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Kurzmitteilung

Vinyl Polymerization. 169*

Copolymerization of Carbon Monoxide with Some Vinyl Monomers

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Recently, carbon monoxide has received considerable attention in the synthetic polymer chemistry, and thus copolymerizations of carbon monoxide with formaldehyde¹⁾, alkylene oxide²⁾ and ethylene imine³⁾ have been studied. With regard to its copolymers with vinyl monomers, however, only few were known in detail in the cases where ethylene⁴⁾, propylene⁵⁾, and vinyl acetate⁶⁾ served as comonomers.

The present paper reports the copolymerization of carbon monoxide with several other vinyl monomers, and some properties of the copolymers are shown.

Carbon monoxide used was a commercial product (Matheson Co., 99.5 per cent purity). Vinyl monomers, such as methyl methacrylate (MMA), acrylonitrile (AN), vinyl chloride (VC), methyl acrylate (MA), styrene (St) and vinylidene chloride (VdC) were purified by the usual methods. After charging vinyl monomer, azobisisobutyronitrile (AIBN) as initiator, and benzene as solvent in a 100 ml autoclave, the content was flushed fully with oxygen-free nitrogen, and then carbon monoxide was allowed to press in. Polymerizations were carried out at constant temperature under stirring. After definite intervals the content was taken out with chilling and the reaction mixture was poured into an excess of precipitants to isolate the copolymer formed, which was then purified by reprecipitation.

The composition of the copolymers was determined by SCHÖNIGER chlorine analysis⁷⁾ in the case of vinyl chloride copolymer, and by usual elementary analysis in all other cases.

Copolymerization of carbon monoxide was carried out at first several sorts of vinyl monomers, where the molar composition of carbon monoxide was kept nearly constant at 35.3 mole per cent. The results were shown in Table I. As can be seen from the table, molar ratios of vinyl monomers in the copolymers showed higher values than that in the monomer compositions in all cases. In the case of MA, carbon monoxide was not incorporated in the polymer obtained. It was found that butadiene could not polymerize and copolymerize with carbon monoxide under the condition used.

*) 168th of the series: K. TSUDA, S. KOBAYASHI, and T. OTSU, *Makromolekulare Chem.* in contribution.

Table 1. Copolymerization of carbon monoxide with vinyl monomers (60°C, [AIBN] = 0.61 mmole in 20 ml of benzene)

	Monomer		Polymeri- zation		Copolymer		
	Vinyl	CO	time (min)	yield (%)	CO	Vinyl	Precipi- tant
	Monomer (mmole)	(kg/cm ²)			(mole-%)	Monomer (mole-%)	
MMA	93.8	21 ^{a)}	60	2.4	13.8	86.2	colorless powder <i>n</i> -hexane
AN	148.8	30	70	6.3	4.6	95.4	colorless powder <i>n</i> -hexane
VC	166.8	30 ^{b)}	150	3.4	4.2	95.8	colorless powder <i>n</i> -hexane
VdC	150.7	33	120	8.3	8.4	91.6	colorless powder <i>n</i> -hexane
St	148.4	32	40	1.8	7.5	92.5	colorless powder methanol
MA	147.7	32	35	50.9	0	100	rubbery <i>n</i> -hexane

^{a)} CO, 37.9 mole-%, 50°C ^{b)} CO, 36.8 mole-%, toluene was used as solvent. ^{c)} measured at 30°C in dimethylformamide solution.

Copolymerization of carbon monoxide with MMA and AN was carried out next more in detail, with different molar ratios of carbon monoxide to vinyl monomer. As can be seen from Fig. 1, the copolymer compositions seemed not to be dependent upon the monomer compositions in both cases, and it was found that carbon monoxide was incorporated in the order of about 10 to 20 per cent in the former case, and about 4 to 8 per cent in the latter case.

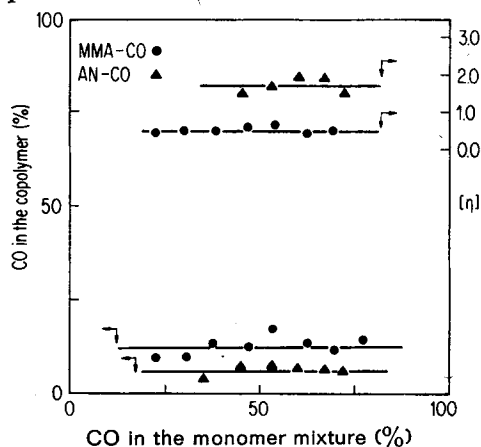


Fig. 1. Copolymerization of carbon monoxide with MMA and AN: monomer-copolymer composition and monomer composition-intrinsic viscosity relationships

Copolymerization of carbon monoxide was then carried out with vinyl chloride as comonomer, and the results obtained were shown in Fig. 2. The monomer reactivity ratios were determined by FINEMAN-ROSS

method: from the slope and intercept the values were determined as follows (Table 2): $r_1 = 13.47$ (VC), $r_2 = 0.15$ (CO)

Table 2. Copolymerization of carbon monoxide with vinyl chloride (60°C, [AIBN] = 0.61 mmole in 10 ml of toluene)

Monomer		Polymerization		Copolymer		F^2/f	$F/f(f-1)$
VC (mmole)	CO (mmole)	time (min)	yield (%)	Cl found (%)	CO calcd. (mole-%)		
166.8	44.5	120	4.0	56.20	2.0	0.291	3.67
166.8	94.1	150	3.4	55.63	4.2	0.138	1.69
168.5	140.9	190	3.3	55.13	6.1	0.092	1.12
82.6	140.9	360	2.8	53.35	12.4	0.049	0.50
84.2	166.5	420	2.3	52.95	13.7	0.041	0.43
84.2	194.2	240	0.6	51.88	17.3	0.039	0.34

All the copolymers obtained were colorless, amorphous powder. It was found for all copolymers that the intrinsic viscosity was tended to decrease with the increasing amount of carbon monoxide in the copolymers, while the solubility of each copolymer was almost the same as well as their homopolymers. As can be seen from Fig. 2, the discoloring points of the carbon monoxide-VC copolymers decreased also with the increasing amount of carbon monoxide in the copolymers, but the $[\eta]$ values of them were lower than that described by WEINTRAUB *et al.*⁸⁾.

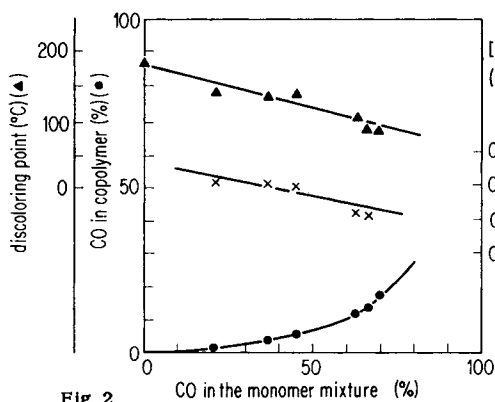


Fig. 2

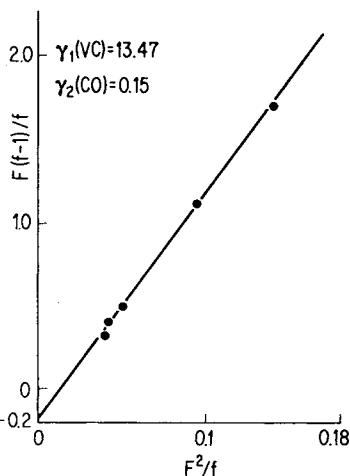


Fig. 3

Fig. 2. Copolymerization of carbon monoxide with VC: monomer-copolymer composition curve together with intrinsic viscosity and discoloring points of the copolymers

Fig. 3. FINEMAN-ROSS plot for the copolymerization of carbon monoxide with VC

An example of IR spectra of the copolymers was shown in Fig. 3. The spectrum shows new absorption band assigned to carbonyl groups, which were responsible to the incorporation of carbon monoxide in the copolymer.

Further study including measurements of the detailed physical properties are now in progress, which will be reported in the near future.

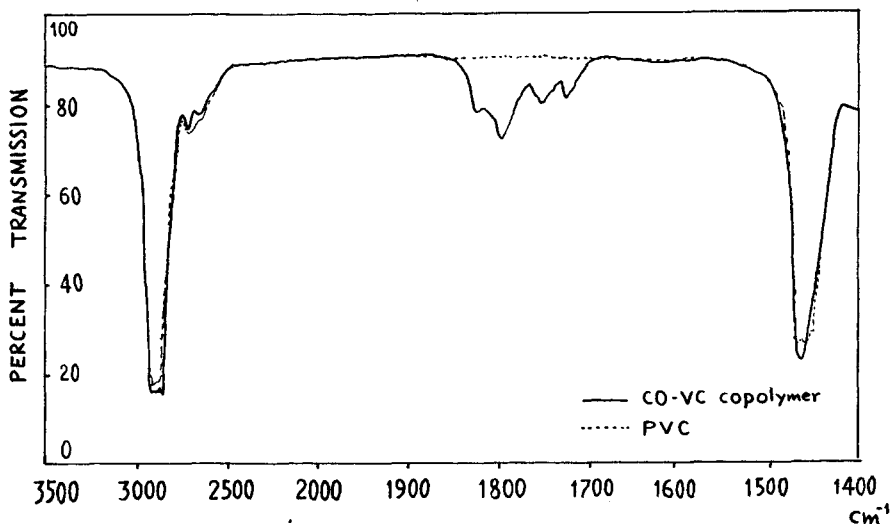


Fig. 4. IR spectrum of carbon monoxide-VC copolymer

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