trans-butene-2 on acidic and basic catalysts could also be attributed to the lack of free rotation in the carbanion.

The unsaturation of the carbanion 2–3 bond could hinder rotation so that return of a proton on either the 1- or 3-carbon atom would result in the formation of butene-1 or reformation of the original reactant butene-2 isomer. The allylic carbanion is likely to retain the steric configuration of the reactant butene-2 isomer and the formation of the other butene-2 isomer would require its rearrangement. The freedom of rotation about the corresponding bond in the carbonium ion would allow the formation of either of the butene-2 isomers thus permitting the energetically more favorable *cis–trans* isomerization to proceed. Butene-1 formation from the carbonium ion will also be possible and will become more important as the temperature increases.

In the discussed mechanisms the intermediate carbonium and carbanions are formally treated as entirely free. Under such conditions it could be expected that all acid catalysts should exhibit the same stereoselectivity at the same conversion and temperature and this should hold also for the basic catalysts.[20] Although it has not been possible in the present work to standardize the experimental conditions and it is therefore difficult to make with certainty comparisons of this kind, there appear to be appreciable individual differences between various catalysts at roughly comparable conditions. Some of these may perhaps be due to duality of character of the catalysts, either as an inherent property of the catalytic material or due to gross inhomogeneities. Also, the intermediate ionic species must be influenced to some extent by the proximity of or direct complexing with the catalyst and the degree of charge transfer is likely to differ in different catalysts. Finally, purely geometric factors[9,15] could come into play to some extent although they are, in general, not likely to play a decisive role in view of the broad distinctions observed in the present work which appear to be primarily associated with the acidity and basicity of the catalytic materials.

The behavior of the metals Ni and Ag cannot be discussed with any certainty. Either the dissociative mechanism or the hydrogen switch mechanism of Turkevitch and Smith[4] would predict lack of selectivity in the butene-1 isomerization and essentially exclusive double bond shift with the two butene-2 isomers, as is observed in the case of silver. The associative mechanism, on the other hand, might be expected to permit easy *cis–trans* isomerization.

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(20) Pointed out by one of the referees of the present work.

[CONTRIBUTION FROM THE MONSANTO CHEMICAL CO., TEXAS CITY, TEX.]

The Reaction of Styryl Radicals with Organoaluminum Compounds

BY TERRY HUFF AND ELI PERRY

RECEIVED FEBRUARY 5, 1960

The chain transfer constants of organoaluminum compounds with the styryl radical have been measured. These transfer constants were found to be unusually large The mechanism appears to be one of radical exchange between the whole group attached to the aluminum atom and the attacking styryl radical.

Introduction

A large number of compounds have been found to be active as transfer agents with free radicals.[1] All of these compounds have a common mode of reaction, the transfer of a single atom to the attacking radical with the generation of a new free radical[2]

$$R_1X + R\cdot_2 \longrightarrow R_2X + R\cdot_1$$

where $R\cdot_1$ and $R\cdot_2$ are free radicals derived from the respective molecules and X is an atom such as H or a halide. Transfer by disulfides may be an exception to this rule.[3] The purpose of this paper is to report a transfer reaction involving a whole group instead of a single atom. The process may be viewed as a radical exchange. The transfer agents are organoaluminum compounds whose reactions with free radicals have not been reported previously. Styrene was used as the monomer.

Results

Chain Transfer Constants.—Representative data are shown in Fig. 1 on a Mayo-type plot[4] for triisobutylaluminum. An example of the primary data from which Fig. 1 was derived is shown in Table I.

TABLE I

PRIMARY DATA AT 110°

Molar ratio of triisobutylaluminum to styrene (× 10^4)

1.11		6.02		10.3	
Time,[a] hours	D.P.[b]	Time, hours	D.P.	Time, hours	D.P.
1.24	1010	0.65	89	0.92	57
2.10	1050	1.29	112	2.22	57
3.18	1035	1.91	152	2.50	76

[a] Time after immersing tube in constant temperature bath. [b] Degree of polymerization.

The chain transfer constant, as computed by least squares, is 28.5. This value remains unchanged over the temperature range of 85 to 110°, giving a value of 6–8 kcal. for the activation energy for the transfer reaction.[5] It is to be noted that the value of the degree of polymerization obtained with no transfer agent present, $(D.P.)_0$, has been ignored in these calculations. The justification for doing this is that the transfer agent is destroyed by reaction with impurities in the monomer when

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(1) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 148–161.

(2) Page 154 of ref. 1.

(3) A. V. Tobolsky and B. Baysal, THIS JOURNAL, **75**, 1757 (1953).

(4) F. R. Mayo, *ibid.*, 2324 (1943).

(5) R. H. Boundy and R. F. Boyer, "Styrene—Its Polymers, Copolymers and Derivatives," Reinhold Publ. Corp., New York, N. Y., 1952, p. 238.

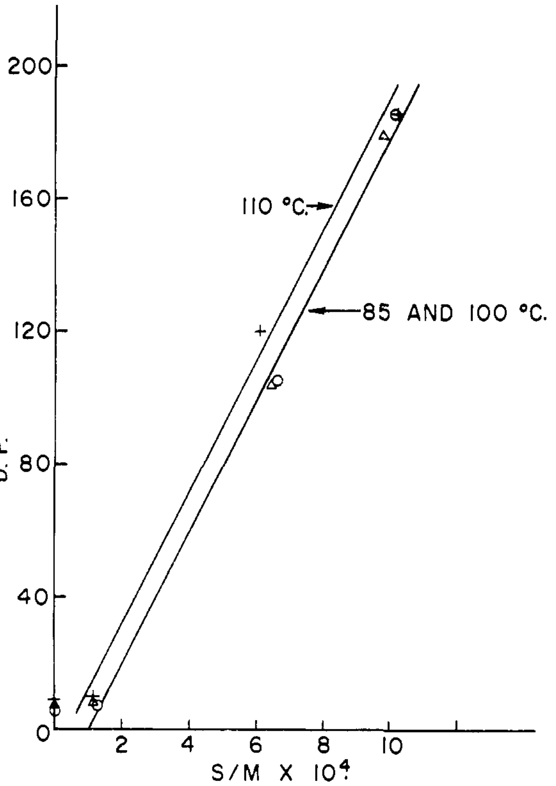

Fig. 1.—Mayo plot for triisobutylaluminum: reciprocal of degree of polymerization versus molar ratio of transfer agent to styrene: O 85°; △ 100°; + 110°.

these impurities contain oxygen or an active hydrogen.[6] All of the points on Fig. 1 should be displaced to the left far enough to permit the lines with their present slopes to pass through the $(D.P.)_0$ values. If the points at $(D.P.)_0$ were included in the least squares calculation, the transfer constant would be reported as 18.6.

The transfer constants for some typical aluminum compounds are summarized in Table II.

TABLE II

CHAIN TRANSFER CONSTANTS

Transfer agent	Molar ratio of transfer agent to styrene ($\times 10^3$)	Polymerization rate (% per hr.)	Chain transfer constant at 100°
"Isoöctane"	1.0- 3.0	2.2	$<10^{-3}$
Triisobutylaluminum	1.0-10.0	2.8	28.5
Diisobutylaluminum hydride	1.0-10.0	1.8	28
Triisobutoxyaluminum	1.0- 3.0	2.5	$<10^{-4}$
Triethylaluminum	0.9- 3.5	2.1	17
Triethoxyaluminum	2.3- 9.3	2.7	$<10^{-5}$
None	......	2.8	....

Mechanism.—The molecular weight obtained by cryoscopy shows good agreement with the molecular weight calculated from the C/H ratio assuming that there is one butyl group per molecule for low molecular weight materials; mol. wt. (from cryoscopy) = 725, mol. wt. (based on the C/H ratio and assuming one butyl group per molecule) = 940. These low molecular weight products, made using large quantities of triisobutylaluminum, have isobutyl rather than *t*-butyl end groups (Table III).

TABLE III

END GROUP DATA ON LOW MOLECULAR WEIGHT POLYMERS

No. of styrene units per isobutyl unit[a]	Calcd. CH_3/CH_2 ratio *t*-Butyl end group	Calcd. CH_3/CH_2 ratio Isobutyl end group	Observed[b] CH_3/CH_2
2.5	0.47	0.31	0.36
4.2[c]	.36	.24	.24
5.2	.33	.24	.26
7.5	.27	.18	.19

[a] From C/H analysis. [b] From infrared measurement. [c] Made using diisobutylaluminum hydride; D.P. from cryoscopy.

The presence of the isobutyl group and the absence of the *t*-butyl group was confirmed by proton n.m.r. studies.

The infrared spectrum of D.P. above 20 is identical with that of polystyrene over the 2 to 23 μ range. None of the polymers of any molecular weight showed significant amounts of carbonyls, ethers or hydroxyl groups in the infrared. Less than 10% of the chains contained a double bond as determined by bromine absorption. No aluminum metal is set free during the polymerization by visual inspection. The aluminum content of the purified polymer samples was less than one p.p.m.

Material of degree of polymerization 4.2 was produced as described under Experimental. The mass was quenched with butanol-O-*t* and freed of excess butanol-O-*t* by repeated washings. The tritium activity of polymer was 860,000 counts per minute per gram. After oxidation with a limited amount of CrO_3, the tritium activity of the polymer was 114,000 c.p.m./g. Therefore, 87% of the tritium was removed preferentially by the oxidation step. The polymer was not destroyed as indicated by the fact that over 70% recovery was obtained in spite of numerous handling and washing losses.

Finally, one-to-one adducts of styrene and triethylaluminum yielded small quantities of *n*-butylbenzene and gave no *sec*-butylbenzene. This identification was accomplished by infrared and mass spectrometer measurements.

Discussion

Organoaluminum compounds are true transfer agents. If the reduction in molecular weight of the polystyrene had been caused by an increased concentration of free radicals when the organoaluminum compounds were added, an increase in rate of polymerization of 8000% would have been required to reduce the D.P. from 1600 to 65 as was found for a molar ratio of transfer agent to monomer of 10^{-3}. If the reduction in molecular weight had been caused by abnormal termination of radicals (*i.e.*, inhibition), a sharp reduction in the rate of polymerization would have been observed. The data in Table II show that the measured rate is always close to the control value. Additional supporting evidence for a chain transfer reaction is the presence of one isobutyl group per polymer chain in low molecular weight compounds where termination by transfer predominates over termination by radical interaction. The size of the transfer constant, 28, is unexpectedly large.

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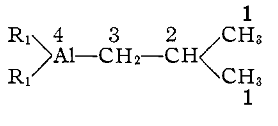
(6) H. Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 494.

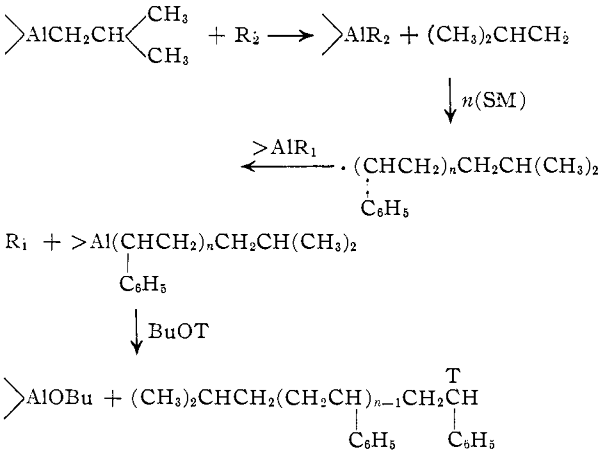
Organoaluminum compounds are among the strongest chain transfer agents known. For example, ethylbenzene has a value of 0.67×10^{-4}, carbon tetrachloride a value of 90×10^{-4} and *n*-butylmercaptan a value of 22 with styryl radicals.[7] The reason for the high reactivity of organoaluminum compounds with free radicals is not clear, but the reactivity may be related to the tendency for organoaluminum compounds to complete their octets as evidenced by dimerization.[8]

This chain transfer action involves the movement of a group rather than a single atom. It should be possible for the triisobutylaluminum molecule to transfer at a number of points

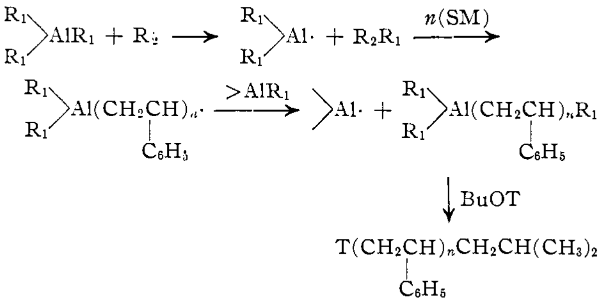


where R_1 is an isobutyl group.

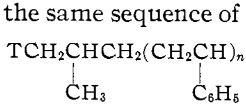
(a) Radical exchange at 3 and 4, not involving a free aluminum radical, is compatible with all of the evidence at hand and has been accepted as the mechanism of the reaction. The reaction scheme is shown below, where $R_2\cdot$ is a free radical and SM is styrene monomer.



(b) For radical exchange at 3 and 4 involving a free aluminum radical

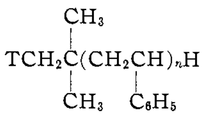


(c) If hydrogen transfer occurs at 1, one would obtain, using the same sequence of reactions



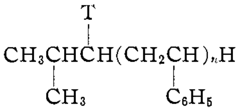
$$\mathrm{TCH_2\underset{CH_3}{CH}CH_2(CH_2\underset{C_6H_5}{CH})_nH}$$

(d) For hydrogen transfer at 2



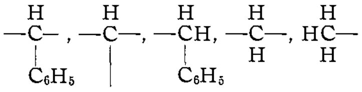
$$\mathrm{TCH_2\overset{CH_3}{\underset{CH_3}{C}}(CH_2\underset{C_6H_5}{CH})_nH}$$

(e) For hydrogen transfer at 3



$$\mathrm{CH_3\underset{CH_3}{CH}\overset{T}{C}H(CH_2\underset{C_6H_5}{CH})_nH}$$

Course b is rejected because the tritium would be difficult to oxidize. The order of decreasing ease of oxidation of a carbon–hydrogen bond is[9–11]



$$\underset{C_6H_5}{\overset{H}{-C-}},\ \underset{|}{\overset{H}{-C-}},\ \underset{C_6H_5}{\overset{H}{-CH}},\ \underset{H}{\overset{H}{-C-}},\ \underset{H}{\overset{H}{HC-}}$$

In addition, the free aluminum radical would not be expected to exist since aluminum lacks electrons even in stable organo compounds. These compounds exist as dimers. Course c would be possible based on the presence of the isobutyl group, but is rejected since the tritium would not be preferentially oxidized in the molecule. Course d is rejected because it requires a *t*-butyl end group and because the tritium would be difficult to oxidize. Course e is rejected because the tritium would be difficult to oxidize.

The infrared spectrum, in its similarity to polystyrene, confirms that the proposed molecular structure is possible. Also, there is negligible aluminum left in the polymer and none is set free during the reaction. The chain transfer constants obtained with the other compounds in Table II are compatible with the proposed mechanism of reaction. All of the organoaluminum compounds in Table II have transfer constants of the same order of magnitude. Such a result is to be expected if transfer of the whole group occurs. The formation of an Al–O–C bond drops the values of the transfer constant markedly. This behavior would be expected for chain transfer *via* radical exchange. The result using "isoöctane" confirms that the high transfer constant does not depend on the iso structure *per se*.

The one-to-one adducts obtained using triethylaluminum and styrene supply further evidence that the sequence of reactions in the chain transfer step does not involve a free aluminum radical. With radical exchange at the Al–C bond *via* a free aluminum radical, one would obtain *sec*-butylbenzene. With radical exchange not involving a free aluminum radical one would obtain *n*-butylbenzene, the product actually detected. It is interesting to note that this mode of chain transfer by radical exchange does not destroy the nature of the transfer agent. A new Al–C bond is formed every time one is broken.

It is not clear whether these results for the chain transfer action of organoaluminum compounds are in conflict with the recent publication of Natta,

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(7) Page 157 of ref. 1.

(8) G. E. Coates, "Organometallic Compounds," John Wiley and Sons. Inc., New York, N. Y., 1956, p. 75.

(9) Jan Rocek, *Chem. Listy*, **51**, 459 (1957).

(10) R. R. Arndt, J. B. Barbour, E. J. Engels, D. H. S. Horn and D. A. Sutton, *J. Chem. Soc.*, 3238 (1959).

(11) L. F. Fieser, *Disc. Faraday Soc.*, **2**, 242 (1947).

et al.,[12] concerning the reaction between styrene and triisobutylaluminum. Those workers, using metallic catalysts in their reaction, replaced the organic ligand with styrene. It seems strange that they did not notice the ability of organoaluminum compounds to act as chain transfer agents.

Experimental

Raw Materials.—The styrene was Monsanto LM-100 polymer grade. It was over 99.7% pure, the balance being predominantly ethylbenzene. Further purification was accomplished by fractionation under vacuum directly before using the monomer. The middle cut, 50% of the total charge to the pot, was used for polymerization studies. All manipulations of monomer were carried out under argon. The triisobutylaluminum was analyzed to be: 90.24% triisobutylaluminum, 5.76% diisobutylaluminum hydride and 4.00% isobutylene. Storage at 0° was necessary to prevent decomposition. The diisobutylaluminum hydride was analyzed to be: 81.0% diisobutylaluminum hydride, 19.0% triisobutylaluminum and less than 0.1% triisobutoxyaluminum.

The triethylaluminum was over 95% pure, the balance being diethylaluminum hydride. The $Al(OC_2H_5)_3$ and $Al(OC_4H_9)_3$ compounds were prepared from the corresponding organoaluminum compounds by allowing them to react with the stoichiometric amount of O_2 contained in dry air. The "isoöctane" was Phillips Petroleum commercial grade. The *n*-dodecylmercaptan had the physical constants $n^{20}D$ 1.4588, sp. gr.$_{20}^{20}$ 0.845, b.p. 146–148° (15 mm.). Argon specifications were: $<0.002\%$ O_2, $<0.002\%$ H_2, $<^1/_2\%$ N_2 and $<0.0008\%$ H_2O. The argon was dried further over Linde No. 5A molecular sieves. The methanol passed Federal Specification O-M-232 July 31, 1950.

Polymerization and Polymer Recovery.—Polymerization was carried out in sealed tubes in a constant temperature bath. The tubes were baked at 130° for over 16 hours and allowed to cool under argon. The purified monomer was charged and then the transfer agent. The monomer was frozen in Dry Ice, the tubes evacuated, sealed, warmed to room temperature, mixed thoroughly, and placed in a constant temperature bath at the desired temperature (bath temperature fluctuation of ±0.25°). Temperatures of 85, 100 and 110° were investigated. A control polymerization using pure monomer was always carried along with the samples to be tested. At a specified time the tubes were cooled quickly to room temperature and the contents were mixed with dilute nitric acid to remove the inorganic materials. The aqueous layer was saturated with NaCl to insolubilize organics. The combined organic layers were poured slowly into 5 volumes of methanol to precipitate the polymer. The precipitate was washed with methanol and dried at 50° and 1 mm. The filtrate was inhibited with *t*-butylcatechol and the solvent was removed under vacuum to isolate any low molecular weight polymeric species. These species were combined with the bulk of the recovered polymer. Usually, the amount of low molecular weight material was negligible. The polymerizations were carried to at least three different conversions for each transfer agent at a particular concentration. The transfer constant was obtained by extrapolating to zero per cent. conversion to obtain the D.P. which was used to make the Mayo plot.

Degree of Polymerization.—The D.P. was measured viscometrically at 36.65 ± 0.05° at a concentration of 0.1 g./100 cc. in toluene using Ostwald–Fenske pipets. The efflux time of the solvent was over 230 sec.

The n_{sp} was converted to $[n]$ using[13]

$$[n] = \frac{\sqrt{1 + 1.5n_{sp}} - 1}{0.75C_v}$$

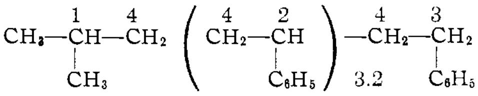
$[n]$ was related to D.P. using[14]

$$[n] = 5.90 \times 10^{-3}\,(\text{D.P.})^{0.78} \qquad (2)$$

Although eq. 1 and 2 were recommended for molecular weights of 10,000 to 600,000, they were found to give satisfactory results down to molecular weights of 800. For example, the D.P. of a low molecular weight material was estimated by three methods: 7.4 (freezing point depression), 8–9 (by eq. 1 and 2), and 9.4 (from the C/H ratio). When Mayo plots of 1/D.P.-S/M are used, the transfer constant determined therefrom is not overly sensitive to the particular $[n]$–D.P. relationship which is used. Equation 2 yields a transfer constant of 28 for triisobutylaluminum. If the relationship $[n] = 4.6 \times 10^{-3}\,(\text{D.P.})^{0.72}$ had been used, the transfer constant would have been reported to be 18.

Reliability.—The over-all technique for measuring transfer constants was verified by determining the constant for *n*-dodecyl mercaptan whose value is given in the literature[15] as 15 at 60°. This transfer constant was found to be 13 at 100°. In addition, the activation energy of 20 kcal. per g.-mole for the polymerization rate for the controls which were carried through at 85, 100 and 110° agreed well with literature values.[16]

CrO_3 Oxidation.—Polystyrene-O-*t* (0.321 g.) of mol. wt. 494 made from styrene and diisobutylaluminum hydride was dispersed in 18 cc. of glacial acetic acid; 0.3 cc. of concentrated H_2SO_4 was added. A total of 57.5 cc. of CrO_3 in glacial acetic acid (0.0085 g. CrO_3/cc.) was added slowly, keeping the reaction mass at 25°. The CrO_3 addition took 2 hours, the green color of the reduced chromium appearing before further increments were added. In this way, the concentration of oxidizing agent was always kept low. The reacted mass was dropped slowly into 3 g. of $FeSO_4 \cdot 7H_2O$ in 100 ml. of H_2O; 200 cc. of ether was added and the phases separated. The aqueous phase was extracted 2 times with 30 cc. of fresh ether before being discarded. The ether phases were combined and were extracted with 50% KOH until the aqueous and organic phases were colorless, then with distilled water until neutral. The ether was evaporated on a sand-bath and the residue dried at 0.5 mm. at 25° for 48 hours. Infrared measurements for the CH_3/CH_2 ratio confirmed the presence of one isobutyl group per molecule for the unoxidized polymer: measured value = 0.24, calcd. value for one isobutyl group = 0.24, calcd. value for one *t*-butyl group = 0.36, and calcd. value without any butyl group = 0.17. The indicated molecular structure was



$$CH_3\text{—}\underset{CH_3}{\overset{1}{CH}}\text{—}\overset{4}{CH_2}\left(\overset{4}{CH_2}\text{—}\underset{C_6H_5}{\overset{2}{CH}}\right)_{3.2}\text{—}\overset{4}{CH_2}\text{—}\underset{C_6H_5}{\overset{3}{CH_2}}$$

For the 0.321-g. sample

g. CrO_3 required to oxidize the hydrogens on 1 to 3 = 0.270
g. CrO_3 actually used (assuming quant. use of the CrO_3) = 0.490
g. CrO_3 required to oxidize hydrogens on 1 to 4 = 0.730

If the tritium is on 1, 2 or 3, there is enough CrO_3 to remove it completely (*i.e.*, 180% of theoretical). If the tritium is on 4, only 66% of the tritium could be removed. Even this amount of removal would require quantitative oxidation by the CrO_3, which is difficult to accomplish.[17] Actually 87% of the tritium was removed.

A Packard Instrument Co. Tri-Carb liquid scintillation counter was used to make the radioactive measurements. The phosphor consisted of 0.05 g./l. of "POPOP" and 3.0 g./l. of "DPO" dissolved in toluene.[18] Internal standards were used as required.

One-to-one Adducts of Styrene and Triethylaluminum.—Triethylaluminum (12.0 g.) was mixed with 6.9 cc. of styrene and 6.9 cc. of *n*-hexane and allowed to react for 20 hours at 100°. The mass was cooled and diluted further with 75 cc. of hexane. A stoichiometric amount of methanol was added slowly at 25°. The solids were removed and the filtrate fractionated under vacuum. The components of the fractions were identified by infrared and mass spectrometry. They contained predominantly hexane and styrene, with small quantities of *n*-butylbenzene. A trace of $CH_3CH_2CH{=}C(C_6H_5)H$ was detected, also, probably due to the equilibrium between

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[12] G. Natta, P. Pino, G. Mazzanti, P. Longi and F. Bernardini, This Journal, **81**, 2561 (1959).

[13] R. A. Gregg and F. R. Mayo, *ibid.*, **70**, 2373 (1948).

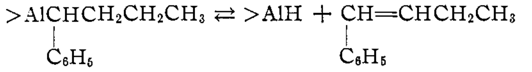
[14] Private communication from Q. A. Trementozzi.

[15] R. A. Gregg, This Journal, **70**, 3740 (1948).

[16] Page 217 of ref. 5.

[17] J. I. Aznarez and J. B. V. Rago, *Anales real. soc. españ. fís. y quim.* (*Madrid*), **50B**, 656 (1954).

[18] H. Kallman and M. Furst, *Nucleonics*, **8**, 32 (1951).



$$>\mathrm{Al}\underset{\mathrm{C_6H_5}}{\mathrm{CH}}\mathrm{CH_2CH_2CH_3} \rightleftarrows >\mathrm{AlH} + \underset{\mathrm{C_6H_5}}{\mathrm{CH}}\mathrm{{=}CHCH_2CH_3}$$

Acknowledgment is due to Dr. H. A. Ory for infrared analyses, Dr. W. T. Cave for infrared and n.m.r. analyses, Mr. K. A. Pinkerton for mass spectrometer analyses, Professor W. H. Urry for his helpful discussions, and Mr. M. Milton who assisted with the experimental work.

[CONTRIBUTION FROM THE MELLON INSTITUTE]

Monodisperse Poly-(α-methylstyrene) by Alkali Metal Initiation[1,2]

BY FRANZ WENGER

RECEIVED FEBRUARY 4, 1960

Short chain dianions, formed in the heterogeneous reaction between sodium and α-methylstyrene in tetrahydrofuran at 25°, are used for the controlled purging of impurities and as initiator in the subsequent polymerization at −78°. Two polymers, synthesized from starting materials with a widely different content of impurities, were fractionated and their $\bar{M}_w/\bar{M}_n$ ratios determined to be 1.05 and 1.06. The results demonstrate the efficacy of the purging process and the inactivity of the reaction products formed. A mechanism for the formation of the initiating short chain dianions is proposed. Further, some potential applications of these materials in the industrial production of poly-(α-methylstyrene), as well as in the polymerization of other monomers, are discussed.

Introduction

Detailed investigations of the kinetics and thermodynamics of the anionic polymerization of α-methylstyrene by Na-naphthalene in tetrahydrofuran have been described recently by Worsfold and Bywater.[3,4] They also made use of a novel polymerization technique with the aim of obtaining a monodisperse product. In their process, the initiator, Na-naphthalene, is added to the monomer above the ceiling temperature, following which the system is cooled rapidly and the polymerization allowed to go to completion at −78°. Qualitative evidence was presented that the polymers had a narrow distribution of chain lengths and that the number average molecular weight was given by the ratio (Monomer in g.)/($^1/_2$ [initiator]).

Although it might appear from the description of these experiments that the initiator added above the ceiling temperature did not react with the monomer, Na-naphthalene actually reacts readily under these conditions yielding short-chain poly-(α-methylstyrene) dianions with ceiling temperatures higher than those reported for long chains.

Since chain initiation—assumed here to require an electron transfer to monomer—should also be possible with metallic sodium[5] we decided to attempt the formation of dianions in a direct (heterogeneous) reaction between metallic sodium and α-methylstyrene. It was found that above the reported ceiling temperature, sodium, as well as lithium and potassium, reacts readily with the monomer yielding the desired dianions. Furthermore, in this heterogeneous reaction it is possible to control the formation of dianions by filtration of the monomer solution from or into the vessel containing the metal. Thus, this technique promised to offer a simple means for purging the system of impurities and for the formation of short chain dianions, which on subsequent polymerization at low temperature should yield a monodisperse product. If practicable, it would be a convenient preparation of monodisperse polymers in large quantities.

Two experiments are described in this paper: A very careful one (II) with pure starting materials, and one (I) in which commercial grade reagents, without special purification, were employed. The aim of the latter experiment was to determine whether the presence of relatively large amounts of products from the reaction of impurities (potential deactivators of propagation centers) with α-methylstyrene anions would influence the molecular weight distribution.

The impurities most likely to be present in the system are water; carbon dioxide and oxygen from the atmosphere; the auto-oxidation products of the monomer,[6] notably peroxides, acetophenone and formaldehyde; and indene[7] from the monomer preparation. None of the reaction products[8] of these substances with α-methylstyrene anions is expected to be further active in the polymerization in tetrahydrofuran.

Experimental

Materials. **α-Methylstyrene** (Eastman Kodak Co., white label): In experiment I, monomer with a relatively large content of auto-oxidation products, evidenced by a white deposit on the walls of the storage bottle, was used. The monomer was freshly distilled under nitrogen at 25 mm. for experiment II.

Tetrahydrofuran (du Pont) was distilled from calcium hydride. In the second experiment an additional distillation from Na-naphthalene was carried out.

Sodium was distilled into the ampoules.

Polymerization. Apparatus.—The reaction vessel was a 1-liter 3-necked flask, containing a glass enclosed magnetic stirring bar. The main outlet had a preformed seal-off constriction and could be connected to the vacuum system by means of a ground joint. The two other outlets led to a break-off ampoule containing methanol and an ampoule containing a sodium mirror. A fritted glass disk between this ampoule and the flask prevented loose sodium particles from

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(1) Presented at the 137th Meeting of the American Chemical Society, Cleveland, Ohio, April, 1960.

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