[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERISTY OF ILLINOIS]

Optically Active Polymers from Active Vinyl Esters. A Convenient Method of Studying the Kinetics of Polymerization[1]

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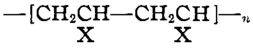
The kinetics of polymerization have been investigated actively in connection with the study of the mechanism of polymerization.[3] The usual method of study has been to isolate the polymer at various stages of the reaction in order to determine the amount formed.[4] Starkweather and Taylor[5] showed that a linear relation existed between the percentage contraction on the volume of the monomer and the degree of polymerization of vinyl acetate and introduced the dilatometer method of following polymerizations. Cuthbertson, Gee and Rideal[6] have used this general procedure to study peroxide catalyzed polymerization of vinyl acetate.

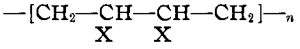
A most convenient method for following the rate of formation of polymer from monomer has now been found in the use of optically active monomeric vinyl derivatives. The monomeric products can be prepared in satisfactory amounts without undue labor and the course of the polymerization can be followed readily by merely observing the change in rotation as the polymerization proceeds. Two optically active monomers of this kind have been prepared and preliminary studies of the rates of polymerization have been made.

d-s-Butyl α-chloroacrylate was prepared by the general methods previously described for related optically inactive esters.[1] The monomer has a specific rotation of +23.5 to +27.5° in dioxane solution depending on the optical purity of the butyl alcohol. The polymer obtained by peroxide catalysis has a specific rotation of +11.04 to +13.05° in dioxane solution. Thus the change in rotation during the polymerization process is sufficient for accurate measurement of the reaction rate. Some difficulty was encountered when the polymerizations were studied at room temperature. The induction period varied over a wide range depending on the exact purity of the sample and polymerization was slow. However, when the polymerizations were carried out at elevated temperatures in the presence of benzoyl peroxide they proceeded rapidly and according to first order kinetics. The corresponding bromoacrylate was prepared but because either hydrogen bromide or *s*-butyl bromide was eliminated in the process, its polymerization was not adaptable to the rate studies.

The second example of active vinyl monomer prepared was vinyl *l*-β-phenylbutyrate. This product was chosen for study because vinyl acetate was known to produce a "head to tail" type of polymer (I)[7] whereas the alkyl chloroacrylates yield a "head to head, tail to tail" type of polymer[8] (II).

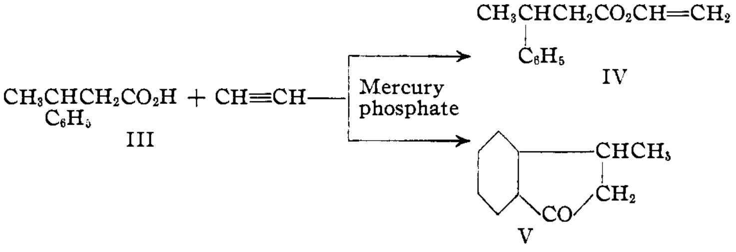

$-[CH_2\underset{X}{C}H-CH_2\underset{X}{C}H]-_n$

I


$-[CH_2-\underset{X}{C}H-\underset{X}{C}H-CH_2]-_n$

II

The vinyl ester (IV) was prepared by adding *l*-β-phenylbutyric acid (III) to acetylene in sealed tubes with mercury phosphate catalyst. The reaction was first worked out with inactive acid. The addition reaction is accompanied by a cyclization reaction to produce the 3-methylindanone (V) which forms a constant boiling mixture with the vinyl ester. The two were separated by use of Girard's Reagent T.[9] The vinyl *l*-β-phenylbutyrate had a specific rotation of −20.4° and its polymer had a specific rotation of −29.2° in dioxane at 25°. The polymerization proceeded smoothly



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[1] This is the eleventh communication on vinyl polymers. For the tenth see THIS JOURNAL, **62**, 3495 (1940).

[2] Du Pont Special Research Assistant in Chemistry, 1940.

[3] For a complete literature survey on this topic see Melville, "Annual Reports on the Progress of Chemistry," 1939, p. 61.

[4] For example, see Schulz and Wittig, *Naturwissenschaften*, **27**, 387 (1939); Schulz, *ibid.*, **27**, 659 (1939); Schulz, Dinglinger and Husemann, *Z. physik. Chem.*, **B43**, 385 (1939); Norrish and Brookman, *Proc. Roy. Soc.* (London), **A171**, 147 (1939).

[5] Starkweather and Taylor, THIS JOURNAL, **52**, 4708 (1930).

[6] Cuthbertson, Gee and Rideal, *Proc. Roy. Soc.*, **A170**, 300 (1939).

[7] Marvel and Denoon, THIS JOURNAL, **60**, 1045 (1938).

[8] Marvel and Cowan, *ibid.*, **61**, 3156 (1939).

[9] Girard and Sandulesco, *Helv. Chim. Acta*, **19**, 1095 (1936).

at elevated temperatures in the presence of peroxides and in dioxane solution. It likewise followed the course of a first order reaction.

The calculations used in determining the order of the reaction take into account the concentrations of the monomer and the polymer at a given time and the amount of rotation contributed by each. In these equations[10] γ_m is the specific rotation of the monomer; γ_p is the specific rotation of the polymer; γ_T is the specific rotation of the solution at time, T; $\left(\gamma_T = \frac{100\alpha_T}{\alpha C_0}\right)$; C_0 is the initial and C_T the concentration at time T of the monomer expressed in grams per 100 cc. of solution.

$$C_0\gamma_T = C_T\gamma_m + (C_0 - C_T)\gamma_p$$

Solving for C_T

$$C_T = \frac{C_0(\gamma_T - \gamma_p)}{\gamma_m - \gamma_p}$$

In setting up these equations it has been assumed that the optical rotation due to each monomeric unit in the polymer chain is independent of the length of the chain.

In the case of vinyl *l*-β-phenylbutyrate the results of the polymerization studies were plotted for zero, first and second order reactions (Figs. 1, 2 and 3). Only the plot for a first order (Fig. 2) reaction gave a straight line. Similarly the polymerization of *d*-*s*-butyl α-chloroacrylate proceeded by a first order mechanism (Figs. 4 and 5).

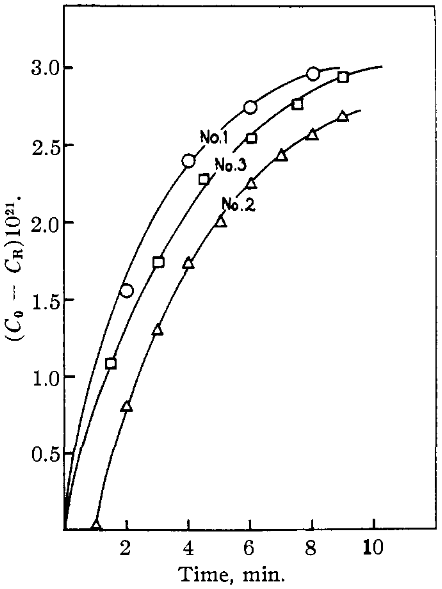

Fig 1.

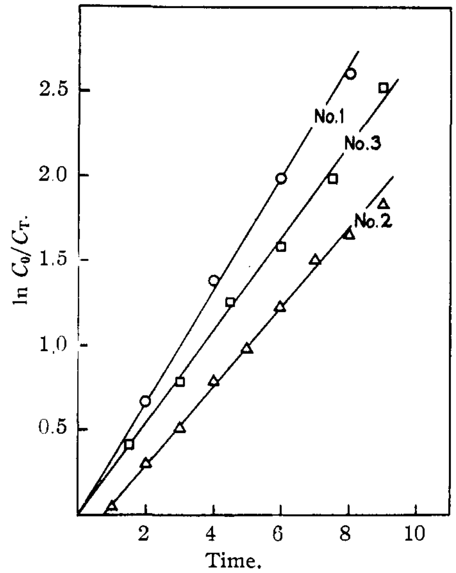

Fig. 2.

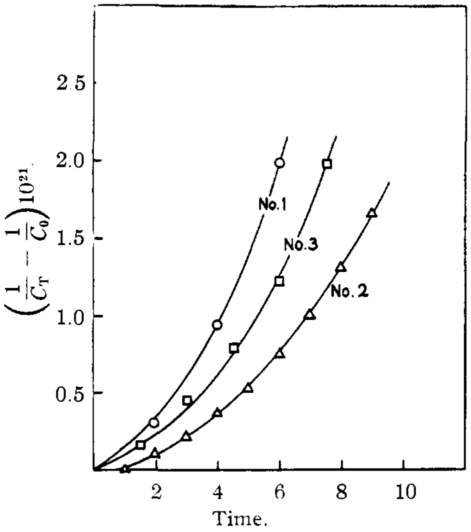

Fig. 3

These results are of interest because they indicate that the activation of the monomer, which is probably the phase of the polymerization process which was measured, is of the same type and proceeds as a first order reaction whether the final polymer has a "head to tail" or a "head to head, tail to tail" structure.

Experimental

***d*-*s*-Butyl α,β-Dichloropropionate.**—Sixteen and two-tenths grams of α,β-dichloropropionyl chloride was added slowly with stirring and cooling to 7.4 g. of *d*-*s*-butyl alcohol ($[\alpha]^{28}_D$ +12.25, 1.50 g. in 25 cc. of dioxane solution). The mixture was allowed to stand at room temperature for about three hours; then warmed for about fifteen minutes at 60–70° before distillation under reduced pressure. The

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[10] We are indebted to Dr. C. C. Price and Dr. F. T. Wall for aid in setting up the equations which were used to calculate the rate of reaction from the change in rotation.

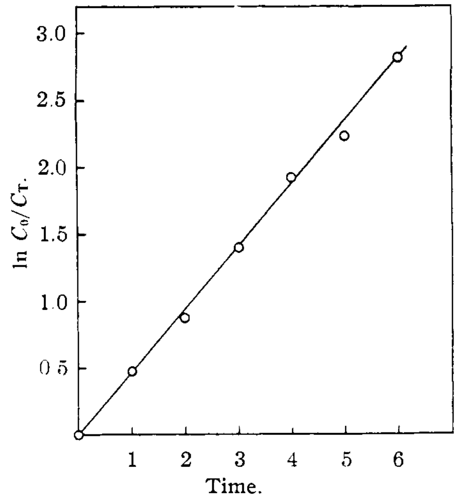

Fig 4

yield was 17.5 g. (88%) of ester boiling at 59–62° (3 mm.), n^{20}_D 1.4423; $[\alpha]^{25}_D$ 12.69 (1.3 g. in 25 cc. of dioxane solution).

Anal. Calcd. for $C_7H_{12}O_2Cl_2$: C, 42.21; H, 6.03. Found: C, 42.53; H, 6.18.

d-s-**Butyl** α-**Chloroacrylate.**—A mixture of 18 g. of quinoline and 18.5 g. of *d-s*-butyl α,β-dichloropropionate was heated in a 100-cc. modified Claisen flask at 80–90° for ten minutes and then distilled under reduced pressure. The distillate boiling at 66–82° (23 mm.) was taken up in chloroform, washed with two 15-cc. portions of 5% sulfuric acid and then with water. The chloroform solution was dried over anhydrous sodium sulfate and distilled under reduced pressure. The yield was 7.2 g. (48%) of ester, b. p. 70–71° (23 mm.); n^{20}_D 1.4360; $[\alpha]^{25}_D$ +26.0 (1.663 g. in 25 cc. of dioxane solution). The rotation of the various samples of ester prepared varied from +23.5 to +27.5°, depending on the optical purity of the alcohol used.

Anal. Calcd. for $C_7H_{11}O_2Cl$: C, 51.83; H, 6.79. Found: C, 51.28; H, 6.77.

Polymer of *d-s*-**Butyl** α-**Chloroacrylate.**—The active ester polymerized readily on standing to give a glassy solid. It was also polymerized by dissolving in dioxane, adding 25% benzoyl peroxide and allowing the mixture to stand for a few days. The polymer was precipitated from this solution as a powder by adding alcohol; $[\alpha]^{26}_D$ +11.04° (1.40 g. in 25 cc. dioxane solution).

Anal. Calcd. for $C_7H_{11}O_2Cl$: Cl, 21.85. Found: Cl, 21.69.

d-s-**Butyl** α,β-**Dibromopropionate.**[11]—From 5 g. of *d-s*-butyl alcohol ($[\alpha]^{20}_D$ +9.06° and 17 g. of α,β-dibromopropionyl chloride was obtained 12 g. (63%) of *d-s*-butyl α,β-dibromopropionate, b. p. 93–95° (8 mm.), $[\alpha]^{30}_D$ +6.15° for pure liquid.

d-s-**Butyl** α-**Bromoacrylate.**[12]—From 8 g. of this dibromo ester and 8 g. of quinoline warmed to 80° for five minutes, 4 g. (70%) of *d-s*-butyl α-bromoacrylate, b. p. 58–60° (8 mm.) was obtained; $[\alpha]^{30}_D$ +19.37° (1.3098 g. diluted to 10 cc. with dioxane). The rotation of the ester was of course dependent on the optical purity of the *d-s*-butyl alcohol used and some samples with a lower rotation were used.

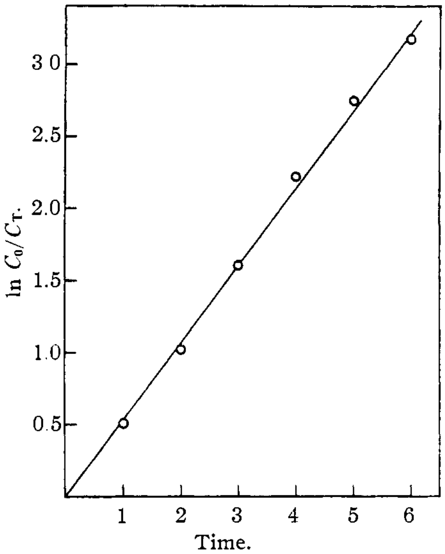

Fig. 5.

Poly *d-s*-**Butyl** α-**Bromoacrylate.**[12]—A solution of 2.569 g. of the *d-s*-butyl α-bromoacrylate ($[\alpha]^{30}_D$ +18.05°) and 0.585 g. of benzoyl peroxide in enough dioxane to give a total volume of 10 cc. was allowed to stand for twenty-seven hours until the rotation became constant. The polymer was then isolated by evaporating the solvent and washing the polymer thoroughly with alcohol. The yield was 0.65 g. A solution of 0.4730 g. of this polymer in 10 cc. of dioxane had a rotation of +0.35°, $[\alpha]^{30}_D$ +7.4°.

Anal. Calcd. for $C_7H_{11}O_2Br$: Br, 38.6. Found: Br, 30.96.

The polymerization was apparently accompanied by a side reaction which caused the loss of either hydrogen bromide or *s*-butyl bromide and hence this ester polymerization was not studied further.

dl-β-**Phenylbutyric Acid.**—This acid was prepared by a modification of the Eÿkman method.[12] A solution of 130 g. of crotonic acid in 400 cc. of dry benzene was added slowly to a well-stirred mixture of 340 g. of anhydrous aluminum chloride in 200 cc. of benzene. This mixture was stirred at room temperature for two days and then decomposed with ice and concentrated hydrochloric acid. The benzene solution was separated, washed thoroughly with water and distilled. The yield of *dl*-β-phenylbutyric acid boiling at 134–136° (6 mm.) was 220 g. (89%).

Vinyl *dl*-β-**Phenylbutyrate.**—*dl*-β-Phenylbutyric acid was mixed with about one-fourth its weight of mercuric phosphate,[13] about 1% of hydroquinone was added and the mixture was placed in a glass-lined shaker tube and treated with acetylene at 200–220 lb. per square inch pressure. The temperature was held at approximately 100° and the tubes were shaken for four to eight hours. For a typical run 37 g. of acid, 10 g. of catalyst and 1 g. of hydroquinone

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(11) These preparations were first carried out by Dr. John Charles Cowan.

(12) Eÿkman, *Chem. Weekblad*, **5**, 655 (1908).

(13) Skirrow and Morrison, U. S. Patent 1,710,197, April 23, 1929.

were used and the mixture was held at 100° for four hours. The tube was opened, the contents diluted with ether and filtered to remove the catalyst, washed with 10% sodium carbonate solution to remove excess acid and then distilled. The fractions taken were 90–97°, 97–100° and 100–135° (3 mm.). The second fraction which was presumably the desired ester weighed 16 g. These various fractions from several runs using a total of 163 g. of acid were mixed and again distilled and the fraction boiling at 112–115° (7 mm.) was collected. The yield of this fraction was 32 g. Redistillation of this fraction gave 24 g. of light yellow oil, b. p. 96–98° (2 mm.), $n^{20}\text{D}$ 1.5252, d^{20}_4 1.1051.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.75; H, 7.44. Found: C, 78.56, 78.72; H, 7.37, 7.42.

Since this analysis indicated that the ester was much too high in carbon it was examined for impurities. Saponification with 10% potassium hydroxide gave *dl*-β-phenylbutyric acid, thus showing that no reaction between the acetylene and the benzene ring of the acid had occurred.

Treatment of 3 g. of the ester fraction with 1 g. of 2,4-dinitrophenylhydrazine in 100 cc. of 95% alcohol and 1.5 cc. of concentrated hydrochloric acid gave 1.6 g. of a derivative (m. p. 235–237°). After crystallization from ethyl alcohol this derivative melted at 239–241°.

Anal. Calcd. for $C_{16}H_{14}O_4N_4$: N, 17.2. Found: N, 17.1.

This analysis checks for the 2,4-dinitrophenylhydrazone of 3-methylindanone-1. A 50–50 mixture of this ketone and the expected vinyl ester have a composition of C, 78.98 and H, 7.30, which checks almost exactly with the results obtained.

The ester and ketone were separated by treating 10 g. of the mixture in 90 cc. of absolute alcohol with 10 cc. of glacial acetic acid and 10 g. of Girard's Reagent T[10] at the boiling point for one hour. About half of the alcohol was removed by distillation and the residue was poured into a mixture of ice, water and 6.5 g. of sodium carbonate. This solution was extracted with two 50-cc. portions of ether, the extract was dried and then distilled. The yield was 6 g. of a clear, white liquid, b. p. 93–94° (2–3 mm.), $n^{20}\text{D}$ 1.5051.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.75; H, 7.44. Found: C, 75.76; H, 7.43.

The sodium carbonate solution from which the ester was extracted was acidified with 10 cc. of concentrated hydrochloric acid and heated on the steam cone for an hour. A dark insoluble oil separated. It was taken up in ether, the extract dried over calcium chloride and then distilled. The yield was 3 g. of light yellow liquid, b. p. 101–102° (3 mm.), $n^{20}\text{D}$ 1.5515. A 2,4-dinitrophenylhydrazone prepared from this material melted at 239–241°. These compounds proved to be identical with synthetic 3-methylindanone-1 and its 2,4-dinitrophenylhydrazone.

3-Methylindanone-1.—This ketone was prepared from 25 g. of β-phenylbutyryl chloride and aluminum chloride by the procedure of von Braun and Kirschbaum.[14] The product boiled at 95–97° (2–3 mm.), $n^{20}\text{D}$ 1.5568. The 2,4-dinitrophenylhydrazone melted at 239–241° and showed no depression in melting point when mixed with the sample isolated from the above vinyl ester.

Polymerization of Vinyl *dl*-β-Phenylbutyrate.—A solution of 1 g. of vinyl *dl*-β-phenylbutyrate and 0.5 g. of benzoyl peroxide in 10 cc. of dioxane was heated on the steam cone for twelve hours. The addition of 95% ethyl alcohol precipitated a soft tacky resin. After drying under reduced pressure the polymer remained tacky.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.75; H, 7.44. Found: C, 75.43; H, 7.72.

Vinyl *l*-β-Phenylbutyrate.—The *dl*-phenylbutyric acid was resolved by the procedure of Rupe and Busolt.[15] The *l*-isomer of the acid was converted to the vinyl ester by the same procedure described for the racemic acid. From 95 g. of the acid there was obtained 24 g. (20%) of ester fraction boiling at 101–107° (4 mm.), $n^{20}\text{D}$ 1.5076.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.75; H, 7.44. Found: C, 76.70; H, 7.83.

A sample of this ester was treated with 2,4-dinitrophenylhydrazine and only a small amount of a 2,4-dinitrophenylhydrazone separated. After recrystallization from ethyl acetate this *l*-2-methylindanone-1 derivative melted at 257–258°.

Anal. Calcd. for $C_{16}H_{14}O_4N_4$: C, 58.89; H, 4.33. Found: C, 58.98; H, 4.34.

A mixture of 22 g. of the above impure ester, 90 cc. of absolute ethyl alcohol, 10 cc. of glacial acetic acid and 15 g. of Girard's Reagent T were refluxed for one hour. The ester was then isolated as described for the racemic isomer. The yield was 16 g., b. p. 93–95° (2 mm.); $n^{20}\text{D}$, 1.5050; $[\alpha]^{25}\text{D}$ $-20.4°$ (0.599 g. in 25 cc. dioxane).

Polymer of Vinyl *l*-β-Phenylbutyrate.—To a solution of 0.3178 g. of the *l*-ester in dioxane was added a solution of 0.3 g. of benzoyl peroxide in dioxane. The solution was heated for twenty-four hours on a steam cone, then cooled and made up to exactly 25 cc. with dioxane. The specific rotation for the polymer at 25° in this solution was $-29.1°$. No attempt was made to isolate the tacky polymer.

Kinetic Studies on Polymerization of Optically Active Esters.—The reactions were carried out in a special polariscope tube 1.76 dm. long of Pyrex glass with an electrically heated oil jacket. The end plates of optical Pyrex glass were sealed to the tube with "Sauereisen Cement." A coil of nichrome wire which had a resistance of 1 ohm per foot was placed in the outer oil jacket and connected through a rheostat. The resistance was adjusted so the oil jacket was maintained at 60°. When the tube was heated, sufficient strain was put on the optical end plates so that readings could not be made. Hence, it was necessary to heat the polymerization mixture a definite time, cool rapidly to room temperature (25°), take a reading and then repeat the process. Three different polymerization experiments were carried out with vinyl *l*-β-phenylbutyrate and they differed only in the time of heating between readings.

The first experiment was made with 0.599 g.

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(14) Von Braun and Kirschbaum, *Ber.*, **46**, 3041 (1913).

(15) Rupe and Busolt, *Ann.*, **369**, 323 (1909).

TABLE I

POLYMERIZATION OF VINYL *l*-PHENYLBUTYRATE

Reading	Rotation	γ_T	$C_T \times 10^{21}$	C_0/C_T	$\ln C_0/C_T$	$\frac{1}{C_T} \times 10^{21}$	$\left(\frac{1}{C_T} - \frac{1}{C_0}\right)^{21}$	$(C_0 - C_T)10^{21}$
0	−0.86	−20.4						
1	−1.04	−24.7	1.63	1.958	0.673	0.614	0.300	1.56
2	−1.14	−27.0	0.797	4.00	1.386	1.255	.941	2.40
3	−1.18	−28.0	.435	7.34	1.993	2.30	1.986	2.75
4	−1.20	−28.5	.235	13.60	2.609	4.26	3.946	2.95
Final	−1.23	−29.2						

TABLE II

POLYMERIZATION OF VINYL *l*-β-PHENYLBUTYRATE

Reading	Rotation	γ_T	$C_T \times 10^{21}$	C_0/C_T	$\ln C_0/C_T$	$\frac{1}{C_T} \times 10^{21}$	$\left(\frac{1}{C_T} - \frac{1}{C_0}\right)10^{21}$	$(C_0 - C_T)10^{21}$
0	−2.64	−20.6						
1	−2.68	−20.9	3.01	1.060	0.058	0.332	0.018	0.18
2	−2.90	−22.6	2.39	1.335	.305	.418	.104	0.80
3	−3.08	−24.0	1.88	1.693	.527	.532	.218	1.31
4	−3.23	−25.2	1.45	2.20	.788	.690	.376	1.74
5	−3.32	−25.9	1.19	2.67	.982	.837	.523	2.00
6	−3.41	−26.6	0.942	3.39	1.221	1.062	.748	2.25
7	−3.48	−27.1	.761	4.19	1.509	1.315	1.001	2.43
8	−3.53	−27.5	.615	5.19	1.647	1.627	1.313	2.57
9	−3.56	−27.8	.507	6.28	1.837	1.975	1.661	2.68
Final	−3.72	−29.1						

TABLE III

POLYMERIZATION OF VINYL *l*-β-PHENYLBUTYRATE

Reading	Rotation	γ_T	$C_T \times 10^{21}$	C_0/C_T	$\ln C_0/C_T$	$\frac{1}{C_T} \times 10^{21}$	$\left(\frac{1}{C_T} - \frac{1}{C_0}\right)10^{21}$	$(C_0 - C_T)10^{21}$
0	−2.20	−20.9						
1	-2.45^-	−23.3	2.10	1.52	0.419	0.476	0.162	1.09
2	-2.64^+	−25.2	1.45	2.20	.788	.759	.445	1.74
3	−2.80	−26.7	0.906	3.52	1.258	1.105	.791	2.28
4	-2.88^-	−27.4	.653	4.89	1.587	1.535	1.221	2.54
5	−2.94	−28.0	.434	7.36	1.996	2.30	1.986	2.76
6	-2.98^+	−28.5	.253	12.60	2.532	3.95	3.636	2.94
Final	−3.07	−29.2						

TABLE IV

POLYMERIZATION OF *d*-*s*-BUTYL α-CHLOROACRYLATE

Reading	Rotation	γ_T	$C_T \times 10^{21}$	C_0/C_T	$\ln C_0/C_T$	$\frac{1}{C_T} \times 10^{21}$	$\left(\frac{1}{C_T} - \frac{1}{C_0}\right)10^{21}$	$(C_0 - C_T)10^{21}$
0	3.04	26.0						
1	2.42	20.7	2.33	1.60	0.470	0.429	0.16	1.40
2	2.08	17.8	1.565	2.38	.867	.64	.37	2.17
3	1.80	15.4	0.929	4.02	1.39	1.08	.81	2.80
4	1.64	14.0	.557	6.80	1.92	1.80	1.53	3.17
5	1.56	13.3^+	.384	9.72	2.27	2.60	2.33	3.35
6	1.48	12.7^+	.224	16.6	2.81	4.46	4.19	3.51
Final	1.39	11.9						

TABLE V

POLYMERIZATION OF *d*-*s*-BUTYL α-CHLOROACRYLATE

Reading	Rotation	γ_T	$C_T \times 10^{21}$	C_0/C_T	$\ln C_0/C_T$	$\frac{1}{C_T} \times 10^{21}$	$\left(\frac{1}{C_T} - \frac{1}{C_0}\right)10^{21}$	$(C_0 - C_T)10^{21}$
0	2.79	25.8						
1	2.20	20.4	2.25	1.67	0.51	0.444	0.176	1.48
2	1.84	17.0^+	1.36	2.74	1.01	.735	.467	2.37
3	1.59	14.7^+	0.75	4.98	1.61	1.33	1.06	2.98
4	1.45	13.4^+	.404	9.25	2.22	2.47	2.20	3.33
5	1.38	12.8^-	.235	15.90	2.75	4.25	3.98	3.49
6	1.35	12.5	.159	23.4	3.17	6.28	6.01	3.57

of the *l*-ester in 25 cc. of dioxane to which 0.5 g. of benzoyl peroxide was added. The solution was placed in the polarimeter cell and heated two hours at 60°, cooled to 25° and read; heated again, etc. The data from this run are given in Table I.

These results are plotted in Curve No. 1, Figs. 1, 2 and 3.

The final reading in each experiment was taken after the cell had been heated overnight in order to determine the rotation of the polymer itself.

In the second experiment on vinyl *l*-butyrate 1.8214 g. of ester and 0.5 g. of benzoyl peroxide in 25 cc. of dioxane were used. The first heating period was forty-five minutes but the change in rotation was so small that the subsequent heating periods were made one hour long. The data for this experiment are collected in Table II and the results are plotted in Curve No. 2 in the Figs. 1, 2 and 3.

The third experiment was made with 1.4914 g. of ester. The heating periods were ninety minutes long. The results are collected in Table III and Curve No. 3 on Figs. 1, 2 and 3.

Two experiments on *d*-*s*-butyl α-chloroacrylate were made with 1.663 g. and 1.538 g. of ester, respectively, with 0.5 g. of benzoyl peroxide each in 25 cc. of dioxane. The heating periods were one hour. The final reading in the first experiment was taken after an overnight heating period to give the rotation of the polymer. The results are summarized in Tables IV and V and are plotted in Figs. 4 and 5.

Summary

d-*s*-Butyl α-chloroacrylate and vinyl *l*-β-phenylbutyrate have been prepared and polymerized. The rate of polymerization can be followed conveniently by means of the polariscope. In the presence of peroxides the polymerization of each ester was a first order reaction.

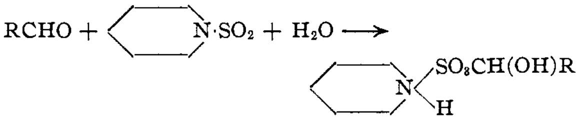
URBANA, ILLINOIS RECEIVED SEPTEMBER 18, 1940

[CONTRIBUTION FROM THE AMMONIA DEPARTMENT OF E. I. DU PONT DE NEMOURS AND COMPANY, INC.]

Analytical Procedures Employing Karl Fischer Reagent.[1]
V. The Determination of Water in the Presence of Carbonyl Compounds

BY W. M. D. BRYANT, J. MITCHELL, JR., AND DONALD MILTON SMITH

The usual Karl Fischer reagent is unsatisfactory for the direct titration of water in the presence of aldehydes and ketones due to the tendency to form acetals and ketals,[1] with the production of additional water. A modified reagent containing a minimum quantity of methanol was found satisfactory for water in the presence of ketones but not aldehydes. With aldehydes low results were obtained where appreciable quantities of water were present. It was possible to show that aldehydes react with water and the $C_5H_5NSO_2$ of the reagent, probably as follows



In the present investigation a procedure was devised by which all types of carbonyl compounds are rendered inert toward the methanol of unmodified Karl Fischer reagent before the titration for water is started. This is accomplished by the reaction of the carbonyl with a dilute solution of hydrocyanic acid in pyridine (or dioxane)

$$\mathrm{RCHO + HCN = RCH(OH)CN} \text{ and}$$
$$\mathrm{RCOR' + HCN = RR'C(OH)CN}$$

The resulting cyanhydrin does not interfere with the titration for water.

Inspection of the experimental data of Lapworth and Manske tabulated by Homer Adkins[2] shows that equilibrium in the above reactions favors cyanhydrin formation in most of the cases studied, the conversion usually exceeding 90% for equimolecular mixtures of carbonyl and hydrogen cyanide.

The aldehydes and ketones less reactive toward hydrogen cyanide also show less tendency to combine with the methanol of Karl Fischer reagent, hence the failure of a few carbonyl compounds to form appreciable amounts of the cyanhydrin

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(1) This reagent, discussed in detail in the first paper of the series (Smith, Bryant and Mitchell, THIS JOURNAL, **61**, 2407 (1939)), consists of a solution of iodine, sulfur dioxide and pyridine in methanol. It is specific for water.

(2) Gilman, "Organic Chemistry," Vol. I, John Wiley and Sons, Inc., 1938, p. 807.