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# Copolymerization of Monoesters of Itaconic Acid with Vinyl Chloride

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#### SUMMARY:

The copolymerization of vinyl chloride with monoesters of itaconic acid  $(CH_2 = C - CH_2COOR)$  in solution in the presence of azobisisobutyronitrile at 60 °C

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was investigated. The reactivity ratios of the monomer pairs: monomethyl itaconatevinyl chloride ( $r_1 = 4.70$ ;  $r_2 = 0.05$ ), monobutyl itaconate-vinyl chloride ( $r_1 = 4.45$ ;  $r_2 = 0.08$ ) and benzyl itaconate-vinyl chloride ( $r_1 = 9.07$ ;  $r_2 = 0.08$ ) are determined by the FINEMAN-Ross method, using a computer programme.

# ZUSAMMENFASSUNG:

Die Copolymerization von Vinylchlorid mit Monoestern der Itaconsäure (CH = C—CH<sub>2</sub>COOR) in Lösung in Gegenwart von Azoisobutyronitril wurde unter-

COOH

sucht bei 60 °C. Die Copolymerisationsparameter der Monomerpaare : Monomethylitaconat-Vinylchlorid ( $r_1 = 4,70$ ;  $r_2 = 0,05$ ), Monobutylitaconat-Vinylchlorid ( $r_1 = 4,45$ ;  $r_2 = 0,08$ ) und Monobenzylitaconat-Vinylchlorid ( $r_1 = 9,07$ ;  $r_2 = 0,08$ ) wurden mit der Methode von FINEMAN und Ross bestimmt unter Verwendung eines Computerprogramms.

Copolymers of vinyl chloride with acrylic monomers have been obtained with the view to improve the processing ability of vinyl chloride polymers by decreasing viscosity of the polymer melt. However, the great difference between the reactivity ratios of these monomers (methyl methacrylate 10 to 15, vinyl chloride 0,00 to 0,10) makes the control of the copolymer composition difficult<sup>1</sup>.

In copolymerizing diesters of itaconic acid with vinyl chloride the copolymerization constants are not so different<sup>2</sup>. Small quantities of dimethyl itaconate decrease both the polymerization rate of vinyl chloride and the viscosity of the polymers<sup>3</sup>. A possible modified approach in the case of vinyl chloride is to copolymerize it with the monoesters of itaconic acid by which procedure simultaneously with the internal plastification are also introduced free carboxyl groups in the copolymer chain. The latter are known to increase adhesion to metals and cellulose materials. Vinyl chloride copolymers containing them may be applied as lacquer coatings.

Terpolymers of the monoesters of itaconic acid with vinyl chloride and acrylonitrile<sup>4</sup> as well as the system vinyl chloride – vinylidene chloride – monobutyl itaconate in ratios of 80:20:1 are described in literature<sup>5</sup>.

This work is an investigation of the copolymerization of vinyl chloride and the monoesters of itaconic acid of the following structure

$$\begin{array}{c} \mathrm{CH}_2 = \mathrm{C} - \mathrm{COOH} \\ | \\ \mathrm{CH}_2\mathrm{COOR} \end{array} \qquad \mathrm{R} = -\mathrm{CH}_3, -\mathrm{C}_4\mathrm{H}_9, -\mathrm{CH}_2 - \overleftarrow{\bigcirc} \ ,$$

thus retaining free the strongly acidic and conjugated carboxyl group. Partial esterification of itaconic acid increases its solubility in organic solvents and yields monomers which facilitate the copolymerization processes. Copolymerization is carried out in solution and in the presence of a free radical initiator.

## Experimental

### Reagents

Monomethyl itaconate (MMI) is obtained by a well-known method<sup>6</sup> from itaconic acid (m.p. 168–168.5 °C) and methanol (mole ratio of 1:3) in the presence of acetyl chloride (1 wt.-%) as catalyst. The excess of methanol is rapidly removed after which the monomethyl itaconate distills at 145-150 °C/8 mm. The resulting liquid crystallizes on standing. The yield is 75%. Recrystallized from toluene, the product has a m.p. of 65–67 °C, acid number 402 (calculated 389) and ester number 399. It is well soluble in water, alcohol and most organic solvents.

Monobutyl itaconate (MBI) is obtained by the same procedure in yield of 89%. It distills at 170-178 °C/12 mm and has a m.p. of 40-42 °C, acid number 285 (calculated 301) and ester number 257. It is soluble in alcohol, acetone and benzene, but is insoluble in water.

Monobenzyl itaconate (MBzI) is also obtained by a described method<sup>6</sup> from itaconic acid (1 mole) and benzyl alcohol (3 moles) in the presence of 2.5% acetyl chloride. After distillation under reduced pressure and crystallization it has a m.p. of 80-82 °C. The yield is 75%. Its acid number is 287 (calculated 254). It is soluble in most organic solvents and insoluble in water and alcohol.

Vinyl chloride (VC), 99.8%, Chemical Works "Devnia" – Bulgaria. Dichloroethane, purum, PPH – Poland. Benzene, purum. Ethyl acetate, purum, PPH – Poland. Azobisisobutyronitrile (ABN) – Fluka, Switzerland, m.p. 102–103°C.

#### Copolymerization in solution

20% solutions of the monomer mixtures in the solvent (dichloroethane for the system MMI-VC and benzene for the systems MBI-VC and MBzI-VC) are introduced into glass ampules and then 0.5-2 mole-% of ABN were added. The ampules are cooled in liquid nitrogen and then sealed and placed in a thermostat at 60 °C. In the course of the polymerization they are continuously and vigorously shaken. After some time the ampules are cooled and opened and the solutions precipitated by means of tenfold excess of n-hexane. The resulting precipitate is washed and then dried in vacuum at room temperature.

The content of itaconic acid monoester in the copolymers is determined by analysis of the acid groups. The polymer is dissolved in ethyl alcohol, acetone or a mixture of both solvents and titrated with 0.1 N alcoholic potassium hydroxide in the presence of phenolphthalein (in alcohol medium) or thymolphthalein (in acetone) as indicator<sup>7</sup>.

Intrinsic viscosities are determined in ethyl acetate at 20 °C and the melting points by a KOFLER microscope.

Copolymerization ratios are computed by a ICL computer programme written in Fortran IV.

# **Results and Discussion**

By copolymerization of VC and monoesters of itaconic acid in solution in the presence of ABN as initiator copolymers are obtained of characteristic properties given in Table 1. The copolymer content of monoester of itaconic acid is high irrespective of the high content of VC in the initial monomer mixture as can be seen from the Table. This is an indication that VC has a low relative reactivity in this copolymerization. The intrinsic viscosity of the copolymer is low too and this is in conformity with the results established by other authors<sup>3, 8</sup> in copolymerization of diesters and VC which could be explained by chain transfers at the labile hydrogen in the methylene group<sup>8</sup>. It should be noted that values of the intrinsic viscosity of the copolymers of VC with MBI and MBzI are higher than those of VC with MMI. The softening point of copolymers of the monoesters of itaconic acid and VC is influenced by the alcohol moiety in the molecule of the monoesters. Copolymers of the aliphatic esters of itaconic acid have a lower softening point than that of pure PVC. The softening point drops with the lengthening of the alkyl unit in the ester. The copolymer of MBzI has a high softening point, close to that of pure PVC.

Copolymers of monomethyl itaconate dissolve in methanol and ethanol because of their major content of monomethyl itaconate but they are insoluble in chlorinated hydrocarbons, ether and hexane. The VC-MBI copolymer swells in ethanol, while the MBzI copolymer is insoluble in this alcohol.

To examine the reactivity of the various monoesters of itaconic acid in their copolymerization with VC experiments were carried out for copolymerization

Itaconic ester	Molar ratio of ester: VC	Monoester in the copolymer wt%	Yield %	Intrinsic viscosity dl/g	Softening point range °C
MMI	1:10	74.0	29.2	0.0275	128-133
MMI	1:7	71.3	32.0	0.0355	
MBI	1:6	73.1	26.6	0.1033	112 - 116
MBI	1:8	69.5	6.2	0.0561	
MBzI	1:8	51.5	17.7	0.0645	165 - 170

 Table 1. Some properties of the copolymers of monoesters of itaconic acid with vinyl chloride.

in solution with varying ratio of the initial monomers and the process was interrupted at low coversion. After precipitation the composition of the copolymers was determined by free carboxyl group analysis. The reactivity ratios were calculated using data from Tables 2, 3 and 4 by a computer programme based on the FINEMAN and Ross method<sup>9</sup>.

MMI in the initial mixture wt%	Time of copolymerization h	Yield %	MMI in the copolymer wt%
69.8	6	2.25	94.7
57.2	4	6.96	85.8
53.7	6	9.70	85.8
53.7	6	11.9	87.1
<b>43.6</b>	6	10.10	85.0
36.7	6	7 14	<i>i</i> .0
31.7	10	6.76	75.7
31.7	4	5.04	70.0
27.9	6	7.80	92.8
24.9	6	13.35	84.5
20.5	4	5.00	69.4
18.8	6	5.18	56.6

Table 2. Copolymerization of MMI with VC in dichloroethane solution at  $60\,^{\circ}$ C in the presence of 1 mole-% of ABN.

The results for reactivity ratios are given in Table 5. Itaconic monoesters have high values for the reactivity ratio  $r_1$ . These values do not vary for aliphatic monoesters of itaconic acid but the reactivity ratio of MBzI is two

MBI in the initial mixture wt%	Time of copolymerization h	Yield %	MBI in the copolymer wt%
75.0	330	4.52	96.4
60.0	4	1.18	85.3
50.4	330	6.79	80.4
<b>43</b> .0	4	0.35	86.9
37.3	330	7.54	85.9
33.3	4	0.50	84.5
30.1	330	1.79	63.4
27.2	6	6.15	75.5
25.1	4	2.41	76.9
23.1	4	0.79	57.0
23.1	4	9.21	66.6

Table 3. Copolymerization of MBI with VC in benzene solution at 60°C in the presence of 1 mole-% of ABN.

Table 4. Copolymerization of MBzI with VC in benzene solution at 60°C in the presence of 1 mole-% of ABN.

MBzI in the initial mixture wt%	Time of copolymerization h	Yield %	MBzI in the copolymer wt%
63.8	12	11.8	95.8
46.9	14	5.3	92.1
41.6	14	6.1	90.5
37.1	14	6.7	85.5
28.4	14	6.3	61.2
26.2	12	11.8	58.2

Table 5.	Reactivity ratios in the copolymerization of monoesters of itaconic acid
	with vinyl chloride.

Copolymer	Total number of exper ments	r <sub>1</sub>	r <sub>2</sub>
MMI-VC	12	$4.697 \pm 0.054$	$0.0531\pm0.784$
MBI-VC	11	$4.454\ \pm\ 0.017$	$0.082  \pm \ 0.286$
MBzI-VC	6	$9.067\stackrel{-}{\pm}0.007$	$0.084 \pm 0.316$

times higher. Reactivity ratios  $r_2$  for VC are of low values close to zero. The great deviations in calculating the  $r_2$  values have an insignificant effect on the shape of the composition curves<sup>10</sup> which are determined mainly from the values for  $r_1$ .

The values obtained for  $r_1$  and  $r_2$  in the copolymerization of the monoesters of itaconic acid and VC are of the same order as those obtained in the copolymerization of diesters<sup>8</sup> which are as follows:  $r_1 = 5,1 \text{ to } 6,0$  for the different types of esters and  $r_2 = 0,053$  to 0,06 for VC.

The copolymer composition curves obtained on the basis of the data for  $r_1$  and  $r_2$  are given in Fig. 1. As they indicate, the monoester of itaconic acid is always predominant in the copolymer irrespective of the initial composition



Fig. 1. Composition curves in copolymerization of monoesters of itaconic acid with vinyl chloride: 1-MMI-VC; 2-MBI-VC; 3-MBzI-VC.

126

of the polymerizing mixture. Vinyl chloride is included in the composition of the MBzI copolymer while it is comparatively more included in the MMI and MBI copolymers. Generally, the major difference in the r values makes the control of the copolymer composition difficult. This difference, however, is less in copolymerization of vinyl chloride with itaconic esters than in its copolymerization with methyl methacrylate ( $r_1 = 10$  to 15,  $r_2 = 0.02$  to 0.1 for VC). Itaconic esters are, therefore, more suitable than methyl methacrylate for modification of vinyl chloride.

Low viscosities of the copolymers are a significant obstacle for their application. But these copolymers could be applied for coatings by mixing them with melamine formaldehyde or epoxy resins since they contain free carboxyl groups which improve adhesion and may undergo cross-linking reactions.

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