Basic Dyeability and Acid Content of High-Conversion Polyacrylonitrile

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Synopsis

Previous data have shown that the basic dyeability of acrylic polymers increases at a given specific viscosity as the peroxydisulfite-to-bisulfite ratio, that is, the catalyst-to-activator (C/A) ratio, is increased. This study represents an effort to understand better the role of the initiator system on the basic dyeability, the acid group composition, and the chain composition of acrylic polymers by preparing model polymers with radioactive initiators. As the C/A ratio is increased, the molecular weight distribution broadens as measured by the $\bar{M}_v/\bar{M}_n$ ratio, the latter obtained by osmometry. There is also a significant effect of both C/A ratio and molecular weight on the sulfate group content per molecule, but there is no effect of C/A ratio on the number of basic dye sites per molecule, the number of sulfonate groups per molecule, or the weak acid groups per molecule. These effects can be explained by invoking a chain transfer to activator reaction in addition to the usual method of chain termination by recombination. The basic dyeability is found to correlate with the number-average molecular weight and with the number of strong acid groups plus the nonchromophoric weak acid groups.

INTRODUCTION

Previous work in this laboratory and elsewhere suggested that the basic dyeability of acrylonitrile copolymers, prepared under heterogeneous conditions with the peroxydisulfate–bisulfite–ion redox initiation system, varied with the catalyst (peroxydisulfate)-to-activator (bisulfite) ratio, while maintaining a nearly constant specific viscosity of the polymer (measured at 0.1 g/dl in DMF at 25°).[1] The present study was initiated to provide a more definitive measure of the strong acid group composition by preparing homopolymers of acrylonitrile with radioactive catalyst ($K_2S^{35}_2O_8$) or activator ($NaHS^{35}O_3$). In addition to the radioassay measurement, a number of other characterization measurements were performed, among them the strong and weak acid content, the number-average molecular weight by osmometry, the intrinsic viscosity, and the basic dye acceptance (BDA). The polymerizations were performed at a lower pH, ca. 2.0, than is normally used in preparing commercial polymers. At the low pH of polymerization, a small but significant amount of hydrolysis oc-

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curred to the polymer. Of the polymers examined, approximately one nitrile group was hydrolyzed to the acid form for every two polymer molecules present. Examination of other polymers prepared by similar methods at higher pH, ca. 3.0, indicated that very little, if any, hydrolysis occurs to the nitrile groups. Therefore, the results to be presented must be interpreted on the basis that we are not dealing with an absolutely pure, 100% homopolymer of acrylonitrile. Because a determined number of nitrile groups were hydrolyzed to the carboxyl function, an additional undetermined number must be hydrolyzed to the amide function. Further, some hydrolysis of the sulfate endgroups may also have occurred. In general, to obtain essentially complete hydrolysis of the sulfate groups requires treatment with 0.1N hydrochloric acid for 3 hr at reflux. The polymers described here were not subjected to anything like these harsh conditions. With these restrictions in mind, we may proceed to consider the results.

EXPERIMENTAL PROCEDURES AND RESULTS

The PAN polymers were prepared on a 100-g scale by a "semibatch" technique at 50°C. The pot was precharged with 22% of the water and purged with nitrogen. Feeds were introduced at constant rates over a 2-hr interval. The final water-to-monomer ratio was 8/1; the ferrous ion concentration was 0.25 ppm, based on monomer. Sufficient 1N H_2SO_4 was added to give a final slurry pH of 1.90–2.25. Sulfur 35-labeled potassium peroxydisulfate and sodium bisulfite were obtained from Tracerlab, Waltham, Massachusetts. The weight per cent of catalyst and activator (based on monomer) used in the polymerization are listed in Table I, columns 1–3. Although sodium bisulfite was used as the activator, the amounts reported in column 2, Table I, are based on SO_2 rather than $NaHSO_3$. Furthermore, it must be kept in mind that the C/A ratio used in this report is on a weight basis. There is always a molar excess of activator. To convert to a mole ratio basis, divide the reported C/A by 4.13. Upon completion of feed addition, the polymer slurry was held at 50°C for an additional half-hour. It was then cooled to 30°C, filtered, and washed with an equal volume of 0.01N H_2SO_4. The polymer was reslurried twice with two volumes of D.I. water and washed with three volumes D.I. water. It was dried in a vacuum oven at 50°C.

Intrinsic viscosity measurements in DMF at 25°C were obtained by standard techniques; they are reported in column 4, Table I. The viscosity-average molecular weights were calculated by means of the Cleland and Stockmayer equation[2]

$$[\eta] = 2.43 \times 10^{-4} \bar{M}_v^{0.75}.$$

Measurements of the number-average molecular weight were made on a Mechrolab high-speed membrane osmometer (column 5, Table I). The solvent was a mixture of distilled butyrolactone containing 3% water and

TABLE I
Recipes and Results on PAN's Prepared by Radioactive Initiators

Type	Redox system Concentration, wt-% b.o.m.ᵃ C/A	C/A ratio	[η] DMF (25°C)	$\bar{M}_v \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	SAG, μeq/g	CWAG, μeq/g	NWAG, μeq/g	Radio sulfur content, μeq/g	DS, μeq/g
KPS/S*O₂	0.46/1.38	1/3	1.57	12.0	5.00	20.9	—	—	18.9	25.9
KPS*/SO₂	0.46/1.38	1/3	1.61	12.5	5.06	21.6	20.7	7.1	3.30	26.2
KPS*/SO₂	0.70/2.10	1/3	1.09	7.41	3.61	39.4	26.5	13.5	2.68	46.9
KPS*/SO₂	0.30/0.90	1/3	2.23	19.2	8.19	13.8	18.2	5.7	3.27	15.8
KPS/S*O₂	1.00/1.00	1/1	1.69	13.2	—	30.4	22.3	4.0	25.3	34.6
KPS*/SO₂	1.00/1.00	1/1	1.48	11.1	4.28	30.2	29.3	11.9	5.80	38.6
KPS*/SO₂	1.50/1.50	1/1	1.18	8.26	3.10	40.3	29.4	11.1	4.80	50.2
KPS*/SO₂	0.75/0.75	1/1	2.00	16.6	5.95	19.9	21.3	6.9	4.24	22.7
KPS/S*O₂	2.10/0.70	3/1	1.64	12.8	4.08	31.2	33.2	11.9	25.3	39.8
KPS*/SO₂	2.10/0.70	3/1	1.36	9.93	3.90	35.1	31.5	21.1	8.23	52.0
KPS*/SO₂	2.85/0.95	3/1	1.39	10.2	3.26	37.9	36.7	14.1	7.73	49.7
KPS*/SO₂	1.74/0.58	3/1	1.86	15.1	5.61	19.6	22.4	8.1	7.24	29.1
Fe²⁺/S*O₂	0.628/0.36	—	1.70	13.4	4.41	46.1	34.6	18.8	42.6	59.0
KPS*	16.0/—	—	7.66	99.6	14.8	5.2	19.4	4.9	—	8.0

ᵃ Based on monomer.

0.1% potassium nitrate. The water was present to improve the solvent power of the butyrolactone and to reduce the influence of adsorbed atmospheric moisture. The salt was present to swamp out the small effects cause by ionization of the polymer or by occlusion of salts in the polymer.

The acid group contents were determined by the nonaqueous titration method of Kirby and Baldwin.[3] Solutions of the polymers in an ethylene carbonate–propylene carbonate solvent were subjected to ion exchange treatment to remove nonpolymeric salts and to place all anions in the acid form. The titrations were followed potentiometrically[3] and photometrically.[4] The results are given in columns 6–8, Table I.

The radioassay results were obtained after ion exchange treatment with mixed-bed resin (MB-3) and corrected for the time lapse between the initial and final assays. The results are reported in column 9, Table I.

The basic dye acceptance (BDA) is the per cent of as-received Sevron Blue 2G (du Pont) dyestuff taken up from a 7-g/l. solution at pH 5.2 at 100°C after 2 hr. Masson[5] has shown that the BDA in per cent is related to the number of basic dye sites (DS) (μeq/g) by the relation

$$DS = 3.87 \, (BDA - 2.48).$$

The parameter 2.48 represents the amount of dyestuff taken up by a polymer of infinite molecular weight. The factor 3.87 is obtained from the best estimate of the molecular weight and the purity of the dyestuff. The calculated number of basic dye sites is listed in column 10, Table I.

DISCUSSION

The polymers investigated in this study were designed to show the influences of the C/A ratio upon the acid group composition and upon the basic dyeability. The polymers were prepared at three levels of specific viscosity within a rather narrow range of specific viscosity to ensure that small fluctuations of the specific viscosity would not adversely affect the conclusions. Thus, valid molecular weight effects may be obscured by the variability observed within the narrow molecular weight range studied. The primary variation in viscosity or molecular weight upon the molecular parameters can be eliminated by multiplying all parameters by the molecular weight to place these parameters on a "per molecule" basis. These new parameters were then subjected to an analysis of the variance to ascertain if there was either an effect of molecular weight or of C/A ratio upon the "parameter per molecule." Since there were no replications, the interaction term was used as the measure of error. The 90% confidence level was used as the criterion of acceptance or rejection of the hypothesis.

The molecular weights were separated into low, medium, and high ranges, as shown in Table II, to calculate the variability of the parameters with molecular weight.

TABLE II
Definition of Molecular Weight Ranges

Molecular weight range	$\bar{M}_v$ values ($\times\,10^{-4}$) from viscometry		
	1/3[a]	1/1[a]	3/1[a]
Low	7.4	8.3	10.2
Medium	12.5	11.1	12.8
High	19.2	16.6	15.1

[a] C/A ratio.

Weak Acid Group Composition

The weak acid group content of these polymers can be separated into a chromophoric (CWAG) and a nonchromophoric (NWAG) species by the procedures given by Kirby et al.[4] The CWAG in these polymers was generated primarily by the chance polymerization of an active radical through a pendant nitrile group, followed by hydrolysis to give a branched molecule which contains a ketonitrile,[6]

$$
\begin{array}{c}
& & & R' & & R' \\
& & & | & & | \\
\text{R—CH}^* + \text{R'CN} \longrightarrow & \text{R—CHC}{=}\text{N}^* \xrightarrow{\ M\ } & \text{R—CHC}{=}\text{N—R''} \xrightarrow{\ H_2{}^+O\ } \\
| & | & | \\
\text{CN} & \text{CN} & \text{CN}
\end{array}
$$

$$
\begin{array}{c}
R' & & & \ominus \\
| & & & \\
\text{R—CHC}{=}\text{O} + \text{H}_2\text{NR''} \xrightarrow{\ base\ } & \text{R—C—C—R'} \\
| & & | \ \ || \\
\text{CN} & & \text{CN O}
\end{array}
$$

the ionized form of which has an intense adsorption at 275 mμ and can be used as a self-indicator in the titration. CWAG's can also be produced by thermal oxidation.[7] The NWAG's are most likely the result of hydrolysis of random nitrile groups to the corresponding carboxyl function. The concentration of the weak acid groups per molecule are given in Table III. There is no effect of C/A ratio or molecular weight on the weak acid content. The average values at the 90% confidence level are:

$$\text{NWAG/molec.} = 0.48 \pm 0.09$$

$$\text{CWAG/molec.} = 1.17 \pm 0.11$$

A constant number of either type of weak acid group per molecule is *not* consistent with a mechanism of random attack on a preformed nitrile group[6]; there should be an increase in the number of weak acid groups per molecule with increasing molecular weight. Perhaps the molecular weight range considered here (a factor of 2.6) is insufficiently broad to show the main effect.

TABLE III
Weak Acid Groups per Molecule

Molecular weight range	CWAG/molec.			NWAG/molec.		
	1/3[a]	1/1	3/1	1/3[a]	1/1	3/1
Low	0.95	0.91	1.19	0.49	0.34	0.46
Medium	1.05	1.25	1.36	0.36	0.50	0.46
High	1.50	1.26	1.25	0.47	0.41	0.46

[a] C/A ratio.

Strong Acid Group Composition and Molecular Weight Distribution

The ratio of radioassayed sulfur to strong acid groups gives the fraction of strong acid groups that arise from either the catalyst or the activator. Under the assumption that the strong acid groups can only arise from the initiator system, the fraction of strong acid groups that come from the activator are listed in Table IV.

TABLE IV
Fraction of Strong Acid Group from Activator

Molecular weight range	SO_3^-/strong acid group		
	1/3[a]	1/1	3/1
Low	0.93	0.88	0.80
Medium	0.85	0.81	0.81
High	0.76	0.79	0.63

[a] C/A ratio.

The proportion of the strong acid group which comes from the activator varies with the C/A ratio *and with the molecular weight*. This must mean that the catalyst and the activator control the molecular weight of the polymer by different mechanisms. We can examine the data further by separating the strong acid groups into the number of sulfate groups per molecule (SO_4^-/molec.) and the number of sulfonate groups per molecule (SO_3^-/molec.). The data of Tables I and IV can be combined to yield Table V.

TABLE V
Sulfate and Sulfonate Groups per Molecule

Molecular weight range	SO_4^-/molec.			SO_3^-/molec.		
	1/3[a]	1/1	3/1	1/3[a]	1/1	3/1
Low	0.10	0.15	0.25	1.32	1.10	0.98
Medium	0.16	0.25	0.24	0.93	1.04	1.03
High	0.27	0.25	0.40	0.86	0.93	0.69

[a] C/A ratio.

Neither the C/A ratio nor the molecular weight has a detectable effect on the number of sulfonate groups per molecule. At the 90% confidence level, the average value is

$$SO_3^-/\text{molec.} = 0.99 \pm 0.11.$$

On the other hand, there is a very significant effect of both C/A ratio and molecular weight on the amount of sulfate groups per molecule. In other words, each molecule, on the average, contains one sulfonate group regardless of the polymerization conditions, whereas the amount of sulfate strong acid groups depends on the polymerization conditions. The accompanying paper[3] shows that these effects will result if we assume that termination of active chains is by combination and we invoke a transfer-to-activator reaction

$$R_n^* + HSO_3 \rightarrow P_nH + SO_3^{-*}.$$
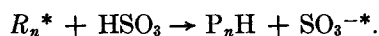
Furthermore, the accompanying paper predicts an effect of C/A ratio on the molecular weight distribution. The viscosity-average molecular weights of these polymers are plotted against number-average molecular weights in Figure 1. Three independent correlation curves are shown, one for each C/A ratio. Statistical evaluation of the $\bar{M}_v/\bar{M}_n$ ratio, Table VI, also shows a definite influence of C/A ratio on the distribution.

TABLE VI
The Heterogeneity Index, $\bar{M}_v/\bar{M}_n$

Molecular weight range	$\bar{M}_v/\bar{M}_n$		
	1/3[a]	1/1	3/1
Low	2.05	2.66	3.13
Medium	2.47	2.59	3.14
High	2.34	2.79	2.69
Average	2.29	2.68	2.99

[a] C/A ratio.

Composition of the Dye Sites

Earlier it was stated that at a given specific viscosity, the basic dyeability increases with an increase in the C/A ratio.[1] However, the number of dye sites should be related to the number of active chain ends of the polymer. As the molecular weight distribution is varying with the C/A ratio, there should be a better correlation between the number of dye sites and the the reciprocal number-average molecular weight (which is one half the number of chain ends, assuming linear molecules) than with the reciprocal viscosity-average molecular weight. Figures 2 and 3 show the correlations
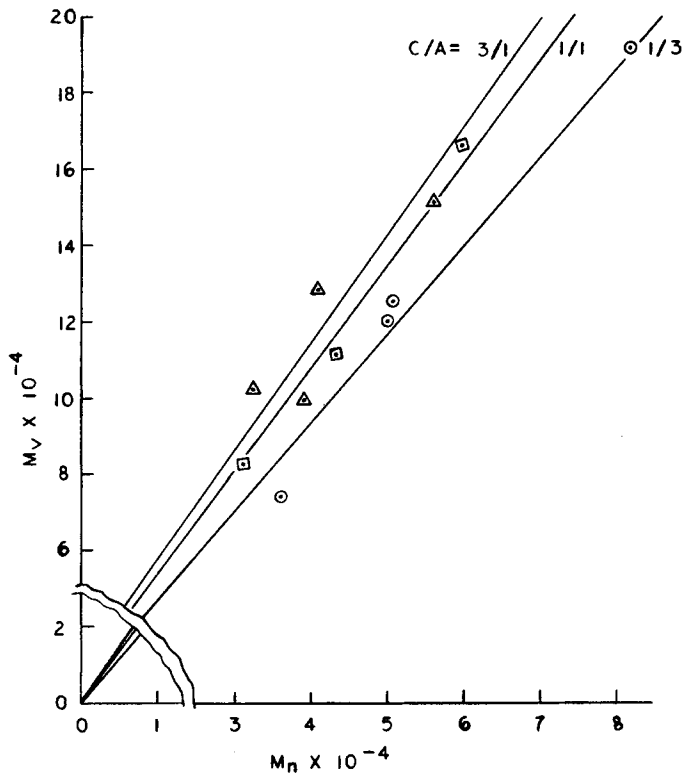
Fig. 1. Viscosity-average molecular weight as a function of the number-average molecular weight as determined by osmometry. Open circles, C/A = 1/3; squares, C/A = 1/1; triangles, C/A = 3/1. The scatter is due in part to examination of high-conversion polymers, but there is a significant effect of C/A ratio on the molecular weight distribution.

obtained. The slope in Figure 2 is 1.6 dye sites per chain, indicating that inactive chain ends exist as predicted by a mechanism of termination by recombination and a transfer-to-activator reaction.

The reason for using an initiator which places strong acid groups in the polymer and including strong or weak acid containing comonomers in the polymer is to increase the basic dyeability of the polymer. Thus, there should be a correlation between the amount of basic dye uptake and the number of acid groups in the polymer. However, independent work in this laboratory and elsewhere have demonstrated that the concentration of strong acid groups in polyacrylonitrile and in acrylonitrile copolymers which do not contain an additional acid function is too low to account for the dye uptake, whereas the concentration of total acid groups is too large. If we speculate that the chromophoric weak acid group is *not* a basic dye site, then there should be a correlation between the dyeability and the sum of the strong acid groups plus the nonchromophoric weak acid groups. Figure 4 shows the DS plotted against SAG + NWAG. The solid line
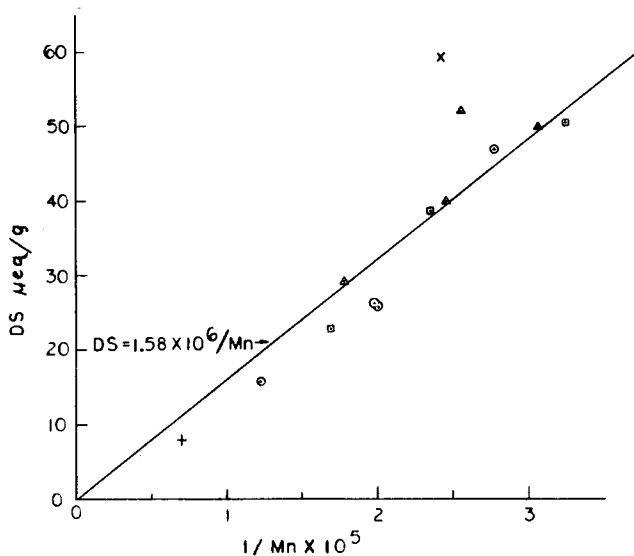
Fig. 2. Number of dye sites as a function of reciprocal number-average molecular weight as determined by osmometry.   Same symbols as in Fig. 1, plus crosses, SO_2 or KPS alone as initiator.
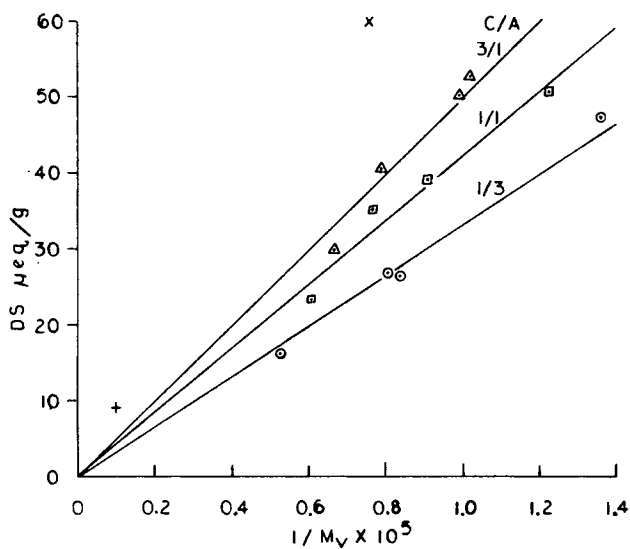

Fig. 3. Number of dye sites as a function of reciprocal viscosity-average molecular weight as determined from viscometry.   Same symbols as in Fig. 2.

is drawn with a slope of unity.   Measurements on other copolymers which do contain added weak acid functions confirm the conclusion that dye uptake is indeed dependent on SAG plus NWAG.   The dye uptake in a fiber, of course, depends also on the accessibility of the dye site to the dyestuff, the kind of dyestuff, and the pH of the dye bath.
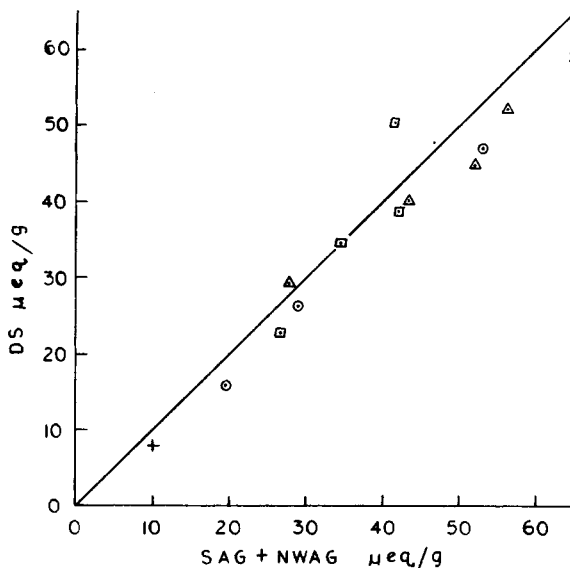
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Fig. 4. Number of dye sites as a function of strong acid group content plus non-chromophoric weak acid content. The solid line is drawn with a unit slope. Same symbols as in Fig. 2.

CONCLUSIONS

The following conclusions have been drawn from a limited number of polyacrylonitrile samples prepared in aqueous medium at pH 2 using an initiator of potassium peroxydisulfate and sulfur dioxide (from sodium bisulfite). The polymers underwent a small amount of hydrolysis, perhaps because of the low pH used in the polymerizations. This amount of hydrolysis does not normally occur.

From the number-average molecular weights, the polyacrylonitrile samples were found to contain 0.99 ± 0.11 sulfonate groups per molecule, 0.48 ± 0.09 nonchromophoric weak acid groups per molecule, and 1.17 ± 0.11 chromophoric weak acid groups per molecule. Statistical analysis of the data failed to show that the C/A ratio or that the molecular weight influenced any of these values.

The sulfate group content arising from the peroxydisulfate initiator increased with increasing C/A ratio and increased with increasing polymer molecular weight.

The constant number of sulfonate groups per molecule and a varying number of sulfate groups per molecule can be explained by assuming that polymer molecules can only be formed by recombination, which produces two strong acid groups per chain, and by transfer to the activator, which produces only one strong acid group per chain. This mechanism also predicts a varying molecular weight distribution with the C/A ratio, which is indeed found.

The number of basic dyesites correlates well with the number of strong acid groups plus the number of nonchromophoric weak acid groups. The chromophoric weak acid groups do not appear to be dye sites. Because of the fairly narrow ranges of molecular weight and C/A ratio used in this study, there is also a good correlation between the number of dye sites and the reciprocal number-average molecular weight. This last correlation may not be generally true.

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