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Chain Transfer in the Polymerization of Styrene. VII. Compounds Containing Halogens, Oxygen and Nitrogen

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Styrene has been polymerized at 60° in the absence of initiator and in the presence of more than fifty organic compounds containing halogen, oxygen or nitrogen. Some compounds were also tested at 100°. In most cases, the added compound had little or no effect on the over-all second-order rate constant of polymerization, and transfer constants were calculated and compared. The abilities of these compounds to reduce the molecular weight of the polystyrene formed are discussed in terms of chain transfer, resonance stabilization of the radical formed by transfer from the added compound, and of polar and steric factors. Several other compounds strongly retarded polymerization; some gave anomalous results in rate and degree of polymerization, and a few gave only inconsistent and irreproducible results.

Previous papers in this series have shown that many solvents reduce the molecular weight of polymerizing styrene without any significant effect on the over-all second-order rate constant of polymerization. The relation between the molecular weight and solvent:monomer ratio in the absence of added initiator is described by the equation[2]

$$1/\bar{P} = C[\mathrm{SX}]/[\mathrm{M}] + 1/\bar{P}_0$$

where $\bar{P}_0$ and $\bar{P}$ are the degrees of polymerization in the absence and presence of solvent, [SX]/[M] is the solvent:monomer ratio and C is the transfer constant of the solvent at the chosen temperature. Since C is the ratio of the rate constants for chain transfer with the solvent and for chain propagation, and since the latter is essentially independent of solvent,[3,4] the transfer constant is a convenient measure of the ability of a radical to capture an atom from a solvent.[5] The present paper presents transfer constants for a variety of organic compounds containing halogen, oxygen or nitrogen.

Experimental.—The purification of styrene, preparation of reaction mixtures and determination of molecular weights from intrinsic viscosities followed procedures described elsewhere.[4a,6] The other reactants (solvents) were purified by fractional distillation or crystallization, but in some cases, in spite of unusual precautions, reproducible polymerization rates and molecular weights could not be obtained. The number of experiments carried out with each reactant was usually limited and some of the results are therefore not as accurate as others we have published.[4] Rather than present the data in full, we have indicated in Table I the number of experiments for each compound, what we consider the most probable value of the transfer constant, and the range of values obtained. In general, the concentration of added compound was adjusted to give polymers of molecular weight above 20,000 and over-all second-order rate constants were within 30% of those obtained in pure styrene.[4a,b]

Discussion.—Studies of copolymerization have established that two factors govern the reactivity of unsaturated compounds toward free radicals,[7] the resonance stabilization of the new free radical to be formed, and the difference between the electron accepting and donating abilities of the reactants. Previous studies have demonstrated the importance in chain transfer of both the resonance stabilization of the radical to be formed from the transfer agent[4b] and of the polar factor.[7,8] However, the effects cannot be resolved until more transfer constants are available for acceptor monomers,[9,10] and the results in Table I will be discussed accordingly.

The measured transfer constants are proportional to the sum of the rates of all the possible transfer reactions of the reactants, but differences between compounds suggest that most of the reactivity is centered in a univalent atom on the most substituted carbon atom of the solvent. Removal of this atom thus forms the most substituted and most stable radical. Aromatic rings or double bonds should particularly facilitate removal of an atom from an adjacent carbon atom, resulting in formation of benzyl or allyl radicals, while other substituents can influence transfer activity by polar factors or by radical stabilization through hyperconjugation.

For most of the solvents, present data do not allow a decision as to which atom is attacked. Toward styryl radicals, cyclohexane has a low reactivity attributable to CH_2 which is dialkyl substituted. The n-alkyl chlorides and bromides, n-butanol and dioxane have only disubstituted CH_2

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[2] F. R. Mayo, THIS JOURNAL, **65**, 2324 (1943).

[3] At least the over-all rate constant of thermal polymerization, which also involves chain initiation and termination, is generally independent of solvent and polymer chain length.

[4] (a) R. A. Gregg and F. R. Mayo, THIS JOURNAL, **70**, 2373 (1948); (b) R. A. Gregg and F. R. Mayo, *Discs. Faraday Soc.*, **2**, 328 (1947); (c) F. R. Mayo, THIS JOURNAL, **70**, 3689 (1948); R. A. Gregg, D. M. Alderman and F. R. Mayo, *ibid.*, **70**, 3740 (1948).

[5] A polymer radical may instead donate an atom to an unsaturated molecule; *cf.* K. E. Wilzbach, F. R. Mayo and R. Van Meter, *ibid.*, **70**, 4069 (1948). Further, a forthcoming paper will show that some aromatic solvents without side-chains reduce the molecular weight of the polymer without being incorporated in the polymer.

[6] As in ref. (4b), the relation $\bar{M}_n = 184{,}000\ [n]^{1.277}$ was used to calculate molecular weights, and the results reported here would not be significantly affected by using the more precise relationships given by F. R. Mayo, R. A. Gregg and M. S. Matheson, THIS JOURNAL, **73**, 1691 (1951).

[7] F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950); pp. 264-270 discuss chain transfer and related reactions.

[8] C. Walling, THIS JOURNAL, **70**, 2561 (1948).

[9] (a) S. Basu, J. N. Sen and S. R. Palit, *Proc. Royal Soc. (London)*, **A202**, 485 (1950); (b) *ibid.*, **A214**, 247 (1952); (c) S. L. Kapur, *J. Sci. Ind. Research (India)*, **10B**, 186 (1951). Although the results on methyl methacrylate in (a) are qualitatively reasonable, the recorded rate of thermal polymerization at 80° is 34 times that found by C. Walling and E. R. Briggs, THIS JOURNAL, **68**, 1141 (1946), at 100°. The trace catalyst probably responsible for this high rate is probably associated with irregularities in the value of $1/\bar{P}_0$. Although study of the catalyzed reaction (b,c) may be more promising, the large disagreements between (a) and (c) in the transfer constant of benzene make the present results difficult to interpret.

[10] Styrene is an electron donor in free radical reactions and the only other monomers known to have received thorough study are also donor monomers: ethylene, unpublished work in this Laboratory by J. R. Little, C. H. Stiteler, L. W. Hartzel, F. O. Guenther and F. R. Mayo; vinyl acetate by W. H. Stockmayer, J. T. Clarke and R. O. Howard, Abstracts of Papers presented at Buffalo Meeting of the American Chemical Society, March 25, 1952, p. 2-O.

TABLE I

TRANSFER CONSTANTS OF COMPOUNDS IN THE POLYMERIZATION OF STYRENE AT 60 AND 100°

Compound	No. of expt.	Expt. at 60° Range of $C \times 10^5$	Most probable $C \times 10^5$	No. of expts.	Expt. at 100° Range of $C \times 10^5$	Most probable $C \times 10^5$
n-Butyl chloride	2	0.36–1.7	0.4	3	2.5–3.8	3.7
i-Butyl chloride	2	13–17	14	4	8–43	30
s-Butyl chloride[b]	3	10–14[b]	12[b]	5	2.4–6.2	3
t-Butyl chloride			Erratic results, see text			
n-Butyl bromide	4	0.5–6.0	0.6	8	2.3–3.9	3.5
n-Butyl iodide	4	16–21.7	18.5	8	54–200	55
n-Amyl chloride	1	....	4.9	...	....	...
Methallyl chloride[c]	3	200–700	240	...	....	...
Methylene chloride[a]	3	0.6–3.0	1.5	1	....	118
Chloroform	5	3.6–7.8	5	...	....	...
Carbon tetrachloride[4a]	...	....	920	...	....	1850
Carbon tetrabromide	4	121,000–144,000	136,000	5	180,000–270,000	235,000
Benzyl chloride	1	....	15.6			
Benzal chloride	2	350–600	500			
Benzotrichloride	3	520–630	575			
Triphenylmethyl chloride			Erratic results, see text			
Ethanol		....	See text			
Butanol	1	....	0.6			
Allyl alcohol	3	14–24	15			
Propargyl alcohol	2	70–130	70			
Hydroquinone	1	....	36			
1,4-Dioxane	3	0	0			
Butyraldehyde	4	52–60	57	3	103–110	110
Acetone	2	0–3	<5			
Benzoin	2	200–570	400			
Dibenzoylmethane	1	....	70			
Acetic acid	...	....	See text			
Propionic acid	3	0.2–0.8	0.5			
Phenylacetic acid	2	59–60	60			
Acetic anhydride	2	6.9–7.2	7			
Diethyl malonate	1	....	4.7			
Methyl chloroacetate	4	2.8–3.4	3	3	5.2–8.0	7.5
Ethyl dichloroacetate[d]	3	12.9–13.9	13	6	0.40–400	?
Ethyl trichloroacetate	5	644–661	650	3	1350–2300	1450
Trichloroacetic acid	3	520–770	660	...	....	...
Diethyl dichloromalonate	3	200–400	300	2	600–640	620
Diethyl bromomalonate	4	5,600–8,000	7000	2	9,000–16,000	12,000
Diethyl dibromomalonate	2	110,000–130,000	120,000	...	....	...
Di-*n*-lauryl disulfide	2	0–23	23			
Dibenzyl disulfide	3	800–1200	1000			
Dibenzyl diselenide	2	120,000–320,000	200,000			
Acetoxime	1	....	22			
Acetonitrile	1	....	4.4			
n-Butylamine	2	4–5	5			
Piperidine	2	9.8–10.1	10			
Aniline	1	....	20			
Pyridine	1	....	6			

[a] J. A. Gannon, E. M. Fettes and A. V. Tobolsky, THIS JOURNAL, **74**, 1854 (1952), give 95×10^{-5} for methylene chloride at 80°. They also give data on several other halides not listed here. [b] At 60°, *s*-butyl chloride exhibited the non-solvent effect and polystyrene of $[\eta] = 4.2$ was obtained at [solvent]/[monomer] of 9.0. [c] $1/\overline{P}$ plotted against [methallyl chloride]/[styrene] extrapolated to a $1/\overline{P}_0$ of 35×10^{-4} instead of to 10^{-4}. [d] [Ethyl dichloroacetate]/[styrene] of less than 0.1 at 60° resulted in higher viscosity. At 100° the transfer constant apparently decreased with increasing solvent concentration while the over-all rate constant held steady.

groups, and since their activities are low and in the same range as cyclohexane, they may be due mainly to CH_2, with a single ether, Br, Cl or OH substituent contributing little more to activity than an alkyl group. This general conclusion is supported by Kenyon's demonstration that methyl radicals react with *s*-butyl chloride to give methane and 2-chloro-2-butyl radicals.[11] The higher and comparable activities of iso- and *s*-butyl chlorides and of chloroform, together with the fact that the hydrogen atom in chloroform is attacked by aliphatic radicals,[12]

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(11) A. S. Kenyon, THIS JOURNAL, **74**, 3372 (1952).

(12) (a) M. S. Kharasch, E. V. Jensen and W. H. Urry, THIS JOURNAL, **69**, 1100 (1947); (b) J. Harmon, T. A. Ford, W. E. Hanford and R. M. Joyce, *ibid.*, **72**, 2213 (1950).

indicate that the behavior of these solvents is due to a C–H bond modified by three substituents. The high transfer activity of carbon tetrachloride compared to chloroform is probably largely a polar effect, best accounted for in terms of contributions to the transition states of ionic resonance structures in which the styryl radical acts as electron donor and the carbon tetrachloride acts as electron acceptor.[7] This conclusion is consistent with the small difference in reactivity of acceptor methyl methacrylate radicals with these two solvents. Basu, Sen and Palit report transfer constants of 14×10^{-5} for chloroform, 24×10^{-5} for carbon tetrachloride at 80°,[9a] and Kapur reports 17.7×10^{-5} and 24×10^{-5}, respectively, at 60°. The greater polarizability of bromine atoms and the lower carbon–halogen bond strength account for the much higher activity of carbon tetrabromide which has been indicated before both qualitatively[12a] and quantitatively.[13] The chloro- and bromomalonates show the same large differences in reactivity. Since differences observed between chloro- and bromobutane are small enough to be masked by reactivities of hydrogen atoms, steric effects may account in part for the easier elimination of bromine from highly substituted compounds.

Iodides have even greater polarizability than bromides and the bond strength to carbon is still lower. The large increase in activity of butyl iodide in the butyl halide series suggests that the iodine atom may be preferentially attacked. Other monosubstituted compounds which have higher transfer constants than the parent hydrocarbon and may be preferentially attacked in the functional group are the amines, the oxime and butyraldehyde. For butyraldehyde, functional group attack has been confirmed by isolation of *n*-propyl ethyl and *n*-propyl butyl ketones using ethylene as the monomer.[14] Thus, a much higher activity for butyraldehyde than for acetone is to be expected.

Among compounds having carbonyl type unsaturated groups, those such as acetone, acetic anhydride and acetonitrile show low activities approximately comparable to that of methylene chloride. Comparison of the activities of methylene chloride, methyl chloroacetate, and diethyl malonate at 60° indicates that a carbalkoxy group activates a C–H bond scarcely more than does a chlorine atom. The tenfold greater activities of dibenzoylmethane and of phenylacetic acid over any of these last three compounds show the greater activating effects of phenyl and benzoyl as compared to carbalkoxy or chlorine. The greater activating effect of phenyl is again evident in comparing the three compounds in each of the chlorinated methyl chloride, acetic ester and toluene series. However, the high transfer constant of dibenzoylmethane, three times that of diphenylmethane,[4b] and fourteen times that of malonic ester, suggests that further investigation of carbonyl compounds would be of interest.

The activating effect of substituents on an atom in a conjugate position for chain transfer with the substituted benzyl radical in polymerizing styrene is: phenyl, benzoyl > carbalkoxyl, carboxyl, carbonyl > halogen > hydroxyl, alkyl > hydrogen. This series presumably corresponds to the abilities of the substituents to stabilize the radical which will be formed from the solvent, and is in good agreement with series based on copolymerization and on the direction of addition of hydrogen bromide to ethylene derivatives.[15]

Hydroquinone and aniline are of similar reactivity, and it may be noted that hydroquinone has no effect on the over-all second-order rate constant in the absence of air. Its oxidation product, quinone, is a well-known and strong inhibitor.

The high activity of dibenzyl disulfide as compared with dilauryl disulfide may be due to the benzyl hydrogen atoms. Even though the transfer activity of the dilauryl disulfide can be spread over many more hydrogen atoms than in the butyl halides, much of the activity must be closely associated with the disulfide group.[16] Reaction of disulfides with free radicals may be like the reactions of diacyl peroxides, one of the very few cases where free radicals attack the skeleton of a molecule (instead of an attached univalent atom). The very high reactivity of dibenzyl diselenide is interesting.

The transfer constants in this paper are not known accurately enough to calculate differences in activation energy between transfer and propagation. Except for a high temperature coefficient with the least reactive compounds, butyl chloride and bromide, and values which indicate considerable experimental error with *s*-butyl chloride and methylene chloride, all the transfer constants are about twice as large at 100° as at 60°, in spite of large differences in reactivity. This correlation suggests that among these compounds, as well as among hydrocarbons,[4b] differences in entropy of activation are as important as differences in energy of activation.

Compounds Behaving Abnormally.—Consistent results were not obtained with *t*-butyl chloride in the absence of initiator or at 60° in the presence of added benzoyl peroxide. At low solvent concentrations, an accelerated rate and an abnormally high viscosity polymer were often obtained, while at high solvent concentrations, almost complete inhibition might result, all without apparent trend. Similar results were obtained with triphenylmethyl chloride.

The following compounds strongly retarded or prevented the thermal polymerization of styrene and their transfer constants were not ascertained: nitrobenzene, nitropropane, acetyl chloride, 1,2-dichlorodiethyl ether, 1,3-dichloropropanone, 1,3-dichloro-2-propanol, dimethylformamide and phenylacetylene.[17] Many of the aliphatic bromides and iodides were inhibitors when impure. Dibenzyl diselenide developed inhibiting properties on standing, possibly due to free selenium.

Glacial acetic acid and ethanol are both non-solv-

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(13) C. H. Bamford and M. J. S. Dewar, *Discs. Faraday Soc.*, **2**, 314 (1947). From their data, C at 60° = 2.7. Data are also given for some other halides. J. W. Breitenbach and H. Karlinger, *Monatsh.*, **82**, 245 (1951), give C = 2–5 at 70°.

(14) C. H. Stiteler and J. R. Little, U. S. Patent 2,517,732; *C. A.*, **44**, 10730 (1950).

(15) Ref. 7, pp. 251, 266.

(16) This point has been proved recently by W. H. Stockmayer, R. O. Howard and J. T. Clarke, This Journal, **75**, 1756 (1953); A. V. Tobolsky and B. Baysal, *ibid.*, 1757.

(17) K. W. Doak, *ibid.*, **72**, 4681 (1950).

ents for polystyrene, and both gave results characteristic of non-solvents.[18] With acetic acid, the intrinsic viscosities of the polymers *increased* with the concentration of solvent. In polymerization at 60° at acetic acid : styrene ratios of 0, 0.5, 1.0 and 5.0, the polystyrenes obtained had intrinsic viscosities of 3.4, 4.2, 4.5 and 5.3. Analogous results were obtained at 100 and 132°. The polymers were not always reproducible and the rates were erratic with a tendency to be low. Separation of polystyrene from solution apparently permits some molecules to grow to unusual size. Carbon analyses of one purified polymer made at an acetic acid : styrene ratio of 1.01 showed only 91.8% carbon (theoretical, 92.28%) indicating incorporation of solvent in the polymers. Ethanol at low concentrations leads to a polymer of lower intrinsic viscosity, but above an ethanol–styrene ratio of about 5, further addition of ethanol gives polymers of *higher* intrinsic viscosity. Dichloroacetic acid combines a non-solvent effect with high transfer activity. As the acid–monomer ratio increases, the intrinsic viscosity of the polymer continues to decrease, but not as much as expected. Malonic, phenoxyacetic and benzoic acids also gave abnormal polymers, but experiments were too limited for further comment.

The behavior of paraformaldehyde was unique and unaccounted for. At concentrations of 0, 0.05 and 0.3% by weight, polystyrenes of intrinsic viscosities 3.4, 4.3 and 5.4 were obtained. The paraformaldehyde appeared to be insoluble in the monomer, and was recovered from the partially polymerized styrene. The high intrinsic viscosity of the polymer was unchanged by shaking a benzene solution with either water or mineral acid but was reduced from 6 to 2.8 by extracting a carbon tetrachloride solution of the polystyrene with water at approximately 40° for one week. Mixing or heating solutions of normal polystyrene with paraformaldehyde produced no increase in viscosity.

PASSAIC, N. J.

(18) J. Abere, G. Goldfinger, H. Naidus and H. Mark, *J. Phys. Chem.*, **49**, 211 (1945); R. N. Haward, *J. Polymer Sci.*, **3**, 10 (1948).

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY AND VIRUS LABORATORY, UNIVERSITY OF CALIFORNIA]

Analysis of a Concentration Anomaly in the Ultracentrifugation of Mixtures[1]

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Dilute solutions of two macromolecular components have been studied in the ultracentrifuge. The boundary area of the slow component of the mixture is found to increase as much as 300% over that of a comparable concentration of that same component alone. Further, the area due to the slow component, corrected for the geometry of the cell and the centrifugal field, decreased as much as 30% as the boundary moved through the cell. By comparison of the experimental results with a theoretical treatment based on the ideas of Johnston and Ogston, it is shown that the magnitude of these anomalies depends on the proximity of the sedimentation constants of the individual components. It is shown that a reasonable prediction of the magnitude of the anomaly can be made from knowledge of the physical properties of the fast component. The existence of convection during the ultracentrifugation of mixtures is discussed.

Introduction

In the course of a study in this Laboratory on the degradation of tobacco mosaic virus using the ultracentrifuge to follow the appearance and disappearance of decomposition products, it became clear that errors, not heretofore realized, can be made by analyzing the ultracentrifuge patterns in terms of concentrations in the conventional manner. It has been known for some time that, in contrast to the study of a single monodisperse protein, the determination of the concentrations of components of a mixture from ultracentrifugal patterns often yields erroneous values.[3-6] Specifically, the concentration of the slower component of a mixture, as obtained from analysis of the ultracentrifuge patterns, is too high, and the concentration of the faster component is too low. Since there has been some discussion[7-9] as to the explanation for this anomaly and because of the unprecedented magnitude of the effect observed in mixtures containing tobacco mosaic virus, detailed ultracentrifugal analyses were conducted with known mixtures. This communication presents the results of such studies and a theoretical interpretation of the results along the lines originally suggested by Johnston and Ogston.[6]

Materials and Methods

Several preparations of tobacco mosaic virus (TMV) and tomato bushy stunt virus (BSV) purified by a series of cycles of alternate high and low-speed centrifugation according to the method of Stanley[10] were used in this study. Bovine plasma albumin (ALB) and β-lactoglobulin (β-lact) obtained from Armour and Company were used in mixture studies with bovine plasma fibrinogen (FIB), also obtained from Armour and Company (fraction I). Some experiments were conducted with a degradation product (DP) of tobacco mosaic virus obtained by treating the virus with sodium dodecyl sulfate.[11] Electron micrographs showed the DP particles to be the same diameter as TMV with lengths about $^3/_4$ those of the virus particles. Ultracentrifuge patterns of this preparation showed a single sharp boundary.

Sedimentation analyses were performed in a Spinco Model E ultracentrifuge equipped with a Philpot–Svensson optical system.[12-14] Centrifuge runs were made at room temperature and sedimentation constants were corrected to a stand-

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(2) Presented in partial fulfillment for the Ph.D. degree in Biochemistry at the University of California, 1952.

(3) A. S. McFarlane, *Biochem. J.*, **29**, 407, 660 (1935).

(4) K. O. Pedersen, *Nature*, **138**, 363 (1936).

(5) K. O. Pedersen, *Compt. rend. Lab. Carlsberg*, **22**, 427 (1938).

(6) J. P. Johnston and A. G. Ogston, *Trans. Faraday Soc.*, **42**, 789 (1946).

(7) B. Enokeson, *Nature*, **161**, 934 (1948).

(8) K. O. Pedersen, *Ann. Rev. Biochem.*, **17**, 187 (1948).

(9) R. Cecil, J. P. Johnston and A. G. Ogston, *Nature*, **163**, 919 (1949).

(10) W. M. Stanley, THIS JOURNAL, **64**, 1804 (1942).

(11) H. K. Schachman, *ibid.*, **73**, 4808 (1951).

(12) J. Thovert, *Ann. Phys.*, **2**, 369 (1914).

(13) J. St. L. Philpot, *Nature*, **141**, 283 (1938).

(14) H. Svensson, *Kolloid Z.*, **87**, 181 (1939).