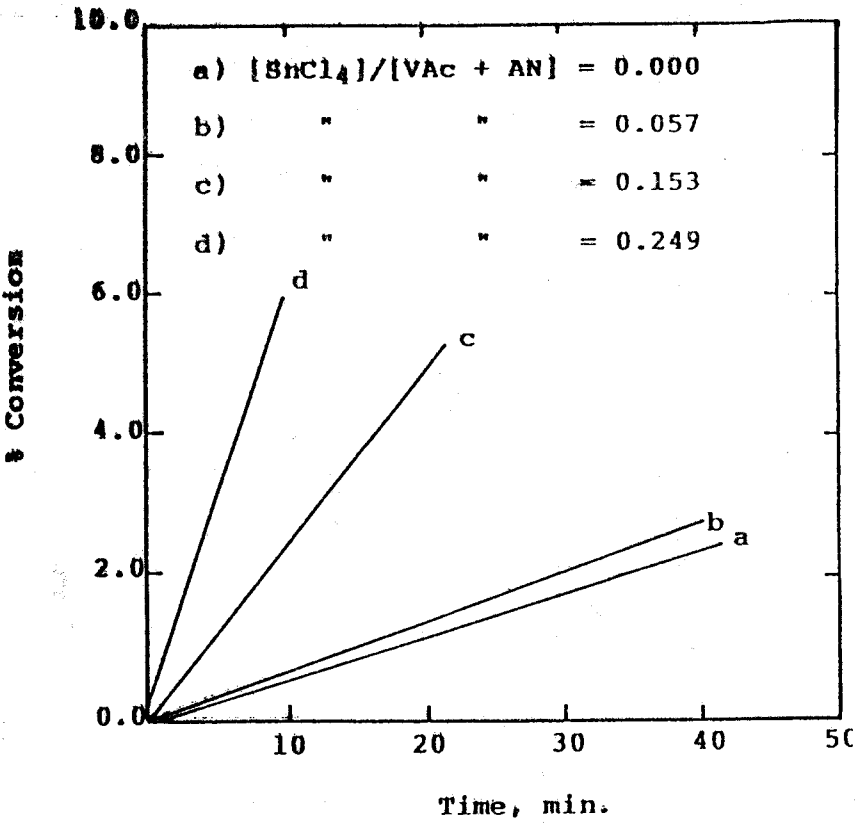

Fig. 3. Percent conversion-time curves for bulk copolymerization on vinyl acetate with acrylonitrile initiated by azobisisobutyronitrile in presence of $SnCl_4$ at 65°C ([VAc]/ [AN] = 50 to 50 molar ratio).

The effect of $SnCl_4$ on the reactivity behaviour of the two monomers during their copolymerization can be confirmed from IR spectra. The IR spectrum of VAc in absence and in presence of various concentrations of $SnCl_4$ shows that (Fig. 5) there is a shift in the frequency of the absorption band of the ester group from 1760 cm^{-1} to 1755 cm^{-1}. Also, $SnCl_4$ intensifies the absorption bands of VAc monomer.

Fig. (6) illustrates the IR spectrum of AN in presence of $SnCl_4$. As shown the absorption band of nitrile group at 2270 cm^{-1} undergo shift to 2260 cm^{-1}. In addition, $SnCl_4$ intensifies the absorption band of the monomer. The IR results suggest that, $SnCl_4$ forms complex with the functional group of each monomer. Thus, it raises their polarity and hence

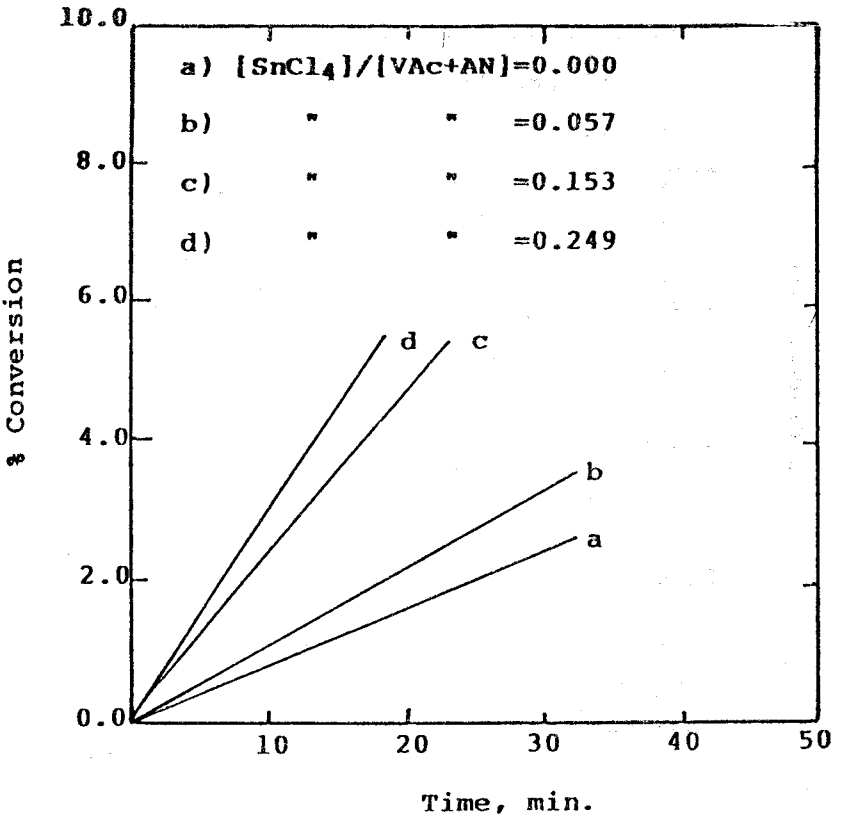

Fig. 4. Percent conversion-time curves for bulk copolymerization of vinyl acetate wth acrylonitrile initiated by azobisisobutyronitrile in presence of $SnCl_4$ at 65°C. ([VAc]/ [AN] = 70 to 30 molar ratio).

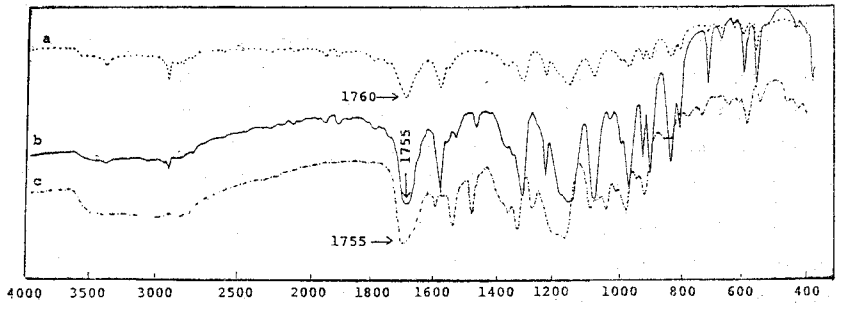

Fig. 5. IR spectra of vinyl acetate: a) in absence of $SnCl_4$, b) in one drop of $SnCl_4$, and c) in excess of $SnCl_4$.

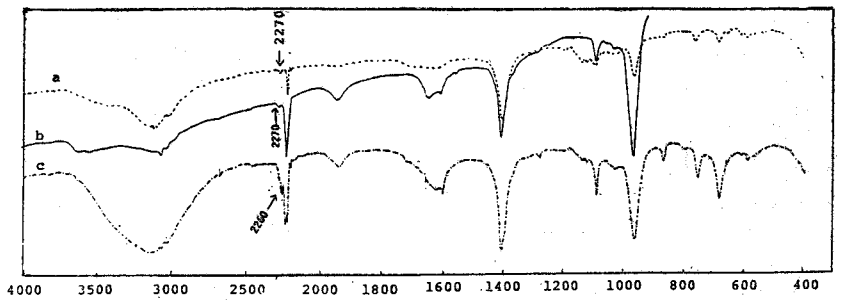

Fig. 6. IR spectra of acrylonitrile: a) in absence of $SnCl_4$, b) in one drop of $SnCl_4$, and c) in excess of $SnCl_4$.

this led to an increase in the conjugation energy of the π-electron of the C=C of the vinyl group. Consequently, $SnCl_4$ increases the reactivity of the two monomers towards the copolymerization reaction.

The action of $SnCl_4$ on the structure of the resulting VAc-AN copolymer was studied from X-ray measurements. Figs. (7) and (8) show the X-ray diffraction diagrams for the copolymer samples obtained during the copolymerization of VAc with AN of 30 to 70 and 80 to 20 molar ratios, respectively, with different concentrations of $SnCl_4$. It was observed that (Fig. 7) in absence of $SnCl_4$ strong reflections appear at $2\theta = 12.3°$, 22.3 and 24.8° and small reflections appear at $2\theta = 28.6°$ and 29.4° (Fig. 7a). However in presence of $SnCl_4$ (Fig. 7b and 7c), the reflection at $2\theta = 22.3°$ and above this range disappear and a new broaden area appears with a maximum reflection at about $2\theta = 21°$. Also, a difference in the X-ray diffraction patterns (Fig. 8) was also observed for VAc-AN copolymer samples prepared from a system of VAc with AN of 80 to 20 (in molar ratio) in absence and in presence of $SnCl_4$. Therefore, it was suggested that $SnCl_4$ affects the structure of the obtained VAc-AN copolymer., ie., order of monomeric unit arrangements in the copolymer chains. Consequently, it affects the properties of the resultant copolymers. This is very important and useful in industry, since VAc-AN copolymers are used for manufacture of membranes (Takao, 1981) and for preparing fibrous activated carbon of high adsorption capacity and strength (Kazuo, 1981).

The composition of the two monomers and the resultant copolymers at the initial stages of copolymerization, i.e. < 10 % conversion, for the

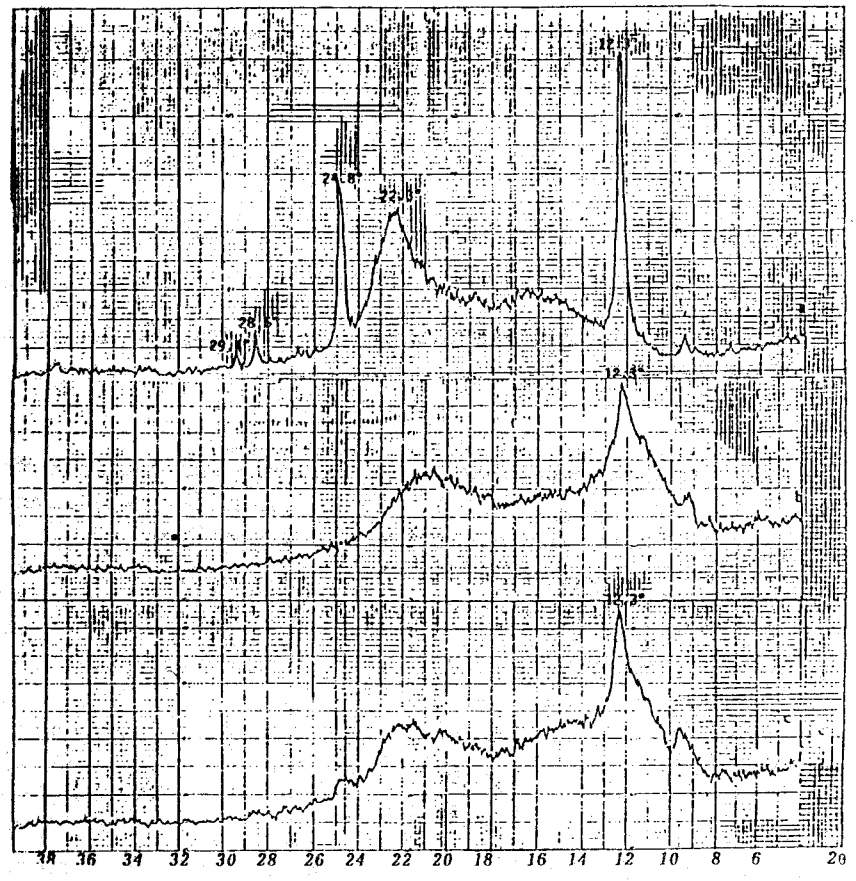

Fig. 7. X-ray diffraction curves of vinyl acetate and acrylonitrile copolymer formed during copolymerization of VAc with AN of 30 to 70 molar ratio in presence of $SnCl_4$ at 65°C using azobisisobutyronitrile as an initiator:

a) $[SnCl_4]/[VAc + AN] = 0.00$.
b) $[SnCl_4]/[VAc + AN] = 0.153$.
c) $[SnCl_4]/[VAc + AN] = 0.249$.

copolymerizing system of VAc and AN in presence of different concentrations of $SnCl_4$ are summerized in Table (1) (A-C). Fig. (9) illustrates the monomer-copolymer composition curves covering the whole range of composition for VAc and AN bulk copolymerization in presence of $SnCl_4$ initiated by AIBN at 65 °C. The concentration of $SnCl_4$ (in molar ratio) to VAc and AN was 0.00, 0.057 and 0.153. It was observed that the content of VAc in the copolymer increases with increasing the concent-

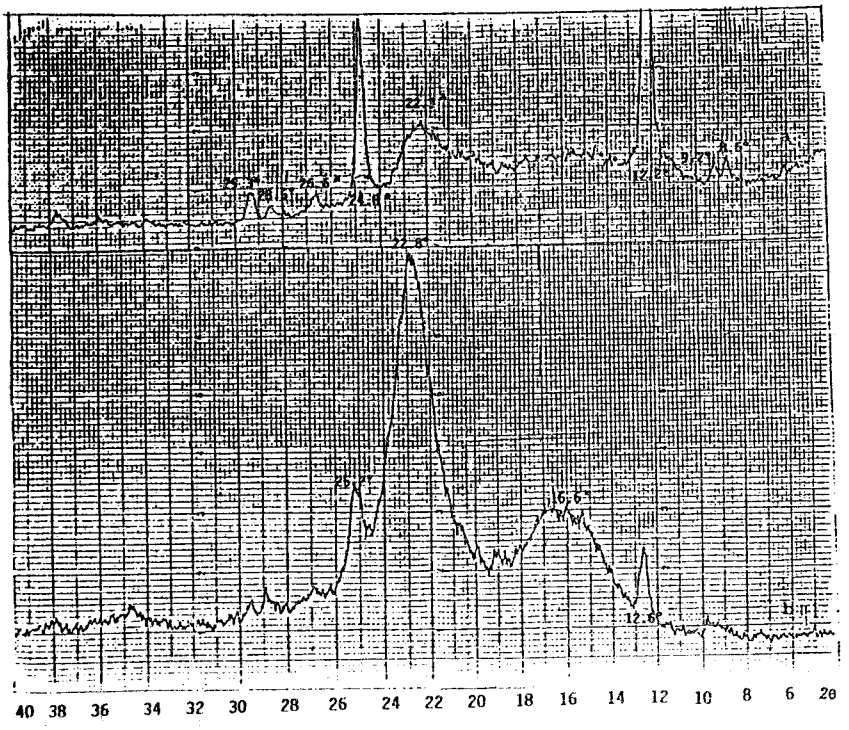

Fig. 8. X-ray diffraction curves of vinyl acetate and acrylonitrile copolymer formed during copolymerization of VAc with AN of 80 to 20 molar ratio in presence of $SnCl_4$ at 65°C using azobisisobutyronitrile as an initiator:

a) $[SnCl_4]/[VAc + AN] = 0.00$.
b) $[SnCl_4]/[VAc + AN] = 0.153$.

Table 1. Copolymerization Of Vinyl Acetate (VAc) With Acrylonitrile (AN) In Presence Of $SnCl_4$ At 65°C Initiated By Azobisisobutyronitrile. (A) $[SnCl_4]/[VAc + AN] = 0.00$

No.	Monomer Composition (%)		N % in copolymer	Copolymer Composition (%)	
	[VAc]	[AN]		[VAc]	[AN]
1	10	90	22.86	8.69	91.31
2	20	80	19.31	18.44	81.56
3	30	70	21.38	12.62	87.38
4	40	60	20.21	15.85	84.15
5	50	50	16.36	27.44	72.56
6	60	40	15.89	28.96	71.04
7	70	30	19.20	18.75	81.25
8	80	20	13.25	37.95	62.05
9	90	10	5.27	71.20	28.80

Table 1. [Cont.]
(B) $[SnCl_4]/[VAc + AN] = 0.057$

No.	Monomer Composition (%)		N% in copolymer	Copolymer Composition (%)	
	[VAc]	[AN]		[VAc]	[AN]
1	10	90	19.02	19.29	80.71
2	15	85	16.92	25.65	74.35
3	20	80	15.65	30.20	69.98
4	35	65	12.76	39.72	60.28
5	50	50	10.96	46.47	53.53
6	60	40	9.91	50.62	49.38
7	70	30	8.81	55.16	44.84
8	90	10	5.19	71.58	28.42

Table 1. [Cont.] (C) $[SnCl_4]/[VAc + AN] = 0.153$

No.	Monomer Composition (%)		N % in copolymer	Copolymer Composition (%)	
	[VAc]	[AN]		[VAc]	[AN]
1	10	90	19.02	19.29	80.71
2	20	80	15.37	30.65	69.35
3	30	70	13.108	38.46	16.54
4	40	60	11.44	44.63	55.37
5	50	50	10.025	50.17	49.83
6	60	40	8.68	55.73	44.27
7	70	30	7.255	61.93	38.07
8	80	20	5.57	69.76	30.24
9	90	10	3.349	80.93	19.07

ration of $SnCl_4$ in the monomer feed. The data of Table (1) were analyzed to determine the copolymerization parameters of VAc and AN using Fineman-Ross method (Ross-1950) and Kelen-Tüdos method (Tüdos-1975). Figs (10) and (11 a, b) are the Fineman-Ross and Kelen-Tüdos plots, respectively, for the copolymerization of VAc and AN in presence of $SnCl_4$. The result of the monomer reactivity ratios r_1 for VAc and r_2 for AN are represented in Table (2). As shown, the copolymerization parameters are of the same values by applying the two methods. From Table (2), the value of r_1 for VAc increases with raising the concentration of $SnCl_4$ in the reaction medium. It increases from 0.044 to 0.370 with increasing the molar ratio of $SnCl_4$ from 0.0 to 0.153, i.e., $[SnCl_4]/[VAc+AN]$ changes from 0.0 to 0.153. However, the value of r_2 for AN decreases with the addition of $SnCl_4$ in the copolymerizing system. Moreover, the values of the copolymerization parameters of the two monomers approach to each other with increasing the concentration of $SnCl_4$ in the reaction medium ($r_1 = r_2 = 0.37$), indicating that, $SnCl_4$

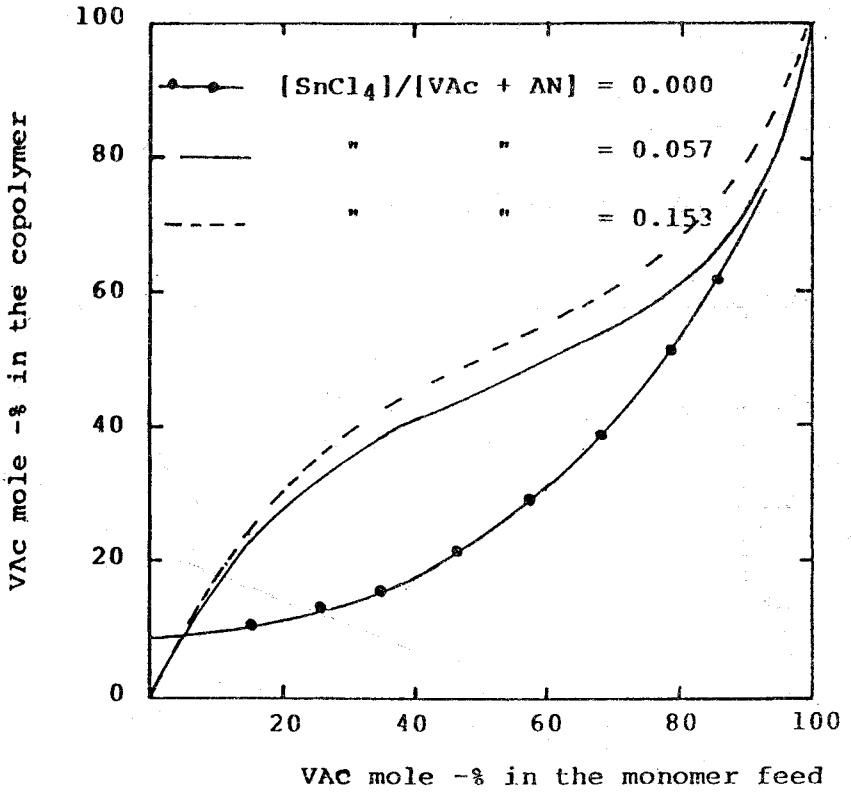

Fig. 9. Monomer-copolymer composition curves for vinyl acetate with acrylonitrile copolymerization in presence of $SnCl_4$ initiated by azobisisobutyronitrile ([AIBN] = 5×10^{-3} mol/litre) at 65°C.

may raise the alternating character of the resultant copolymers (Kabanov, 1980). The increase in the value of r_1 and the decrease in the value of r_2 indicate that, the content of VAc during copolymerization of VAc with AN, at the early stages of polymerization, increases while the content of AN decreases. Considering these results, we can conclude that the presence of $SnCl_4$ increases the reactivity of VAc towards the copolymerization process and the resultant copolymers are of alternating character.

On the basis of the obtained results, the copolymerization of VAc and AN in the presence of $SnCl_4$ can be considered as a multicomponent system, since the two monomers can form complexes with $SnCl_4$ and the

following sixteen elementary polymerization reactions have to be taken into consideration during the propagation process:

(i) $\sim \text{VAc}^{\cdot} + \text{VAc} \xrightarrow{\text{Kp1}} \sim \text{VAc} - \text{VAc}^{\cdot}$

(ii) $\sim \text{VAc}^{\cdot} + \text{AN} \xrightarrow{\text{Kp2}} \sim \text{VAc} - \text{AN}^{\cdot}$

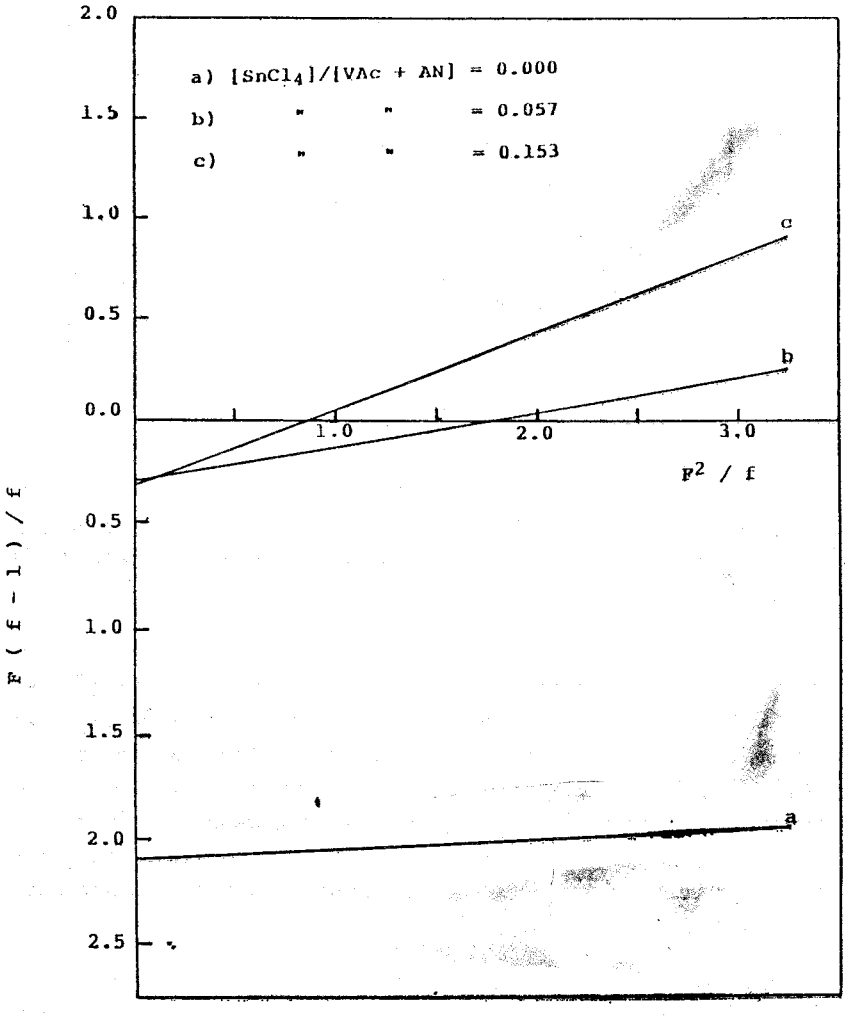

Fig. 10. Bulk copolymerization of vinyl acetate with acrylonitrile in presence of $SnCl_4$. Plots used to determine relative reactivity ratios by the method of Fineman and Ross.

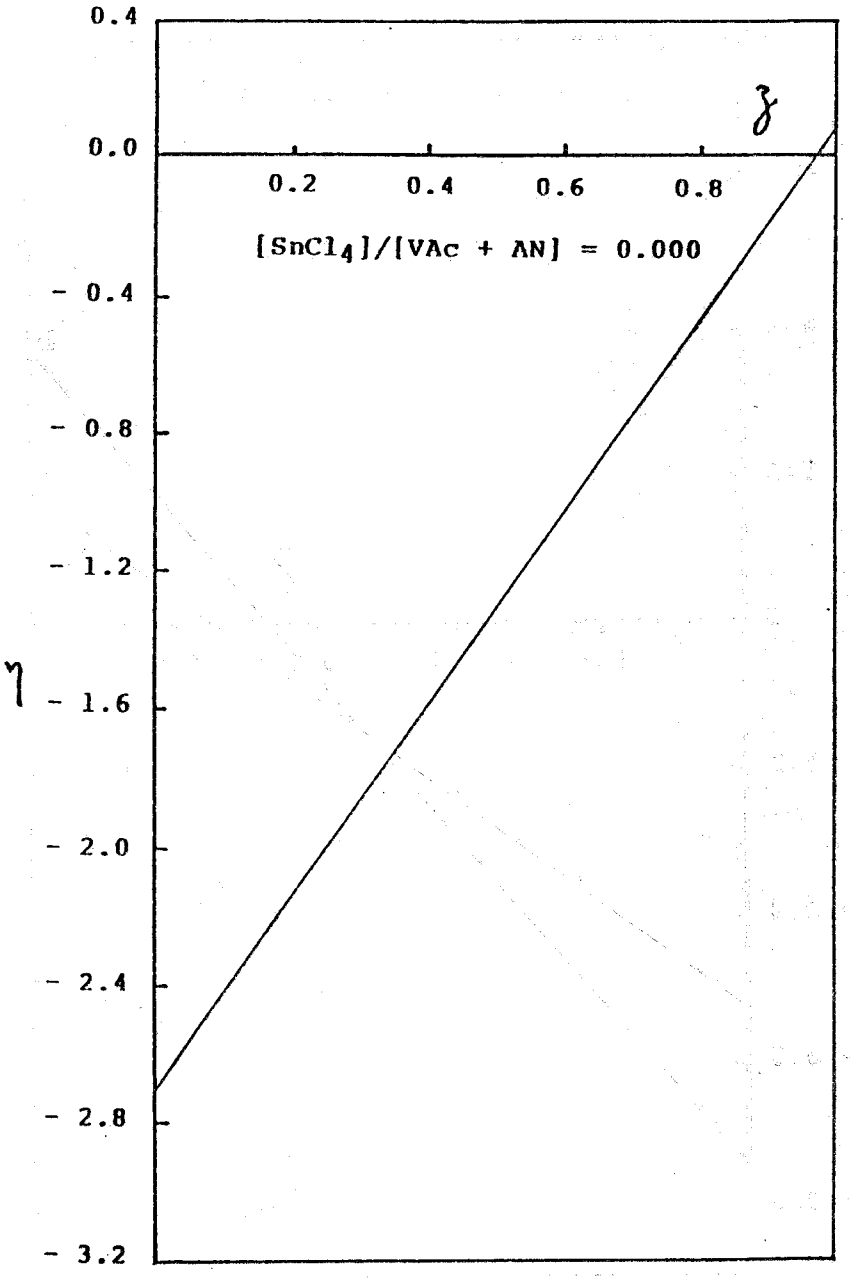

Fig. 11a. Bulk copolymerization of vinyl acetate with acrylonitrile in absence of $SnCl_4$. Plots used to determine relative reactivity ratios by the method of Kelen and Tüdos.

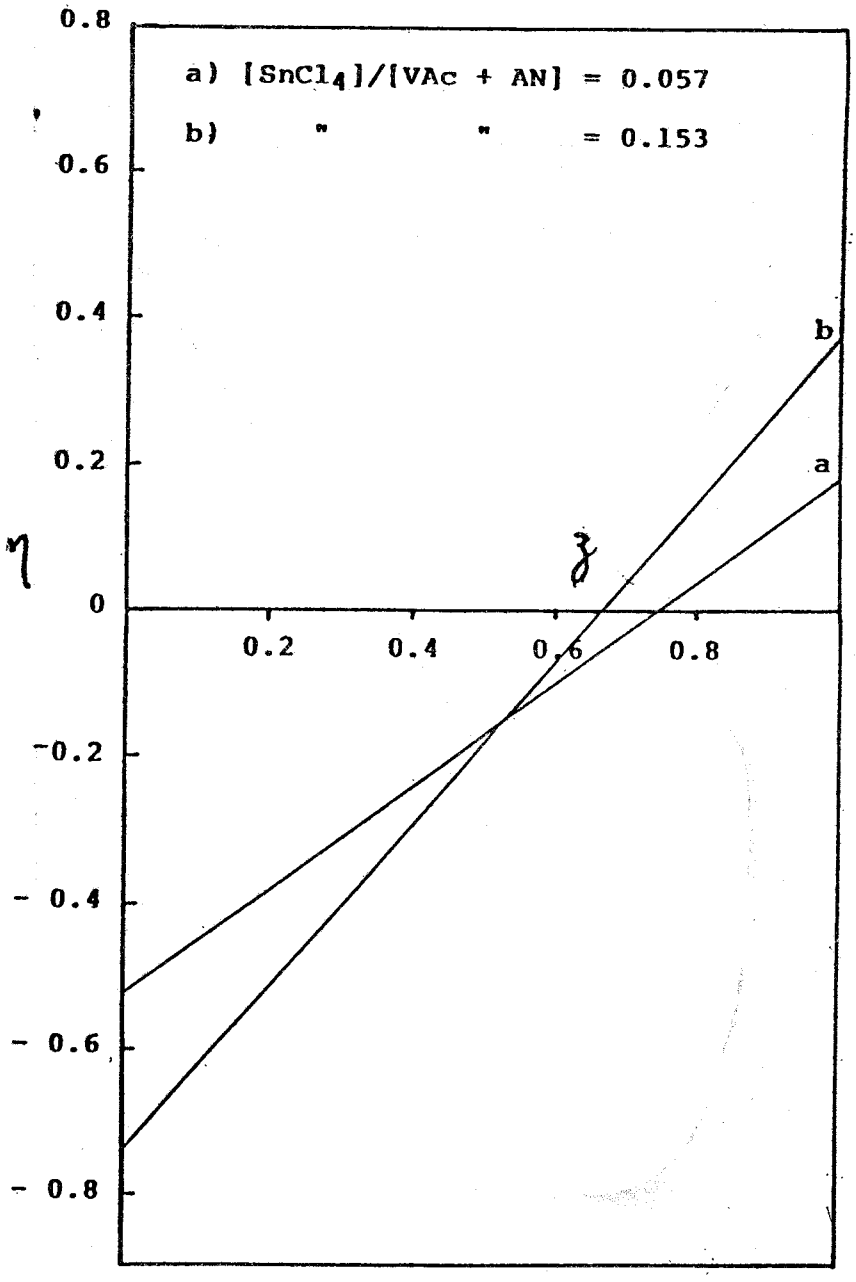

Fig. 11b. Bulk copolymerization of vinyl acetate with acrylonitrile in presence of $SnCl_4$. Plots used to determine relative reactivity ratios by the method of Kelen and Tüdos.

Table 2. Apparent Reactivity Ratios For The Bulk Copolymerization Of Vinyl Acetate (VAc) And Acrylonitrile (AN) in Different Cincentrations Of $SnCl_4$ At 65°C

$[SnCl_4]/[VAc+AN]$	Fineman-Ross		Kelen-Tüdos	
	r_{VAc}	r_{AN}	r_{VAc}	r_{AN}
0.00	0.044	2.110	0.045	2.340
0.057	0.180	0.358	0.180	0.359
0.153	0.373	0.370	0.370	0.370

(iii) $\sim VAc^{\cdot} + VAc \ldots SnCl_4 \xrightarrow{Kp3} \sim VAc - VAc^{\cdot} \ldots SnCl_4$

(iv) $\sim VAc^{\cdot} + AN \ldots SnCl_4 \xrightarrow{Kp4} \sim VAc - AN^{\cdot} \ldots SnCl_4$

(v) $\sim VAc^{\cdot} \ldots SnCl_4 + VAc \xrightarrow{Kp5} \sim VAc - VAc^{\cdot} \ldots SnCl_4$

(vi) $\sim VAc^{\cdot} \ldots SnCl_4 + AN \xrightarrow{Kp6} \sim VAc - AN^{\cdot} \ldots SnCl_4$

(vii) $\sim Vac^{\cdot} \ldots SnCl_4 + VAc \ldots SnCl_4 \xrightarrow{Kp7} \sim VAc(SnCl_4) - VAc^{\cdot} \ldots SnCl_4$

(viii) $\sim VAc^{\cdot} \ldots SnCl_4 + AN \ldots SnCl_4 \xrightarrow{Kp8} \sim VAc\,(SnCl_4) - AN^{\cdot} \ldots SnCl_4$

(ix) $\sim AN^{\cdot} + VAc \xrightarrow{Kp9} \sim AN - VAc^{\cdot}$

(x) $\sim AN^{\cdot} + AN \xrightarrow{Kp10} \sim AN - AN^{\cdot}$

(xi) $\sim AN^{\cdot} + VAc \ldots SnCl_4 \xrightarrow{Kp11} \sim AN - VAc^{\cdot} \ldots SnCl_4$

(xii) $\sim AN^{\cdot} + AN \ldots SnCl_4 \xrightarrow{Kp12} \sim AN - AN^{\cdot} \ldots SnCl_4$

(xiii) $\sim AN^{\cdot} \ldots SnCl_4 + VAc \xrightarrow{Kp13} \sim AN - VAc^{\cdot} \ldots SnCl_4$

(xiv) $\sim AN^{\cdot} \ldots SnCl_4 + AN \xrightarrow{Kp14} \sim AN^{\cdot} - AN \ldots SnCl_4$

(xv) $\sim AN^{\cdot} \ldots SnCl_4 + VAc \ldots SnCl_4 \xrightarrow{Kp15} \sim AN\,(SnCl_4) - VAc^{\cdot} \ldots SnCl_4$

(xvi) $\sim AN^{\cdot}\ldots SnCl_4 + AN\ldots SnCl_4 \xrightarrow{Kp16} \sim AN\,(SnCl_4)—AN^{\cdot}\ldots SnCl_4$

Where VAc, AN, VAc ... $SnCl_4$ and AN ... $SnCl_4$ are free and complexed monomers; Kpi is the propagation rate constant and $\sim VAc,^{\cdot}$ $\sim AN,^{\cdot} \sim VAc^{\cdot}\ldots SnCl_4$ and $\sim AN^{\cdot}\ldots SnCl_4$ are free and complexed propagating radicals.

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