

**Mechanochemically Initiated Copolymerizations****3. Copolymerization of Acrylonitrile with Vinyl Acetate and with Alpha-Methyl Styrene****Cleopatra Vasiliu Oprea and Marcel Popa**

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SUMMARY

The mechanochemically initiated copolymerization (by vibratory milling) of acrylonitrile (AN) with vinyl acetate (VA) and with alpha-methyl styrene (MS), at room temperature, was studied. The reactivity ratio values:

$$\begin{array}{lll} \text{AN - VA} & r_{\text{AN}} = 2.850 & r_{\text{VA}} = 0.159 \\ \text{AN - MS} & r_{\text{AN}} = 2.550 & r_{\text{MS}} = 0.272 \end{array}$$

calculated according to an analytic procedure, as well as by the Kelen-Tüdös method, are quite different from those already given in literature, indicating the existence of a different copolymerization mechanism.

INTRODUCTION

The mechanochemically initiated copolymerization of binary mixtures of vinylic monomers was investigated only in a limited number of papers; the initiation step was realised in the presence of inorganic "mechano-activators", such as oxides, halides, sulphides (PLATE and KARGIN, 1963; PLATE and STROGANOV, 1972; ANTONOVA et al., 1976; BARAMBOIM and ANTONOVA, 1976). Recently, the possibility of activating the mechanochemical copolymerization by vibratory milling, without "initiators", was proved (SIMIONESCU et al., 1980; VASILIU OPREA et al., 1980; VASILIU OPREA and POPA, 1982; VASILIU OPREA and WEINER, 1982). The method yielded acrylonitrile - based copolymers, and the present paper is concerned with the determination of reactivity ratio values of acrylonitrile (AN) - vinyl acetate (VA) and AN - alpha-methyl styrene (MS) systems.

EXPERIMENTAL

Eight different mixtures have been studied for each copolymerization system. The syntheses were accomplished on a LABOWILS-60 type (VEB Kefama/Katzhütte Thüringen, DDR) vibration mill, working at a frequency of 25 Hz and vibration amplitudes of 2 - 4 mm. The reactions were carried out in a V<sub>2</sub>A steel vessel, at 18±2°C, under nitrogen. Six kg of grinding balls (Ø 9 mm) were introduced in the vessel, the filling ratio (defined as (grams of monomer/ grams of grinding balls) x 100) being 0,5 %. The copolymerizations were stopped at conversions less than 15 %; the resulted products were extracted with methanol, in a Soxhlet apparatus. The composition of the copolymers was determined based on nitrogen content (Kjeldahl me-

thod).

### RESULTS AND DISCUSSION

The vibratory milling mechanochemically synthesised polymers generally present a smaller solubility, as compared with their analogues obtained by classical methods (SIMIONESCU et al., 1980; VASILIU OPREA and POPA, 1982). This behaviour is due to the structural modifications appearing as a consequence of the presence of metallic atoms yielded by the vessel walls and chemically bounded to the macromolecular chains. As determined by elemental analysis, the percent of metal increases with conversion. The solubility in polar solvents (DMF) decreases with the increase of the bonded metal. For the copolymers under study, the solubility values vary between 70 % and 90 %. The composition of the studied copolymers were established based on elemental analysis data, both for the raw products and for the soluble fractions.

The molar fraction of AN in the raw product was determined by recalculating the nitrogen content related to the quantity of organic product. The later one was corrected by using the residium content, determined following polymer combustion. The results obtained for four copolymers from each series are given in Tables 1 and 2.

TABLE 1  
AN - VA copolymer composition

f <sub>AN</sub>	residium following elemental analysis (%)	nitrogen content in the raw product (%)	nitrogen content		F <sub>AN</sub>	
			recalculated for the organic product existing in the raw product (%)	in the DMF soluble fraction (%)	in the organic product existing in the raw product	in the DMF soluble fraction
0.135	12.7	8.16	9.35	9.45	0.471	0.475
0.345	9.15	13.55	14.91	14.83	0.678	0.675
0.615	8.30	18.20	19.85	20.00	0.831	0.835
0.830	3.25	22.88	23.65	23.74	0.933	0.935

One can see that the same amount of AN appears in both the raw product and in the DMF soluble fraction.

Based on these data, the composition of the two series of copolymers was further determined only for the fractions soluble in DMF.

The reactivity ration values were determined analitically, based on Mayo-Lewis and Fineman-Ross equations (EZRIELEV et al., 1969), and using the Kelen-Tudós method.

In the first case, the experimental results were processed on a FELIX C-256 computer, performing successive calculations, until the  $\Delta_{10}$  and  $\Delta_{20}$  corrections of the reactivity ratio values became of no value.

The copolymerization data of the AN - VA system are presented in Table 3.

TABLE 2  
AN - MS copolymer composition

f <sub>AN</sub>	residuum following elemental analysis (%)	nitrogen content in the raw product (%)	nitrogen content		F <sub>AN</sub>	
			recalculated for the organic product existing in the raw product (%)	in the DMF soluble fraction (%)	in the organic product existing in the raw product	in the DMF soluble fraction
0.200	12.2	4.66	6.87	7.00	0.439	0.445
0.430	8.7	11.82	12.95	12.90	0.682	0.680
0.685	7.1	17.96	19.33	19.50	0.858	0.860
0.880	3.1	22.98	23.72	23.64	0.952	0.951

TABLE 3  
Copolymerization data of AN(M<sub>1</sub>) - VA(M<sub>2</sub>) system.

Sample	f <sub>AN</sub>	F <sub>AN</sub>	Initial mixture $x_1 = [M_1] / [M_2]$	Copolymer composition $y_1 = d[M_1] / d[M_2]$	$n_1 = y_1 / x_1$
1	0.100	0.325	0.111	0.481	4.333
2	0.135	0.475	0.156	0.905	5.801
3	0.235	0.550	0.307	1.222	3.980
4	0.345	0.675	0.527	2.077	3.941
5	0.445	0.725	0.802	2.636	3.287
6	0.615	0.835	1.597	5.061	3.169
7	0.715	0.915	2.509	10.765	4.290
8	0.830	0.935	4.882	14.385	2.947

The analytical method gave the reactivity ratio values

$$r_{AN} = 2.933 \quad r_{VA} = 0.137$$

About the same results appeared from the Kelen-Tüdös plot:

$$r_{AN} = 2.850 \quad r_{VA} = 0.159$$

Figure 1 presents the copolymerization diagram of the AN -VA system, and Figure 2 the Kelen-Tüdös plot. The data attest the high reactivity of AN in mechanically initiated copolymerization. Without being identical with literature data concerning the same system, one can see that they are of the same order of magnitude (Table 4). The existing differences had to be attributed to a different mechanism of polymerization in vibratory milling conditions and to the formation of copolymers with special characteristics. Under the action of the shock energy, developed by vibratory milling, and following the interactions of the monomer with the metallic walls, fine traces of metal, in colloidal state, strongly activated, are released in the reaction medium and are chemically bonded to the polymeric chains. The metalopolymer thus resulted was previously characterised by RES and Mössbauer spectroscopy (SIMIONESCU et al., 1980; VASILIU

OPREA and POPA, 1982).

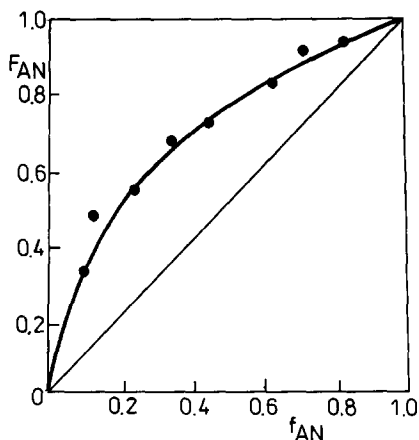


Figure 1. Copolymerization diagram (AN - VA system).

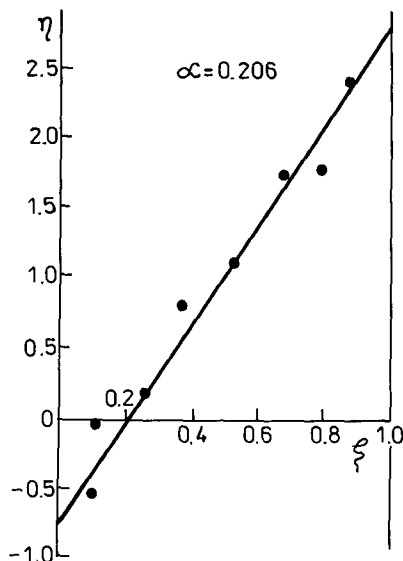
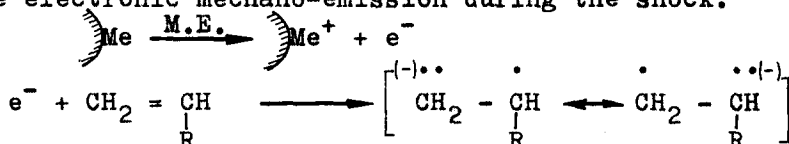


Figure 2. The Kelen-Tüdös plot (AN - VA system).

TABLE 4  
AN - VA system reactivity ratio values.

$r_{AN}$	$r_{VA}$	$T(^{\circ}C)$	Initiation	References
3.88	0.009	25	-	TANIYAMA and OSTER, 1957
5.60	0.02	40	cationic, $R_3B$	ASHIKARI and NISHIMURA, 1958
6.00	0.2	-196	$\gamma$ -rays	ISHIGURE et al., 1967
6 + 2	0.02	60	peroxides	FORDYCE et al., 1948
1.94	0.364	50	peroxides	BUTLER and KASAT, 1965

Nowadays, for this type of synthesis, an anionic-radical mechanism is generally accepted, the promoter role being attributed to the electronic mechano-emission during the shock.



Thus, the initiation period yields anion-radicals which can grow either at the anionic end, or at the radical one, this explaining, at least in part, the values of  $r_{AN}$  and  $r_{VA}$ . One has to observe that even literature data present large enough variations as concerns the reactivity ratio values, depending on the initiation mechanism and reaction temperature. Results quite different from literature data were obtained for AN - MS copolymerization system. The copolymerization data used to calculate the reactivity ratio values, according to both mentioned methods, are presented in Table 5. The analytical method gave  $r_{AN} = 2.55$  and  $r_{MS} = 0.272$ .

TABLE 5  
Copolymerization data of AN( $M_1$ ) - MS( $M_2$ ) system.

Sample	$f_{AN}$	$F_{AN}$	Initial mixture $x_i = [M_1] / [M_2]$	Copolymer composition $y_i = d[M_1] / d[M_2]$	$n_i = y_i / x_i$
1	0.110	0.290	0.124	0.408	3.290
2	0.200	0.445	0.250	0.802	3.208
3	0.330	0.600	0.493	1.500	3.043
4	0.430	0.680	0.754	2.125	2.818
5	0.525	0.765	1.105	3.255	2.946
6	0.685	0.860	2.175	6.143	2.824
7	0.815	0.925	4.405	12.333	2.800
8	0.880	0.950	7.333	19.000	2.591

Once again, the Kelen-Tüdös method yielded about the same results ( $r_{AN} = 2.675$  and  $r_{MS} = 0.268$ ).

Figure 3 presents the copolymerization diagram and Figure 4 the Kelen-Tüdös plot of AN - MS system.

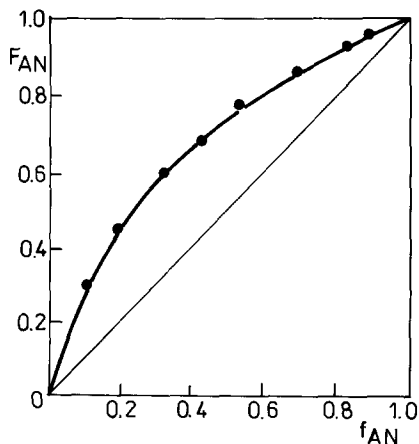


Figure 3. Copolymerization diagram (AN - MS system).

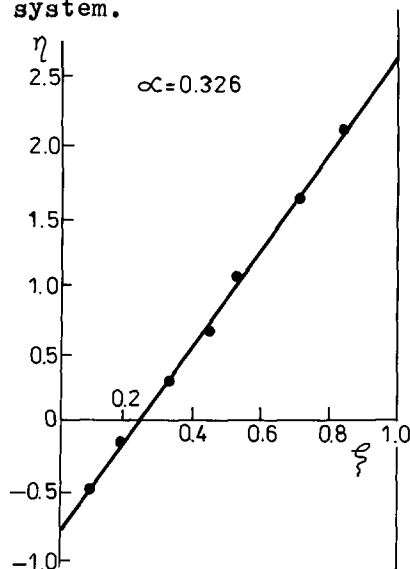


Figure 4. The Kelen-Tüdös plot (AN - MS system).

The present data emphasize the great reactivity of AN towards MS; for the radical copolymerization of the two comonomers, literature data indicate  $r_{AN} = 0.04$  and  $r_{VA} = 0.20$  (WITTMER, 1967).

The explanation has to be found in the different mechanism of mechanochemically initiated copolymerizations. Having a strong polar substituent, AN will present a greater tendency to polymerize by an anionic mechanism. In the presence of MS, a monomer not easily polymerizable by an anionic mechanism, the growth of the copolymer chain proceeds mainly at the anionic end of the growing particle, and mainly by adding AN.

CONCLUSIONS

1. Vibratory milling can be used to activate copolymerization reactions of binary systems based on AN.
2. The reactivity ratio values of the mechanochemically copolymerized systems are different from the literature ones.
3. The mechanism of the mechanochemically activated copolymerization requires mainly the participation of anionic centers during the initiation step.

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