trans-1-(4-Chlorophenyl)-4-phenyl-2-butene-1,4-dione.—A mixture of 14.4 g. of phenylglyoxal, 15.4 g. of *p*-chloroacetophenone and 250 g. of acetic anhydride was refluxed for 2 hours and hydrolyzed with ice–water. The precipitated oil was crystallized from ethanol; 4 g. (15%), m.p. 120.5–121.5° (yellow).

An improved preparation[22] of di-(*p*-methoxybenzoyl)-ethylene is: To a stirred mixture of 114 g. of anhydrous aluminum chloride in 550 ml. of benzene at 70° was added 68 g. (0.63 mole) of anisole, and this was followed by dropwise addition over 4–5 min. of a mixture of 60 g. (0.39 mole) of fumaryl chloride and 40 g. (0.37 mole) of additional anisole. Refluxing occurred and was continued for an additional 10 min. The mixture was then cooled and poured into ice containing 30 ml. of concd. hydrochloric acid. The resulting suspension of the bulk of the product (an orange solid) was filtered, and a small additional crop was obtained from the benzene solution; yield, nearly pure, 44 g. (41%). Recrystallization was from butanone–ethanol mixture; m.p. 168–168.5° (lit.[16] 165.5°).

Di-(*m*-nitrobenzoyl)-ethylene. (1,4-Di-3-nitrophenyl-2-butene-1,4-dione).—The method for nitrating β-benzoylacrylic acid to its 3-nitro derivative[23] was used. A solution of 11 g. of 1,2-dibenzoylethylene was made in 25 ml. of fuming nitric acid at 0°, and was poured into ice-water. The product was washed and crystallized from ethanol–benzene mixture; yield 6 g. (40%), m.p. 205–205.5° (pale yellow).

Anal. Calcd. for $C_{16}H_{10}N_2O_6$: C, 58.85; H, 3.09. Found: C, 58.80; H, 2.99.

Aqueous alkaline permanganate oxidation gave a little over one equivalent of *m*-nitrobenzoic acid (identified).

An isomer was obtained by evaporation of the solvent from the above crystallizations; m.p. 129–130°.

Anal. Calcd. for $C_{16}H_{10}N_2O_6$: C, 58.85; H, 3.09. Found: C, 59.10; H, 2.93.

The nitro compounds were too insoluble in methanol for kinetic study by the procedure used for the rest of the series.

(22) (a) J. D. Hutcheson, (b) N. H. Shearer, Theses, University of Virginia, 1933, 1944, resp.

(23) M. T. Bogert and J. J. Ritter, *J. Am. Chem. Soc.*, **47**, 526 (1925).

Procedure.—A solution about 5×10^{-5} *M* in the dibenzoylethylene, also containing the buffer components, was prepared using reagent grade methanol as solvent. All reactions were run at 25.0°. The optical density at the wave length of maximum absorption of the substrate was determined at intervals.

The spectra of the reaction mixtures from *p*-methoxy-, *p*-bromo- and *p*-chlorodibenzoylethylene, when compared with the spectra of the methoxyethanes, prepared by addition of methanol as described above, showed that equilibrium was reached at about 90% reaction, as in the parent compound.[9] Any effect of substituents on the equilibrium constant was smaller than the experimental error. The kinetic runs were plotted by calculating the concentration of dibenzoylethylene from the optical density and the known absorptivities of reactant and product, and using this concentration in the simple first-order equation, $\ln A_0/A = kt$, for the first 25% reaction. Values of k_2 were then obtained by dividing k by the methoxide-ion concentration, except in the more detailed study of the parent dibenzoylethylene. For the remaining six compounds of Table II, the products were not prepared but their absorptivities were estimated from values for similar compounds and from the observed equilibrium mixture. It should be noted that the ratio of the two isomeric addition products from each unsymmetrical dibenzoylethylene was not measured.

After standing from 1 to 4 months, *trans*-dibenzoylethylene in methanol or in triethylamine–triethylammonium chloride buffers, and *cis*-dibenzoylethylene in acid solutions show spectral evidence of the cyclic methoxydiphenylfuran, known to be formed under such conditions.[24] Our observation that cyclization to this stable product occurs after the faster dibenzoylmethoxyethane formation is in accord with the results of Bailey and Kelley,[24b] who started with the latter compound and isolated both dibenzoylethylene and methoxydiphenylfuran after refluxing with methanolic triethylamine hydrochloride and hydrogen chloride.

(24) (a) P. S. Bailey and R. E. Lutz, *ibid.*, **69**, 498 (1947); (b) P. S. Bailey and J. T. Kelley, *ibid.*, **70**, 3442 (1948); (c) R. E. Lutz and M. G. Reese, *ibid.*, **81**, 3397 (1959).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN, BROOKLYN 1, N. Y.]

Solvent Effects in Cationic Polymerization and Copolymerization[1]

BY C. G. OVERBERGER AND V. G. KAMATH[2]

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The cationic reactivity ratios for the copolymerization of *p*-chlorostyrene and isobutylene and for chloroprene and styrene were determined in various solvents. The results obtained in hydrocarbon solvents strongly indicate that the solvation of the growing ion pair by the more polar monomer was the predominant effect.

Monomer reactivity ratios have been established to be generally independent of the dielectric constant of the solvent or the initiator in free radical copolymerizations. The effect of temperature on the reactivity ratios has also been found to be negligible in radical polymerizations. It was interesting to investigate how far these monomer reactivity ratios are affected by changes in solvent in cationic-initiated copolymerizations where ions or ion pairs are involved. A preliminary communication on our findings has been reported earlier.

Small variations in the values of r_1 and r_2 were reported by Florin[4] in the cationic copolymerization of styrene and 3,4-dichlorostyrene using different initiators. Changes were also observed when nitrobenzene was used as solvent instead of carbon tetrachloride. No attempt was made to explain these observations and since some of the polymerizations were heterogeneous, interpretation was difficult. Overberger, *et al.*,[5] did not observe any major changes in the reactivity ratios of styrene and *p*-chlorostyrene copolymerizations in mixed solvents of nitrobenzene and carbon tetrachloride. Neither was any change observed for the r_1 and r_2 values of these monomers using different initiators such as titanium tetrachloride and stannic chloride.[6] The cationic copolymerization of α-methylstyrenes with 2-chloroethyl vinyl ether in benzene as well as nitrobenzene solvents has been reported recently by Marvel.[7] Only in the case of α-methylstyrene itself was some change observed in the maximum reactivity ratios.

Results and Discussion

One of the objections that can be raised to the use of mixed solvents is that the measured dielectric constant of the mixture may not accurately describe the system on a molecular level. To eliminate this possibility it was desirable to measure the reactivity ratios in pure solvents. Isobutylene was copolymerized with *p*-chlorostyrene in different solvents and the results are given in Table I. This particular monomer pair was chosen because of the expected differences in the reactivities of the carbonium ions derived from the

(1) This is the 21st in a series of papers concerned with ionic polymerization; for the previous paper in this series, see G. F. Endres, V. G. Kamath and C. G. Overberger, *J. Am. Chem. Soc.*, **84**, 4813 (1962).

(2) This paper comprises a portion of the Dissertation submitted by V. G. Kamath in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Polytechnic Institute of Brooklyn.

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

(4) R. E. Florin, *ibid.*, **71**, 1867 (1949); **73**, 4468 (1951).

(5) C. G. Overberger, L. H. Arond and J. J. Taylor, *ibid.*, **73**, 5541 (1951).

(6) C. G. Overberger, R. J. Ehrig and D. Tanner, *ibid.*, **76**, 772 (1954).

(7) C. S. Marvel and J. F. Dunphy, *J. Org. Chem.*, **25**, 2209 (1960).

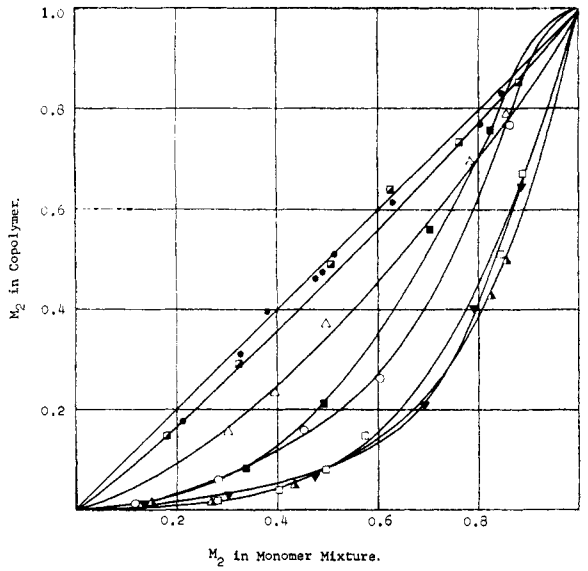

Fig. 1.—Copolymerization of isobutylene (M_1) and *p*-chlorostyrene (M_2): ●, *n*-hexane solvent, $AlBr_3$ catalyst; Δ, ethylene dichloride, $AlBr_3$; ■, benzene, $SnCl_4$; O, nitrobenzene, $SnCl_4$; □, benzene–nitrobenzene, $AlBr_3$; ▼, nitrobenzene, $AlBr_3$; ▲, nitromethane, $AlBr_3$; ◪, benzene, $AlBr_3$.

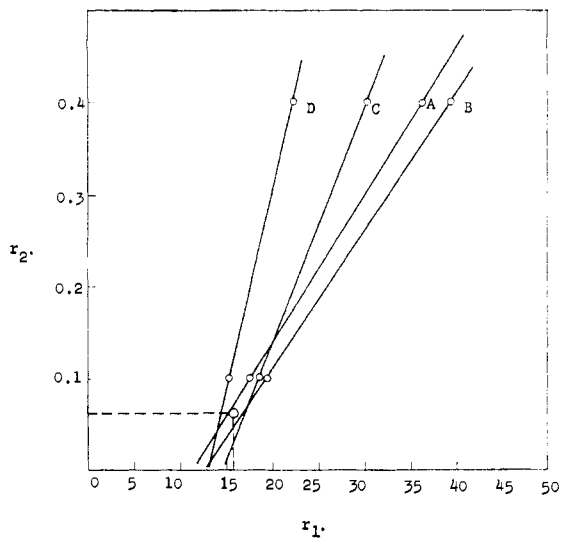

Fig. 2.—Copolymerization of styrene (M_1) and chloroprene (M_2) in nitrobenzene using $AlBr_3$ as initiator: A, 80 mole % M_2; B, 80.2 mole % M_2; C, 70 mole % M_2; D, 60.5 mole % M_2.

monomers and the potential difference in the solvation of the corresponding iron pairs in different solvents. Copolymerization of styrene with isobutylene has been reported earlier.[8,9]

As can be seen from Table I, significant differences are noted for the reactivity ratios in different solvents. No copolymer was obtained using aluminum bromide initiator and acetonitrile or benzonitrile as solvents.

TABLE I

REACTIVITY RATIOS r_1 AND r_2 FOR THE COPOLYMERIZATION OF ISOBUTYLENE (M_1) AND *p*-CHLOROSTYRENE (M_2) IN VARIOUS SOLVENTS

Solvents	Dielectric constant of solvent	Initiator	r_1	r_2
Benzene	2.28	$SnCl_4$	12.2 ± 1.0	2.8 ± 0.03
Nitrobenzene	36.0	$SnCl_4$	8.6 ± 0.20	1.25 ± 0.1
n-Hexane	1.82	$AlBr_3$	1.1	1.04
Benzene	2.28	$AlBr_3$	1.14 ± 0.10	0.99 ± 0.10
Ethylene dichloride	10	$AlBr_3$	2.80	0.89
Nitrobenzene	36	$AlBr_3$	14.9 ± 0.2	0.53 ± 0.04
Nitromethane	38	$AlBr_3$	22.2 ± 0.5	0.73 ± 0.05
Mixt. of benzene–nitrobenzene (50% vol.)		$AlBr_3$	18.0	0.75

The reason for this may be formation of stable complexes between the catalyst and these solvents. In all other cases, copolymers were obtained. The copolymer composition was evaluated by analyzing the copolymer for its chlorine content. It has been previously proved[8] by control experiments using styrene alone that in these solvents no catalyst or solvent fragments were incorporated in the copolymer, and hence chlorine analysis of the copolymer should indicate accurately the *p*-chlorostyrene content of the copolymer. The reactivity ratios were calculated by the intersection method; the conversions in most of the experiments being kept below 7%. The copolymer composition curves are plotted in Fig. 1.

The Lewis acids used as initiators for these copolymerizations are also well known as alkylation catalysts in aromatic systems. If the calculated reactivities were to be meaningful, it was necessary to demonstrate that all the isobutylene incorporated in the copolymer came from polymerization and not from any nuclear alkylation reaction. In order to determine whether under the copolymerization conditions any alkylation of the monomer took place, experiments were carried out using isobutylene and *p*-chlorotoluene (instead of *p*-chlorostyrene) with aluminum bromide as the catalyst. This was also repeated with chlorobenzene. Complete recovery of the *p*-chlorotoluene as well as chlorobenzene showed that under the conditions of polymerization, alkylation of the monomer did not occur.

The results outlined in Table I indicate that in some of the solvents used the product of the reactivity ratios r_1r_2 was greater than unity. With such high values of the product r_1 and r_2, it was conceivable that instead of a true copolymer being formed a block copolymer may have resulted. One of the standard methods of obtaining evidence for this possibility is to fractionate the copolymer formed and to analyze the fractions for chemical homogeneity as well as molecular weight. The sample of copolymer obtained using isobutylene and *p*-chlorostyrene monomers in nitrobenzene solvent with stannic chloride initiator was fractionated using butanone as the solvent and methanol as nonsolvent by the conventional method. The fractions obtained showed a regular decrease in the intrinsic viscosity and an almost uniform chemical composition as determined by its chlorine analysis (Table IV). This is an indication that a true copolymer has been formed and that if blocks were present they were small blocks which could not be separated by a single fractionation technique.

Attempts were made to study the effect of solvents on the cationic copolymerization of the monomer pair isobutylene and 2-chloroethyl vinyl ether. No copolymer was obtained using either stannic chloride or aluminum bromide as the initiators; but with boron trifluoride etherate as initiator clear semi-solid polymers were obtained which turned dark on exposure to air. These polymer samples on analysis proved to be mostly homopolymers of the chlorovinyl ether.

(8) J. Rehner, R. L. Zapp and W. J. Sparks, *J. Polymer Sci.*, **11**, 21 (1953).

(9) E. B. Ludvig, A. R. Gantnakhar and S. S. Medvedev, *Polymer Science* (USSR), **1**, No. 3, 516 (1960)[10].

Translated from *Vysokomol. Soedin.*, **1**, No. 9, 1333 (1959).

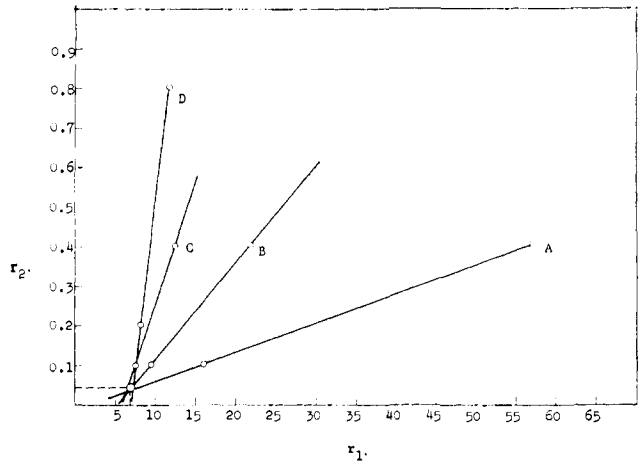

Fig. 3.—Copolymerization of styrene (M_1) and chloroprene (M_2) in benzene using $AlBr_3$ as initiator: A, 83.5 mole % M_2; B, 80.2 mole % M_2; C, 70.0 mole % M_2; D, 60.5 mole % M_2.

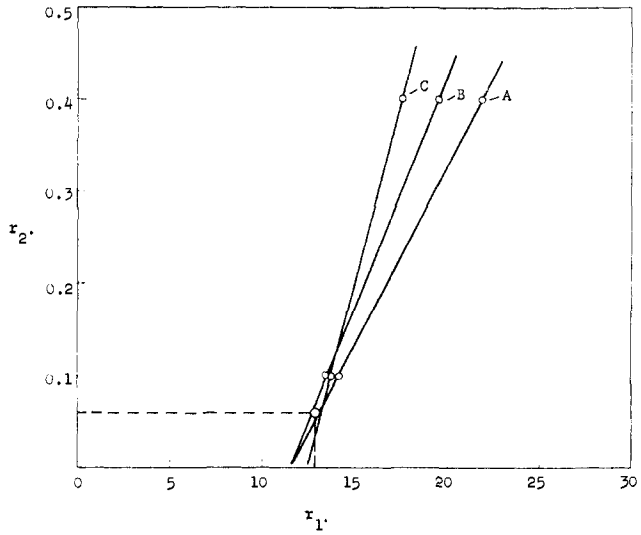

Fig. 4.—Copolymerization of styrene (M_1) and chloroprene (M_2) in *n*-hexane using BF_3 etherate as initiator: A, 71.0 mole % M_2; B, 60.5 mole % M_2; C, 51.2 mole % M_2.

A second monomer pair, styrene (M_1) and chloroprene (M_2), was copolymerized using boron trifluoride etherate as the initiator. Foster[11] has copolymerized this monomer pair using cyclohexane as solvent and boron trifluoride etherate as the initiator and obtained reactivity ratios of $r_1 = 15.6$ and $r_2 = 0.24$ compared to free radical initiated reactivity ratios of $r_1 = 0.005$ and $r_2 = 6.3$ for the same pair. Experimental results for this monomer pair are given in Table II. The method of intersection was employed to calculate the reactivity ratios as illustrated in Fig. 2, 3, 4 and 5. The reactivity ratios thus obtained are given in Table III with the solvent dielectric constants.

Although the general trend observed in Table I indicates an increase in the r_1 values and a decrease in the r_2 values, as the solvent dielectric constant increases, some anomalies do appear; *i.e.*, the $SnCl_4$ initiated case where the r_1 values decrease as the solvent dielectric constant increases. This may be attributed to the inability of the macroscopic parameter, the dielectric constant, to adequately describe the actual microscopic environment of the growing ion pair. Thus structural effects in solvents undoubtedly contribute to the ease of solvation and thus are difficult to define accurately. A solvent such as nitrobenzene or nitromethane being highly polar complexes with the

(11) F. Foster, *J. Polymer Sci.*, **5**, 369 (1950).

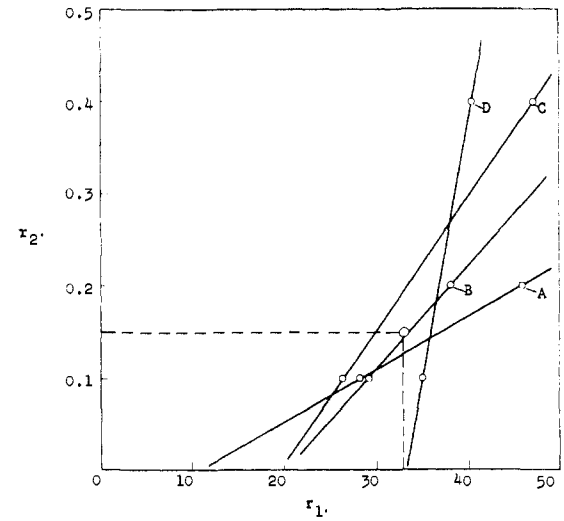

Fig. 5.—Copolymerization of styrene (M_1) and chloroprene (M_2) in nitroethane using BF_3 etherate as initiator: A, 90.0 mole % M_2; B, 80.6 mole % M_2; C, 59.2 mole % M_2; D, 34.6 mole % M_2.

ion pair; *i.e.*, the ion pair is solvated by the solvent and the two monomers have to diffuse through this cage of solvent to yield the copolymer. In the case of the hydrocarbon solvent such as *n*-hexane which has a lower solvating power, the solvent does not complex with the ion pair and one of the monomers which has a higher solvating power complexes with the growing ion pair. Thus instead of an envelope of solvent we have an effective envelope of one of the monomers around the ion pair. It is reasonable to suggest that *p*-chlorostyrene can solvate the ion pair more easily than isobutylene. The result of such a preferential solvation of the ion pair would be that more *p*-chlorostyrene gets incorporated in the copolymer as the concentration of this monomer in the immediate vicinity of the growing ion pair is higher.

In the case of the $SnCl_4$-initiated copolymer in nitrobenzene, the decrease in r_1 may be due to the formation of a stable solvent cage around the growing ion pair which decreases the rate of diffusion of isobutylene to the active site. Note that the r_2 values show a comparatively larger decrease as the solvent dielectric constant increases, which is consistent with the proposed solvent effect.

In the case of chloroprene and styrene copolymerization, chloroprene has a higher solvating power than styrene and hence becomes incorporated into the copolymer more in hydrocarbon solvents. The increase in r_1 values as the solvent polarity increases, as shown in Table III, is consistent with this assumption. The r_2 values also appear to increase, but this change is within the magnitude of the experimental error. Therefore, the trend was not considered significant in view of the strong evidence to the contrary exhibited by the results in Table I.

Marvel's results with 2-chloroethyl vinyl ether–α-methylstyrene also indicate a similar trend. The chlorovinyl ether which is more polar is incorporated into the copolymer to a greater extent in a hydrocarbon solvent (benzene) than in nitrobenzene as a solvent. Similar results have been obtained by Higashimura[12] with styrene and isobutylene using *n*-hexane and nitroethane. Additional evidence for this suggestion is found in the results with a mixture of nitrobenzene and benzene as solvent. The more polar nitrobenzene can solvate the ion pair and the result should be the same as

(12) T. Higashimura, *Chemistry* (Japan), *Special Issue No. 7, Synthesis of High Polymers*, **33** (1961).

TABLE II

COPOLYMERIZATION OF STYRENE (M_1) AND CHLOROPRENE (M_2) IN DIFFERENT SOLVENTS

M_2 in monomer mixt. (mole %)	Reaction time, min.	Conversion, %	Chlorine,[a] %	m_2[b] in copolymer
In nitrobenzene using $AlBr_3$ as initiator (system I)				
0.6371 (80)	72	1.5	7.04	0.202
.6353 (80.2)	165	2.5	6.86	.199
.5660 (70)	120	4.0	4.37	.127
.4855 (60.5)	22	8.0	3.25	.094
In benzene using $AlBr_3$ as initiator (system II)				
0.7236 (83.5)	150	1.1	13.08	0.3887
.6395 (80.2)	240	2.7	10.32	.2907
.5578 (70.0)	105	2.7	8.14	.2292
.3874 (49.2)	90	10.0	4.07	.1146
In *n*-hexane using BF_3 etherate as initiator (system III)				
0.2864 (71.0)	240	2.5	5.27	0.1485
.2401 (60.5)	130	3.0	3.59	.1011
.1994 (51.2)	110	3.0	2.38	.0670
In nitroethane using BF_3 etherate as initiator (system IV)				
0.716 (90.0)	137	2.0	11.39	0.320
.654 (80.6)	25	4.0	4.14	.117
.481 (59.2)	17	4.0	1.57	.0440
.293 (34.6)	17	5.0	0.53	.0149

[a] Analysis by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. [b] Mole fraction of chloroprene in copolymer.

TABLE III

COPOLYMERIZATION OF STYRENE (M_1) AND CHLOROPRENE (M_2) IN DIFFERENT SOLVENTS

Solvent	Dielectric constant of solvent	Initiator	r_1	r_2
Nitrobenzene	36	$AlBr_3$	16.0 ± 0.05	0.065 ± 0.01
Benzene	2.2	$AlBr_3$	6.9 ± 0.5	.04 ± .01
n-Hexane	1.8	BF_3 etherate	12.8 ± .3	.06 ± .01
Nitroethane	30	BF_3 etherate	33.0 ± .5	.15 ± .05

TABLE IV

FRACTIONATION OF A COPOLYMER OF *p*-CHLOROSTYRENE AND ISOBUTYLENE POLYMERIZED IN NITROBENZENE SOLVENT; 2.8 G. OF POLYMER IN BUTANONE

Fraction	Weight in g. of fraction	In benzene $[\eta]$, dl./g.	Analysis, % Cl
A	0.3283	0.0658	19.33
B	.3788	.049	18.0
C	.4720	.0405	17.98
D	.4280	.040	19.2
E	.3020	.0380	17.14
F	.240	.0370	17.85
G	.4200	—	17.41
Original	—	.040	18.90

if the copolymerizations were carried out in pure nitrobenzene as solvent. This assumption has been observed to be correct as evidenced by the r_1 and r_2 values obtained in solvent mixtures of nitrobenzene and benzene in the copolymerization of *p*-chlorostyrene and isobutylene. The r_1 and r_2 values were almost identical with the values obtained for this monomer pair in pure nitrobenzene solvent. This also explains why previous results using mixed solvents showed no variations in the value of r_1 and r_2 for the styrene–*p*-chlorostyrene pair.

Experimental[13]

p-Chlorostyrene was prepared from *p*-chlorophenylmethylcarbinol according to a known procedure[5]; 141 g. (1.0 mole) of *p*-chlorobenzaldehyde gave 128 g. (82%) of *p*-chlorophenyl methyl carbinol, b.p. 89–90° (2 mm.), $n^{25}D$ 1.5423 (b.p. 89–91° (2 mm.), $n^{20}D$ 1.5504).[14,15] The alcohol was either directly dehydrated over activated alumina at 300°[16] to give *p*-chlorostyrene in 55% yield or it was acetylated to give a 40% yield of the acetate, b.p. 70–75° (1 mm.), $n^{25}D$ 1.5120 (b.p. 75–80° (18 mm.), $n^{9}D$ 1.5118).[17] The acetate was pyrolyzed at 500° according to the previously described procedure[18] and *p*-chlorostyrene was isolated from the product in 90% yield, b.p. 38–39° (2 mm.), $n^{25}D$ 1.5630 (b.p. 38–39° (2 mm.), $n^{20}D$ 1.5648).[19]

Isobutylene was used directly after drying. Chloroprene was washed with water, dried, and distilled through a packed column before use; b.p. 56–57° (755 mm.), $n^{25}D$ 1.4580 (b.p. 59.4° (760 mm.), $n^{20}D$ 1.4583).[20] Stannic chloride and aluminum bromide were distilled and filled in ampoules by a procedure reported previously.[21] *n*-Hexane was purified by washing with sulfuric acid, water, sodium carbonate solution, drying and fractional distillation; b.p. 67°, $n^{25}D$ 1.3752 ($n^{25}D$ 1.3751).[22] Nitrobenzene was similarly purified; b.p. 70° (3 mm.), $n^{25}D$ 1.5498, (b.p. 210° (atm.), $n^{25}D$ 1.5500).[23] Nitromethane was purified by a series of distillations as suggested by Thompson[24]; b.p. 101° (atm.), $n^{25}D$ 1.3805 ($n^{25}D$ 1.37963). Nitroethane was purified by a similar procedure; b.p. 114° (atm.), $n^{25}D$ 1.3899 (b.p. 115, $n^{25}D$ 1.3900).[25]

Copolymerizations were carried out in bottles with screw caps as described by Overberger, *et al.*[21] Conversions were kept below 10% in all cases, and the copolymer was analyzed for its chlorine content for determining the copolymer composition. The total monomer concentration in all cases was kept at 2 moles per liter and the initiator concentration was adjusted to give about 5 to 10% conversion in a reasonable time. The time needed was determined by initial preliminary experiments in each solvent and catalyst system. The results for the copolymerization of styrene and chloroprene are shown in Table II.

Fractionation was carried out on a copolymer of *p*-chlorostyrene and isobutylene prepared in nitrobenzene solvent using stannic chloride as initiator. The copolymer was dissolved in butanone solvent (0.5% solution) and fractions were separated by addition of methanol as the non-solvent. The fractionation was carried out at a constant temperature of 25°, the methanol being added till sufficient turbidity was obtained. The flask was then heated slowly till the turbidity just disappeared and then allowed to cool slowly to again give the turbid fraction. The separated fraction was redissolved and reprecipitated once more from butanone into methanol. Several fractions were thus collected. The last fraction was obtained by evaporation of the remaining solution. The intrinsic viscosities of the fractions were determined in benzene solution using a Ubbelohde viscometer with a built-in filter.

Acknowledgment.—We wish to thank the Shell Chemical Company and the Wright Air Development Division of the United States Air Force for their generous support of this work.

(13) Analysis by Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.

(14) S. N. Ushakov and P. A. Natuzov, *J. Gen. Chem. USSR*, **14**, 120 (1944).[15]

(15) See *Chem. Abstr.*, **39**, 916 (1945).

(16) W. S. Emerson and V. E. Lucas, *J. Am. Chem. Soc.*, **70**, 1180 (1948).

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(25) J. Timmermans, "Physicochemical Constants of Pure Organic Compounds," Elsevier Publishing Co., New York, N. Y., 1950.