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Studies on Telomerization of Vinyl Chloride with Carbon Tetrabromide

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The radical telomerization of vinyl chloride with carbon tetrabromide was investigated. The telomers with $n=1$ and 2 in $Br(CHClCH_2)_nCBr_3$ were isolated and identified. The molecular weight distribution of the telomers was determined by thin-layer chromatography (TLC), and it was found that the distribution varied a little with the variation of reaction conditions. From the results of the TLC, the chain transfer constants (C_n) of polylvinyl chloride radical to carbon tetrabromide were calculated, and a monotonous increase in C_n with the increasing n was found. The effects of initial ratio of vinyl chloride to carbon tetrabromide, reaction time and temperature on the conversion of vinyl chloride and the average molecular weight of the telomer were investigated. Bromoform was also used as a telogen instead of carbon tetrabromide, and the results were compared in both systems.

There are few studies on telomerization of vinyl chloride as a taxogen. Akiyoshi *et al.*[1] carried out this reaction using carbon tetrachloride as a telogen and the formation of telomers with 1 : 1 and 1 : 2 of the ratio of telogen to taxogen was confirmed. Ali *et al.*[2] investigated this reaction using carbon tetrabromide as a telogen, but liquid telomers were not obtained, probably because the amount of the chain transfer agent was low in this investigation. In order to confirm further the possibility of the preparation of oligo (vinyl chloride), the present investigation was designed under the various reaction conditions such as telogen-taxogen ratio, reaction time and temperature. Further, the separation of products by means of thin-layer chromatography was undertaken. The result will be presented in this paper.

Experimental

Materials. Vinyl chloride was purified by washing with a 30% KOH aqueous solution and drying over calcium chloride. Carbon tetrabromide was prepared from the reaction of acetone and bromine in potassium

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[1] S. Akiyoshi, T. Aso and S. Imoto, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **57**, 58 (1954).

[2] D. Ali, H. F. Mark and R. B. Mesrobian, *Ind. & Eng. Chem.*, **42**, 484 (1950).

Table 1. Properties of monomer and dimer

	Monomer (n=1)				Dimer (n=2)			
Mol wt	390 (calcd 395)				460 (calcd 457)			
bp	80—87°C/2 mmHg				120—125°C/2 mmHg			
n_D^{27}	1.6490				1.6948			
	(%)				(%)			
Anal.	C	H	Cl	Br	C	H	Cl	Br
Calcd[a]	9.14	0.76	8.99	81.1	13.15	1.32	15.53	69.99
Found	9.23	0.78	8.98	81.0	13.36	1.48	15.46	69.70

a) Calculated for $Br_3C(CH_2CHCl)Br$ and $Br_3C(CH_2CHCl)_2Br$.

hydroxide solutions and purified by recrystallization. α,α'-Azobisisobutyronitrile was purified by recrystallization from methanol before use.

Telomerizations. Into a glass ampoule with a 100 m*l* capacity, definite amounts of carbon tetrabromide and ABIN were taken and a definite amount of vinyl chloride was charged while cooling in dry ice and then sealed. Reactions were carried out in a reaction oven at a given temperature, being shut from light.

Analyses of Products. After the reaction, unreacted vinyl chloride was removed initially at room temperature under atmospheric pressure and completely under reduced pressure. The number-average molecular weights of the products (telomers) were measured cryoscopically. The lower telomers were separated with distillation and the lower and higher telomers were separated by thin-layer chromatography on silica gel.

Results and Discussions

Separation and Identification of Reaction Products. Residues of reaction mixtures after removing the unreacted vinyl chloride are colorless at lower molar ratio, vinyl chloride/carbon tetrabromide, and pale yellow or brown at higher ratios, higher temperatures and prolonged reaction time. However, it is considered that the main components of the residues are telomers of vinyl chloride and carbon tetrabromide, with a small amount of complicated products resulting from the initiator, because the measured mean molecular weights of the residues are in good agreement with those calculated from the results of quantitative analyses of telomers, as will be shown later.

Two fractions were obtained with the distillation at 2 mmHg. Properties of these products are shown in Table 1. From these results and NMR spectra (Fraction 1, 4.0 and 5.9 ppm; Fraction 2, 3.9, 5.7, 6.3 and 7.1 ppm) and IR spectra (CBr; 610; CBr_3, 630; CCl, 685 cm^{-1}), it was confirmed that these fractions are the telomers, $Br(CHClCH_2)_nCBr_3$, with n=1 and 2 respectively.

Separation of telomers higher than n=3 was impossible by distillation, for they are unstable at elevated temperatures. Thus thin-layer chromatographic separation was carried out. Thin plates (size 20×20 cm², depth 0.15 mm) were prepared of Silica Gel G (Merck) and the spots of product mixtures (0.01—0.03 m*l*) were developed with cyclohexane-chloroform (8: 1.5 by volume) on the vertical plates. Detection of developed spots was made by exposure with iodine vapor or by carbonization with 50% sulfuric acid. The results of the TLC analysis are shown in Table 2, in terms of R_f (the ratio of the origin-spot distance to the origin-developing front distance) and $R_m=\log(1/R_f-1)$. It was confirmed from the development of authentic samples that the spots 1 and 2 are the telomers of n=1 and 2, respectively. Although direct identification of the other spots is impossible, it is plausible that they are the telomers with successively increasing n, for the linearity is found between R_m values and spot numbers. Thus, the spots 1, 2, 3, ⋯ would be assigned to be telomers

Table 2. R_f and R_m values of telomer mixture

Spot	R_f	R_m
1	0.837	−0.710
2	0.740	−0.460
3	0.641	−0.250
4	0.530	−0.052
5	0.409	0.160
6	0.287	0.359
7	0.222	0.545

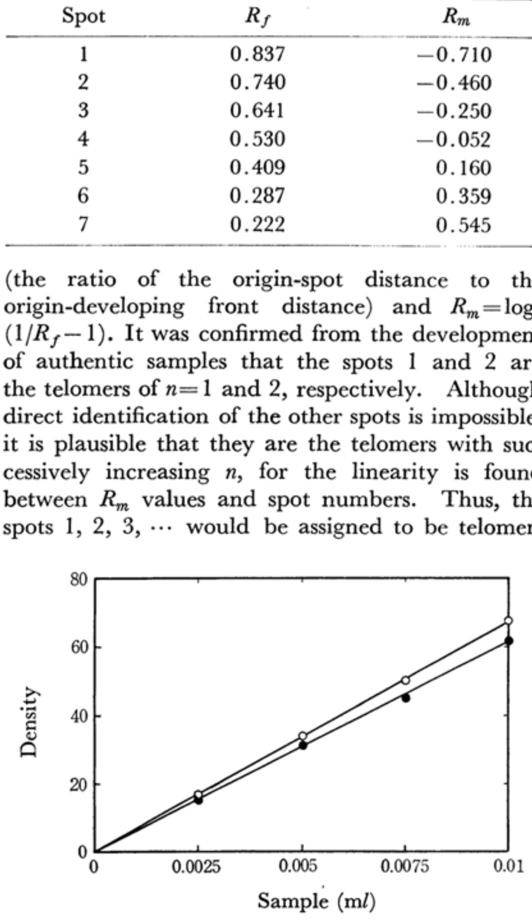

Fig. 1. Relationship between the amounts of telomers and the TLC densities.
○ n=2 telomer; ● n=3 telomer

with $n=1, 2, 3, \cdots$, respectively.

The coloration of spots carbonized with 50% sulfuric acid was measured quantitatively by a TLC densitometer (Seikyo Rika SS-7). The calibration curves for telomers with $n=2$ and 3 were obtained by using the samples separated by distillation as shown in Fig. 1. For the other telomers, it was assumed that the absorption density per mole is proportional to the carbon number in each molecule. This seems to be plausible for molecules in a homolog. The average molecular weights calculated from the results of TLC analysis agree well with the average molecular weights measured cryoscopically.

Effects of Reaction Conditions. From the analyses of the reaction product, it is considered that the telomerization of vinyl chloride with carbon tetrabromide takes place in the present reaction system. Thus, the reaction scheme would be as follows.

$$CBr_4 + R\cdot \rightarrow \cdot CBr_3 + RBr$$

$$\cdot CBr_3 + nCH_2{=}CHCl \rightarrow CBr_3(CH_2CHCl)_{n-1}CH_2\dot{C}HCl$$

$$CBr_3(CH_2CHCl)_{n-1}CH_2\dot{C}HCl + CBr_4 \rightarrow CBr_3(CH_2CHCl)_nBr + \cdot CBr_3$$

$$CBr_3(CH_2CHCl)_n\cdot + CBr_3(CH_2CHCl)_m\cdot \rightarrow CBr_3(CH_2CHCl)_{n+m}CBr_3$$

Total yields, average molecular weights and molecular weight distribution of the telomers are mainly affected by the experimental factors such as the molar ratio of vinyl chloride to carbon tetrabromide, reaction time and temperature. The results for these examinations are summarized in Table 3.

As is expected from the reaction scheme, the conversion of vinyl chloride decreases and the average n value increases with the increasing molar ratio. The increasing reaction time results in slight increases in the conversion and the average n value. Moreover, the increasing temperatures are followed by decreases in the conversion and the average n value. This might be due to the increasing reactivity in telogen molecules at higher temperatures. These results are plausible from the reaction scheme and characterize the telomerization reaction. It should be cited that Bengough *et al.*[3] investigated the telomerization reaction of vinyl chloride and bromotrichloromethane (TBr) and obtained the 1:1 adduct at the molar ratio of vinyl chloride to TBr lower than 10.

TABLE 3. TELOMERIZATION OF VINYL CHLORIDE AND CARBON TETRABROMIDE

No.	Mol ratio[a]	Time (hr)	Temp. (°C)	Conversion of V.C. (%)	Av. mol wt	$\bar{n}$
1	3	5	60	65.0	470	2.2
2	3	5	60	65.2	471	2.2
3	5	5	60	42.5	489	2.5
4	5	5	60	42.1	487	2.5
5	10	5	60	39.0	530	3.2
6	10	5	60	39.2	530	3.2
11	3	1	60	50.5	443	1.8
12	3	1	60	50.0	442	1.8
13	3	3	60	56.3	456	2.0
14	3	3	60	56.0	452	2.0
15	3	5	60	60.9	469	2.2
16	3	5	60	60.5	465	2.2
21	3	3	60	56.3	457	2.0
22	3	3	60	56.5	457	2.0
23	3	3	80	51.0	450	1.9
24	3	3	80	51.2	451	1.9
25	3	3	100	47.9	442	1.8
26	3	3	100	48.0	441	1.8

a) Molar ratio of vinyl chloride to carbon tetrabromide.

Molecular Weight Distribution. The regulation of molecular weight distribution is essentially important for practical purposes. This is difficult in the present stage but the examination was made to get the information for the effect of reaction conditions. The results at various molar ratios of vinyl chloride to carbon tetrabromide are shown in Table 4. The yield in the mole unit decreases when n increases. This is expected in general for the telomerization where the content of telogen is high. When vinyl chloride/carbon tetrabromide is 3, the telomers with $n=1$—6 are obtained and the higher telomers are formed when the molar ratio

TABLE 4. DISTRIBUTION OF DEGREE OF POLYMERIZATION

Mol ratio[a]	Mol% of telomers with n mol units of V.C.							
	1	2	3	4	5	6	7	Others
3	35.34	26.15	25.44	9.54	3.20	0.33	0	0
5	41.50	28.00	25.50	8.25	2.25	1.90	—	3.10
10	30.64	20.83	17.46	10.15	5.51	4.65	3.67	7.09

a) Molar ratio of vinyl chloride to carbon tetrabomide.

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[3] W. I. Bengough, R. A. M. Thomson, *Trans. Faraday Soc.*, **61**, 1735 (1965).

Table 5. Distribution of degree of polymerization at low conversions

Mol ratio[a]	Reaction time (hr)	Mol% of telomers with n mol units of V.C.					
		1	2	3	4	5	6
2	1	53.35	35.57	10.10	1.20	0	0
2.2	1	48.20	32.77	15.20	3.18	0.39	0.26
2.5	1	45.12	31.11	15.20	3.89	0.60	0.08
4	0.5	44.21	31.13	17.49	5.79	1.21	0.18
10	0.5	35.43	26.24	17.49	8.75	3.12	0.79

a) Molar ratio of vinyl chloride to carbon tetrabromide.

becomes high. However, the yield of the telomer with $n=1$ is always the largest. When the reaction time is prolonged, the distribution extends to higher telomers. The main products are the telomers with $n=1$ and 2 at the molar ratio 3, 1 hr and 60°C. When the reaction temperature is higher, the distribution shifts into lower telomers. Thus, at the molar ratio 3 and the reaction time 3 hr, he telomers with $n=1$—7, $n=1$—5 and $n=1$—3 are formed at 60, 80 and 100°C, respectively.

It was, therefore, found that the selective formation of the telomer with $n=1$, *i. e.*, $Br_3CCH_2CHClBr$, is possible in the present reaction system under the conditions of the lower mole ratio, vinyl chloride/carbon tetrabromide, shorter reaction time and higher temperature, but the selective formation of the telomers with medium adduct numbers of vinyl chloride is impossible under the reaction conditions examined in the present investigation.

Chain Transfer Constants. The chain transfer constants C_n of poly(vinyl chloride) radicals $CBr_3(CH_2CHCl)_n^{\cdot}$ to carbon tetrabromide were calculated from the Mayo equation

$$\frac{F_n}{F_{n+1}} = C_n\frac{[S]}{[M]} + \frac{C_n}{C_{n+1}},$$

where F_n is the mole number of active species $CBr_3(CH_2CHCl)_n^{\cdot}$, [S] and [M] are molar concentrations of carbon tetrabromide and vinyl chloride respectively. The conversion must be depressed for the successful use of this relationship. In order to satisfy this requirement and get a wider distribution of molecular weight, experimental data were obtained at the higher mole ratios and the shorter reaction time, the results of which are presented in Table 5. The chain transfer coefficients thus obtained are listed in Table 6. A monotonous increase in C_n with the increasing n is found. This result is consistent with ones obtained by Lewis and Mayo,[4] in different reaction systems and may be attributed to the inductive effect

Table 6. Chain transfer constants

C_1	C_2	C_3	C_4
0.33	1.85	7.45	12.15

Table 7. Telomerization of vinyl chloride with bromoform

Mol ratio[a]	Time (hr)	Temp. (°C)	Conversion of V.C. (%)
0.3	3	60	61.5
0.5	3	60	51.5
1.0	0.5	60	24.1
1.0	1	60	26.5
1.0	2	60	30.0
1.0	3	60	34.4
1.0	3	80	25.8
1.0	3	100	18.0
1.0	5	60	55.9
2.0	3	60	50.0

a) Molar ratio of vinyl chloride to bromoform.

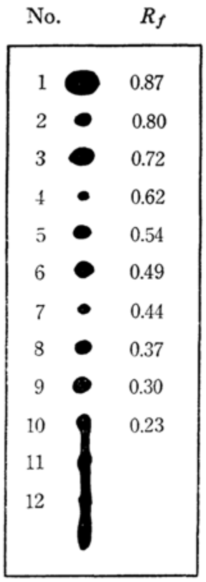

Fig. 2. Thin-layer chromatogram of the telomerization product of vinylchloride and bromoform.

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[4] F. M. Lewis and F. R. Mayo, *J. Am. Chem. Soc.*, **76**, 457 (1954).

of the CBr_3 group as suggested by Walling[5] and Karapetyan.[6]

Telomerization of Vinyl Chloride - Bromoform. Using bromoform instead of carbon tetrabromide as telogen, the telomerization of vinyl chloride was carried out under similar conditions and the results are compared in both systems. The experimental conditions and results are summarized in Table 7.

It was found from the results that both systems show a similar behavior when the taxogen/telogen ratio is lower than unity. That is to say, the conversion of vinyl chloride decreases when the mole ratio increases, the reaction time shortens, and temperature becomes higher. However, when the taxogen/telogen ratio increases over unity, the solid product is formed in a small amount and the conversion increases, making a minimum around unity. The solid product is confirmed to be poly(vinyl chloride). Further, a complicated pattern was found when the product mixture was developed by the thin-layer chromatography. A typical example is shown in Fig. 2. These results are interpreted from the possibilities that the chain transfer of the growing ends is not feasible to bromoform in comparison with carbon tetrabromide and the subtraction by the initiator and growing end radicals takes place at the two alternative positions of bromoform, *i. e.*, H-subtraction and Br-subtraction. For a detailed discussion, identification of products and further examinations under various conditions are necessary and are now in progress.

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5) C. Walling, "Free Radicals in Solution," John Wiley and Sons, New York (1957), p. 257

6) Sh. A. Karapetyan, *Izv. Akad. Nauk*, **1963**, 1346.