piperidone diacetate was effected with 2.4 g. (0.036 mole) of potassium hydroxide in 25 ml. of 85% ethanol. After stirring at room temperature for 10 hr., the mixture was cooled and acidified with concd. hydrochloric acid to the Congo red paper end point. Evaporation of the solution to one fourth the original volume yielded a white solid which could not be purified by recrystallization.

The polymeric lead mercaptide was prepared from lead diacetate and the dithiol in ethanol. The dithiol was regenerated by bubbling hydrogen sulfide into an ether suspension of the yellow mercaptide, filtration of the lead sulfide, and evaporation of the ether. Recrystallization of the crude solid from cyclohexane yielded 2.0 g. (91%) of the product, m.p. 83.5–85°. The infrared spectrum showed absorption maxima assignable to a δ-lactam (3380, 3080, and 1645 cm.$^{-1}$) and thiol (2550 cm.$^{-1}$).

Anal. Calcd. for $C_{11}H_{21}ONS_2$: C, 53.44; H, 8.50; N, 5.67; S, 25.87. Found: C, 53.17; H, 8.39; N, 5.45; S, 25.98.

Polymerization of 3,6-bis(3-mercaptopropyl)-2-piperidone to the polydisulfide (V). A method similar to that employed by Marvel and Olson[6] and the apparatus and temperature modification reported by Marvel, Bonsignore and Banerjee were utilized. The following procedure was employed in all the oxidative emulsion polymerizations conducted at 77°: 3,6-Bis-(3-mercaptopropyl)-2-piperidone, 2.0 g.; potassium hydroxide, 2.0 g.; lauric acid, C.P., 1.5 g.; distilled water, 25 ml.; selenious acid, 15 mg.; Antifoam A (Dow-Corning), 1 drop.

During all polymerization runs some polymer precoagulated which prevented an accurate recording of the yield. After a 7-day polymerization period, the polymer latices were coagulated by pouring slowly into 600 ml. of 50% aqueous methanol containing approximately 5 ml. of concd. hydrochloric acid. A yellow to pink powdery solid was obtained which was soluble in hot formic acid, hot tetrachloroethane, and a hot 1:1 mixture of chloroform and glacial acetic acid. The polymer was purified by dissolution in hot tetrachloroethane, filtration of the hot solution and reprecipitation into 80% aqueous methanol. A white solid polymer was obtained, m.p. 212–259°. The infrared spectrum showed absorption maxima for a δ-lactam (3380, 3140, 1650, and 960 cm.$^{-1}$).

Anal. Calcd. for $C_{11}H_{19}ONS_2$: C, 53.87; H, 7.75. Found: C, 50.48; H, 7.13.

Upon correction for a water-soluble residue obtained upon combustion of the polymer sample, the analytical values were:

Found: C, 53.58; H, 7.56.

Hydrolysis of polymer to polyampholyte. The method of Marvel and Schniepp[10] for the hydrolysis of 2-piperidone was employed. One-half gram of the polymer was refluxed in 25 ml. of concd. hydrochloric acid for 24 hr. The finely divided polymer remained suspended in part in the acid and with heating changed color to dark brown. The residue was filtered and dried and showed absorption maxima in the infrared which indicated hydrolysis of several isolated lactam functions.

The acid filtrate was evaporated to dryness, and the yellow residue was dissolved in water, decolorized with charcoal, and filtered. Lyophilization of the aqueous solution yielded a white rubbery polymer, m.p. 247–264° (83%) with an inherent viscosity of 0.784 in water. The infrared spectrum showed major absorption maxima for acid (2500–2700, 1705, and 950 cm.$^{-1}$) and amine hydrochloride (3100–3500, 2400–2500, 2050, 1615, 935, and 965 cm.$^{-1}$).

Anal. Calcd. for $C_{11}H_{26}O_4NS_2Cl \cdot 2H_2O$: C, 39.34; H, 7.14. Found: C, 39.82; H, 7.77.

Neutralization of the amine hydrochloride with potassium hydroxide yielded a white rubbery solid which was insoluble in hot water and wet and dry tetrahydrofuran and dioxane.

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[10] C. S. Marvel and L. E. Schniepp, *J. Am. Chem. Soc.*, **57**, 1557 (1935).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Cationic Copolymerization of Some α-Methylstyrenes with Vinyl 2-Chloroethyl Ether. Solvent Effects[1]

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Reactivity ratios for vinyl 2-chloroethyl ether with α-methylstyrene, α,*p*-dimethylstyrene and *p*-methoxy-α-methylstyrene in a cationic system in the solvents benzene and nitrobenzene have been determined. No solvent effect was apparent.

Although it is well known that the rates of cationic homopolymerization of styrene and α-methylstyrene are markedly enhanced by an increase in the dielectric constant of the medium,[2] the relative reactivity ratios of monomer pairs in cationic copolymerization had been shown not to vary with the dielectric constant of the medium. Thus, Overberger, Arond, and Taylor[3] have shown that the composition of the initial copolymer formed in the stannic chloride–initiated copolymerization of styrene and *p*-chlorostyrene is independent of the dielectric constant of the medium. Similar results were obtained using titanium tetrachloride and aluminum bromide.[4] It was suggested that the lack of solvent effects was due to the similarity in structure of the monomers studied. The concept

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[1] This is a partial report of work done under contract with three Utilization Research and Development Divisions, Agricultural Research Service, U. S. Department of Agriculture, and authorized by the Research and Marketing Act. The contract was supervised by Dr. J. C. Cowan of the Northern Division. This paper is based on portions of a thesis submitted by James F. Dunphy to the Graduate College of the University of Illinois in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] D. C. Pepper, *Nature*, **158**, 789 (1940); D. C. Pepper, *Trans. Faraday Soc.*, **45**, 397 (1949).

[3] C. G. Overberger, L. H. Arond, and J. J. Taylor, *J. Am. Chem. Soc.*, **73**, 5541 (1951).

[4] C. G. Overberger, R. J. Ehrig, and D. Tanner, *J. Am. Chem. Soc.*, **76**, 772 (1954).

of "solvent clusters" was invoked; *i.e.*, the propagating ion-pairs were solvated preferentially by one component of the system being thereby rendered insensitive to changes in the gross dielectric constant of the system. Structurally similar ion-pairs would be expected to be similarly solvated. As a test of this hypothesis, Overberger and Kamath[5] have recently reported the results of their study of the system *p*-chlorostyrene-isobutylene; they observed extremely wide fluctuations in the values of the monomer reactivity ratios as the dielectric constant of the medium was varied.

During the course of a general study of the cationic copolymerization of vinyl ethers, we have determined the reactivity ratios of vinyl 2-chloroethyl ether in copolymerization with α-methylstyrene, α,*p*-dimethylstyrene, and *p*-methoxy-α-methylstyrene. Benzene and nitrobenzene were the solvents employed. The results of this study are summarized in Table I. The vinyl ether was considered as monomer 2 in the calculations.

TABLE I

CATIONIC COPOLYMERIZATION OF VINYL 2-CHLOROETHYL ETHER WITH SOME α-METHYLSTYRENES

	Solvent			
	Benzene		Nitrobenzene	
Comonomer	r_1	r_2	r_1	r_2
α-Methyl-styrene	0.33	5.0	0.34, 0.42	2.6, 3.3
α,*p*-Dimethyl-styrene	0.54, 0.51	1.7, 1.7	0.64	1.7
p-Methoxy-α-methyl-styrene	1.1	0.42	1.3	0.73

It is clear from the data in Table I that, with the possible exception of r_2 for the system α-methylstyrene-vinyl 2-chloroethyl ether, the changes in the reactivity ratios are very small, in spite of the widely differing structures of the monomer pair.

EXPERIMENTAL[6]

Materials. The vinyl 2-chloroethyl ether (Monomer-Polymer Inc.) was purified by the method of Schildknecht, Zoss and McKinley[7]; it was redistilled immediately before use; b.p. 106–107°; $n_{\rm D}^{25}$ 1.4357. α-Methylstyrene (Dow Chemical Co.) was redistilled; b.p. 62°/21 mm.; $n_{\rm D}^{25}$ 1.5357. α,*p*-Dimethylstyrene, b.p. 79–80°/15 mm.; $n_{\rm D}^{25}$ 1.5322, and *p*-methoxy-α-methylstyrene, b.p. 107–110°/17 mm., were synthesized by dehydration of the carbinol obtained by reaction of the appropriate *p*-substituted acetophenone with methylmagnesium bromide.[8] Mallinckrodt benzene and absolute methyl alcohol (Analytical Reagent grade) were used without further purification. Commercial nitrobenzene was redistilled before use. The stannic chloride employed was Baker's C.P. anhydrous material, without further purification. Catalyst solutions were prepared immediately before use by dissolving the stannic chloride in sufficient solvent to make a 1% (by weight) solution.

Copolymerization procedure. Copolymerizations were carried out in 2-ounce screw-cap bottles at room temperature. To a solution of 5.000 g. of the monomer mixture in 5.00 g. of benzene or nitrobenzene was added from 0.10 to 0.25 ml. of the appropriate catalyst solution. Polymerization was interrupted by the addition of a large excess of absolute methyl alcohol as soon as the solution exhibited a temperature increase; this served to precipitate the polymer which was purified by repeated triturations with methyl alcohol. The polymers were then dissolved in 30–40 ml. of benzene and quantitatively transferred to clean, dry, tared bottles by means of suction filtration through a sintered-glass funnel. The benzene solutions were frozen and the benzene removed by sublimation at 0.2 to 0.3 mm. for 36 hr. Polymers which were prepared in nitrobenzene were subjected to an additional 24 hr. at 45° in a vacuum oven. Reweighing the tared bottles furnished the yield of polymer. Data for the polymerization experiments are gathered in Table II.

TABLE II

	Monomer Charge, g.	M_2[a]	Yield, %	Chloride, %	m_2[a]
α-Methylstyrene-Vinyl 2-Chloroethyl Ether					
Benzene 30°	4.984	0.699	5.58	29.87	0.907
	4.997	0.489	7.34	26.93	0.825
	4.992	0.298	2.95	20.52	0.641
	5.008	0.101	0.44	8.94	0.289
Nitrobenzene 30°	4.991	0.700	40.21	28.16	0.859
	4.991	0.499	13.48	29.33	0.779
	5.003	0.301	2.38	15.10	0.479
	5.003	0.099	1.13	6.87	0.224
α,*p*-Dimethylstyrene-Vinyl 2-Chloroethyl Ether					
Benzene 30°	5.006	0.900	2.45	30.72	0.937
	4.985	0.701	1.64	26.33	0.825
	4.988	0.499	3.85	17.95	0.592
	4.991	0.298	3.68	11.45	0.394
	5.022	0.101	1.22	5.55	0.199
Nitrobenzene 30°	5.003	0.900	11.89	30.02	0.919
	5.008	0.700	17.93	25.19	0.794
	5.004	0.502	19.46	18.32	0.603
	4.997	0.301	13.68	10.25	0.356
	4.998	0.094	0.98	1.96	0.072
p-Methoxy-α-methylstyrene-Vinyl 2-Chloroethyl Ether					
Benzene 30°	4.989	0.900	2.27	27.22	0.862
	4.986	0.706	7.33	15.76	0.556
	5.005	0.501	2.61	10.42	0.388
	4.993	0.301	2.17	7.17	0.276
Nitrobenzene 25°	5.008	0.901	9.42	28.14	0.884
	5.004	0.699	22.14	18.13	0.624
	4.999	0.500	22.50	11.83	0.434
	5.017	0.302	15.16	6.96	0.247
	4.990	0.018	5.13	0.27	0.011

[a] M_2 is the mole fraction of vinyl 2-chloroethyl ether in the monomer mixture; m_2 is the mole fraction in the copolymer.

The method of calculating the reactivity ratios varied with the yield of polymer. For yields up to 6%, the differential form of the copolymer composition equation was

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(5) C. G. Overberger and V. G. Kamath, *J. Am. Chem. Soc.*, **81**, 2910 (1959).

(6) We are indebted to Mr. Josef Nemeth of the University of Illinois and to the Clark Microanalytical Laboratory, Urbana, Ill., for the microanalyses.

(7) C. E. Schildknecht, A. O. Zoss, and C. McKinley, *Ind. Eng. Chem.*, **39**, 180 (1947).

(8) P. Epple and S. Ruhemann, *Ber.*, **59**, 294 (1926); G. B. Bachman and R. W. Finholt, *J. Am. Chem. Soc.*, **70**, 622 (1948).

used[9]; for yields in the range 6–12%, corrected values of M_1 and M_2 were used in the differential form.[10] In the range 12–40%, the integrated form of the copolymer composition equation was used, the concentrations of monomers present at the time the reaction was stopped being estimated from the yield and composition of the copolymer.[11]

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[9] T. Alfrey, Jr., J. J. Bohrer, and H. Mark, *Copolymerization,* Interscience Publishers, Inc., New York, 1952, p. 12.

[10] C. G. Overberger, D. Tanner, and E. M. Pearce, *J. Am. Chem. Soc.,* **80,** 4500 (1958).

[11] F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.,* **66,** 1594 (1944).