

Determination of Halogen in Copolymers by Dye-Partition Technique and Calculation of r_1 Therefrom

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Synopsis

Halogen-bearing polymers have been prepared by copolymerization of monomers (M_1) such as styrene, methyl methacrylate, methyl acrylate, and vinyl acetate with traces of chlorine-bearing monomers (M_2) such as allyl chloride and tetrachloroethylene at varying $M_1:M_2$ ratios in the 100:1 composition range. The halogen atoms in the copolymers were transformed to quaternary pyridinium halide groups by quaternization with pyridine. The copolymer compositions and the monomer reactivity ratio r_1 were determined by the estimation of the quaternary halide groups in the copolymers by the dye-partition technique, with aqueous disulfine blue VN150 in 0.01M hydrochloric acid as the dye reagent.

Functional groups can be well incorporated in polymers by copolymerization with monomers bearing the specific groups. Estimation of the specific groups thus introduced in the copolymers provides an easy and simple determination of copolymer composition and monomer reactivity ratio. This has been done for carboxyl-bearing monomers¹ by using a dye-interaction method of estimation of carboxyl groups in copolymers.

Recently, a dye-partition method,² described herein in detail, has been developed for the determination of halogen atoms in polymers. Copolymers at low conversions from monomers (M_1) such as styrene, methyl methacrylate, methyl acrylate, or vinyl acetate with a chlorine-bearing monomer (M_2) such as allyl chloride and tetrachloroethylene at varying $M_1:M_2$ ratios in the 100:1 composition range have been prepared, and the copolymer composition determined by the dye-partition method. The monomer reactivity ratio, i.e., the r_1 value for each copolymer is obtained with the help of the following simplified equation,¹

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

where $(M_2/M_1)_f$ and $(M_2/M_1)_p$ represent the molar ratio of the component monomers M_2 and M_1 in the feed and the copolymer, respectively.

EXPERIMENTAL

Materials

Monomers. Styrene, methyl methacrylate, and methyl acrylate were purified as usual by washing with 5% caustic soda solution until free of inhibitors, subsequently washed with distilled water, dried over fused calcium chloride for 24 hr., and finally purified by vacuum fractional distillation. Allyl chloride and tetrachloroethylene were purified by vacuum fractional distillation. Vinyl acetate was also purified by the usual procedure.³ The purified vinyl monomers were stored in a refrigerator.

Other Reagents. Chloroform (E. Merck) was used as the solvent for the copolymers. Pure pyridine (E. Merck) was used to quaternize halogen atoms in polymers to quaternary pyridinium halide groups. Analytical grade benzoyl peroxide (Eastman Kodak) was used as initiator of all copolymerization reactions. Disulfine blue VN150 was the dye used for the dye-partition test.

Preparation of Copolymers

For the preparation of polymers, known quantities of the required monomers were mixed together in clean Pyrex sealing tubes containing weighed amounts of benzoyl peroxide. The tubes were then flushed with nitrogen, frozen in liquid oxygen, and finally sealed under vacuum. Copolymerizations were carried out at a temperature of $60 \pm 0.1^\circ\text{C}$. to low conversions.

Quaternization of the Halogen Atoms in Polymers to Quaternary Pyridinium Halide Groups

The copolymers obtained were then quaternized with pyridine. About 0.2–0.3 g. of a copolymer was dissolved in about 2–5 ml. of pyridine in a clean Pyrex sealing tube. The solution was then frozen in liquid oxygen, and the tube was sealed under vacuum. The sealed tubes containing the halogen-bearing polymers in pyridine solution were then placed in a thermostated bath maintained at $90 \pm 1^\circ\text{C}$., and the quaternization was allowed to continue for 90 hr.

Purification of the Quaternized Copolymers

The quaternized copolymers were then precipitated with petroleum ether or alcohol. The precipitated polymers were further purified by repeated precipitation from their benzene solutions with a mixture of alcohol and petroleum ether as the nonsolvent. The process was repeated 5 to 6 times to ensure complete removal of all impurities. The finally precipitated polymers were then washed with petroleum ether and dried in air.

Dye-Partition Method for the Determination of Quaternary Halide Groups

The test for quaternary halide groups in polymers was carried out with an aqueous disulfine blue reagent prepared by dissolving 80 mg. of the

disulfine blue VN150 dye in one liter of 0.01*M* hydrochloric acid. A 10-ml. portion of the purified quaternized copolymer solution of known concentration in chloroform in a well-stoppered centrifuge tube was then well shaken with an equal volume of the aqueous disulfine blue reagent for a period of 1-2 hr. The two-phase system was then allowed to stand for about 2 hours. A distinct blue color in the chloroform layer indicates the presence of quaternary halide groups in the polymer. This dye-partition test is specific only for quaternary halide endgroups (ammonium or pyridinium chloride, bromide, or iodide).

The chloroform layer was then separated from the aqueous layer and then centrifuged, if necessary, to get a clear solution, and the color developed was measured in a Hilger spectrophotometer at 630 $m\mu$ with the use of stoppered 1 cm. cells. The quantity of quaternary halide endgroup present in a polymer was obtained by comparing the experimental optical density values with a calibration curve of laurylpyridinium chloride (LPC) or laurylpyridinium bromide (LPB), obtained by following a similar procedure. Complications sometimes arise, particularly with methyl methacrylate polymers of high molecular weight owing to the tendency for

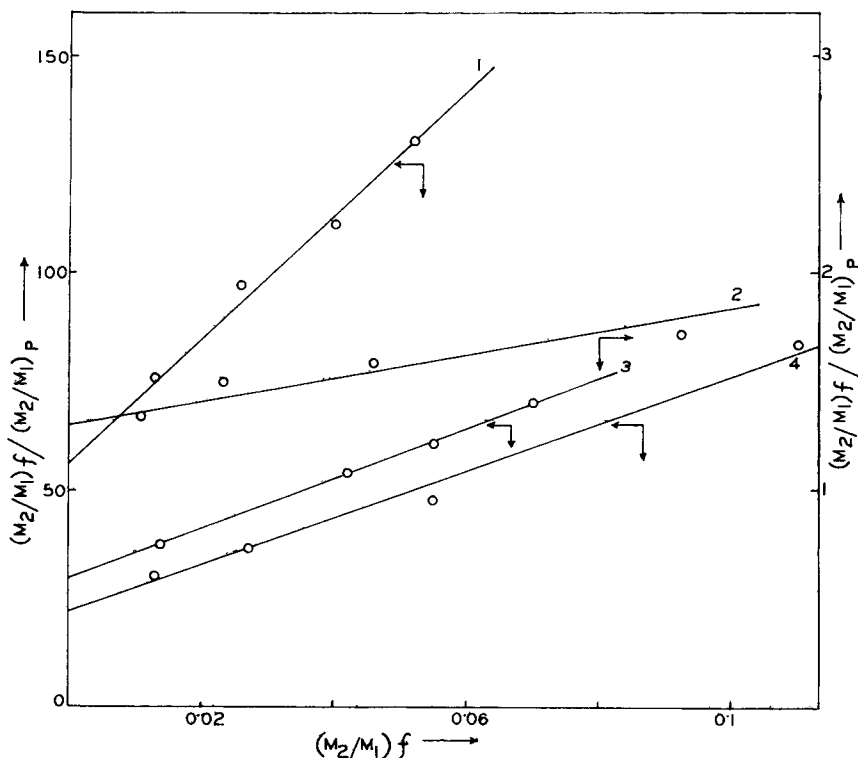


Fig. 1. Plot of $(M_2/M_1)_f / (M_2/M_1)_p$ vs. $(M_2/M_1)_f$ for copolymers: (1) methyl methacrylate-allyl chloride; (2) vinyl acetate-allyl chloride; (3) styrene-allyl chloride; (4) methyl acrylate-allyl chloride.

Copolymer Composition and Monomer Re-

Copolymer	$(M_2/M_1)_f$	Conditions of polymerization	Conver- sion, %	Po so. (q ni
Styrene (M_1)– allyl chloride (M_2)	0.070 0.055 0.042 0.014	60°C., 0.1 mole- % Bz_2O_2 , bulk	6.5 4.6 4.4 2.5	0. 0. 0. 0.
Styrene (M_1)– tetrachloro- ethylene (M_2)	0.113 0.091 0.056 0.022	60°C., 0.15 mole- % Bz_2O_2 , bulk	5.8 6.1 6.1 7.0	0. 0. 0. 0.
Methyl methacrylate (M_1)– allyl chloride (M_2)	0.052 0.040 0.026 0.013	60°C., 0.2 mole-% Bz_2O_2 , bulk	4.5 2.5 2.2 2.1	0. 0. 0. 0.
Methyl methacrylate (M_1)– tetrachloro- ethylene (M_2)	0.052 0.042 0.021 0.011	60°C., 0.1 mole- % Bz_2O_2 , bulk	3.2 2.8 2.5 2.5	0. 0. 0. 0.
Methyl acrylate (M_1)– allyl chloride (M_2)	0.110 0.055 0.027 0.013	60°C., 0.4 mole- % Bz_2O_2 , bulk	12.0 2.1 5.0 2.2	0. 0. 0. 0.
Vinyl acetate (M_1)– allyl chloride (M_2)	0.092 0.046 0.023 0.011	60°C., 0.4 mole- % Bz_2O_2 , bulk	11.2 10.8 12.6 12.9	0. 0. 0. 0.

formation of emulsions in the organic phase. The complications may however, be greatly overcome on long standing and centrifugation. For polystyrene and polyvinyl acetate and for relatively low molecular weight polyacrylates and methacrylates, no such complications generally arise.

RESULTS AND DISCUSSION

The results of copolymerization are shown in Table I. The monomer reactivity ratio r_1 was obtained with the help of eq. (1). For each copolymer, $(M_2/M_1)_f/(M_2/M_1)_p$ values were plotted against $(M_2/M_1)_f$ values. The plots follow a straight line. The intercept, obtained by extrapolating the straight line to zero $(M_2/M_1)_f$ value, gives the r_1 value for the copolymer (Figs. 1 and 2). The copolymer composition $(M_2/M_1)_p$ was obtained by

as Determined by Dye-Partition Method

λ , at 630 μ using disulfine blue reagent	Corre- sponding LPC concn., $10^{-4}N$	$(M_2/M_1)_p$ $\times 10^{-3}$	$(M_2/M_1)_f$ $(M_2/M_1)_p$	r_1	
				Experi- mental	Litera- ture
1.4	13.9	1.0	70	30	31.2 ± 4
1.29	12.9	0.91	60.1		
1.14	11.5	0.78	53.6		
0.54	5.36	0.37	37.8		
0.24	2.36	0.062	1800	200 ± 20	185 ± 20 , 208
0.23	2.29	0.058	1520		
0.20	1.98	0.052	1080		
0.17	1.7	0.043	528		
0.78	7.8	0.39	130	56	42
0.70	7.0	0.35	111		
0.53	5.3	0.27	97		
0.34	3.42	0.17	76		
0.30	3.0	0.030	1733	240 ± 20	—
0.32	3.2	0.032	1313		
0.26	2.62	0.026	808		
0.20	1.99	0.020	550		
0.78	7.78	1.34	83.2	22 ± 4	—
0.675	6.8	1.18	47.4		
0.43	4.3	0.74	36.1		
0.25	2.5	0.433	30.0		
0.85	8.5	53.8	1.70	1.30	0.7
0.58	5.8	29.1	1.58		
1.20	12.0	15.4	1.50		
0.64	6.4	8.17	1.34		

the application of dye partition test, taking laurylpyridinium chloride (or bromide) as the basis of comparison.

An important step in the present method of determination of specific quaternary groups in a polymer is the process of quaternization, which is generally slow and sluggish.^{4,5} In our present method of quaternization we used the quaternizing agent (pyridine) as the solvent to dissolve the substrates to be quaternized. Fairly high temperature (90°C.) and sufficiently long hours of heating (90 hr.) were allowed to ensure that the quaternization be complete as far as practicable. It is known that in a long chain polymer the quaternization with pyridine is highly dependent on steric factors. When allyl chloride was used as a component monomer in copolymerization, this steric factor is negligible and all the chlorine atoms

in the copolymer are presumably quaternizable. But when tetrachloroethylene bearing two chlorine atoms on each of the two carbon atoms, is used as a component monomer in copolymerization, the steric factor probably plays a great part in the quaternization process. The bulky quaternary pyridinium groups formed when one chlorine atom from each of the two carbon atoms of a tetrachloroethylene segment of a copolymer is quaternized shield the other two chlorine atoms of the same tetrachloroethylene segment from being quaternized, and we assume that two chlorine

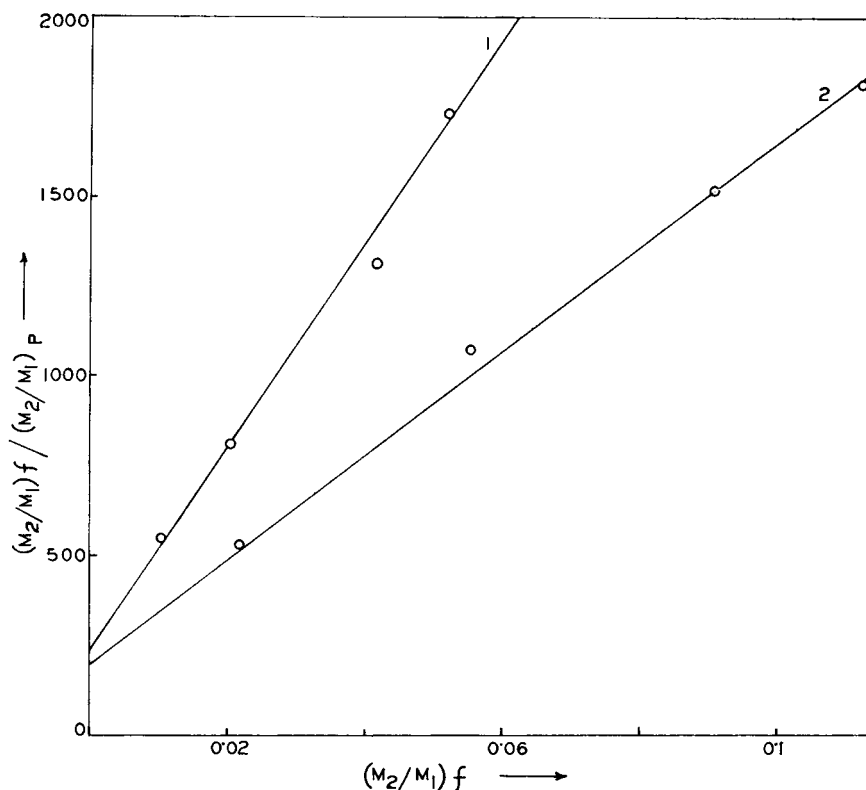


Fig. 2. Plot of $(M_2/M_1)_f / (M_2/M_1)_p$ vs. $(M_2/M_1)_f$ for copolymers: (1) methyl methacrylate-tetrachloroethylene; (2) styrene-tetrachloroethylene.

atoms, on the average, of each tetrachloroethylene segment of a copolymer are quaternized. The results (r_1 values) presented in Table I are obtained on the basis of these assumptions and are found to compare well with some values given in the literature.^{6,7} Some of our experimental r_1 values, e.g., those for methyl methacrylate-allyl chloride and vinyl acetate-allyl chloride do not agree closely with the literature values,^{9,10} but nevertheless our experimental values are of the same order as those given in the literature.

There may be some uncertainty in the quantitative aspects of the present method because the r_1 values for the copolymers have been obtained by empirical comparison with a long chain pyridinium chloride (LPC), and it is difficult to make an independent check at the present stage. Allowing for this uncertainty, it may be seen from Table I that the experimental r_1 values for styrene allyl chloride⁶ and styrene-tetrachloroethylene^{7,8} copolymers are in close agreement with the literature values, while those for MMA-allyl chloride⁹ and vinyl acetate-allyl chloride¹⁰ are higher than the values given in the literature. The r_1 values for the other two copolymers could not be checked from the literature.

Quaternization of polyvinylpyridine with butyl bromide has been extensively studied by Fuoss,^{4,5,11} and it has been shown that the extent of quaternization in this system is not always complete and varies from about 70 to 100%. In our present method for the determination of copolymer composition, it is apparent that incomplete quaternization will always lead to a higher r_1 value. From the fair agreement of the experimental r_1 values with the existing literature values, it may be concluded that the dye-partition method gives a fairly reasonable estimate of halogen content in copolymers.

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Résumé

Des polymères porteurs d'halogènes ont été préparés par copolymérisation de monomères (M_1) tels que le styrène, le méthacrylate de méthyle, l'acrylate de méthyle et l'acétate de vinyle avec des traces de monomères (M_2) porteurs de chlore tels que le chlorure d'allyle et le tétrachloroéthylène en variant les rapports $M_1:M_2$ dans le rapport et composition de 100:1. Les atomes d'halogènes dans les copolymères ont été transformés en groupement halogénure de pyridine quaternée en recourant à la quaternation avec la pyridine. Les compositions du copolymère et de là, le rapport de réactivité du monomère (r_1) ont été déterminés par estimation des groupes quaternaires halogénés dans les copolymères au moyen de la technique de partition de couleurs en employant une solution aqueuse de bleu de disulfine VN150 dans 0.01M d'acide chlorhydrique comme réactif coloré.

Zusammenfassung

Durch Copolymerisation von Monomeren (M_1) wie Styrol, Methylmethacrylat, Methacrylat und Vinylacetat mit Spuren von halogenhaltigen Monomeren (M_2) wie Allylchlorid und Tetrachloräthylen bei wechselndem Verhältnis $M_1:M_2$ im Bereich von etwa 1 Molprozent M_2 wurden halogenhaltige Polymere hergestellt. Die Halogenatome in den Copolymeren wurden durch Quaternisierung mit Pyridin in quaternäre Pyridiniumhalogenid-Gruppen übergeführt. Die Zusammensetzung des Copolymeren und damit das Monomerreaktivitätsverhältnis r_1 wurde durch Bestimmung der quaternären Halogenid-Gruppen mittels einer Anfärbemethode mit wässrigem Disulfonblau VN150 in 0,01M HCl als Farbreagens ermittelt.

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