Some Problems Encountered in Copolymerization Studies Using Ziegler-Natta Type Catalysts[1]

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INTRODUCTION

It was hoped to obtain copolymerization parameters for a series of copolymers obtained by initiation with Ziegler-Natta catalysts. Preliminary experimentation restricted the list of monomers to just the styrene-acryonitrile pair. Vinyl acetate was found to enter into copolymerization with styrene in only trace amounts, methyl acrylate produced a tacky semi-solid which proved impossible to handle; other monomers such as ethyl vinyl ether and allyl chloride were eliminated because of vigorous reaction with catalyst components.

Preliminary copolymerization of styrene and acrylonitrile with a TIBAL-$VOCl_3$ catalyst system indicated, Fig. 1, the following reac-

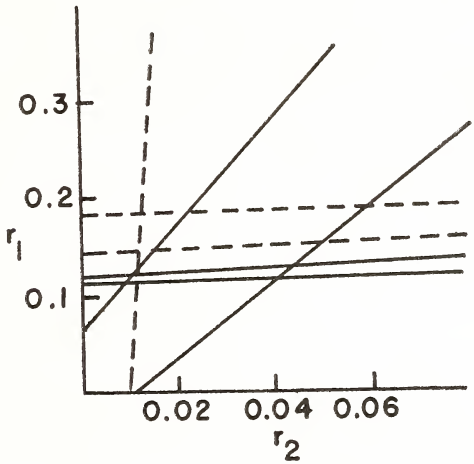

Figure 1. Copolymerization:

Styrene (M_1) and Acrylonitrile

(Preliminary Data)

Carbon Analysis: ————

Nitrogen Analysis: - - - -

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tivity ratios: (styrene = M_1) : $r_1 = 0.12 \pm 0.01$, $r_2 = 0.03 \pm 0.02$. It was decided then, to study the copolymerization of this monomer pair in greater detail, to compare results at different temperatures and with another catalyst system.

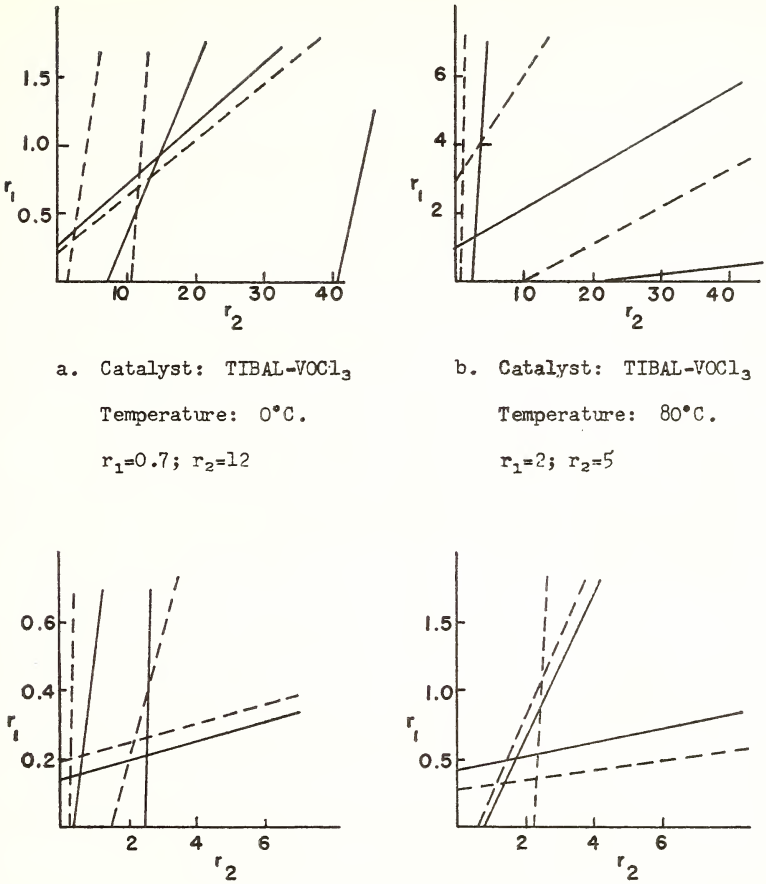
Experimental Methods

Monomers and solvents were purified in the usual way with special precautions to exclude oxygen and water at all times. TIBAL was transferred under nitrogen in a polyethylene glove bag to amber bottles stoppered with perforated, Buma S rubber-lined crown caps. Otherwise, TIBAL was used as received in a 25% solution in hexane. Vanadium oxytrichloride was distilled under nitrogen at atmospheric pressure in all-glass apparatus, and diluted under nitrogen in a polyethylene glove bag with cyclohexane to a 25% solution. The solution was stored in an amber bottle fitted with a three-way stopcock to permit removal with a syringe under a flow of nitrogen. Titanium trichloride was weighed under nitrogen in the glove bag into glass stoppered weighing bottles which were stored in a desiccator under nitrogen.

Copolymerizations were carried out in 3-neck, glass joint, 100 ml., flat bottom flasks equipped with a thermometer, condenser, three-way stopcock and magnetic stirring bar. The apparatus was oven dried, assembled, flushed with nitrogen for at least one hour and charged by use of syringes through the 3-way stopcock under a constant flow of nitrogen entering the system through one arm of the stopcock. The open end of the condenser was protected from the atmosphere with a dibutyl phthalate seal-bubbler. The $TiCl_3$ was dumped into the flask through an open neck shielded from the atmosphere with a large funnel through which nitrogen was passed rapidly.

The order of addition of reagents and a typical recipe are given in Table 1. Monomers were mixed and flushed with nitrogen before addition to the flask. Reactions were carried out at two temperatures: (1) 0° to 5° C. was maintained through the initial vigorous reaction of monomer with catalyst and for several hours thereafter by immersing the flask in an ice bath, then the temperature was allowed to reach room temperature; and (2) the contents of the flask, before addition of monomers, were heated to 72° C. with the addition of monomers raising the temperature to 80° C. or to a lower reflux temperature which was maintained throughout the reaction.

After sixteen to eighteen hours, the reaction was quenched by pouring the contents of the flask into methanol containing 1.5% of hydrogen chloride (45 ml. of concentrated HCl in 1 liter of methanol). The copolymer was filtered off on sintered glass crucibles and redissolved in an appropriate mixture of solvents selected from benzene, N,N-dimethylformamide, tetralin and butyrolactone. Great difficulty was experienced repeatedly in dissolving completely the copolymers even though many different mixtures of the above solvents were attempted. In several instances, a reprecipitated copolymer would not dissolve in a solvent mixture previously found satisfactory for that particular sample. After redissolving, the copolymer was reprecipitated in acidified methanol in a Waring blender to avoid formation of a



a. Catalyst: TIBAL-$VOCl_3$
Temperature: 0°C.
r_1=0.7; r_2=12

b. Catalyst: TIBAL-$VOCl_3$
Temperature: 80°C.
r_1=2; r_2=5

c. Catalyst: TIBAL-$TiCl_3$
Temperature: 0°C.
r_1=0.2; r_2=1.5

d. Catalyst: TIBAL-$TiCl_3$
Temperature: 80°C.
r_1=0.5; r_2=2

Figure 2. Copolymerization: Styrene (M_1) and Acrylonitrile (M_2).
Carbon Analysis ———; Nitrogen Analysis – – – – –

ropey precipitate which would trap solvent and catalyst residues. Copolymers were reprecipitated at least six times with the final copolymer solution also filtered through a sintered glass crucible. The copolymer finally was washed with methanol and pentane and dried in a vacuum oven at 80° C. to give a friable material of light tan color. Catalyst and monomer ratios and analytical data are summarized in Table 2.

Table 1. Typical Copolymerization Recipe

Reagent	Milli-moles	Quantity measured	Mole fraction
Cyclohexane	92.6	10 ml.	0.593[a]
TIBAL (25% in hexane solution)	22.5	24.5 ml.	0.028
$VOCl_3$ (25% in cyclosexane solution	7.5	5.7 ml.	0.009
Cyclohexane	185	20 ml.	——
Styrene	150	15.6 g.[b]	0.185
Acrylonitrile	150	7.96 g.[b]	0.185

[a]Reported here as 0.593 mole fraction of total diluents.

[b]Weighed to nearest 0.01 g., mixed together and flushed with nitrogen before adding to the reaction flask.

Table 2. Copolymerization of Styrene (M_1) with Acrylonitrile

Catalyst[a]	Temp.	M_1	%C	%H	%N	M_1(C)[b]	M_1 (N)[c]
$VOCl_3$	0°C.	0.895	85.46	7.60	5.73	0.768	0.744
$VOCl_3$	0°C.	0.501	65.96	6.34	15.69	0.107	0.296
$VOCl_3$	0°C.	0.100	62.89	6.39	22.04	0.0027	0.010
$VOCl_3$	80°C.	0.900	89.55	7.90	0.81	0.905	0.964
$VOCl_3$	80°C.	0.502	63.94	6.43	20.47	0.038	0.082
$VOCl_3$	80°C.	0.104	64.09	6.77	19.06	0.043	0.145
$TiCl_3$	0°C.	0.897	81.62	7.62	5.25	0.683	0.714
$TiCl_3$	0°C.	0.512	72.69	7.05	12.97	0.416	0.295
$TiCl_3$	0°C.	0.100	60.14	6.84	14.70	0.042	0.200
$TiCl_3$	80°C.	0.914	87.03	7.86	3.79	0.845	0.794
$TiCl_3$	80°C.	0.499	70.55	7.15	11.52	0.352	0.373
$TiCl_3$	80°C.	0.101	57.91	7.33	17.51	——	0.046

[a]Catalyst was TIBAL plus $VOCl_3$ or $TiCl_3$ as indicated.

[b]Mole fraction of styrene in the copolymer as calculated from carbon content.

[c]Mole fraction of styrene in the copolymer as calculated from nitrogen content.

Table 3 Elemental Analysis of Polyacrylonitrile

Catalyst	%C	%H	%N	%Cl	%0	% ash
TIBAL-$VOCl_3$	62.81	6.27	22.30	——	——	0.63
TIBAL-$TiCl_3$	59.32	6.95	17.59	——	——	0.09
TIBAL-$TiCl_3$*	58.17	63.0	19.18	——	——	0.09
(Theory	67.90	5.70	26.40)			

*Repeat analysis of the preceding sample.

In determining mole fractions of monomers in the copolymers, percentage composition obtained from elemental analysis of polyacrylonitrile (Table 3) was used rather than theoretical percentage. Figure 2 shows the plots obtained from the data by the "intersection method" of Mayo and Lewis (1). Accepted r_1, r_2 values for styrene and acrylonitrile by free-radical polymerization are $r_1=0.41$, $r_2=0.04$ (2), and by anionic copolymerization, $r_1=0.20$, $r_2=11\text{-}14$ (3). Reactivity ratios obtained in this work as approximated in Figure 2, lie generally between the values for free-radical and anionic copolymerization possibly indicating simultaneous copolymerization by both methods (4).

Further complicating the picture is the indication of homopolymerization possibly taking place. A small portion of the copolymer was usually found to be soluble in benzene. One copolymer sample gave a nitrogen content of 11.6% whereas the benzene-insoluble fraction after solvent fractionation contaied 13.07% nitrogen.

Summary

The work has raised more questions than it answered. Reactivity ratios for the styrene (M_1) acrylonitrile monomer pair appear to be for TIBAL- $VOCl_3$ at 0° C., $r_1=0.7$ and $R_2=12$, for TIBAL-$VOCl_3$ at 80°C, $r_1=2$ and $r_2=5$ for TIBAL-$TiCl_3$ at 0°C, $r_1=0.2$ and $r_2=1.5$ and for TIBAL-$TiCl_3$ at 80°, $r_1=0.5$ and $r_2=2$. Plots for the solution of these reactvity ratios give approximations only. Discrepancies and nonreproductibility may be caused by any combination of the following factors: faulty technique and procedure, excessive homopolymerization, block copolymerization, and simultaneous copolymerization by free-radical and anionic mechanism. Further study should include the nature of the reactions by which ogygen and chlorine are introduced into the copolymer.

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