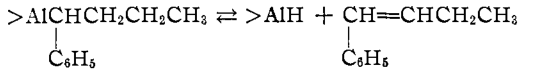

$$>\underset{\substack{|\\ C_6H_5}}{\mathrm{AlCH}}CH_2CH_2CH_3 \rightleftarrows >AlH + \underset{\substack{|\\ C_6H_5}}{\mathrm{CH}}{=}CHCH_2CH_3$$

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

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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.

[2] F. Wenger, Mellon Institute Quarterly Report of Fundamental Research No. FR-201-A (January 1 through March 31, 1959).

[3] D. J. Worsfold and S. Bywater, *J. Polymer Sci.*, **26**, 299 (1957).

[4] D. J. Worsforld and S. Bywater, *Can. J. Chem.*, **36**, 1141 (1958).

[5] E. Bergmann, H. Taubadel and H. Weiss, *Ber.*, **64**, 1493 (1931).

[6] Tiffeneau, *Ann. chim. et phys.*, [8] **10**, 155 in "Beilstein," Vol. 5, p. 484.

[7] G. D. Jones and R. E. Friedrich, *Ind. Eng. Chem.*, **51**, 745 (1959).

[8] J. Schmidt, Organo-Metallverbindungen, Stuttgart, 1934.

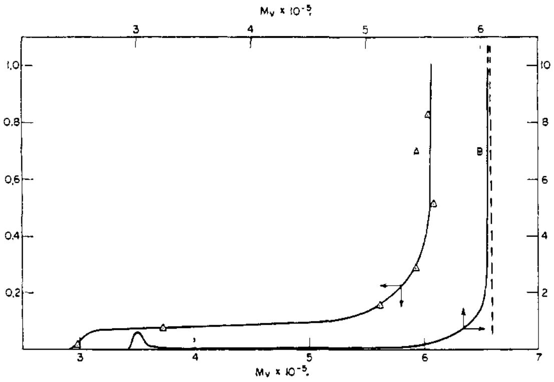

Fig. 1.—Poly-(α-methylstyrene), sample I; integral (A) and differential (B) weight distribution; data are from Table I.

entering the reaction mixture. An additional sidearm connected to a vacuum jacketed absorption cell fitting to a Bausch & Lomb colorimeter (Spectronic 20).

Polymerization Procedure.—The monomer (15 ml.) was placed in the flask with a syringe. For sample II, the flask had previously been evacuated and degassed and the vacuum broken with nitrogen. The flask containing the monomer was attached to the vacuum system, degassed and cooled to −78°; 500 ml. of tetrahydrofuran was then distilled in. The polymerization flask was sealed off at the preformed constriction and its contents warmed to room temperature. The seal to the ampoule containing sodium was then crushed and the monomer solution brought in contact with the metal by tilting until the red color from the α-methylstyrene anions persisted. The active solution was then drained back into the polymerization flask where the color discharged immediately upon reaction with impurities. This procedure was repeated until almost all the impurities had reacted, as indicated by a slower disappearance of the red anions. At this stage, the formation of dianions in the ampoule was carried out in small incremental steps. While draining the solution back into the flask it was made certain that the equivalent point for the removal of impurities was being approached carefully (an overtitration would lead to deactivation of dianions at one end). After the impurities had been deactivated in the described fashion—a process comparable to ordinary titration—further dianions were formed in the appropriate concentration for the subsequent polymerization. The contents of the flask were then cooled to −78° and the polymerization allowed to proceed until terminated by methanol. The initial cooling was achieved by swirling the flask in a Dry Ice–methanol slurry; the time required to reduce the temperature from 25 to −50°, the critical temperature interval,[4] was less than 2 minutes. Subsequently, a magnetic stirrer was sufficient for maintaining a uniform temperature throughout the reaction mixture.

The polymer was isolated by precipitation in 5000 ml. of methanol–water mixture 1:1, at 0°, filtered, washed with methanol and then dried in the vaccum oven (60°) for 24 hours. No effort was made to collect the precipitated polymers quantitatively; the yields reported are probably 2 to 3% too low. A portion of each of the two polymers was separated into six fractions by fractional precipitation at 30° by the addition of methanol to 1% solution in toluene.

In the experiment with the impure starting materials (polymer I) the course of the reaction was followed spectrophotometrically at regular intervals. For this purpose solution from the reaction flask was poured into the measuring cell and the cell, vacuum jacket and connecting tubing were kept at −78°. The measurement was made after the vacuum jacket had been warmed to room temperature, to avoid frosting of the glass. Afterwards, the cell contents were poured back into the main flask. Throughout the whole operation the active polymer solution was always kept at −78° and uniform polymerization conditions were therefore maintained. It should be noted that the procedure described can also be employed in the spectrophotometric determination of number average molecular weights if a calibration curve has been established previously.

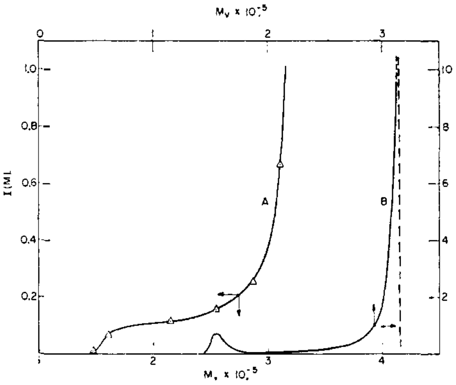

Fig. 2.—Poly-(α-methylstyrene), sample II: integral (A) and differential (B) weight distribution; data are from Table II.

Results

The results of the fractionations of the two poly-(α-methylstyrene) samples:

Polymer I, $\bar{M}_v$ 575,000: monomer and solvent without special purification; reac. time 12 hr.; yield 96%

Polymer II, $\bar{M}_v$ 289,000: monomer and solvent purified; reac. time 2.5 hr.; yield 51%

are summarized in Tables I and II and in Figs. 1 and 2.

TABLE I

FRACTIONATION OF POLY-(α-METHYLSTYRENE), SAMPLE I, 1% IN TOLUENE, PRECIPITANT METHANOL, 29.8°

Fraction	$\frac{\text{Ml. methanol}}{\text{100 ml. toluene}}$	G.	w_i	Σw_i	$[\eta]^a$	$\bar{M}_v \times 10^{-5\,b}$
Cloud pt.	25.6					
1	26.6	1.833	0.366	0.366	1.17	6.03
2	27.6	1.265	.253	.619	1.18	6.08
3	28.6	1.027	.205	.824	1.16	5.94
4	29.6	0.297	.059	.883	1.12	5.62
5	31.6	.464	.093	.976	0.86	3.72
6	37.6	.159	.031	1.007	0.74	2.97
Unfract. polymer					1.14^c	5.75

[a] $[\eta]$ in toluene 30°, from: $[\eta] = \frac{1}{c}\left[\ln \eta_{rel} + \frac{1}{4}\left(\eta_{spec} - \ln \eta_{rel}\right]\right)$- [b] $[\eta] = 1.92 \times 10^{-4} \times \bar{M}^{0.655,10}$ [c] $[\eta]_{cald.} = \Sigma w_i[\eta]_i = 1.14$.

In the latter the integral weight distribution curves were constructed according to the method of Schulz[9] while the differential weight distribution curves were obtained from a graphical evaluation of the integral functions. Both differential distribution curves exhibit two peaks, the minor one occurring at lower molecular weight. The molecular weights corresponding to these maxima differ by a factor of two in each case.

The measured intrinsic viscosities of the unfractionated polymers are in good agreement with the calculated values $[\eta]_{cald} = \Sigma w_i[\eta]_i$. The discrepancy between the weight and viscosity average molecular weight of polymer II (Table III) may be partly attributable to uncertainty in the absolute molecular weight scales both in the light scattering determination of $\bar{M}_w$ and in the preliminary $[\eta]$–$\bar{M}_v$

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[9] G. V. Schulz and A. Dinglinger, *Z. physik. Chem.*, **B43**, 47 (1939).

TABLE II

FRACTIONATION OF POLY-(α-METHYLSTYRENE), SAMPLE II, 1% IN TOLUENE, PRECIPITANT METHANOL, 30°

Fraction	Ml. methanol / 100 ml. toluene	G.	w_i	Σw_i	$[\eta]$	$\bar{M}_v \times 10^{-5}$
1	28	1.376	0.688	0.688	0.760	3.11
2	29	0.280	.140	.828	.726	2.87
3	30	.106	.053	.881	.665	2.54
4	31	.052	.026	.907	.599	2.16
5	33	.166	.083	.990	.493	1.61
6	38	.041	.020	1.010	.468	1.48
Unfract. polymer					.725[a]	2.89

[a] $[\eta]_{\text{calcd}} = \Sigma w_i[\eta]_i = 0.73$.

relation employed.[10] The uncertainty in the absolute molecular weight scale has, however, little effect on the value of the ratio $\bar{M}_w/\bar{M}_n$ as obtained here calculated from the fractionation data.

Discussion

Whether the primary step in the reaction of sodium with unsaturated hydrocarbons would involve a one-electron transfer to give a radical-ion, followed by dimerization, or a two-electron transfer to yield a dianion was a matter of controversy, notably between Schlenk[11] and Ziegler.[12] The problem was elucidated for some hydrocarbons on the basis of data from polarography.[13] No polarographic data are available for α-methylstyrene, but some qualitative information can be obtained from data for styrene. The half-wave potential for styrene has been measured by Laitinen and Wawzonek[14] and found to be -2.35 volts. In the reduction of this hydrocarbon, the same investigators obtained only one polarographic wave. This, together with the independence of the half-wave potential of the *p*H, in the range investigated, led them to conclude that the over-all reaction was a two-electron addition. Hoijtink[15] had drawn attention to the fact that the measured half-wave potential of styrene differs by -0.3 volt from the value calculated semi-empirically from a relation which was found to hold closely for a series of hydrocarbons investigated. He attributed the relatively high value found for styrene to a high reactivity of the radical-ion toward proton addition. From the same work by Hoijtink it is known also that the addition of a second electron to such radical-anions, requires an electrode-potential probably at least 0.2 volt more negative than for the first one. On the basis of a comparison of the structures of styrene with α-methylstyrene we should assume slightly more negative potentials required for the formation of α-methylstyrene dianions, presumably around -2.9 volt, a value approximately 0.2 volt more negative than the reported standard potential for sodium in tetrahydrofuran.[16] We shall therefore assume that the initial step is the formation of radical-anions (1).

$$\text{e} + \text{M} \longrightarrow \bar{M} \qquad (1)$$

$$\bar{M} + \text{M} \longrightarrow \bar{M}\text{–M}\cdot \qquad (2)$$

$$2\ \bar{M} \longrightarrow \bar{M}\text{–}\bar{M} \qquad (3)$$

$$2\ \bar{M}\text{–M}\cdot \longrightarrow \bar{M}\text{–M–M–}\bar{M} \qquad (4)$$

$$\bar{M} + \cdot\text{M–}\bar{M} \longrightarrow \text{M} + \bar{M}\text{–}\bar{M} \qquad (5)$$

$$\text{e} + \cdot\text{M–}\bar{M} \longrightarrow \bar{M}\text{–}\bar{M} \qquad (6)$$

The radical-anions formed in step 1 are then further assumed to disappear either by recombination (3) and (4) or by electron transfer reactions after addition of at least one monomer unit (2),[17] to give dianions. In the latter case the radical-anions may react either with other radical-anions (5) or with sodium (6). The postulated reactions 4, 5 and 6 should be visualized as occurring not only in the monomeric and dimeric forms, respectively, but also after the species have grown anionically to some extent. The chain length of the dianions formed is then eventually limited by the ceiling temperature phenomenon. Assuming no termination, the number average molecular weight of polymers thus obtained would be given by the ratio $\bar{M}_n$ = polymer in g./($^1/_2$ mols. of chain-ends), a relationship which can be tested by any method for chain-end analysis such as the spectral photometric procedure outlined in the Experimental part.

The occurrence of two maxima in the differential weight distribution curves (Figs. 1 and 2) with the corresponding molecular weights differing by a factor of two, must be attributed to the presence of both short chain monoanions and dianions in the early stages of the polymerization. The formation of monoanions arises from partial deactivation of dianions. Possible explanations for such chain-end deactivation will be discussed later.

From a comparison of Figs. 1 and 2 it would appear that the polydispersity of the two samples is not related to the amounts of impurities present in the starting materials. The inactivity of the products of the purging reaction is indicated by the absence of measurable amounts of polymers between the two peaks in the distribution curves of sample I. Thus, after the initial destruction of propagation centers (responsible for the peak at lower molecular weights) no further deactivation takes place. This point is evidenced also by the spectrophotometric measurements in which no change in the absorbancy during the reaction time could be observed. The process of using the short chain dianions as a purging agent seems therefore to be quite efficient.

On the basis of the results obtained (Table III) the polymerization process can be regarded as a simple and satisfactory tool for the preparation of essentially monodisperse poly-(α-methylsytrene). The homogeneity of the polymers can be further enhanced, by a one-step fractionation, to a degree such that the polydispersity of the resulting fraction

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(10) D. J. Worsfold, private communication.

(11) W. Schlenk and E. Bergmann, *Ann.*, **479**, 58 (1930).

(12) K. Ziegler, H. Colonius and O. Schafer, *ibid.*, **473**, 36 (1929).

(13) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1952.

(14) H. A. Laitinen and S. Wawzonek, THIS JOURNAL, **64**, 1765 (1942).

(15) G. J. Hoijtink, *Rec. trav. chim.*, **74**, 1525 (1955).

(16) G. J. Hoijtink, E. de Boer, R. H. van der Maij and W. P. Weijland, *ibid.*, **75**, 487 (1956).

(17) The nature of the dimeric radical-anion postulated in step 2 is not known. Thermodynamically a structure with a phenyl group at each end is more likely,[18] whereas the kinetics would probably favor a head to tail arrangement—to be expected from a reaction *via* an anionic mechanism.

(18) M. Szwarc, *Advances in Chem. Phys.*, **2**, 147 (1959).

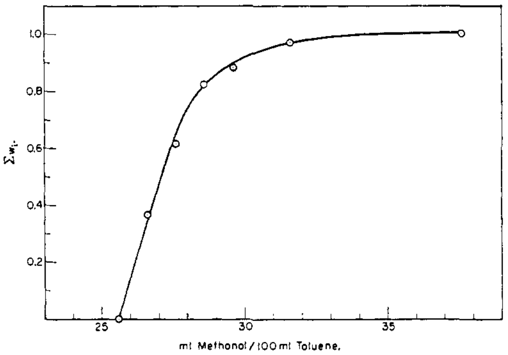

Fig. 3.—Fractional precipitation of poly-(α-methylstyrene), sample I; data are from Table I.

could probably not be detected by ordinary means.[19] The ease with which such a fractionation could be performed is apparent from the plot in Fig. 3 and the statement with regard to the polydispersity of the fraction thus obtainable is substantiated by the data in Table I. It should be mentioned also that the experimental conditions were chosen for convenience; modifications can be made easily so as to permit higher product yields without affecting the homogeneity of the polymers obtained.

TABLE III

MOLECULAR WEIGHTS OF POLY-(α-METHYLSTYRENE), SAMPLES I AND II

$\bar{M}_v$ measured	5.74×10^5	2.89×10^5
$\bar{M}_n = 1/\Sigma w_i/M_i$	5.47×10^5	2.72×10^5
$\bar{M}_w = \Sigma w_i M_i$	5.73×10^5	2.89×10^5
$\bar{M}_w$ measured		2.65×10^5[a]
$\bar{M}_w/\bar{M}_w$	1.05	1.06

[a] From light scattering by Dr. E. F. Casassa of these laboratories.

The formation of monoanions at the beginning of the polymerization could arise from two effects; a too rapid overtitration in the purging process or destruction of chain-ends during the build-up of the dianion concentration for the initiator proper. Calculations from data on molecular weights and yields (Tables I, II and III) show that the initial concentration of dianions was roughly the same in the two experiments and that the extent of chain-end deactivation was approximately 10% in each case. This extent of deactivation is too large to be accounted for by the first effect. Deactivation due to the second effect could be explained by assuming the presence of a relatively inactive impurity, which reacts only slowly and incompletely upon careful approach to the end-point of the titration. Deactivation of it would then take place only at a higher concentration of dianions, *i.e.*, during the initiator build-up. We have checked this hypothesis and have found that the concentrations of dianions formed initially under the conditions of experiments I and II decreased on standing. A polymerization was then carried out in which the apparent end-point for impurity removal was intentionally exceeded. After the color of the dianions had disappeared again completely, the temperature was lowered to 0° and the appropriate concentrarion of dianions was formed by the reaction of monomer and sodium as before. It is expected that the polymer obtained under these conditions will have only one maximum in the differential weight distribution curve and will be monodisperse to a degree that fractionation cannot further improve. The fractionation data, however, are not yet available and will be reported elsewhere.

Although it appears that the short chain dianions of α-methylstyrene which can be easily obtained should be useful as initiators in the preparation of other monodisperse polymers such as polystyrene or poly-(methacrylates), the possible disadvantage arising from the incorporation of a thermally unstable block of α-methylstyrene into the middle of an otherwise relatively stable chain must be recognized. Such a disadvantage is not as serious if short chain monoanions of α-methylstyrene, which can be prepared conveniently by the addition of monomer to butyllithium, are used as initiator, since thermal degradation of this block at one end of the chain would, in the presence of a suitable radical scavenger, cause only a negligible change in the chain length. We have reported elsewhere on the subject of other initiators such as Na-biphenyl for the synthesis of other monodisperse bifunctional polymers such as styrene.[21]

The difficulties inherent in the adaptation of the sodium-catalyzed polymerization of α-methylstyrene for industrial purposes are indicated in a recent publication.[7] The present process, involving the controlled purging of impurities and production of an appropriate concentration of dianions above the ceiling temperature, with subsequent homogeneous polymerization at a lower temperature, could be adapted to industrial scale production. Such a process can yield not only monodisperse products, but if desired, by partial deactivation at suitable intervals, polymers of an arbitrarily chosen molecular weight distribution.

NOTE ADDED IN PROOF.—Based on osmotic pressure measurements and light scattering on nearly homogeneous poly-(α-methylstyrene), Sirianni, Worsfold and Bywater[22] have published recently a new [η]–M relationship

$$[\eta] = 1.08 \times 10^{-4} \times M^{0.71}$$

In the range of our absolute molecular weight determinations from 1.8×10^5 [23] to 2.6×10^5 the difference in the molecular weights derived from the new and the preliminary equations is relatively small; our measurements are rather in support of the preliminary relationship.[10] It is stressed that the statements and conclusions of this work are valid regardless of which equation is employed. For Sample I, application of the new equation yields $\bar{M}_v = 4.64 \times 10^5$ and a $\bar{M}_w/\bar{M}_n$ ratio of 1.04.

This work was supported in part by the Office of Naval Research.

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[19] In the characterization of polymers for which $\bar{M}_w/\bar{M}_n$ is nearly unity, the value of this ratio is an inadequate measure of the polydispersity of the sample. Even if a sufficiently precise value of $\bar{M}_w/\bar{M}_n$ is experimentally obtainable, its relationship to the nature and extent of polydispersity is ambiguous. Thus, a polymer sample for which $\bar{M}_w/\bar{M}_n$ is unity within the limits of the experimental error involved in its determination may perhaps still be readily separable by fractionation into component portions more nearly homogeneous in molecular weight than the original sample. This problem will be discussed further in a forthcoming publication.[20]

(20) T. A. Orofino and F. Wenger, to be published.

(21) F. Wenger, *Makromol. Chem.*, **36**, 200 (1960).

(22) A. F. Sirianni, D. J. Worsfold and S. Bywater, *Trans. Faraday Soc.*, **55**, 2124 (1959).

(23) F. Wenger, *Makromol. Chem.*, **37**, 143 (1960).