Polymer Journal, Vol. 10, No. 3, pp 281—285 (1978)

Sequence Length Required for Poly(vinyl acetate)—Iodine and Poly(vinyl alcohol)—Iodine Color Reactions

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(Received October 5, 1977)

ABSTRACT: An oligomeric mixture of poly(vinyl acetate) (PVAc) was subjected to preparative gel-permeation chromatography, yielding pure n-mer in the range of $n=$ 4—14. These n-mers, fractionated poly(vinyl acetate), and derived poly(vinyl alcohol) were used to study their color reaction with iodine in order to find the lower limits of the degree of polymerization for these reactions. In the poly(vinyl acetate)—iodine reaction the red-violet color began to appear at 12-mer. Tetradecamer was not long enough for the blue-color reaction of poly(vinyl alcohol)—iodine.

KEY WORDS Poly(vinyl acetate) / Poly(vinyl alcohol) / Iodine / Color Reaction / Degree of Polymerization / Oligomer / Gel-Permeation Chromatography /

It is understood on the red-violet complex of poly(vinyl acetate) (PVAc)—iodine[1] and the blue complex of poly(vinyl alcohol) (PVA)—iodine[2] that a linear alignment of iodine atoms is included by the molecules of PVAc and PVA, respectively. It is known for the reactions that high-molecular-weight polymers yield stable complexes but that the dimer or trimer does not. Thus, it is important to the understanding of these complexes to determine at what degree of polymerization the complex formation begin to take place.

Information up to this point on the dependency of the reactions on the degree of polymerization is as follows. The PVAc—iodine reaction was reported by Hayashi, *et al.*,[3] to be independent of the degree of polymerization in the range from 280 to 2380. The PVA—iodine reaction, according to Imai, *et al.*, was linearly dependent on the degree of polymerization in the range from several hundreds to 4000.[4] Using the fact that the 1,2-glycol unit in PVA sensitively damages the color reaction, we estimated the lower limit of the required degree of polymerization to be around 120.[5]

Thus, since the threshold degree of polymerization of these reactions was expected to be rather low, we attempted to isolate individual oligomers in the pure state and to study the lower limit of the degree of polymerization required for these reactions.

EXPERIMENTAL

Preparation of Vinyl Acetate Oligomers

Telomerization. Into a 1-*l* three-necked flask containing 1 mol of chloroform, was added a solution of vinyl acetate (1 mol) and benzoyl peroxide (0.01 mol) in 1 mol of coloroform at 60°C under nitrogen in 8 hr. The reaction was continued for additional 2 hr. The chloroform solution was washed with 500 m*l* of a 10-% aqueous $NaHCO_3$ in 3 portions, washed with water, and then dried over $MgSO_4$. Evaporation of chloroform *in vacuo* gave 74.0 g of a telomer mixture.

To remove a high-molecular-weight portion, the telomer was subjected to chromatography using a Sephadex LH-20 column (100×2.5 cm). In each run, 5 g of the telomer in 5 m*l* of methanol was charged and eluted with methanol. The first fraction of 50 m*l* out of the total 210 m*l* after a void volume of 90 m*l* was discarded. The residual fraction showed the gel-permeation

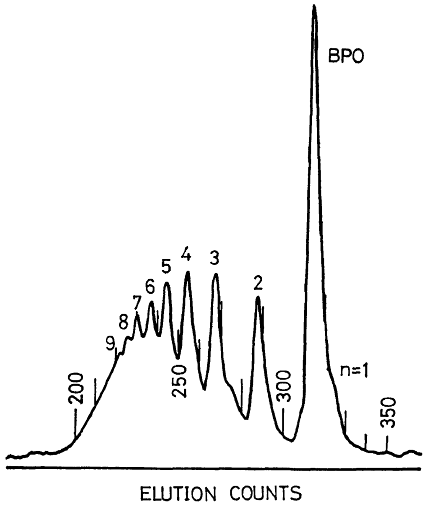

Figure 1. GPC of vinyl acetate telomers as polymerized. *n* represents the degree of polymerization.

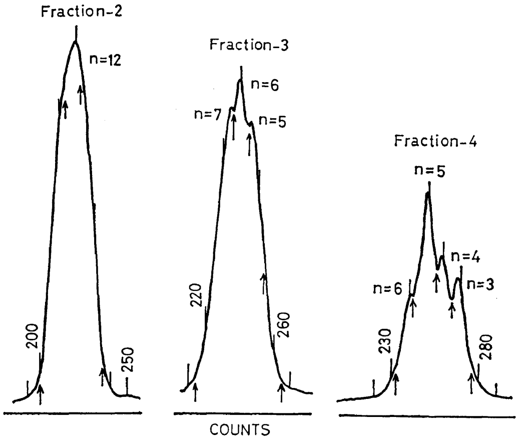

Figure 2. GPC of roughly fractionated telomers. End group was reduced.

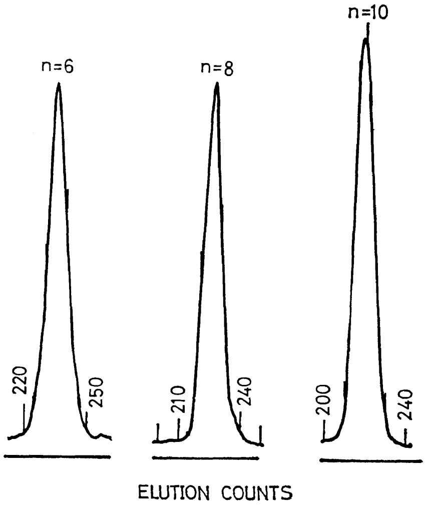

Figure 3. GPC of purified telomers.

chromatogram (GPC) shown in Figure 1.

Reduction of the End Group. Since the terminal trichloromethyl group might not be stable during subsequent treatment and reactions, it was converted into the methyl group by a procedure described elsewhere.[6] To remove a trace of tin originating from the reductant, the reduced oligomer was solvolyzed with NaOH in methanol, deionized with Dowex 50W-X2 and Dowex I-X8, dried, and reacetylated with pyridine—acetic anhydride (v/v=2/1) at 40—50°C for 10 hr. The reaction mixture was evaporated *in vacuo*, the residue was dissolved in chloroform, washed with aqueous $NaHCO_3$ and with water, dried over $MgSO_4$, and chloroform was evaporated, leaving a purified oligomer. Infrared, absorptions of ν_{C-Cl} at 780 and 700 cm^{-1} completely disappeared on reduction. The yield was 1.89 g out of 5.04 g of the telomer.

Isolation of n-mer. The reduced telomer was roughly fractionated using a Sephadex LH-20 column (180×2.5 cm). The telomer (5 g) in 5 m*l* of methanol was charged and eluted with methanol, giving 5 fractions of each 100 m*l* after a void volume of 300 m*l*. GPC of the middle 3 fractions is shown in Figure 2 and the fractions were subjected to detailed GPC separation using a Toyo Soda HLC 807 preparative gel-permeation chromatograph (column TSK GEL G2000H) at 37°C with a charge of 100 mg in chloroform. Fraction 2 was separated into 3 fractions, fraction 3 into 4 fractions and fraction 4 into 4 fractions as shown by arrows in Figure 2. A further GPC separation was continued until each fraction was obtained in the monodisperse state as shown in Figure 3. M_w/M_n values calculated from the GPC curve were 1.017 for pentamer and 1.028 for dodecamer, for example. The infrared spectrum of hexamer is shown in Figure 4 and refractive indexes of isolated telomers are shown in Table I.

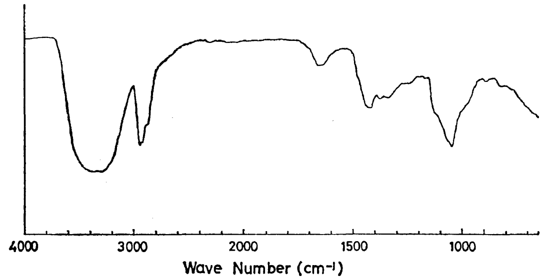

Figure 4. Infrared spectrum of vinyl alcohol hexamer.

Table I. Refractive index of fractionated telomers

Mer No.	Refractive index n_D^{20}	
	As telomerized	End group reduced
4	1.4700	1.4519
5	1.4700	1.4600
6	1.4699	1.4628
7	1.4695	1.4614
8	—	1.4650
9	—	1.4667
10	—	1.4681
11	—	1.4689
12	—	1.4682

Conversion into PVA. Conversion of the reduced oligomeric PVAc into PVA was not successful by the usual methanolysis with sodium hydroxide in methanol or sodium methoxide in methanol but rather by the reduction with lithium aluminum hydride in tetrahydrofuran. To a solution of the reduced telomer (0.1 g) in 5 m*l* of tetrahydrofuran was added a solution of $LiAlH_4$ (0.45 g) in 5 m*l* of tetrahydrofuran at room temperature within a period of one hour. The reaction mixture was poured into cold water, filtered, deionized through ion-exchange resins Dowex 50W-X2 and Dowex 1-X8, and the water was evaporated. The obtained PVA had a very weak absorption due to unsaturation at 213 nm. The degree of the estimated unsaturation assuming $\varepsilon=10000$ was one per 170 monomeric units for hexamer, for example.

Fractionation of Poly(*vinyl acetate*)

In order to obtain specimens of a larger degree of polymerization than 14, the fractionation of commercial poly(vinyl acetate) was carried out by adding water to the 2-% aqueous solutions in acetone. A fractionation was carried out with poly(vinyl acetate) whose PVA (DP=390) was cleaved beforehand by periodate. Specimens used in the following experiments are shown in Table II. Conversion of PVAc into PVA in this case was carried out by the usual methanolysis method.

Table II. Molecular weight of fractionated poly(vinyl acetate)

Starting material[a]	$M_w(\times 10^4)$	$M_n(\times 10^4)$	M_w/M_n	DP
A (DP=1220)	20.3	10.6	1.92	1230
	10.4	6.55	1.59	760
B (DP=390)	7.21	4.40	1.64	510
	5.13	3.04	1.69	350
	3.46	2.27	1.52	260
	1.81	1.32	1.73	150
Periodate-treated B	2.11	1.38	1.53	160
	1.63	1.07	1.52	120
	1.06	0.65	1.63	80

[a] Commercial PVA was supplied by Nippon Gohsei Chem. Ind. Co., Ltd.

Complex Formation

Poly(*vinyl acetate*)*—Iodine.* A 0.3-m*l* portion of a poly(vinyl acetate) solution in methanol (26.05 mmol/*l*) and 3 m*l* of an aqueous I_2—KI solution ($[I_2]=5$ mmol/*l*, [KI]=20 mmol/*l*) was mixed and was kept standing for 20 hr at room temperature. Absorption spectra were measured using an I_2—KI solution ($[I_2]=4.55$ mmol/*l*, [KI]=18.2 mmol/*l*, $H_2O/CH_3OH=10/1$(v/v) as a reference and a Hitachi-124 Spectrophotometer at 15°C. Ethyl acetate, 2,4-diacetoxypentane, and 2,4,6-triacetoxyheptane were used as the monomer, dimer, and trimer, respectively.

Poly(*vinyl alcohol*)*—Iodine.* A 2.5-m*l* portion of a PVA solution (80 mmol/*l*), 0.4 m*l* of an aqueous I_2—KI solution ($[I_2]=50$ mmol/*l*, [KI]=200 mmol/*l*), and 0.8 m*l* of 5-% aqueous boric acid were mixed, made up to 4 m*l* and the whole solution was kept in a refregerator for 20 hr. Absorption spectra were taken at 5°C using an I_2—KI—H_3BO_3 solution ($[I_2]=5$ mmol/*l*, [KI]=20 mmol/*l*, $[H_3BO_3]=160$ mmol/*l*) as reference.

RESULTS AND DISCUSSIONS

As shown in Figures 5 and 6 of the

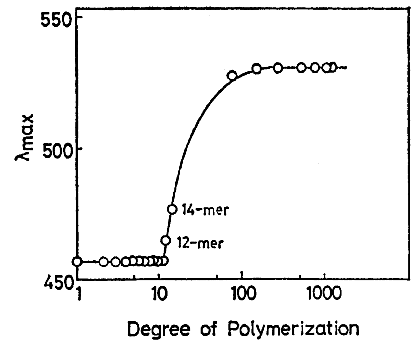

Figure 5. Poly(vinyl acetate)—iodine reaction: [PVAc], 2.37 mmol/*l*; [I_2], 4.55 mmol/*l*; [KI], 18.2 mmol/*l*; 15°C.

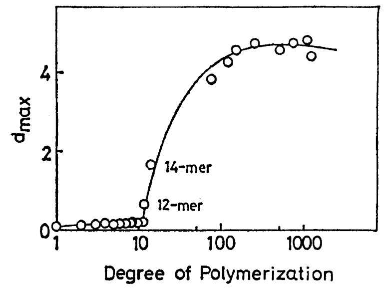

Figure 6. Poly(vinyl acetate)—iodine reaction. Reaction conditions are the same as in Figure 5.

poly(vinyl acetate)—iodine reaction a weak absorption was observed at 457 nm for up to 11-mer irrespective of degree of polymerization, and a red shift of the absorption maximum began at DP=12 and leveled off at around DP=100. Thus, the lower limit of the degree of polymerization for this color reaction was found to be 12-mer.

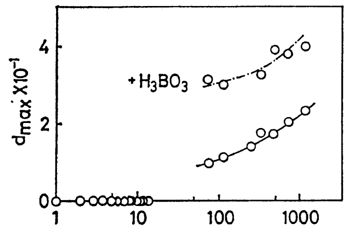

Figure 7. Poly(vinyl alcohol)—iodine reaction: [PVA], 50 mmol/*l*; [I_2], 5 mmol/*l*; [KI], 20 mmol/*l*; 5°C. (—), without H_3BO_3; (-·-), 160 mmol/*l* H_3BO_3 added.

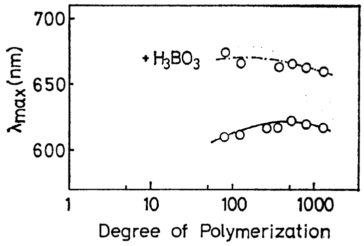

Figure 8. Poly(vinyl alcohol)—iodine reaction. Reaction conditions are the same as in Figure 7.

Figures 7 and 8 show the relation of the degree of polymerization to absorption maxima and absorbance of the poly(vinyl alcohol)—iodine reaction, respectively, in the presence and the absence of boric acid. The blue color did not appear up to 14-mer, even in the presence of boric acid. The polymer with a higher average degree of polymerization than 80 showed an absorption maximum at around 620 nm in the absence of boric acid and 670 nm in its presence. Neither absorption maxima shifted much with the degree of polymerization, and absorbances were larger with a higher degree of polymerization, this being in accordance with observation of Imai, *et al.*[4]

The fact that an average degree of polymerization of 80 is large enough for the color reaction seems to conflict with the previous finding that the lower limit of the chain length required for the coloration is about 120.[5] This discrepancy is not due to the fact that the specimen with DP=80 has a distribution of degree of polymerization (Table II), because the color reaction with this specimen was saturated with respect to absorption maximum and absorbance (Figures 7 and 8). This discrepancy is probably due to the fact that the previous estimation is, in principle, likely to overestimate the lower limit of the degree of polymerization.

Thus, the threshold degree of polymerization of the PVA—iodine reaction is considered to be larger than that of the poly(vinyl acetate)—iodine reaction. This difference may be ascribed to the difference in length of the included polyiodide chain which, in turn, is reflected in the difference in the absorption maxima, 530 nm for PVAc and 620 nm for PVA. The chain length of the included polyiodide was estimated by Cramer, *et al.*,[7] to be 14 iodine atoms for 611.6-nm absorption, by Murakami, *et al.*,[8] to be eight iodine atoms for 521.4-nm absorption, and by Pjojosubroto, *et al.*,[9] to be seven iodine atoms for 620-nm absorption. In all treatments, the longer polyiodide chain corresponds to the longer wavelength of the absorption maxima.

The spatial structure of the host molecules including the polyiodide chain was proposed by Zwick[2] to be a helix and a nonhelical structure by Tebelev[10] for PVA. The degree of polymerization of 12 necessary for the poly(vinyl acetate)—iodine reaction may be too small to form a helical structure of the Zwick's type. The spatial arrangement of PVAc molecules in such a poor solvent as aqueous methanol might provide a kind of void structure necessary for the inclusion of the polyiodide chain. The size of this void might be larger in the case of PVA than in the case of PVAc, resulting in a larger threshold degree of polymerization and longer absorption maximum in the former.

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