Polymer Bulletin 18, 9–12 (1987)

Polymer Bulletin

Effect of $ZnCl_2$ on the copolymerization of acrylonitrile with N-2-chlorophenylmaleimide

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SUMMARY

The effect of $ZnCl_2$ addition on the reactivity ratios of the system acrylonitrile (AN)-N-2-Chlorophenylmaleimide (2CMI) has been investigated. It has been found that the addition of small amount of $ZnCl_2$ doubles the reactivity of AN while drastically decreasing that of the 2CMI. The viscosity of the copolymers has been measured and was found to decrease with increasing the maleimide and the $ZnCl_2$ concentrations.

INTRODUCTION

The rate constants of chain propagation in radical polymerization are determined mainly by the chemical structure of the monomer (at given temperature, pressure, solvent, and initiator), however, the situation changes if substances capable of interacting specifically with monomers and radicals are introduced into the reaction medium. The complexation of monomers and radicals with Lewis acids is one of the important types of such interactions (KABANOV 1980).

The radical polymerization of acrylonitrile in the presence of Lewis acids has been intensively investigated (IMOTO 1963,-GAYLORD 1968, 1970, PATNAIK 1970). Two cases have been identified for this type of interaction : at low and at high concentrations of the complexing agent (Lewis acid). In the former case, the rate of AN polymerization increases due to interaction between the propagating radicals and the complexing agent (BAMFORD 1958);in the latter the rate increase was attributed to the formation of a stable complex with the monomer (IMOTO 1963). The IR spectrum of the AN-$ZnCl_2$ complex showed only a shift in the absorption band of the nitrile group. This indicates the involvement of this group in the fromation of a complexed structure which could be considered as a new substituent attached to the monomer. The conjugation energy and the electron orbital polarization of the molecule as a whole will be changed.

$ZnCl_2$ was found to increase the rate of polymerization of the N-substituted maleimides (ELSABEE and MOKHTAR 1983) in solvents of low polarity. The rate enhancement was attributed to the interaction of Lewis acid with the propagating maleimide radicals.

In continuation of our interest in the copolymerization

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behaviour of AN with various substituted maleimides, it was planned to see the effect of the addition of various amounts of $ZnCl_2$ to a selected monomer pair AN/2CMI. This system was found to produce acrylonitrile copolymer with enhanced thermal and dyeing characteristics (SABAA et al.1986).

EXPERIMENTAL

Materials:

AN (BDH) was purified by distillation before use. 2CMI was prepared by the procedure of Searle (SEARLE 1948). Azobisisobutyronitrile (AIBN) was recrystalized from ethanol mp.- 104°C. Zinc Chloride (Merck) was heated for three hours at 140°C and stored over P_2O_5. The copolymerization procedure was described in a previous publication (SABAA et al. 1986).

Viscosity measurements:

Viscosity measurements were carried out in an Ubbelohde suspended level dilution viscometer. DMF was used as a solvent with a flow time of 125 seconds at 30°C.

Elemental analysis:

All elemental analyses were conducted at the Central Microanalytical Unit in Cairo University.

RESULTS AND DISCUSSION

Five AN-2CMI systems with different $ZnCl_2$/AN molar ratios have been copolymerized in DMF. The formed copolymers were precipitated in ethanol keeping always the conversion below 10%. The copolymers were filtered, reprecipitated and finally dried in an air oven at 60°C. The dried copolymers were analyzed by estimating the chlorine content and the five copolymer composition diagrams are given in Fig.1, together with that for the AN/2CMI system without $ZnCl_2$ (SABAA et al.1986).

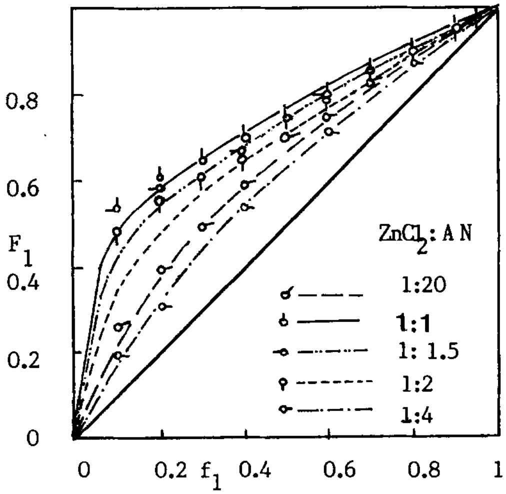

Fig.1: Copolymer composition diagram of AN (M_1) with 2CMI in the presence of different ratios of $ZnCl_2$. Total monomer concentration 2 mol/L.

The data from Fig.1 were analysed by the Kelen-Tüdös method (KELEN and TÜDÖS 1975), and are plotted in Fig.2
The reactivity ratios r_1(AN) and r_2(2CMI) were determined and are given in Table 1.

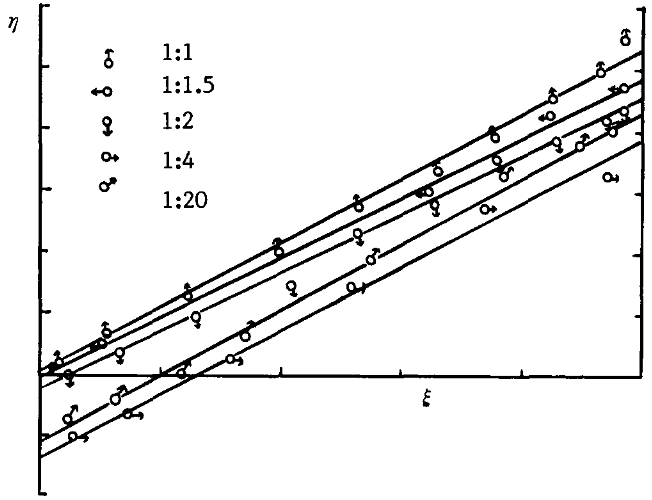

Fig.2 Kelen-Tudos plots for the investigated systems

TABLE 1: Reactivity ratios of the AN and 2CMI system in the presence of $ZnCl_2$.

$ZnCl_2$/AN	r_1	r_2
1.0	2.14	0.006
0.66	1.93	0.016
0.50	1.82	0.041
0.25	1.52	0.32
0.05	1.80	0.27
0.00	0.96	1.04

One can notice an appreciable increase in the value of r_1 with the addition of small percent of $ZnCl_2$ (5%) followed by a gradual rise of the reactivity on further increase of $ZnCl_2$ concentration. The relatively high value of r_1 in case of low $ZnCl_2$ might be attributed to the coordination of the latter with the propagating AN radical, whose concentration is also small. At higher $ZnCl_2$ concentration, the AN monomer is complexed with the Lewis acid to a greater extent relative to its complexation with the radical (GOLUBEV et al. 1970).

On the other hand, the observed decrease of r_2 is probably due to the increase of the value of the rate constant K_{21}. The complexed AN monomer should add to the maleimide radical with a higher rate than that of the uncomplexed AN monomer, where as the K_{22} is not expected to increase since the chance of complexation of 2CMI with $ZnCl_2$ in DMF is small (ELSABEE et al. 1983).

Viscosity measurements:

The intrinsic viscosity [η] values of some prepared copolymers in DMF at 30°C are given in Fig.3. $[\eta]$ for PAN prepared under the same experimental conditions is equal to 0.59.

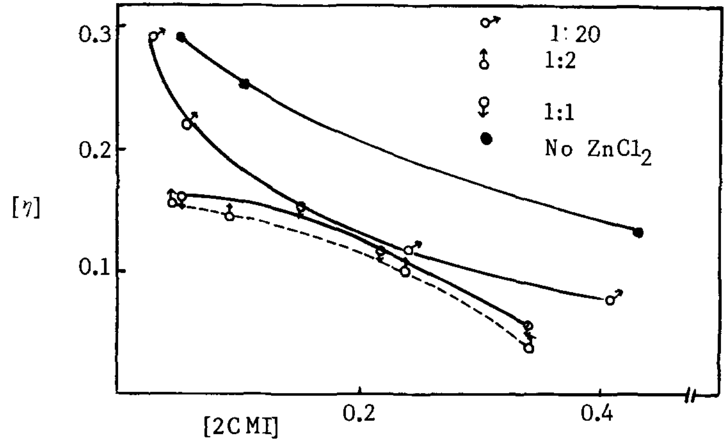

Figure 3. Effect of [2CMI],and $[ZnCl_2]$ concentration on the intrinsic viscosity of the copolymers.

The obtained values show a gradual decrease of $[\eta]$ with increasing the maleimide content which suggest a strong tendency for a chain-transfer to monomer. Chain-transfer to similar 1,2-disubstituted olefins has been reported(SOSANWO et al. 1982, LOKAJ and HRABAK 1979) and explained through migration of a H-atom from an α-carbon atom to the growing C-radical of the poly(N-arylmaleimide) to the monomer with the formation of a C-radical of N-arylsuccinimide and a terminal double bond in the inactive polymer chain. The gradual decrease in the value of $[\eta]$ by increasing the $ZnCl_2$ concentration is probably due to the effect of $ZnCl_2$ on the various steps of the polymerization process (KABANOV 1980).

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Accepted May 25, 1987 C