Distribution of End Groups and Comonomer of the Acrylonitrile-Vinyl Acetate Copolymer

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Synopsis

The number average molecular weight and strong acid end groups (SAG) of fractionated polymers were measured for the acrylonitrile-vinyl acetate copolymers (93:7 in weight), which were prepared by continuous polymerization in aqueous medium with the persulfate-bisulfite-ion redox system. Average number of SAG per polymer molecule was nearly 1 for fractionated portions of the polymers prepared under the polymerization conditions of water/monomer ratio in the range 4.0–2.5 in weight. No marked difference existed in comonomer content in fractions of these polymers. For unfractionated polymers prepared under the conditions of water/monomer ratio varied from 4.0 to 1.75, average number of SAG was roughly 0.8–1. The proportion of sulfoxy end groups to SAG was estimated to be roughly from 0.5 to 0.6 and increased slightly with increased bisulfite/persulfate ratio. Based on the above results, disproportionation and transfer to bisulfite-ion are considered to be the main processes of termination of polymer radicals in the studied range of polymerization conditions.

INTRODUCTION

In the preparation of acrylonitrile (AN)-vinyl acetate (VAc) copolymer (93:7 in weight) by continuous polymerization in aqueous medium with the persulfate-bisulfite-ion redox initiation system, properties of the polymer slurry and structures of the polymer particles in the range of water/monomer ratio from 4.0 to 1.5 in weight were studied by the authors.[1] In this paper the results of end-group analysis and number average molecular weight ($\overline{M}_n$) measurements of the polymer mentioned above are dealt with. Moreover, based on these measurements, some discussion is made on the mechanism of the polymerization.

EXPERIMENTAL

Material

Commercial-grade AN and VAc, chemically first-grade potassiumm persulfate (KPS), and sodium hydrogen carbonate ($NaHCO_3$), chemically special-grade sulfur dioxide (SO_2), and ferrous sulfate ($FeSO_4$) were used with-

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out further purification. Deionized water was used. Chemically first-grade N, N-dimethylformamide (DMF) was distilled before use. Chemically special-grade dimethylsulfoxide (DMSO), chemically first-grade lauryl alcohol (LA), and chemically special-grade sodium thiocyanate (NaSCN) were used without further purification.

PREPARATION OF THE POLYMERS

The reaction vessel and procedures for the polymerization were the same as those previously described.[1] The slurries of polymer were taken from the reaction vessel as samples for evaluation at least 6–8 hours after the start of polymerization. The polymerization conditions are shown in Tables I and II.

FRACTIONATION OF POLYMERS

Precipitation fractionation of sample of Experiments 1 and 2 were carried out at 30°C, DMSO being used as solvent, LA as nonsolvent, NaSCN was added to mask the charge of SAG. Fractionation was performed as follows. After a polymer sample 20.00 g was dissolved in DMSO 2270 mL in a fractionation flask, a certain amount of LA was added to cause a precipitation. The solution was then warmed through several degrees to dissolve the precipitation again, and was further cooled to the original temperature to cause liquid–liquid phase separation. The dilute phase was transferred to another flask by a suction aspirator. The concentrated phase was diluted by DMSO, then precipitated and washed with methanol. The polymer obtained was dried at 50°C overnight. A certain amount of LA was added to the dilute phase and the same procedure described above was repeated. Thus, 10 fractions for sample of Experiment No. 1 (the yield of recovered polymer = 99.5%) and for sample of Experiment No. 2 (the yield = 95.2%) were obtained.

MOLECULAR WEIGHT DETERMINATION

Number average molecular weight ($\overline{M}_n$) was determined by osmometry previously described[2] for unfractionated samples.

For fractionated samples, intrinsic viscosity (η), weight average molecular weight ($\overline{M}_w$), viscosity average molecular weight ($\overline{M}_v$), and $\overline{M}_n$ were calculated by gel permeation chromatograph (high speed GPC) measurement previously described.[2]

END-GROUP ANALYSIS

Strong acid end group (SAG) of polymers were determined by the following method described in the literature.[3,4] A 2% polymer solution in DMF was ion exchanged with a mixed bed of cation exchange resin and anion exchange resin to remove inorganic electrolytes. After the solution was ion exchanged with cation exchange resin to convert end groups to acid types, SAG were determined either by PH titration or by potentiometric titration.

It has been ascertained that sulfate end groups were completely hydrolyzed by boiling treatment in 0.5 N H_2SO_4 solution for 2 hours. Therefore,

TABLE I

Number of Strong Acid Groups (SAG eq./mol), Comonomer Content, and $\overline{M}_n$ of the Polymer Prepared under Various Polymerization Conditions[a]

	Polymerization conditions				Polymer characteristics			
Expt. no.	Water/ monomer (wt. ratio)	Dwell time (min)	SO$_2$/KPS (mol. ratio)	Temp. (°C)	VAc (%)	SAG (× 10^5 eq./g)	$\overline{M}_n \times 10^{-4}$ [b]	SAG (eq./mol)
1.	4.0	60	10	50	7.02	3.63	2.51	0.91
2.	2.5	70	10	50	7.13	4.42	2.07	0.91
3.	3.0	60	10	50	7.60	3.88	2.11	0.82
4.	3.0	60	4.3	60	7.19	4.35	2.18	0.95
5.	3.0	60	10	50	7.30	3.87	1.95	0.75
6.	2.0	82	10	50	7.06	3.97	2.60	1.03
7.	2.0	82	10	60	7.04	4.08	2.10	0.86
8.	1.75	89	10	50	7.17	3.82	2.60	0.99
9.	1.75	89	10	60	7.12	4.05	2.02	0.82
10.	1.75	89	4.3	50	6.51	3.91	2.29	0.90

[a] Molar ratio of SO$_2$ to NaHCO$_3$ was fixed to 1.3 in order to keep pH of the polymerization system 3.0 Fe^{2+} ion was fed 0.4 ppm by weight of monomer.
[b] Obtained by osmometry.

TABLE II

SAG and SAG* (SAG Hydrolysed) and Comonomer Content of the Polymer Prepared Under Various Polymerization Conditions[a]

Expt. no.	Polymerization conditions				Polymer characteristics			
	Water/ monomer (wt. ratio)	Dwell time (min)	SO_2/KPS (mol. ratio)	Temp. (°C)	VAc (%)	SAG ($\times 10^5$ eq./g)	SAG*[b] ($\times 10^5$ eq./g)	SAG*/SAG
11.	4.0	60	10	50	6.54	3.60	2.08	0.58
12.	4.0	60	4.3	50	6.96	3.89	1.88	0.48
13.	2.5	70	10	50	6.98	3.70	2.33	0.63
14.	2.5	70	6.5	50	7.24	3.81	2.26	0.59
15.	1.75	89	10	50	7.17	3.82	2.25	0.59
16.	1.75	89	4.3	50	6.51	3.91	2.08	0.53

[a] Molar ratio of SO_2 to $NaHCO_3$ waas fixed to 1.3 in order to keep pH of the polymerizing system 3.0. Fe^{2+} ion was fed 0.4 ppm by weight of monomer.
[b] Sulfoxy end groups.

when the SAG content after this treatment is expressed as SAG* (eq./g), sulfoxy and sulfate end groups are roughly estimated by Eqs. (1) and (2).

$$\text{Sulfoxy end groups (eq./g)} = \text{SAG*} \qquad (1)$$

$$\text{Sulfate end groups (eq./g)} = \text{SAG} - \text{SAG*} \qquad (2)$$

SAG and SAG* for a whole polymer and SAG for a fractionated polymer were obtained.

COMONOMER ANALYSIS

VAc content in polymers, both fractionated and unfractionated, was determined from absorbance of carbony groups of VAc on the infrared (IR) spectra.

AN content in polymers was calculated from nitrogen content measured from the CHN coder (Yanagimoto MT-2).

RESULTS AND DISCUSSION

Effect of the Polymerization Conditions on SAG Content

SAG of the polymers prepared under the polymerization conditions of water/monomer ratio, SO_2/KPS ratio and temperature varied are shown in Table I. Values of $\overline{M}_n$ obtained by osmometry are also shown in Table I.

Average number of SAG (eq./mol) of a polymer molecule can be calculated by Eq. (3).

$$\text{SAG (eq./mol)} = \text{SAG (eq./g)} \times \overline{M}_n \qquad (3)$$

Average number of SAG (eq./mol) of a polymer molecule calculated from $\overline{M}_n$ and SAG (eq./g) is nearly in the range 0.8–1. SAG are composed of both sulfate end groups and sulfoxy end groups. The amount of both end groups estimated by the above-described procedure are shown in Table II. From Table II, it is inferred that the estimated amount of sulfoxy end groups in SAG increased with the increase of SO_2/KPS ratio. From Table II, the average number of sulfoxy end groups seems to be larger than that of sulfate end groups.

THE DISTRIBUTION OF CHEMICAL COMPOSITION

(η), $\overline{M}_n$, $\overline{M}_v$, and $\overline{M}_n$ of the fraction of the polymer prepared under the condition of water/monomer ratio 4.0 are shown in Table III. The analytical results of the composition of the fraction of the polymers prepared under the water/monomer ratio conditions 4.0 and 2.5 are shown in Tables IV and V.

No marked difference was observed among the VAc content of the fractions. Hence, it seems that there is fairly good uniformity in the composition of AN and VAc in the polymers.

TABLE III
Calculated Intrinsic Viscosity and Average Molecular Weights $\overline{M}_v$, $\overline{M}_w$, and $\overline{M}_n$ of the
Polymer Prepared Under the Condition[a] of Water-to-Monomer Ratio 4.0

Fraction no.	(η) (dL/g)	$\overline{M}_n \times 10^{-4}$	$\overline{M}_v \times 10^{-4}$	$\overline{M}_w \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$
Whole polymer	1.37	2.80	10.4	12.5	4.46
1	2.28	8.74	22.9	25.9	2.96
3	2.01	(5.61)[b]	18.8	21.2	3.78
3	1.86	8.06	16.7	18.6	2.30
4	1.77	8.42	15.5	17.1	2.03
5	1.62	6.75	13.5	15.0	2.22
6	1.37	5.19	10.4	11.7	2.25
7	1.16	3.97	8.09	9.03	2.28
8	1.01	3.22	6.51	7.34	2.28
9	0.730	1.78	3.97	4.56	2.56
10	0.360	(0.337)[b]	1.34	1.64	(4.87)[c]

[a] Corresponds to Expt. No. 1 in Table I.
[b] Smaller than expected.
[c] Larger than expected owing to the smaller value of $\overline{M}_n$.

Average number of SAG of a polymer molecule prepared under the condition of water/monomer ratio 4.0 is nearly 1, irrespective of the molecular weight of the fraction as shown in Table IV. That of a polymer molecule prepared under the water/monomer ratio condition 2.5 seems nearly 1, too.

In this polymerization system it is considered[4-6] that the polymerization is initiated mainly either by SO_4^- or by $HSO_3^.$[5-11] Therefore, taking into consideration that average number of SAG is nearly 1, it is apparent that SAG originated from fragments of initiators.

As the estimated amount of sulfoxy end groups in SAG increased with

TABLE IV
The Distribution of Chemical Composition of the Polymer Prepared under the Condition[a] of
Water-to-Monomer Ratio 4.0

Fraction no.	VAc (%)	AN (%)	SAG ($\times 10^5$ eq./g)	SAG (eq./mol)
Whole polymer	7.62	90.9	3.63	1.0
				(0.91)[b]
1	7.65	86.2	1.55	1.4
2	7.38	89.3	1.55	0.86
3	7.35	86.3	1.33	1.1
4	7.15	86.1	1.23	1.0
5	6.90	85.7	1.41	0.95
6	7.15	85.8	2.18	1.1
7	7.20	85.3	2.29	0.91
8	5.95	88.5	4.10	1.3
9	6.75	88.0	4.57	0.81
10	6.85	84.9	9.66	—

[a] Corresponds to Expt. No. 1 in Table I.
[b] The value of $\overline{M}_n$ obtained by osmometry was used. The calcd. value of $\overline{M}_n$ from GPC data was used for the other SAG.

TABLE V

The Distribution of Chemical Composition of the Polymer Prepared Under the Condition[a] of Water-to-Monomer Ratio 2.5

Fraction no.	VAc (%)	AN (%)	SAG ($\times 10^{-5}$ eq./g)	SAG (eq./mol)	$\overline{M}_n \times 10^{-4}$ [b]
Whole polymer	7.13	91.45	4.42	0.91	2.07
1	7.31	90.95	1.66	—	—
2	7.12	89.02	1.56	—	—
3	6.70	89.89	1.80	—	—
4	6.62	90.61	1.76	—	—
5	7.08	90.99	2.16	1.1	5.30
6	6.76	89.67	2.26	—	—
7	6.60	90.54	2.70	1.1	4.21
8	6.47	90.95	2.86	—	—
9	6.62	89.33	3.06	(0.56)[c]	1.82
10	7.10	78.73	13.22		

[a] Corresponds to Expt. No. 2 in Table I.
[b] Obtained by osmometry.
[c] Smaller than expected.

the increase of SO_2/KPS ratio, it seems that polymer chain transfer to HSO_3^- cannot be neglected.

As already stated,[5,12,13] Bamford et al.[12] and Bailey and Jenkins[13] have shown that the termination in AN polymerization in DMF or ethylene carbonate (EC) mainly occurs by recombination of polymer radicals. L. H. Peebles and co-workers[4] have shown that more than one strong acid end group per molecule exists as to polyacrylonitrile with persulfate-bisulfite ion initiator system, where they considered bimolecular termination.

J. Ubricht[14] has shown that termination mainly takes place by disproportionation of radicals in EC and butyrolactone. Tsuda[15] has shown that

TABLE VI

Comparison of the System Used by Us With Those Used by Peebles and His Co-workers

Items	Our case	Peebles' case
Polymer composition	AN/VAc 93/7 in weight	AN homopolymer
(η) (DMF 25°C)	1.4 ~ 1.7	1 ~ 2
Polymerization condition		
Water/monomer ratio[a]	1.75 ~ 4.00	8.00
pH	3.0	1.90 ~ 2.25
Bisulfite/persulfate ratio[b]	4 ~ 10	1 ~ 8
Reactor conditions	83 liter continuous	100 g semibatch
Results obtained		
Strong acid groups Per polymer molecule	0.8 ~ 1.0	1.0 ~ 1.5

[a] Weight ratio.
[b] Molar ratio.

termination consists of disproportionation in AN polymerization in aqueous medium using S^{35} labeled KPS.

Differences between our results described in this paper and those[4] obtained by L. H. Peebles are roughly compared in Table VI. It is apparent that polymer compositions and polymerization conditions are different in both systems. In the polymerization system used by Peebles, bimolecular termination is supposed to occur in a different state of the system owing to difference in polymer composition (homopolymer and copolymer) and possibly owing to difference in water-to-monomer ratio and in the state of micromixing in comparison with our system. In the case of acrylonitrile homopolymer, the existence of 1.5 ~ 2.0 strong acid groups per polymer molecule was also assured by T. Masuzawa, K. Kamada, and T. Yoshihara.[16] Hence, we consider it is not strange that there exist differences between results obtained by Peebles and our results. Based on these results and considerations, it is considered that the termination of active polymer radicals occurs mainly by disproportionation or by chain transfer to bisulfite ion in our polymerization system.

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