

Solvent Sensitized Dye Interaction Technique for End Group Analysis of Acrylonitrile Polymers. Part II—Verification by Calculation of r_1 in Acrylonitrile Copolymers.

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Manuscript received 28 October 1976, revised 11 April 1977, accepted 16 April 1977

Based on a newly developed solvent sensitized dye interaction technique (SSDIT) for the determination of carboxyl groups in acrylonitrile polymers, the copolymer reactivity ratio (r_1) for the following pairs of monomers (1) acrylonitrile (M_1)—acrylic acid (M_2); (2) acrylonitrile (M_1)—sodium acrylate (M_2); (3) acrylonitrile (M_1)—methacrylic acid (M_2); (4) acrylonitrile (M_1)—maleic anhydride (M_2); (5) acrylonitrile (M_1)—crotonic acid (M_2); at varying $M_1 : M_2$ ratios (100 : 1 to 1000 : 1), were determined. The experimental r_1 values compare reasonably well with the literature values where known. This proves the validity of the SSDIT for the estimation of carboxyl groups in acrylonitrile polymers.

A solvent sensitized dye interaction technique¹ (SSDIT) has recently been developed for the estimation of carboxyl end groups in acrylonitrile polymers. Copolymers of acrylonitrile (M_1) as predominant monomer and other carboxyl bearing monomers (M_2) e.g., acrylic acid, sodium acrylate, etc., have been prepared and the monomer reactivity ratio r_1 has been determined by measuring the carboxyl group content in those copolymers by using the equation (1)^{2,3}:

$$\lim_{(M_2/M_1)_f \rightarrow 0} \frac{(M_2/M_1)_f}{(M_2/M_1)_p} = r_1 \quad (1)$$

where $(M_2/M_1)_f$ and $(M_2/M_1)_p$ represent the molar ratio of the component monomers M_1 and M_2 in the feed and copolymer respectively. A comparison of the experimental r_1 values with the literature values will thus verify the quantitative accuracy obtainable by the present method¹.

Experimental

Acrylonitrile was purified by the usual procedure. Acrylic acid and methacrylic acid were purified by freezing them several times in a refrigerator and finally by distillation under reduced pressure in presence of a copper salt. The major middle fraction was always used. Sodium acrylate⁴ was prepared by titration of acrylic acid to neutrality (pH-7.0) which corresponds to 99% of sodium acrylate.

Purification of N,N-dimethylformamide (DMF) was described elsewhere¹. Benzene (thiophene free), methanol and petroleum ether were freshly distilled before use.

Preparation and Purification of Copolymers: The copolymers of acrylonitrile (M_1) and other carboxyl bearing monomers (M_2) were prepared both in aqueous and non-aqueous (DMF) medium at varying $M_1 : M_2$ ratios in the composition range 100 : 1 to 1000 : 1. In aqueous medium, the polymerization was achieved in an atmosphere of nitrogen using the initiating system Fe^{2+} - H_2O_2 or, H_2O_2 -u.v. at desired temperatures. Copolymers with different ratios of the monomers were obtained for acrylonitrile-acrylic acid, acrylonitrile-sodium acrylate, acrylonitrile-methacrylic acid pairs. The conversion of monomers in all cases was limited to 10-15%. The copolymer precipitated on formation was filtered, washed free from iron and dried under vacuum. The polymerization in DMF was carried out with benzoyl peroxide (Bz_2O_2) as initiator in vacuum sealed pyrex glass tubes at desired temperatures to low conversion. Copolymers with different ratios of the monomers were obtained for acrylonitrile-acrylic acid, acrylonitrile-methacrylic acid, acrylonitrile-maleic anhydride, acrylonitrile-crotonic acid, pairs. Polymers were precipitated from their viscous solutions with cold methanol.

The copolymers were rigorously purified by reprecipitation with cold methanol from their DMF solutions, cold methanol was selected as the precipitant

since this was not a nonsolvent for the homopolymers of the co-monomers used in the present study but it precipitated quantitatively both polyacrylonitrile and acrylonitrile copolymers from their DMF solutions. As the presence of methanol might affect the dye interaction, test (SSDIT) the copolymers were, after rigorous purification, washed with petroleum ether for four or, five times to remove any trace of methanol. These purified polymers were finally dried under vacuum.

Preparation of the Dye-Reagent: The methylene-blue MT dye reagent was obtained by immediate extraction from an approximately 0.4% strong caustic soda solution of the dye (8-10 mg. in 5 ml) with 100 ml. of thiophene free pure benzene¹. This red coloured dye extract was then stored over solid caustic soda in dark.

Determination of the Copolymer Composition from SSDIT: The resulting polymers were subjected to solvent-sensitized dye interaction test (SSDIT) for the evaluation of the composition of the copolymers. This was done by preparing solutions of the copolymers in such a manner that the approximate carboxyl content in the solutions lay within the concentration range of 1.0×10^{-5} mol.l.⁻¹ to 1.0×10^{-4} mol.l.⁻¹. In each case, all the copolymers were dissolved in 3 ml of DMF and 2 ml of the benzene extract of the Methylene Blue MT dye reagent¹ was used. The O.D.'s of the resulting polymer solution in benzene-DMF mixed solvent were measured at 650 m μ with the Hilger Uvispek Spectrophotometer and were compared with the calibration curve obtained with a standard polymeric acid as well as cyanoacetic acid¹.

Results and Discussion

The experimental results for the copolymerisations studied are presented in Table-1, and their graphical representations are shown in the Figs. 1 to 3. The

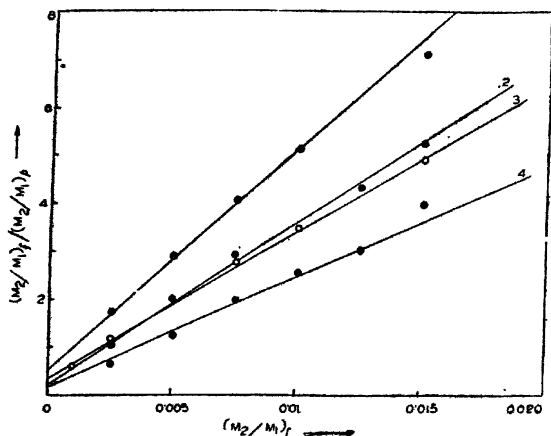


Fig. 1. Plot of $(M_2/M_1)_f / (M_2/M_1)_p$ against $(M_2/M_1)_f$ for copolymers to determine r_1 .
1. acrylonitrile (M_1)-acrylic acid (M_2); 30°C,
2. acrylonitrile (M_1)-sodium acrylate (M_2); 50°C,
3. acrylonitrile (M_1)-acrylic acid (M_2); 50°C,
4. acrylonitrile (M_1)-sodium acrylate (M_2); 30°C.

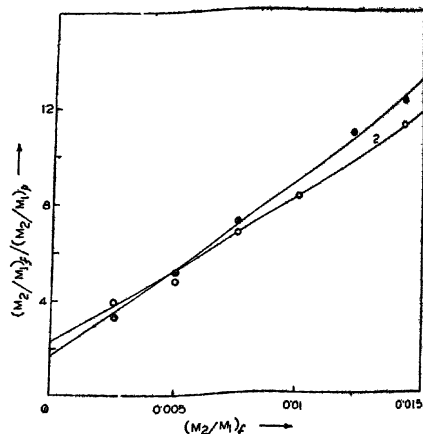


Fig. 2. Plot of $(M_2/M_1)_f / (M_2/M_1)_p$ against $(M_2/M_1)_f$ for copolymers to determine r_1 in acrylonitrile (M_1)-methacrylic acid (M_2) copolymerization 1. 60°C, 2. 30°C.

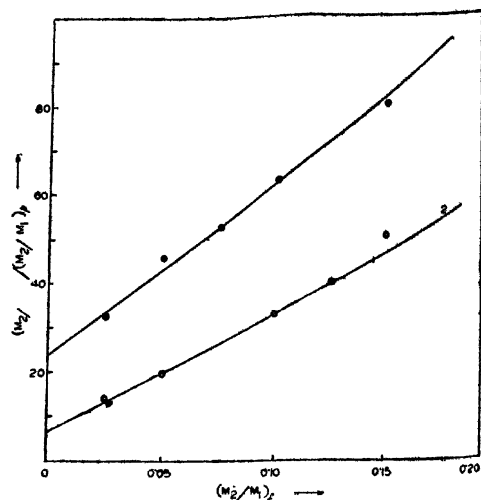


Fig. 3. Plot of $(M_2/M_1)_f / (M_2/M_1)_p$ against $(M_2/M_1)_f$ for copolymers to determine r_1 .
1. acrylonitrile (M_1)-crotonic acid (M_2); 60°C,
2. acrylonitrile (M_1)-maleic anhydride (M_2); 60°C.

monomer reactivity ratio r_1 for each monomer pair was calculated by the application of equation (1). For each copolymer $(M_2/M_1)_f / (M_2/M_1)_p$ values were plotted against respective $(M_2/M_1)_f$ values. The plots, in general, followed a straight line. The r_1 value of the copolymer concerned was given by the intercept obtained by extrapolation of this straight line to zero value of $(M_2/M_1)_f$. The estimation of the copolymer composition, i.e. $(M_2/M_1)_p$ was done with the help of the newly developed solvent sensitized dye interaction test by the determination of the carboxyl content in the polymer. Cyanoacetic acid and polyacrylonitrile were taken as the basis of comparison.

TABLE I—COPOLYMER COMPOSITION AND MONOMER REACTIVITY RATIOS AS DETERMINED BY THE SOLVENT SENSITIZED DYE INTERACTION TECHNIQUE (SSDIT).

Copolymer	$(M_2/M_1)_f$	Condition of polymerisation	% concn. of polymer solution	Optical density at 650 $m\mu$	Corresponding concn. from calibration curve $\times 10^5$	$(M_2/M_1)_p \times 10^3$	$(M_2/M_1)_t$ $(M_2/M_1)_p$	r_1 values	
								experimental	Literature
Acrylonitrile (M_1) Acrylic acid (M_2)	0.0025	Aqueous, 30°C H_2O_2 - u.v. 0.08 m/l	0.100	0.308	2.75	1.461	1.711	0.50	—
	0.0050		"	0.354	3.30	1.755	2.850		
	0.0075		"	0.372	3.50	1.850	4.053		
	0.0100		"	0.387	3.70	1.955	5.113		
	0.0150		"	0.408	3.95	2.105	7.127		
Acrylonitrile (M_1) Acrylic acid (M_2)	0.0010	Aqueous, 50°C $Fe^{++}(2.5 \times 10^{-4}$ m/l) - $H_2O_2(0.04$ m/l)	0.100	0.342	3.15	1.661	0.602	0.36	0.35 (3)
	0.0025		"	0.421	4.10	2.178	1.148		
	0.0075		"	0.509	5.15	2.727	2.751		
	0.0100		"	0.534	5.45	2.879	3.473		
	0.0150		"	0.562	5.78	3.062	4.899		
Acrylonitrile (M_1) Acrylic acid (M_2)	0.0050	Non-aqueous DMF, 80°C Bz_2O_2 (4.0×10^{-3} m/l)	0.050	0.402	3.87	4.099	1.220	0.15	0.13 \pm 0.02 (6)
	0.0075		"	0.381	3.63	3.845	1.951		
	0.0100		"	0.395	3.77	3.997	2.502		
	0.0125		"	0.406	3.93	4.164	3.003		
	0.0150		"	0.380	3.62	3.839	3.907		
Acrylonitrile (M_1) Sodium acrylate (M_2)	0.0025	Aqueous, 50°C $H_2O_2(0.04$ m/l) $Fe^{++}(2.5 \times 10^{-4})$ m/l)	0.100	0.452	4.48	2.376	1.052	0.20	0.21 (5)
	0.0050		"	0.476	4.75	2.513	1.990		
	0.0075		"	0.484	4.85	2.579	2.908		
	0.0125		"	0.534	5.45	2.894	4.320		
	0.0150		"	0.530	5.40	2.856	5.252		
Acrylonitrile (M_1) Methacrylic acid (M_2)	0.0025	Aqueous, 30°C H_2O_2 - u.v. (0.08 m/l)	0.100	0.176	1.22	0.6427	3.890	2.22	—
	0.0050		"	0.245	2.00	1.062	4.708		
	0.0075		"	0.258	2.15	1.137	6.595		
	0.0100		"	0.270	2.30	1.221	8.188		
	0.0150		"	0.289	2.53	1.340	11.20		
Acrylonitrile (M_1) Methacrylic acid (M_2)	0.0025	DMF medium 60°C, Bz_2O_2 (2.0×10^{-3} m/l)	0.100	0.200	1.45	0.7672	3.258	1.68	—
	0.0050		"	0.232	1.83	0.9692	5.160		
	0.0075		"	0.244	1.98	1.049	7.151		
	0.0125		"	0.258	2.15	1.148	10.89		
	0.0150		"	0.270	2.30	1.227	12.23		
Acrylonitrile (M_1) Crotonic acid (M_2)	0.025	DMF medium 60°C, Bz_2O_2 (4.0×10^{-3} m/l)	0.100	0.200	1.45	0.7686	32.52	23.8	21.0 \pm 10 (7)
	0.050		"	0.249	2.05	1.085	46.08		
	0.075		"	0.303	2.70	1.430	52.47		
	0.100		"	0.328	3.00	1.586	63.05		
	0.150		"	0.373	3.53	1.873	80.11		
Acrylonitrile (M_1) Maleic anhydride (M_2)	0.025	DMF medium 60°C, Bz_2O_2 (4.0×10^{-3} m/l)	0.100	0.358	3.35	1.769	14.13	6.5	6.0 (8)
	0.050		"	0.478	4.78	2.535	19.50		
	0.100		"	0.563	5.80	3.078	32.49		
	0.125		"	0.572	5.90	3.116	40.12		
	0.150		"	0.548	5.62	2.977	50.40		

Figures shown within brackets in the last column indicate references.

It may be observed that the results of the r_1 values presented in the Table-1 (obtained on the basis of the introductory assumptions) are found to compare reasonably well with most of the available values given in the literature. This produces an evidence in favour of the present method in regard to the order of attainable accuracy for the determination of end groups in polymers.

There might have been some doubt in the quantitative aspect of the method, had it been only cyanoacetic acid as the sole basis of comparison for the calculation of r_1 values for the copolymers. This suspicion, however, has been mostly removed by using polyacrylonitrile with known carboxyl content for calibration¹. It may be mentioned in this connection that both of them give the same calibration curve¹. The r_1 values for the copolymer of acrylonitrile with methacrylic acid could not be checked from the literature. However, from the fair agreement of most of the experimental r_1 values with the existing literature values, it may be quite logically concluded that the

present dye interaction method gives a fairly reasonable estimate of the carboxyl content in acrylonitrile copolymers.

References

1. C. KANJILAL, B. C. MITRA, S. R. PALIT and A. K. BANTHIA, *J. Indian Chem. Soc.*, (communicated).
2. S. R. PALIT and P. GHOSH, *J. Poly. Sci.*, 1962, 58, 1225.
3. M. K. SAHA, P. GHOSH, and S. R. PALIT, *J. Poly. Sci. A*, 1964, 2, 1365.
4. J. BOURDAIS, *Bull. Chem. Soc.*, France, 1955, 485.
5. H. ITO and S. SUZUKI, *Kogyo Kagaku Zasshi.*, 1955, 58, 627; *Chem. Abs.*, 1956, 50, 7501e.
6. L. J. YOUNG, Unpublished data, quoted in *J. Poly. Sci.*, 1961, 54, 411.
7. K. W. DOAK, quoted in *Chem. Rev.*, 1950, 46, 191.
8. H. GILBERT, F. F. MILLER, S. J. AVERILL, E. J. CARLSON, V. L. FOLT, H. J. HELLER, F. D. STEWART, R. F. SCHMIDT and H. L. TRUMBULL, *J. Amer. Chem. Soc.*, 1956, 78, 1669.