NOTES

Influence of Stannic Chloride on the Copolymerization Behaviour of Vinyl Acetate with Acrylonitrile

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Free radical polymerization is one of the most important methods of obtaining synthetic polymers. However, the polymerization reaction by free radical mechanism cannot be controlled easily, and this is the main disadvantage of this process. As 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. Extensive studies have been published on homo- and copolymerization of vinyl monomers in presence of some inorganic salts, such as: LiCl , ZnCl_2 , AlBr_3 and SnCl_4 .^{1–3} These salts form complexes with functional groups of such monomers and show considerable effect on the reaction rate and composition of the resulting polymers.⁴

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

Copolymerization rates were measured

using a dilatometer. The copolymer compositions were calculated on the basis of nitrogen content of the copolymers. Copolymerization parameters were calculated by the Fineman–Ross method⁵ and the Kelen–Tüdös method.⁶ The infrared spectra were recorded by a double beam spectrophotometer Perkin-Elmer 398. X-ray diffraction patterns were obtained by philips apparatus (pW 1390 channel control and pW 1373 goniometer supply) using a Cu-K_α beam by the film method.

Figure 1 illustrates the results of the percent conversion-time for the copolymerizations of vinyl acetate (VAc) and acrylonitrile (AN) of 20 to 80 mol% at various concentrations of SnCl_4 . It was found that as the concentration of SnCl_4 increased, the overall rate of the reaction increased. Figure 2 shows the relative rates of VAc and AN copolymerization in the absence and 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. These results indicate that SnCl_4 is more effective on the reaction kinetics of VAc–AN copolymerization than ZnCl_2 .⁴ Similar behaviour was also observed for the

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Figure 1. Percent conversion-time curves for bulk copolymerization of vinyl acetate with acrylonitrile (20 to 80 mol%) initiated by azobisisobutyronitrile in the presence of SnCl_4 at 65°C .

Figure 2. Dependence of the relative rates of VAc-AN copolymerization in the presence of azobisisobutyronitrile initiator on SnCl_4 concentration at 65°C : a, $[\text{VAc}]/[\text{AN}] = 20$ to 80 mol%; b, $[\text{VAc}]/[\text{AN}] = 50$ to 50 mol%; c, $[\text{VAc}]/[\text{AN}] = 70$ to 30 mol%.

copolymerization system of VAc and AN of 50 to 50 and of 70 to 30 mol%, respectively (*cf.* Figures 2 and 3). In addition the copolymerization reaction of VAc and AN is more efficient to produce a copolymer with a higher rate with increasing the content of both AN and SnCl_4 in the monomer feed. The same trend was reported previously for the copolymerizations of some vinyl monomers in

Figure 3. Percent conversion-time curves for bulk copolymerization of vinyl acetate with acrylonitrile initiated by azobisisobutyronitrile in the presence of SnCl_4 at 65°C : —, $[\text{VAc}]/[\text{AN}] = 50$ to 50 mol%; ----, $[\text{VAc}]/[\text{AN}] = 70$ to 30 mol%.

presence of Lewis acids.³

The effect of SnCl_4 on the reactivity behaviour of comonomers during their copolymerization can be confirmed from IR spectra. The IR spectrum of VAc in presence of SnCl_4 shows that there is a shift in the frequency of the absorption band of the ester group from 1760 cm^{-1} to 1755 cm^{-1} . Also, the absorption band of nitrile group of AN at 2270 cm^{-1} undergoes a shift to 2260 cm^{-1} in presence of SnCl_4 . These results suggest that SnCl_4 forms complex with the functional group of each monomer. Thus, it raises their polarity, leading to increased conjugation energy of the π -electron of the $\text{C}=\text{C}$ 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 by X-ray measurements. Figure 4 shows the X-ray diffraction diagrams for the copolymer samples obtained during the copolymerization of VAc with AN of 30 to 70 with various concentrations of SnCl_4 . It was observed that in the absence of SnCl_4 strong reflections

Figure 4. X-Ray diffraction curves of vinyl acetate and acrylonitrile copolymer formed during copolymerization of VAc with AN of 30 to 70 in the presence of SnCl_4 at 65°C using azobisisobutyronitrile as an initiator: a, $[\text{SnCl}_4]/[\text{VAc} + \text{AN}] = 0.00$; b, $[\text{SnCl}_4]/[\text{VAc} + \text{AN}] = 0.153$; c, $[\text{SnCl}_4]/[\text{VAc} + \text{AN}] = 0.249$.

appeared at $2\theta = 12.3^\circ$, 22.3° and 24.8° and small reflections appeared at $2\theta = 28.6^\circ$ and 29.4° (Figure 4a). However in presence of SnCl_4 (Figures 4b and 4c), the reflection at $2\theta = 22.3^\circ$ and above this range disappeared and a new broaden area appeared with a maximum reflection at about $2\theta = 21^\circ$. Therefore, SnCl_4 may affect the structure of the obtained VAc-AN copolymer, *i.e.*, 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 the manufacture of membranes⁷ and preparing fibrous activated carbon of high adsorption capacity and strength.⁸

The compositions of the comonomers and resultant copolymers at the initial stages of polymerization, *i.e.*, $< 10\%$ conversion, for the copolymerizing system of VAc and AN in

Figure 5. Monomer-copolymer composition curves for vinyl acetate with acrylonitrile copolymerization in the presence of SnCl_4 initiated by azobisisobutyronitrile ($[\text{AIBN}] = 5 \times 10^{-3} \text{ mol l}^{-1}$) at 65°C .

Table I. Apparent reactivity ratios for the bulk copolymerization of vinyl acetate (VAc) and acrylonitrile (AN) in different concentrations of SnCl_4 at 65°C

$[\text{SnCl}_4]$	Fineman-Ross		Kelen-Tüdös	
	$[\text{VAc} + \text{AN}]$	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

^a In molar ratio.

presence of various concentrations of SnCl_4 are shown in Figure 5. It was observed that the content of VAc in the copolymer increases with increasing the concentration of SnCl_4 in the monomer feed. These data were analyzed to determine the apparent copolymerization parameters of VAc and AN using the Fineman-Ross method⁵ and Kelen-Tüdös method.⁶ The results of the apparent monomer reactivity ratios r_1 for VAc and r_2 for AN are represented in Table I. As shown the apparent copolymerization parameters are similar in the two methods. From Table I the value of r_1 for VAc increases on raising the concentration of SnCl_4 in the reaction medium. It increases

from 0.044 to 0.370 on increasing the concentration of SnCl_4 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 apparent copolymerization parameters of the two monomers approach each other with increasing concentration of SnCl_4 in the reaction medium ($r_1 = r_2 = 0.37$), indicating that SnCl_4 increases the reactivity of VAc monomer towards the copolymerization process.

On the basis of the obtained results, the copolymerization of VAc and AN in the presence of SnCl_4 can be considered a multicomponent system, since the two monomers can form complexes with SnCl_4 and sixteen elementary polymerization reactions have to be taken into consideration during the propa-

gation process.

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