The Copolymerization of Vinyl Chloride and Ethylene by a Ziegler-Natta Catalyst

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Recently, Yamazaki et al. have reported the copolymerization of vinyl chloride with propylene by the use of the catalyst systems consisting of $Ti(n\text{-}OBu)_4$ and organoaluminum compounds.[1] In the course of the studies of the copolymerization of vinyl chloride with ethylene, the present authors have also found that the same catalyst systems can copolymerize these monomers in a manner quite different from the radical copolymerization which they previously reported.[2] This paper will deal with the copolymerization by the use of the $Ti(n\text{-}OBu)_4$-$AlEtCl_2$ catalyst system.

The reaction was carried out in a stainless-steel autoclave equipped with an agitating device. The resultant copolymer was treated and purified in the usual manner. The composition of the product was calculated from the elemental analyses data. The reduced specific viscosity of the tetrahydrofuran-soluble polymer was measured using a 0.5 g./100 ml. cyclohexanone solution at 30.0°C.

Typical copolymerization results, including the results of successive solvent extraction, are shown in Table I. The copolymerizates obtained by the use of the present catalyst system were considerably richer in ethylene than those obtained in the radical copolymerization using trialkylboron-peroxide systems.[2] The copolymerizate became richer in ethylene with an increase in the aluminum/titanium molar ratio. At aluminum/titanium molar ratios higher than 5, only polyethylene was obtained at any composition of the monomer mixture.

In order to investigate the composition distribution of the copolymerizate, successive solvent extraction, using tetrahydrofuran and monochlorobenzene, of the products obtained at aluminum/titanium molar ratios of 1.8, 2.5 and 3 were carried out. These results are shown in Table I. The copolymerizates being extracted not only according to the difference in molecular weight, but also according to the difference in composition, it was considered that the copolymerizates consisted of copolymers of different compositions. There may exist several active sites in the catalyst system, each with different reactivity ratios and each producing its own type of polymer.

The catalyst system was active for vinyl chloride homopolymerization, but it showed little activity for ethylene at aluminum/titanium molar ratios lower than 2.5. However, the catalyst changed its activity for each monomer at an aluminum/titanium molar ratio slightly higher than 2.5. From the infrared spectroscopy of the extracted fractions of the copolymerizates, particularly investigating the 900—700 cm^{-1} region where absorptions due to the methylene rocking mode of polyvinyl chloride (833 cm^{-1}), the vinyl chloride-ethylene random copolymer (750 cm^{-1}) and polyethylene (730 and 720 cm^{-1}) are observed, it was proved that a random copolymer with a broad composition distribution was obtained at aluminum/titanium molar ratios lower than 2.5, whereas, at an aluminum/titanium molar ratio of 3, a block copolymer rich in ethylene was formed, along with a random copolymer rich in vinyl chloride.

Detailed experimental results and a discussion of the reaction mechanism will be reported in the near future.

TABLE I. COPOLYMERIZATION RESULTS WITH USE OF $Ti(n\text{-}OBu)_4$-$AlEtCl_2$ CATALYST SYSTEM

				THF extract			MCB extract		Residue	
Al/Ti	VCl mol.% in feed	yield %	VCl mol.% in product	wt.%	VCl mol.%	η_{sp}/C	wt.%	VCl mol.%	wt.%	VCl mol.%
1.8	40	5.97	44.85	40.12	66.41	0.1734	3.81	5.16	56.07	0
2.5	70	5.80	48.87	40.54	77.58	0.3068	42.40	20.42	17.06	—
3.0	90	8.22	53.26	43.76	77.49	0.4234	39.30	34.96	16.94	—
Polyvinyl chloride				100			0		0	
Polyethylene				2.47			29.63		67.90	

vinyl chloride + ethylene: 0.5 mol., $Ti(n\text{-}OBu)_4$: 2 mmol., $AlEtCl_2$: varied *n*-heptane: 50 ml., 50°C, 3 hr.

1) N. Yamazaki, M. Aritomi and S. Kambara, Preprint of the 19th Annual Meeting of the Chemical Society of Japan, Tokyo, 4T103 (1966).

2) A. Misono, Y. Uchida and K. Yamada, Preprint of the 19th Annual Meeting of the Chemical Society of Japan, Tokyo, 4U226 (1966).